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Complexes of heterocyclic thionates. Part 1. Complexes of monodentate and chelating ligands

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Contents

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Abstract

The monodentate and chelating behaviour of deprotonated heterocyclic thiones, otherwise known as the heterocyclic thionates, with transition and other metals is reported. The range of ligands involved is large and includes pyrimidine, imidazole, triazole, quinoline, purine, thiazole, thiadiazole and oxazole molecules, mostly as their monothionate derivatives. Some dithionate derivatives of mostly pyrimidine, quinoxaline and thiadiazole are also included. The preparation, spectroscopy and, in some cases, the electrochemical properties of the complexes are described. The review emphasizes the resultant geometries and dimensions derived from the crystal structures of the complexes contained in almost 180 references.

Heterocyclic thionates are ambidentate monodentate ligands. They are sulphur donating towards organomercury(II) and aurophosphine(I) cations with supplementary intramolecular attachments to the thioamido nitrogen atoms in many cases. The alternative monodentate nitrogen-donating behaviour is mostly limited to zinc(II) complexes of benzo-1,3-thiazoline-2-thionate. Monosubstituted heterocyclic thionates are S,N-chelating and mostly generate four-membered rings. Some quinoline thionate derivatives are also S,N-chelating and generate five-membered rings. The dithionate derivatives are generally S,S-chelating and also generate five-membered rings. The complexes are mostly mononuclear with coordination at the metal ranging from two, for monodentate ligands, to eight for tetrachelates.

The effect of deprotonation and coordination on the dimensions of parent heterocyclic thiones, especially those of pyridine-2-thione and benzo-1,3-thiazoline-2-thione, are also reported and discussed.

Keywords: Heterocyclic thionates; Metal complexes; Monodentate ligands; Bidentate ligands; Molecular geometry

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Abbreviations

bzimSH$_2$	benzo-1,3-imidazoline-2-thione
bzoxSH	benzo-1,3-oxazoline-2-thione
bztzSH	benzo-1,3-thiazoline-2-thione
cytSH	thiocytosine (4-aminopyrimidine-2-thione)
dtucH$_2$	2,4-dithiouracil (pyrimidine-2,4-dithione)
2,6dtz(SH)$_2$	2,6-dithioxanthine
imzSH$_2$	1,3-imidazoline-2-thione
imzdSH$_2$	1,3-imidazolidine-2-thione
pur6SH	purine-6-thione
pur8SH	purine-8-thione
py2SH	pyridine-2-thione
py4SH	pyridine-4-thione
pym2SH	pyrimidine-2-thione
pym4,6(SH)$_2$	pyrimidine-4,6-dithione
qun8SH	quinoline-8-thione
qun2SH	quinoline-2-thione
quzOSH$_2$	4-oxo-quinazaline-2-thione (2-thioquinazolinone)
qnx(SH)$_2$	quinoxaline-2,3-dithione

tcpSH	thiocaprolactam (hexamethyleneimine-2-thione)
1,3,4tdz(SH)$_2$	1,3,4-thiadiazole-2,5-dithione
1,2,5tdz(SH)$_2$	1,2,5-thiadiazole-3,4-dithione
theo8SH	theophylline-8-thione
6-thgSH	6-thioguanine
trzSH$_2$	1,2,4-triazoline-3(5)-thione
tucH$_2$	thiouracil (4-oxopyrimidine-2-thione)
tzSH	1,3,-thiazoline-2-thione
tzdSH	1,3-thiazolidine-2-thione
tzd4SH	1,3-thiazolidine-4-thione

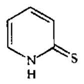
Alkyl, aryl, amino, nitro, trialkylsilyl and other derivatives are distinguished from the parent heterocycle by the addition of suitable prefixes (e.g. me, ph, am, no SiR$_3$ etc.) to the above abbreviations.

1. Introduction

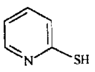
1.1. Scope of the review

This review is concerned with the coordinating properties of heterocyclic thionates. Monodentate and chelating ligand behaviour are reviewed in this part. Part 2 will deal with the complexes of bridging heterocyclic thionates.

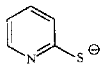
The parent molecules, the heterocyclic thiones, are characterized by thione–thiol tautomerism (**Ia** and **Ib**) [1]. They have wide-ranging applications [2] and a coordination chemistry that makes extensive use of the exocylic thione sulphur atom in both conventional [2,3] and organometallic complexes [4].



Ia



Ib



Ic

Heterocyclic thionates are readily obtained by deprotonating the parent thione (**Ic**). The term "thionate" is deliberately chosen so as to relate the anion to the parent heterocycle. It also distinguishes the series from "thiolates", such as alkyl and aryl thiolates [5,6], and dithiolates [7] which have an extensively reported coordination chemistry. Also excluded from this review are the thiolates derived from 4,5-dimercapto-1,3-dithiole-2-thione [8] and related ligands which lack the heterocyclic thioamide group. Zwitterionic species, such as the piperidine-thiones, which also mostly function as thiolates [9] are also excluded.

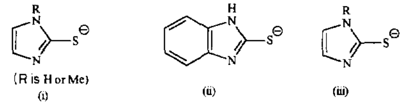
This review concentrates on ligands that are derived from heterocyclic thiones and contain at least one deprotonated heterocyclic thioamide group (N–C–S)$^-$. No attempt has been made to limit the complexes surveyed to those which contain a majority of heterocyclic thionate ligands. The presence of such a ligand in a complex is sufficient to justify its inclusion.

Heterocyclic thionates are electron-rich and, in many instances, polyfunctional ligands. Although complexes of these ligands have been known for some time [10], many were initially formulated empirically. They were generally regarded as polynuclear species with S,N-bridging, rather than S,N-chelating, ligands primarily because of the presumed inherent instability of the latter [11]. This situation has changed somewhat in recent years, primarily as a result of the increase in the number of crystal structure determinations that have established several coordinating modes of these ligands [12]. Consequently, the major theme of this review, in addition to the preparation, spectroscopy and electrochemistry of the complexes, is their structural chemistry. The effect of coordination on the thioamide dimensions of the parent ligands is also considered, where the data are available.

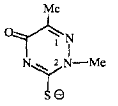
1.2. The ligands

Most heterocyclic bases form thione–thiol derivatives, and the tautomeric balance in these molecules is of long-standing interest. Typical of recent studies in this area is the solvent-balanced tautomerism among pyridine and pyrimidine-2-thiones [13].

Most of the molecules are monosubstituted such as the pyridine (**IIc**), imidazole (**IIa**), quinoline (**IIi**), purine (**III**), thiazole (**IIm**), triazole (**IIb**) and oxazole (**IIp**) derivatives. Dithionate derivatives are common among pyrimidine (**IId**), thiadiazole (**IIn**) and some purine (**III**) derivatives, while sym-1,3,5-triazoline-2,4,6-trithione, (thiocyanuric acid) (**IIg**) is a rare example of a trisubstituted derivative with a relatively underdeveloped coordination chemistry [2].



IIa



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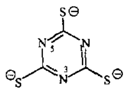
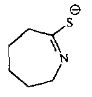


IIg



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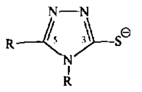
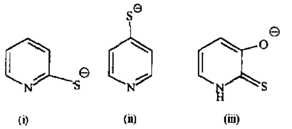
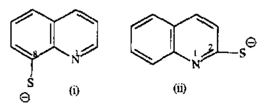


IIb



IIc



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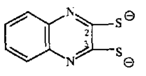
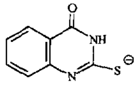
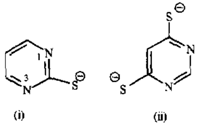


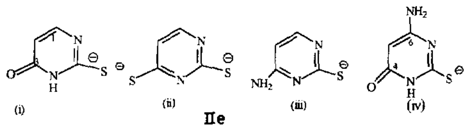
IIj



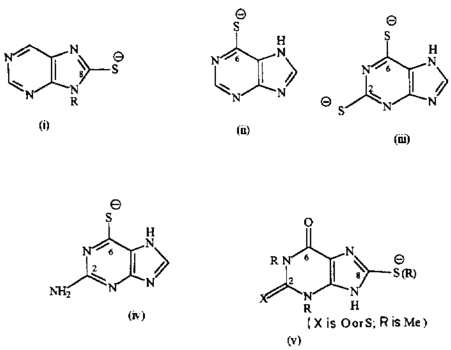
IIk



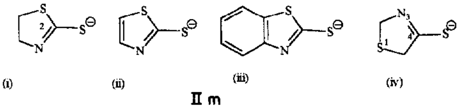
IId



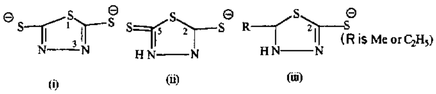
IIe



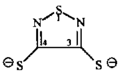
IIl



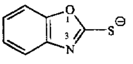
II m



IIn



IIo



IIp

All the monosubstituted derivatives adopt the thione form (**Ia**) in the solid [1,2]. The crystal structures of a number of complexes of heterocyclic thionates have been reported. The ligands involved are shown in **II** in their commonly deprotonated forms. With relatively few exceptions, such as hexamethyleneimine-2-thione (ω-thiocaprolactam) (**IIh**) and thiazolidine-2-thione (**IIm(i)**), they are planar molecules. The range of structurally characterized complexes varies for each group of ligands. Pyridine-2-thione (**IIc(i)**) and its derivatives, including a number of 3-, 6- and 3,6-substituted trialkyl silyls, are the most commonly used ligands with a significant number of reported structures. Consequently, the effect of coordination on the thioamide dimensions of the parent ligand is considered throughout this review.

Heterocyclic thiones are weak acids with pK_a values in the range 5–11. The pK_a of the imidazoline-2-thione derivatives (**IIa(i)**) are in the region of 11 [14]. The molecules are readily deprotonated by either aqueous or alcoholic sodium hydroxide [15] or potassium hydroxide [16]. Organic solvents also deprotonate some heterocyclic thiones, especially in the presence of a metal salt. Pyridine-2-thione is deprotonated in this manner by methanol [17], ethanol [18] and tetrahydrofuran [19]. However, not all ligands are affected in this way. Benzo-1,3-thiazoline-2-thione is deprotonated in aqueous ethanol or in mixed solvents, but remains unaffected in absolute ethanol [20]. Organic bases, such as trimethylamine [21] and triethylamine [22], are invariably effective deprotonating agents in most organic solvents. Metal-based procedures include sodium in methanol [23] or ethanol [24] as well as sodium hydride in ether [25]. Metal alkyls, such as n-butyl lithium in hexane with benzo-1,3-thiazoline-2-thione in tetrahydrofuran, are also effective [26].

Heterocyclic thionates can be prepared in situ by splitting the disulphide bond of the appropriate heterocyclic disulphide, such as 2,2′-dipyridyl disulphide, either thermally [27] or photochemically [28]. These are popular routes for organometallic complexes of both aryl thiolates and heterocyclic thionates. Organometallic [29] and chelate [30–32] complexes of heterocyclic thionates have been prepared by these means.

Electrochemical generation of heterocyclic thionato complexes from the parent ligand in acetonitrile has also been used in conjunction with sacrificial metal anodes such as nickel, zinc and copper. Nitrogen bases or phosphine derivatives have also been used to produce crystalline complexes from the initially intractable products resulting from this method [33].

Most heterocyclic monothiones have one replaceable proton and function readily as monoanions, notably pyridine-2-thionate (**IIc**). Imidazole-2-thionates, such as benzoimidazoline-2-thionate (**IIa(i)**) also function as monothionate anions despite the presence of an additional replaceable but weakly acidic proton. The disubstituted pyrimidines 2-thiouracil and 2,4-dithiouracil (**IIe**) may function as monoanions or dianions. Variations in the stages of deprotonation occasionally affect the tautomeric balance, as is the case with 2-thiouracil [34] and 2-thioquinazolineone (**IIk**) [15].

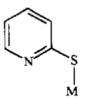
Complete deprotonation of a heterocyclic thione molecule frequently simplifies the tautomeric possibilities in most instances. An interesting example is that of 1,3,4-thiadiazole-2,5-dithione which exists as a mixed thione–thiol tautomer in the solid and as the dithionate ion (**IIn(i)**) in some of its complexes. The tautomeric arrangement in the parent molecule facilitates intermolecular (NH---S) hydrogen bonding [35].

The existence of the thioureide entity among the parent molecules and their anions, particularly those of imidazole-2-thionates (**IIa**) and purine-8-thionates (**III**), makes them useful biomimetic agents. Cysteinyl sulphur coordination occurs naturally in a number of metalloenzymes [36], and specifically in both bridging and terminal modes in (Cd, Zn) metallothionein [37]. It also plays a major role in the detoxification and sequestration of heavy metals. Consequently, the involvement of heterocyclic thionates in this topic has been directed towards heavy metals, such as mercury, and the η^1-S donating behaviour of the anions (see Section 2.2). Metalloenzymes with established S,N-coordination sites include the copper "blue" proteins [38]. Heterocyclic thionato S,N- and S_2N_2-coordination has been used to mimic the electronic and structural properties of the active sites in these proteins [39,40]. The occurrence of a predominantly sulphur-coordinated environment for molybdenum in nitrogenase has stimulated investigations into molybdenum–sulphur coordination chemistry involving both aryl thiolate and heterocyclic thionate ligands [41]. In addition, S,N-chelated molybdenum is believed to be relevant to the reduction of nitrogen by nitrogenase [42]. Finally, the use of sulphur-coordinated gold(I) complexes in the treatment of rheumatoid arthritis [43] has also stimulated interest in heterocyclic thiones and thionates as a source of sulphur-donating ligands (see Section 2.3).

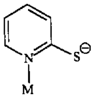
2. Complexes of monodentate ligands

2.1. Introduction

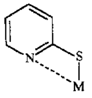
Heterocyclic thionates are ambidentate ligands that are capable of involving either the exocyclic sulphur (η^1-S) (**IIIa**) or the endocyclic nitrogen (η^1-N) (**IIIb**) atoms of their thioamide groups in monodentate coordination. Many linearly bi-coordinate heterocyclic thionato complexes involve heavy metals, such as the alkyl derivatives of mercury(II), tin(II) and thallium(I) as well as auro(I)phosphines. Consequently, the involvement of η^1-S coordination in such complexes accords nicely with the principles of hard and soft donor–acceptor behaviour [44]. However, η^1-N donor behaviour is also known (see Section 2.4). Secondary bonding among these complexes is also of significance, particularly intermolecular M---S and S---S contacts [45]. There is also a tendency for η^1–S donation to be supported by intramolecular M---N contacts in the solid (**IIIc**). Such contacts are frequently labile in solution and may be of relevance to the mobility of the methylmercury(II) ion in biological systems [46].



IIIa



IIIb

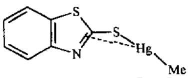


IIIc

2.2. *Organomercury and other organometallic complexes*

Much of the interest in the coordination chemistry of methylmercury $(MeHg)^+$ and other metal–alkyl systems results from the methylation of the metal and its coordination to cysteinyl sulphur residues in biosystems [46]. The latter phenomenon is also important in relieving the effects of heavy metal toxicity in living systems [37]. Such activity has led to the modelling of mercury–cysteinyl sulphur interactions by heterocyclic thionates and other sulphur donor systems [47]. The preparation and crystal structures of a number of organomercury and related complexes have been reported. Selected dimensions from these complexes are listed in Table 1 and some structural details are shown in (**IV–XI**).

The preparation of a heterocyclic thionato organomercury complex typically involves either methylmercury or phenylmercury hydroxide, often obtained from the corresponding chloride and silver(I) oxide, together with the ligand in methanol or ethanol. The complexes [RHg(bztzS)] (R = Ph or Me) are produced in such a manner [46]. The crystal structure of the methyl derivative shows the complex to be virtually planar with the mercury atom η^1-S coordinated by the exocyclic sulphur atom of the benzo-1,3-thiazoline-2-thionato anion (**IIm(iii)**). The complex has an essentially linear Me–Hg–S arrangement and relatively small Hg–S–C angles. The latter probably reflect the relatively short intramolecular interaction (3.05(2) Å) between the mercury atom and the thioamido (>C=N) portion of the thiazole ring (**IV**).



Adapted from [46]

IV

Intermolecular Hg---S contacts to both exocyclic and endocyclic sulphur atoms of neighbouring complexes (3.363(7)–3.507(7) Å), as well as a detailed analysis of the vibrational spectrum of the complex, have also been reported. Pyrimidine-2-thionate

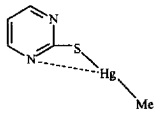
Table 1
Selected bond distances and angles for organomercury(II) and related metal complexes

Complex	M–S (Å)	M–N and M–N (Å)	Me–M–S (deg)	M–S–C (deg)	Reference
[MeHg(bztzts)][a]	2.369(6)	—	177.7(1)	97.4(8)	[46]
	2.375(6)	—	178.8(6)	99.4(7)	
[MeHg(pym2S)][b]	2.39(2)	2.83(3)	174(1)	107.7(6)	[47]
[MeHg(5-mecytos)]	2.393(4)	2.80(2)	178.6(4)	94.1(4)	[48]
[MeHg(6-oxo-cytos)]	2.390(6)	2.95(3)	178.6(9)	95.2(6)	[49]
[MeHg(tzdS)]	2.358(4)	—	175.7(10)	105.4(13)	[50]
[$(MeHg)_2$(tzds)](NO_3)	2.368(7)	2.05(2)	176.0(10)	102.5(10)	[50]
			(Me–Hg–N = 174.3(12))		
[{$(MeHg)_2(tdzS_2)$}$_2$]	2.40(1)	2.76(3)–2.93(3)	177(1)	98.1(1)	[51]
	2.37(1)		178(1)	97(1)	
[$(Me_2Tl)_2$(tdzS)]	3.05(2)–3.46(1)	2.70(4)	81(1)–110(1)	98.2(2)	[51]
		2.70(4)		110(1)	
[Me_2Tl(tucH)]	2.869(8)	2.55(2)	149(1)		[53]
			95(1)		
[MeHg(MeS)tucH]	—	2.12(1)	176.3(5)		[34]
			(Me–Hg–N)		
[Hg((3-$SiMe_3$)py2S)$_2$]	2.341(4)	2.789(5)	178.0(2)	95.3(4)	[47]
	2.345(2)	2.799(5)		95.9(4)	

[a] Two independent molecules.

[b] Chiral molecule: Hg–C(Me), 2.00(3)–2.11(2) Å; Tl–C(Me), 2.14(7)–2.35(5) Å.

[48] and two cytosine derivatives [49] form a closely related series of methylmercury complexes (**V**) with similar Hg–S distances (2.390(6)–2.393(4) Å) (Table 1).



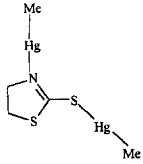
Adapted from [48]

V

The Me–Hg–S group bends out of the plane of the pyrimidine ring in all cases and so enables the mercury atom to interact quite strongly with the N(3) atom of the pyrimidine ring (2.80(2)–2.95(2) Å). This is reflected in significantly smaller Hg–S–C angles in the case of the cytosine complexes. Proton NMR studies of the pyrimidine-2-thionate complex show that the Hg---N interaction is labile in solution.

Thiazolidine-2-thione forms three complexes with the methylmercury cation [50]. In [MeHg(tzdSH)](NO_3) the neutral ligand is thione sulphur donating (Hg–S = 2.391(4) Å). The 1,3-thiazolidine-2-thionate anion (**IIm(i)**) forms two complexes, neutral [MeHg(tzdS)] and [$(MeHg)_2$(tzdS)](NO_3). In the neutral complex the coordination is essentially the same as that in **V** with an essentially linear Me–Hg–S arrangement. Intermolecular Hg---N (2.88 Å), rather than intramolecular contacts, are formed with the endocyclic nitrogen atoms in neighbouring complexes. In the

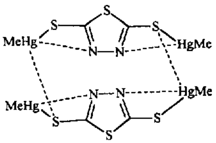
$[(MeHg)_2(tzdS)]^+$ cation the ligand S,N-bridges the methylmercury cations by means of its exocyclic sulphur and endocyclic nitrogen atoms (**VI**); the geometry of both methylmercury cations is essentially linear.



Adapted from [50]
VI

Intermolecular contacts consist of a complex series of interactions involving the mercury, exocyclic sulphur and nitrate oxygen atoms. In both the complexes involving the 1,3-thiazolidine-2-thionate anion the Hg–S distances are shorter than the corresponding distance in the complex involving the neutral parent ligand. Clearly, the anion binds more effectively to mercury(II) than does the parent ligand.

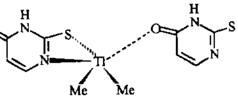
Two 1,3,4-thiadiazole-2,5-dithionate anions (**IIn(i)**) bind two mercury(II) atoms through their exocyclic sulphur atoms in the dimeric complex $[\{(MeHg)_2(tdzS_2)\}_2]$ (**VII**) [51].



Adapted from [51]
VII

The primary contacts are straightforward with normal Hg–S distances and virtually linear Me–Hg–S angles; secondary Hg---S'_{exo} (3.35(3) Å) contacts generate symmetry-related dimers. The dimerisation process is facilitated by a small Hg–S–C–N torsion angle (7(3)°), and a relatively small Hg–S–C angle (Table 1). Strong intramolecular Hg---N contacts (2.76(3)–2.93(3) Å) supplement the bonding within the dimers. The complex $[(Me_2Tl)_2(tdzS_2)]$ is formed from dimethyl thallium iodide silver(I) oxide and the ligand in methanol. The ligand in this complex binds to the thallium atom by means of an intricate network of Tl---S_{exo} and Tl---N_{endo} interactions which probably have a significant electrostatic contribution [52]. The thallium atoms are axially bound to two methyl groups and have four equatorially bonded atoms consisting of one exocyclic sulphur, from each of three different ligands, and one endocyclic nitrogen atom from one of these ligands. The range of Tl---S distances involved is rather large (Table 1), but they are shorter than the sum of the van der Waals radii (Tl---S = 3.76 Å). There are some similarities between this structure and that of $[\{(MeHg)_2(tdzS_2)\}_2]$. Both complexes have asymmetric sulphur bridges between metal centres and use all their exocyclic sulphur and endocyclic nitrogen atoms in the coordination process. There are also important differences. In the thallium complex the metal–sulphur distance is longer and the metal–nitrogen distance is shorter than in the mercury complex (Table 1); consequently the thallium–nitrogen bond is probably stronger than the thallium–sulphur bond, as it is in other systems [52]. Furthermore, both the exocyclic sulphur atoms form asymmetric bridges in the thallium complex, whereas only one is involved in the mercury complex. Consequently, thallium is more extensively coordinated than mercury in these two complexes.

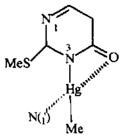
A number of complexes involving RHg^+ and R_2Tl^+ cations have been prepared from 2-thiouracil, 2,4-dithiouracil and 2-thioquinazolinone. Interest in these complexes centres on the differing toxicological properties of the two cations and their influence on the tautomeric balance. This is wide ranging in the parent molecules but mostly limited to the thione–thiol balance among the deprotonated ligands [15]. The harder dimethyl thallium cation is considered to be generally less effective than the methylmercury cation in generating "thiol" character in the thiouracilate ion because it forms stronger bonds to the ligand's endocyclic nitrogen atom [15,34]. Thiouracil forms monoanionic $[R_nM(tucH)]$ and dianionic $[(R_nM)_2(tuc)]$ complexes ($R = Me$ or Ph; $M = Hg$ or Tl; $n = 1$ or 2). NMR spectra indicate that the monoanionic ligand is exocyclic sulphur donating in the [(RHg)(tucH)] complexes. In the $[(R_2Tl)(tucH)]$ complexes the ligand is endocyclic nitrogen donating, while in the $[(RHg)_2(tuc)]$ complexes it is intermediate in character. The latter suggests that the organometallic fragment is rapidly exchanging its coordinating character in these complexes [34]. The crystal structure of $[(Me_2Tl)(tucH)]$ [53] shows that the cation is coordinated by one S,N-donating thiouracilate anion and the carbonyl oxygen of an adjacent 2-thiouracilate ligand (Tl–O = 2.72(3) Å). These contacts, together with the methyl carbon atom, form a distorted five-coordinate square-based pyramid about the thallium atom (**VIII**).



Adapted from [53]

VIII

The C–Tl–C angle (106(1)°) is narrower than the normal values for this cation (163.5°–190°), presumably because of the steric crowding at the metal. The thallium–ligand bonds also vary in strength, with the thallium–nitrogen bond considered to be relatively short and strong. The thallium–sulphur bond is intermediate in character between the asymmetric bridging distances (Tl–S) reported for $[(Me_2Tl)_2(\mu\text{-}PhS)]$ [54], while the Tl---O distance is indicative of a relatively weak contact, as expected. Monometallated complexes of the 2-S-methylthiouracilate anion $[(R_nM)(tucSMe)]$ ($R = Me$ or Ph; $M = Hg$ or Tl; $n = 1$ or 2) have also been prepared. The crystal structure of [(MeHg)(tucSMe)] has been reported [34]. With the exocyclic sulphur site blocked through methylation, the mercury(II) atom is strongly η^1-N bonded through the N(3) atom of the ligand (**IX**) and the Me–Hg–N angle is effectively linear (Table 1).

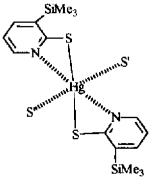


Adapted from [34]

IX

The choice of N(3) rather than N(1) as the ligand donor site is considered to be consistent with the charge distribution calculated for the "thiol" tautomer [55]. Additional intramolecular contacts (Hg---O = 2.91(2)Å; Hg---N(1) = 3.02(2) Å) are also reported for this complex.

Several series of methylmercury(II) and mercury(II) complexes have been prepared from 3-, 6- and 3,6-triorganosilyl pyridine-2-thionate, as well as similarly substituted methyl and phenyl thiolates [47]. Typically, [MeHg(3-SiR_3-py2S)] and [Hg(3-SiR_3-$py2S)_2$] are prepared from methylmercury chloride and mercury(II) chloride in methanol with the ligands deprotonated by triethylamine. The crystal structure of [Hg(3-$SiMe_3$-$py2S)_2$] (**X**), shows that the ligands coordinate to the metal primarily through exocyclic sulphur with secondary Hg---N_{endo} contacts from the same ligands (Hg---N = 2.789(5) Å and 2.799(5) Å) and additional intramolecular Hg---S'_{exo} contacts to neighbouring ligands (Hg---S'_{exo} = 3.239(3) Å).



Adapted from [47]

X

The HgS_4 polyhedron is a flattened tetrahedron in which the S–Hg–S angle is virtually linear (Table 1). The Hg---N contacts are significant and force a contraction in the Hg–S–C angles; ^{13}C NMR spectra suggest that the Hg---N contacts persist in solution.

Detailed analysis of the changes in ligand dimensions upon coordination in these complexes is hampered by the fact that so much of the scattering is caused by the cations and the sulphur atoms. However, there is a clear indication that, in general, the thione (>C=S) distances are increased, relative to the corresponding free-ligand value, as a result of deprotonation and coordination.

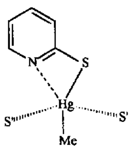
Pyridine-2-thionate (**IIc(i)**) has been complexed with alkylmercury [56], alkylthallium and alkyltin [57] cations. Crystal structures have been reported for [MeHg(py2S)], [Me_2Tl(py2S)] and [$Me_2Sn(py2S)_2$]. Selected dimensions of these complexes, and that of the free ligand, are listed in Table 2.

The ligand in [MeHg(py2S)] is η^1-S donating with secondary bonds to the endocyclic nitrogen atom and to neighbouring thionato sulphur atoms. Consequently, the overall geometry at the metal is distorted trigonal bipyramidal (**XIa**).

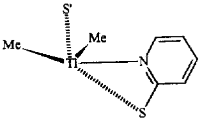
Table 2
Selected bond distances and angles for methylmetal complexes of pyridine-2-thionate

	[MeHg(py2S)] [56]	[$Me_2Sn(py2S)_2$] [57]	[$Me_2Tl(py2S)$] [57]
M–S (Å)	2.374(2)	2.487(2)	3.160(3)^a
M–N (Å)	2.980(5)	2.702(5)	2.494(7)
C–S (Å)	1.776(1)	1.751(3)	1.730(8)
C–N (Å)	1.350(7)	1.36(1)	1.33(1)
S–C–N (deg)	116.6	114.4	119.5
M–S–C (deg)	99.0	91.9	75.6
N–M–S (deg)	58.5	60.5	54.2
M–N–C (deg)	85.9	93.1	110.5
pySH(mean values X-ray data) [58]	C–S = 1.695(2) Å	C–N = 1.356(3) Å	S–C–N = 120.6(1)°

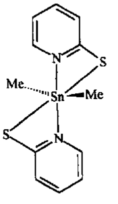
[a] Tl–S′ = 2.870(4) Å.



Adapted from [56]
XIa



Adapted from [57]
XIb



Adapted from [57]
XIc

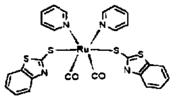
In [$Me_2Tl(py2S)$] the metal is η^1-N donating with secondary Tl---S_{exo} bonds to the original as well as to a neighbouring ligand. The latter contact (Tl---S_{exo} = 2.870(2) Å) is shorter than the former (Table 2), and the S---Tl---S′ angle is 136.7(1)°. If all the contacts are considered, then the metal is five-coordinate and approximates to octahedral coordination with one of its sites vacant (**XIb**). Both the ligands in [$Me_2Sn(py2S)_2$] are S,N-chelating and, together with the metal, occupy a mirror plane; only one of the ligands is crystallographically independent. The metal is six-coordinate, if the two methyl groups are included in the coordination sphere (**XIc**), and is variously described as a distorted octahedron [59], a skewed trapezoidal bipyramid or a bicapped tetrahedron [60]. The extent of the distortion is evident from the range of angles at the metal (60.5(1)°–152.1(2)°); the smallest angle is the S_{exo}–Sn–N_{endo} chelating angle.

These three complexes of pyridine-2-thionate form a self-contained group in which ligand coordination varies with the metal. The S,N-chelating mode is included here in order to complete the survey. Differences in coordination are accompanied by variations in metal–ligand distances in these complexes, as well as by differences in the bond lengths of the thioamido (N_{endo}–C–S_{exo}) portion of the ligand. Such variations merit careful consideration (Table 2). According to the bond lengths, the metal–nitrogen bond is strong in the thallium complex, weak in the mercury complex and of intermediate strength in the tin complex. As the metal–nitrogen bond weakens, the cation moves away from the direction in which the charge density of the donating electron pair is greatest; consequently, the C(2)–N–M angle closes and the M–S–C(2) angle opens (**XIc**). In addition, the thione ($>C{=}S$) distance in the ligands varies considerably, increasing as the metal–sulphur distance decreases but always remaining longer than in the parent molecule [58] (Table 2). The distance is greatest in the mercury complex and closest to the carbon–sulphur single-bond value (1.81 Å) [61], with only 13.1% π character. In the parent molecule the π character of the corresponding bond is 44.2% [62]. These trends allow the cations to be ranked according to their "softness" towards pyridine-2-thionate:

$$Me_2Tl^+ < Me_2Sn^{2+} < MeHg^+$$

The authors also argue that the same trend denotes the increasing ability of the cations to transform the ligand from essentially "thione" to "thionate" character. In fact the deprotonation is responsible for the conversion from "thione" to "thionate", and the above sequence reflects the ability of the cations to generate decreasing π character in the exocyclic carbon–sulphur distance of the pyridine-2-thionate ligands.

Conventional organometallic complexes are rather less numerous than those described above, but benzo-1,3-thiazoline-2-thione reacts with trirutheniumdodecacarbonyl with consequent break up of the trinuclear cluster giving a red product containing several crystalline phases including $[Ru_2(bztzS)_2(CO)_6]$ [63]. Recrystallization of this product in aqueous pyridine gives yellow crystalline mononuclear $[Ru(bztzS)_2(CO)_2(py)_2]$ [64]. The ruthenium atom in this complex has distorted six-coordinate geometry and occupies a crystallographic C_2 site. The pairs of carbonyl groups and pyridine molecules (Ru–C = 1.872(3); Ru–N = 2.181(2) Å) are each *cis*-related, while the η^1-S donating benzo-1,3-thiazoline-2-thionate anions (Ru–S = 2.406(4) Å) occupy *trans* positions (**XII**) with an Ru–S–C angle of 109.0(1)°.



Adapted from [64]

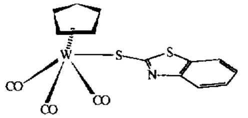
XII

The effect of deprotonation and coordination on the heterocyclic S_{endo}–C–(S_{exo})–N_{endo} portion of the ligand dimensions [65] is significant. The C–S_{endo} distance increases from 1.740(4) to 1.760(4) Å and the C–S_{exo} distance increases from 1.662(4) to 1.724(3) Å, whereas the C–N_{endo} distance decreases from 1.353(6) to 1.287(3) Å. The major angular changes occur at the thioamido carbon atom. The overall dimensional changes signify a major drift of π character towards the thoamido C–N_{endo} portion of the ligand.

Metal carbonyl dimers react with organic disulphides either photochemically [66] or thermally [67], producing metal carbonyl thiolates:

$$[(\eta^5\text{-}C_5H_5)_2(CO)_6M_2] + RSSR \rightarrow 2[(\eta^5\text{-}C_5H_5)(CO)_3MSR]$$

Photochemical reactions of $[\{(\eta^5\text{-}C_5H_5)(CO)_3W\}_2]$ with 2,2′-dipyridyldisulphide and bis(*o*-aminophenyl)disulphide, using 366 nm radiation, produce mononuclear tungsten carbonyl complexes containing η^1-S donating heterocyclic thionates [29]. The crystal structure of $[(\eta^5\text{-}C_5H_5)(CO)_3(\eta^1\text{-S-bztz2S})W]$ shows that the metal has a square-pyramidal "piano-stool" geometry in which the carbonyl groups and the heterocyclic ligand form the basal plane and the cyclopentadienyl ligand occupies the apex (**XIII**).



Adapted from [29]

XIII

Bond angles about the metal in the basal plane average 77(2)°. The centroid of the cyclopentadienyl group is positioned slightly away (2.0 Å) from the metal towards the benzo-1,3-thiazoline-2-thionate ligand. The W–S distance (2.500(3) Å) and the W–S–C angle are normal (109.3(4)°), with the endocyclic nitrogen (W---N = 3.650 Å) too distant for coordination to occur. The heterocyclic ligand dimensions ($C\text{–}S_{exo}$ = 1.728(14), $C\text{–}S_{endo}$ = 1.764(12), $C\text{–}N_{endo}$ = 1.287(16) Å; $N_{endo}\text{–}C\text{–}S_{exo}$ = 115(1)°) show the characteristic deviations from those of the neutral molecule [65]. In addition, carbonyl loss from $[(\eta^5\text{-}C_5H_5)(CO)_3WSR]$ (R = 2-pyridyl or 2-benzothiazolyl) can be induced thermally or photochemically with the subsequent production of complexes containing S,N-chelating heterocyclic thionates [67] (**XIV**).

XIV

Similar reactions with *o*-aminophenol as the organic group generate oligomers.

2.3. Aurophosphine complexes

Although gold compounds had been in therapeutic use since medieval times, the period covering the end of the nineteenth and early twentieth century saw a revival of interest in the application of "chrysotherapy" in the treatment of tuberculosis and other infectious diseases [68]. The first reported application of gold compounds in the treatment of rheumatoid arthritis in 1935 [69] led to the subsequent development of a range of water-soluble polymeric gold thiolates such as auro(I) sodium thiomalate (Myocrysin) and auro(I) sodium thiosulphate (Sanochrysin) [43]. Although the popularity of gold compounds in the treatment of rheumatoid arthritis declined somewhat because of the toxicity associated with the large doses employed, they have been the "second-line" agents for the treatment of the disease for 60 years [68]. The monomeric lipid-soluble orally administered triethylphosphine gold(I) thioglucose derivative Auranofin [(2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-glucopyranosal-*S*)(triethylphosphine)gold(I)] is an improvement on its polymeric predecessors and is an essentially linear P–Au–S containing aurophosphine thiolate (Table 3) [70]. In addition to being a potent anti-arthritic drug, Auranofin has proved to be an effective cytotoxic agent against melanoma and leukaemia cells. The search for other aurophosphinethiolate anticancer drugs has been extended to thiopyrimidine [71] and thiopurine [72] derivatives, including 2-dithiouracil and 6-thioguanine. Also of current medical importance is the discovery that aurothioglucose and aurothiomalate have anti-HIV-1 activity in vitro. Such activity requires the formation of a reactive intermediate with a molar equivalent of a thiol ligand. This activates gold(I) ligand exchange between the reactive species, auro(I) thiomalate and acidic thiol groups on protein surfaces [73].

Inevitably, such wide-ranging activity has broadened the search for sulphur donor ligands. In addition to organothiolates [74] heterocyclic thiones and thionates have been used as sources of sulphur donor ligands with auro(I) phosphines and other gold salts. Recent studies involving heterocyclic thiones and thionates have shown that dimethyl sulphide in [AuCl][SMe_2] is readily replaced with pyridine-2-thione and pyridine-4-thione in tetrahydrofuran, giving [AuCl][RSH] (RSH = py2SH and py4SH) [75]. The crystal structure of [AuCl][pySH] shows that the molecule contains an essentially linear Au–S–Cl arrangement (171.7(1)°) with the neutral heterocyclic ligand thione sulphur bonded to the metal (Au–S = 2.261(5) Å; Au–S–C = 110.0(5)°). A combination of weak hydrogen bonding (NH---Cl = 2.42 Å and 146°) and short intermolecular metal---metal contacts (Au---Au = 3.215 Å)

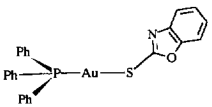
Table 3
Aurophosphine complexes of heterocyclic thionates: selected distances and angles

Complex	Au–S (Å)	Au–P (Å)	P–Au–S (deg)	Au–S–C (deg)	Reference
'Auranofin'	2.293(3)	2.259(3)	173.6(1)	105.6(3)	[70]
[Au(PPh_3)(bzox2S)]	2.299(2)	2.258(2)	176.4(1)	103.1(3)	[78]
[Au(PPh_3)(py2S)]	2.297(2)	2.258(2)	177.9(1)	102.0(2)	[79]
[Au(PPh_3)(pym2S)]	2.310(3)	2.253(2)	174.7(2)	98.9(3)	[79]
[Au(PC_6H_{11})(meimzS)]	2.331(3)	2.292(3)	172.0(1)	106.6(3)	[80]
[Au(PPh_3)(tucH)][a]	2.296(2)	2.248(2)	175.2(2)	103.8(3)	[81]
	2.300(2)	2.248(2)	177.0(2)	100.8(2)	
[Au(PEt_3)(tucH)][a]	2.310(2)	2.248(2)	176.9(1)	101.4(3)	[81]
[Au(PPh_3)(6pr-tucH)]	2.328(4)	2.248(2)	175.4(2)	101.3(6)	[16]
	2.314(5)	2.248(2)	176.9(2)	100.3(6)	
[Au(PPh_3)(theo8S)]	2.308(2)	2.256(2)	178.6(2)	100.3(2)	[72]
[Au(PPh_3)(pur6S)]	2.287(1)	2.237(2)	173.71(6)	105.9(2)	[82]
[Au(PPh_3)($(CF_3)_4$(tzd4S)]	2.312(2)	2.259(2)	178.4(1)	101.6(2)	[83]

[a] Two independent molecules.

are also reported. Replacement of dimethylsulphide in [AuCl][Me_2S] with pyridine-2 or pyridine-4 thionate (**IIc**) generates intractable polymers [$\{Au(RS)\}_n$]. Tetrahydrothiophene (tht) in [AuX(tht)], [$Au(tht)_2$](ClO_4) and [$Au(PPh_3)$(tht)]-(ClO_3) (X = Cl or C_6F_5) is replaced with 1,3-thiazolidine-2-thione, pyrimidine-2-thione, benzo-1,3-thiazolidine-2-thione and benzoimidazoline-2-thione in the production of complexes containing the appropriate thione sulphur-donating heterocycle [76]. The crystal structure of [$Au(py2SH)_2$](ClO_4) contains two complete and two half cations in the asymmetric unit with linear S–Au–S coordination of the metal and a maximum deviation of 5.7° in the S–Au–S angle. The neutral ligand is thione sulphur donating (Au–S = 2.288(3)–2.291(3) Å). Five of the six cations in the cell form a centrosymmetric linear chain (Au---Au ≈ 3.3 Å). Deprotonation of the thioamido nitrogen in the cationic complexes with solid sodium carbonate leads to neutral monomeric and binuclear complexes, with S,N-bridging ligands proposed for the latter.

A number of studies have also been devoted exclusively to the production of heterocyclic thionato auro(I)phosphine complexes. Preparative routes for these complexes have been known for some time, and typically involve the addition of sodium hydroxide and the neutral ligand, in ethanol, to [Et_3PAuCl], also in ethanol, in 1 : 1 : 1 molar ratio followed by recovery and crystallization of the initial product [77]. This method has been used for benzo-1,3-oxazoline-2-thionate (**IIp**) [78]. Pyrimidine-2-thionate (**IId(i)**) and pyridine-2-thionate (**IIc(i)**), as well as alkyl and aryl thiolates (R′S), have also been used to generate complexes with a variety of tertiary phosphines [$Au(PR_3)$(R′S)] (R = Et, Ph and C_6H_{11}) [79]. Tertiary phosphine complexes of purine-6-thionate and its 5-trifluoromethyl derivative (**III(i)**), together with imidazoline-2-thionate and its 1-methyl derivative (**IIa(i)**) [80] have also been prepared. These complexes have been characterized by a combination of IR, ^1H and ^{13}C NMR, and FABS methods. The crystal structures of mononuclear [AuR_3P(R′S)], (R = Ph, R′S = bzox2S, py2S, pym2S; R = C_6H_{11}, R′S = meimzSH) show them to have essentially linear P–Au–S arrangements with monodentate η^1–S donating heterocyclic thionates (Table 3 and **XV**). The ^1H NMR spectra of the pyridine and pyrimidine complexes in deuterated acetone indicate free rotation of the heterocyclic ligands about their thionate (>C–S$^-$) bonds, in contrast with the rigidity observed in the solid state.



XV

The discovery of carcinostatic activity in gold complexes of pyrimidine and purine thionates [71] has prompted structural studies on 2-thiouracilate (**IIe(i)**) and oxopurinethionato (**III(v)**) aurophosphine complexes. 2-Thiouracilate and its 6-n-propyl derivative replace the chloride ion in [$Au(R_3P)Cl$] (R = Et and Ph), producing complexes that contain the corresponding η^1-S-donating heterocyclic thionate [16,80,81]. An attempted reaction between the bischelated complex [$Au(dppe)_2Cl$]

(dppe = 1,2-bis(diphenylphosphino)ethane) and 2-thiouracil produced [Au(dppe)$_2$]-[(tucH)(tucH$_2$)] instead of the anticipated gold complex of the 2-thiouracilate anion. An assessment of the anti-arthritic activity of the [Au(R$_3$P)(tucH)] (R = Et and Ph) complexes in a gold-sensitive rat strain revealed the triphenylphosphine derivative to be the more effective prophylactic [81]. Interactions between [Au(PPh$_3$)Cl], [Au$_2$(dppe)Br$_2$] and the oxopurinethiones, theophylline-8-thione, 2-thiotheophylline-8-thione and 8-(methylthio)-theophylline (**III(v)**) in alcoholic potassium hydroxide produced a number of complexes including [(Au-(PPh$_3$)RS], [{Au(PPh$_3$)}$_2$(μ-RS)] and [Au(μ-dppe)(μ-RS)Au] (RS$^-$ = oxopurinethionato anion) [72]. These complexes, characterized by a combination of IR and NMR techniques, contain either one S(8)-bonded or two N(7)S(8)-bonded oxopurinethionato anions. In addition, the crystal structure of [Au(PPh$_3$)(theo8S)] established the existence of hydrogen-bonded dimers (N(7)H---O), an η^1-S-donating heterocycle and essentially linear P–Au–S coordination at the metal (Table 3). A number of complexes of the purine-6-thionate anion (**III(ii)**) have been prepared [R$_3$PAu(pur6S)] and characterized by spectroscopic methods [82]. Preliminary testing for anti-arthritic activity in rats showed that some of the complexes (a wide range of alkyl and aryl phosphine substituents was used) are both more potent and less toxic than the gold(I) thiolates currently in use. The crystal structure of [Ph$_3$PAu(pur6S)] is also reported (Table 3).

Addition of potassium thiocyanate to 2,2,4,4-tetrakis(tetrafluoromethyl)-1,2-dithietane produces the potassium salt of 2,2,5,5-tetrakis(trifluoromethyl)-1,3-thiazolidine-4-thionate ((CF$_3$)$_4$(tzd4S) (**IIm(iv)**)) which replaces the chloride ion in [Au(PPh$_3$)Cl] [83]. The crystal structure of the resultant complex showed that the heterocyclic thionate is η^1-S donating (Table 3).

Selected dimensions of the reported bi-coordinate aurophosphine complexes are given in Table 3. The Au–S distances (2.287(2)–2.331(3) Å) are closely related and appear to be independent of the nature of the heterocycle; even the value for Auranofin is within the range. However, the Au–S distance in [AuCl(pySH)] (2.261(5) Å) [75] is significantly shorter than the corresponding distance in [Au(PPh$_3$)(py2S)] (2.297(2) Å). This is an unexpected result that is probably due to the greater *trans* effect of the phosphine. In the absence of the *trans* effect, the anionic thionate would be expected to bind more strongly to the metal than the neutral ligand. This is the case with the methylmercury(II) complexes of thiazolidine-2-thione and thionate [50]. The Au–P distances, which are generally shorter than the Au–S distances, also form a compact series (2.237(2)–2.259(3) Å); only the value for the bulky tri-(cyclohexyl) phosphine ligand (2.292(3) Å) lies outside this range. All the complexes exhibit distorted linear P–Au–S geometry with the distortion ranging from 1.4° to 8.0°. In addition, the Au–S–C angles vary significantly from 98.9(3)° to 106.6(3)°. In some complexes both these angles correlate well with the distance between the metal and the thioamido nitrogen atom of the coordinated heterocyclic thionate. In [Au(PPh$_3$)pym2S] the relatively short Au---N distance (2.957(8) Å) generates a small Au–S–C angle and a larger than average deviation in the linearity of the P–Au–S angle (Table 3). In [Au(PPh$_3$)py2S] the Au---N separation is larger (3.118(4) Å) and consequently the P–Au–S angle is closer to the ideal and the Au–S–C angle is increased (Table 3). The pyridine-2-thionate ligand is also twisted by about 14° out of the Au–S–C plane in this complex; similar effects have been observed in complexes of the 2-thiouracilate anion [16,81,84].

The effect of coordination on the ligand dimensions can be assessed by the effect on pyridine-2-thione [78]. In the pyridine-2-thionate anion the exocyclic thione (>C=S) distance is increased from 1.695(2) to 1.750(6) Å. The thioamide C(2)–N(1) distance decreases slightly, from 1.356(3) to 1.336(7) Å, as does the N–C–S angle, from 120.6(1)° to 118.2(7)°. Similar effects have been observed for the 2-thiouracilate anion [16,81,84]. The thione bond lengths in the other ligands range from 1.704(9) to 1.766(7) Å. They are all shorter than the single-bond (>C–S) distance (1.81 Å) [61]. However, changes in the ligand dimensions of pyridine-2-thionate are consistent with the shift of π-electron density to the amide (C–N) portion of the thioamide group, concentration of the negative charge on the sulphur atom of the anion and enhancement of the thionate character in the ligand.

2.4. *Copper(I) and zinc(II) complexes of benzo-1,3-thiazoline-2-thionate*

Binuclear complexes with terminal η^1-S-donating heterocyclic thionates are relatively rare and are currently limited to the benzo-1,3-thiazoline-2-thionato (**IIm(iii)**) complex $[Cu_2(bztzS)_2(dppe)_3]$ [85].

This copper(I) complex resulted from a reinvestigation of the reaction between copper(II) salts and benzo-1,3-thiazoline-2-thione in ethanol. Other heterocyclic thiones were also involved in this study. The initial product $[Cu(bztzS)_2]$, obtained from the parent ligand and copper sulphate pentahydrate, proved to be intractable and was treated with dppe in hot acetone, from which the dimeric complex was obtained. The complex is centrosymmetric with the centre of symmetry located between the two methylene carbon atoms of the bridging dppe ligand. The distorted tetrahedral geometry at each copper(I) atom is completed by a chelating dppe ligand and a η^1-S-donating heterocyclic thionate; consequently, each metal atom has a P_3S donor set. There are two similar independent molecules in the unit cell that generate mean Cu–S and Cu–P distances of 2.318(6) Å and 2.306(9) Å respectively.

As a result of deprotonation and coordination to copper(I), the $C–S_{exo}$ and $C–S_{endo}$ distances of the parent ligand [65] (1.662(6) and 1.732(6) Å) increase (to 1.675(25) and 1.795(25) Å) and the thioamide C–N distance (1.353(6) Å) decreases (to 1.295(45) Å). In addition, the thioamide $N–C–S_{exo}$ angle increases from 127.4(2)° in the parent ligand to 132.5(20)° in the complex. This causes the non-bonded Cu···N distance to lengthen and helps to maintain the monodentate character of the ligand. Changes in the ligand dimensions, despite the rather large errors, are indicative of a shift of π-electron density to the amide (C–N) portion of the thioamide group and enhancement of the thionate ($C–S^-$) character.

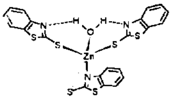
All the reported mononuclear complexes of divalent zinc involve benzo-1,3-thiazoline-2-thionate in a variety of mixed-ligand environments that involve either nitrogen bases or S,S-chelating dithiocarbamates.

The complex $[Zn(bztzS)_2(bipy)]$ (bipy = 2,2′-bipyridine) [86] results from the electrochemical oxidation of the metal, in acetonitrile, in the presence of the parent thione ligand and 2,2′-bipyridine. The same complex may also be prepared from [Zn(bztz2S)$_2$], obtained from zinc(II) acetate dihydrate and benzo-1,3-thiazoline-2-thione in ethanol by the addition of 2,2′-bipyridine in chloroform. In addition, [Zn(bztz2S)$_2$(py)$_2$] and [Zn(bztz2S)$_2$(phen)] were prepared from [Zn(bztz2S)$_2$] by similar methods [87].

The crystal structures of the 2,2′-bipyridine [86], as well as those of the pyridine (py) and *o*-phenanthroline (phen) [87], adducts have been reported. All three complexes have pseudo-tetrahedral geometry with N_2S_2 donor sets formed from two η^1-S-donating benzo-1,3-thiazoline-2-thionate ligands and either two pyridine molecules or one N,N′-chelating nitrogen base. Angles at the metal are in the range from 78.8(1)° to 122.4(1)°, with the smallest angle formed by the N,N′-chelates. The η^1-S-donating heterocyclic thionates generate Zn–S distances (2.294(5)–2.324(1) Å) which are typical of other tetrahedral Zn–S systems (2.25–2.36 Å) [86]. The mean thioamide C–S (1.72 Å) and C–N (1.30 Å) distances are typical of deprotonated and coordinated heterocyclic thionates.

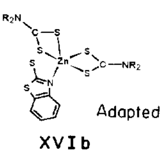
The involvement of the thionato sulphur and the non-involvement of the thioamido nitrogen atom as donor atoms in these complexes clearly results from the greater nucleophilicity and steric favorability of the exocyclic sulphur atom.

The involvement of benzo-1,3-thiazoline-2-thione as an accelerator in the vulcanization of natural rubber has generated a number of complexes including (n-Bu$_4$N)[Zn(bztzS)$_3$(H$_2$O)] [88], (n-Bu$_4$N)[Zn(dtc)(bztzS)$_2$] and (n-Bu$_4$N)-[Zn(dtc)$_2$(bztzS)] [89] (dtc = dithiocarbamate). In the [Zn(bztzS)$_3$(H$_2$O)]$^-$ anion two of the heterocyclic ligands are η^1-S donating (mean Zn–S = 2.338 Å). They are also hydrogen bonded to the coordinated water molecule (Zn–O = 2.02 Å) through their thioamido nitrogen atoms. The remaining heterocyclic ligand is η^1-N bonded to zinc(II) (Zn–N = 2.019(4) Å) with the thionato sulphur atom 3.125(2) Å from the metal. The coordination at the metal is considered to be four-coordinate (S$_2$ON) or five-coordinate (S$_3$ON) (**XVIa**). In the tetrahedral [Zn(dtc)$_2$(bztzS)]$^-$ anion the dithiocarbamate anions are S,S′-chelating and the heterocyclic ligand is η^1-N bonded to zinc(II) (Zn–N = 2.061 Å); the thionato sulphur atom is 3.43 Å from the metal (**XVIb**). The metal geometry, excluding the thionato sulphur interaction, is square-based pyramidal. Similarly, the [Zn(dtc)(bztz2S)$_2$]$^-$ anion contains two η^1-N donating heterocyclic ligands (mean Zn–N = 1.997 Å) and a bidentate dithiocarbamate anion. The metal has distorted tetrahedral geometry.



Adapted from [86]

XVIa



Adapted from [87]

XVIb

The varied donor behaviour of the benzo-1,3-thiazoline-2-thionate anion in the presence of these dithiocarabamate ligands is in marked contrast to its behaviour in the presence of nitrogen bases. The involvement of the thioamido nitrogen atoms in hydrogen bonding with the coordinated water molecule probably accounts for the η^1-S-donating behaviour of two of the heterocyclic ligands in the

$[Zn(bztzS)_3(H_2O)]^-$ anion but not for the predominantly thioamido nitrogen η^1-N-donating behaviour in the third heterocyclic ligand (**XVIa**).

Furthermore, the η^1-N-donating behaviour of the heterocyclic ligands in $[Zn(dtc)(bztzS)_2]^-$ and $[Zn(dtc)_2(bztzS)]^-$ (**XVIb**) is more consistent but equally intriguing. The involvement of the thioamido nitrogen atoms in the coordination scheme is probably not due to steric factors, since such considerations will consistently favour the exocyclic sulphur atoms. However, the position of zinc as a borderline acceptor atom probably means that the balance of electronic factors favours neither the thioamido nitrogen nor the thionato sulphur atoms in these ambidentate ligands, but depends on the other donor atoms in the individual complexes. In this respect the presence of the S,S-chelating dithiocarbamates appears to be crucial.

3. Chelate complexes

3.1. Introduction

The four-membered ring formed by a S,N-chelating heterocyclic thionate is inherently strained. Consequently, many complexes were formerly presumed to contain S,N-bridging rather than S,N-chelating ligands [2]. However, the publication of the crystal structure of *cis*-$[Ru(py2S)_2(PPh_3)_2]$ in 1972 [90] established the S,N-chelating capability of pyridine-2-thionate with its characteristically narrow bite (2.56 Å) and chelating angle (mean $S–Ru–N = 67.9(2)°$). Subsequently, monochelate (Section 3.2), bischelate (Section 3.3), trischelate (Section 3.4) and tetrachelate (Section 3.5) complexes, involving a range of heterocyclic monothionates, have been structurally established. In addition, the dithionates quinazoline-2,3-dithionate and 1,2,5-triazoline-3,4-dithionate form bischelates with slightly less strained five-membered rings (Section 3.3). Bridging chelating dithionates will be dealt with in Part 2 of this review.

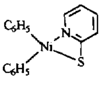
Many of the complexes adopt octahedral and square-planar geometries which, together with the asymmetric character of the S,N-chelating ligands, generate extensive isomeric possibilities. These include geometric isomers among six-coordinate $[M(chel\text{-}S,N)_2A_2]$ complexes (Section 3.3), as well as optically active trischelates (Section 3.4). Fluxional behaviour, which invariably arises from the juxtaposition of *cis*-related sulphur-donating and S,N-chelating ligands, has also been monitored by variable-temperature NMR data in a number of complexes [19,91].

3.2. Monochelates

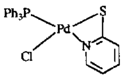
3.2.1. Four-coordinate complexes

These species are relatively rare and are limited to the square-planar geometries that are typical of nickel(II), palladium(II) and platinum(II). Although a number of heterocyclic thionates have been used, the crystal structures are limited to the pyridine-2-thionate complexes of nickel(II) and platinum(II).

Addition of stoichiometric quantities of pyridine-2-thione, pyrimidine-2-thione, methylimidazoline-2(3H)-thione, 1,3-thiazolidine-2-thione, benzoimidazoline-2-thione, benzoxazoline-2-thione and 2,6-dimethyl-5-oxo-1,2,4-triazine-3-thione (see structures **II**) to $(NBu_4)[\{Ni(C_6H_5)_2(\mu\text{-}OH)\}_2]$ in dichloromethane, followed by reduction of the reaction volume and addition of diethyl ether, produces the air-stable complexes of the corresponding heterocyclic thionate (RSN^-), $(NBu_4)[Ni(C_6H_5)_2(RSN)]$ [92]. In this reaction the heterocyclic thione is deprotonated by the μ-hydroxo anion of the precursor complex. The complexes are 1:1 electrolytes in ethanol and have been characterized by IR, UV–visible and NMR techniques. The electronic spectra of all the complexes contain a ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition typical of square-planar low-spin d^8 systems. Square-planar geometry was confirmed in the crystal structure of $(NBu_4)[Ni(C_6H_5)_2(py2S)]$, together with a C_2NS donor set; the metal is also slightly displaced from the coordination plane (**XVIIa**). Angles at the metal are irregular, largely because of the small bite of the chelating ligand (N–Ni–S = 73.8(2)°). The Ni–N (1.919(5) Å) and Ni–S (2.257(2) Å) distances are somewhat shorter than the distances reported for the corresponding octahedral trischelates [23]. Similar structures have been deduced for the other members of this series.

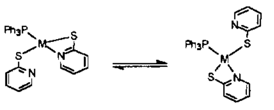


XVIIa



XVIIb

Several mononuclear pyridine-2-thionate complexes have been reported [19]: $[M(py2S)_2(PPh_3)_2]$, $[MCl(py2S)(PPh_3)]$ and $[M(py2S)_2(PPh_3)]$ (M = Pd(II) and Pt(II)). A variety of synthetic routes have been employed for these complexes. The oxidative addition of dipyridyl-2,2′-disulphide to $[M(PPh_3)_4]$ in toluene and in a nitrogen atmosphere produced *trans*-$[M(py2S)_2(PPh_3)_2]$ (M = Pd(II) and Pt(II)) in high yield. The metals have a *trans*-S_2P_2 donor set with monodentate sulphur-donating pyridine-2-thionate ligands. A combination of molecular weight determinations and NMR spectra (${}^1H$ and ${}^{31}P\{1H\}$) of the $[M(py2S)_2(PPh_3)_2]$ complexes suggested the occurrence of phosphine exchange and ligand scrambling in solution. The phosphine exchange involves loss of a phosphine molecule, and ligand scrambling involves conversion of one monodentate sulphur-donating ligand into a S,N-chelating ligand. The latter process is shown in **XVIII**. In the palladium(II) complex the ligand-scrambling process is more rapid than that of phosphine exchange, and both processes are extremely slow in the platinum(II) complex.



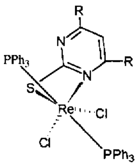
XVIII

Pyridine-2-thione and sodium methoxide were added to $[Pd_2Cl_4(PPh_3)_2]$ in tetrahydrofuran with the aim of replacing a bridging chlorine with μ_2-S bridging pyridine-2-thionate in [{PdCl(μ-py2S)(PPh_3)}$_2$], similar to the arrangement previously established for the corresponding trimethyl phosphine structure [93]. However, the unexpected product of the reaction was mononuclear [PdCl(py2S)(PPh_3)]. In this complex the metal has distorted square-planar geometry with a N, S, P, Cl donor set, a *trans*-(P,N) structure and S,N-chelating pyridine-2-thionate (**XVIIb**). There are two independent molecules in the unit cell that differ in the disposition of their pyridine rings. Some significant differences are also evident in the bond distances (Pd–S = 2.320(7) and 2.289(5); Pd–N = 2.112(13) and 2.046(14) Å) and angles (S–Pd–N = 73.9(4)° and 67.3(4)°). Increase in the thioamide–thione distance of the ligands is evident in both these complexes.

3.2.2. *Six-coordinate complexes*

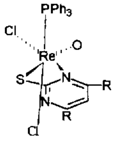
These mixed-ligand complexes are limited to the cations and oxy-cations of the heavier transition metals with a range of ligands occupying the remaining coordination sites.

Addition of solid 4,6-dimethylpyrimidine-2(1H)-thione to *trans*-[$ReOX_2(PPh_3)_2$] (X = Cl, Br), in boiling acetone produces two types of crystalline product, *trans*-[Re(III)X_2(me_2pym2S)(PPh_3)$_2$]·C_3H_6O and [Re(V)OX_2(me_2pym2S)(PPh_3)] (X = Cl, Br); the ligand proton is removed as the hydrohalic acid [94]. The crystal structures of the chloro complex of each type of product have been reported, with all the complexes further characterized by spectroscopic methods. Reaction pathways have been proposed to account for the production of a rhenium(III) complex from a rhenium(V) precursor. These involve either a partial *trans*→*cis* isomerization of the phosphine ligands or partial oxidation of the parent thione to the corresponding disulphide. Although no positive identification of the latter was provided in this case, the analogous production of disulphides is common in copper(II)/(I) heterocyclic thione redox chemistry [3]. Both complexes adopt distorted octahedral geometry. In *trans*-[$ReCl_2$(me_2pym2S)(PPh_3)$_2$] (**XIXa**) the two phosphine ligands occupy *trans* axial positions (P–Re–P = 173.9(2)°), with the chlorine atoms and the S,N-chelating heterocyclic ligand occupying the equatorial positions. The *cis* angles at the metal are in the range from 67.1(3)° to 100.5(2)°, with the former the chelating angle (N–Re–S) and the latter involving the *cis*-chlorine atoms. The Re(III)–S (2.409(4) Å) and the Re–N (2.115(10) Å) distances are similar to other reported values (2.354(4)–2.483(4) Å [95] and (2.139(9)–2.143(12) Å) [96] respectively. In [$ReOCl_2$(me_2pym2S)(PPh_3)] (**XIXb**) the phosphine is *trans* to a chlorine atom (Cl–Re–P = 169.1(1)°) with the rhenyl(V) oxygen (Re–O = 1.670(7) Å), the S,N-chelating heterocycle and the second chlorine atom in the equatorial plane. The Re–N distance (2.117(7) Å) is similar to that in the Re(III) complex, but the Re–S distance (2.507(2) Å) is slightly longer. Angles at the metal are significantly distorted from their ideal octahedral values and range from 65.4(2)° for the S–Re–N chelating angle to 110.3(2)° for the Cl–Re–O angle. The significant variation in the two *cis*-Re–Cl distances (2.293(2) and 2.370(3) Å) is attributed to differences in repulsive interactions (Cl---Cl′ = 3.624(5) Å and Cl---O′ = 3.278(6) Å) exerted by neighbouring octahedra. The mean ligand dimensions in both complexes (C–S = 1.701 Å, C–N = 1.36 Å and N–C–S = 110.3°) are consistent with deprotonation and coordination of the heterocycle.



XIXa

(R is Me)



XIXb

Adapted from [94]

Addition of pyridine-2-thione to *mer*-[$IrH_3(PPh_3)$] in boiling benzene produced pale yellow crystals of *trans*-[$IrH_2(py2S)(PPh_3)_2$] [97]. This highly distorted structure is similar to that of **XIXa** with *trans*-phosphines (P–Ir–P = 168.9(3)°) and a significant variation in the *cis* angles ranging from 64.7(8)°, the S–Ir–N chelate angle, to 95.5(8)°, the P–Ir–N angle. The equatorial positions are occupied by the S,N-chelate and the two *cis*-hydrogen atoms (Ir–S = 2.497(9) Å, Ir–N = 2.15(2) Å). The ligand thioamide dimensions (C–S = 1.77(3) Å, C–N = 1.38(4) Å and N–C–S 105(2)°) are indicative of deprotonate chelating pyridine-2-thionate [58].

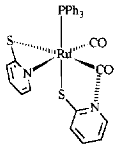
A range of halide complexes of molybdenum(III), (IV) and (V) have been prepared from mono and di-silylated derivatives of pyridine-2-thione [98]. Most of the complexes, of which [$MoBr_3$(3-$SiMe_3$-py2SH)] is typical, contain terminal sulphur-donating neutral thione derivatives. However, (Ph_4P)[$MoOBr_3$(3-$SiMe_3$-py2S)] was obtained by treating the filtrate from the reaction of [$MoBr_2(CO)_4$] and (3-$SiMe_3$)pyridine-2-thione in acetonitrile with dichloromethane and its crystal structure was determined. Two of the bromine atoms are *trans* with the remaining bromine (Mo–Br = 2.509(3)–2.525(3) Å), the molybdenyl oxygen (Mo–O = 1.64(2) Å) and the S,N-chelating heterocycle (Mo–S = 2.467(7) Å, Mo–N = 2.282(2) Å and S–Mo–N = 64.0(5)°) in equatorial positions. The halogen atoms in these complexes are readily displaced by a variety of donors including organohydrazine and pseudo-halide ligands.

3.2.3. *Organometallic complexes*

The majority of organometallic complexes have been derived from carbonyl precursors and include a number which contain a *cis*-related combination of one S,N-chelating and one monodentate sulphur-donating ligand. Complexes have also been reported which contain alkyne groups as the major organometallic fragment as well as a quinoline-2-thionate derivative which was obtained from the novel internal cyclization of an alkenyl-*N*-arylthioamide ligand.

A number of osmium, ruthenium and iridium carbonyls react with 1,3,4- thiadiazole-2-thiol-5-thione, generally in boiling toluene, to give complexes of the monodeprotonated anion 1,3,4-thiadiazole-2-thiolate-5-thione (**IIn(ii)**). *Trans*-[$Ru(II)(tdzS_2H)_2(PPh_3)_2(CO)$] is typical of this series [91]. A similar reaction involving [$Os(CF_3CO_2)_2(CO)_4$] and pyridine-2-thione in refluxing toluene produced the *fac* isomer of [$Os(py2S)_2(CO)_3$] [99], while the reaction involving [$Ru(CO)_3(PPh_3)_2$] and 2.2′-dipyridyldisulphide in boiling toluene produced *cis*-

[Ru(II)(py2S)$_2$(CO)$_2$(PPh$_3$)] [100]. Further loss of carbonyl in the latter complex, in dichloromethane/n-hexane, is facilitated by a short (2.782(7) Å) intramolecular contact between a carbonyl carbon and an adjacent thioamido nitrogen atom (**XX**), which leads to the formation of the *cis*-bischelate [Ru(py2S)$_2$(PPh$_3$)$_2$] (see Section 3.3). The final member of this group [Rh(3-SiMe3-py2S)$_2$(C$_5$Me$_5$)] was obtained from [{Rh(C$_5$Me$_5$)Cl$_2$}$_2$] and a suspension of (3-trimethylsilyl)pyridine-2-thione in acetonitrile, followed by concentration of the reaction solution and the addition of diethyl ether [101]. The three carbonyl complexes all adopt highly distorted pseudo-octahedral geometry with *trans*-phosphines in *trans*-[Ru(II)(tdzS$_2$H)$_2$(PPh$_3$)$_2$(CO)], a group of three confacial carbonyls in *fac*-[Os(py2S)$_2$(CO)$_3$] and *cis*-carbonyls in *cis*-[Ru(II)(py2S)$_2$(CO)$_2$(PPh$_3$)]. In contrast, the pentamethylcyclopentadienyl complex [Rh(3-SiMe$_3$-py2S)$_2$(C$_5$Me$_5$)] adopts a pyramidal structure with η^5-C$_5$Me$_5$ at the apex. The ring carbons are essentially equidistant from the metal in this complex (mean Rh–C = 2.176(5) Å), the S$_2$N atoms from the heterocyclic ligands form the base and the metal atom is significantly displaced from the basal plane. The major structural interest in these complexes centres on the unusual combination of a *cis*-related pair of one S,N-chelating and one monodentate sulphur-donating heterocyclic thionate ligand in each complex (**XX**).



Adapted from [100]

XX

Structures in which two potentially bidentate ligands share three adjacent sites frequently display fluxional behaviour. Consequently, variable-temperature proton NMR studies in CDCl$_3$ have revealed dynamic interchange between the S,N-chelating and the sulphur-donating heterocyclic ligands in [M(II)(tdzS$_2$H)$_2$(PPh$_3$)$_2$(CO)] (M = Ru, Os) [91]. A summary of the essential structural details of these complexes (Table 4) shows that the M–S distances generated by the chelating ligands (M–S = 2.408(2)–2.478(5) Å) are consistently longer than those generated by the sulphur-donating heterocyclic thionates (M–S = 2.360(2)–2.424(3) Å). This indicates more effective overlap of the metal–sulphur orbitals in the case of the sterically more favourable monodentate ligands.

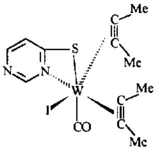
The inherent strain in these four-membered chelate rings is again evident in the small S–M–N chelating angles (64.8(4)°–67.6(1)°) and the fact that the M–S–C angles (79.7(2)°–80.9(6)°) are significantly more constrained than those of the monodentate ligands (109.6(3)°–114(6)°). Three of the latter are close to the average tetrahedral value for monodentate sulphur-donating neutral ligands [102]. The C–S$_{\mathrm{exo}}$ dimensions of the heterocyclic ligands in *trans*-[Ru(II)(tdzS$_2$H)$_2$(PPh$_3$)$_2$(CO)] (C(2)–S(2) = 1.73(2) Å, 1.71(2) Å; C(5)=S(5) = 1.58(2) Å, 1.67(2) Å, 1.67(2) Å) are consistent with the 1,3,4,thiadiazole-2-thiolate-5-

Table 4
Selected bond distances and angles of S,N-chelating and monodentate sulphur-donating ligands in monochelate complexes

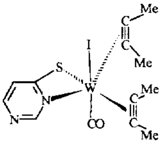
S,N-chelate				Monodentate-S	
M–S (Å)	M–N (Å)	M–S–C (deg)	S–M–N (deg)	M–S (Å)	M–S–C (deg)
[Ru(tzdtH)$_2$(PPh$_3$)$_2$CO] [91]					
2.478(5)	2.18(1)	80.2(6)	64.8(4)	2.385(5)	114(6)
[Os(py2S)$_2$(CO)$_3$] [99]					
2.446(3)	2.129(3)	79.9(4)	67.4(2)	2.424(3)	109.7(4)
[Ru(py2S)$_2$(CO)$_2$(PPh$_3$)] [100]					
2.453(1)	2.114(4)	79.7(2)	67.6(1)	2.419(1)	109.6(3)
[Ru((3-SiMe$_3$)py2S)$_2$(C$_5$Me$_5$)] [101]					
2.408(2)	2.089(4)	80.9(6)	67.44(9)	2.360(3)	109.9(2)

thione tautomer. Although the symmetrical nature of the ligand makes the numbering somewhat arbitrary, the ligand dimensions are consistent with deprotonation of the thiol (C–SH) rather than of the thione–thioamide portion of the molecule [35]. The $>$C–S$_{exo}$ dimensions of all the heterocyclic thionates (1.71(2)–1.76(1) Å) are consistent with deprotonation and coordination. In general, the dimensions of the thioamide moieties among the heterocyclic thionates show no significant differences between chelating and monodentate donors. In *cis*-[Ru(II)(py2S)$_2$(PPh$_3$)(CO)$_2$] the C–S and the C–N distances of the pyridine-2-thionate ligands are 1.756(7) and 1.747(6) Å for the chelating donors, and 1.353(7) and 1.320(7) Å for the monodentate donors. The difference between the N–C–S angles of monodentate and chelating pyridine-2-thionate in this complex (109.9(4)° and 121.3(4)°) results from the geometric strain of chelation.

Alkyne complexes of molybdenum(II) and tungsten(II) have been reported, reviewed [103] and recently extended to include the S,N-chelating heterocyclic thionates pyrimidine-2-thionate [104], pyridine-2-thionate [105] and a pyrollidine dithiocarbamato complex [106]. The starting material for this sequence of complexes is [WI$_2$(CO)(NCMe)(η^2-MeC$_2$Me)$_2$]·0.5CH$_2$Cl$_2$ which, when treated with an equimolar quantity of potassium pyrimidine-2-thionate in ether, produces [WI(CO)(pym2S)(η^2-MeC$_2$Me)$_2$]. The addition of potassium pyridine-2-thionate to the same precursor in CH$_2$Cl$_2$, followed by the addition of Na(BPh$_4$), produces the cationic complex [W(CO)(NCMe)(py2S)(η^2-MeC$_2$Me)$_2$](BPh$_4$). A similar procedure produces the corresponding pyrrolidine–dithiocarbamato complex. This synthetic route has been extended to include bis-heterocycles, phenanthrene and diphosphines. Two isomeric forms of the pyrimidine-2-thionate complex are possible (**XXI**).



XXIa

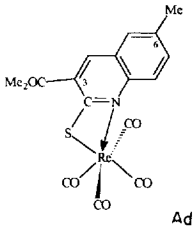


Adapted from [104]
XXIb

Variable-temperature proton NMR revealed fluxional behaviour for the pyrimidine-2-thionate complex, with the isomer **XXIa** being the most abundant at room temperature. This was confirmed by the crystal structure of the complex which revealed distorted octahedral geometry with *trans*-related thionato sulphur and carbonyl as well as *cis*-related but-2-yne ligands (mean W–C = 2.076(5) Å). The extent of the distortion from regular octahedral geometry is indicated by the *cis* angles at the metal which range from 64.4(2)° for the chelating angle to 97.2(2)° for the C–W–N angle. The *trans* angles range from 104.1(2)° to 165.9(1)°. Metal–ligand distances generated by the S,N-chelating ligand are W–S = 2.544(4) Å and W–N = 2.210(4) Å, with the W–S–C angle (81.1(2)°), like the chelating angle, typical of the inherently strained four-membered chelate ring. The ligand dimensions (C–S = 1.739(5) Å, C–N = 1.346(5) Å and N–C–S = 110.7(3)°) are typical of deprotonated chelating ligands. The triple-bonded but-2-yne ligands are parallel to the W–CO axis which permits maximum overlap of both pπ orbitals of the coordinated alkynes and optimizes their π-acceptor and π-donor properties [103]. The ν(CO) value at 2044 cm^{-1} reflects the small amount of electron density on the metal that is available for back donation to the π^* orbitals of the carbonyl. Replacement of the iodine atom in **XXIb** with an acetonitrile group generates the isomeric form typical of the pyridine-2-thionate complex. In this structure the acetonitrile and carbonyl groups occupy the axial positions, and the but-2-yne and heterocyclic thionato ligands occupy the equatorial sites. The alkyne ligands are again oriented so that their triple bonds are parallel to the W–CO axis with a mean W–C distance of 2.054 Å. This arrangement maximizes pπ-orbital overlap. The distances generated by pyridine-2-thionate (W–S = 2.551(5) Å, W–N = 2.217(22) Å and S–W–N = 63.6(5)°) are similar to those of the pyrimidine-2-thionate complex.

NMR studies show that these structures adopt the isomeric form **XXIb** in solution. The acetonitrile group in these complexes is readily replaced with both neutral mono- and bidentate ligands.

A recent development in the organometallic chemistry of organic isothiocyanates involves the reaction between aryl isothiocyanates and the lightly stabilized dimetallated olefin complex $Re(CO)_4[trans\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ which results in the displacement of the acetonitrile ligand and insertion of the organic isothiocyanate into the carboxylate-substituted rhenium–carbon bond [107]. The product $Re(CO)_4[(E)\text{-}HC{=}C(CO_2MeC{=}N(C_6H_4\text{-}p\text{-}R)S)]Re(CO)_4$ (R = H, Me, Cl), contains an alkenyl-*N*-arylthioamide ligand. Irradiation of this complex in the presence of iodine causes it to undergo an unusual cyclization reaction in which the aryl ring is coupled at its *ortho* position to the unsubstituted olefin. This results in the production of bridged binuclear and mononuclear S,N-chelate complexes of quinoline-2-thionate (**IIi(ii)**) derivatives. One of the mononuclear complexes (**XXII**) obtained from this reaction contains six-coordinate rhenium with four linear terminal carbonyls and S,N-chelating 3-carbomethoxy-6-methyl-quinoline-2-thionate.



Adapted from [107]

XXII

The heterocyclic ligand generates tyical contacts with the metal (Re–S = 2.505(2) Å, Re–N = 2.196(5) Å and S–Re–N = 64.9(2)°). The ligand dimensions are characteristic of deprotonated chelating species (C–S = 1.731(7) Å, C–N = 1.383(9) Å and S–C–N = 110.3(5)°).

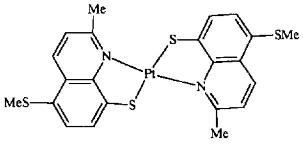
In common with other chelating heterocyclic thionates in organometallic environments, the quinoline-2-thionate derivative behaves as a three-electron donor.

3.3. Bischelates

This group is one of the most populous categories, with complexes formed by the main group and by transition metals in conventional and organometallic environments. Metal coordination among the complexes ranges from four-coordinate, in distorted tetrahedral and square-planar forms, to a fluxional seven-coordinate complex with capped-octahedral/"piano-stool" geometry. The asymmetric character of the S,N-chelating heterocyclic thionates generates a large number of geometric isomers, particularly among complexes with $[M(\text{chel-S,N})_2A_2]$ stoichiometry. The ligands involved range from pyridine-2-thionate, which typically generates four-membered S,N-chelates, to quinoline-8-thionates, which generate five-membered S,N-chelates, to the dithiolene analogues quinoxaline-2,3-dithionate and 1,2,5-thiadiazole-3,4-dithionate, both of which generate five-membered S,S-chelates.

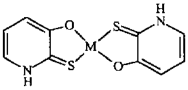
3.3.1. Four-coordinate complexes

Lead(II) [108] and zinc(II) [109] bis S,N-chelates of 2-methyl-5-methylthioquinoline-8-thionate (**IIi(i)**) adopt distorted tetrahedral geometry with the following mean dimensions: Pb–S = 2.635(4) Å, Pb–N = 2.58(1) Å and S–Pb–N = 72(1)°; Zn–S = 2.263(2) Å, Zn–N = 2.100(6) Å and S–Zn–N = 89.1(1)°. The chelating angle in the zinc(II) complex appears to be more typical of this type of ligand (87.6(1)°–90.5(8)°) [109] than does that of the lead complex. Typical mean ligand dimensions reported for these complexes are C–S = 1.760(7) Å and C–N = 1.380(7) Å; the mean Zn–S–C angle (95.3(2)°) is significantly smaller than that expected for four-membered S,N-chelating ligands. The same ligand also forms a centrosymmetric bischelate of platinum(II) with a *trans*-S,S geometry and dimensions Pt–S = 2.302(1) Å, Pt–N = 2.029(5) Å and S–Pt–N = 84.5(1)° [110] (**XXIII**).



XXIII Adapted from [110]

The crystal structure of 3-hydroxy-6-methyl-pyridine-2-thione [111] established the existence of the thione tautomeric form of the molecule in the solid. Consequently, the anion is capable of generating either four-membered S,N-chelating species or five-membered S,O-chelating species (**IIc(iii)**). Highly coloured complexes of transition metals have been reported for this ligand without identification of the chelating mode [18]. Bischelates of nickel(II) and copper(II) have been prepared from nickel(II) chloride hexahydrate in aqueous ethanol and copper(II) oxide in ethanol hydrochloric acid, with the ligand deprotonated by the addition of dilute ammonium hydroxide, and their crystal structures have been reported [18]. The complexes are isostructural and centrosymmetric at the metal, as well as being almost planar but with slight dihedral angles between the pyridine and the chelating rings of 2.6(1)° for the nickel(II) complex and 4.2(1)° for the copper(II) complex. Chelation involves the oxygen and sulphur atoms and results from deprotonation of the hydroxo, rather than the thione, group, with the formation of five-membered S,O-chelating rings rather than the more strained four-membered S,N-chelating rings (**XXIV**).



(M is Ni and Cu) Adapted from [18]
XXIV

The M–O (2.204(1) and 2.292(2) Å) and M–S (1.856(3) and 1.902(4) Å) distances for nickel(II) and copper(II) respectively are unexceptional, their respective M–S–C angles (95.1(1)° and 93.7(2)°) are larger than would be expected for S,N-chelation and the ligand C–S distance of 1.716(4) Å for both complexes is more indicative of thione than of thionate character [2].

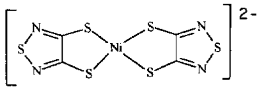
Several diamagnetic and electrochemically active mononuclear nickel(ii) complexes of sterically hindered alkyl and aryl thiolates, as well as those of pyridine-2-thionate derivatives, have been reported [112]. A combination of nickel chloride hexahydrate, 3-substituted trimethylsilyl pyridine-2-thione and trimethylamine in ethanol, refluxed for an hour, followed by recrystallization of the initial product produced crystalline $[Ni((3\text{-}SiMe_3)py2S)_2]$. This centrosymmetric square-planar complex has a *trans*-S_2N_2 donor set with Ni–S = 2.2281(8) Å, Ni–N = 1.873(2) Å and N–Ni–S = 74.30(8)° with ligand dimensions C–S = 1.756(3) Å and C–N = 1.336(4) Å. The complex exhibits a one-electron Ni(II)/Ni(III) oxidation potential at +0.42 V vs. SCE in acetonitrile at 25 °C; this value is typical of similar complexes [113].

Bis-1,2-dithiolene metal complexes have generated significant interest as precursors for molecular metals, and even superconductors, in recent years [114]. Although heterocyclic thionato analogues of 1,2-dithiolenes are relatively rare, both quinoxaline-2,3-dithionate (**IIj**) and 1,2,5-thiadiazole-3,4-dithionate (**IIo**) contain the $S_2C_2N_2$ moiety, which is characteristic of 1,2-dithiolenes, and also form bis S,S-donating chelates. The crystal structures, UV–visible spectra and electrochemical properties of the copper(II) and copper(III) complexes of quinoxaline-2,3-dithionate-$(PPh_4)_2[Cu(II)(qnxS_2)_2]$ and $(PPh_4)[Cu(III)(qnxS_2)_2]$ have been reported [115]. Both bischelate anions contain square-planar CuS_4 cores, with their major structural difference limited to the copper–sulphur bond lengths (mean Cu(III)–S = 2.187(1) Å; mean Cu(II)–S = 2.260(1) Å).

The copper–sulphur bond lengths in the corresponding complexes of dithiomaleonitrile have a similar relationship [116]. Dimensions of the $N_2C_2S_2$ portion of the ligand are dependent on the oxidation number of the metal. Consequently, the copper(III) complex has significantly shorter carbon–carbon distances (mean C–C = 1.439(3) Å) and longer carbon–sulphur distances (mean C–S = 1.748(3) Å) than the corresponding copper(II) complex (mean C–C = 1.459(3) Å, mean C–S = 1.739(3) Å). The five-membered chelate produces S–Cu–S chelating angles of 90.5(1)° in the centrosymmetric copper(III) complex and a mean of 91.9(1)° for the two independent anions of the copper(II) complex. Furthermore, the Cu–S–C angles (102.8(1)°–104.8(1)°) reflect the decreased strain at the thionato sulphur atoms expected of five-membered chelates. The cyclic voltammetric curves of the quinoxaline-2,3-dithionate complexes in dimethyl formamide have also been reported. Two redox reactions have been observed at $E_{\frac{1}{2}}$ values of −0.18 and −1.38 V vs. SCE. The first value corresponds to the $[Cu(qnxS_2)_2]^-/[Cu(qnxS_2)_2]^{2-}$ couple and is fully reversible; the second value corresponds to the $[Cu(qnxS_2)_2]^{2-}/[Cu(qnxS_2)_2]^{3-}$ couple and is quasi-reversible. This variation in electrochemical behaviour has been attributed to structural differences between the complexes.

Addition of 3,4-dichloro-1,2,5-thiadiazoline to disodium sulphide in aqueous ethanol, followed by extraction and drying of the product, produces the disodium salt of 1,2,5-thiadiazoline-3,4-dithionate, i.e. $(tdzS_2)Na_2$. The complexes $(R_4N)_2[Ni(tdzS_2)_2]$ (R = Et, Bu) were obtained by reacting $(tdzS_2)Na_2$ and nickel(II) chloride hexahydrate in methanol followed by addition of the reaction mixture to methanolic solutions of both ethyl and butyl ammonium bromide; the initial product was recrystallized [117].

The crystal structures of both complexes contain essentially planar centrosymmetric square-planar anions (**XXV**) (mean Ni–S = 2.200(1) Å); the nickel–sulphur distances in the complexes are equivalent within experimental error.



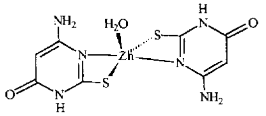
XXV Adapted from [117]

The smaller ethylammonium anion allows a layered stacking of the ionic components, with the packing of the butylammonium structure somewhat looser in character. The carbon–carbon and carbon–sulphur distances of the anionic dithionates (mean C–C = 1.503(2) Å; mean C–S = 1.722(5) Å) are similar to those of the quinoxaline-2,3-dithionate anions. These heterocyclic vicinal dithionates are clearly useful additions to the range of 1,2-dithiolene ligands which share with other ligands in this range the ability to produce oxidizable precursors with the potential to produce compounds with novel magnetic and electrical properties. Such properties will undoubtedly be developed in the future.

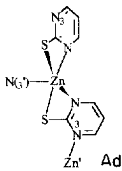
3.3.2. *Five-coordinate complexes*

Two of the complexes in this category have [Zn(chel-S,N)$_2$adduct] stoichiometry with distorted trigonal bipyramidal geometry formed from pyrimidine-2-thionate derivatives with the thioamido nitrogen atoms of the ligands in the apical sites and the remaining donor atoms in the equatorial sites.

A hydrated zinc complex of the 6-amino-2-thiouracilate anion (**IIe(iv)**) (6-am-tucH) [Zn(6-am-tucH)$_2$(H$_2$O)]·2H$_2$O was one of the products of a series of reactions involving divalent metal acetates (M(II) = Ni, Co, Zn, Cd, Cu) and the ligand in aqueous solution [118]. In the crystal structure of the zinc(II) complex the metal and the coordinated water molecule (Zn–O = 1.968(4) Å) occupy a crystallographic two-fold axis with the thioamido nitrogen atoms occupying apical sites (Zn–N = 2.235(2) Å, N–Zn–N = 171.0(1) Å) while the water molecule and the thionato sulphur atoms occupy the equatorial sites. The sulphur atoms deviate slightly from the equatorial plane because of the four-membered chelate ring (Zn–S = 2.353(1) Å, N–Zn–S = 69.16(7)°, Zn–S–C = 80.0(1)°) (**XXVIa**).



Adapted from [118]
XXVIa



Adapted from [120]
XXVIb

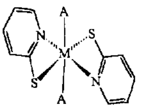
The ligand's thioamide dimensions (C–S = 1.721(3) Å, C–N = 1.322(4) Å and N–C–S = 117.2(2)°) show characteristic deviations from the corresponding values of the free ligand (C–S = 1.671(1) Å, C–N = 1.349(2) Å and N–C–S = 121.9(1)°) [119], with the major angular changes occurring at the thioamido carbon atom. Diffuse reflectance spectra suggest that [Co(6-am-tucH)$_2$(H$_2$O)]·2H$_2$O has a similar structure to that of the zinc(II) complex.

Electrochemical oxidation of a zinc anode together with deprotonation of 4,6-dimethylpyrimidine-2-thione (4,6-me$_2$-pym2SH) in acetonitrile produced [Zn(4,6-me$_2$-pym2S$_2$)]. Addition of pyridine, 2,2′-bipyridine and 1,10-phenanthroline to the electrolytic phase produced the 1:1 adducts of the complex [33]. These adducts were characterized by IR and by proton and ^{13}C NMR methods, and the crystal structure of the pyridine adduct was reported. In this complex the thioamido nitrogen atoms of the chelating ligands again occupy the apical sites (N–Zn–N = 168.1(2)°, Zn–N = 2.264(5), 2.219(5) Å), while the thionato sulphur atoms and the pyridine molecule are in an approximately equatorial plane which is again distorted because of the four-membered chelate (Zn–S = 2.347(2), 2.369(2) Å; Zn–py = 2.057(4) Å; N–Zn–S = 68.2(2)°; Zn–S–C = 82.8(2)°, 81.5(2)°). The ligands have mean thioamide dimensions which are similar to those of the 2-thiouracilate derivative (C-2 = 1.736(5) Å, C–N = 1.350(6) Å and N–C–S = 113.5(4)°).

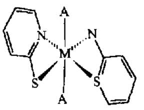
Pyrimidine-2-thionates (**IId(i)**) have an additional donor site, the N(3) atom, which appears to be rarely used in complex formation. However, in [Zn(4,6-me$_2$-pym2S)$_2$], obtained by the addition of potassium hydroxide and zinc chloride to a stirred aqueous solution of the parent ligand, the metal is pentacoordinated with a N_3S_2 donor set provided by the two ligands, of which one is S,N-chelating and the other is tridentate N_2S-bridging (**XXVIb**) [120]. Within each molecular unit the zinc(II) atom is S_2N_2 coordinated by the thioamido sulphur and nitrogen atoms of each ligand. One ligand is S,N-chelating with a thioamido nitrogen atom in an apical site (Zn–N = 2.369(6) Å) and the thionato sulphur atom in an equatorial site (Zn–S = 2.319(2) Å). The second ligand is tridentate bridging with the thioamido nitrogen atom in an equatorial site (Zn–N = 2.061(5) Å) and the thionato sulphur atom in an apical site (Zn–S = 2.679(2) Å) and the pyrimidino-N(3) atom occupying the remaining equatorial site in a neighbouring symmetry-related fragment (Zn′–N = 2.040(5) Å). The latter contact generates infinite chains. The long Zn–S distance formed by the tridentate ligand appears to be primarily due to the fact that the two ligands are twisted by 113.3(1)° relative to each other in order to avoid steric crowding of the thionato sulphur atoms (S---S = 3.875(3) Å). Angles at the metal reflect the distortion from regular trigonal bipyramidal geometry and range from the S,N-chelating angle (67.6(1)°) to the *trans* N–Zn–S angle (168.6(1)°). The structure is described as intermediate between trigonal bipyramidal and square pyramidal.

3.3.3. Six-coordinate complexes

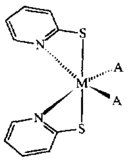
Octahedral complexes of stoichiometry [M(chel-S,N)$_2$A$_2$] generate both *trans* and *cis* isomers. Because of the asymmetric nature of the chelating ligand there are two *trans* isomers, defined in terms of $MS_2N_2A_2$ stoichiometry as *cis-cis-trans* (*cct*) and



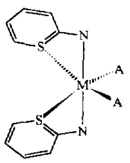
trans (ttt)
XXVIIa



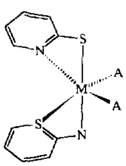
trans (cct)
XXVIIb



cis (tcc)
XXVIIc



cis (ctc)
XXVIId

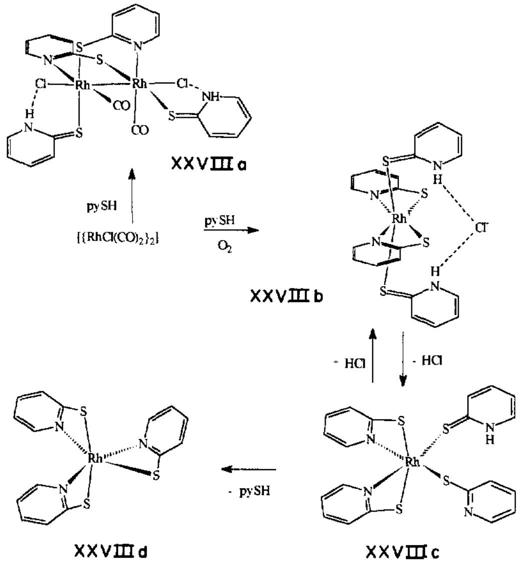


cis (ccc)
XXVIIe

trans-trans-trans (*ttt*). There are also three*cis* isomers, similarly defined as *trans-cis-cis* (*tcc*), *cis-trans-cis* (*ctc*) and *cis-cis-cis* (*ccc*). These isomers are illustrated in **XXVII**; the corresponding enantiomeric *cis*-isomers are also possible.

The *trans* isomers of the complexes of $[\mathrm{M(chel\text{-}S,N)_2A_2}]$ stoichiometry are numerically fewer than those of the *cis* isomers but their derivation involves some intriguing chemistry.

A combination of *trans*-$[\mathrm{Rh(III)(py2S\text{-}S,N)_2(pySH\text{-}S)_2}]\mathrm{Cl}$, *cis*-$[\mathrm{Rh(III)(py2S\text{-}S,N)_2(py2S\text{-}S)(py2SH\text{-}S)}]$ and *mer*-$[\mathrm{Rh(III)(py2S\text{-}S,N)_3}]$ result from the treatment of a chloroform solution of the dinuclear complex $[\mathrm{Rh_2(I)Cl_2(CO)_4}]$ with an excess of pyridine-2-thione. The reaction initially produces solutions containing air-sensitive rhodium(I) carbonyl complexes of pyridine-2-thione [121] (**XXVIII**).



Adapted from [123]

On standing in the absence of air such solutions slowly deposit blue-black crystals of dinuclear $[\{\mathrm{Rh(II)Cl(\mu_2\text{-}py2S\text{-}SN)(py2SH\text{-}S)(CO)}\}_2]$ (**XXVIIIa**) whose "open-book" structure results from the *cis* "head-to-tail" arrangement of the S,N-bridging pyridine-2-thionate ligands [122]. However, the addition of a ten-fold excess of pyridine-2-thione to $[\{\mathrm{RhCl(CO)_2}\}_2]$ in chloroform, in the presence of air, results in the oxidation of the metal together with total loss of the carbonyl ligands and the slow production of pale orange crystals of *trans*-$[\mathrm{Rh(III)(py2S\text{-}SN)_2(py2SH\text{-}S)_2}]\mathrm{Cl}$ (**XXVIIIb**), which is a 1:1 electrolyte in dichloromethane/acetonitrile. Deprotonation and dechlorination of **XXVIIIb**, by stirring the complex with basic alumina or by the addition of triethylammine in chloroform, results in a major redistribution of the ligands and production of *cis*-$[\mathrm{Rh(III)(py2S\text{-}S,N)_2(py2S\text{-}S)(py2SH\text{-}S)}]$ (**XXVIIIc**). Removal of the neutral ligand in **XXVIIIc** is readily achieved by sublimation of the complex or by melting it and recovering *mer*-[Rh-

(III)(py2S-S,N)$_3$] (**XXVIIId**) by chromatographic extraction of a dichloromethane solution of the cooled product.

Some preliminary structural information about these complexes has been deduced from proton NMR studies. Two equally populated ligand environments in (**XXVIIIb**) indicated the presence of pyridine-2-thionate and pyridine-2-thione in the complex. Despite the presence of four non-equivalent ligands in **XXVIIIc**, the proton NMR spectrum consists of two sets of ligand resonances of equivalent intensity, even down to −60 °C, resulting from rapid proton exchange between the two monodentate ligands. The existence of three sets of ligand resonances in **XXVIIId** is more consistent with the *mer* than with the *fac* isomer.

The structures of the mononuclear complexes have also been confirmed by crystal structure analyses [123]; that of *mer*-[Rh(py2S)$_3$] is discussed in Section 3.4.2. The *trans*-octahedral (*cct*) geometry of **XXVIIIb** is significantly distorted as a result of S,N-chelation (mean values Rh–S = 2.375(4) Å, Rh–N = 2.072(8) Å, N–Rh–S = 86.1(3)° and Rh–S–C = 80.1(4)°) and the fact that the *trans*-pyridine-2-thione ligands (mean values Rh–S = 2.360(4) Å, S–Rh–S = 171.2(1)° and Rh–S–C = 114.2(4)°) are positioned so as to maximize their relatively weak hydrogen-bonding interactions with the chloride anion (N---Cl = 3.156 Å, 3.105 Å). The presence of both neutral and deprotonated pyridine-2-thione in the complex affords some interesting comparisons of the dimensions within the ligands and the contacts which they generate. The shorter Rh–S distances generated by the neutral ligand are indicative of the extent to which the longer anionic Rh–S distances ameliorate the steric strain within the chelating ligands. The effect of deprotonation and coordination on the ligand's thioamide dimensions is also more marked in the S,N-chelating anion (mean values C–S = 1.740(10) Å, C–N = 1.344(11) Å and N–C–S = 109.3(3)°) than in the monodentate sulphur-donating neutral ligand (mean values C–S = 1.707(11) Å, C–N = 1.348(11) Å and N–C–S = 123.4(7)°). Selected dimensions of *cis*-[Rh(III)(py2S-S,N)$_2$(py2S-S)(py2SH-S)] (**XXVIIIc**) are listed in Table 5 and are discussed below.

Oxidation of [Os(II)(py2S)$_2$(PPh$_3$)$_2$] by cerium(IV) in dichloromethane acetonitrile produced [Os(III)(py2S)$_2$(PPh$_3$)$_2$]PF$_6$·nH$_2$O in two geometrically isomeric forms, green ($n = 1$) and red ($n = 0$), with the latter the minor constituent [124]. Crystal structures of the two isomers revealed that they both adopt *trans*-[M(chel-S,N)$_2$A$_2$] geometry with OsS$_2$N$_2$P$_2$ *cct* configurations (**XXVIIb**) in the green form and *ttt* (**XXVIIa**) in the centrosymmetric red form. Both structures exhibit substantial angular distortion with values in the green (*cct*) form ranging from the chelating angle (S–Os–N = 67.4(3)°) to the *trans* angle (P–Os–P = 177.6(1)°); the corresponding values in the red (*ttt*) form are 68.2(2)° and 180°. The {Os(py2S)$_2$} fragment in the *ttt* isomer is rigidly planar (Os–S = 2.374(3) Å; Os–N = 2.099(9) Å) while both the non-planarity of the otherwise separately planar {Os(py2S)} fragments and the longer osmium–sulphur distance of the *cct* isomer (Os–S = 2.395(3) Å; Os–N = 2.100(10) Å) are attributed to the presence of *cis*-sulphur atoms in the latter. Each isomer displays a quasi-reversible one-electron cyclic voltammetric curve in dichloromethane due to Os(III)/Os(II), with the *cct* isomer easier to oxidize than the *ttt* isomer: $E_{\frac{1}{2}}$ (*cct*) = $E_{\frac{1}{2}}$ (*ttt*) + 0.5 V vs. SCE. Analysis of the EPR spectra of these

Table 5
Selected bond distances and angles for the *trans-cis-cis* isomeric forms of *cis*-[M(chel-S,N)$_2$A$_2$] complexes

M–S (Å)	M–N (Å)	Chelating angle S–M–N (deg)	*Trans* angle S–M–S (deg)	*Cis* angle A–M–A(B) (deg)	M–S–C (deg)
[Sn(py2S)$_2$Cl$_2$] [128]					
2.467(3)	2.396(3)	66.2(3)			81.8(4)
2.462(3)	2.382(1)	66.0(3)	154.2(1)	94.8(1)	81.9(4)
[Sn(py2S-S,N)$_2$(py2S-S)$_2$]·py2SH [31]					
2.542(2)	2.332(5)	64.2(2)			83.0(2)
2.483(2)	2.324(5)	65.1(2)	148.22(6)	105.48(6)	82.3(2)
2.475(2) (py2S-S)					93.7(2)
2.463(2) (py2S-S)					101.7(2)
[Co(bztz2S)$_2$(py)$_2$][a] [129]					
2.585(1)	2.156(4)	66.3(1)	166.7(1)	94.8(2)	74.1(2)
2.605(1)	2.159(4)	66.3(1)	167.1(1)	96.1(2)	74.4(2)
[Ru(py2S)$_2$(PPh$_3$)$_2$] [90]					
2.434(2)	2.115(6)	66.2(2)			80.1(3)
2.437(2)	2.132(7)	67.7(2)	154.7(1)	96.8(1)	80.6(3)
[Mo(VI)O(NNMePh)(3-SiMe$_3$-py2S)$_2$] [131]					
2.514(1)	2.323(3)	63.45(8)			
2.432(1)	2.245(3)	65.88(8)	148.23(4)	104.9(1)	NR
[Mo(VI)(NNMePh)$_2$(3SiMe$_3$-py2S)$_2$][b] [132]					
2.496(1)	2.276(1)	64.2(1)	152.1(2)	NR	84.8(5)
[Mo(V)OCl(3SiMe$_3$-py2S)$_2$*]* [132]					
2.429(4)	2.18(1)	64.4(3)	152.1(2)	104.6(4)	82.2(5)
2.456(4)	2.30(1)	66.6(3)			84.8(5)
[Rh(py2S-S,N)$_2$(py2S-S)(py2SH-S)] [123]					
2.374(3)	2.051(4)	69.0(2)			79.2(2)
2.396(3)	2.077(4)	69.2(2)	163.1(1)	95.0(1)	80.3(2)
2.343(3)-(py2S-S)					108.5(2)
2.318(3)-(py2SH-S)					115.0(2)
[Os(py2S)$_2$(CO)$_2$] [99]					
2.441(1)	2.149(4)	66.7(1)			80.7(2)
2.419(2)	2.120(5)	67.5(1)	152.6[c]	91.4(3)	81.2(2)
[Ru(py2S)$_2$(CO)(PPh$_3$)] [133]					
2.429(1)	2.138(2)	67.8(1)			80.2(2)
2.422(1)	2.118(2)	67.5(1)	157.96(3)	90.9(1)	80.2(1)
[Cd(py2S)$_2$(py)$_2$][b] [87]					
2.715(2)	2.392(5)	62.1(1)	163.9(1)	93.1(3)	NR
2.696(2)	2.451(5)	62.1(1)	161.8(1)	97.1(3)	

NR, Not reported.

[a] C$_2$ axis and two independent molecules in the unit cell.

[b] C$_2$ axis.

[c] Calculated by the author.

paramagnetic complexes ($\mu_B = 1.83$ (*cct*) and 1.92 (*ttt*) at 298 K) revealed substantial splitting of the t_2 shell with corresponding ligand field transitions in the near-IR region (7400 cm^{-1} (*cct*) and 8300 cm^{-1} (*ttt*)). Formation of the green (*cct*) and red (*ttt*) isomers in such unequal proportions (ca. 1% red form) is ascribed to the presence of the *trans*-[Os(II)$(py2S)_2(PPh_3)_2$] precursor, in the *cct* form, in solution prior to oxidation and production of the trivalent osmium complexes [125].

The *trans* octahedral (*cct*) isomers may also adopt a skewed trapezoidal bipyramidal structure. This arrangement arises from a combination of two asymmetric chelating ligands, in an equatorial plane, and two mutually *trans* monodentate ligands. In order to minimize intraligand repulsions, the planar chelating ligands distort to form a trapezium with the *trans* monodentate ligands skewed towards its long edge [126].

Such distortion is slight in the *trans*-[Os(III)$(py2S)_2(PPh_3)_2]^+$ cation (P–Os–P = 177.6(1)°) and is the reverse of what is predicted in the *trans*-[Rh(III)$(py2S\text{-}SN)_2(py2SH\text{-}S)_2]^+$ cation where the internal hydrogen bonding distorts the *trans* ligands (S–Rh–S = 171.2(1)°) towards the short (N...N) edge of the trapezium. In [$(Ph)_2Sn(py2S)_2$], however, the *trans* octahedral (*cct*) structure consists of *trans* phenyl groups (C–Sn–C = 125.5(1)°) and two *cis*-chelating pyridine-2-thionate ligands (mean Sn–S = 2.481(1) Å, Sn–N = 2.667(4) Å, N–Sn–S = 60.70(8)° and Sn–S–C = 90.8(2)°), with the C–Sn–C axis significantly bent towards the longer (N---N) edge of the trapezium. Unusually, the Sn–N distances are longer than the Sn–S distances in this structure, presumably in order to accommodate the relatively narrow chelating angles [127]. Mean ligand thioamide dimensions in this structure (C–S = 1.754(4) Å, C–N = 1.331(7) Å and N–C–S = 114.6(3)°) are typical of deprotonated S,N-chelating ligands.

Of the three possible isomeric forms of the *cis*-[M(chel-S,N)$_2$A$_2$] bischelates, all the reported structures adopt *tcc* form (**XXVIIc**). Selected dimensions of the reported crystal structures are listed in Table 5.

There is no single identifiable preparative route to the *tcc* isomeric forms of *cis*-[M(chel-S,N)$_2$A$_2$] bischelates. The tin(IV) complexes are prepared by the oxidative addition of 2,2′-dipyridyl disulphide to either tin(II) chloride or metallic tin in organic solvents [30,31]. The pyridine adduct of the benzo-1,3-thiazoline-2-thionate complex [$Co(bztz2S)_2(py)_2$] is produced by the addition of [$Co(bztz2S)_2$] to pyridine [129], while the seminal pyridine-2-thionate complex [$Ru(py2S)_2(PPh_3)_2$] is obtained by the addition of pyridine-2-thione and triphenylphosphine to solutions of "blue" ruthenium chloride [130]. Molybdenum(VI) complexes with hydrazido ligands and sterically hindered pyridine-2-thionates are obtained by reacting [$Mo_2O_3(3SiMe_3\text{-}py2S)_4$] with 1,1-methylphenylhydrazine in dichloromethane [131] and by the addition of 1,1-methylphenylhydrazine to [$MoCl_2(3SiMe_3\text{-}py2S)_2$] in dry methanol [132]. The resultant molybdenum–hydrazido nitrogen distances (1.787(3) Å [131] and 1.75(1) Å [132]) are short and strong. A variety of methods have been used for the preparation of the carbonyl complexes. For example, *cis*-[$Ru(py2S)_2(CO)_2$] has been prepared by the thermolysis of triruthenium dodecacarbonyl [134] and by the reductive carbonylation of ruthenium trichloride, both in the presence of the parent ligand [134].

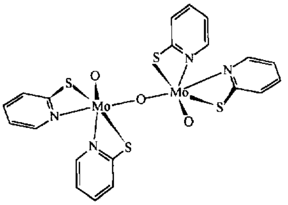
The reported crystal structures show that all the complexes have distorted octahedral geometry (Table 5) with *cis* A–M–A angles ranging from 90.9(1)°, for a combination of carbonyl and phosphine ligands, to 96.8(1)°, for a pair of triphenyl phosphines. However, the largest *cis* angle occurs between the two monodentate sulphur-donating pyridine-2-thionate ligands in [Sn(py2S-S,N)$_2$(py2S-S)$_2$]·py2SH [31]. Variations among the *trans* S–M–S angles range from 148.22(6)°, for two pyridine-2-thionate ligands, to 167.1(1)°, for the more bulky benzo-1,3-thiazoline-2-thionate ligands. The chelating ligands generate typically small S,N-chelating angles (63.45(8)°–69.2(2)°), short metal–nitrogen distances (2.051(4)–2.396(3) Å) and relatively long *trans* metal–sulphur distances (2.374(3)–2.605(1) Å). The exception to these general observations is [Cd(py2S)$_2$(py)$_2$] with the smallest chelating angles and the longest metal–ligand distances in the series [87].

There are two complexes which contain pyridine-2-thione molecules and pyridine-2-thionate anions, with the latter both S,N-chelating and monodentate sulphur donating. The ^{13}C NMR spectrum of *cis*-[Sn(py2S-S,N)$_2$(py2S-S)$_2$]·py2SH, recorded in deuterated chloroform at ambient temperature, contains separated signals for the *cis*-[Sn(py2S-SN)$_2$(py2S-S)$_2$] complex and the pyridine-2-thione molecule which are averaged at 178 K owing to slow intermolecular exchange between the thioamido proton of the parent molecule and the deprotonated ligands [135]. In the solid state the parent molecule is hydrogen bonded to the thioamido nitrogen of one of the monodentate ligands (NH---N = 1.92(7) Å). Furthermore, the metal–sulphur distances of the monodentate ligands are shorter than those of the chelating anions, primarily as a result of the absence of steric constraints in the former; the M–S–C angles also reflect the decreased strain of monodentate coordination (Table 5). The proton exchange which occurs between the two *cis*-related monodentate ligands in *cis*-[Rh(III)(py2S-S,N)$_2$(py2S-S)(py2SH-S)] (**XXVIc**) has already been alluded to above [123]. The metal–sulphur distances of the monodentate ligands are unequal, with that of the anion surprisingly longer than that of the neutral molecule; their M–S–C angles are also unequal. Both the monodentate ligands have metal–sulphur distances which are significantly shorter than those of the S,N-chelating anions (Table 5).

A combination of electronic and steric factors are probably responsible for the adoption of the *tcc* isomeric form of these complexes. A *cis* arrangement of carbonyl and phosphine ligands clearly favours dπ–dπ overlap of their respective orbitals, while the *trans*oid sulphur arrangement appears to be more steric than electronic in character.

Various combinations of neutral and anionic pyridine-2-thione ligands in the complexes listed in Table 5 have produced a range of thioamide ligand dimensions. Among the chelating ligands the mean C–N and C–S distances (1.347 Å and 1.741 Å) compare with the corresponding free ligand values [58] (1.356(3) Å and 1.695(2) Å); the N–C–S angle also decreases from 120.6(2)° in the parent molecule to a mean of 110.9° in the complexes. For the monodentate anions, the mean values are 1.375 Å and 1.763 Å for the C–N and C–S distances respectively, with the N–C–S angle at 118.1° remaining fairly close to the value in the parent molecule. The one reported monodentate neutral ligand has values of 1.343(5) Å and 1.704(5) Å for C–N and C–S with a N–C–S angle of 123.5(3)°. The increase in the C–S distance is the most sensitive indicator of coordination for the monodentate ligands. Reduction of both the N–C–S angle and the C–N distance, together with an increase in the C–S distance, characterizes the effects of chelation on the dimensions of the parent ligand.

Aerial oxidation of the dark green precipitate obtained from molybdenum(II) acetate and sodium pyridine-2-thionate in ethanol followed by recrystallization in chloroform produces the deep red crystalline binuclear complex $[(Mo(V)O)_2(\mu\text{-}O)(py2S\text{-}S,N)_4]$ [25]. This complex consists of two *cis*(*tcc*) distorted octahedral $(MoO_2(py2S)_2)$ isomeric units with *cis* oxygen atoms (O–Mo–O = 105.9(2)°, $Mo–O_{br} = 1.853(1)$ Å and $Mo–O_t = 1.673(4)$ Å) which are centrosymmetrically related through a Mo–O–Mo bridge (**XXIX**).



Adapted from [25]

XXIX

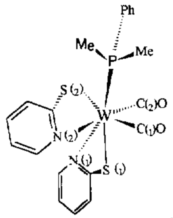
Consequently, the central Mo_2O_3 core is rigidly planar with *anti* geometry. The chelating anions generate mean dimensions similar to those reported in Table 5 (Mo–S = 2.460(4) Å, Mo–N = 2.245(5) Å, S–Mo–N = 65.3(1)° and S–Mo–S = 149.6(1)°), with the thioamido nitrogen atoms occupying positions which are *trans* to the strongly pπ-bonding oxo groups. The strong *trans* effect of the terminal oxo group is responsible for the disparity in the resultant molybdenum–nitrogen distances (Mo–N = 2.305(5) Å and 2.185(5) Å). A similar structure has been reported for $[Mo_2O_3(3SiMe_3(py2S)_4]$ [132].

3.3.4. Organometallic complexes

In addition to the carbonyl complexes listed in Table 5, other complexes with organometallic ligands have also been reported.

The polymeric halogen bridged diene $[\{Ru(diene)Cl_2\}_n]$ (diene = 1,5-cyclooctadiene) reacts with a variety of ligands, including heterocyclic thiones, in dimethylformamide in the presence of anhydrous sodium carbonate, giving complexes of the type $[Ru(diene)(chel)_2]$ [136]. With bicyclo[2.2.1]hepta-1,4-diene(nbd) as the organometallic ligand, pyridine-2-thione gives $[Ru(nbd)(py2S\text{-}SN)_2]$ by the above method. A *trans* (*tcc*) isomeric structure has been proposed for the complex on the basis of proton and ^{13}C NMR spectra [137]. The crystal structure of the air-stable orange-red crystalline complex confirmed the spectroscopic predictions [138]. The *cis*-related pyridine-2-thionate ligands generate dimensions (Ru–S = 2.427(1) Å, Ru–N = 2.105(4) Å, S–Ru–N = 67.6(1)° and S–Ru–S = 149.9(1)°) which are similar to those reported for $[Ru(py2S)_2(CO)(PPh_3)]$ [133], except for slightly shorter Ru–N distances and a smaller *trans* S–Ru–S angle.

The reaction of $[W(CO)_3(MeCN)]$ with pyridine-2-thione in acetonitrile at room temperature gives [$W(CO)_3(py2S)_2$] as the major product together with some [$W(CO)_5(py2SH)$ [139]. Both IR and proton NMR data identified the latter as a six-coordinate complex containing monodentate sulphur-donating pyridine-2-thione. Two strong ν(CO) IR bands in [$W(CO)_3(py2S)_2$], consistent with confacial tris-carbonyls. These two *cis*-S,N-chelating pyridine-2-thionate anions generate a seven-coordinate complex with the proton NMR spectra consisting of one set of pyridine-2-thionate resonances down to −90 °C, most probably as a result of fluxional exchange in the complex. In order to suppress the supposed fluxionality, dimethylphenylphosphine was added to the complex in cyclohexane and [$W(py2S\text{-}S,N)_2(CO)_2(PhMe_2P)$] was produced. The molybdenum(II) analogue was also reported. The crystal structure revealed the presumed seven-coordinate complex and an 18-electron configuration at the metal, with *cis*-related pyridine-2-thionate chelating ligands (mean values W–S = 2.529(3) Å, W–N = 2.220(6) Å, S–W–N = 65.5(2)° and S–W–S = 139.9(1)°) (**XXX**).



Adapted from [139]

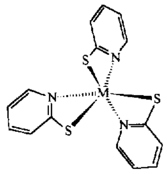
XXX

The two carbonyls and the dimethylphosphine ligands form an approximately *fac*-related set. Neither of the two idealized seven-coordinate geometries is adopted. For the face-capped octahedral geometry the atom in the capping position (C(1)) should form three angles close to 75° to three adjacent ligands (C(2), P, S(1)) and three angles close to 130° to three more distant ligands (S(2), N(1), N(2)). The actual angles (71.5(3)°–76.8(3)°) and 122.3(3)°–134.9(2)°) are distorted from the ideal because of the narrow bite of the chelating ligands. The alternative 4:3 "piano-stool" arrangement requires a P, N(2), S(1) C(1): N(2), S(2), C(2) arrangement. No quantitative assessment of the extent of distortion from the ideal was made. The fluxional character of the complex was revealed by the proton NMR spectra which consist of two sets of pyridine-2-thionate signals and two methyl doublets at −53 °C, consistent with non-equivalent pyridine-2-thionate and dimethylphosphine groups, which merge at room temperature. The complicated nature of the fluxional character requires an intermediate structure with a mirror plane through the tungsten–phosphorus bond which also relates the two pyridine-2-thionate ligands. None of the possible structures with these requirements relates directly to the reported structure.

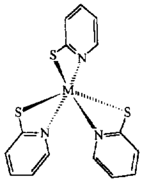
3.4. Trischelates

In addition to homoleptic trischelates, this category also contains two types of mixed-ligand trischelates that contain either one or two chelating heterocyclic thionates in combination with other invariably *N,N′*-chelating ligands such as diaminoethane and 2,2′-bipyridine. There are also examples of seven-coordinate complexes that are based on trischelates of the formula $[\mathrm{M(het\text{-}S,N)_3L}]$ (L = *p*-tolyl and phenylhydrazide).

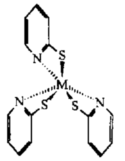
There are three possible geometric isomers for trischelates of the general formula $[\mathrm{M(het\text{-}S,N)_3}]^n$ ($n=0$ or -1) two of which (**XXXIa** and **XXXIb**) also give rise to the corresponding enantiomers. However, trigonal prismatic geometry (**XXXIc**) is more typical of *S,S′*-chelating 1,2-dithiolates, such as 1,2-diphenylethene-1,2-dithiolate (dpdt) which generated $[\mathrm{Re(dptp)_3}]$, the first reported complex with this geometry [140].



Confacial
XXXIa



Meridional
XXXIb



Trigonal prismatic
XXX Ic

The restricted bite (approximately 2.5 Å) of heterocyclic thionates should favour the formation of trigonal prismatic geometry among trischelates of heterocyclic thionates, at least in principle [141]. No homoleptic trischelates with trigonal prismatic geometry are known, but one mixed-ligand trischelate with this geometry has been reported $[\mathrm{Cd(bztz2S)_2(bipy)}]$ [142]. In addition, examples have been reported in which the geometry is intermediate between that of trigonal prismatic and *fac*-octahedral for both homoleptic and mixed-ligand complexes. However, most authors do not report the extent of the distortion from octahedral to trigonal prismatic geometry. Although no resolution of optical isomers has been reported among homoleptic trischelates, such resolution has been observed among mixed-ligand complexes. Substituted heterocyclic thionates also give rise to structural isomerism among complexes containing substituted pyrimidine-2-thionates and 2-thiouracilates [143,144].

3.4.1. Homoleptic complexes

The majority of these complexes involve the lighter transition metals; selected details of their reported crystal structures are given in Table 6.

A variety of routes have been used in the preparation of these complexes. Iron(II) complexes of pyridine-2-thionate and pyrimidine-2-thionate have been obtained from

Table 6
Selected bond distances and angles for homoleptic trischelate complexes

M–S (Å)	M–N (Å)	Chelating angle S–M–N (deg)	*Trans* angle S–M–S (N) (deg)	M–S–C (deg)	N–N–C (deg)
mer-(Et$_4$N)[Fe(py2S)$_3$] [23]					
2.568(1)-2.589(1)	2.141(4)-2.173(4)	65.9(1)-66.3(1)	152.7(1)-158.7(1)	77.0(2)-77.9(2)	101.6(3)-102.8(3)
mer-(Me$_4$N)[Fe(pym2S)$_3$] [145]					
2.523(1)-2.537(1)	2.149(2)-2.182(2)	66.5(1)-66.7(1)	154.1(2)-164.0(2)	78.3-79.3(1)	100.7(2)-101.9(2)
mer-(Me$_4$N)[Fe(pym2S)$_3$] [22]					
2.523(2)-2.536(2)	2.149(4)-2.180(4)	66.2(1)-66.3(1)	153.9(1)-163.5(1)	78.5(2)[a]	102.0(3)[a]
mer-[Co(py2S)$_3$] [17]					
2.286(1)-2.306(1)	1.903(3)-1.938(3)	72.3(1)-72.8(1)	164.5(1)-167.4(1)	77.1(1)-77.4(1)	101.0(2)-102.0(2)
mer-[Co(py2S)$_3$] [146]					
2.292(3)-2.313(3)	1.912(6)-1.923(6)	71.9(7)-72.3(7)	164.36(9)-166.8(3)	NR	NR
mer-[Co(3SiMe$_3$-py2S)$_3$] [146]					
2.241(8)-2.315(8)	1.86(1)-1.91(1)	71.4(8)-72.6(8)	164.0(9)-164.9(7)	NR	NR
fac-[Co(4,6-me$_2$-pym2S)$_3$]C$_6$H$_3$O [147]					
2.252(2)-2.259(2)	1.975(5)-1.986(5)	72.4(1)-72.6(1)	164.73(14)-167.44(14)	79.2(2)-79.5(2)	98.9(3)-100.3(3)
fac-[Co(4,6-me$_2$-pym2S)$_3$]H$_2$O [148]					
2.247(2)-2.271(2)	1.956(5)-1.991(5)	NR	NR	NR	NR
mer-(Et$_4$N)[Ni(py2S)$_3$] [24]					
2.518(1)-2.541(1)	2.034(4)-2.081(4)	67.4(1)-67.8(1)	156.0(1)-161.3(2)	75.6(2)-77.0(2)	102.3(3)-103.7(3)
mer-(Ph$_4$P)[Ni(pym2S)$_3$] [24]					
2.460(2)-2.545(2)	2.025(5)-2.053(5)	67.1(2)-68.3(2)	154.8(1)-163.4(1)	75.6(2)-75.6(2)	101.1(4)-103.5(4)
fac-(Et$_4$N)[Ni(bztz2S)$_3$] [21]					
2.533(2)-2.588(2)	2.058(3)-2.087(3)	67.3(1)-68.1(1)	161.0(1)-161.8(1)	72.7(2)-73.8(2)	98.2(2)-100.0(3)
mer-[Rh(py2S)$_3$] [123]					
2.361(0.5)-2.392(0.5)	2.034(1)-2.050(2)	69.2(0.5)-69.5(0.5)	161.0(0.5)-167.8(1)	78.9(2)-79.6(2)	102.0(2)-102.3(2)
mer-[Rh(3SiMe$_3$-py2S)$_3$] [101]					
2.377(3)-2.395(3)	1.992(9)-2.051(9)	68.3(3)-69.4(3)	161.9(3)-171.4(4)	78.8(4)-79.9(4)	NR

Table 6 (*continued*)

M–S (Å)	M–N (Å)	Chelating angle S–M–N (deg)	*Trans* angle S–M–S (N) (deg)	M–S–C (deg)	M–N–C (deg)
fac-(Et$_4$N)[Cd(bztz2S)$_3$]^b [149]					
2.667(6)	2.474(11)	62.0(3)	149.6(3)	79.5(5)	94.5(8)
fac-[Sb(py2S)$_3$]^b [150]					
2.472(2)	2.830(7)	59.3(1)	120.0	93.9(2)	89.9(4)

NR, not reported.

[a] One value reported.

[b] C_3 symmetry.

the appropriate metal halide with the ligand deprotonated by sodium hydroxide in ethanol [23] or by triethylamine in tetrahydrofuran [22]. Cobalt(III) complexes have been obtained by a transmetallation reaction involving [Zn_4O(py2S)$_6$] and hydrated cobalt(II) chloride in methanol with the assistance of ultrasonic radiation [17]. They have also been prepared by addition of pyridine-2-thione and triethylamine in ethanol to [Co(pentane-2,4-dionate)$_3$] in methanol [146], and by the addition of 4,6-dimethyl-pyridine-2-thione to hydrated cobalt perchlorate in warm acetone in a ligand-to-metal ratio of 3 : 1 which results in simultaneous deprotonation and coordination of the ligand [147]. In contrast with these routes, nickel(II) complexes of pyridine-2-thionate [24], pyrimidine-2-thionates [21,24] and benzo-1,3-thiazoline-2-thionate [21] need aprotic solvents and a specific order of addition of the reactants. This invariably requires the addition of tetraethylammonium tetranickelate(II) to a slurry of the ligand and triethylamine in acetonitrile. This procedure also yields complexes other than trischelates with thiazole-2-thione derivatives [21]. A range of spectroscopic techniques have been used to characterize the complexes. The proton NMR spectra of [Co(py2S)$_3$] [17], like those of [Rh(py2S)$_3$] [123], consist of three sets of resonances, which overlap in the case of the cobalt(III) complex, and are consistent with *mer* geometry. The oxidation state of the iron(II) complexes was obtained by Mössbauer spectroscopy on the crystalline solid. Room temperature magnetic moments ($\mu_B = 5.83$) and a single d–d transition in the visible spectrum of both complexes confirmed high-spin d^5 iron(II) and Jahn–Teller distorted octahedral geometry. The presence of absorptions (1440 and 940 nm) in the pyrimidine-2-thionate complex which are blue-shifted relative to the pyridine-2-thionate complex (1270 and 900 nm) confirmed that the former exerts the stronger ligand field. The cobalt(III) complexes are diamagnetic with a low-spin d^6 configuration [17,146,147]. The nickel(II) complexes have room temperature magnetic moments ($\mu_B = 2.90$–3.40) and three d–d transitions in the visible region consistent with high-spin octahedral d^8 configurations. The $\nu_1(^3A_{2g} \rightarrow {}^3T_{2g})$ transition in the pyridine-2-thionate and pyrimidine-2-thionate nickel(II) complexes is split and consistent with the less symmetrical *mer* isomer [24]. In contrast, the benzo-1,3-thiazoline-

2-thionate complex has a smooth transition that is consistent with the more symmetrical *fac* isomer [21]. The cyclic voltammetry profiles of the cobalt(II) and nickel(II) complexes are irreversible and consistent with ligand-centred oxidation. The corresponding profiles of the iron(II) complexes consist of a clean one-electron redox process with the $E_{\frac{1}{2}}$ values indicating that pyrimidine-2-thionate ($E_{\frac{1}{2}} = -0.08$ V vs. SCE) stabilizes iron(II) more effectively than does pyridine-2-thionate ($E_{\frac{1}{2}} = -0.21$ V vs. SCE) [23,145].

The reported crystal structures are limited to complexes of pyridine-2-thionate (**IIc(i)**), pyrimidine-2-thionate (**IId(i)**) and benzo-1,3-thiazoline-2-thionate (**IIm(iii)**). These heterocyclic thionates generate three four-membered chelate rings and highly distorted octahedral structures in mostly *mer* isomeric forms (**XXXIb**) (Table 6). Metal–sulphur distances, excluding those of the cadmium(II) and antimony(III) complexes, range from 2.241(8) to 2.589(1) Å, with the shorter distances formed by the tripositive ions. The shorter and stronger metal–nitrogen distances (1.86(1)–2.182(2) Å) are a more closely related series with occasional evidence of a modest *trans* effect. Such an effect occurs in the $[Fe(py2S)_3]^-$ anion where the metal–nitrogen distance *trans* to the appropriate metal–sulphur bond is 0.025 Å longer than the other iron–nitrogen distances in the complex [23]. The extent of the angular distortion is evident in the closely related chelate angles S–M–N (65.9(1)°–72.8(1)°) and the wider range of *trans* S–M–S(N) angles (152.7(1)°–171.4(4)°). The ligands form the characteristic "propeller-shaped" distribution about the metal with the angles between them distorted from the ideal because of their narrow bite. In the $[Fe(py2S)_3]^-$ anion the angles between the ligands (72.4°–97.5°) are representative of this distortion, with the dihedral angles between the pyridine and chelate rings (1.35°–3.0°) indicating that the two rings are effectively coplanar. Formation of four-membered chelate rings induces considerable strain on the ligand framework. The M–N–C angles of the complexes (98.2(2)°–103.7(3)°) (Table 6) and the N–C–S angles of the pyridine-2-thionate ligands (107.8(4)°–114.5(3)°) are extensively distorted from the 120° expected for trigonally hybridized atoms. In addition, the M–S–C angles (72.7(2)°–79.9(2)°) are significantly narrower than those reported for monodentate sulphur-donating heterocyclic thiones [102] and aryl thiolates [5], which invariably have average values in the region of the tetrahedral angle. The mean thioamide dimensions of pyridine-2-thionate (C–S = 1.731 Å; C–N = 1.351 Å) show the characteristic increase and decrease respectively, relative to the free ligand, which is typical of deprotonation and chelation. Similar mean dimensional changes are also observed with pyrimidine-2-thionates (C–S = 1.728 Å; C–N = 1.357 Å) and benzo-1,3-thiazoline-2-thionate (C–S = 1.695 Å; C–N = 1.300 Å). The relative planarity of most four-membered chelate rings suggests that the inherent strain in these systems is moderated, to a greater or lesser extent, by all the atoms in the ring [147]. However, with short strong metal–nitrogen bonds and long metal–sulphur bonds, the latter are longer and weaker than those formed by monodentate metal–thione [2,102] and metal–thiolate interactions [5]. In addition, the M–S–C angles are substantially reduced from the tetrahedral angle which is typical of monodentate thione–sulphur interactions. It is the thionato sulphur atom which appears to possess the requisite flexibility to ameliorate the strain of S,N-chelation.

The *fac*-$[Cd(Bztz2S)_3]^-$ anion [149] has dimensions which are closer, in some crucial respects, to those of $[Cd(py2S)_2(py)_2]$ [87] rather than to the other complexes in this series. This may be due, in part, to the presence of constrained C_3 symmetry in the *fac*-$[Cd(bztz2S)_3]^-$ anion which also exhibits a significant angular distortion (25.8° or 43%) from trigonal-prismatic towards octahedral geometry (**XXXIc**). In *mer*-$[Rh(py2S)_3]$ [123] the distortion is 16.4° or about 27%, and a 60° rotation is required for complete transformation. The small chelating angle (62.0(3)°) probably accounts for the fact that the cadmium–sulphur and cadmium–nitrogen distances are the longest and the *trans* S–Cd–N angle is the smallest in the series (Table 6). The ligand framework is typically strained, with small M–N–C and M–S–C angles as well as an N–C–S angle (124.0(11)°) that is only slightly less than that of the free ligand (127.4(2)°) [65]. The thioamide distances in the anionic ligand (C–S = 1.693(14) Å and C–N = 1.303(17) Å) are respectively longer (C–S = 1.662(6) Å) and shorter (C–N = 1.352(6) Å) than the free-ligand values [65]. The $[Sb(py2S)_3]$ complex [150] also has C_3 symmetry with unusual metal–ligand distances (Sb–S = 2.472(2) Å and Sb–N = 2.830(7) Å). Furthermore, the Sb–N distance, although shorter than the sum of the van der Waals radii of the two atoms (3.58 Å) [151], is longer than that of a normal single bond (2.53–2.64 Å) [150]. This suggests that the ligand is intermediate in character between S,N-chelating and monodentate sulphur-donating, although ν(Sb–S) and ν(Sb–N) at 630 and 390 cm^{-1} are indicative of S,N-coordination. Considerable intermolecular activity (Sb---Sb = 3.657(1) Å) is also reported to occur along the C_3 crystal axis.

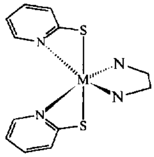
Steric factors appear to be largely responsible for the adoption of both *fac*- and *mer*-isomers, and Burdett [152] has concluded that the confacial isomer is the most stable configuration for a low-spin d^6 trischelate. This is certainly the case for some complexes including $[Co(\text{L-cys})_3]$ [153] in which the L-cysteinate ligand is S,N-chelating. It is also the case for *fac*-$[Co(4,6\text{-me-2-pym2S})_3]$ but not for *mer*-$[Co(pyt2S)_3]$ (Table 6). Among heterocyclic thionate trischelates, the *fac* isomer maximizes the S---S and minimizes the intraligand interactions. The reverse relationship is valid in the *mer* isomer **XXXIc**, with 6-substitution maximizing the intraligand repulsion. The dominance of the *mer* isomers among these complexes suggests that non-bonding S---S interactions are the major consideration. It appears that the *fac* isomer is adopted only when intraligand interactions are maximized by substitution, as in 4,6-dimethyl-pyrimidine-2-thionate and benzo-1,3-thiazoline-2-thionate. Substitution at the 3-position, even with the bulky trimethylsilyl group, still results in production of *mer*-$[Co((3SiMe_3)py2S)_3]$ [146], which is to be expected.

The 4-phenyl-quinoline-8-thionate anion **IIII(i)** generates three five-membered S,N-chelate rings in $[Sb(4\text{-ph-qun8S})_3]$ [154]. The metal–sulphur distances (2.521(2)–2.536(2) Å) are longer than those of the listed tripositive ions (Table 6). In addition, the metal–nitrogen distances are also significantly longer (2.582(6)–2.676(6) Å) and the chelating angles (S–Sb–N = 70.9(2)°–72.4(2)°) are slightly larger than the corresponding values in Table 6. The larger M–S–C angles

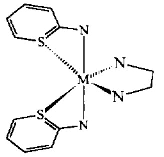
(105.9(9)°–107.7(9)° are also indicative of the decreased strain inherent in five-membered chelates compared with that in four-membered chelates.

3.4.2. Mixed-ligand complexes with two chelating heterocyclic thionates

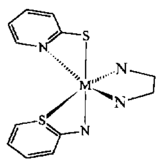
Mixed-ligand trischelates with two chelating heterocyclic thionates [M(het-S,N)$_2$(chel)] (chel-N,N or P,P-chelate) give rise to three geometric isomers, similar to those of six coordinate bischelates. With a $MS_2N_2N_2$ or $MS_2N_2P_2$ stoichiometry the *tcc* isomer (**XXXIIa**) and the *ctt* isomer (**XXXIIb**) have a two-fold axis bisecting the symmetric N,N-chelate. The *ccc* isomer (**XXXIIc**) is asymmetric, and all the isomers are optically active.



trans-cis-cis (*tcc*)
XXXIIa



cis-trans-cis (*ctc*)
XXXIIb



cis-cis-cis (*ccc*)
XXXIIc

Trigonal prismatic geometry is also possible (**XXXIc**). Selected dimensions of the reported crystal structures of these complexes which involve pyridine-2-thionate (**IIc(i)**), pyrimidine-2-thionate (**IId(i)**) and benzo-1,3-thiazoline-2-thionate (**IIm(iii)**) are listed in Table 7.

Preparative routes vary, with [V(py2S)$_2$(tmen)] (tmen = tetramethyldiaminoethane) obtained by the addition of sodium pyridine-2-thionate to [VCl$_2$(tmen)] in dichloromethane [155] and [Cd(bztz2S)$_2$(dipy)] obtained from [Cd(bztz2S)$_2$] and 2,2′-bipyridine in chloroform [142]. Production of the ruthenium(II) complexes involves addition of the appropriate diphosphine to [Ru(py2S)$_2$(PPh$_3$)$_2$] [156, 157]. The remaining complexes in this series were obtained by the electrochemical oxidation of the metal (nickel, zinc or cadmium). The reactions were performed in non-aqueous media with a platinum cathode and a supporting electrolyte in the presence of the appropriate heterocyclic thione (pyridine-2-thione, pyrimidine-2-thione or benzo-1,3-thiazoline-2-thione). This electrolytic method results in the evolution of hydrogen gas at the cathode and production of the appropriate deprotonated complex: [M(py2S)$_2$] (M = Zn, Cd) [158], [M(pym2S)$_2$] (M = Zn, Cd) [159], [Ni(het-S,N)$_2$] (het-S,N = py2S [160], tzd2S or bztz2S [161]). Introduction of a bidentate ligand, in order to modify the generally intractable products, invariably leads to the production of the appropriate adducts [M(het-S,N)$_2$(N–N)] (N–N = phenanthroline or 2,2′-bipyridine). Electrochemical efficiency experiments show that the adducts are formed after production of the deprotonated complexes. Deprotonation of pyridine-2-thione is invariably indicated by the absence of both the ν(NH) vibration (3160 cm^{-1}) and the broad singlet of the thioamido proton (13.43 ppm) in the resultant complex [158]. The most important feature of the ^{13}C NMR spectra of coordinated heterocyclic thionates is that of the C(2) carbon, which shows a high field shift relative to that of the free ligand. This is consistent with the generally observed increase in the thione (>C=S) distance of the parent ligand on

Table 7
Selected bond distances and angles for mixed-ligand trischelate complexes with two heterocyclic thionate ligands

M–S (Å)	M–N (Å)	Chelating angle S–M–N (deg)	*Trans* angle S(N)–M–S(N) (deg)	M–S–C (deg)	M–N–C (deg)
[V(py2S)$_2$(tmen)][a] [155]					
2.547(1)	2.124(2)	66.85(8)	156.05(5)	NR	NR
[Ru(py2S)$_2$(dppb)] [156]					
2.427(1)	2.135(3)	NR	155.6(1)	NR	NR
2.416(1)	2.151(3)	NR		NR	NR
[Ru(py2S)$_2$(dppe)] [157]					
2.413(3)	2.131(8)	67.0(2)	155.0(1)	81.1(4)	102.1(6)
2.428(3)	2.136(3)	67.6(2)		81.0(3)	102.1(6)
[Zn(py2S)$_2$(phen)] [158]					
2.627(2)	2.085(6)	65.1(2)	160.7(1)	NR	NR
2.546(3)	2.128(7)	66.2(2)			
[Ni(pym2S)$_2$(bipy)] [159]					
2.532(1)	2.078(5)	68.6(2)	154.26(7)	NR	NR
2.480(3)	2.072(4)	67.5(1)			
[Ni(py2S)$_2$(bipy)]0.5 bipy [160]					
2.475(2)	2.053(3)	67.98(8)	155.96(3)	NR	NR
2.495(2)	2.068(2)	68.48(8)			
[Ni(bztz2S)$_2$(dmp)] [161]					
2.485(2)	2.118(6)	67.3(2)	167.5(1)	NR	NR
2.532(2)	2.106(6)	68.5(2)		NR	NR
[Cd(pym2S)$_2$(phen)] [162]					
2.588(3)	2.394(9)	61.4(3)	157.2(3)	NR	NR
2.549(3)	2.36(1)	62.8(3)			
[Cd(bztz2S)$_2$(bipy)$_2$][a] [142]					
2.618(2)	2.529(5)	62.55(13)	131.15(8)	81.3(2)	122.0(5)

[a] C_2 axis with one independent molecule.

tmen; tetramethyl diaminoethane; dppe, diphenylphosphinoethane; dppb, diphenylphosphinobutane; bipy, 2,2′-bipyridine.

NR, not reported.

deprotonation and coordination. The nickel(II) complexes have electronic absorption spectra typical of distorted octahedral environments [160].

All the complexes listed in Table 7, except those with cadmium(II) adopt the *tcc* arrangement (**XXXIIa**). The structures generate relatively long metal–sulphur distances (2.416(1)–2.627(2) Å), short strong metal–nitrogen distances (2.053(3)–2.151(3) Å), small chelating angles (S–M–N = 65.1(2)°–68.6(2)°) and *trans* S–M–S angles that deviate substantially from 180° (154.26(7)°–167.5(1)°). There is limited evidence in the literature of induced strain on the ligand framework, but the mean reported M–S–C (81.0°) and M–N–C (102.1°) angles (Table 7) are extensively distorted from the value of 120° expected for trigonally hybridized atoms. The mean thioamide dimensions of pyridine-2-thionate (C–S = 1.727 Å; C–N = 1.350 Å) show variations, relative to the free ligand, which are typical of deprotonation and chelation. Similar mean distances also occur in pyrimidine-2-thionate (C–S = 1.720 Å; C–N = 1.355 Å). In addition to changes in the thioamide distances (C–S = 1.703 Å; C–N = 1.318 Å) the C–S_{endo} distance (1.754(5) Å) increases and the thioamido carbon angle decreases (S_{endo}–C–N = 113.9(5)°) in the benzo-1,3-thiazoline-2-thionate anion [142] relative to the free-ligand values (1.732(4) Å and 109.2(2)°) [65].

The two cadmium(II) complexes are structurally different from the rest of the series. [Cd(pym2S)$_2$(phen)] [162] adopts the *ctc* isomeric form (**XXXIIb**) and [Cd(bztz2S)$_2$(bipy)] [159] is effectively trigonal prismatic (**XXXIc**). The metal–ligand dimensions in these two complexes are similar to those of the [Cd(bztz2S)$_3$]$^-$ anion (Table 6) and [Cd(bztz2S)$_2$(py)$_2$] (Table 5). The mean cadmium–sulphur distance (2.585 Å) is 0.103 Å longer than the mean metal–sulphur distance in Table 7, except for that of [Zn(py2S)$_2$(phen)] (2.627(2) Å) [158]. In contrast, the mean cadmium–nitrogen distance (2.428 Å) is 0.265 Å longer than the corresponding mean distance in Table 7. It is also 0.139 Å longer than the mean cadmium–nitrogen distance formed by the N,N′-chelates in these complexes. The mean chelating angle (S–Cd–N = 62.5°) is also similar to the mean value reported for other S,N-chelated cadmium complexes (62.3°) [87, 149] and is 4.9° less, on average, than the other values reported in Table 7. The contrasting *trans* S–Cd–S(N) angles are a consequence of the structural differences between the two complexes. Longer and weaker metal–ligand distances, particularly cadmium–nitrogen distances, and unusually small chelating angles are the major characteristics of cadmium heterocyclic thionates. Baggio et al. [87] have proposed that the excess electron density on the cadmium(II) atom due to the four nitrogen donors in [Cd(bztz2S)$_2$(py)$_2$] is compensated by lengthening of the axial cadmium–sulphur bonds (mean Cd–S = 2.705 Å). However, the fact that S,S′-chelating ligands, such as *cis*-1-methylthiostilbene-2-thiolate [163] and diethyldithiocarbamate [149] also generate cadmium–sulphur (thiolate) distances in the range 2.525(1)–2.755(3) Å suggests that the dominant factor governing cadmium–ligand distances in S,S- and S,N-chelates is probably the size of the cadmium(II) ion [163].

3.4.3. Mixed-ligand complexes with one chelating heterocyclic thionate

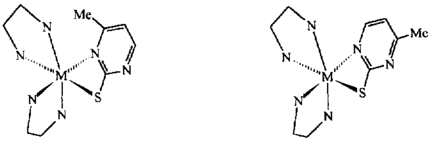
Reduction of the number of heterocyclic thionate ligands in these complexes from two to one removes the possibility of geometrical isomerism but not optical isomerism in the cationic cobalt(III) complexes. The complexes have been characterized by UV–visible, CD, MCD and ^{13}C NMR spectra. Some optical isomers have also been resolved.

A series of complexes of general formula [Co(py2S)$_{3-n}$(diamine)$_n$]$^{n+}$ (n = 0, 1, 2; diamine = 1,2-diaminoethane, (*R*)-1,2-diaminopropane and 2,2′-bipyridine) have been prepared from the diamine, hydrated cobalt(II) perchlorate and 2,2′-dipyridyldisulphide in ethanol [32]. Dissolving the product in hot water and cooling to 5 °C produced crystals of the spontaneously resolved complex $[Co(py2S)(en)_2](ClO_4)_2$ whose CD spectrum in water confirmed the presence of a single isomer. Optical resolution was also achieved by the addition of potassium antimony tartrate $K_2[Sb_2\{(R,R)\text{-}C_4H_2O_6\}_2]\cdot 3H_2O$ to an aqueous solution of the complex, followed by subsequent fractional crystallization of the resultant diasterioisomers. Selected dimensions of the crystal structure of $[Co(py2S)(en)_2](ClO_4)_2$ are listed in Table 8 [164].

Other complexes of general formula $[Co(chel\text{-}S,N)_{3-n}(diamine)_n]^{n+}$ ($n=0, 1, 2$; chel-S,N = py2S, pym2S, 4-me-pym2S and 4,6-me$_2$-pym2S) have been obtained in moderate yield from $[Co(en)_3]Cl_3$ and 1,2-diaminoethane by a photochemical method [165]. The reaction products were separated by column chromatography. Recrystallization of $[Co(pym2S)(en)_2]^{2+}$ and $[Co(4\text{-}me\text{-}pym2S)(en)_2]^{2+}$ from acidic media produced the corresponding protonated species $[Co(pymSH)(en)_2]^{3+}$, with proton NMR confirming the thioamido nitrogen of pyrimidine-2-thionate as the protonation site. Resolution of the optical isomers of $[Co(chel\text{-}S,N)(en)_2]^{2+}$ (chel-S,N = pym2S and 4-me-pym2S) was achieved by the addition of potassium antimony tartrate to aqueous solutions of the complexes followed by fractional crystallization of the diasteroisomers. The CD spectrum of $(+)_{520}[Co(pym2S)(en)_2]^{2+}$ has two components and is similar to that of $\Lambda(+)_{520}[Co(py2S)(en)_2]^{2+}$. Since 4-methylpyrimidine-2-thionate is an asymmetrical ligand, S,N-chelation to a metal centre generates linkage isomers. These consist of a *remote* isomer with the C(4) methyl group distant from the two 1,2-diaminoethane chelates and an *adjacent* isomer with the methyl group near the N,N-chelates (**XXXIIIa**) and **XXXIIIb**).

Table 8
Selected bond distances and angles for mixed-ligand trischelate cobalt(III) complexes with one heterocyclic thionate ligand

M–S (Å)	M–N (Å)	Chelating angle S–M–N (deg)	*Trans* angle S–M–N (deg)	M–S–C (deg)	M–N–C (deg)
$[Co(py2S)(en)_2](ClO_4)_2$ [164]					
2.282(2)	1.975(6)	72.6(2)	170.0(2)	77.7(2)	101.8(4)
cis $Co\text{–}N_{(mean)} = 1.973$ Å; *trans* Co–N = 1.993(6) Å; *cis* $N\text{–}Co\text{–}N_{(mean)} = 93.7°$					
$[Co(4\text{-}me\text{-}pym2S)(en)_2](ClO_4)_2$ [165]					
2.294(2)	1.911(3)	72.4(1)	167.8(1)	77.7(1)	101.0(2)
cis $Co\text{–}N_{(mean)} = 1.952$ Å; *trans* Co–N = 1.977(6) Å; *cis* $N\text{–}Co\text{–}N_{(mean)} = 85.7°$					
$[Co(tuc)(en)_2](ClO_4)\cdot H_2O$ [143]					
2.278(2)	1.911(5)	72.7(2)	168.7(2)	77.8(3)	101.9(4)
cis $Co\text{–}N_{(mean)} = 1.952$ Å; *trans* Co–N = 1.977(6) Å; *cis* $N\text{–}Co\text{–}N_{(mean)} = 85.7°$					
$[Co(di\text{-}6\text{-}am\text{-}tuc)](ClO_4)\cdot H_2O$ [144]					
2.273(2)	1.919(4)	72.6(1)	167.1(2)	77.7(2)	101.6(3)
cis $Co\text{–}N_{(mean)} = 1.951$ Å; *trans* Co–N = 1.954(6) Å					



Adjacent isomer
XXXIII a

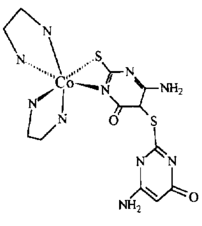
Remote isomer
XXXIII b

The two isomeric forms are readily distinguished by means of proton NMR. Selected dimensions of the *remote* isomer of $[Co(4\text{-me-pym2S})(en)_2]^{2+}$ are listed in Table 8.

Cobalt(III) complexes have been prepared with 2-thiouracil and its methyl derivatives ($tucH_2$, 5-me-$tucH_2$, 6-me-$tucH_2$) from $[Co(en)_3]Cl_3$ by a photochemical method with the products separated on a cation exchange column. A similar method has been used to prepare complexes of 2,3-dihydroquinazoline-4-oxo-(1H)-2-thione ($qunzO2SH_2$). Complexes of both uninegative $[Co(tucH)(en)_2]^{2+}$ and dinegative $[Co(tuc)(en)_2]^{2+}$ 2-thiouracilates (**IIe(i)**) and of the 4-oxo-quinazoline-2-thionate derivatives ($quzOSH^-$ and $quzOS^{2-}$) (**IIk**) have been obtained and characterized. Both *remote* and *adjacent* linkage isomers of 4-methyl-2-thiouracilate are also possible, with the *adjacent* form readily distinguished by proton and ^{13}C NMR spectra. Details of the crystal structure of the *adjacent* form of $[Co(4\text{-me-tuc})(en)_2](ClO_4)\cdot H_2O$, in which the sterically less favourable *adjacent* isomer is stabilized by intermolecular hydrogen bond formation involving amino and ketonic groups on adjacent ligands (N–H---O = 2.876(8) Å), are summarized in Table 8 [143, 144].

An attempted preparation of a cobalt(III) complex of 6-amino-2-thiouracil in water from *trans*-$[CoCl_2(en)_2]Cl$ and sodium hydroxide, in the presence of activated charcoal, eventually produced two red complexes. One of these complexes $[Co(6\text{-am-tucH})(en)_2]^{2+}$ contains one 6-amino-2-thiouracilate anion (6-amtucH) (**IIe(iv)**) with N_5S coordination at the metal and the anion S,N-chelating at the N(2), S(3) site. With twelve ^{13}C NMR signals in the second complex, eight of which are due to the heterocyclic ligand, there are two amino-thiouracilate anions in the structure and N_5S coordination at the metal. A crystal structure analysis established the two anions to be present as an S,N-chelating mono-sulphur-bridged dimeric ligand ([5-((1′-H)-4′-oxo-6′-aminopyrimidino-2′-yl)thio]-6-amino-2-thiouracilate (di-6-amtuc)).

Structural details of $[Co(\text{di-6-am-tuc})(en)_2](ClO_4)\cdot H_2O$ (**XXXIV**) are summarized in Table 8 [144].



Adapted from [144]
XXXIV

The complexes listed in Table 8 all crystallize with distorted octahedral geometry. They present a consistent set of geometric parameters in which the dimensions generated by the heterocyclic thionate ligands are similar to those observed in the corresponding cobalt(III) trischelates (Table 5). The relatively short metal–ligand distances generated by the cobalt(III) ion are compensated by a slight increase in the chelating angle (S–Co–N = 72.5°). A modest *trans* effect is evident in the complexes with the cobalt–nitrogen distances *trans* to the cobalt–sulphur about 0.025 Å longer than the equatorial cobalt–nitrogen distance (Table 9). The modest *trans* effect in these complexes is probably due to the inefficient overlap between the cobalt 3d and the sulphur lone-pair orbitals as a result of the narrow bite of the ligand and the consistent deviation of the axial S–Co–N angles from 180°. Angles at the thioamido sulphur and nitrogen atoms are consistently less than the tetrahedral and trigonal angles and are typical of inherently strained ligand frameworks. Thioamide ligand dimensions for pyridine-2-thionates (C–S = 1.754(7) Å; C–N = 1.339(9) Å), pyrimidine-2-thionate (C–S = 1.738(7) Å; C–N = 1.379(9) Å) and 2-thiouracilate (C–S = 1.732(4) Å; C–N = 1.352(5) Å) are similar and typical of deprotonated S,N-chelating ligands.

Production of the (di-6-amtuc)$^{2-}$ ligand is novel and similar to the oxidized products obtained from 1,3-thiazolidine-2-thione and imidazoline-2-thione derivatives with copper(II) salts [3]. Not surprisingly, the production of [Co(di-6-amtuc)(en)$_2$](ClO$_4$)·H$_2$O is increased substantially by means of aerial oxidation of the reaction solution. The crystal structure of the complex shows the heterocyclic ligand to be S,N-chelating through the N(2), S(3) atoms of the first pyrimidine fraction with the thionato sulphur atom of the second pyrimidine fraction attached to the first at the (C5) atom (C–S = 1.745(4) and 1.771(5) Å). The two rings are almost mutually perpendicular (C4–C5–S2–C2 = 89.8(4)°) with pairs of *trans*-related amino and oxo substituents. The presence of the water molecule causes an unusual self-generated molecular assembly by means of a double-bridged centrosymmetric hydrogen-bonding scheme that also persists in solution. Pairs of water molecules link pairs of complexes into an infinite chain through double NH---O bridges (2.750(5) Å) which involve amino and oxo groups on adjacent ligands.

3.4.4. Seven-coordinate complexes of bis- and trischelates

The structural principles and reported crystal structures of seven-coordinate complexes have been reviewed by Kepert [166]. Since this review was published, a group of such complexes based on bis and tris S,N-chelating heterocyclic thionates, which adopt distorted pentagonal bipyramidal geometry, have also been reported.

Seven-coordinate molybdenum-hydrazido and diazenido complexes are well known and are derived from S,N-chelating heterocyclic thionates [132,167] and S,S-chelating dithiocarbamates [168,169]. Other combinations of ligands include tridentate thiolates [170] and dithiocarbazates [171]. In addition, the crystal structure of [(*p*-tolyl)Sn(IV)(py2S)$_3$] has also been reported [172].

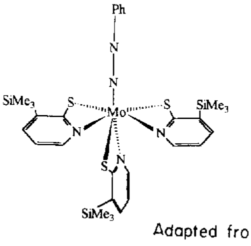
Interest in hydrazido and diazenido complexes of molybdenum results from the role of such complexes as intermediates in the reduction of coordinated dinitrogen. Synthetic routes are variable. A red crystalline material [MoCl$_2$(N$_2$MePH)(3SiMe$_3$-

Table 9
Selected bond distances and angles for seven-coordinate pentagonal bipyramidal complexes

Axial donor atoms and M–L(axial) (Å)	Equatorial donor atoms and M–L(equatorial) (Å)	*Trans* angle L–M–L (deg)	Chelating angle S–M–N (deg)
[MoCl$_2$(N$_2$MePh)(3-SiMe$_3$-py2S)$_3$] [132]			
Cl 2.451(4) N 1.75(1)(hydrazide)	2S 2.496(5), 2.508(4) 2N 2.21(1), 2.21(1) Cl 2.416(4)	176.0(4)	64.3(4)
[Mo(N$_2$Ph)(3-SiMe$_3$-py2S)$_3$] [167]			
N 1.814(3)(hydrazide) N 2.201(3)	3S 2.493(1)–2.524(1) 2N 2.203(4), 2.218(4)	169.8(1)	63.6(1)–65.4(1)
[Sn(p-tolyl)(py2S)$_3$)] [172]			
C 2.119(9) S 2.486(3)	3N 2.444(8)–2.487(7) 2S 2.571(3), 2.571(3)	156.0(3)	61.9(2)–63.3(2)

py2S)$_2$] is obtained by the addition of the parent ligand to methanolic solutions of [MoCl$_2$(N$_2$MePh)] [166]. [Mo(N$_2$Ph)-(3SiMe$_3$py2S)$_3$] results from the addition of phenylhydrazine to [Mo$_2$Cl$_4$(μ-S$_2$)(μ$_2$-S-3SiMe$_3$-py2S)(3SiMe$_3$-py2S)] in dichloromethane [132]. Production of [Sn(IV)(*p*-tolyl)(py2S)$_3$] involves the stoichiometric addition of methanolic sodium pyridine-2-thionate to *p*-tolyltin trichloride in chloroform [172].

All three complexes adopt distorted pentagonal bipyramidal geometry with a range of axial and equatorial donor atoms. The selected dimensions of the structures are summarized in Table 9 and the structure of [Mo(N$_2$Ph)(3SiMe$_3$-py2S)$_3$] is illustrated in **XXXV**.



Adapted from [167]

XXXV

The various combinations of donor atoms generate significant differences in axial distances and angles. In the molybdenum complexes the hydrazido anions always occupy one of the axial sites (Mo–N = 1.75(1) and 1.814(3) Å) with either chlorine or thioamido nitrogen in the *trans* position. In the tin(IV) complex the axial atoms are tolyl carbon and thionato sulphur which generate the smallest *trans* angle in the series. The equatorial atoms are invariably displaced from the mean plane, largely as a result of the non-bonding interactions resulting from the narrow bite of the chelating ligands. The metal–sulphur (2.493(1)–2.524(1) Å) and the metal–nitrogen

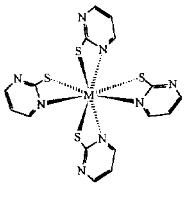
(2.203(4)–2.487(4) Å) distances are both relatively closely related series with values similar to those of other S,N-chelating heterocyclic thionates. The chelating angles are also closely related (61.9(1)–65.4(1)°), with the largest value resulting from the accommodation of an axial thioamido nitrogen atom. The mean dimensions of pyridine-2-thionate in [(*p*-tolyl)Sn(IV)(py2S)$_3$] [172] (C–S = 1.73(1) Å; C–N = 1.33(1) Å) are typical of the ligand.

Cyclic voltammetry of [Mo(N$_2$Ph)(3SiMe$_3$-py2S)$_3$] in acetonitrile consists of two one-electron oxidations at +0.31 and +0.96 V vs. SCE. The first process is a diffusion-controlled reversible one-electron oxidation and the second is irreversible. Both processes involve the metal rather than the ligands.

3.5. *Tetrachelates*

The geometric and isomeric possibilities of complexes with the general formula [M(bidentate)$_4$] have been discussed at length in relation to both symmetric and asymmetric chelating ligands [173–176]. For complexes of formula [M(S,N)$_4$], where M is a d^2 ion, dodecahedral geometry is predicted with the thionato sulphur atoms (π donors) occupying the A vertices and the thioamido nitrogen atoms (π acceptors) occupying the B vertices [174, 175]. Furthermore, the 42 antiprismatic isomers are eliminated and the 93 dodecahedral isomers are reduced to four limiting possibilities for such complexes [176]. The structural possibilities for the mixed-ligand complexes of formula [W(5-tert-buyl-pyrimidine-2-thionate)$_n$(pyrimidine-2-thionate)$_{4-n}$] are further reduced to that of the $D_{2d}(mmmm)$ isomer [177]. This is a consequence of the fact that the *m* edges are the only ones capable of accommodating the narrow ligand bite (about 2.50 Å) which is characteristic of S,N-chelating heterocyclic thionates.

The three reported structures in this class of compounds involve pyrimidine-2-thionate (**IId**(**i**)) and a substituted pyridine-2-thionate (**IIc**(**i**)) derivative. The two complexes involving d^2 ions, [M(pym2S)$_4$] (M = W, Mo), are obtained respectively from tungsten hexacarbonyl and pyrimidine-2-thione in diglyme [178] and from [MoCl$_4$(thf)$_4$] with the parent ligand deprotonated by triethylamine in tetrahydrofuran [22]. These two complexes adopt the predicted arrangement of dodecahedral symmetry with the sulphur atoms in the A sites and the nitrogen atoms in the B sites. Alternatively, the chelating atoms can be described as occupying interlocking slightly flattened tetrahedra (**XXXVI**).



XXXVI (M is Mo and W)

The complexes have similar mean dimensions (Mo–S = 2.532 Å, W–S = 2.519 Å, Mo–N = 2.179 Å, W–S = 2.162 Å, S–N = 2.51 Å (Mo), 2.50 Å (W); S–M–N = 63.9° (Mo and W)). In addition, two short (about 3.0 Å) interactions are reported to involve thionato sulphur atoms in the molybdenum complex, which is indicative of sulphur---sulphur bonding. Cyclic voltammetry in dichloromethane shows that the molybdenum complex undergoes a reversible diffusion-controlled one-electron oxidation at +0.40 V vs. SCE, giving cationic $[Mo(pym2s)_4]^+$. The tungsten complex is similarly oxidized, but at +0.20 V vs. SCE. Both complexes are also reversibly reduced to the anion $[M(pym2S)_4]^-$, which is a 19-electron species. Reduction of the tungsten complex ($E_p = -1.95$ V vs. SCE) is less reversible than that of its molybdenum counterpart ($E_p = -1.17$ V vs. SCE), probably because molybdenum(III) is more accessible than tungsten(III) [22].

In the tin complex $[Sn(3SiMe_3\text{-}py2S)_4]$ [179] obtained by the disproportionation of $[Sn(3SiMe\text{-}py2S)_2]$ in acetonitrile, the disposition of the sulphur and nitrogen atoms is the reverse of that previously described for the tungsten and molybdenum complexes. This is clearly illustrated by the fact that the mean *trans* angles (N–Sn–N = 67.5°, S–Sn–S = 137.9°) are the reverse of those reported for the tungsten and molybdenum complexes (N–M–N = 159.9°(W), 160.4°(Mo); S–M–S = 72.3°(W), 72.3°(Mo)). Otherwise, the reported dimensions are rather similar (Sn–S = 2.482(4), 2.510(4) Å; Sn–N = 2.60(1), 2.52(1) Å).

4. Final comments

Deprotonation of heterocyclic thiones produces the corresponding thionates in which the negative charge is localized on the thionato sulphur atom and the thioamide π-electron density is concentrated between the carbon and nitrogen atoms of the thioamide.

Consequently, the predominantly monodenate sulphur donating character of heterocyclic thionates results primarily from the steric favourability and enhanced nucleophilicity of the thionato sulphur atom. However, monodentate metal–sulphur bonding is frequently supported, in the solid state, by secondary intramolecular contacts to the thioamido nitrogen atom. In contrast, the alternative thioamido nitrogen-donating character of heterocyclic thionates is relatively rare. Furthermore, such bonding appears to be dependent on the presence of other ligands, particularly that of S,S-chelating ligands, in the complex.

The formation of four-membered S,N-chelates by heterocyclic thionates is clearly more widespread than was previously appreciated. Such coordination is characterized by short strong metal–nitrogen bonds, relatively long metal–sulphur bonds, small chelating angles and mostly planar chelate rings. In the absence of extraneous structural effects, the metal–sulphur bonds formed by S,N-chelating heterocyclic thionates are invariably slightly longer than those formed by the monodentate ligands. In addition, the slightly more relaxed five-membered rings formed by the S,S-chelating heterocyclic dithionates permit shorter metal–sulphur bonds than those formed by the S,N-chelates. The overall impression is that the inherent flexibility of the thionato sulphur atoms is responsible for much of the varied donor behaviour of heterocyclic thionate ligands.

Although the reported complexes are primarily mononuclear species, there is some evidence that those ligands containing heterocyclic groups with additional donor sites, such as the N(3) atom of some pyrimidine derivatives, may be induced to generate polynuclear species. Such activity could well be further exploited in the future.

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