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INORGANIC (CARBON-FREE) CHELATE RINGS

IONEL HAIDUC * and IOAN SILAGHI-DUMITRESCU

Chemistry Department, Babes-Bolyai University, R-3400 Cluj-Napoca (Romania)

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* Author to whom correspondence should be addressed.

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A. INTRODUCTION

Any textbook of inorganic or coordination chemistry devotes many pages to chelate complexes, i.e. cyclic compounds in which a ring is closed by a bidentate (or polydentate) ligand, attached with at least two donor sites to the same metal atom. The most familiar chelate rings are those derived from organic ligands, containing nitrogen, phosphorus, arsenic, oxygen, sulfur atoms [1]. Such metal chelates play an important role in analytical chemistry, bioinorganic chemistry and many other fields.

Although some chelate rings, formed by ligands which do not contain carbon atoms in their main chain (skeleton) are well established, it seems that inorganic (carbon-free) chelate rings have not been yet recognized as a self-consistent chapter of coordination chemistry. For the inorganic chemist it is important to realize that the possibility of closing a chelate ring with, and indeed by, a ligand that is purely inorganic does exist, as it also does for a ligand which bears organic groups attached only as external substituents to an inorganic chain. The purpose of this review is to emphasize this type of compound. It should be mentioned that some metal chelates of this type have already received considerable attention (e.g. dithiophosphates and dithiophosphinates, pyrazolylborates, etc.).

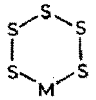
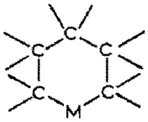
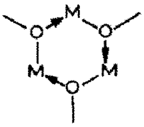
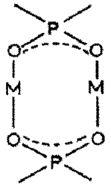
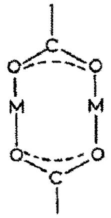
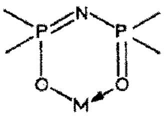
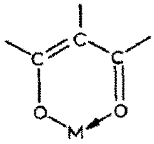
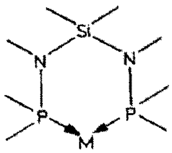
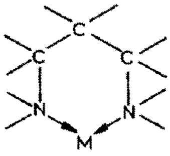
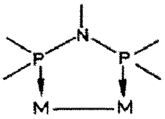
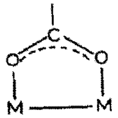
The inorganic chelate rings bridge the gap between the chemistry of traditional inorganic ring systems or heterocycles [2–5] (built up mainly of non-metallic main group elements) and coordination chemistry (dealing mainly with transition elements), and cross, to some extent, the borders of organometallic chemistry (if the metal center bears organic groups).

Inorganic chelates can also be considered as part of a larger family of rings, *metallocycles*, comprising metal-containing heterocycles in either an organic or inorganic ring. The metallocycles can be regarded as organic or inorganic, depending upon the presence or absence of carbon in the ring. Furthermore, parallel classes of compounds can be distinguished as is illustrated in Table 1.

This review deals with rings classified in Table 1 under (d) and (e). Since heterocycles of type (a) with inorganic ligands are also described as metal chelates, (e.g. polysulfides) these will also be included in this review. Originally we endeavoured to provide an exhaustive review, but during its

TABLE 1

Classification of metallocycles

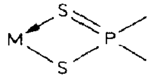
Type of ring	Examples	
	Inorganic	Organic
(a) True heterocycles		
(b) Coordinative rings		
(c) Cyclic dimers with bridging ligands		
(d) Metal chelates of anionic ligands		
(e) Metal chelates of neutral ligands		
(f) Metal–metal bond heterocycles with bridging ligands		

preparation it became clear that the search and finding of new references is a never-ending process. Therefore we claim no completeness, and the literature cited should be regarded only as illustrative, although the selection is fairly comprehensive. The subject could easily be expanded into a book, and we would be appreciative if any reader could drop us a post-card or letter bringing to our attention additional references (preferably with reprints or xerox copies of the articles).

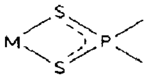
B. A GRAPH-BASED CLASSIFICATION OF INORGANIC CHELATE RINGS

A cyclic structure can be represented by a cyclic graph [6] i.e. a closed arrangement of connected points (called nodes). Thus, all six-membered rings are represented by the same graph, a hexagon. By replacing the nodes with atom symbols, the abstract graph is transformed into a *chemical graph* (Fig. 1). A chemical graph shows only the atoms forming a given chemical structure, without providing much information about the oxidation states and valencies of the atoms or about the nature of the chemical bonds involved. In fact it represents only the σ bond skeleton. As shown in Fig. 1, different actual chelate rings can be obtained from the same graph by adding double bonds (to indicate π-orbital participation), arrows (to indicate the donor–acceptor bonding), and plus and minus signs (to indicate electrical charges, etc.). In this review we will use the conventional arrow bond notation, but when the nature of the bonding can not be specified, a simple line notation will be employed.

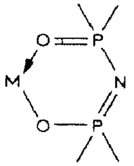
The notation raises some difficult questions. It is common practice to use either double bond or delocalized formulae, e.g. for dithiophosphinates or imidodiphosphinates:



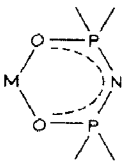
1a



1b



2a



2b

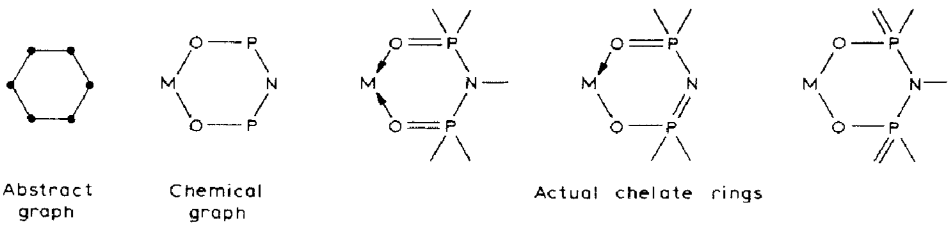
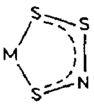


Fig. 1. The relationship between abstract graphs, chemical graphs and chemical structure formulae.

This is especially so when interatomic distances suggest that actual bonds have character that is intermediate between single and double bonds. In some cases, particularly those of sulfur–nitrogen ligands, a Lewis type structure, with localized bonds, is difficult to write and delocalized formulae (which probably correctly reflect the electronic distribution) will be used here:

3



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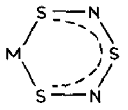

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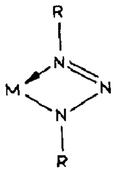
In an inorganic chelate ring the following components can be distinguished: (a) the coordinated metal atom, M; (b) the donor sites, i.e. the atoms directly connected to the metal; (c) the chain of atoms connecting the donor sites. Accordingly, our classification will use the following criteria: (a) the size of the graph (ring size), and, (b) the nature of the donor sites.

A linear formula for each type of cyclic graph is suggested, indicating the central atom and the donor sites, that incorporates the so called "chromophore" (in square brackets) and the other atoms that are present in the chelated chain (in parentheses), e.g. [M : NN](⊃ N), [M : NN](⊃ NN), [M : OO](⊃ PNP). These formulae represent triazenido, tetrazene and imidodiphosphinato chelates, respectively. Table 2 gives a comprehensive list of cyclic graphs from which various inorganic chelate rings derive. Both homoatomic and heteroatomic chains can form chelating ligands. This is clearly reflected by the linear formula.

In most cases the ligands encountered in this review form chelate rings. However, this is not the only way they coordinate. Usually, a bidentate ligand can either close a chelate ring or form a bridge between two metal centers, leading to binuclear complexes. This can be nicely illustrated for triazenido and bis(difluorophosphino)amine ligands, which form either chelate rings or metallocycles with or without metal–metal bonds:



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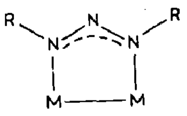

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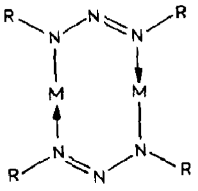

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TABLE 2

Classification of inorganic (carbon-free) chelate rings

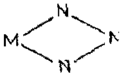
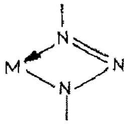
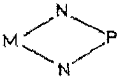
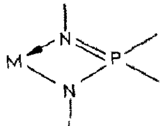
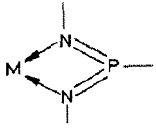
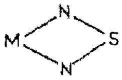
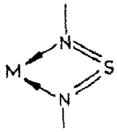
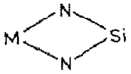
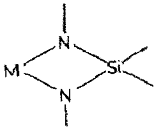
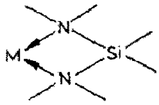
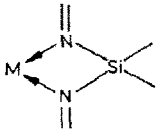
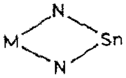
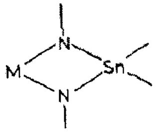
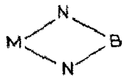
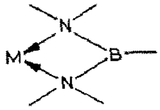
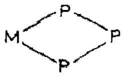
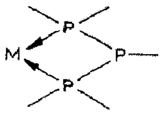
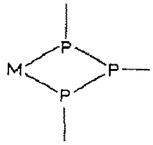
Linear notation	Chemical graph	Chelate rings	Nomenclature
FOUR MEMBERED-RINGS			
(i) Nitrogen donor sites			
[M:NN](⊃ N)			Triazenido chelates
[M:NN](⊃ P)			Diimidophosphinato- and -phosphato chelates
			Diiminophosphorane chelates
[M:NN](⊃ S)			Sulfur diimine chelates
[M:NN](⊃ Si)			Diimidosilane chelates
			Diaminosilane chelates
			Diiminosilane chelates
[M:NN](⊃ Sn)			Diimidostannane chelates
[M:NN](⊃ B)			Diaminoborane chelates
(ii) Phosphorus donor sites			
[M:PP](⊃ P)			Triphosphine chelates
			Triphosphido chelates

TABLE 2 (continued)

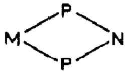
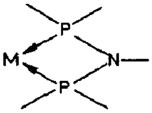
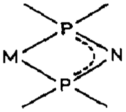
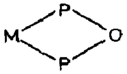
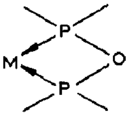
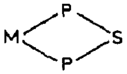
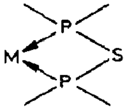
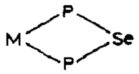
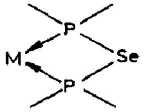
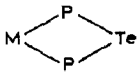
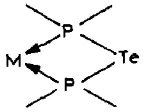
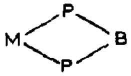
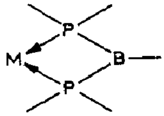
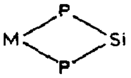
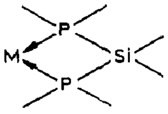
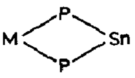
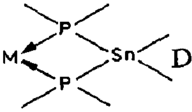
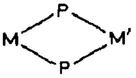
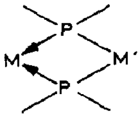
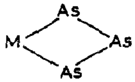
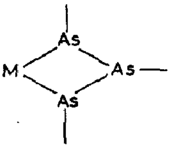
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : PP](⊃ N)			Diphosphinoamine chelates
			Diphosphineamido chelates
[M : PP](⊃ O)			Diphosphineoxide chelates
[M : PP](⊃ S)			Diphosphinosulfide chelates
[M : PP](⊃ Se)			Diphosphinoselenide chelates
[M : PP](⊃ Te)			Diphosphinotelluride chelates
[M : PP](⊃ B)			Diphosphinoborine chelates
[M : PP](⊃ Si)			Diphosphinosilane chelates
[M : PP](⊃ Sn)			Diphosphinostannane chelates
[M : PP](⊃ M′)			Diphosphidometal chelates (M′ = Ti, Zr
(iii) Arsenic donor sites			
[M : AsAs](⊃ As)			Triarsenido chelates

TABLE 2 (continued)

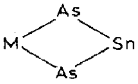
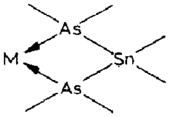
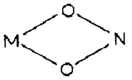
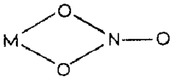
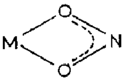
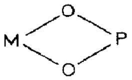
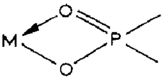
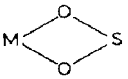
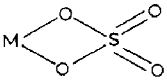
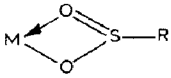
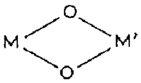
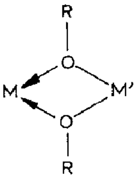
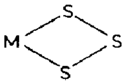
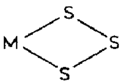
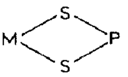
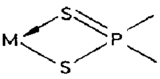
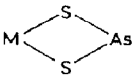
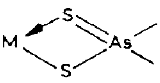
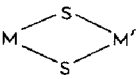
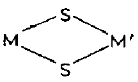
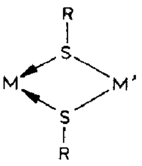
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : AsAs]($\supset$ Sn)			Diarsenidostannane chelates
(iv) Oxygen donor sites			
[M : OO]($\supset$ N)			Nitrato chelates
			Nitrito chelates
[M : OO]($\supset$ P)			Phosphinato- and phosphato chelates
[M : OO]($\supset$ S)			Sulfato chelates
			Sulfinato chelates
[M : OO]($\supset$ M′)			Dialkoxometal chelates
(v) Sulfur donor sites			
[M : SS]($\supset$ S)			Trisulfido chelates
[M : SS]($\supset$ P)			Dithiophosphinato- and dithiophosphato-chelates
[M : SS]($\supset$ As)			Dithioarsinato chelates
[M : SS]($\supset$ M′)			Tetrathiometallato (molybdato, tungstato, etc.) chelates
			Dithiolatometal chelates

TABLE 2 (continued)

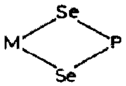
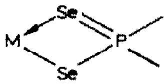
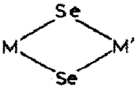
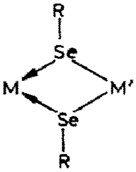
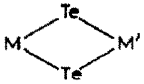
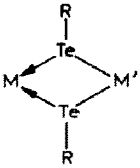
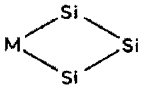
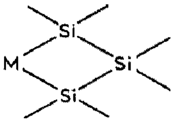
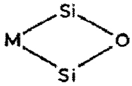
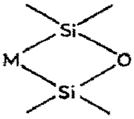
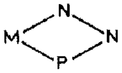
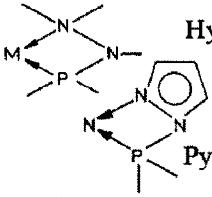
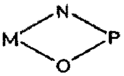
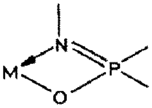
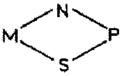
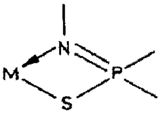
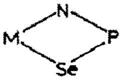
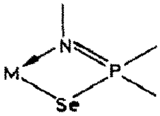
Linear notation	Chemical graph	Chelate rings	Nomenclature
(vi) Selenium donor sites			
[M : SeSe](⊃ P)			Diselenophosphinato and diselenophosphato chelates
[M : SeSe](⊃ M′)			Bis(alkylseleno)metal chelates
(vii) Tellurium donor sites			
[M : TeTe](⊃ M′)			Bis(alkyltellurol)metal chelates
(viii) Silicon donor sites			
[M : SiSi](⊃ Si)			Trisilanido chelates
			Disiloxanido chelates
(ix) Heteronuclear (mixed) donor sites			
[M : NP](⊃ N)			Hydrazine phosphine chelates Pyrazolylphosphine chelates
[M : NO](⊃ P)			Iminophosphinato and -phosphato chelates
[M : NS](⊃ P)			Iminothiophosphinato and -phosphato chelates
[M : NSe](⊃ P)			Iminoselenophosphinato (phosphato) chelates

TABLE 2 (continued)

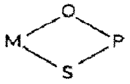
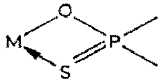
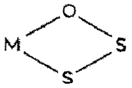
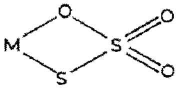
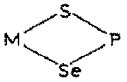
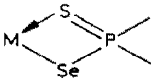
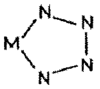
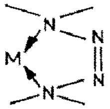
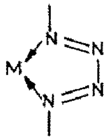
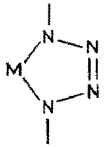
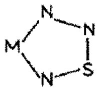
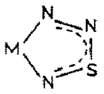
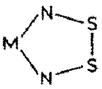
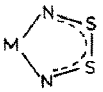
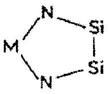
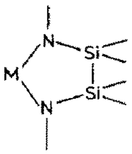
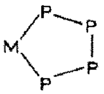
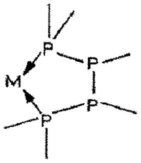
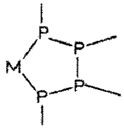
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : OS](⊃ P)			Monothiophosphinato and -phosphato chelates
[M : OS](⊃ S)			Thiosulfato chelates
[M : SSe](⊃ P)			Selenothiophosphates (-phosphinates)
FIVE-MEMBERED RINGS *(i) Nitrogen donor sites*			
[M : NN](⊃ NN)			Tetrazene-2 chelates
			Tetrazadiene-1,3 chelates
			Tetrazene-2 chelates
[M : NN](⊃ NS)			Triazathio chelates
[M : NN](⊃ SS)			Diazadithio chelates
[M : NN](⊃ SiSi)			Disilanediamido chelates
(ii) Phosphorus donor sites			
[M : PP](⊃ PP)			Tetraphosphine chelates
			Tetraphosphido chelates

TABLE 2 (continued)

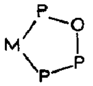
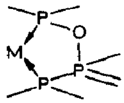
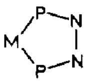
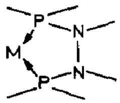
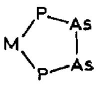
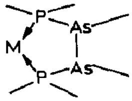
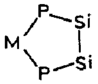
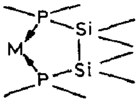
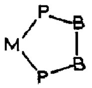
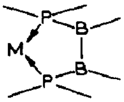
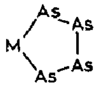
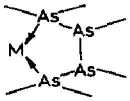
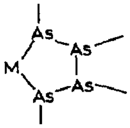
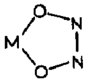
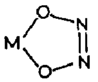
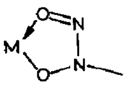
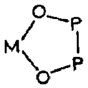
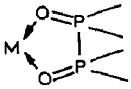
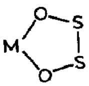
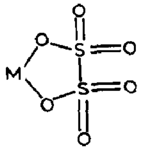
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : PP](⊃ PO)			Oxatriphosphine
[M : PP](⊃ NN)			Diphosphinohydrazine chelates
[M : PP](⊃ AsAs)			Diphosphinodiarsine chelates
[M : PP](⊃ SiSi)			Diphosphinodisilane chelates
[M : PP](⊃ BB)			Diphosphinodiborine chelates
(iii) Arsenic donor sites			
[M : AsAs](⊃ AsAs)			Tetraarsane chelates
			Tetraarsenido chelates
(iv) Oxygen donor sites			
[M : OO](⊃ NN)			Dioxodiazeno chelates
			Nitrosohydroxylamino chelates
[M : OO](⊃ PP)			Diphosphine dioxide chelates
[M : OO](⊃ SS)			Dithionato chelates

TABLE 2 (continued)

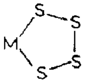
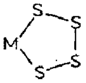
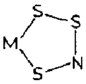
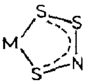
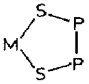
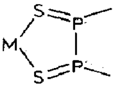
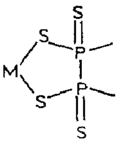
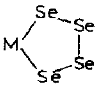
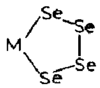
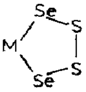
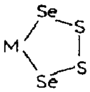
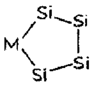
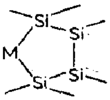
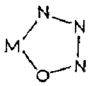
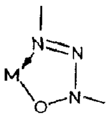
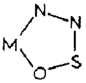
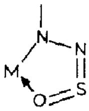
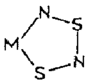
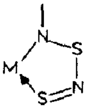
Linear notation	Chemical graph	Chelate rings	Nomenclature
(v) Sulfur donor sites			
[M : SS](⊃ SS)			Tetrasulfido chelates
[M : SS](⊃ NS)			Azatrithio chelates
[M : SS](⊃ PP)			Diphosphine disulfide chelates
			Tetrathiodiphosphinito chelates
(vi) Selenium donor sites			
[M : SeSe](⊃ SeSe)			Tetraselenido chelates
[M : SeSe](⊃ SS)			Diselenodisulfido chelates
(vii) Silicon donor sites			
[M : SiSi](⊃ SiSi)			Tetrasilanido chelates
(viii) Heteronuclear (mixed) donor sites			
[M : NO](⊃ NN)			Triazene-1-oxide chelates
[M : NO](⊃ NS)			N-Sulfinyl hydrazido chelates
[M : NS](⊃ NS)			Diazadithiochelates

TABLE 2 (continued)

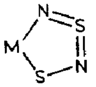
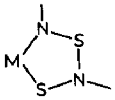
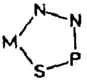
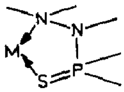
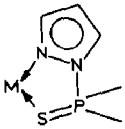
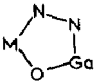
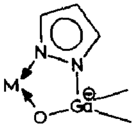
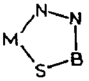
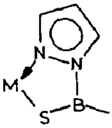
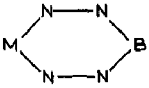
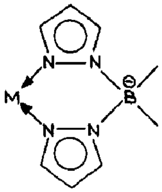
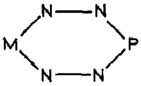
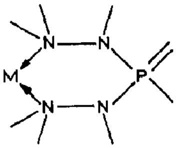
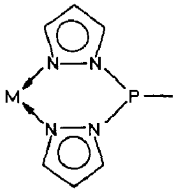
Linear notation	Chemical graph	Chelate rings	Nomenclature
			Diazadithio chelates
			Diazadithio chelates
[M : NS](⊃ NP)			Hydrazinothiophosphine chelates
			Pyrazolylthiophosphine chelates
[M : NO](⊃ NGa)			Pyrazolyloxogallato chelates
[M : NS](⊃ NB)			Pyrazolylthioborato chelates
E. SIX-MEMBERED RINGS			
(i) Nitrogen donor sites			
[M : NN](⊃ NBN)			Bis(pyrazolyl)borato chelates
[M : NN](⊃ NPN)			Bis(hydrazino)phosphonate chelates
			Bis(pyrazolyl)phosphino chelates

TABLE 2 (continued)

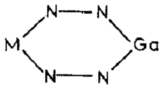
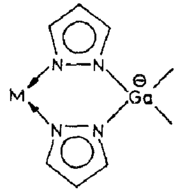
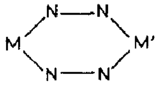
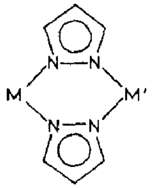
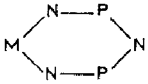
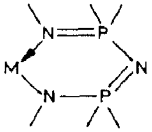
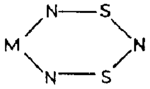
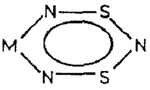
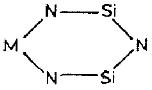
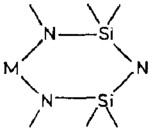
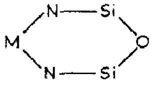
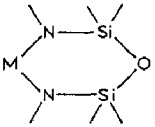
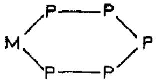
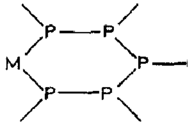
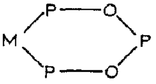
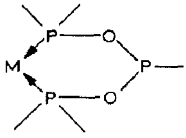
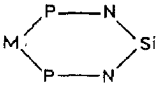
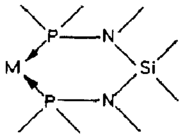
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : NN](⊃ NGaN)			Bis(pyrazolyl)gallato chelates
[M : NN](⊃ NM′N)			Bis(pyrazolyl)metal chelates
[M : NN](⊃ PNP)			Triamidodiphosphinato chelates
[M : NN](⊃ SNS)			Triazadithio chelates
[M : NN](⊃ SiNSi)			Disilazanediamido chelates
[M : NN](⊃ SiOSi)			Disiloxanediamido chelates
(ii) Phosphorus donor sites			
[M : PP](⊃ PPP)			Pentaphosphido chelates
[M : PP](⊃ OPO)			Bis(phosphinoxo)phosphine chelates
[M : PP](⊃ NSiN)			Bis(phosphinoamino)silane chelates

TABLE 2 (continued)

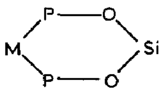
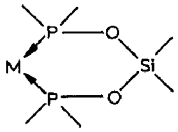
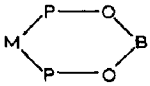
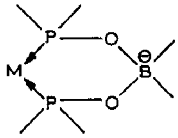
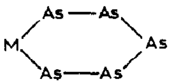
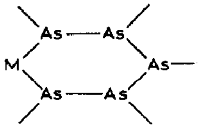
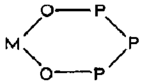
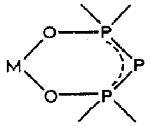
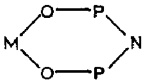
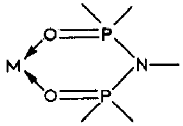
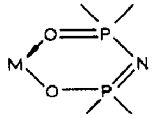
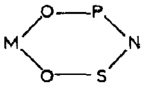
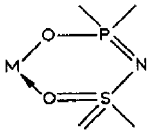
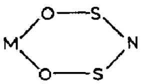
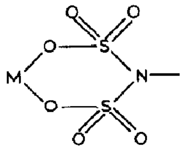
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : PP]($\supset$ OSiO)			Bis(phosphinoxo)silane chelates
[M ; PP]($\supset$ OBO)			Bis(phosphinoxo)borata chelates
(iii) Arsenic donor sites			
[M : AsAs]($\supset$ AsAsAs)			Pentaarsenido chelates
(iv) Oxygen donor sites			
[M:OO]($\supset$ PPP)			Dioxotriphosphino chelates
[M:OO]($\supset$ PNP)			Bis(oxophosphino)amine chelates
			Amidodiphosphinato chelates
[M:OO]($\supset$ PNS)			Sulfonylimidophosphato chelates
[M:OO]($\supset$ SNS)			Amine-N-disulfonato chelates

TABLE 2 (continued)

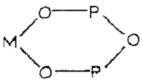
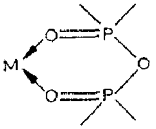
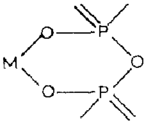
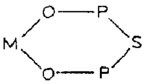
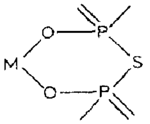
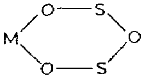
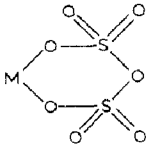
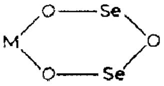
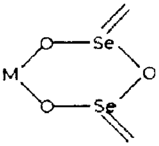
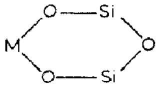
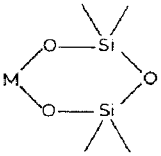
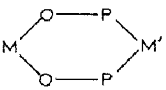
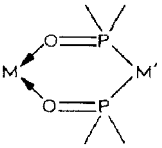
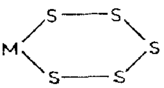
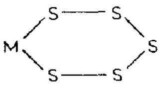
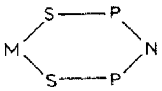
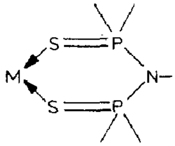
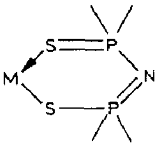
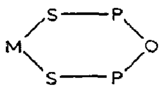
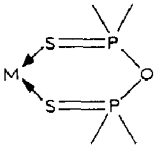
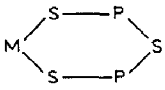
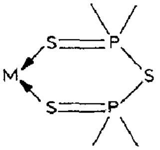
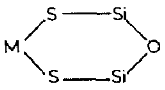
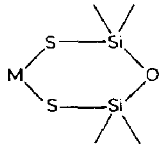
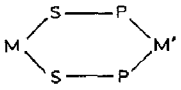
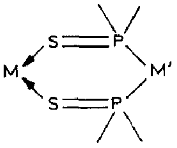
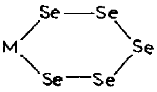
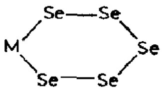
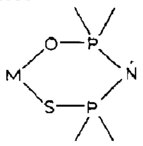
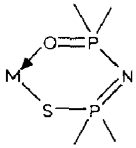
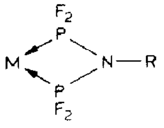
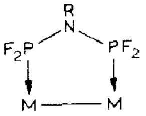
Linear notation	Chemical graph	Chelate rings	Nomenclature
[M : OO](⊃ POP)			Phosphinic anhydride chelates
			Diphosphato chelates (pyrophosphato)
[M : OO](⊃ PSP)			Thiopyrophosphato chelates
[M : OO](⊃ SOS)			Disulfato (pyrosulfato) chelates
[M : OO](⊃ SeOSe)			Diselenito chelates
[M : OO](⊃ SiOSi)			Disiloxanediolato chelates
[M : OO](⊃ PM′P)			Bis(oxophosphino)metal chelates
(v) Sulfur donor sites			
[M : SS](⊃ SSS)			Pentasulfido chelates
[M : SS](⊃ PNP)			Bis(thiophosphinyl)amido chelates

TABLE 2 (continued)

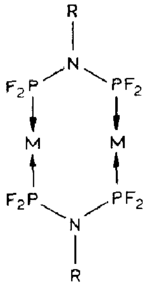
Linear notation	Chemical graph	Chelate rings	Nomenclature
			Amidodithiodiphosphinato chelates
[M : SS](⊃ POP)			Bis(thiophosphinyl)oxide chelates
[M : SS](⊃ PSP)			Bis(thiophosphinyl)sulfide chelates
[M : SS](⊃ SiOSi)			Disiloxanedithiolato chelates
[M : SS](⊃ PM′P)			Bis(thiophosphino)metal chelates
(vi) Selenium donor sites			
[M : SeSe](⊃ SeSeSe)			Pentaselenido chelates
(vii) Heteronuclear donor sites			
[M : OS](⊃ PNP)			(Thiodiphosphinyl)amido chelates



9



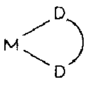
10



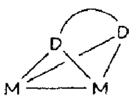
11

Only the first type will be discussed in this review, although the second type could be considered as chelate rings containing two coordination centers. The same ligands, in rare cases, may also coordinate as monodentate. More subtle peculiarities of coordination patterns (e.g. resulting from iso- and anisobidentate coordination) have been discussed for dithiophosphato and -phosphinato ligands [7] and the review cited is recommended as an addition to the present one.

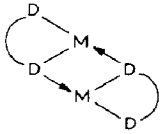
In some cases the closure of a chelate ring **12** does not entirely fulfil the coordination potential of the donor sites, i.e. when these possess additional lone pairs (e.g. $D = S, P^-, As^-$). In these cases additional coordination may lead to bridge chelating (**13a**) (in dinuclear compounds with metal–metal bonds) or to dimerization (**13b**) or trimerization (**13c**) of the chelate species. Some examples of each type will be encountered later in this review.



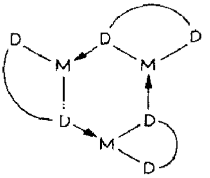
12



13a



13b



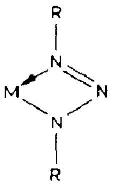
13c

C. FOUR-MEMBERED RINGS

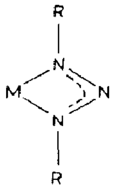
(i) Nitrogen donor sites

(a) [M : NN](⊃ N) Systems: triazenido chelates

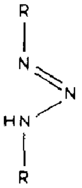
Four-membered chelate rings (**14a–b**) derive from deprotonated diaryltriazenes (**14c**). The ability of diphenyltriazene (**14c**, R = Ph) to form



14a

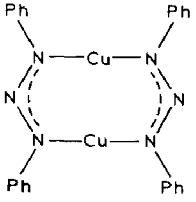


14b



14c

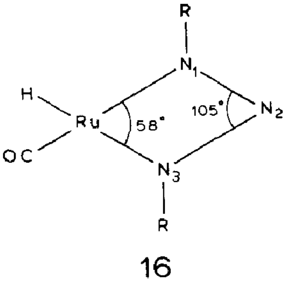
metal complexes was discovered many years ago [8,9], but the formation of small ring chelates was first considered improbable [10] on the grounds that a marked ring strain would occur in a four-membered cycle. This view was supported by the finding that some Cu(I), Ni(II) and Pd(II) compounds were found to be dimeric [10]; indeed, an early X-ray diffraction study of the dimeric diphenyltriazenido copper(I) [11] established an eight-membered ring structure (**15**):



15

The first confirmation of a four-membered chelate ring structure (**14a**–**b**) was obtained by an X-ray diffraction analysis of tris(diphenyltriazenido)cobalt(III), $Co(PhN_3Ph)_3$ [12], but the same authors [13] also discovered that the Ni(II) derivative has a dinuclear structure, with four bridging triazenido ligands. In the cobalt compound, $Co(PhN_3Ph)_3$ the four-membered CoN_3 ring is planar, with Co–N 1.94 Å, N–N 1.31 Å, ∠N–Co–N 65°, ∠N–N–N 105°; these bond angles indicate ring strain [12].

Chelating triazenido ligands were later found in ruthenium [14–16], rhodium [14,17], iridium [14,17–20], chromium [21,22], palladium [23,24] (see, however ref. [24a], describing bridged palladium triazenido complexes), thallium [25] and mercury [26–28] complexes. Several of these compounds were investigated by X-ray diffraction. Thus, for example, in the ruthenium complex $[RuH(CO)(PPh_3)_2(RNNNR)]$ (R = *p*-tolyl) (**16**) the X-ray investigation established a symmetrical structure for the ligand (N_1–N_2 1.32 Å, N_2–N_3 1.31 Å) with slightly differing Ru–N bond lengths (Ru–N_1 2.149(3) Å and Ru–N_3 2.179(3) Å), which is probably due to a *trans*-influence for the hydrido that is greater than that of the carbonyl ligand [15]. The bond angles (∠N–Ru–N 58°, ∠N–N–N 105°) suggest that the four-membered ring is strained [15].



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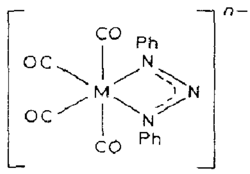
A large number of organometallic complexes containing bidentate diphenyltriazenido ligands were also reported. These include anionic chromium, molybdenum and tungsten tetracarbonyl derivatives $[M(CO)_4(PhN_3Ph)]^-$ (M = Cr, Mo, W) (**17**), isoelectronic neutral manganese and rhenium tetracarbonyl derivatives $[M(CO)_4(PhN_3Ph)]$ (M = Mn, Re) (**17**) [29,30] and related complexes [30a].

The η^5-cyclopentadienylmolybdenum dicarbonyl derivatives, η^5-$C_5H_5Mo(CO)_2(PhN_3Ph)$ (**18**) [29–33], η^5-$C_5H_5Mo(NO)X(RN_3R)$ [33a]; neutral η^5-cyclopentadienylcobalt derivatives, η^5-$C_5H_5Co(\sigma$-$C_3F_7)(PhN_3Ph)$ (**19**) [29], η^5-$C_5H_5Co^{II}(PPh_3)(PhN_3Ph)$ [34] and salt-like complexes $[\eta^5$-$C_5H_5Co^{III}(PR_3)(R'N_3R')]^+PF_6^-$ [34a]; rhodium complexes $[(\eta^5$-$C_5Me_5)RhL(PhN_3Ph)]^+PF_6^-$ (L = MeCN, $P(OMe)_3$), $[\eta^5$-$C_5H_5RhCl(RN_3R)]$ (R = Ph, *p*-tolyl, *p*-ClC_6H_4) [35]; and cyclopentadienyliron complexes $[\eta^5$-$C_5H_5Fe(PR_3)(R'N_3R')]$ (R = Ph, OMe, OPh; R′ = *p*-tolyl, *p*-ClC_6H_4) [36] are other examples of organometallic triazenido chelate complexes, demonstrating the versatility of this ligand. An X-ray structural analysis of η^5-$C_5H_5Mo(CO)_2(RN_3R)$, with R = 3,5-$(CF_3)_2C_6H_3$, confirmed the symmetrical chelate ring structure of type **18**, with Mo–N 2.12 Å, ∠N–Mo–N 56° and ∠N–N–N 101° [33].



M = Cr, Mo, W ; n = 1
M = Mn, Re ; n = 0

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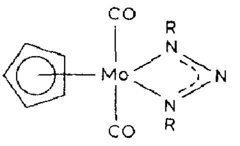

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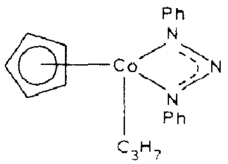

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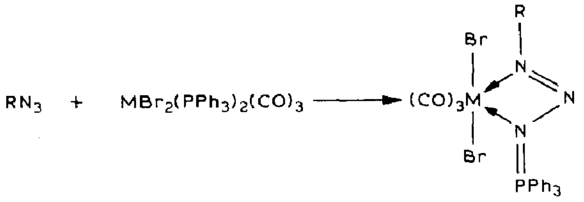
An interesting compound is $W_2(NMe_2)_4(PhN_3Ph)_2$; although the triazenido ligand is expected to form bridges in this derivative, the two PhN_3Ph groups are in fact chelating to separate tungsten atoms bonded to each other through W≡W (triple) bonds [37]. An analogous molybdenum compound $Mo_2(NMe_2)_2(RN_3R)_2$ (R = *p*-tolyl) has also been reported [38].

Related complexes (**20**) containing an N_3 fragment, coordinated as a chelating group, are formed by the insertion of arylazides into M–P bonds of molybdenum and tungsten triphenylphosphine complexes (R = Ph, *p*-tolyl) [39]. An X-ray investigation of the tungsten compound $W(CO)_3Br_2(RN_3R)$ (R = *p*-tolyl) showed the metal to be seven coordinate, and the WN_3 metallocycle to be nearly planar. The R–N=N–N=PR_3 ligand cannot exist free and is stabilized through coordination [39].

In some metal complexes, e.g. M(PPh$_3$)Cl(RN$_3$R) (where M = Pt(II), Pd(II) and R = *p*-tolyl) the diaryltriazenido ligand is monodentate, but ^{1}H NMR and other physico-chemical studies indicate fluxional behavior; the nonrigid process occurs via pseudo-pentacoordinate intermediates, containing a chelating bidentate triazenido ligand [16,40].



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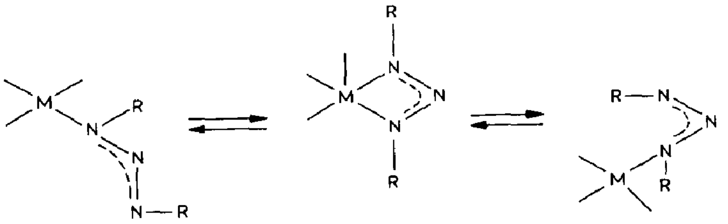
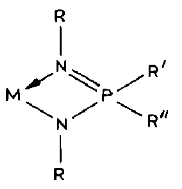


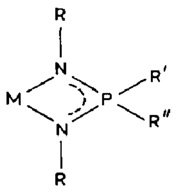
An interesting type of compound is formed by pentaazadiene R–N=N–NH–N=N–R (R = *p*-tolyl) on coordination to nickel(II); the binuclear complex formed contains both four membered [Ni : NN](⊃ N) chelate rings (by coordination of a ligand fragment) and Ni–NNN–Ni bridges [40a].

(b) [M : NN](⊃ P) Systems: diimidophosphinato chelates

Four-membered chelate rings [M : NN](⊃ P), which can be depicted using three canonical forms (**21a–c**), derived from diiminophosphinic (or -phosphoric, -phosphonic) anions (**22**), are obtained by reacting the appropriate N-lithium derivatives with metal halides or halogeno complexes. Thus, Me$_2$P(: NMe)NMeLi with Zeise's salt gave a platinum chelate (**23**) (R = Me) [41].



21a



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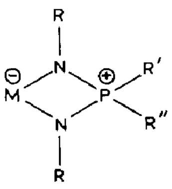
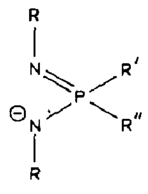


21c



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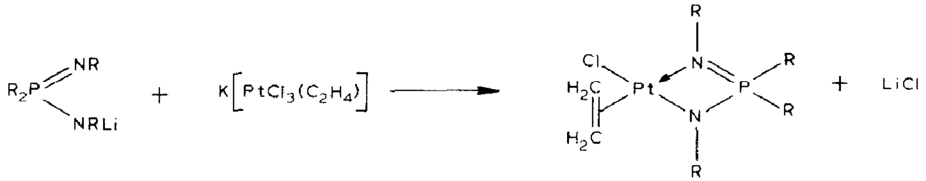

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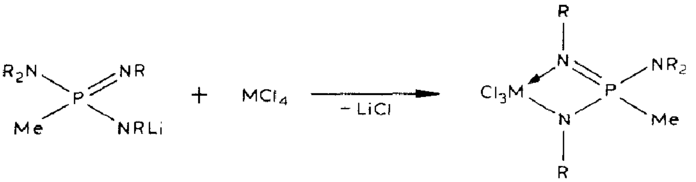
The structure of (**23**) has been confirmed by X-ray diffraction. Similar compounds were obtained with tin(IV), titanium(IV) [42,42a] and zirconium [42b] chlorides (R = $SiMe_3)_3$:



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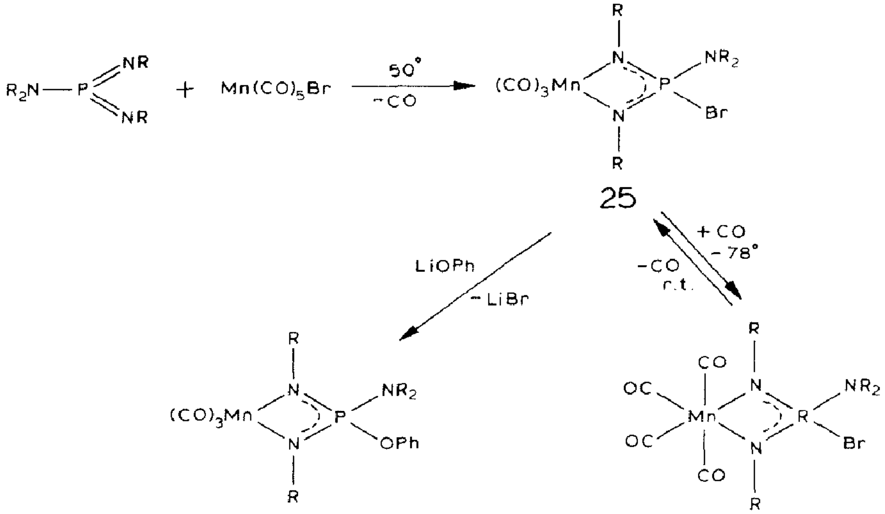
Amino-bis(imino)phosphoranes react with metal carbonyl halides and the resulting chelate ring (**25**) withstands further substituent exchange reactions (R = $SiMe_3$) [43,44].



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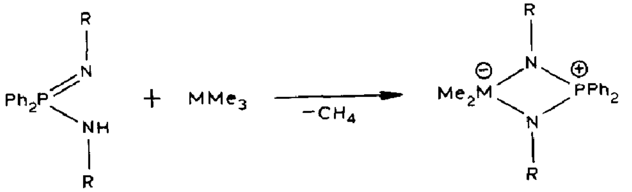
27

An X-ray diffraction analysis of (**26**) showed that the manganese atom exhibits an unusual (for this element) square pyramidal coordination [44].

The mobile hydrogen atom of diiminophosphinato ligands can be replaced by group IIIA trialkylmetal derivatives, to form chelate rings which are capable of being formulated as zwitterionic compounds (**28**) (R = $SiMe_3$, M = Al, In, Ga) [45]:



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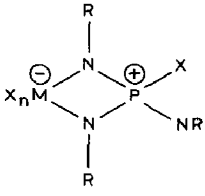
Infrared and NMR spectroscopic data support this formulation. The formation of [M : NN](⊃ P) chelate rings has been found to be quite general and a number of other derivatives, such as (**29**) with MX_n = $AlCl_2$, $FeCl_2$, $TiCl_3$, $NbCl_4$, SnCl (X = Cl, R = R′ = $SiMe_3$) [46], MX_n = $AuMe_2$, (X = Cl, R = R′ = $SiMe_3$) [46a], MX_n = $AlMe_2$ R = Bu^t, NR'_2 = $N(SiMe_3)_2$, $NBu^t(SiMe_3)$ [47], (**30**) (R = Me) [48] and (**31**) (M = Ni, Pd, R = $SiMe_3$) [49] have been reported.



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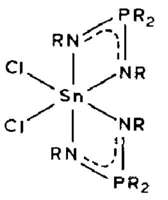

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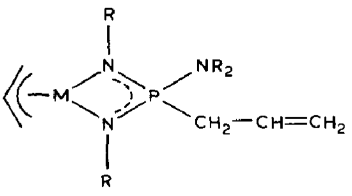

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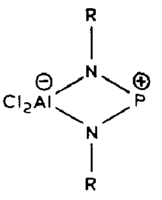
Compounds (**29**) are formed in the reactions of amino-bis(imino)-phosphoranes $R'_2N-P(:NR)_2$ with appropriate metal halides [46,46a] or $AlMe_3$ [47] while (**30**) is obtained from $Me_2P(:NMe)_2Li$ with $SnCl_4$ [48] and (**31**) from $(Me_3Si)_2N-P(:NSiMe_3)_2$ with $M(\eta^3\text{-allyl})_2$ [49].

X-ray diffraction analysis [46,49] confirms the four-membered MN_2P chelate ring structures of (**29**) (M = Ti, X = Cl) and (**31**) (M = Pd). The phosphorus–nitrogen (endocyclic) bond lengths (1.61, 1.59 Å in (**29**) and 1.598Å in (**31**)) indicate a high degree of P–N π-bonding (compare this with the sum of the covalent radii of phosphorus and nitrogen, which is 1.84 Å).

The trimethylsilylated amino-iminophosphine $R_2N-P=NR$ (R = $SiMe_3$) reacts with anhydrous aluminum chloride at 40°, and a dicoordinate phosphorus derivative (**32**) is formed [50], with elimination of RCl.

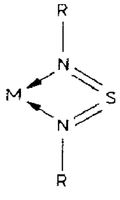


32

The compound is remarkably stable to hydrolysis. The structure has been confirmed by X-ray diffraction [51].

(c) [M : NN](⊃ S) Systems: sulfur diimine chelates

Four-membered [M : NN] (⊃ S) rings (**33**) are formed by bidentate coordination of sulfur diimines (**34**) to some metals. These ligands frequently coordinate as monodentate or bridging to form a large variety of complexes [52]. Bidentate (chelating) behavior is usually observed when R in (**34**) is a bulky organic group (e.g. tert-butyl, mesityl, $SiMe_3$).



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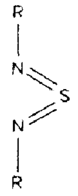


34

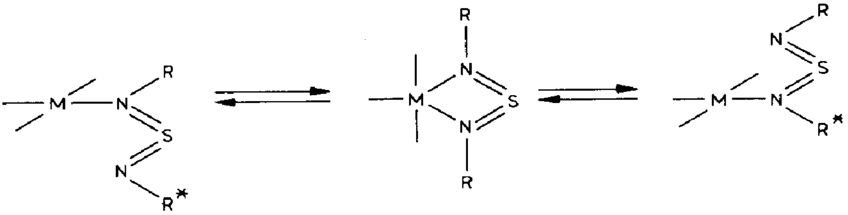
The best examples of such chelates are the Group VI metal carbonyl derivatives $[M(CO)_4(RNSNR)]$ (**33**, M = Cr, Mo, W, R = Bu^t [53,53a,54] and Pr^i [54]). An X-ray diffraction study [55] of (**33**) (M = $W(CO)_4$, R = Bu^t) confirmed the presence of a planar four membered ring, with N–S 1.58 Å, (1.33 Å in the free ligand) and ∠NSN 93.4° (in the free ligand (**34**), R = Me ∠NSN = 113.6°) thus suggesting a certain ring strain, which, however, does not prevent cyclization. These complexes were readily prepared by reacting (**34**) with $M(CO)_6$ (M = Cr, Mo, W) [53,54] but a similar reaction with $Fe_2(CO)_9$ resulted in the rupture of some S–N bonds, with formation of completely different complexes, containing RNS and RNC(O)S ligands [56].

The reduction of $[M(CO)_4(RNSNR)]$ (M = Cr, Mo, W; R = Bu^t) with a potassium mirror in ethereal solvents produces anions with well defined ESR spectra, which suggest that the unpaired electron is localized mainly on the ligand [57].

Trimethylsilylated sulfur diimine, (**34**) (R = $SiMe_3$) has been reported to form a 1 : 1 adduct with $SnCl_4$, which has a chelate structure (**33**) (M = $SnCl_4$) as established by X-ray diffraction [58].

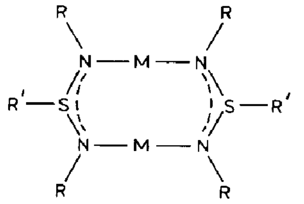
Chelate rings are also present in the complexes *trans*-$[M(CO)(PPh_3)_2(RN{=}S{=}NR)]ClO_4$, M = Rh(I), Ir(I), when R = Bu^t or Pr^i (five coordinate central atom); when R = Me or Et the ligand is monodentate and in solution they are present as two isomers which interconvert by N–N jump, via five-coordinate cyclic complexes [59]. A similar process has been observed for dialkyl- [60] and diaryl- [61,61a] sulfur diimine platinum(II) complexes,

$[PtX_2(RNSNR)L]$ (L = PR_3, AsR_3, SbR_3, SR_2, etc.):



This process starts at temperatures varying between −45° and +60° (depending on the metal and its surroundings); the rate of exchange decreases in the order Rh(I), Ir(I) > neutral Pd(II) > cationic Pt(II) > neutral Pt(II) [59].

Sulfur diimines can be S-alkylated with LiR′ or R′MgX derivatives, to give M[RNS(R′)NR] derivatives (M = Li, MgX) [62–64]. The new anions



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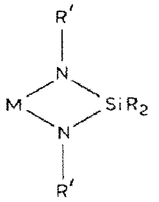
form dimeric bridged Ag(I) and Cu(I) complexes [62,63] with structure (**35**), but chelate ring complexes like $[Pd\{RNS(R^1)NR\}(\eta^3\text{-}R^2C_3H_4)]$ (R = aryl, R^1 = Me, Bu^t, R^2 = H, Me) [65] and $[Rh\{RNS(R')NR\}(CO)_2]$ (R = mesityl, R′ = Bu^t) [66] are known. For the palladium compounds two interconvertive isomers were observed by NMR in solution, the structure of each depending on the orientation of the allyl groups [65]. The rhodium compound has been investigated by X-ray diffraction, which established a symmetrical chelate ring structure of type (**33**) (N–S 1.65 Å, Rh–N 2.06 Å) [66]. Trimethyltin derivatives $[Me_3Sn\{RNS(Me)NR'\}]$ (R,R′ = Bu^t or $SiMe_3$), probably containing five-coordinate tin(IV) in a chelate ring (**33**), have been prepared from $Li[MeS(NR)(NR')]$ and Me_3SnCl [64].

Closely related ligands are the *S*,*S*-dialkylsulfur(VI) diimides, $R_2S(NR')_2$ (R = Me, Et, R′ = $SiMe_3$). These were found to form 1 : 1 adducts with trimethylaluminum which might be chelate compounds containing an [Al : NN]($\supset$ S) ring and five-coordinate aluminum [67].

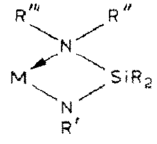
(d) [M : NN]($\supset$ Si) Systems

Four different types of chelate rings (**36a–d**) all described by the

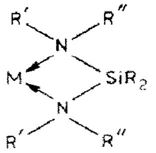
[M : NN](⊃ Si) graph, and containig diimidosilane, diaminosilane and diiminosilane, respectively, can be obtained.



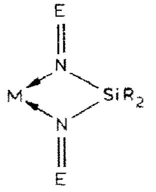
36a



36b

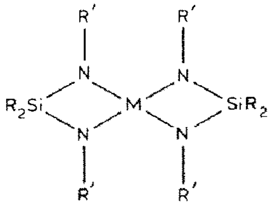


36c



36d

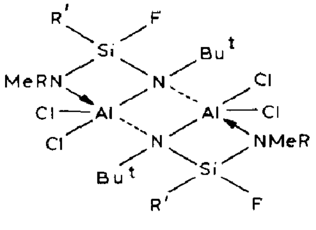
Type (**36a**) with $M = (\eta^5\text{-}C_5H_5)_2Ti$, R = Me and $R' = CMe(CF_3)_2$ has been obtained from $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $Me_2Si[N{=}C(CF_3)_2]_2$ and methyllithium [68]. Several compounds of type (**36a**) ($M = AlMe_2$, $GaMe_2$, $InMe_2$, R = Me, $R' = Bu^t$) have been prepared by three different routes and investigated spectroscopically in considerable detail [68a]. Tin derivatives, (**36a**) and (**37**) (M = Sn, R = Me, $R' = Bu^t$) have also been prepared and investigated in considerable detail [68b,68c]. The reaction of dilithiated $Me_2Si(NHR')_2$ with $TiCl_4$ and $ZrCl_4$ gave spirocyclic derivatives (**37**) (M = Ti, Zr, R = Me, $R' = Pr^i$, Bu^t, $SiMe_3$), both of which have been investigated by X-ray diffraction (Si–N 1.742 Å and 1.753 Å; ∠N–M–N 83.4 and 77.9°, ∠N–Si–N 92.4 and 94.8° for M = Ti and Zr respectively) [69,69a]. Similar compounds (**37**) (M = Ti, Zr, Hf, R = Me, $R' = SiMe_3$) were prepared by treating dilithiated $Me_2Si(NHSiMe_3)_2$ with MCl_4; by changing the molar ratio of the reactants, compounds (**36a**) with $M = ZrCl_2$ and $HfCl_2$ were also obtained [70]. Another derivative of type (**36a**) ($M = TiCl_2$, R = Me, $R' = Bu^t$) has been prepared and investigated by X-ray diffraction [71].



37

A chelate ring of type (**36b**) with $M = V(:NBu^t)Cl_2$, R = Me, $R' = R'' = Bu^t$, $R''' = H$ has been prepared from $Me_2Si(NHBu^t)_2$ and $VO(OEt)Cl_2$ and its structure confirmed by X-ray diffraction [71a]. A related compound (**36b**) ($M = Sn(C_5H_5)$, R = Me, $R' = R'' = Bu^t$, $R''' = H$) was formed in the reaction of $Me_2Si(NBu^t)_2Sn$ (**36a**), (M = Sn(II), R = Me, $R' = Bu^t$) with cyclopentadiene [71b].

The reaction of $(Me_3SiNMe)_2SiFNBu^tLi$ with anhydrous aluminum chloride gave a derivative of (**36b**) with M = $AlCl_2$, which was found, by X-ray diffraction, to have a dimeric structure (**38**) R = $SiMe_3$, R′ = $NMe(SiMe_3)$, containing five coordinate aluminum [72].



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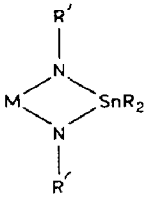
Diaminosilanes $R_2Si(NR'R'')_2$ as donors seem to be too weak and so far no chelate ring of type (**36c**) seems to have been reported, but derivatives of type (**36d**) are known. Thus, the phosphinimino derivative $Me_2Si(-N{=}PMe_3)_2$ reacted with trimethylaluminum, -gallium and -indium to form (**36d**) (M = $AlMe_2^+$, $GaMe_2^+$, $InMe_2^+$, R = Me, E = PMe_3), which are all cationic species [73]; neutral compounds (**36d**) (M = ZnR_2, CdR_2; R = Me, E = PMe_3) were obtained with zinc and cadmium dialkyls [74].

(e) [M : NN](⊃ Sn) Systems

Tin-containing analogues of (**36a**) with structure (**39**) have been prepared

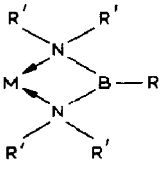


39

by reacting $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with a bis(imino)stannane $Me_2Sn[-N{=}C(CF_3)_2]_2$ and methyllithium [68].

(f) [M : NN](⊃ B) Systems

This type of ring is little known. Tris(dimethylamino)borane $B(NMe_2)_3$



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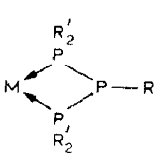
forms a 1 : 2 adduct with $GaCl_3$, for which an ionic structure $[Me_2B(NMe_2)_2GaCl_2]^+GaCl_4^-$, containing a chelate ring of type (**40**) (M = $GaCl_2$, R = NMe_2, R′ = Me) has been suggested [75].

(ii) Phosphorus donor sites

(a) [M : PP](⊃ P) Systems: triphosphine and triphosphido chelates

The graph [M : PP](⊃ P) describes two types of possible chelate ring; (**41**) (derived from triphosphine ligands) and (**42**) (derived from triphosphido ligands).



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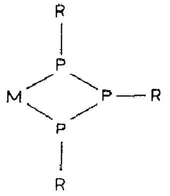

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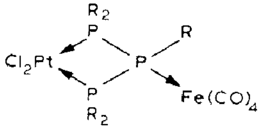
Molybdenum derivatives of type (**41**), *cis*-$(CO)_4Mo(Me_2P–PR–PMe_2)$ (R = Me, Ph, Bu^t), have been obtained by reactions of coordinated ligands; treatment of *cis*-$[(CO)_4Mo(PMe_2H)_2]$ with butyllithium, followed by Bu^tPCl_2 [76] or $MePCl_2$ [77], or by reacting *cis*-$[(CO)_4Mo(PR'_2Cl)_2]$ with Li_2PPh (R′ = Me, Ph) [77].

In compounds of type (**41**) the phosphorus atom P(2) is coordinatively unsaturated and can act as a further donor. Thus, a platinum complex (**41**, M = $PtCl_2$, R = R′ = Ph) can coordinate as a ligand to a $Fe(CO)_4$ group, leading to the formation of (**43**). This compound has been prepared by



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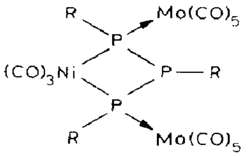


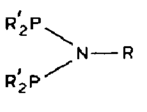
44

reacting $(CO)_4Fe \leftarrow PPh(PPh_2)_2$ with $PtCl_2$ and the structure has been established by X-ray diffraction [78]. Triphosphido chelates (**42**) with M = $(\eta^5\text{-}C_5H_5)_2Ti$ (R = Ph) [79,80] and M = $(\eta^5\text{-}C_5H_5)_2Zr$, $(\eta^5\text{-}C_5H_5)_2Hf$ (R = Me, Et, Ph, Bu^t) [80] have been obtained by reacting bis(cyclopentadienyl) metal dichlorides with alkali metal polyphosphides, $M^I_2(PR)_n$ (M^I = Na, K, Li, n = 3–5) in THF or dioxane.

The chelates (**42**) exhibit donor ability and a dimolybdenum complex (**44**), R = Ph, with $Mo(CO)_5$ groups coordinated at P(1) and P(3) sites, has been prepared and investigated by X-ray diffraction [81].

(b) $[M:PP](\supset N)$ Systems: bis(diphosphino)amine and related chelates

Variously substituted bis(diphosphino)amines (**45**) are versatile ligands, able to form four-membered chelate rings (**46**), with many metals. The substituents at nitrogen and phosphorus may vary considerably to give a large diversity of bis(diphosphino)amine ligands. Of these, bis(difluorophosphino)amines, $(F_2P)_2NR$ (R = Me, Et, Ph), discovered by J.F. Nixon [82] have been the most thoroughly investigated, mainly by R.B. King and his coworkers, and the results were reviewed [83,84]. These are useful chelating ligands, with good σ-donor and π-acceptor properties, able to stabilize low oxidation states.



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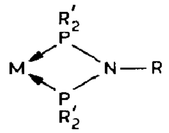


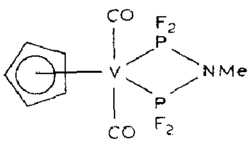
46

Bis(difluorophosphino)amine complexes can be readily obtained by displacement reactions. Thus, *cis*-$[(CO)_4M(F_2P)_2NR]$ (M = Cr, Mo, W, R = Me, Et, Ph) can be prepared by displacing norbornadiene from $C_7H_8M(CO)_4$ [85–87]. The reaction of $RN(PR'_2)_2$ with metal carbonyls $M(CO)_6$ or $C_7H_8M(CO)_4$ is equally useful for the preparation of $[M(CO)_4(R'_2P)_2NR]$ M = Cr, R = H, Me, Ph, R′ = Ph [88,89]; M = Mo, R = H, Me, Et, Pr^n, R′ = Ph [90]; M = Cr, Mo, W, R = Et, R′ = OPh, [91]. Rhodium(I) chelates of $(Ph_2P)_2NR$ (R = Me, Et, Ph, *p*-tol.) have also been prepared [91a].

Group VI metal hexacarbonyls react with excess ligand under UV irradiation, losing all six CO groups, to form air stable tris-chelates $M[(R'_2P)_2NR]_3$ (M = Cr, Mo, W; R′ = F, R = Me [92,93] R = Ph [94]). The co-condensation of metal vapor with (**45**) or with mixtures of (**45**) and dimethylaminodifluorophosphine, $Me_2N{-}PF_2(L)$ affords $M[(F_2P)_2NMe]_3$ (M = Cr) [95,96] or other interesting mixed ligand complexes like $L_4Cr(F_2P)_2NMe$ [96] and $L_3Fe(F_2P)_2NMe$ [97], containing only phosphorus atoms coordinated to the metal center. The X-ray crystal structure determination found a very small P–Cr–P angle (66°) in the $[Cr:PP](\supset N)$ chelate ring [95].

The *N,N*-bis(diphenylphosphino)-*N′,N′*-dimethylhydrazine (DPH) complexes, $[M(CO)_5(DPH)]$, eliminate carbon monoxide to form $[M(CO)_4DPH]$ (M = Cr, Mo, W) containing a chelate ring (**46**), with R = NMe_2, R′ = Ph [97a].

Vanadium [98], molybdenum [99], tungsten [99] and manganese [99,100] cyclopentadienyl derivatives (**47**–**49**) have also been reported. An iron derivative [η^5-$C_5H_5Fe\{(F_2P)_2NMe\}$(pyrrole)] has also been reported [101].



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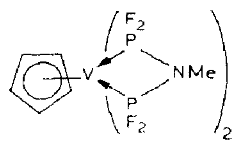

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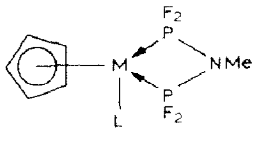
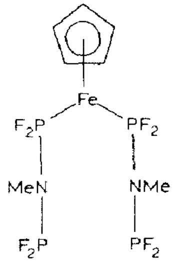


(M = Mo, W)

49

The ligands (**45**) may also be monodentate, as in some η^5-cyclopentadienyliron complexes, (**50**) [102], and frequently form bridges in dinuclear compounds with and without metal–metal bonds. Thus, metal–metal bond, five-membered metallocycles based on skeleton (**51**) can be cited for molybdenum (Mo≡Mo triple bond) [103], iron [104,105], cobalt [106–109] and rhodium [110,111]. An eight-membered metallocycle, (**52**) (R = Me), without metal–metal bonds is known for iron [105].



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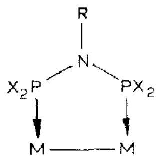

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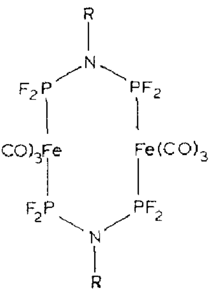


52

An excess of ligand can open the four-membered chelate ring, making the bis(difluorophosphino)amine monodentate; this reaction was used for the preparation of mixed ligand complexes [87]:

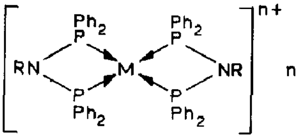
$$cis\text{-}PhN(PF_2)_2Cr(CO)_4 + PhN(PF_2)_2 \rightarrow trans\text{-}\{PhN(PF_2)_2\}_2Cr(CO)_4$$

$$cis\text{-}MeN(PF_2)_2Cr(CO)_4 + PhN(PF_2)_2 \rightarrow trans\text{-}\{PhN(PF_2)_2\}\text{-}\{MeN(PF_2)_2\}Cr(CO)_4$$

Other nucleophilic ligands, like triphenylphosphine, can effect both ring opening reactions to give derivatives with monodentate ligand $\{MeN(PF_2)_2\}Cr(CO)_4PPh_3$ (major product), and CO group replacement, to give $\{MeN(PF_2)_2\}Cr(CO)_2(PPh_3)_2$ [87].

Chiral bis(diphenylphosphino)aminoacid esters $(Ph_2P)_2N-CHR-COOMe$ ($R = H$, Me, Pr^i, CH_2Ph) react with $(\eta^5-C_5H_5)M(CO)_3Cl$ ($M = Mo$, W) and other metal derivatives to form diastereoisomeric derivatives of the chelate ring (**46**) some of which can be separated [112,113].

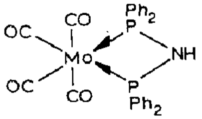
Square planar chelates (**53**) of iridium(I) ($R = H$, $X = Cl^-$, BPh_4^-, $n = 1$) [114], rhodium(I) ($R = H$, $X = Cl^-$, PF_6^-, $n = 1$) [115–117], nickel(II) ($R =$ Ph, $n = 2$), palladium(II) ($R = Ph$, $n = 2$) [118] and platinum(II) ($R = H$, $X = Cl$, $n = 2$) [114] have been prepared using bis(diphenylphosphino)amines as ligands. An interesting feature of (**53**) ($M = Ir$, Rh) is their ability for oxidative addition, resulting in adduct formation with one mole of CO [114,115], O_2, S_2, [115], and having square pyramidal geometry.



53

Cyclopentadienylnickel compounds $[(\eta^5-C_5H_5)Ni(Ph_2P)_2NR]^+X^-$ ($R =$ Me, Ph, $X = Cl^-$, BF_4^-) have also been reported. Such compounds undergo chelate ring opening with cyanide, to form $[(\eta^5-C_5H_5)Ni(Ph_2P-NR-PPh_2)(CN)]$ [119].

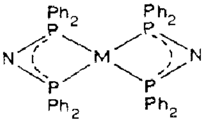
A molybdenum carbonyl derivative, *cis*-$[Mo(CO)_4(Ph_2P)_2NH]$ (**54**), was formed by intermolecular condensation of the coordinated aminophosphine ligands in *cis*-$[Mo(CO)_4(PPh_2NH_2)_2]$ on treatment with $BF_3.OEt_2$ [120].



54

The chromium analogue of **54** has also been prepared [120a]; the compound $[(CO)_4Cr(Ph_2P)_2NH]$ can be metalated with *n*-BuLi and further treatment with $ClPPh_2$ gives $[(CO)_4Cr(Ph_2P)_2N-PPh_2]$ [120a]. Bis(diphenylphosphino)amine, $(Ph_2P)_2NH$, reacts with metal carbonyls $M(CO)_6$ ($M = Cr$, Mo) to form bis-chelate derivatives, *cis*-$[(CO)_2M\{(Ph_2P)_2NH\}_2]$ ($M = Cr$, Mo) [121] but dinuclear complexes with PNP ligand bridges were obtained with $Fe(NO)_2(CO)_2$ [121] and $[Rh(CO)_2Cl]_2$ [122]. With $Co_2(CO)_8$ the ligand $(Ph_2P)_2NH$ formed a bridged compound, $Co_2(CO)_6\{(Ph_2P)_2NH\}$, containing a five-membered metallocycle of type (**51**) [123].

Neutral chelate rings, (**55**), ($M = Pt$, Pd), were synthesized from lithiated bis(diphenylphosphino)amine, $(Ph_2P)_2N^-Li^+$, in reactions with K_2PtCl_4 and $PtCl_2$ [124].



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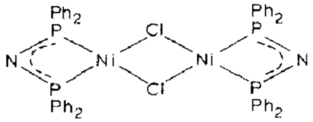
With nickel(II) chloride, in the presence of trimethylphosphine, a dimeric complex (**56**) is obtained [124], while $Ph_3P.AuCl$ forms a dinuclear metallocycle **57** [125].



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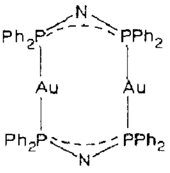

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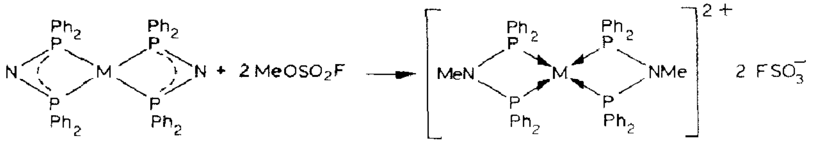
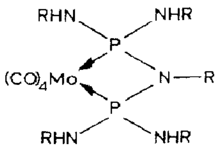
The neutral Pt(II) and Pd(II) complexes (**55**) can be *N*-methylated with $MeOSO_2F$, to yield cationic species of type (**53**) [124].



The X-ray structure determination of $[Pd\{(Ph_2P)_2NMe\}_2](FSO_3)_2.2MeNO_2$ thus obtained, established that the N, P, and Pd atoms and the Me groups are all coplanar [124].

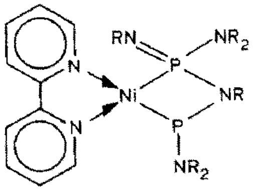
Another compound containing a [Mo : PP]($\supset$ N) chelate ring, *cis*-$(CO)_4Mo\{[(PhNH)_2P]_2NPh\}$ (structure (**58**), R = Ph), has been obtained by three different routes: the reaction of *cis*-$[(CO)_4Mo\{(Cl_2P)_2NPh\}]$ with aniline, by treatment of *cis*-$[Mo(CO)_4(PCl_3)_2]$ with aniline and from



58

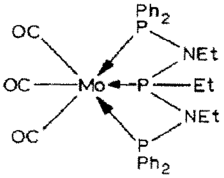
$[Mo(CO)_4(NBD)]$ (NBD = norbornadiene) with $P(NHPh)_3$ [126]. The structure of (**58**) (R = Ph) has been determined by X-ray diffraction [126].

A rather unusual compound, (**58a**) ($R = SiMe_3$), containing a formally pentavalent phosphorus donor, has been prepared by treating $Ni(COD)_2$ (COD = cyclooctadiene-1,5) with $R_2N{-}P{=}NR$ and then with bipyridine [126a].



58a

The [M : PP]($\supset$ N) ring can be incorporated in bicyclic systems. Thus, the terdentate ligand $Ph_2P{-}NEt{-}PPh{-}NEt{-}PPh_2$ replaces three carbonyl groups in $Mo(CO)_6$ to form the bicyclic system (**59**) [127].



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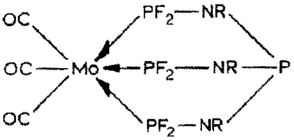
An unexpected transformation of the ligand $(F_2P)_2NPh$ (**45**), (R = Ph, R′ = F) occurred during its reaction with *fac*-$[(MeCN)_3Mo(CO)_3]$ in acetonitrile. Instead of the expected derivative of the chelate ring (**46**), a novel tridentate ligand (unknown in the free state), coordinated to molybdenum in $P(NPhPF_2)_3Mo(CO)_3$, was formed. The structure (**60**) of this compound has been established by X-ray diffraction [128].



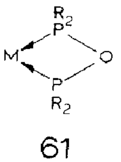
60

In fact, compound (**60**) contains two new chelate rings (six-membered) [M : PP]($\supset$ NPN) unknown in any other compounds. The bridgehead phosphorus(III) atom can further coordinate, and an iron complex, $(CO)_4Fe \cdot P(NPHPF_2)_3Mo(CO)_3$, is obtained by reacting (**60**) with $Fe_2(CO)_9$ in refluxing diethyl ether [129].

The data presented above demonstrate both the versatility of bis(diphosphino)amine ligands (**45**), and the complexity of their metal chemistry, which is caused by various coordination patterns (bidentate chelating or bridging and monodentate) and sometimes by unexpected reactions.

(c) [M : PP]($\supset$ O) Systems: diphosphineoxide chelates

Diphosphineoxide chelates (**61**) have only recently been obtained and characterized structurally. The first compound (**62**) (M = Mo, R = Ph) has



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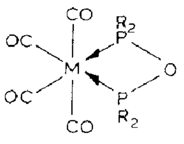
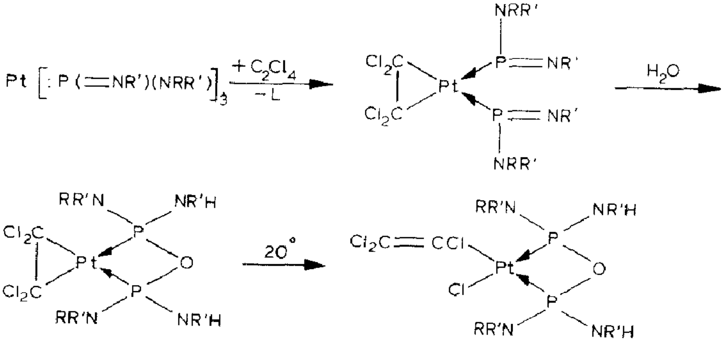


62

been obtained by an intramolecular condensation of coordinated ligands in $[Et_3NH]^+[cis\text{-}Mo(CO)_4(PPh_2O)_2H]^-$ under the action of acetyl chloride, phosphorus trichloride or $(MeO)P(O)Cl_2$ [120]. Similar compounds (**62**) (M = Cr, Mo, W, R = Ph) are obtained by a thermal reaction of $[M(CO)_5PPh_2P(O)Ph_2]$ [130]. The structure has been confirmed by X-ray diffraction of two compounds (**62**), with M = Cr and Mo, R = Ph. The P–O distances are 1.66 and 1.67 Å and ∠P–O–P 103.3 and 100.2° respectively; the four membered [M : PP]($\supset$ O) chelate ring is planar [131].

Other compounds containing this ring, (**63**) and (**64**), were formed in a series of successive transformations of a platinum complex of an imino-aminophosphine complex [132] (R = $SiMe_3$, R′ = Bu^t). The structure of (**64**) has been determined by X-ray diffraction [132].



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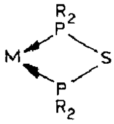
64

A rhenium compound $HRe[P(OMe)_3][(MeO)_2POP(OMe)_2]$, formed in some reactions of rhenium complexes with $P(OMe)_3$ [133] probably contains a ring (**61**) (R = OMe).

For monodentate and bridging coordination of $(Ph_2P)_2O$ see ref. [134].

(d) [M : PP](⊃ S) Systems: diphosphinosulfide chelates

Chelate rings (**65**) were first obtained in the reaction of $F_2P{-}S{-}PF_2$ with [Mo(CO)$_4$(NBD)] (NBD = norbornadiene) which gave *cis*-[(CO)$_4$Mo(F$_2$P-SPF$_2$)], (**66**) (R = F) [135]. The reaction of *cis*-[(CO)$_4$Mo(PPh$_2$Cl)$_2$] with H_2S produced (**66**), R = Ph [120]; this compound was investigated by X-ray diffraction [136]; the chelate ring is planar, with bond angles P–Mo–P 72.02° and P–S–P 86.9° indicating ring strain.



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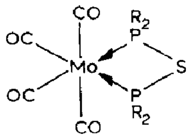

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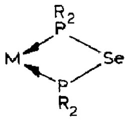
(e) [M : PP](⊃ Se) Systems: diphosphinoselenide chelates

The only known compound containing the chelate ring (**67**) is *cis*-[(CO)$_4$Mo(F$_2$PSePF$_2$)] prepared from [Mo(CO)$_4$(NBD)] and $F_2P{-}Se{-}PF_2$ [135].



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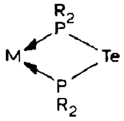
(f) [M : PP](⊃ Te) Systems: diphosphinotelluride chelates

The tellurium analogues (**68**) of the above rings, were prepared by similar methods. A chromium derivative (**68**) M = Cr(CO)$_4$, R = Bu^t [137,138] was obtained in 70% yield from [Cr(CO)$_4$(NBD)] at room temperature and molybdenum and tungsten analogues (**68**) M = Mo(CO)$_4$ and W(CO)$_4$, R = Bu^t were prepared similarly from [Mo(CO)$_4$(NBD)] and [W(CO)$_4$(MeCN)$_2$] or [W(CO)$_3$(MeCN)$_3$], respectively [138,138a].



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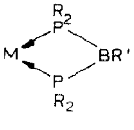
(g) [M : PP]($\supset$ B) Systems: diphosphinoborine chelates

The four membered [M : PP]($\supset$ B) system (**69**) is represented by tetracarbonyl–chromium, –molybdenum and –tungsten chelates, (**70**) (R = Ph), prepared by treating *cis*-$[(CO)_4M(PPh_2Li)_2]$ with $Cl_2B–NEt_2$ [139].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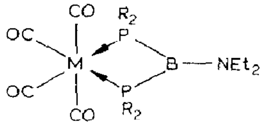
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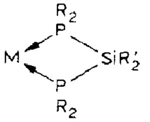
Although these chelate complexes are crystalline, no X-ray structure analysis was performed and the new compounds were characterized only by spectroscopic methods–IR, ^{31}P, ^{11}B and ^{1}H NMR.

(h) [M : PP]($\supset$ Si) Systems: diphosphinosilane chelates

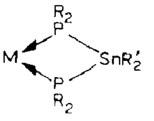
There is only one report [140] concerning chelate rings of type (**71**)


71

derived from diphosphinosilanes. Thus, $Me_2Si[PBu^t(SiMe_3)]_2$ reacted with nickel tetracarbonyl to form (**71**), M = $Ni(CO)_2$.

(i) [M : PP]($\supset$ Sn) Systems: diphosphinostannane and related chelates

Four membered chelate rings [M : PP]($\supset$ Sn) were described as early as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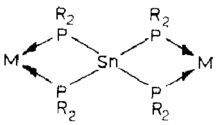
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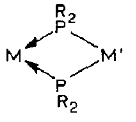
1968, when a nickel compound (**72**) M = $Ni(CO)_2$, R = Ph, R′ = Me was prepared from the appropriate diphosphinostannane and nickel tetracarbonyl [141]. More recently, a chromium complex (**72**) M = $Cr(CO)_4$, R = Bu^t, R′ = Me was prepared similarly, using $Cr(CO)_6$ or $[Cr(CO)_4(NBD)]$ [142]. Tetraphosphinostannanes, $Sn(PR_2)_4$, form rather unusual spirobicyclic chelates (**73**), in which the tin atom is the spirocenter and two metal atoms are incorporated in the rings. Thus, with the appropriate metal carbonyl derivatives, compounds (**73**) with R = Ph, M = $Fe(NO)_2$, Co(NO)(CO), $Ni(CO)_2$ and $M'(CO)_4$ (M′ = Cr, Mo, W) have been obtained [143].

(j) [M : PP](⊃ M′) Systems: metaldiphosphido chelates

Transition metal diphosphides can act as chelating ligands to form chelate



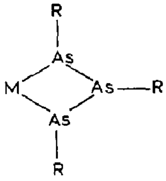
74

rings of type (**74**). Thus the reaction of *cis*-$[(CO)_4Mo(PMe_2Li)_2]$ with $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ gave cyclopentadienylmetaldiphosphido chelates of molybdenum, (**74**), M = $Mo(CO)_4$, M′ = $TiCp_2$, $ZrCp_2$, R = Me [76]; M′ = $TiCp_2$, $ZrCp_2$, R_2 = PhH, $Ph(SiMe_3)$ [144]. This type of compound was considerably extended recently, by the synthesis of many new derivatives, (**74**), with M = $Ni(CO)_2$, M′ = $Th(\eta^5\text{-}C_5H_5)_2$, R = Ph [144a], M = $W(CO)_4$ or $Fe(CO)_3$, M′ = $ZrCp_2$ and $Ti(\eta^5\text{-}C_5Me_5)_2$, R = Ph or Cy [144b], M = $Mo(CO)_4$, $Fe(CO)_3$, $Ni(CO)_2$, M′ = $HfCp_2$, R = Et [144c], M = $W(CO)_4$, M′ = $Re(CO)_3H$, R = Ph [144d]. The structures of some of these compounds were investigated by X-ray diffraction.

(iii) Arsenic donor sites

(a) [M : AsAs](⊃ As) Systems: triarsenido chelates

Although analogy with polyphosphido (and polyphosphine) chelates can be expected, arsenic systems have been much less investigated, and only chelate rings (**75**) containing the triarsenido ligand have been reported.



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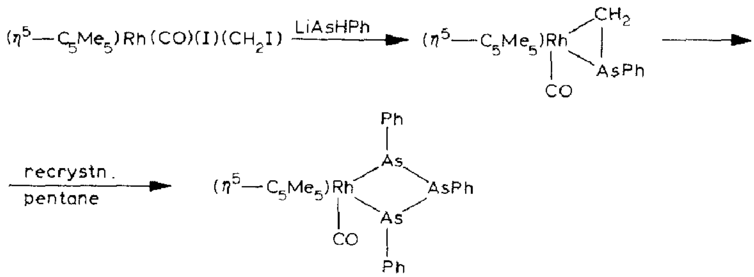
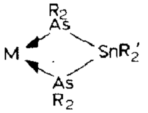
Thus, dipotassium polyarsenides $K_2(AsEt)_n$ ($n = 2$ and 5) react with biscyclopentadienyltitanium dichloride, to give the same product, (**75**), R = Et, M = $(\eta^5\text{-}C_5H_5)_2Ti$ [145]. A rhodium derivative, (**75**), R = Ph, M = $Rh(\eta^5\text{-}C_5Me_5)(CO)$, was formed in the following reaction [146]:



the chelate ring structure of this compound has been confirmed by X-ray diffraction [146].

(b) [M : AsAs](⊃ Sn) Systems: diarsinostannane chelates

The analogy with phosphorus is also extended to substituted stannanes.



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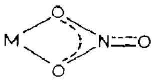
Thus, a chelate ring (**76**) $R = R' = Me$, $M = Cr(CO)_4$ has been reported [141].

(iv) Oxygen donor sites

(a) [M : OO](⊃ N) Systems: nitrato and nitrito chelates

Four membered rings [M : OO](⊃ N), (**77**) and (**78**) are formed by bidentate coordination of nitrate and nitrito groups, respectively. Although this type of coordination is somewhat surprising, it is quite common [147], especially in complexes of metal ions with large coordination numbers [148]. An exhaustive list of complexes containing chelating nitrato ligands cannot be given here, but this type is well illustrated by the structures of numerous anhydrous metal nitrates [147–151], nitrato complexes of lanthanoids, e.g.



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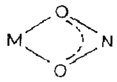


78

$[La(NO_3)_3(H_2O)_5] \cdot H_2O$ [152]
$[La(NO)_3)_3(TEG)]$ (TEG = tetraethyleneglycol) [153]
$[La(NO_3)_3\{OP(NMe_2)_3\}_3]_2$ [154]
$[La(NO_3)_3(DPPB)]$ (DPPB = 2,6-diacetylpyridine-bis(benzoic acid hydrazone) [155]

$[Ce(NO_3)_3(H_2O)_5] \cdot H_2O$ [156]
$(BIPY \cdot H)^+[Ce^{III}(NO_3)_4(H_2O)(BIPY)]$ (BIPY = bipyridyl) [157]
$K_2[Ce(NO_3)_6]$ [158]
$(Ph_4As)_2[M(NO_3)_5]$ (M = Pr, Nd, Sm, Eu [159], Ho, Er, Tm, Yb [160])
$(BIPY \cdot H)^+[Nd(NO_3)_4(H_2O)_2(BIPY)]$ [161]
$La(NO_3)_3L$ (L = macrocyclic ligand) [162]
$(Ph_4As)_2[Eu(NO_3)_5]$ [163]
$K_2[Er(NO_3)_5]$ [164]
$(Ph_4As)_2[Er(NO_3)_5]$ [160]
$M(NO_3)_2 \cdot 3DMA$ (M = Er, Sm; DMA = dimethylacetamide) [165]
$[Yb(NO_3)_3(DMSO)_3]$ (DMSO = dimethylsulfoxide) [166]
$[Yb(NO_3)_3(H_2O)_4]NO_3 \cdot 2BIPY$ [161]
nitrato complexes of actinoids e.g.:
$Th(NO_3)_4 \cdot 3OP(NMe_2)_3$ [167]
$(BIPY \cdot H)^+ [Th(NO_3)_6]NO_3$ [168]
$UO_2(NO_3)_2 \cdot 6H_2O$ [169]
$[UO_2(NO_3)_2(H_2O)]_2 \cdot 2IMIDAZOLE$ [170]
$UO_2(NO_3)_2 \cdot 2THF$ [171]
$UO_2(NO_3)_2 \cdot OP(OMe)_3$ [172]
$UO_2(NO_3)_2 \cdot 2OPBu_3$ [173]
$UO_2(NO_3)_2 \cdot 2OPPh_3$ [174]
$(CHOLINE)_2[(UO_2)_2(NO_3)_4(\mu\text{-}OH)]_2$ [175]
$NpO_2(NO_3)_2 \cdot 2OPPh_3$ [174]
$Rb[NpO_2(NO_3)_3]$ [176]

Ring forming bidentate coordination of nitrato groups has also been found in chelate complexes containing bismuth, e.g. $Cs_2[Bi(NO_3)_5] \cdot H_2O$ [177], iron, e.g. $(Ph_4As)[Fe(NO_3)_4]$ [178] and $(NO^+)_3[Fe(NO_3)_4]_2(NO_3)$ [179], cobalt, e.g.
$Co(NO_3)_2 \cdot 2OP(NMe_2)_3$ [180]
$Co(NO_3)_2 \cdot 2OPMe_3$ [181]
$Co(NO_3)_2 \cdot 2OPPh_3$ [182]
$[Co(NO_3)_3MeCN][CoP(OCH_2)_3CMe]_5$ [183]
$Co(NO_3)_2 \cdot 2DEMP$ (DEMP = 1H-3,5-diethyl-4-methylpyrazole) [184]
nickel, e.g.
$Ni(NO_3)_2 \cdot 2DEMP$ [185]
$Ni(NO_3)_2 \cdot DAPA$ (DAPA = 2,6-diacetylpyridine-bis(anyl)) [186]
$Ni(NO_3)_2 \cdot DMPE$ (DMPE = 3,5-dimethylpyrazol-1-yl-methylaminoethane) [187]
copper, e.g.
$Cu^I(NO_3) \cdot 2PPh_3$ [188]
$Cu^{II}(NO_3)_2 \cdot 2DEMP$ [189]
and various platinum metals (for review see ref. [190]).

Bidentate coordination of nitrato groups also occurs in some organometallic nitrates, e.g. $(\eta^5\text{-}C_5Me_5)Rh(NO_3)_2$ [191] and various organotin compounds like:

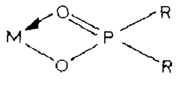
$[Ph_2Sn(NO_3)(DMSO)](NO_3)$ [192]
$[Ph_2Sn(NO_3)(ABT)]$ (ABT = 2-aminobenzenethiazolato) [193]
$[Ph_2Sn(NO_3)(OPPh_3)]$ [194]
$[Ph_2Sn(NO_3)_2(OAsPh_3)]$ [195]
$[Ph_2Sn(NO_3)(OAsPh_3)]_2(C_2O_4)$ [196]
$[Ag(PPh_3)_4][PhSn(NO_3)_2(Cl, NO_3)]$ [197]

Chelating coordination of nitrito groups, as shown in (**78**), has been observed in $[Ni(NO_2)_2(TMED)]$ (TMED = tetramethylethylenediamine) [198], *cis*-$[Zn(ENDA)_2(NO_2)](NO_2)$ (ENDA = ethane-1,2-diamine) and *trans*-$[Zn(DMED)(NO_2)_2]$ (DMED = *N*,*N*-dimethylethane-1,2-diamine) [199] $[Ni(DPED)_2(NO_2)Cl]$ (DPED = *meso*-1,2-diphenylethane-1,2-diamine) [200] and *cis*-$[Ni(MIMD)_4(NO_2)]NO_3 \cdot 2MeOH$ (MIMD = 2-methylimidazole) [201].

In some case nitro derivatives, RNO_2, in *aci*-form, like the nitromethylbenzenato $PhCH_2NO_2^-$ group, can coordinate in the same manner as nitrato groups, to form chelate rings, as found in $[Ni(PhCH_2NO_2)_2 \cdot TMED]$ (TMED = tetramethylethylenediamine) [202].

(b) [M : OO](⊃ P) Systems: phosphinato and related chelates

Various oxygen-containing anions of phosphorus, $R_2PO_2^-$, including phosphinates (R = alkyl, aryl), hypophosphites (R = H), phosphoric acid esters (R = OR′), fluorophosphates (R = F), or orthophosphates ($R = O^-$) can coordinate as bidentate ligands, to form chelate rings, represented as (**79a**) or better as (**79b**) (due to symmetrical structure of the OPO fragment). These phosphorus–oxygen ligands seem, however, to act preferentially as bridge forming groups (**80**) [203], leading to formation of dimers, (**81**) (M = Cr, R = Ph [204], M = Au, R = OPh [205]), trimers [206] and polymers, (**82**) [203,207]. The presence of single or multiple metal–metal bonds greatly favors the bridge formation, and several examples of ring systems such as (**83**) are now known (e.g. M = Mo [208,209], Pt [210], Rh [211]). The simultaneous presence of bridging and chelating R_2PO_2 groups in a compound seems possible [207].



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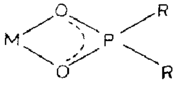

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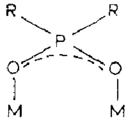

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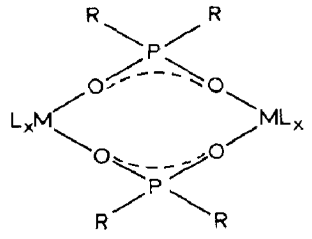

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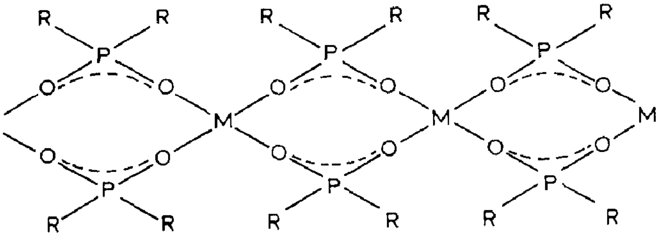

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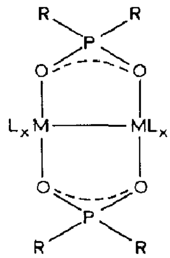


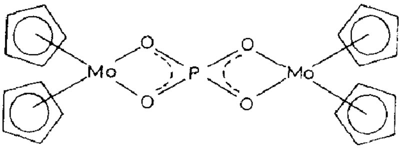
83

Many dialkyl(aryl)phosphato complexes $M[O_2P(OR)_2]_n$, (e.g. $n = 2$, M = Mn [212], Fe [213], Cu [212–214]; $n = 3$, M = Al, Ga, In, Sc, Y, Dy, Ti, Cr, Fe [212–216], Nd [217]; $n = 4$, M = Th, U [216,218], UO_2 [218a]) and their amine adducts, (e.g. $Co[O_2P(OR)_2]_2 \cdot 2L$ where L = py, β-picoline, γ-picoline, isoquinoline) [219], phosphonato complexes $M[O_2P(OR)R']_n$ (e.g. $n = 2$, M = Fe, VO [220]; $n = 3$, M = Sc, Y, lanthanide [221]) and phosphinato complexes $M[O_2PR_2]_n$ (e.g. $n = 2$, M = Cr, Mn, Fe, Ni, Cu [222]; $n = 3$, M = Y, lanthanide [223]) have been prepared. Early workers [224] suggested monomeric chelate ring structures (type (**79**)) but the insolubility of these materials is more in favour of polymeric structures (based upon bridging ligands, type (**80**)) [203,207]. Because of the impossibility of obtaining single crystals and carrying out an X-ray diffraction investigation of these materials, no unambiguous structural characterization was possible. The compound $UO_2[O_2P(OBu^n)_2]_2$ has, however, been investigated by X-ray diffraction, and the polymeric structure of type (**82**) (M = UO_2, R = OBu^n) has been confirmed [218a].

An authentic example of a phosphato chelate ring system, (**79**) (R = O^-) confirmed by X-ray diffraction, [225] is the compound $[Co(PO_4)(NH_3)_4] \cdot 3H_2O$. It contains a strained four-membered ring, with ∠O–P–O 97.7° and ∠Co–O–P 93.1°. Probably similar structures have *cis*-[Co(CYCLEN)(PO_4)] (CYCLEN = 1,4,7,9-tetraazacyclododecane) [226] and *cis*-[Co(ENDA)(PO_4)] (ENDA = ethane-1,2-diamine) [226,227].

A compound containing the ring (**79**), namely $Cu[O_2P(OSiMe_3)_2]_2$ has also been claimed; it was obtained from $OP(OSiMe_3)_3$ and $Cu(OAc)_2$ [228].

Unusual coordination (double bite chelating) of the phosphato group, as



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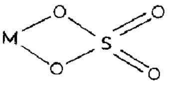
shown in (**84**) was found by X-ray diffraction in $[Mo_2(\eta^5\text{-}C_5H_5)_4(PO_4)](PF_6)_2$ [229].

(c) [M : OO](⊃ S) Systems: sulfato and related chelates

Some similarity in the coordinating properties of sulfato, phosphato and nitrato ligands can be expected. Bidentate coordination of sulfato groups should lead to four-membered rings (**85**).



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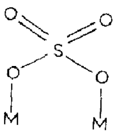

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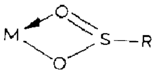

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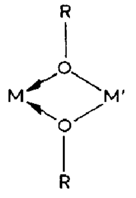
Authentic examples of such chelate complexes, based upon X-ray diffraction studies, are: $K_3[Nb(SO_4)_4]$ (with dodecahedral coordination around niobium, produced by chelating SO_4 ligands) [230]; $(guanidinium)_2[Zn(SO_4)_2]$ (with tetrahedrally coordinated zinc) [231] and $Th(SO_4)_2 \cdot 8H_2O$ (ten-coordinated thorium from two chelating SO_4 ligands and eight coordinated water molecules) [232]. On the basis that vibrational spectra seem to allow one to distinguish between bidentate chelating (**85**) and bridging (**86**) sulfato groups [233,234], many more examples of bidentate coordination (**85**) have been reported in the literature. Thus, in $[Fe(LNO)(SO_4)]$ and $[Ni(LNO)(SO_4)]$ (where LNO = 2,6-lutidine-*N*-oxide) [235], $[Co(en)_2(SO_4)]X$ ($X = Br^-$, ClO_4^-) [236], $[Pd(PHEN)]SO_4$, $[Pdpy_2SO_4]$ and $[Pd(DMSO)_2SO_4]$ [237], $[Cu(DMP)SO_4]$ and $[Zn(DMP)SO_4]$ (DMP = 2,9-dimethyl-1,10-phenanthroline) [238] and $[Pt(PPh_3)_2SO_4]$ [239–241], the sulfato groups are believed to be chelating (structure (**85**)). In compounds containing metal–metal bonds, e.g. in the anion $[Mo_2(SO_4)_4]^{4-}$ [242], the sulfato ligand coordinates as bridging (**86**).

The coordinating properties of the sulfato groups are much more numerous and a classification of sulfate structures, based on these, has been attempted [243].

In sulfinato complexes [244] among other coordinating possibilities, chelating behavior (as shown in (**87**)) is observed; examples are [Ni(BIPY)RSO_2] [245] and [Fe(BIPY)RSO_2] (R = *p*-tolyl) [246].

(d) [M : OO](⊃ M') Systems: metal alkoxo chelates

Alkoxo groups in metal alkoxides can use the electron lone pairs of oxygen to coordinate to further metal atoms, and this often leads to chelate rings, (**88**);



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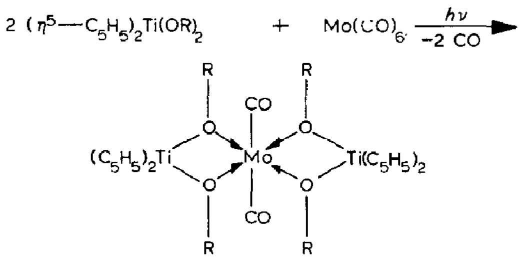
Thus, bis(cyclopentadienyl)titanium diphenoxide reacts with molybdenum hexacarbonyl, to form a bis-chelate complex [247].

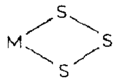


This behavior is common in double metal alkoxides. Among the compounds reported in the literature, [Ln{Al$(OR)_4$}$_3$] (Ln = lanthanoid) [248], [M{Al$(OPr^i)_4$}$_n$] (M = Cr, Fe, $n = 3$; M = Mn, Co, Ni, Cu, $n = 2$) [249], [M{M'$(OPr^i)_6$}$_2$] (M = Mg, Ca, Sr, Ba, M' = Nb, Ta) [250], and [$(Pr^iO)_3M(\mu\text{-}OPr^i)_2Be(\mu\text{-}OPr^i)_2Al(OPr^i)_2$] (M = Ti, Zr, Hf) [251] can be cited. Many more examples can be found in the book of Bradley et al. [252]. In these compounds an alkoxo anion like $[Al(OR)_4]^-$ or $[Nb(OR)_6]^-$ can be regarded as the chelating ligand; an alternative view is to consider these compounds as alkoxo-bridged polynuclear oligomers, without defining a ligand and a central atom.

(v) Sulfur donor sites

(a) [M : SS](⊃ S) Systems: trisulfido chelates

A trisulfido chelate ring (**89**), M = Ti(η^5-C_5H_5)$_2$, was suggested some time ago [253], but this report has not been confirmed. Bis(pentamethylcyclopentadienyl)titanium dichloride reacted with dilithium disulfide to form



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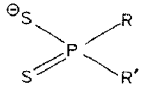
$(\eta^5\text{-}C_5Me_5)_2TiS_3$, the structure of which has been confirmed by X-ray diffraction [254]. It was recently shown that $(\eta^5\text{-}C_5Me_5)_2MCl_2$ (M = Ti, Zr, Hf) react with Li_2S_3, Li_2S_5 or $Li[HBEt_3]$ and excess sulfur, to form $(\eta^5\text{-}C_5Me_5)_2MS_3$, containing four-membered chelate rings (**89**) [255].

(b) [M : SS](⊃ P) Systems: dithiophosphato, dithiophosphinato and dithiophosphonato chelates

Dithiophosphorus anions (**90**) (R, R′ = alkoxy, aroxy [dithiophosphates], R, R′ = alkyl, aryl [dithiophosphinates], R = alkyl, aryl, R′ = alkoxy, aroxy [dithiophosphonates]) form an extensive class of metal complexes.



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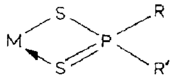

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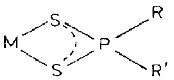

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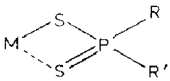
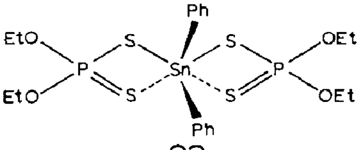


92

The chemistry of transition metal dithiophosphates [256] and dithiophosphinates [257] was reviewed some years ago, whereas that of main group metal dithiophosphate derivatives was reviewed quite recently [258]. A large amount of literature dealing with these compounds has been published in the last fifteen years; it cannot possibly be fully surveyed here and indeed could form the subject matter of a large review in itself.

Dithiophosphorus ligands exhibit a remarkable diversity of coordination pattern [7]; of interest here is the bidentate, chelating behavior. Formulae (**91a**) and (**91b**) are usually considered to be equivalent, and represent isobidentate coordination, i.e. symmetrical bonding of the dithiophosphorus fragment to the transition metal atom. However, there is one, unique example of a dithiophosphonato complex, namely $Ni[S_2P(OPr^i)(Et)]_2$, in which the P–S bonds are not equal (P–S 2.030 Å, P=S 1.901 Å, comparable with known bond lengths of single and double phosphorus–sulfur bonds, respectively) [259]. Strangely, the related compounds $M[S_2P(OEt)Ph]_2$ (M = Pt, Pd) exhibit isobidentate (symmetrical) coordination [260]. In the indium compound, $In[S_2P(OEt)_2]_3$, the coordination of the dithiophosphato ligand can also be depicted as (**91a**) (with P–S 2.137 Å, P=S 1.902 Å and In–S 2.578 Å, In ← S 2.607 Å) [261]. The anisobidentate (unsymmetrical) coordination (**92**) is observed mainly in nontransition metal derivatives; in (**92**) the dotted line represents a semi-bonding interaction, reflected by an interatomic distance which is longer than a covalent bond but shorter than the sum of the Van der Waals radii of the two atoms involved [7]. Some examples of this can be cited; $Sb[S_2P(OMe)_2]_3$ (structure (**92**), P–S 2.029–2.036 Å, P=S 1.927–1.941 Å, Sb–S 2.522–2.535 Å and Sb···S 3.002–3.008 Å) [262] and $Sb(S_2PPh_2)_3$ (P–S 2.044–2.089 Å, P=S 1.959–1.981 Å, Sb–S 2.456–2.598 Å and Sb···S 2.923–3.187 Å) [263]. In the compound $Ph_2Sn[S_2P(OEt)_2]_2$ the dithiophosphato ligand is also anisobidentate (structure (**93**)) with P–S 2.03–2.04 Å, P=S 1.92–1.94 Å and Sn–S 2.48–2.49 Å, Sn···S 3.20–3.23 Å [264] but, surprisingly, in the closely related compound $Ph_2Sn[S_2P(OPr^i)_2]_2$ the ligand is isobidentate (symmetrical structure (**94**)) with P–S 1.998–2.006 Å and Sn–S 2.678–2.689 Å [265].



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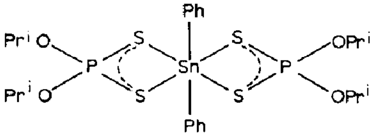
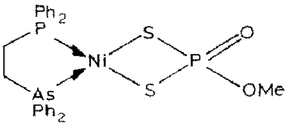


94

In (**93**) the Ph–Sn–Ph angle is 135°, whereas in (**94**) this group is colinear (Ph–Sn–Ph 180°). This difference in coordination patterns has not been satisfactorily explained as yet. Anisobidentate coordination of type (**92**) was also observed in $Me_2Sn(S_2PMe_2)_2$ [266].

Most transition metal dithiophosphates and dithiophosphinates exhibit symmetrical (isobidentate) coordination of type (**91b**). Numerous chelates of this type have been investigated by X-ray diffraction including these following examples for nickel (of square planar structure); dithiophosphates $Ni[S_2P(OR)_2]_2$, with R = Me [267], Et [268,269], Pr^i [270], 1,1′-binaphthyl-2,2′-diyl [271]; dithiophosphinates $Ni(S_2PR_2)_2$, with R = Me [272–274], Ph [275] and $Ni(S_2PRR')_2$ with R = Me, R′ = Et [276] and R = Me, R′ = 2-thienyl [277], their amine adducts, e.g.
$Ni[S_2P(OMe)_2]_2 \cdot$ PHEN [278,279] (PHEN = 1,10-phenanthroline)
$Ni[S_2P(OMe)_2]_2 \cdot$ BIPY [280]
$Ni[S_2P(OEt)_2]_2 \cdot$ PHEN [281]
$Ni[S_2P(OEt)_2]_2 \cdot$ TMED [282] (TMED = *N,N,N′,N′*-tetramethylethylenediamine)

$Ni[S_2P(OEt)_2]_2 \cdot DPED$ [283] (DPED = *N*,*N*′-diphenylethylenediamine)
$Ni[S_2P(OEt)_2]_2 \cdot TED$ [284] (TED = triethylenediamine or diazabicyclooctane DABCO)
$Ni(S_2PEt_2)_2 \cdot 2py$ [285]
$Ni(S_2PEt_2)_2 \cdot QUIN$ [278] (QUIN = quinoline)
$Ni(S_2PPh_2)_2 \cdot 2py$ [286]
Closely related structures are those of the *O*-monomethyl dithiophosphate (**95**) [287,288] and ethyldithiophosphonate (**96**) [289]:



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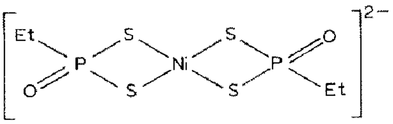

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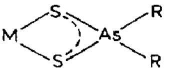
In addition to nickel complexes, many dithiophosphato and dithiophosphinato chelates of other transition metals were investigated structurally by diffraction methods. These include the platinum compound $Pt[S_2P(OPr^i)_2]_2$ [290], the cobalt complexes $Co[S_2P(OMe)_2]_3$ [291] and $Co[S_2P(OMe)_2]_2 \cdot PPh_3$ [292], the derivatives of chromium(III) $Cr[S_2P(OEt)_2]_3$ [293],
molybdenum(III) $Mo[S_2P(OMe)_2]_3$ [294],
molybdenum(IV) $Mo_2O_3[S_2P(OEt)_2]_4 \cdot 2C_6H_4Cl_2$ [295], $Mo_2O_3[S_2P(OPr^i)_2]_4$ [296], $Mo_2O_3(S_4)[S_2P(OPr^i)_2]_4$ [297], $Mo_2O_3(NH)[S_2P(OEt)_2]_2 \cdot THF$ [298], $Mo_2O_3(S)[S_2P(OPr^i)_2]_2$ [299], $Mo(N\text{-}p\text{-tol})[S_2P(OEt)_2]_3$ [300], $\{Mo(N\text{-}p\text{-tol})(\mu_3\text{-}S)[S_2P(OEt)_2]\}_4$ [301], $[Mo_3S(S_2)_3(S_2PEt_2)_3]^+(S_2PEt_2)^-$ [302],
niobium(IV) $Nb[S_2P(OPr^i)_2]_4$ [303,304],
vanadium(III) $V[S_2P(OEt)_2]_3$ [305],
titanium(IV) $TiCl_2[S_2PEt_2]_2$ [306],
zirconium(IV) $Zr[S_2P(OPr^i)_2]_4$ [304],
lanthanoids $Ln(S_2PCy_2)_3$ (Ln = Pr, Sm [307], Dy, Lu [308] (Cy = cyclohexyl), $La[S_2P(OEt)_2]_3 \cdot 2OPPh_3$ [309], $[Ln\{S_2P(OR)_2\}_4]^-$ (Ln = La, Ce, Nd, Ho, Er, R = Me, Et or Pr^i) [310,311], $[Ln(S_2PMe_2)_4]^-$ (Ln = Ce, Pr, Tm) [312,313],
actinoids $Th(S_2PR_2)_4$ (R = Me, Cy) [314], $UO_2(S_2PR_2)_2 \cdot EtOH$ (R = Ph, Cy), $UO_2(S_2PMe_2)_2 \cdot OPMe_3$ and $[UO_2(S_2PR_2)_2Cl]^-$ (R = Me, Ph) [315],
zinc $Zn(S_2PR_2)_2$ R = OEt [316], OPr^i [317], Et [318], Pr^n [319]; $[Zn(S_2PR_2)_3]^-$ R = O-*p*-tol, Ph [320,321],
cadmium $Cd(S_2PR_2)_2$ R = OPr^i [317].
The zinc and cadmium compounds, $M(S_2PR_2)_2$ (M = Zn, Cd), are dimers containing bidentate chelating and bridging dithioligands, whereas the an-

ions $[Zn(S_2PR_2)_3]^-$ contain both bidentate and monodentate ligands.

The discussion, in this review, of dithiophosphorus ligand complexes has been limited to structural investigations (by diffraction methods) which are relevant to the problem of chelate ring formation. Other aspects (synthesis, spectroscopy, applications of these compounds), which were much investigated, will not be treated but are discussed in the reviews cited above.

(c) [M : SS](⊃ As) Systems: dithioarsinato chelates

Although the first metal dithioarsinates, $M(S_2AsR_2)_n$, were prepared more than a century ago [322,323], it is only recently that diorganodithioarsinates have been used as chelate ring forming ligands, (**97**). Since



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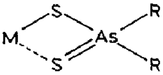
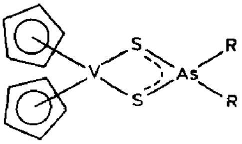


98

X-ray structure determinations are lacking, it is generally assumed (by analogy with dithiophosphinates and dithiophosphates) that dithioarsinates coordinate as isobidentate ligands, at least in transition metal derivatives. The anisobidentate structure (**98**) should also be considered possible in some cases.

Dimethyldithioarsinato chelates, $M(S_2AsMe_2)_n$ with M = Zn(II) [324,325], cadmium(II) [324], cobalt(II) [324,325] ($n = 2$); M = Cr(III), $n = 3$ [324–326]; Mn(II) [325], Cu(II) [325] ($n = 2$); and indium(III), $n = 3$ [325] have all been described previously. Similar diphenyldithioarsinates, $M(S_2AsPh_2)_n$, with M = Zn(II), Co(II), Ni(II), $n = 2$; and M = In(III), Cr(III), and V(III), $n = 3$ [327] and a dibenzyldithioarsinate $Co[S_2As(CH_2Ph)_2]_2$ [328] have also been reported. In addition, compounds with organometallic coordination centers have been prepared, containing a bis(cyclopentadienyl)vanadium unit, (**99**), (R = Me) [329] or a manganese or rhenium tetracarbonyl unit (**100**) (R = Me) [330].



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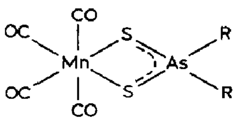
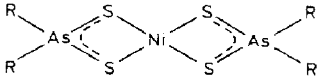


100

The composition of $(CO)_4Mn(S_2AsMe_2)$ requires the dimethyldithioarsinate ligand to be a three-electron donor in order to satisfy the 18-electron rule; thus, it should be bidentate.

All nickel dithioarsinates described are diamagnetic and their electronic spectra are similar to those of nickel(II) dithiophosphates and dithiophosphinates [325,327,328,331]; this suggests a square planar coordination (structure (**101**))



101

The electronic spectra and magnetic properties of cobalt(II) dithioarsinato complexes [331] indicate a tetrahedral coordination by two chelating ligands. The e.s.r. spectrum of oxovanadium(IV) dithioarsinate $OV(S_2AsMe_2)_2$ with 27 discernible lines, was interpreted in terms of superhyperfine splitting caused by two equivalent ^{75}As nuclei, in a square pyramidal coordination geometry [332].

Since νAsS_2 vibrations of dithioarsinates $R_2AsS_2^-$ are almost pure group vibrations [333], infrared spectroscopy can be a useful tool in distinguishing between mono-and bidentate dithioarsinato ligands. On this basis, it was suggested that $R_3Pb(S_2AsPh_2)$ and $R_2Pb(S_2AsPh_2)_2$ contain PbS_2As chelate rings (**97**), while in the analogous organosilicon and -germanium derivatives, the dithioarsinato ligand is monodentate [334].

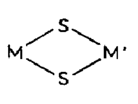
Several organotin dimethyl- and diphenyldithioarsinates have been prepared; an X-ray structure analysis of $Me_2Sn(S_2AsMe_2)_2$ showed that the dithioarsinato ligand is anisobidentate, as shown in (**98**) [335].

The compound $Zn_4S(S_2AsMe_2)_6$ has also been investigated by X-ray diffraction [336]; in this molecule each dimethyldithioarsinato ligand is connected to two different zinc atoms located on the vertices of a tetrahedron, thus acting as a bridge.

The limited amount of information available, suggests that the diorganodithioarsinato groups behave in the same manner as their phosphorus analogues and may exhibit similar coordination patterns.

(d) [M : SS](⊃ M') Systems: thiometallato chelates and dithiolatometal chelates

The chelate rings discussed in this section belong to the same graph, (**102**), of composition [M : SS](⊃ M′), which describes two main types of structure: (a) rings with diconnective sulfur atoms, (**103**), which occur in complexes of thiometallato anions, attached to the coordination center M through sulfur; and (b) rings with triconnective sulfur atoms (**104**), which are formed by electron donation from two thiolato groups of a metal dithiolate to the coordination center M.



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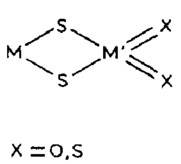

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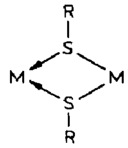
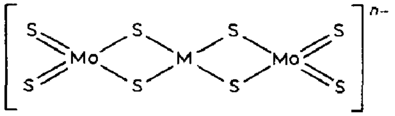


104

Thiometallato chelates. To form rings of type (**102**) the thioanion must contain at least two sulfur atoms. Such ligands include tetrathiomolybdato MoS_4^{2-}, tetrathiotungstato WS_4^{2-}, tetrathiovanadato VS_4^{2-} and related oxothioanions $MoO_2S_2^{2-}$, $MoOS_3^{2-}$, $WO_2S_2^{2-}$, WOS_3^{2-}. All these form transition metal complexes which have been investigated extensively in recent years; the interest in these compounds is stimulated by their biological relevance (modelling of molybdenum enzymes) [337–344].

Tetrathiomolybdates, MoS_4^{2-}, form anionic complexes with two coordinated ligands $[M(MoS_4)_2]^{n-}$ (structure (**105**)) and with one coordinated ligand$[L_nM(MoS_4)]^{n-}$ (structure (**106**)):



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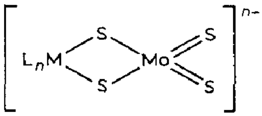

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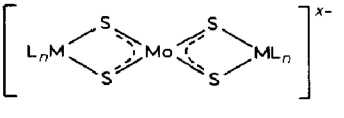
Complexes of type (**105**) are known for iron ($n = 2$ and 3) [345–349], cobalt ($n = 2$ and 3) [350–352], nickel ($n = 2$) [345,350,353–355], palladium ($n = 2$) [353], platinum ($n = 2$) [353] and zinc ($n = 2$) [345,350,356]. The trimolybdenum compounds $(PPh_4)_2[MoO(MoS_4)_2]$ and $(PPh_4)_4[MoS(MoS_4)_2]$ have a similar structure (**105**) (M = MoO and MoS) [351,357].

Complexes of type (**106**) are known in which $ML_n = FeCl_2$ [358–364], $Fe(NO)_2$ [365], $Fe(SAr)_2$ [359,366–368], $FeS_2Fe(SPh)_2$ [369], $Fe(OPh)_2$ [370], $Fe(OAc)_2$ [368], $Fe(S_5)$ [367,371], $Nien_2$, $Ni(phen)_2$, $Ni(bipy)_2$ [372], $Ni[S_2C{=}C(CN)_2]$ [373], $Ni(S_2C{-}NEt_2)$ [373a], $Pd(S_2C{-}NEt_2)$ [373a], CuCN [374–376], CuSPh [377], AgCN [378,379], $(\eta^5\text{-}C_5H_5)_2Mo$ [380], $(\eta^5\text{-}C_5H_5)_2W$ [381], $Mo(NNMe_2)_2(PPh_3)$ [382] and $Ru(bipy)_2$ [383]. Four MoS_4 ligands can also coordinate to the iron atoms of a Fe_4S_4 core [384].

Tetrathiomolybdates are able to act as doubly bidentate chelating ligands, to form trinuclear complexes (**107**) and (**108**).



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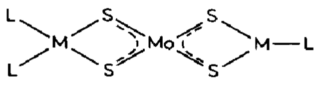
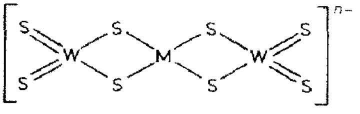


108

Symmetrical compounds, (**107**), are known with $ML_n = FeCl_2$ [385,386], CuCN [375], $CuPy_2$ [387], $Ru(bipy)_2$ [383] and unsymmetrical compounds (**108**) are described with M = Cu, L = PPh_3, [385,388], M = Ag, L = PPh_3 [385,389] and M = Au, L = PEt_3 [390].

Most of the compounds cited above have been investigated by X-ray diffraction and their structures thus confirmed. There is no room here to discuss in detail the structure and properties of these chelate ring compounds. Much detailed information can be found in the reviews cited above [337–344] and in the original literature.

Tetrathiotungstate, WS_4^{2-}, behaves very much like the tetrathiomolybdate and forms similar chelates. Thus, bis(tetrathiotungstato) metal chelates, (**109**) are formed with M = iron ($n = 2$ and 3) [349,391,392], cobalt ($n = 2$ and 3) [350,393–396], nickel ($n = 2$) [350,353,397–399], palladium ($n = 2$) [353], platinum ($n = 2$) [353,400], zinc ($n = 2$) [350,393,399,401]. Oxotungsten- and thiotungsten bis(tetrathiotungstates) $[XW(WS_4)_2]^{2-}$ (X = O, S) are also known [402–405].



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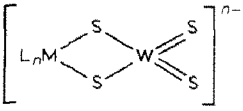

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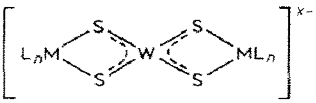
Complexes of type (**110**) are known with $ML_n = FeCl_2$ [358,361,362,406], $Fe(NO)_2$ [365], $Fe(SPh)_2$ [367,371], $Fe(OAc)_2$ [368], $Fe(S_5)$ [367,371], $Nien_2$ [407], $Ni[S_2C{=}C(CN)_2]$ [373], $Ni(S_2C{-}NEt_2)$ [373a], $Pd(S_2C{-}NEt_2)$ [373a], $Pt(PR_3)_2$ (R = Et, Ph) [408].

Like tetrathiomolybdates, the tetrathiotungstate anions can act as doubly bidentate chelating ligands, to form symmetrical compounds, (**111**) with $ML_n = FeCl_2$ [358,364,386], $Cu(PMePh_2)$ [409], $Ag(PMePh_2)$ [409], $Au(PMePh_2)$ [409] and unsymmetrical compounds, (**112**) with M = Cu,



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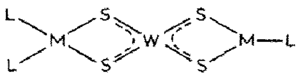

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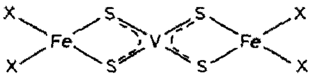
L = PPh_3 [389], M = Ag, L = PPh_3 [410]. The tetrathiotungstate can also be coordinated to a Fe_3S_2 cluster [411] and to a W_2S_4 core [412], to form the anions $[Fe_3S_2(WS_4)_3]^{4-}$ and $[W_2S_4(WS_4)_2]^{2-}$, respectively.

Oxothiomolybdates and -tungstates, containing at least two sulfur atoms, form similar complexes by coordinating through sulfur. Among such compounds $[M(MoO_2S_2)_2]^{2-}$ (M = Fe [368], Co, Ni [413]), $[M(MoOS_3)_2]^{2-}$ (M = Zn, Ni [413]), $[M(WO_2S_2)_2]^{2-}$ (M = Ni, Co [414]) and $[M(WOS_3)_2]^{2-}$ (M = Co, Ni, Zn [415]) can be cited as examples.

Although other thiometallate anions are also known, these have been much less used as ligands. Thus, *tetrathiovanadates* were reported to form doubly bidentate chelate complexes, (**113**), with X = Cl, SPh [416], which are similar to those of molybdenum (**107**) and tungsten (**111**), cited above.



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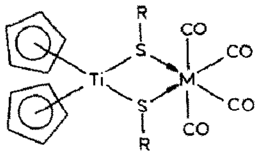
Dithiolatometal chelates. Bis(cyclopentadienyl)titanium dithiolates [417] were found to react photochemically with chromium [418], molybdenum [247,418], and tungsten [418] hexacarbonyls, to form compounds of type (**114**), which contain four-membered chelate rings:



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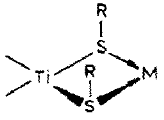
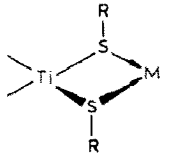
This type of structure has been confirmed by X-ray diffraction analysis of $\{(\eta^5\text{-}C_5H_5)_2Ti(SMe)_2\}Mo(CO)_4$ [419]. Similar chelate compounds, $\{(\eta^5\text{-}C_5H_5)_2Ti(SR)_2\}Fe(NO)_2$ (R = Me, Ph) [420], $\{(\eta^5\text{-}C_5H_5)_2Ti(SPh)_2\}PdCl_2$ [421] and $[\{(C_5H_5)_2Ti(S\text{-}CH_2CH_2PPh_2)\}Cu]^+BF_4^-$ [422] were also reported.

This type of compound is of interest for two reasons: (a) the planarity of the four-membered ring affords the formation of two geometrical (*cis* and *trans*) isomers (**115a**, **b**) (b) there is evidence that the electron transfer from



cis

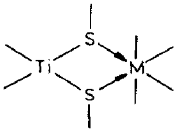
115 a



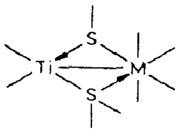
trans

115 b

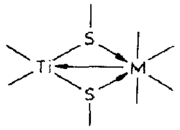
M to empty *d* orbitals of Ti is appreciable, which leads to the alternative formulations (**116a**, **b**, **c**) [423] that attempt to reflect the transannular metal–metal interactions:



116a



116 b



116 c

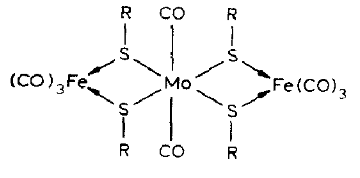
Each of these canonical structures probably contributes to some extent to the bonding in the four-membered rings.

Analogous compounds are known, for other bis(cyclopentadienyl) metal dithiolates, as chelating ligands. Thus, niobium derivatives $[\{(\eta^5\text{-}C_5H_5)_2Nb(SMe)_2\}_2M]^{2+}2X^-$ (X = Cl, BF_4, M = Ni, Pd, Pt) [424,425] and $\{(\eta^5\text{-}C_5H_5)_2Nb(SR)_2\}MCl_2$ (M = Ni, Cu, Mn) [426] and tantalum dithiolate chelates $[\{(\eta^5\text{-}C_5H_5)_2Ta(SMe)_2\}_2Pt]^+X^-$ (X = Cl, PF_6) [427] have been prepared.

Bis(cyclopentadienyl)molybdenum and -tungsten dithiolates were found to form similar chelates [428]. Among the compounds prepared, some were examined by X-ray diffraction, confirming the presence of four-membered chelate rings. These include $\{(\eta^5\text{-}C_5H_5)_2M'(SR)_2\}MX_2$ with M′ = Mo, W, M = Fe, X = Cl [429] (X-ray: M′ = Mo, $MX_2 = FeCl_2$, R = Bu^n [430]); M = Co, X = Cl, Br, SCN [429]; $[\{(\eta^5\text{-}C_5H_5)_2M'(SR)_2\}M]^{2+}2X^-$ with M′ = Mo, W, M = Ni, Pd, Pt [431] (X-ray: M′ = Mo, M = Ni, R = Me, X = BF_4 [425]); $\{(\eta^5\text{-}C_5H_5)_2M'(SR)_2\}M(CO)_4$, with M′ = W, M = Cr, Mo, W [428] (X-ray [432,433]). A rhodium compound $[\{(\eta^5\text{-}C_5H_5)_2Mo(SMe)_2\}Rh(\eta^3\text{-}C_3H_5)_2]^+PF_6^-$ has also been reported [434].

Other molybdenum dithiolates can behave similarly. Thus, $[(RNC)_4Mo(SBu^t)_2]$ (R = Bu^t, Cy) reacts with FeX_2 to form $\{(RNC)_4Mo(SBu^t)_2\}FeX_2$ (X = Cl, Br) [435] and $[(CO)_4Mo(SR)_2]^{2-}$ (R = Ph, CH_2Ph) reacts to form complexes with iron(II) and cobalt(II) halides [436].

Tetrathiolates can act as doubly bidentate chelating ligands, as found (by X-ray diffraction) in the structure of compound (**117**), obtained from $Mo(SR)_4$ (R = Bu^t) and $Fe_2(CO)_9$ [437].



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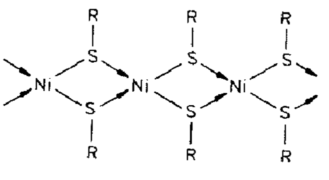


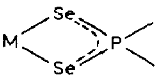
118

The polymerization (up to the degree of hexamer) of palladium [438], nickel [439–442] and cobalt [443] dithiolates, is due to similar chelate ring formation, as shown in (**118**).

The formation of chelate rings (**104**) is based, in fact, upon the ability of thiolato groups to act as bridges between two different or identical metal atoms. The examples cited suggest a great versatility of metal dithiolates as ligands, especially towards soft base metals, and thus, an extremely large number of new compounds synthesized on this basis, can be envisaged.

(vi) Selenium donor sites

(a) [M : SeSe]($\supset$ P) systems: diselenophosphato and diselenophosphinato chelates



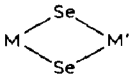
119

From the limited data available, it appears that diselenophosphato, $(RO)_2PSe_2^-$, and diselenophosphinato, $R_2PSe_2^-$, anions are able to form four-membered chelate rings (**119**), analogous to those described above for sulfur analogues. Thus, diselenophosphato chelates $M[Se_2P(OR)_2]_n$ with main group elements, M = Tl(I), In(III), Sn(II), Pb(II), As(III), Sb(III) and Bi(III) [444] and transition metals, M = Cr(III) [445–447], Co(III) [447,448], Rh(III) [445], Ir(III) [445,448], Ni(II) [448], Ag(I), Cu(I), Zn(II), Cd(II) [448] have been investigated. An X-ray structure analysis of $Ni[Se_2P(OEt)_2]_2$ showed that this contains a square planar, four-membered chelate ring, (**119**), the compound being isomorphous with the dithio analogue [449].

Diselenophosphinato complexes $M(Se_2PPh_2)_n$, have also been reported [450,451].

(b) [M : SeSe]($\supset$ M′) systems: selenometallato chelates and diselenometal chelates

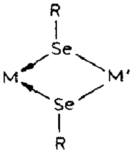
Selenium-containing analogues of (**102**), i.e. four-membered chelates (**120**), are less well known.



120

The first tetraselenometallato complex was the zinc anion $[Zn(WSe_4)_2]^{2-}$ [345]. Copper(I) and silver(I) analogues of (**112**) i.e. $[(PPh_3)_2CuSe_2WSe_2Cu(PPh_3)]$ and $[(PPh_3)_2AgSe_2WSe_2Ag(PPh_3)]$ have also been obtained [379], and the thiometallato-selenometallato analogy has been limited to these examples.

Diselenolmetal chelates, (**121**), are known only for bis(cyclopentadienyl)titanium ligands, and include $\{(\eta^5\text{-}(C_5H_5)_2Ti(SeR)_2\}Mo(CO)_4$ (R = Ph) [247] and $\{(\eta^5\text{-}C_5H_5)_2Ti(SeR)_2\}Fe(NO)_2$ (R = Me, Ph) [420].

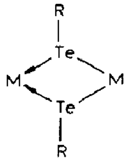


121

(vii) Tellurium donor sites

(a) [M : TeTe](⊃ M') Systems

Four-membered chelate rings with tellurium donor sites, (**122**), are known only as analogues of dithiol and diselenol metal complexes. Thus, compounds $\{(\eta^5\text{-}C_5H_5)_2Ti(TePh)_2\}Fe(NO)_2$, $\{(\eta^5\text{-}C_5H_5)_2Nb(TePh)_2\}Fe(NO)(CO)$ and $\{(\eta^5\text{-}C_5H_5)_2Nb(TePh)_2\}Co(CO)_2$ have been prepared [420].

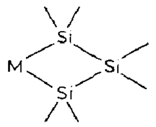


122

(viii) Silicon donor sites

(a) [M : SiSi](⊃ Si) Systems: trisilanido chelates

The four-membered ring (**123**), containing a rare trisilanido ligand (**124**) is



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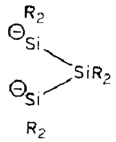
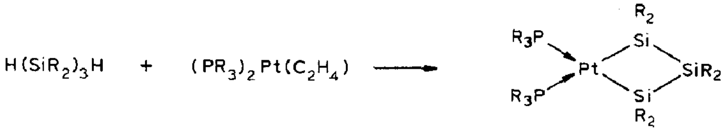


124

known in a platinum compound, (**125**) (R = Ph), which has been obtained from the reaction of hexaphenyltrisilane with bis(triphenylphosphine)(ethylene)platinum(0) [452]:

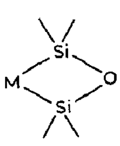


125

Although other transition metals are able to react with Si–H bonds, to form Si–M bonds, this reaction has not yet been exploited as a method for extending this new class of chelate ring.

(b) [M : SiSi](⊃ O) Systems: disiloxanido chelates

Another silicon-donor chelate ring system, (**126**), derived from (hypothetical) disiloxanido anions (**127**), is known to occur in several noble metal derivatives, (**128**). Such compounds are known to exist with ML$_n$ = IrH(CO)(PPh$_3$)$_2$ [453–457], Pd(PPh$_3$)$_2$ [453,456,458], Pd(PPh$_3$)$_2$ [453,456, 458] and Pt(PPh$_3$)$_2$ [453,456,457,459–461] or Pt(PR'$_2$Ph)$_2$ (R' = Me, Et) [461]. When the silicon atoms bear two different substituents, geometrical isomers can be isolated, both for platinum and iridium compounds (L = PPh$_3$, R = Ph or PhCH$_2$) [456,457]. These complexes act as catalysts in the disproportionation of HMe$_2$SiOSiMe$_2$H into Me$_2$SiH$_2$ and linear polysiloxanes at room temperature [453]. An X-ray diffraction study of (PPh$_3$)$_2$(CO)HIr(Me$_2$SiOSiMe$_2$) revealed an abnormally low Si–O–Si bond angle (99.8°) suggesting considerable ring strain, which explains the catalytic activity of the chelate [455].



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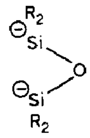

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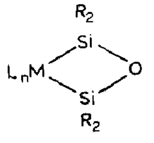

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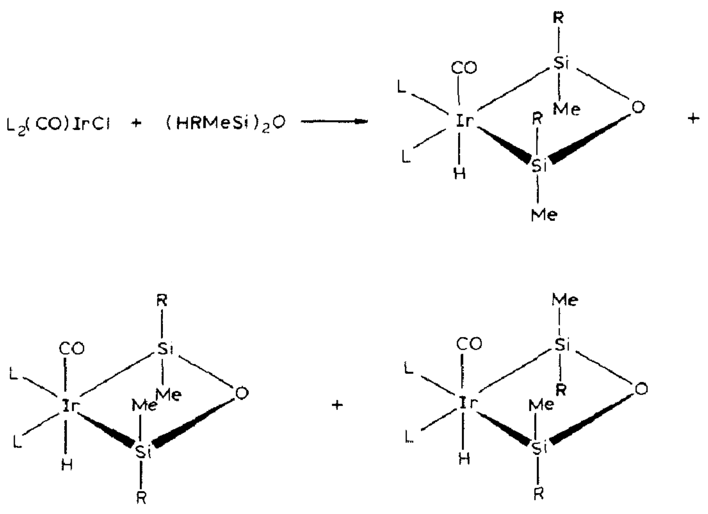
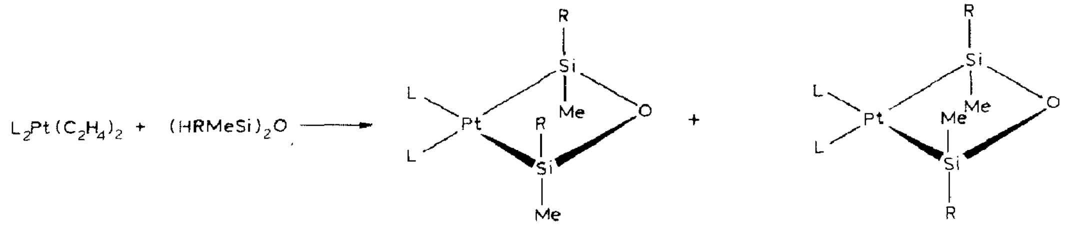


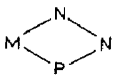


(ix) Heteronuclear donor sites

This section will deal with four-membered chelate rings in which the donor sites are not identical. Instead, the ligand is attached to the metal through two chemically different donor sites. Any pair-wise combination of donors is, in principle, possible, and chelate rings with paired N, P, O, S and Se donors are known.

(a) [M : NP](⊃ N) Systems

The chelate ring represented by the graph (**129**) occurs in hy-



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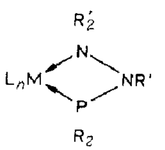

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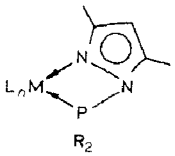


131

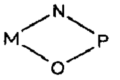
drazinophosphine complexes, (**130**), with $ML_n = Cr(CO)_4$ or $Mo(CO)_4$ (R = Ph, R′ = Me) [97a], prepared by heating $[M(CO)_5(TMPH)]$ (TMPH = *N*-trimethyl-*P*-diphenylhydrazine) in refluxing toluene, with elimination of carbon monoxide. Similar chelate rings are probably present in some complexes of divalent metals with hydrazidothiophosphoric acid esters [462] but no structure has been unambiguously demonstrated.

The same ring (**129**) was found in some complexes of pyrazolylphosphines, which, unexpectedly, coordinate through both phosphorus and nitrogen atoms, to form four-membered chelates, (**131**) [463–465,465a]. Thus, 3,5-dimethylpyrazolyl-*P*-diphenylphosphine (L) forms $[LM(CO)_4]$ (M = Mo, W) and $[LM(CO)_2(PF_3)_2]$ [463,464].

Manganese and rhenium compounds, (e.g. **131**, $ML_n = Mn(CO)_3X$; M = Mn, X = Cl; M = Re, X = Br) have been prepared and the former has been investigated by X-ray diffraction, which confirmed the presence of the four-membered chelate ring [465a,466].

(b) [M : NO]($\supset$ P) Systems

The four-membered chelate ring (**132**) is known to occur only in organoaluminum compounds, (**133**) ($ML_n = AlMe_2$, R = Me, Et, Pr^i, Bu^i, R′ = Me),



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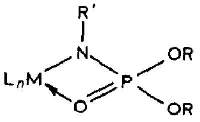


133

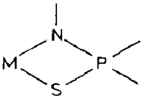
obtained by reacting trimethylaluminum with phosphoric methylamidoesters $(RO)_2P(O)NHMe$. The four-membered compounds (**133**) are in equilibrium with eight-membered ring dimers [467] (see also ref. [467a]). Bulky substituents reduce the tendency towards dimerization and favour the formation of chelate ring (**133**). It is surprising that no chelates of type (**132**) have been reported for other metals.

(c) [M : NS]($\supset$ P) Systems

Unlike previous systems, those containing the N–S (**134**) donor set have been investigated extensively. Thus, four-membered chelate ring compounds (**135**) have been reported for such different metals as M = Al, Sn, Ti, Mn, Re, Ni, Au, demonstrating the versatility of amidothiophosphorus derivatives as ligands.

Aluminum chelates (**135**, $ML_n = AlEt_2$, R = R′ = R″ = Et) were prepared from triethylaluminum and diethylthiophosphinic acid ethylamide, $Et_2P(S)NHEt$; the cyclic structure was assigned on the basis of spectroscopic data

[468]. Other compounds, (**135**), $ML_n = AlMe_2$, $R = Me$, $R' = N(SiMe_3)_2$, $R'' = Bu^t$ [42,47a,469] and $ML_n = AlPh_2$, $R = Ph$, $R' = N(SiMe_3)_2$ or



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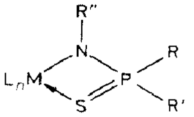

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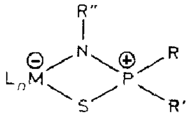


135 a

$NBu^t(SiMe_3)$ or $Si(Me_3)$, $R'' = Bu^t$ [47a] have been prepared by reacting $AlMe_3$ or $AlPh_3$ with $(Me_3Si)_2N{-}P(=S)(=NBu^t)$ or $(Me_3Si)Bu^tN{-}P(=S)(=NBu^t)$. The structure of (**135**), $ML_n = AlPh_2$, $R = Ph$, $R' = N(SiMe_3)_2$, $R'' = Bu^t$ has been determined by X-ray diffraction [47a] and the alternative representation (**135a**) has been suggested as a result.

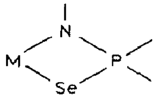
The compounds $R_2N{-}P(=S)(=NBu^t)$ react with methyllithium to give $(R_2N)MeP(=S)(NBu^tLi)$ and the latter form chelate rings (**135**), $ML_n = SnCl_3$ and $TiCl_3$, after reacting with tin(IV) and titanium(IV) chlorides [42].

Manganese and rhenium derivatives, (**135**) ($ML_n = Mn(CO)_4$ and $Re(CO)_4$, $R = Cl$, $R' = NBu^t(SiMe_3)$, $R'' = Bu^t$) were prepared by reacting $Bu^t(SiMe_3)N{-}P(=S)(=NBu^t)$ with $M(CO)_5Cl$ ($M = Mn, Re$) [46a]; a similar reaction with Me_2AuCl gave (**135**) $ML_n = AuMe_2$, (R, R′ and R″ as above) [46a].

A nickel complex (**135**), $ML_n = Ni/2$, $R = R' = Et$, $R'' = CHMePh$, has been prepared and was the first paramagnetic complex investigated by the 2D-NMR technique [470].

(d) [M : NSe](⊃ P) Systems

The compounds containing the chelate ring (**136**) are very similar to those



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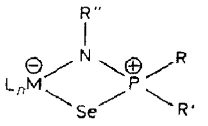
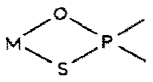


137

described in the previous Section. Thus, organoaluminum amidoselenophosphinates (**137**) ($ML_n = AlMe_2$, $R = Me$, $R' = N(SiMe_3)_2$ or $NBu^t(SiMe_3)$, $R'' = Bu^t$) were prepared by reacting trimethylaluminum with $(Me_3Si)_2N{-}P(=Se)(=NBu^t)$ or $(Me_3Si)Bu^tN{-}P(=Se)(=NBu^t)$ [47a,469]. Manganese, rhenium and gold compounds, similar to those of the sulfur analogues cited in the previous section, have also been reported [46a].

(e) [M : OS](⊃ P) Systems

The chelate rings (**138**) are expected to occur in metal complexes (**139**) of monothiophosphato- and -phosphinato ligands.



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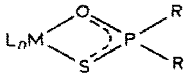
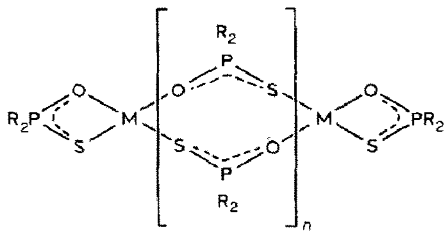


139

Many transition metal monothiophosphates $M[OSP(OR)_2]_n$ [471–473] and monothiophosphinates, $M(OSPR_2)_n$ [474] have been prepared, but their lack of solubility in water and organic solvents, suggests a polymeric structure, with bridging monothiophosphorus ligands. In some cases the simultaneous presence of bridging and chelating thiophosphinato groups (structure **140**) has been inferred [475]. In other cases, the bridging behavior of the monothiophosphinate or monothiophosphate leads to dimer formation, e.g. structure (**141**), $ML_n = Ni(H_2O)_3(ClO_4)$ and $Cu(H_2O)_2$ [476] or $ML_n = AlMe_2$, $GaMe_2$ and $InMe_2$ [477].



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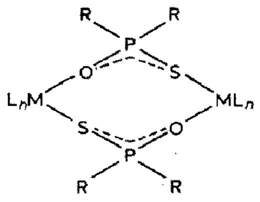
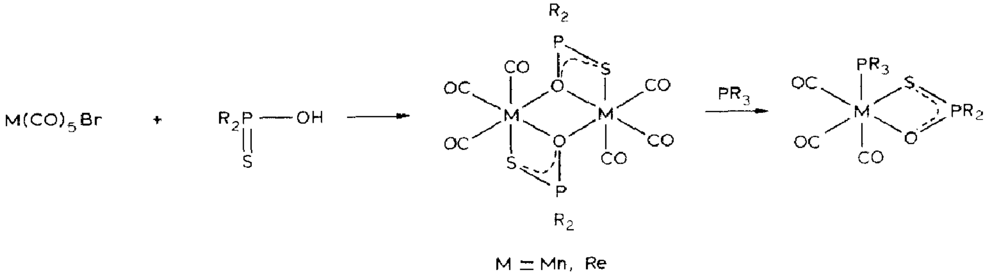


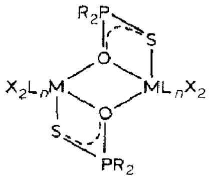
141

In manganese and rhenium carbonyl complexes the monothiophosphinato ligand coordinates in a peculiar way, simultaneously chelating and bridging (structure **142**), but a monomeric rhenium compound with a chelate structure (**143**) can also be obtained [478–480]:



142 143

Recent X-ray diffraction investigation of some lanthanide monothiophosphinates $M(SOPR_2)_3 \cdot xH_2O$ ($R = Me$, $M = Er$, $x = 2$; $M = Pr$, $x = 7$ [481] and $R = Cy$, $M = Nd$, $x = 2$ [482]) and $NH_4[Er(SOPCy_2)_4(H_2O)_2]$ [482] established the same chelating–bridging coordination of the ligand with the simultaneous presence of monodentate thiophosphinato ligand (X) coordinated through oxygen. The neodymium compound $[Nd(SOPCy_2)_3(H_2O)]_2$ is even more interesting as it contains three kinds of monothiophosphinato ligand (monodentate, bidentate chelating and chelating–bridging) as shown in (**145**) [482] ($L = H_2O$).



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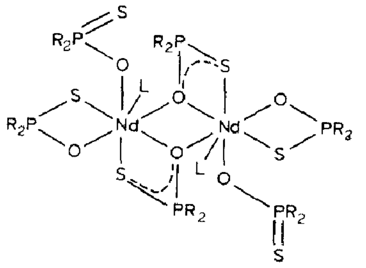
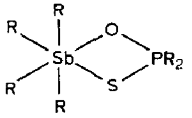


145

While in $Me_4SbOSPMe_2$, the vibrational spectra indicate bidentate chelating coordination of the ligand (structure **146**, $R = Me$) [483], an X-ray diffraction study of $Sb(OSPR_2)_3$ shows anisobidentate coordination (structure **147**, $R = Cy$) [484].

The data cited above suggest that monothiophosphates and -phosphinates are able to exhibit various coordination patterns which are, like as with dithiophosphorus ligands [7], rather unpredictable. Therefore, every possible effort should be made to study their structure by X-ray diffraction.



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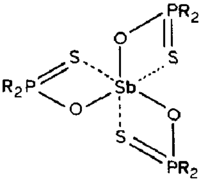

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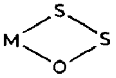
(f) [M : OS](⊃ S) Systems

The unusual chelate ring illustrated by graph (**148**), has been discovered in the thiosulfato complexes (**149**) of bis(cyclopentadienyl)molybdenum and -tungsten, ($(\eta^5\text{-}C_5H_5)_2M(S_2O_3)$) and was confirmed by X-ray diffraction. The compounds are formed quantitatively in the reaction of the hydrides $(C_5H_5)_2MH_2$ with sulfur dioxide [485]. This type of thiosulfato coordination is unique to the best of our knowledge, and it is not yet clear whether a large class of thiosulfato chelates can be obtained.



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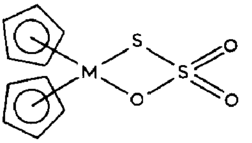

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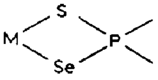
(g) [M : SSe](⊃ P) Systems

A rather close analogy between dithiophosphato, diselenophosphato- and selenothiophosphato (or -phosphinato) complexes is to be expected. The



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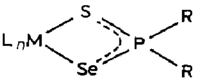

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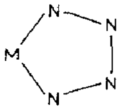
four-membered chelate ring (**150**) is probably present in the transition and main group metal phosphato [486,487] and -phosphinato [446a,451,488,489] complexes reported in the literature. The investigation of these complexes is confined to spectroscopic techniques and the lack of X-ray diffraction analyses prevents further comment on their structure. Very likely, the diversity of coordination patterns observed for dithiophosphates and -phosphinates [7] is also possible for selenothio analogues.

D. FIVE-MEMBERED RINGS

(i) Nitrogen donor sites

(a) [M : NN](⊃ NN) Systems: tetrazene and tetrazadiene chelates

The five-membered graph (**152**) is the basis of two chelate ring systems: tetrazene chelates, (**153**), and tetrazadiene chelates, (**154**). A third type, (**155**), in which the metal is formally bound as a heteroatom, in a cyclometallatetrazene through normal covalent bonds rather than donor–acceptor bonds, is also known, but to a lesser extent.



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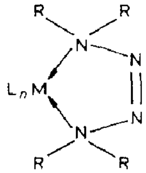

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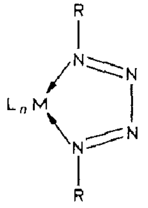

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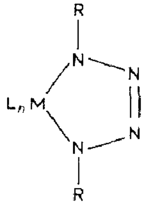

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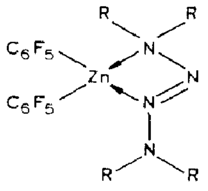
The first reported tetrazene chelates were cadmium, mercury and aluminum derivatives of tetramethyltetrazene (**153**, R = Me; $ML_n = CdX_2$, HgX_2, $AlCl_3$; X = Cl, Br) [490]. Zinc compounds ($ML_n = ZnR'_2$ with R′ = Bu, Ph, C_6F_5 [491], and Cl [492]) organoberyllium derivatives ($ML_n = BeR'_2$ with R′ = Et, Pr^i, Bu^t [493]) and organoaluminum complexes ($ML_n = AlMe_3$ [494–496] and $AlEt_3$ [497]) were also described. All these compounds were formulated as five-membered chelates (**153**) on the basis of spectroscopic evidence (single ^1H NMR peaks for NMe_2 and MMe_n groups, respectively), but an X-ray diffraction investigation of $(C_6F_5)_2ZnN_4Me_4$ established that



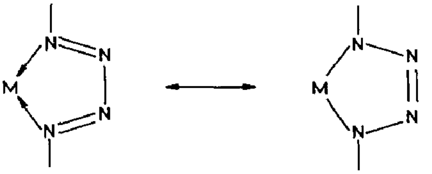
156

this compound contains a four-membered ring and is actually a triazene chelate (**156**) [498]. This observation creates some suspicion about the structures assigned (**153**) to all tetramethyltetrazene complexes, and until more X-ray diffraction investigations are performed, these structures should be treated with some caution.

Although the free 1,4-diorganotetrazadiene-1,3 ligands are unstable and cannot be isolated, remarkably stable complexes, (**154**), with various metals, can be prepared in situ from organic azides RN_3, and appropriate metal compounds.

An iron tricarbonyl complex (**154**, $ML_n = Fe(CO)_3$, R = Me), prepared from MeN_3 and $Fe_2(CO)_9$ [499] was the first representative of this class. X-ray diffraction [500] reveals a nearly planar five-membered ring. Theoretical calculations were performed [501,502] to explain the electronic structure of this compound, which was described as "aromatic". Carbonyl groups can be partially replaced by phosphine and phosphites, without destruction of the metallocycle [502,503].

Cyclopentadienylcobalt tetrazadiene chelates, (**154**) ($ML_n = Co(\eta^5\text{-}C_5H_5)$, R = Me, Ph, C_6F_5, 2,4-$F_2C_6H_3$, 2,6-$Me_2C_6H_3$) have been prepared and investigated in some detail [504–509]. These are formed in the reaction of $\eta^5\text{-}C_5H_5Co(CO)_2$ with organic azides. An X-ray investigation of $\eta^5\text{-}C_5H_5CoN_4(C_6F_5)_2$ (**154**, $R = C_6F_5$, $ML_n = \eta^5\text{-}C_5H_5Co$) established that the five-membered ring is planar; the molecular structure shows evidence for Co–N π-bonding at the expense of N–N π-bonding [506,507]. Thus, the bond distances N_1–N_2 1.360 Å, N_3–N_4 1.355 Å and N_2–N_3 1.279 Å suggest that the contribution of canonic form (**155a**) is more important than (**154a**)



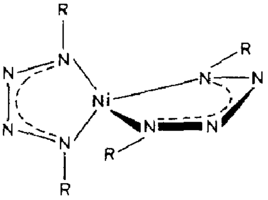
154a 155a

The bonding in this chelate ring has been discussed in terms of a delocalization of the π-electrons over the entire ring, including the metal atom [506]. Electrochemistry, electronic and ESR spectra of the 19e anionic complexes derived from the cobalt chelate [508] and the photolysis, which produces an unusual transformation [505,506,508,509], have been investigated.

Rhodium chelates, (**154**) ($ML_n = Rh(NO)(PPh_3)$, $R = SO_2C_6H_4Me\text{-}p$), have also been prepared from $Rh(NO)(PPh_3)_3$ and $p\text{-}MeC_6H_4SO_2N_3$ and their physico-chemical behavior and structure were investigated [510,511].

Iridium analogues (**154**, $ML_n = Ir(CO)(PR_3)_2$, R = Ph, p-FC_6H_4, p-ClC_6H_4, p-BrC_6H_4, p-$CF_3C_6H_4$ and p-MeC_6H_4) have been synthesized by reacting Vaska's complex *trans*-$Ir(CO)Cl(PPh_3)_2$ with p-substituted phenyldiazonium tetrafluoroborates; an X-ray structure investigation of $[Ir(CO)(PPh_3)_2(N_4C_6H_4F_2)]^+BF_4^-$ again revealed shorter N_2–N_3 distances than N_1–N_2 and N_3–N_4, thus suggesting an important contribution of (**155a**) [512,513].

Several nickel complexes, of type $Ni(N_4R_2)_2$ (R = aryl), were prepared by various methods, including treatment of aryl azides with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) or $Ni(\eta^5\text{-}C_5H_5)_2$ [514,515] and by ligand transfer reactions [516]. An X-ray investigation of $Ni(N_4R_2)_2$ (R = 3,5-$Me_2C_6H_3$) revealed a structure (**157**) with two planar NiN_4 rings, perpendicular to each other [514,515].



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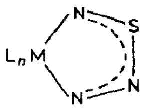
It is interesting to note that all the N–N bond distances within the ring are practically equal (1.322 Å), suggesting full π-electron delocalization. Mixed ligand complexes (**154**) with $ML_n = Ni(CNBu^t)_2$ and $Ni(COD)_2$ [516,517] and $Ni(\eta^5\text{-}C_5H_5)_2$ [518] have also been described, as well as some interesting molecular rearrangements [518]. Similar platinum chelates have also been investigated [516–518].

A six-coordinate platinum compound $[Pt(N_4R_2)(C{\equiv}CPh)_2(PEt_3)_2]$, prepared from $[(PhC{\equiv}C)_2Pt(PEt_3)_2]$ and RN_3 (R = p-$O_2NC_6H_4$) has been investigated by X-ray diffraction and formulated as (**155**) $ML_n = Pt(C{\equiv}CPh)(PEt_3)_2$ [519].

Tin derivatives, (**155**) (R = Bu, Ph, CH_2Ph, p-MeC_6H_4, C_6F_5, $ML_n = Sn[N(SiMe_3)_2]_2$), have been prepared from the stannylene: $Sn[N(SiMe_3)_2]_2$ and organic azides [520].

(b) [M : NN](⊃ NS) Systems

The chelate ring (**158**) is known in only one example, a nickel complex with M = Ni, L = $P(OPh)_3$, $n = 2$, isolated from the reaction between $Ni[P(OPh)_3]_4$ and S_4N_4, in benzene, at room temperature; although there has been no direct determination, structure (**158**) is highly likely [521].



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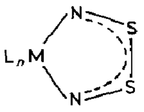
(c) [M: NN](⊃ SS) Systems

The ring (**159**) is known in two complexes: an osmium compound $OsCl_4(N_2S_2)$, obtained from $OsCl_5$ and $(ClSN)_3$, followed by treatment with Ph_4AsCl or $GaCl_3$ [522] and a rhenium compound $[PPh_3Cl]^+[ReCl_4(N_2S_2)]^-$, prepared by reacting $[ReCl_3(NSCl)_2(POCl_3)]$ with PPh_3 [523]. In the rhenium compound, the ReN_2S_2 ring is planar and contains a very long (2.530 Å) S · · · S bond [523].



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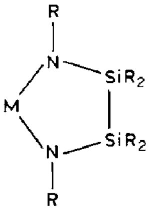
(d) [M: NN](⊃ SiSi) Systems

The ring (**160**) has first been obtained as a titanium derivative (M = Ti/2, R = Me), prepared by the reaction of $(Me_2Si{-}NMeLi)_2$ with $TiBr_4$.



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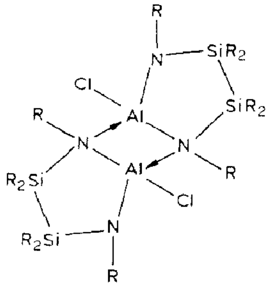
The spirocyclic structure with a tetrahedrally coordinated titanium center has been confirmed by X-ray diffraction [524]. A monocyclic compound (**160**, M = $TiBr_4$, R = Me) has also been obtained, by reacting the spiro compound with $TiBr_4$ (ligand redistribution) [525].

The reaction of $(Me_2Si{-}NMeLi)_2$ with $BeCl_2$ gave a beryllium derivative (**160**, M = Be, R = Me), which is associated in solution and in the solid state, probably through N → Be bonds [526]. An aluminum compound (**160**, M = AlCl, R = Me), was prepared similarly using anhydrous aluminum chloride; its dimeric structure, (**161**), has been confirmed by an X-ray diffraction analysis [527].



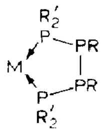
161

In the same way, an organotin derivative (**160**, M = SnBu$_2$, R = Me), was obtained from (Me$_2$Si–NMeLi)$_2$ and Cl$_2$SnBu$_2$ [528].

(ii) Phosphorus donor sites

(a) [M : PP](⊃ PP) Systems

Several chelate ring compounds (**162**), containing a tetraphosphane ligand



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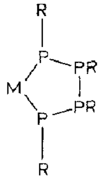

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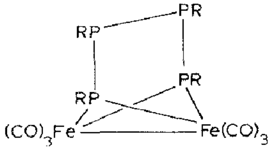


164

have been reported in the literature. Tetraphosphido chelate rings (**163**) are also known.

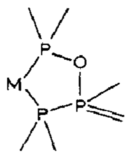
Molybdenum derivatives (**162**), M = Mo(CO)$_4$, were prepared from *cis*-[Mo(CO)$_4$(PR$'_2$Cl)$_2$] (R$'$ = Me, Ph) and Li$_2$PPh [77] or from *cis*-[Mo(CO)$_4$(PMe$_2$Li)$_2$] and Cl$_2$PR, (R = Ph, Bu^t [77] and R = Me [529,530]). The ring structure has been confirmed by X-ray diffraction analysis of (**162**), M = Mo(CO)$_4$, R = R$'$ = Me; the P–P bond lengths are 2.200 Å (P$_1$–P$_2$) and 2.142 Å (P$_2$–P$_3$) [531]. The formation of five-membered rings [M : PP](⊃ PP) rather than the expected [M : PP](⊃ P) systems in these reactions is somewhat surprising.

The tetraphosphido chelate ring (**163**) was first suggested for magnesium compounds (M = Mg, R = Me, Et) [532] and later described in several other compounds, with R = Cy, M = SnR'_2, $Ti(\eta^5\text{-}C_5H_5)_2$ and $Zr(\eta^5\text{-}C_5H_5)_2$ [533].

In tetraphosphido chelates the donor ability is not exhausted by chelate ring formation and the P-atoms in positions 1 and 4 can further coordinate, leading to tetraphosphido bridges, of type (**164**), that have been established by X-ray diffraction to be present in the diiron hexacarbonyl compound $Fe_2(CO)_6(PR)_4$ (R = Me, Ph) [534].

(b) [M : PP]($\supset$ PO) Systems

An interesting chelate ring type (**165**) is formed in the reaction of



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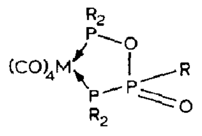

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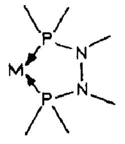
cis-$[(CO)_4Mo(PR_2O)_2H]^-$ salts with $RPCl_2$. Several compounds, (**166**) R = Ph, M = Cr, Mo, W, have been prepared; the structure of the molybdenum derivative has been confirmed by X-ray diffraction [535].

(c) [M : PP]($\supset$ NN) Systems

The chelate ring (**167**) is formed in the reaction of *cis*-$[(CO)_4Mo(R_2PCl)_2]$



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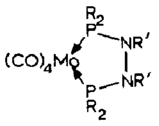

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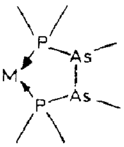
with symmetrical hydrazine hydrochlorides in the presence of triethylamine; thus, several derivatives (**168**), with R = Me, Ph and R′ = H, Me [536] and R′ = $SiMe_3$ [536a] were synthesized. Perhaps this type of chelate can be extended to other metals.

(d) [M : PP]($\supset$ AsAs) Systems

The ring (**169**) is known in several compounds formed by reactions of coordinated ligands. Thus, *cis*-$[(CO)_4Mo(PR'_2Li)_2]$ reacts with $RAsCl_2$ to give (**170**).



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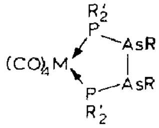

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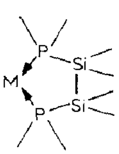
(M = Mo, R = R′ = Me) [529,530]. The molecular structure of the compound formed was confirmed by an X-ray diffraction analysis [537].

(e) [M : PP](⊃ SiSi) Systems

The silicon analogue of the previously cited rings has also been prepared and confirmed by an X-ray diffraction study of compound (**172**) [538].



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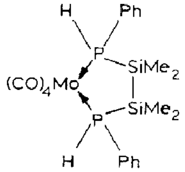

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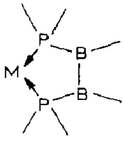
(f) [M : PP](⊃ BB) Systems

Diphosphinodiborane ligands can form five-membered rings of type (**173**).



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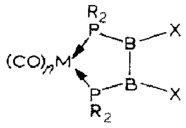

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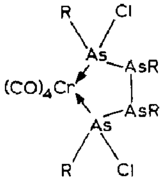
Thus, a nickel complex (**174**, M = Ni, $n = 2$, R = Et, X = NEt_2) was formed in the reaction of $B_2(PEt_2)_2(NEt_2)_2$ with $Ni(CO)_4$ [539]. From *cis*-$[(CO)_4M(PPh_2H)_2]$ lithiated with $LiBu^n$ and then treated with $Cl(Me_2N)B\text{-}B(NMe_2)Cl$, compounds (**174**) with M = Cr, Mo, W, $n = 4$, R = Ph, X = NMe_2 can be obtained [139]. These compounds were characterized only by spectroscopic techniques, and no X-ray molecular structure determination has been performed to date.

(iii) Arsenic donor sites

(a) [M : AsAs](⊃ AsAs) Systems

Arsenic donor chelates are rather scarce, and five-membered rings are known in fact only as derivatives of tetraarsines. Thus, compound (**175**)

($R = Bu^t$) is formed in a rather unusual reaction, from $Na_2[Cr_2(CO)_{10}]$ with Bu^t_2AsCl, after addition of $[Ph_3P{-}N{-}PPh_3]^+Cl^-$ [540].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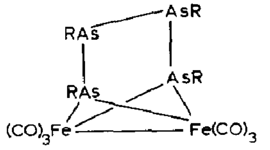
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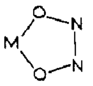
Tetraarsenido groups can form bridged dinuclear compounds (**176**) ($R = Me$) [541] which can be regarded as chelate rings, $FeAs_4$, coordinated to a second iron atom.

(iv) Oxygen donor sites

(a) [M : OO](⊃ NN) Systems

There are two types of chelate compounds containing the [M : OO])(⊃ NN) system (**177**): hyponitrite complexes (**178**) and *N*-alkyl(aryl)-*N*-nitrosohydroxylamine chelates (**179**).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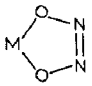
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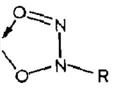
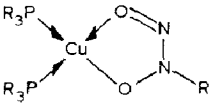

179

A compound of type (**178**), with $M = Pt(PPh_3)_2$, was obtained by treating $Pt(PPh_3)_4$ with nitric oxide, NO [542–544] and the molecular structure was confirmed by X-ray diffraction.

Chelate compounds containing the ring (**179**) are formed in the reactions of organometallic compounds with nitric oxide. Thus, organometallic derivatives of Group II and III elements, MR_n ($n = 2, 3$) absorb two moles of NO, while $R_{n-1}MX$ absorb one mole of NO; the reaction mechanism involves coordination of one NO molecule through oxygen to the metal, followed by a 1,3-shift by the R group and attack of a second NO molecule, to form the five-membered ring (**179**). Thus, ZnR_2 gives $ROZn(O_2N_2R)$ and $Zn(O_2N_2R)_2$ ($R = Pr^n$) and RMgCl yields $RMg(O_2N_2R)$ ($R = Bu^i$) [544a]. The reaction was applied to other zinc dialkyls [545], and also aluminum [546] and gallium [547] trimethyls. The latter form $Me_2M(O_2N_2Me)$ (structure (**179**), $M = AlMe_2$ or $GaMe_2$, $R = Me$).

Similar compounds were obtained in the reactions of nitric oxide with titanium, zirconium, vanadium, niobium and tantalum σ-alkyls [548] and with hexamethyl tungsten [549]. The presence of the chelate ring (**179**) in the products of these reactions was confirmed by an X-ray diffraction analysis of $MeCl_2Ta(O_2N_2Me)_2$ [550] and $Me_4W(O_2N_2Me)_2$ [551].

N-Phenyl-*N*-nitrosohydroxylamine is a versatile analytical reagent, well known under the name cupferron. It forms copper, zinc, manganese, iron, nickel and cobalt complexes, $M(O_2N_2Ph)_2$, and pyridine adducts of these [552]. The copper complex $Cu(O_2N_2Ph)_2$ reacts with triphenylphosphine to form (**180**) (R = Ph), whose structure has been determined by X-ray diffraction [552].



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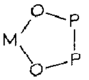
X-ray diffraction studies were also performed on several cupferron chelates, including $Cu(O_2N_2Ph)_2$ [553], $Fe(O_2N_2Ph)_3$ [554], $Zr(O_2N_2Ph)_4$ [555] and $NH_4[UO_2(O_2N_2Ph)_3]$ [556]. All these were found to contain planar, five-membered chelate rings (**179**).

There is a vast literature on the analytical uses of cupferron based upon the formation of chelate complexes, but this will not be cited here. The formation of chelates (**179**) (R = cyclohexyl) can be used in the solvent extraction of lanthanoids, thorium and other metals [556a].

The trioxodinitrato complexes $[M(N_2O_3)]^{4-}$ (M = Mn, Fe, Co, Ni) probably contain chelate rings of type (**179**) with $R = O^-$, but their structure has been incompletely investigated, using only infrared spectroscopy [557].

(b) [M : OO](⊃ PP) Systems

The ring (**181**) is scarce but may occur in dioxodiphosphino chelates



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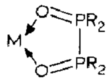
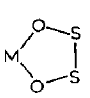


182

(**182**). The only known representative seems to be $[Zn(O_2P_2Ph_4)](AsF_6)_2$ formed in the reaction of $[Zn(SO_3)_3](AsF_6)_2$ with $Ph_2P–PPh_2$ [558].

(c) [M : OO](⊃ SS) Systems

Five-membered rings (**183**) can be present in the chelate complexes (**184**) of dithionato ligands. This type is illustrated by the chromium complex, containing the $[Cr(S_2O_6)(NH_3)_4]^+$ cation [559]. The dithionato group,



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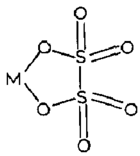


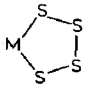
184

$S_2O_6^{2-}$, could probably be used as a ligand with other metals as well, in order to generate a larger number of representatives for this chelate ring.

(v) Sulfur donor sites

(a) [M : SS](⊃ SS) Systems: tetrasulfido chelates

Tetrasulfido chelate rings, (**185**), are typical representatives of a larger family of polysulfido complexes that has received considerable attention in recent years [560–561].



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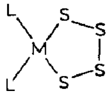

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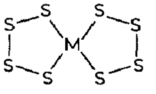

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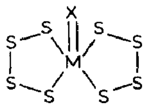

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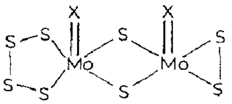
The tetrasulfido chelate ring (**185**) occurs in both monocyclic chelates (**186**) (M = Mo, W, Ni, Pd, Pt) and in spirocyclic derivatives (**187**) (M = Ni, Pd) or (**188**) (M = Mo, X = O, S).

The first member of this class was bis(cyclopentadienyl)molybdenum tetrasulfide $(\eta^5\text{-}C_5H_5)_2MoS_4$ (**186**, M = Mo, L = $\eta^5\text{-}C_5H_5$) [562–564], followed soon by a tungsten analogue, $(\eta^5\text{-}C_5H_5)_2WS_4$ (**186**, M = W, L = $\eta^5\text{-}C_5H_5$) [563,564]. The molecular structures of both molybdenum [565] and tungsten [566,567] compounds were confirmed by X-ray diffraction, which established the presence of a nonplanar, five-membered chelate ring, with envelope conformation. The compounds can be prepared by the reaction of bis(cyclopentadienyl)metal dichlorides with ammonium polysulfide [562,563] or by reacting the hydrides $(\eta^5\text{-}C_5H_5)_2MH_2$ with elemental sulfur [564].

Tetrathiomolybdates, e.g. $(NH_4)_2MoS_4$, reacted with dibenzyl trisulfide or ammonium polysulfide, to form the spirocyclic anion $[MoS(S_4)_2]^{2-}$ (structure **188**, X = S), isolated as a tetraethylammonium salt [568,569]; the reaction of this anion with DMSO [568] or its controlled hydrolysis in MeCN or DMF [569] produced the oxoderivative, (**188**), M = Mo, X = O. The molecular structures of the anions $[MoS(S_4)_2]^{2-}$ [568,569] and $[MoO(S_4)_2]^{2-}$ [569,570] were determined by X-ray diffraction. In addition, the anions $Mo_2S_{10}^{2-}$ (structure **189**, X = S) [569,570], $Mo_2S_8O_2^{2-}$ (structure **189**, X = O) [571], $Mo_2S_{12}^{2-}$ (structure **190**, X = S) [569] and $Mo_2S_{10}O_2^{2-}$

(structure **190**, X = O) [570] have been obtained and then investigated by X-ray diffraction.



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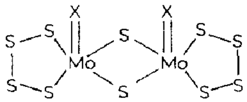

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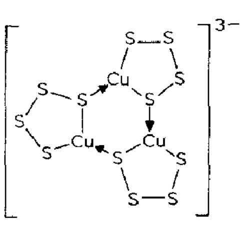
Nickel chelates of type (**186**) (M = Ni, 2L = DIPHOS) (DIPHOS = $Ph_2PCH_2CH_2PPh_2$) were prepared by reacting $(DIPHOS)NiCl_2$ with alkali metal polysulfides [572]; spirocyclic anions $[Ni(S_4)_2]^{2-}$ (structure **187**, M = Ni) were obtained by treating $Ni(OAc)_2 \cdot 4H_2O$ ($Ac = CH_3COO^-$) with ammonium polysulfide and $[NEt_4]Br$ [573] or by reacting $[Ni(SPh)_4]^{2-}$ with dibenzyltrisulfide or sulfur [574]. In the anion (**187**) the nickel atom exhibits square planar coordination [573,574]. The reaction of $(DIPHOS)Ni(SH)_2$ with H_2S or NaHS also gave $(DIPHOS)NiS_4$ [575].

Similar palladium compounds, including $(DIPHOS)PdS_4$ [572,575] and $[Pd(S_4)_2]^{2-}$ [573] were also reported.

The platinum compound $(DIPHOS)PtS_4$ (structure **186**, M = Pt, 2L = DIPHOS) was obtained from the corresponding dichloride by reaction with sodium polysulfide, and its structure was determined by X-ray diffraction [576,577]. The degradation of $[Pt(S_5)_2]^{2-}$ with DIPHOS [572] and triphenylphosphine [578,579] produced (**186**), M = Pt with 2L = DIPHOS and L = PPh_3, respectively. The compound $(PPh_3)_2PtS_4$ was also formed in the reaction of $Pt(PPh_3)_4$ with elemental sulfur in benzene [580].

A cobalt-containing ring, $LCoS_4$, is formed in the reaction of $LCo(SH)_2$ with sulfur or of $LCo(NCS)_2$ with Na_2S_4 ($L = Me\text{–}C(CH_2PPh_3)_3$ [581]).

Copper(I) behaves in a more complex manner. Thus, the CuS_4 ring trimerizes to form a $[Cu_3(S_4)_3]^{3-}$ anion, (**191**) which can be isolated as a mixed PPh_4/NH_4 salt from the reaction product of $Cu(OAc)_2 \cdot H_2O$, treated with ammonia and then with H_2S, in the presence of elemental sulfur and $[PPh_4]Br$. The structure was established by X-ray diffraction [582,583]. Other polysulfido copper(I) anions, prepared similarly but in other solvent media, $[Cu_4S_x]^{2-}$ (x = 13, 14) contain CuS_4 and CuS_5 chelate rings simultaneously and can be written as $[Cu_4(S_4)_2(S_5)]^{2-}$ and $[Cu_4(S_4)(S_5)_2]^{2-}$



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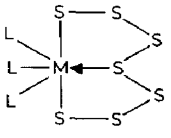
[584,585]. The hexanuclear anion $[Cu_6S_{17}]^{2-}$ also contains CuS_4 rings and it should be formulated as $[Cu_6(S_4)_3(S_5)]^{2-}$; this anion is formed by treating $Cu(acac)_2$ in DMF with ethanolic ammonium polysulfide [586] or by reacting $CuCl_2 \cdot 2H_2O$ with sodium thiolates, NaSR (R = Me, CH_2Ph), and sulfur [587]. The tetrathiocuprate NH_4CuS_4 was found (by X-ray diffraction) to consist of CuS_4 chelate rings, linked via additional Cu–S bonds to form monodimensional polymeric anions [588].

A zinc complex $[Zn(S_4)_2]^{2-}$ (structure **187**, M = Zn) was isolated as a NEt_4^+ salt from the reaction of $[Zn(SPh)_4]^{2-}$ with sulfur or dibenzyl trisulfide and its structure was determined by X-ray diffraction [574].

Tin-containing anions $[Sn^{IV}(S_4)_3]^{2-}$ and $[Sn^{IV}(S_4)_2(S_6)]^{2-}$ were formed on treating $SnCl_2 \cdot 2H_2O$ with polysulfides; the X-ray diffraction analysis of the mixed salt $(NEt_4)_2\{[Sn(S_4)_3]_{0.4}[Sn(S_4)_2(S_6)]_{0.6}\}$ showed that the tin(IV) atom is octahedrally coordinated [589].

As interesting bicyclic structure, (**192**) (L = PMe_3), containing two fused MS_4 rings was found in the compounds $M[(PMe_3)S_7]$ (M = Ru, Os) obtained in the reaction of $MH(PMe_3)_3(CH_2PMe_2)$ with elemental sulfur in benzene. This type of structure was established by X-ray diffraction analysis of the osmium compound [590].

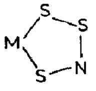


192

The examples shown in this section suggest that a still larger class of MS_4 chelate rings, derived from the versatile ligand S_4^{2-}, can be anticipated.

(b) [M : SS](⊃ SN) Systems

The ring system (**193**) is present in several transition metal complexes, which have been reviewed [591,592]. According to Lewis valence bond concepts structure (**194a**) should be taken as correct, but bond distances in several known compounds, indicating a shorter S_2–N and N–S_4 bond, suggest that formula (**194b**) reflects more correctly the bonding in these rings. A non-committal formulation (**194c**) can be used in most cases.



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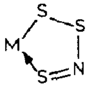

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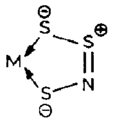

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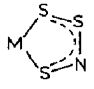


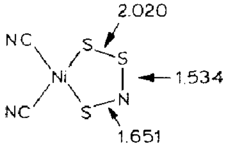
194c

This ring is formed in reactions of cyclotetrathiazene, S_4N_4, with metal chlorides in alcoholic media; in addition to bis-chelate complexes $[M(S_3N)_2]$, mixed ligand compounds $[M(S_3N)(S_2N_2H)]$ and other related species such as $[M(S_2N_2H)_2]$ (M = Co, Ni, Pd, Pt) are formed [593,594]. These reactions are very sensitive to slight changes in reaction conditions; thus, the compound $[Pd_2(S_3N)_2(\mu\text{-}S_3N_2)]$ can be prepared from the same reagents [595]. The mixed ligand complex $[Co(S_3N)(NO)_2]$ is obtained by treating, with NO, the primary product of the reaction between $Co_2(CO)_8$ and S_4N_4 [596]. Three different products, namely $[Pt(S_3N)_2]$, $[Pt(S_3N)(S_2N_2H)]$ and $[Pt(S_2N_2H)_2]$ which can be separated by column chromatography, can be isolated from the reaction of $H_2PtCl_6 \cdot 6H_2O$ with S_4N_4 [597]. Similar compounds are formed in the reaction of S_4N_4 with $NiCl_2$ in refluxing methanol [598].

The isolation of the free ligand, the S_3N^- anion, as $[N(PPh_3)_2]^+$ or $AsPh_4^+$ salts, afforded the direct synthesis of cobalt and nickel complexes, $[M(S_3N)_2]$ [599,600]. Some copper and silver complexes $[M(S_3N)_2]^-$ (M = Cu^I, Ag) were also reported [600a].

An interesting and unexpected observation was the degradation of cycloazaheptathiane, S_7NH, under various conditions, with the formation of S_3N–metal complexes. Thus, the reaction of S_7NH with $NiCl_2$ in alkaline media gave $(NBu^t_4)[(NiS_3N)_3S_2]$, containing a Ni_3S_2 cluster with three chelating S_3N^- ligands attached to the metal atoms [601]. The reaction of S_7NH with n-BuLi at $-78°C$ in ether, followed by addition of $HAuCl_4$ gave $[Cl_2Au(S_3N)]$ [602]. The compound $[Cu(S_3N)(SPPh_3)]$ was obtained from S_7NH and $ClCu(PPh_3)_3$ [603]; the salts $(AsPh_4)[Cu(S_3N)_2]$, $(AsPh_4)[Cu(S_3N)Cl]$ and $(NMe_4)[Ni(S_3N)(CN)_2]$ were prepared from S_7NH and appropriate copper and nickel salts, in basic media [604].

The crystal and molecular structures of several compounds cited above have been determined. These include, among others, $[Pd(S_3N)_2]$ [605], $[Pd_2(S_3N)_2(\mu\text{-}S_3N_2)]$ [595], $[Co(S_3N)(NO)_2]$ [596], $(NBu^t_4)[(NiS_3N)_3S_2]$ [601], $[Cu(S_3N)(SPPh_3)]$ [603], $[Ni(S_3N)(CN)_2]$, $(AsPh_4)[Cu(S_3N)_2]$ and $(AsPh_4)[Cu(S_3N)Cl]$ [604]. In all these, the five-membered metallocycle was found to be planar, and the S_2–N distance was shorter than the N–S_4 distance as shown for example, in (**195**) and (**196**).



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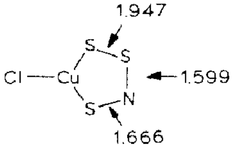

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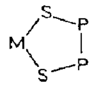
A detailed investigation of the vibrational spectra (infrared, Raman) and a normal coordinate analysis of $[Pd(S_3N)_2]$ were performed [606].

(c) [M : SS]($\supset$ PP) Systems

The five-membered ring (**198**) may be found in two types of chelates, (**198**) and (**199**), the former being much more common.



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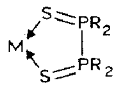

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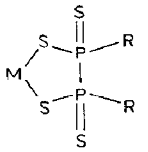

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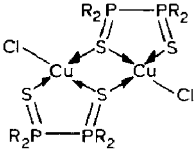
Type (**198**) is formed in the reactions of diphosphine disulfides with various metal compounds. The ligand is a rather weak donor and the complexes exhibit only moderate stability. They readily decompose to metal sulfides and some are even explosive. The first report on such complexes [607] described the formation of copper(I) chelates of tetramethyl- and tetraethyldiphosphine disulfides in the reactions of the ligand with copper(II) salts, during which the metal is reduced. The complexes were formulated as $[Cu^{I}(S_2P_2R_4)][CuCl_2]$ on the basis of conductometric and spectroscopic (infrared) investigations. An X-ray study of the white methyl derivative showed that the compound is a molecular dimer, in which two puckered five-membered rings are joined by bridging sulfur atoms (structure **200**, R = Me) [608]. Copper is tetrahedrally coordinated.



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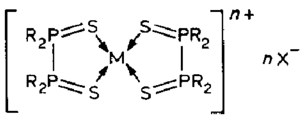

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A second minor, brown, product, isolated from the reaction of $CuCl_2 \cdot 2H_2O$ with tetramethyldiphosphine disulfide, $[CuCl_2(S_2P_2Me_4)]$ was found to be a polymer, in which $CuCl_2$ groups are connected by $Me_4P_2S_2$ bridges, and which contains no chelate rings [609]. This is a precursor of the cyclic copper(I) compound, since on standing it converts into the white dimer.

Other 1 : 1 complexes were obtained in the reaction of tetramethyldiphosphine disulfide with zinc, mercury, copper, tin, antimony and bismuth halides; these were treated with alkalis to give tetramethyldiphosphine [610,610a]. Some of these were reinvestigated in much greater detail at a later stage. Thus, a large number of tetramethyldiphosphine disulfide complexes of the types $[M(S_2P_2R_4)_2]X_2$ (M = Co, Cd, $X = NO_3^-$, ClO_4^-) (structure **201**); $MX_2 \cdot S_2P_2R_4$ (M = Zn, X = Cl, Br; M = Cd, X = Cl, Br, I;

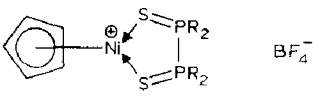
M = Fe, X = Cl, Br; M = Hg, X = Cl, Br) and $MX_4 \cdot S_2P_2R_4$ (M = Sn, X = Cl) [611]; $ZnCl_2 \cdot S_2P_2Me_4$ and $ZnCl_2 \cdot S_2P_2(CD_3)_4$ [612] and, in addition, other alkyl derivatives such as $MX_2 \cdot S_2P_2R_4$ (R = Et, Pr, Bu, M = Zn, X = Cl, Br; M = Cd, X = Br, I; M = Hg, X = Cl, Br; M = Co, R = Et, Pr, Bu, X = Br) [613] and $MX_2 \cdot S_2P_2R_4$ (R = allyl, M = Zn, Hg, X = Cl; M = Co, X = Br, I) [614] were recently isolated and investigated by vibrational spectroscopic methods. The results are in agreement with cyclic chelate structures involving the ring (**198**).

Other diphosphine disulfide complexes reported include $TiX_4 \cdot S_2P_2R_4$ (X = Cl, Br, R = Me, Et) [615,615a], $VCl_4 \cdot S_2P_2R_4$ (R = Me, Et) [615a], $SnX_4 \cdot S_2P_2R_4$ (X = Cl, Br, R = Me, Et) [616], $MoOCl_3 \cdot S_2P_2Et_4$, $MoOCl_3(S_2P_2Me_4)(\mu\text{-}S_2P_2Me_4)$ [617] and $VOCl_3 \cdot S_2P_2R_4$ [615a]. The chelate ring structures assumed for these compounds is based upon spectroscopic evidence alone.

In the reaction of PtL_4 where L = PPh_3, $PMePh_2$ or $P(OPh)_3$, with tetraalkyldiphosphine disulfides, $R_4P_2S_2$ (R = Me, Et), the cyclic intermediate (**198**) (M = PtL_2) undergoes a cleavage of the P–P bond, with the formation of a thiophosphinato-bridged platinum complex [618].

Chelate ring structures were postulated for the dinitrosyl metal derivatives $[M(NO)_2(S_2P_2Me_4)]^+X^-$ (M = Fe, Co, X = Br) [619,620].

An interesting compound with an organometallic coordination center (structure **202**) is formed in the reaction of $[\eta^5\text{-}C_5H_5Ni(C_5H_6)]BF_4$ with tetramethyldiphosphinedisulfide. The inorganic chelate ring is readily cleaved by tetraphenyldiphosphinoethane (DIPHOS), which displaces the diphosphine disulfide [621].



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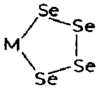
More recent investigations, [622], showed that the basicity of the two sulfur atoms of diphosphine disulfides can be modified by an appropriate selection of substituents for the phosphorus atoms. Thus, dialkylamino derivatives, $(Et_2N)RP(S)P(S)R(NEt_2)$ (R = NEt_2, cyclo-C_6H_{11}, Ph) seem to be very good donors; several copper(I), palladium(II), platinum(II) complexes were obtained and investigated in the solid state and in solution, by spectroscopic, and in some cases, by diffraction methods [622–624]. The copper complexes were of type $[CuL_2]ClO_4$, L = $(Et_2N)_2P(S)\text{–}P(S)(NEt_2)_2$, [LCuCl], L = $Et_2N(Cy)P(S)\text{–}P(S)(Cy)(NEt_2)$, while the palladium(II) and platinum compounds were of the $[LMCl_2]$ type [622]. The molecular structure of a palladium chelate complex with $(Et_2N)(Cy)P(S){-}P(S)(Cy)(NEt_2)$ was determined by X-ray diffraction analysis [624a].

The other five-membered [M : SS]($\supset$ PP) metallocycle, (**199**) M = Ti(η^5-$C_5H_4X)_2$ was obtained in the reaction of $(\eta^5\text{-}C_5H_4X)_2Ti(CO)_2$ with cyclic disulfides, $[RP(\mu\text{-}S)S]_2$ in tetrahydrofuran (X = H, Me, R = p-$MeOC_6H_4$, p-$EtOC_6H_4$, Bu^t or 3-cyclohexenyl) [625]. The same type of compound is formed in the reaction of $(MeC_5H_4)_2TiCl_2$ with Li_2RPS_3.

(vi) Selenium donor sites

(a) [M : SeSe]($\supset$ SeSe) Systems

The five-membered ring (**203**) was first obtained as bis(cyclopentadienyl)molybdenum and tungsten derivatives [M = $Mo(C_5H_5)_2$, $W(C_5H_5)_2$] [563].



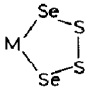
203

The complex $[Ir(Se_4)(TMPE)_2]Cl$ obtained from the reaction of $[Ir(TMPE)_2]Cl$ with elemental selenium (TMPE = tetramethyldiphosphinoethane) was found by X-ray diffraction to contain a half-chair five-membered $IrSe_4$ ring [626].

A cobalt complex, $Me{-}C(CH_2PPh_2)_3CoSe_4$, was formed from the corresponding bis(thiocyanate) and disodium tetraselenide, or sodium hydroselenide, in reactions similar to those used for the sulfur analogue [581].

(b) [M : SeSe]($\supset$ SS) Systems

A platinum compound, obtained by the reaction of $(PPh_3)_2Pt(SeH)_2$ with elemental sulfur, having composition $(PPh_3)_2PtSe_2S_2$, contains the unusual chelate ring (**204**).



204

The compound was characterized only by spectroscopic methods [575]. An X-ray structure determination would be of extreme interest, in view of the difficulty of isolating individual sulfur–selenium heterocycles.

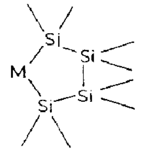
(vii) Tellurium donor sites

No chelate rings of this nature are known.

(viii) Silicon donor sites

(a) [M : SiSi]($\supset$ SiSi) Systems

The tetrasilanide dianion $R_8Si_4^{2-}$ forms five-membered chelate rings (**205**) with some transition metals.



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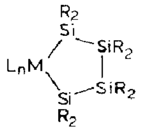


206

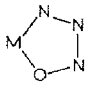
Thus, a platinum compound (**206**) (M = Pt, L = PPh_3, R = Ph) is formed in the reaction of $[(PPh_3)_2Pt(C_2H_4)]$ with $H(SiPh_2)_4H$ or by the reaction of *cis*-$[Pt(PPh_3)_2Cl_2]$ with $Li(SiPh_2)_4Li$; interestingly, the pentasilane $H(SiPh_2)_5H$ reacts with $[(PPh_3)_2Pt(C_2H_4)]$ to form (**206**), with a tetrasilanido ligand [627].

A titanium derivative (**206**) (M = Ti, L = η^5-C_5H_5, R = Ph) can be prepared in 19% yield by reacting $Li(SiPh_2)_4Li$ with $(\eta^5\text{-}C_5H_5)_2TiCl_2$; some cyclopentasilane $(SiPh_2)_5$ is formed as a by-product (12% yield) [628].

(ix) Heteronuclear donor sites

(a) [M : ON]($\supset$ NN) Systems

The five-membered ring graph (**207**) is typical of triazenide-1-oxido complexes (**208**). These were reviewed recently [629], and only some subsequent results will be briefly illustrated here.



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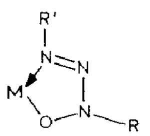

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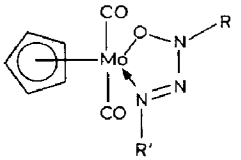
A ruthenium(III) complex of 1-ethyl-3-*p*-tolyltriazene oxide, $[RuCl_2(ONEt : NNC_6H_4Me)_2]$, was selected from several analogous compounds for an X-ray diffraction determination of the molecular structure [630]. A copper(II) complex, containing two [CuNO]($\supset$ NN) rings, connected through two biphenylyl bridges, was also investigated structurally by X-ray diffraction [631].

Spectral and Mössbauer studies of several triazene-1-oxide complexes of iron(III) were reported [632].

Non-transition metals, like lead(II) and tin(II), are also able to form triazene-1-oxide chelates, and a large number of derivatives have been prepared [633].

Triazene-1-oxide chelates with organometallic centers are much rarer, although this could possibly constitute a large class of compounds. An interesting example illustrating this possibility is the η^5-cyclopentadienylmolybdenum dicarbonyl derivative (**209**), reported some years ago [33a].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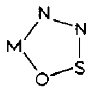
(b) [M : NO](⊃ NS) Systems

The ring system (**210**) has been identified in metal complexes of *N*-sulfinylhydroxylamines. Copper(II) and Ni(II) chelates (**211**) (R = Ph, M = Cu/2, Ni/2) have been prepared and investigated spectroscopically [634], but a cobalt complex, isolated as a bis-pyridine adduct, *trans*-Co(PhNNSO)$_2$ · 2Py, has been investigated by X-ray diffraction [635].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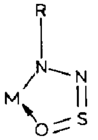
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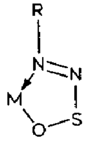
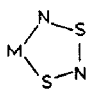

211b

(c) [M : NS](⊃ SN) Systems

The five-membered rings (**212**) occur in a large number of thiazeno chelates, of type (**213**). These compounds have been known for quite some time, have been reviewed [2,591,636] and are also treated in a recent Gmelin volume [592]. Therefore, only newer results will be quoted here.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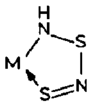
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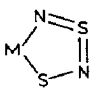
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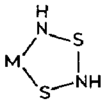
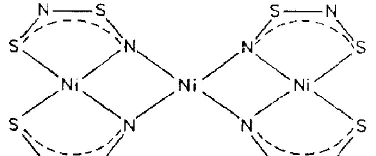

215

Both derivatives of the $S_2N_2H^-$ ligand (**213**) and of the $S_2N_2^{2-}$ ligand (**214**) are known, and even a chelate of the fully hydrogenated ligand (**215**) has been reported. The use of Lewis bond formulae e.g. (**213**) and (**214**), for thiazeno chelates should be regarded only as conventional, since the actual bonding situation is more complex and (at least some) electron delocalization within the ring more than likely occurs.

Although known for many years [2,591,592,636] the chelates (**213**) derived from the $S_2N_2H^-$ ligand have continued to attract interest in recent years. Thus, improved preparations for $M(S_2N_2H)_2$ derivatives (M = Co [594], Ni [594,598], Pd [594], Pt [594,597]) have been reported. Vibrational [637–640], electronic [594], ESR (cobalt complex) [594] and mass spectra [637] were all investigated in detail. Theoretical calculations (e.g. CNDO) were performed to determine the atomic charge densities [641,642] and the results were compared with X-ray photoelectron spectroscopy data [643]. A new X-ray structure determination of $Ni(S_2N_2H)_2$ (β-modification) has been published [644] and the structure of $K[Ni(S_2N_2H)(CN)_2]$ has also been determined by X-ray diffraction [645].

Some interesting reactions of $[M(S_2N_2H)_2]$ chelates have been discovered. Thus, $[Ni(S_2N_2H)_2]$ can be deprotonated in alkaline media, with KOH to form $K_2[Ni(S_2N_2)_2]$ and with $[ER_4]OH$ (E = N, R = Me, Et, Bu; E = P, As, R = Ph) to give $ER_4[Ni(S_2N_2H)(S_2N_2)]$ [646]. The structure of $AsPh_4[Ni(S_2N_2H)(S_2N_2)]$ was determined by X-ray diffraction [646]. In the presence of potassium cyanide, strong bases like KOH convert $[Ni(S_2N_2H)_2]$ into $K[Ni(S_2N_2H)(CN)_2]$ [645], while in the presence of milder bases like $KHCO_3$ the dinuclear complex $K_2[Ni_2(S_2N_2)_2(CN)_2]$ is formed [647].

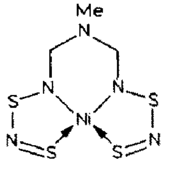
The anion $[Ni(S_2N_2)_2]^{2-}$ formed in the deprotonation of $Ni(S_2N_2H)_2$, can itself act as a chelating ligand. Thus a mixture of $Ni(S_2N_2H)_2$, $[PPh_4]OH$ and $NiCl_2 \cdot 6H_2O$ in methanol gave an unusual complex, $[PPh_4]_2[Ni_3N_8S_8]$, containing a planar anion of structure (**215a**) [648].



215 a

The reactivity of NH groups in $[M(S_2N_2H)_2]$ can be exploited in several ways for preparative purposes. Thus, $[Ni(S_2N_2H)_2]$ reacted with formaldehyde in the presence of methanol to give $[Ni(S_2N_2H)(S_2N_2CH_2OMe)]$ [649]. With paraformaldehyde and methylamine, $[Ni(S_2N_2H)_2]$ forms a tricyclic compound (**216**) in which the two *cis*-nitrogen atoms of two different chelate rings are bridged by a $-CH_2-NMe-CH_2-$ fragment [650]. Similar compounds are formed with other aldehydes and amines [651,652].

Tricyclic compounds with disiloxane and disilazane bridges (**217**) were also prepared from nickel and cobalt chelates $[M(S_2N_2H)_2]$ with the appropriate dichloro organosilicon derivatives (E = O, NR, NMeNMe) [653–655].



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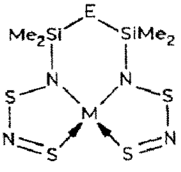
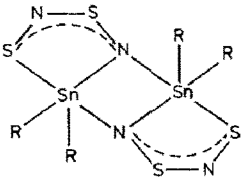


217

In addition to the two [M : NS](⊃ NS) chelate rings, compounds (**217**) contain a fused six-membered [M : NN](⊃ SiESi) chelate ring.

Chelate rings derived from the $S_2N_2^{2-}$ ligand, of type (**214**), have been investigated to a somewhat lesser extent.

Dimethyltin derivatives $Me_2SnS_2N_2$, have been obtained from the reaction of $N(SnMe_3)_3$ with S_4N_4 or S_2Cl_2, and an X-ray diffraction study showed that these are nitrogen-bridged dimers, (**218**), (R = Me), containing five-coordinate tin [656–658].



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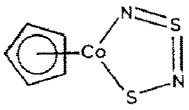


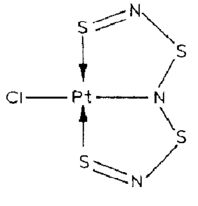
219

Two lead compounds, PbS_2N_2 and $PbS_2N_2 \cdot NH_3$, were also found by X-ray diffraction, to contain five-membered chelate rings (**214**) (M = Pb) [659].

A fine example is the cyclopentadienylcobalt derivative, (**219**), prepared in 25% yield from η^5-$C_5H_5Co(CO)_2$ and S_4N_4 in benzene; its structure was established by X-ray diffraction [660].

An iridium derivative $[L_2Ir(S_2N_2)]BPh_4$ (where L = $Ph_2P–CH=CH–PPh_2$) prepared from $[L_2Ir(CO)]BPh_4$ and S_4N_4 in THF at 50°C, was also investigated by X-ray diffraction which confirmed the presence of a planar IrS_2N_2 chelate ring [661]. Platinum complexes, $[(PPh_3)_2Pt(S_2N_2)]$ and $[P(OPh)_3]_2Pt(S_2N_2)$, were obtained from S_4N_4 and $Pt(PPh_3)_4$ and $Pt[P(OPh)_3]_4$, respectively [662].

The bicyclic compound (**220**), obtained from *cis*-$[PtCl_2(NCPh)_2]$ and S_4N_4, can be regarded as a close relative of compounds just discussed, since it contains two fused PtS_2N_2 rings [663].

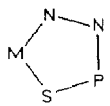


220

The fully saturated chelate ring (**215**), containing the $S_2N_2H_2^{2-}$ ligand, has been very little investigated. The reaction of $(SNH)_4$ with $Pt(PPh_3)_4$ in benzene gave $[(PPh_3)_2Pt(S_2N_2H_2)_2]$ (assigned structure (**215**) with M = $Pt(PPh_3)_2$) [662], and that of $(SNH)_4$ in acetone with an aqueous solution of K_2PtCl_4 gave $[(S_2N_2H_2)Pt(OSNH)_2]$ (structure **215** with M = $Pt(OSNH)_2$) [664].

(d) [M : NS](⊃ NP) Systems

The five-membered ring system (**221**) may occur in metal complexes of



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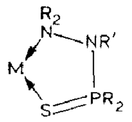
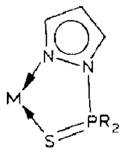


222a

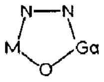


222b

thiophosphino hydrazine derivatives (**222a**) or thiophosphinato pyrazole derivatives (**222b**). Thus, the nickel complexes of dihydrazidothiophosphoric acid phenyl ester, $PhO\text{-}P(S)(NHNH_2)_2$, seem to contain five-membered [M : NS](⊃ NP) rings in addition to six-membered [M : NN](⊃ NPN) rings [665]. Of the several thiophosphato- and thiophosphinato hydrazine complexes investigated, e.g. $(RO)_2P(S)NHNH_2$ and $Ph_2P(S)NHNH_2$ (L) [666–668], apparently the only chelates are the palladium compounds of type $LPdCl_2$ (structure **222a**, R = Ph, OEt, R′ = H) [667]. A rhenium compound (**222b**) M = $Re(CO)_3Br$, R = Ph, was reported as a reaction product of diphenylthiophosphinatopyrazole and an appropriate rhenium carbonyl derivative [456a].

(e) [M : ON](⊃ GaN) Systems

The rather exotic chelate ring (**223**) occurs in several pyrazolylgallate derivatives.



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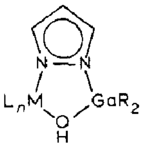

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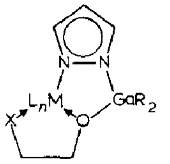


225

The parent complex (**224**) (R = Me) was obtained only recently as a rhenium derivative of the novel ligand $[Me_2Ga(Pyz)OH]^-$ (Pyz = pyrazolyl, 3,5-dimethylpyrazolyl) [669], but a large number of type (**225**) complexes, with a second donor group (X = NR'_2 or SR′) were investigated earlier.

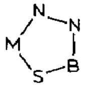
The sodium salt of the novel ligand, pyrazolylhydroxodimethylgallato anion, $Na^+[Me_2Ga(Pyz)OH]^-$ can be readily obtained from $[Me_2Ga(OH)]_4$ and Na^+Pyz^-, and reacts with the rhenium carbonyl chloride $[Re(CO)_4Cl]_2$ to form (**224**) [ML_n = $Re(CO)_4$] [669]. Molybdenum derivatives of $[MeGa(Pyz)_2O]^-$ were also reported [670,671].

Several complexes containing the skeleton (**225**), in which X = NMe_2 and M = molybdenum [672–674], tungsten [673,674], manganese [673], iron [675], nickel [676,677] and copper [678–680] have prepared and investigated by X-ray diffraction.

Derivatives of type (**225**) with X = SR (R = Et or Ph) and M = molybdenum [681,682], tungsten [681], manganese [681,682], copper [681] and nickel [681,682] have also been described and structurally characterized by X-ray diffraction.

(f) [M : NS](⊃ NB) Systems

The five-membered chelate ring (**226**) is known only in a cobalt bis(di-



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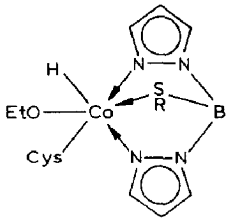


227

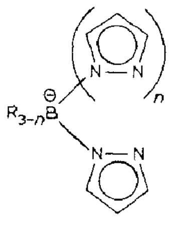
methylpyrazolyl)tolylmercaptoborato complex, which also contains a six-membered [CoNN]($\supset$NBN) chelate ring. This complex approximates the active site of poplar plastocyanin [683].

E. SIX-MEMBERED RINGS

(i) Nitrogen donor sites

(a) [M : NN]($\supset$ NBN) Systems: pyrazolylborato chelates

Among the most versatile chelating ligands are the bis- and tris(pyrazolyl) borates (**228**, $n = 1, 2$). These were first prepared twenty years ago and were



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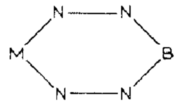

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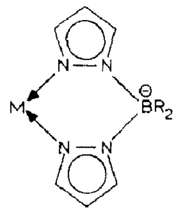


230

found to be excellent complexing reagents [684–686]. Bis(pyrazolyl)borates (**228**, $n = 1$) behave as uninegative bidentate ligands, whereas tris(pyrazolyl)borates (**228**, $n = 2$) exhibit the rare feature of being uninegative tridentate ligands (thus forming neutral complexes with six-coordinate divalent metals). Both these types of ligand form six-membered chelate rings corresponding to the graph **229**, as shown in (**230**) for the bis(pyrazolyl)borato ligand. The tris derivatives contain a second [M : NN]($\supset$ NBN) chelate ring.

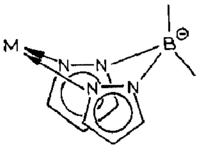
The basic chemistry of pyrazolylborato chelates was reviewed some years ago [687–689] and the work discussed there will not be cited in this review. The interest towards pyrazolylborato chelates has not decreased with time and much has been published since the appearance of the cited reviews. To review these results in any detail would require a comprehensive article by itself and this cannot be done here. As a result of intensive research, pyrazolylborato chelates are now known for nearly every transition metal and for some main group metals as well.

The recent publications on pyrazolylborato chelates deal with the synthesis, structure determination (by X-ray diffraction) and, in some cases, reactivity of a large diversity of chelate complexes containing titanium [690–690b], zirconium [691–694], vanadium [690a,695], niobium [696,697], tantalum [698,698a], chromium [695,699], molybdenum [700–722], tungsten [708,721,723–725], manganese [726–728], rhenium [726,729], iron [728,730–730d], ruthenium [731,732], cobalt [728,733–737], rhodium [731,738–742], iridium [738,739], nickel [728,734,743–746], palladium [747–752], platinum [753,754], copper [728,734,735,755–763a], silver [763–765], gold [766,767] and zinc [734]. Lanthanoid pyrazolylborates were also described [768]. Of the actinoids only thorium [769,770] and uranium [770–772] were reported to form pyrazolylborato chelates.

Among pyrazolylborato chelates of the main group metals those of thallium [773] and tin [774] can be cited.

Many of the pyrazolylborato chelates contain organometallic coordination centers. In the early years, the pyrazolylborato chelates were mainly complexes of the simple ions, whereas the tendency to attach such a ligand to an organometallic moiety is frequently observed in recent years, thus enormously enlarging the number of potential compounds described under this headline.

Many X-ray structure determinations revealed that the six-membered chelate ring adopts a tube conformation (**231**), determined by the peculiar geometry of the ligand itself.



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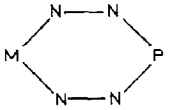
Similar complexes containing the ring (**229**) might be obtained with hydrazinoborane anions, e.g. $[R_2B(NR'-NR'_2)_2]^-$, but such complexes have not so far been reported.

(b) [M : NN]($\supset$ NPN) Systems

The cyclic graph (**232**) describes chelate rings found in metal complexes of phosphoric acid dihydrazides and pyrazolylphosphines, which, unlike pyrazolylborates are neutral ligands.



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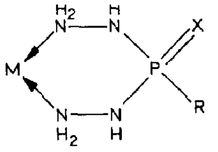

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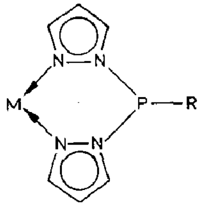
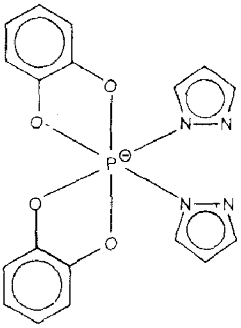


234

Only manganese [462] and nickel [665] complexes containing the ring (**233**) have been reported (with X = S and R = OPh).

There are several pyrazolylphosphine derivatives containing the unit (**234**). Thus, rhenium tricarbonyl bromide complexes of phenyl bis(3,5-dimethylpyrazolyl)phosphines have been prepared and investigated by X-ray diffraction [465a,775]. The reactions of various molybdenum and tungsten carbonyl derivatives with various pyrazolylphosphines gave several similar chelates [463,465,776]. Less usual are the palladium and platinum complexes of pyrazolylcyclophosphazenes: in these chelates the bis(pyrazolyl) phosphorus moiety is part of a cyclic PN ring system $(L_2PN)_n$ (L = pyrazolyl, 3,5-dimethylpyrazolyl, 3-methylpyrazolyl, n = 3–6) [777,777a].

An anionic bis(pyrazolyl)phosphorane (**235**), isolated as a sodium salt [778] might be an interesting chelating ligand, but apparently its complexing ability has not been investigated.



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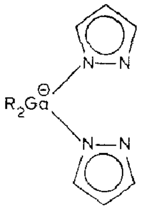
(c) [M : NN](⊃ NGaN) Systems: pyrazolylgallato chelates

Bis(pyrazolyl)dimethylgallato anions (**236**) are formally analogous to the bis(pyrazolyl)borates cited above, and can form similar complexes.



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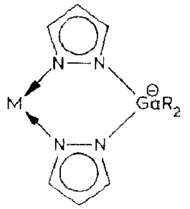


237

Aluminato- and indato-analogues have also been prepared, but strangely enough, they do not react with transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) to form chelate ring complexes [779]. Thus, only the chelate ring (**237**) can be formed with various metals, and a rather large number of such complexes are known.

The bis(pyrazolyl)dimethylgallato anion $[Me_2Ga(Pyz)_2]^{2-}$ (Pyz = pyrazolyl or 3,5-dimethylpyrazolyl) reacts with cobalt(II), nickel(II), copper(II) and zinc(II) salts to form simple chelate complexes of the type (**237**) (R = Me, M = Co/2, Ni/2, Cu/2, Zn/2) [779].

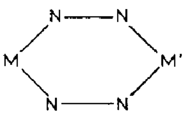
Bis(pyrazolyl)dimethylgallato chelates of molybdenum [780], tungsten [780], manganese [780] and rhenium [669,780a] carbonyls were obtained by reacting the sodium salt of (**236**) with $M(CO)_6$, $C_7H_7M(CO)_2I$ or $(MeCN)_3M(CO)_3$ (M = Mo, W), $Mn(CO)_5Br$, and $Re(CO)_4Cl$, respectively. The structures of some manganese, molybdenum [780] and rhenium [780a] derivatives were established by X-ray diffraction, confirming the presence of a chelate ring. Several rhodium complexes, containing one chelate ring (**237**) and additional ligands to the metal (L = 1,5-cyclooctadiene, CO, PPh_3) have been prepared; the molecular structures of some species were determined by X-ray diffraction, which showed that the six-membered chelate ring [RhNN](⊃ NGaN) exhibits a nonplanar, tube conformation [781,781a].

A number of nickel derivatives, containing the ligand (**236**) and additional η^3-allyl [782] and nitrosyl [676] groups coordinated to the metal have been prepared and investigated by X-ray diffraction. The same ring (**237**) (M = Ni, R = Me) is present in another complex, which also contains a five-membered chelate ring [677].

Derivatives of the tridentate tris(pyrazolyl)methylgallato ligand $[MeGa(Pyz)_3]^-$ which contain two six-membered chelate rings (**237**), have also been reported with molybdenum [783,784], rhenium [785] and nickel [676] coordination centers.

(d) [M : NN](⊃ NM′N) Systems

Chelate rings, containing two transition metals, described by the chemical graph (**238**) are obtained when pyrazolyl complexes of some transition metals (**239**) coordinate through the free nitrogen atoms of pyrazolido groups to a second transition metal atom M, to form chelate rings (**240**). Thus, several metal(II) chelates (**240**) (M = Co, Cu, Zn, Cd) are formed when their salts react with palladium and platinum complexes *cis*-$[L_2M'(Pyz)_2]$ (M′ = Pd, Pt; L_2 = DIPHOS, BIPY) [786,786a]. Similarly, *cis*-$[PtL_2(Pyz)_2]$ (Pyz = pyrazolyl) reacts with chromium hexacarbonyl, to



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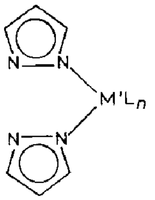

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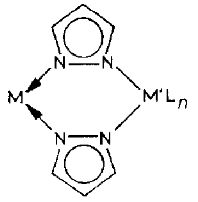

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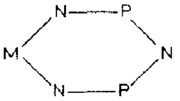
form [{$L_2Pt(Pyz)_2$}$Cr(CO)_4$] (structure **240**, M = $Cr(CO)_4$, M′ = Pt, L = PEt_3, PMe_2Ph) [787].

(e) [M : NN](⊃ PNP) Systems

The cyclic graph (**241**) represents some chelate rings (**242**) derived from



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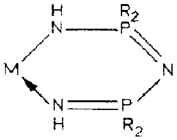

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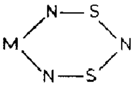
imidodiphosphinates. Only nickel [788] and copper [788,789] derivatives of type (**242**) (M = Ni/2, Cu/2) have been reported so far, although this class of ligands deserves more attention.

(f) [M : NN](⊃ SNS) Systems

The cyclic graph (**243**) represents a chelate ring derived from an N_3S_2



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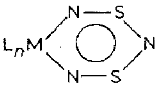

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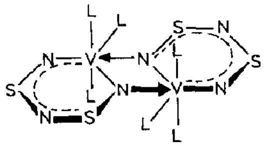
ligand, which cannot be depicted by usual valence bond Lewis structures (a situation frequently encountered in sulfur–nitrogen compounds). The bond lengths determined in several compounds do not clarify the picture and a delocalized formulation (**244**) will be used here for the chelate rings containing the N_3S_2 ligand.

The first compound synthesized containing a chelate ring (**244**) was the vanadium derivative [$Cl_2V(N_3S_2)$] obtained from a reaction of S_4N_4 with VCl_4 in methylene chloride. An X-ray structure analysis showed that the compound is a chlorine bridged dimer, containing planar VN_3S_2 six-membered rings. Weak V ··· N interactions lead to association of the dimeric molecules into a polymer [790]. The same compound has been obtained from VCl_4 or $VOCl_3$ and $S(=NSiMe_3)_2$ in methylene chloride at room temperature [791], and also from $VOCl_3$ and $(ClSN)_3$ [792]. With excess $(ClSN)_3$ the latter reaction gives [$Cl_2V(N_3S_2)(NSCl)$]$_2$. The compound [$Cl_2V(N_3S_2)$] reacts with [$AsPh_4$]Cl to give a salt [$AsPh_4$][$VCl_3(N_3S_2)$]$_2$ which on treatment with silver azide yields [$AsPh_4$][$V(N_3)_3(N_3S_2)$]$_2$ · CH_2Cl_2; an X-ray investigation of this compound shows that dimerization occurs through V–N bonds, in a planar structure (**245**, L = N_3) [792]. In the



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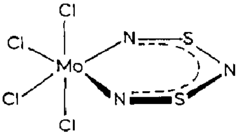
six-membered chelate ring the V–N bond lengths are 1.89 and 1.72 Å, whereas in the four-membered V_2N_2 ring formed via dimerization the V–N bond lengths are 2.24 Å, and the $V{-}N_{azido}$ bonds are 2.00–2.04 Å, thus suggesting some double bond character in the VN_3S_2 ring [792].

The reactions of Mo_2Cl_{10} with S_4N_4 or $S_3N_2Cl_2$ gave a compound of formulation $[Cl_3Mo(N_3S_2)]$ [791,793]; the same composition was obtained from $Mo(CO)_6$ and $(ClSN)_3$ [791], and from reactions of $MoNCl_3$ with $(ClSN)_3$ [794] or S_4N_4 [791]. The compound $[Cl_3Mo(N_3S_2)]$ was described as a chlorine-bridged dimer [794]. With $[AsPh_4]Cl$ it forms a salt, $[AsPh_4]^+[Cl_4Mo(N_3S_2)]^-$ [793,794], which was investigated by X-ray diffraction; this contains a planar six-membered ring and six-coordinate molybdenum, with S–N 1.55–1.66 Å (structure **246**) [793].



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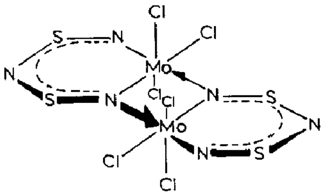

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The reaction of $Mo(CO)_6$ with $(ClSN)_3$ in methylene chloride at 30 °C and the reaction of $MoBr_4$ with S_4N_4 in boiling bromine(!) were reported to give $[X_3Mo(N_3S_2)]_2(\mu\text{-}N_2S_2)$ (X = Cl or Br); the chloro compound reacts with $[PPh_4]Cl$ in CH_2Cl_2 to give $(PPh_4)_2[Cl_3Mo(N_3S_2)]_2$, which was found (by X-ray diffraction) to be a planar dimeric anion (**247**), with S–N in the range 1.56–1.63 Å and Mo–N (in the six-membered ring) 1.97 and 1.77 Å [795,795a]. The chelate $[Cl_3Mo(N_2S_3)]$ reacts with $MoCl_4$ to form $[N(SCl)_2]^+[MoCl_5(NSCl)]^-$ [796]. The reaction of $MoCl_5$ with $(ClSN)_3$ in CH_2Cl_2 gives $[Cl_4Mo(NSCl)]_2(\mu\text{-}S_2N_2)$ which does not incorporate the metal in a chelate ring [797].

Several tungsten analogues of the molybdenum chelates cited above were also investigated. Thus, the reactions of WCl_6 or $WNCl_3$ with S_4N_4 in CH_2Cl_2 [791], of $WOCl_4$ or $WSCl_4$ with excess $(ClSN)_3$ [794], of WCl_6 with S_4N_4 [791,793] and $(ClSN)_3$ [797] all give $[Cl_3W(N_3S_2)]_2$.

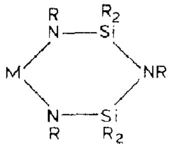
The salts $[EPh_4][Cl_4W(N_3S_2)]$ (E = P or As) were also prepared [794] and a methyl cyanide adduct, $[Cl_3W(N_3S_2)] \cdot MeCN$, was obtained [791,793] by treating $[Cl_3W(N_3S_2)]_2$ with $[EPh_4]Cl$ and MeCN, respectively.

The reactions of $W(CO)_6$ with $(ClSN)_3$ in CH_2Cl_2 and of WBr_6 with S_4N_4 in boiling bromine gave $[X_3W(N_3S_2)]_2(\mu\text{-}N_2S_2)$ (X = Cl, Br) [795,795a]. The reaction of $W(CO)_6$ with $(ClSN)_3$ in 1 : 1 ratio in CH_2Cl_2 was also reported to give $[Cl_3W(N_3S_2)]$ [791]. The structures of $[Cl_3W(N_3S_2)] \cdot MeCN$ [793] and $[AsPh_4][Cl_4W(N_3S_2)]$ [794] were determined by X-ray diffraction. The WN_3S_2 ring is planar in both compounds.

The data cited above illustrate the unpredictable chemistry of the versatile N_3S_2 ligand. Many interesting results can be expected in the future concerning complexes of these little-studied inorganic chelate rings.

(g) [M : NN](⊃ SiNSi) Systems

The six-membered chelate ring of type (**248**), incorporates a metal attached to the terminal nitrogens of a (deprotonated) 1,3-diaminodisilazane. In all the cyclic compounds (**248**) reported so far R = Me, and their synthesis is usually based upon the general reaction of metal halides with dilithiated diaminodisilazane, $LiNR{-}SiR_2{-}NR{-}SiR_2{-}NRLi$.



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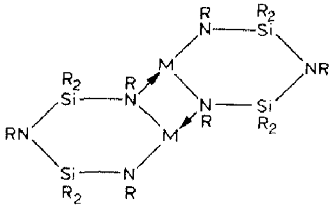
The beryllium derivative (**248**) (M = Be) is dimeric in the solid state (X-ray diffraction) and solution, owing to coordinative unsaturation in a monomeric chelate, thus adopting structure (**249**) (M = Be). This compound was prepared by methane elimination between $BeMe_2$ and the diaminodisilazane $[(RNH)SiR_2]_2NR$ (R = Me) [526].

The reaction of anhydrous aluminum chloride with $RN(SiR_2NRLi)_2$ at −60°C gave an aluminum derivative (**248**) (M = AlCl) which is also dimeric



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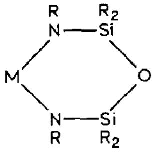
(structure **249**, M = AlCl). An X-ray structure analysis showed that the central Al_2N_2 ring is planar (N–Al 1.947 Å) whereas the chelate six-membered ring is puckered (N–Al 1.803 Å) [798].

In a similar reaction, titanium tetrabromide produced a spiro bicyclic compound (**248**) (M = Ti/2) [799], but monocyclic compounds (**248**) (M = $TiCl_2$, $TiBr_2$, $Ti(NMe_2)_2$ and $Ti(NEt_2)_2$) have also been obtained from the appropriate titanium halide; all these titanium chelates are monomeric [525]. A vanadium spirocyclic compound, containing two chelate rings (**248**) (M = V/2) has been prepared from VCl_4 and characterized by several spectroscopic methods [800].

Some compounds in which [M : NN]($\supset$ SiNSi) chelate rings (M = Ni) are fused to two [M : NS]($\supset$ SN) chelate rings, to form a tricyclic system (**217**) (E = NR) were cited above (Section D(ix)(c)) [653–655].

(h) [M : NN]($\supset$ SiOSi) Systems

Six-membered disiloxanediamido chelates (**250**) are formed in a manner similar to that of the [M : NN]($\supset$ SiNSi) ring (**248**), and the compounds are very similar. Thus, dimeric beryllium derivatives of (**250**) (M = Be) [526], spirocyclic (**250**) (M = Ti/2) [799] and monomeric (**250**) M = $TiBr_2$, $Ti(NMe_2)_2$ and $Ti(NEt_2)_2$ titanium derivatives were synthesised. Tricyclic compounds with structure (**217**) (E = O, M = Ni, Co) were also reported [653–655].



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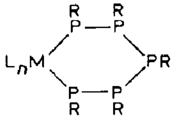
(ii) Phosphorus donor sites

(a) [M : PP]($\supset$ PPP) Systems

The six-membered ring (**251**) may represent a large class of pentaphosphido chelates, but so far only a magnesium representative (**251**, M = Mg) has been reported [801]. To the extent that polyphosphido chains are



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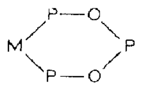
analogous with polysulfido anions, a much larger number of pentaphosphido chelates could be expected, provided that convenient preparation methods could be found.

(b) [M : PP]($\supset$ OPO) Systems

Unusual chelate ring compounds are known to exist that contain the ring described by the graph (**252**). Thus, a molybdenum chelate ring, acting itself



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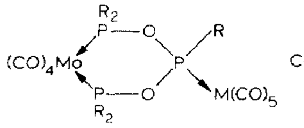

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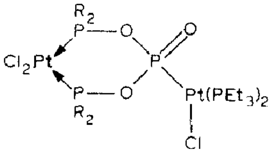

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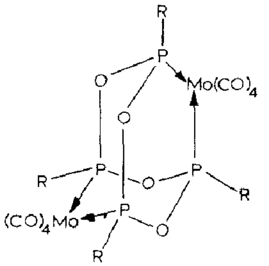
as a ligand to an $M(CO)_5$ group (M = Cr, Mo), as shown in (**253**) (R = Ph) has been reported not long ago [535]. The compounds were prepared by treating $[(CO)_4Mo(PR_2Cl)_2]$ with $[(CO)_5MPPh(OH)O]^-$. A somewhat analogous compound containing platinum (**254**, R = OEt) has been prepared by hydrolysis of $[Cl_2Pt\{PCl(OEt)_2\}(PEt_3)]$ or by reacting *trans*-$[Pt_2Cl_4(PEt_3)_2]$ with tetraethyldiphosphate [802].

A truly remarkable adamantane type structure (**255**) (R = NPr^i_2), containing two [Mo : PP]($\supset$ OPO) chelate rings, is formed in the reaction of



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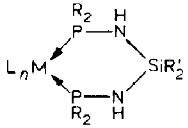
$(Pr^i_2N)_2P(O)H$ with $Mo(CO)_6$. A closer look shows that this structure contains a cyclic tetramer $(Pr^i_2N\text{-}PO)_4$, formed by elimination of $HNPr^i_2$ from $(Pr^i_2N)_2P(O)H$; the $P_4^{III}O_4$ ring is folded in such a way as to coordinate two pairs of opposite phosphorus atoms (in *cis*-positions) to molybdenum atoms [803].

(c) [M : PP]($\supset$ NSiN) Systems

A class of chelate rings (**256**) that derive from bis(phosphinylamino)silanes $(R'_2P\text{-}NH)_2SiR_2$ have not been isolated as such, but are formed by reactions of coordinated ligands. Thus, *cis*-$[(CO)_4Mo(R_2PNH_2)_2]$ reacts with Me_2SiCl_2 in the presence of triethylamine, to give (**256**) R = Me or Ph,



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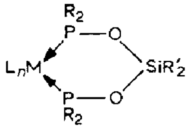
R′ = Me, $ML_n = M(CO)_4$ [536,536a] or similarly by treating lithiated *cis*-$[(CO)_4Mo(R_2PNH_2)_2]$ or the salt $Na^+[Mo(CO)_4(PR_2O)_2H]^-$ with R'_2SiCl_2 (R = Ph, R′ = Me) [804]. Extensive spectroscopic investigations (^{13}C, ^{17}O, ^{29}Si, and ^{31}P NMR, etc.) were performed on some of these compounds [805].

(d) [M : PP](⊃ OSiO) Systems

Closely related to the previous rings, are the bis(phosphinoxy)silane chelates, containing a ring of type (**257**). These are also formed by the reactions of coordinated ligands. Thus, the anion *cis*-$[Mo(CO)_4(PPh_2O)_2H]^-$ reacts with R'_2SiCl_2 to form (**257**) $ML_n = Mo(CO)_4$, R = Ph, R′ = Me [804]; a spiro compound, (**258**), containing two such chelate rings was similarly prepared with $SiCl_4$ [806]. These chelate rings were recently investigated in detail by spectroscopic methods [805–807].



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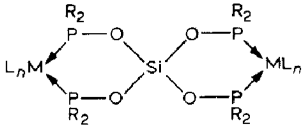
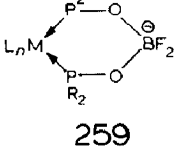


258

It can be expected that the chemistry of both the chelates (**256**) and (**257**) can be greatly expanded, to include other transition metals.

(e) [M : PP](⊃ OBO) Systems

The ring (**259**) is present in chelates prepared by treatment of complexes containing two PR_2OH ligands in the *cis*-position, with boron trifluoride. Thus, the first such compound, (**259**) $ML_n = Mo(CO)_4$, R = Ph was prepared by reacting salts of *cis*-$[Mo(CO)_4(PPh_2O)_2H]^-$ with BF_3OEt_2 [804]. Similarly prepared were rhodium [808], iridium [809] and platinum [810,811] chelates. The structures of (**259**) $ML_n = Pt(PEt_3)Cl$, R = OMe, [810] and



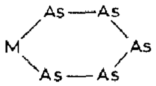
259

(**259**) ($M = Pt/2$, $R = OMe$) [811] were determined by X-ray diffraction; in both compounds the chelate rings exhibit a chair conformation.

(iii) Arsenic donor sites

(a) [M : AsAs](⊃ AsAsAs) Systems

The six-membered ring (**260**) is known only in a molybdenum derivative



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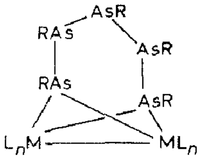

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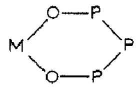
(**261**) $ML_n = Mo(CO)(\eta^5\text{-}C_5H_5)$, $R = Me$, in which the coordinated terminal atoms of the pentaarsenido chain, still maintain donor properties and coordinate to a second metal atom, thereby forming a bridge. The structure was established by X-ray diffraction and the compound can be prepared by reacting $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ with $(AsMe)_5$ [812].

(iv) Oxygen donor sites

(a) [M : OO](⊃ PPP) Systems

The chelate rings containing the atom sequence shown in graph (**262**)



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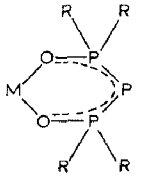

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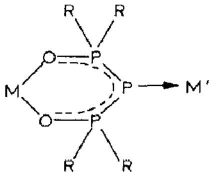
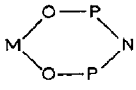


264

derive from an unusual ligand, obtained as a sodium or lithium salt, by reacting yellow phosphorus (P_4) with $MOPR_2$ ($M = Na$, Li). The lithium salt was investigated by X-ray diffraction and found to be a dimer containing a chelate ring of type (**263**) ($R = Ph$) [813]. The same type of ring was shown to be present in the compound $(CO)_5W : P\{P(O)(OEt)_2\}_2SnCl$ (structure **264**, $M = SnCl$, $M' = W(CO)_5$, $R = OEt$) [814]. Two fused [Zn : OO](⊃ PPP) chelate rings are also present in the compound $Zn[P\{P(O)(OEt)_2\}_3]_2(AsF_6)$, obtained from $Zn(SO_2)_3(AsF_6)_2$ and $P\{P(O)(OEt)_2\}_3$ [558].

(b) [M : OO](⊃ PNP) Systems

The graph (**265**), represents two types of chelate rings, (**266**) (donors: two phosphoryl oxygens) and (**267a–b**) containing a delocalized electron system. The ligands in (**266**) and (**267**), when R′ = H, are in tautomeric relationship, but this is not possible if R′ = alkyl or aryl: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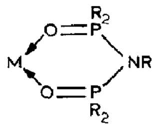
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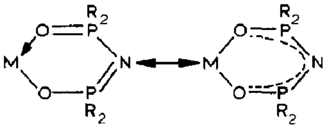
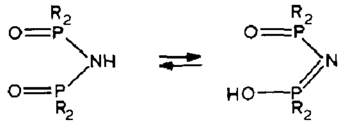
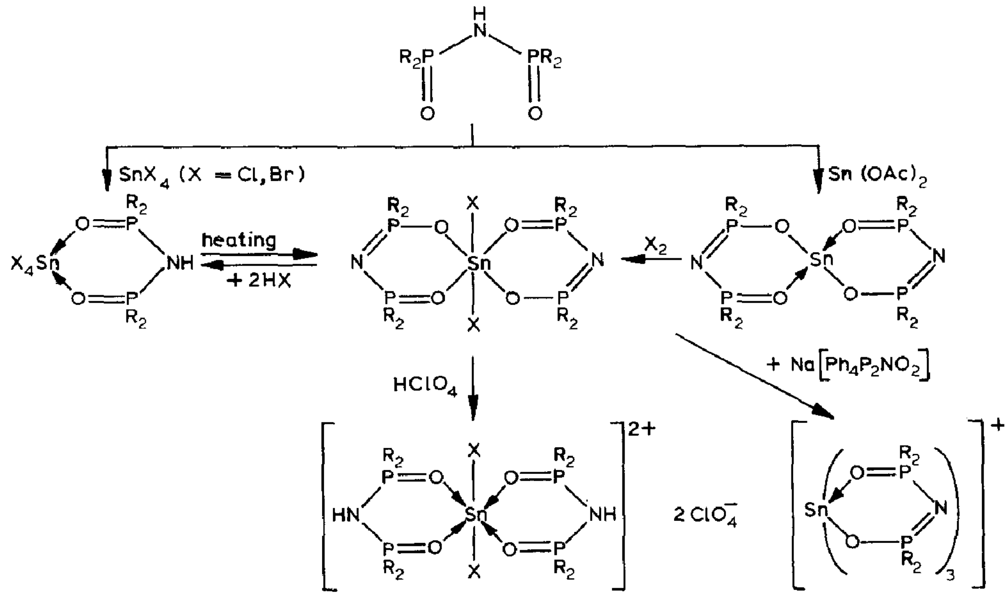

267a 267b


268a 268b

Therefore, both type of chelates can be obtained from imidodiphosphinates (**268**), and interconversions are possible. This is illustrated by the tin complexes of tetraphenylimidodiphosphinate (**268**, R = Ph), which undergo the reactions shown in the following scheme [815,816]:



Ready deprotonation of (**268a**) (R = NMe$_2$) also occurs with sodium methoxide in methanol, and the sodium salt thus formed reacts with lanthanoid chlorides MCl_3 (M = Ce, Pr, Nd, Sm, Gd, Dy, Ho) to form neutral tris-chelates ML_3 ($L = {}^-N\{PO(NMe_2)_2\}_2$) and anionic tetrakis chelates, $Na[ML_4]$ containing the ring (**267**) (R = NMe_2) [817].

A powerful bidentate neutral ligand, which forms chelate rings (**266**) (R = R′ = Me) is nonamethylimidodiphosphoramide (NIPA). This ligand was found to form chelate complexes with many metal ions, including magnesium, calcium, strontium [818,819], calcium, barium, aluminum, manganese, iron, cobalt, nickel, copper, zinc, mercury, thorium and dioxouranium [818]. Spectroscopic evidence (mainly infrared) supports coordination through the phosphoryl oxygen [818]. It was found that replacement of the NMe_2 groups in the ligand with –O– or –CH_2– groups has little effect upon the stability of the complexes [820]. The number of chelate rings (**266**) in the complex is determined by the coordination number of the metal; thus four-coordinate $[Cu(NIPA)_2](ClO_4)_2$ (containing two rings), and six-coordinate $[M(NIPA)_3](ClO_4)_n$ ($M^{n+} = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Zn^{2+}, Hg^{2+}$) (containing three rings) were established [818]. In the dioxouranium complex $[UO_2(NIPA)_3](ClO_4)_2$, ^{31}P NMR spectroscopy in CH_3NO_2 and CH_2Cl_2 solution established a pentacoordinate arrangement of the two bidentate and one monodentate NIPA ligands around central UO_2^{2+}, with fast intramolecular exchange (at −60°C) yielding full dynamic equivalence of all phosphorus atoms at 30°C [821]. In $[UO_2(NIPA)_2(EtOH)](ClO_4)_2$, X-ray diffraction established that the two NIPA ligands are bidentate, with an EtOH molecule occupying the fifth coordination site at the central UO_2 group [822]; NMR investigations also revealed intramolecular ligand-exchange [822a].

NIPA is also an excellent ligand for lanthanoid ions, and chelate complexes of the types $[Ln(NIPA)_3](NCS)_3$ (with Ln = Ce, Pr, Nd, Sm, Eu), $[Ln(NIPA)_3(NCS)_2][Ln(NIPA)_2(NCS)_4]$ (with Ln = Er, Tm, Lu) [823], $[Ln(NIPA)_2(EtOH)_n](NO_3)_3$ (with $n = 1$, Ln = La, Ce, Pr, Nd, Sm; $n = 2$, Ln = Eu, Gd, Tb, Dy, Er) [824, 825], and $[Ln(NIPA)_2](NCS)_3$ (with Ln = Pr, Nd, Sm, Gd, Tb, Er, Tm, Lu) [826] have been investigated.

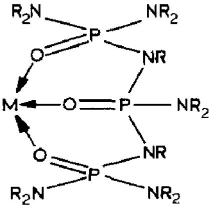
The cobalt(III) paramagnetic tris-chelate complex was found to be stereochemically non-rigid, a somewhat unexpected result [827].

In addition to NIPA, other imidophosphoramides, $R'N\{P(O)(NMe_2)_2\}_2$ (R′ = n-C_6H_{13}, CH_2Ph, n-$C_{12}H_{25}$), also exhibit powerful donor properties and can be used as reagents for the solvent extraction of several metal cations, owing to formation of neutral chelates of type (**266**) [828].

Another class of good chelating ligands are the imidodiphosphate tetraesters, $(RO)_2P(O)NHP(O)(OR)_2$, which can readily be prepared [829]. Thus deprotonated tetraphenyl ester was reported to form chelates (**267**) (R = OPh) with M = Ba, Ca, Cu, Fe [830] and lanthanoids [831,832]. An X-ray investigation of the ytterbium chelate (**267**) (R = OPh, M = Yb/3) showed it to contain a six-coordinate metal with three bidentate ligands [833,834].

Tetraphenylimidodiphosphinate, $Ph_2P(O)NHP(O)Ph_2$, forms chelate rings (**267**) (R = Ph) with beryllium [835], zinc [836], bismuth [837], tin [815,816], copper [789], cobalt [838,839], nickel [838], cadmium, mercury [839], manganese [839], dioxouranium [839]. An aluminum derivative (**267**) M = $Al(OPr^i)_2$, R = Ph has also been obtained [839].

Bicyclic systems, containing two fused [M : OO]($\supset$ PNP) chelate rings (**269**) are formed by tridentate coordination of *N*-dodecamethyl-bis-imidotriphosphoric amide (TRIPA), $(R_2N)(O)P\{NR{-}P(O)(NR_2)_2\}_2$ (R = Me), which forms complexes with many transition metal [839a] and lanthanoid [839b,c] cations.



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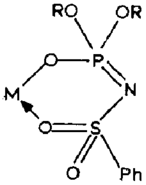
(c) [M : OO]($\supset$ PNS) Systems

Partial replacement of phosphorus for sulfur in the previous ligands, leads to a new class of chelates (**270**).



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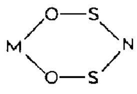
Such rings are derived from phenylsulfonylimidophosphato ligands (R = alkyl); they are formed when these ligands are used as extraction reagents for alkaline earths (Ca, Sr, Ba) [840–843] and lead [844]. The investigations of these chelates is limited to their use in solvent extraction and so far no detailed structural study has been reported.

(d) [M : OO]($\supset$ SNS) Systems

A potentially interesting class of chelate rings based upon the graph (**271**) might be expected both as *N*-substituted types (**272a**) or *N*-unsubstituted types (**272b**) (with X = aryl, alkyl, O^-, etc.). However so far, to the best of our knowledge, only heavy metal cation complexes of hydroxylamine-*N*,*N*-disulfonates (R = OH) are known as representatives of this class [845].



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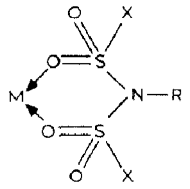

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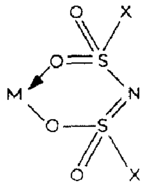
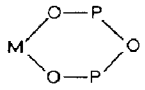


272b

(e) [M : OO](⊃ POP) Systems

The cyclic graph (**273**) represents two possible types of chelate rings: type (**274**), derived from ligands containing the pyrophosphoryl group O=P–O–P=O, in which the doubly bonded oxygens are the donors, and type (**275**), in which the doubly bonded oxygens are exocyclic; a potential mixed type (**276**) (note the asymmetry of the ligand !) has not yet been described.



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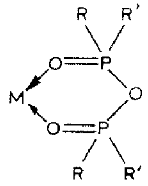

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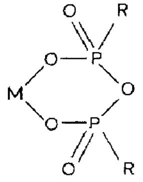

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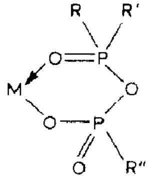


276

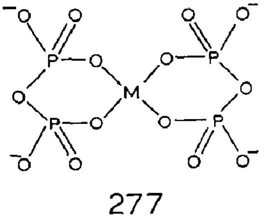
Regardless of the nature of R and R′ groups, the phosphoryl ligands readily close six-membered chelate rings (**274**). Even when either R or R′ or both R and R′ are dialkylamino groups the coordination occurs through the phosphoryl oxygens, rather than through nitrogen. The most frequently used ligand of this class was octamethylpyrophosphoramide ($R = R' = NMe_2$) (abbreviated OMPA). This versatile ligand was intensively investigated two decades ago [846–853] when formation of chelate rings **274** ($R = R' = NMe_2$, $M = Fe^{3+}$, Co^{2+}, Cu^{2+}, Ag^{1+}, Hg^{2+}, Mg^{2+}) were established, and firmly supported by X-ray investigation of the copper(II) [851–853], cobalt(II) [852] and magnesium [853] complexes. The six-membered chelate ring was found to exhibit planar conformation. Similar chelates of lanthanoids (M = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb) [854], thorium [855,856] and uranium [828,855–857] were later reported. The X-ray diffraction analysis of $[U(OMPA)_2(NSC)_4]$ and $[ThCl_4(OMPA)_2]$ [856] was also performed. The cobalt(III) chelate of OMPA is stereochemically nonrigid [827].

Similar chelate compounds were described with ethyl dimethylamidopyrophosphates (**274**) ($R = OEt$, $R' = NMe_2$ and other combinations of NMe_2 and OEt substituents at phosphorus sites) [858,859], *P*-dialkyl-*N*-tetramethylpyrophosphoramides (**274**) ($R = Me, Et, Pr^i$, $R' = NMe_2$) [860], tetraethylpyrophosphate (**274**) ($R = R' = OEt$) [859] and dialkyl(aryl)phosphinic anhydrides (**274**) ($R = R'$ = alkyl or aryl) [861–863].

Chelates of type (**275**) are best illustrated by complexes of dialkylpyrophosphates. Thus, the good extractability of uranium with dialkylpyrophosphates was explained in terms of a stable compound containing six-membered chelate rings (**275**) (R = OR′, R′ = alkyl) [864]. However, this type of chelates has not been widely investigated. Magnesium complexes of methyl and aryl pyrophosphate esters were investigated with the aim of elucidating the role played by the Mg^{2+} ions in phosphoryl transfer reactions [864a].

By contrast many chelates of purely inorganic pyrophosphates (**275**), (R = OH or O^-) were studied in considerable detail. The extensive literature dealing with complexes of $P_2O_7^{4-}$ or $H_2P_2O_7^{2-}$ ligands, cannot be fully reviewed here, and only some significant examples will be cited to illustrate this type of chelate. The chelating behavior of the pyrophosphato ligand was confirmed by X-ray diffraction investigation of $Na_6[Cu(P_2O_7)_2]\cdot 16H_2O$ [865], $Na_6[VO(P_2O_7)_2]\cdot 16H_2O$ [866], $[Co(NH_3)_4(HP_2O_7)]\cdot 2H_2O$ [867], $[Cr(H_2O)_4(HP_2O_7)]\cdot H_2O$ [868] and $[Cr(NH_3)_4(HP_2O_7)]\cdot 2H_2O$ [869]. Although not investigated by diffraction methods, it seems obvious that the complexes $[Cu(BIPY)(H_2P_2O_7)]$ [870], $[Co(en)_2(HP_2O_7)]\cdot 2H_2O$, $Ba[Co(en)_2(P_2O_7)]\cdot 4H_2O$ [871,872] and $[Rh(H_2O)_4(P_2O_7)]$ [873] also contain chelated pyrophosphato ligands.

The formation of 1 : 1 $M:P_2O_7^{n-}$ and 1 : 2 $M:P_2O_7^{n-}$ complexes was established in aqueous solutions. In the 1 : 1 complexes the coordination sphere of the metal is probably completed by water molecules, whereas 1 : 2 complexes are spirocyclic chelates (**277**). Such compounds have been reported for M = Mo(V) [874,875], Fe(III) [876–879], Co(II) [878,880,881,882], Ni(II) [878,880–882], Cu(II) [876–878,881–883], Zn(II) [881,882,884], Cd(II) [882], Al(III) [879,885], Ga(III) [879,885], In(III) [885], Sn(II) [886], Pb(II) [887], lanthanoids [888] and uranium [889].



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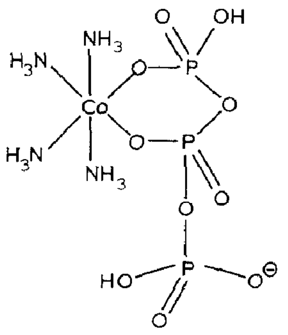
An interesting observation was the possibility of linear triphosphate coordinating as a bidentate ligand in two ways, firstly to form a *β*, *γ*-isomer (containing a six-membered chelate ring (**278**)) and secondly an *α*,*γ*-isomer (containing an eight-membered chelate ring (**279**)). This isomerism was investigated in the cobalt complex $[Co(NH_3)_4(H_2P_3O_{10})]$ [890–894].



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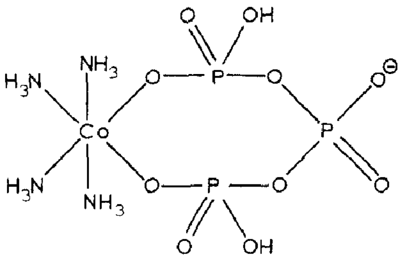

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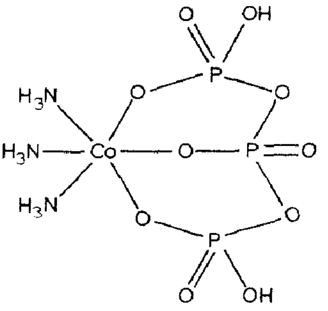

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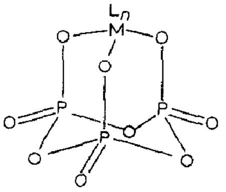
An additional possibility is tridentate coordination of the triphosphate, with the formation of a bicyclic chelate structure, discovered in $[Co(NH_3)_3(H_2P_3O_{10})]$ [895] (structure **280**) and $Na_3[Cd(H_2O)_3(P_3O_{10})] \cdot 9H_2O$ [896].

Tridentate chelating behavior has also been observed, in complexes of the trimetaphosphate ligand. Thus, the ions $[(NBD)Rh(P_3O_9)]^-$ and $[M(CO)_3(P_3O_9)]^+$ (M = Mn, Re) exhibit an adamantane-like structure (**281**), in which the six-membered chelate rings [M : OO]($\supset$ OPO) are readily noticed [897].



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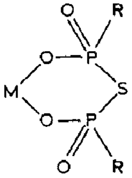
The chelating behavior of pyrophosphato and triphosphato ligands is of interest for modeling the interactions of nucleic acids with metal ions [898]. Thus, various adenosinediphosphate and -triphosphate complexes of molybdenum(V) [899], manganese(III) [900], ruthenium(II and III) [901], cobalt(II) [900], rhodium(III) [873,901], iridium(III) [901], copper(II) [900,902,903] and zinc [900,904,905] have been reported, with chelating coordination of the di- or triphosphato fragment to the metal. The copper(II) complex of thiamine pyrophosphate, investigated by X-ray diffraction, was also found to contain a six-membered ring of type (**275**) [906].

(f) [M : OO]($\supset$ PSP) Systems

Chelate rings containing the pyrothiophosphato ligand (**282**) (with R = O^- or OR′) have been reported, mainly as dinuclear compounds, containing two



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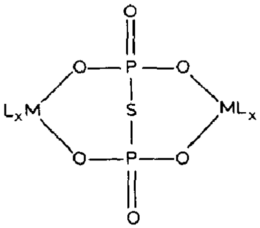

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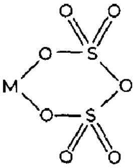
fused six-membered rings (**283**) or related types [907]; these are formed on heating metal complexes of trialkylthiophosphates. However, this type of chelate is not yet firmly established, since none of the assumed structures are based upon a diffraction investigation.

(g) [M : OO](⊃ OSO) Systems

A potentially large class of chelate rings, (**284**) could be derived from the

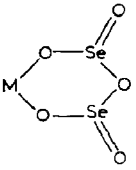


284

disulfato (pyrosulfato) ligand but to the best of our knowledge, this ring (M = Sb) has been identified only in $Sb_2(S_2O_7)_3$; this was done by X-ray diffraction [908].

(h) [M : OO](⊃ OSeO) Systems

Chelate rings derived from diselenito ligand, (**285**), are equally rare. This



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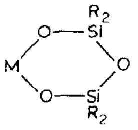
cyclic unit was found (by X-ray diffraction) as a building unit in $[Y(Se_2O_5)(NO_3) \cdot 3H_2O]$ [909] but we know of no other example.

(i) [M : OO](⊃ SiOSi) Systems

The dianions resulting from deprotonation of organodisiloxane-1,3-diols



286

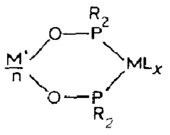
can coordinate as chelating bidentate ligands, to form rings of type (**286**). This chelate ring (M = Al) was identified by X-ray diffraction [910,911] as a structure fragment in the crystalline products formed in the reactions of alkylcyclosiloxanes with anhydrous aluminum chloride [912–916]. Spirobicyclic titanosiloxanes (**286**, M = Ti/2) were also described [917] and similar but larger rings were suggested in other spirocyclic siloxane derivatives [918,919].

An X-ray investigation of $[Et_2NH_2]^+[Zr(Ph_4Si_2O_3)_3]^-$, obtained from $Zr(NEt_2)_4$ and $Ph_2Si(OH)_2$, revealed the presence of three chelate rings of type (**286**), formed by chelating the disiloxanediolato ligand to a six-coordinated zirconium atom [920].

It can be anticipated that disiloxane-1,3-diolates will prove, eventually, to become a much more versatile class of ligands than is presently recognized.

(j) [M : OO](⊃ PM′P) Systems

Heterobimetallic chelate rings of type (**287**), in which one metal atom, M,



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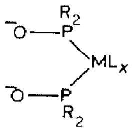

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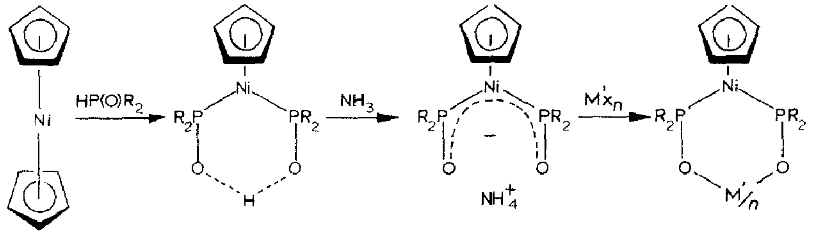
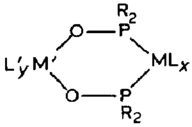
is part of the ligand, are formed by coordination of bis(dialkylphosphinito) ligands (**288**), to a second metal atom, M′. In known examples M = Ni, Pd, Pt, Rh, Ru, Mo and M′ is one from a large range of main Group and transition metal ions.

η^5-Cyclopentadienylnickel-bis(dialkylphosphinito) complexes are formed on treatment of nickelocene with the dialkyl (usually methyl)ester of phosphinous acid (R = OMe, etc.), followed by treatment with ammonia and then with a metal salt:



Thus, bis-chelates ($n = 2$) with M' = Co(II) [921–923], Ni(II) [921,923], Cu(II) [921,923], Zn(II) [921–923], VO(II) [921–923], tris-chelates ($n = 3$) with M' = Cr(III) [921,923], Fe(III) [921,923], Al(III) [921,923] and tetrakis-chelates ($n = 4$) with M' = U(IV) [924] (R = OMe) were prepared by this procedure.

Compounds, containing only one chelate ring, (**289**) (R = OMe) with



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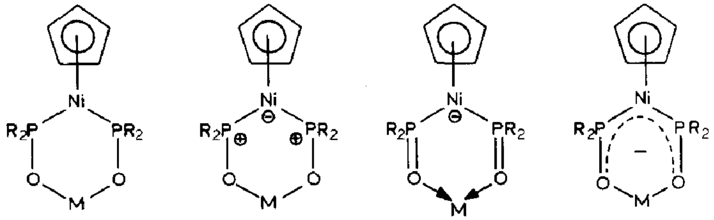
$ML_x = Ni(\eta^5\text{-}C_5H_5)$ and $M'L'_y$ = VO(acac), $Ni(NH_3)_2$, Ni(acac), $Pd(\eta^3\text{-}C_3H_4R)$, $Rh(C_8H_{12})$ and Tl have also been reported [921–923].

Palladium analogues of types (**288**) and (**289**) (M = Pd) with the same central atoms (M') have been similarly prepared [921–923,925].

The chelate rings discussed here can be written with the aid of several canonical formulae (**290a–d**), and it is difficult to say which one is the best representation of the actual bonding in the ring:



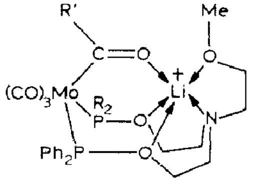
290a 290b 290c 290d

Therefore, formulae (**287**) and (**289**) are to be regarded only as conventional representations of this type of chelate ring.

Several platinum bis(phosphinato) chelates, of type (**287**) with ML_x = $Pt(PEt_3)Cl$, R = Ph, $n = 2$, M' = VO [926], R = Ph or OMe, $n = 2$, M' = Co(II), Cu(II), UO_2, $n = 2$ [927,928]; $n = 4$, M' = Th, [928] and ML_x = $Pt(S_2C\text{-}NEt_2)$, R = Ph, $n = 2$, M' = VO, Co(II), Ni(II), Cu(II), [929] M' = Co(II) [811a]; Mn(III), Cr(III), $n = 3$ [929] have been prepared and investigated by spectroscopic methods. A similar ruthenium compounds, (**287**), $ML_x = Ru(Me_2PS_2)$, R = Ph, $n = 2$, M' = Co, has been described [811a].

η^5-Cyclopentadienylrhodium ligands, of type (**288**) can readily be generated as alkali metal salts and additionally thallium(I), cobalt(II), zinc(II), iron(III) and aluminum(III) chelates (**287**), $ML_x = Rh(\eta^5\text{-}C_5H_5)Me$, R = OMe, have been prepared [930,931].

A novel, interesting type of structure, incorporating an inorganic chelating fragment into a macrocyclic ligand, which forms strong lithium complexes is illustrated by formula (**291**); the compound has been prepared by



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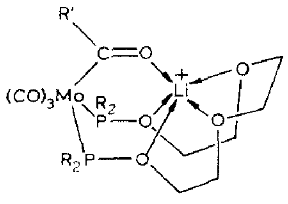

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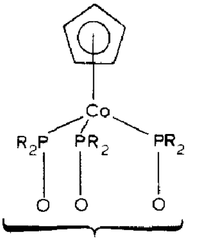
reacting $(Ph_2POCH_2CH_2)_2NCH_2CH_2OMe$ with $[Mo(CO)_4(NBD)]$ then with R′Li (R = Me, Ph) [932]; this unusual complex, containing a boat shaped chelate ring, has been confirmed by X-ray diffraction. A related compound is shown in formula (**292**) [932]. This type of ligand promises to be very versatile.

A large number of complexes, derived from the tripod (uninegative tridentate) ligand (**293**) and containing two fused chelate rings, (**294**), have been reported with various metals, including alkali metals [933,934], Mg(II),



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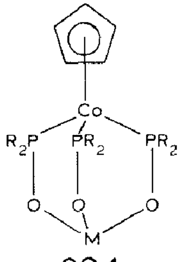

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Ca(II), Sr(II), Ba(II) [934–936], VO [937], Mn(II) [934–936], Fe(II) [936], Co(II and III) [935,936,938–941], Ni(II), Cu(II) [934–936], Ag(I) [934], Zn(II), Cd(II), Hg(II) [934–936], Al(III), Ga(III), In(III), Tl(III) [933], Sn(II) [937], Pb(II) [934–936], La(III) [934], $Cr(CO)_3$, $Mo(CO)_3$, $W(CO)_3$ [942], $Mn(CO)_3$, $Re(CO)_3$ [943] and $Rh(CO)_3$ [944].

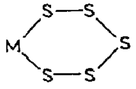
The tripod ligand is a powerful complexing reagent, and in this respect it is worth mentioning that the sodium chelate is more stable than the crown ether complexes [934] that are known.

The cobalt atom in the tripod ligand can be replaced by other metals. Thus, a ruthenium ligand $[(Me_2PS_2)Ru(PPh_2O)_3H_2]$ was reported to form oxovanadium and cobalt(III) chelates [811a].

(v) Sulfur donor sites

(a) [M : SS](⊃ SSS) Systems: pentasulfido chelates

In addition to tetrasulfido chelates, discussed in Section D(v)(a), the six-membered rings (**295**) illustrate the ability of polysulfur chains to act as chelating bidentate ligands [560,561]. At the present time several metals are known to form such rings; these will be discussed here according to the position of the metal in the Periodic Table.



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Probably the most investigated pentasulfido chelate is bis(η^5-cyclopentadienyl)titanium pentasulfide (η^5-C_5H_5)$_2$TiS_5 and its substituted derivatives [945]. The compound was prepared by reaction of (η^5 – C_5H_5)$_2$TiCl_2 with alkali metal or ammonium polysulfides [946–950]; (η^5-C_5H_5)$_2$Ti(SH)$_2$ with iodine, sulfur dichlorides S_xCl_2 ($x = 1, 2, 3$) [951] or bis(benzimidazolyl)sulfides [255,952]; by reacting (η^5-C_5H_5)$_2$TiCl_2 with Li_2S_2, with Li[Et_3BH] and sulfur or Li_2S_2 and sulfur [255,952] and also by reacting (η^5-C_5H_5)$_2$ Ti(CO)$_2$ with elemental sulfur [953,954].

Substituted derivatives reported include pentamethyl [255], methyl [955] and 1,1′-dimethylsilyl [956] cyclopentadienyls.

The cyclic structure of (η^5-C_5H_5)$_2$TiS_5 [957,958] and (η^5-Me_3Si-C_5H_4)$_2$ TiS_5 [959] was confirmed by X-ray diffraction. The six-membered chelate ring, TiS_5, exhibits the chair conformation. Molecular orbital calculations have been reported [960,961] and the photochemistry and electronic structure of (η^5-C_5H_5)$_2$TiS_5 was also investigated [962,963].

Several interesting reactions of (η^5-C_5H_5)$_2$TiS_5 have been reported. When heated in refluxing xylene, the compound rearranges to a η^5-cyclopentadienyltitanium derivative of 1,2-dimercapto-3-trisulfidocyclopentene [964]. The methylcyclopentadienyl derivative can be desulfurated with an iridium(I) complex or with PPh_3 to form cyclic [(η^5-MeC_5H_4)$_2$Ti(μ-S_2)$_2$Ti(η^5-C_5H_4Me)$_2$] [965]. Reactions of the TiS_5 ring derivatives with ketones and CH_2Br_2 were reported to replace a sulfur atom in the ring with a CRR′ or CH_2 group, respectively [966]. The reactions of (η^5-C_5H_5)$_2$TiS_5 with various sulfur dichlorides, S_xCl_2 [967–969] and sulfuryl chlorides [970] serve as reactants for the synthesis of several cyclopolysulfur rings; the reaction with Se_2Cl_2 yields cyclic 1,2-Se_2S_5, SeS_5 and 1,2,3-Se_3S_3 [971] and with oxalyl chloride produces the macrocyclic compound S_{10}(CO)$_4$ [972]. The cited examples suggest that interesting chemistry of this compound can be envisaged in the future.

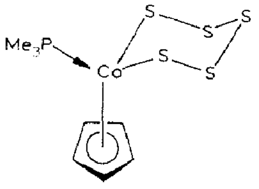
Six-membered chelate rings, (**295**), with M = $(\eta^5\text{-}C_5H_5)_2Zr$ [255,952,973], $(\eta^5\text{-}C_5H_5)_2Hf$ [255,952,973], and $(\eta^5\text{-}C_5H_5)_2V$ [953,954,974,975] were prepared by procedures similar to those used for the titanium derivative. Of these, the vanadium compound was investigated by X-ray diffraction; the VS_5 ring also exhibits chair conformation [953,954].

The only known chromium pentasulfido chelate is the anion of $PPh_4[Cr(NH_3)_2(S_5)_2]$ obtained from chromium(II) acetate and an alkali metal polysulfide; X-ray diffraction shows that the compound contains two *cis*-CrS_5 chelate rings, of chair conformation [589].

The MnS_5 ring is associated with an MnS_6 ring in the complex $(PPh_4)_2[Mn(S_5)(S_6)]$ prepared by oxidation of $[Mn(SPh)_4]^{2-}$ with dibenzyltrisulfide [574].

The iron pentasulfido chelate ring FeS_5 was identified in two anionic species: $[Fe(S_5)WS_4]^{2-}$ (investigated by X-ray diffraction) [976] and $[Fe_2S_2(S_5)_2]^{2-}$ [977]. The isolation of the latter from various reaction mixtures consisting of $FeCl_3$ with sodium or CaH_2 and cyclooctasulfur, S_8, in dimethylformamide, or with $Et_2N\text{-}P(S)(SH)_2 + S_8$, $(p\text{-}MeC_6H_4)_2PS_2Na$ plus Na_2S_4 systems [977] demonstrates a strong tendency for it to be formed.

A chair-shaped CoS_5 ring was found (by X-ray diffraction) in the compound $(\eta^5\text{-}C_5H_5)(PMe_3)CoS_5$, structure (**296**), obtained by treating $(\eta^5\text{-}C_5H_5)(PMe_3)Co(\eta^2\text{-}CS_2)$ or $(\eta^5\text{-}C_5H_5)(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)(\eta^5\text{-}C_5H_4Me)$ with cyclooctasulfur [978]. A rhodium analogue of (**296**), namely $(\eta^5\text{-}C_5H_5)(PPh_3)RhS_5$ was obtained in the reaction of $(\eta^5\text{-}C_5H_5)Rh(PPh_3)_2$ with cyclooctasulfur in hot benzene [979]. The RhS_5 chelate ring is also present in $(NH_4)_3[Rh(S_5)_3]$ which is formed in the reaction of $RhCl_3$ with ammonium pentasulfide [980].



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A nickel pentasulfido chelate ring, isolated as $[PPh_4]^+$ or $[AsPh_4]^+$ salts of the $[Ni(CN)_2(S_5)]^{2-}$ anion, is formed in the reaction of $K_2[Ni(CN)_4]$ with cyclooctasulfur and potassium hydroxide in DMF [981].

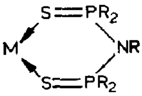
The platinum pentasulfido chelate is present in the anion $[Pt(S_5)_3]^{2-}$, prepared by reaction of $H_2[PtCl_6]$ with ammonium [982,983] or potassium [984] polysulfides. Desulfuration of $[Pt(S_5)_3]^{2-}$ with various nucleophiles yields $[Pt(S_5)_2]^{2-}$ [982,985]. The structure of $[Pt(S_5)_3]^{2-}$ has been confirmed by X-ray diffraction [984,986,987]. These anions are optically active [983]. The ^{195}Pt NMR spectrum of $[Pt(S_5)_3]^{2-}$ has been reported [988].

Some copper containing MS_5 chelate rings were cited above, in Section D(v)(a). Zinc and cadmium chelates $[Zn(S_{4-6})_2]^{2-}$ and $[Cd(S_5)_2]^{2-}$ containing MS_5 rings, have also been reported [574].

Finally, it should be noted that the identification (by analysis) of an S_5 unit in the composition of a coordination compound does not necessarily imply the presence of an MS_5 chelate ring. This is especially true in dinuclear compounds, since the pentasulfido ligand may act as a bridge, as in $[Os_2(\mu\text{-}S_5)(S_3C\text{-}NMe_2)(S_2C\text{-}NMe_2)_3]$ [989] or in $(NH_4)_3[Mo_2(\mu\text{-}S_5)(\mu\text{-}OH)(\mu\text{-}S_2)_3(NO)_2]$ [990], or, alternatively, five sulfur atoms in a molecule may be distributed as S_3 and S_2 bridges, as in $(\mu^5\text{-}C_5H_5)_2Re_2(CO)_2S_5$, containing a $Re(\mu\text{-}S_2)(\mu\text{-}S_3)Re$ cyclic skeleton [991].

(b) [M : SS](⊃ PNP) Systems

The chelates discussed in this Section are thioanalogues of those treated in Section E(iv)(b). There are few ring derivatives of type (**297**) and most known compounds are chelates of type (**298**).



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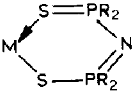

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Both types of chelate ring derive from tetraalkyl(aryl)dithioimidodiphosphinic acids, $[R_2P(S)]_2NH$, (usually R = Me, Ph) [992]; although in the solid state the free ligand adopts a *trans*-configuration [993], chelate cyclization requires a rotation about one of the R–N bonds.

The (**297**) type chelates are derived from the protonated form (R′ = H) of the ligand. Phenylated derivatives (**297**) (R = Ph) are formed when cobalt(II) perchlorate, zinc(II) halides, copper(I) bromide and palladium(II) bromide react with the ligand under mild conditions, to form $[Co\{(Ph_2PS)_2NH\}_2](ClO_4)_2$, $[ZnCl_2(Ph_2PS)_2NH]$, $[CuBr(Ph_2PS)_2NH]$ and $[PdBr_2(Ph_2PS)_2NH]$, respectively. On heating, the deprotonated type (**298**) is formed [994]. Probably the titanium tetrahalide adducts, $[TiX_4(Me_2PS)_2NH]$ (X = Cl, Br), are also complexes, of type (**297**), of the protonated ligand (R′ = H) [995].

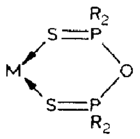
There are many chelate ring compounds of type (**298**) (derived from the deprotonated ligand). These contain transition metals with M =

manganese(II) [839,996–998], iron(II) [838,999,1000], cobalt(II) [838,839, 994,1000], nickel(II) [788,838,839,1001,1002], palladium(II) [838,994], platinum(II) [838,994], copper(I and II) [1000,1003–1006], zinc(II) [838,994], cadmium(II) [836,839,994], mercury(II) [839,994] and dioxouranium [839]. Of the main group metals, bismuth(III) [837,1007] and tellurium(II) [1008] form similar chelates. Several of these compounds were investigated by X-ray diffraction (M = Mn(II) [997], Fe(II) [999], Ni(II) [1001,1002], Bi(III) [1007] and Te(II) [1008]). Monovalent copper forms polynuclear complexes containing a tetrahedral Cu_4 cluster in which the ligand L simultaneously chelates and bridges; thus $[Cu_4L_3]^+$ species (containing a tetrahedral Cu_4 cluster) were investigated by X-ray diffraction [1005,1006] and Cu_3L_3 and Cu_3L_4 species were also identified [1003,1005].

Tetraphenyl esters of imidodithiophosphoric acid, $[(PhO)_2P(S)]_2NH$, were reported to form scandium, ytterbium, mercury, silver, gold, hafnium and palladium chelates; these can be used for the solvent extraction of the metals cited [1009].

(c) [M : SS](⊃ POP) and [M : SS](⊃ PSP) Systems

The chelate ring (**299**) (R = Me) is formed when $[Me_2P(S)]_2O$ reacts with



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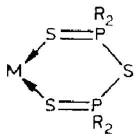

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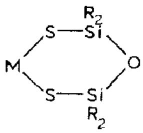
either cadmium(II), mercury(II) or copper(II) bromide; however, phenyl analogues cannot be obtained since $[Ph_2P(S)]_2O$ does not form complexes [1010].

Although the ligand can be prepared, chelate rings of type (**300**) could not be obtained since $[R_2P(S)]_2S$ (R = Me and Ph) undergo cleavage in reactions with divalent metal salts, to form dithiophosphinato complexes, $M(S_2PR_2)_2$ [1010].

(d) [M : SS](⊃ SiOSi) Systems

Deprotonated organosiloxane-1,3-dithiols can form chelate rings of type



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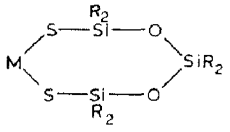
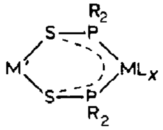


302

(**301**), which are thioanalogues of related siloxanediolato chelates. So far only a bis(η^5-cyclopentadienyl)titanium derivative (**301**), M = Ti(η^5-C_5H_5)$_2$, R = Me has been reported; it was prepared by reacting (η^5-C_5H_5)$_2$Ti(SH)$_2$ and $(ClMe_2Si)_2O$ [1011]. In addition, an eight-membered ring (**302**), was similarly prepared [1011].

(e) [M : SS](⊃ PM′P) Systems

Some thioanalogues of the chelate ring (**293**) (described in Section E(iv)(j) are known. Thus, the sulfur chelate ring (**303**) is formed ML_x = Ni(η^5-C_5H_5),



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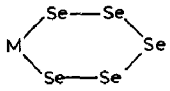
M′ = Zn, $n = 2$, R = OMe), when nickelocene reacts with $(MeO)_2P(S)H$ in the presence of Zn^{2+} ions [1012].

A platinum derivative, (**303**) ML_x = $(R_2N\text{-}CS_2)Pt$, M′ = $Pt(S_2C\text{-}NR_2)$ has also been reported [1013].

(vi) Selenium donor sites

(a) [M : SeSe](⊃ SeSeSe) Systems

Pentaselenido chelate rings, (**304**), can be prepared by methods similar to those used for the sulfur analogues. The best investigated are the bis(η^5-cyclopentadienyl)titanium derivatives. Thus, (η^5-C_5H_5)$_2$TiSe$_5$ can be prepared by reacting (η^5-C_5H_5)$_2$TiCl$_2$ with disodium pentaselenide, hydrogen selenide in the presence to triethylamine [949], or dilithium polyselenide [255]. A methylcyclopentadienyl derivative has also been reported [955,965]. The compound (η^5-C_5H_5)$_2$TiSe$_5$ reacts with organoboron halides, and the reaction was used to prepare $Me_2B\text{-}SeSe\text{-}BMe_2$ [1014] and $R_2B_2Se_3$ [1015].



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Bis(η^5-cyclopentadienyl)vanadium pentaselenide, (**304**) M = (η^5-C_5H_5)$_2$-V, has been prepared from (η^5-C_5H_5)$_2$VCl$_2$ and alkali metal polyselenide [974].

The reaction of iron(II) chloride with elemental selenium and sodium metal (1 : 6 : 3 molar ratio) in DMF at 70°C in the presence of $[PPh_4]Br$

yielded $(PPh_4)_2[Fe_2Se_2(Se_5)_2]$, which contains two $FeSe_5$ rings (**304**, M = Fe) joined by a double selenium bridge [977].

No other inorganic chelate rings containing selenium donors seem to have been prepared.

(vii) Tellurium donor sites

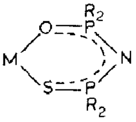
No chelate rings of this nature are known.

(viii) Silicon donor sites

No chelate rings with silicon donor sites have been reported.

(ix) Heteronuclear donor sites

Six-membered chelate rings containing two different donor atoms are poorly represented. The only such chelate which can be cited is the ring (**305**). Copper(II) and nickel(II) chelates, (**305**), are obtained from $Ph_2P(O)-NH-P(S)Ph_2$ [1003].



305

The tetraphenylester of imidothiodiphosphoric acid, $(PhO)_2P(O)-NH-P(S)(OPh)_2$ was used as a reagent for solvent extraction of several metals (including scandium, mercury, silver, gold, palladium) based upon the formation of chelate rings of type (**305**) (R = OPh) [1009].

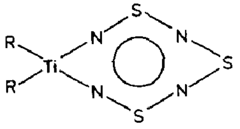
F. LARGER CHELATE RINGS

There are few chelates containing a carbon free ring with more than six atoms.

(i) Nitrogen donor sites

An eight-membered chelate ring, (**306**) ($R = \eta^5\text{-}C_5H_5$) is formed in the reaction of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ with S_4N_4 in THF [1016]. An X-ray diffraction investigation of this compound revealed a nearly planar ring conformation, with the titanium atom only 0.58 Å above the mean plane [1016].

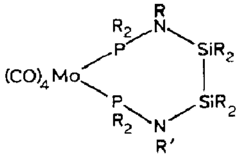
No other large chelate ring with nitrogen donor atoms seems to be known.



306

(ii) Phosphorus donor sites

The only representative of this class is the seven-membered ring (**307**) (R = Me, R′ = $SiMe_3$), formed in the reaction of *cis*-$[Mo(CO)_4(R_2P\text{-}NH_2)_2]$ with 1,2-dichlorotetramethyldisilane [536a].



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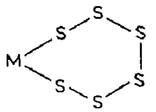
(iii) Sulfur donor sites

The class of polysulfido chelates contains some large ring representatives, including seven- (**308**), eight- (**309**) and ten-membered (**310**) rings.



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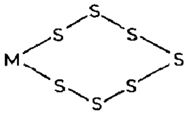

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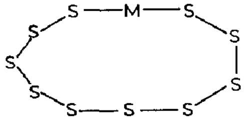

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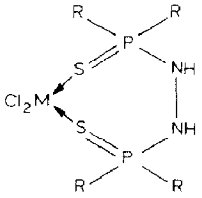
Hexasulfido chelates (**308**) are known in the complex ions $[Mn(S_5)_x(S_6)_{2-x}]^{2-}$ [574], $[(S_6)Cu(\mu\text{-}S_8)Cu(S_6)]^{4-}$ [582], $[Cu(S_6)_3]^{3-}$ [1017], $[(S_6)Ag(\mu\text{-}S_8)Ag(S_6)]^{4-}$ [1018], $[Ag(S_6)_2]^{2-}$ [1019], $[Hg(S_6)_2]^{2-}$ [1020] and $[Sn^{IV}(S_4)_2(S_6)]^{2-}$ [589]. Tetraorgano ammonium or phosphonium salts of all these anions were prepared from various polysulfides and appropriate metal salts. The chelate ring structures were established by X-ray diffraction.

The eight-membered heptasulfido chelate ring (**309**) is represented by the tellurium heptasulfido dihalides X_2TeS_7. This structure was confirmed by X-ray diffraction [1021].

The ten-membered ring (**310**) was found in silver $[Ag^{I}(S_9)]^-$ [589,1019] and gold $[Au^I(S_9)]^-$ [1022] chelates, isolated as $[PPh_4]^+$ and $[AsPh_4]^+$ salts, respectively. X-ray diffraction investigation of both compounds revealed highly puckered ring conformations, with nearly linear S–M–S coordination (e.g. S–Au–S 176°).

A set of heteronuclear chelating ligands, forming seven-membered rings, could possibly be the bis(thiophosphinyl)hydrazines, $R_2P(S)–NHNH–P(S)R_2$ (R = OEt, Ph) which form palladium and platinum complexes, probably by coordination through sulfur [667] as shown in (**311**) (M = Pd, Pt).



311

In the absence of an X-ray diffraction study this assignment should only be regarded as tentative.

(iv) Oxygen donor sites

An eight-membered chelate ring has been cited earlier in this review, as one of the coordination possibilities of the triphosphate ion (structure **285**). This is confirmed by an X-ray diffraction investigation of $[Co(NH_3)_4(H_2P_3O_{10})]\cdot H_2O$, which contains an α,γ-bidentate dihydrogentriphosphato ligand [1023].

Other large chelate rings with oxygen donors are not known.

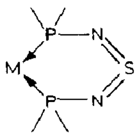
G. FINAL COMMENTS

We hope that this review fulfills, at least in part, three of our aims.

The first aim was to demonstrate that carbon-free chelates represent a well-defined, self-consistent chapter of coordination chemistry. We hope that our review will contribute to the recognition of this chapter and its specific treatment in future inorganic and coordination chemistry textbooks or monographs.

The second aim was to identify gaps in this new chapter and suggest possibilities for further research. This review reveals some potentially very versatile ligands, used only to a limited extent as yet, the chemistry of which could be greatly expanded by the use of other metal ions or organometallic groups as coordination centers. Interesting preparative and structural results could thus be obtained, especially with the use of less traditional ligands, such as sulfur–nitrogen, polysulfur, polyphosphine or polysilane derivatives.

The third aim was to generate ideas for further research by suggesting new carbon-free chain compounds for use as inorganic ligands. In principle, any flexible inorganic chain (regardless of its external substituents) bearing terminal donor atoms can serve as such a ligand. Therefore, the design of new carbon-free ligands would seem a rather simple matter, bearing in mind that some are rather unpredictable, such as the N_3S_2 ligands for example. Thus, hundreds of new ligands can in principle be designed and their synthesis is only a matter of overcoming any experimental difficulties that may arise. Some chelate rings, which have not yet been reported, are suggested here (**312**–**319**):



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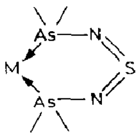

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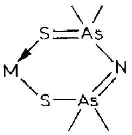

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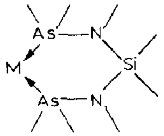

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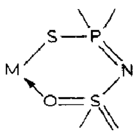

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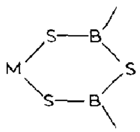

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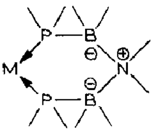

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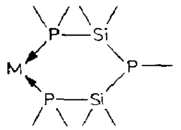
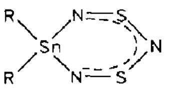


319

Potential arsenic-donor ligands have been much less studied than their phosphorus analogues. Boron- and silicon-containing ligands (with N, P^{III}, As^{III} or S^{II} donor sites) have also been rarely considered. It is quite a challenge to the inorganic synthetic chemist to prepare new ligands of this type and to investigate their coordinating ability.

A final comment stems from our combination of interests in inorganic heterocycles, organometallic and coordination chemistry. The study of inorganic (carbon-free) chelate rings is a junction of these three branches of inorganic chemistry. Thus, chelate ring compounds such as (**320**) and (**321**), for example, both with an organometallic coordination centre, and a carbon-free ligand, would belong simultaneously to all three chapters:



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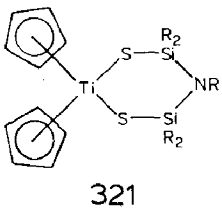

321

In conclusion, we express great optimism with regard to the future of the chemistry of inorganic (carbon-free) chelate rings and invite the reader to join us in this optimism.

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