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Complexes of heterocyclic thionates Part 2: complexes of bridging ligands

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Abstract

The bridging behaviour of deprotonated heterocyclic thiones, the heterocyclic thionates, is reported. The anions are effective bridging ligands among binuclear, trinuclear, tetranuclear, hexanuclear and polynuclear metallic species. The metals involved are mostly from the second and third series of transition metals together with some from the first transition series. Some examples involving main group metals are also included.

The anionic ligands included in the review mostly involve the monothionate derivatives of pyridine, imidazole, triazole, quinoline, thiazole, and thiadiazole derivatives. Dithionate derivatives are few in number and are limited to μ_2-S,N bridging pyrimidine and μ_2-S,S bridging 1,2,5-thiadiazole bases. Several bridging modes are described. These may involve the exclusive use of the thionate sulphur atom in the rare edge-bridging, μ_2-S(η^2-S), of two metal centres. Alternatively, both the sulphur and the nitrogen atoms of the thioamide groups may be involved in the formation of either binuclear double-bridging, μ_2-(η^1-S;η^1-N), or binuclear triple-bridging, μ_2-(η^2-S;η^1-N) systems. Trinuclear face-bridging, μ_3-(η^2-S;η^1-N), ligands occur among trinuclear, tetranuclear and octahedral complexes. Relatively rare tetranuclear, μ_4-(η^3-S;η^1-N), bridging ligands generate polymeric and oligomeric complexes. Combinations of similar, or different, bridging arrangements are also involved in the formation of double or multiple bridges among binuclear and polynuclear metal centres.

Preparative routes, vibrational and electronic spectra as well as the electrochemistry of the complexes are described and discussed. Isomeric forms of the complexes, arising mostly from a combination of the bifunctional and polydentate character of the bridging ligands towards the metal centres, are also described and discussed.

The review emphasises the structures and dimensions derived from the X-ray crystallographic study of a large number of binuclear and polynuclear complexes. The effect of deprotonation and coordination on the dimensions of some of the parent ligands is also reported and discussed. Some structures, as well as some structural changes, derived from solution NMR spectra, are also reported.

Keywords: Binuclear and polynuclear metal complexes; Bridging heterocyclic thionate ligands; Molecular geometry; Preparations and spectroscopy

Major ligand abbreviations

py2SH	pyridine-2-thione
py4SH	pyridine-4-thione
tcpSH	thiocaprolactam (hexamethyleneimine-2-thione)
imzSH$_2$	1,3-imidazoline-2-thione

$imzdSH_2$	1,3-imidazolidine-2-thione
$bzimSH_2$	benzo-1,3-imidazoline-2-thione
pym2SH	pyrimidine-2-thione
$pym4,6(SH)_2$	pyrimidine-4,6-dithione
$pym2,4(SH)_2$	pyrimidine-2,4-dithione
$tucH_2$	2-thiouracil (4-oxopyrimidine-2-thione)
$dtucH_2$	2,4-dithiouracil (pyrimidine-2,4-dithione)
cytSH	thiocytosine (4-aminopyrimidine-2-thione)
$trzSH_2$	1,2,4-triazoline-3(5)-thione
qun2SH	quinoline-2-thione
tzSH	1,3-thiazoline-2-thione
bztzSH	benzo-1,3-thiazoline-2-thione
tzdSH	1,3-thiazolidine-2-thione
1,3,4tdzSH	1,3,4-thiadiazole-2-dithione
$1,2,5tdz(SH)_2$	1,2,5-thiadiazole-3,4-dithione
bzoxSH	benzo-1,3-oxazoline-2-thione

(Alkyl, aryl, amino, trialkylsilyl and other derivatives are distinguished from the parent heterocycle by the addition of suitable prefixes, e.g. me, ph, am, SiR_3 etc., to the above abbreviations.)

Miscellaneous abbreviations

dppm	bis(diphenylphosphino)methane
dppe	bis(diphenylphosphino)ethane
COD	cycloocta-1,5-diene
nbd	norborna-2,5-diene

tfbb tetraflurorobenzo[5,6]bicyclo[2,2,2]octa-2,5,7-triene (tetrafluorobenzobarrelene)

py pyridine

thf tetrahydrofuran

1. Introduction

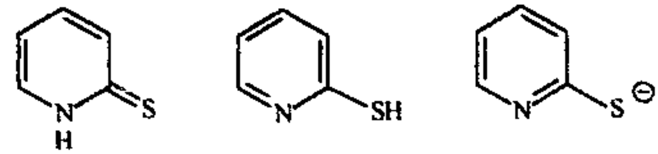
The first part of this review [1] dealt with the monodentate (η^1-S and η^1-N) as well as the S,N-chelating character of heterocyclic thionates. This second part is concerned exclusively with the behaviour of heterocyclic thionates as bridging ligands in binuclear and polynuclear complexes. The review is intended to be comprehensive in character with the literature surveyed from about 1980 to the summer of 1996.

The relationships between multinuclear metallic complexes, homogeneous catalysis, magnetic exchange phenomena and metalloprotein chemistry have been explored by many authors [2,3]. Macrocyclic dinucleating ligands, which are capable of bridging two metals in close proximity, have served as the essential precursors of homo- and hetero-bimetallic complexes since 1970 [4]. However, the range of bridging ligands has been extended considerably in recent years. Some recent examples include diphosphines, with the P–C_n–P skeleton [5], as well as diphosphinoamines and cyclodiphosphazenes [6]. Compartmental ligands, derived from a variety of mostly ketonic precursors, have also been developed and employed, together with phosphorus containing ligands, in the successful generation of bimetallic complexes [7,8]. The increasing use of alkyl and arly thiolates has also broadened the range of bridging ligands and made sulphur-bridged polynuclear metallic systems more accessible [9,10].

Aromatic nitrogen containing heterocyclic molecules, such as diazines and azolates, have been increasingly used in a variety of bridging capacities in recent years [11]. Bi-heterocyclics such as 2,2′-bipyridine are effective N,N′-bridging and chelating ligands towards copper and other metals [11,12]. The growing interest in the production of self-assembled inorganic clusters has given rise to the design of specific open-chain bridging heterocyclic ligands [13]. A variety of heterocyclic amides, including some thioamides, have been used to bridge multiply bound bimetallic clusters [14].

The extensive use of heterocyclic thionates as bridging ligands stems from the presence of the thioamide N–C–S$^-$ group, in a variety of heterocyclic environments. The involvement of thioamide sulphur and nitrogen atoms enable the formation of either μ_2-S or μ_2-S,N bridges between binuclear and polynuclear metal centres. The parent ligands adopt the thione form in the solid **(Ia)** but may exist, at least in part, as the thiol form **(Ib)** in solution, particularly in non-polar solvents [14].

Deprotonation of the parent thione is readily achieved in a variety of aqueous and non-aqueous media [1]. As in Part 1 the term heterocyclic thionate **(Ic)** is deliberately chosen so as to avoid confusion with alkyl and aryl thiolates, as well as related ligands. Complexes of organo-thiolate ligands are, however, constantly used

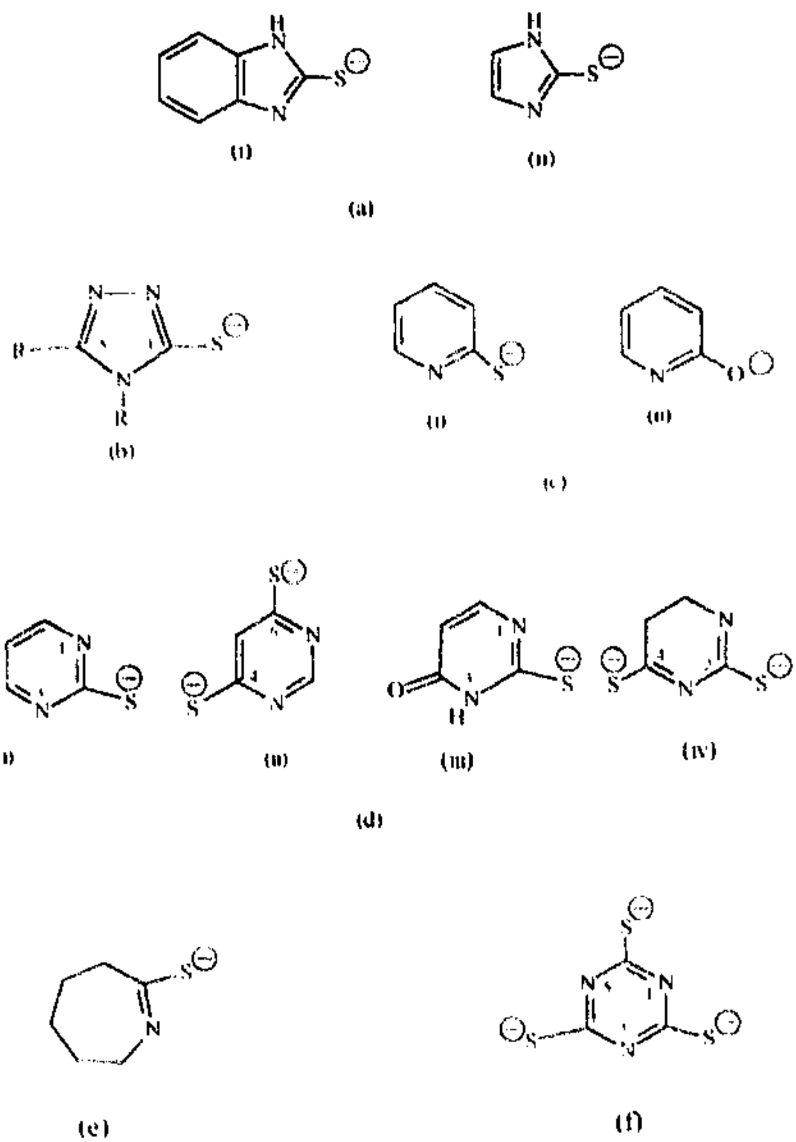


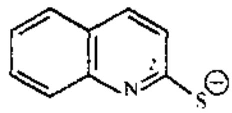
(a) (b) (c)

(I)

for comparative purposes in this review. An additional advantage of the nomenclature is that it relates the anion directly to the principle tautomeric form of the parent molecule (see abbreviations section). The heterocyclic thionates most frequently involved as bridging ligands are shown in **(II)** in their commonly deprotonated forms.

Most of the ligands are monothionate in character and are derived primarily from





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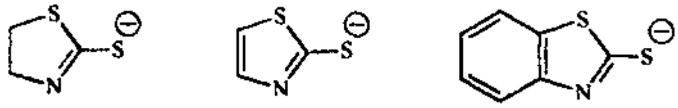
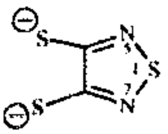
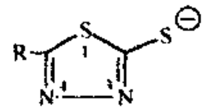


(i) (ii) (iii)

(h)



(i)

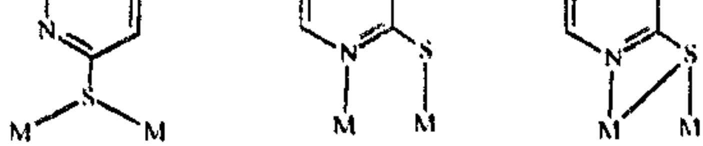


(j)

(II)

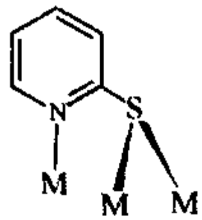
imidazole (**IIa**), pyridine (**IIc**), pyrimidine (**IId**), 1,3,4-triazole (**IIb**), quinoline (**IIg**), 1,3-thiazole (**IIh**) and 1,3,4-thiadiazole (**IIj**) bases. Some double-bridging, μ_2-S,N, dithionates are also reported but they are mostly limited to pyrimidine derivatives such as 2,4-dithiouracil (**IIdiv**) and to 1,2,5-thiadiazole-3,4-dithionate (**IIi**) which is a rare example of an S,S-bridging heterocyclic thionate. A rare trithionate, *sym*-1,3,5-triazoline-2,4,6-trithionate (**IIf**) is derived from thiocyanuric acid and reportedly functions as a bridging tris-chelating ligand (see Section 2.1. It is however a relatively neglected ligand, despite its bridging potential.

With both thionate sulphur and thioamide nitrogen atoms available for coordination heterocyclic thionates are versatile, electron rich, bridging ligands (**III**).



(a) (b) (c)

Binuclear bridging, in either single or multiple combinations, is achieved by the relatively rare, edge-bridging, μ_2-S(η^2-S) system (**IIIa**) and by the much more common μ_2-S,N(η^1-S;η^1-N) (**IIIb**) system. Both of these examples are three electron donors. The binuclear triple-bridging system, μ_2-S,N(η^2-S;η^1-N) (**IIIc**), is a five electron donor and is simultaneously η^2-S bridging and S,N-chelating. This arrange-



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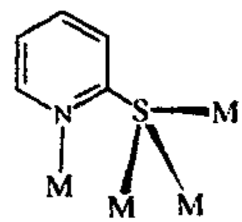

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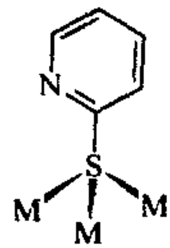


(f)

(a) μ_2–S(η^2–S) (b) μ_2–S,N(η^1–S;η^1–N) (c) μ_2–S,N(η^2–S;η^1–N)

(d) μ_3–S,N(η^2–S;η^1–N) (e) μ_4–S,N(η^3–S;η^1–N) (f) μ_3(η^3-S)

(III)

ment generates a unique combination of three four-membered rings around the central metals in bimetallic complexes (see Section 2.3.3.3. The trinuclear triple-bridging system, μ_3-S,N(η^2-S;η^1-N) **(IIId)**, is also a five-electron donor. This system is ideally adapted for coordination to individual triangular metallic clusters (see Section 3.2 as well as for the triangular faces of tetrahedral (see Section 4.2 and octahedral (see Section 5.2 metal aggregates. Maximum involvement of the thionate sulphur atom's valence electrons produces the extremely rare tetranuclear bridging, μ_4-S,N(η^3-S;η^1-N) system **(IIIe)**, a seven-electron donor. An exclusively sulphur donating trinuclear triple-bridging μ_3-S(η^3-S) system **(IIIf)** is also possible but has currently not been reported. As has been observed in thiolate chemistry, the greater the electron involvement of the thionate sulphur atom the fewer are the reported complexes. Typical of this generalisation is the fact that the μ_4-S,N bridging anion has been shown to be an effective means of linking discrete tetranuclear metallic aggregates into polymetallic species in only one instance (see Section 4.2. More examples of this type of bridging must surely arise in the future.

Configurational isomerism is common among binuclear complexes with two and four, double-bridging, μ_2-S,N, ligands (see Sections 2.3 and 2.5. Such arrangements generate pairs of *"head to head"* and *"head to tail"* isomers (see Section 2.1. Pyramidal inversion about coordinated sulphur is a common cause of fluxionality among thiolate complexes [16]. Among binuclear heterocyclic thionate containing complexes, low energy conversion between μ_2-S,N and μ_2-S(η^2-S) bridging modes **(IV)** is also an occasional cause of fluxionality.

The structure of this review is based upon the increasing nuclearity of the complexes. Subsidiary classifications involve a flexible combination of the number of bridging ligands, metal coordination numbers, compound stoichiometry and the type of bridging ligand. Some flexibility is required because some complexes contain more than one type of bridging ligand. In this case the complex is categorised with those complexes that contain the most extensively bridging ligand. Some approxima-

(a) (b)

(IV)

tion of the coordination number is also required in the presence of terminal organometallic dienes.

As in Part 1 the review describes the preparation as well as the vibrational and electronic spectra of the complexes. The redox chemistry and electrochemistry of the complexes are also included wherever possible. The isomeric possibilities arising from the bifunctional character of the ligands are described and discussed. In particular, the review emphasises the structural chemistry of the complexes obtained primarily, from X-ray crystallographic studies. The effects of deprotonation and coordination on the thioamide dimensions of the parent ligands are reported and discussed, especially for pyridine and 1,3-thiazole derivatives. Some structures, as well as dynamic structural changes, derived from solution NMR spectra, are also reported.

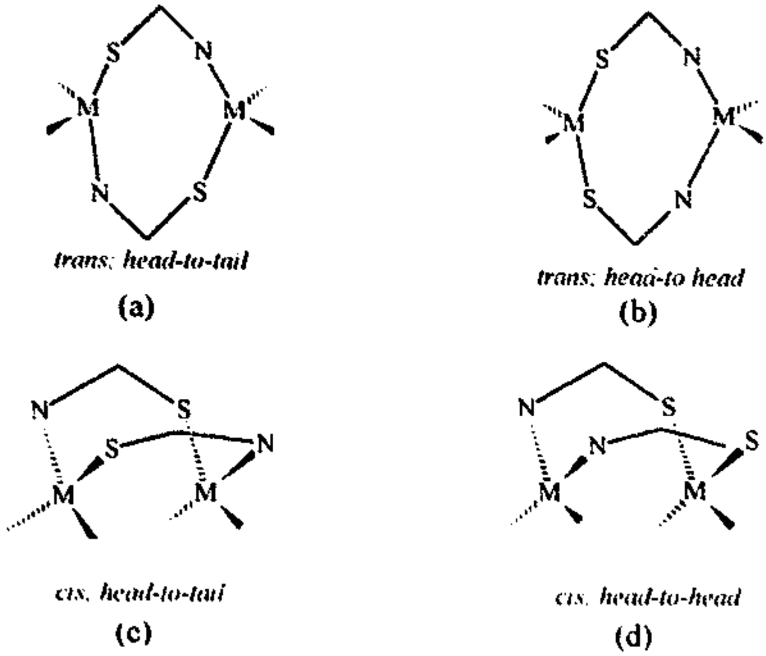
2. Binuclear complexes

2.1. Introduction

Interest in binuclear metallic complexes has been sustained at a high level since the early 1970s and the literature is now enormous. Many reviews are now available that survey neutral, anionic, symmetric and bifunctional bridging ligands of both homometallic and heterometallic systems.

Among bridged binuclear complexes with heterocyclic thionate ligands the number of bridging ligands may range from one to four. Homolepticity among the complexes is rare and limited mostly to the $[M_2(\text{het-S,N})_4]$ species. For the remaining complexes the coordination at the metal is made up of various combinations of terminal monodentate (halide, carbonyl, phosphine), chelating (1,2-diaminoethane, heterocyclic thionates) and organometallic (allyls, dienes) ligands. With bifunctional ligands, such as the heterocyclic thionates, there are numerous isomeric possibilities. Furthermore, they may also be complicated, on occasions, by the occurrence of conformational isomerism among terminal chelating ligands, such as 1,2-diaminoethane, as well as by the presence of other bridging ligands.

With two bridging ligands both *head-to-tail* and *head-to-head* isomers are possible in either *trans*-related planar "A-frame" (**Va, b**) or *cis*-related non-planar forms (**Vc, d**). A variety of terms have been used to define the *cis*-related isomeric form, notably, "open-book", "face-to-face", "vicinal" and "cradle".



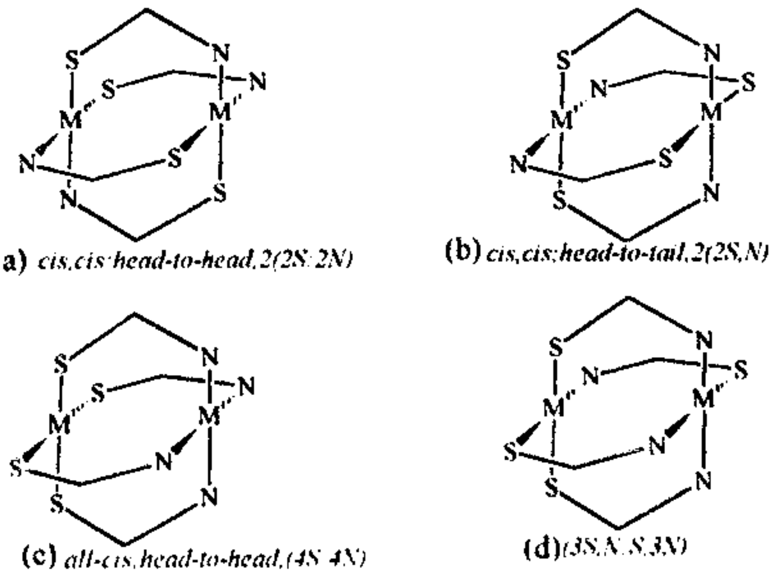
(V)

Four bridging ligands generate four possible isomeric forms. The *cis,cis;head-to-head;2(2S:2N)* isomer contains two pairs of *cis*-related sulphur and nitrogen donor atoms (**VIa**). The *cis,cis;head-to-tail;2(2S,N)* isomer contains two pairs of both *cis*- and *trans*-related sulphur and nitrogen donor atoms and may be described in terms of either arrangement (**VIb**). The two remaining isomers involve four bridging ligands in the *all-cis;head-to-head;(4S:4N)*, (**VIc**) arrangement and an intermediate isomer with three *cis*-related ligands and a *(3S,N: S,3N)* arrangement (**VId**). The *italicised* nomenclature used relates to both the ligand and to the donor atom distribution.

With ligand bites in the region of 2.6 Å and metal–metal distances varying from 2.6 to in excess of 3.0 Å the resultant structure is frequently distorted. With disparate ligand bite and metal–metal separation distances the distortion generally involves "tilting" (**VIIa**) of the coordination spheres on each metal towards the centre of the complex as well as "twisting" of the same coordination spheres out of the formally eclipsed configuration (**VIIb**).

Other modes of binuclear bridging, such as (**IIIc**), are also capable, at least in principle, of *trans* "A-frame" and *cis* "open-book" configurations. Both *head-to-tail* (**VIIIa,c**) and *head-to-head* (**VIIIb,d**) ligand combinations are possible. An additional structural feature, in the case of this mode of attachment, involves the proliferation of rings around the binuclear centre involving the heterocycle, its donor atoms and the metal atoms (**VIII**). The formation of *head-to-head* attachments (**VIIIb,d**) in this isomeric form is manifestly unlikely.

Ligand deprotonation relies heavily on the use of metal derivatives such as sodium-alkoxides [40–43] and *n*-butyl lithium [64–66], or their hydrides [54], in the presence of anhydrous organic solvents (ethanol, ether, thf). A variety of preparative routes



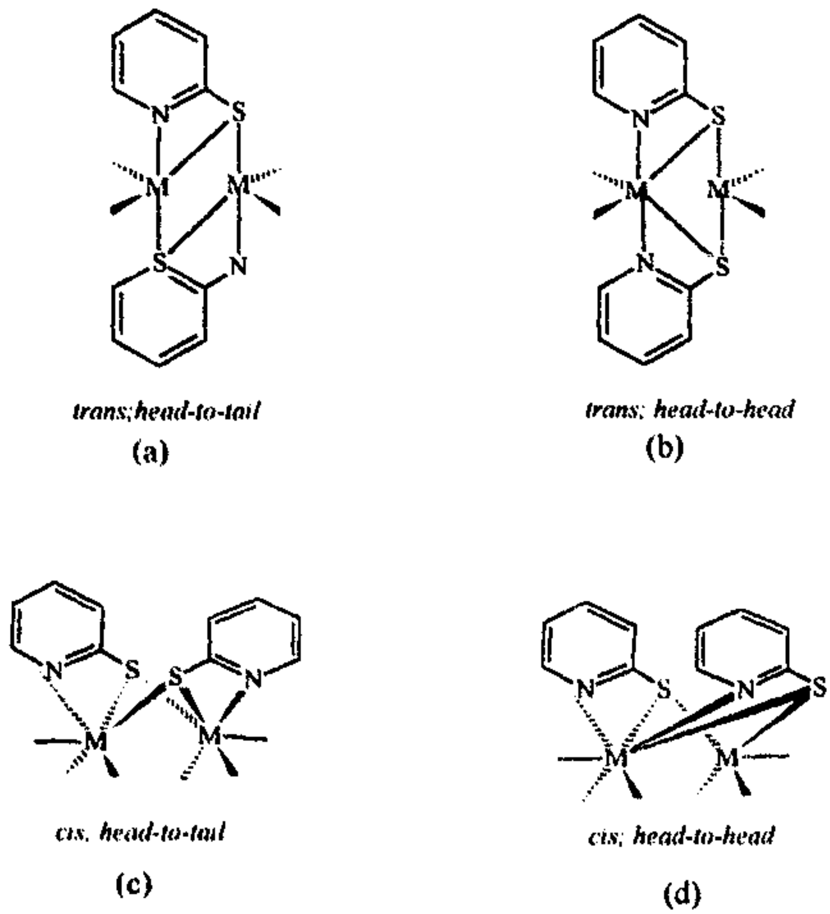
(VI)

(a) (VII) (b)

have been used for the complexes. The classic technique of replacing bridging halide, invariably chloride, with bridging thiolate [17], in this case heterocyclic thionate, is extensively used. It is also possible to start from mononuclear precursors [19], or even the parent metal [30], and to rely on the bridging ability of the ligands to produce the required complex. Such procedures have been successful with many examples, and numbers, of bridging ligands. The double-bridging acetate groups in binuclear metal tetra-acetates are readily replaced with bridging heterocyclic thionates [96]. Occasionally the breakdown of a trinuclear cluster, such as $Ru_3(CO)_{12}$, has been used to generate a binuclear product [73].

Trans-annular oxidation–addition reactions [18], that result in the formal one-electron oxidation of each metal and the generation of metal–metal bonds, are a particular feature of bridged binuclear complexes. The metals most affected by such reactions include: platinum(II) [see Section 2.5.2], rhodium(I) [56] and iridium(II) [71].

Some of the aspects of the solution chemistry of these complexes that have attracted attention include: low-energy isomeric (IV) [27] and structural changes as well as scrambling among terminal ligands, especially carbonyl–phosphine exchange [64–66].

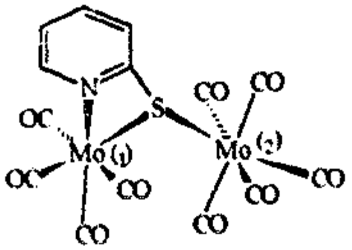


(VIII)

2.2. *Complexes with one bridging heterocyclic thionate ligand*

This is a relatively rare class of complexes. In spite of the three possible means by which a binuclear metal group may be bridged by one heterocyclic thionate (**IIIa–c**) only one established example has been reported.

The two molybdenum(0) atoms in $(C_8H_{20}N)[Mo_2(\mu\text{-py2S})(CO)_9]$ [19] have distorted octahedral geometry and are μ_2-S,N(η^2-S,η^1-N), triple-bridged, by a single pyridine-2-thionate anion. The complex is obtained, under nitrogen, from molybdenum hexacarbonyl, pyridine-2-thione, sodium methoxide and tetraethyl ammonium chloride, in 1:1:1:1 molar ratio in thf at 318–323 K. Because of the asymmetric triple-bridging nature of the anion the molybdenum atoms have different donor sets (**IX**). Furthermore, the separation distance (Mo...Mo = 4.5609(7) Å) is consistent with the absence of a metal...metal interaction [20]. The extent of the octahedral distortion is indicated by the range of bonding angles at each metal (Mo(1) 63.6(1)–173.0(2)°; Mo(2) 89.0(2)–177.5(2)°). The narrowest value is the S–Mo(1)–N chelating angle and the largest is the *trans* S–Mo(2)–$C_{(carbonyl)}$ angle. The asymmetric bridging ligand generates a relatively short molybdenum–nitrogen distance, non-equivalent molybdenum–sulphur distances and a substantial bridging angle at the thionate sulphur atom (Mo–N = 2.284(4), Mo(1)–S = 2.617(1), Mo(2)–S = 2.582(1) Å; Mo–S–Mo = 122.59(6) Å). Inequivalence among metal–sulphur bridging distances is not unusual [21]. In this complex however, the inequivalence probably reflects the unequal electron donations to the two molybdenum(0) atoms. Inequivalence is also reflected in the bridging angles at the sulphur atom (Mo(1)–S–C = 80.9(1), Mo(2)–S–C = 112.0(2)°); the smaller of the two values is within the four-membered chelate ring. The molybdenum–carbonyl bond distances are unexceptional, apart from the distances *trans* to the bridging sulphur atom (Mo(1)–C = 1.934(5) and Mo(2)–C = 1.991(6)°). These distances show evidence of modest *trans*-effects.



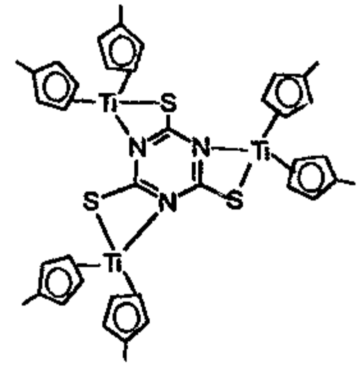
(adapted from [19])

(IX)

The thioamide distances in the pyridine-2-thionate anion are insignificantly different from the corresponding values in the parent ligand [22]. However, the N–C–S thioamide angle is reduced from 120.6(2)°, in the parent ligand, to 111.8(3)° in the complex, in order to accommodate binuclear triple-bridging (Table 2).

The production of mononuclear, binuclear and trinuclear complexes of bis(methylcyclopentadienyl)titanium(III) species from 2-hydroxypyridinato (**IIcii**), 2,4-dihydroxypyridinato (uracilate) and 2,4,6-trihydroxycyanurate anions [23] established the bridging capability of otherwise mostly N,O-chelating pyrimidine derivatives. This success led to the attempted preparation of the corresponding complexes with 2-thiouracilate (**IIdiii**), 2,4-dithiouracilate (**IIdiv**), 4,6-pyrimidinedithionate (**IIdii**) and 2,4,6-trithiocyanurate (**IIf**) anions [24]. The complexes are prepared by heating the sodium salt of the appropriate heterocyclic thione and bis(methylcyclopentadienyl)- titanium monochloride, in thf, for several days at 50 °C under helium. All the products are air sensitive. Unusual trinuclear, triangular arrangements (see Section 3.2 have been proposed for the trithiocyanurate complex [{Ti(η^5-MeC$_5$H$_4$)$_2$}$_3$(ten3S)] (**X**) and its oxygen analogue. Binuclear monobridged structures have been proposed for the complexes of the pyrimidine–thione derivatives and established for that of the 2,4-dithiouracilate anion [{Ti(η^5-MeC$_5$H$_4$)$_2$}$_2$(dtuc)] by crystal structure analysis (**XI**).

The dianionic 2,4-dithiouracilate anion simultaneously bis-S,N-chelates and monobridges the two bis(methylcyclopentadienyl)titanium(III) units (Ti...Ti = 6.075(2) Å). The two titanium atoms are nearly coplanar with the bridging dithiouracilate anion. The titanium-cyclopentadienyl ring dimensions (Ti–C = 2.282(11)–2.538(12) Å) and "tilt-angles" are unexceptional. The S,N-chelating char-



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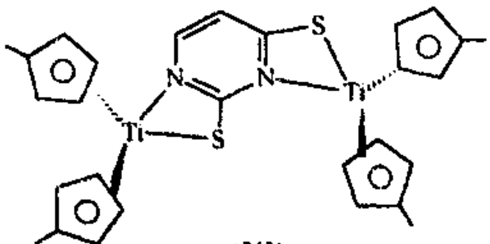


(XI)

(adapted from [24])

acter of the bridging dianion is manifest in the average distances and angles generated (Ti–S = 2.594, Ti–N = 2.206 Å; N–Ti–S = 66.0, Ti–N–C = 101.8, Ti–S–C = 79.0°). These are similar to those reported for other S,N-chelating anions [1].

Variable temperature (4.2–244 K) magnetic susceptibility and EPR data have been reported for the heterocyclic thionate complexes [24,25] and those of their oxygen analogues [23]. The magnetic properties generated by the dithiouracilate and the trithiocyanurate anions are significantly different from those reported for those of their oxygen analogues. Significantly, the former group of complexes exhibit weak ferromagnetic behaviour ($J = +2.0$ and $+3.1\ cm^{-1}$) while the latter exhibit weak anti-ferromagnetic exchange interactions ($J = -2.2$ and $-0.93\ cm^{-1}$). These differences in magnetic properties are ascribed to the presence of an acute Ti–S–C angle in the heterocyclic thionate complexes that assists the formation of a net ferromagnetic interaction. In addition, the EPR spectra of the two heterocyclic thionate complexes, in toluene glass at liquid nitrogen temperatures, show zero-field splitting energies that are about four times greater than those of their oxygen analogues. Larger values for the heterocyclic thionate complexes are rationalised in terms of substantial pseudo-dipolar through-space interactions.

2.3. Complexes with two bridging heterocyclic thionate ligands

This is the most extensive group of complexes contained in any section of this review. Metal coordination includes four, five and six-coordinated systems.

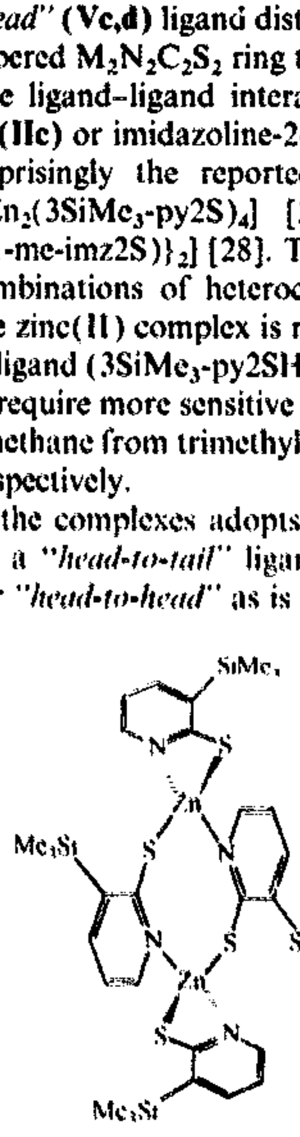
Conventional terminal, as well as organometallic, ligands are involved in the coordination together with double and triple-bridging, asymmetric, heterocyclic thionates. There are numerous isomeric possibilities resulting from the various ligand combinations and most of them have been structurally established.

2.3.1. Four-coordinate (tetrahedral) complexes

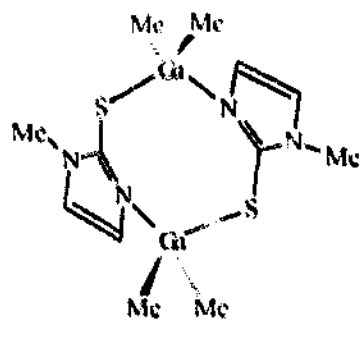
The combination of two double-bridging, μ_2-S,N(η^1-S;η^1-N), ligands and two tetrahedrally coordinated metals generate isomers derived from *cis "head-to-tail"* or *"head-to-head"* (**Vc,d**) ligand distributions. Each isomer contains an unusual central eight-membered $M_2N_2C_2S_2$ ring that tends to be folded, rather than planar, in order to minimise ligand–ligand interactions. The bridging ligands are either pyridine-2-thionate (**IIc**) or imidazoline-2-thionate derivatives (**IIa**).

Not surprisingly the reported complexes involve metals from either group twelve, [Zn_2(3SiMe$_3$-py2S)$_4$] [26] or thirteen [{(Me)$_2$Al(py2S)}$_2$] [27] and [{Me$_2$Ga(1-me-imz2S)}$_2$] [28]. The group thirteen metal complexes are rare examples of combinations of heterocyclic thionate bridging ligands with main group metals. The zinc(II) complex is readily prepared from zinc nitrate hexahydrate and the parent ligand (3SiMe$_3$-py2SH) in ethanol. The aluminium(III) and gallium(III) complexes require more sensitive handling since their preparations involve the elimination of methane from trimethyl metal precursors with the parent ligands in toluene and thf, respectively.

Each of the complexes adopts a somewhat folded double-bridged configuration with either a *"head-to-tail"* ligand arrangement, in the case of zinc and gallium, (**XIIa,b**) or *"head-to-head"* as is the case with the aluminium complex (**XIIc**).

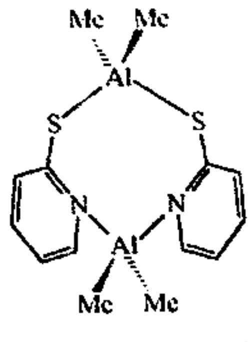


(a) (adapted from [26])



(b) (adapted from [28])

A variable temperature ^{1}H NMR study of the aluminium complex in benzene-d_6 indicates dynamic behaviour in solution. This consists of rapid rearrangement of the dimeric structure at room temperature and above. At intermediate temperatures two species of unequal population undergo slow exchange and at low temperatures (< -35 °C) one form occurs. The latter is consistent with the solid state structure



(c) (adapted from [27])

(XII)

Possible rearrangements involve conversion to *"head-to-tail"* or to μ_2-S bridged species (**IV**). More complicated structural alternatives, based on five- or six-coordinated species, are also suggested [27].

The structure of the zinc complex consists of two *"head-to-tail"* double-bridging, μ_2-S,N(η^1-S;η^1-N), ligands and two terminal S,N-chelating ligands (**XIIa**). Each metal therefore has an S_2N_2 donor set. The zinc–nitrogen distances (Table 1a) of both ligand types are not significantly different. However, the zinc–sulphur distances of the terminal chelating ligands are significantly longer than those of the bridging ligands. This is clearly a consequence of the acute chelating angle (average S–Zn–N = 70.2°). The slightly larger angles at the metal and longer bond distances for the centrosymmetric gallium complex, compared with the values for the aluminium complex, are due to the larger size of the gallium atom. The radically different bridging angles at the aluminium atoms (S–Al–S = 97.34(9), N–Al–N = 129.5(2)°) are the result of different donor sets. In addition, there appears to be a real possibility of residual attraction between the two thionate sulphur atoms in this complex. The bridging angle in the gallium complex (S–Ga–N = 100.90(07)°) is also significantly less than the average of the values reported for the aluminium complex. In other respects the different donor sets: S_2C_2 and N_2C_2, for aluminium, and S,NC_2 for both of the gallium atoms, do not appear to cause significantly different dimensions in the complexes. Furthermore, there is no obvious reason why the two metals adopt different bridging ligand arrangements.

The average thioamide dimensions of 1-methylimidazoline-2-thione [29] (C–S = 1.685, C–N = 1.345 Å) show some sensitivity to deprotonation and coordination. These distances are respectively longer and shorter (C–S = 1.733(3), C–N = 1.335(3) Å) in [{Me_2Ga}$_2$(μ-1-meimz2S)}$_2$] than they are in the parent ligand. The thioamide angle, in the complexed ligand however (N–C–S = 127.0(2)°) readily accommodates μ_2-S,N(η^1-S;η^1-N) bridging without any significant change to the average free ligand value (N–C–S = 127.1°). The fact that the imidazoline ring is a five-membered, rather than a six-membered ring, undoubtedly helps the bridging process in this respect.

Table 1
Binuclear complexes with two double-bridging, μ_2-(S,N)(η^1-S;η^1-N), heterocyclic thionate ligands; selected dimensions (Å and °)

Complex and metal...metal distances	Reference angles at the metal	M–S	M–N	M–N–C	M–S–C
(a) Four-coordinate (tetrahedral) complexes					
[Zn(μ-3SiMe$_3$-py2S)$_2$(3SiMe$_3$-py2S)$_2$] [26]					
NR	123.8(1)–	2.335(3)–	2.066(7)–	NR	NR
	141.7(3)	2.337(3)	2.055(6)		
S,N-chelating	69.9(2)	2.405(3)–	2.055(6)–	NR	NR
ligands	2.410(3)	2.072(6)			
[{Me$_2$Al(μ-py2S)}$_2$] [27]					
NR	97.34(9)–	2.335(3)–	1.992(4)–	120.7(3)–	NR
	129.5(2)	2.341(3)	1.993(4)	121.2(3)	
[{Me$_2$Ga(μ-1meimz2S)}$_2$]^a [28]					
NR	100.90(07)–	2.3697(8)	2.019(2)	122.2(02)	100.97(09)
	124.9(02)				
(b) Five-coordinate complexes					
[Cd$_2$(μ-3SiMe$_3$-py2S)$_2$(3SiMe$_3$-py2S)$_2$]^a [30]					
3.4374(5)	64.84(9)	2..597(2)	2.380(4)	NR	NR
	158.1(1)	2.667(2)			
S,N-chelating	62.02(9)	2.495(1)	2.381(4)		
3SiMe$_3$-py2S					
(c) Four-coordinate (square-planar) and six-coordinate (octahedral) complexes					
[Pd(μ-quin2S)$_2$(quin2S)$_2$(PMe$_3$)$_2$] [40]					
3.224(2)	85.4(2)	2.317(5)	2.14(1)	NR	103.7(6)
	176.8(2)	2.363(5)	2.15(1)	NR	104.0(6)
η^1-S		2.325(5)			104.2(7)
quin2S		2.335(5)			105.0(7)
[{Pd(dmba)(μ-quin2S)}$_2$] [41]					
2.99(2)	81.0(2)	2.297(1)	2.158(3)	NR	114.7(4)–
	174.7(2)	2.296(1)	2.163(4)	NR	113.9(4)
[{Pd(μ-py2S)(PMe$_3$)Cl}$_2$] [42]					
2.942(2)	88.092)	2.284(3)	2.137(9)	NR	114.7(4)
	176.9(1)	2.386(3)	2.131(1)		113.9(4)
[{Pd(μ-pym2S)(PMe$_3$)Cl}$_2$]^a [43]					
2.915(1)	NR	2.293(1)	2.143(3)	NR	NR
[{Pd(μ-4-mepym2S)(PMe$_3$)Cl}$_2$]^a [43]					
2.924(1)	NR	2.287(1)	2.120(2)	NR	NR
[{Pd(μ-1-meimz2S)(PMe$_3$)Cl}$_2$] [43]					
3.104(2)	NR	2.307(3)	2.092(7)	NR	NR
		2.296(3)	2.096(7)		

Table 1 (*continued*)

Complex and metal...metal distances	Reference angles at the metal	M–S	M–N	M–N–C	M–S–C
$[\{Pt(μ\text{-}py2S)(en)\}_2]$ [48]					
3.083(1)	83.1(5)–	2.302(4)–	2.059(10)–	123.9(7)–	112.0(5)–
	94.8(1)	2.299(4)	2.041(11)	122.4(10)	110.4(4)
$[\{Pt(μ\text{-}4\text{-}mepy2S)(en)\}_2]$ [48]					
3.101(1)	83.3(3)–	2.294(2)	2.042(6)–	124.2(4)	112.0(3)–
	94.6(1)	2.291(2)	2.024(7)	121.7(6)	108.6(2)
$[\{Rh(μ\text{-}tzd2S)(COD)\}_2]$. $2CH_2Cl_2$ [54]					
3.7154(4)	90.3(1)	2.358(1)	2.079(3)	127.4(3)	107.4(1)
	166.4(2)	2.362(1)	2.102(3)	129.1(3)	108.5(1)
$[\{Ir(μ\text{-}tzd2S)(COD)\}_2]$ [54]					
3.5434(4)	92.6(1)	2.329(2)	2.087(5)	129.5(5)	106.7(2)
	169.9(3)	2.337(2)	2.096(5)	130.1(5)	106.7(2)
$[\{Rh(μ\text{-}tzd2S)(CO)(PPh_3)\}_2]$.2THF [55]					
3.2435(3)	88.3(1)	2.378(1)	2.102(4)	126.3(2)	106.1(1)
	175.7(1)	2.379(1)	2.104(4)	127.0(2)	106.3(1)
$[\{Rh(μ\text{-}tzd2S)(CO)(PMe_3)\}_2]$ [55]					
3.0524(4)	87.71(9)	2.394(1)	2.097(3)	125.6(3)	103.8(1)
	177.8(2)	2.396(1)	2.105(2)	128.1(3)	104.4(1)
$[Rh_2I_2(μ\text{-}tzd2S)_2(dppe)]$ 0.5THF [56]					
2.748(1)	83.22(6)	2.382(2)	2.099(5)	123.0(4)	99.8(2)
	176.6(1)	2.418(2)	2.132(5)	124.8(5)	100.3(2)
$[Rh_2(μ\text{-}tzdS)(CO)_2(dppm)_2]Cl.CH_2Cl_2$ [56]					
2.9957(7)	86.69(2)	2.422(2)	2.097(5)	120.5(4)	117.1(2)
	175.27(6)				
$[\{Rh(μ\text{-}py2S)(tfb)\}_2].(CH_3)_2CO$ [66]					
3.028(2)	70.3(3)	2.320(2)	2.112(6)	119.1(5)	113.1(3)
	176.5(3)				
$μ_2$-S bridging Rh–S–Rh–					
py2S	80.5(1)	2.339(2)			105.5(2)
		2.349(2)			117.0(2)
$[\{Rh(μ\text{-}py2S)(CO)_2\}_2]$ [66]					
2.941(2)	87.4(2)	2.364(2)	2.118(6)	120.9(5)	105.6(2)
	177.3(3)				
$[Rh_2(μ\text{-}bztz2S)_2(PPh_3)(CO)_3]$ [68]					
3.0351(5)	88.3(1)	2.370(1)	2.100(3)	120.9(2)	104.1(1)
	175.4(2)	2.376(1)	2.107(2)	121.8(2)	106.2(1)

Table 1 (*continued*)

Complex and metal...metal distances	Reference angles at the metal	M–S	M–N	M–N–C	M–S–C
[(PPh$_3$)Pt(μ-bztz2S)$_2$RhCl(CO)] [70]					
2.6266(4)	83.7(1)– 177.9(1)	2.306(1) 2.3103(1) (Pt–S)	2.040(4) 2.045(4) (Rh–N)	123.5(3) 124.7(3) (Rh–N–C)	105.5(2) 105.7(2) (Pt–S–C)
[Ir$_2$(μ-py2S)$_2$(CO)$_4$I(CH$_2$I)] [71]					
2.695(2)	88.4(4)– 172.6(4)	2.360(4) 2.361(4)	2.109(11) 2.112(12)	NR	NR
[Ir$_2$(μ-bztz2S)$_2$(CO)$_4$I$_2$)] [130]					
2.676(2)	Ir–Ir–I 174.3$_{(average)}$	2.386(5) 2.395(6)	2.10(2) 2.13(6)	NR	NR
[{RhCl(μ-py2S)(η^1-py2SH)(CO)}$_2$][a] [72]					
2.652(4)	83.6(1)– 99.4(1)	2.339(3)	2.123(4)	NR	NR
η^1-py2SH ligand		2.427(3)			NR
[{Ru(μ-bztz2S)(py)(CO)$_2$}$_2$] [73]					
2.759(4)	83.2(2) 93.4(2)	2.445(4) 2.449(5)	2.177(6) 2.198(6)	120.0(4) 120.6(4)	NR

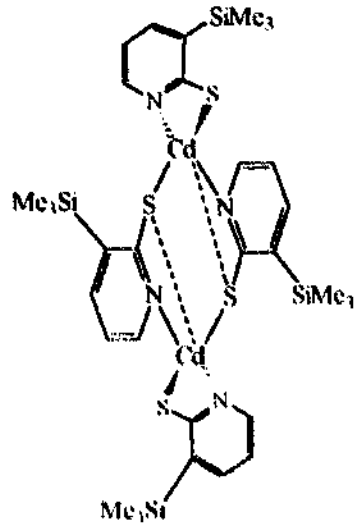
NR not reported.
[a] Symmetrical complex

2.3.2. *Five-coordinate complexes*

Among [{M(het-S,N)$_2$}$_2$] complexes, that contain binuclear double-bridging ligands, pyramidal five-coordinate metal coordination is readily achieved by conversion of the ligand to a binuclear triple-bridging (**IIIb**→**IIIc**) system. Such coordination occurs in [Cd(μ-3SiMe$_3$-py2S)$_2$(3SiMe$_3$-py2S)$_2$] [30]. This complex is one of the products of a series of preparations involving the electrochemical oxidation of metals (nickel, zinc, cadmium and copper) in acetonitrile in the presence of the parent ligand, (3-trimethylsilyl)-pyridine-2-thione. Empirical stoichiometries of the products are [M(3SiMe$_3$-py2S)$_2$], for the divalent metals, and [Cu(3SiMe$_3$-py2S)], for the copper(I) complex. Adducts of the nickel complex [Ni(3SiMe$_3$-py2S)$_2$(add)], with 2,2'-bipyridyl and 1,10-phenanthroline, and with 1,2-bis(diphenylphosphino)ethane (dppe) for the copper complex [Cu$_2$(3SiMe$_3$-py2S)$_2$(dppe)$_3$], are obtained by the common practice of adding the appropriate chelate to the electrolysing solution.

The room-temperature magnetic moments and the electronic spectra of the nickel complexes are all consistent with mononuclear products and pseudo-octahedral geometry. The NMR (^{1}H, ^{13}C, ^{31}P) spectra of the [Cu$_2$(3SiMe$_3$-py2S)$_2$(dppe)$_3$] complex are consistent with terminal η^1-S donating heterocyclic thionates and a combination of terminal and bridging diphosphines. The similarity with the corresponding 1,3-benzothiazoline-2-thionate complex is striking and suggests the two complexes to be isostructural [31].

The absence of both the ligand ν(NH) band in the IR spectrum (3140 cm^{-1}) and the broad signal of the NH proton (13.37 ppm) in the ^1H NMR spectrum, of the cadmium complex, together with the upfield shift of the thioamide (C2) carbon atom, are indicative of sulphur donating heterocyclic thionates [32]. The crystal structure of $[\{Cd(\mu\text{-}3SiMe_3\text{-}py2S)_2\}_2]$ consists of centrosymmetric, discrete, neutral binuclear units. Each cadmium atom is coordinated by one terminal S,N-chelate and one binuclear triple-bridging, μ_2-S,N(η^2-S; η^1-N), ligand, in a distorted five-coordinate trigonal-bipyramidal environment (**XIII**). Each S_3N_2 donor set in the complex consists of three equatorial sulphur atoms, two of which are bridging and one is terminal, and two apical nitrogen atoms.



(adapted from [30])

(XIII)

Much of the distortion in the structure is caused by the characteristically narrow angles of the terminal and bridging S,N-chelating ligands (S–Cd–N = 62.06(9), 64.84(9)°), respectively. These ligands form a *trans*-$N_{(terminal)}$–Cd–$N_{(bridging)}$ angle (158.1(1)°) which deviates significantly from the ideal value. The cadmium–nitrogen distances however are effectively identical (Table 1b). The cadmium–sulphur distances show some interesting variations that correlate well with the relative degrees of strain induced at the sulphur atoms by, binuclear triple-bridging and terminal S,N-chelating ligands, respectively. The two bridging ligands form a *trans* (*2-anti*) arrangement across the centre of the structure that produces a centrosymmetric Cd_2S_2 core. This core is itself at the centre of a five-ring sequence, which also includes two four-membered S,N-chelates, (see Section 2.3.3.2. The core dimensions (Cd–S = 2.597(2), Cd–S′ = 2.667(2), S...S′ = 3.985(1), Cd...Cd = 3.4374(5) Å; Cd–S–Cd′ = 81.56(4), S–Cd–S′ = 98.45(3)°) are typical of many M_2S_2 cores that are generated by organo thiolates [9,10] as well as by heterocyclic thiones [33] and thionates (see Section 4. The cadmium–sulphur distances within the core are significantly longer than those of the terminal S,N-chelates (Cd–S = 2.495(1) Å). Clearly, the combined steric and electronic demands on the bridging sulphur atom are greater than those on the terminal chelating sulphur atom, in this structure. This is in direct contrast to the situation described for the μ_2-S,N(η^1-S, η^1-N) double-bridging and S,N-chelating ligands in $[Zn_2(\mu\text{-}3SiMe_3\text{-}py2S)_4]$ described above (see Section 2.3.2).

The effects of deprotonation and coordination on the thioamide dimensions of the bridging and chelating ligands are very similar (Table 2). The carbon–nitrogen distances of both ligands are comparable with the corresponding distance in the parent (pyridine-2-thione) ligand [22]. The carbon–sulphur distances in the bridging and chelating ligands are both significantly longer than the corresponding value in the parent ligand. The most significant effect however is seen in the thioamide angles of the bridging and chelating ligands (N–C–S = 113.0(3), 114.4(4)°), respectively. Both of these values are significantly reduced relative to that of the parent ligand (120.6(2)°).

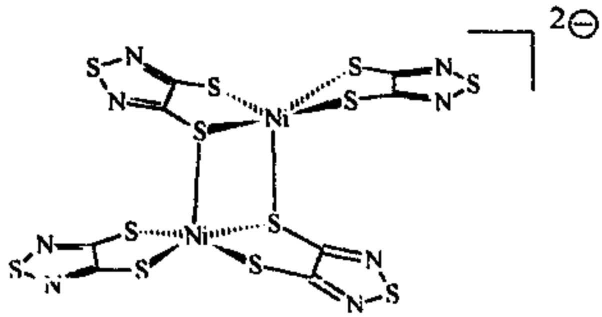
The ability of metal complexes of multisulphur π-acceptor ligands to generate molecular metals, superconductors and materials with novel optical properties has intensified the search for such materials. Vicinal dithione derivatives, such as 1,2,5-thiadiazole-3,4-dithione (**III**), are sulphur rich and contain adjacent thioamide (N–C=S) groups. In this respect the molecule is similar to dithiomaleonitrile. The bis S,S-chelating ability of this ligand has been reported [35] as well as the crystal

Table 2
Pyridine-2-thionate complexes; average thioamide dimensions (Å and °)

Complex and reference	C–S	C–N	N–C–S
Pyridine-2-thione [22]	1.692(2)	1.357(3)	120.6(2)
(a) μ_2-S,N bridging ligands			
$[\{Pt(py2S)(en)\}_2]$ [47]	1.754	NP	122.1
$[\{Pt(4\text{-}Mepy2S)(en)\}_2]$ [48]	1.733	NP	122.7
$[\{Rh(\mu\text{-}py2S)(tfb)\}_2]$. CH_2Cl_2 [66]	1.742(6)	1.341(11)	116.9(6)
μ_3-py2S ligand	1.782(6)	1.323(11)	117.6(5)
$[\{Rh(\mu\text{-}py2S)(CO)_2\}_2]$* [66]	1.738(8)	1.350(10)	120.8(5)
$[Pt_2Cl_2(\mu\text{-}py2S)_4]$.2$CHCl_3$ [88]	1.753	NR	121.5
$[Pt_2Cl_2(\mu\text{-}4Mepy2S)_4]$. 0.5$C_7H_8$ [89]	1.733	NR	122.7
$[Mo_2(\mu\text{-}py2S)(CO)_6]$ [19]	1.765(5)	1.361(6)	118.3(3)
$[Cd(\mu\text{-}3SiMe_3\text{-}py2S)_2(py2S)_2]$ [30]	1.770(4)	1.352(5)	113.0(3)
S,N-chelate	1.749(4)	1.353(5)	114.4(4)
(b) μ_3-S,N bridging ligands			
$[Ru_3(\mu\text{-}H)(\mu\text{-}py2S)(CO)_9]$ [113]	1.76(1)	1.35(1)	118.5(7)
$[Rh_3(\mu\text{-}py2S)_2(CO)_6](ClO_4)$ [64,119]	1.783	1.353	119.8
(c) μ_4-S,N bridging ligands			
$[\{Ru_3(\mu\text{-}H)(\mu\text{-}py2S)(CO)_7\}_3]$ [113]	1.777	1.383	115.5

* Symmetrical molecule.

structures of two dianionic nickel(II) salts [36]. A monoanionic, nickel(III), complex $(PBu_4)[Ni(1,2,5\text{-tdzS2})_2]$ has also been reported [37]. The nickel(III) complex is obtained from the nickel(II) precursor by iodine oxidation in degassed acetone under nitrogen. The crystal structure of $(PBu_4)[Ni(\mu\text{-}1,2,5\text{-tdzS2})_2]$ consists of anionic dimeric pairs in which each five-coordinate nickel(III) atom has an S_5 donor set and square-pyramidal geometry (**XIV**).



(adapted from [37])

(XIV)

Within the dimeric pairs the anions are staggered, relative to one another, so as to facilitate additional nickel–sulphur contacts and the formation of a central Ni_2S_2 core. Similar arrangements have been reported among corresponding dithiolene complexes [38]. Within the monoanion the nickel–sulphur distances are about 2.22 Å in those cases where the sulphur atom is not involved in interdimer interactions. In those instances where the Ni(III) atom is involved in such interactions the distance is slightly shorter at 2.207 Å. The central Ni_2S_2 core is typically asymmetric with an intradimer nickel–sulphur distance of 2.385 Å. The slight difference in nickel sulphur bond distances between the monoanion (average Ni S = 2.200 Å) and the dianion is considered to be consistent with the addition of an extra electron to a delocalised $^3b_{2g}$ molecular orbital on the dianion. Bond distances in the heterocyclic ligand are also consistent with extensive delocalisation of the π-electron density. Cyclic voltammetric studies of $(PBu_4)[Ni(\mu\text{-}1,2,5\text{-tdzS2})_2]$ in acetonitrile (vs SCE) show an irreversible oxidation at +0.87 V which is ascribed to the formation of the insoluble neutral complex. Differences between solid and solution electronic spectra are attributed to the formation of discrete monoanions in solution and dimeric species in the solid.

2.3.3. *Four-coordinate (square-planar) and six-coordinate (octahedral) complexes*

In principle, both planar *trans*-related ("A"-frame) (**Va,b**) and non-planar *cis*-related ("open-book") (**Vc,d**) configurations are possible for square-planar complexes. However, only *cis*-related isomers are generally observed for complexes with square-planar metal geometry with two double-bridging, μ_2-S,N(η^1-S;η^1-N), ligands. These arise from the possibility of either *"head-to-tail"* (**Vc**) or *"head-to-head"* (**Vd**) double-bridged ligand arrangements. Each isomer contains an unusual central eight-membered $M_2N_2C_2S_2$ ring which is invariably folded, rather than planar, in order to minimise ligand–ligand interactions. Planar *trans*-related configurations are commonly observed with neutral planar diphosphine ligands [5] and also for one mixed-metal double-bridged heterocyclic thionate complex.

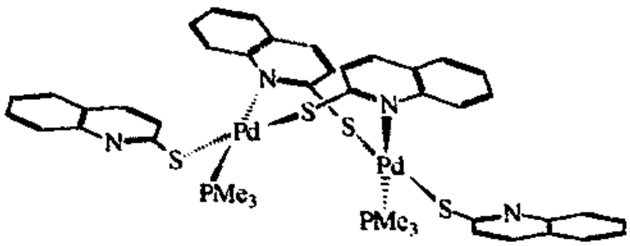
Octahedral six coordinate metal coordination, in combination with two double-bridging, μ_2-S,N(η^1-S; η^1-N), heterocyclic thionate ligands, however, generate both planar *trans*-related ("A"-frame) **(Va,b)** and non-planar *cis*-related ("open-book") **(Vc,d)** configurations.

In addition to the inherent structural interest of the isomers, cooperative interactions with substrate molecules, dynamic ligand exchange in solution **(IV)**, *trans*-annular oxidation of the metal centres and the translation of bridging ligands to terminal sites are all salient features of interest among this class of complexes.

2.3.3.1. Palladium(II) and platinum(II) complexes. Addition of the 2-(dimethylaminomethyl)phenyl (dmp) palladum(II) chloro-bridged complex [Pd_2Cl_2(dmp)$_2$] to pyridine-2-thione or its 6-methyl derivative, in the presence of triethylamine, generates the binuclear complexes [Pd_2(dmp)$_2$(het-S,N)$_2$] (het-S,N = py2S and 6-mepy2S) [39]. These complexes exist as "*head-to-tail*" *cis*-isomers with the palladium coordination planes approximately parallel. Because both ligands are unsymmetrical the bridged complexes exist in five diastreoisomeric forms. Two of these have "*head-to-head*" and three have "*head-to-tail*" arrangements of the bridging pyridine-2-thionate ligands. Only one "*head-to-tail*" isomer is present in solution with a ^{1}H NMR spectrum consistent with two-fold symmetry. Variable temperature ^{1}H NMR spectra of [Pd_2(dmp)$_2$(6-mepy2S)$_2$] have been interpreted in terms of fluxional enantiomerisation. Rates of exchange of the diasteroscopic ligand N-methyl groups have also been reported. These bridged dimers behave as neutral cyclic bridging ligands towards other metal centres in the formation of trinuclear complexes (see Section 3.

The ability of quinoline-2-thionate **(IIg)** to μ_2-S,N bridge binuclear palladium(II) centres has been reported [40]. In addition, reaction of the dimeric palladium complex [{PdCl(PMe_3)μ-Cl}$_2$] with quinoline-2-thione produces monomeric [Pd(quinSH)Cl_2(PMe_3)] in acetone. Under more forcing conditions, [Pd(quinSH)$_2$Cl(PMe_3)]Cl is produced in ethanol. Both complexes contain distorted square-planar geometry and monodentate, η^1-S, quinoline-2-thione ligands (average Pd–S = 2.317 Å). Both the terminal and bridging chlorine atoms in the same binuclear palladium(II) precursor, are replaced with monodentate, η^1-S, and double-bridging, μ_2-S,N, quinoline-2-thionate anions, respectively, in the production of [{Pd(quin2S)$_2$(PMe_3)}$_2$] **(XV)**.

This complex is prepared by reacting the binuclear precursor with sodium quinoline-2-thionate in ethanol under nitrogen. The azido groups in dimeric [{Pd(dmba)N_3}$_2$] (dmba = dimethylbenzylamine) are similarly replaced with double-bridging quinoline-2-thionate anions by reacting the complex with sodium quinoline-2-thionate in ethanol, also under nitrogen [41]. Both complexes effectively have two-fold symmetry. Geometry at the metal is essentially square-planar with *cis*-related, and somewhat "folded", "*head-to-tail*" double-bridging, μ_2-S,N(η^1-S;η^1-N), quinoline-2-thionate ligands. The remaining coordination sites in the two complexes are

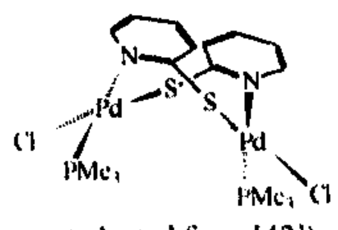


(adapted from [40])

(XV)

occupied by *trans*-related monodentate η^1-S donating quinoline-2-thionate and cyclopalladated C,N-donating dimethylbenzylamine ligands, respectively. Selected dimensions of these two similar complexes are given in Table 1c. Particularly noteworthy are the dimensions of the terminal and bridging quinoline-2-thionate ligands in [{Pd(quin2S)$_2$(PMe$_3$)}$_2$]. The average terminal and bridging palladium–sulphur distances (Pd–S$_{(terminal)}$ = 2.330, Pd–S$_{(bridging)}$ = 2.350 Å) are just significantly different ($\Delta\sigma = 4$) while the average angles at the corresponding thionate sulphur atoms are equivalent (Pd–S–C = 104.2°), within experimental error (Table 1c). These relative values suggest that the similarity in the angles is achieved by a slight relaxation in the bridging palladium–sulphur distance. Furthermore, the average thioamide distance (C–S = 1.73 Å) is the same for both terminal and bridging quinoline-2-thionate ligands.

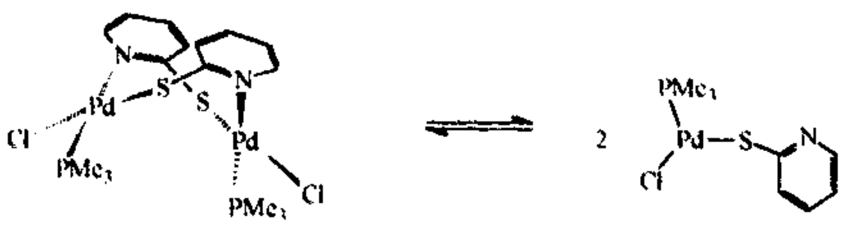
A group of complexes with the general formula [{Pd(het-S,N)(PMe$_3$)Cl}$_2$] (het-S,N = py2S [42], pym2S [43], 4-mepym2S [43], 1-meimz2S [43]) has been prepared by treating [{PdCl(PMe$_3$)μ-Cl}$_2$] with the sodium salts of the corresponding heterocyclic thionate in ethanol. Their crystal structures have also been reported. The complexes are effectively isostructural with the palladium atoms bridged by *cis*-related "*head-to-tail*" μ_2-S,N(η^1-S; η^1-N) double-bridging heterocyclic thionates. The metal geometry is distorted square-planar with the terminal chlorine and trimethylphosphine ligands *trans* to the thioamide sulphur and nitrogen atoms, respectively (**XVI**). Selected dimensions of these structures are given in Table 1c.



(adapted from [42])

(XVI)

The metal separation distances (2.915(1)–3.104(2) Å) lie outside the range (2.595–2.848 Å) reported for binuclear palladium(II) complexes with strong metal–metal bonds [44]. Of the remaining bond distances (M–S and M–N in Table 1c) those of the six-membered heterocycles are similar while the metal nitrogen distance formed by 1-methylimidazoline-2-thionate is slightly smaller than the others in the series. Interesting and varied dynamic behaviour in solution has been reported for these complexes on the basis of ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra together with molecular weight measurements. Variable temperature NMR spectra have established that all of the complexes are fluxional in character, with the exception of $[\{Pd(\mu\text{-}1\text{-meimz2S})\text{-}(PMe_3)Cl\}_2]$. This fluxionality is based on a reversible dimer–monomer equilibrium that involves rupture of the palladium–nitrogen bond. The monomeric species are more stable at higher temperatures (XVII).



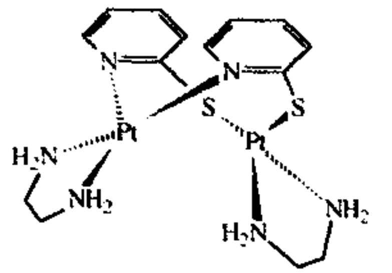
(XVII)

In contrast, the variable temperature (−50 to +100 °C) ^{1}H NMR spectra of $[\{Pd(1\text{-meimz2S})(PMe_3)Cl\}_2]$ are static and indicative of the absence of any rapid equilibrium process on the NMR time-scale. The crystal structures of the pyridine- and pyrimidine-2-thionate complexes suggest that there are no inherent structural differences among the double-bridging anions, despite significant differences in the basicities of the parent ligands. They have relatively narrow ligand thioamide angles (N–C–S = 121.9(2) to 124.5(8)°) which restrict metal ligand coordination and weaken the resultant metal nitrogen interactions. These thioamide angles are also responsible for the similarity in dynamic behaviour among the complexes. The 1-methylimidazoline-2-thionate anion, a five-membered heterocycle, has a larger thioamide angle (N–C–S = 128.4(7)°), which is similar to the average value in the parent molecule (127.1°) [29], and is able to form stronger palladium–nitrogen bonds. This accounts for the static variable temperature ^{1}H NMR spectra of the $[\{Pd(\mu\text{-}1\text{-meimz2S})(PMe_3)Cl\}_2]$ complex [43].

The preparation and characterisation of binuclear platinum(II) complexes of 2-pyridonate (**HeII**) and 1,2-diaminoethane (en) $[\{Pt(pyNO)(en)\}_2]$ [45,46] has led to the preparation of the corresponding complexes of pyridine-2-thionate and its 4-methyl derivative [47,48]. Preparation of the complexes involves the addition of potassium hydroxide (0.1M) to an aqueous solution of $[Pt(en)Cl_2]$ and the parent ligand; the yellow complexes are obtained at neutral pH. Both of the complexes adopt a "*head-to-head*" configuration of the double-bridging, μ_2-S,N(η^1-S:η^1-N), pyridine-2-thionate ligands (**XVIII**).

The study also involved the preparation and characterisation of a binuclear complex of 2-aminoethyl-2-pyridylsulphide (aps) $[\{Pt(aps)Cl\}_2]Cl_2.3H_2O$, which contains a "*head-to-tail*" configuration of the bridging ligands in the solid state.

Selected dimensions of the pyridine-2-thionate complexes are in given Table 1c. The PtN_4 and PtS_2N_2 coordination spheres are approximately planar with angles at



(adapted from [48])

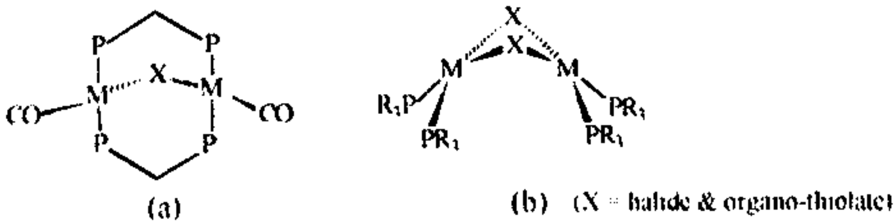
(XVIII)

the metal deviating significantly from the regular values and Pt...Pt distances that are too long for metal–metal bonding. The coordination planes in both complexes are also tilted (31.0(3) and 31.9(2)°) (**VIIa**). In addition, the average values of the (S–Pt–Pt–N) torsion angles (32.6 and 34.3°), in both complexes, indicate the extent by which the coordination planes are twisted out of the eclipsed position (**VIIb**). Such distortions are common among binuclear complexes with planar metal coordination especially when metal...metal distances significantly exceed ligand bite distances. The λλ (or δδ) conformations of the 1,2-diaminoethane ligands in the solid are presumed to undergo rapid conformational (λ↔δ) interconversion in solution. The metal–ligand dimensions are very similar in the two complexes (Table 1c).

The ligand thioamide dimensions however do show some characteristic differences relative to those of pyridine-2-thione [22] (Table 2). The average carbon–sulphur distance in the complexes is significantly longer than it is in the free ligand. Among the ligand angles the average thioamide angle (N–C–S = 122.1, 122.7°) and those at the thioamide nitrogen atoms (Pt–N–C = 123.1, 123.0°) are increased slightly relative to the free ligand values (120.6(2), 121.0(10)°), respectively. The average angle at the thionate sulphur atoms (Pt–S–C = 111.7, 110.3°) is in the middle of a relatively extensive range of values (104–115°; Table 1c), for this series of complexes. The evidence suggests a redistribution of the thioamide π-electron density, probably towards the carbon–nitrogen bond. Accommodation of the modest steric demands required by the double-bridging binuclear ligands is probably assisted by the angular flexibility of the thionato sulphur atom. Both complexes exist as centrosymmetric dimeric pairs in the solid (Pt...Pt′ = 3.613(1), 3.72(2) Å).

Cyclic voltammetric studies show that both complexes exhibit irreversible oxidation and reduction in dimethylformamide (+0.77 and +0.55 V; +1.20 and +0.86 V) relative to a silver/silver chloride reference electrode. This behaviour is attributed to a two-electron metal centred (2Pt(II)→2Pt(III)+2e) oxidation. Similar behaviour also occurs with the corresponding 2-pyridonate complex [49]. Production of the *"head-to-head"* isomer is ascribed to the initial replacement of the chlorine atoms in [Pt(en)Cl_2] with monodentate η^1-S donating pyridine-2-thionates.

2.3.3.2. Rhodium and iridium complexes. Prior to the use of bifunctional ligands, such as heterocyclic thionates, halide [50] and organo-thiolate [51] were frequently used in the production of *cis*-related double bridged square-planar complexes (**XIX**). Hoffmann and Hoffmann pointed out that such structures, based on square-planar d^8–d^8 complexes, have a vacant coordination site between the metals as well as similar valence orbitals [52]. Considerable effort has been expended recently to increase the range of bridging ligands that are capable of generating bridged binuclear complexes with the heavier transition metals such as rhodium and iridium.

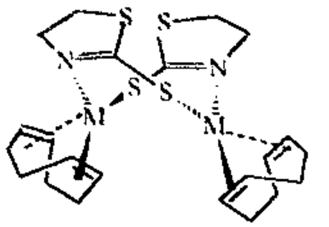


(XIX)

Cowie and his co-workers have made a useful contribution in this area by describing the synthesis and characterisation of a series of binuclear complexes of rhodium and iridium with bifunctional ligands such as 2-pyridinonate (**IIcii**), pyrazolate [53], pyridine-2-thionate (**IIci**) [54] and 1,3-thiazolidine-2-thionate (**IIhi**) [54–56] as well as diphosphines [56]. Structural interest in these complexes centres on how the bridging groups affect the "tilt" of the two coordination planes (**VIIa**) and on the resulting metal–metal distances. The latter is significant in the photochemical activation of such complexes in two-centre oxidation–addition reactions [71]. The transference of bridging anions to terminal sites as a result of their replacement by diphosphines is also of interest. Such "bridge-opened" species have been proposed as key intermediates in the activation of substrates by binuclear "*cis*-related" double-bridged complexes [57]. The use of diphosphines, to facilitate the transference of bridging ligands, raises the question of whether the resultant structures adopt planar *trans*-related or non-planar *cis*-related structures (**XIX**).

The preparation of complexes with the general formula [{M(μ-anion)(COD)}$_2$] (COD = 1,5-cyclooctadiene; M = Rh, Ir) involves addition of the parent ligand (e.g. 1,3-thiazolidine-2-thione) and sodium hydride, in thf, to the precursor complex [{M(μ-Cl)(COD)}$_2$], under nitrogen [54]. The terminal dienes in [{M(μ-tzd2S)(COD)}$_2$] may also be replaced with carbon monoxide giving the corresponding tetracarbonyl complex. Further addition of tri-phenyl and tri-methyl phosphines to the tetracarbonyl, in thf, results in the production of *trans*-[{M(μ-tzd2S)(CO)L}$_2$] (L = Ph_3P, Me_3P) [55]. The crystal structures of the 1,3-thiazolidine-2-thionate complexes have been reported; selected dimensions are listed in Table 1c. The [{Rh(μ-tzd2S)(COD)}$_2$] complex crystallises from dichloromethane, with two molecules of the solvent, as a *cis*-related "*head-to-tail*" double bridged dimer (**XX**).

The coordination planes are tilted (54.3(2)°) and are also twisted out of the totally eclipsed position (ca. 40°), about the metal–metal axis. This is a consequence of the need to avoid interactions between the hydrogen atoms of the terminal ligands. In other respects terminal ligand geometry is normal. Variable temperature (−40 to



(adapted from [55])

(XX)

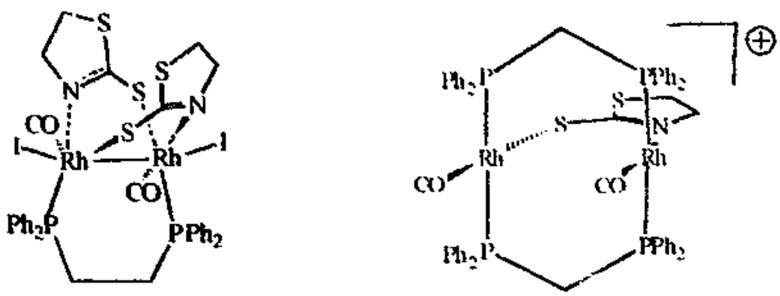
+38 °C) ^{1}H NMR spectra are ascribed to fluxionality in the complex due to facile rotation of the diene ligand about the metal–diene axis. Bridging ligand geometry consists of a short strong rhodium–nitrogen bond (average 2.091 Å), similar to that observed for a related pyrazolylate bridged complex [58], and a rhodium–sulphur bond (average 2.361 Å) that is comparable to the value observed in a related thiolate bridged complex [58]. Similarly, average angles at the bridging atoms (Rh–N–C = 128.2, Rh–S–C = 108.0°) reflect the modest steric demands of the μ_2-S,N(η^1-S;η^1-N) bridging ligands. Inclination of the coordination planes, mentioned above, involves both a degree of "folding" about the bridging groups and "twisting", of the planes, about the metal–metal axis, in order to stagger the terminal diene ligands. Although there is no precise measurement of the degree of folding required in this structure the dihedral angle is 54.3(2)°. This indicates a greater degree of folding than is observed with double-bridged thiolate and halide complexes, where the dihedral angle is generally about 120°, or in the case of double-bridged pyrazolate complexes where the dihedral angle is about 79° [53]. Cowie argues convincingly [54] that the degree of folding, decreasing dihedral angle, is related to the different constraints imposed by the one- (thiolate), two- (pyrazolylate) or three-atom (heterocyclic thionate) bridging units. In order to maintain normal unstrained angles at the bridging atoms, and to generate optimum orbital overlap, it is necessary for the folding to increase as the number of bridging atoms increases. Such a degree of folding is not accompanied by compression of the rhodium–rhodium distance in this structure (Rh–Rh = 3.7154(5) Å).

The [{Ir(μ-tzd2S)(COD)}$_2$] complex is virtually isostructural with that of the binuclear rhodium analogue [54]. The coordination planes are folded to effectively the same degree (55.2(2)°) and twisted about the iridium–iridium axis (37.3°) so as to stagger the terminal diene ligands. A smaller metal–metal separation (Ir–Ir = 3.5434(4) Å) is the only significant difference between the two structures.

With the exception of the *trans*-related pairs of carbonyl and phosphine ligands the crystal structures of the *trans*-[{Rh(μ-tzd2S)(CO)(R_3P)}$_2$] (R = Ph and Me) [55] complexes are similar to that of the corresponding diene. Each metal atom has approximately square-planar geometry formed by an N,S,P,C-donor set, pairs of *cis*-related *"head-to-tail"* bridging ligands (**XX**) and approximately two-fold symmetry about the rhodium–rhodium axis. Selected dimensions are given in Table 1c. The coordination planes are staggered (ca. 30.9°), as are the phenyl groups of the terminal triphenyl phosphine ligands, in order to minimise intra-ligand interactions. The dihedral angle between the inclined coordination planes (38.5°) in these structures is less than that observed for the corresponding diene complex (54.3(2)°) and is accompanied by a decrease in rhodium–rhodium separation distance (3.2435(3) Å). This is probably due to the reduced steric interaction caused by replacing COD ligands with carbonyl and phosphine. The metal–ligand dimensions are generally similar to those of the corresponding dirhodium complex (Table 1c). Differences between the average rhodium–sulphur distances (2.379, 2.395 Å) in the two complexes are attributed to differences in the degree of the *trans*-effect generated by the phenyl- and methyl-phosphine ligands. Furthermore, the smaller trimethylphosphine ligand permits a shorter metal–metal separation distance (3.0524(4) Å) and a more acute angle (30.0°) between the coordination planes.

Attempts have been made to combine the structural features of both *trans*-("A"-frame) and *cis*-related ("open-book") binuclear complexes in one complex. This has been achieved by the incorporation of diphosphine ligands, such as bisdiphenylphosphinomethane or ethane (dppm, dppe) into a binuclear *cis*-related structure [56]. The chosen starting point for these reactions are complexes of the type $[\{M(\mu\text{-tzd2S})(CO)_2\}_2]$ (M = Rh, Ir) where the metal–metal separation distances (3.05 Å) are comparable to the bite of the diphosphine ligands. A range of complexes has been prepared. Treatment of the precursor complex with one equivalent of the diphosphine ligand in thf gives complexes of the type $[M_2(\mu\text{-tzd2S})_2(CO)_2(\mu\text{-dppm})]$. The oxidative-addition of iodine atoms to these complexes, in some cases, gives $[M_2I_2(\mu\text{-tzd2S})_2(CO)_2(\mu\text{-dppm})]$. With two equivalents of the diphosphine *trans*-related ("A-frame") complexes of the type $[M_2(CO)_2(\mu\text{-tzd2S})(\eta^1\text{-tzd2S})(\mu\text{-dppm})_2]$ are produced. In solution, the terminal monodentate η^1-S donating 1,3-thiazolidine-2-thionate anion in these complexes exchanges with both the corresponding bridging and free heterocyclic thionate anions. Treatment of *trans*-$[\{MCl(CO)(dppm)\}_2]$ with two equivalents of the 1,3-thiazolidine-2-thionate anion also gives $[M_2Cl(CO)_2(\mu\text{-tzd2S})(dppm)_2]$. The rhodium dimer undergoes reversible halide dissociation to give $[Rh_2(CO)_2(\mu\text{-tzd2S})(dppm)_2]Cl$. These complexes have been characterised by IR and NMR methods. Complexes of formula $[M_2(\mu\text{-tzd2S})_2(CO)_2(\mu\text{-dppm})]$ have *cis*-related 1,3-thiazolidine-2-thionate anions, one bridging diphosphine *trans* to a bridging thionate, and terminal carbonyls. They may consequently be regarded as either "A-frame" or "open-book" in character. The relatively clean *trans*-annular oxidation–addition of iodine to $[Rh_2(\mu\text{-tzd2S})_2(CO)_2(\mu\text{-dppm})]$ permitted the isolation of $[Rh_2I_2(\mu\text{-tzd2S})_2(CO)_2(\mu\text{-dppe})]$ 0.5THF, whose crystal structure has been reported [56] (**XXIa**).

This structure consists of pairs of *cis*-related, "*head-to-tail*" 1,3-thiazolidine-2-thionate bridging anions, that produce a distorted "open-book" arrangement because of the narrow ligand bite (S…N = 2.685(6) Å). The bridging diphosphine (average Rh–P = 2.325 Å) is *trans* to one of the bridging heterocyclic thionates with which it forms a distorted "A-frame" arrangement due to the dimensional disparity between the two bridging ligands (P…P = 3.841(3) Å). The remaining bridging heterocyclic thionate atoms effectively occupy apical positions *trans* to the two carbonyls. With the two rhodium(II) atoms separated by a single bond (Rh–Rh =



(a) (b)

(adapted from [56])

(XXI)

2.748(1) Å) the six-coordinate geometry is completed by terminal iodo ligands slightly offset from the Rh–Rh vector (average Rh–Rh–I = 169.8°). Selected dimensions are summarised in Table 1c. Angles at the metal signify the extent of distortion from regular geometry in the complex. Average angles at the bridging thoamide nitrogen (123.8°) and thionate sulphur atoms (100°) are typical of binuclear double-bridging heterocyclic thionates. Differences in the rhodium–sulphur and rhodium–nitrogen distances, *trans* to the phosphorus atoms or to the carbonyl groups, are the reverse of that reported for $[\{Rh(CO)(PPh_3)(\mu\text{-}PhS)\}_2]$ [59]. The two sets of octahedra in the complex are offset by inclination (16.4°) about the axial direction, parallel to the rhodium–phosphorus bonds. They are also staggered about the rhodium–rhodium bond by an average torsion angle of approximately 33°.

The reversible dissociation of $[Rh_2(CO)_2(\mu\text{-}tzd2S)Cl(dppm)_2]$ in dichloromethane (**XXII**) permits isolation of the cationic complex $[Rh_2(CO)_2(\mu\text{-}tzd2S)(dppm)_2]Cl.CH_2Cl_2$. The crystal structure of this complex has also been reported [56] (**XXIb**).

$$[Rh_2(CO)_2(tzd2S)Cl(dppm)_2] \rightleftharpoons [Rh_2(CO)_2(tzd2S)(dppm)_2]Cl$$

(XXII)

The complex cation $[Rh_2(CO)_2(\mu\text{-}tzd2S)(dppm)_2]^+$ shows considerable resemblance to conventional "A-frame" structures with the diphosphines in the *trans*-bridging positions. The 1,3-thiazolidine-2-thionate anion is at the apex and *trans* to the carbonyl ligands. Selected dimensions are listed in Table 1c. Square planar geometry at the metals is significantly distorted with the N–Rh–C and S–Rh–C angles (172.9(2), 151.9(2)°), respectively, resulting from the displacement of the carbonyls. The distance between the rhodium(I) atoms (2.9957(7) Å) is slightly compressed relative to the average diphosphine intraligand distance (P...P = 3.062 Å). Cowie regards this as a consequence of crystal packing of the bulky phenyl groups, rather than the result of metal...metal bonding. In conventional "A-frame" structures where the capping ligand is a single atom, such as halide or sulphide (see **XIX**), the resultant tilting of the coordination planes is substantial (ca. 83°). In this binuclear rhodium structure, and in **(XXIa)**, the capping ligand binds to the two metals through two well separated donor atoms. This opens up the "A-frame" with more closely parallel coordination planes in which the dihedral angle is only 16(2)°. Consequently, the dimeric cation adopts a geometry similar to that of "*face-to-face*" dimers such as *trans*-[{Rh(CO)Cl(dppm)}$_2$] [60]. In other respects the dimensions of the complex are similar to those of **(XXIa)**.

This group of complexes permits careful analysis of the effects of deprotonation and coordination on the dimensions of the parent 1,3-thiazolidine-2-thione ligand [61]. The relevant dimensions are summarised in Table 3. Because of the ethylenic backbone in the parent ligand the bulk of the π-electron density, conveniently expressed as the percentage of double-bond character, is concentrated in the heterocyclic portion of the molecule (C–N = 77%, C–S$_{exo}$ = 55%, C–S$_{endo}$ = 37%) [62,63]. The effect of deprotonation and coordination is to concentrate the π-electron density in the thioamide carbon–nitrogen bond, with an average of about 95% double-bond character [62]. This is achieved at the expense of the carbon–sulphur bonds, where the corresponding double-bond character is about 20% (C–S$_{endo}$) and 33% (C–S$_{exo}$), respectively [63]. In contrast the thioamide, N–C–S$_{exo}$, angle is scarcely affected by coordination (Table 3). This is also indicative of the modest steric demands of binuclear, double-bridging ligands, as are the Rh–N–C and Rh–S–C angles in Table 1. All the other angles in Table 3 are affected by deprotonation and coordination to some extent.

Oro and his co-workers have also extended the range of asymmetrically bridged binuclear rhodium and iridium complexes by using pyridine-2-thionate **(IIei)** and benzo-1,3-thiazoline-2-thionate **(IIhiII)** [64–66]. The general synthetic strategy adopted involves deprotonation of the parent ligands in diethyl ether with *n*-butyl lithium in hexane followed by addition of the general precursor complex [{Rh(μ-Cl)(olefin)}$_2$] (olefin = COD, nb and tetrafluorobenzo-[5,6]-bicyclo-[2,2,2]-octa-2,5,7-triene (tfbb)). All reactions were carried out under nitrogen. Replacement of the bridging chloro ligands by the heterocyclic thionates generates the corresponding binuclear double-bridged complexes, [{Rh(μ-het-S,N)(olefin)}$_2$]. Replacement of the terminal η^2-olefins in these complexes, by carbonylation in dichloromethane, produces the corresponding carbonyl complexes [{Rh(μ-het-S,N)(CO)$_2$}$_2$]. Subsequent replacement of a pair of carbonyls with triphenylphosphine is also possible in some cases giving [{Rh(μ-py2S)(PPh$_3$)(CO)}$_2$]. The intensity and pattern of the major IR bands in this, and similar complexes, is consistent with a "*face-to-face*" disposition of the two Rh(CO)$_2$ groups. Detailed analysis of the ^{1}H NMR spectrum of [{Rh(μ-py2S)(CO)$_2$}$_2$] has also enabled the more intractable aspects of the NMR spectra of the olefin complexes [{Rh(μ-py2S)(olefin)$_2$] to be rationalised. Although the ^{1}H NMR spectrum of the carbonyl complex is invariant in the range −20 to +50 °C fluxional behaviour is manifest in the form of two doublet resonances arising from two sets of equivalent carbonyl groups in its ^{13}C{^{1}H} spectrum at −50 °C. At higher temperatures the four carbonyl groups become equivalent and generate a resonance doublet. This spectral change, in which the coupling constant is also retained above coalescence, is ascribed to carbonyl scrambling without their dissociation. The fluxionality in the complex is ascribed to the reversible conversion

Table 3
1,3-Thiazolidine-2-thionate complexes; selected ligand dimensions (Å and °)

▶(a) μ_2-S,N double bridging ligands in binuclear rhodium and iridium complexes
Bond lengths and angles
Complex and reference

$C-S_{endo}$	C–N	$C-S_{exo}$	C–N–C	$N-C-S_{endo}$	$N-C-S_{exo}$	$S_{endo}-C-S_{exo}$	$C-S_{endo}-C$
1,3-Thiazolidine-2-thione(average dimensions) [61]							
1.725	1.315	1.626	118.5	111.7	126.2	122.1	93.1
[{Rh(μ-tzd2S)(COD)}$_2$] [54]							
1.756	1.283	1.731	113.5	115.6	126.3	117.4	91.3
1.767	1.272	1.737	114.5	116.2	126.5	118.2	91.0
[{Ir(μ-tzd2S)(COD)}$_2$] [54]							
1.755	1.282	1.723	112.9	116.6	126.4	117.4	91.1
1.753	1.282	1.733	112.4	115.9	126.6	117.5	91.3
[{Rh(μ-tzd2S)(CO)(PMe$_3$)}$_2$] [55]							
1.772	1.286	1.696	114.0	114.9	127.1	117.8	90.5
1.767	1.286	1.753	112.8	115.6	126.6	118.0	90.2
[{Rh(μ-tzd2S)(CO)(PPh$_3$)}$_2$] [55]							
1.781	1.278	1.696	113.4	114.1	128.3	117.7	89.6
1.753	1.287	1.753	114.1	115.7	126.5	117.6	90.6
[Rh$_2$I$_2$(μ-tzd2S)$_2$(CO)$_2$(dppm)] [56]							
1.758	1.270	1.737	111.7	116.9	127.4	117.5	89.2
1.754	1.280	1.724	111.7	116.8	125.7	115.7	90.1
[Rh$_2$(μ-tzd2S)(CO)$_2$(dppm)]$^+$ [56]							
1.775	1.283	1.719	111.7	115.1	128.8	116.1	89.7

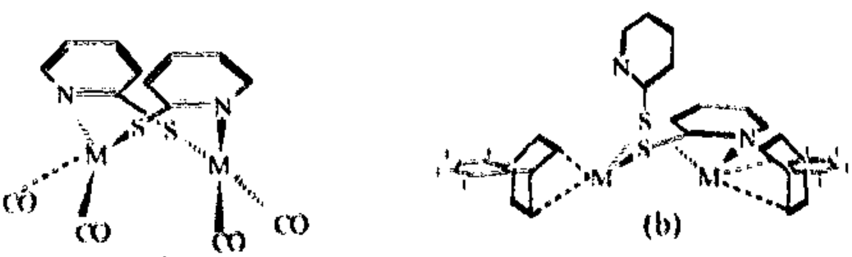
(b) Miscellaneous 1,3-thiazolidine-2-thionate bridging complexes

Complex and reference	$C-S_{exo}$	C–N	$C-S_{endo}$	N–C–S
[(η^6-C$_6$H$_6$)$_2$Ru$_2$(μ-tzd2S)$_2$Cl] Cl.2H$_2$O [80]				
μ_2-S,N double-bridging ligand	1.728(14)	1.277(15)	1.765(11)	130.6(9)
μ_3-S,N triple-bridging ligand	1.772(12)	1.280(15)	1.731(14)	109.2(10)
[Os$_3$(μ-H)(μ-tzd2S)(CO)$_{10}$] [109] (average dimensions of two independent molecules)				
μ_2-S, edge-bridging ligand	1.74	1.29	1.79	127.4
[{Cu(μ-tzd2S)}$_4$.(toluene)}$_n$] [133] (average dimensions)				
μ_3-S,N bridging ligand	1.744	1.277	1.770	125.4
μ_4-S,N bridging ligand	1.755	1.277	1.781	126.8
[{Cu(μ-tzd2S)}$_4$(tzd2SH)$_2$]^a [134]				
μ_3-S,N bridging ligand	1.727	1.287	1.767	127.8
η^1-S monodentate ligand	1.681(7)	1.373(12)	1.675(6)	123.8(6)
[{Ni(μ-OH)(py)(μ-tzd2S)}$_4$].2py ^{a} [137]				
μ_2-S,N double-bridging ligands	1.74(2)	1.26(3)	1.77(2)	129(1)

e.s.d's 0.003–0.007 Å and 0.2–0.5°.
^{a} Symmetrical molecule.

of one of the binuclear pyridine-2-thionate ligands from a double-bridging, μ_2-S,N(η^1-S;η^1-N), to an edge-bridging, μ_2-S (η^2-S), mode (**IV**). Isomeric interconversions are successfully avoided in the correspondingly bulkier benzo-1,3-thiazoline-2-thionate complexes. An additional interesting characteristic of [{Rh(μ-py2S)(CO)$_2$}$_2$] is the smooth double oxidative-addition of methyl iodide giving the binuclear diacyl complex [{Rh(μ-py2S)(COMe)I(CO)$_2$}$_2$]. This behaviour contrasts with that of a similar tertiary-butylthiolate complex in which oxidative-addition of methyl iodide occurs readily on only one of the metal centres. Oro argues that this contrasting behaviour illustrates the enhanced activity of pyridine-2-thionate complexes, relative to that of analogous alkanethiolate complexes, in this type of reaction.

The crystal structures of [{Rh(μ-py2S)(tfbb)}$_2$] and [{Rh(μ-py2S)(CO)$_2$}$_2$] provide definitive evidence of binuclearity and the contrasting nature of the double-bridging systems utilised in these complexes. Both structures involve binuclear rhodium(I) species with bridging pyridine-2-thionate anions as well as terminal η^2-donating olefin or carbonyl ligands. The carbonyl complex (**XXIIIa**) has a crystallographic two-fold axis and two *cis*-related, "*head-to-tail*" μ_2-S,N(η^1-S;η^1-N) double-bridging, pyridine-2-thionate anions. The olefinic complex (**XXIIIb**) contains the rare combination of one double-bridging, μ_2-S,N(η^1-S;η^1-N), and one slightly asymmetric and also double-bridging, μ_2-S(η^2-S), pyridine-2-thionate ligand. Selected dimensions of these complexes are summarised in Table 1c.



(adapted from [66])

(XXIII)

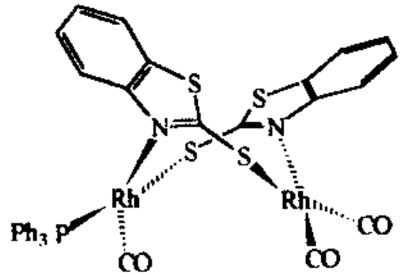
There are slight differences in the metal–ligand and metal–metal distances formed by the double-bridging, μ_2-S,N(η^1-S;η^1-N), ligands in the two complexes. The slightly longer distances in the olefin complex clearly result from the additional steric demands of the double-bridging, μ_2-S(η^2-S), pyridine-2-thionate anion (Rh–S = 2.349(2), 2.339(2) Å; Rh–S–Rh = 80.5(1)°). The two complexes have slightly different donor sets as well as distorted square-planar geometry. Furthermore, the inclination of the pairs of coordination planes in the two complexes is significantly different. In the olefinic complex the dihedral angle is 81.2(1)° whereas in the carbonyl complex the value is 18.9(2)°; a clear indication of the extent by which single atom bridges distort the binuclear geometry. In the carbonyl complex the angles at the bridging ligands (Rh–N–C, Rh–S–C) are normal (Table 1c). The slightly asymmetric character of the double-bridging, μ_2-S(η^2-S), pyridine-2-thionate anion in the olefinic complex is more apparent in the angles at the donor atom (Rh–S–C = 105.5(2), 117.0(2)°) than in the corresponding rhodium–sulphur distances. There is no marked effect on the angles at the donor atoms in the other bridging ligand in this complex however (Rh–S–C = 113.1(3), Rh–N–C = 119.1(5)°). Nor are there any significant differences in the bite (S...N) distances of the planar bridging pyridine-2-thionate ligands in these two complexes. In the μ_2-S(η^2-S) bridging ligand, the bite distance is 2.666(7) Å, with a corresponding distance of 2.636(6) Å, for the μ_2-S,N bridging ligand. In the carbonyl complex the distance is 2.692(7) Å. Clearly these distances do not seem to affect, or to be affected by, differences in bridging function.

The most significant consequences of deprotonation and coordination on the thioamide dimensions of pyridine-2-thione are observed for the μ_2-S(η^2-S) bridging ligand in the olefin complex (Table 2). This ligand shows the largest increase in the C–S distance and the largest reduction in the C–N distance, the N–C–S angle is also significantly reduced. The corresponding values for the μ_2-S,N bridging ligand in this complex show a significant reduction in the thioamide angle which is also due to the additional steric demands of the μ_2-S(η^2-S) bridging ligand. The thioamide dimensions of the crystallographically unique bridging ligand in the carbonyl complex are normal in comparison (Table 2).

The production of disubstituted phosphines of the type [{Rh(μ-py2S)(PPh$_3$)(CO)}$_2$] from the corresponding tetracarbonyl complex has been alluded to above [66]. The monosubstituted complexes [Rh$_2$(μ-het-S,N)$_2$(PPh$_3$)(CO)$_3$] however are less well known. They are probably relatively rare because of their tendency to disproportionate and to exist in equilibrium with the tetracarbonyl and disubstituted complexes. Such behaviour has been shown to occur among similar iridium-thiolate complexes [67]. In addition, the production of [{Rh(μ-py2S)(CO)}$_2$] from solutions of [Rh$_2$(μ-het-S,N)$_2$(PPh$_3$)(CO)$_3$], at low temperature, is also known to occur [66]. Oro has described the preparation of dark-red crystalline [Rh$_2$(μ-bztz2S)$_2$(PPh$_3$)(CO)$_3$] from the carbonylation of [{Rh$_2$(μ-bztz2S)(CO)}$_2$] followed by the addition of one-equivalent of trimethylphosphine [68]. Careful monitoring of the reaction medium by ^{31}P{^{1}H} NMR spectroscopy revealed the existence of both the monosubstituted and disubstituted complexes in solution. However, the monosubstituted complex is insoluble at lower temperatures because of its reduced solubility. In addition, the presence of three strong carbonyl bands in the IR spectrum indicated the monosubstituted character of the product. This was confirmed by crystal structure analysis.

The tetracarbonyl precursor exists in solution in both *"head-to-head"* and *"head-to-tail"* isomeric forms. Consequently, several isomeric forms of [Rh$_2$(μ-bztz2S)$_2$(PMe$_3$)(CO)$_3$] are possible depending on the distribution of the bridging ligands and on the position of the phosphine ligand. The structure of the complex is shown in **(XXIV)**.

The complex consists of two distorted square-planar metallic centres bridged by two *cis*-related, *"head-to-tail"* double-bridging, μ_2-S,N(η^1-S;η^1-N), benzo-



(adapted from [68])

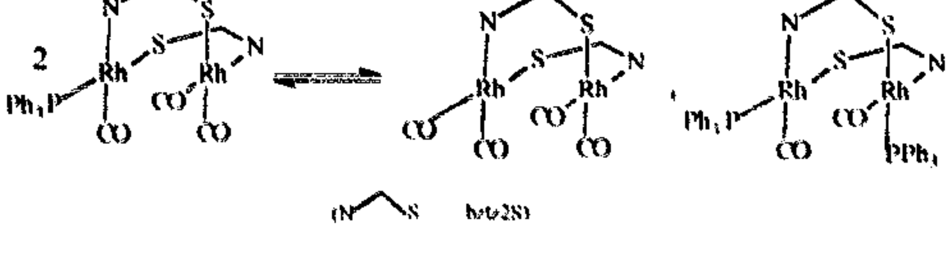
(XXIV)

1,3-thiazoline-2-thionate ligands. Disparity in the donor sets and the narrow bite of the bridging ligand cause distortion in the angles at the metal (Table 1c) as well as their displacement from the coordination planes. The coordination planes are also tilted (30.3(1)°) and twisted (38.5(1)°) in order to minimise intra-ligand interactions. The major dimensions of the complex (Table 1c) are similar to those of related complexes with the metal–metal distance too long for metal–metal bonding.

The effects of deprotonation and coordination on the dimensions of benzo-1,3-thiazoline-2-thione [69] are similar to those reported for 1,3-thiazolidine-2-thione (Table 3) and are summarised in Table 4. The average thioamide distances for the ligand show the characteristic increase and decrease in the carbon–sulphur and carbon–nitrogen distances, respectively. Although the thioamide angle remains relatively unaffected by coordination some perturbation (ca. 2–7°) of the remaining angles in the heterocyclic portion of the molecule occurs.

As a result of disproportionation in dichloromethane $[Rh_2(\mu\text{-bztz2S})_2(PMe_3)(CO)_3]$ is immediately in equilibrium with the tetracarbonyl complex and it's disubstituted product (**XXV**). The temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum shows the complexes to be in a dynamic equilibrium that shifts towards the monosubstituted complex as the temperature rises. Equilibrium is also reached when equimolar quantities of (**XXVa and b**) are mixed. Scrambling experiments, carried out with the analogous 6-methyl-benzo-1,3,-thiazoline-2-thione complexes, suggest that polynuclear intermediates are responsible for the ligand-redistribution equilibrium.

The bifunctional nature of heterocyclic thionates should facilitate the



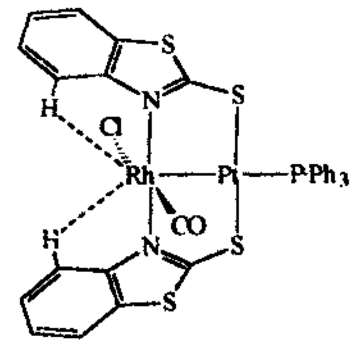
(XXV)

Table 4
Benzo-1,3-thiazoline-2-thionate complexes; selected average ligand dimensions (Å and °)

Complex and reference	C–Sexo	C–N	C–Sendo	N–C–S
Benzo-1,3-thiazoline-2-thione [69]	1.662(4)	1.353(6)	1.732(3)	127.4(3)
(a) μ_2-S,N bridging ligands				
$[Rh_2(\mu\text{-bztz2S})_2(PPh_3)(CO)_3]$ [68]	1.713	1.319	1.738	125.8
$[(Ph_3P)Pt(II)(\mu\text{-bztz2S})_2Rh(I)Cl(CO)]$ [70]	1.726	1.303	1.740	127.2
$[\{Ru(\mu\text{-bztz2S})(CO)_2(py)\}_2]$ [73]	1.746	1.306	1.719	128.1
$[Pd_2(\mu\text{-bztz2S})_4]$ [90]	1.715	1.325	1.745	130.0
$[Pt_2(\mu\text{-bztz2S})_4]$ [91]	1.706	1.342	1.753	130.5
(b) μ_3-S,N bridging ligands				
$[Ru_3(\mu\text{-H})(\mu\text{-bztz2S})(CO)_9]$ [112]	1.73(1)	1.30(1)	1.75(1)	124.4(5)
$[Rh_3(\mu\text{-bztz2S})_2(CO)_2(PPh_3)_2(tfb)](ClO_4)$ [119]	1.73	1.33	1.675	123.4
$[(COD)_2Rh_2(\mu\text{-bztz2S})2Ag(O_2ClO_2)]_2$[a] [120,121]	1.757(14)	1.298(16)	1.729(14)	116.0(10)

[a] Symmetrical molecule.

generation of heterobimetallic complexes. Accordingly, reactions of $[\{Rh(\mu\text{-bztz2S})(PPh_3)(CO)\}_2]$ with $[MCl_2(COD)]$ (M = Pd, Pt) in toluene were used to generate the diamagnetic heterobimetallic species $[(Ph_3P)M(\mu\text{-bztz2S})_2RhCl(CO)]$ (M = Pd, Pt) together with $[MCl_2(PPh_3)_2]$ and $[\{Rh(\mu\text{-Cl})(COD)\}_2]$ [70]. The complicated nature of the underlying processes controlling these reactions has been studied by ^{31}P NMR spectroscopy of the reaction solution. An alternative route to the heterobimetallic complexes involves reacting species such as *trans*-$[Pt(bztz2S)_2(PPh_3)_2]$ with $[\{Rh(\mu\text{-Cl})(CO)_2\}_2]$. Structural characterisation of $[(Ph_3P)Pt(\mu\text{-bztz2S})_2RhCl(CO)]$ has been achieved by spectral and crystal structure analysis. The ^{31}P NMR spectrum of the complex indicates the presence of a P–Pt–Rh unit. In addition, the equivalence of the ^1H NMR spectra of the benzo-1,3-thiazoline-2-thionate ligands suggest an unusual *trans*-related "*head-to-head*" distribution of the double-bridging ligands. These features of this currently unique structure were confirmed by crystal structure analysis of the dichloromethane solvate. The structure is shown in **(XXVI)** and selected dimensions are summarised in Table 1c.

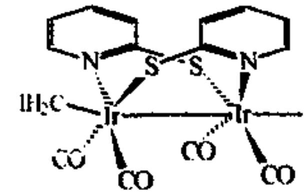


(adapted from [70])

(XXVI)

The metallic centres are connected by a short metal–metal bond (2.6266(4) Å) and bridged by two *trans*-related, *"head-to-head"* benzo-1,3-thiazoline-2-thionate, μ_2-S,N (η^1-S;η^1-N), double-bridging ligands. Unusually, the average ligand bite distance (S...N = 2.710 Å) is comparable with the metal–metal distance in this complex. The presence of a metal–metal bond, a consequence of the thirty electron count, denies the structure some flexibility. In addition, the *"head-to-head"* ligand distribution, coupled with the proximity of metal–metal and ligand bite distances, require a *trans*-, rather than a *cis*-related arrangement, of double-bridging ligands; primarily for steric reasons. Such an arrangement, which persists in solution, is unique among this class of complexes. Terminal sites are occupied by the remaining monodentate ligands. Coordination at platinum(II) is square planar with octahedral geometry at rhodium(I). The extent of the relatively slight distortion at both metals is manifest in the angles at the platinum(II) (83.7(1)–176.39(5)°) and rhodium(I) atoms (89.0(1)–177.9(1)°), respectively. The dihedral angle formed by the ligand planes is 12.5(1)°. They also form an average dihedral angle with the coordination plane about the platinum(II) of 13.1°, providing further evidence of the slight geometric distortion. Oro attributes the absence of an additional terminal ligand at the rhodium(I) atom to intramolecular contacts between the metal and adjacent hydrogen atoms (average Rh–H = 2.880 Å). These rhodium...hydrogen contacts are also detectable in the ^{1}H NMR spectrum. The average thioamide dimensions of the bridging ligands show the characteristic changes resulting from deprotonation and coordination (Table 4).

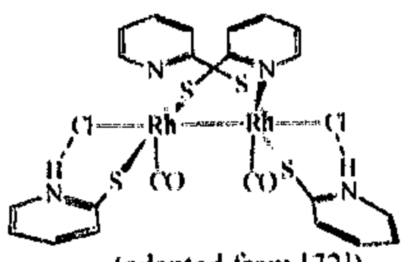
Replacement of the diolefin molecules in [{Ir(μ-py2S)(COD)}$_2$] with carbonyl ligands, in toluene, produces deep-purple air-sensitive solutions of [{Ir(μ-py2S)(CO)$_2$}$_2$] from which black-violet crystals of the complex are obtained [71]. The IR and ^{1}H NMR spectra of this complex are consistent with a *cis*-related *"head-to-tail"* distribution, of μ_2-S,N(η^1-S;η^1-N), double-bridging ligands. This complex undergoes *trans*-annular oxidative-addition of iodine, methyl iodide or methylene iodide, upon exposure to sunlight or UV-light, giving air-stable iridium(II) complexes [{Ir(μ-py2S)(CO)$_2$R}$_2$] (R = I, CH_2I, Me). The crystal structure of $[Ir_2(\mu\text{-py2S})_2(CO)_4I(CH_2I)]$ shows that the complex consists of the anticipated distribution of bridging ligands, four terminal carbonyls and a separation distance (Ir–Ir = 2.695(2) Å) consistent with a metal–metal bond. Octahedral coordination about the metals is completed by an iodo atom in one case and by a methylene iodide group in the other. Consequently, each metal has a slightly different donor set. The structure is shown in **(XXVII)** and selected dimensions are given in Table 1c. A free-radical mechanism is proposed for the formation of the complex.



(adapted from [71])

(XXVII)

Two complexes have been reported with metal–metal bonded d^7–d^7 systems involving rhodium(II) [72] and ruthenium(I) [73]. Yellow solutions of $[Rh_2Cl_2(CO)_4]$ react with pyridine-2-thione, in 1:2 molar ratio in chloroform and a nitrogen atmosphere, slowly giving blue-black crystals of the double-bridged binuclear rhodium(II) complex $[Rh_2Cl_2(\mu\text{-py2S})_2(\eta^1\text{-pySH})_2(CO)_2].2CHCl_3$. Aerial oxidation of chloroform solutions of $[Rh_2Cl_2(CO)_4]$ and pyridine-2-thione (in 1:3 molar ratio) also produce the tris-chelate $[Rh(py2S)_3]$. The crystal structure of $[Rh_2Cl_2(\mu\text{-py2S})_2(\eta^1\text{-pySH})_2(CO)_2].2CHCl_3$ shows that the molecule has two-fold crystallographic symmetry about the metal–metal axis **(XXVIII)**

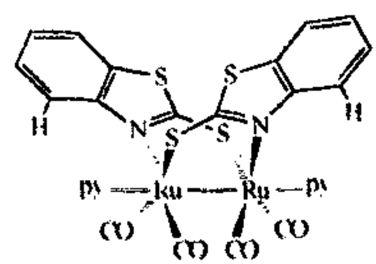


(adapted from [72])

(XXVIII)

The metallic centres are connected by a short metal–metal bond (2.652(4) Å) and bridged by two *cis*-related, *"head-to-tail"* μ_2-S,N (η^1-S:η^1-N) double-bridging, pyridine-2-thionate ligands. The neutral pyridine-2-thione ligands are terminal monodentate (η^1-S) donating. There are significant differences between the bridging and terminal rhodium–sulphur distances with the bridging anion, as expected, binding more strongly than the terminal neutral molecule. In addition, the terminal chloro ligands form intra-molecular hydrogen bonds with the terminal pyridine-2-thione molecules (N–H...Cl = 3.003 Å). This results in the generation of pseudo-chelate rings. Coordination planes about the metals are also staggered rather than eclipsed (S–Rh–Rh–N = 37°). Selected dimensions are summarised in Table 1c.

Conversion of a trinuclear ruthenium cluster to a binuclear ruthenium(I) complex is achieved by heating a mixture of $Ru_3(CO)_{12}$ and benzo-1,3-thiazoline-2-thione (1:3 molar ratio) in air-free toluene and a nitrogen atmosphere. This reaction produces red-orange crystals of the binuclear complex $[\{Ru(bztz2S)(CO)_3\}_2]$. Recrystallisation of this product from pyridine produces orange air-stable crystals of the pyridine adduct $[\{Ru(\mu\text{-}bztz2S)(py)(CO)_2\}_2]$ [73]. The structure of the complex consists of six-coordinate metal and a pair of *cis*-related, "*head-to tail*" double-bridging, heterocyclic thionate ligands (average N–Ru–S = 87.1°). Terminal pyridine molecules, *trans* to the metal–metal axis, together with pairs of *cis*-related carbonyl ligands, *trans* to the thioamide nitrogen and sulphur atoms, complete the coordination. The structure is shown in (**XXIX**) and selected dimensions are given in Table 1c.



(adapted from [73])

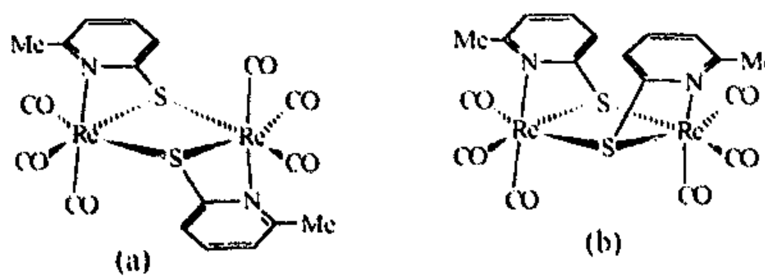
(XXIX)

The metal–metal distance in this structure is similar to that in the preceding rhodium(II) complex. Slight distortion about the metal octahedra (Table 1c) is ascribed to the difference between the metal–metal distance and the bridging ligand bite. Breakdown of the triangular ruthenium cluster is also ascribed to initial replacement of axial carbonyls, by benzo-1,3-thiazoline-2-thionate anions, followed by ejection of one ruthenium atom by the second bridging ligand. Average thioamide group dimensions in the bridging ligands show the characteristic concentration of the π-electron density in the carbon–nitrogen thioamide distance at the expense of the carbon–sulphur distances (Table 4).

With the exception of $[(Ph_3P)Pt(\mu\text{-}bztz2S)_2RhCl(CO)]$ [70] this structurally well-characterised group of complexes all contain pairs of binuclear *cis*-related, double-bridging, heterocyclic thionate ligands. These bridging ligands are securely bonded to the metal through strong contacts to the thioamide nitrogen (Table 1c). Both the ligand thioamide (N–C–S) angles, and those of the thioamide nitrogen (Rh–N–C), are close to the values in the free ligand. This is consistent with the absence of a significant degree of strain in the bridging ligands. The requisite flexibility in the bridging function however is achieved through modest variations in distances and angles at the thionate sulphur atoms (Table 1c). In addition, differences between the bridging ligand bite (S...N) and the metal...metal separation distances in the complexes are accommodated by varying degrees of tilting and twisting of the coordination planes.

2.3.3.3. Complexes with μ_2-S,N(η^2-s;η^1-N) bridging ligands. An increase in the electron involvement of the thionate sulphur atom in binuclear, double-bridging ligands, enables the production of binuclear, triple-bridging, μ_2-S,N (η^2-S;η^1-N) **(IIIc)**, heterocyclic thionates. The change, from a three- to a five-electron donating system, clearly involves increased metal coordination by the thionate sulphur atom (see Section 2.3.2.

A group of binuclear complexes have been reported with six-coordinate metals and pairs of binuclear triple-bridging ligands in either centrosymmetric, *trans*-related (chair), or chiral, (C_2) *cis*-related (boat), configurations. Each complex incorporates a central combination of three fused four-membered rings consisting of two S,N-chelates, grouped around a central M_2S_2 core **(XXX)**. The bridging ligands involve imidazoline-2-thionate **(IIaii)**, pyridine-2-thionate **(IIci)**, quinoline-2-thionate **(IIg)**, benzo-1,3-thiazoline-2-thionate **(IIhiii)** and 2-thiouracilate **(IIdiii)** derivatives.



(XXX)

Dirhenium dodeca-carbonyl is a useful precursor for complexes of the formula [{Re(μ-het-S,N)(CO)$_3$}$_2$] (het-S,N = bztz2S [74], 6-mepy2S [75]). The yellow crystalline benzo-1,3-thiazoline-2-thionate complex is obtained by prolonged heating of [$Re_2(CO)_{10}$] with benzo-1,3-thiazoline-2-thione in dimethyleneglycol diethylether followed by slow cooling of the reaction mixture. Refluxing in xylene is preferred for the 6-methylpyridine-2-thionate complex followed by chromatographic separation of the product. An analogous manganese complex of benzo-1,3-thiazoline-2-thione has also been prepared from [$Mn(CO)_5Br$] [74]. Infrared and mass spectral observations on some manganese-thioamide complexes had previously indicated that the chair form was preferred in the solid state **(XXXa)**, primarily for steric reasons [76]. However, except for [{Re(μ-6-mepy2S)(CO)$_3$}$_2$], the above rhenium and manganese complexes possess a crystallographic two-fold axis and are therefore constrained to adopt the boat form. Furthermore, the presence of five IR carbonyl bands (1917–2039 cm^{-1}) suggests that [{Re(μ-6-mepy2S)(CO)$_3$}$_2$] also adopts the boat form **(XXXb)**. In addition, a crystallographic two-fold axis also constrains [{Mo(1-meimz2S)(η^3-allyl) (carbonyl)}$_2$] to adopt the boat form [28]. Selected dimensions for these complexes are listed in Table 5; no structural data have been reported for [{Mn(μ-bztz2S)(CO)$_3$}$_2$].

The metal...metal separation distances confirm the absence of metal–metal bonds in the rhenium(I) and molybdenum(II) structures. A variety of terminal ligands, including *fac*-carbonyl and η^3-2-methylallyl groups, complete the distorted octahedral coordination at the metals. The bridging ligands are securely held by strong

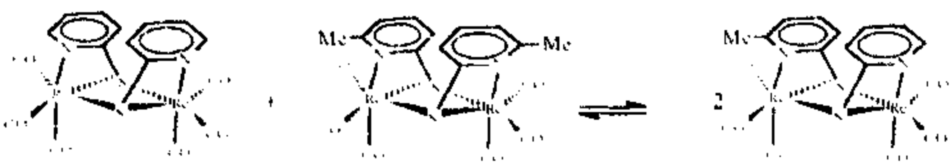
Table 5
Binuclear complexes with triple-bridging, μ_2-(S,N)(η^2-S:η^1-N), ligands: selected dimensions (Å and °)

►Complex and reference							
M–M	M–S	M–N	M–S–M	S–M–S	M–S–C	M–N–C	S–M–N
[Re_2(μ-6-mepy2S)$_2$(CO)$_6$] [75]							
NR	2.529(6)–	2.181(10)	95.3(2)	80.7(2)	NR	NR	65.8(3)
	2.556(6)	2.194(10)	96.2(2)	81.1(1)			65.6(3)
[Re_2(μ-bztz2S)$_2$(CO)$_6$]ᵃ [74]							
3.754(6)	2.541(7)	2.18(1)	94.1(7)	82.5(7)	76.9(5)	NR	63.9(3)
	2.586(7)				109.1(7)		
[Mo_2(η^3-allyl)$_2$(μ-1-meimz2S)$_2$(CO)$_4$]ᵃ [28]							
3.8313(4)	2.5876(7)	2.253(2)	93.83(2)	80.96(2)	75.66(9)	101.2(2)	63.89(6)
	2.6868(7)				111.06(2)		
[(VO)$_2$(μ-py2S)$_2$(py2S)$_2$]ᵃ [77]							
3.989(2)	2.457(4)	2.106(7)	98.65(9)	NR	NR	NR	62.35(2)
	2.798(3)						
S,N-chelating py2S							
	2.427(3)	2.088(7)			NR	NR	68.51(9)
[Re_2(μ-I)(μ-6-me-3(CO_2Me)quin-2-S)(CO)$_7$] [79]							
3.933(4)	2.519(3)	2.20(1)					
	2.533(3)		(Re–I 2.788(3), 2.803(3))				
[(η^6-C_6H_6)$_2$$Ru_2$(μ-tzd2S)$_2$Cl] Cl.2$H_2O$ [80]							
3.675(7)	2.427(3)	2.090(8)	117.8(1)	90.3(1)	78.7(1)	104.5(4)	66.9(3)
	2.361(3)				110.3(4)		
μ_2-S,N(η^1-S:η^1-N) ligand							
	2.395(3)	2.104(8)			112.8(4)	126.5(9)	
[(η^6-p-cymene)Ru_2(μ-Cl) Cl(μ-4,5-ph$_2$-meimz2S)] Cl. 0.5CH_3OH [80]							
3.700(1)	2.465(1)	2.121(4)	98.2(1)	80.1(1)	77.5(2)	100.9(3)	67.9(1)
	2.4[illegible]			80.0(1)	103.3(2)		
	Ru–Cl_{br} 2.427(2)					(Cl–Ru–S)	
	2.459(2)		Ru–Cl_{br}–Ru				
	Ru–Cl_t 2.391(2)		98.5(1)				

NR not reported.
ᵃ Symmetrical molecule.

metal nitrogen bonds that are incorporated into S,N-chelating bridges. Consequently, the S–M–N, M–S–C and M–N–C angles (Table 5) are highly strained. The central M_2S_2 core in the complexes is invariably puckered, as is indicated by the torsion angle in the molybdenum complex (S–Mo–S′–Mo′ = 24°). The extent of the asymmetry in the metal–sulphur bonds is variable. However, the M–S–M angles are fairly constant (93.83(2)–96.2(2)°) and the larger M–S–C angles (ca. 110°) are in the range observed for the less strained, binuclear double-bridging μ_2-S,N(η^1-S; η^1-N), ligands (Table 1). The thioamide dimensions in the 1-methylimidazoline-2-thionate ligand (C–S = 1.744(3), C–N = 1.309(3) Å; N–C–S = 118.9(2)°) [28] all show characteristic differences relative to the average dimensions in the parent ligand (C–S = 1.685, C–N = 1.345 Å; N–C–S = 127.4°) [29]. The consequences of S,N-chelation are clearly evident in the reduced thioamide angle.

In spite of the strained bridging ligand the complexes are reputedly thermally stable. Significantly, the ^{1}H NMR spectra of a deuterated chloroform solution of equimolar quantities of (**XXXI a** and **b**) show separate signals for the two compounds [75]. During several days at room temperature however, an equilibrium is reached which involves (**XXXI a, b** and **c**). Several processes have been proposed to rationalise this novel ligand distribution; most of them involve either cleavage of the rhenium–nitrogen bond or of the dimer itself. The results of substitution reactions involving phosphine derivatives are also reported. All these observations highlight a structurally labile system [75].



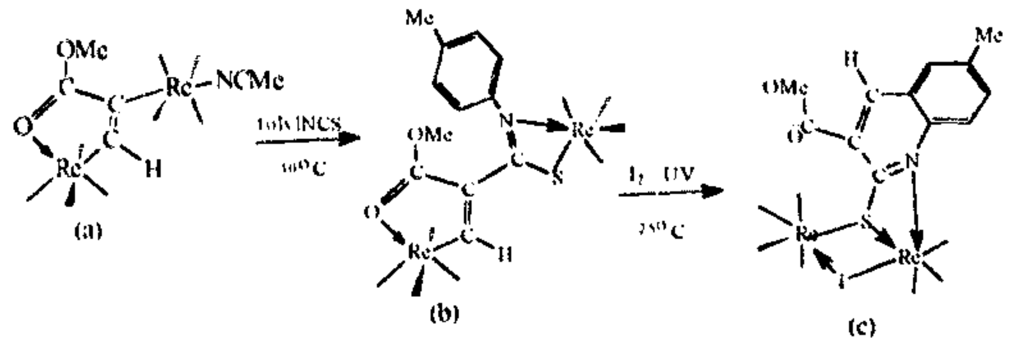
(a) (b) (c)

(XXXI)

Adoption of the boat form by the above complexes, even in the absence of the relevant crystallographic constraints, contrasts markedly with binuclear copper(I) complexes of heterocyclic thiones. These complexes, of which [{Cu(1-meimz2SH)(Cl)$_2$}$_2$] [78] and [{Cu(1-meimz2SH)$_3$}$_2$](BF$_4$)$_2$ [79] are typical, have centrosymmetric Cu_2S_2 cores which adopt a *trans* (*2-anti*) disposition of the bridging ligands. Such a disposition favours the formation of intramolecular (N–H... Cl) hydrogen bonds in the former and intermolecular (N–H...F) hydrogen bonds in the latter. Removal of the thioamide proton prevents the corresponding thionate anion from generating hydrogen bonds. However, a possible advantage of the boat form is that it is more compact than the chair form. Consequently, molecular packing is probably a deciding factor in the production of the boat form in the solid state.

The vanadyl(IV) complex [(VO)$_2$(μ-py2S)$_2$(η^2-S,N-py2S)$_2$], is obtained by the addition of sodium pyridine-2-thionate to [VOCl$_2$(thf)$_2$] in thf [77]. This complex is crystallographically centrosymmetric and consequently adopts the chair (**XXXa**) configuration in the solid, with consequent reduction of intra-ligand repulsion. Metal coordination in the complex is distorted square-pyramidal and consists of terminal vanadyl-oxygen, together with terminal S,N-chelating and binuclear triple-bridging, pyridine-2-thionate ligands. Metal–metal separation distances and ligand generated dimensions are similar to the other complexes in Table 5. Of particular interest however, is the fact that the terminal chelating angle (68.5(2)°) is significantly larger than that of its bridging (62.4°) counterpart.

The remaining complexes in this section involve mixed bridging ligands. A novel means of synthesising complexes of quinoline-2-thionate (**IIg**) derivatives has been established. The method involves the metal assisted coupling and cyclisation of aryl isothiocyanates to alkyne ligands [79]. The reported route involves reacting the lightly stabilised metallated complex (**XXXIIa**) with *p*-tolyl isothiocyanate. The product (**XXXIIb**) results from insertion of isothiocyanate into the substituted rhenium–carbon bond. Treating (**XXXIIb**) with iodine and ultra-violet radiation causes the tolyl ring to cyclise with the unsubstituted end of the metalated olefin yielding the quinoline-2-thionate rhenium complex (**XXXIIc**).



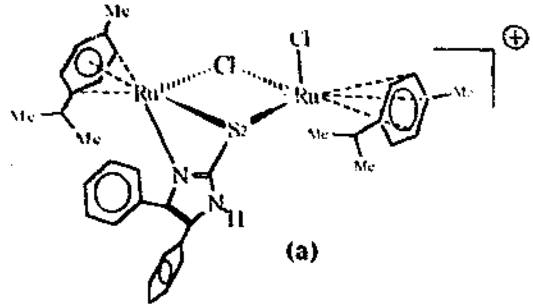
(adapted from [79])

XXXII

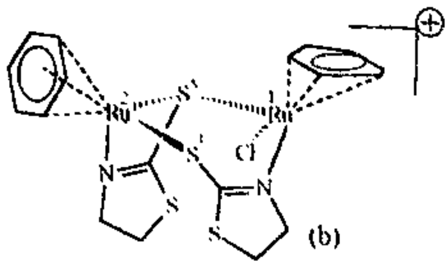
The products (**XXXIIb and c**) were characterised by IR, ^1H NMR and single-crystal X-ray methods. In (**XXXIIc**) the Re $(CO)_4$ and Re $(CO)_3$ groups are bridged by an iodo atom and by a binuclear triple-bridging, quinoline-2-thionate derivative. The metal…metal and the metal ligand distances in (**XXXIIc**) are comparable with those of similar complexes in Table 5. Attempts to prepare a variety of complexed quinoline-2-thionate derivatives by varying the substituents on the alkyne and aryl groups are also reported.

Binuclear complexes with mixed bridging ligands have been prepared from the ruthenium(II) precursor $[\{(\eta^6\text{-}p\text{-cymene})_2RuCl_2\}_2]$ (*p*-cymene = $MeC_6H_4CHMe_2$). Preparations involve equimolar quantities of the ruthenium complex and, either the 1-methyl (1-meimz2SH) or the 4,5-biphenyl (4,5-ph$_2$-imz2SH) imidazoline-2-thione derivatives (**IIaii**), in aqueous methanol and an organic base [80]. The resultant complexes have the formula $[(\eta^6\text{-}p\text{-cymene})_2Ru_2(\mu\text{-RS})(\mu\text{-Cl})Cl]Cl$ (RS = meimz2S, 4,5-ph$_2$-imz2S) (**XXXIIIa**). A similar preparation with 1,3-thiazolidine-2-thione (tzd2SH) and $[\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2]$ gives the red crystalline cationic complex $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu\text{-tzd2S})_2Cl]Cl$. (**XXXIIIb**). A mononuclear 1,3-thiazolidine-2-thione complex $[(\eta^6\text{-}p\text{-cymene})_2\ Ru(\mu\text{-tzd2SH})Cl_2]$ is also obtained, from a 1:2 molar ratio (metal complex:ligand) of the components in aqueous methanol. A trinuclear product $[(\eta^6\text{-}p\text{-cymene})_3Ru_3(\mu_3\text{-4,5-Ph}_2\text{-imz2S})(\mu\text{-Cl})Cl_2]$ has also been reported (see Section 3.2. All these complexes crystallise with added solvent.

The mononuclear complex has monodentate (η^1-S) donating 1,3-thiazolidine-2-thione (Ru–S = 2.400(1), C–S_{exo} = 1.691(4) Å; N–S–C = 128.6(3), Ru–S–C = 114.4(1)°) and approximately tetrahedral metal geometry. Proton NMR spectra, in



(a)



(b)

(adapted from [80])

(XXXIII)

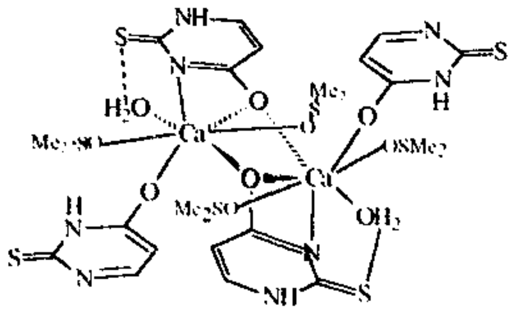
deuterated methanol, of the benzenoid protons in $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu\text{-tzd2S})_2Cl]Cl$ clearly indicate the two ruthenium atoms to be coordinated by different combinations of ligands. Crystal structure analysis revealed a combination of, double-bridging, μ_2-S,N(η-S;η^1-N), and triple-bridging, μ_2-S,N(η^2-S;η^1-N), binuclear 1,3-thiazolidine-2-thionate ligands, in the complex cation **(XXXIIIb)**. With two terminal η^6-arene groups and one terminal chloro atom (Ru–Cl = 2.419(4) Å) each metal has different donor sets. The unique composition of the complex enables the geometry of each bridging ligand to be assessed (Table 5). One common feature of both bridging ligands is the equivalence of the metal–nitrogen distances. The ruthenium–sulphur distance (Ru(2)–S(1) = 2.395(1) Å), formed by the double-bridging ligand, is similar to that formed by the neutral ligand in the mononuclear complex above. In addition, the significant angular parameters (Ru–N–C and Ru–S–C, Table 5) are similar to those of other binuclear double-bridging ligands (Table 1). The ligand thioamide dimensions formed by the binuclear double-bridging ligand (Table 3), despite rather large errors, indicate the typical accumulation of double-bond character in the carbon–nitrogen bond. This is achieved at the expense of the double-bond character in the carbon–sulphur bonds, with only a slight extension to the thioamide angle. In contrast, the binuclear triple-bridging ligand generates asymmetric ruthenium–sulphur distances, and a Ru–S(5)–Ru angle that is larger than those generally observed for such ligands (Table 5). The remaining angular parameters (M–S–C, M–N–C and S–M–N) are comparable with similar bridging ligands (Table 5). The thioamide dimensions of the binuclear triple-bridging ligand (Table 3) show increased lengthening of the carbon–sulphur bonds and added strain in the thioamide angle. These dimensional differences in the complex are clearly a consequence of the additional electronic demands of triple-bridging, μ_2-S,N(η^2-S;η^1-N), relative to those of double-bridging, μ_2-S,N(η^1-S;η^1-N), binuclear ligands.

The similarity of the ^{1}H NMR spectra of the [(η^6-*p*-cymene)$_2$Ru$_2$(μ-RS)(μ-Cl)Cl]Cl (RS = meimz2S, 4,5-ph$_2$-imz2S) complexes, both of which indicate dissimilar environments for the ruthenium(II) atoms, suggest the complexes to be isostructural [80]. A crystal structure analysis of the 4,5-biphenyl-imidazoline-2-thionate complex cation showed the structural differences to be due to differences in the donor sets and in the metal geometries. The complex cation is shown in **(XXXIIIa)** and selected dimensions are given in Table 5. The central asymmetric Ru(1)-Cl-Ru(2)-S(2) core of the complex is folded with modest atomic displacements (±0.146 Å) from the best least-squares mean-plane. Angles at the bridging chloro (98.5(1)°) and thionate sulphur atoms (98.2(1)°) are remarkably similar to one another. They are also similar to the bridging angles formed by other binuclear triple-bridging ligands (Table 5). The disparity in the bridging atoms however causes a slight contraction in the angles (Cl–Ru(1)–S and Cl–Ru(2)–S) normally formed at the metals by pairs of triple-bridging binuclear ligands (Table 5). This angular contraction is also matched by a slight increase in the metal...metal separation distance. Significantly, the ruthenium–sulphur distances are slightly longer than those reported for the [(η^6-C$_6$H$_6$)$_2$Ru$_2$(μ-tzd2S)$_2$Cl]$^+$ cation. The ruthenium–nitrogen distance and the remaining, significant, angular parameters (M–S–C, M–N–C and S–M–N) are similar to those listed in Table 5. Such similar dimensions reflect the similarity in geometric requirements for binuclear triple-bridging ligands.

The thioamide dimensions of the imidazoline-2-thionate derivative (C–S$_{exo}$ = 1.751(5), C–N = 1.313(6) Å; N–C–S = 113.7(4)°) differ from those of the unsubstituted imidazoline-2-thione molecule (C–S$_{exo}$ = 1.698(2), C–N = 1.346(3) Å; N–C–S = 126.8(2)°) [81]. The observed changes are characteristic of binuclear double-bridging, heterocyclic thionate ligands.

Examples of binuclear triple-bridging ligands in both homoleptic and mixed-ligand complexes are clearly scarce. This probably owes much to the fine balance between the benefits of additional metal-thionate sulphur coordination and the added steric demands of triple-bridging, in such ligands.

A hot solution of 2-thiouracil **(IIdiii)** in dimethyl sulphoxide dissolves calcium hydroxide from which colourless crystals of [{Ca(2-thiouracilate)$_2$.DMSO.H$_2$O}$_2$] are obtained in high yield. The bridging monoanion is unusual since it is not based on the deprotonated thione, but on the deprotonated hydroxy tautomer. Consequently, the ligand is N,O-, rather than S,N-bridging [82]. The crystallographically centrosymmetric dimeric complex contains pairs of terminal monodentate oxygen donating and N,O-bridging 2-thiouracilate anions. Dimethyl sulphoxide solvent molecules are also terminal oxygen donating. The seven coordinate metal has pseudo-pentagonal bipyramidal geometry with six of the attachments to oxygen donors (Ca–O = 2.324(4)–2.366(3) Å) and the seventh to a 2-thiouracilate nitrogen atom (Ca–N = 2.557(4) Å) **(XXXIV)**. There are no calcium contacts to thione sulphur. The thione-sulphur atom of the bridging anions form hydrogen bonds with terminal water molecules (S...O = 3.203(5) Å). Every potential donor centre not involved in coordination, to calcium(II), is involved in an intricate system of intra- and intermolecular hydrogen bonding. Two tautomeric forms of the 2-thiouracilate anion are present that differ only in the positions of the remaining proton. One of these tautomers is terminal and the other is bridging. The role of calcium in this complex and its preference for oxygen, rather than sulphur donors, is responsible for the alternative coordination mode of the 2-thiouracilate anion.



(adapted from [82])

(XXXIV)

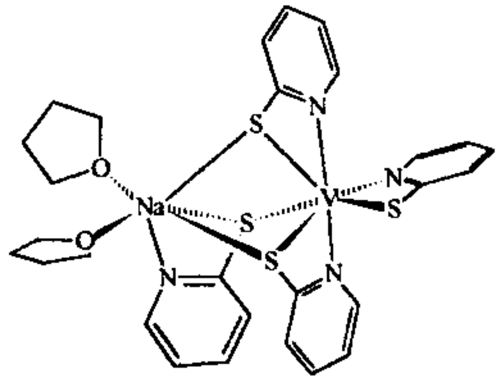
A solution of the complex in dimethylsulphoxide dissolves solid platinum dichloride. Addition of a mixture of alcohol and toluene to this solution precipitates a gold coloured, water soluble, powder with the composition $[\{Ca(2\text{-thiouracilate})_2.DMSO.H_2O)\}_2]_2.PtCl_2$.

2.4. Complexes with three bridging heterocyclic thionate ligands

In contrast to the large number of complexes based on two bridging ligands in Section 2.3 only one example has been reported for this class of complexes.

In addition to the binuclear complex $[(VO)_2(py2S)_4]$, involving a combination of bridging and chelating pyridine-2-thionate anions, referred to above (see Section 2.3.3.2 the same report contains details of a binuclear, mixed-metal, sodium–vanadium(III) complex $[NaV(\mu\text{-S,N-py2S})_3(py2S)(thf)_2]$ [77]. This complex is obtained by the addition of four equivalents of sodium pyridine-2-thionate to the vanadium(III) complex $[VCl_3(thf)_3]$, in thf. The seven coordinate vanadium(III) atom has a N_3S_4-donor set consisting of one S,N-chelating and three triple-bridging, μ_2-S,N(η^2-S:η^1-N), pyridine-2-thionate anions. The three bridging thionate sulphur atoms and one of the pyridine-2-thionate nitrogen atoms are connected to the second metallic centre in the dimer, the six-coordinate sodium atom, which has a NS_3O_2 donor set. Two terminal thf molecules provide the oxygen atoms (**XXXV**).

In addition to the six heterocyclic molecules the complex contains four, four-membered S,N-chelate and three, four-membered puckered, $NaVS_2$ rings. This is an extraordinary profusion of rings in such a relatively small structure. Distances to the sodium atom ($Na–S = 2.960_{average}$; $Na–N = 2.400(3)$; $Na–O = 2.286(3)$, 2.325(3) Å) are generally longer than those to vanadium(III) ($V–S = 2.534_{average}$;



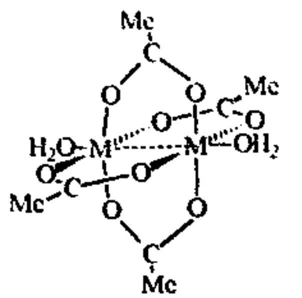
(adapted from [77])

(XXXV)

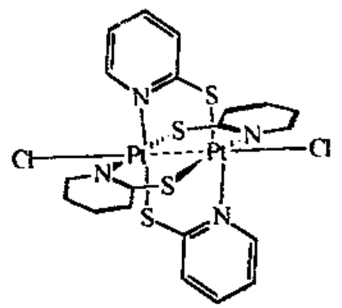
V–N = 2.162$_{average}$ Å). The S,N-chelating angles (S–V–N = 65.18$_{average}$°) are typically narrow. In addition, angles at the bridging thionate sulphur atoms within the central $NaVS_2$ cores (Na–S–V = 79.18$_{average}$°) are narrower than the corresponding angles in Table 5 (M–S–M = 93.83–117.8(1)°). This is presumably due to a relatively short sodium–vanadium(III) separation distance that is unfortunately not reported.

2.5. Complexes with four bridging heterocyclic thionate ligands

Divalent, dimeric acetates of general formula [{M(μ-CH_3CO_2)$_2$(H_2O)}$_2$] (M = Cu, Cr, Rh, Mo) formed the first series of complexes to be characterised with the classic "lantern" structure (**XXXVIa**). Such an arrangement is typical of binuclear complexes with four double-bridging ligands of which hundreds of examples are now known [14]. The progressive reduction in metal–metal separation distances (2.64–2.10 Å) for the above series of dimeric tetra-acetates also confirmed the increasing bond order [83]. Subsequently, the search for bridging ligands with bite distances comparable to those of the short metal–metal distances in the complexes, has been intensified. The production of binuclear rhodium(II) complexes with bridging dialkylaminoformamide, 2-pyridinate or related organic or inorganic ligands is typical of such research [84]. More recently, heterocyclic thionates have also been shown to be capable of replacing the double-bridging acetate ligands of mostly divalent metals with the resultant formation of comparable binuclear complexes. The metals involved in this series of complexes mostly involve molybdenum(II), rhodium(II) and those from group ten. The latter readily generate d^8–d^8 metal pairs with square-planar geometry that undergo oxidative-addition reactions which produce metal–metal bonded (d^7–d^7) halogenated complexes. A wide range of heterocyclic thionates have been involved in the production of this series of complexes including: pyridine-2-thionate (**IIei**), pyrimidine-2-thionate (**IIdi**), imidazoline-2-thionate (**IIaii**), 1,2,4-triazoline-3-thionate (**IIb**), 1,3-thiazole-2-thionate (**IIh**) and hexamethyleneimine-2-thionate (**IIe**) derivatives. The bifunctional nature of the ligand generates a number of isomeric possibilities (**VI**) all of which have been structurally characterised.



(M = Cu, Cr, Rh, Mo)
(a)



(adapted from [89])
(b)

(XXXVI)

2.5.1. Palladium(II) and platinum(II) complexes

The production and characterisation of binuclear platinum(II) complexes with pairs of N,O-bridging 2-pyridonate anions **(IIcii)**, the "platinum pyridone blue" complexes [85] and their halogenated oxidation products [86] prompted attempts to prepare the corresponding pyridine-2-thionate complexes. The structural similarity of the ligands and the longer bite of the pyridine-2-thionate anion (S...N = 2.7; N...O = 2.3 Å) being the major reasons for repeating the work with the thionate anion [87].

The room-temperature reaction of palladium(II) acetate with pyridine-2-thione, in a 1:2 molar ratio in dioxane, initially gives a brown product that redissolves yielding a red solution from which an orange solid is produced. Such a sequence of coloured products is typical of complicated metal:ligand redox reactions. Recrystallisation of the orange product from chloroform gives $[Pd_2(\mu\text{-py2S})_4]$. $2CHCl_3$. This is an easily oxidised crystalline solid with a centre of symmetry at the mid-point of the palladium...palladium axis (Pd...Pd = 2.677(1) Å). The bridging ligands also have a *cis,cis;head-to-head;2(2S:2N)* distribution **(VIa)** with the PdS_2N_2 coordination squares slightly twisted about the palladium...palladium axis (average S–Pd–Pd–N = 1.5°). Addition of iodine to a solution of the complex, a 2:1 molar ratio in chloroform, produces tetrameric crystalline $[Pd_4(\mu\text{-py2S})_6I_2]$ rather than an oxidised product.

The lemon-yellow mixed ligand complexes $[Pt_2(en)_2(\mu\text{-het,S,N})_2]Cl_2.3H_2O$ (het-S,N = py2S, 4-mepy2S) [88] are obtained from $[Pt(en)Cl_2]$ and the parent ligands in water with the bridging ligand deprotonated by dilute aqueous potassium hydroxide. Their crystal structures have been reported, together with that of $[Pt_2(Cl)_2(\mu\text{-aps})_2]Cl_2.3H_2O$ (aps = 2-aminoethyl-2-pyridylsulphide). Selected dimensions of the pyridine-2-thionate complexes are listed in Table 6a. Both complexes have a combination of two N,N-chelating 1,2-diaminoethane and two *cis*-related, *head-to-head* binuclear double-bridging, μ_2-S,N(η^1-S:η^1-N), pyridine-2-thionate ligands **(Vd)**. These generate a combination of PtN_4 and *cis*-PtS_2N_2 coordination squares. The dissimilar metal...metal and ligand bite distances cause the two platinum(II) atoms to deviate out of the coordination planes towards each other (ca. 0.10 Å). The coordination planes also tilt **(VIIa)** towards one another (average

Table 6
Binuclear complexes with four double-bridging, μ_2-(S,N)(η^1-S:η^1-N), ligands: selected dimensions (Å and °)

▶Complex and reference Isomeric form	Metal-metal	Angles at the metal	M–S	M–N	M–S–C	M–N–C
(a) Palladium(II) and platinum(II) complexes						
[$Pt_2(en)_2(\mu$-py2S$)_2]Cl_2.3H_2O$ [88]						
Vd	3.083(1)	83.1(1)–	2.299(4)	2.041(11)	110.4(4)	123.9(7)
		94.8(1)	2.302(4)	2.059(11)	112.9(5)	122.4(10)
[$Pt_2(en)_2(\mu$-4mepy2S$)_2]Cl_2.3H_2O$ [88]						
Vd	3.101(1)	83.3(1)–	2.291(2)	2.024(7)	108.6(2)	121.7(6)
		94.6(1)	2.294(2)	2.042(6)	112.0(3)	124.2(4)
[$Pt_2(\mu$-4mepy2S$)_4]^a$. 0.5C_7H_8 [89]						
VIa	2.680(2)	88.6(5)	2.274(7)	2.04(2)	109.4(8)	122.1(15)
		91.7(3)	2.293(7)	2.11(2)	111.1(8)	125.8(16)
[$Pd_2(\mu$-bztz2S$)_4]^a$ [90]						
VIa	2.745(1)	88.4(1)	2.285(2)	2.078(5)	104.0(2)	126.1(4)
		90.6(2)	2.289(2)	2.084(5)	104.7(2)	126.3(4)
[$Pt_2(\mu$-bztz2S$)_4$].DMF[b] [91]						
VIa	2.761(1)	88.6(1)	2.282(3)	2.070(4)	104.4(3)	122.7(4)
	2.753(1)	90.2(1)	2.287(3)	2.081(4)	107.6(2)	125.2(4)
(b) Platinum(III) complexes						
[$Pt_2Cl_2(\mu$-4mepy2S$)_4].2CHCl_3$ [89]						
VIa	2.532(1)	88.5(3)	2.291(3)	2.103(8)	106.7(4)	120.8(7)
		91.1(3)	2.304(3)	2.106(9)	107.2(3)	122.2(5)
			Pt–Cl = 2.458(2); Pt–Pt–Cl = 172.6(1)			
[$Pt_2I_2(\mu$-pym2S$)_4$] [93]						
VIa	2.554(1)	NR	2.285(2)	2.087(13)	Pt–I = 2.774(mean)	
			2.301(4)	2.131(12)	I–Pt–Pt = 173.2 (mean)	
[$Pt_2Cl_2(\mu$-pym2S$)_4$] [94]						
VId	2.518(1)	88.5(2)	2.210(1)	2.055(10)	103.1(4)	119.8(8)
		92.1(2)	2.346(3)	2.121(10)	104.6(4)	121.6(7)
				Pt–Cl = 2.452(mean); Pt–Pt–Cl = 178.7(1)		
[$Pt_2I_2(\mu$-tucH$)_4$] [94]						
VIa	2.546(2)	84.5(3)	2.284(10)	2.007(34)	104.7(12)	118.5(27)
		94.7(8)	2.304(10)	2.127(29)	106.1(15)	124.4(21)
			Pt–I = 2.771(mean); Pt–Pt–I = 176.2			
[$Pt_2Cl(\mu$-pym2S$)_4(\eta^1$-S, pym2S)] [95]						
VIa	2.547(2)	86.6(3)	2.292(8)	2.046(23)	NR	NR
		93.5(6)	2.307(8)	2.096(26)		
		Pt–Cl = 2.494(7); Pt–Pt–Cl = 175.8(2)				
		η^1-S, pym2S Pt–S = 2.438(8)				

Table 6 (*continued*)

►Complex and reference Isomeric form	Metal–metal	Angles at the metal	M–S	M–N	M–S–C	M–N–C
(c) Molybdenum(II) and rhodium(II) complexes						
$[Mo_2(\mu\text{-}4,6\text{-me2pym2S})_4].CH_2Cl_2$ [96]						
VIb	2.083(2)	87.5(3)– 97.9(5)	2.444(4)– 2.454(4)	2.18(1)– 2.22(1)	102.7(5)– 103.9(5)	120.1(9)– 124.0(1)
$[Mo_2(O_2CBu^t)_3(\mu\text{-imdz2S})(py)_2]$ [97]						
–	2.116(1)	89.9(2) 98.8(3)	2.487(4)	2.124(1)	101.9(6)	121.9(9)
		Mo–O(mean) = 2.120 Mo–N(py) = 2.631(12), 2.966(19)				
$[Rh_2(\mu\text{-tep2S})_4(\eta_1{}^1\text{-S tep2S})]$ [101]						
VIc	2.497(1)	88.51(2)– 92.55(1)	2.343(1)– 2.359(1)	2.016(2)– 2.032(2)	104.6(1)– 106.5(1)	124.7(1)– 125.7(1)
(η^1-S tep2S)			2.388(1)		114.8(1)	
$[Rh_2(\mu\text{-tep2S})_4(CO)]^a$ [101]						
VIc	2.495(1)	87.43(3)– 92.57(3)	2.373(1)	2.033(1)	105.1(1)	125.0(2)
$[Rh_2(\mu\text{-5-MeS-1,3,4-tdz2S})_4(PPh_3)]$ [99]						
VIc	2.603(1)	86.6(1)– 97.3(1)	2.355(2)– 2.379(3)	2.002(7) 2.020(8)	NR	NR
(d) Nickel(II) complex						
$[Ni_2(\mu\text{-tz2S})_4Cl]^a$ [104]						
VIc	2.648(2)	85.3(1) 92.5(1)	2.217(1) 2.233(2)	2.068(4) 2.086(5)	101.0(2) 102.3(1)	123.6(3) 125.4(3)

NR not reported.
[a] Symmetrical molecule.
[b] Two half complexes per asymmetric unit.

interplanar angle = 31.8°) and twist (**VIIb**) out of the totally eclipsed position (average S–Pt–Pt–S torsion angle = 33.2°). Although the two complexes are asymmetric in the solid state the two coordination planes undergo rapid thermal oscillation about the metal...metal axis in solution with each 1,2-diaminoethane ligand undergoing rapid conformational ($\lambda \leftrightarrow \delta$) interconversion. In the $[Pt_2(Cl)_2(\mu\text{-aps})_2]Cl_2.3H_2O$ (aps = see above) complex the bridging ligands have a *head-to-tail* distribution with the coordination planes in the eclipsed configuration.

Preparation of binuclear platinum(II) and platinum(III) complexes of pyridine-2-thionate and its 4-methyl derivative initially involves production of the lemon-yellow binuclear complexes [89]. The procedure involves reaction of pyridine-2-thione with *cis*-$[PtCl_2(NH_3)_2]$ in dioxane under argon, and addition of the potassium salt of 4-methylpyridine-2-thionate to *cis*-$[PtCl_2(CH_3CN)_2]$ in toluene, also under argon. Slow evaporation of chloroform solutions of these complexes gives the red crystalline binuclear platinum(III) complexes $[Pt_2Cl_2(\mu\text{-py2S})_4].2CHCl_3$ and $[Pt_2Cl_2(\mu\text{-4-mepy2S})_4]$. $0.5C_7H_8$. The crystal structures of both of these complexes have been reported; the binuclear platinum(III) complex will be considered with other platinum(III) complexes (Section 2.5.2. The bridging ligands in the $[Pt_2(\mu\text{-4-mepy2S})_4]$ $0.5C_7H_8$ complex have the *cis,cis;head-to-head;2(2S:2N)* distribution (**VIa**). Selected dimensions are listed in Table 6a. The two coordination planes are twisted slightly out of the eclipsed configuration (average torsion angle N–Pt–Pt–S = 13.4°). This is probably why the complex has the shortest metal... metal distance (Pt...Pt = 2.680(2) Å) of this set of binuclear platinum(II) complexes (Table 6a). The metal–nitrogen and metal–sulphur distances in Table 6a are very similar to other listed values while the angles at the ligand donor atoms (M–S–C and M–N–C) show little sign of angular stress. The latter are similar to those of other binuclear double-bridging ligands (Table 1). The average thioamide carbon–sulphur distance and thioamide angle of the pyridine-2-thionate ligands show the characteristic variations, relative to the parent ligand [22], that are typical of binuclear bridging ligands (Table 2). The $[Pt_2(\mu\text{-4-mepy2S})_4]$ complex exhibits metal-centred, quasi-reversible, cyclo-voltammetric peaks in dimethylformamide (vs $(Ag/Ag(Crypt(2,2))^+)$ centred at +0.282 V.

Addition of aqueous-ethanolic solutions of benzo-1,3-thiazoline-2-thione to aqueous potassium tetrachloropalladate, and the equivalent platinum(II) chloro-anion, produces isostructural complexes with four double-bridging ligands $[M_2(\mu\text{-bztz2S})_4]$ (M = Pd, Pt) [90,91]. The presence of the anion in the platinum(II) complex is clearly indicated, in the IR spectrum, by the absence of the ν(NH) band and the presence of ν(Pt–N) and ν(Pt–S) bands. Selected dimensions are given in Table 6a. Both complexes consist of pairs of metal atoms with *cis,cis;head-to-head;2(2S:2N)*, double-bridging, binuclear ligands (**VIa**); and a centre of symmetry at the mid-point of the metal...metal axis. The *cis*-MS_2N_2 coordination planes are essentially square-planar and in the eclipsed position; displacement of platinum(II) atoms from the coordination planes is minimal. Metal separation distances are similar to one another and shorter than the distances in the parent metal (Pd–Pd = 2.751, Pt–Pt = 2.775 Å) [20]. The remaining distances and angles in the two structures are also similar. In particular, the metal–sulphur distances (2.282(3)–2.289(2) Å) resemble metal–thiolate distances and are shorter than those of the corresponding metal–thione values (2.339–2.362 Å) [91]. Average thioamide dimensions among the bridging ligands (Table 4), coupled with significant perturbation of the angles (2–7°) at the thioamide carbon atom, are indicative of the redistribution of π-electron density in the bridging anions (Table 4).

2.5.2. *Platinum(III) complexes*

The oxidative-addition of halogen atoms to binuclear platinum(II) complexes is a ready general source of the corresponding binuclear platinum(III) species [92]. Successful preparative routes include: addition of iodine to the binuclear platinum(II) complex in chloroform [87] and recrystallisation of the binuclear platinum(II) complex from chloroform, from which chlorine atoms are abstracted [89]. The addition of the tetraiodoplatinate(II) ion to monomeric $[Pt(pym2S)_2]$ in hot methanol is also effective [93]. Direct reactions of the tetrachloroplatinate(II) ion with pyrimidine 2-thione derivatives in hot methanol [94,95], have also been used. All the reported platinum(III) complexes seem to require axial terminal ligands to effect their stabilisation. Consequently, the metals effectively have octahedral geometry with metal–metal separation distances (2.518(1)–2.547(2) Å) that are inevitably shorter than those of the corresponding binuclear platinum(II) complexes (2.680(2)–3.101(1) Å). Selected dimensions of the reported crystal structures, which are inherently similar, are given in Table 6b.

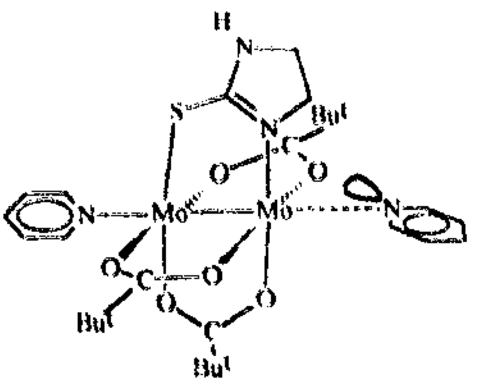
In $[Pt_2Cl_2(\mu\text{-py2S})_4].2CHCl_3$ [89] the chlorine atoms occupy the expected axial sites (Cl–Pt–Pt = 172.6(1)°) with the four double-bridging, μ_2-S,N(η^1-S:η^1-N), pyridine-2-thionate ligands arranged in a *cis,cis;head-to-head;2(2S:2N)* arrangement **(XXXVIb)**. The structure has an approximate two-fold axis perpendicular to the Cl–Pt–Pt–Cl axis. The two *cis*-PtS_2N_2 coordination squares twist out of the eclipsed configuration with an average torsion angle (N–Pt–Pt–S = 23.3°) larger than that of its sister complex $[Pt_2(\mu\text{-4-Mepy2S})_4]$ [89]. The larger twisting angle is primarily due to the shorter metal–metal distance generated by the platinum(III) atoms. Metal–ligand distances and angles are similar to those of the binuclear platinum(II) complexes listed in Table 6a. Average thioamide ligand dimensions (C–S = 1.733 Å; N–C–S = 122.2°) show the characteristic changes relative to the parent ligand [22]. The $[Pt_2Cl_2(\mu\text{-py2S})_4]$ complex exhibits a pseudo-reversible cyclic voltammetric curve ($E_{1/2}$ = +0.257 V), in dimethylformamide. A redox cycle involving a two-electron exchange together with complicated loss and uptake of chlorine atoms and solvent molecules is proposed for the complex. The structure of $[Pt_2I_2(\mu\text{-pym2S})_4]$ is similar to that shown in **(XXXVIb)**. The *cis*-PtS_2N_2 coordination squares are twisted about the metal–metal axis, and out of the eclipsed position, by about 26° [93]. The (3S,N:S,3N) **(VId)** disposition of the four bridging ligands in the $[Pt_2Cl_2(\mu\text{-pym2S})_4]$ complex generates PtS_3N and $PtSN_3$ coordination squares that are twisted by approximately 29° about the metal–metal axis. In addition, the metal atoms are slightly displaced towards the axial chlorine atoms [94]. There is also some evidence of *trans*-effects among the metal–ligand bonds. In the 2-thiouracilate complex $[Pt_2I_2(\mu\text{-2-tucH})_4]$ the ligand distribution is as shown in **(VIa)** with *cis*-PtS_2N_2 coordination squares rotated about the metal–metal axis by 25°. The average thioamide dimensions of the 2-thiouracilate anion (C–S = 1.719, C–N = 1.349 Å; N–C–S = 124.0°) are characteristic of bridging heterocyclic thionates [94]. The five pyrimidine-2-thionate ligands in $[Pt_2Cl(pym2S)_5]$ [95] consist of one terminal, (η^1-S), and four double-bridging, μ_2-S,N(η^1-S:η^1-N), anions. The latter adopt the *cis,cis;head-to-head;2(2S:2N)* arrangement **(VIa)**. Consequently, the donor sets, S_2N_2Cl and S_3N_2, of the platinum(III) atoms are different. Of particular interest is the fact that the terminal platinum–sulphur distance is longer (2.438(8) Å) than those involving the bridging ligands (2.292(8)–2.307(8) Å).

2.5.3. *Molybdenum(II) and rhodium(II) complexes*

Complexes containing multiple metal–metal bonds generally possess wide ranging optical, magnetic and electrochemical properties [14]. Such desirable behaviour has prompted the search for suitable bridging ligands.

Quadruply-bonded binuclear molybdenum(II) complexes with a range of bridging ligands have been prepared and characterised. The acetate groups in dimolybdenum tetra-acetate are readily replaced by the addition of sodium 4,6-dimethylpyrimidine-2-thionate, in absolute ethanol, under nitrogen [96]. Recrystallisation of the red product in dichloromethane produces the solvated complex $[Mo_2(\mu\text{-}4,6\text{-}me_2pym2S)_4].CH_2Cl_2$. The four bridging ligands all adopt the *cis,cis;-head-to-tail;2(2S,N)* arrangement **(VIb)** in this complex and virtual D_{2d} symmetry. There are no capping ligands in this structure. Selected dimensions are given in Table 6c. The metal–metal distance (Mo–Mo = 2.083(2) Å) is the longest in a series of binuclear molybdenum structures that involve bifunctional bridging ligands with carbon, oxygen or nitrogen donors (2.064(1)–2.072(2) Å) [96]. The remaining metal–ligand distances and angles are typical of those generated by binuclear double-bridging ligands (Table 1). The average thioamide dimensions of the 4,6-dimethylpyrimidine-2-thionate ligand (C–S = 1.72, C–N = 1.375 Å; N–C–S = 120.0°) are also similar to other heterocyclic thionates.

Attempts to prepare polymers based on quadruply bonded dimetal tetra-carboxylate subunits bridged by conjugated aromatic ligands have led to the isolation of $[Mo_2(O_2CBu^t)_3(\mu\text{-imdz2S})(py)_2]$ [97]. The amber crystalline complex is obtained from the sodium salt of imidazolidine-2-thionate and $[Mo_2(O_2CBu^t)_3(CH_3CN)_2](BF_4)$ in a dichloromethane–acetonitrile–methanol solvent mixture. Recrystallisation from pyridine gives the bis-adduct in which the two axial pyridine molecules are weakly bound to the metals. The more weakly bound pyridine (2.966(14) Å) is accompanied by a tilting of the molecule so that the nitrogen lone pair is not optimised for bonding **(XXXVII)**.



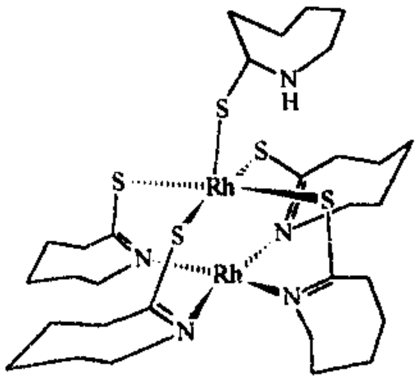
(adapted from [97])

(XXXVII)

The metal–metal distance (Mo–Mo = 2.116(1) Å; Table 6c) is slightly longer than that in $[Mo_2(\mu\text{-}4,6\text{-}me_2pym2S)_4]$ but is typical of carboxylato coordinated systems [96]. The metal ligand distances and angles generated by the imidazolidine-2-thionate ligand are typical of a binuclear double-bridging, μ_2-S,N(η^1-S;η^1-N), ligand (Table 6c). The thioamide dimensions (C–S = 1.693(6), C–N = 1.362(19) Å; N–C–S = 122.7(11)°) of the bridging imidazolidine-2-thionate ligand show some evidence for the concentration of the thioamide π-electron density in the carbon–nitrogen bond and a slight narrowing of the thioamide angle [98].

A group of air-stable orange or brown dirhodium(II) complexes have been prepared by partial or complete replacement of the acetate groups in dirhodium tetra-acetate with a range of heterocyclic thionates [99]. Typically, preparation of the bis-substituted complexes $[Rh_2(het\text{-}S,N)_2(CH_3COO)_4L_2]$ initially involves abstraction of the sodium salt of the heterocyclic thionate from sodium hydride in ether. The recovered sodium salt is then refluxed in benzene with $[Rh_2(CH_3COO)_4(CH_3OH)_2]$, in a 1:2 (metal:ligand) molar ratio, in the presence of bases, such as triphenylphosphine or one of its derivatives. Tetra-substituted products $[Rh_2(het\text{-}S,N)_4L]$ are invariably produced by reacting a large excess of the sodium salt of the heterocyclic thionate with $[Rh_2(CH_3COO)_4(CH_3OH)_2]$, in ethanol, followed by the addition of triphenylphosphine. The heterocyclic thionates used include 5-methylthio-1,3,4-thiadiazole-2-thionate **(IIj)**, 4,5-disubstituted-1,2,4-triazoline-3-thionate **(IIb)** and 1,3-thiazolidine-2-thionate **(IIhi)**. The bases used involve triphenylphosphine or its methoxy, isopropyloxy and phenoxy derivatives. Some twenty complexes are reported together with the crystal structure of the $[Rh_2(5\text{-}MeS\text{-}1,3,4\text{-}tdz2S)_4(PPh_3)]$ complex. A combination of IR, laser Raman, ^1H NMR and UV spectral data confirmed the presence of deprotonated ligands, Rh–Rh bonds (287–289 cm^{-1}) and essentially octahedral coordination at the metal, in the complexes. The crystal structure of $[Rh_2(\mu\text{-}5\text{-}MeS\text{-}1,3,4\text{-}tdz2S)_4(PPh_3)]$ established the presence of four binuclear double-bridging, μ_2-S,N(η^1-S; η^1-N), ligands in an *all-cis;head-to-head;(4S:4N)* arrangement **(VIc)**. Consequently, one rhodium atom has square-pyramidal coordination formed from a N_4 donor set. The other rhodium atom has octahedral coordination and a terminal S_4P donor set. The disparity in donor sets does not significantly affect the *cis*-angles at the rhodium(II) metal. In each case the average angle is close to 90°. The coordination squares however twist about the metal–metal axis (S–Rh–Rh–N = 23.8°). The resultant metal–metal distance (Rh–Rh = 2.603(1) Å), as well as the metal–ligand dimensions (Table 6c), are comparable (Rh–Rh = 2.550 Å) with other dirhodium(II) systems such as $[Rh_2(SOCCH_3)_4(HSOCCH_3)_2]$ [100].

The non-planar anion ω-thiocaprolactamate **(IIe)** also replaces the bridging acetate groups in dirhodium tetra-acetate [101]. Heating a mixture of dirhodium tetra-acetate and the parent ligand until molten and extracting the product with dichloromethane produces large green-black crystals of $[Rh_2(tcp2S)_4(tcpSH)]$, after evaporation of the solvent. The terminal monodentate η^1-S donating parent ligand is slowly and irreversibly replaced in $[Rh_2(\mu\text{-}tcp2S)_4(\eta^1\text{-}tcpSH)]$ with carbon monoxide in dichloromethane. The product $[Rh_2(\mu\text{-}tcp2S)_4(CO)]$ is removed as either a brown powder or as green crystals. Attempts to perform similar exchange reactions with pyridine, phosphines and other ligands were not successful. Both of the axially coordinated dirhodium complexes adopt essentially the same structure with the axial ligands attached to the RhS_4 site **(XXXVIII)**. The metal–metal axis in $[Rh_2(\mu\text{-}tcp2S)_4(CO)]$ however occupies a crystallographic four-fold axis. Selected dimensions of both structures are given in Table 6c.



(adapted from [101])

XXXVIII

In $[Rh_2(\mu\text{-tcp2S})_4(\eta^1\text{-tcpSH})]$ the average equatorial distance (Rh–S = 2.354 Å) is shorter than the axial distance formed by the ω-thiocaprolactam molecule (Rh–S = 2.388(1) Å). The latter also has a larger Rh–S–C angle (114.8°) than that of the bridging anions ($Rh\text{–}S\text{–}C_{average}$ = 105.3°). The shorter equatorial distances and smaller Rh–S–C angles formed by the thionate sulphur atoms are clearly a consequence of steric restrictions caused by the binuclear double-bridging ligands. The coordination cores twist about the metal–metal axis (S–Rh–Rh–N = 21.1°); the extent of the twist is similar to that in the dirhodium(II) 5-methylthio-1,3,4-thiadiazole-2-thionate complex. The metal–metal separation distances are similar in the two ω-thiocaprolactamate complexes and are slightly shorter than that in the dirhodium(II) 5-methylthio-1,3,4-thiadiazole-2-thionate complex. The relationship between metal–metal separation distances and the bite angle of bridging ligands in dirhodium complexes has been discussed [102]. However, similar ligand bite distances (S...N = ca. 2.7 Å), similar torsion angles (N–Rh–Rh–S = ca. 22°) and thioamide angles (N–C–S = 122–125°) generate dissimilar metal distances in $[Rh_2(\mu\text{-5-MeS-1,3,4-tdz2S})_4(PPh_3)]$ and $[Rh_2(\mu\text{-tcp2S})_4L]$ (L = tcpSH and CO). These observations would seem to negate a direct relationship between ligand bite and metal–metal separation distances, at least for dirhodium heterocyclic thionate complexes. Production of the 4S:4N isomer, rather than that of any other form, is also ascribed to the steric and electronic consequences following attachment of the first ω-thiocaprolactamate double-bridging anion [101]. The remaining metal–ligand dimensions are similar in both of the dirhodium ω-thiocaprolactamate complexes.

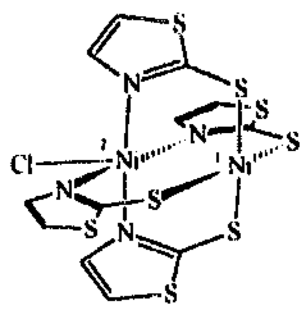
The electrochemical properties of dirhodium complexes with bifunctional ligands are quite different from those of dirhodium tetra-carboxylates. While the tetra-carboxylates only undergo a single electro-oxidation the ω-thiocaprolactamate complexes undergo two reversible one-electron oxidations to form Rh(II) Rh(III) and Rh(III) Rh(II) species. The half-wave oxidation potentials, in dichloromethane, increase (+0.31–0.71 V) in the order:

$$[Rh_2(tcp2S)_4] < [Rh_2(tcp2S)_4(tcp2SH)] < [Rh_2(tcp2S)_4(CO)]$$

This is consistent with a lowering of the HOMO upon axial binding of either the ω-thiocaprolactam or carbonyl ligands. In the case of the carbonyl adduct lowering of the HOMO is particularly large (0.45 V). The complex nature of the oxidation products and ligand–solvent exchanges involved are evident from the fact that the ESR spectra of the mono-oxidised products $[Rh_2(tcp2S)_4(tcpSH)]^+$ are different in dichloromethane and acetonitrile.

2.5.4. *Nickel(II) complexes*

The relative absence of binuclear nickel(II) complexes, with four double-bridging heterocyclic thionate ligands, is in striking contrast to the behaviour of other group ten metals (see Section 2.5.1). However, nickel(II) readily forms mononuclear S,N-chelates with heterocyclic thionates [1] as well as mostly diamagnetic sulphur-bridged binuclear complexes with thiolate ligands [9,10]. One of the problems with nickel(II) complexes is that deprotonation of the parent ligand in aqueous solution, in the presence of a nickel(II) salt, invariably generates intractable solids [103]. More recently, the brown crystalline, binuclear complex $(Et_4N)[Ni_2(\mu\text{-tz2S})_4Cl]$, has been prepared by adding triethylamine to a mixture of $(Et_4N)[NiCl_4]$ and 1,3-thiazoline-2-thione (**IIhii**) in acetonitrile [104]. Aprotic solvents, complexed nickel(II), in situ ligand deprotonation and the correct order of addition of the reactants are apparently essential for the successful preparation of crystalline nickel(II) heterocyclic-thionate complexes. Absence of the ν(NH) band and the presence of ν(Ni–N) and ν(Ni–S) bands in the IR spectrum confirmed the presence of both deprotonated and S,N-coordinating ligands in the complex. The crystal structure of the complex shows that the nickel and chlorine atoms of the binuclear anion occupy a crystallographic two-fold axis with the four double-bridging, μ_2-S,N(η^1-S;η^1-N), ligands in the eclipsed *all-cis;head-to-head;4S:4N* configuration (**VIe**). The capping ligand occupies the NiN_4 (average Ni–N = 2.077 Å), rather than the NiS_4 (average Ni–S = 2.225 Å), site (**XXXIX**). In this respect the nickel(II) complex differs from those of the heavier metals described in this section.



(adapted from [104])

XXXIX

Furthermore, the nickel(1) atom has diamagnetic square-planar NiS_4 and nickel(2) has paramagnetic square-based pyramidal NiN_4Cl (Ni–Ni = 2.648(2) Å), coordination. This distribution rationalises the room-temperature magnetic moment of the complex ($\mu_B = 1.92$ per nickel(II) atom). The reported angular dimensions (Table 6d) are similar to those generated by other binuclear double-bridging ligands (Table 1). The complex undergoes ligand-centred irreversible oxidation ($E_p = +0.6$ V; vs SCE) in acetonitrile.

The effects of deprotonation and coordination on the parent ligand dimensions [105] are similar to those reported for 1,3-thiazolidine-2-thione (Table 3) and benzo-1,3-thiazoline-2-thione (Table 4) [90,91]. All of the central thioamide dimensions of the parent ligand [105] ($C-S_{exo} = 1.657(4)$, $C-N = 1.335(5)$, $C-S_{endo} = 1.767(4)$ Å; $N-C-S_{exo} = 127.4(3)°$) are affected to some extent. The corresponding average dimensions in the complex ($C-S_{exo} = 1.726$, $C-N = 1.314$, $C-S_{endo} = 1.735$ Å; $N-C-S_{exo} = 127.1°$) show lengthening of the carbon–sulphur and shortening of the carbon–nitrogen bonds. Although the thioamide angle ($N-C-S_{exo}$) is scarcely affected by the coordination process all of the remaining angles show some degree of perturbation.

3. Trinuclear complexes

3.1. Introduction

The bridging ability of organothiolates and the established trinuclear character of some metalloprotein systems have collectively stimulated considerable activity in trimetallic systems in recent years. A typical product of this activity is the $[Fe_3(\mu_2\text{-}PhS)_3Cl_6]^{3-}$ anion with a planar hexagonal Fe_3S_3 core, μ_2-S edge-bridging phenyl thiolates, terminal chlorine and tetrahedral coordination at the metal [9,10]. More recently, biomimetic activity of the active sites in nickel hydrogenases has produced linear [106] and cyclic [107] trinuclear thiolate bridged nickel(II) complexes.

Heterocyclic thionates rarely utilise μ_2-S edge-bridging modes **(IIIa)**. Consequently, most of the research effort has concentrated on μ_2-S,N **(IIIb)** and μ_3-S,N **(IIId)** bridging modes in the controlled production of polynuclear, including trinuclear, metal complexes. The μ_3-S,N(η^2-S;η^1-N), face-bridging mode **(IIId)**, is particularly suitable for trinuclear sites and is involved in the formation of homo- and hetero-trimetallic clusters.

Several methods are available for the synthesis of trinuclear heterocyclic thionate complexes. Thermolysis of trimetallic carbonyls in the presence of heterocyclic thiones [108] and the controlled addition of solvated $ML_x^{\prime}$ species to binuclear double-bridged, μ_2-S,N, heterocyclic thionate complexes [64,65] have been particularly successful. A combination of the parent ligand and a suitable mononuclear precursor has also occasionally been successful [126]. All of the established compound stoichiometries involve one trinuclear unit in combination with one, two or six bridging ligands. The established trimetallic cores are either cyclic or angular. No linear species have been characterised. A large number of heterocyclic thionate ligands have been used in the production of the known complexes but established crystal structures are limited to complexes of imidazoline-2-thionate (**IIa**), pyridine-2-thionate (**IIc**) and benzo-1,3-thiazoline-2-thionate (**IIh**) derivatives.

3.2. Complexes with one bridging heterocyclic thionate

Trinuclear ruthenium and osmium polycarbonyls form readily available starting materials from which trimetallic complexes with one bridging heterocyclic thionate ligand have been obtained.

Thermolysis of $[Ru_3(CO)_{12}]$ with pyridine-2-thione gives the trinuclear complex $[Ru_3(\mu\text{-H})(\mu\text{-py2S})(CO)_9]$. This complex may be converted into polymeric $[\{Ru_3(\mu\text{-py2S})(CO)_7\}_n]$ which, on further reaction with pyridine-2-thione gives the S,N-chelated mononuclear complex $[Ru(py2S)_2(CO)_2]$ [108]. A combination of IR and NMR (^1H, $^{31}P\{^1H\}$) spectral data established the presence of bridging hydride and μ_3-S,N bridging pyridine-2-thionate in the trinuclear and polymeric complexes.

Triosmium clusters readily react with organosulphur compounds, including heterocyclic thioamides. The acetonitrile substituted triosmium carbonyl $[Os_3(CO)_{10}(MeCN)_2]$ reacts with several heterocyclic thione molecules under gentle reflux, in benzene or hexane, giving complexes of general formula: $[Os_3(CO)_{10}(H)(\text{het-S,N})]$ (het-S,N = imzd2S, bzimz2S, 1-meimz2S, bztz2S, tzd2S, bzoxz2S) [109]. All the complexes were characterised by ^1H and ^{13}C NMR spectra. The upfield shift shown by the thioamide (C(2)) carbon atom of benzo-1,3-thiazoline-2-thionate (189.9 to 171.6 ppm), upon coordination, is typical of the series and is consistent with both thione–thionate conversion and thionate sulphur coordination.

The crystal structure of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-tzd2S})]$ revealed a complex with a trinuclear osmium cluster and terminal carbonyl ligands. Six coordinate geometry at the metal limits the 1,3-thiazolidine-2-thionate anion to μ_2-S, rather than μ_2-S,N bridging (**XL**). The presence of a bridging hydride anion implies two isomers with the symmetric isomer (**XLa**) confirmed by ^1H NMR spectra. Selected dimensions are given in Table 7.

The metal–metal separation distances in $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-tzd2S})]$ are slightly shorter than the average corresponding distance in $[Os_3(CO)_{12}]$ ($Os\text{–}Os_{av}$ = 2.887 Å) [110]. A narrow Os–S–Os angle, together with metal–sulphur distances and M–S–C angles that are similar to those of μ_3-S,N bridging heterocyclic thionate anions in this series (Table 7a), characterise the μ_2-S bridging anion. Average thioamide dimensions of the 1,3-thiazolidine-2-thionate ligand are in Table 3. The non-involvement of the thioamide nitrogen atom leaves the thioamide ($N\text{–}C\text{–}S_{exo}$) angle virtually the same as that in the parent ligand.

Mono-decarbonylation of the $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-tzd2S})]$ complex leads to production of the corresponding nonacarbonyl and conversion of the μ_2-S bridging anion to a μ_3-S,N bridging mode [109]. Two isomers are again possible (**XLb,c**) with room-temperature ^1H and ^{13}C NMR spectra consistent with the symmetric isomer. More extensive thermolysis of $[Os_3(CO)_9(\mu\text{-H})(\mu\text{-tzd2S})]$, by refluxing the nonacarbonyl in refluxing octane, results in thionate ($>C-S^-_{exo}$) bond cleavage, desulphurisation of the bridging ligand and production of the sulphur-capped

Table 7
Trinuclear complexes; selected dimensions (Å and °)

▶Complex and reference M–M	Angles at the metal	M–S	M–N	M–S–M	M–S–C	M–N–C
(a) Complexes with one bridging ligand						
$[Os_3(\mu\text{-}H)(\mu\text{-tzd2S})(CO)_{10}]^b$ [109]						
2.837(2)	59.5(1)	2.416(11)		72.0(3)	106.4(17)	–
2.865(2)	72.7(2)	2.419(9)			109.4(17)	
$[Ru_3(\mu\text{-}H)(\mu\text{-bztzd2S})(CO)_9]$ [112]						
2.786(5)	59.3(1)	2.404(5)	2.177(9)	72.3(2)	105.0(3)	118.3(7)
2.836(5)	61.0(1)	2.405(5)			105.1(4)	
$[Ru_3(\mu\text{-}H)(\mu\text{-py2S})(CO)_9]$ [113]						
2.774(1)	79.7(1)	2.398(3)	2.174(7)	72.6(1)	106.8(4)	121.0(6)
2.841(1)	80.1(1) (Ru Ru S)	2.401(3)			107.9(4)	
$[\{Ru_3(\mu_3\text{-}H)(\mu_4\text{-py2S})(CO)_7\}_2]$ [113]						
2.702(1)	79.26(6)	2.421(3)	2.171(8)	75.11(7)	104.8(2)	122.2(1)
3.289(1)	80.61(6) (Ru Ru S)	2.510(3)	2.197(7)	75.68(7)	111.7(2)	124.1(1)
(b) Complexes with two bridging ligands						
$[Rh_3(\mu\text{-py2S})_2(CO)_6](ClO_4).CH_2Cl_2$ [64,119]						
2.891(5)	112.4(2)	2.365(5)	2.080(14)	74.8(2)	107.1(6)	123.1(11)
2.927(5)	112.7(2)	2.451(6)	2.106(13)	75.8(2)	114.0(6)	126.6(11)
$[Rh_3(\mu\text{-bztz2S})_2(CO)_2(PPh_3)_2(tfb)](ClO_4)$ [119]						
2.994(4)	112.0(1)	2.374(6)	2.136(11)	77.3(2)	108.7(7)	119.4(13)
3.033(1)		2.386(6)	2.180(17)	79.2(2)	113.6(8)	120.0(14)
$[(COD)_2Rh_2(\mu\text{-bztz2S})_2Ag(O_2ClO_2)_2]^a$ [120,121]						
Rh Ag	Rh Ag Rh′	Rh S	Rh N	Rh S Ag	Ag S C	Rh N C
2.796(3)	110.5(1)	2.358(4)	2.080(9)	68.3(1)	102.7(4)	128.9(8)
		Ag S			Rh S C	
		2.609(4)			104.7(4)	
$[Pd_3(dmp)_4(\mu\text{-py2S})_2](BF_4)^b$ [39]						
2.925(4)	106.3(2)	2.308(6)	2.130(13)	75.3(2)	NR	102.1(6)
2.958(4)	107.7(2)	2.494(5)	2.174(17)	79.2(2)		115.5(5)
$[RhPd_2(\mu\text{-py2S})_4(\eta^3\text{-}C_4H_7)_2](BF_4)$ [122]						
Pd Pd	Pd S	Pd N	Rh S Pd	Pd S C		
2.963(4)	2.373(6)	2.130(7)	113.0(2)	104.5(3)		
Pd Rh	2.361(4)	2.150(8)	104.5(3)	104.8(3)		
3.920(4)						
3.929(4)						

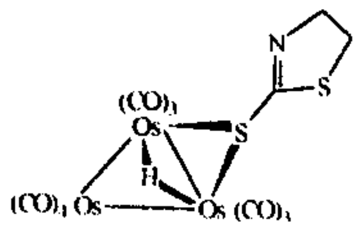
Table 7 (*continued*)

►Complex and reference						
M–M	Angles at the metal	M–S	M–N	M–S–M	M–S–C	M–N–C
S,N-chelate	Rh–S	Rh–N	S–Rh–N	S–Rh–S	Rh–S–C	
	2.327(4)–	2.070(8)	68.9(3)	90.0(2)–	98.8(2)	
	2.394(4)	2.078(7)	68.9(3)	161.2(1)	100.0(3)	
(c) Complexes with six bridging ligands						
$[Pb_3(\mu\text{-}3SiMe_3\text{-}py2S)_6]^a$ [125]						
Pb...Pb	S–Pb–S	Pb–S	Pb–N			
2.89(3)	56.2(6)–	2.707(9)–	2.51(2)			
	94.8(2)	3.318(8)	2.81(3)			

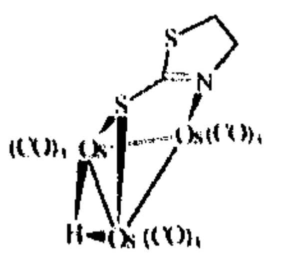
NR not reported.

[a] Symmetrical molecule.

[b] Two independent molecules (cations) in the unit cell.



(a)



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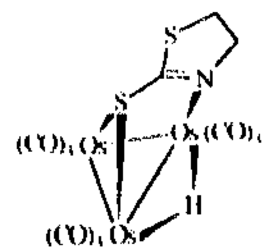
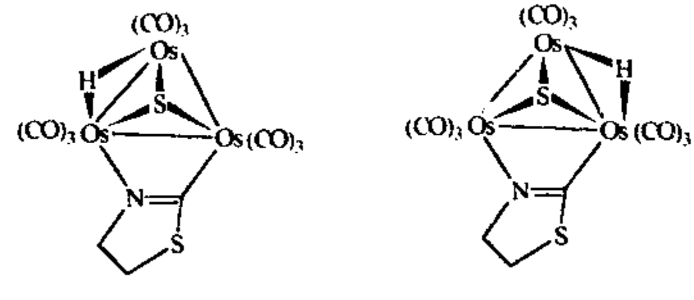


(c)

complex $[Os_3(CO)_9(H)(\mu_3\text{-}S)(tzd)]$ (tzd = 1,3-thiazolidinyl). The ^1H NMR spectrum of this complex shows a broad hydride resonance at 0 °C that resolves into two lines at −60 °C. This is consistent with hydride ligand migration across two edges of the osmium triangle. Hydride migration is suppressed at room temperature (**XLd,e**).

In addition to thionate ($>C-S_{oxo}$) bond cleavage oxidative desulphurisation of 1,3-thiazolidine-2-thione is also possible in certain circumstances. For example, production of both sulphate and (2-oxo-1,3-thiazolidin-3-yl)carbonylthioethylammonium ions occurs by reacting the ligand with zinc dichloride and hydrogen peroxide [111]

Heating suspensions of $[Ru_3(CO)_{12}]$ with benzo-1,3-thiazoline-2-thione [112] or



(d) (e)

(adapted from [109])

(XL)

pyridine-2-thione [113] in refluxing toluene and cyclohexane, respectively, under nitrogen, produces crystalline complexes of formula $[Ru_3(CO)_9(H)(het\text{-}S,N)]$. Red crystalline $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}bztz2S)]$ is obtained at low temperature with the yellow pyridine-2-thionate complex obtained by chromatographic (TLC) separation. These products are in agreement with the model proposed for reactions involving $[Ru_3(CO)_{12}]$ and thiols in which three carbonyls are replaced by one μ_3-S,N bridging heterocyclic thionate ligand [114]. Infrared data on both complexes are consistent with deprotonation of the parent molecule and S,N-coordination of the anion. Bridging hydride ligands were characterised by a high field ^{1}H NMR signal in both complexes. The complexes are effectively isostructural and adopt the symmetric configuration similar to that shown in **(XLb)**, with six-coordinate metal and the μ_3-S,N bridging ligand approximately perpendicular to the plane of the triruthenium cluster. Selected dimensions are given in Table 7a.

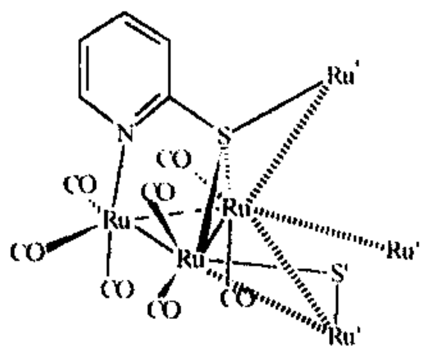
The presence of the bridging thionate sulphur atom and the hydride ion on the same edge of the triruthenium cluster scarcely affect the original metal metal distances (Ru–Ru = 2.848 Å in $Ru_3(CO)_{12}$) [115]. The arrangement also causes only slight perturbation of the angles at the metal. Angular dimensions are very similar in the two complexes. Narrow angles (Ru–S–Ru) characterise the double bridging thionate sulphur atom. Approximately tetrahedral (M–S–C) angles are inevitably narrower than most values usually observed for μ_2-S,N bridging ligands (Table 1). Trigonal (M–N–C) angles are consistent with minimum angular perturbation of the thioamide nitrogen donor atom. Selected thioamide ligand dimensions for the pyridine-2-thionate and benzo-1,3-thiazoline-2-thionate anions are in Table 2 and Table 4, respectively. The values lack the precision to justify detailed analysis but the established trends are indicated.

Double decarbonylation of $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}py2S)]$ occurs in refluxing cyclohexane with the production of trimeric dark red crystalline $[\{Ru_3(CO)_7(\mu_3\text{-}H)(\mu_4\text{-}py2S)\}_3]$ [113]. Proton NMR spectra indicated the presence of hydride and pyridyl groups in the trimer and gave no indication of thionate ($C–S_{exo}$) bond cleavage. Regeneration of the starting product, on passing carbon monoxide through a toluene solution of the trimeric complex, indicated that the thionate ($C–S_{exo}$) bond was unchanged during thermolytic production of the trimer.

However, the anticipated thermolysis product $[Ru_3(CO)_9(\mu\text{-H})(\mu\text{-2-pyridyl})(\mu\text{-S})]$ does require cleavage of the exocyclic thionate ($C-S^-_{exo}$) bond and the resultant migration of the sulphur atom. This product was not obtained.

Crystals of the electron precise trimer are trigonal and contain three independent trimers in the unit cell; two of the trimers are structurally equivalent. Each trimer contains three symmetry-related triruthenium clusters linked by an Ru_3S_3 ring, in a chair conformation, and with an overall screw arrangement. One of the trimers possesses a right-handed screw and the other is left-handed. The unit cell contains equal numbers of the enantiomeric molecules.

Production of the trimer is facilitated by conversion of the μ_3-S,N bridging pyridine-2-thionate, in the precursor complex, to a μ_4-S,N bridging mode **(IIIe)** in the trimer. This enables the thionate sulphur atoms to generate additional sulphur bridges to neighbouring triruthenium clusters **(XLI)** and to function in a manner similar to that of the sulphide ion in $[\{Ru_3(CO)_8(\mu\text{-H})_2(\mu_4\text{-S})\}_3]$ [116].

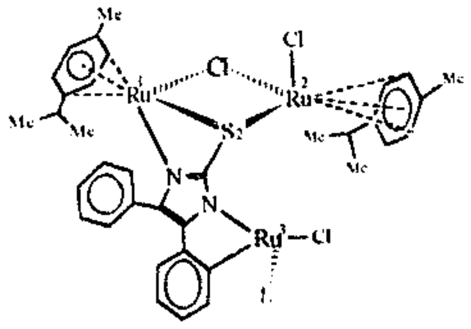


(adapted from [113])

(XLI)

However, the generation of three ruthenium sulphur bonds per molecule in the formation of the trimer is insufficient for saturation. Consequently, the formation of six additional, long-range, ruthenium ruthenium bonds is necessary to achieve this. Attempts to cleave the long-range bonds in the trimer, by the selective addition of carbon monoxide, lead to complete carbonylation with regeneration of the precursor complex. Selected dimensions are listed in Table 7a. Both normal (2.705–2.975 Å) and long-range (3.2–3.3 Å) metal–metal distances are reported. The ruthenium–sulphur distances are slightly longer than those reported for μ_3-S,N bridging pyridine-2-thionate in the precursor complex (Table 7a) but the ruthenium–nitrogen distances are effectively the same. Angles at the ligand donor atoms remain close to the tetrahedral (Ru–S–C) and trigonal (Ru–N–C) values typical of μ_3-S,N bridging heterocyclic thionates (Table 7a). Average thioamide bridging ligand distances are summarised in Table 2. It is clear that lengthening of the thione distance and reduction of the thioamide (N–C–S) angle occur in the bridging anion.

Dimeric $[\{\eta^6\text{-}p\text{-cymene})RuCl_2\}_2]$ reacts with 4,5-biphenyl-1-methylimidazoline-2-thione in methanol–sodium methoxide. Solvent removal, addition of aqueous methanol and cooling (−40 °C) of the reaction medium produce deep-red crystalline $[(\eta^6\text{-}p\text{-cymene})_3Ru_3(\mu\text{-Cl})(\mu_3\text{-4,5-ph}_2\text{-imz2S})Cl_2]$ [80]. Structural details of this complex have been reported although poor crystal quality prevented a detailed analysis of the molecular dimensions. The structure is similar to that of the dinuclear cation **(XXXIIIa)** and is shown in **(XLII)**.



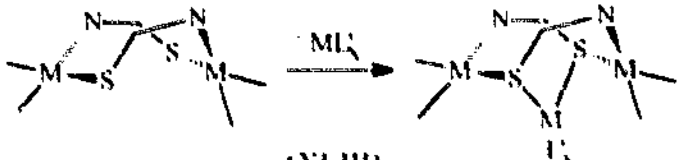
(L = p-cymene)

(adapted from [80])
(XLII)

Deprotonation and cyclometallation of the bridging imidazoline-2-thionate derivative result in the production of the pentadentate trianion. Incorporation of the third ruthenium atom is achieved by means of the deprotonated imidazoline N(3) atom and the ortho-carbon atom of the phenyl group attached to the imidazole carbon (C(4)) atom. Such a reaction appears to be of general applicability, especially with heterocyclic thionates that contain an additional replaceable proton.

3.3. Complexes with two bridging heterocyclic thionate ligands

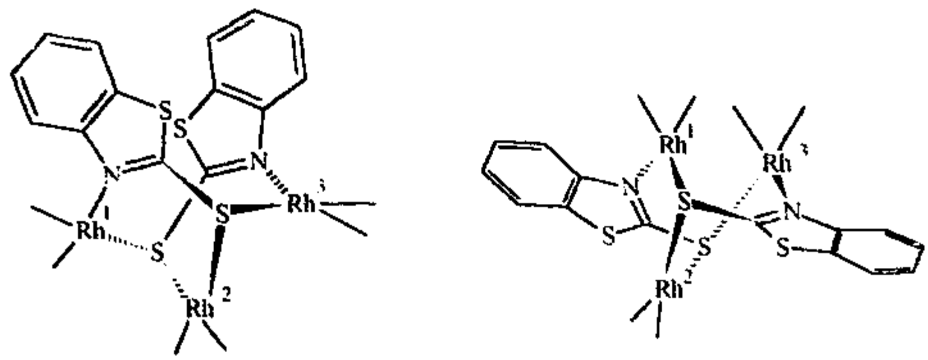
The controlled production of polynuclear complexes is a topic of considerable interest, especially in relation to the design of new materials [117]. In this respect, the use of ligands with small bites, such as 1,8-naphthyridin-2-onate, in the synthesis of trinuclear linear aggregates of rhodium is typical [118]. Of more general applicability is the controlled addition of a metal fragment to a binuclear complex that contains two μ_2-S,N bridging heterocyclic thionate ligands. This results in a trinuclear μ_3-S,N bridged complex of predetermined structure **(XLIII)**.



(XLIII)

This synthetic route has been used in the successful production of trinuclear rhodium complexes with pyridine-2-thionate and benzo-1,3-thiazoline-2-thionate [64–66,119]. Hetero-trinuclear complexes involving rhodium, iridium and palladium have also been successfully produced [120–123]. The isomeric possibilities associated with the cyclic, or non-linear, trinuclear double-bridged metal aggregates,

"$M_3(\mu_3$-het-S,N$)_2$" (**XLIV**), have been described. The reaction pathways involved in their production have also been discussed [119].



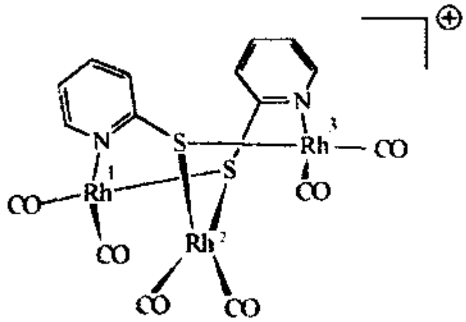
(a) (b)

idealised [$Rh_3(\mu_3$-bztz2S$)_2$] conformers

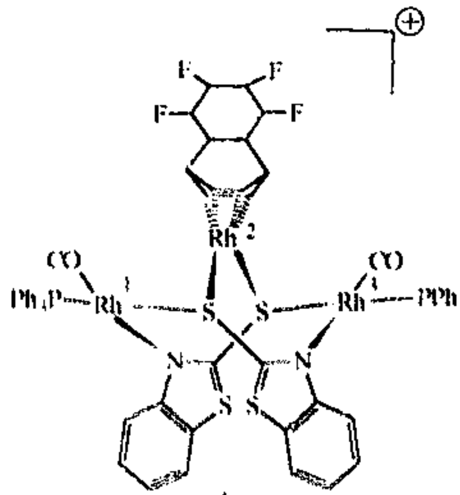
(XLIV)

Single isomers of trinuclear cationic complexes have been obtained as the perchlorate salts. The series are of general formulae [$Rh_3(\mu_3$-het-S,N$)_2$(diolefin)$_3]^+$ (het-S,N = py2S, bztz2S; diolefin = COD, nbd, tfb), [$Rh_3(\mu_3$-het-S,N$)_2(CO)_6]^+$ (het-S,N = py2S, bztz2S) and [Rh_3(bztz2S)$_2(PPh_3)_2$(diolefin)$_2]^+$ (diolefin = COD, nbd, tfb) [119]. Deep-green solutions of cationic [$Rh_3(\mu_3$-py2S$)_2$(diolefin)$_3]^+$ are readily obtained from the binuclear precursors [{Rh(μ_2-py2S)(diolefin)}$_2$] and [{Rh(μ-Cl)(diolefin)}$_2$] in polar solvents. Addition of perchlorate ion enables isolation of the crude complex. No reaction occurs in a non-coordinating solvent so the solvent plays a crucial part in providing cationic rhodium species. An alternative, and more general route, involves addition of a solvated metallic fragment [Rh(diolefin)($Me_2CO)_x]^+$ to the appropriate binuclear complex [{Rh(μ_2-py2S)(diolefin)}$_2$]. Carbonylation at room temperature replaces the diolefin molecules giving [$Rh_3(\mu_2$-py2S$)_2(CO)_6$] (ClO_4), after the addition of perchlorate ion. All the complexes were characterised by a combination of IR, ^1H and ^{31}P NMR and UV-visible electron spectroscopy. The unit cell of [$Rh_3(\mu$-py2S$)_2(CO)_6$] (ClO_4) CH_2Cl_2 consists of two chemically identical but crystallographically independent cations together with perchlorate ions and solvent molecules. The structure of the cation is shown in (**XLVa**) with selected dimensions in Table 7b.

The trirhodium group is angular rather than cyclic (Rh(1)–Rh(2)–Rh(3)$_{(av)}$ = 112.5°) with metal–metal separation distances consistent with weak metal–metal bonding. Each rhodium(I) atom has distorted square-planar geometry and donor sets of either S,N$(CO)_2$, for Rh(1) and Rh(3) or $S_2(CO)_2$, for Rh(2). Angular distortion at the central Rh(2) atom is greater than that at the terminal rhodium atoms, probably because of the steric demands of the bridging thionate sulphur atoms. Each pyridine-2-thionate ligand is μ_3-S,N(η^2S;η^1N) donating and contributes



(a)



(b)

(adapted from [119])

(XLV)

two of the donor atoms at each of the metals. The remaining coordination is provided by the terminal carbonyl ligands. While the rhodium sulphur bonds are comparable with those formed by other μ_3-S,N bridging ligands (Table 7a), the rhodium nitrogen bond lengths are slightly shorter. This may be due to the rather more open geometry of the trirhodium cluster. Angles at the thioamide donor atoms (M-S-M, M-S-C, M-N-C) are similar to those of other μ_3-S,N bridging ligands (Table 7a). Apart from a slight extension to the exocyclic thionate ($>$C–S_{exo}) distances the average thioamide dimensions of the bridging ligands (Table 2) show little change from those of the parent ligand.

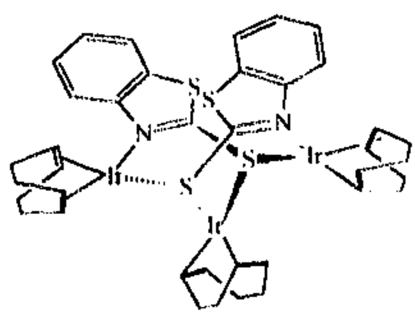
Addition of the appropriate solvated metal species to [{Rh(μ-bztz2S)$_2$(diolefin)}$_2$] (diolefin = COD, nbd, tfb) yields the air-stable [Rh_3(μ-bztz2S)$_2$(diolefin)$_3$] complexes in good yield. Carbonylation of the diolefin complexes in dichloromethane also produces the hexacarbonyl complex [Rh_3(μ-bztz2S)$_2$(CO)$_6$](ClO$_4$). This hexacarbonyl complex reacts cleanly with triphenyl phosphine to give single isomers of [Rh_3(μ-bztz2S)$_2$(CO)$_3$(PPh$_3$)$_2$] (ClO$_4$).

Production of one of the two enantiomeric conformers of the "Rh_3(N–C–S)$_2$"

fragment (**XLIV**) depends on which of the three possible conformations of the "$M_2(NCS)_2$" group reacts with the additional metallic fragment "ML_x". Proposed reaction pathways for the formation of the trinuclear complexes have also been tested and extensively discussed [119]. Deduction of the proposed reaction pathways involved the preparation and characterisation of $[Rh_3(\mu\text{-bztz2S})_2(CO)_2(PPh_3)_2(tffb)](ClO_4)$ and other complexes. Equivalence of the carbonyl and phosphine ligands as well as that of the bridging ligands, in the mono-tetrafluorobarrelene complex, have all been demonstrated by NMR spectral data. Crystal structure analysis confirms that this equivalence arises because the cation has effectively two-fold symmetry (**XLVb**). Selected dimensions are given in Table 7b. The structure of the cation is very similar to that of the pyridine-2-thionate complex (**XLVa**) with an open angular arrangement of three rhodium atoms bridged by two μ_3-S,N(η^2S;η^1N) donating ligands. Square-planar four-coordination at the metals is completed by a combination of terminal carbonyl, phosphine and η^2-donating tetraflourobarrelene ligands. Coordination at the metals is slightly more distorted than in the pyridine-2-thionate complex. The rhodium–sulphur bonds are comparable in the two complexes but the rhodium–nitrogen distances are slightly longer in the benzo-1,3-thiazoline-2-thionate complex. Angles, at the donor atoms of the bridging ligands (M–S–M, M–S–C, M–N–C), are very similar to those in the pyridine-2-thionate complex. Average thioamide dimensions of the bridging ligands are in Table 4. The most significant change in these dimensions occurs in the heterocyclic thione (>C–S_{endo}) distance that is, unusually, significantly reduced.

The general synthetic strategy used above for the production of single isomers of trinuclear rhodium(I) complexes, of predetermined structure, is manifestly capable of extension to other systems. Oro has done this and has successfully produced a number of both homo- and hetero-trinuclear angular aggregates involving rhodium, iridium, palladium and group eleven metals [120,121].

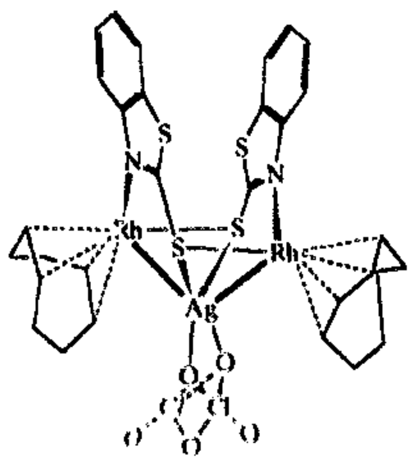
The trinuclear cations $[Ir_3(\mu\text{-bztz2S})_2(\eta^2\text{-COD})_3]^+$ and $[Pd_3(\mu\text{-bztz2S})_2(\eta^2\text{-C}_3H_6)_3]^+$ are obtained by addition of the solvated metal species to the appropriate binuclear metal complex (**XLIII**) and are isolated as the perchlorate salts [120]. The structures consist of symmetrical μ_3-S,N(η^2S;η^1N) bridging ligands, four coordinate metals and terminal η^2-donating diene ligands (**XLVI**).



(adapted from [120])

(XLVI)

Production of single isomers of hetero-trinuclear aggregates with a predetermined structure requires addition of solvated metal species with metals other than those of the binuclear precursor (**XLIII**). A large number of neutral hetero-trinuclear complexes have been prepared from binuclear rhodium and iridium precursors in this manner. Copper, silver or gold chlorides, tetrafluoroborates or perchlorates, provide the third metal. A neutral, symmetrical, tetranuclear product has also been reported $[(Ph_3P)_2(CO)_2Rh_2(bztz2S)Ag_2(OClO_3)_2]$ [121]. This complex contains weakly coordinated perchlorates in the solid and is conducting in polar solvents. In non-polar solvents the complex retains its characteristic combination of symmetrical bridging and terminal phosphine ligands as well as coordinated perchlorate ions. The trinuclear aggregates have been characterised by IR, ^1H and ^{31}P NMR spectra. The crystal structure of $[(\eta^2\text{-COD})_2Rh_2(\mu\text{-bztz2S})_2Ag(O_2ClO_2)]$ also provides definitive structural data for the series. This symmetrical structure is shown in (**XLVII**) and selected dimensions are given in Table 7b.

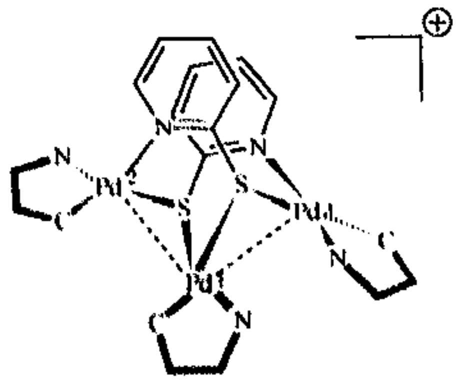


(adapted from [121])
(XLVII)

A two-fold crystallographic axis bisects the bridging ligands and the angular arrangement of the metal atoms in the hetero-trinuclear complex. The μ_3-S,N(η^2S;η^1N) bridging ligands interact with all three metal atoms. Terminal η^2-donating diene ligands complete the square-planar coordination at the rhodium atoms. A disordered O,O-chelating perchlorate ion completes the tetrahedral coordination at the silver atom. The rhodium–silver separation distance (2.796(3) Å) in the heterometallic aggregate is considered to be an attractive interaction rather than a metal–metal bond. The distorted coordination at the silver atom is the result of a S_2O_2 donor set and the consequent disparity in the bond lengths (Ag–O = 2.532(17) Å). The narrow angle (O–Ag–O = 52.2(5)°) also results from the short bite (O...O′ = 2.22(3) Å) of the perchlorate ligand. The major differences between this hetero-trinuclear structure and that of the trinuclear rhodium(I) counterparts (Table 7b) are a shorter metal–metal (Rh–Ag) separation, asymmetry in the metal–sulphur bridging distances and a decrease in the sulphur bridging angle (Rh–S–Ag). The rhodium–nitrogen separation distance remains unaffected. However, the angular dimensions (M–S–C and M–N–C) of the μ_3-S,N bridging ligands are respectively slightly smaller and larger than those reported for the corresponding trinuclear rhodium(I) complex. Clearly, a slight modification of the trirhodium aggregate has been necessary in order to accommodate the silver atom. Rather large errors in the thioamide dimensions of the bridging ligands inhibit meaningful analysis. However, the thioamide angle (N–C–S_{exo}) is significantly smaller than that of the free ligand (Table 4).

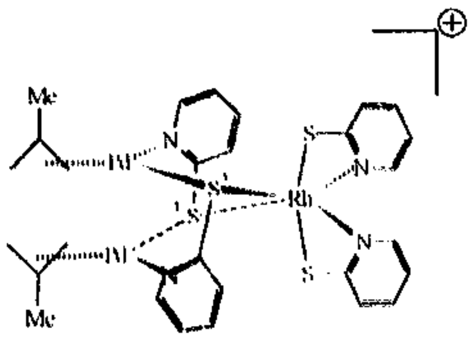
The remaining complexes in the series all have structures similar to that in (**XLVII**) with the hetero-atom utilising the electron rich sulphur atoms to enter the structure. Coordination at the hetero-atom is completed by either O,O-chelating perchlorate or monodentate, chlorine or triphenylphosphine, ligands

Addition of solvated pyridine(II) complexes [Pd(dmp)(solvent)]$^+$ to pyridine-2-thionate symmetrically bridged binuclear palladium complexes [Pd_2(dmp)$_2$(py2S)$_2$] (dmp = 2-(dimethylaminomethyl)phenyl; solvent = H_2O or $(Me)_2CO$) gives trinuclear cationic [Pd_3(dmp)$_3$(py2S)$_2$](BF_4) [39]. Complicated ^{1}H NMR spectra indicated asymmetry in the molecular cation. Crystal structure analysis showed that the cation contains a trinuclear, double-bridged (Pd_3(μ_3-py2S)$_2$) unit and three terminal cyclometallated 2-(dimethylaminomethyl)phenyl ligands. There are two crystallographically independent cations in the unit cell. The structure is shown in (**XLVIIIa**) with selected dimensions in Table 7b.



(adapted from [39])

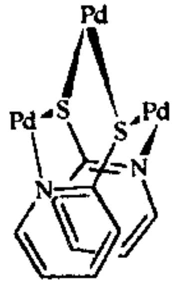
(a)



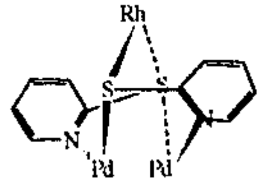
(adapted from [122])

(b)

In spite of the relatively short metal...metal separation distances no palladium–palladium bonds are proposed for this structure. The trinuclear palladium unit is considered to be angular (Pd–Pd–Pd$_{av}$ = 107.0°) in which each metal atom has distorted square-planar geometry. The non-equivalence of the Pd(2) and Pd(3) atoms results from the unsymmetrical nature of the cyclometallated chelate(dmp) at the Pd(1) atom. This feature also removes the two-fold molecular symmetry and accounts for the complicated nature of the ^{1}H NMR spectra. The different *trans* influences of the C,N-chelate are also responsible for the variations in palladium–sulphur bond lengths and angles (Pd–S–Pd, Pd–S–C) at the bridging thionate sulphur atoms (Table 7b).



(c)



(d)

('M3(μ3–py2S)2' conformers)

(XLVIII)

A novel variation of the combination of a metallo-ligand and solvated metallo-species has been described. The procedure involves monomeric $[Rh(py2S)_3(py2SH)]$ in combination with two equivalents of the solvated 2-methylallyl complex cation $[Pd(\eta^3\text{-}C_4H_7)(solvent)_2](BF_4)$ (solvent = H_2O or Me_2CO) and trimethylamine in dichloromethane [122]. The six-coordinate rhodium(III) complex contains three pyridine-2-thionate anions. Two of the anions are *cis*-S,N chelating and one is monodentate sulphur donating. The pyridine-2-thione ligand is monodentate sulphur donating. The ^1H NMR spectra of the salmon-pink trinuclear heterometallic product $[RhPd_2(py2S)_4(\eta^3\text{-}C_4H_7)_2](BF_4)$ indicated the allyl groups to be equivalent but unsymmetrical. Two equally populated sites for the pyridine-2-thionate ligands and molecular rigidity up to 80 °C were also indicated. The crystal structure established the presence of an approximately two-fold axis bisecting the S(3) Rh S(4) angle and pairs of S,N-chelating and μ_3-S,N(η^2S:η^1N) bridging pyridine-2-thionate ligands. The structure is shown in **(XLVIIIb)** and selected dimensions are given in Table 7b. Metal metal separation distances are too long for metal metal bonding. Coordination is octahedral at the rhodium(III) atom and square-planar at the palladium(II) atoms. Both arrangements are distorted and consistent with the retention of the original oxidation states. The rhodium has a S_4N_2 donor set with dimensions that are typical of S,N-chelating pyridine-2-thionate and similar to those reported for $[Rh(py2S)_3(py2SH)]$ [123]. Each palladium atom has S,N,(η^3-C_4H_7) coordination. The geometry of the $\{RhPd_2(\mu\text{-}py2S)_2\}$group is biycyclic with the heterometallic core capped above and below by the bridging ligands. The metal ligand distances and angles of the bridged trinuclear species are similar to related systems (Table 7b). The bridging angles at the thionate sulphur atoms (Pd S Rh) however, do reflect the open nature of the central hetero-metallic core. Various ways of forming a "$M_3(\mu_3\text{-}py2S)_2$" cage, by the addition of metal atoms to pyridine-2-thionate coordinated metal species, are also considered.

Deeming [39] also points out that the "$Pd_3(\mu_3\text{-}py2S)_2$" **(XLVIIIc)** and "$Pd_2Rh(\mu_3\text{-}py2S)_2$" **(XLVIIId)** cages, although apparently different, are topologically equivalent. The "$Pd_3(\mu_3\text{-}py2S)_2$" cage has two long (Pd...Pd) and one short (Pd...Pd) distances while the "$Pd_2Rh(\mu_3\text{-}py2S)_2$" cage has one short (Pd...Pd) and two long (Pd...Rh) distances. However, the two structures are inter-convertible conformations that can be mutually transformed by rotating the ligands about the bonds to the thionate sulphur atoms without these bonds being broken. The conformations (**XLVIIIc,d**) appear to be close to the limit of the two extreme possibilities that can be adopted by "$M_3(\mu_3$-het-S,N$)_2$" cages.

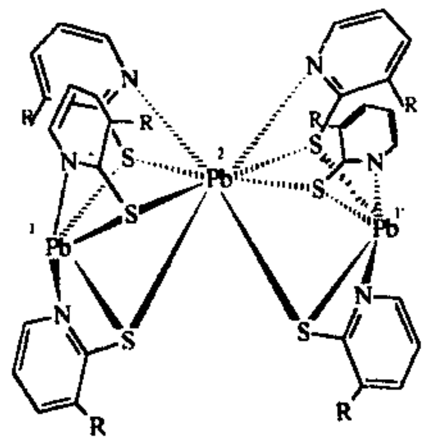
3.4. *Complexes with six bridging ligands*

The combination of a cyclic, or angular, trinuclear aggregate and six bridging heterocyclic thionate ligands presents some interesting structural possibilities. The simplest combination involves divalent metals and six μ_2-S double-bridging ligands spanning each edge of the polygon. A similar arrangement has been proposed for organothiolate ligands [9] and observed in [$Co_3(CO)_3(\mu$-CO)(μ-SEt$)_5$] [124]. With six μ_2-S,N bridging ligands, also arranged in double-bridging pairs: several isomeric forms are possible because of the asymmetric nature of the bridging ligands. Six, μ_3-S,N, trinuclear-bridging ligands generate eighteen metal–ligand contacts that clearly may be distributed about three acceptor atoms in a variety of ways. There is one reported example to consider, [Pb_3(3SiMe$_3$-py2S$)_6$].

The complex is readily prepared by the addition of two equivalents of 3-trimethylsilyl pyridine-2-thione to lead(II) nitrate in ethanol. Production of [Pb_3(3SiMe$_3$-py2S$)_6$] is clearly a "ligand driven" process in which the presence of the triorganosilyl substituent confers enhanced solubility to the product and assists in the generation of discrete molecular species. The same ligand also reacts with tin(II) chloride producing monomeric [Sn(3SiMe$_3$-py2S$)_4$]. This complex contains four S,N-chelating ligands [125].

The complex [Pb_3(3SiMe$_3$-py2S$)_6$] occupies a two-fold crystallographic axis in the solid. There are two distinct geometries about the three lead(II) atoms that involve an asymmetric distribution of the metal–ligand contacts. Furthermore, each binuclear bridging μ_2-S,N(η^2S:η^1N) ligand involves three metal–ligand contacts (**IIIc**). Consequently, such an arrangement generates a total of eighteen metal ligand contacts in the complex. The structure is shown in (**XLIX**). Selected dimensions are given in Table 7c.

The trinuclear aggregate is angular with the central metal atom (Pb(2)) occupying the two-fold axis. The symmetry-related lead(II) atoms (Pb(1 and 1')) have a S_3N_2 donor set provided by three separate ligands. The donor set consists of three primary contacts with thionate sulphur atoms and two additional secondary interactions to thioamide nitrogen atoms. This arrangement generates distorted trigonal-pyramidal, five-coordinate geometry, with the lead(II) atom at the apex. The central lead(II) atom has an S_6N_2 donor set that is also formed by a combination of primary and secondary attachments to all of the ligands. This arrangement results in distorted eight coordinate geometry. The irregular geometries associated with the metal atoms are ascribed to the influence of each stereochemically active lone-pair. The overall geometry of the complex is similar to that reported for [$Pb_3(SCH_2-2,4,6-Pr^i_3)_6$] [126].



(R = $SiMe_3$, adapted from [125])

(XLVIX)

4. Tetranuclear complexes

4.1. Introduction

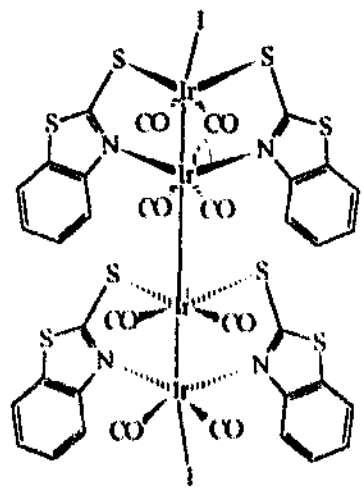
The structures of a variety of organo-thiolate bridged cyclic tetranuclear complexes have been established. They have arisen primarily as a consequence of the biological relevance, and the structural diversity, of metal thiolate interactions [9,10]. Investigation of copper(I) sulphur cores is particularly active with tetrahedral $[\{Cu(RS)\}_4]$, as well as octahedral $[\{Cu(RS)\}_6]$ and dodecahedral $[\{Cu(RS)\}_{12}]$ (RS = trimethyl silylphenyl thiolate derivatives) species recently reported [127]. The structures and luminescent properties of tetranuclear copper(I) halide complexes with heterocyclic nitrogen donors, such as $[\{CuI(py)\}_4]$, have also attracted particular interest [128]. In addition binuclear double-bridging, μ_2-S(η^2-S), heterocylic thiones, tend to produce tetranuclear copper(I) aggregates with planar rhomboid metallic cores of varied stoichiometry [129].

There are, however, relatively few fully characterised tetranuclear complexes of heterocyclic thionates. Such complexes that are known to occur involve pyridine-2-thionate (**IIc**), imidazole-2-thionate (**IIa**) and 1,3-thiazole-2-thionate (**IIh**) derivatives. They include cyclic and acyclic as well as homo- and hetero-metallic tetranuclear cores. Preparative routes involve the *trans*-annular oxidative-addition of binuclear iridium(I) complexes [130]. Degradation of polymeric heterocyclic thionate complexes with pyridine or phosphine derivatives [136]. Direct electrochemical synthesis from the parent ligand, in acetonitrile, also provides effective routes to tetranuclear nickel(II) [137] and copper(I) [132] complexes. A direct route to hetero-metallic tetranuclear complexes involves controlled reactions between binuclear rhenium(I) complexes and triruthenium dodecacarbonyl. Such reactions involve a combination of oxidation addition with thionate (>C–S–) bond cleavage [138–140].

4.2. Acyclic and cyclic complexes

Transannular oxidation–addition reactions of bridged binuclear complexes [18], having been used successfully in the stabilisation of otherwise reactive binuclear iridium species [71], have also been used in the production of a linear tetrairidium cluster [130]. Oxidative-addition of iodine to $[Ir_2(\mu\text{-bztz2S})_2(CO)_4]$ in toluene produces tetranuclear $[Ir_4(\mu\text{-bztz2S})_4(CO)_4I_2]$, in the presence of UV radiation. This tetrairidium complex is of structural and mechanistic significance. It is an intermediate in the oxidative-addition of iodine to $[Ir_2(\mu\text{-bztz2S})_2(CO)_4]$ that ultimately results in the binuclear end-product $[Ir_2(\mu\text{-bztz2S})_2(CO)_4I_2]$, in dichloromethane. Further oxidative-addition of iodine to the tetrairidum complex also produces the same binuclear end-product. Crystal structures of both the tetrairidium cluster and the iodo end-product have been reported. The structure of $[Ir_2(\mu\text{-bztz2S})_2(CO)_4I_2]$ is similar to that of $[Ir_2(\mu\text{-py2S})_2(CO)_4I(CH_2I)]$ **(XXVII)** in which an iodine atom replaces the terminal methylene iodide group [71]. The dimensions (Table 1) of the two binuclear complexes are also similar.

The tetrairidium cluster contains two binuclear sections related by a two-fold axis and is shown in **(L)**. Selected dimensions of the structure are given in Table 8.



(adapted from [130])

(L)

Each binuclear section contains the $\{Ir_2(\mu\text{-bztz2S})_2\}$ group with two metal–metal bonded iridium atoms and two *cis-head-to-head*, μ_2-S,N(η^1S;η^1N), double-bridging ligands. Both of the outer iridium atoms complete their coordination with terminal iodine (Ir–I = 2.731(2) Å) while the inner iridium atoms form a non-bridged metal–metal bonded contact with its symmetry related partner. The almost linear tetrairidium chain results in an EPR silent complex. Furthermore, the structure of the complex indicates that iodine attacks one of the metal centres in the binuclear precursor giving the metal–metal bonded complex radical $\{Ir_2(\mu\text{-bztz2S})_2I(CO)_4\}^{\bullet}$; this fragment rapidly dimerises. In this way the second metal centre involved in the formation of the tetrameric complex provides anchimeric

Table 8
Tetranuclear complexes; selected dimensions (Å and °)

►Complex and reference M_4-core dimensions	Angles at the metal	M–S	M–N	M–S–M	M–N–C	M–S–C
$[Ir_4(\mu\text{-bztz2S})I_2(CO)_8]$.(toluene)[a] [130]						
2.731(2), 2.828(2),	Ir–Ir–I 168.5(1), 170.2(1)	2.382(2), 2.408(6)	2.09(2), 2.11(2)	–	NR	NR
$[\{Cu(\mu\text{-meimz2S})\}_4]$[a] [132]						
2.671(2), 3.132(2); 71.8(1)	109.3(2) 133.1(2)	2.233(2), 2.307(2)	1.995(6)	72.1(1)	119.2(5)	106.8(2) 96.8(2)
$[\{Cu(\mu\text{-tzd2S})\}_4$.(toluene)$]_n$ [133]						
2.692(4) 3.687(6); 57.23(11) 110.15(12)	92.51(11) 130.85(9)	2.273(4) 2.790(3)	1.993(4) 2.023(4)	70.53(12) 87.49(12)	117.2(3)– 127.5(3)	97.7(2)– 118.4(2)
$[\{Cu(\mu\text{-tzd2S})\}_4(\eta\text{-tzd2SH})_2]$[a] [134]						
2.889(2)	102.4(1) 129.2(2)	2.225(2) 2.310(2)	1.996(7) 2.017(5)	78.00(8) 86.95(7)	122.0(5) 128.1(5)	99.4(2) 111.3(3)
$(\eta^1\text{-S})$tzd2SH		2.491(2)				105.3(2)
$[\{Cu(\mu\text{-tzd2S})\}_4L_n]$ (L = py, n = 1; L = PPh_3, n = 2) [136]						
2.672(2) 4.127(1)	NR	2.191(2) 2.424(2)	1.996(6) 2.063(7)			
$[Cu_2E_2(E_4)(\mu\text{-tzd2S})_4(PPh_3)_2]$ (E = Ag) [136]						
2.817(1) 4.275(1)	NR	2.191(2)	1.996(6) 2.424(2)	2.063(7)		
$[\{Ni(\mu\text{-OH})(\mu\text{-tzd2S})(py)\}_4]$[a] [137]						
2.04((1) 2.08(1) Ni–O–Ni 95.6(4) 103.2(4)	76.8(4) 175.1(6)	2.44(1)	2.11(2) Ni–Py 2.13(1)		130(1)	NR
$[ReRu_3(\mu\text{-S})(\mu\text{-}C_5H_4N)(CO)_{14}]$ [140]						
Ru–Re 2.894(1) Ru–Ru 2.719(1)						
μ_4-S		2.380(2) 2.417(3)		69.6(1) 134.8(1)		
2-Pyridyl		Ru–C 2.100(9)		Ru–N 2.10(1)		
$[Re_2Ru_2(\mu\text{-S})(\mu\text{-}C_5H_4N)(py2S)(CO)_{13}]$[b] [140]						
Ru–Ru	Re–S	Re–N	Re–S–Re	Re–S–C		
2.701(1) 2.715(2)	2.508(2) 2.514(2)	2.170(6) 2.19(2)	96.9(2) 97.70(7)	79.5(5) 80.3(3)		

Table 8 (*continued*)

▶Complex and reference M$_4$-core dimensions	Angles at the metal	M–S	M–N	M–S–M	M–N–C	M–S–C
μ_4-S		2.409(2)–2.553(2)		68.05(6)–125.63(8)		
2-Pyridyl		Ru–C = 2.07(1)		Ru–N = 2.114(8)–2.124(9)		
[$Re_3Ru(\mu$-S)(μ-C_5H_4N)(py2S)$_2$(CO)$_{11}$]^b [138]						
Ru–Re	Ru–S	Re–S	Re–N			
2.884(1)–2.902(1)	2.443(4)–2.525(4)	2.500(3)–2.610(4)	2.15(1)–2.17(1)			
μ_4-S	2.384(3)–2.537(3)		72.5(1)–139.5(1)			
2-Pyridyl(average)		Ru–C = 2.04	Ru–N = 2.21			

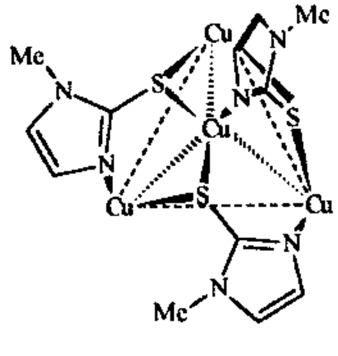
NR not reported.
[a] Symmetrical molecule.
[b] Range of values reported for two isomers.

assistance in cleaving the added molecular iodine. Orientational changes in the μ_2-S,N bridging ligands, between the tetranuclear complex and its binuclear precursor, are probably a result of their inherent mobility; both complexes are fluxional. Metal–ligand dimensions generated by the μ_2-S,N bridging ligands are similar to those of the binuclear end-product (Table 1).

Organothiolate ligands form double, (μ_2-S), bridges along the six edges of the tetrahedral core in the [$Cu_4(PhS)_6$]$^{2-}$ ion [131]. A more extensive series of tetranuclear complex anions is also formed with additional terminal monodentate ligands and [$M^{n}_4(RS)_{10}$]$^{(10-4n)-}$ stoichiometry [9]. Although similar arrangements are possible with binuclear bridging heterocyclic thionates (**IIIa**) it is the five-electron donating trinuclear, μ_3-S,N(η^2S;η^1N), face-bridging mode (**IIId**), that dominates the tetranuclear copper(I) cores of complexes with general stoichiometry [{Cu(het-S,N)}$_4$].

Colourless, crystalline, diamagnetic, air-stable [{Cu(μ-meimz2S)}$_4$] is obtained electrochemically by means of a platinum cathode, a copper anode and 1-methylimidazoline-2(3H)-thione in acetonitrile in the presence of a supporting electrolyte [132]. The complex may also be obtained from equimolar solutions of hydrated copper acetate and 1-methylimidazoline-2(3H)-thione. In situ ligand deprotonation is achieved by the addition of aqueous ammonia. The same reactants in dry ethanol with metallic sodium as the deprotonating agent was also successful. The IR spectra of all the products indicated both ligand deprotonation and S,N-coordination. The structure of the complex is shown in (**LI**) and selected dimensions are given in Table 8.

The tetranuclear complex occupies a crystallographic four-fold inversion axis and possesses a slightly flattened Cu_4 tetrahedron. The anionic ligands are virtually



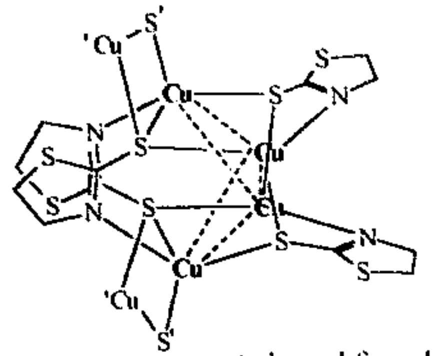
(adapted from [132])

(LI)

normal to the isosceles triangular faces of the Cu_4 tetrahedron and form trinuclear, μ_3-S,N(η^2S;η^1N), bridges with the copper(I) atoms on each triangular plane. Consequently, each copper(I) atom has an S_2N donor set and distorted trigonal geometry formed by three separate ligands. The bridging ligands form short metal–nitrogen bonds and metal–sulphur distances that are broadly comparable with those observed for trinuclear heterocyclic thionate complexes (Table 7). Angles at the thioamide donor atoms are close to the expected trigonal value in the case of the thioamide nitrogen (Cu–N–C). The double-bridging thionate sulphur atom generates characteristically narrow (Cu–S–Cu) and asymmetric (M–S–C) angles (Table 8). Ligand thioamide dimensions show changes, (C–S = 1.751(7), C–N = 1.329(9) Å; N–C–S = 127.2(5)°), relative to the average values of the free ligand (C–S = 1.685, C–N = 1.345 Å; N–C–S = 127.1°) [29], that are characteristic of μ_3-S,N bridging ligands. The complex undergoes irreversible ligand centred oxidation (E_p = +0.50 V; vs SCE) in acetonitrile.

A similar electrochemical procedure with 1,3-thiazolidine-2-thione in toluene produced pale-yellow crystals of toluene-solvated polymeric $[\{Cu(\mu\text{-tzd2S})\}_4(\text{toluene})]_n$ [133]. The same reaction mixture subsequently produced a small quantity of deep-yellow crystals of the tetranuclear complex $[\{Cu(\mu\text{-tzd2S})\}_4(\eta\text{-tzd2SH})_2]$ [134]. The polymeric toluene solvate consists of self-assembled $[\{Cu(\mu\text{-tzd2S})\}_4]$ tetramers that are sulphur bridged through the "wing-tip" copper atoms into polymeric chains. A section of the structure is shown in **(LII)** and selected dimensions are given in Table 8.

The central tetranuclear copper(I) core of the complex has an "open-butterfly" configuration. The "spinal" copper atoms (Cu...Cu = 2.882(5) Å) have distorted trigonal S_2N coordination involving three separate ligands. The "wing-tip" copper atoms (Cu...Cu = 3.687(6) Å) have distorted tetrahedral coordination from three different ligands within an individual tetramer plus an additional contact from a thionate sulphur atom in a neighbouring tetramer. The latter contact generates asymmetric, centrosymmetrically related Cu_2S_2 units (Cu–S = 2.539(3)–2.790(3) Å; Cu–S–Cu′ = 129.72(12), 131.68(7)°) that link the "wing-tip" atoms into a polymeric chain. These are the longest copper–sulphur distances in the structure (Table 8), the



(adapted from [133])

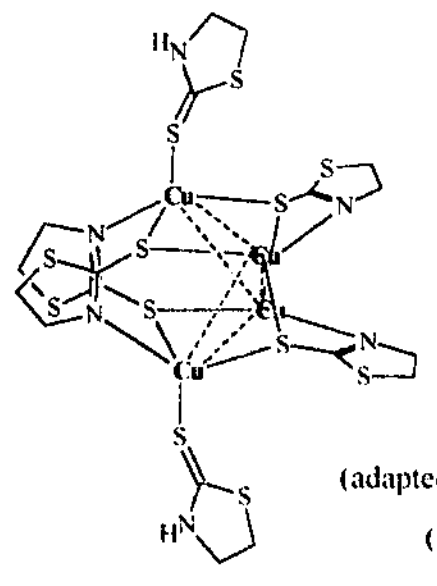
(LII)

remaining distances being mostly comparable with those of trinuclear μ_3-S,N bridging ligands. Consequently, the four ligands in each tetramer consist of two pairs of μ_3-S,N(η^2S;η^1N) and μ_4-S,N(η^3S;η^1N) bridging ligands. This unique combination of bridging ligands is necessary in order to accommodate the coordination requirements of the two types of copper atoms. The arrangement also facilitates polymer formation. The remaining angles at the thioamide donor atoms (Cu–N–C, Cu–S–Cu, and Cu–S–C) are similar to those reported for [{Cu(μ-meimz2S)}$_4$] (Table 8), for similar reasons. Average ligand thioamide dimensions are summarised in Table 3b. These show the characteristic shift of π-electron density from the carbon–sulphur bonds to the carbon–nitrogen bond, for both types of bridging ligand. As has been observed with other 1,3-thiazolidine-2-thionate complexes (Table 3a) all of the thioamide angles are also perturbed by between 2–7°. The complex undergoes irreversible two-stage, ligand-centred oxidation, in acetonitrile (E_p = −0.5 and +0.5 V vs SCE).

The structure of the central tetranuclear core in [Cu$_4$(μ-tzd2S)$_4$(η-tzd2SH)$_2$] is essentially similar to that of the polymeric product. It consists of an open-butterfly arrangement of copper(I) atoms, μ_3-S,N(η^2S;η^1N) bridging ligands and similar metal–ligand dimensions [134]. The structure is shown in **(LIII)** and selected dimensions are given in Table 8.

The terminal, neutral, monodentate (η^1-S) ligands are attached to the "wing-tip" atoms. Consequently, these atoms have distorted tetrahedral geometry and an S_3N donor set. The "spinal atoms" in the tetranuclear aggregate have distorted trigonal coordination generated from S_2N donor sets involving three separate ligands. The "spinal" copper atoms also form long-range contacts (Cu–S = 3.006 Å) with the thione sulphur atoms of terminal monodentate ligands in neighbouring tetramers. Clearly, the copper atoms, and especially the "wing-tip" copper atoms, have a marked preference for four-coordinate tetrahedral geometry in these complexes. This is achieved by additional copper–sulphur interactions between adjacent tetramers in the polymer and by monodentate, or long-range, contacts to neutral ligands in the case of [Cu$_4$(μ-tzd2S)$_4$(η-tzd2SH)$_2$]. The fact that the polymer is always the major product indicates that polymerisation is the preferred option.

Thioamide ligand dimensions are given in Table 3b. The average dimensions of the μ_3-S,N bridging ligands are comparable with those of the solvated tetranuclear



(adapted from [134])

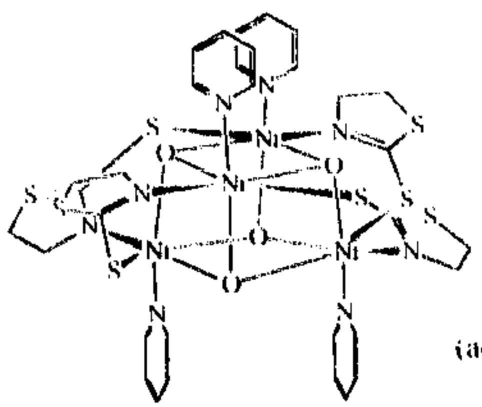
(LIII)

polymer. The dimensions of the disordered monodentate (η^1-S) ligands are somewhat anomalous.

Prior to the publication of polymeric $[\{Cu(\mu\text{-tzd2S})\}_4.(toluene)]_n$ copper complexes of deprotonated 1,3-thiazolidine-2-thione have had a somewhat uncertain history. Both [Cu(tzd2S)] [103] and $[Cu(tzd2S)_2]$ [135] had been known for some time, the latter with an anomalous room-temperature magnetic moment. The first reliable attempt to establish the nuclearity and to rationalise the structure of [Cu(tzd2S)] involved preparation of the complex from hydrated copper(II) acetate and the parent ligand [136]. Treatment of the insoluble product with pyridine, and also with triphenylphosphine, generated polymeric $[\{Cu(\mu\text{-tzd2S})\}_4(py)]_n]$ and $[Cu_4(\mu\text{-tzd2S})_4(PPh_3)_2]$, respectively. Similar reactions were performed with silver acetate and a mixture of copper and silver acetates. These generated $[\{Ag(\mu\text{-tzd2S})\}_4]$ and $[Cu_2Ag_2(\mu\text{-tzd2S})_4]$, respectively. Selected dimensions of the resultant structures are given in Table 8. All the complexes, except that of the pyridine adduct, have structures similar to that of $[\{Cu(\mu\text{-tzd2S})\}_4(\eta\text{-tzd2SH})_2]$. Each structure consists of an "open-butterfly" tetranuclear metallic core, together with four μ_3-S,N(η^2S;η^1N) bridging ligands. Terminal phosphine ligands are attached to the "wing-tip" copper atoms. In the mixed-metal complex the silver(I) atoms occupy the "wing-tip" sites. The pyridine complex is unusual in that only one molecule of pyridine, also attached to a "wing-tip" atom, is involved in each tetranuclear unit. This enables the other "wing-tip" atom in each tetramer to interact with an endocyclic sulphur atom of a bridging ligand in a neighbouring tetramer (Cu–S_{endo} = 2.723(3) Å). This is the most novel manner by means of which a "wing-tip" atom achieves tetrahedral four-coordination in this series of complexes. The proposed interactions also result in the production of a polymeric complex. It would appear that an excess of pyridine disrupts the polymeric arrangement in the parent complex $[\{Cu(\mu\text{-tzd2S})\}_4]$, replacing it with the proposed alternative. As is observed in the other complexes in this series the "wing-tip" separation (3.6–4.2 Å) exceeds that of the "spinal-atoms" (2.7–3.1 Å) as well as the distance between "wing-tip" and "spinal-atoms" (2.9–3.0 Å). Metal–ligand distances are similar to the others in the series.

In addition to the production of [Cu(tzd2S)], described above [103], the same report also describes the production of other complexes of the 1,3-thiazolidine-2-thionate anion. These complexes involve divalent metals [M(tzd2S)$_2$] (M = Zn, Cd, Hg, Co, Ni, Pd, Pt, Au, Mn) as well as Ag(tzd2S)] and [Ir(tzd2S)$_3$]. These products are mostly intractable solids and are described as polymeric with μ_2-S,N bridging ligands, largely on the basis of IR data. Except for the tetranuclear copper(I) complexes the wealth of coordination chemistry inherent in this report has provided relatively little definitive structural chemistry [1,90,91]. However, complexes derived from the diamagnetic nickel(II) complex [Ni(tzd2S)$_2$] have been reported [137].

The preparation of monomeric, green, paramagnetic, microcrystalline [Ni(tzd2S)$_2$(py)$_2$], involves the dissolution of polymeric [Ni(tzd2S)$_2$] in dry pyridine followed by the addition of dry ethyl ether. The IR and UV-visible spectra of this complex are consistent with S,N-chelating ligands and distorted octahedral metal geometry. In the absence of pyridine this complex reverts to its polymeric precursor. However, addition of water to a solution of [Ni(tzd2S)$_2$] in dry pyridine produces the tetranuclear complex [{Ni(μ-OH)(μ-tzd2S)(py)}$_4$].2py. The IR and UV-visible spectra of this tetrameric product are similar to those of the monomeric product. The structure of [{Ni(μ-OH)(μ-tzd2S)(py)}$_4$] is shown in (LIV) and selected dimensions are given in Table 8.



(adapted from [137])
(LIV)

The structure consists of a central cubane {(Ni(μ-OH))$_4$} arrangement with four terminal pyridine and four μ_2-S,N(η^1S:η^1N) bridging heterocyclic ligands. The heterocyclic-thionate ligands bridge the nickel atoms outside the tetrameric core. Each metal has distorted octahedral geometry and an O$_3$(py)(S,N) donor set. The donor set is formed from apical pyridine, three bridging hydroxo groups together with thionate sulphur and thioamide nitrogen atoms from two different bridging heterocyclic ligands. The nickel–oxygen distances (Ni–O = 2.04(1)–2.08(1) Å) are reputedly slightly larger than those formed by other Ni$_4$O$_4$ cores. Furthermore, the metal–ligand distances formed by the bridging ligands are comparable with related values in the tetranuclear [{Cu(μ-tzd2S)}$_4$] complexes (Table 8). The metal–metal distances involved preclude the formation of metal–metal bonds within the Ni$_4$O$_4$

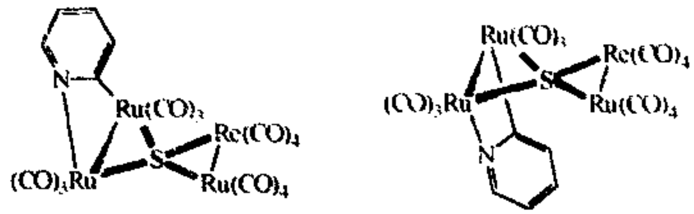
cores. Thioamide dimensions (Table 3b) broadly indicate the characteristic modification of the ligands' π-electron density following deprotonation and coordination.

Low-temperature (295–4 K) magnetic susceptibility measurements revealed the compound to be antiferromagnetic. Intra-cluster nickel–nickel interactions account for the maximum susceptibility at 60 K while a sharp decrease in the susceptibility at lower temperatures indicated the compound to have a diamagnetic ground state. Detailed analysis of the magnetic exchange parameters revealed the antiferromagnetic behaviour to be due to distortions in the cubane core induced by the 1,3-thiazolidine-2-thionate bridging ligands.

Some novel synthetic routes have been devised for the preparation of polynuclear heterometallic complexes. Some methods rely on the controlled addition of solvated metal species in order to progressively increase nuclearity. Other routes result from the development of fortuitous discoveries. Reactions involving dimeric $[Re_2(py2S)_2(CO)_6]$ and trimeric $[Ru_3(CO)_{12}]$ are in the latter category. Instead of producing dinuclear heterometallic complexes, the desired objective, tetranuclear heterometallic complexes containing various combinations of ruthenium and rhenium atoms were obtained [138–140]. Oxidative addition reactions with cleavage of pyridine-2-thionate ($>$C–S$^-$) groups and the production of complexes containing bridging sulphido, μ_4-S, and μ_2-pyridyl groups are responsible for the unexpected products. Mixtures of the complexes are obtained by heating equimolar quantities of the reactants, in refluxing xylene, followed by successive separation (TLC) into several components. These consist of yellow crystalline isomers of $[ReRu_3(\mu\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$, lemon-yellow crystalline isomers of $[Re_2Ru_2(\mu\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}py2S)(CO)_{13}]$ and orange crystalline isomers of $[Re_3Ru(\mu\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}py2S)_2(CO)_{11}]$.

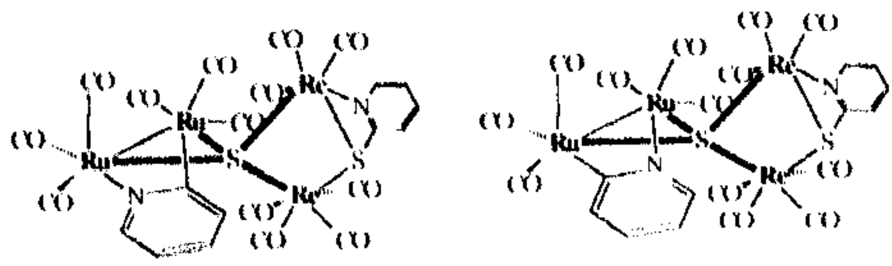
The complexes have been thoroughly characterised by means of IR, ^{1}H NMR and single-crystal X-ray methods. Production of $[ReRu_3(\mu\text{-}S)(\mu\text{-}C_5H_4N)(CO)_{14}]$ results from the thionate bond ($>$C–S$^-$) cleavage of a bridging pyridine-2-thionate ligand in the binuclear precursor. Although the hetero-trinuclear complex was originally believed to be a single product it actually exists as two interconverting, but inseparable, isomers in solution. A single crystal, obtained from a dichloromethane–hexane mixture, containing just one pure diastereoisomer as a mixture of disordered enantiomers, was used to determine the crystal structure of the complex. The molecular structure of the electron precise complex is essentially that of the isomer shown in **(LVa)**. The structure shows that the products of thionate bond cleavage, a sulphido atom and a 2-pyridyl group, bridge the metallo-carbonyl fragments in the complex. The distorted tetrahedral sulphido atom is μ_4-S bridging and links two metal–metal bonded dinuclear units. The disordered 2-pyridyl ligand bridges the metal–metal bonded $Ru_2(CO)_6$ group; metal geometry is distorted octahedral. In solution the isomeric forms of the complex result from the interchange of $Re(CO)_4$ and $Ru(CO)_4$ units **(LVa,b)**.

Two non-interconverting isomers of $[Re_2Ru_2(\mu\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}py2S)(CO)_{13}]$ were separated from diastereochemically pure samples and each was structurally classified. Their structures **(LVIa,b)** differ only in the orientation of the 2-pyridyl ligands that bridge the dinuclear $Ru_2(CO)_6$ units. Each isomer is also electron



(a) (b)
(adapted from [140])
(LV)

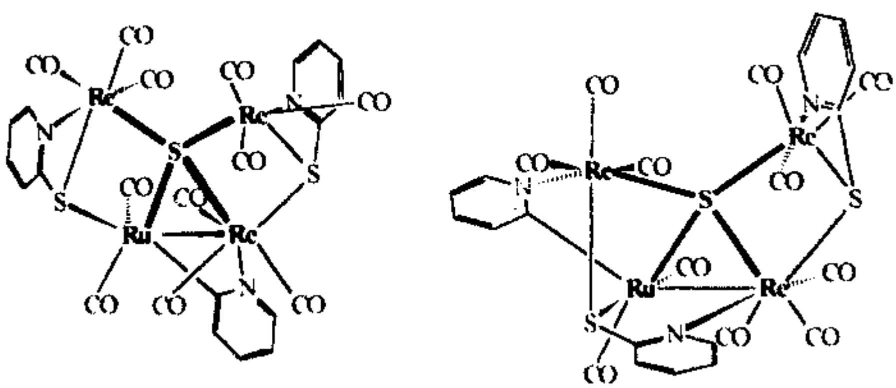
precise and contains only one metal–metal bonded pair of ruthenium atoms. The $Re_2(CO)_7$ unit is bridged by means of a binuclear triple-bridging, μ_2-S,N(η^2S;η^1N), pyridine-2-thionate ligand. Angles at the bridging thionate sulphur atom (Table 8) are similar to those of other binuclear triple-bridging ligands (Table 5). These angles are also significantly more strained than those of binuclear double-bridging, μ_2-S,N(η^1S;η^1N), ligands in other tetranuclear complexes (Table 8). Average thioamide bond distances (C–S = 1.763, C–N = 1.34 Å) are similar to those of other binuclear triple-bridging ligands (Table 2 and Table 5). The μ_4-S atom links the two metal–metal bonded dinuclear units in a distorted tetrahedral arrangement (Table 8). Metal geometry is distorted octahedral.



(a) (adapted from [140]) (b)
(LVI)

Two isomers of [$Re_3Ru(\mu$-S)(μ-C_5H_4N)(μ-py2S$)_2(CO)_{11}$] have also been isolated. The bridging pyridine-2-thionate ligands have different functions in these two electron-precise complexes. These two isomeric forms have been confirmed by crystal structure analysis. That of **(LVIIa)** shows both pyridine-2-thionate ligands to be μ_2-S,N(η^2S;η^1N) bridging. In contrast, that of **(LVIIb)** shows one ligand is binuclear μ_2-S,N(η^2S;η^1N) and the other is trinuclear μ_3-S,N(η^2-S;η^1-N) in character. Selected dimensions are given in Table 8.

In spite of geometric differences the metal atoms in both isomers have similar coordination spheres and distorted octahedral geometry. The ^{1}H NMR spectrum of each isomer is consistent with its established structure and shows the presence of three non-equivalent 2-pyridyl rings. There is severe distortion at the μ_4-S atom in both of these structures with three relatively narrow and three relatively large angles



(a) (adapted from [138]) (b)

(LVII)

in each case. Although the isomers are interconvertible, in principle, no evidence for such interconversion has been found.

These complexes demonstrate that reactions between coordinated pyridine-2-thionate ligands and polynuclear carbonyls provide a general route for the formation of strongly bound cages involving various combinations of bridging sulphido, 2-pyridyl and also pyridine-2-thionate ligands.

5. Hexanuclear and polynuclear complexes

5.1. Introduction

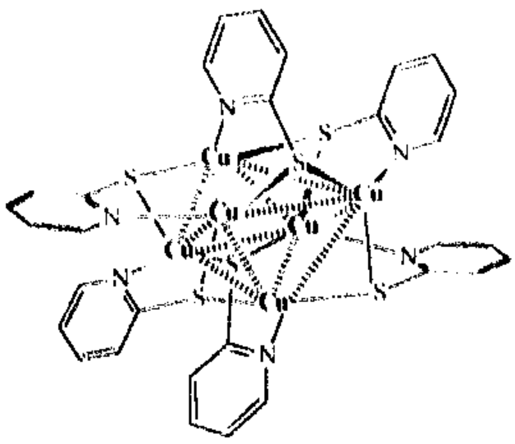
The structural diversity of metal-thiolate coordination is nowhere more evident than among complexes with six or more metal atoms [9,10]. Complexes are known with a range of metals and with up to fourteen metal atoms in the structure [9]. The corresponding series of heterocyclic thionate complexes is limited to those of the d^{10} metals copper(I), silver(I) and cadmium(II) with a maximum of twelve atoms in the structure. The ligands involved in the formation of this series of heterocyclic thionate complexes involve imidazoline-2-thionate **(IIa)**, pyridine-2-thionate **(IIc)**, pyrimidine-2-thionate **(IId)** and quinoline-2-thionate **(IIg)** derivatives.

5.2. Hexanuclear and dodecanuclear copper and silver complexes

Hexanuclear complexes have the common formulation $[\{M(\text{het-S,N})\}_6]$ (M = Cu or Ag). Preparation of the complexes involves the addition of the parent ligand with an organic base such as triethylamine, in acetone or methanol, to solutions of $[Cu(CH_3CN)_4](PF_6)$ in acetonitrile. Inert atmospheres are used in some instances [141,142]. Production of the yellow or orange products also invariably involves limiting the molar ratio (1:1) of the reactants and recrystallisation of the crude products from chlorohydrocarbon solvents such as dichloromethane. The 4,6-dimethylpyrimidine-2-thionate copper(I) complex was prepared electrochemically, in acetonitrile, from the parent ligand and a copper anode. The crude product was recrystallised in acetonitrile [143]. The hexanuclear silver(I) complex was prepared from an excess of silver nitrate [144,145].

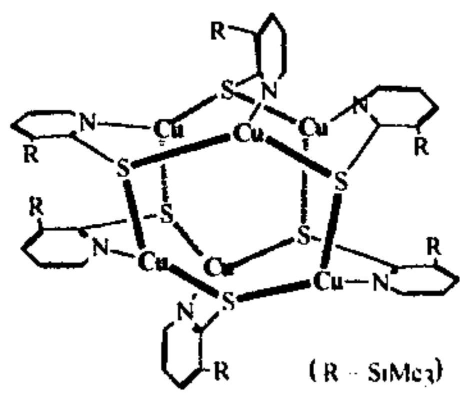
The reaction between pyridine-2-thione and copper(I) was monitored by ^{1}H NMR spectroscopy. As a result, production of several low molecular weight copper(I)/heterocyclic-thione species was revealed, in solution, prior to the formation of [{Cu(μ-py2S)}$_6$] [141]. Similar studies on the quinoline-2-thione copper(I) reaction revealed the production of polymeric [{[Cu(quin2SH)$_2$]X}$_n$] ($X=ClO_4$ or PO_2F_2) prior to the formation and production of [{Cu(μ-quin2S)}$_6$] [142]. Consequently, it would appear that deprotonation occurs with the heterocyclic ligand already thione-sulphur coordinated to copper(I) in these reactions. In addition, the ^{1}H and ^{13}C NMR spectra of [{Cu(μ-me$_2$pym2S)}$_6$] have been shown to be consistent with the solid state structure of the complex [143]. Presumably, all of the hexanuclear complexes retain their integrity in solution. Some adducts of the electrochemically generated [{Cu(μ-me$_2$pym2S)}$_6$] have been reported with 1,2-bis(diphenylphosphino)methane, and its ethane analogue. The adducts have also been characterised by NMR spectra [143].

Selected dimensions of the copper(I) and silver(I) hexanuclear complexes are given in Table 9. The structures of [{Cu(μ-py2S)}$_6$] and [{Cu(μ-3SiMe$_3$-py2S)}$_6$] are shown in **(LVIIIa and LVIIIb)**, respectively.



(a)
(adapted from [141])

All of the hexanuclear complexes occupy crystallographic centres of symmetry except [{Cu(μ-me$_2$pym2S)}$_6$]. The pyridine-2-thionate complex is typical of this group of complexes with a structure that consists of a distorted octahedral hexametallic core with six of the eight triangular trimetallic faces bridged by μ_3-S,N(η^2S;η^1N) donating pyridine-2-thionate ligands. Consequently, the hexanuclear copper(I) core has two large centrosymmetrically related *trans*-equilateral, sulphur-bridged, triangular faces. The remaining six smaller, and approximately isosceles triangular metallic faces, are all μ_3-S,N bridged. The average metal–metal



(b)

(adapted from [145])

LVIII

distance within the two *trans*-related faces (3.073 Å) is longer than the corresponding distance within the remaining six isosceles triangular faces (2.950 Å). There are no metal–metal bonds between the copper(I) atoms. Each copper(I) atom has distorted trigonal geometry and an S_2N donor set provided by three separate ligands. The thioamide nitrogen atom of the bridging ligands forms relatively short bonds with the copper(I) atoms of the hexanuclear core (Table 9). These contacts firmly anchor the bridging ligands to the trimetallic faces of the octahedral core. They also ensure that the ligands are virtually normal to the plane of the triangular faces. The thionate sulphur atoms form typically asymmetric distances and narrow (Cu–S–Cu) angles (Table 9) that are characteristic of μ_3-S,N bridging ligands (Table 7). The thionate character of the bridging ligands is characterised by C–S and C–N bonds in the region of 1.76 and 1.35 Å, respectively.

A rather novel description has been adopted for the hexanuclear silver complex that has been the result of preliminary [144] and final reports [145]. The description involves viewing the complex down the distorted C_3 axis of the metal octahedron and consists of two Ag_3S_3 rings linked by means of silver–nitrogen bonds. This alternative description has also been used to describe the analogous copper(I) complex and is shown in **(LVIIIb)**.

The crystal structures of two radically different dodecanuclear complexes of copper [146] and of silver [145] have also been reported.

The mixed-valent copper aggregate $[Cu_2Cu_{10}(\mu\text{-meimz2S})_{12}(MeCN)_4](BPh_4)_2$ [146] is obtained from $[Cu(MeCN)_4](ClO_4)$, hydrated copper acetate and 1-methylimidazoline-2(3H)-thione in an acetonitrile–methanol mixture followed by the addition of sodium tetraphenylborate. Recrystallisation from acetonitrile produces dark-blue crystals of the acetonitrile solvate. The skeletal structure of the centrosymetric cation is shown in **(LIX)** and selected dimensions are given in Table 9.

The complex cation consists of a ring of eight four-coordinate copper(I) atoms with either S_4 or S_3N donor sets from a combination of μ_3-S_2N and μ_4-S_3N bridging ligands. Two further copper(I) sites are three-coordinate with N_3 donor sets formed

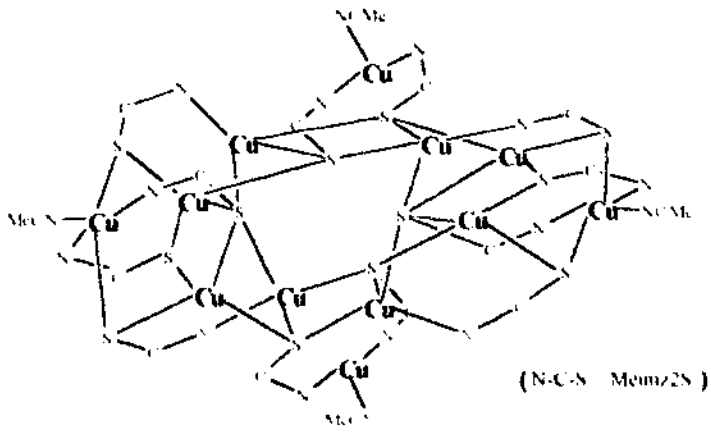
Table 9
Hexanuclear and dodecanuclear complexes of copper(I) and silver(I); selected dimensions (Å and °)

►Complex and reference Metal core dimensions	Ligand generated angles at the metal	M–S	M–N	M–S–M
$[\{Cu(py2S)\}_6]^a$ [141]				
2.795(1)–3.160(1)	109.7(2)–124.8(2)	2.220(2)–	2.024(6)–	NR
51.85(3)–91.99(4)	2.249(2)	2.041(7)		
$[\{Cu(quin2S)\}_6]^a$ [142]				
2.786(2)–3.151(2)	113.5(1)–121.9(2)	2.243(3)–	2.034(7)–	87.97(9)–
55.34(4)–90.16(6)		2.260(3)	2.047(7)	88.67(9)
$[\{Cu(me_2pym2S)\}_6]^b$ [143]				
2.711(2)–3.433(2)	105.6(1)–133.0(2)	2.212(3)	2.016(8)–	NR
48.62(5)–93.43(5)		2.279(3)	2.025(8)	
$[\{Cu(3SiMe_3\text{-}py2S)\}_6]^a$ [144]				
$3.139_{(average)}$	112.1(2)–119.2(1)	2.236(2)–	2.019(9)	82.6(1)–
		2.254(2)	2.041(5)	88.5(1)
$[\{Ag(3SiMe_3\text{-}py2S)\}_6]^a$ [144]				
$3.323_{(average)}$	117.0(2)–124.8(2)	2.474(2)	2.300(6)	77.4(1)
		2.479(2)	2.312(9)	83.9(1)
$[\{Ag(3SiMe_3\text{-}py2S)\}_6]^a$ [145]				
$3.157_{(average)}$	109.7(3)–126.1(1)	2.464(3)	2.300(10)–	NR
$3.016_{(average)}$		2.495(3)	2.321(10)	
$[Ag_8(3SiMe_3\text{-}py2S)_6][AgNO_3]_2 \cdot 2CH_3OH \cdot CH_2Cl_2^a$ [145]				
2.856(1)–3.660(1)	84.0(2)–171.6(2)	2.382(3)	2.179(5)	NR
		2.784(2)	2.208(5)	
		Ag–O = 2.360(7)	2.624(5)	
$[Cu(I)_{10}Cu(II)_2(meimz2S)_{12}(MeCN)_4](BPh_4)_2 \cdot (MeCN)_3^a$ [146]				
2.547(1)–2.724(1)	150.9(1)–175.4(3)	2.280(2)	1.867(8)	NR
		2.645(2)	1.984(4)	

NR not reported.
[a] Symmetrical molecule.
[b] Two independent molecules in the unit cell.

by a combination of two heterocyclic ligands and an acetonitrile molecule. The copper(II) sites are five-coordinate with *trans*-N_2S_2 donor sets from four heterocyclic ligands and a terminal acetonitrile nitrogen atom. The copper(II) atoms are magnetically free from other interactions and have electronic ($\lambda = 635$ nm) and ESR spectra similar to those of the copper "blue" proteins.

Production of the mixed-valent complex depends on a rather complicated copper(II)-thione reduction process and subsequent stabilisation of the copper(II) sites at the extremities of the copper(I)-thionate matrix. [147]. Furthermore,

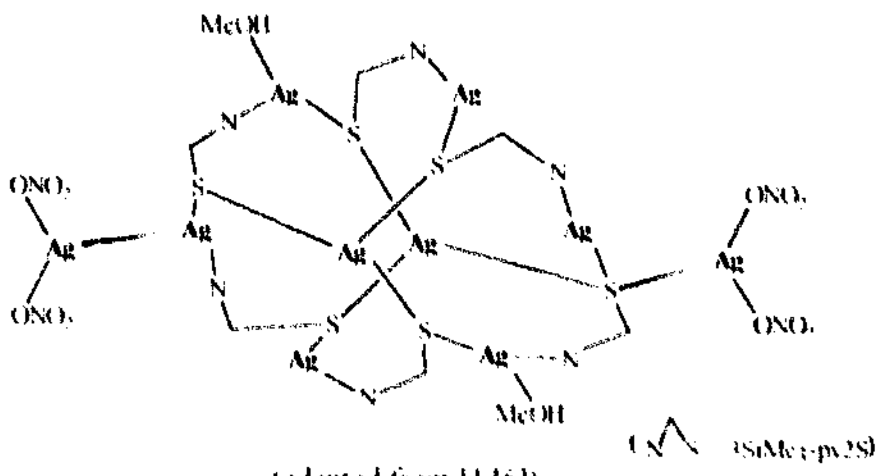


(adapted from [146])

LIX

a detailed study of the reactions between hydrated copper acetate and 1-methylimidazoline-2(3H)-thione has shown that the solvated cations $[Cu_2Cu_{10}(\mu\text{-meimz2S})_{12}(solvent)_4]^{2+}$ are remarkably stable in solution [148].

Production of the dodecanuclear silver(I) complex $[Ag_8(\mu\text{-3SiMe}_3\text{-py2S})_6][Ag(NO_3)_2]_2 \cdot 2CH_3OH \cdot CH_2Cl_2$ [145] relies upon the use of a bulky substituent in the pyridine-2-thionate anion to control the degree of aggregation [144]. In contrast to the production of the corresponding hexanuclear silver(I) complex, which relied on the use of excess 3-trimethylsilylpyridine-2-thione, successful production of the dodecanuclear complex relies on the use of an excess of silver(I) nitrate under otherwise identical conditions. A skeletal version of the structure is shown in (**LX**) and selected dimensions are given in Table 9.



(adapted from [145])

LX

The structure consists of an octanuclear complex cation $[Ag_8(\mu\text{-3SiMe}_3\text{-py2S})_6]^{2+}$ associated, by means of secondary interactions, to two complex anions $[Ag(NO_3)_2]^-$ and two methanol molecules. The complex is crystallographically centrosymmetric and consists of five chemically and structurally distinct silver sites. Four of the silver sites have distorted trigonal geometry. Two of these arrangements involve an S,N donor set from different ligands plus a long contact to a nitrate oxygen atom. A third contact involves an S_3 donor set from three different ligands. The fourth site involves a combination of one thionate sulphur and two contacts to nitrate oxygen atoms. The fifth silver site is diagonally coordinated by an S,N donor set from two different ligands.

The eight silver atoms of the central metallic core adopt a hexagonal bipyramidal arrangement with the two silver atoms of the $[Ag(NO_3)_2]^-$ anions associated as two interacting arms. The bridging heterocyclic thionate ligands are either μ_3-S_2N or μ_4-S_3N donating and are disposed as three above and three below the equatorial plane of the metallic core. Alternate "spokes" to the axial silver sites from the equatorial sites are bridged by thionate sulphur atoms while the thioamide nitrogen atoms bridge the adjacent silver sites of the hexagonal plane. Axial silver sites have trigonal-planar geometry and an S_3 donor set. Equatorial silver sites have S,N donor sets that are distorted by secondary interactions.

5.3. Hexanuclear and polynuclear cadmium(II) complexes

A number of heterocyclic thionate ligands have been reported to form neutral complexes with cadmium(II) of general formulation [Cd(het-S,N)$_2$] [149]. Apart from spectroscopic evidence implicating involvement of the thioamide sulphur and nitrogen atoms the complexes were mostly described as polymeric with S,N-bridging ligands. In contrast, many structural types have been characterised for cadmium(II) complexes with thiolate ligands ranging from mononuclear to dodecanuclear species as well as non-molecular solids [150].

One of the observations of general applicability resulting from the work on thiolate complexes is the ability of bulky ligands to stabilise mononuclear and small oligomeric species. This principle has been applied to the successful production of cadmium complexes with heterocyclic thionates.

The electrochemical method used in the successful synthesis of the hexanuclear complex [{Cu(μ-me$_2$pym2S)}$_6$] [143] has been adapted for the synthesis of a range of nickel(II) and cadmium(II) complexes by using either elemental nickel or cadmium as the sacrificial anode [151]. Mixed ligand complexes of both metals were obtained by the usual method of adding 2,2′-bipyridyl or 1,10-phenanthroline to the electrolysing medium. The nickel(II) complexes, of general formula [Ni(me$_2$pym2S)$_2$(N,N-chel)], are spectroscopically typical of tris-chelates with distorted octahedral geometry. In addition, crystalline [Cd(me$_2$pym2S)$_2$] has also been obtained and its crystal structure determined. The calixerene-like skeletal structure is shown in (**LXI**) and selected dimensions are given in Table 10.

The complex consists of discrete hexanuclear [{Cd(μ-me$_2$pym2S)$_2$}$_6$] species with imposed crystallographic C_3 symmetry. The separation distances between the cadmium(II) atoms (ca. 3.716 Å) preclude metal–metal bond formation. The regular non-planar hexagon of cadmium(II) atoms is bridged above and below the plane by twelve μ_3-S,N(η^2S:η^1N) donating ligands. The thionate sulphur atoms belong

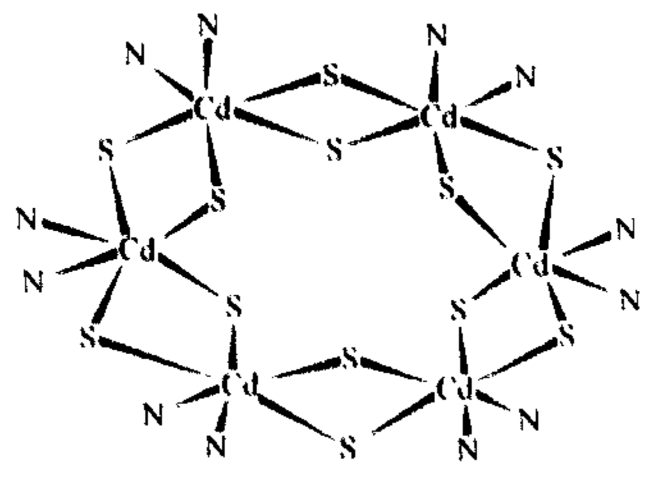
Table 10
Polynuclear complexes of cadmium(II); selected dimensions (Å and °)

Cd–S	Cd–N	S–Cd–S(N)	Cd–S–Cd	Cd–S–C	Cd–N–C
$[\{Cd(me_2pym2S)_2\}_6]^a$ [151]					
2.638(8)– 2.761(8)	2.36(2)– 2.38(2)	60.4(8)– 168.0(2)	86.4(2) 88.9(2)	100(1) 106(1)	103(2) 104(3)
$[\{Cd(py2S)_2\}_n]^a$ [152]					
2.543(5)– 2.809(4)	2.342(4)– 2.343(4)	57.2(2)– 103.4(3)	NR	NR	NR
$[\{Cd(bztz2S)_2\}_n]^a$ [152]					
2.547(4)– 3.061(5)	2.283(4)– 2.328(3)	57.7(3) 96.8(3)	NR	NR	NR

Complex and reference given in the first column of each group.

NR not reported.
[a] Symmetrical molecule.

to two sets of six, each set being approximately planar, with three atoms above and three below the plane. These planes are mutually parallel and are also parallel with the best mean-plane through the six cadmium(II) atoms. Each cadmium atom has distorted octahedral geometry and *cis*-S_4N_2 coordination with *cis*-thioamide nitrogen atoms. The donor set is formed from two bridging ligands and two additional thionate sulphur atoms from two other ligands that bridge other cadmium(II) atoms. The bridging thionate sulphur atoms also generate Cd_2S_2 units with narrow angles at the metal and asymmetric metal sulphur distances. The plane of the bridging ligand is almost normal to that of the Cd_2S_2 unit (Table 10). Angles at the metal generally show substantial deviation from those expected of regular octahedral geometry.

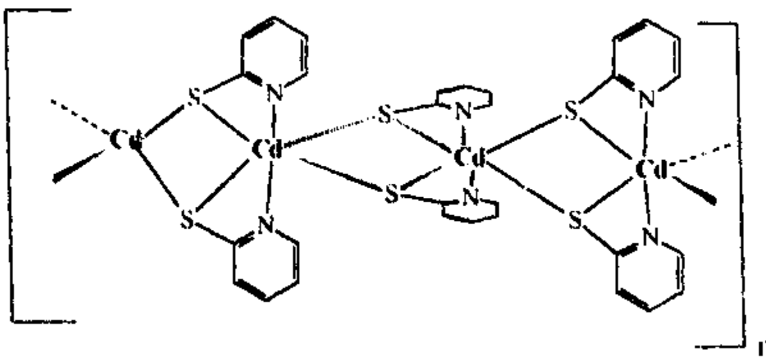


(adapted from [151])

LXI

Average thioamide dimensions of the bridging ligands (C–S = 1.71, C–N = 1.38 Å; N–C–S = 114°) are consistent with the extension and contraction of the relevant bonds in the parent ligand (Table 2).

The addition of stoichiometric quantities of pyridine-2-thione and benz-1,3-thiazoline-2-thione to aqueous solutions of cadmium acetate produces polymeric complexes [152]. Crystalline products were obtained by slow recrystallisation of the crude products from either hot pyridine (py2S) or dimethylformamide (bztz2S). The complexes sublime (150 °C) at low pressure and decompose to cadmium(II) sulphide (CdS) on heating in air. Both complexes occupy crystallographic C_2 axes. They are genuine polymeric substances with approximately octahedral metal geometry. The N_2S_4 donor sets are formed by μ_2-S,N(η^2S;η^1N) bridging ligands. Selected dimensions are given in Table 10 and the structure of the pyridine-2-thionate complex is shown, in part, in (**LXII**).



(adapted from [152])

LXII

In the pyridine-2-thionate complex one pair of bridging ligands is approximately parallel and one pair is approximately normal to the polymer chain. The perpendicular ligand is S,N-coordinating to one cadmium atom and also S-bridges the adjacent, symmetry-related cadmium atom. The second, parallel ligand, similarly bridges two cadmium atoms but with slightly longer cadmium–sulphur (3.04 Å) distances. The sequence of asymmetric Cd_2S_2 units form the essential repetitive core of the polymeric chain. The benz-1,3-thiazoline-2-thionate complex is structurally similar to that of the pyridine-2-thionate complex.

6. Summary

This is the fourth in a series of reviews that have sought to establish the factors that govern the coordination chemistry of heterocyclic thiones and thionates [1,149,153]. Consequently, this is a convenient point to summarise the major observations resulting from these reviews.

With the thione form of the parent molecules dominant in neutral, polar and acidic media their coordination chemistry is limited to thione-sulphur coordination in either monodentate thione sulphur, (η^1-S), or binuclear, μ_2-S(η^2-S), double-bridging modes. The latter invariably generate asymmetric metal–sulphur contacts with narrow angles at the thione sulphur atom. Of all the donor characteristics of these molecules monodentate (η^1-S) coordination is the most widespread throughout the periodic table.

The neutral molecules are only involved in S,N-coordination when they possess an additional heterocyclic nitrogen atom adjacent to the thioamide group. Such arrangements occur in pyrimidine-2-thione derivatives. Previous proposals that the thioamide nitrogen atoms of neutral heterocyclic thione molecules, such as 1,3-thiazolidine-2-thione, are also monodentate nitrogen donors, are spurious.

Although the structures of the parent molecules are dominated by thione tautomers a variable degree of delocalisation of the thioamide π-electron density is also evident. Among imidazole-2-thione derivatives, for instance, the distribution amounts to about 50% π-character in the exocyclic carbon–sulphur bonds. This proportion is reduced, on average, by about 13% on the formation of either monodentate (η^1-S) or double-bridging (μ_2-S) contacts.

Deprotonation, as the most recent reviews have shown, substantially enhances the coordination potential of the molecules particularly towards the heavier metals. The most extensive coordination mode of heterocyclic thionates involves the formation of four-membered S,N-chelates. These generate short metal–nitrogen bonds, relatively long metal–sulphur bonds, narrow chelating angles and mostly planar chelate rings. Monodentate thionate, (η^1-S) coordination, is also known although it is limited to large "soft" acceptors. Monodentate nitrogen coordination is even more limited in scope than that of monodentate thionate (η^1-S) coordination.

Heterocyclic thionates form μ-S,N bridged complexes that also involve short metal–nitrogen bonds with the electron rich thionate sulphur atoms providing geometrically flexible contacts to the neighbouring metal, or metals, as required.

The distribution of complexes with μ-S,N bridging heterocyclic thionates follows the sequence:

$$\mu_2-\mathrm{S,N(double-bridging)} \gg \mu_2-\mathrm{S,N(triple-bridging)} \sim \mu_3-\mathrm{S,N} \gg \mu_4-\mathrm{S,N}$$

The predominance of the binuclear double-bridging, μ_2-S,N species, probably arises because it represents the least geometrically and electronically demanding of all the bridging systems. Consequently, this series of complexes, with between two and four bridging ligands, modest coordination numbers at the metal and occasional metal–metal bonded species, is structurally the best defined. The solution chemistry of the complexes has also been profitably investigated, in some cases.

In contrast, binuclear triple-bridging is much less common. Furthermore, the benefits of additional ligand donor capacity, exhibited by this system, are offset by longer metal–metal distances. Further disadvantages include added geometrical complexity and crowding, especially in the centre of what are invariably double-bridged complexes. Nevertheless, the structural possibilities generated by this bridging mode in the solid, as well as an example of some novel rearrangements in solution, have been characterised.

As has been observed for thiolate chemistry, increased polynuclearity among heterocyclic thionate complexes is accompanied by the formation of progressively fewer examples. Consequently, the total number of polynuclear complexes is significantly less than those of binuclear species. The structural diversity of the established tri-, tetra- and hexa-nuclear complexes arises mostly from the variations in metal–ligand combinations, which are by no means exhausted, and the extensive use of μ_3-S,N five-electron donating anions about a central metal core. Occasional examples, in which μ_2-S,N double-bridging, three-electron anions, are also involved, add to the structural diversity. Polymeric systems are extremely rare and invariably involve either μ_3-S,N or μ_4-S,N bridging anions. The longest of the three metal–sulphur contacts formed by the μ_4-S,N anions is inter-molecular in character and enables the concatenation of neighbouring metallic cores into oligomeric and polymeric species. This bridging mode could prove to be extremely useful in the design of new materials in the future, especially if it could be used to concatenate metal–metal bonded clusters.

With limited exceptions the structural consequences of additional electron involvement are indicated by increased angular variations at the sulphur atom rather than by significant increases in metal–sulphur bond lengths. However, the ligand bites generally remain unaffected by increases in the total electron involvement of the anion, despite substantial changes to the thioamide (N–C–S_{exo}) angle, in some instances.

The effects of deprotonation and coordination on the thioamide dimensions of the anions are universal. They consist of the accumulation of both anionic charge at the thionate sulphur atom and of π-electron density in the carbon–nitrogen bond. In addition, the narrow thioamide angles of six-membered heterocyclic molecules are more distorted than are the larger values of five-membered molecules. Furthermore, among thiazole-2-thionate derivatives, and similar molecules containing overlapping thioamide groups, the effects of deprotonation and coordination are more extensive than they are among molecules in which the thioamide portion is more localised. All of the carbon–sulphur bonds in thiazole derivatives lose π-electron density to the carbon–nitrogen bond. It would appear that perturbation of the coordinating thionate portion of such molecules subsequently affects all of the heterocyclic bonds in the molecule.

The chemical integrity of heterocyclic thiones and thionates is generally retained during coordination processes. However, heterocyclic thiones may be oxidised with the production of N,N-donating disulphides and monosulphides as well as S,N-donating heteroyl substituted heterocyclic thiones. While heterocyclic thionates are resistant to such oxidation they may be induced to undergo fission of the thionate ($>$C–S$^-$) bonds with the production of C,N-chelating heteroyl species and polydentate sulphide ions.

With the structural principles governing the coordination chemistry of heterocyclic thionates now more apparent and a wider range of preparative routes also available it should now be possible for synthetic strategies to be planned with more certainty than before. Biomimetic activity and the design of new materials, as well as an intrinsic interest in the controlled coordination chemistry of these ligands, will undoubtedly drive the subject forward. What is still lacking from this scenario however is complete control of the reactants/products process. There will undoubtedly be plenty of surprises in store.[15,34]

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