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THIOLATO-COMPLEXES OF THE TRANSITION METALS

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CONTENTS

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A. INTRODUCTION

This review aims to survey the transition metal thiolato-complexes containing a high proportion of thiolate sulphur in the coordination sphere. The literature coverage is approximately to May 1985. To keep the account within reasonable bounds, an arbitrary lower limit of thiolate sulphur comprising 50% of the coordinated atoms has been chosen. This is justified in that if less than 50% of the ligand atoms are thiolate sulphur then the other ligands are likely to dominate the properties of the complex, or at least obscure the role of the thiolato-ligands. The compounds that qualify for inclusion on this basis illustrate all of the notable properties of thiolato-ligands, and in any case complexes in which only a minor proportion of the ligands are thiolates are far too numerous and disparate to be drawn together in a useful way. Departure from the arbitrary limit will only be made when required to illustrate features of metal thiolate chemistry of particular interest. Complexes with "1,2-dithiolene" and 1,1-dithiolato-ligands have not been included since their structural and electronic properties are often largely a result of the characteristic π-delocalisation in such ligands, and in any case their chemistry has been reviewed elsewhere [1]. Other reviews of relevance usually cover sulphur ligands in general without special reference to thiolates [2–9].

The review is divided into sections according to the principal mode of ligation of the thiolates, i.e. terminal, μ^2-bridging,, μ^3-bridging and finally a discussion of general chemical and electronic properties of thiolato-complexes, making comparisons with conclusions about divalent sulphur bonding drawn from organosulphur chemistry where appropriate.

B. COMPLEXES WITH TERMINAL THIOLATO-LIGANDS

(i) Mononuclear homoleptic complexes with mono- and bi-dentate thiolates

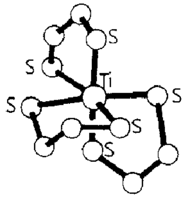
The known mononuclear homoleptic thiolato-complexes are summarised in Table 1. The only reported six-coordinate homoleptic thiolato-complexes are the anions $[M(SCH_2CH_2S)_3]^{n-}$ (M=Nb, n=1 [10], Ti, n=2 (**1**) [11]) and $[Re\{(SCH_2)_3CCH_3\}_2]^-$ (**2**) [11a]. The X-ray crystal structures of the anions

TABLE 1

Mononuclear homoleptic thiolate complexes

Complex	SR	Structure [a]	References
$[Nb(SCH_2CH_2S)_3]^-$		intermediate octahedral trigonal prismatic	10
$[Ti(SCH_2CH_2S)_3]^{2-}$		trigonal prismatic	11
$[Cr(SCH_2CH_2S)_2]^{2-}$		planar	11
$[Mo(SBu^t)_4]$		distorted tetrahedral	13
$[Mn(SR)_4]^{2-}$	SPh	distorted tetrahedral	18, 19, 20
	$\frac{1}{2}(SCH_2CH_2S)$	distorted tetrahedral	19, 28
$[Re\{(SCM_2)_3CCH_3\}_2]^-$		trigonal prismatic	11a
$[Fe(SR)_4]^{2-}$	SPh	distorted tetrahedral	17, 18
	SEt		31
	$\frac{1}{2}$(S_2-*o*-xylyl)	tetrahedral	25, 26
$[Fe(SR)_4]^-$	Boc–(Gly–L–Cys–Gly)$_4$–NH_2		30
	SPh, SEt, SCH_2Ph, SBu^t	distorted tetrahedral	24
	1/2(S_2-*o*-xylyl)	tetrahedral	25, 26
$[Co(SR)_4]^{2-}$	SPh	distorted tetrahedral	18, 20, 21
	SEt		33
	SC_6H-2,3,5,6-Me_4, 1/2(SCH_2CH_2S)		11
	1/2(S_2-*o*-xylyl)		25
	SC_6F_5		
$[Co(SCH_2CH_2S)_2]^-$		planar	11
$[Ni(SR)_4]^{2-}$	SPh	distorted tetrahedral	18, 20
	SC_6F_5		21
	SC_6Cl_5		43
	$\frac{1}{2}(SCH_2CH_2S)$		36a
$[Pd(SR)_4]^{2-}$	SC_6F_5		39, 40
	SC_6Cl_5		43
$[Pt(SC_6F_5)_4]^{2-}$			39, 40, 41
$[Cu(SPh)_3]^{2-}$		trigonal planar	37, 38
$[Cu(SR)_2]^-$	SC_6F_5		39, 40
$[Ag(SC_6F_5)_2]^-$			39, 40
$[Au(SR)_2]^-$	SMe, SBu^t, SPh		42
	SC_6F_5		39, 40, 41
$[Au(SC_6F_5)_4]^-$			41
$[Zn(SR)_4]^{2-}$	SPh	distorted tetrahedral	18, 20
	SC_6F_5		21, 39, 40
	SC_6Cl_5		43
$[Zn(SPh)_2]$			21
$[Cd(SR)_4]^{2-}$	SPh	distorted tetrahedral	20
	SC_6F_5		39, 40
$[Hg(SR)_4]^{2-}$	SPh		22
	SC_6H_4-4-Cl	distorted tetrahedral	23
$[Hg(SPh)_3]^-$			22
$[Hg(SR)_2]$	SEt	linear	46, 49
	SPr^n, $Samyl^n$, $Shexyl^n$, $Sheptyl^n$, $Soctyl^n$		44
	SBu^n, SPh		49
	SC_6H_4-4-Me	linear	47
	$SCH_2CH(S)CH_2CH_2OH$		49

show them to have a geometry intermediate between trigonal prismatic and octahedral, with trigonal twist angles from the pure prismatic structure of 33°(Nb), 35–40°(Ti) and 6°(Re). It would therefore appear that the tendency towards trigonal prismatic coordination exhibited in the 1,2-dithiolene complexes [1] is not entirely due to the ligand unsaturation. Another interesting feature of these complexes is that the metals are in high formal oxidation states in spite of the strong reducing ability of thiolates apparent with complexes of other metals. This probably reflects the highly reducing nature of the Nb(IV) or Ti(III) dianion. (Ep^{red} for $\mathrm{Ti(IV)} \rightarrow \mathrm{Ti(III)} = -2.0$ V vs. SCE in MeCN) [11].



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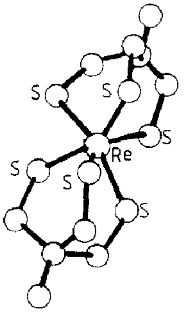

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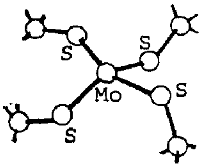
Homoleptic thiophenolato-complexes $[\mathrm{Ti(SPh)_4}]$, $[\mathrm{Zr(SPh)_4}]$, $[\mathrm{Nb(SPh)_5}]$ and $[\mathrm{Ta(SPh)_5}]$ have been reported. They are soluble in donor solvents but there is no structural evidence concerning their nuclearity. Their reported preparations are unusual in that the source of thiolate is $\mathrm{Al(SPh)_3 \cdot Et_2O}$ [12].

All of the four-coordinate homoleptic thiolato-complexes structurally characterised have approximate tetrahedral structures distorted to varying degrees towards D_{2d} symmetry. Group VI is represented only by planar $[\mathrm{Cr(SCH_2CH_2S)_2}]^{2-}$ [11] and tetrahedral $[\mathrm{Mo(SBu^t)_4}]$ [13]. The synthesis of the latter complex is critically solvent dependent, involving the reaction of $\mathrm{MoCl_4}$ with $\mathrm{LiSBu^t}$ in 1,2-dimethoxyethane. The X-ray structure (**3**) of this compound shows it to be a tetrahedron distorted towards approximate D_{2d} core symmetry. This distortion is apparently sufficient to render the complex diamagnetic, and has been ascribed to an interaction between a sulphur $3p$ lone pair and the vacant metal d_{z^2} orbital. This gives rise to the observed "W"-configuration (**4**) with a small S–Mo–S angle of 95.6(1)°.

This view, however, is inconsistent with the results of ultraviolet photoelectronic and theoretical studies [14] (see below). The X-ray structure (**3**) can be described in terms of two of these planar "W"-units intersecting orthogonally ("double-W" structure), giving rise to two distinct S–Mo–S angles of ca. 117° and 96°. The rather large Mo–S–C bond angles



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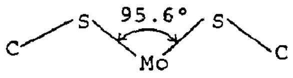

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(116–119°) result from repulsion between the molybdenum and the bulky $\mathrm{Bu^t}$ groups, which may also contribute to the narrowing of the S–Mo–S angle within each "W" structure. The Mo–S bond lengths (2.235(3) Å) are among the shortest known for molybdenum thiolato-complexes. $[\mathrm{Mo(SBu^t)_4}]$ is a reactive material but in most cases the $\mathrm{Mo(SBu^t)_4}$ unit is not retained in the products. Some of the reported reactions are summarised by eqns. 1, 2, 3 [15] and 4 [16].

$$[\mathrm{Mo(SBu^t)_4}] + 4\ \mathrm{Bu^tNC} \rightarrow cis\text{-}[\mathrm{Mo(SBu^t)_2(CNBu^t)_4}] + \mathrm{Bu^tSSBu^t} \qquad (1)$$

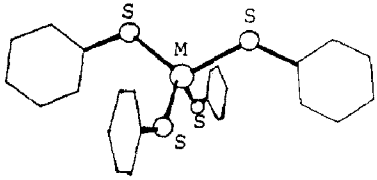
$$2[\mathrm{Mo(SBu^t)_4}] + 8\ \mathrm{CO} \rightarrow [\mathrm{Mo_2(\mu\text{-}SBu^t)_2(CO)_8}] + 3\ \mathrm{Bu^tSSBu^t} \qquad (2)$$

$$2[\mathrm{Mo(SBu^t)_4}] + 2\ \mathrm{PMe_2Ph} \rightarrow [\mathrm{Mo_2(\mu\text{-}S)_2(SBu^t)_4(PMe_2Ph)_2}] + 2\ \mathrm{Bu^tSH} + 2\ \mathrm{CH_2{=}CMe_2} \qquad (3)$$

$$[\mathrm{Mo(SBu^t)_4}] + [\mathrm{CuBr(CNBu^t)_3}] \rightarrow [\mathrm{(Bu^tNC)_4Mo(\mu\text{-}SBu^t)_2CuBr}] + \text{byproducts} \qquad (4)$$

Several features common to the chemistry of metal thiolato-complexes are illustrated by these reactions, viz. ligand oxidations by the metal to give a disulphide (eqns. 1 and 2) dealkylation of coordinated alkanethiolates (eqn. 3), cleavage of the metal–sulphur bond to give thiol or thiolate (eqns. 3 and 4) and the bridging ability of thiolato-ligands (eqn. 4). The complexes $[\mathrm{M(SPh)_4}]^{2-}$ are well characterised for M=Mn [18–20], Fe [17,18], Co [18,20,21], Ni [18,20], Zn [18,20], Cd [20], and Hg [22,23]. All are tetrahedral and have a similar "double W" configuration to $[\mathrm{Mo(SBu^t)_4}]$, with the coplanarity within the "W" subunit extended to include the phenyl groups. This arrangement allows an interaction between S(3p) and $\mathrm{M}(nd_{z^2})$ and $((n+1)p_z)$ orbitals while the sulphur is conjugated to the aromatic ring, i.e. a partial contribution from sp^2 hybridisation at sulphur which is sufficient to impose coplanarity (**5**) in spite of the steric preference for a configuration (**6**) in which the Ph ring is perpendicular to the Me–S–C plane. Thus in these cases electronic factors appear to outweigh steric factors in defining the structure.

Like $[\mathrm{Mo(SBu^t)_4}]$, all the complexes $[\mathrm{M(SPh)_4}]^{2-}$ show to varying de-



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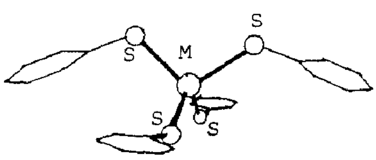

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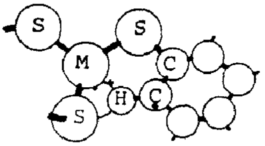
grees a distortion towards D_{2d} symmetry, involving a diminution of the angle θ within the "W" planes (**8**). A bonding interaction between Mo($4d_{z^2}$) and S($3p$) orbitals invoked to account for this in the case of [Mo(SBu^t)$_4$] [13] is inconsistent with MO calculations on the hypothetical complexes [Mo(SH)$_4$] and [Mo(SMe)$_4$] and UV-PES studies on [Mo(SBu^t)$_4$] [14], which suggest that the HOMO consists largely of Mo($4d_{z^2}$), with small contributions from S($3p$) and S($3d$). The principal contribution to the distortion is more likely to be the result of steric interaction between methyl hydrogens and metal and sulphur atoms causing the angle θ to be diminished and ϕ to be increased (**7**), (**8**).



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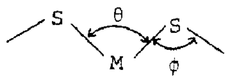

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This is a similar interaction to that described by Coucouvanis et al., to account for the same type of distortion observed in [Fe(SPh)$_4$]$^{2-}$ [17], and presumably applies to other complexes of general type [M(SPh)$_4$]$^{2-}$ (**7**). It seems unlikely that in the [M(SPh)$_4$]$^{2-}$ complexes the distortions arise entirely from the *ortho*-hydrogen steric interactions since examination of the structural data reveals no correlation between M–S distances and the degree of deviation from tetrahedral geometry. It may be significant that the largest distortion is observed for [Ni(SPh)$_4$]$^{2-}$, since four-coordinate Ni(II) ions are most likely to be square planar. The similarity of the distortion for the thiophenolate complexes of Mn, Co, Cd, Zn and Ni, as the tetraphenylphosphonium salts, which are all isomorphous, suggests that there may be a contribution from crystal packing effects. However, the same distortion occurs in the tetramethylammonium salt [NMe$_4$]$_2$[Hg(SC$_6$H$_4$-4-Cl)$_4$] [23]. It seems that, since no systematic variation can be found in these distortions, the conformations are due to combinations of electronic interactions between metal and ligands (other than simple σ-bonds), steric effects, crystal packing effects and, in some cases, a possible Jahn–Teller effect. With reference to the steric contribution it is notable that $[Fe(SEt)_4]^-$ [24], $[Fe(S_2\text{-}o\text{-xyl})_2]^-$ and $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ [24,26] (which have no hydrogens in close proximity to metal or other ligand atoms) and $[Fe(SC_6H\text{-}2,3,5,6\text{-}Me_4)_4]^-$ [27] (in which, paradoxically, the steric bulk of the *ortho*-substituents removes the source of the distortion by imposing a different ligand orientation) show only small deviations from tetrahedral geometry.

The $[Mn(SCH_2CH_2S)_2]^{2-}$ anion [19] also has a distorted tetrahedral MS_4 coordination unit of approximate D_{2d} symmetry. The observed geometry is presumably due to the small bite angle of the bidentate ligand. This complex is oxygen sensitive, being oxidised to the dimeric Mn(III) species $[Mn_2(SCH_2CH_2S)_4]^-$, which is partially dissociated in solution to give solvated mononuclear monoanions. The dimer is irreversibly reduced at a cathode to give ultimately $[Mn(SCH_2CH_2S)_2]^{2-}$ [19,28].

Considerable interest has focused on the synthesis and physical properties of tetrahedral thiolato-complexes of Fe(II) and Fe(III), principally in an effort to model the spectroscopic and electrochemical properties of the Fe centre of the redox active rubredoxins [29]. The protected polypeptide ligand Boc–(Gly–L–Cys–Gly)$_4$–NH_2, which contains four cysteinyl thiol groups, has been used to form an Fe(II) complex, solutions of which after exposure to air show good spectroscopic similarity to the oxidised form of rubredoxin (Rb_{ox}) [30]. The anionic species $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ and $[Fe(S_2\text{-}o\text{-xyl})_2]^-$ [25] have inner core geometries close to tetrahedral, as reflected in the range of S–Fe–S angles (103.5(2)–114.9(2)°) for the Fe(II) dianion and 105.82(7) to 112.60(8)° for the Fe(III) monoanion. The major difference between the two structures is the decrease in mean Fe–S distance from Fe(II) to Fe(III) of 0.089(13) Å. This difference also gives rise to a slight conformational change in the chelate rings.

The electronic properties of $[Fe(SPh)_4]^{2-}$ [17], $[Fe(S_2\text{-}o\text{-xyl})_2]^-$ and $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ [25,26] have been the subject of considerable study. $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ is converted to $[Fe(S_2\text{-}o\text{-xyl})_2]^-$ by reaction with dioxygen and by a reversible one-electron electrochemical oxidation [25]. $[Fe(SPh)_4]^{2-}$ can also be reversibly oxidised electrochemically to $[Fe(SPh)_4]^-$ [31]. Results of Mössbauer [31], electronic spectra, magnetic susceptibility and e.p.r. measurements lead to the conclusion that the electronic states of these complexes and rubredoxin are closely similar in their corresponding oxidation states [17,25].

The reactions involved in synthesis of these mononuclear iron species are not trivial, with complications due to reduction to Fe(II) by monothiolates and concentration-dependent equilibria between mononuclear species and species of higher nuclearity (see section C(ii)(d)) containing bridging thiolato-ligands [25,32,33].

It has been demonstrated that the complexes $[Fe(SR)_4]^{2-}$ (R = Ph, Et) can act as precursors in the sequential synthesis of Fe–S protein analogues from mononuclear iron–sulphur species through sulphido-bridged dinuclear species to the tetranuclear Fe_4S_4 clusters. Thus, $[Fe(SPh)_4]^{2-}$ is the first identifiable intermediate in the cluster synthesis based on solutions containing $FeCl_3$, PhS^- and elemental sulphur, if more than a five-fold excess of PhS^- is present. The reaction in acetonitrile then proceeds by incorporation of sulphur to give $[Fe_2S_2(SPh)_4]^{2-}$, which can react further with sulphur in methanol solution to give $[Fe_4S_4(SPh)_4]^{2-}$ [34]. Similar sequential steps in cluster formations have been demonstrated for $[Fe(SEt)_4]^{2-}$ [35]. $[Fe(S_2\text{-}o\text{-}xyl)_2]^-$ is also reactive towards sulphide sources, affording $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ on reaction with sodium hydrosulphide [36].

Except for $[Ni(SPh)_4]^{2-}$, homoleptic mononuclear thiolato-complexes of the nickel subgroup are not well characterised. Although $[Ni(SPh)_4]^{2-}$ displays a greater distortion from ideal tetrahedral geometry [18,19] than analogous complexes of other metals, it still does not approach the square-planar geometry characteristic of d^8 species. A square-planar geometry for $[Ni(SC_6F_5)_4]^{2-}$ has been inferred from its diamagnetism [21], but in the light of the subsequent structural characterisation of $[Ni(SPh)_4]^-$ it seems unnecessary to invoke such an extreme distortion from tetrahedral. The anion $[Ni(SCH_2CH_2S)_2]^{2-}$ has been detected spectrophotometrically in solution and its equilibrium with $[Ni_2(SCH_2CH_2S)_3]^{2-}$ has been studied [36a]. However, it has not been isolated and characterised as a crystalline material.

The coordination number for homoleptic monomeric copper-subgroup metal thiolato-complexes ranges from 2 to 4. The planar anion $[Cu(SPh)_3]^{2-}$ has been isolated from the reaction of the copper(II) species $[Cu(S_2C_4O_2)_2]^{2-}$ with potassium benzenethiolate. In solution equilibrium (7) exists, and the crystal structure of the $[Cu(SPh)_3]^{2-}$ salt shows that the ion is distorted, with two small S–Cu–S angles (ca. 112°) and one large (135°), with the Cu–S bond opposite the larger angle longer (2.335(4) Å) than the other two (2.274(4) and 2.276(4) Å), suggesting that one thiolate is more weakly coordinated [37,38].

$$[Cu(SPh)_3]^{2-} \rightleftharpoons [Cu(SPh)_2]^- + PhS^- \qquad (7)$$

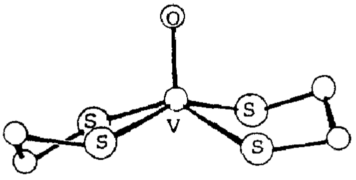
The two-coordinate, presumably linear complexes, $[M(SC_6F_5)_2]^-$ have been characterised for M = Cu, Ag and Au [39–41]. No monomeric Cu(II) thiolato complexes have been reported. All reactions of Cu(II) with thiolate reported so far have led to reduction with formation of RSSR and Cu(I) species. The gold(I) complex $[Au(SC_6F_5)_2]^-$ was also synthesised by reduction of Au^{3+} with pentafluorothiophenolate [39]. Salts of $[Au(SR)_2]^-$ with aliphatic and aromatic thiolates have been isolated (R = Me, Bu^t, Ph). No evidence for dimers or oligomers was found among these anions, and their IR spectra (Au–S stretching and S–Au–S bending modes) are consistent with linear two coordination [42]. A four-coordinate gold(III) pentafluorothiophenolato complex has also been isolated, and found to be similar spectroscopically to its chloride analogue $[AuCl_4]^-$ [41].

The zinc subgroup metals also show two, three and four-coordinate thiolate species. The most studied zinc complexes are the tetrahedral anions $[Zn(SR)_4]^{2-}$ with SR = SPh [18,20,21], SC_6Cl_5 [43] and SC_6F_5 [21,39,40]. All are colourless species, suggesting that the low energy charge transfer absorptions which give rise to the strong colours of the transition metal thiolates are $L \rightarrow M$ in origin [21]. These complexes have been synthesised by reaction of $[ZnCl_4]^{2-}$ with the required thallium thiolate TlSR, (a method also used for Co and Ni complexes [21]) and of $[Zn(dts)_2]^{2-}$ with KSPh (also found to be a general method [18,20]). The tetrahedral mercury thiolates show an enhanced tendency towards dissociation to form $[Hg(SR)_3]^-$ and $[Hg(SR)_2]$ in solution compared with the Zn species, although $[Zn(SPh)_2]$ has been isolated as a soluble, yellow material which is monomeric in solution, presumably with linear two coordination [21]. $[Hg(SPh)_3]^-$ has been isolated as a tetraphenylphosphonium salt [22], but the most common type of mercury thiolate complex is $[Hg(SR)_2]$. Most of these, with aliphatic and aromatic thiolates, are monomeric in solution [44], the possible exception being $[Hg(SMe)_2]$ [45]. Although a monomer in solution, $[Hg(SEt)_2]$ in the crystal has essentially linear coordination with four other sulphurs at a distance of 3.54 Å, in what may be described as a highly distorted octahedral structure. The large Hg–S distances for these bridging sulphurs, together with the low melting point, suggests that these intermolecular bonds are not very significant [46]. The structure of $[Hg(SMe)_2]$ is quite different, with the coordination sphere of Hg containing two sulphurs at 2.36 Å and three distant sulphurs at 3.26 Å. Here again, the closely bonded thiolates are linearly coordinated [45]. The structure of $[Hg(SC_6H_4\text{-}4\text{-}Me)_2]$ consists of discrete linear monomeric units [47]. In the light of these results, the polymeric structure of $[Hg(SBu^t)_2]$ is surprising. The mercury is four-coordinate in a distorted tetrahedron, and the tetrahedra share edges to form an infinite chain polymer [48]. $[Hg(SBu^t)_2]$ appears to be monomeric in solution, however. [Hg(BALH)] ($BALH_3 = HSCH_2CH(SH)CH_2CH_2OH$) is polymeric with mercury coordinated only by sulphur. IR studies suggest that the polymeric structure is not due to bridging thiolate but to non-chelation of the bidentate ligand with the mercury being linearly two-coordinate [49].

(ii) Mononuclear complexes with heteroligands

(a) Oxo-complexes

Studies of oxo-thiolato-complexes have largely been confined to the group VI and VII metals. The exception is the vanadium(IV) complex $[VO(SCH_2CH_2S)_2]^{2-}$, prepared by the reaction of $[VO(acac)_2]$ with sodium ethanedithiolate [51]. The structure of this dianion is square-pyramidal (**9**), with the oxo-ligand apical, an arrangement shared also by the Mo(IV), Mo(V), and Re(V) analogues. The V–O distance in $[VO(SCH_2CH_2S)_2]^-$ is 1.625(2) Å, rather longer than usual for VO^{2+} in this geometry, and correspondingly $\nu(V{=}O)$ is rather low at 928 cm^{-1}. This is a reflection of the double negative charge and of the strong electron-donating ability of thiolato-ligands. The EPR spectrum has been interpreted as suggesting significant π-donation from the sulphur lone pairs, which may contribute to the weakening of the V=O bond [51].



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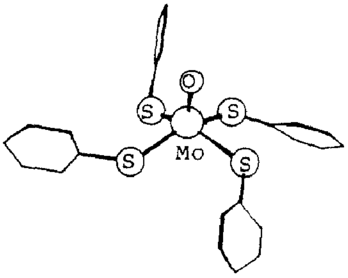

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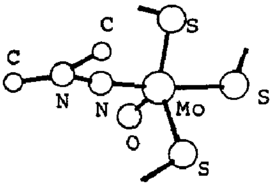
Molybdenum(V) and (IV) oxo-complexes have been synthesised with both monodentate and bidentate thiolato-ligands. Salts of $[MoO(SPh)_4]^-$ (**10**), have been very extensively studied. They have been synthesised by a variety of methods [52–54], and are intensely blue stable solids which decompose only slowly in air. Their tungsten analogues have also been characterised. The structure is again square pyramidal with an apical oxo-group and the Mo displaced from the basal plane [54]. The electronic properties have been interpreted in terms of a d^1 $(S = 1/2)$ system in a tetragonal field (consistent with the observed structure) with the singly-occupied HOMO consisting largely of $Mo(d_{xy})$ [55]. $[MoO(SPh)_4]^-$ is irreversibly oxidised electrochemically, with thiolate being the ultimate electron donor, as the Mo(IV) species reacts further with eventual elimination of PhSSPh and formation of Mo(V) dinuclear species $[Mo_2O_2(SPh)_6(MeCN)]$. One-electron reduction generates $[MoO(SPh)_4]^{2-}$ [56]. The complexes with chelating aliphatic thiolates e.g. $[MoO(SCH_2CH_2CH_2S)_2]^-$ behave similarly, generating stable Mo(IV) species such as $[MoO(SCH_2CH_2CH_2S)_2]^{2-}$ [57].

The reactivity of these oxo-species is dominated by electrophilic attack at sulphur, particularly by protic species HX, e.g. HOR, HSR, and HN_3 to give dinuclear oxo-complexes $[Mo_2O_2(SR)_6X]^-$ in which X occupies a bridging position *trans* to the oxo-groups [58,59]. Reaction with excess HCl gives $[MoOCl_4]^-$, but if the stoichiometry is controlled $[Mo_2O_2Cl_5(SPh)_2]^-$, in which the bridging thiolates are *cis* to oxygen, is isolable [60]. $[MoO(SPh)_4]^-$ reacts with 1,1-dimethylhydrazine, again with elimination of HSPh, to give $[Mo(NNMe_2)O(SPh)_3]$, a Mo(VI) hydrazido(2 −) complex which has a highly distorted square-pyramidal geometry with an apical oxo-group (**11**) [53]. The analogous Re complex $[ReO(NNMe_2)(SPh)_3]$ has been shown to be isostructural [61].



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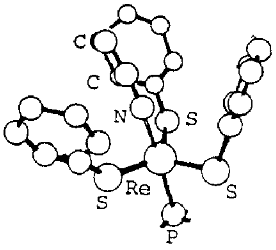
Mo(IV) analogues $[MoO(SR)_4]^{2-}$ can be synthesised either chemically, or electrochemically by controlled potential reduction (e.g. of $[MoO(SCH_2CH_2CH_2S)_2]^-$ [57]. The Mo(IV) species $[MoO(SCH_2CH_2S)_2]^{2-}$ [62], $[MoO(tdt)_2]^{2-}$ [62] (tdt = 2,3-toluenedithiolate), and $[MoO(SCH_2CH_2CH_2S)_2]^{2-}$ are orange diamagnetic materials which are oxidised to the Mo(IV) species by oxygen [62]. They can be prepared chemically by reaction of $K_4[Mo(CN)_4(O)_2] \cdot 6\ H_2O$ with the dithiol in water [62]. The square-pyramidal geometry has been proven for $[MoO(SOCCOS)_2]^{2-}$ by an X-ray structure determination [63].

The Re(V) and Tc(V) oxo-complexes are isostructural and isoelectronic with the Mo(IV) complexes described above. Crystal structure determinations have been carried out for $[ReO(SPh)_4]^-$ [64], $[ReO(SCH_2CH_2S)_2]^-$ [65], $[TcO(SCH_2CH_2S)_2]^-$ [66,69], and $[TcO(SCH_2COS)_2]^-$ [67]. All are square pyramidal, with the chelating ligands causing little or no distortion of the square base of the pyramid. The Tc series includes complexes with 1,1-alkenedithiolato-ligands [68]. The ν(Re–O) stretching frequencies of the rhenium complexes are lower than for the analogous square-pyramidal $[ReOCl_4]^-$, with ν(Re–O) being increased by electron-withdrawing substituents on the chelating dithiol backbone, which also facilitate electrochemical reductions [70].

No studies of the reactivity of the Re or Tc complexes with chelating thiols have been reported, but $[ReO(SPh)_4]^-$ reacts with triphenylphosphine in acetonitrile solution in a deoxygenation reaction to give $[Re(SPh)_3$

(MeCN)(PPh_3)], a trigonal bipyramidal complex with equatorial thiolates (**12**) [71]. This arrangement maximises π-donation from sulphur to rhenium, and from rhenium to the axial π-acceptor ligands. With less bulky monophosphines and diphosphines, $[Re(SPh)_3(PR_3)_2]$ is obtained ($(PR_3)_2 = (PMe_2Ph)_2$ or $Ph_2PCH_2CH_2PPh_2$) [72].



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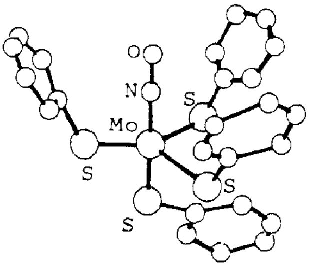
Only two mononuclear sulphido-thiolato-complexes have so far been reported $[VS(SCH_2CH_2S)_2]^{2-}$ [51] and $[ReS(SCH_2CH_2S)_2]^-$ [50]. These both have square pyramidal structures with apical sulphido-groups.

(b) Complexes with metal–nitrogen multiple bonds

A series of anionic molybdenum and tungsten nitrosyl complexes of general type $[M(SPh)_3X(NO)]^-$ (($M = Mo$, $X = SPh$ (**13**); $M = W$, $X = Cl$ (**14**)) have been synthesised and characterised by X-ray crystal structures [73]. Both have trigonal bipyramidal structures with equatorial thiolato-ligands. The N–O stretching frequency is comparatively low at 1650 cm^{-1}, consistent with strong back donation to the NO π^* orbitals.



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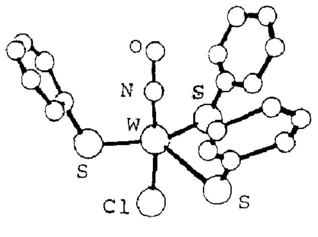

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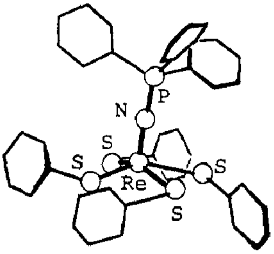
The Re(V) nitrido-complex $[ReNCl_2(PPh_3)_2]$ reacts with thiophenolate ion in the presence of oxygen to give the triphenylphosphiniminato-complex (**15**). An X-ray crystal structure [71] showed a square-pyramidal structure with an axial $NPPh_3$ group. The Re–N and N–P distances are indicative of both Re–N and N–P multiple bonding. The Re(VI) nitrido complex $[ReN(SPh)_4]^-$ may be an intermediate and such a species can be isolated using bulky aromatic thiols (see Section B(iii)(b)). Attempts to synthesise arylimido-complexes by reaction of $[ReCl_3(NPh)(PPh_3)_2]$ with thiophenolate ion invariably led to loss of the NPh ligand and $[ReO(SPh)_4]^-$ was the only isolable species [72]. However, use of bulky aromatic thiols permits the isolation of imido-complexes (see Section B(iii)(b)).



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(c) Miscellaneous monomeric thiolato complexes with other heteroligands

In contrast to the reaction of $TiCl_4$ with $[Al(SPh_3)_3 \cdot Et_2O]$ which gives molecular species, $[Ti(NR_2)_4]$ (R = Me, Et) reacts with four or more equivalents of R′SH (R′ = Me, Et or Pr^i) to give polymeric species. With lower thiol : titanium ratios mononuclear species $[Ti(SR')_n(NR_2)_{4-n}]$ are formed amongst other products. These complexes are thermally and hydrolytically unstable [74]. Bis(cyclopentadienyl) complexes of Ti, Zr and Hf can be prepared according to eqn. 8.

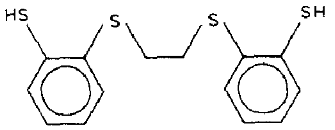
$$[Cp_2ZrCl_2] + 2\ MSPh \rightarrow [Cp_2Zr(SPh)_2] + 2\ MCl \tag{8}$$

Analogues have been prepared with a variety of thiolates [75,76] and the thiolato-sulphurs are sufficiently basic to form dimers as in $[Cp_2Ti(\mu\text{-}SMe)_2Mo(CO)_4]$. A review of such species is presented in ref. 77.

A vast number of complexes have been reported of polydentate ligands involving thiolate in combination with nitrogen, phosphorus, thioether sulphur, or oxygen donor atoms. Space does not permit a comprehensive survey but we here present some recent results for molybdenum and iron. There has been considerable activity in this area as efforts are made to provide viable models for oxygen transfer molybdoenzymes and for nitrogenase.

The Mo(IV) precursor $[MoCl_4(thf)_2]$ reacts with H_2dttd (**16**) to give $[Mo(dttd)Cl_2]$ [78,79], which on reduction under CO yields $[Mo(dttd)(CO)_3]$ [78]. This tricarbonyl can also be prepared directly by reaction of $[MoCl_2(CO)_4]$ with Na_2dttd. The related bidentate ligand (*o*-methylthio)-thiophenol (mttph) (**17**) gives an analogous tricarbonyl $[Mo(mttp)_2(CO)_3]$ [78].

A series of iron carbonyl complexes of these polydentate ligands has also been prepared and characterised. The complex $[Fe(dttd)(CO)_2]$ (**18**) has



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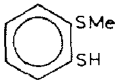

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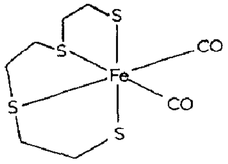
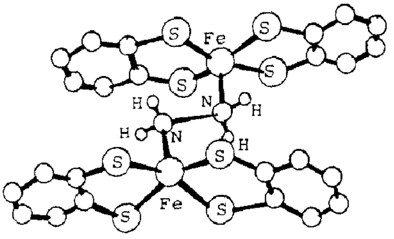


(18)

been synthesised by the template reaction of $[Fe(S_2C_6H_4)_2(CO)_2]^{2-}$ with 1,2-$C_2H_4Br_2$ in DMSO at room temperature. An X-ray crystal structure showed the presence of *cis* CO groups (**18**) [80]. The reaction of $FeCl_2$ with the dianion of dttd in a donor solvent gives [Fe(dttd)(solvate)] [81], which reacts rapidly with a range of neutral and anionic reagents. Thus it reacts with hydrazine to give a bridged N_2H_4 complex, the presence of the μ-N_2H_4 group being suggested by an X-ray crystal structure determination for the related $[(\mu\text{-}N_2H_4)\{Fe(S_2C_6H_4)_2\}_2]$ (**19**) [82]. Nucleophilic attack at iron occurs on reaction of (**18**) with LiPh to give $[Fe(Ph)(CO)_2(dttd)]^-$ with cleavage of a thioether sulphur [81] iron bond. However, with $Li[Et_3BH]$ complex (**18**) undergoes nucleophilic attack at co-ordinated carbon monoxide to generate the formyl complex $[Fe(HCO)(CO)(dttd)]^-$. The nature of the product of the reactions of PhLi is strongly dependent on the identity of the thioether–thiolate ligand. Thus $[Fe(mttp)_2(CO)_3]$ reacts with PhLi to produce the carbene complex $[Fe\{C(Ph)OLi(thf)_3\}(mttp)_2(CO)]$. The presence of the carbene ligand was established by an X-ray crystal structure [81].



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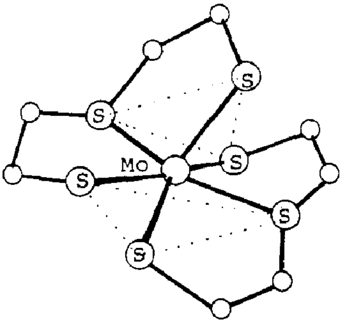
The tridentate thioether–thiolato-ligand $HSCH_2CH_2SCH_2CH_2SH$, dimercaptoethylsulphide, dmesH_2, reacts with $[MoCl_4(thf)_2]$ to give the trigonal prismatic complex [Mo(dmes)$_2$] (**20**) [83]. Short interligand S ··· S contacts are probably important in stabilising the observed trigonal prismatic geometry. It is interesting that the related complex $[Mo\{PhP(CH_2CH_2S)_2\}_2]$ with phosphorus replacing the thioether sulphur has a distorted octahedral geometry (**21**) [84].



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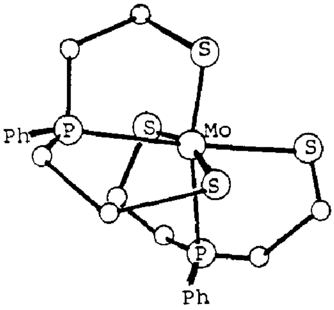
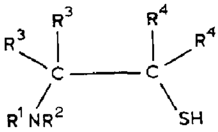


21

There has been considerable recent interest in the chemistry of molybdenum bisoxo-complexes with bi and tetradentate aminothiolato-ligands of types (**22**), (**23**), (**24**) and (**25**). This has largely been stimulated by EPR and EXAFS evidence that molybdenum-containing enzymes what catalyse oxygen transfer reactions contain Mo ligated by at least one oxo and at least two thiolato-sulphur ligands.



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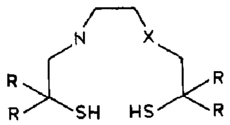

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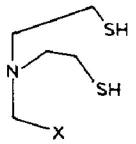

$X = CH_2NR_2$, SCH_3

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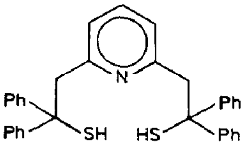

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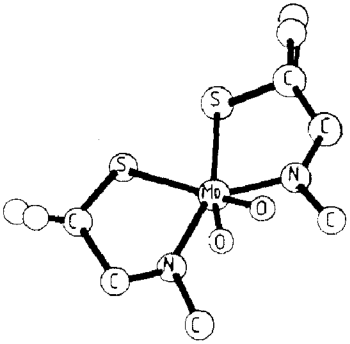
The bidentate ligands of type (**22**) readily react with $[MoO_2(acac)_2]$ (acac = acetylacetonate) to give bis(oxo) complexes $[MoO_2L_2]$ (L = bidentate aminothiolate) [85,86]. The X-ray crystal structures of the complex with $L = H_2NCMe_2CMe_2SH$ revealed a highly distorted octahedral structure described as a skew trapezoidal bipyramid (**26**) [87]. A short S · · · S interaction of about 2.8 Å may be at least in part responsible for the distorted geometry. Steric effects at sulphur are clearly also important as the complex $[MoO_2(H_2NCMe_2CH_2S]$ has a reasonably regular octahedral geometry [87].



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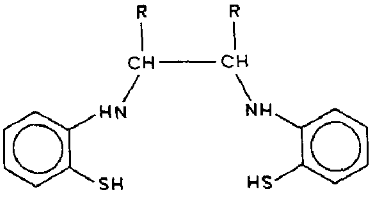
The linear and tripodal tetradentate ligands (**23**) (X = O, S) and (**24**) also form Mo(VI) bis(oxo)-complexes of the type $[MoO_2L]$ and a number of crystal structures with different backbone substituents have been reported [88,89]. The complex with the tripodal type of ligand (**24**) with $X = SCH_3$ is of interest as its EXAFS spectrum is extremely similar to that of oxidised sulphite oxidase.

Generally when Mo(VI) bis(oxo)-complexes with the MoO_2^{2+} core are reduced, Mo(V) dimers are produced. However, the use of bulky ligands to prevent dimer formation permits one-electron reduction to monomeric Mo(V) species [85]. In the case of the bulky tridentate ligand NS_2H_2 (**25**), the five-coordinate bis(oxo)-complex $[MoO_2(NS_2)]$ is formed. An X-ray crystal structure revealed an unusual distorted trigonal-bipyramidal geometry [90]. Triphenylphosphine reduction of this Mo(VI) species gave the Mo(IV) oxo-complex $[MoO(OPPh_3)(NS_2)]$ in quantitative yield, without μ-oxo Mo(V) dimer formation. The Mo(IV) DMF solvate $[MoO(DMF)(NS_2)]$ reacts with Me_2SO to generate Me_2S with reformation of the Mo(VI) bis(oxo) complex. This reaction is of interest in the context of the fact that *d*-biotin-*d*-sulfoxide reductase is a molybdenum co-factor-dependent enzyme.

In the case of the tetradentate aminothiol (**27**), two-electron reduction of the Mo(VI) complex leads to deprotonation of the amine nitrogens with formation of the Mo(IV) complex $[MoOL]^{2-}$. This Mo(IV) species can be oxidised electrochemically to $[MoOL]^-$. This last Mo(V) complex can also be synthesised directly by reaction of $[MoO(SPh)_4]^-$ with the free ligand in acetonitrile [91].



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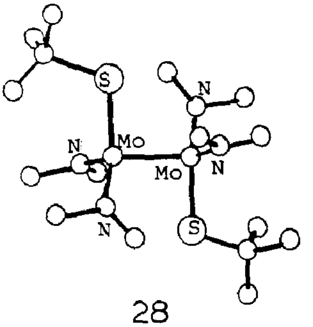
For the purposes of this review, a metal–metal multiple bond unsupported by bridging ligands is classified as a heteroligand. Complexes containing heteroligands of this type include $[\{Mo(SR)(NMe_2)_2\}_2]$ (M≡M) (R = Me or Bu^t) (**28**) [92], $[\{Mo(OR)(SR')_2\}_2]$ (M≡M) (SR′ = 2,4,6-trimethylbenzenethiolate) (**29**) [93], and $[\{Mo(SR')_3\}_2]$ (M≡M) (**30**) [94]. Among these complexes, careful comparison [92,93] of Mo–S, Mo–N and Mo–O distances suggests that thiolate can act as a weak π-donor ligand, the sequence of π-donor ability being $NR_2 > OR > SR > Cl$. $[\{Mo(SBu^t)(NMe_2)_2\}_2]$ reacts further with Bu^tSH, resulting in dealkylation of the thiol to form a μ-sulphido complex $[\{Mo(SBu^t)_2(NMe_2)\}_2(\mu\text{-}S)_2]$ [92,95], and with alcohols to give $[\{Mo(OR)_3\}_2]$, in spite of the weaker acidity of the alcohol compared with the thiol [95].



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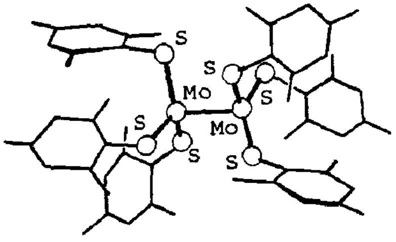

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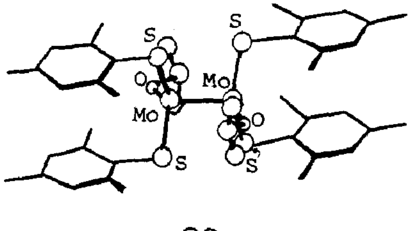

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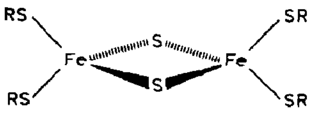
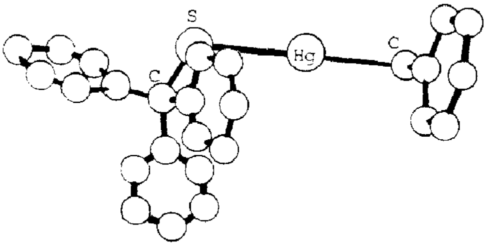


31

The tetrahedral FeS_4 core observed in the $[Fe(SR)_4]^-$ and $[Fe(SR)_4]^{2-}$ complexes discussed earlier occurs in the dinuclear sulphido-bridged complexes $[Fe_2S_2(SR)_4]^{2-}$ (**31**). These can be synthesised by reaction of $FeCl_3$ with thiol and sodium hydrosulphide under basic conditions, giving for example $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$, which has been studied as a possible model for 2-Fe protein-active sites. The chelating dithiolates in this complex can be substituted by the more acidic arene-thiols, to give, for example, $[Fe_2S_2(SPh)_4]^{2-}$ [96]. The thiolates can be replaced by chloride ligands by using the nucleophilic character of the coordinated thiolates, as in eqn. (9) [97].

$$[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-} + 4\ RCOCl \rightarrow [Fe_2S_2Cl_4]^{2-} + 2(RCOS)_2\text{-}o\text{-xyl} \qquad (9)$$

Several monomeric nickel, palladium and platinum thiolato-complexes are known with coordinated tertiary phosphines and arsines. The four-coordinate species $[Ni(SR)_2(PR_3)_2]$ can be synthesised by metathesis of sodium alkanethiolate with $[NiCl_2(PR_3)_2]$ and by oxidative addition of dialkyldisulphides to $[Ni(CO)_2(PR_3)_2]$ ($PR_3 = PEt_3$, PMe_2Ph or $1/2(Ph_2PCH_2CH_2PPh_2)$). The analogous palladium complexes are prepared similarly. They are apparently square planar, and dissociate to some degree in solution [98]. It is also possible to synthesise complexes of this type by treatment of the polymeric $[M(SC_6F_5)_2]$ ($M = Pd$ or Pt) with tertiary phosphines to give $[M(SC_6F_5)_2(PR_3)_2]$ [99], and by oxidative addition of 1,2-ethanedithiol to $[M(PPh_3)_4]$ [100]. If the thiol $HSCM_2CM_2SMe$ is used in a reaction of the latter type, the hydrido-complex $[PtH(SCM_2CM_2SMe)(PPh_3)_2]$ can be isolated, suggesting that a hydrido-complex of this type may be intermediate in the reaction of $[M(PPh_3)_4]$ with 1,2-ethanedithiol [100].



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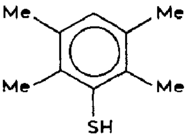
Finally, the structure of the complex $[Hg(SCPh_3)(CH_2Ph)]$ (**32**) is of interest, as it contains the extremely bulky 'trityl' thiolate ligand. The molecule is linear, and the Hg–C–C angle in the benzyl ligand is opened out to 112°, presumably because of steric pressure from the bulky thiolate substituent. Surprisingly, this interaction does not appear to cause a significant distortion of the Hg–S–C angle which is only 104° [101].

(iii) Complexes with sterically hindered thiolato-ligands

As discussed in more detail in Section F two of the principal complications encountered in the coordination chemistry of thiolato-ligands are C–S bond cleavage and the formation of thiolate-bridged oligomers. Both can be circumvented by the use of aromatic thiolates with *ortho*-substituents. Steric hindrance prevents bridge formation while the aromatic C–S bond is resistant to cleavage. Representative examples are shown [(**33**), (**34**), (**35**) and (**36**)] together with the abbreviations used.



TEMPTH
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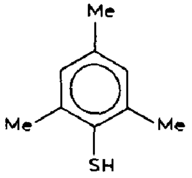

TRMPTH
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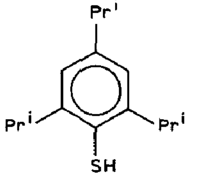

TIPTH
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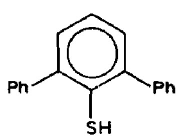
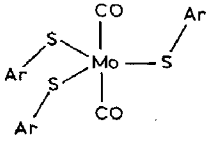


DPTH
36

(a) Chromium, molybdenum and tungsten

The reaction of $[MoCl_4(thf)_2]$ with NaTIPT under CO in thf (thf = tetrahydrofuran) gives the anionic Mo(II) carbonyl complex $[Mo(TIPT)_3(CO)_2]^-$. The complex can also be prepared by reaction of $[MoBr_2(CO)_4]$ with 3 equivalents of $TIPT^-$ in methanol in high yield [102]. An X-ray crystal structure revealed a trigonal bypyramidal structure with axial CO groups (**37**). The analogous tungsten complex is isostructural. The bulk of the thiolato-ligands causes two of the three arene groups to be disposed to one side of the equatorial plane. This configuration is common to all the five-coordinate complexes with such ligands discussed below. The complex (**37**) undergoes facile substitution reactions with a range of neutral donors to give $[Mo(TIPT)_3(CO)L]^-$ ($L = MeCN$, Bu^tCN, Bu^tNC, PMe_2Ph). Decarbonylation of (**37**) occurs rapidly on reaction with $[PhN_2]BF_4$ in acetonitrile to give green, air-stable $[Mo(N_2Ph)(TIPT)_3(NCMe)]$ [103]. An X-ray crystal structure showed an analogous trigonal bipyramidal structure with axial N_2Ph and NCMe ligands [103]. A closely-related nitrosyl complex $[Mo(NO)(TIPT)_3(NH_3)]$ can be prepared by reaction of $\{Mo(NO)(NH_2O)(H_2O)_n\}_n$ [104] with excess $TIPT^-$ in refluxing methanol. The NH_3 ligand arises from thiolate reduction of the coordinated hydroxylamido-ligand [105].



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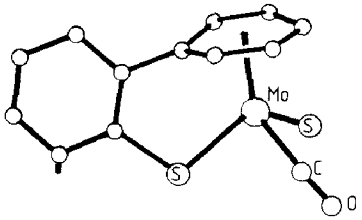
The nature of the products obtained by reaction of halido-precursors with the aromatic thiolates is strongly solvent dependent. Thus reaction of $MoCl_4$ with NaTIPT in 1,2-dimethoxyethane gives a mixture of two products, $[Mo_2(TIPT)_6]$ and $[MoO(TIPT)_4]^-$ [106]. An X-ray crystal structure of $[Mo_2(TIPT)_6]$ revealed the presence of an $Mo{\equiv}Mo$ triple bond and the overall geometry is similar to that for $[Mo_2(TMT)_6]$ discussed in the previous section. This represents a particularly convenient one-step synthesis of the metal–metal multiply-bonded species from $MoCl_4$.

The Mo(V) oxo-species $[MoO(TIPT)_4]^-$ has a very similar EPR spectrum to $[MoO(SPh)_4]^-$ and probably has the same square-pyramidal geometry. The thiolate systems have a very high affinity for oxygen, and it is extremely difficult to avoid the formation of oxo-complexes. Thus in the reaction of $[MoCl_4(PPh_3)_2]$ with NaTIPT in toluene the principal product isolated is $[Mo_2O_4(TIPT)_2(PPh_3)_2]$. This has a symmetric structure with two bridging and two terminal oxo-groups [107]. The oxo-complexes $[MoO(TIPT)_4]^-$ (M = Mo, W) can be prepared in high yield by reaction of $[MoOCl_4]^-$ or $WOCl_4$ with NaTIPT in THF [103].

The molybdenum(III) precursor $[MoCl_3(MeCN)_3]$ reacts with NaTIPT in MeCN with oxidation of the metal to give a complex formulated as $[Mo(TIPT)_4(MeCN)]$ [108]. The unsolvated $[Mo(TIPT)_4]$ has recently been reported as the product of sodium amalgam reduction of $[MoCl(TIPT)_4]$. The red Mo(V) chloro complex is unexpectedly prepared in 40% yield by reaction of $MoCl_4$ with 2 equivalents of $Me_3SiTIPT$ [109].



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If the thiolate ligand bears *o*-phenyl substituents, then the observed chemistry is entirely different. Thus NaDPT (**36**) reacts with $[MoBr_2(CO)_4]$ in 1,2-dimethyoxyethane to give a bright-green complex of stoichiometry $[Mo(DPT)_2(CO)]$ [110]. ^1H NMR data suggested the presence of an η^6-bonded phenyl group and this was confirmed by an X-ray crystal structure (**38**). The molybdenum has what is best described as a distorted piano-stool geometry with one of the *o*-phenyl thiolate groups η^6-bonded to the molybdenum. The phenyl group is labile and can readily be displaced by a range of two electron donor ligands. However, the displacement chemistry is not entirely straightforward. Thus (**38**) reacts with bipyridyl to give *cis*-

$[Mo(DPT)_2(CO)_2(bipy)]$ in less than 50% yield. The formation of the dicarbonyl product from a monocarbonyl precursor suggests that a species with bridging carbonyl ligands may be involved. The reaction of (**38**) with the diphosphine dppe is more straightforward giving the stable 5-coordinate species $[Mo(DPT)_2(CO)(dppe)]$ [111]. The lability of the η^6-arene group therefore permits ready access to a range of Mo(II) thiolato-complexes.

(b) Manganese, technetium and rhenium

Rhenium is the only element of this triad to have any reported chemistry with bulky aromatic thiolates. The Re(V) oxo-complex $[ReOCl_3(PPh_2)_2]$ reacts readily with TIPTH (or other bulky aromatic thiols) in methanol in the presence of Et_3N to give $[ReO(TIPT)_4]^-$. An X-ray crystal structure of the related $[ReO(TMT)_4]^-$ anion [112] revealed a square-pyramidal geometry with an apical oxo group as found for $[ReO(SPh)_4]^-$ [64].

The rhenium(IV) precursor $K_2[ReCl_6]$ reacts with excess NaTIPT in MeCN to give violet crystalline $[Re(TIPT)_3(NCMe)_2]$ in high yield. The acetonitrile ligands are very labile and can readily be replaced by CO or Bu^{t}NC. All these d^4 five-coordinate species have the same trigonal-bipyramidal structures as $[Mo(TIPT)_3(CO)_2]^-$ (Mo(II), d^4) discussed above. The nitrosyl complexes $[Re(TIPT)_4(NO)]$ have been synthesised by reaction of $[ReCl_2(OMe)(NO)(PPh_3)_2]$ with $TIPT^-$ in methanol [112a].

As described in Section B(ii)(b), the phenylimido-ligand in $[ReCl_3(NPh)(PPh_3)_2]$ is lost on reaction with thiophenolate anion. However, with $TIPT^-$, the brown crystalline species $[Re(NPh)(TIPT)_4]^-$ can be isolated in high yield [113]. The Re(V) nitrido-complex $[ReNCl_2(PPh_3)_2]$ reacts with $TIPT^-$ in the absence of air to give the yellow, very oxygen-sensitive nitride di-anion $[ReN(TIPT)_4]^{2-}$. Aerial oxidation of this produces the air-stable Re(VI) nitrido-complex $[ReN(TIPT)_4]^-$ [113]. The bulk of the aromatic thiolate ligands may preclude interaction of the nitride nitrogen with PPh_3 to give a phosphiniminato-complex.

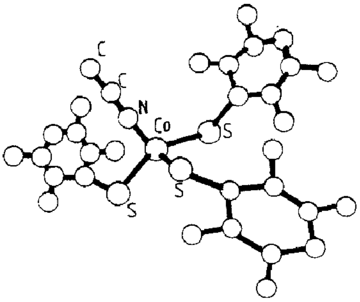
(c) Iron, ruthenium and osmium

Reaction of $FeCl_3$ with thiophenolate anion in methanol causes reduction to Fe(II) with formation of $[Fe(SPh)_4]^{2-}$. However, with $TIPT^-$, no reduction occurs and the stable Fe(III) complex $[Fe(TIPT)_4]^-$ can be isolated in high yield [114]. An X-ray crystal structure has been reported [114]. The Fe(III)thiophenolate complex can, however, be prepared by reaction of $[Fe(OC_6H_3,2,6\text{-}Me_2)_4]^-$ with PhS^- in methanol [115]. This supports the contention that steric bulk prevents the formation of thiolato-bridged dimers which mediate electron transfer. The iron(II) carbonyl $[FeI_2(CO)_4]$ is reduced by 2 equivalents of NaTIPT in THF to give the dimer $[\{(CO)_3Fe(\mu\text{-}TIPT)\}_2]$. Without any more bulky ligands than CO terminally coordinated to the iron even the sterically demanding *o*-disubstituted TIPT ligand bridges the two irons [116].

The five-coordinate Ru and Os complexes $[M(TEMTP)_4(NCMe)]$ ($M =$ Ru, Os) have been prepared by reaction of $[RuCl_4(MeCN)]^-$ or $OsCl_3$ with LiTEMTP and half an equivalent of the disulphide in refluxing acetonitrile. An X-ray crystal structure of the Ru(IV) (d^4) system showed a trigonal bipyramidal structure with an axial MeCN group [117]. Analogous complexes were also obtained with the more sterically demanding TIPT ligand. Both the Ru and Os complexes can be successively, and reversibly electrochemically reduced or oxidised to give $[M(TEMTP)_4(NCMe)]^-$ and $[M(TEMPT)_4(NCMe)]^+$ respectively [117].

(d) Cobalt, rhodium and iridium

Cobalt(II) chloride, $CoCl_2$, reacts with 3 equivalents of K[TMETP] in refluxing acetonitrile to give $[Co(TMETP)_3(NCMe)]^-$ in high yield [118]. An X-ray crystal structure (**39**) revealed a distorted tetrahedral geometry with large deviations from the normal tetrahedral bond angles due to steric interactions and mixed ligand coordination.



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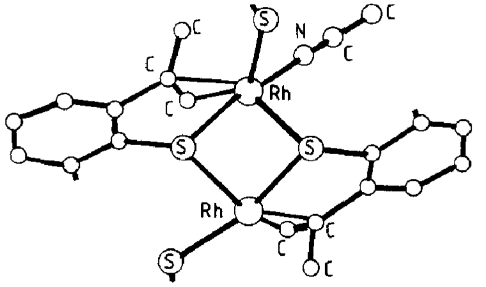
By contrast $RhCl_3$ reacts with TIPT anion in acetonitrile at room temperature to give the novel asymmetric dimer (**40**). The presence of the bridged thiolate-olefinic ligands was verified by an X-ray crystal structure study [119]. The presence of a rhodium–rhodium bond [Rh–Rh, 2.756(1) Å) is manifested in the non-planar Rh_2S_2 system. The chelated thiolate-olefin ligand is related to the π-arene molybdenum complex (**38**) discussed above. However, the *o*-phenylated thiolate DPT reacts with $RhCl_3$ in acetonitrile to give the symmetry binuclear complex (**41**). An X-ray crystal structure (**41**) revealed the presence of bridging thiolato-ligands with the *o*-phenyl groups *ortho*-metallated to provide one Rh–C bond to each rhodium. Each Rh atom achieves a formal sixteen electron count without a rhodium–rhodium bond [120].



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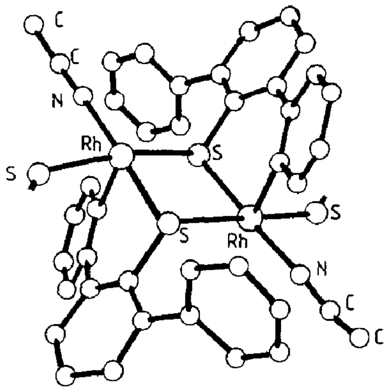

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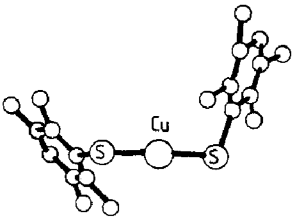
(e) Copper, silver and gold

The two-coordinate complex $[Cu(TEMTP)_2]^-$ can be prepared by reaction of $[Cu(NCMe)_4]BF_4$ with 3 equivalents of Li[TEMTP] in ethanol. The linear coordination of the copper ion was confirmed by an X-ray crystal structure (**42**) [118]. In contrast to the reactions of Cu(I) with thiophenolate ion the bulky aromatic thiol shows no sign of forming any polymeric species.



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C. COMPLEXES WITH μ^2-BRIDGING THIOLATO-LIGANDS

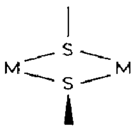
(i) Introduction

A great deal of the chemistry of metal thiolates involves thiolate as a bridging ligand. Thiolates can bridge between two or three metals, to give dinuclear, linear or three-dimensional cluster compounds, or high polymers, and the bridges can consist of one, two, three of four thiolate sulphur atoms. Discussion of complexes with bridging thiolates is here separated into dinuclear and linear polynuclear complexes with μ^2-thiolates (Sections C(ii) to C(iv)), and cluster species with nuclearity greater than two (Section C(v)). Section D deals with clusters containing μ^3-bridging thiolates.

(ii) Dinuclear and linear polynuclear complexes with two μ^2-thiolato-ligands

Enormous numbers of complexes containing (μ-SR)$_2$ bridges have been reported. They are too numerous to be fully discussed here, and attention will be confined to those in which thiolate ligands predominate.

It appears from a limited survey that the general tendency is towards a planar conformation of the M_2S_2 rings in (μ-SR)$_2$ bridges, as might be expected from consideration of intra-ring, 1,3-non-bonded interactions, and bond angle deformation at metal and ligand. It has been suggested [121] that M(μ-SR)$_2$M bridges might in general be intrinsically bent, adopting the "butterfly" conformation, in the absence of steric or other effects, but there seems to be little evidence for this. The presence of metal–metal interactions can result in bending, as can asymmetric distribution of bulky bridging or terminal ligands. An *anti*-orientation of thiolate substituents (**43**) usually allows planarity, whereas the *syn*-isomer (**44**) may be slightly bent as a result of steric interaction across the bridging system. Several ring geometries are possible (**43**–**47**), and examples of all but the *syn-exo* form are found.



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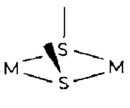

syn

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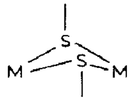

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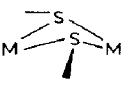

syn-endo

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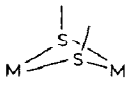

syn-exo

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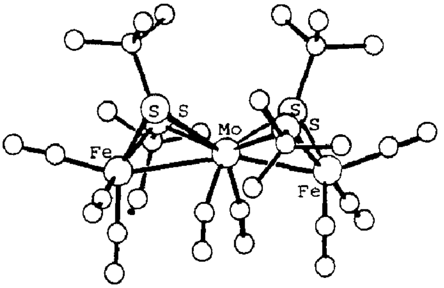
NON-PLANAR

Angles subtended at the bridging thiolate sulphurs are very varied and it appears that they open and close easily to accommodate various degrees of M–M interaction. For example [$Cp_2W(\mu$-$SPh)_2Mo(CO)_4$] has "normal" Mo–S–W angles of around 104° [122], while in [{$(CO)_3Fe$}$_2(\mu$-$SEt)_2$] the Fe–S–Fe angles are 68° [123], as a result of a strong Fe–Fe bond. In general, metal to bridging thiolate sulphur bonds are longer than those to terminal thiolate sulphur in the same complex.

(a) Molybdenum

The puckering of a M_2S_2 ring as a result of a metal–metal bonding interaction is illustrated by the novel Mo–Fe cluster $[\{(CO)_3Fe(\mu\text{-}SBu^t)_2\}_2Mo(CO)_2]$ (**48**), formed in the reaction between $[Mo(SBu^t)_4]$ and $[Fe_2(CO)_9]$ [124]. The pentacoordinate Fe atoms have approximate tetragonal pyramidal geometry. The orbital available for the formation of a strong Fe–Mo bond is d_{z^2}, and in order to achieve a favourable overlap with the Mo orbitals the MoS_2Fe ring is drastically folded along the S–S vector. Thus, folding of the bridge is imposed by the symmetry of the metal ions in order for the orbitals involved in M–M bonding to overlap. The molybdenum atom in this complex has a highly distorted trigonal prismatic geometry as a result of this Mo–Fe bonding. The CO ligands coordinated to Mo are slightly bent due to a small attractive interaction with a Fe atom, in a semi-bridging arrangement.



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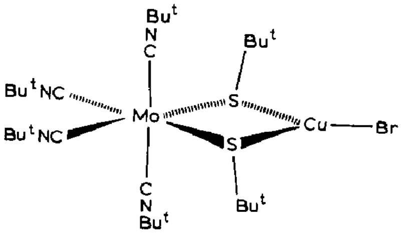
The effect on the molybdenum in $[Mo(SBu^t)_2(CNBu^t)_4]$ of coordination of the sulphur ligands to a copper atom has been considered [16]. Thus $[Mo(SBu^t)_2(CNBu^t)_4]$ reacts with $[CuBr(CNBu^t)_3]$ to form $[(Bu^tNC)_4Mo(\mu\text{-}SBu^t)_2CuBr]$ (**49**) which has a planar bridge with narrow Mo–S–Cu angles (ca. 69°), indicating metal–metal bonding. Both *syn* and *anti* isomers have been structurally characterised [16]. The change in ν(C–N) for the isonitrile ligands is very small, and this was taken as an indication that there is no net electron transfer to the copper atom, with electron donation via sulphur from Mo to Cu being returned through the metal–metal bond [16].



(*anti*-isomer)

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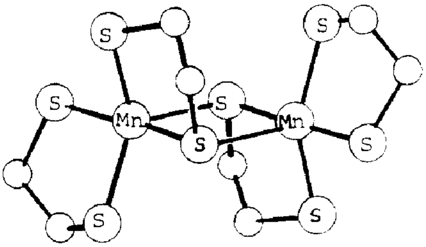
(b) Manganese, technetium and rhenium

The dimeric manganese(III) complex $[Mn_2(SCH_2CH_2S)_4]^{2-}$ has a planar double thiolate bridge (**50**) [19,28]. The complex may be described as a weakly-associated pair of $[Mn(SCH_2CH_2S)_2]^-$ units, since each sulphur atom is more closely associated with one metal than the other to form a rectangular bridge with a non-bonding Mn–Mn distance. This is consistent with the solution behaviour. The complex partially dissociates in donor solvents to give green $[Mn(SCH_2CH_2S)_2(solv)_2]^-$. The $[Mn(dithiolate)_2(py)_2]^-$ species analogous to this may be responsible for the green colour generated by $[Mn(OAc)_2]$ in colorimetric tests for dithiols [125]. The dinuclear Mn(III) species is irreversbily reduced electrochemically to $[Mn(SCH_2CH_2S)_2]^{2-}$ [19,28]. Other Group VII metal complexes with $(\mu\text{-}SR)_2$ bridges include the oxo-complex $[Tc_2O_2\{S(CH_2)_nS\}_3]$ ($n = 2$ or 3) [126] and $[\{M(CO)_4\}_2(\mu^2\text{-}SR)_2]$ (M = Mn or Re, R = C_6H_5 or C_6F_5) formed in the reaction of $[MH(CO)_5]$ with HSR [127]. This reaction illustrates the difference between SPh and the relatively poor electron donor SC_6F_5 in their tendency to act as bridging ligands. The monomeric species $[Re(SPh)(CO)_5]$ is unknown, whereas under certain conditions, $[Re(SC_6F_5)(CO)_5]$ is isolable from this reaction [127].



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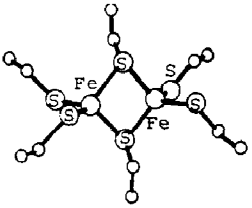
(c) Iron

The tetrahedral dimeric iron thiolato-complexes $[Fe_2(SR)_6]^{2-}$ (SR = SEt or $\frac{1}{2}S_2\text{-}o\text{-xyl}$) have been structurally characterised [33,128] (**51**). $[Fe_2(SEt)_6]^{2-}$ has a planar $(\mu\text{-}SEt)_2$ bridge with the *anti* configuration. Two isomers of the complex $[Fe_2(S_2\text{-}o\text{-xyl})_3]^{2-}$, in which the Fe_2S_2 rings are slightly distorted, have been characterised by X-ray structural studies, and have the chelate ring arrangements (**52**) [33] and (**53**) [128]. This is illustrative of the flexibility of the S_2-*o*-xyl ligand, and intra-ligand S–S distances lie in the range 3.7–4.3 Å in these compounds. The ligand $SCH_2CH(S)CH_2CH_2OH$ forms a dimer of the $[Fe_2(SR)_6]^{2-}$ type, $[Fe_2\{SCH_2CH(S)CH_2CH_2OH\}_3]^{2-}$ which has been identified in solution [129]. In $[Fe_2(S_2\text{-}o\text{-xyl})_2(SPh)_2]^{2-}$ the benzene-thiolate ligands occupy terminal positions, consistent with the view that the more strongly donating alkylthiolates are the more likely to act as bridging ligands.



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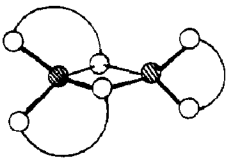

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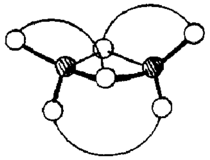

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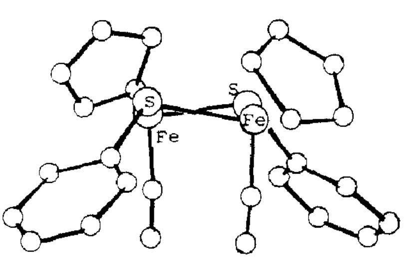
The dimer $[\{Fe(SCH_2CH_2S)_2\}_2]^{2-}$ [130] has a structure completely analogous to that of $[\{Mn(SCH_2CH_2S\}_2]^{2-}$ (**50**). The magnetic properties of the iron complex have been studied in some detail [131]. The iron atoms are antiferromagnetically coupled, and the J value was found to be much larger than in $[\{Fe(salen)Cl\}_2]$ which has a $(\mu\text{-}OR)_2$ bridge of similar geometric parameters. This it was concluded that the SR bridge is more effective than OR at mediating this type of magnetic interaction.

The combined effects of steric and metal–metal bonding interactions on the M_2S_2 ring geometry are illustrated by the complexes $[\{Cp(CO)Fe\}_2(\mu\text{-}SR)_2]^{n+}$ ($R = Me$, $n = 1$ or $R = Ph$, $n = 0$). $[\{Cp(CO)Fe\}_2(\mu\text{-}SPh)_2]$ (**54**) has a *syn*-orientation of SPh groups, which is presumably enforced by steric interaction between the Cp and SPh ligands. The resulting steric repulsion across the Fe_2S_2 ring between the phenyl groups causes a significant bending of the bridge unit (dihedral angles between the Fe_2S planes and between the S_2Fe planes are 164° and 161° respectively). The Fe–Fe distance is 3.39 Å, which is not indicative of significant Fe–Fe attraction [132]. One-electron oxidation of $[\{Cp(CO)Fe\}_2(\mu\text{-}SMe)_2]$ gives the stable monocation $[\{Cp(CO)Fe\}_2(\mu\text{-}SMe)_2]^+$ (**55**) [133]. This oxidation corresponds to removal of an electron from a Fe–Fe antibonding orbital resulting in a one-electron Fe–Fe bond (formal bond order 0.5). Because of the distortion imposed by the steric effect of the Cp ligands, the overlap of Fe–Fe orbitals results in bonding electron density slightly out of the Fe_2S_2 plane, so that there is a "bent" Fe–Fe bond and further folding of the ring occurs along the S–S vector [133]. This is reflected in the decreased dihedral angles (with respect to the neutral SR analogue) of 156° and 153°, and a decrease in the Fe–Fe distance to 2.93 Å [133].

The bridge geometry in $[\{(CO)_3Fe\}_2(\mu\text{-}SEt)_2]$ (**56**) [123] is comparable with that in $[\{(CO)_3Fe(\mu\text{-}SBu^t)_2)_2\}_2Mo(CO)_2]$ (**48**) in which the Fe coordination is very similar, and again the Fe_2S_2 ring is folded about the S–S vector to accommodate overlap between the $Fe(d_{z^2})$ orbitals in a "bent" Fe–Fe bond [133]. It can be seen by comparison with the isoelectronic $[\{(NO)_2Fe\}_2(\mu\text{-}SEt)_2]$ (**57**) [134] ("Roussin's red ethyl ester"), which is



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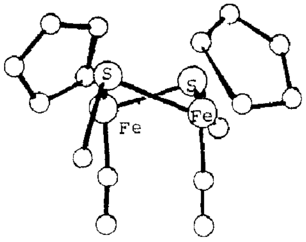

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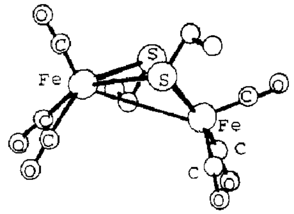
Fe–Fe bonded but with a planar bridge, that when symmetry allows a strong M–M bond within the M_2S_2 plane, the distortion of the ring involves only expansion of S–M–S angles and contraction of M–S–M angles, while the M_2S_2 ring remains planar. The high stability of the $Fe_2(SR)_2$ bridge system is demonstrated by mass spectral studies of $[\{(NO)_2Fe\}_2(\mu\text{-}SR)_2]$, and its cobalt analogue. The molecules remain dimeric in the gas phase, and the bridging system remains intact, the major decomposition being loss of NO [135].



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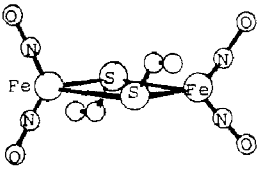

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(d) Cobalt

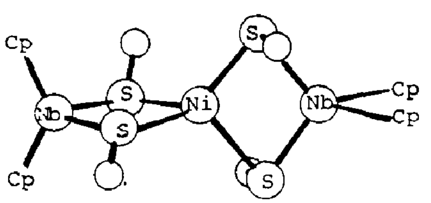
Cobalt(II) forms complexes analogous to $[Fe_2(SEt)_6]^{2-}$ (**51**). Both *syn*- and *anti*-isomers of $[Co_2(SEt)_6]^{2-}$ have been characterised by X-ray structure determination [33]. As noted in other systems, the *syn*-orientation results in a slightly non-planar bridge. The isotropically shifted ^1H NMR spectra of the complexes $[M_2(SEt)_6]^{2-}$ (M = Fe or Co) are consistent with the equilibrium

$$3[M_2(SEt)_6]^{2-} \overset{K}{\rightleftharpoons} 2[M(SEt)_4]^{2-} + [M_4(SEt)_{10}]^{2-} \qquad (11)$$

taking place in CD_3CN solution. K is much larger for the cobalt complexes than for the iron complexes.

(e) Nickel, palladium and platinum

A remarkable dependence of geometry on electron population is shown by the complexes $[\{Cp_2M(\mu\text{-}SMe)_2\}_2Ni]^{2+}$ (M = Nb (**58**) or Mo (**59**) [136]. The Nb complex has the nickel atom in an approximately tetrahedral array of thiolato-ligands, which together with the diamagnetism of the complex prompted a formal assignment of oxidation state zero for the nickel atoms. There is a metal–metal bond with a Ni–Nb distance of 2.78 Å, and the bridge has a planar, *anti*-configuration. In contrast the molybdenum system (**59**) which has two more valence electrons, has a square planar-coordinated nickel and is assigned the formal oxidation state II. There is no significant Ni–Mo bonding (Mo–Ni 3.39 Å, Mo–S–Ni 92°), but the $NiMoS_2$ rings are decidedly bent with a dihedral angle between NiS_2 and MoS_2 planes of 132.7°.



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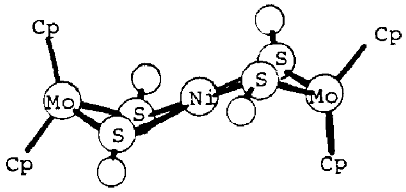

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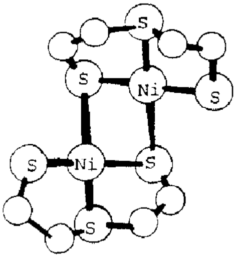
No entirely satisfactory rationalisation has been provided for this, and construction of models shows that larger Mo–Ni distances and more reasonable intra-ring bond angles could be achieved by adopting a planar conformation [136]. However, further examination shows that, far from minimising *trans*-annular S–S contacts, the bent arrangement allows a very short S–S distance of around 2.88 Å. This is well within the range for which attractive S–S interactions have been suggested (see Section F(iv)), and perhaps in this case an out-of-plane S–S bonding electron density is the cause of the bent arrangement. It is interesting that here Ni(II) when coordinated by four μ^2-thiolates is square planar whereas the monomeric $[Ni(SR)_4]^{2-}$ complexes have distorted tetrahedral structures. Several other complexes containing the square planar Ni(II) coordinated by four μ_2-SR ligands have been identified. Examples are the complexes, $[\{L_2M(\mu\text{-}SR)_2\}_2Ni]$ (L = tertiary phosphine, R = Pr^i, Ph, M = Ni, Pd, Pt) [137] which probably have a similar bridge structure to $[\{Cp_2Mo(\mu\text{-}SMe)_2\}_2Ni]^{2+}$ (**59**).

Dinuclear nickel complexes with dithiolate ligands include $[Ni_2(S_2\text{-}o\text{-}xyl)_3]^{2-}$, which is formed even in the presence of excess thiolate, there being no evidence for monomeric $[Ni(S_2\text{-}o\text{-}xyl)_2]^{2-}$ [25]. $[Ni(SCH_2CH_2S)_2]^{2-}$ has, however, been detected in solution, [36a] in equilibrium with the dinuclear species $[Ni_2(SCH_2CH_2S)_3]^{2-}$. The properties of the species with $SCH_2CH(S)CH_2CH_2OH$ ligands are similar suggesting that in these the OH group is not coordinated [360]. Complexes of nickel and palladium with 2-

mercaptoethyl sulphide ($SCH_2CH_2SCH_2CH_2S$) ligands have been characterised. $[Ni_2(SCH_2CH_2LCH_2CH_2S)_2]$ (L = S, NMe or NEt) all appear to be of similar structure [138], and two independent determinations of the structure for L = S [139,140] show a dimeric unit, with approximate square-planar coordination to nickel (**60**). The nickel atoms are within bonding distance at 2.73 Å, and the bridging atoms are thiolate sulphur. The bridge is non-planar, apparently due to chelate constraints. The palladium complex of this ligand is trimeric, again with square-planar metal atoms, in a triangular array. The molecule is bent at the bridging sulphur resulting in the "basin-shaped" structure (**61**) [139,141].



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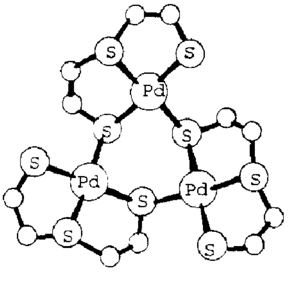

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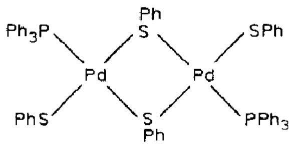
Dinuclear di-μ-SR bridged palladium species $[\{Pd(SPh)_2(PPh_3)\}_2]$ (**62**) can be synthesised by treatment of polymeric $[Pd(SPh)_2]_n$ with triphenylphosphine [39], or by oxidative addition of RSSR to $[Pd(PPh_3)_4]$ [142], and similar complexes $[\{Pt(PR_3)Cl(SR)\}_2]$ are known in which the chloride ligands are terminal [143]. In the last complexes it was found (on the basis of dipole moment data) that the *cis*-isomers (**63**) were more stable than the *trans*-isomers (**64**).



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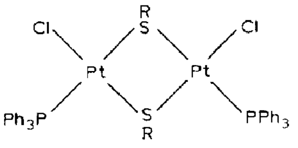

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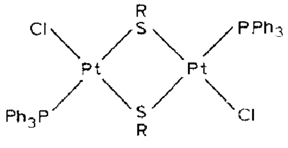

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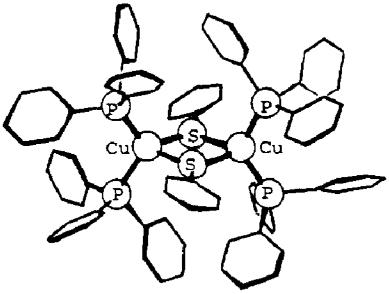
It has been suggested [143] that the Pt_2S_2 ring might be an "inorganic aromatic ring", with a $d\pi$–$d\pi$ system covering both Pt and S atoms. On the basis of dipole moment measurements it was concluded that the sulphur atoms are not planar in these compounds, so that sulphur *p*-orbitals could not contribute strongly to such a system. The potential for significant involvement of sulphur *d*-orbitals in such a system has yet to be assessed, and relevant ab initio or semi-empirical calculations are conspicuously absent.

(f) Copper, silver and gold

A (μ-SR)$_2$ bridge involving copper was mentioned earlier. Another example worthy of comment is [(Cu(SPh)(PPh$_3$)$_2$}$_2$] (**65**) [144]. The sulphur atoms in this complex, which has a planar Cu$_2$S$_2$ ring, are very close to planar with neither *syn*- nor *anti*-descriptions of the bridge geometry being entirely appropriate. This appears to be the result of the steric constraint imposed by the terminal PPh$_3$ ligands rather than an electronic effect involving sulphur *p*-orbitals. This observation suggests that bond angles at thiolate sulphur are easily deformed and as noted earlier a wide range of angles can be accommodated with little strain. Deformation energies of this type have been quantified by NMR studies of inversion processes at bridging thiolate sulphur atoms and found to be quite small (see Section F(ii)). The dinuclear species [Au$_2$(SC$_6$F$_5$)$_6$]$^{2-}$ has been isolated [41] and characterised and appears to have a doubly thiolato-bridged structure.



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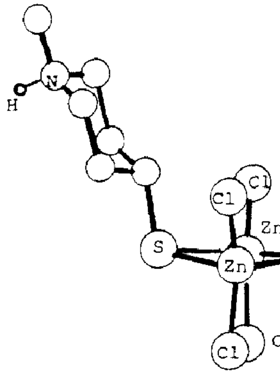
(g) Zinc, cadmium and mercury

[Zn$_2$Cl$_4$(SR)$_2$] (SR = 4-thiolato-*N*-methylpiperidinium) (**66**) has a (μ-SR)$_2$ bridge with a **syn**-conformation which causes deformation of the Zn$_2$S$_2$ ring [145]. Polymeric [Cd(SR)$_2$]$_n$ with the same ligand (in this case unprotonated) consists of infinite chains of edge-shared tetrahedra, (**67**) with planar (μ-SR)$_2$ bridges [146]. The same structure is found in crystals of [Hg(SBu^t)$_2$] although this compound is monomeric in solution [48].

(iii) Complexes with three μ^2-thiolato-ligands

Discrete complexes with triple thiolate bridges are confined almost exclusively to those containing iron, molybdenum or tungsten. In many cases the triple bridge is supported by a metal–metal bond, resulting in M–S–M



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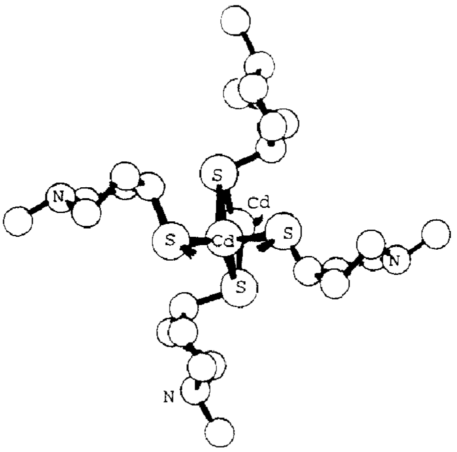

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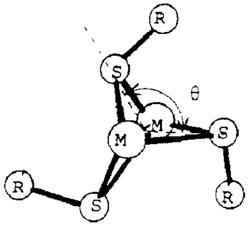
angles in the bridge as acute as 62°. In the absence of sources of asymmetry in the terminal ligands the bridge unit may have one of two isomeric forms (**68**) and (**69**).



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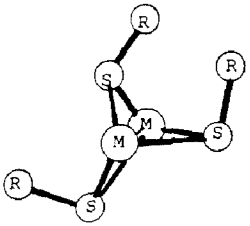

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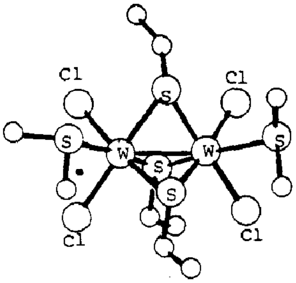
In form (**69**), steric interaction between the thiolate substituents might be expected to cause a distortion from the symmetric $\theta = 120°$ structure. This is indeed found to be the case in the example discussed below. More often the threefold symmetry is destroyed by the terminal ligands which may cause distortion of the (**68**) isomer or render the (**69**) isomer the more stable, again resulting in deviation from the $\theta = 120°$ ideal. Particularly important in this respect are the relative *trans*-influences of the terminal ligands. For example, in the mixed oxidation state cluster $[\{(SMe_2)Cl_2W\}_2(\mu\text{-}SEt)_3]$ (**70**), prepared by the reaction of $[WCl_4(SMe_2)_2]$ with Me_3SiSEt, the μ-SEt *trans* to the SMe_2 ligands has shorter W–S distances than the other two which are *trans* to chloride ligands [147]. The W–S–W angles in the bridge of this compound are exceedingly acute, lying in the range 61.7° to 62.9° as a result of a strong W–W bond (W–W distance is 2.505(1) Å) [147].

The red dinuclear species $[Mo_2O_2(SCH_2Ph)_7]^-$ results from treatment of $[MoOCl_3(thf)_2]$ with benzylthiolate. This reflects the stronger electron



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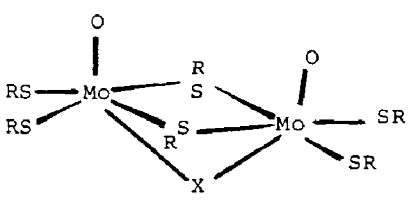
donating ability and resulting stronger bridging tendency of the alkanethiolate compared with arenethiolates, which give $[MoO(SR)_4]^-$ (R = aryl). The structure of the red dinuclear species is not known unequivocally, but is probably similar to (**71**) [158]. It is a member of a series of dinuclear molybdenum(V) oxo-complexes containing six thiolates, while the third bridging position *trans*- to the oxo-ligands is occupied by some heteroligand. This series includes the anions $[Mo_2O_2(SPh)_6(OR)]^-$ (R = Me, Et, Pr^i) [58] and $[Mo_2O_2(SC_6H_4\text{-4-Me})_6OMe)]^-$ [148]. The latter two anions have been characterised recently by an X-ray structure determination confirming the supposed general structure (**71**) for the series.



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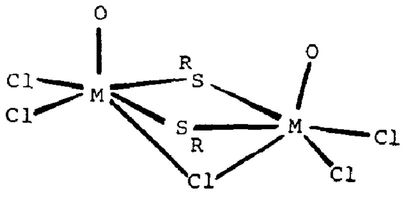

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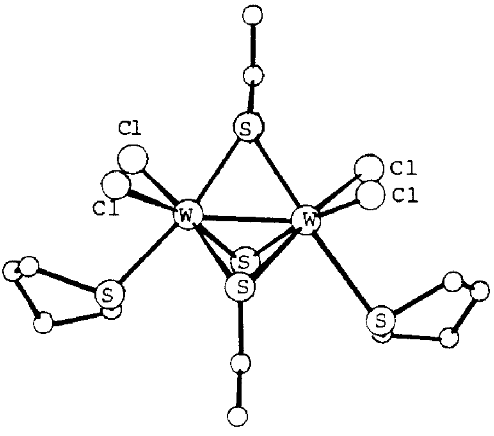
Other examples of triple bridges consisting of two thiolates and one other ligand are $[(Cl_2OM)_2(\mu\text{-SR})_2(\mu\text{-Cl})]^-$ (M = Mo, R = Ph [60] or M = W, R = Bu^t [149]) (**72**) (which have the bridging chloride ligand approximately *trans* to the oxo-group), $[\{Cl_2(tht)W\}_2(\mu\text{-SEt})_2(\mu\text{-S})]$ (tht = tetrahydrothiophene) (**73**) [150], and $[\{(dtc)OMo\}_2(\mu\text{-SPh})_2(\mu\text{-0})]$ (dtc = dialkyldithiocarbamate) (**74**) [61,151] among others. The last complex has the narrowest M–S–M angle (59.89(7) Å) reported for thiolate bridges. In each of these complexes the metal–metal distances are rather short, and M–S–M angles acute suggesting varying degrees of metal–metal bonding. The iridium hydride-complex $[\{(PPh_3)_2HIr)_2(\mu\text{-SPh})_2(\mu\text{-Cl})]^+$ (**75**) has been isolated and structurally characterised and again the bridging chloride ligand is *trans* to the high *trans*-influence ligand, in this case hydride [152].

As previously mentioned, complexes are known in which the threefold



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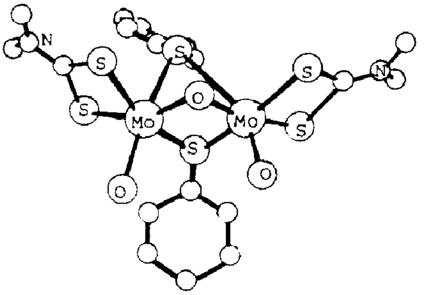

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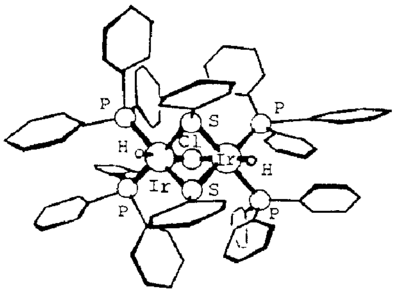

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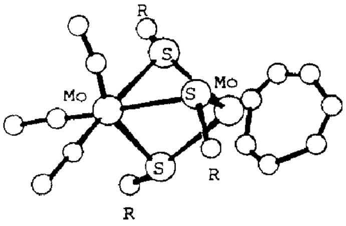
symmetry of the bridging sulphur atoms is destroyed even when there is no apparent asymmetry in the terminal ligands. This is invariably the result of isomeric form (**69**) being adopted. For example, the complex $[(\eta^7\text{-}C_7H_7)Mo(\mu\text{-}SR)_3Mo(CO)_3]$ ($R = Bu^n$ or Bu^t) (**76**) has been shown by ^1H



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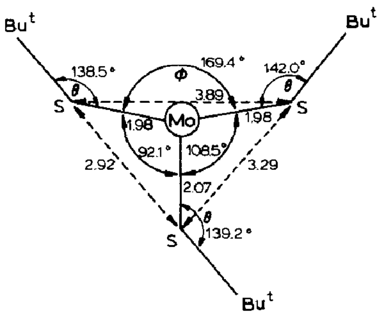
NMR studies (for $R = Bu^t$) to exist in both isomeric forms (**68**) and (**69**) which are interconvertible in solution by an inversion process at a bridging sulphur atom [153]. The (**68**) form shows only one signal for the bridging thiolate Bu^t protons, suggesting a threefold symmetry axis along the Mo–Mo vector, while the (**53**) isomer [154] shows a very considerable distortion of the bridge (shown by (**77**) which is a projection along the Mo–Mo axis). Formula (**78**) shows the same projection for the R = $\mathrm{Bu^n}$ analogue [154], and demonstrates the steric effect of the $\mathrm{Bu^t}$ groups which are pushed apart so as to increase the angles θ where the steric interactions are strongest. As expected the R = $\mathrm{Bu^n}$ analogue has smaller angles θ and also a marginally smaller angle ϕ. Whether these steric interactions alone are sufficient to account for the considerable distortion is open to question. A somewhat similar complex with a triple methoxide bridge, $[(\eta^3\text{-}C_7H_7)(CO)_2Mo(\mu\text{-}OMe)_3Mo(\eta^7\text{-}C_7H_7)]$ which also has the (**69**) isomeric form, has θ in the range 118.7 to 121.8°, [155] i.e. there is very little distortion compared to the triple $\mathrm{SBu^n}$ bridge (**78**), contrary to the supposition that a methyl group might be expected to show a similar steric effect to a $\mathrm{Bu^n}$ group in the most stable arrangement. The ease of distortion thus appears to be a property of the thiolate bridge in particular. Compounds (**71**) and (**78**) reveal that the shortest sulphur–sulphur distance in the bridge is that between the sulphurs whose non-bonding electron pairs are directed approximately towards each other, and has the value 2.92 Å for the R = $\mathrm{Bu^t}$ species. This is in the range for which attractive sulphur–sulphur interactions have been invoked to account for unusual structural features of monomeric complexes (see Section F(iv)). Such a S–S interaction, involving a stabilising rather than repulsive contribution from the sulphur lone-pairs may be effective in stabilising the (**69**) isomer where steric effects would favour the (**68**) isomer. The NMR spectrum of the R = $\mathrm{Bu^t}$ compound [153] and the crystallization of its (**69**) isomer [154] implies a comparable stability of the two isomers. The asymmetric complexes $[CpCl_2Mo(\mu\text{-}SMe)_2(\mu\text{-}OH)MoClCp]$ and $[CpCl_2Mo(\mu\text{-}SMe)_3MoClCp]$ have stronger M–M interactions [156] and similar arguments may be applicable. They show similarly distorted bridge structures, but severe disorder problems in the $(\mu\text{-}SMe)_3$ species prevented detailed analysis of the structure. The complex $[(CpCr)_2(\mu\text{-}SMe)_3]$, obtained by the



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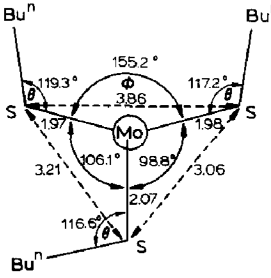

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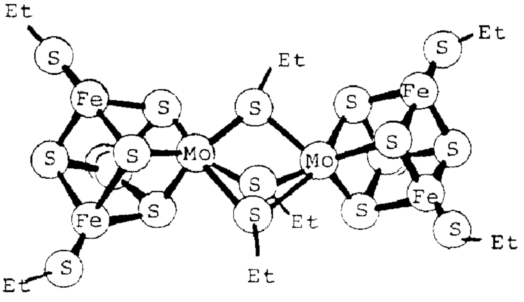
reaction of $[CpCr(CO)_3]$ with MeSSMe, is unstable and incompletely characterised [157].



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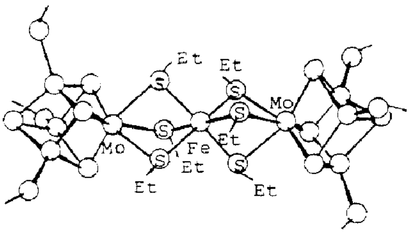
In contrast to the systems described above, the triple thiolate bridge in the "double-cubane" cluster $[\{(SEt)_3Fe_3MoS_4\}_2(\mu\text{-SEt})_3]^{3-}$ (**79**) [158] has a threefold axis along the Mo–Mo vector, and the three bridging thiolate substituents are oriented in the same sense around that vector. The long Mo–Mo distance (3.668(4) Å) and wide Mo–S–Mo angles (ca. 91°) preclude significant attraction between the metals. The analogue containing thiophenolate ligands in place of ethanethiolate has also been characterised [159] and has a similar structure. These complexes were synthesised during studies aimed at elucidating the structure of the iron–molybdenum cofactor of nitrogenase, and while they may not be close mimics of the structure and reactivity of nitrogenase, they are excellent spectroscopic models. They show sequential reversible electrochemical reductions to the 4^- and 5^- anions, and the reduced species evolve H_2 from thiophenol, with formation of thiophenolate anion and oxidation of the cluster to the 3^- anion [160]. The terminal ethanethiolate ligands in $[\{(EtS)_3FeMoS_4\}_2(\mu\text{-SEt})_3]^-$ can be exchanged by SPh using excess thiophenol, the rate determining step in this reaction being protonation of coordinated thiolate by thiophenol [161]. This type of exchange has been used to synthesise water-soluble analogues of the cluster with the thiol $HSCH_2CH_2OH$ [162]. The terminal thiolates can also be exchanged for chloride ligands with use of acyl chloride MeCOCl [161].



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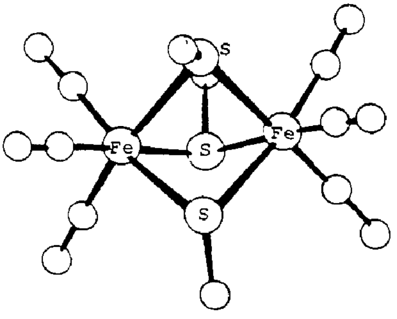
The triple thiolate bridge may serve to link iron and molybdenum atoms as in the iron-bridged double cubane complexes $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**80**) and $[Mo_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$ which has a similar structure [163]. The central Fe atom is coordinated by six bridging thiolates in an axially elongated trigonal antiprismatic environment, with three approximately equivalent S–S distances within each bridge. The triple thiolate bridge in the complex cation $[(CO)_3Fe(\mu\text{-}SMe)_3Fe(CO)_3]^+$ (**81**) has been identified crystallographically as the (**68**) isomer, and as expected the thiolate groups are equivalent, with no distortion from threefold symmetry. There is no suggestion of a strong metal–metal bond in this complex [164] which is isolated by a complicated reaction between $[(CO)_3Fe(\mu\text{-}SMe)_2Fe(CO)_3]$ and the dithiolene $(CF_3)_2C_2S_2$, as a salt of the $[Fe_2\{(CF_3)_2C_2S_2\}_4]^-$ anion [165]. The complex $[Re_2(NO)_2(SPh)_7]^-$ [112a] also has a triple thiolate bridge but in this instance the Re–Re distance of 2.783(1) Å is indicative of an Re–Re bond.



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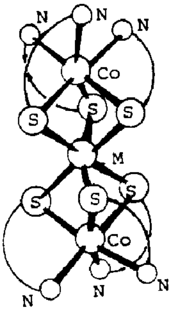
The complex cation $[\{Co(SCH_2CH_2NH_2)_3\}_2M]^{3+}$ (M = Fe or Ru) (**82**) has been shown by EPR spectroscopy to have a central atom M coordinated by six bridging thiolates with a distortion along the threefold axis [166]. It seems likely that the M atom has a similar environment to that of the central iron atoms in the iron bridged double cubane described above.

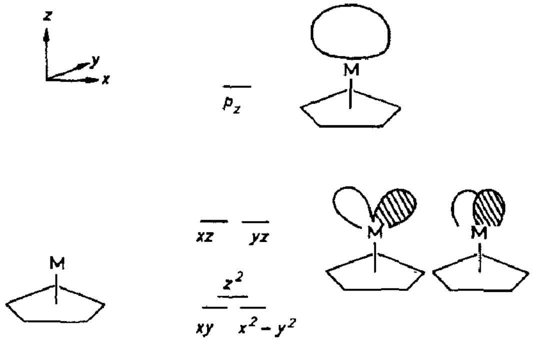


82

(iv) Complexes with quadruple μ^2-thiolato-ligands

Virtually all complexes with quadruple thiolate bridges have π-cyclopentadienyl or π-arene terminal ligands. This is not surprising since the frontier orbitals of the Cp–M fragment (**83**) are correctly aligned for interaction with four such bridging ligands [167]. The first reported complex of this type was $[(CpV)_2(\mu\text{-SMe})_4]$, which shows a low magnetic moment suggesting strong magnetic exchange through the sulphur bridges or possibly via a direct metal–metal interaction [168]. It is synthesised by oxidative displacement of carbon monoxide from $[CpV(CO)_4]$ using dimethyldisulphide. This type of reaction can also be used to synthesise the analogous molybdenum complex $[(CpMo)_2(\mu\text{-SMe})_4]$. This complex is diamagnetic, consistent with a direct metal–metal bonding interaction [157], confirmed by a crystal structure determination [169] which shows a Mo–Mo distance of 2.603(2) Å, and Mo–S–Mo angles in the range 63.6(1)–63.9(1)°. The S–C vectors are all oriented in the same sense about the Mo–Mo axis so as to maintain C_{4h} symmetry (**84**). The complex can be oxidised using $AgBF_4$ to the corresponding cation $[(CpMo)_2(\mu\text{-SMe})_4]^+$, whose structure is almost isodimensional with the neutral parent [169]. Neutral quadruply thiolate-bridged species can also be generated by addition of alkenes to the complex $[\{(MeCp)Mo\}_2(\mu\text{-S})_2(\mu\text{-SH})_2]$ to yield for example $[\{(MeCp)Mo\}_2(\mu\text{-SCH}_2CH_2S)_2]$ (**85**) [170]. These reactions are readily reversible with the facile occurrence of C–S bond cleavage, evident in the reversible displacement of ethylene from the latter complex by isocyanides to give dithiocarbonimidate ligands [171]. $[\{(MeCp)Mo\}_2(\mu\text{-SCH}_2CH_2S)_2]$ acts as an efficient catalyst for the hydrogenation of acetylene to ethylene [172], in a reaction sequence entirely localised at the bridging sulphur atoms. It is proposed, on the basis of this chemistry and extended Hückel calculations on these systems, that the four bridging sulphur atoms have acceptor and donor properties similar to those normally associated with transition metals [173]. The related complex cation $[\{(\eta^6\text{-CH}_3C_6H_5)Mo\}_2(\mu\text{-SMe})_4]^{2+}$ has a similar structure to the Cp analogues [174]. Mo–Mo bonding is indicated by the Mo–S–Mo angles of ca. 64°. A facile exchange of the methyl hydrogens of the toluene ligands occurs under basic conditions, demonstrated by disappearance of the corresponding methyl resonance from the ^1H NMR spectrum in D_2O–NaOD solution. The rate of exchange is dependent on the base concentration [174].

That the terminal Cp or π-arene ligands are not a requirement for quadruple bridge formation is demonstrated by the vanadium(III) dimer $[V_2(SCH_2CH_2S)_4]^{2-}$ (**86**) [51]. Although the formula is analogous to the $[M_2(SCH_2CH_2S)_4]^{2-}$ (M = Mn or Fe) complexes described earlier, the structure is not. Instead of a double bridge the vanadium species contains a



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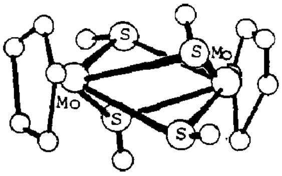

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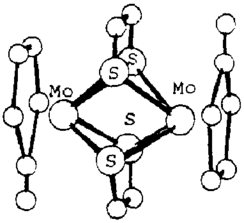

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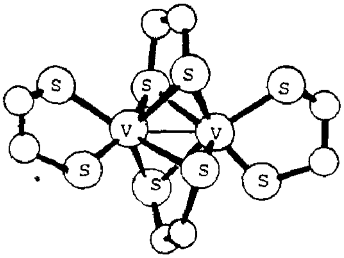
quadruple bridge probably supported by a metal–metal bond (V–V distance = 2.6 Å). The geometry of the dimer is best described as two orthogonally intersecting distorted square-planar units [51].

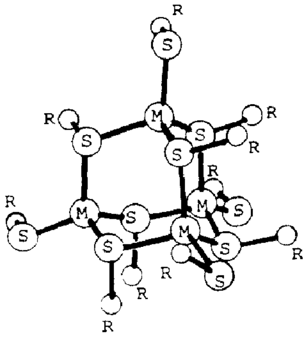


86

(v) Three-dimensional clusters

(a) Clusters with tetrahedral metal centres

The most common structural types of homoleptic thiolate clusters are the $[M_4(SR)_{10}]^{2-}$ adamantane-like unit and related structures, based on assemblies of $M(SR)_4$ tetrahedra. The general structure is that represented by (**87**).



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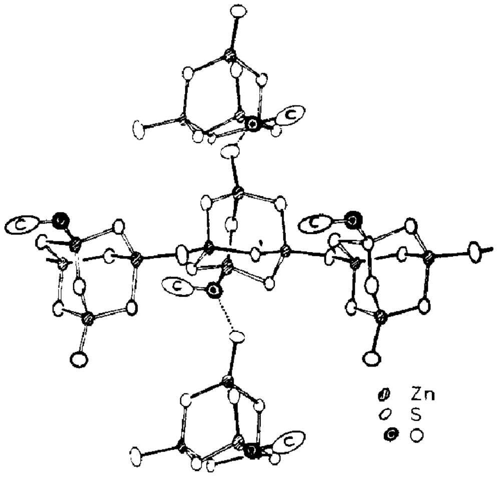
There is no evidence for metal–metal bonding in any complexes of this type. Such structures are known for M = Fe [33,175–177], Co [33,178,179], Zn [180–184], and Cd [184,185] and with alkyl (SEt) and aryl (SPh) thiolates. Synthetic procedures usually involve careful adjustments of equilibria between monomeric, dimeric and higher nuclearity species by varying the relative concentrations of M^{2+} (as halide or other salts) and thiolate anion. Related structures may be formed during the sequestration of metal ions by the cysteine-rich metallothionein proteins in biological systems. This process has been studied for M = Cd by ^{113}Cd NMR spectroscopy [186], with the conclusion that 4 and 3-Cd clusters are formed. Suggested structural units are $[Cd_3(SR)_9]$ and $[Cd_4(SR)_{11}]$ (SR = cysteinyl thiolate). The $[M_4(SR)_{10}]$ complexes undergo a variety of dynamic processes in solution. Rapid inversion at bridging sulphur atoms can be detected in the NMR spectra [176]. In addition, scrambling of terminal and bridging thiolates occurs [176]. In solutions containing $[M_4(SR)_{10}]^{2-}$ and $[M'_4(SR)_{10}]^{2-}$, exchange occurs leading to mixed metal complexes of the same general structure, with the statistically expected distribution of M and M′ seen approximately among the clusters [176]. These processes probably occur via the equilibria between the tetranuclear clusters and mononuclear and dinuclear species [33]. $[Fe_4(SPh)_{10}]^{2-}$ has been observed as an early intermediate in the cluster "self assembly" reactions in mixtures containing thiophenolate, $FeCl_3$ and elemental sulphur [34]. It reacts with elemental sulphur to form the $[Fe_4S_4(SPh)_4]^{2-}$ cubane cluster directly, illustrating the ease with which these labile systems undergo conversion to the biologically-relevant thermodynamically-stable clusters [34]. A reaction with elemental sulphur is also observed for $[M_4(SPh)_{10}]^{2-}$ (M = Zn or Cd) [184] to give a different type of cluster, $[M_{10}S_4(SPh)_{16}]^{4-}$ with a $M_6S_4^{4+}$ adamantane-like cluster rather than a cubane type cluster. Each of the four exposed M_3 faces of the $M_6S_4^{4+}$ core is capped by a $[M(SPh)_4]^{2-}$ unit [184].

In addition to variation in terminal ligands in such structural analogues as $[Zn_4(SPh)_8X_2]^{2-}$ (X = Cl, Br) [180], $[Co_4(SPh)_8Cl_2]^{2-}$ [178], $[Fe_4(SPh)_6$



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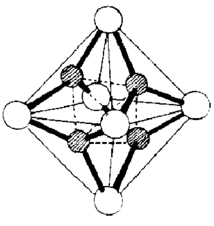
$Cl_4]^{2-}$ [177], and $[Zn_4(SPh)_9Cl]^{2-}$ [180], the clusters may be linked in chains as in *catena*-(μ-SPh) $[(\mu\text{-SPh})_6Zn_4(CH_3OH)(SPh)]$ (**88**) [183]. The four "terminal" ligands attached to each $Zn_4(SPh)_6$ core in this cluster are two thiolates bridging between clusters, one terminal thiolate and a molecule of methanol. This complex is described as a pertinent structural model for substrate-bound alcohol dehydrogenases as well as metallothionein proteins. The Zn–S–Zn angle at the linking thiolate is unusually large at 140°, compared with corresponding angles of ca. 109° within the cluster core [183].

The tetrahedral coordination at zinc is preserved in the cluster $[Zn_8Cl(SPh)_{16}]^-$ [182]. This structure is comprised of a central chloride atom surrounded by a tetrahedron of zinc atoms, which are linked by twelve thiolate bridges to an outer tetrahedron of zinc atoms. The coordination of each of the outer zinc atoms is completed by a terminal thiolate ligand [182].

(b) Copper and silver

The preference of copper(I) for three and two-coordination results in a different type of cluster system based on assemblies of approximately trigonal-planar and sometimes linearly coordinated copper. The tetranuclear clusters $[Cu_4(SR)_6]^{2-}$ are known for R = Me [187–189] or Ph [37,38,188,189]. They consist of a tetrahedron of copper atoms, with each of the six edges bridged by a μ^2-SR (**89**) so that each of the copper atoms has roughly trigonal-planar coordination [37,188,189]. The structure $[Cu_5(SR)_6]^-$ has been identified ($R = \mathrm{Bu}^t$) [190]. Its topological relationship to $[Cu_4(SR)_6]^{2-}$ can be described as a replacement of the three thiolates in one triangular face of the octahedron of sulphur atoms of $[Cu_4(SR)_6]^{2-}$ by a $[Cu(SR)_3]^{2-}$ unit (**90**). Similarly the structurally-characterised $[Cu_5(SR)_7]^{2-}$



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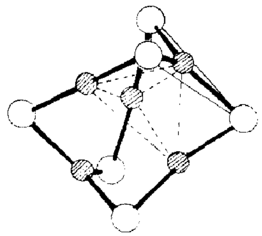

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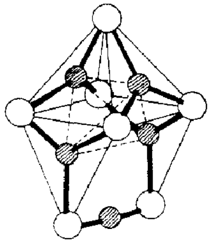

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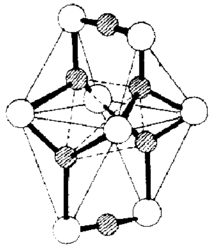


92

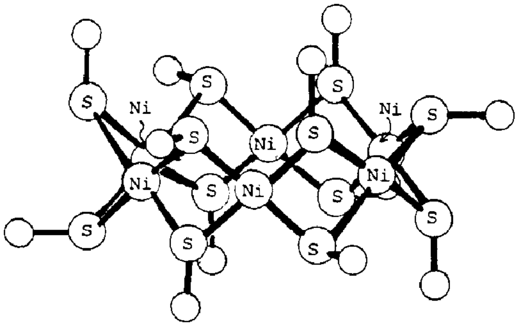
▨ Metal

○ Sulphur

(R = Ph) [192] can be described as a $[Cu_4(SR)_6]^{2-}$ unit with one of the edge-bridging thiolates replaced by a roughly linear $[Cu(SR)_2]^-$ unit (**91**). The silver(I) analogues of some of these clusters have been isolated. $[Ag_5(SPh)_7]^{2-}$ has the same structure as its copper analogue (**91**) [191] and $[Ag_5(SBu^t)_6]^-$ [187] (which has not been subjected to a crystal structure determination) is presumably similar to $[Cu_5(SBu^t)_6]^-$. The series has been extended by crystallisation of $[Ag_6(SPh)_8]^{2-}$ (**92**) which is related to $[M_4(SR)_6]^{2-}$ by a formal replacement of two opposite edge-bridging thiolates by the $[M(SR)_2]^-$ unit [193].

The series of cations $[Ag(RSAg)_n]^+$ (R = $CH_2C(CH_2OH)_3$ has been identified in aqueous solution [194], with $n = 9$ apparently the most stable member. The suggested structure is a chain of alternating S and linear Ag atoms, with each end terminated by Ag [194]. Formally, cyclisation of these chains by removal of a terminal Ag^+ results in the cyclic species $[Ag(SR)]_n$. These have been detected in solution by molecular weight measurements and the X-ray crystal structure of $[Ag(Scy)]_n$ (cy = cyclohexyl) reveals cyclic molecules, $n = 12$, with weak linkages across the ring between sulphur and silver atoms. As expected the silver atoms have approximately linear coordination [195]. The one-dimensionally non-molecular crystal structure of $[Ag(SR)]_\infty$ [196] (SR = 3-methyl-3-pentanethiolate) has been interpreted as containing remnants of the presumably cyclic solution structure $[\{Ag(SR)\}_8]$

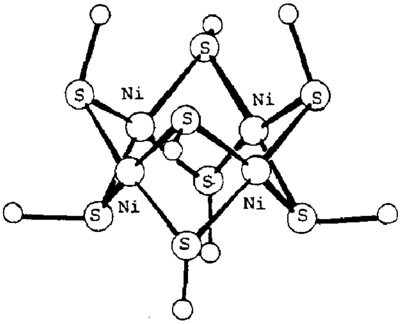
which was characterised by molecular weight measurement [197]. The ring size was found to be dependent on the steric properties of the thiol; thus primary alkanethiolates give only polymeric $[AgSR]_n$, while some secondary alkanethiolates give $[\{Ag(SR)\}_{12}]$ and tertiary alkanethiolates give $[\{Ag(SR)\}_8]$ [197,198].



93

(c) Nickel, palladium and platinum

Nickel(II), palladium(II) and platinum(II) thiolates, $[M(SR)_2]_n$ form cyclic structures with $n = 6$ [98,199–203] as well as infinite polymers [190,204]. The "tiara" structure of these hexamers is represented in (**93**) (R = Et) [200]. Crystal structures have also been determined for $R = CH_2CH_2OH$, M = Ni or Pd [202,203] and for $R = Pr^n$, M = Pd [203]. Each metal has approximate square-planar coordination and each sulphur is doubly bridging. The nickel atoms are all coplanar. Cryoscopic molecular weight measurements show that $n = 6$ is maintained in solution, but at high temperature dissociation occurs and solubility decreases [204].



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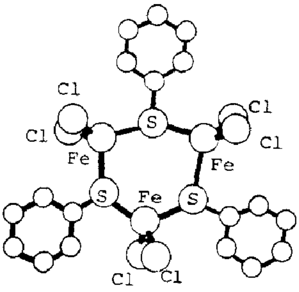
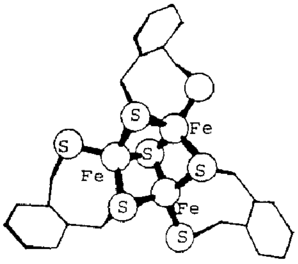
A similar structure type with $n = 4$, $[\{Ni(SR)_2\}_4]$ (SR = 4-thiolato-*N*-methylpiperidine), has been identified (**94**) [205]. The nickel atoms are displaced from the least squares planes of their coordinated sulphur atoms presumably as a result of strain in the cyclic structure. It has also been suggested [205] that S–S bonding interactions perpendicular to the Ni_4 plane (S–S = 2.993 Å) may be important in determining the exact geometry. The tetramer structure is maintained in solution [205].



95

(d) Other cluster types

A new structural type of iron-thiolate complex, represented by $[Fe_3(SPh)_3Cl_6]^{3-}$ (**95**) has recently been identified [32]. This cluster contains the $Fe_3(SPh)_3$ ring present in the $[M_4(SR)_{10}]^{2-}$ clusters, but remarkably the ring is planar and the Ph groups of the thiophenolate ligands lie in the same plane as the Fe_3S_3 ring. Thus the sulphur atoms have planar geometry with very large Fe–S–Fe angles (140–142°) and small S–Fe–S angles (99–102°). The roughly tetrahedral coordination of each Fe is completed by two chloride ligands. The reason why this unusual planar structure is adopted is not clear but evidently does not lie in steric considerations.



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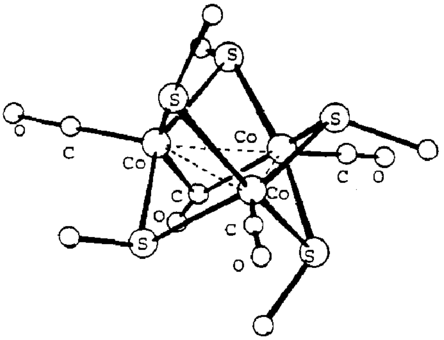
A trinuclear Fe(II) cluster $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ illustrates a topological similarity between μ^3-bridging sulphide and μ^2-bridging thiolate, since its structure (**96**) [206,207] resembles the $Fe_4S_4(SR)_4$ cubane cluster unit with one Fe(SR) group removed. It is emphasised that this relationship is topological rather than chemical or electronic since thiolate is less able to mediate electronic interactions than sulphide.



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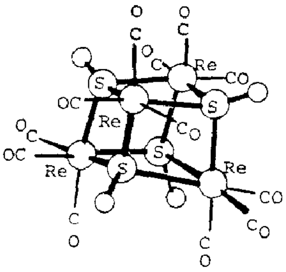
Another form of trinuclear species supported by thiolate bridges is $[Co_3(SEt)_5(CO)_4]$ (**97**) [208]. The cobalt atoms form a triangle with each edge bridged by two thiolates or a thiolate and a carbonyl group. The remaining three carbonyls are terminally bonded to the metals; thus each cobalt is approximately a tetragonal pyramid with an apical CO group [208].

Existence in solution of a mixed valence copper cluster with the formula $[Cu^{II}\{(RS)Cu^{I}\}_4]$ (SR = thiomalic acid) has been proposed. A structure involving a tetrahedral Cu(II) ligated via sulphur to four Cu(I)(SR) units is suggested, but this is based on optical titration and polarographic data and is not unequivocal [209].

The eight cadmium atoms in $[Cd_8I(SCH_2CH_2OH)_{12}]I_3$ form a cube at the centre of which is an iodine atom. Each of the twelve edges of the cube are bridged by a thiolate sulphur, so that each cadmium is bonded to three sulphurs in a trigonal planar array, and the trigonal bipyramidal coordination of the metals is completed by the axial ligands, one being the central iodine, the other being a hydroxyl group of the thioglycollate ligand [210].

D. COMPLEXES WITH μ^3-BRIDGING THIOLATO-LIGANDS

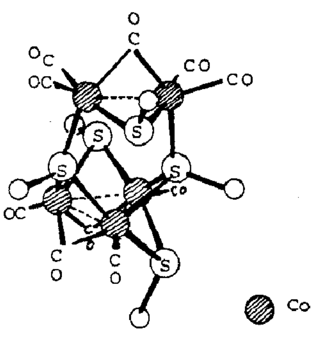
Since the thiolate anion possesses three lone pairs of electrons it may in principle coordinate to three metal centres, and this has indeed been observed in several cluster species. There are many more instances in which a nominally μ^2-bridging thiolate is weakly coordinated to a metal atom in an inter-molecular association in the crystalline state and these will not be considered here.



98

The simplest example is the tetranuclear carbonyl species $[\{M(SMe)(CO)_3\}_4]$ (M = Mn or Re) (**98**), synthesised in the reaction of $[MBr(CO)_5]$ with $Me_2Sn(SMe)_2$. These complexes were originally formulated as trinuclear clusters on the basis of misleading cryoscopic molecular weight measurements [211]. After various proposals for the structure had appeared (some erroneous [211,212] and some correct [213–215]) on the basis of cryoscopic molecular weight measurements, mass spectroscopy and vibrational spectroscopy, the structure of $[\{Re(SMe)(CO)_3\}_4]$ was elucidated unequivocally by a crystal structure determination [216]. The four rhenium atoms form a tetrahedron with each face capped by a thiolate ligand bonded equally to three metals (**98**).

Pentanuclear cobalt thiolate clusters containing the subunit $Co_3(\mu^2\text{-}SEt)_4(\mu^2\text{-}CO)_2(CO)_3$ (which has a similar structure to $[Co_3(SEt)_5(CO)_4]$, (**97**)), are formally adducts formed by coordination of the bridging thiolates of the subunit to another cluster fragment. Thus in $[Co_5(SEt)_5(CO)_{10}]$ (**99**) [217] two of the bridging thiolates of the triangular subunit are coordinated to a $Co_2(SEt)(CO)_5$ fragment and thus become triply bridging. Similarly in $[Co_6(SEt)_4(CO)_{11}S]$ [217] the triangular subunit is linked to a $[Co_3(\mu^3\text{-}S)(\mu^2\text{-}CO)_3(CO)_3]$ fragment (**100**). A series of mixed valence copper clusters, $[Cu^{II}_6Cu^{I}_8(SL)_{12}Cl]^n$ (**101**) with bidentate chelating thiolate ligands ($SL = SC(CH_3)_2CH_2NH_2$, $n = 7^+$ [218], $SL = SC(CH_3)_2COO$ [219], or penicillamine $SC(CH_3)_2CH(COO)NH_2$, $n = 5^-$ [220]) are supported by μ^3-thiolate bridges. The structure consists of a central chlorine atom inside a cube of eight Cu(I) atoms. Each of the six faces of the cube is capped by a Cu(II) atom, and each Cu(II) is linked to two Cu(I) atoms via a thiolate bridge. Thus each thiolate is bonded to three metal atoms. The Cu(I) atoms have approximate trigonal-planar coordination to three sulphurs, while the Cu(II) atoms are approximately square planar with two thiolate sulphurs and two other donor groups L of two chelate ligands. The presence of chloride ion in solution, chelation, and the methyl-substituents are apparently required for the stability of the mixed valence clusters. The intense colour is due to a strong absorption at ca. 485 nm, which has been variously assigned as S(3p) → Cu(II) ($d_{x^2-y^2}$) or S(3p) → Cu(I)(4s, 4p).



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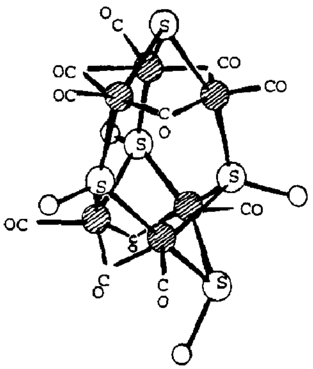

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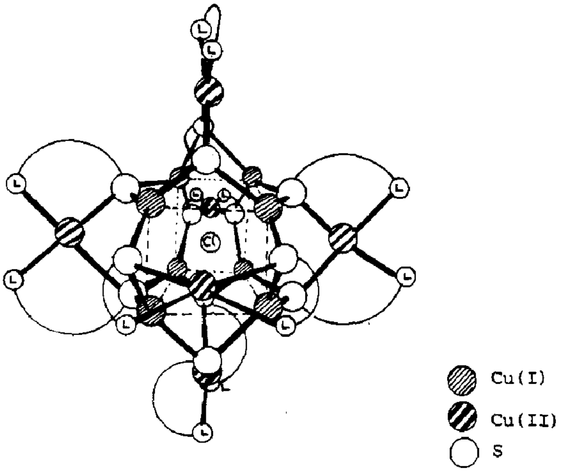
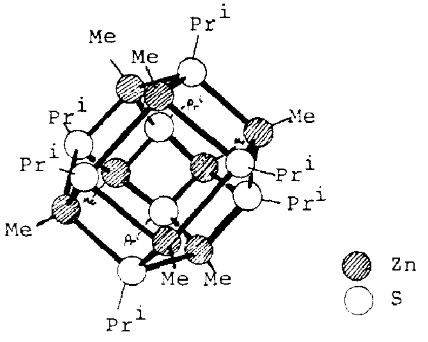


101

An oligomeric methyl zinc cluster $[ZnMe(SPr^i)]_n$ (**102**) has $n = 6$ in solution but crystallises as an octamer [221] in which tetrahedrally-coordinated zinc is bonded to three thiolates and one methyl, while each thiolate sulphur is bonded to three zinc atoms [221]. Finally the cluster species $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$ (**103**) contains some μ^3-bridging thiolate and Cd atoms in a variety of coordination environments, tetrahedral (4S), trigonal bipyramidal (4S + O) and octahedral (3S + 3O). The arrangement of Cd and S atoms approximately mimics a fragment of the cubic ZnS (sphalerite) lattice [222].



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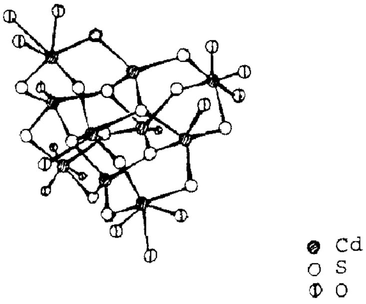


103

E. SYNTHESIS OF THIOLATO-COMPLEXES

A wide variety of synthetic methods has been used for incorporation of thiolate into transition metal complexes. The simplest and most direct involve the displacement of halide ion by thiolate anion, which has an advantage over use of RSH because of formation of an insoluble halide as a thermodynamic driving force. Lithium, sodium and potassium salts of thiols are commonly used in non-aqueous solvents for reactions of this type but do not invariably give the same products. More covalent thiolate sources have also been employed in halide substitution reactions. Thus $Pb(SR)_2$, AgSR, TlSr and $Al(SR)_3$ on reaction with transition metal halide complexes give insoluble halide by-products which are easily removed by filtration. An alternative method which is attractive because of the ease of removal of volatile Me_3SiCl involves reaction of metal halide complexes with Me_3SiSR. Equations (12) [13], (13) [19], (14) [12], (15) [20], and (16) [147] illustrate reactions of this type.

$$MoCl_4 + 4\ LiSBu^t \xrightarrow{\text{1,2-dimethoxyethane}} [Mo(SBu^t)_4] + 4\ LiCl \tag{12}$$

$$MnCl_2 \cdot 4\ H_2O + 4\ NaSPh \rightarrow Na_2[Mn(SPh)_4] + 2\ NaCl + 4\ H_2O \tag{13}$$

$$NbCl_5 + \tfrac{5}{3}(Al(SPh)_3 \cdot Et_2O) \rightarrow [Nb(SPh)_5] + \tfrac{5}{3}(AlCl_3) + Et_2O \tag{14}$$

$$ZnCl_4^{2-} + 4\ TlSPh \rightarrow [Zn(SPh)_4]^{2-} + 4\ TlCl \tag{15}$$

$$[WCl_4(SMe_2)_2] + 3\ Me_3SiSEt \rightarrow [W_2Cl_2(SEt)_3(SMe_2)] + \text{by-products} \tag{16}$$

Thiolate anions may be generated in solution by addition of base to the reaction mixture containing thiol (eqn. 17) [102]

$$[MoCl_2(CO)_4] + 3\ HSC_6H_2Pr^i_3 + 3\ NEt_3 \xrightarrow{MeOH}$$
$$[HNEt_3][Mo(SC_6H_2Pr^i_3)_3(CO)_2] + 2[HNEt_3]Cl + 2\ CO \tag{17}$$

Alternatively the base may be present in the precursor complex, as in the reaction between thiols and dialkylamido-complexes [74], (eqn. 18).

$$n[\mathrm{Ti(NR_2)_4}] + 4n\mathrm{HSR} \rightarrow [\mathrm{Ti(SR)_4}]_n + 4n\mathrm{HNR_2} \qquad (18)$$

This approach can also be used to synthesise thiolate complexes by thiol exchange; for example the terminal ethanethiolate ligands in the double cubane cluster $[\{(\mathrm{SEt})_3\mathrm{MoFe_3S_4}\}_2(\mu\text{-SEt})_3]^{3-}$ can be replaced by thiophenolate by treatment with excess thiophenol [161].

Another approach involves use of either disulphides (RSSR) or thiols as oxidative–addition type reagents with low-valent metal complexes, particularly metal(0) carbonyl or tertiary phosphine species (eqns. 19, 20 [168] and 21 [142]).

$$2[\mathrm{CpV(CO)_4}] + 2\ \mathrm{MeSSMe} \rightarrow [\{\mathrm{CpV(SMe)_2}\}_2] + 8\ \mathrm{CO} \qquad (19)$$

$$2[\mathrm{CpV(CO)_4}] + 4\ \mathrm{MeSH} \rightarrow [\{\mathrm{CpV(SMe)_2}\}_2] + 2\ \mathrm{H_2} + 8\ \mathrm{CO} \qquad (20)$$

$$2[\mathrm{Pd(PPh_3)_4}] + 2\ \mathrm{PhSSPh} \rightarrow [\{\mathrm{Pd(SPh)_2(PPh_3)}\}_2] + 6\ \mathrm{PPh_3} \qquad (21)$$

The reactions involving disulphides are usually carried out under vigorous conditions, e.g. in refluxing toluene under UV irradiation. The addition reaction of RSH probably proceeds via a hydrido-intermediate since such a species has been isolated (eqn. 22) [100].

$$[\mathrm{Pt(PPh_3)_4}] + \mathrm{HSCH_2CH_2SMe} \rightarrow [\mathrm{PtH(SCH_2CH_2SMe)(PPh_3)}] + 3\ \mathrm{PPh_3} \qquad (22)$$

Synthesis of compounds with bridging thiolate ligands has relied on two basic approaches. One is a logical method involving coordination of monomeric species with terminal thiolates to another metal centre either by an addition or a ligand displacement reaction. Equation (23) gives an example of this [124].

$$[\mathrm{Mo(SBu^t)_4}] + [\mathrm{Fe_2(CO)_9}] \rightarrow [\{(\mathrm{CO})_3\mathrm{Fe}(\mu\text{-SBu}^t)_2\}_2\mathrm{Mo(CO)_2}] \qquad (23)$$

The other relies on spontaneous and uncontrolled formation of thiolate bridges, a mode of reactivity usually more difficult to avoid than to achieve.

The methods described so far are general and also simple. However, in many cases the synthesis of thiolate complexes is not trivial, but is hampered by difficulties inherent in thiolate chemistry. The most important of these are:

(i) That thiolates frequently act as bridging ligands, a tendency which has been an obstruction to the synthesis of mononuclear compounds.

(ii) The tendency for thiolates to act as reducing agents with formation of disulphides, which has hampered synthesis of complexes of metals in their higher oxidation states.

(iii) The facility with which the C–S bond cleavage may occur in coordinated alkanethiolates to give sulphide complexes.

All of these are illustrated in the previous sections. A variety of approaches has been used to circumvent them. Much use has been made of electron-withdrawing substituents on arenethiolates to make the sulphur a weaker donor and thus decrease its ability to bridge. The prime example is pentafluorothiophenol, use of which has led to isolation of monomeric species where only dimers or polymers could otherwise be obtained. An example is the reaction of $[MH(CO)_5]$ (M = Mn or Re) with thiols [127] discussed earlier (Section C(ii)). Another way round the problem which has been employed is the use of thiols containing bulky substituents (see Section B(iii)).

The problem of reduction by thiolates is less straightforward and consideration of the mechanism is required in design of synthetic approaches to its solution. A good illustration is the synthesis of the mononuclear iron(III) thiolates $[Fe(SR)_4]^-$. The use of Fe(III) precursors containing sterically demanding alkoxide ligands, and of bulky thiols is discussed in Section B(iii)(c). While the use of these bulky thiols has led to success in isolation of low coordination number complexes (Section B(iii)) no routes have yet been found to Cu(II) thiolates except in mixed oxidation state clusters, although there is evidence for the formation of $[\{Cu^{II}(SR)\}_2]^{2+}$ as an intermediate in cluster formation [223].

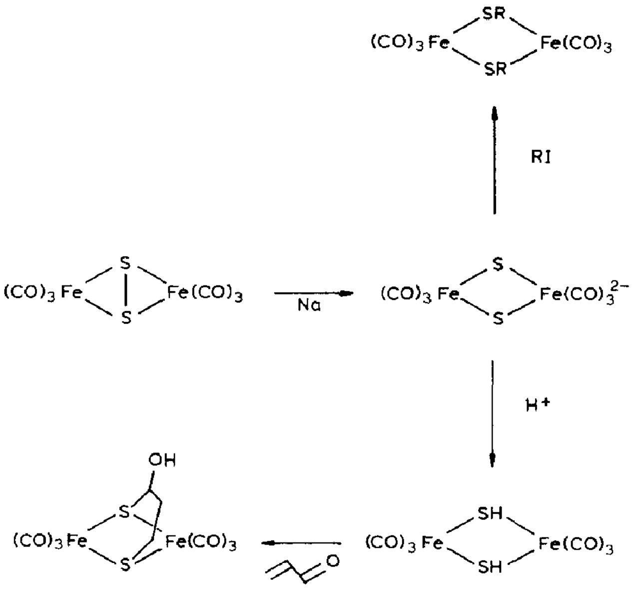
Pathways involving C–S bond cleavage are limited to the alkanethiols and therefore the simplest approach is to avoid their use and synthesise complexes of arenethiolates. With careful design of aliphatic thiolate ligands based on mechanistic considerations (see below, Section F(i)) it may prove possible to circumvent this problem. The use of neo pentyl derivatives as the ligand side chain might prove effective for example.

Recently new approaches to synthesis of M–SR bonds by alkylation of sulphido-ligands have been developed. An example is the extensive chemistry found to occur at the sulphur sites in $[\{CpMo(SCH_2CH_2S)\}_2]$ and related complexes. Another is illustrated by Scheme 1 [224,225].
Another example of sulphide alkylation is the reaction of NiS with tetraethyl tin to give the $[\{Ni(SEt)_3\}_6]$ structure (Section C(v)).

F. REACTIVITY AND REDOX CHEMISTRY OF THIOLATO-COMPLEXES

(i) Reactivity of sulphur

Several reviews are available covering all aspects of the reactivity of sulphur ligands [2,6,8,9], and although thiolate complexes have received little special attention the combined reviews give reasonably adequate coverage.



Scheme 1

This section will therefore be a brief summary of material specific to thiolate ligands.

One of the principal factors governing the reactivity of thiolate complexes is the availability of electron density on the sulphur atoms which encourages attack by electrophiles at the sulphur atoms of thiolate complexes. An extreme example is $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, which undergoes facile protonation or alkylation reactions at the sulphur atom [226]. As might be expected, alkylation at terminal thiolates is more often observed than at bridging thiolate [227] and has been used in "template synthesis" reactions to give chelating thioether ligands [80,228]. An example is shown in eqn. (24) [80].

$$[Fe(SCH_2CH_2S)_2(CO)_2]^{2-} + BrCH_2CH_2Br \rightarrow [Fe\{S(CH_2)_2S(CH_2)_2S(CH_2)_2S\}(CO)_2] + 2\ Br^- \qquad (24)$$

Alkylation of bridging thiolates may also be carried out under mild conditions in some cases, as in the reaction of polymeric $[(Pd\{S(CH_2)_mS\})_n]$ ($m = 2$ or 3) with alkyl bromides and iodides [229].

The thiolate substitution reactions in the iron–molybdenum–sulphur cubane clusters are dependent on nucleophilic and basic properties of the coordinated thiolate, making use of protonation and acylation by thiol and acyl halide [97,161,230]. As indicated by this type of reactivity, the availability of electron density at the sulphur atoms is much greater than at the oxygen atoms of analogous alkoxide complexes, largely because the thiolate ligand is less able to transfer electron density to the metal atom by

π-donation, in spite of the smaller electronegativity of sulphur. This can be understood by reference to the organic chemistry of divalent sulphur and oxygen where differences in electronic effects between the two are interpreted by differentiating between σ- and π-effects. Various studies using ^1H and ^{19}F NMR, and dipole moment measurements, in suitable series of aliphatic compounds, indicate that the inductive withdrawing ability ($-I$ effect) is greater for oxygen (and nitrogen) than sulphur [231], as might be expected on grounds of electronegativity. However, in compounds with orbitals capable of engaging in π-interaction with the oxygen or sulphur, such as aromatic compounds, oxygen appears to be the more effective electron donor, $-OH$ and $-OR$ being more ring-activating than sulphur counterparts in analogous pairs of aromatic compounds. For example, 4-(methylthio)-benzoic acid, $CH_3SC_6H_4COOH$, is a stronger acid than 4-methoxybenzoic acid, $CH_3OC_6H_4COOH$ [232]. The relative weakness of this $+R$ resonance effect ((**104**), X = 0 or S) for sulphur may be attributed to its poor *S* (3*p*) overlap with the ring π-orbitals.


104

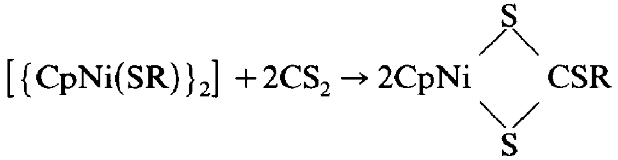
As mentioned above, dealkylation of thiolate ligands to sulphide is a commonly observed reaction. The reaction of Me_3SiSR with WCl_6 has been studied in some detail and proceeds as shown by eqn. (25) [233].

$$WCl_6 + Me_3SiSR \rightarrow WCl_4S + Me_3SiCl + RCl \qquad (25)$$

The rate at which this C–S cleavage occurs depends on the R group in the sequence $Bu^t \gg EtS > MeS$ and indeed the intermediate $[WCl_5(SMe)]$ is stable. Dealkylation of the SBu^t ligand is particularly common, and is observed for example in the reaction of $[Mo_2(NMe_2)_6]$ with excess $HSBu^t$ resulting in a double sulphido-bridge [95], and in the reaction of $[Mo(SBu^t)_4]$ with dimethylphenylphosphine, also with formation of a double sulphide bridge [15]. Isobutylene has been identified as the side-produce of dealkylation in the latter reaction. Reversible C–S bond cleavage is an important property of the quadruple μ^2-thiolate bridges in $[(CpMo)_2(\mu^2\text{-}SR)_4]$ complexes which has led to the development of an extensive chemistry at these ligands (see Section C(iv). S–C bond cleavage has not been observed in arene-thiolate ligands.

The reactions of some iron, zinc and cadmium thiolate complexes with sulphur to give metal sulphido–thiolato-clusters were described earlier. Thiolate complexes may also react with elemental sulphur via insertion into the M–SR bond. Copper thiolates also react with elemental sulphur although the products are not well characterised [214].

Several examples have been reported of insertion of carbon disulphide into a M–SR bond, as in eqn. (26) [234].



$$[\{\mathrm{CpNi(SR)}\}_2] + 2\mathrm{CS}_2 \rightarrow 2\mathrm{CpNi}\overset{\mathrm{S}}{\underset{\mathrm{S}}{\diamond}}\mathrm{CSR} \qquad (26)$$

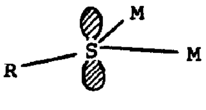
(R = Me or Et)

This type of reactivity is more fully discussed in a review of CS_2 activation [235].

(ii) Inversion at sulphur

Several kinetic studies have been made of interconversion of isomers by inversion at three-coordinate sulphur, i.e. for the thiolate complexes at μ^2-thiolate ligands. Dialkyl sulphides coordinated to transition metals show much lower energy barriers ($\Delta G^\ddagger = 55$–70 kJ mol^{-1}) to the inversion process than do sulphoxides and sulphonium ions ($\Delta G^{\neq} = 100$–150 kJ mol^{-1}) and stabilisation of a planar transition state by sulphur to metal $p\pi \rightarrow d\pi$ overlap has been suggested as the basis for this [153].

A survey of activation energies for inversion processes at bridging thiolate sulphur [16,124,128,149,153,211,212,236,237] reveals that most studies (using variable temperature NMR) obtain values of $\Delta G^{\neq}$ in the range 45 to 77 kJ mol^{-1}, similar to terminal R_2S ligands. Some discussion has appeared in the literature [236,237] concerning which of the two transition states (**105**) or (**106**) are appropriate. In (**105**) a planar transition state occurs with possible interaction of the sulphur *p*-orbital with the two metal centres. In (**106**) both lone pairs of the sulphur are directed to one or other metal alternately and the process is described as a rotation rather than an inversion with sp^3 hybridisation at sulphur maintained throughout. However, these arguments seem rather futile since any distinction between the two is purely a matter of formalism, and the decisive factor in the choice is therefore one of personal preference, as remarked by Abel et al. [238].



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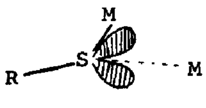

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(iii) Redox chemistry

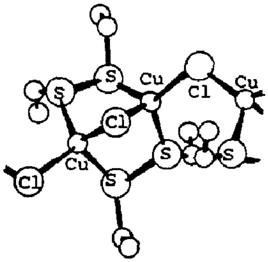
The redox chemistry of thiolate complexes is concerned to a large extent with the formation and cleavage of sulphur–sulphur bonds, and oxidative addition of disulphides to low oxidation state metal complexes is a useful synthetic reaction. Sulphur–sulphur bond formation may occur in thiolate complexes with reduction of the metal or of some external oxidant. For example, in the reaction of WCl_6 with MeSiSR, the initial substitution product $[WCl_5(SR)]$ is stable to disulphide formation but a second substitution to give presumably $[WCl_4(SR)_2]$ results in elimination of RSSR [233] with concomitant reduction of the metal. For disulphide elimination to occur it is not always necessary for two thiolates to be present at the same site. Electrochemical oxidation of $[Cp_2M(MeCN)(SR)]^+$ and $[Cp_2M(SR)_2]$ (M = Mo or W) proceeds by one electron transfer followed by dissociation of thiol radical $RS^\cdot$, which subsequently further reacts to give disulphide [239]. A similar process may occur in electrochemical oxidation of $[MoO(SPh)_4]^-$ (see Section B(ii)). Although oxidation of thiolate ligands occurs with formation of sulphur–sulphur bonds the disulphide group may be retained in the complex. Thus $[CpFe(SPh)(CO)_2]$ reacts with $NO[PF_6]$ to give what appears to be a phenyldisulphide-bridged dimer, $[\{CpFe(CO)_2\}_2(\mu\text{-PhSSPh})]^{2+}$. Other types of oxidation at coordinated thiolate include formation of S=0 bonds by reaction with H_2O_2 [241]. Oxidative pathways of coordinated thiolates have been summarised as follows [241]:

(1) 1 e oxidation at sulphur followed by M–S bond cleavage, with ultimate formation of free disulphide.
(2) Oxidation at sulphur with formation of coordinated RSSR (either in a mononuclear complex containing *cis*-thiolates or via a dinuclear intermediate) usually followed by M–S cleavage to give free disulphide.
(3) Oxidation at sulphur to yield S-bonded sulphonic acid complexes.
(4) Oxidation at carbon adjacent to sulphur to give S-bonded thioacid complexes.

In spite of the tendency towards ligand-centred redox behaviour, well-behaved electrochemical and chemical redox reactions are common and indeed thiolate ligands are now recognised as very efficient mediators of electron-transfer. Aspects of this behaviour are fully discussed in ref. 6. Reversible electrochemical processes may be ligand-centred as in complexes with "dithiolene" type ligands but also metal-centred reversible processes are often found. These are important to the understanding of redox processes occurring at the thiolate-coordinated metal ions in the active sites of redox-active enzymes.

(iv) *Sulphur–sulphur interactions*

Unusual structural features of several thiolato-complexes, particularly those with chelating ligands, have been rationalised by invoking weak bonding interactions between nominally non-bonded sulphur atoms. Examples of such features include trigonal prismatic geometry [11a] or distortions of octahedral complexes towards the trigonal prismatic limit [10,11,83], unexpectedly close *cis*-S–S contacts with narrow S–M–S angles between terminal thiolate ligands [243,244], and distortion of M_2S_2 rings in thiolate bridged structures [1(d)]. Examples of close contacts between terminal thiolate ligands are $[MoO_2L_2]$ ($L = SC(Me)_2CH_2NHMe$), in which the S–Mo–S angle is ca. 70° and the S–S contact distance 2.76 Å [243] and $[Mo_2O_4(SPh)_4]^{2-}$, with S–Mo–S angles of ca. 74° and 82°, and S–S contacts of ca. 2.9 and 3.2 Å [244]. The angles in the latter complex are narrow by comparison with the chloride analogue $[Mo_2O_2Cl_4]^{2-}$ (92°). These S–S contact distances may be compared to the bonded S–S distance of 2.04 Å and 2.06 Å in ethyldisulphide complexes of copper, $\{CuX(Et_2S_2)\}_n$ (**107**) (in which there is a definite "normal" S–S bond) [245,246] and with the sum of the van der Waals radii of two sulphur atoms (ca. 3.7 Å). Where comparison is possible, these S–S contacts are invariably shorter when the sulphur lone pairs (assuming approximate sp^3 hybridisation) are oriented so as to allow overlap, resulting in an interaction which would normally be considered repulsive. Close examination of the structural data for many thiolate complexes shows S–S contacts closer than 3 Å and it must be queried whether these close contacts are the result of a steric compression forcing the sulphur together, or whether there is an intrinsic attraction between the sulphurs atoms as a result of orbital overlap. In many cases there is no obvious steric contribution, and some S–S attraction is therefore suggested. This is supported by a variety of circumstantial evidence. For example, although the S_8 ring shows no contacts between non-bonded sulphurs of less than 4.7 Å, the oxidised form S_8^{2+} (**108**) shows a different ring conformation allowing contra-ring contacts of as little as 2.86 Å



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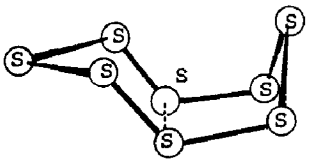

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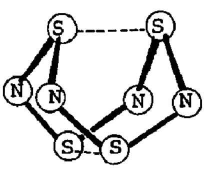

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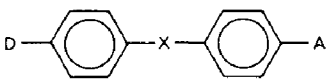
suggesting a distinct degree of bonding across the ring. An even more notable interaction occurs between the sulphur atoms in the S_4N_4 ring (**109**) (in which there are no proper bonds between sulphur atoms) resulting in S–S distances of 2.58 Å and a folded ring conformation [247]. There are many such examples in sulphur chemistry. Further evidence that nominally non-bonded sulphur atoms may be attracted together comes from the coordination chemistry of thioethers. In the octahedral complexes $[(NH_3)_5RuL]^{3-}$ (L = dithioether ligand coordinted by one sulphur), the presence of the second (non-coordinated) thioether group in the ligand has very distinct effects on the electronic spectra and redox potentials, but only if the flexibility of the ligand is such as to allow close contact between the sulphur atoms [6].

These structural and electronic observations suggest that sulphur–sulphur attractions can be intrinsic and can occur without, for example, the intermediacy of vacant metal orbitals. Of course, this does not preclude a stabilising effect of metal orbitals in favourable cases. It is not yet possible to predict in what types of complexes sulphur–sulphur attractions may be important, and neither can it be said that the orbital origin of the interaction is fully understood. Because structural effects are often evident, it must be assumed that they also have effects on the electronic structure of the metal and variation in the strength of attraction between coordinated sulphur atoms may contribute towards stabilisation of a gradation of oxidation states of the metal. Thus, a pair of coordinated thiolate ligands may be separate one-electron donors or at the other extreme a disulphide ligand with a S–S bond of length ca. 2 Å, with a more or less continuous variation in between. The interesting possibility of a role of this type for sulphur ligands in biological systems has received consideration [243].

G. CONCLUSIONS

Thiolates are strong donor ligands with a high affinity for most metal ions. An enormous structural variety of complex and cluster species has been identified, and the potential for sophisticated design of the thiolate substituent group should lead to still greater diversity. Some evidence based on structural considerations and bond length data has indicated thiolates to be capable of a degree of π-donation from S(3p) to metal in favourable arrangements. To add to this evidence (discussed earlier) a detailed study of the structure of $[Mo(CNR)_2(PhCCPh)(SBu^t)_2]$ including extended Hückel MO calculations shows that all aspects of the geometry may be accounted for by taking into account maximisation of sulphur–metal π-interaction [248]. The π-donor effect is much weaker than for oxygen in spite of the lower electronegativity of sulphur. This is to be expected from the many



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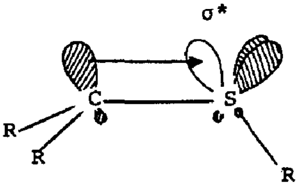

111

comparisons of divalent oxygen and sulphur in organic compounds.

Thiolato (and particularly sulfido) ligands are effective at mediating electron transfer in redox reactions, and indeed at transmitting other types of electronic influences. The suggestion that divalent sulphur possesses such properties is reinforced by parallels in organosulphur chemistry. In particular, NMR studies of shifts of electron density from one aromatic ring to another through various "transmitter" groups X under the influence of electron donating and accepting groups (D and A) in compounds of the type (**110**) indicate that while O, CH_2, SO and SO_2 groups X are poor "transmitters", S and NH are quite effective in this respect [249]. The observation that SO and SO_2, which have sulphur in high oxidation states, are less effective suggests that the origin of the difference between S and O is not the availability of 3*d*-orbitals on sulphur (which is expected to be greater in higher oxidation states), but rather is a consequence of the high polarisability of sulphur (which is expected to be most evident in low oxidation states). The limited information available suggests that this property is transferable to divalent sulphur ligated to transition metals. Fackler [1(d)] remarks that sulphur ligands are very effective at averaging the electronic charge over all atoms to which they are bound, as illustrated by the 4 Fe protein active site models $[Fe_4S_4(SR)_4]^{2-}$ in which it has not proved possible to define distinct Fe(II) and Fe(III) atoms [250]. The levelling of charge has been attributed [1(d)] to several factors including low-lying empty S(3*d*) orbitals, high polarisability of low valent sulphur and a shallowness of the potential energy minimum along the M–S coordinate. The notion of the involvement of sulphur 3*d* orbitals has often been invoked to explain properties of certain organo–sulphur compounds and occasionally metal thiolate complexes, but recent studies suggest that S(3*d*) orbitals are much less significant than had been supposed [251–253]. A prominent example is the stabilisation of carbanionic centres by adjacent sulphur atoms, often suggested to be the result of electron transfer to S(3*d*) orbitals [254], but calculations and physical studies [255–257] suggest that it would be more appropriate to consider the polarisability of sulphur [258], or a vacant relatively low-energy S–C σ^* antibonding orbital [259,260] of an SR group as the stabilising influence (**111**)..

The role of S($3d$) orbitals, S($3p$) → M(nd) donation, the polarisability of sulphur, and interactions such as (**111**) has yet to be elucidated by theoretical study. Another area which deserves further consideration is the role of sulphur–sulphur interactions in stabilising various structural and electronic features of complexes, and the detailed electronic origin of such interactions.

The factors discussed in this section contribute to the utility and widespread occurrence of thiolate and sulphide as ligands for transition metals in metalloenzymes, in particular those active in redox processes. It is hoped that this review has illustrated the variety of structural types, and the wide range of co-ligands stable at metal sites with a high proportion of thiolate ligands. However, there are several notable biologically and catalytically relevant co-ligand types which have yet to be stabilised and studied at such sites. Notably absent are those ligands relevant to the biological reduction of dinitrogen, in particular dinitrogen and hydride. However, there seems little doubt that the increasing sophistication being utilised in thiolate ligand design will lead to complexes capable of binding and activating a range of small molecules. There will doubtless also be further progress towards the synthesis of viable models for a range of metalloenzymes involving thiolate-ligated metal ions. Whatever metal thiolate complexes emerge it is clear that the diversity of chemistry of which thiolato-ligands are capable will ensure further interesting and exciting developments in this area.

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