Coordination Chemistry Reviews, 61 (1985) 115–184
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPLEXES OF HETEROCYCLIC THIONE DONORS

ERIC S. RAPER

School of Chemical and Life Sciences, The Polytechnic, Ellison Building, Newcastle upon Tyne NE1 8ST (Gt. Britain)

(Received 10 April 1984)

CONTENTS

0010-8545/85/$24.50

MAJOR LIGAND ABBREVIATIONS

pyrdtH	pyrrolidine-2-thione
imdtH$_2$	1,3-imidazolidine-2-thione
imtH$_2$	1,3-imidazoline-2-thione
trztH$_2$	1,2,4-triazoline-3(5)-thione
ttztH	1,2,3,4-tetrazoline-5-thione
dtzt	2,3-diphenyl-2,3-dehydrotetrazolium-5-thione (dehydrodithizone)
pptH	*N*(1)-methyl-4-mercaptopiperidine
tmptH	thiomorpholine-2-thione
tcptH	ε-thiocaprolactam
pytH	pyridine-2-thione
pymtH	pyrimidine-2-thione
tucH$_2$	2-thiouracil
dtucH$_2$	2,4-dithiouracil
tcytH	2-thiocytosine
qnxtH$_2$	quinoxazoline-2,3-dithione
tztH	1,3-thiazoline-2-thione
tzdtH	1,3-thiazolidine-2-thione
rdtH	rhodanine (1,3-thiazolidine-2-thione-5-one)
tdzt$_2$H$_2$	1,3,4-thiadiazoline-2,5-dithione (Bismuthiol I)
oxdtH	1,3-oxazolidine-2-thione
bzoxtH	benz-1,3-oxazoline-2-thione
oxdztH	1,3,4-oxadiazoline-2-thione

(alkyl, aryl, amino and other derivatives are distinguished from the parent heterocycle by adding suitable prefixes e.g., me, ph, am, to the above abbreviations)

A. INTRODUCTION

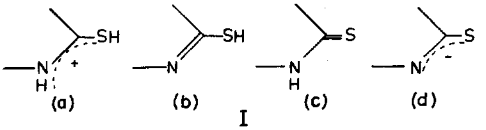
Many reviews in recent years have been devoted to various aspects of the donor behaviour of sulphur-containing systems [1–23]. Among heterocyclic molecules, on the other hand, attention has mostly been concentrated on the donor behaviour of nitrogen-containing molecules [24–26].

This review is concerned with heterocyclic thiones and involves aspects of the donor behaviour of both sulphur-containing systems and heterocyclic molecules. The molecules concerned all contain thioketonic (thione) and occasionally thiol (mercapto) groups directly attached to the carbon atoms of heterocyclic molecules. They represent a novel group of ligands which, to the author's knowledge, have not been previously reviewed as a class, although some individual molecules have been considered within other classifications

[14,25]. The complexes considered in this review involve the coordinated atoms in their normal (i.e. non-zero) oxidation states.

B. GENERAL ASPECTS OF HETEROCYCLIC THIONE DONORS

The combination of an exocyclic thione (thioketo) group and a heterocyclic molecule, which may contain nitrogen, oxygen, sulphur or a combination of these, generates a group of molecules with considerable coordination potential. An important factor in realising such potential is that of prototropic tautomerism [27] and in particular, which tautomer is present, in solution, immediately prior to the formation of the metal–ligand bond. A common feature of all nitrogen-containing heterocyclic thiones is 'thione' (**Ic**) 'thiol' (**Ib**) tautomerism (**I**). Structural evidence, particularly from X-ray crystallographic studies, indicates a tendency for the thione form to dominate in the solid (Table 1). Determination of the proportion of SCF-π character [28] in the resultant carbon–sulphur bond however points to a variable degree of delocalisation of the π-electron density within the heterocyclic 'thioamide' (Table 1). Infrared spectra support the dominance of the thione form in the solid with the presence of ν(NH) bands (ca 3100 cm^{-1}) [29], the absence of ν(SH) (ca 2500 cm^{-1}) and the production of characteristic 'thioamide' bands (Table 2) due to extensive coupling of (CH), (NH), (CN)



I

TABLE 1

Thione (C–S) dimensions and π-character for typical heterocyclic thiones

Molecule	C–S (Å)	π-character (%)	Ref.
1,3-Imidazoline-2-thione	1.698(2)	46.9	104
Benz-1,3-imidazoline-2-thione	1.671(8)	57.3	57
1,2,4-Triazoline-3-hydrazino-4-amino-5-thione	1.681(4)	51.9	131
Pyridine-2-thione	1.68(2)	53.9	172
Tetrahydropyrimidine-2-thione	1.722(7)	37.7	195
Purine-6-thione monohydrate	1.676(5)	55.4	221
1,3-Thiazolidine-2-thione	1.676(7)	55.4	263
Benzo-1,3-thiazoline-2-thione	1.662(4)	60.7	233
1,3-Thiazoline-2-thione-3-methyl-4-one	1.679(11)	54.2	270
1,3,4-Thiadiazoline-2-thione-5-amine	1.678(7)	54.6	292
Benz-1,3-oxazoline-3-methyl-2-thione	1.629(7)	73.5	296

TABLE 2

Major IR bands (cm^{-1}) for some heterocyclic thiones

Molecule	ν(NH)	Thioamide bands				Ref.
		I	II	III	IV	
1,3-Imidazoline-2-thione	3130	1480	1228	1070	740	61
1,2,4-Triazoline-5-thione	3050	1580	1275	1080	650	129,130
1,2,3,4-Tetrazoline-5-thione	3050	1508	1358	990	755–782	141
Thiomorpholine-3-thione	3225	1590–1560	1345	1100	620–700	161
2,4-Dithiouracil	3000	1565	1230	1128	780	206
Pyridazine-3,4,5-trithione	3100	1450–1550	1310	1060	815	222
Benzo-1,3-thiazoline-2-thione	3110	1490	1320	1010	860	237
1,3-Thiazolidine-2-thione	3160	1490	1245	990	650–690	262
1,3,4-Thiadiazoline-2,5-dithione	2860–3060	1500	1265	1050	940	279
1,3,4-Thiadiazoline-2-thione-5-amine	3200	1600	1350	1050	750	289
Benz-1,3-oxazoline-2-thione	3100	1505	1245	1010	745	298

and (CS) vibrational activity [30,31]. More detailed assignments have been achieved for imidazolidine-2-thione (see p. 128) and thiazolidine-2-thione (see p. 160) by a combination of N-deuteration, selenation, S-methylation and normal coordinate analysis. X-ray photoelectron spectroscopy (X-ray PES) provides further evidence of thione dominance with the nitrogen ($1s$) spectra of benz-1,3-imidazoline-2-thione (see p. 123) and benz-1,3-oxazoline-2-thione (see p. 170) consisting of a single peak and with electron core binding energies (ca. 400 eV) consistent with the presence of imido (NH) groups. Proton NMR measurements usually support the presence of thione tautomers in solution with chemical shifts (δ, ppm) consistent with imido (NH) (ca. 8–11) rather than thiol (δ, ppm; 3–4) groups [32]. Both thione and thiol forms are occasionally reported for the same molecule as occurs, for instance, with tetrahydropyrimidine-2-thione (see p. 148). The production of the thiol form immediately prior to coordination is also reported for benzo-1,3-thiazoline-2-thione (see p. 156).

Tautomeric equilibria may be further modified in solution by changes in pH. In highly acid media fully protonated species (**Ia**) are likely and may appear to have all available coordination sites blocked. Alternatively, because imido (NH) protons are labile, species such as (**Ia**) are also potentially ambidentate. With p*K*a values varying from about 5 to 11 de-protonation is possible over a wide pH range. The resultant thiolate anion (**Id** and **VIIIe**) is capable of monodentate, bidentate or bridging coordination behaviour and of involving either, or both, sulphur and nitrogen in these processes.

Extensive use has been made of spectroscopic methods in determining the coordinating character of heterocyclic thione molecules. For many neutral molecules the choice reduces to either nitrogen or sulphur donation. Shifts in specific IR bands have been extensively used in order to diagnose donor activity. Negative shifts in the thioamide (IV) band as well as in the low frequency (CS) absorptions are associated with sulphur donation (see p. 124). Positive shifts in thioamide (I) bands together with negative shifts in ν(NH) absorptions are associated with nitrogen donation (see p. 162). Supporting evidence is frequently obtained from related low-frequency IR activity with ν(M–S) absorptions in the range 200–480 cm^{-1} [33,34] and ν(M–N) bands occurring between 148 and 540 cm^{-1} (see Tables 9 and 10). Where both atoms are involved in coordination clear distinctions in low-frequency vibrational activity become difficult to make (see p. 148).

Although both ^{1}H and ^{13}C NMR spectra have been used in the detection of coordination activity the former is rarely successful owing to the difficulty of evaluating the contribution of the thioamide group anisotropy to the chemical shift [88]. The application of ^{13}C NMR spectra in the detection of coordination activity is more encouraging with the carbon atoms of the thione groups moved high field when the sulphur is coordinated (see p. 130).

The combination of Mössbauer, ^{13}C NMR and IR spectra has been used to study organotin complexes of a variety of heterocyclic thiones. These suggest the possibility that both thione sulphur and heterocyclic nitrogen are involved in the coordination of benzo-1,3-thiazoline-2-thione and 1,3,4-thiadiazoline-2,5-dithione to tris (*n*-butyl) and trimethyltin, respectively [35]. Mössbauer spectra have also been used in the detection of iron–sulphur bond formation (see p. 142).

Ligand field splitting energies (*Dq*, cm^{-1}) and Racah (B′, β) parameters have been particularly useful for detecting cobalt–sulphur interactions in tetrahedral environments. Some typical values are listed in Table 3. These show *Dq* values in the range 326–476 cm^{-1} and Racah (β) parameters between 60 and 74% of the free-ion value. Although the corresponding values for nitrogen-donating heterocyclic thiones show a significant overlap with those of sulphur donors (*Dq* 430–549 cm^{-1}; β 0.60–0.75) such data have been used for complexes of thiomorpholine-2-thione (see p. 141), thiazolidine-2-thione (see Table 9) and benzoxazoline-2-thione (see Table 11).

The ability of X-ray PES to distinguish between atoms of the same elemental type in differing chemical environments has enabled the donor behaviour of heterocyclic thiones to be studied [6]. In uncoordinated molecules the electron binding energies of thione sulphur ($2p_{3/2}$) electrons are in the region of 162.0 eV (see p. 123). Coordination generally causes a decrease

TABLE 3

Spectrochemical parameters for $[Co–S_4(thione)]^{2+}$ chromophores

Thione-donor	Dq (cm^{-1})	B′ (cm^{-1})	β	Ref.
Thiourea	425	600	0.62	92
Pyrrolidine-2-thione	326	718	0.74	51
1-Methyl-1,3-imidazoline-2-thione	402	651	0.67	69
1,3-Imidazolidine-2-thione	378	651	0.67	83
2,3-Diphenyl-2,3-dehydrotetrazolium-5-thione	408	500	0.62	145
ε-Thiocaprolactam	391	634	0.64	165
Pyridine-2-thione	396	635	0.65	167
1,3-Thiazolidine-2-thione	476	576	0.60	259
1,3-Oxazolidine-2-thione	425	500	0.62	295

in the electron density of the coordinating atoms and produces a consequent increase in their electron binding energies. For the ($2p_{3/2}$) electrons of thione sulphur atoms such increases upon coordination are reported to be of the order 0.3–0.9 eV (see pp. 123 and 156).

The technique has been particularly successful in the study of molecules such as 1,3-thiazoline-2-thiones which contain both thioether and thione sulphur. Among the silver(I) complexes of a group of such molecules, increases of the order 0.3–0.9 eV in the thione sulphur ($2p_{3/2}$) electron binding energies confirmed the donor atom [36].

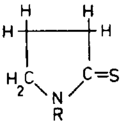
Increases in the nitrogen ($1s$) electron binding energies of the order 0.5–0.9 eV have also been reported among complexes of S,N-donating thiolate ions (see p. 173).

The stimulus for much of the research into the coordination chemistry of heterocyclic thione donors stems from their wide ranging applications. These include: *Analytical Chemistry* Both gravimetric [37] and spectrophotometric [38,39] analyses have been developed for many metals; *Polymers and Plastics* Pyridine thione complexes of zinc [40(a)] and tin [40(b)] have been patented for use as polyolefin stabilisers. A cobalt complex of tetrahydropyrimidinethione has been patented as a vulcanisation accelerator [40(c)]; *Medical–Biological Systems* Bacteriostatic activity has been related to coordinating ability for a series of imidazoline and thiazoline-thiones [41]; the bacteriostatic ability of the zinc pyridine thione system has been extensively patented [42]. Other applications include thyrotoxic activity [43], central nervous system depressant and anti-convulsant activity [44]. Carcinostatic activity among heavy metal complexes has been reported [45] and a platinum pyridine thione complex has been patented for clinical use in cancer treatment [46]. Fungicidal activity has also been reported [47]. *Metal Treatment* Industrial applications have tended to centre around the metal finishing and electroplating industries as well as the inhibition of metallic corrosion [48–50].

C. COMPLEXES OF NITROGEN CONTAINING HETEROCYCLIC THIONES

(i) Pyrrolidine-thiones

Pyrrolidine-2-thione, pyrdtH (**IIa**), and its *N*-methyl derivative (**IIb**) form pseudo-tetrahedral ML_2X_2 and tetrahedral $[ML_4]X_2$ complexes with a variety of metals [M(II) = Co, Zn, Cd, Hg; X = Cl, Br, I, NO_3, NCS, ClO_4] [51,52]. The sulphur-donating character of these molecules has been established either by a lowering of the ν(CS) (1100 cm^{-1}) band [51] or by a raising of the δ(CS) (332 cm^{-1}) band [52] of the coordinated ligand. In addition, the spectrochemical (Dq, β) parameters of the cobalt(II) complexes occur in the range 309–378 and 0.68–0.75 cm^{-1}, respectively [51].



II

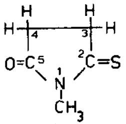
a: R=H

b: R=Me

Tetragonal complexes are formed with nickel(II) and tellurium(IV) in which the ligand is sulphur donating [53,54].

With copper(I) pyrdtH forms complexes of type $Cu(LH)_3X$ ($X = NO_3$, $\frac{1}{2}SO_4$, BF_4). These are 1 : 1 electrolytes and trigonal planar geometries are proposed with sulphur-donating ligands [56].

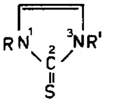
N-Methyl pyrrolidine-2-thione-5-one (**III**) reacts with metal halides and perchlorates, [M = Ag(I), Cu(I), Ni(II), Hg(II)] producing complexes with formulae ranging from Ag(L)I to $Hg(L)_5(ClO_4)_2$. Thione sulphur donation has been established for the ligand by a lowering of the ν(CS) (1123 cm^{-1}) band [55].



III

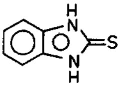
(ii) 1,3-Imidazoline-2-thiones

The parent molecule, together with various derivatives (**IV–VII**), are structurally well characterised, with the thione form the dominant solid-state tautomer in each case (Table 4). The range of bond lengths observed in the thioamide portion of the molecules suggests that a combination of thione

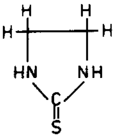


IV

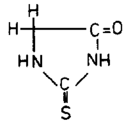
a: R=R'=H
b: R=Me, R'=H
c: R=R'=Me



V



VI

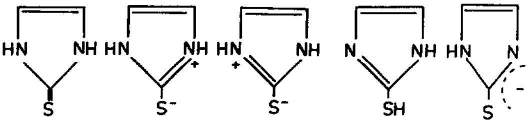


VII

and other canonical forms are required to rationalise the delocalised π-electron distribution (**VIIIa–d**).

Donor sites are limited to nitrogen and sulphur but monodentate, bidentate or bridging coordination modes are possible depending on the reaction conditions.

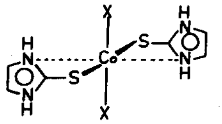
In neutral media 1,3-imidazoline-2-thione, imtH$_2$ (**IVa**), forms two types of complex with cobalt and zinc: M(LH$_2$)$_2$X$_2$ (X = Cl, Br, I) and M(LH$_2$)$_4$X$_2$ (X = NO$_3$, ClO$_4$) [61]. Electronic spectra indicate octahedral coordination for the cobalt complexes in the solid with either terminal halides (**IX**) or ionic nitrates and perchlorates. In nitromethane the iodo and perchlorate complexes change to tetrahedral CoS$_2$I$_2$ and CoS$_4$ chromophores which suggests a tenuous cobalt–nitrogen link for the S,N-chelating imtH$_2$ molecule in the solid complexes. S,N-chelation is also proposed for Pd(imtH$_2$)$_2$ which is formed in acid conditions (pH 0–3) [63] and for the aluminium, copper and iron complexes of the thiolate anions imtH$^-$, meimt$^-$ and bzimtH$^-$ [41]. High stability constants are reported for these latter complexes in alkaline media (log β 19.60–20.30 for copper). The



(a) (b) (c) (d) (e)

Adapted from Ref. 61

VIII



IX

TABLE 4

Imidazole thiones: dimensions (Å) of the heterocyclic thioamide groups

Molecule	C(2)–S(2)	C(2)–N(1)	C(2)–N(3)	Ref.
1,3-Imidazoline-2-thione	1.698(2)	1.346(3)	1.344(3)	104
Benz-1,3-imidazoline-2-thione	1.671(8)	1.362(6) [a]	1.362(6) [a]	57
1-Methylimidazoline-2-thione	1.685(2)	1.351(4)	1.344(3)	64
1,3-Dimethylimidazoline-2-thione	1.696(5)	1.349(6) [a]	1.349(6) [a]	78
Imidazolidine-2-thione	1.708	1.322	1.322	82
1,3-Dimethylimidazolidine-2-thione	1.673(5)	1.342(5)	1.334(5)	103
Imidazolidine-4-one-2-thione (thiohydantoin)	1.642(3)	1.393(3)	1.322(4)	98

[a] Molecules have crystallographic mirror symmetry.

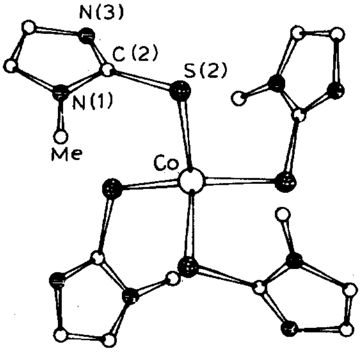
oxidation state of the copper complex (+II) is unusual in view of the reducing ability of imidazole-thiones towards copper(II). Complexes of copper(I) with $imtH_2$ and meimtH have been obtained either by reduction of copper(II) halides by the ligands in ethanol [118] or by direct combination of copper(I) halides in acetonitrile and the ligands in ethanol [105]. The complexes are in the formula range $Cu(LH)_nX$ ($LH = imtH_2$, meimtH, me_2imt; $n = 1$ or 2; X = Cl, Br, I).

Several nickel complexes involving monodentate and sulphur-donating $imtH_2$ have been prepared in neutral media: $Ni(LH_2)_4X_2$ (X = Cl, Br, I, NO_3, ClO_4, BF_4) and $Ni(LH)_2(NCS)_2$ with ν(Ni–S) in the range 290–340 cm^{-1} [60]. These tetragonal paramagnetic (μ 2.76–3.42 B.M.) complexes exhibit increasing tetragonality in the sequence $Cl < SCN < NO_3 < Br < I < ClO_4 < BF_4$ on the basis of their Dq_z values. Tetragonal distortion in the chloro complex is so slight that no splitting of the ν_1 band is observed in the solid state electronic spectrum which suggests similar positions for chloride and $imtH_2$ in the spectrochemical series and a Dq value in the region of 780 cm^{-1} for the heterocyclic molecule. The crystal structure of $Cd(imtH_2)_2Cl_2$ has monodentate sulphur-donating $imtH_2$ with Cd–S (2.45 Å) and Cd–S–C angles of 105.6° [62].

Benz-1,3-imidazoline-2-thione, $bzimtH_2$ (**V**), is a widely used analytical reagent for inorganic ions either in acid or in alkaline media [37,38]. An X-ray PES study of the molecule and some of its metal complexes [Ag(I), Hg(II), Cd(II), Pb(II), Cu(I), Ni(II), Pt(II), Pd(II)] shows binding energies of 400.6 eV(N1s) and 162.4 eV ($S2p_{3/2}$) for the free molecule [58]. The presence of two types of nitrogen ($1s$) spectra for complexes of the deprotonated ligand together with chemical shifts in the range 0.2–1.2 eV suggests coordination involves both sulphur and one of the imidazole nitrogen atoms. Only the sulphur atom is involved in coordination for complexes which contain $bzimtH_2$. An anionic zinc complex containing $bzimtH^-$ and piperidinedithiocarbamate has been reported; similar complexes containing the benzothiazolethiolate anion and di-alkyldithiocarbamates have also been prepared, and in some instances, structurally classified [59], (see p. 159).

Complex formation between 1-methyl-1,3-imidazoline-2(3*H*)-thione, meimtH (**IVb**), and a variety of metals [M(II) = Cu, Zn, Pd, Cd and Ag(I)] in aqueous solutions has been studied potentiometrically [66]. Two types of product are reported with copper (II): a navy blue polynuclear form is produced at 1 : 1 (metal : ligand) ratios and a green form at higher ligand ratios. Deprotonation of the ligand occurs during production of the navy blue material; consequently the thiolate anion, $meimt^-$, is the coordinated species in this instance whereas both $meimt^-$ and meimtH are involved in the green compound. The electronic spectra of the two complexes are clearly different with the blue material absorbing at 13000 cm^{-1} and the green substance in the range 16–17000 cm^{-1}. Of the remaining complexes, $Pd(meimt)_2$ also involves the thiolate anion and $[Ag(meimtH)_3]^+$, $[Cd(meimtH)_2]^{2+}$ and $[Zn(meimtH)_4]^{2+}$ all involve the neutral molecule with coordination apparently occurring through the imido (NH) nitrogen atom. In alkaline media the thiolate anion also produces $Co(meimt)_2$ which is a polymeric S,N-bridged complex with an anomalously low room temperature magnetic moment (μ 4.0 B.M.) [70]. With cobalt(II) and zinc(II) halides and perchlorates in neutral alcoholic media pseudo-tetrahedral $M(LH)_2X_2$ (X = Cl, Br, I) and tetrahedral $M(LH)_4(ClO_4)_2$ complexes are produced [69,70]. Spectrochemical parameters classify these complexes as CoS_2X_2 or CoS_4 chromophores with Racah (β) values in the range 0.60–0.69. The nitrate complexes $M(LH)_4(NO_3)_2$ (M = Co, Zn, Cd) also contain CoS_4 groups; $Co(LH)_2(NO_3)_2$ however has a Racah (β) value of 0.75 which is consistent with a CoS_2N_2 environment [71].

Infrared spectra support the spectrochemical data with respect to the monodentate sulphur-donating character of meimtH in these complexes. The thioamide (IV) band (770 and 740 cm^{-1}) is the most significantly affected of all the ligand bands upon coordination; ν(M–L) bands also appear in the range 300–330 cm^{-1} and these are believed to be essentially ν(M–S) in character [69,71]. The results of single crystal X-ray studies of meimtH complexes are summarised in Table 5. These show that the thione (C–S) distance of meimtH is lengthened upon coordination or, alternatively, the π-character [28] in this bond is reduced. The M–S–C angles suggest an approximately tetrahedral value at the sulphur atom (Table 5) and the ligands 'twist' about the M–S–C plane (X).



X

Adapted from Ref. 71

Nickel(II) complexes of meimtH are formulated; $Ni(LH)_4X_2$ (X = Cl, Br, I, NO_3, BF_4, ClO_4) or $Ni(LH)_2(NCS)_2$ [65]. The chloride and thiocyanate are paramagnetic at room temperature (μ 3.26 and 3.09 B.M. respectively) and tetragonal, the remainder are diamagnetic and either tetragonal or

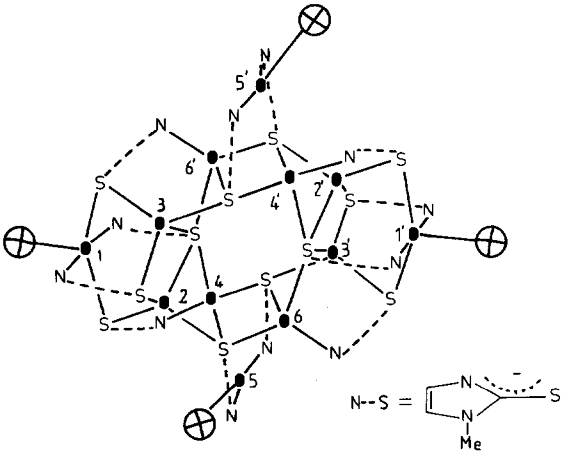
TABLE 5

Selected structural details of imidazole-thione complexes

Ligand and complex	Average bond lengths (Å) and angle (°)				Ref.
	M–S	C–S	C–N	M–S–C	
(a) *Imidazoline-2-thione (LH_2)*					
$Cd(LH_2)_2Cl_2$	2.45			105.6	62
(b) *1-Methylimidazoline-2-thione (LH)*					
$[Co(LH)_4](ClO_4)_2$	2.302	1.717	1.339	104.2	71
$[Co(LH)_4](NO_3)_2$	2.326	1.731	1.351	103.6	127
$[Zn(LH)_4](NO_3)_2$	2.339	1.708	1.333	101.4	72
$[Ni(LH)_4(ClO_4)_2]$	2.225	1.713	1.333	108.4	73
$[Ni(LH)_4]Br_2$	2.213	1.724	1.340	109.4	125
$[Pt(LH)_4]Cl_2 \cdot 2H_2O$	2.323	1.719	1.346	106.5	68
$[Pt(LH)_4]Cl_2 \cdot 2H_2O$	2.321	1.714	1.341	106.9	107
$[Pd(LH)_4]Cl_2 \cdot 2H_2O$	2.332	1.703	1.351	107.5	106
(c) *1,3-Dimethylimidazoline-2-thione (L)*					
CoL_2Br_2	2.334	1.696	1.362	103.6	79
$AsLCl_3$	2.301	1.729	1.359	105.5	81
$SbLCl_3$	2.511	1.743	1.335		108
$BiLCl_3$	2.845	1.719	1.349	100.5	109
(d) *Imidazolidine-2-thione (LH_2) and its N-ethyl derivatives*					
$Co(LH_2)_2(CH_3CO_2)_2$	2.328	1.693	1.298	102.5	84
$Ni(LH_2)_2(NCS)_2$	2.507	1.70	1.32	116.9	112
$Cd(LH_2)_2(NCS)_2$	2.60	1.74	1.31	111.6	116
$[Cu(LH_2)_4](NO_3)_2$	2.342	1.700	1.330	109.8	89
$Cu(LH_2)_2Cl$					89
	Cu(a)2.269	1.698	1.322	108.2	
	Cu(b)2.196	1.686	1.321	108.8	
bridging $(LH)_2$	(a)2.631 (b)2.204	1.717	1.309	(a) 114.6 (b) 107.3	
$[Cu(LH_2)_3]_2SO_4$	2.270	1.700	1.33	104.8	114
$[Cu_4(LH_2)_9](NO_3)_4$	2.390	1.72		107.1	115
$Cu(EtimdtH)_2Cl$	2.216	1.702	1.322	108.3	91
$Cu(Et_2imdt)_2Cl$	2.229	1.698	1.330	110.5	119
$Ag(LH_2)_2(SCN)$	2.482	1.688	1.332	107.6	99
$Au(LH_2)_2Cl \cdot H_2O$	2.278	1.718	1.296	110.5	101
$[Os(Et_2imdt)_4Cl_2](ClO_4)_2$	2.386	1.745	1.323	109.7	117
$[Te_2(LH_2)_4Br_2]Br_2$	2.495	1.745	1.319	103.3	100

square planar. A ^1H NMR study of meimtH and its nickel complexes in dimethylsulphoxide gives chemical shifts (δ, ppm) in the region 6.30–7.00 (two bands), 2.80–4.00 and 11.50–12.00 consistent with ethylenic protons, methyl protons and the imido (N–H) protons, respectively. The absence of any evidence for the thiol (–SH) proton (δ, 3–5 ppm) confirms the thione tautomer as the dominant species both in the free molecule and in the complexes studied [65]. The crystal structure of Ni(meimtH)$_4$(ClO$_4$)$_2$ has rather short Ni–S distances (Table 5) and H-bonded perchlorate groups in approximately apical positions (Ni–O, 3.620 Å) relative to the tetrahedrally distorted square NiS$_4$ plane of the complex [73]. This complex is tetragonal whereas Ni(meimtH)$_4$Br$_2$ is square planar and also has a distorted NiS$_4$ environment with the bromide ions H-bonded to heterocyclic imido (NH) groups but not in apical positions (Table 5) [125].

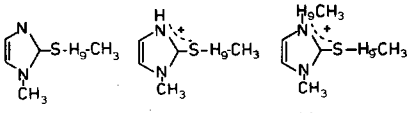
Interest in modelling environments analogous to those in blue (type 1) copper proteins has led to the study of reactions involving meimtH and copper salts. An EPR study at 77 K of Cu(meimt)$_2$ suggests a partially binuclear structure with strongly coupled [copper(II)–copper(II)] species; a similar study of [Cu(II)(Cu(I)(meimt))$_5$]meimt, ClO$_4$, suggests it to be monomeric. Both complexes absorb intensely in the region 610–620 nm. [75,76]. The mixed valence [copper(II)–copper(I)] aggregate [Cu$_{12}$(meimt)$_{12}$(MeCN)$_4$] [BPh$_4$]$_2$(MeCN)$_4$ is prepared from [Cu(I)(MeCN)$_4$]ClO$_4$, [Cu(II)(MeCO$_2$)$_2$(H$_2$O)$_2$]$_2$ and meimtH in (1 : 1) acetonitrile–methanol. The dark blue crystalline solid is obtained by redissolving the product in acetonitrile. The structure (**XI**) consists of a ring of eight four-coordinated copper(I) atoms with sulphur bridging between the metal centres. Two further copper(I) sites are three coordinate and the two copper(II) sites are five coordinated by a *trans*-N$_2$S$_2$ donor set and an acetonitrile molecule. The sulphur atoms form double, triple and quadruple bridges between the copper(I) sites. The copper(II) atom is magnetically free from other interactions and has electronic absorption and EPR spectra similar to those of blue copper proteins [77].



XI • = Cu ⊕ =MeCN Adapted from ref. 77.

The behaviour of meimtH towards palladium(II) and platinum(II) generates two possible modes of coordination in the pH range 0–6. One report [67] suggests that the molecule is completely protonated below pH 3.5 and all coordination sites are blocked. Between pH 3.5 and 6.0 the ligand nitrogen donates in both *cis*-$Pt(LH)_2X_2$ and *trans*-$Pd(LH)_2X_2$ (X = Cl, I). Between pH 6 and 10.0 deprotonation of the heterocycle occurs and polymeric products $[M(meimt)_2]$ (M = Pd, Pt) are obtained which contain S,N-bridging thiolate ions. These observations are supported by IR and ^1H NMR measurements. The latter also suggest the presence of both thiol and thione forms of the molecule in solution.

In contrast to the above behaviour, reactions of meimtH with palladium(II) and platinum(II) in both neutral and strongly acid media produce $M(LH)_4Cl_2 \cdot 2H_2O$ as the major product although variations in the stoichiometric (metal : ligand) ratios do generate other complexes. Monodentate sulphur donation appears to be the dominant coordination mode among these complexes and is generally indicated by perturbation of the thioamide (IV) band (740–770 cm^{-1}) and the presence of ν(M–L) absorptions in the region of 340 cm^{-1} [68]. X-ray analysis of the major products confirms these observations and shows the structures to consist of essentially regular square MS_4 environments, ionic chlorides and H-bonded water molecules (Table 5). A further report [102] on the ^1H NMR spectrum of meimtH refutes the previous assertion [67] that the thione and thiol forms co-exist in solution and supports the claim [65] that the thione form is the dominant tautomer on the basis of chemical shifts (δ, ppm) of 12.00 ± 0.02 (> NH), 3.45 ± 0.01 ($-CH_3$), 6.87 ± 0.01 [CH(4)] and 7.05 ± 0.01 [CH(5)]. In addition, coordination of meimtH towards methylmercury(II) also appears to be dependent on both pH and stoichiometric ratios of the reactants [102]. With 1 : 1 (metal : ligand) ratios Hg–S bonds are formed in basic (**XIIa**) and acidic (**XIIb**) media whereas with 2 : 1 (metal : ligand) ratios in basic media both Hg–N and Hg–S bonds are formed (**XIIc**). In each complex coordination has been deduced on the basis of $[^2J(^{199}Hg-^1H)]$ coupling constants (184.6–207.8 Hz) and ^1H NMR chemical shifts.



(a) (b) (c)

XII

Adapted from Ref. 102

Reactions of nitrogen bonded *cis*-$M(meimtH)_2Cl_2$ [M(II) = Pd, Pt] with guanosine (guo), cytidine (cyd), and adenosine (ado) have been studied in neutral solutions. Two types of complex have been isolated, $[M(meimtH)_2L_2]$ (L = guo or cyd) and $[ML_4]X_2$ (L = cyd, ado; X = Cl, PF_6). Infrared, ^1H NMR and ^{13}C NMR studies confirm the coordination of palladium and platinum to the N(7) atom in guo and ado and to the N(6) atom in cyd. The

NMR data reflect electronic modifications in the ring system of the coordinated nucleoside [74].

The *N*,*N*′(1,3)-dimethylimidazoline-2-thione molecule, me$_2$imt (**IVc**), is clearly an exclusive sulphur donor which readily coordinates to cobalt(II), zinc(II) and nickel(II) [79,80,110]. Pseudo-tetrahedral complexes ML_2X_2 [M(II) = Co, Zn, Ni; X = Cl, Br, I] are formed in neutral alcoholic media. Racah (β) parameters for the cobalt complexes range from 0.72 to 0.78 and 0.63 to 0.79 for the nickel complexes; ν(M–S) absorptions are in the range 310–327 cm^{-1} [79]. An X-ray study of pseudo-tetrahedral Co(me$_2$imt)$_2$Br$_2$ confirms the monodentate sulphur donating character of the ligand (Table 5). Non-halo counter ions generate CoS_4 chromophores (Dq 394 cm^{-1}; β 0.65) with ν(M–S) absorptions in the range 300–320 cm^{-1} [80]. Tetragonal nickel(II) complexes, NiL_4X_2 (X = NO_3, ClO_4, BF_4) and $NiL_2(NCS)_2$ are paramagnetic at room temperature (μ 2.88–3.34 B.M.) [110]. In solution they behave as 1 : 2 electrolytes and generate electronic spectra consistent with square planar environments with the exception of the thiocyanate complex which is polymeric.

Group V trihalides form two types of complex with me$_2$imt (Table 5); M(me$_2$imt)Cl$_3$ [M(III) = As, Sb] [81,108] and Bi(me$_2$imt)$_2$Cl$_3$ [109]. The basic structural unit in the (1 : 1) complexes is a distorted pyramid with additional and longer metal–chlorine contacts modifying the environment of the central atoms to that of a distorted trigonal bipyramid in the case of arsenic, and distorted octahedral for antimony. With bismuth the structure consists of two centrosymmetrically related octahedra which share a common edge through chlorine bridges.

Imidazolidine-2-thione, imdtH$_2$ (**VI**), is widely known by its trivial name, ethylenethiourea, and contains a formally saturated 1,3-imidazolidine ring. The C(2)–S and C(2)–N(1,3) distances suggest that a delocalised π-MO component is centered on the thioamide portion of the molecule [82] (Table 4).

A detailed analysis of the IR spectra of imdtH$_2$ as well as its *N*- and *N*,*N*-dialkyl derivatives has been undertaken by a combination of N-deuteration, S-methylation and selenation [122–124]. The major IR activity of imdtH$_2$ consists of symmetric and antisymmetric ν(NH) at 3275 and 3250, ν(CN) at 1528 and 1508 and two ν(CS) bands at 925 and 516 cm^{-1} [122]. The alkylated derivatives have ν(CS) activity concentrated in the range 230–620 cm^{-1} [124]. In its metal complexes [M(II) = Co, Ni, Zn, Cd, Hg] the IR spectrum of imdtH$_2$ undergoes positive shifts to ν(NH) and the ν(CN) bands and negative shifts to the ν(CS) bands. These changes are consistent with thione sulphur donation by the ligand [123].

An X-ray PES study of imdtH$_2$ has produced electron core binding energies of 399.6 eV for the nitrogen (1*s*) and 162.0 eV for the sulphur

($2p_{3/2}$) electrons. In its complexes, $M(LH_2)_2Cl_2$ [M(II) = Co, Zn, Cd, Hg], positive shifts of the order of 1 eV are observed for the binding energies of the sulphur atoms whereas for nitrogen the binding energies vary by ±0.5 eV [111]. Sulphur donation is proposed for $imdtH_2$ from these observations.

With cobalt(II), $imdtH_2$ forms both $Co(LH_2)_2X_2$ (X = Cl, Br, I) and $[Co(LH_2)_4](ClO_4)_2$ [83], whereas the alkyl derivatives of the heterocycle are restricted to $Co(LH_2)_2X_2$ (X = Cl, Br, I) [93,94]; The acetate complex, $Co(imdtH_2)_2(CH_3CO_2)_2$, is pseudo-tetrahedral with two long [2.923(7) Å] cobalt–oxygen distances as well as monodentate sulphur-donating $imdtH_2$ (Table 5) [84]. The spectrochemical parameters of a range of cobalt(II) complexes containing saturated and unsaturated imidazole-thiones are listed in Table 6. The unsaturated molecules appear to generate larger ligand field strengths and greater covalent character in the cobalt–sulphur bonds than the saturated molecules. Infrared spectra are also indicative of sulphur donation with ν(Co–S) values in the range 320–340 cm^{-1} [93].

A ^1H NMR study suggests that of the complexes of $imdtH_2$ and its *N*-alkyl derivatives those with imido (NH) groups appear to be more stable in solution because of their ability to form hydrogen bonds with neighbouring halogens [95].

With nickel(II), $imdtH_2$ forms planar and tetragonal complexes $Ni(LH)_4X_2$ (X = Cl, Br, I, ClO_4, NO_3) as well as an octahedral complex $[Ni(LH_2)_6](ClO_4)_2$ [85]. The tetragonal chlorides and bromides exist as *cis* and *trans* isomers and together with the octahedral perchlorate complex are paramagnetic (μ 3.12–3.00 B.M.) at room temperature. The remaining complexes are diamagnetic at room temperature. All the complexes lose $imdtH_2$ molecules in solution and retain coordinated anions. Electronic

TABLE 6

Spectrochemical parameters of $[CoS_4]^{2+}$ imidazole-thione chromophores

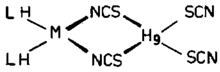
Molecule	Dq (cm^{-1})	B′ (cm^{-1})	β	Ref.
Imidazolidine-2-thione	378	651	0.67	83
1-Methylimidazolidine-2-thione [a]	382	668	0.69	93
1,3-Dimethylimidazolidine-2-thione [a]	371	663	0.69	94
1-Ethylimidazolidine-2-thione [a]	397	651	0.67	93
1,3-Diethylimidazolidine-2-thione [a]	374	662	0.68	94
Imidazoline-2-thione [b]	449	588	0.60	61
1-Methylimidazoline-2-thione	402	651	0.67	69
1,3-Dimethylimidazoline-2-thione	397	630	0.65	80

[a] Calculated values from the ligand field approximation method. [b] Solution values.

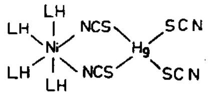
spectra give Dq and β for the octahedral $[Ni(imdtH_2)_6]^{2+}$ system of 800 and 0.56 cm^{-1}, respectively, which are consistent with thione sulphur donation by the ligand. Structural relationships among the square and tetragonal complexes are rationalised on the basis of the relative positions in the spectrochemical series of the heterocyclic molecules and the counter ions. Because of the proximity of heterocycle and counter ion in the spectrochemical series the average ligand field approximates to octahedral in $Ni(LH_2)_4Cl_2$ ($Dq = 782$ cm^{-1}) whereas with iodide the separation between the components in the series leads to a tetragonal diamagnetic complex.

With metal thiocyanates $imdtH_2$ forms complexes of type $M(LH_2)_2(NCS)_2$ with a variety of metals [M(II) = Mn, Co, Ni, Zn, Cd, Pb, Mg] [120] [M(II) = Co, Ni, Cd, Zn] [126]. The anion is either nitrogen bonded or S,N-bridging in these complexes. Infrared spectra suggest monodentate sulphur donation for the ligand with ν(M–S) in the range 275–285 cm^{-1} and negative shifts (ca. 75 cm^{-1}) to a mixed vibrational mode $\nu(C{-}S) + \delta(NCS)$ of the ligand at 1270 cm^{-1} [126]. Structural studies show the cadmium and lead complexes to be isostructural with octahedral coordination of the metal consisting of apically sulphur-donating $imdtH_2$ [Cd–S 2.60(1) Å] and pairs of bridging anions [Cd–S 2.73(2); Cd–N 2.53(13) Å] in the equatorial plane [116] (Table 5). The bridging thiocyanate groups in $Ni(imdtH_2)_2(NCS)_2$ are unusual inasmuch that they provide apical nitrogen and equatorial sulphur in adjacent complexes which, together with the sulphur donating $imdtH_2$ molecules, generate tetragonal NiS_4N_2 units [112] (Table 5).

Two types of bimetallic thiocyanate complexes are formed by $imdtH_2$ [86]. Those of formula $[M(imdtH_2)_n][Cd(SCN)_4]$ are 1 : 1 electrolytes [M(II) = Co($n = 4$); Ni($n = 6$)] with either tetrahedral cobalt or octahedral nickel. Both $imdtH_2$ and thiocyanate are monodentate sulphur donating in these complexes. The compounds of type $(LH_2)_nM(NCS)_2Hg(SCN)_2$ are nonelectrolytes with terminal and bridging thiocyanates (**XIII**). When M is cobalt or zinc ($n = 2$) both electronic ($Dq = 408$ cm^{-1}, $\beta = 0.78$) and IR spectra are indicative of tetrahedral environments. With nickel ($n = 4$) the coordination is octahedral (**XIV**). The (imido) nitrogen is the proposed donor atom in the bridged monomeric complexes on the basis of rather high Racah



XIII



XIV

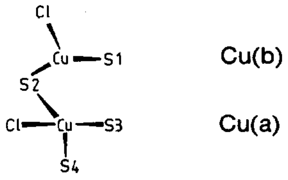
(β) parameters, shifts to salient ligand vibrational modes [ν(NH), δ(NH), ν(C–S)] and ν(M–N) in the range 210–275 cm^{-1}. Similar complexes are also reported for thiohydantoin, (see p. 132) and thiazolidine-2-thione, (see p. 161).

With zinc and cadmium halides *N*-mono and *N*,*N'*-dialkyl substituted $imdtH_2$ molecules form pseudo-tetrahedral $M(LH_2)_2Cl_2$ complexes with monodentate sulphur-donating heterocyclic ligands. The reported ν(M–S) values are 250–230 cm^{-1} (Zn) and 140–215 cm^{-1} (Cd) [96].

Complexes of copper with $imdtH_2$ have been known for some time [113] and continue to be investigated. The reducing power of the heterocyclic thioamide group towards copper(II) and the unpredictability of both the stoichiometry and the stereochemistry of the reaction products are underlying themes of many investigations.

Many of the complexes may be formulated: $M(LH_2)_nX$ ($n = 1$ to 4; X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$, BF_4), but more complicated stoichiometries are also known.

A ^{13}C NMR study of $Cu(LH_2)_2X$ (X = Cl, Br) shows chemical shifts (δ, ppm) for the C(2) thione carbon atom of $imdtH_2$ of 184.5 for the free molecule and 180.8 in both the reported complexes [88]. A high-field shift of this magnitude is a useful diagnostic test for thione-sulphur donation. The crystal structure of $Cu(imdtH_2)_2Cl$ shows it to be binuclear (**XV**) with two types of copper [89]. Atom (a) is tetrahedrally coordinated to three ligand sulphur atoms (S2, S3, S4) and one chlorine atom. Atom (b) is trigonally coordinated to two ligand sulphur atoms (S1, S2) and one chlorine atom. Clearly one of the ligand sulphur atoms (S2) is bridging, the remainder are terminal and the bridging ligand is more loosely bound to the tetrahedral copper atom [Cu(a)–S2 = 2.631(3); Cu(b)–S2 = 2.204(3) Å; Cu(a)–S2–Cu(b) = 137.3°] than are the terminal ones [Cu(a)–S(av) = 2.269(3) Å), Table 5]. In $Cu(imdtH_2)_4(NO_3)_2$ the metal is tetrahedrally coordinated by four sulphur-donating thione molecules, the nitrate groups are ionic [89] (Table 5). Complexes of type $Cu(LH_2)_2X$ and $Cu(LH_2)_3X$ (X = NO_3, BF_4, $\frac{1}{2}SO_4$) are reported for $imdtH_2$ and its *N*-alkyl substituted derivatives, respectively [56]. The 1 : 2 (metal : ligand) complexes are non-electrolytes which are subject to extensive solvolysis in solution and the 1 : 3 complexes are 1 : 1 electrolytes.



XV

Adapted from Ref. 89

In all cases coordination to copper is by means of the sulphur atom; trigonal planar structures are also proposed.

Structural studies have established trigonal environments for the metal in chloro-bis(*N*-ethylimidazolidine-2-thione) copper(I) [91]; chloro-bis(N,N^1-di-ethylimidazolidine-2-thione) copper(I) [119] and tris(imidazolidine-2-thione) copper(I) sulphate [114] (Table 5). In general, copper–sulphur distances are longer in tetrahedral than they are in trigonal environments.

The tetranuclear copper(I) complex, $Cu_4(imdtH)_9(NO_3)_4 \cdot 6H_2O$, contains a discrete copper cluster involving one-, two- and four-coordinating $imdtH_2$ molecules [115]. The four copper atoms have a common tetrahedral coordination with significant differences among Cu–S distances which range from 2.243 to 2.515(2) Å (Table 5). Three distinct types of Cu–S bonding environment occur in this structure. Monodentate $imdtH_2$ molecules coordinate by donation of an electron pair from a sulphur sp^2 orbital into a vacant sp^3 copper orbital. Bridging (μ_2) $imdtH_2$ ligands coordinate by means of an sp^2 electron pair as well as through the sulphur $p\pi$ orbital producing an eight-membered ring with alternating Cu–S bonds. Especially interesting is the bridging (μ_4) $imdtH_2$ molecule which shares two sp^2 non-bonded electron pairs with four vacant copper sp^3 orbitals forming a pair of electron-deficient three-centre bonds. Such an interaction generates shorter copper–copper separation distances [2.849(1) Å] relative to those formed by two-coordinate (μ_2) bridging environments [3.362(1) Å].

Complexes with other IB metals are significantly less numerous than those for copper; crystal structures of both $Ag(imdtH_2)_2(SCN)$ [99] and $Au(imdtH_2)_2Cl \cdot H_2O$ [101] have been reported however (Table 5). The silver complex contains trigonal planar AgS_3 units formed from two $imdtH_2$ ligands and the thiocyanate group all of which are sulphur donating. These units are associated through weak [$Ag \cdots S = 3.105(2)$ Å] contacts into centrosymmetric dimers which contain Ag_2S_2 rings. The gold complex contains distorted [$S–Au–S = 167.1(2)$ Å] linearly coordinated cations. The distortion and *cis* configuration of the ligands is ascribed to H-bonding between the imido (> NH) groups of the heterocyclic molecules and the water molecule.

The reaction of platinum dichloride or potassium tetrachloroplatinate(II) with $imdtH_2$ produces $[Pt(LH_2)_4]Cl_2$, $[Pt(LH_2)Cl_2]_2$ and $Pt(LH_2)_2Cl_2$ [97]. A ^{13}C NMR study gives high field shifts in the range 3.0–11.0 ppm for the thione carbon atoms of $imdtH_2$ in these complexes and suggests sulphur donation by the ligand. Proton NMR spectra also suggest involvement of the imido (N–H) group of the ligand in the coordination process for $[Pt(LH_2)_4]Cl_2$. Infrared spectra show ν(Pt–Cl) for $[Pt(LH_2)Cl_2]_2$ and $Pt(LH_2)_2Cl_2$ (300–320 cm^{-1}) but not for $[Pt(LH_2)_4]Cl_2$. Mixed valence complexes containing platinum II and IV have been reported with formulae

$[Pt(imdtH_2)_4][PtCl_6]$ and $[Pt(imdtH_2)_2Cl_2][Pt(imdtH_2)_2Cl_4]$ [90]. Halogen bridges link the square cations and octahedral anions in the solid; X-ray PES has been used to establish the oxidation states of the platinum atoms. Similar complexes have been reported for ϵ-thiocaprolactam (see p. 142), tetrahydropyrimidine-2-thione (see p. 148), pyrimidine-2-thione (see p. 145) and thiohydantoin (see p. 132).

An X-ray study of $[Te_2(imdtH_2)_4Br_2]^{2+}$ shows an essentially square distribution about tellurium, bridging bromines and terminally sulphur-donating $imdtH_2$ [100] (Table 5).

Osmium tetroxide reacts with $imdtH_2$, as well as its *N*-methyl and *N*-ethyl derivatives, in acidified 1 : 1 (volume) water : ethanol to give $[Os(L)_6]^{3+}$ species in the presence of perchloric and tetrafluoroboric acids. Magnetic measurements are consistent with low-spin osmium(III). Positive shifts in the $\nu(CS)$ region (490–518 cm^{-1}) suggest sulphur-donating ligands. The kinetics of $[OsL_6]^{3+}$ formation are pseudo-first order and linear with respect to both acid and ligand concentrations [121]. An X-ray study of $[Os(Et_2\text{-}imdt)_4Cl_2](ClO_4)_2$ shows the metal to be octahedrally coordinated by four sulphur-donating Et_2imdt molecules and a pair of *trans* chlorines (Table 5) [117]. Since no chloride ion was added to the reaction mixture it is deduced to have originated from reduction of the perchlorate ion [121].

It is suggested that with titanium(IV) and tin(IV) $imdtH_2$ forms nitrogen-bonded complexes $M(imdtH_2)_2X_4$ (X = Cl, Br, I). Support for the donor atom comes from positive shifts to the thioamide I band (1420 cm^{-1}) and to the mixed vibration $[\gamma(C{=}S) + \delta(NCS)]$ at 1265 cm^{-1} [87].

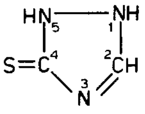
The crystal structure of 2-thiohydantoin (imidazolidine-2-thione-4-one, thnH, **VII**) has established the thione form as the dominant solid-state tautomer [98]. Some aspects of the coordination chemistry of thnH have been previously indicated in this section.

In bimetallic thiocyanates coordination is the same as that previously described for $imdtH_2$ (see p. 130) with sulphur donation in the ionic complexes and (imido) nitrogen donating in the thiocyanate-bridged complexes (**XIII**) [86]. With copper(I) two complexes $Cu(LH)_2X$ (X = Cl, Br) are known. Sulphur donation has been demonstrated for the chloro complex from ^{13}C NMR spectra which show the thione carbon of thnH (183.5 : δ ppm) to have moved very slightly high field (183.3 : δ ppm) in the complex [88]. With platinum(II) the complex $[Pt(thnH)_4]Cl_2$ is formed in which the heterocyclic molecule is again sulphur donating [97].

The coordination chemistry of thnH is similar to that of $imdtH_2$ although the range of metals studied is narrow. No involvement of the ketonic oxygen atom of thnH in its complexes has so far been observed.

(iii) Triazoline-thiones

The 1,2,4-triazoline-3(5)-thione molecule, trztH$_2$ (**XVI**), is di-protic and



XVI

may coordinate in the neutral (LH$_2$) or anionic (LH$^-$, L^{2-}) forms. A maximum of four possible donor sites may be further modified by substitution (**XVIIa,b**). The presence of ν(NH) at 3050 cm^{-1}, as well as four thioamide bands (1580, 1275, 1080, 650 cm^{-1}) (Table 2), suggests the thione form (**XVI**) to be the dominant solid-state tautomer [129,130].

Coordination of trztH$_2$ occurs with a range of metals producing mostly polymeric and insoluble products. The most commonly coordinated form of the molecule is the monoanion, LH$^-$ (Table 7), which is invariably S,N-bridging. This is suggested by IR spectra which indicate an increase in bond order of the ν(CN)-containing vibrations [129,130] and by low frequency ν(M–L) activity.

The electronic spectrum of the nickel(II) complex (*Dq* 1016 cm^{-1}, β 0.74), suggests both fairly strong ligand fields and a moderate degree of covalency in the metal–ligand bonds. The parent molecule is monodentate sulphur donating with platinum(II) in Pt(trztH$_2$)$_4$Cl$_2$ and the dianion, L^{2-}, forms a highly distorted octahedral complex with cobalt(II), CoL · 3H$_2$O. The copper

TABLE 7

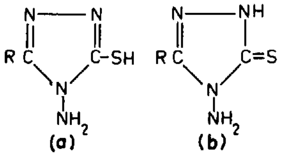
Metal complexes of 1,2,4-triazoline-3-thione

Metal	Ligand type and stoichiometry (metal : ligand)	Proposed structure	Magnetic and spectroscopic data		Ref.
			μ	ν(M–L)	
Co(II)	LH$^-$(1 : 2)	octahedral		300–400	129
	L^{2-}(1 : 1)	dist. octahedral	4.5	300–400	129
Ni(II)	LH$^-$(1 : 2)	octahedral	3.2	300–400	129
Cu(II)/Cu(I)	LH$^-$,LH$_2$(1 : 1)	square	0.9	300–400	129
Ag(I), Au(I), Tl(I)	LH$^-$(1 : 1)	linear	dia.	300–400	129,130
Cd(II), Hg(II)	LH$^-$(1 : 2)	tetrahedral	dia.		130
Zn(II), Pb(II)	LH$^-$(1 : 1)		dia.		130
Rh(III)	LH$_2$(1 : 1) LH$^-$(1 : 2)	octahedral	dia.	300–400	129
Ru(II)	LH$^-$(1 : 3)	octahedral	dia.		129
Pd(II)	LH$^-$(1 : 2)	square	dia.	300–400	129
Pt(II)	LH$_2$(1 : 4)	square	dia.	280–325	129

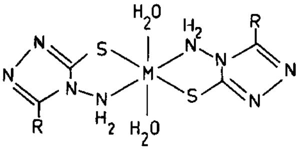
complex contains both +I and +II states of the metal as well as LH_2 and LH^- forms of the ligand and rhodium(III) coordinates with both the free molecule (LH_2) and the monoanion.

Infrared spectra of the *N*(4)- and C(5)-alkyl substituted derivatives of $trztH_2$ suggest the thione forms are present in the solid and that coordination to silver(I) occurs through the sulphur [128,139].

Complexes have been reported of the 3-alkyl substituted derivatives of 1,2,4-triazoline-4-amino-5-thione (**XVII**) [133,134]. The IR spectrum of the molecule contains both ν(SH) (2500 cm^{-1}) and ν(CS) (750 cm^{-1}) and suggests that both the thione and thiol forms of (**XVIIa,b**) exist in the solid; the complexes however do not possess ν(SH). Coincidentally, the crystal structure of 1,2,4-triazoline-3-hydrazino-4-amino-5-thione shows the thione tautomer to be dominant in the solid with a C(5)–S distance of 1.681(5) Å [131]. Coordination of (**XVII**) occurs with deprotonation of the ligand in ammonia. Cobalt(II) and nickel(II) form hydrated octahedral chelates (**XVIII**) [133]; zinc(II) and cadmium(II) produce tetrahedral (ML_2) chelates; copper(I), silver(I) and thallium(I) produce polymeric (ML) products [134]. Fairly high *Dq* (Co = 902–933 cm^{-1}, Ni = 996–103 cm^{-1}) and β(0.8–0.87) values, together with ν(M–S) at 360 cm^{-1} and ν(M–N) at 400 cm^{-1}, are consistent with S,N-coordination involving thiolate sulphur and amino nitrogen [133,134].

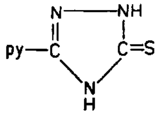


XVII



XVIII

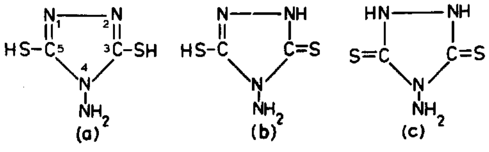
The 3-(4-pyridyl) derivative of $trztH_2$ (**XIX**) is readily deprotonated at the N(4) position with the production of S,N-chelates [Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Pt(II), Rh(III)] or S,N-bridged polymers [Cu(II), Pt(IV)] [135–137]. The parent molecule monodentate sulphur donates to



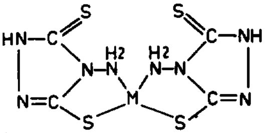
XIX

rhodium(I) [135]. All the complexes have 1 : 2 (metal : ligand) stoichiometry; the rhodium (+ I and + III) complexes are dinuclear with chlorine bridging. Ligand donation has been deduced from relevant shifts to thioamide bands (1570, 1200, 990, 850 cm^{-1}) as well as *Dq* and β values for the cobalt (850 cm^{-1}, 0.70) and nickel (1040 cm^{-1}, 0.55) complexes.

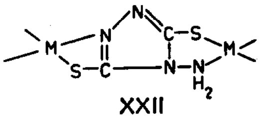
At least three forms of 1,2,4-triazoline-4-amino-3,5-dithione (**XX**) are possible, with the thione forms (**XXb**, **c**), suggested from the IR spectra. The molecule is diprotic and is capable of coordinating in LH_2, LH^- and L^{2-} forms. Two types of complex are reported; $M(LH)_2(H_2O)_n$ [M(II) = Co or Ni, $n = 2$; M(II) = Zn, Cd, Pb, $n = 0$] and $M(L)(H_2O)_n$ [M(II) = Ni, Co, $n = 4$; M(II) = Cu, Zn, $n = 2$; M(II) = Pd, Cd, $n = 1$] [138]. Electronic spectra suggest octahedral cobalt ($Dq = 952$ cm^{-1}, $\beta = 0.92$), octahedral or tetragonal nickel and copper, as well as square palladium; zinc and cadmium are presumed to be tetrahedral. Infrared spectra suggest that the complexes of the mono anion involve thiolate sulphur and amino nitrogen in S,N-chelation (**XXI**), whereas those of the dianion involve both thiolate sulphur atoms together with amino nitrogen and heterocyclic nitrogen in the formation of S,N-bridged polymers (**XXII**). The latter complexes are insoluble in common organic solvents. Most of the complexes also contain coordinated water.



XX

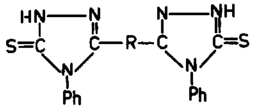


XXI



XXII

Bridging of pairs of *N*(4)-phenyl substituted $trztH_2$ molecules at the C(5) and C(5′) positions has been achieved by using ethylene glycol [132] and propyl [140] groups (**XXIII**). Complexes of these molecules have a 1 : 1



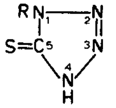
XXIII

(metal : ligand) stoichiometry [L = **XXIIIa**, M = Cu(II), Ni(II), Hg(II), Zn(II), Fe(III)] and are readily formed in aqueous methanols. The nickel(II) and iron(III) complexes are octahedral and paramagnetic, the iron complex is high spin (μ 5.2 B.M.). The remaining complexes are diamagnetic with either tetrahedral [Zn(II), Hg(II)] or tetragonal [Cu(II)] structures. The diamagnetism of the copper(II) complex has led to the suggestion that metal–metal interactions occur in the solid. Coordination occurs by means of thione sulphur donation in these polymeric complexes [132].

The bulk of the complexes formed by (**XXIIIb**) have a 1 : 2 (metal : ligand) stoichiometry [M(II) = Co, Ni, Zn] in addition to $CuLCl_2$ and $NH_4FeL(SO_4)_2 \cdot 4H_2O$. The nickel and zinc complexes are diamagnetic, the former is square and the latter tetrahedral. The remaining complexes are paramagnetic with tetragonal [Cu(II)] or octahedral [Co(II), Fe(III)] environments; the iron complex is also low spin (μ 1.20 B.M.). Coordination involves both of the thione sulphur atoms or a combination of thione sulphur and heterocyclic nitrogen [140].

(iv) Tetrazoline-thiones

1,2,3,4-Tetrazoline-5-thiones (ttztH) have been studied exclusively as their 1-substituted derivatives (**XXIV**). The substituent is usually an alkyl or an aryl group together with their halo, amino or methoxy derivatives. Coordination invariably involves the mono anion, L^-, which is obtained by *in situ* deprotonation or used as the sodium salt.

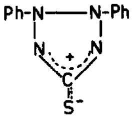


XXIV

Complexes of type ML_2 [M(II) = Co, Ni, Cu, Cd, Pd] are reported [141,142]. The four thioamide bands of the ligands (1508, 1358, 990, 755–782 cm^{-1}) are replaced by two new bands (1140, 1065 cm^{-1}) in the complexes, the ν(NH) band (3050 cm^{-1}) also disappears [141]. Spectrochemical and magnetic studies of the cobalt(II) complexes (Dq 484–526 cm^{-1}, β 0.59–0.61, μ 4.33–4.41 B.M.) are consistent with tetrahedral structures and suggest that the ligand is primarily sulphur donating [142].

A variety of complexes is formed with the heavier metals, ML_3 [M(III) = Ru, Rh], PtL_3Cl, $RuL_2 \cdot 2H_2O$, RhL_2X (X = py, H_2O) and PtL_2. All the complexes are diamagnetic which suggests dimeric formulae and metal–metal interactions for the rhodium(II) and ruthenium(III) complexes. Planar structures are proposed for rhodium(II) and platinum(II) and octahedral for the remainder. Major changes to the thioamide bands, the absence of ν(NH) and the production of ν(M–N) and ν(M–S) at 500 and 400 cm^{-1} suggest S,N-donating ligands in these complexes [143].

Complexes of type ML_3 are formed with some of the lanthanides [M(III) = La, Ce, Pr, Nd, Sm] [144]; all except that of lanthanum are paramagnetic. The complexes are insoluble polymers with S,N-bridging ligands.



XXV

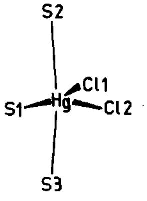
TABLE 8

Metal complexes of 2,3-diphenyl-2,3-dehydrotetrazolium-5-thione (dehydrodithizone)

Metal	Stoichiometry (metal : ligand)	Proposed structure	Magnetic and spectrochemical properties				Ref.
			μ	Dq	β	ν(M–L)	
Co(II)	1:2	tetrahedral	4.40–4.46	319–322	0.71–0.74	315–320	145
	1:3	tetrahedral	4.59	392	0.67		145
	1:4	tetrahedral	4.55–4.75	293–443	0.62–0.73	245–318	145
Ni(II)	1:2	tetrahedral	3.24–2.99	402–457	0.77–0.94	271–252	152
Cu(II)	1:2	tetrahedral	1.98			245–250	152
	1:2	dist.octahedral	0.77–0.83			244–346	152
Zn(II), Cd(II)	1:2	tetrahedral	dia.			198–292	148
Zn(II), Hg(II)	1:2	tetrahedral	dia.			194–297	148
Zn(II)	$[1:2]_n$	polym.octahedral	dia			292, 200	148
Hg(II)	$[1:1]_2$	dimeric tetrahedral	dia			252–260	148
Cd(II), Hg(II)	1:4	octahedral	dia.			205–269	148
Au(III)	1:1	square	dia				151
As(III),Sb(II), Bi(III)	1:2	square-pyramidal	dia.			288–327 329, 315	149
As(III), Sb(III), Bi(III)	1:5	square-pyramidal	dia.			203–334	149

The orange oxidation product of dithizone, 2,3-diphenyl-2,3-dehydrotetrazolium-5-thione (**XXV**), commonly known as dehydrodithione, dtzt, has the molecular structure of a meso-ionic sydnone [C–S = 1.687(5), C–N = 1.360(4), N–N = 1.316(4) Å] [147]. A detailed interpretation of the IR spectrum of dtzt has also been reported [150].

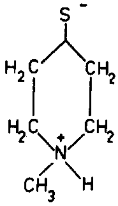
The essential features of the complexes of dtzt are summarised in Table 8. A variety of cobalt(II) complexes is reported all of which have tetrahedral geometry. The spectral parameters, *Dq* 408 cm^{-1} and β 0.62 for $[Co(dtzt)_4]^{2+}$, are consistent with a CoS_4 chromophore [145]; ν(Cu–S) occurs in the range 315–320 cm^{-1} [145]. Nickel(II) complexes, NiL_2X_2 ($X = Cl, ClO_4$), have tetrahedral structures with nitrogen-donating dtzt and coordinated anions. The bromo complex, $NiL_7Br_2 \cdot 2EtOH$, probably contains uncoordinated ligands, and the iodo complex, $NiL_4I_2 \cdot 2EtOH$, probably contains both tetrahedral and tetragonal chromophores; both contain nitrogen-donating dtzt [152]. Of the copper complexes the chloride is tetrahedral with nitrogen-donating dtzt, the others contain coordinated anions, as well as S,N-bridging dtzt and distorted octahedral structures. The abnormal magnetic moments are due to metal–metal interactions or superexchange phenomena [152]. Both tetrahedral and octahedral environments are reported for zinc(II), cadmium(II) and mercury(II) with the ligand either monodentate or bridging bidentate through its thione sulphur atom [148]. The crystal structure of the 1 : 1 adduct formed between mercury(II) chloride and dtzt consists of alternating chains of mercury and sulphur atoms. The coordination polyhedron around the mercury atom is a distorted trigonal bipyramid (**XXVI**) with two apical sulphur atoms [Hg–S = 3.28(2) Å], one equatorial sulphur [Hg–S = 2.40(1) Å] and two equatorial chlorine atoms [Hg–Cl = 2.34(1), 2.57(1) Å] [146]. A planar complex of gold(III), $AuLCl_3$, also contains sulphur-donating dtzt [151]. With arsenic, antimony and bismuth two types of square pyramidal arrangement are proposed, ML_2X_3 and ML_5^{3+}, both of which contain sulphur-donating dtzt [149].



XXVI

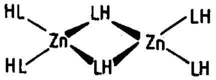
(v) Piperidine-thiones

The non-planar molecule *N*(1)-methyl-4-mercaptopiperidine, pptH, coordinates readily in aqueous or alcoholic media with zinc, cadmium and mercury halides and perchlorates [153–158]. Structural studies have shown that pptH, which is a weak acid (p*K*a 10.6) [159], behaves as a sulphur-donating unidentate neutral zwitterionic ligand (**XXVII**) [155–157].

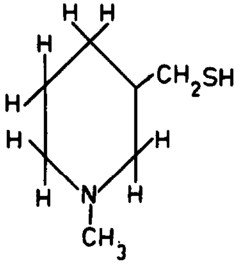


XXVII

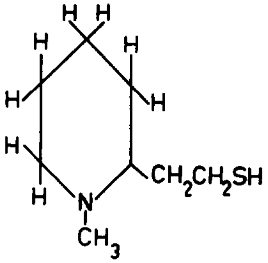
The reaction between pptH and zinc(II) has been studied electrochemically in aqueous methanol at room temperature in the pH range 4–9 [153]. The data are indicative of the production of soluble polymeric thiolates of formula $[Zn_2(LH)_6]^{4+}$ (log *K* 35.26), $[Zn_3(LH)_6]^{6+}$ (log *K* 39.71) and $[Zn_5(LH)_{12}]^{10+}$ (log *K* 79.87). Structural forms of the complexes are proposed on the basis of tetrahedral zinc and a combination of bridging and terminal ligands (**XXVIII**).



XXVIII

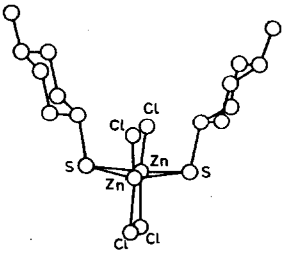


XXIX



XXX

Solid complexes are also reported [154]. Those of type $[M_2(LH)_2X_4]H_2O$ (M = Zn, Cd, Hg; X = Cl, Br, I) heave the same structure as $[Zn_2(LH)_2Cl_4]$ [157]. This complex has bidentate sulphur-bridging pptH, tetrahedral zinc, an average Zn–S distance of 2.371 Å and terminal chlorines (**XXXI**). The C–S distance in the coordinated heterocycle, 1.843(12) Å, is consistent with the thiolate form of the molecule (**XXVII**), which also adopts the chair form in the complex.



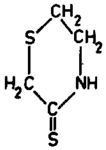
XXXI

Adapted from Ref. 157

Polymeric structures are proposed for $[Cd(LH)Cl_2]_n$ and $[Hg_2(LH)Cl_4]_n$ [154]. The cadmium complex has octahedrally coordinated metal, bridging halogen and bridging pptH. The mercury complex is effectively an adduct of mercury(II) chloride, $[HgCl_2LH]$, with the sulphur-bridging pptH molecules linking chlorine-bridged $HgCl_2$ chains. The complex $[Cd(pptH)_2](ClO_4)_2 \cdot 2H_2O$ consists of infinite chains of tetrahedral cadmium each being coordinated by four sulphur atoms from four different pptH molecules. Each sulphur atom bridges pairs of cadmium atoms with an average Cd–S distance of 2.548 Å [155,156]. Complexes of (**XXVII**), (**XXIX**) and (**XXX**) have been prepared with mercury(II) perchlorates. The resulting stoichiometries are $[Hg(LH)_n]^{2+}$ ($n = 1$ and 2) for all three ligands [158]. The crystal structure of $[Hg(pptH)_2](ClO_4)_2$ contains monodentate ligands and an essentially linear S–Hg–S arrangement [Hg–S = 2.329(4) Å]. Vibrational spectra of the complexes show strong bands at 395 cm^{-1} (IR) and 372 cm^{-1} (R) which have been assigned to asymmetric and symmetric ν(Hg–S), respectively [158].

(vi) Thiomorpholine-3-thione

The presence of ν(NH) at 3225 cm^{-1} and thioamide (I–IV) bands at 1560–1590, 1345, 1100 and 620–700 cm^{-1} in the solid-state IR spectrum of thiomorpholine-3-thione, tmtH (**XXXII**), establishes the thione form as the dominant solid state tautomer [161].



XXXII

Although tmtH contains three potential donor sites, complexes are reported in which the (imido) nitrogen coordinates to a variety of metals [Cr(III), Co(II), Ni(II), Cu(I), Bi(III)] and the thione sulphur coordinates to palladium(II), platinum(II), rhodium(III) and osmium(IV). No complexes are reported in which the thioethereal sulphur is involved. Nitrogen donation is invariably deduced from a combination of negative shifts to ν(NH), which occur between 3100 and 3200 cm^{-1} in the complexes, and positive shifts to ν(CS) bands, as well as low frequency ν(M–N) bands in the range 212–440 cm^{-1}.

The chromium(III) complexes are neutral monomeric six coordinate, CrN_3X_3 (X = Cl, Br, I), chromophores (Dq 1410–1475 cm^{-1}; β 0.63–0.65) with ν(Cr–N) between 230 and 245 cm^{-1} [160].

Cobalt(II) complexes of formulae $Co(LH)_2X_2$ (X = Cl, Br, I) and

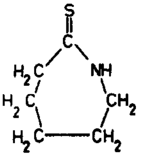
$Co(LH)_4X_2$ ($X = ClO_4$, BF_4) have tetrahedral environments with room temperature magnetic moments in the range 4.1–4.9 B.M. and spectral parameters (*Dq* 430–487 cm^{-1}; β 0.58–0.75) indicative of nitrogen-donating ligands [148]. Complexes of formula $Co(LH)_4(Ac)_2$ and $Co(LH)_6X_2$ ($X = ClO_4$, BF_4) have magnetic moments (μ 4.9–5.5 B.M.) and spectral parameters (*Dq* 949–967 cm^{-1}; β 0.88–0.91) consistent with octahedral environments [162].

Nickel(II) complexes have either tetrahedral $Ni(LH)_2I_2$ (μ 3.2 B.M; *Dq* 458 cm^{-1}; β 0.95); polymeric octahedral, $Ni(LH)_2X_2$ (X = Cl, Br: μ 3.6–3.7; *Dq* 826–855 cm^{-1}; β 0.85–0.95) or square environments [162]. The anion is also coordinated in the copper(I) complex, $Cu(LH)_3(BF_4)$ [162]. Either octahedral *mer*-isomers ($BiX_3 \cdot 3LH$) (X = Cl, I) or pyramidal environments ($BiBr_3 \cdot LH$) are proposed for bismuth [164].

Thione sulphur donation is deduced from a combination of positive shifts to ν(NH) and negative shifts to ν(CS) bands of the coordinated ligands as well as a low Racah (β 0.36) parameter for the rhodium(III) complex [163]. Among the heavier metals, square environments are proposed for the palladium and platinum complexes: $[M(LH)_4]X_2$ (X = Cl, Br); octahedral environments are proposed for the rhodium(III) and osmium(IV) complexes: $[Rh(LH)_3Cl_3]$ and $[Os(LH)_6][PtCl_4]$ [163].

(vii) ε-Thiocaprolactam

The presence of ν(NH) at 3180 cm^{-1} in the solid state IR spectrum [166], and NMR (^1H, ^{13}C) chemical shifts (δ, ppm) of 8.81 for the imido (NH) proton [88], as well as 209.7 [88] and 209.9 [166] for the thione carbon atom confirms the presence of the thione form of (**XXXIII**) in the solid and solution. The trivial name, ε-thiocaprolactam (tcpH), is invariably used for this molecule which is reported to coordinate to cobalt [165], copper [88], platinum [166,90,97] and rhodium [90].

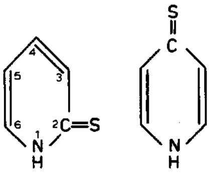


XXXIII

The cobalt complexes $Co(LH)_2X_2$ (X = Cl, Br, I) and $Co(LH)_4(ClO_4)_2$ are tetrahedral (μ 4.64–4.68 B.M.). Spectral data (*Dq* 391 cm^{-1}, β 0.64, ν(Co–L) 390 cm^{-1}) suggest monodentate sulphur donation by tcpH. Two types of complex are formed with copper(I), Cu(LH)X and $Cu(LH)_2X$ (X = Cl, Br). Sulphur donation is indicated by high-field shifts (δ) in the region of 4.0 ppm to the thioketo carbon atom of the ligand in these complexes. The same technique provides useful evidence for sulphur donation with high-field shifts (49 ppm) to the thioketo carbon atoms in $[Pt(LH)_4Cl_2]$ [97,166]. In addition, ν(Pt–S) is reported in the region 375–395 cm^{-1} [97]. A mixed valence complex, $[Pt(tcpH)_4][PtCl_6]$, contains chlorine-bridged planar cations and octahedral anions with sulphur-donating tcpH [90]. The rhodium(III) complex, $[Rh(LH)_4Cl_2]Cl$, has three ^{13}C resonance signals for the thioketo carbon atom (δ, ppm) at 200.0, 200.4 and 202.3, all of which are shifted high-field in relation to that of the free molecule (209.9) [166]. The presence of these three signals is thought to be due to structural isomerism.

(viii) Pyridine-thiones

Measurement of the basicities and electronic spectra of 2- and 4-mercaptopyridine and their *N*- and *S*-alkyl derivatives confirms the presence of the thione forms (**XXXIV**) in solution [171]. A structural analysis of the 2-isomer supports these observations for the solid also (Table 1) [172].

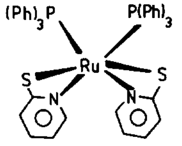


XXXIV

Pyridine-2-thione, pytH (**XXXIV**), is a monodentate sulphur donor towards many elements. Complexes have also been reported for pyridine-4-thione and 2-methyl-6-pyridine-thione, both of which are also monodentate sulphur donors towards cobalt(II), zinc(II) and mercury(II) [167].

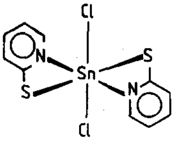
Mössbauer spectra of $Fe(pytH)_2X_2$ (X = Cl, Br) [168] consist of a doublet of isomer shift 0.87 mm s^{-1}, and quadrupole splitting, 3.48 mm s^{-1}, which are consistent with tetrahedral iron(II) and sulphur-donating ligands [168]. Spectral parameters of the cobalt(II) complexes (*Dq* 396–450 cm^{-1}, β 0.64–0.69) are in the range of CoS_4 chromophores (Table 3) [167]. The crystal structure of pseudo-tetrahedral $Co(pytH)_2Cl_2$ supports this assignment [Co–S 2.320(1), Co–Cl 2.265 Å] [169].

The nickel(II) complexes, $Ni(LH)_2X_2$ (X = Cl, Br, I), have polymeric octahedral structures with bridging sulphur atoms [167]; $Ni(LH)_4X_2$ is *trans*-octahedral on the basis of a single ν(Ni–Cl) at 242 cm^{-1} [168]; the remainder, $Ni(LH)_4X_2$ (X = Br, I, NO_3), are diamagnetic and square [167,168]. Tetrahedral environments have been proposed for halo complexes of copper(I) [168]; a trigonal arrangement has been established for $Cu(pytH)_3(NO_3)$ by X-ray analysis [Cu–S(av) = 2.222 Å] [177]. While copper(I) is the normal state of the metal in combination with the mildly reducing heterocyclic thiones, a copper(II) complex, $[Cu(phen)_2(pytH)](ClO_4)_2$, has been prepared with a normal magnetic moment and an electronic spectrum consistent with a five-coordinate environment [168]. Reactions with copper(II) oxyanione (SO_4^{2-}, Ac^-, ClO_4^-) give insoluble polymeric products. A thiolato complex CuL_n is also reported [168]. The silver(I) complexes are poorly characterised and those of zinc, cadmium and mercury have uniform tetrahedral environments. A complex of the deprotonated molecule, $Hg(pyt)_2$, has also been reported [167]. Among the heavy metals, $M(pytH)_4Cl_2$ [M(II) = Pd, Pt] are probably square in the solid with sulphur-donating ligands and ionic chloride. In solution the molar conductivities in methanol are somewhat less than expected for 1 : 2 electrolytes [167,168]. A reaction involving palladous acetate and pytH produces $PdL_2(LH)$, which is presumed to be five coordinate [168]. No displacement of coordinated acetate was achieved with dimeric rhodium acetate; the adduct $Rh_2(CH_3COO)_4 \cdot 2(LH)$ was obtained with sulphur-bonded pytH [168]. Treatment of a methanolic solution of the dirhodium cation, Rh_2^{4+}, with a slight excess of triphenylphosphine followed by a stoichiometric quantity of pytH, also in methanol, produces $[Rh(pyt)_2(PPh_3)_2(BF_4)]$. The presence of ν(Rh–S) at 344 cm^{-1} suggests monodentate sulphur donation by the thiolate anion with the octahedral coordination of the rhodium(III) atom completed by coordination from the tetrafluoroborate anion [173]. Similar behaviour is reported for the benzo-1,3-thiazole thiolate anion (see p. 157). Reaction of pytH with blue ruthenium(II) chloride, $[Ru_5Cl_{12}]^{2-}$, in methanol produces insoluble polymeric species, $[RuCl_2(pytH)_2]_n$. However, reaction of the polymeric material with triphenylphosphine produces $Ru(pyt)_2(PPh_3)_2$ [175]. Structural analysis shows the complex to be distorted octahedral with *cis*-phosphine groups, *trans*-sulphur atoms and S,N-chelating thiolate anions [174] (**XXXV**). The structural dimensions [Ru–S = 2.436(2); Ru–N = 2.124(7) Å; Ru–N–C = 102.5(6); Ru–S–C = 80.4(3)°] suggest the pyridine nitrogen is more strongly bonded to the metal than is the thiolate sulphur.



XXXV

The reaction between di-2-pyridyldisulphide and tin(II) halides produces dihalogeno bis-(2-pyridinethiolato) tin(IV). The same product may be obtained from pytH and tin(IV) chloride [176]. The complex has a distorted octahedral structure with *trans*-chlorine and sulphur but *cis*-nitrogen atoms (**XXXVI**) [170]. Structural dimensions [Sn–S = 2.465(2); Sn–N = 2.264(9) Å;



XXXVI

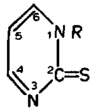
Sn–N–C = 98.1–140.1(8); Sn–S–C = 81.9(4)°] again suggest stronger bonds to the nitrogen with the sulphur atom taking most of the strain in the four-membered chelate [170]. Similar chelates are believed to be formed in a series of organotin complexes, $R_2Sn(pyt)_2$ (R = Me, Ph, Bu), for which quadrupole splittings and isomer shifts from Mössbauer spectra suggest *trans* C–Sn–C bonds [178]. A *trans* octahedral structure has been proposed for $SnCl_4(LH)_2$ with presumably sulphur-donating pytH [167]. The bismuth complex, $BiCl_3(pytH)_2$, is of uncertain stereochemistry [167]. The ν(M–S) absorptions for pytH complexes appear to fall into quite well defined groups with the lighter elements in the range 210–240 cm^{-1}, cadmium and mercury at about 200 cm^{-1}, silver in the range 240–280 cm^{-1} and palladium, platinum and rhodium between 330 and 380 cm^{-1}.

Optical electronegativities have also been calculated from the charge-transfer spectra which for pytH are centred around 29000 cm^{-1} and are assumed to be ligand (sulphur) to metal in character [167]. The values calculated on this assumption range from 2.35 to 2.5 with an average of 2.43 for a variety of metals [Hg(II), Cd(II), Zn(II), Sn(IV), Ni(II), Co(II), Pt(II), Bi(III)] [167]. These values are similar to those of the sulphide ion (S^{2-}) itself from which it appears that the availability of electron density on the thione sulphur atom is comparable to that of free sulphide and certainly greater than that in thiophosphate and thioethers [167].

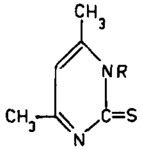
Pyridine-1-oxo-2-thiolate forms either bis-chelates or oligomers with d^8 ions [M(II) = Ni, Pd, Pt] [179].

(ix) Pyrimidine-thiones

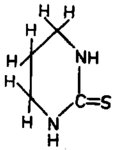
In addition to the parent molecule, pyrimidine-2-thione, pymtH (**XXXVIIa**), the 1-methyl, mepymtH, (**XXXVIIb**); 4-6 dimethyl, me_2pymtH, (**XXXVIIIa**); 1,4,6-trimethyl, me_3pymtH, (**XXXVIIIb**); and tetrahydro,



XXXVII
a: R=H
b: R=Me



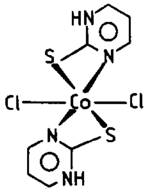
XXXVIII
a: R=H
b: R=Me



XXXIX

H_4pymtH (**XXXIX**) derivatives are all known to coordinate to a wide range of metals in a variety of reaction conditions.

With MX_2 halides [M(II) = Mn, Fe, Co, Ni, Zn, X = Cl, Br; M = Cd, X = Cl, Br, I] [180] pymtH forms complexes of formula $M(LH)_2X_2$ in hot ethanol [180]. Distorted monomeric octahedral structures are proposed for these complexes on the basis of ν(M–Cl) absorptions, electronic spectra, Mössbauer spectra [Fe(II)] and X-band EPR spectra [Mn(II)]. The crystal structure of $Co(pymtH)_2Cl_2$ (**XL**) shows that coordination of pymtH involves the N(3) and S(2) atoms in the production of an asymmetric four-membered chelate [180]. The dimensions [Co–N = 2.098(4); Co–S = 2.960(2), Co–Cl = 2.369(2) Å] suggest octahedral coordination about the metal and stronger bonds to the nitrogen than to the sulphur. Low frequency ν(M–L) bands (230–260 cm^{-1}) are also reported for these complexes. Similar structures are expected for manganese, iron and nickel but greater tetrahedral character is expected for zinc and cadmium with further lengthening of the metal–sulphur bond. With metal acetates, complexes of the deprotonated ligand are produced, $M(pymt)_2$ [M(II) = Co, Ni]. These are believed to be polymeric in character with tetrahedral cobalt and octahedral nickel environments based on their electronic spectra [180].



XL

Adapted from Ref. 180

In a reaction involving tungsten hexacarbonyl and pymtH in refluxing diglyme, the compound $W(pymt)_4$ is produced [193]. The dodecahedral structure has virtually D_{2d} symmetry, in which the *A* vertices are occupied by sulphur and the *B* vertices by the nitrogen atoms of the deprotonated thiolate anions. Average dimensions are 2.520 (W–S), 2.162 (W–N) and 1.72 Å for the C–S bonds of the anion [193].

Sulphur donation is also reported for pymtH in $Pt(LH)_4Cl_2$ and $[Pt(LH)_4][PtCl_6]$ [90].

Complexes of formula $[M(LH)_4](ClO_4)_2 2Me_2CO$ [M(II) = Mn, Co, Ni, Cu, Zn] are formed with mepymtH. Tetrahedral cations are proposed for these complexes and nitrogen-donating ligands with ν(M–N) in the range 210–224 cm^{-1}. Spectral parameters for the cobalt complex (*Dq* 628 cm^{-1}, β 0.68) suggest a moderately strong ligand field [191].

The crystal structure of the zinc complex confirms the tetrahedral geometry (N–Zn–N = 107–113°) and nitrogen-donating ligands [Zn–N(av) 2.059

Å]. The zinc–sulphur distances [3.206 and 3.255(1) Å] also indicate that the thione sulphur is not coordinated to the metal. The manganese and cobalt complexes are believed to be isomorphous with that of zinc [181]. Octahedral geometries are proposed for $[Co(mepymtH)_3](ClO_4)_2$ and $[Co(mepymtH)_2(H_2O)_2](ClO_4)_2$. The absence of splitting in the ν_1 band of the former complex suggests a *fac* arrangement of the S,N-chelating ligands [191]. The halo complexes, $M(mepymtH)_2X_2$ (M = Mn, Co, Ni; X = Cl, Br), are also octahedral with S,N-chelating ligands and coordinated halogens [191]. With copper(II) salts mepymtH produces copper(I) complexes of formula, $Cu_2(LH)_3X_2$ ($X = ClO_4$, BF_4) [191]. No reduction of the metal occurs with copper(II) halides however and complexes of formula $Cu(LH)X_2$ (X = Cl, Br) are produced [191]. Monodentate sulphur donation is proposed for the ligand with copper(I) and S,N-chelation for the *cis*-planar copper(II) complexes. Three different modes of bonding have been observed for mepymtH in the dark-red diamagnetic complex, $Cu_4(LH)_4(BF_4)_4$ [182]. The cation contains a planar centrosymmetric array of copper(I) atoms which form a parallelogram with copper ··· copper distances of 2.713(1) and 2.824(1) Å with a short diagonal of 2.839(1) Å. This Cu_4 cluster is coordinated by six thione molecules which bind in three different ways: type I, in which a pair of copper atoms is bridged by sulphur and a third is coordinated by the N(3) atom; type II, in which a pair of copper atoms is bridged by sulphur; and type III, which involves terminally bonded sulphur. Each copper atom has a distorted trigonal environment and either an S_3 or an S_2N donor set; Cu–S bond lengths range from 2.241(1) to 2.356(1) Å; the Cu–N bond length is 2.035(3) Å.

Reaction between mepymtH and methyl mercury hydroxide in aqueous solution produces MeHg(mepymt). The ligand is deprotonated in the process and the resultant S,N-chelate [Hg–S = 2.39(2); Hg–N = 2.83(3) Å; Hg–S–C = 107.7(8)°] contains a mercury–nitrogen bond which is labile in solution [192]. With zinc, cadmium and mercury, mepymtH forms complexes of formula $M(LH)X_2$ (M = Cd, X = Cl, Br); $M(LH)_2X_2$ [M(II) = Zn, X = Cl, Br, I; M(II) = Cd, X = Br, I] and $[Hg(LH)_3][HgX_4]$ (X = Cl, Br) in which the ligand is S,N-chelating [185].

With divalent manganese, cobalt, nickel, zinc, cadmium and mercury, me_2pymtH is invariably S,N-chelating [183]. The cobalt complexes exist in isomeric forms with blue tetrahedral $[Co(LH)_2]^{2+}$ (Dq 500 cm^{-1}, β 0.78); pink octahedral $[Co(LH)_2(H_2O)_2]^{2+}$ and green $[Co(LH)_2X_2]$ forms with the latter having structures intermediate between those of the blue and pink forms. Octahedral structures are proposed for the manganese, nickel and cadmium complexes and tetrahedral arrangements for those of zinc and mercury in which the ligand is a monodentate nitrogen donor.

Deprotonation of me_2pymtH is readily achieved by reaction of the appropriate metal acetate with the ligand in alcoholic media; bis-thiolate complexes, $M(me_2pymt)_2$ (M = Ni, Cd, Hg), as well as $Zn(me_2pymt)_2$-(me_2pymtH) are reported [183]. A tris-thiolate complex, $Co(me_2pymt)_3$, is obtained from cobalt(II) perchlorate and the ligand in warm acetone [189,190]. The structure is *fac*-octahedral which allows maximum π-back-bonding to the three sulphur atoms since each of them may overlap different metal orbitals. Mean dimensions (Co–S = 2.259; Co–N = 1.979 Å) for the S,N-chelate complex show that both the Co–S and the Co–N bonds appear to be quite strong and although the angle at the nitrogen atom (Co–N–C = 100.0°) appears to show the greater distortion, the strain of the four-membered chelate is taken up by the whole ring rather than by any one atom. The distortion from octahedral symmetry (S–Co–N = 72.0°) is also quite severe and is probably a consequence of the limited bite of the ligand.

With zinc(II), cadmium(II) and mercury(II) me_2pymtH forms two types of complex; $M(LH)_2X_2$ (X = Cl, Br, I) and $M(LH)_3A_2$ (A = ClO_4, BF_4, CF_3COO) [186]. The ligand is mostly S,N-bonded to the metal with the metal–nitrogen bond [ν(M–N), 270–330 cm^{-1}] stronger than that of metal–sulphur [ν(M–S), 166–227 cm^{-1}]. The cadmium chloride and bromide complexes appear to contain nitrogen-bonded heterocyclic molecules and bridging halide. Most of the complexes appear to have distorted six-coordinate structures. Complexes of the deprotonated ligand are also reported; ML_2 (M = Cd, Hg) and $ZnL_2 \cdot LH$. A slight increase in the position of the ν(M–S) band in these complexes, relative to the corresponding value for the neutral molecule, suggests some strengthening of the metal–sulphur bond [186].

The neutral, deprotonated and protonated form of me_2pymtH are reported to complex with copper(I) [187] and silver(I) [188]. The neutral molecules are S,N-chelating in complexes such as M(LH)X, $M(LH)_2X$ and $Cu_2(LH)_3Br_2$; for copper the anion is restricted to halide but for silver a wide range of anions is involved. The deprotonated ligand behaves as a terdentate, N,N,S-bridging anion in complexes of type ML as well as those which also involve the neutral molecule such as $Cu_3(LH)_3(L)Br_2$ and $Ag(L) \cdot [Ag(LH)ClO_4]_2$. In the protonated form complexes of formula $M_mX_n(LH_2)_{m-n}$ are produced in which the ligand is a monodentate sulphur donor. The metal–ligand bands have almost the same frequencies for both metals; ν(M–N), 288–317 and 272–322; ν(M–S), 191–225 and 176–257; for copper and silver, respectively. Copper has the greater tendency to retain trigonal coordination with non-equivalent copper–halogen bond lengths in the case of bridging halide giving rise to one high and one low ν(Cu–X) frequency. The greater tendency of silver to adopt tetrahedral coordination makes the silver–halogen bands more equivalent giving rise to two very close and usually rather low ν(Ag–X) frequencies. This difference is evident for the $M_mX_n(LH_2)_{m-n}$ complexes which show for copper(I) only the $Cu(I)X_2(LH_2)$ ($X = Cl$, Br) stoichiometry while for silver more complicated species occur.

Reaction between dimolybdenum tetracetate and the sodium salt of me_2pymtH produces $Mo_2(me_2pymt)_4$. The thiolate anion bridges the dinuclear molybdenum group [Mo–Mo = 2.083(2) Å] producing pairs of *trans* sulphur and nitrogen atoms with average distances of 2.449 (Mo–S) and 2.20 Å (Mo–N) [194].

Towards divalent metals [M(II) = Mn, Co, Ni, Cu, Zn, Cd, Hg] me_3pymtH is mostly S,N-chelating. With metal halides a range of complexes are formed: $M(LH)_2X_2$ [M(II) = Mn, Ni, Zn; X = Cl, Br; M(II) = Cd, Hg; X = Cl, Br, I] as well as $Cu(LH)X_2$ (X = Cl, Br); $Ni(LH)_3Br_2$ and $[Co(LH)_3][CoX_4]$ (X = Cl, Br) [185].

Electronic spectra suggest six-coordinate environments for $Ni(LH)_3Br_2$ and the cobalt complexes; X-band EPR spectra suggest a similar environment for manganese. The $Ni(LH)_2X_2$ complexes have halogen-bridged octahedral structures and the copper complexes have *cis*-planar geometry. Metal–halogen frequencies are in the range 220–325 cm^{-1}; ν(M–L) bands occur between 223 and 248 cm^{-1} and contain both ν(M–N) and ν(M–S) contributions. For zinc, cadmium and mercury the position of ν(M–X) (125–269 cm^{-1}) frequencies are intermediate between those expected of tetrahedral and octahedral geometries and suggest distorted $MS_2N_2X_2$ environments.

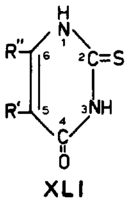
With anions of low coordinating ability tris-chelates are formed; $M(LH)_3X_2$ [M(II) = Mn, Co, Ni, Cu, Zn; X from NO_3, ClO_4, BF_4, I]. The complex cations have a *fac* arrangement of sulphur and nitrogen atoms and the spectral parameters for the cobalt(II) complexes (Dq 1040–1080 cm^{-1}, β 0.80–0.81) are consistent with substantial ligand field strength and only moderate covalent character in the resultant bonds [184].

In the solid state tetrahydropyrimidine-2-thione, H_4pymtH (**XXXIX**), adopts the chair configuration and the thione form [C–S = 1.722(7), C–N = 1.334(6) Å] [195]. Complexes with metal chlorides have the formula $M(LH)_2Cl_2$ (M = Co, Ni, Zn, Cd, Hg). The ligand is reported as sulphur donating on the basis of shifts to ν(C–S), 642 cm^{-1}; δ(C–S), 340 cm^{-1}; and π(C–S) 320 cm^{-1} bands; ν(M–S) bands also occur in the range 230–282 cm^{-1} [196]. Complexes of copper(I) and platinum(II) have been reported with formulae: $Cu(LH)X$ (X = Cl, Br); $Cu(LH)_2X$ (X = Cl, Br) [88]; $Pt(LH)_4Cl_2$, $[Pt(LH)Cl_2]_2$ and $Pt(LH)_2Cl_2$ [97]. The presence of thiol (SH) groups is intimated in the ligand and in both sets of complexes from ^1H NMR spectra with peaks (δ, ppm) in the region 3.27–3.40. Sulphur donation by the ligand is also deduced from ^{13}C NMR spectra on the basis of high-field shifts (δ, ppm) to the thione-carbon atom (176.9, free ligand value) in the range 4–10 ppm. Structural analysis of $Cu(H_4pymtH)_2Cl$ shows a monomeric system with trigonally coordinated copper and dimensions of 2.317(3) (Cu–Cl), 2.206(2) (Cu–S), 1.727(7) Å (C–S) and angles around the copper ranging from 118.3 to 123.4(2)° [197]. The ligand is present in the thione form in the structure which contrasts with the previously mentioned conclusions drawn from ^1H NMR data. The complex also shows a single ^{63}Cu NQR line at two fixed temperatures (77 and 273 K) [197].

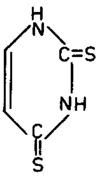
A mixed valence $[Pt(LH)_4][PtCl_6]$ complex is also known which is similar to those reported for other heterocyclic thione ligands (see p. 132) [90].

(x) *Thiouracils and thiocytosines*

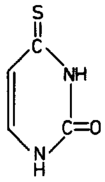
Several tautomeric forms are possible for both thiouracil, **XLI**, **XLII**, **XLIII** and thiocytosine, **XLIV**, **XLV** derivatives.



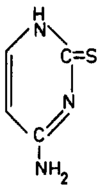
XLI
a: R'=R''=H
b: R'=H, R''=Me



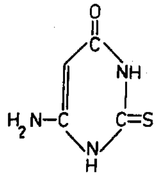
XLII



XLIII



XLIV



XLV

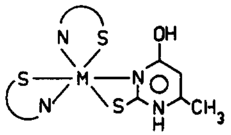
Structural analysis of sodium 5,6-dihydro-2-thiouracil sulphonate monohydrate shows the molecule to be puckered at the C5 and C6 positions and the presence of thione [C–S = 1.673(2) Å] as well as ketone [C–O = 1.220(2) Å] groups [201]. The protonated thiocytosine (**XLIV**) cation is nearly planar and also contains thione [C–S = 1.659(6) Å] and amino groups [C–N = 1.309(6) Å] [202].

Although oxygen appears to be a possible donor atom in some of these molecules coordination invariably involves sulphur and nitrogen in bonding modes ranging from mono to tetradentate together with neutral (LH) as well as anionic (LH^-, L^{2-}) forms of the molecules.

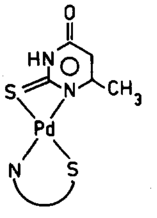
In neutral media 2-thiouracil, $tucH_2$ (**XLIa**), reacts with metal halides MX_2 (M(II) = Mn, Co, Ni, Zn, Cd, Hg; X = Cl, Br, I) producing mostly $M(LH_2)_2X_2$ complexes with the exception of $Co(LH_2)_4X_2$. The ligand is believed to be sulphur donating with octahedral environments proposed for manganese, cobalt and nickel [199]. The addition of solid $tucH_2$ to a solution (0.2 M) of copper(II), followed by recrystallisation in dimethylformamide (dmf) produces $Cu(tucH_2)_2Cl \cdot dmf$. Structural analysis shows an essentially trigonal environment for the metal with monodentate sulphur-donating $tucH_2$ [Cu–S(av) 2.227 Å; Cu–S–C(av) 109.2°] and terminal chlorine [Cu–Cl 2.260(1) Å] [212].

The bulk of the reported complexes however involve the deprotonated ligand (LH^-) with transition metals [Fe(III), Co(II), Ni(II), Cu(II)] [198]; [Rh(III), Pd(II), Pt(IV), Pt(II)] [203] and non-transition metals [Zn(II), Cd(II), Hg(II), Pb(II), Tl(I)] [204]. The complexes are mostly insoluble and polymeric with the ligand invariably S,N-bridging; metal–ligand frequencies are observed between 300 and 400 cm^{-1}. Structural environments have been deduced in some instances from room temperature magnetic measurements and electronic spectra. Nickel(II) is octahedral (μ 3.32 B.M.) with spectral parameters (Dq 926 cm^{-1}; β 0.96) which suggest little covalent contribution to the metal–ligand bond. Cobalt(II) is tetrahedral (μ 4.45 B.M.) and iron(III) is low-spin (μ 2.44 B.M.) octahedral. The copper(II) complex, $[CuL(H_2O)_2]$ involves the dianion and has an unusually low magnetic moment (μ 1.07 B.M.). The heavy metal complexes are diamagnetic and have low Racah (β) values (0.34–0.42).

Heavy metal complexes are formed by (**XLIb**) with $M(LH_2)_3Cl_3$ [M(III) = Rh, Ir] obtained from solutions of the acidified chlorides and $M(LH)_2$ [M(II) = Pd, Pt] obtained from solutions of the deprotonated ligand in ethanol [200]. The ligands are S,N-bidentate with octahedral (Rh, Ir) and square (Pd, Pt) arrangements proposed for the metals. Infrared spectra indicate nitrogen donation from ν(M–N) frequencies at 258 cm^{-1} (Rh) and 260 cm^{-1} (Ir) with sulphur donation deduced from perturbation of the thioamide bands at 1560, 1160, 805 and 650 cm^{-1}. X-ray PES data suggest that a tautomeric rearrangement of the ligand occurs in the octahedral complexes on the basis of a broad (528–534 eV) oxygen (1*s*) peak (**XLVI**). The palladium and platinum complexes involve the thiolate anion (**XLVII**).



XLVI



XLVII

A number of 6-substituted thiouracil derivatives (**XLI**) (R′ = H; R″ = H, Me, C_3H_7, NH_2) form complexes of formula $Cu(LH)_2 \cdot n$ (solvent) [n = 2,3,4(H_2O); 3(CH_3OH)] from copper(II) salts and the ligand in either strongly alkaline (10% NaOH) or methanolic media [205]. The resultant thiolate anion S,N-chelates to copper(II) on the basis of changes to the IR spectrum of the ligand (1800–700 cm^{-1}) upon coordination.

The presence of two thione sulphur atoms, two imido (> NH) groups and the ability to coordinate in neutral (LH_2) as well as anionic (LH^-, L^{2-}) forms poses interesting possibilities for 2,4-dithiouracil, dtucH_2 (**XLII**). The coordination mode of the ligand in its complexes has been determined from shifts to thioamide bands (1565, 1230, 1128, 780 cm^{-1}) and the production of metal–ligand bands in the range 300–425 cm^{-1}. From these observations the ligand is deduced to be tetradentate towards Cd(II), Ni(II), Pb(II) and Ru(II); bidentate towards Co(II), Tl(I), Rh(I), Rh(II), Rh(IIII), Ru(III), Pd(II), Pd(IV), Pt(II) and Pt(IV) as well as tridentate with copper(II) and monodentate with silver(I) and palladium(O) [206–208]. With the exception of $Pd(LH_2)_2(PPh_3)_2$ the complexes are polymeric and insoluble in common organic solvents. The most common form of the coordinated ligand is the S,N-bridging (μ_2) monoanion (LH^-), which is also occasionally S,N,S terdentate (μ_3) bridging; the dianion is tetradentate and bis-(S,N)-bridging (μ_2) while the neutral molecule is sulphur donating. Some complexes combine both neutral and anionic forms of the ligand. Structural assignments have been made on the basis of magnetic and electronic spectral data such as octahedral nickel(II) (μ 2.81 B.M.) and tetragonal copper(II) (μ 1.85 B.M.). Others have uncertain environments such as $Co_4(ligand)_9(H_2O)_2$ which has an unusual magnetic moment (μ 1.44 B.M.). The diamagnetism of rhodium(II) is attributed to strong spin–spin interactions or a superexchange mechanism.

An antiferromagnetic copper(II) complex, $Cu(LH)(OH) \cdot H_2O$, involving the terdentate $dtucH^-$ monoanion, combines S,N-chelation with sulphur and hydroxy bridging of the metal centres [209].

The 2-thiocytosine molecule, tcytH (**XLIV**), is S,N-chelating to copper(II) in $Cu(LH)Cl_2$ and $Cu(LH)_4Cl_2 \cdot 2H_2O$. Very strong antiferromagnetic coupling occurs between the metal centres in both complexes with values for the exchange interaction parameter ($-2J$) in the region of 1400 ± 200 cm^{-1}. Electronic spectra suggest the metals possess D_{4h} [$Cu(LH)Cl_2$] and C_{2v} [$Cu(LH)_4Cl_2 \cdot 2H_2O$] microsymmetries [209].

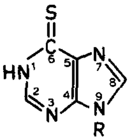
Infrared spectra suggest that (**XLIII**) adopts the form shown and reacts with metals generally as the monoanion (LH^-).

Shifts to the relevant IR bands in the complexes suggest either N,O-chelation [Cd(II), Ag(I), Tl(I)] or S,N-chelation [Ni(II), Co(II), Fe(II), Hg(II), Zn(II), Au(III), Pb(II)] for the monoanion. Tetradentate bridging is proposed for the dianion with copper(II) and lead(II) while the presence of both tetradentate and bidentate species is proposed for zinc(II) and gold(III) [210].

The cytosine derivative (**XLV**) reacts with methyl mercury(I) acetate in aqueous sodium hydrogen carbonate producing MeHg(LH). Structural analysis shows the monoanion (LH^-) bonds strongly to mercury(I) through the sulphur atom [Hg–S = 2.393(4) Å] with a weaker secondary interaction through the deprotonated nitrogen atoms [Hg–N = 2.80(2) Å]. The mercury(I) is linearly coordinated with a S–Hg–Me angle of 178.6(4)° [211].

(xi) Purine-thiones

Complexes of the anionic form of purine-6-thione (**XLVIIIa**) with transition metals have been reported [213–215]. They are amorphous, hydrated materials which are insoluble in common organic solvents. Two types of metal attachment have been proposed involving either N(3)–N(9) or S(6)–N(7) chelation. The former involves a four-membered and the latter a five-membered chelate [214]. The latter arrangement has been established by structural analysis of bis-(6-thionato-9-benzylpurine)palladium(II)-dimethylacetamide solvate [216]; blocking of the 9-position (**XLVIIIb** is done in order to simulate a riboside. The coordination geometry is slightly distorted square planar with pairs of *cis*-sulphur and nitrogen atoms [Pd–S(av) 2.308; Pd–N(av) 2.063 Å]. The angle C(6)–N(1)–C(2) is reduced from about 126° in the free ligand to 117° in the complex confirming deprotonation of the N(1)–H(1) group on coordination [217]. The thione, C–S, distance in the ligand increases from 1.68 to 1.72 Å upon coordination [221].



XLVIII
a: R=H
b: R=benzyl
c: R=methyl

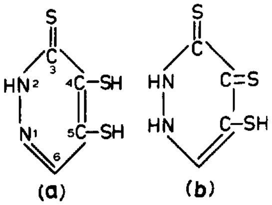
With copper(II) chloride and 6-thione-9-methyl purine (**XLVIIIc**) in hydrochloric acid the complex $Cu(LH)Cl_2 \cdot H_2O$ is produced. Structural analysis shows the copper coordination is square pyramidal. The ligand is S,N-bidentate with average dimensions Cu–S = 2.424 and Cu–N = 1.992 Å; the equatorial plane is completed by two chlorines [Cu–Cl(1) = 2.301(4); Cu–Cl(2) = 2.244(4) Å]. The complex forms centrosymmetrical dimers in which the equatorial chlorine, Cl(1), in one unit, occupies the apical position in an adjacent unit with the resultant Cu–Cl(1′) distance 2.736(6) Å [218]. The thione, C–S, bond is significantly lengthened [1.692(6) Å] upon coordination while the adjacent, C(6)–N(1) [1.357(4) Å] and C(6)–C(5) [1.378(4) Å], bonds are significantly shortened, relative to the corresponding distances in purine-6-thione [221]. The ligand bite is also reduced by about 0.3 Å upon coordination.

A 1 : 1 (ligand–metal) mixture of (**XLVIIIa**) and copper(II) chloride dihydrate in 20% aqueous hydrochloric acid produces a dimeric complex of the protonated ligand (LH_2^+) and copper(I): $Cu_2(LH_2)_2Cl_4$ [220]. The dimeric structure consists of a pair of copper(I) atoms bridged, asymmetrically [Cu–S(av) 2.253, 2.736 Å], by the sulphur atoms of the thiopurines. The tetrahedral environment around each copper atom is complemented by pairs of chlorines [Cu–Cl(av) 2.303 Å] [220].

Reacting hot solutions of copper(II) dichloride dihydrate and purine-8-thione in molar hydrochloric acid produces a $CuCl_2$ ligand adduct. Magnetic measurements showed the oxidation state of the metal to be +I, consequently the ligand is presumably protonated in the complex. Structural analysis shows the complex to be a helical polymer (Cu–Cu = 4.1 Å) with pairs of copper atoms sulphur bridged by the ligand [Cu–S = 2.289(2) and 2.375(2) Å] and the tetrahedral coordination around each metal completed by pairs of chlorine atoms [Cu–Cl = 2.276(2) and 2.423(2) Å] [219]. The C–S distance in the ligand is surprisingly short [1.683(6) Å] and is comparable with the corresponding distance in purine-6-thione (**XLVIIIa**) [221].

(xii) Pyridazine-thiones

The IR spectrum of pyridazine-3,4,5-trithiol contains four thioamide bands (1450–1550, 1310, 1060, 815 cm^{-1}) as well as ν(NH) at 3100 cm^{-1} and dithiol, ν(SH), bands in the region of 2400 cm^{-1} which suggest the presence of both thione and thiol forms of (**XLIXa,b**) in the solid [222].

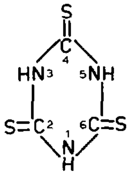


XLIX

Complexes are reported with a number of metals: Co(II), Fe(III), Cr(III) [222]; Pd(0), Pd(II), Rh(I), Rh(III), Ru(II), Ru(III), Pt(II), Pt(IV) [223]; Au(III), Pb(II), Cd(II), Ag(I), Tl(I), Hg(II) [224]. These involve the free molecule $Pd(LH_3)_2(PPh_3)_2$ as well as the anionic forms: $Co(LH_2)_2 \cdot 6H_2O$, Ni(LH) and CrL. Deprotonation is readily achieved in aqueous alcoholic media in the presence of the relevant metal salt. The coordination mode of the various forms of the ligand has been deduced from shifts to relevant IR bands together with metal–ligand bands in the range 350–375 cm^{-1}. Both sulphur and/or nitrogen may be involved in a variety of bridging modes (S,S; S,N; N,N) for these polymeric complexes. Magnetic moments are reported for the first-row metals [Co(II) 2.7; Ni(II) 1.69; Cu(II) 0.7; Fe(III) 4.4; Cr(III) 0.7 B.M.] while the heavy transition metals are diamagnetic. Spin–spin interactions or superexchange phenomena are proposed in order to account for unusually low magnetic moments.

(xiii) 1,3,5-Triazine-2,4,6-trithione

The IR spectrum of (**L**) supports the thione form of the molecule in the solid [225]. Polymeric complexes are formed by addition of an aqueous solution of the metal salt [Cu(II), Cd(II), Hg(II), Pb(II), Pd(II), Ag(I), Bi(III)] to that of the ligand in sodium hydroxide solution (2 M) [226].

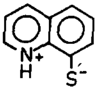


L

It is proposed that the ligand, as the trianion, simultaneously (S,N)-chelates to three separate metal centres. The copper(II) complex is diamagnetic and is, together with the nickel and palladium complexes, semiconducting [226].

(xiv) Quinoline-8-thione

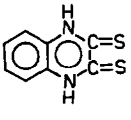
Complexes of quinoline-8-thione have been reviewed previously and S,N-chelation established as the normal mode of coordination [14]. Complexes have subsequently been reported with palladium(II) and dioxomolybdenum(IV) [227] as well as molybdenum(V) and (VI) [228]. It has also been proposed that between pH 4 and 7 the ligand exists in aqueous solution primarily in the zwitterion form (**LI**) [229].



LI

(xv) Quinoxazoline-di-thione

The dithione tautomer (**LII**) is the proposed form of quinoxazoline-2,3-dithione ($qnxtH_2$) [230].



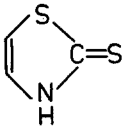
LII

Cobalt complexes, $(n\text{-}Bu_4N)_2[Co(qnxtH_2)]$ and $(n\text{-}Bu_4N)_3[Co(qnxtH_3)]$, are prepared from a solution of the ligand in sodium methoxide–methanol. The cobalt(II) complex is square (μ 2.40 B.M.); the cobalt(III) complex is octahedral and diamagnetic. An iron(III) complex has a magnetic moment of 3.02 B.M. consistent with a spin-triplet ground state and an electronic spectrum indicative of a trigonally distorted octahedral structure [230]; the ligand coordinates as a 1,2-dithiolate anion. Zinc complexes have also been reported, $R_2[ZnL_2]$, where R is a quaternary ammonium salt and the ligand is a nitro substituted quinoxazoline-dithiolate [231].

D. COMPLEXES OF SULPHUR AND NITROGEN CONTAINING HETEROCYCLIC THIONES

(i) Thiazoline-thiones

A normal coordinate analysis of 1,3-thiazoline-2-thione, tztH (**LIII**), and N-deuterated tzt-*d*, produces ν(NH) at 3080 and 3120 cm^{-1}, and extensively coupled (CH), (CN) and (CS) vibrational activity [232].

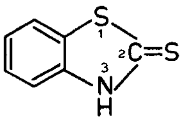


LIII

The molecule forms $M(LH)_2Cl_2$ complexes with nickel and mercury as well as $M(LH)Cl_2$ complexes with copper and cadmium. Largely on the basis of shifts in ν(NH) vibrational activity, monodentate nitrogen donation is proposed for cadmium and sulphur donation for the remaining metals [232].

(ii) Benzo-1,3-thiazoline-2-thione

The thione nature of benzothiazoline-2-thione, bztzH (**LIV**), in the solid has been established by structural analysis (Table 1) [233]. X-ray PES has also shown the presence of two different types of sulphur atom in bztztH with electron core binding energies for $2p_{3/2}$ electrons of 164.5 eV (thione) and 162.3 eV (thioether) [234].



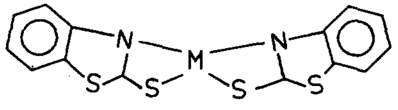
LIV

The presence of thiol-(SH) (δ, 1.95 ppm) and imido (NH) nitrogen (δ, 10.20 ppm) has been demonstrated for bztztH in solution by ^{1}H NMR studies. The effect of pH on the coordination properties of the molecule has also been studied. In acid media complexes of type $M(LH)_2X_2$ (M = Pd, Pt; X = Cl, I) are formed. Nitrogen-donating ligands are proposed on the basis of ν(M–N) bands between 257 and 290 cm^{-1}. Location of thiol (SH) groups (δ, 2.10 ppm) in the complexed molecules suggests nitrogen donation is facilitated by proton migration. In basic media ML_2 (M = Pd, Pt) complexes are formed and are described as polymeric with bridging thiolate anions [67]. Reactions between bztztH and heavy metals in acid media have produced $M(LH)_2Cl_2$ (M = Pd, Pt) and $M(LH)_2Cl_3$ (M = Rh, Ru, Ir) as well as $Pt(LH)_4Cl_2$ and $Pt(LH)_2Br_2$. Proton NMR has shown that the molecule exists in the thione form in the free molecule, with the location of the –NH signal (δ = 3.59 ppm), and as the thiol form in the complexes on the basis of (–SH) signals in the region of 2.07 ppm (δ). The complexes all contain nitrogen-donating ligands [244].

Complexes of the benzothiazolate anion, bztzt (L^-), have received the most attention. With a pK_a of 6.9 [247] bztztH is readily deprotonated by reacting the molecule with a metal salt in aqueous alcoholic media. Alternatively, an aqueous solution of the ligand is neutralised with aqueous alkali prior to reaction with the metal salt. The resultant complexes are invariably insoluble in water but slightly soluble in organic solvents. Stoichiometries have been established for metals in the following oxidation states: +1 (M = Cu, Ag, Tl), +2 (M = Mn, Co, Ni, Cu, Zn, Cd, Pb, Rh, Pd, Pt) and +3 (M = Pr, Nd, Sm, Gd, Dy, Er, Th, Ru).

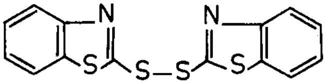
Coordination has been deduced on the basis of shifts to thioamide bands (1490, 1320, 1010, 860 cm^{-1}) [237], as well as ν(C–S) at 667 cm^{-1} [235], and the production of ν(M–N) and ν(M–S) bands in the range 230–284 and 315–382 cm^{-1}, respectively [235]. Chemical shifts to N(1s) and S($2p_{3/2}$) electron core binding energies have also been used [234]. In HgL_2, PbL_2, AgL and CuL_3H_2Cl the ligand is sulphur donating. In CuL, CuL_2 and ML_2 (M = Ni, Pd, Pt, Cd) complexes both sulphur and nitrogen donation occurs. All copper complexes are in the +1 state. Chemical shifts are of the order of 0.2–0.9 eV for the thione sulphur and 0.5–0.9 eV for the nitrogen atom [234].

Most authors describe the anion as S,N-bridging, however S,N-chelation has also been proposed for the *cis*-square nickel, palladium and platinum complexes (ML_2) (LV) [235], as well as for the halogen-bridged dimer,



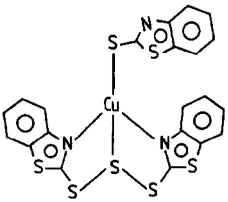
LV

$[Co(L)Cl]_2$, which also contains tetrahedral cobalt (μ 4.40 B.M.) [238]. Tetrahedral cobalt is indicated for [Co(L)Cl] (μ 4.49 B.M.) [237] and either square or tetrahedral for CoL_2 (μ 2.5–3.4 B.M.) [236]. Nickel complexes, NiL_2, are either diamagnetic and square [235,237,238] or paramagnetic (μ 2.75 B.M.) and octahedral [236]. Tetrahedral geometries are presumed for cadmium, zinc and lead, (ML_2), [237] and linear for silver, (AgL) [235,237]. A number of copper complexes have been reported. Yellow insoluble CuL is obtained from copper(I) chloride and bztztH in hydrochloric acid. The complex contains copper(I) and is polymeric with the ligand sulphur bridging [245]. Orange CuL_2, obtained from copper(II) chloride and bztztH in aqueous alcohol, is diamagnetic over the temperature range 89–303 K and contains copper(I) [235]. Yellow diamagnetic CuL_2 is described as a copper(II) complex with the diamagnetism attributed to spin–spin interactions [236–238]; a polymeric structure is proposed with the metal coordinated by pairs of *trans* thione sulphur and heterocyclic nitrogen atoms. Both $Cu_2L_3H_2Cl$ [234] and $[CuL_2]L\text{–}L$ [235] contain copper(I) with part of the ligand in the oxidised form (L–L) [bis(benzothiazol-2-yl)disulphide] (**LVI**).



LVI

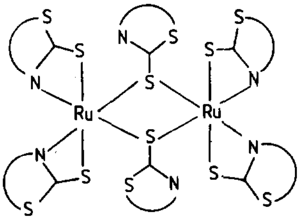
The compound $[Cu(bztztH)(bztzt\text{-}S\text{-}bztzt)](ClO_4)\cdot 2CHCl_3$ is prepared from bztztH and solid hydrated copper perchlorate in methanol. Structural analysis shows the metal to be tetrahedrally coordinated by a thione sulphur from a bztztH molecule [Cu–S, 2.221(4) Å], by two nitrogen atoms [Cu–N, 2.04(1); 2.01(1) Å], and an additional sulphur atom [Cu–S, 2.486(4) Å] from an oxidised form of the ligand, (bztzt-S-bztzt) [240], (**LVII**).



LVII

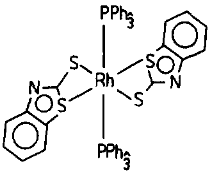
Adapted from Ref. 240

The complex $[Ru(bztzt)_3]$ is dimeric in chloroform, contains weakly paramagnetic octahedral and metal–metal bonded ruthenium(III) together with both S,N-chelating and sulphur-bridging ligands [175] (**LVIII**). The presence of ν(Rh–S) at 319(ν_s) and 408 cm^{-1} (ν_{as}) suggests that $[Rh(bztzt)_2(PPh_3)_2]BF_4$ contains octahedral rhodium(III) *trans* S,S-chelating ligands and apical phosphines [173] (**LIX**).



LVIII

Adapted from Ref. 175



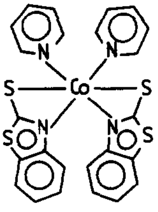
LIX

Adapted from Ref. 173

With lanthanides [M(III) = Pr, Nd, Sm, Gd, Dy, Er, Tm] the complexes are formulated $MLCl_2$ and the thiolate anion is presumed to be monodentate sulphur donating [246].

Cleavage of bridging ligands in polymeric complexes containing the bztzt⁻ anion may be achieved by reacting the appropriate complex with a variety of heterocyclic bases. Reaction between $Cu(bztzt)_2$ and pyridine produces a dimeric blue complex, $[Cu(bztzt)_2(bztztH)py]_2$, which contains paramagnetic copper(II) (μ 2.07 B.M; g_{av} 2.06). Five-coordinate copper(II) with sulphur-donating anions in terminal positions, neutral molecules in bridging environments as well as apical pyridine are proposed for this complex [238].

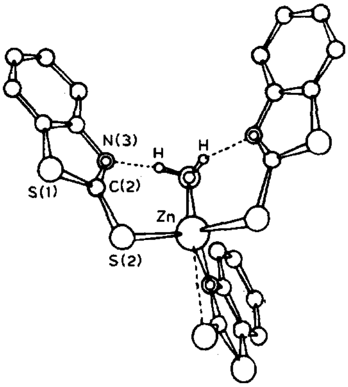
Pyridine adducts, ML_2py_2, are also formed from $M(bztzt)_2$ (M = Co, Ni). Structural analysis shows the cobalt atom is coordinated by two *cis*-thiazole nitrogens [Co–Ni, 2.156(4) Å], two *trans*-thione sulphurs [Co–S, 2.585(4) Å] and two *cis*-pyridine nitrogens (Co–N, 2.127(4) Å). The thioamide portion of the bztzt⁻ anion may be regarded as 'allylic' in character with L–Co–L angles in the range 95–129°. The electronic spectrum of the complex is consistent with octahedral cobalt(II); the nickel and cobalt complexes are isostructural [239] (**LX**).



LX Adapted from Ref. 239

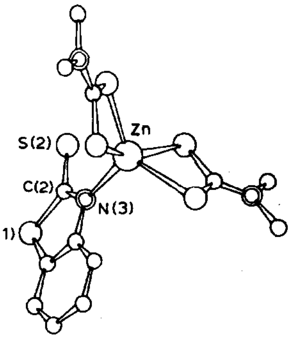
A sequence of reactions related to the inorganic chemistry of rubber vulcanisation has produced a variety of zinc and cadmium complexes containing the bztzt⁻ anion, some of which have been thoroughly characterised by crystallographic methods.

$[n\text{-}Bu_4N][Zn(bztzt)_3]H_2O$ (**LXI**) contains two sulphur-donating bztzt ions [Zn–S (av) 2.338 Å] which also form intramolecular hydrogen bonds with a coordinated water molecule. The remaining anion forms a Zn–N bond [2.019(4) Å] and a weak Zn–S [3.125(2) Å] bond. The zinc atom has a tetrahedrally distorted trigonal bipyramidal geometry [241,242,59]. [*n*-Bu_4N][$Zn(S_2CNMe_2)_2$(bztzt)]EtOH (**LXII**) contains, in addition to two bidentate dithiocarbamate anions, one nitrogen-donating [Zn–N, 2.061(8) Å] bztzt anion. The coordination geometry of the zinc atom is a rectangular based pyramid [59]. [*n*-Bu_4N] [$Zn(S_2CNMe_2)$(bztzt)$_2$] (**LXIII**) contains two nitrogen-donating bztzt anions [Zn–N (av) 1.997 Å] and a bidentate dithiocarbamate anion. The zinc atom has a distorted tetrahedral environment [59]. In [NEt_4][Cd(bztzt)$_3$] (**LXIV**) the complex anion contains three-fold crystallographic symmetry with each heterocyclic anion bonded to the metal through sulphur [Cd–S, 2.667(6) Å] and nitrogen [Cd–N, 2.474(11) Å]. The small bite of the thioamide linkage leads to a slight distortion (25.8°) from trigonal prismatic to octahedral geometry [243]. The presence of a more regular arrangement of ligands around cadmium than is observed for zinc is attributed to the greater size of the former.



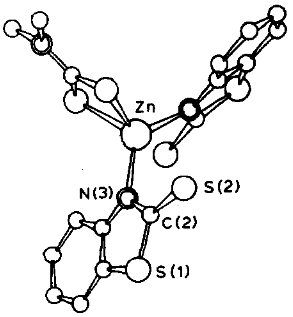
LXI

Adapted from Ref. 59



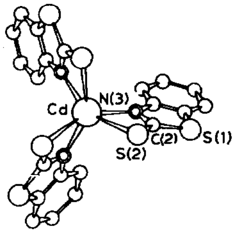
LXII

Adapted from Ref. 59



LXIII

Adapted from Ref. 59

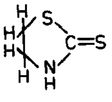


LXIV

Adapted from Ref. 243

(iii) 1,3-Thiazolidine-2-thione

The thione nature of 1,3-thiazolidine-2-thione, tzdtH (**LXV**), has been established by a crystallographic study (Table 1) [263].



LXV

Normal coordinate analysis of tzdtH as well as its N-monodeuterated [257] and selenated derivatives [267] has provided an assignment of their IR spectra. The ν(NH) band occurs at 3420 cm^{-1} in chloroform and at 3130 cm^{-1} in the solid. The ν(CN) activity occurs in the region 1000–1510 cm^{-1} and the ν(CS) vibrations occur between 700 and 1100 cm^{-1}; low frequency (CS) activity is reported between 300 and 600 cm^{-1}. Four thioamide bands are reported at 1490, 1245, 990 and 690–650 cm^{-1} [262].

Proton NMR has produced chemical shifts (δ) consistent with imido (NH) nitrogen (10.00 ppm), methylenic carbon atoms (3.60, 3.90 ppm)

TABLE 9

Complexes of N-donating 1,3-thiazolidine-2-thione

Metal	Stoichiometry (metal: ligand)	Proposed Structure	Magnetic and spectral data				Ref.
			μ	Dq	β	ν(M–N)	
Sn(IV)	1:2	octahedral	dia.			380	248
Ti(IV)	1:2	octahedral	dia.			382	248
Sb(III)		distorted				250	
Bi(III)	1:2	square-pyramidal	dia.			to 430	164
Mn(II)	1:4	octahedral	5.9–6.0	536–657		213–215	249
	1:4	tetrahedral	5.8	678		210	249
	1:2	tetrahedral	5.9	to		to	249
	$[1:1]_n$	polymeric tetrahedral	5.5	787		212	249
Cr(III)	1:3	octahedral	3.9–4.2	1390–1430	0.62–0.64	225–238	160
Fe(II)	1:2	tetrahedral	4.6–5.2			330–380	250
	1:3	tetrahedral	5.2			220	250
	1:4	tetrahedral	5.6			to	
	1:6	octahedral	5.7			230	250

TABLE 9 (continued)

Metal	Stoichiometry (metal : ligand)	Proposed Structure	Magnetic and spectral data				Ref.
			μ	Dq	β	ν(M–N)	
Fe(III)	1 : 2	tetrahedral					250
	1 : 3	tetrahedral	5.9			230	250
	1 : 4	octahedral				to	250
	1 : 6	octahedral	5.8			235	250
Co(II)	1 : 2	tetrahedral	4.67– 5.01	326– 466	0.60– 0.86	326– 341	251, 252 162,126,86
	1 : 4	tetrahedral	4.50– 4.98	338– 476	0.60– 0.78	172– 375	251,252,162
	1 : 2	polymeric octahedral	4.87– 5.46	850– 940	0.88– 0.99	207– 260	258
	1 : 4	octahedral	5.0	891	0.98	219	252
Ni(II)	1 : 2	tetrahedral	3.5	566	0.48	219	252
	1 : 4	tetrahedral	3.3	478	0.74	220	162
	1 : 2	polymeric octahedral	3.15– 3.32	911– 980	0.76– 0.93	209– 245	126,258
	1 : 4	octahedral	3.40	932	0.85	218	252,86
	1 : 6	octahedral	3.30	850	0.87	215	162
	1 : 2	square	dia.	$\Delta_I = 19470$		228	162
Cu(I)	1 : 1		dia.			315	162
	1 : 3		dia.			306– 329	162,253
Ag(I)	1 : 1		dia.				139
Zn(II), Cd(II) Hg(II)	1 : 2	tetrahedral	dia.			170– 268(Zn) 136–320(Cd) 147–148(Hg)	254,255,257
Zn(II), Cd(II)	1 : 4	tetrahedral	dia.			165– 172	252
Pd(II), Pt(II)	1 : 2,3,4		dia.			217– 239	253
Pt(II)	1 : 2	*cis*-square	dia.			252,262	255
Pd(II)	1 : 2	*trans*-square	dia.			190,232	255
Pt(II)	1 : 4	square	dia.			236	255
Ru(III)	1 : 3	*mer*- octahedral	1.8– 2.0	2465– 2760		250– 280	256
Os(III)	1 : 3	*mer*- octahedral	1.8– 1.9	2500– 2905		250– 285	256
Ir(III)	1 : 3	*mer*- octahedral	dia.	$[\Delta = 34400]$	0.33	216– 274	256
Rh(III)	1 : 3	octahedral	dia.	$[\Delta = 27000]$	0.64		256
Rh(III)	1 : 4						67
Rh(I)	1 : 3	octahedral	dia.				67

[253,255] and thiol (SH) sulphur at 1.8 ppm, which suggests both thione and thiol forms exist in solution [67].

Complexes are reported for many elements in which the molecule donates either through the imido (NH) nitrogen or thione sulphur atoms; the monoanion, tzdt$^-$, forms S,N-bridges.

Some properties of complexes containing nitrogen-donating tzdtH are summarised in Table 9. The imido (NH) donating character of tzdtH is invariably diagnosed from the IR spectrum of the relevant complex by virtue of shifts to ν(NH)- and ν(CN)-containing absorptions. Typically [160], the ν(NH) band is sharp in the complexes and shows a negative shift in the region of 300 cm^{-1} relative to the value in solution. The thioamide(I) band shows slight positive shifts while the ν(C–S) bands are unaffected by coordination. These observations are supported by ν(M–N) bands in the range 136–430 cm^{-1} although the bulk of the absorptions for M(II) species occur in the region 200–260 cm^{-1}. Ligand field parameters show the production of moderate field strengths for first row transition metals whose complexes are invariably high spin although a diamagnetic complex of nickel(II) is also reported. The Racah, B′, parameter is usually 60–80% of the free-ion value for tetrahedral complexes with the exception of a tetrahedral nickel(II) complex for which a value of 0.48 is reported [252]; for octahedral complexes the β values are within 76.0–93.0% of the free-ion values with the exception of chromium(III) whose values (62.0–64.0%) are outside this range [160].

Some structural assignments have been proposed on the basis of either electronic or IR spectra; these are also summarised in Table 9.

Among the heavier metals tetrahedral structures are proposed for cadmium and mercury; square for palladium and platinum and *mer*-octahedral for ruthenium, osmium, iridium and rhodium; low-spin configurations are also observed among the octahedral complexes. Proton NMR measurements show the presence of (NH) in both the free ligand (δ, 10.05 ppm) and the octahedral (Ru, Os, Ir, Rh) complexes with a low-field shift (δ, 12.00 ppm) upon coordination [256]. Nitrogen donation, at least among some of the heavy metals, has been rationalised on the basis of migration of the labile proton from the nitrogen to the exocyclic sulphur atom after reaction with the metal. This is supported by the absence of ν(NH) in the IR spectra of the complexes and by the appearance of δ(SH) (ca. 2.0 ppm) in their ^{1}H NMR spectra [67].

Coordination of tzdtH by means of its thione sulphur occurs with a variety of metals but the range of complexes is significantly less extensive than that reported for (imido) nitrogen donation.

Sulphur donation is typically deduced from the IR spectra of the complexes in which the ν(NH) band usually occurs between 3100 and 3170

cm^{-1}; the ν(CS) band in the 600–700 cm^{-1} region is lowered by 40–50 cm^{-1} and ν(M–S) bands occur between 300 and 400 cm^{-1} [257,259].

Complexes of type $M(LH)_2X_2$ are formed with cobalt(II) (X = Cl, Br, I), nickel(II) (X = Cl, Br, I) [259] as well as $Cu(LH)_2Cl_2$ and $Hg(LH)_2Cl_2$ [257]. Pseudo-tetrahedral structures are proposed for the cobalt complexes as well as $Ni(LH)_2I_2$ and polymeric octahedral forms for the remaining nickel complexes on the basis of electronic spectra. Ligand field parameters give *Dq* values in the range 360–460 cm^{-1} for the tetrahedral and 810–830 cm^{-1} for the octahedral fields with the free-ion Racah parameter (B) reduced by between 62.0 and 73.0% in tetrahedral and 86.0 to 90.0% in octahedral fields [259]. Copper chemistry has received a great deal of attention with both Cu(I), $Cu(LH)_3X$ (X = Cl, Br, I, NO_3, $\frac{1}{2}SO_4$, BF_4) [253,56,268], $Cu(LH)_2X$ (X = Cl, Br) [268] and a copper(II) complex, $Cu(LH)_2Cl_2$ [257,265] reported. The copper(I) complexes are yellow diamagnetic species for which trigonal structures are proposed. The copper(II) complex has an octahedral halogen-bridged structure; a combination of variable temperature (126.6–293.8 K) magnetic measurements and EPR data indicate the possibility of exchange interactions in the solid. In addition to a downward shift in the ν(CS) band in the complex a ν(Cu–S) band at 390 cm^{-1} confirms the sulphur-donating character of the ligand [265].

An alkyl-substituted derivative of tzdtH produces only copper(I) complexes, Cu(LH)X (X = Cl, Br), as well as mixed complexes with the parent heterocycle [266]; a detailed analysis of the IR spectrum of *N*-methyl thiazolidine-2-thione has also been reported [269].

The crystal structure of $Pd(tzdtH)_4Cl_2$ consists of square $Pd(LH)_4^{2+}$ units with the ligand sulphur-donating [Pd–S (av) 2.325 Å] [264].

In alkaline media the deprotonated thiolate anion, $tzdt^-$, forms complexes of formulae ML_2 [M(II) = Zn, Cd, Hg, Co, Ni, Pd, Pt, Au, Mn], ML [M(I) = Cu, Ag] and IrL_3 [262]. The involvement of both the thiolate sulphur and heterocyclic nitrogen in complex formation is indicated by the presence of ν(M–N) and ν(M–S) in their respective ranges; 185–313 and 240–380 cm^{-1}.

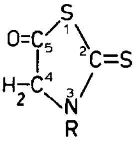
In general, the formation of four-membered chelates is rejected in favour of S,N-bridging and polymeric structures for these complexes. Magnetic measurements and electronic spectral data suggest a tetrahedral environment for cobalt(II) (*Dq* 436 cm^{-1}, β 0.74); square planar environments are suggested for nickel(II), palladium(II) and platinum(II) with octahedral for iridium(III) and manganese(II). In a reaction with copper(II) it has been proposed that tzdtH changes to the thiol form in solution prior to bonding through the thiolate sulphur together with either heterocyclic nitrogen or sulphur. The resultant complex, $Cu(tzdt)_2$, contains +2 copper and has a room temperature magnetic moment of 0.79 B.M. [261]. A diamagnetic complex of +1 copper is also reported [262].

Chelation with tellurium(II) is suggested on the basis of ν(Te–S) at 201–245 cm^{-1} and ν(Te–N) at 300–376 cm^{-1} [260].

Anionic complexes $[PtL_2Cl_2]^{2-}$, $[PtL_4]^2$ and $[RhL_4Cl_2]^{3-}$ are reported to contain monodentate sulphur-donating thiolate anions [67].

(iv) 1,3-Thiazolidine-2-thione-5-one

The thione form of (**LXVI**), commonly known as rhodanine (rdtH), has been established by X-ray methods as the dominant solid-state tautomer [270]. A number of coordination sites are available which may be further modified by substitution at the 3-position notably by methyl (merdt), allyl (allrdt), phenyl (phrdt) and amino (amrdt) groups. Potentiometric titrations have shown rdtH to be a weak acid with a pK_a value in the region of 5.2 [275].

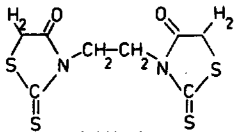


LXVI

With copper(I), rdtH and its 3-alkyl derivatives (R = Me, *n*-Bu) form complexes of formula $Cu(LH)_nX$ ($n = 1,2,3; X = Cl, Br, I$) in acid media. The presence of ν(Cu–S) in the region of 300 cm^{-1} suggests thione sulphur donation by the ligands; this is supported by a ^1H NMR study which shows the thione form of the ligands to be retained in the complexes. Polymeric structures are proposed for these insoluble complexes [274], which is supported by the crystal structure of Cu(merdtH)I.

This complex contains a chain of copper atoms [Cu–Cu(av) 2.984 Å] connected by bridging iodine [Cu–I(av), 2.658 Å]. Each copper is tetrahedrally coordinated by three iodine atoms and one thione sulphur [Cu–S, 2.301(3) Å] [272]. Polymeric complexes are also formed with 5-methylrhodanine and copper(I) in acid media: Cu(LH)I, $Cu(LH)_2Br$ and $Cu_3(LH)_4Cl_3$. Thione sulphur donation is proposed on the basis of ν(Cu–S) in the region of 300 cm^{-1} [276]. Infrared spectra of the complexes, M(allrdtH)Cl [M = Cu(I), Pd(II), Pt(IV)], suggest that the metal is bonded by both the thione sulphur and the olefinic double bond of the ligand [276]. Silver(I) complexes, $Ag(rdtH)_3Cl_2$ and Ag(rdtH)Cl, are reported to be formed in strong acid (6 M HCl) [274]. Ethylene bis rhodanine (**LXVII**) (enrdt), and the related butylene derivative are possibly bidentate with palladium(II) and platinum(II) [276].

A large negative shift in the ν(CO) absorption of the complexed ligands in $Pt(LH)(PPh_3)_2$ (LH = rdtH, merdt, enrdt) is equated with ring opening due



LXVII

to fission of the C(2)–S(1) bond and the production of Pt(II) complexes with the resultant S,S-chelating anion, $SCNROCOCH_2S^{2-}$ [271]. The complex $RuCl_3(merdt)_2 \cdot H_2O$ is insoluble in common organic solvents which suggests a dimeric or polymeric structure. The room temperature magnetic moment (μ 2.1 B.M.) is normal for low-spin ruthenium(III) [271]. The mercury complexes, $Hg(rdtH)X_2$ (X = Cl, Br) and $Hg(merdt)Br_2$, contain ν(Hg–S) in the region of 350 cm^{-1} and thione sulphur-donating ligands [271].

In acid solution (M · HX) (X = Cl, Br, I), substituted rhodanines form complexes of formula $M(LH)_2X_2$ (M = Pd, Pt; LH = merdt, burdt, phrdt; X = Cl, Br, I). Infrared spectra show ν(M–X) (215–335 cm^{-1}) and ν(M–S) (300–388 cm^{-1}) frequencies which are consistent with *cis*-isomers and thione sulphur-donating ligands [277].

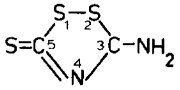
With K_2MCl_4 (M = Pd, Pt) and rdtH in ethanol, insoluble polymeric complexes, $M(rdt)_2$, are produced. The absence of ν(NH), lowering of the (CS) vibrations (1080–1235 cm^{-1}) and the production of ν(M–S) (300–370 cm^{-1}) in the IR spectra of the complexes suggest that the thiolate anion is S,N-coordinating, although no ν(M–N) activity was detected [277]. Potentiometric titrations of silver(I) with rdtH in acidified and non-acidified media have produced 1 : 1 complexes containing the deprotonated anion. A polymeric structure is proposed for the complex with S,N-bridging ligands [275]. Similar behaviour is reported for 2-thiohydantoin and pyrrolidine-2-thione [275].

Complexes of *N*-amino rhodanine (**LXVI**) ($R = NH_2$) are formulated: ML_2X_2 (M = Co, X = Cl, I; M = Ni, X = Cl, Br); $ML_{2.5}X_2$ (M = Co, X = Br(H_2O); M = Ni, X = I); $ML_3(ClO_4)_2$ (M = Co, Cu); $NiL_4(ClO_4)_2$; $CuLX_2$ (X = Cl, Br). Infrared spectra contain ν(M–S) and ν(M–N) in the ranges 329–296 and 404–512 cm^{-1}, respectively and suggest that coordination involves amino nitrogen and thione sulphur. Electronic spectra suggest distorted octahedral environments for cobalt(II) (*Dq* 910–916 cm^{-1}; β 0.71–0.88) as well as tetragonal nickel(II) and copper(II) [273].

(v) 1,2,4-Dithiazoline-3-amino-5-thione

1,2,4-Dithiazoline-3-amino-5-thione (**LXVIII**), also known as xanthan hydride and isoperthiocyanic acid, forms *cis*-square planar complexes with platinum(II) and palladium(II) $[M(LH)_2Cl_2]$. The copper(I) complex,

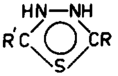
$Cu(LH)_2Cl$, contains halogen-bridged tetrahedral species. X-ray PES data distinguish between the two types of sulphur atom on the basis of their ($2p_{3/2}$) binding energies with thioether at 164.3 eV and thione at 162.3 eV. The thioethereal sulphur binding energies are unchanged in the complexes but those of the thione sulphur show positive shifts (0.6–0.9 eV) thus confirming the donor atom [278].



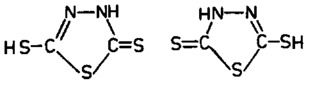
LXVIII

(vi) 1,3,4-Thiadiazoline-thiones

Several thione-substituted 1,3,4-thiadiazoles are known to form complexes. The 2,5-dithione (Bismuthiol I) derivative, $tdzt_2H_2$ (**LXIXc**), and its *N*(3)-phenyl substituted derivative (Bismuthiol II), $phtdzt_2H$, are probably the best known ligands due to their use as analytical reagents [281].



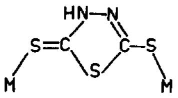
LXIX
a: R'=Me, R=S
b: R'=S, R=NH$_2$
c: R'=R=S



LXX

Several forms of $tdzt_2H_2$ are possible involving various combinations of thione and thiol tautomers. The presence of both ν(NH) (2860–3060 cm^{-1}) and ν(SH) (2470 cm^{-1}) in the infrared suggests (**LXX**) to be the most likely combination in the solid [279,280]. In solution, the electronic spectra of $tdzt_2H_2$ and its derivatives support the existence of the di-thione (**LXIXc**) [285]. The four thioamide bands are reported at 1200, 1265, 1050 and 940 cm^{-1} [279].

Complexes of formula $M(LH_2)_2(PPh_3)_2$ [M(O) = Pd, Pt] are produced from $tdzt_2H_2$ and the appropriate metal phosphine in benzene. The presence of ν(M–N) in the region of 400 cm^{-1} suggests the molecule to be monodentate nitrogen donating and present in the (**LXX**) form in these monomeric complexes [280].



LXXI

The readily deprotonated $tdzt_2H_2$ molecule reacts with a wide range of elements either as the free molecule or its mono-potassium salt producing

TABLE 10

Complexes of 1,3,4-thiadiazoline-3-thiolate-5-thione

Metal	Stoichiometry (metal : ligand)	Proposed structure	Magnetic and spectroscopic data			Ref.
			μ	ν(M–N)	ν(M–S)	
Cu(I), Ag(I), Tl(I)	1 : 1	linear	dia.		350	280
Cu(I)	1 : 1		dia.			284
Cu(II)/Cu(I)	1 : 1		0.92	540	380	283
Zn(II),Cd(II),Pb(II)	1 : 2	tetrahedral	dia.		350	280
Co(II)	1 : 2	square	2.74		338	281
		tetrahedral	4.3		385	282
Ni(II)	1 : 2	square	1.40		330	281
	1 : 2	octahedral	3.5		370	282
Cu(II)	1 : 2	square	0.38		380	282
Zn(II)	1 : 1	tetrahedral	dia.		390	282
Zn(II),Cd(II),Hg(II)	1 : 2	tetrahedral	dia	540	332	281
Pd(II), Pt(II)	1 : 2	octahedral	dia		350	279
Ru(III), Rh(III)	1 : 2	octahedral	dia.		350	279
Ru(II)	1 : 2	octahedral	dia.		350	279
Ir(III)	1 : 3	octahedral	dia.		350	279

largely insoluble polymeric species (Table 10). The monoanion (LH$^-$) is present in these complexes and is characterised in the infrared by the absence of ν(SH) and the presence of ν(CN) (1440–1470 cm^{-1}), ν(CS) (1020–1050 cm^{-1}) and ν(NH) (2800–3300 cm^{-1}) [281]. The anion normally uses both of its exocyclic thione sulphur atoms in the formation of S,S-bridges (**LXXI**), which are characterised by a combination of negative shifts to the ν(CS) bands and the production of ν(M–S) bands (330–390 cm^{-1}) (Table 10). S,N-bridging has been proposed for the zinc, cadmium and mercury complexes largely on the basis of the presence of ν(M–N) and ν(M–S) (Table 10).

Structural evidence is sparse for these polymeric materials. Square planar [CoS$_4$] species are proposed on the basis of the room temperature magnetic moment, the electronic spectrum being inconclusive [281]. Square planar NiS$_4$ species are deduced from the electronic spectra; the magnetic moment (μ 1.40 B.M.) however is anomalous [281]. Tetrahedral cobalt(II) and octahedral nickel(II) are also proposed on the basis of typical magnetic moments (Table 10) and electronic spectra [282]. Both diamagnetic copper(I) [280,284] and paramagnetic copper(II) [282,283] are proposed; lowering of the magnetic moment in the latter is ascribed to superexchange phenomena [282] or to mixed valence complexes [283]. Tetrahedral zinc and cadmium complexes may contain either S,S-bridging [280] or S,N-bridging ligands

[282]. Octahedral environments dominate the heavier transition metals with the ligand S,S-bridging. Diamagnetism in the ruthenium(III) complex is due to the occurrence of superexchange phenomena operating through ruthenium–chlorine bridges [279]. Ligand field (Dq, cm^{-1}) values are in the range 2500–2778 and Racah (β) parameters range from 0.21 to 0.45 [279].

Complexes of $phtdzt_2H$ invariably involve the monoanion (L^-) and are formulated ML_2 [M(II) = Co, Ni, Cu, Cd, Zn] [282]. There are also insoluble polymeric species in which the presence of ν(M–S) in the region 375 ± 15 cm^{-1} suggests S,S-bridging by means of the thione sulphur atoms. Magnetic measurements suggest tetrahedral cobalt(II) (μ 4.58 B.M.) and octahedral nickel(II) (μ 3.20 B.M.). The low magnetic moment (μ 0.58 B.M.) in the copper(II) complex is ascribed to either metal–metal bonding or superexchange phenomena; the metal has a square environment. Another copper complex is diamagnetic and contains equivalent amounts of Cu_2L_2 and an insoluble disulphide $(C_8H_5N_2S_3)_2$ [284].

Complexes are formed between tin [287]; zinc, cadmium and mercury [288]; cobalt, nickel and copper [286] and 1,3,4-thiadiazole-2-methyl-5-thione, metdztH (**LXIXa**). Infrared spectra of the deuterated derivative suggest that the thione tautomer occurs in the solid [287].

Cobalt(II) complexes, $[Co(LH)_2X_2$, (X = Cl, Br, I)], have pseudo-tetrahedral structures (μ 4.40–4.48 B.M.; Dq 342–382 cm^{-1}; β 0.62–0.70) in which the ligand is monodentate thione sulphur donating [ν(Co–S) 270–297 cm^{-1}].

Nickel(II) complexes, $[Ni(LH)X_2$, X = Cl, Br], are polymeric with the metal in tetragonal (μ 3.08–3.34) environments (Dq 722–765 cm^{-1}; β 0.73–0.78). The ligand is S,N-bridging with ν(Ni–S) at 280–298 cm^{-1} and ν(M–N) at 218–220 cm^{-1}. Both copper(I) $[Cu(LH)_2X$, X = Cl, Br, $ClO_4]$ and copper(II) $[Cu_3(LH)_4Cl_6$, $Cu_5(LH)_6Br_{10}]$ complexes are reported. The former have asymmetric halogen-bridged structures with the ligand thione sulphur donating [ν(Cu–S) 300 cm^{-1}]. The latter are polymeric with either tetrahedral (chloro) or octahedral (bromo) metal sites and nitrogen-donating ligands [ν(Cu–N) 217–280 cm^{-1}].

The zinc(II), cadmium(II) and mercury(II) complexes of metdztH are formulated: $M(LH)_2X_2$ (M = Zn, X = Cl, Br, I; M = Cd, Hg, X = Cl, Br); ML_2 (M = Zn, Cd); $CdL_2 \cdot LH \cdot NH_3$; $HgL \cdot NO_3$; $HgL_2(LH)$; $HgL_2 \cdot NH_3$.

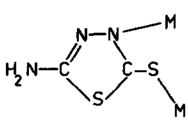
In the $M(LH)_2X_2$ complexes the ligand is thione sulphur donating to the metal with ν(M–S) in the range 184–300 cm^{-1} (Zn), 270–290 (Cd) and 300–390 (Hg). Tetrahedral environments are proposed for zinc and mercury and octahedral for cadmium. The remaining complexes contain the deprotonated thiolate S,N-bridging anion.

The tin(IV) complexes $Sn(LH)_2X_4$ (X = Cl, Br) are *trans*-octahedral with the ligand coordinated through the unprotonated ring nitrogen atoms.

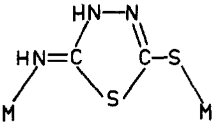
X-ray analysis has shown that the amino-thione form of 1,3,4-thiadiazole-5-amino-2-thione (amtdztH) is the dominant tautomer in the solid (**LXIXb**) [292].

The solid state IR spectrum of amtdztH is complicated by the presence of several contributions to the usual thioamide bands (Table 2) as well as to ν(NH). In solution however ν(SH) is reported (2570 cm^{-1}) [289].

The neutral thiol form of amtdztH is a monodentate heterocyclic nitrogen donor ν(M–N) ca. 400 cm^{-1} with rhodium(I) [290] palladium(0) and platinum(0) [291]. The majority of the complexes however are insoluble polymeric materials which contain the deprotonated (L$^-$) ligand. Formulations range from ML, ML$_2$ to ML$_3$ and involve M(I) (Cu, Ag, Tl) [291]; M(II) (Fe, Co, Cu, Zn, Cd, Pd, Pt, Pb) [289–291]; and Au(III) [290]. Chloro complexes are also reported; MLCl [M(II) = Fe, Co] [289]; ML$_2$Cl [M(III) = Ru, Rh, Ir] [289]. The ligand is invariably S,N-bridging in these complexes and the distinction as to whether the heterocyclic nitrogen (**LXXII**) or the imino nitrogen (**LXXIII**) is involved, together with the thiolate sulphur, has been made from an analysis of ν(NH), ν(CN) and thioamide (I–IV) band (1600, 1350, 1060 and 750 cm^{-1}) activity [289–291]. Most of the complexes also possess ν(M–L) bands in the range 350–450 cm^{-1}. The most common coordination mode appears to be (**LXXIII**).



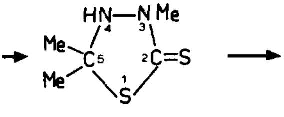
LXXII



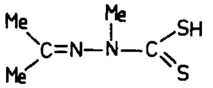
LXXIII

Some structural assignments have been suggested on the basis of magnetic moments and electronic spectra. Tetrahedral environments are proposed for iron(II) (μ 5.09 B.M.) and cobalt(II) (μ 4.49 B.M.) and tetragonal for nickel(II) (μ 3.01 ± 0.1 B.M.). Diamagnetism among ruthenium(III) and copper(II) complexes is rationalised on the basis of superexchange phenomena. The preparation of a paramagnetic (μ 1.77 B.M.) pyridine adduct has been used as evidence for the existence of +2 copper in CuL$_2$ [290].

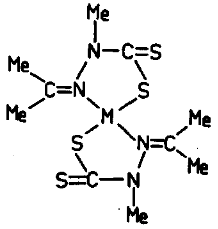
In the presence of some metal salts [Ni(II), Cu(II), Pd(II)], 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione (**LXXIV**) undergoes rearrangement producing initially the corresponding Schiff's base, α-*N*-methyl-β-*N*-isopropylidenedithiocarbazoic acid (**LXXV**), followed by the metal chelate (**LXXVI**). The nickel and palladium complexes are diamagnetic; that of copper is paramagnetic (μ 1.90 B.M.). The presence of ν(C–N) at 1640 cm^{-1} for all the complexes suggests the Schiff's base to be involved in coordination. Similar behaviour is reported for 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione with nickel(II), cobalt(II) and palladium(II) and for 5-(2-pyridyl)-1,3,4-thiadiazolidine-2-thione with nickel(II) [293].



LXXIV



LXXV

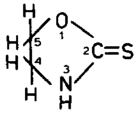


LXXVI

E. COMPLEXES OF NITROGEN AND OXYGEN CONTAINING HETEROCYCLIC THIONES

(i) 1,3-Oxazolidine-2-thione

Complexes of 1,3-oxazolidine-2-thione, oxdtH (**LXXVII**) , are reported with cobalt [295], cadmium and mercury [294] as well as copper [56]. Reaction with zinc halides catalyses ring opening of oxdtH at the $H_2C(5)$–O (1) position and the production of white polymeric materials of indefinite composition [294].

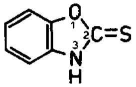


LXXVII

The cobalt complexes, $Co(LH)_2X_2$ (X = Cl, Br, I), have pseudo-tetrahedral structures (*Dq* 333–365 cm^{-1}) and sulphur-donating ligands (β 0.65–0.72; ν(Co–S) 234 cm^{-1}). The cadmium(II) complexes are similar to those of the cobalt(II) with ν(Cd–S) at 200 cm^{-1} while the mercury(II) complexes are either monomeric pseudo-tetrahedral $[Hg(LH)_2Br_2]$ or polymeric octahedral with chlorine bridges $[Hg(LH)_2Cl_2]$. Two types of copper complex are reported: $Cu(LH)_3X$ (X = NO_3, BF_4) and $Cu(LH)_{2\frac{1}{2}}SO_4$; the former are 1 : 1 and the latter is a 2 : 1 electrolyte. Trigonal planar arrangements are proposed with the ligand sulphur donating.

(ii) Benz-1,3-oxazoline-2-thione

The thione form of benz-1,3-oxazoline-2-thione, bzoxtH (**LXXVIII**), has been established by a variety of techniques. Crystallographic analysis of the *N*(3)-methyl derivative shows a thione (C–S) distance of 1.629(7) Å [296]. X-ray PES data gives electron core binding energies (eV) for imido (NH) nitrogen (1*s*) (400.9), thione sulphur ($2p_{3/2}$) (162.8) and heterocyclic oxygen (1*s*) (534.6) for bzoxtH [58]. Infrared spectra are consistent with hydrogen-bonded dimers [29,302] and thioamide bands (I–IV) are reported to occur at 1505, 1245, 1010 and 745 cm^{-1} [298].



LXXVIII

The coordination chemistry of bzoxtH is pH dependent with (imido) nitrogen donation reported in acid or neutral media [297–300] and S,N-bridging occurring in alkaline media [58,301].

Nitrogen donation is invariably deduced from the infrared on the basis of negative (ca. 300 cm^{-1}) shifts to ν(NH) relative to the solution value of 3450 cm^{-1}; ν(NH) is usually present as a sharp band in the solid complexes. Small positive shifts to thioamide *I* bands are also cited as supporting evidence as well as ν(M–L) bands in the range 150–320 cm^{-1} (Table 11).

Magnetic moments and electronic spectra suggest that the bulk of the first row transition elements [Mn(II), Fe(II), Fe(III), Co(II), Ni(II)], as well as zinc, adopt tetrahedral geometries; chromium(III) and also iron(III) are octahedral. Tetrahedral ligand field parameters (Dq) range from 300 to 773 cm^{-1} with the Racah (β) parameter reduced to between 70 and 80% of the free-ion value, although a lower value (59%) is reported for cobalt(II). Complexes of both +I and +II copper are reported with the metal occupying planar coordination sites in both cases. With symmetric quadridentate carboxylate anions polymeric linear complexes are formed in which the metals [Co(II), Ni(II)] are octahedrally coordinated and bzoxtH is nitrogen donating [258].

Among the heavier metals, [Cd(II), Hg(II), Ru(III), Ir(III), Pd(II), Pt(II), Ru(III), Os(III)], the complexes are generally low-spin [Table 11] and either octahedral or square except for cadmium and mercury which are tetrahedral. Low frequency IR data have assisted in the identification of the *mer*-isomers of ruthenium and osmium; ν(M–N) bands are observed in the region 215–295 cm^{-1}.

Of the complexes formed with antimony and bismuth trihalides, $MX_3(LH)$ (M = Bi, X = Cl, Br, I; M = Sb, X = Cl, I) are monomeric pyramidal and $SbBr_3(LH)_{1.5}$ is polymeric. The ligand is monodentate nitrogen donating [164].

With a pK_a of 6.58 the monoanion (L$^-$), bzoxt$^-$, is readily produced and complexes formed from the appropriate metal salt and the neutral molecule in ethanol–dimethylsulfoxide media [301]. Complexes have the formulae: ML [M(I) = Cu, Ag, Au]; ML_2 [M(II) = Co, Ni, Zn, Cd, Hg, Pd, Pt] and ML_3 [M(III) = Rh, Ir]; many are hydrated.

The IR spectra of the complexes contain no vibrational activity due to the imido (NH) group. Thioamide bands I and IV have slight (ca. 20 cm^{-1})

TABLE 11

Metal complexes of N-donating benz-1,3-oxazoline-2-thione

Metal	Stoichiometry (metal: ligand)	Proposed structure	Magnetic and spectrochemical parameters				Ref.
			μ	Dq	β	ν(M–N)	
Cr(III)	1:3	octahedral	3.5–4.1	1482–1538	0.70–0.78	251	298
Mn(II)	1:2	tetrahedral	5.6	678–773	B 626–696 C 3922–4082	211–219	300
Fe(II)	1:2	tetrahedral	5.4			232	300
Fe(III)	1:1 1:2	tetrahedral	5.5–6.1	294–362	B 240–311 C 2732–2856	229	300
	1:3	octahedral	5.9			229	300
Co(II)	1:2	tetrahedral	4.5	472–549	0.59	224	297
Ni(II)	1:2	tetrahedral	3.5	395–406	0.78	220	297
Cu(II)	1:2	planar	2.0	1666–1826		318	298
Cu(I)	1:2	planar	dia.			319	298
Zn(II)	1:2	tetrahedral	dia.			152–172	298
Cd(II)	[1:1]$_2$	dimeric halogen-bridged tetrahedral	dia.			160	298
	1:2	tetrahedral	dia.			164	298
Hg(II)	[1:1]$_2$	dimeric halogen-bridged tetrahedral	dia.			168	298
	1:2	tetrahedral	dia.			162	298
Ru(III)	1:3	*mer*-octahedral	1.7	2620–2755	B 445–446 C 1780–1824	255–297	300
Os(III)	1:3	*mer*-octahedral	2.0	2944–3008	B 345–350 C 1380–1800	259–295	300
Rh(III)	1:3	*mer*-octahedral	dia.	2838–2896	0.53	215–250	299
Ir(III)	1:3	*mer*-octahedral	dia.	3069–3168	0.38	216–270	299
Pd(II)	1:2	*cis*-square	dia.	2482–2499		255–296	299
	1:4	square	dia.	2447		250	299
Pt(II)	1:2	*cis*-square	dia.	2729–2855		224–251	299

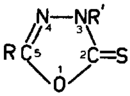
negative shifts and band II undergoes a positive shift. Low frequency data provide further support for S,N-bonding with ν(M–N) bands in the range 190–410 cm^{-1} and ν(M–S) between 226 and 382 cm^{-1}. S,N-bridging, rather than chelation, is proposed for the bzoxt$^-$ thiolate anion [301].

The cobalt(II) complex is paramagnetic (μ 4.40 B.M.) and tetrahedral (Dq 440 cm^{-1}) with a Racah (β) parameter (0.77) significantly higher than that reported for Co(bzoxtH)$_2$Cl$_2$ [297] (Table 11). The remaining complexes are diamagnetic with square [Ni(II), Pd(II), Pt(II)] and octahedral [Rh(III), Ir(III)] geometries proposed from electronic spectra [301].

X-ray PES measurements on some metal complexes [Ni(II), Cu(I), Ag(I), Cd(II), Hg(II), Pd(II), Pt(II)] of the bzoxt$^-$ ion show shifts to the binding energies for the nitrogen ($1s$) (0.3–1.0 eV) and sulphur ($2p_{3/2}$) (0.1–0.7 eV) electrons with the oxygen ($1s$) electron unaffected by coordination [58].

(iii) 1,3,4-Oxadiazoline-2-thione

Complexes have been reported for two derivatives of 1,3,4-oxadiazoline-2-thione (**LXXIXa,b**)



LXXIX

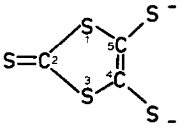
where, in (a), R = phenyl, R' = H; in (b), R = hydroxyphenyl, R' = diphenylaminomethyl.

The 5-phenyl derivative (**LXXIXa**) forms complexes of formulae: ML [M(I) = Cu, Ag]; ML_2 [M(II) = Co, Ni, Zn] and FeL_3; in which it behaves as an S,N-chelating thiolate anion. All the complexes are paramagnetic, except zinc and silver, with iron(III) high-spin (μ 5.58 B.M.) and copper (μ 1.73 B.M.) in the +2 state. Infrared spectra suggests S,N-chelation involves the deprotonated N(3) and sulphur atoms [303].

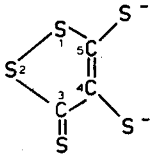
The 5-hydroxyphenyl-3-diphenylaminomethyl derivative, (**LXXIXb**), is sulphur donating towards silver(I) and nitrogen donating with iron(III), cobalt(II), nickel(II), copper(I) and zinc(II). Tetrahedral environments are proposed for the latter group of metals with the exception of copper [304].

F. COMPLEXES OF SULPHUR CONTAINING HETEROCYCLIC THIONES

A mixture of dimethylformamide, alkali metal and carbon disulphide reacts to give 1,3-dithiole-2-thione-4,5-dithiolate [305,306] (**LXXX**) (iso-C_3S_5). Further heating of (iso-C_3S_5) in dimethylformamide yields the thermodynamically more stable 1,2-dithiole-3-thione-4,5-dithiolate (**LXXXI**). Bis-chelates have been reported for both dithiolates [307]. With (**LXXX**) the complexes have the formula $(n\text{-}Bu_4)_2[ML_2]$ [M(II) = Cu, Ni, Zn, Pd, Pt, Cd, VO], and with (**LXXXI**) similar complexes are formed [M(II) = Ni, Pd, Pt, Cu, VO] [307]. Crystal structures of nickel(II) complexes with both thiolates show that the Ni-S distances [2.179, 2.197(4) Å] for (**LXXXI**) [308] are shorter than those for (**LXXX**) [2.211, 2.221(4) Å] [306] and that both complex anions are essentially planar.



LXXX



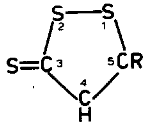
LXXXI

Reversible one-electron transfer reactions:

$[ML_2]^- + e \rightleftarrows [ML_2]^{2-}$

are reported for complexes of both dithiolates. The half-wave potentials of the nickel(II) chelates (iso-C_3S_5, -0.19 V; C_3S_5, -0.07 V) indicate the possibility of them being readily oxidised by moderately strong oxidising agents [307]. Consequently $(n\text{-}Bu_4)_2[Ni(II)(isoC_3S_5)_2]$ is oxidised to $(n\text{-}Bu_4)[Ni(III)(iso\text{-}C_3S_5)_2]$ in quantitative yield by either iodine oxidation in acetone or by aerial oxidation in glacial acetic acid [307]. Crystallographic analysis of the (iso-C_3S_5) nickel(III) chelate shows that a major consequence of oxidation is a reduction in the nickel–sulphur distance to an average value of 2.156(3) Å [309]. Stronger oxidising agents are required to oxidise the nickel(III) chelate to that of nickel(IV) for which an $E_{1/2}$ value of about $+0.7$ V is estimated [307]. Oxidation reactions similar to that described for $(n\text{-}Bu_4)[Ni(III)(iso\text{-}C_3S_5)_2]$ have produced related complexes of other metals [M(III) = Fe, Co, Cu, Ag, Pd, Pt] [307].

Cobalt(II) complexes of 1,2-dithiole-3-thione and its 5-substituted derivatives (**LXXXII**) are formulated: $Co(L)_2X_2$ (X = Cl, Br, I). Room temperature magnetic moments (4.50–4.75 B.M.) and Dq values (327–404 cm^{-1}) suggest pseudo-tetrahedral structures. Racah (β) parameters (0.60–0.75) and ν(Co–S) bands (305–319 cm^{-1}) suggest that the molecules use their thione sulphur rather than their heterocyclic thiole sulphur atoms for coordination [310].



LXXXII

G. FINAL COMMENTS

Heterocyclic thiones generally retain their identity during chemical reactions with metal salts, only rarely does ring fission or fusion disrupt the coordination process.

Of the various coordination modes which have been deduced, largely from vibrational and electronic spectra, some, for example monodentate thione sulphur, monodentate (unprotonated) nitrogen, S,N-chelation, as well as several types of thione sulphur bridging, have been thoroughly characterised by single crystal X-ray methods. In some cases, X-ray PES has also proved to be a reliable indicator of donor atom involvement. Monodentate (imido) nitrogen donation, which has been proposed as the major coordination mode for several heterocyclic thiones, is not so firmly established. Structural data on such systems would be particularly interesting in view of the fact that similar contacts for imidazole have only been observed in solution. Furthermore, the electron distribution at the (imido) nitrogen, even among formally saturated heterocyclic thiones such as tzdtH, does not immediately favour coordination, and major changes in electron distribution may be necessary in order to enable coordination to occur.

Structural data have also indicated the inherent flexibility of S,N-chelating thiolate anions. Asymmetric four-membered chelation may, in fact, be more common than is currently supposed among "polymeric" thiolates.

Of the various factors which govern the coordination characteristics of heterocyclic thiones the role of the acceptor atom appears to be of minor importance, at least among the oxidation states reviewed, and bearing in mind that the range of metals studied is limited for some molecules. One possible exception to this generalisation is copper(I) which shows an affinity for thione sulphur. The factors which appear to dominate the coordination behaviour of an individual heterocyclic thione are its molecular and electronic configuration together with the reaction media employed.

ACKNOWLEDGEMENTS

The author is grateful to Dr. Marion O'Neill for assistance during the initial stages of the work and to Jeremy Atkinson, Janet Hart and Ian Winship of the Newcastle upon Tyne Polytechnic Library for their help with the literature.

REFERENCES

1 H. Vahrenkamp, Angew. Chem., Int. Ed. Engl., 14 (1975) 322.
2 E.W. Ainscough and A.M. Brodie, Coord. Chem. Rev., 27 (1978) 59.
3 C.G. Kuehn and S.S. Isied, Prog. Inorg. Chem., 27 (1980) 1953.
4 A. Mueller, W. Jaegerman and J.H. Enemark, Coord. Chem. Rev., 46 (1982) 245.
5 L.R. Balsenc, Struct. Bonding (Berlin), 39 (1980) 83.
6 R.A. Walton, Coord. Chem. Rev., 31 (1980) 183.
7 A. Müller, E. Diomann and C.K. Jörgensen, Struct. Bonding (Berlin), 14 (1973) 23.
8 A. Müller, E.J.C. Baran and R.O. Carter, Struct. Bonding (Berlin), 26 (1976) 81.
9 J.A. McCleverty, Prog. Inorg. Chem., 10 (1968) 49.

10 D. Coucouvanis, Prog. Inorg. Chem., 11 (1969) 233.
11 R. Eisenberg, Prog. Inorg. Chem., 12 (1970) 295.
12 T.N. Lockyer and R.L. Martin, Prog. Inorg. Chem., 27 (1980) 223.
13 S.E. Livingstone, Coord. Chem. Rev., 7 (1971) 59.
14 M. Akbar Ali and S.E. Livingstone, Coord. Chem. Rev., 13 (1974) 101.
15 U. Casellato, M. Vidali and P.A. Vigato, Coord. Chem. Rev., 28 (1979) 231.
16 M.J.M. Cambell, Coord. Chem. Rev., 15 (1975) 279.
17 E.W. Abel and B.C. Crosse, Organomet. Chem. Rev., 2 (1967) 443.
18 I. Omae, Coord. Chem. Rev., 28 (1979) 97.
19 P.V. Jarett, Coord. Chem. Rev., 23 (1977) 183.
20 P.J. Vergamini and G.J. Kubas, Prog. Inorg. Chem., 21 (1976) 261.
21 A.U. Xavier, J.J.G. Moura and J. Moura, Struct. Bonding (Berlin), 43 (1981) 187.
22 B.A. Averill, Struct. Bonding (Berlin), 53 (1983) 59.
23 J.P. Fackler, Jr., Prog. Inorg. Chem., 21 (1976) 55.
24 M. Inoue and M. Kubo, Coord. Chem. Rev., 21 (1976) 1.
25 D.K. Hodgson, Prog. Inorg. Chem., 23 (1977) 211.
26 R.J. Sundberg and R.B. Martin, Chem. Rev., 4 (1974) 471.
27 A.R. Katritzky and J.M. Lagowski, Advances in Heterocyclic Chemistry, Academic Press, New York and London: Vol. 1 (1961); Vol. 2 (1963).
28 N. Trinajstic, Tetrahedron Lett., 12 (1968) 1529.
29 M.St.C. Flett, J. Chem. Soc., 1 (1953) 347.
30 B. Singh and K.P. Thakur, J. Inorg. Nucl. Chem., 36 (1974) 1735.
31 C.N. Rao and R. Venkataraghavan, Spectrochim. Acta, 18 (1962) 541.
32 F. Scheinman, An Introduction to Spectroscopic Methods for the Identification of Organic Compounds, Vol. 2, Pergamon Press, Oxford, 1970.
33 D.M. Adams, Metal–Ligand and Related Vibrations, St. Martin's Press, New York, 1968.
34 D.M. Adams and J.B. Cornell, J. Chem. Soc. A, (1968) 1299.
35 G. Domazetis, R.J. Magee and R.D. James, J. Inorg. Nucl. Chem., 43 (1981) 1351.
36 L.J. Gerenser, M.G. Mason and P.J. Trotter, J. Phys. Chem., 80 (1976) 2384.
37 F.J. Welcher, Organic Analytical Reagents, Vol. 4, Van Nostrand, New York, 1948.
38 B.C. Bera and M.M. Chakrabarty, Anal. Chem., 38 (1966) 1419.
39 M.J. Stiff, Analyst, 97 (1972) 146.
40 (a) Japanese Patent: JP7513318 (750203). (b) Japanese Patent: JP75126668 (751004). (c) Russian Patent: SU929662 (820523).
41 W.O. Foye and J.R. Lo, J. Pharm. Sci., 61 (1972) 1209.
42 United States Patent: US3590035 (710629). British Patent: GB1202716 (700819). French Patent: FR1506349 (671222).
43 Martindale Extra Pharmacopoeia, 27th edn., Pharmaceutical Press, London, 1977, p. 300.
44 H. Kohn, B.A. Kohn, M.L. Steenberg and J.P. Buckley, J. Med. Chem., 20 (1977) 158.
45 J. Dehand, J. Jordanov and J.P. Beck, Chem–Biol. Interactions, 11 (1975) 605.
46 Japanese Patent: JP8061522 (800509).
47 V.J. Ram and H.N. Pandey, Agric. Biol. Chem., 36 (1973) 1465.
48 Yu.P. Aronson and S.M. Belen'kii, Zashch. Met., 1 (1965) 125.
49 B. Donnelly, T.C. Downie, R. Grzeskowiak, H.R. Hamburg and D. Short, Corros. Sci., 18 (1978) 109.
50 S. Zen, M. Hirooka, R. Nakazato and S. Koto, Kogyo Kagaku Zasshi, 73 (1970) 2060.
51 S.K. Madan and M. Sulich, Inorg. Chem., 5 (1966) 1662.
52 F. Cristiani, F.A. Devillanova and G. Verani, Transition Met. Chem., 2 (1977) 50.

53 S.K. Madan and M. Sulich, J. Inorg. Nucl. Chem., 29 (1967) 2765.
54 E.R. Clark and M.A. Al-Turaihi, J. Inorg. Nucl. Chem., 39 (1977) 765.
55 P. Rechberger and G. Gritznev, Inorg. Chim. Acta, 31 (1978) 125.
56 F.A. Devillanova, F. Isaia and G. Verani, J. Inorg. Nucl. Chem., 43 (1981) 2749.
57 G.R. Form, E.S. Raper and T.C. Downie, Acta Crystallogr. Sect. B, 32 (1976) 345.
58 T. Yoshida, Bull. Chem. Soc. Jpn., 53 (1980) 1449.
59 J.A. McCleverty, N.J. Morrison, N. Spencer, C.A. Ashworth, N.A. Bailey, M.R. Johnson, J.M.A. Smith, B.A. Tabbiner and C.R. Taylor, J. Chem. Soc., Dalton Trans., (1980) 1945.
60 E.S. Raper, M.E. O'Neill and J.A. Daniels, Inorg. Chim. Acta, 41 (1980) 201.
61 E.S. Raper and P.H. Crackett, Inorg. Chim. Acta, 50 (1981) 159.
62 L. Cavalca, P. Domiano, A. Musatti and P. Sgarabotto, J. Chem. Soc., Chem. Commun., (1968) 1136.
63 P.O. Knishko, M.I. Michaelenko and K.V. Tsepkasovich, Zh. Neorg. Khim., 14 (1969) 3039.
64 E.S. Raper, J.R. Creighton, R.E. Oughtred and I .W. Nowell, Acta Crystallogr., Sect. B, 39 (1983) 355.
65 E.S. Raper, M.E. O'Neill and J.A. Daniels, Inorg. Chim. Acta, 41 (1980) 145.
66 B. Lenarcik and M. Wisniewski, Ann. Soc. Chim. Polon, 51 (1977) 1625.
67 J. Dehand and J. Jordanov, Inorg. Chim. Acta, 17 (1976) 37.
68 M.E. O'Neill, E.S. Raper, J.A. Daniels and I.W. Nowell, Inorg. Chim. Acta, 66 (1982) 79.
69 E.S. Raper and J.L. Brooks, J. Inorg. Nucl. Chem., 39 (1977) 2163.
70 A. Bult and W. Rakhorst, J. Inorg. Nucl. Chem., 38 (1976) 1221.
71 E.S. Raper and I.W. Nowell, Acta Crystallogr., Sect. B, 35 (1979) 1600.
72 I.W. Nowell, A.G. Cox and E.S. Raper, Acta Crystallogr., Sect. B, 35 (1979) 3047.
73 M.E. O'Neill, E.S. Raper, I.W. Nowell and J.A. Daniels, Inorg. Chim. Acta, 54 (1981) L243.
74 J. Dehand and J. Jordanov, J. Chem. Soc., Dalton Trans., (1978) 1588.
75 A. Dobry-Ducleaux and P. Perrichon, J. Chim. Phys., 73 (1976) 1058.
76 Y. Henry and A. Dobry-Ducleaux, J. Chim. Phys., 73 (1976) 1068.
77 Y. Agnus, R. Louis and R. Weiss, J. Chem. Soc., Chem. Commun., (1980) 946.
78 G.B. Ansell, J. Chem. Soc. Perkin Trans., (1972) 841.
79 N. Kheddar, J. Protas, M. Le Baccon, R. Guglielmetti and J.E. Guerchais, Bull. Soc. Chim. Fr., 2 (1976) 803.
80 E.S. Raper and I.S. Rowell, J. Inorg. Nucl. Chem., 43 (1981) 3137.
81 D.J. Williams, C.O. Quicksall and K.J. Wynne, Inorg. Chem., 17 (1978) 2071.
82 P.J. Wheatley, Acta Crystallogr., 6 (1953) 369.
83 D.L. Carlin and S.L. Holt, Inorg. Chem., 1 (1963) 849.
84 E.M. Holt, S.L. Holt and K.J. Watson, J. Am. Chem. Soc., 92 (1970) 2721.
85 S.L. Holt and R.L. Carlin, J. Am. Chem. Soc., 86 (1964) 3017.
86 P.P. Singh, S.A. Khan, M. Dubey and O.P. Agarwal, Inorg. Chim. Acta, 33 (1979) 15.
87 P.P. Singh and I.M. Pande, J. Inorg. Nucl. Chem., 34 (1972) 591.
88 P. Castan, Transition Met. Chem., 6 (1981) 14.
89 L.P. Battaglia, A.B. Corradi, M. Nardelli and M.E. Vidoni Tani, J. Chem. Soc. A, (1976) 143.
90 J.M. Bret, P. Castan and J.P. Laurent, Inorg. Chim. Acta, 51 (1981) 103.
91 L.P. Battaglia, A.B. Corradi, F.A. Devillanova and G. Verani, Transition Met. Chem., 4 (1979) 264.
92 F.A. Cotton, O.D. Faut and J.T. Mague, Inorg. Chem., 3 (1964) 17.
93 F.A. Devillanova and G. Verani, Inorg. Chim. Acta, 30 (1978) 209.

94 F.A. Devillanova and G. Verani, Transition Met. Chem., 5 (1980) 42.
95 F.A. Devillanova, A. Lai, M. Monduzzi, G. Saba and G. Verani, Inorg. Chim. Acta, 41 (1980) 35.
96 F.A. Devillanova and G. Verani, J. Inorg. Nucl. Chem., 42 (1980) 623.
97 P. Castan and J.P. Laurent, Transition Met. Chem., 5 (1980) 154.
98 L.A. Walter, K. Folting and L.A. Merritt, Acta Crystallogr., Sect. B, 25 (1969) 88.
99 M.B. Ferrari, C.G. Fava and M.E. Vidoni Tani, Cryst. Struct. Commun., 10 (1981) 571.
100 P. Herland, M. Lundeland and K. Maroy, Acta Chem. Scand., A30 (1976) 719.
101 P.C. Jones, J.J. Guy and G.M. Sheldrick, Acta Crystallogr., Sect. B, 32 (1976) 3321.
102 E. Buncel, A.R. Norris, S.E. Taylor and W.J. Racz, Can. J. Chem., 60 (1982) 3033.
103 C. Chieh and S.K. Cheung, Can. J. Chem., 61 (1983) 211.
104 E.S. Raper, A.R.W. Jackson and D.J. Gardiner, Inorg. Chim. Acta, 84 (1984) L1.
105 E.S. Raper, A.R.W. Jackson and D.J. Gardiner, unpublished work.
106 L.M. Butler, J.R. Creighton, R.E. Oughtred, E.S. Raper and I.W. Nowell, Inorg. Chim. Acta, 75 (1983) 149.
107 P.J.M.W.L. Birker, J. Reedijk, G.C. Verschoor and J. Jordanov, Acta Crystallogr., Sect. B, 38 (1982) 2245.
108 B. Rubin, F.J. Heldrich, W.K. Dean, D.J. Williams and A. Viehlbeck, Inorg. Chem., 20 (1981) 4434.
109 D.J. Williams, B. Rubin, J. Epstein, W.K. Dears and A. Viehlbeck, Cryst. Struct. Commun., 11 (1982) 1.
110 M.E. O'Neill, E.S. Raper and J.A. Daniels, Inorg. Chim. Acta, 54 (1981) L25.
111 F.A. Devillanova, C. Furlani, G. Mattogno, G. Verani and R. Zanoni, Gazz. Chim. Ital., 110 (1980) 19.
112 M. Nardelli, G. Fava Gaspari, A. Musatti and A. Manfredotti, Acta Crystallogr., 21 (1966) 910.
113 T. Morgan and H. Burstall, J. Chem. Soc., (1925) 143.
114 M.S. Weiniger, G.W. Hunt and E.L. Amma, J. Chem. Soc., Chem. Commun., (1970) 1140.
115 A.L. Crumbliss, L.J. Gestaut, R.C. Rickard and A.T. McPhail, J. Chem. Soc., Chem. Commun., (1974) 545.
116 L. Cavalca, M. Nardelli and G. Fava, Acta Crystallogr., 13 (1960) 125.
117 L. Antolini, F. Cristiani, F.A. Devillanova, A. Diaz and G. Verani, J. Chem. Soc., Dalton Trans., (1983) 1261.
118 R. Shunmugan and D.N. Sathyanarayana, J. Coord. Chem., 12 (1983) 151.
119 F.A. Devillanova, G. Verani, L.P. Battaglia and A.B. Corradi, Transition Met. Chem., 5 (1980) 362.
120 M. Nardelli and I. Chierici, Gazz. Chim. Ital., 88 (1958) 248.
121 F. Cristiani, F.A. Devillanova, A. Diaz and G. Verani, Transition Met. Chem., 7 (1982) 69.
122 K. Dwarakanath and D.N. Sathyanarayana, Bull. Chem. Soc. Jpn., 52 (1979) 2699.
123 K. Dwarakanath and D.N. Sathyanarayana, Indian J. Chem., 18A (1979) 302.
124 F.A. Devillanova and G. Verani, J. Chem. Res. (S) (1978) 24; J. Chem. Res. (M) (1978) 0239.
125 E.S. Raper, R.E. Oughtred and I.W. Nowell, Inorg. Chim. Acta, 84 (1984) L5.
126 P.P. Singh, O.P. Agrawal and M.K. Singh, Indian J. Chem., 15A (1977) 1045.
127 E.S. Raper and I.W. Nowell, Inorg. Chim. Acta, 43 (1980) 165.
128 L.H. Little and R.H. Ottewill, Can. J. Chem., 40 (1962) 2110.
129 B.K. Gupta, D.S. Gupta and U.C. Agarwala, Bull. Chem. Soc. Jpn., 51 (1978) 2724.

130 B.K. Gupta, D.S. Gupta, S.K. Dikshit and U. Agarwal, Indian J. Chem., 15 (1977) 624.
131 N.W. Isaacs and C.H.L. Kennard, J. Chem. Soc. (B) (1971) 1270.
132 V.J. Ram, L. Mishra and H.N. Pandey, Transition Met. Chem., 4 (1979) 237.
133 R.U. Gadag and M.R. Gajendragad, Indian J. Chem., 19 (1980) 705.
134 R.U. Gadag and M.R. Gajendragad, Indian J. Chem., 16A (1978) 703.
135 B. Singh, R. Singh, K.P. Thakur and M. Chandra, Indian J. Chem., 12 (1974) 631.
136 B. Singh and R. Singh, J. Inorg. Nucl. Chem., 34 (1972) 3449.
137 B. Singh and R. Singh, Indian J. Chem., 9 (1971) 1013.
138 B.K. Sinha, R. Singh and J.P. Srivastava, J. Inorg. Nucl. Chem., 39 (1977) 1797.
139 A. Parentich, L.H. Little and R.H. Ottewill, J. Inorg. Nucl. Chem., 35 (1973) 2271.
140 H.N. Pandey, V.J. Ram and L. Mishra, Transition Met. Chem., 2 (1977) 26.
141 U. Agarwala, V.A. Narayan and S.K. Dikshit, Can. J. Chem., 45 (1967) 1057.
142 U. Agarwala and S.K. Dikshit, J. Inorg. Nucl. Chem., 30 (1968) 1245.
143 U. Agarwala and B. Singh, J. Inorg. Nucl. Chem., 31 (1969) 2515.
144 L. Agarwala and U. Agarwala, J. Inorg. Nucl. Chem., 34 (1972) 2255.
145 A.C. Fabretti, G. Peyronel and G.C. Franchi, J. Coord. Chem., 6 (1976) 47.
146 W.J. Kozarek and Q. Fernando, J. Chem. Soc., Chem. Commun., (1972) 604; Inorg. Chem., 12 (1973) 2129.
147 Y. Kushi and Q. Fernando, J. Chem. Soc., Chem. Commun., (1969) 1240; J. Am. Chem. Soc., 92 (1970) 1965.
148 A.C. Fabretti, G. Peyronel and G.C. Franchini, Spectrochim. Acta, Part A, 33 (1977) 7.
149 A.C. Fabretti, G. Peyronel and G.C. Franchini, Spectrochim. Acta, Part A, 33 (1977) 377.
150 A. Bigotto, G. de Alti and A.C. Fabretti, Gazz. Chim. Ital., 106 (1976) 585.
151 J.J. Cox and D.M. Servant, Anal. Chim. Acta, 74 (1975) 200.
152 G. Peyronel and A.C. Fabretti, J. Coord. Chem., 7 (1977) 119.
153 J.C. Bayon and P. Gonzalez-Duarte, J. Chem. Soc., Dalton Trans., (1982) 487.
154 J.C. Bayon, I. Casals, W. Gaete, P. Gonzalez-Duarte and J. Ros, Polyhedron, 1 (1982) 157.
155 J.C. Bayon, M.C. Brianso, J.L. Brianso and P. Gonzalez-Duarte, Inorg. Chem., 18 (1979) 3478.
156 J.C. Bayon, M.C. Brianso, J.L. Brianso and P. Gonzalez-Duarte, Sixth European Crystallographic Meeting, Barcelona, Spain, July 1980.
157 M.C. Brianso, J.L. Brianso, W. Gaete, J. Ros and C. Suñer, J. Chem. Soc., Dalton Trans., (1981) 852.
158 H. Barrera, J.C. Bayon, P. Gonzalez-Duarte, J. Sola, J.M. Vinas, J.L. Brianso, M.C. Brianso and X. Solans, Polyhedron, 1 (1982) 647.
159 H. Barrera, J.C. Bayon, P. Gonzalez-Duarte and J. Sola, J. Chim. Phys. Phys–Chim. Biol., 76 (1979) 987.
160 C. Preti and G. Tosi, Can. J. Chem., 52 (1974) 2845.
161 C. Preti, G. Tosi, D. De Filippo and G. Verani, Can. J. Chem., 52 (1974) 2021.
162 C. Preti and G. Tosi, Can. J. Chem., 53 (1975) 177.
163 D. De Filippo, P. Deplano, A. Diaz and E.F. Trogu, Rend. Semin. Fac. Sci., Univ. Cagliari, 46 (1974) 203.
164 C. Preti and G. Tosi, J. Mol. Struct., 50 (1978) 7.
165 S.K. Madan and C. Goldstein, J. Inorg. Nucl. Chem., 28 (1966) 1251.
166 P. Dini, J.C.J. Bart, E. Santoro, G. Cum and N. Giordano, Inorg. Chim. Acta, 17 (1976) 97.
167 B.P. Kennedy and A.B.P. Lever, Can. J. Chem., 50 (1972) 3489.

168 I.P. Evans and G. Wilkinson, J. Chem. Soc., Dalton Trans., (1974) 946.

169 E. Binamira-Soriaga, M. Lundeen and K. Seff, Acta Crystallogr., Sect. B, 35 (1975) 2875.

170 M. Masaki, S. Matsunami and H. Ueda, Bull. Chem. Soc. Jpn., 51 (1978) 3298.

171 R.A. Jones and R.A. Katritzky, J. Chem. Soc., (1958) 3610.

172 B. Penfold, Acta Crystallogr., 6 (1953) 707.

173 R.W. Mitchell, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. A, (1971) 3224.

174 S.R. Fletcher and A.C. Skapski, J. Chem. Soc., Dalton Trans., (1972) 635.

175 J.D. Gilbert, D. Rose and G.A. Wilkinson, J. Chem. Soc. A (1968) 1749.

176 M. Masaki and S. Matsunami, Bull. Chem. Soc. Jpn., 49 (1976) 3274.

177 S.C. Kokkou, S. Fortier, P.J. Rentzepris and P. Karagiannidis, Acta Crystallogr., Sect. C, 39 (1983) 178.

178 F.P. Mullins, J. Inorg. Nucl. Chem., 41 (1979) 463.

179 J.L. Davidson, P.N. Preston and M.V. Russo, J. Chem. Soc., Dalton Trans., (1983) 783.

180 J. Abbott, D.M.L. Goodgame and I. Jeeves, J. Chem. Soc., Dalton Trans., (1978) 880.

181 A.C. Skapski and K.A. Woode, Acta Crystallogr., Sect. B, 35 (1979) 59.

182 D.M.L. Goodgame, G.A. Leach, A.C. Skapski and K.A. Woode, Inorg. Chim. Acta, 31 (1978) L375.

183 D.M.L. Goodgame, I. Jeeves and G.A. Leach, Inorg. Chim. Acta, 39 (1980) 247.

184 D.M.L. Goodgame and G.A. Leach, Inorg. Chim. Acta, 25 (1977) L127.

185 D.M.L. Goodgame and G.A. Leach, Inorg. Chim. Acta, 32 (1979) 69.

186 R. Battistuzzi and G. Peyronel, Spectrochim. Acta, Part A, 36 (1980) 113.

187 R. Battistuzzi and G. Peyronel, Transition Met. Chem., 3 (1978) 345.

188 R. Battistuzzi and G. Peyronel, Can. J. Chem., 59 (1981) 591.

189 B.A. Cartwright, D.M.L. Goodgame, I. Jeeves, P.O. Langguth, Jr. and A.C. Skapski, Inorg. Chim. Acta, 24 (1977) L45.

190 B.A. Cartwright, P.O. Langguth Jr. and A.C. Skapski, Acta Crystallogr., Sect. B, 35 (1979) 63.

191 D.M.L. Goodgame and C.A. Leach, J. Chem. Soc., Dalton Trans., (1978) 1705.

192 C. Chieh, Can. J. Chem., 56 (1978) 560.

193 F.A. Cotton and W.M. Ilsley, Inorg. Chem., 20 (1981) 614.

194 F.A. Cotton, R.H. Niswander and J.C. Sekutowski, Inorg. Chem., 18 (1979) 1149.

195 H.W. Dias and M.R. Truter, Acta Crystallogr., 17 (1964) 937.

196 S. Manogaran and D.N. Sathyanarayana, Bull. Soc. Chim. Belg., 90 (1981) 427.

197 J.M. Bret, P. Castan, G. Jugie and A. Dubourg, J. Chem. Soc., Dalton Trans., (1983) 301.

198 I.P. Khullar and U. Agarwala, Aust. J. Chem., 27 (1974) 1877.

199 D.M.L. Goodgame and G.A. Leach, Inorg. Chim. Acta, 37 (1979) L505.

200 J.R. Lusty, J. Peeling and M.A. Abdel-Aal, Inorg. Chim. Acta, 56 (1981) 21.

201 N.B. Jain, B. Lee, K.B. Mertis and I.H. Pitman, Acta Crystallogr., Sect. B, 34 (1978) 927.

202 L.J. DeLucas, R.A. Hearn and C.E. Bugg, Acta Crystallogr., Sect. B, 33 (1977) 2611.

203 I.P. Khullar and U. Agarwala, Aust. J. Chem., 28 (1975) 1529.

204 I.P. Khullar and U. Agarwala, Indian J. Chem., 12 (1974) 1096.

205 J.F. Villa and H.C. Nelson, J. Indian Chem. Soc., LV (1978) 631.

206 J.S. Dwivedi and U. Agarwala, Indian J. Chem., 10 (1972) 652.

207 J.S. Dwivedi and U. Agarwala, Indian J. Chem., 10 (1972) 657.

208 J.S. Dwivedi and U. Agarwala, Z. Anorg. Allg. Chem., 397 (1973) 74.

209 H.C. Nelson and J.F. Villa, Inorg. Chim. Acta, 34 (1979) L235.

210 I.P. Khullar and U. Agarwala, Indian J. Chem., 12 (1974) 1096.

211 D.A. Stuart, L.R. Nassimbeni, A.T. Hutton and K.R. Koch, Acta Crystallogr., Sect. B, 36 (1980) 2227.

212 G.W. Hunt and E.L. Amma, J. Chem. Soc., Chem. Commun., (1973) 869.
213 A.A. Grinberg, N.A. Kustova and M.I. Gelfman. Russ, J. Inorg. Chem., 13 (1969) 1230.
214 A.A. Grinberg, Yu.A. Varshavskii, M.I. Gelfman and D.B. Smolenskaya, Russ. J. Inorg. Chem., 13 (1969) 422.
215 S. Kirschner, Y. Wei, D. Francis and J.G. Bergman, J. Med. Chem., 9 (1961) 366.
216 H.I. Meitner and S.J. Lippard, Inorg. Chem., 13 (1974) 815.
217 C. Singh, Acta Crystallogr., 19 (1965) 861.
218 E. Sletten and A. Apeland, Acta Crystallogr., Sect. B, 31 (1975) 2019.
219 M.R. Caira and R. Nassimbeni, J. Chem. Soc., Dalton Trans., (1976) 4.
220 M.R. Caira and R. Nassimbeni, Acta Crystallogr., Sect. B, 31 (1975) 1339.
221 E. Sletten, J. Sletten and L.H. Jensen, Acta Crystallogr., Sect. B, 25 (1969) 1330.
222 J.S. Dwivedi and U. Agarwala, J. Inorg. Nucl. Chem., 35 (1973) 2229.
223 J.S. Dwivedi and U. Agarwala, Indian J. Chem., 174 (1979) 276.
224 J.S. Dwivedi and U. Agarwala, Indian J. Chem., 13 (1975) 501.
225 M.L. Tosato and L. Pasolini, J. Chem. Soc., Chem. Commun., (1966) 909.
226 J.C. Chudy and J.A.W. Dalziel, J. Inorg. Nucl. Chem., 37 (1975) 2459.
227 H.R. Zuicke and Z.H. Brovers, Koord. Khim., 8 (1982) 282.
228 K. Yamanouchi and J.H. Enemark, Inorg. Chem., 18 (1979) 1626.
229 E. Sekido, T. Kobayashi and Y. Masuda, Bull. Chem. Soc. Jpn., 55 (1982) 1321.
230 K.K. Ganguli, G.O. Carlisle, M.J. Hu, L.J. Theriot and I. Bernal, J. Inorg. Nucl. Chem., 33 (1971) 3581.
231 N. Muresan and V. Muresan, Rev. Roum. Chim., 24 (1979) 1123.
232 K. Geertharani and D.N. Sathyanarayana, Indian J. Chem., 14A (1976) 925.
233 J.P. Chesick and J. Donohue, Acta Crystallogr., Sect. B, 27 (1971) 1441.
234 T. Yoshida, K. Yamsaki and S. Sawada, Bull. Chem. Soc. Jpn., 52 (1979) 2908.
235 S. Banerji, R.E. Byrne and S.E. Livingstone, Transition Met. Chem., 7 (1982) 5.
236 F. Pruchnik and D. Chwolka, Ann. Soc. Chim. Polon, 51 (1977) 653.
237 I.P. Khullar and U. Agarwala, Can. J. Chem., 53 (1975) 1165.
238 M.F. El-Shazly, T. Salem, M.A. El-Sayed and S. Hedewy, Inorg. Chim. Acta, 29 (1978) 155.
239 I.G. Dance and D. Isaac, Aust. J. Chem., 30 (1977) 2425.
240 S. Jeannin, Y. Jeannin and G. Lavigne, Inorg. Chem., 18 (1979) 3528.
241 C.C. Ashworth, N.A. Bailey, M. Johnson, J.A. McCleverty, N. Morrison and B. Tabbiner, J. Chem. Soc., Chem. Commun., (1976) 743.
242 J.A. McCleverty, N. Spencer, N.A. Bailey and S.L. Shackleton. J. Chem. Soc., Dalton Trans., (1980) 1939.
243 J.A. McCleverty, S.A. Gill, R.S.Z. Kowalski, N.A. Bailey, H. Adams, K.W. Lumbard and M.A. Murphy, J. Chem. Soc., Dalton Trans., (1982) 493.
244 R.F. Wilson and P. Merchant, J. Inorg. Nucl. Chem., 29 (1967) 1993.
245 M.M. Khan and A.U. Malik, J. Inorg. Nucl. Chem., 34 (1972) 1847.
246 A.U. Malik and F.R. Rahmani, J. Inorg. Nucl. Chem., 37 (1975) 1553.
247 O. Narratil and J. Liska, Collect. Czech. Chem. Commun., 33 (1968) 987.
248 P.P. Singh, O.P. Agrawal and A.K. Gupta, Inorg. Chim. Acta, 18 (1976) 19.
249 C. Preti and G. Tosi, Aust. J. Chem., 29 (1976) 543.
250 C. Fregni, C. Preti, C. Tosi and G. Verani, J. Inorg. Nucl. Chem., 37 (1975) 1837.
251 P.P. Singh and R. Rivest, Can. J. Chem., 46 (1968) 2361.
252 C. Preti and G. Tosi, J. Chem. Soc., Dalton Trans., (1976) 685.
253 D. DeFilippo, F. Devillanova, E.F. Trogu, G. Verani, C. Preti and P. Viglino, Can. J. Chem., 51 (1973) 1172.

254 D. DeFilippo, F. Devillanova, C. Preti and G. Verani, J. Chem. Soc. A, (1971) 1465.
255 G. Colombini and C. Preti, J. Inorg. Nucl. Chem., 87 (1975) 1159.
256 C. Preti and G. Tosi, Transition Met. Chem., 3 (1978) 17.
257 K. Geertharani and D.N. Sathyanarayana, Indian J. Chem., 14A (1976) 170.
258 C. Preti and G. Tosi, Aust. J. Chem., 32 (1974) 989.
259 D. DeFilippo and C. Preti, J. Chem. Soc. A, (1970) 1904.
260 E.R. Clark and M.A. Al-Turaihi, J. Inorg. Nucl. Chem., 38 (1976) 1443.
261 W.D. Basson and A.L. du Preez, J. Chem. Soc., Dalton Trans., (1974) 1708.
262 C. Preti and G. Tosi, Can. J. Chem., 54 (1976) 1558.
263 E.S. Raper, R.E. Oughtred and I.W. Nowell, Inorg. Chim. Acta, 77 (1983) L89.
264 M. Fabiak and T. Glowiak, Acta Crystallogr., Sect. B, 38 (1982) 2031.
265 A.C. Fabretti, M. Ferrari, G.C. Franchini, C. Preti, L. Tassi and G. Tosi, Transition Met. Chem., 7 (1982) 279.
266 F. Cristiani, F.A. Devillanova and G. Verani, Spectrochim. Acta, 38A (1982) 1299.
267 F.A. Devillanova, K.R. Gayathui Devi, D.N. Sathyanarayana and G. Verani, Spectrochim. Acta, Part A, 35 (1979) 1083.
268 F.A. Devillanova and G. Verani, Transition Met. Chem., 2 (1977) 217.
269 F.A. Devillanova, D.N. Sathyanarayana and G. Verani, J. Heterocycl. Chem., 15 (1978) 945.
270 R. van der Helm, A.E. Lessor and I. Merritt, Acta Crystallogr., 15 (1962) 1227.
271 F.G. Moers and A. Soesman, J. Inorg. Nucl. Chem., 43 (1981) 299.
272 F.G. Moers, W.P.J.H. Bosman and P.T. Buerskens, J. Cryst. Mol. Struct., 2 (1972) 23.
273 A.C. Fabretti, G.C. Franchini and G. Peyronel, Inorg. Chim. Acta, 52 (1981) 11.
274 F.G. Moers and J.J. Steggerda, J. Inorg. Nucl. Chem., 30 (1968) 3217.
275 W.I. Stephen and A. Townshend, J. Chem. Soc., (1965) 3738.
276 F.G. Moers, J.W.M. Goosens and J.P.M. Langhout, J. Inorg. Nucl. Chem., 35 (1973) 855.
277 F.G. Moers and J.P. Langhout, Rec. Trav. Chim. Pays-Bas, 89 (1970) 1237.
278 D.A. Edwards, R. Richards, R.E. Myers and R.A. Walton, Inorg. Chim. Acta, 23 (1977) 215.
279 M.R. Gajendragad and U. Agarwala, Aust. J. Chem., 28 (1975) 763.
280 M.R. Gajendragad and U. Agarwala, Indian J. Chem., 13 (1975) 697.
281 S.A.A. Zaidi, A.S. Farooqi, D.K. Varshney, V. Islam and K.S. Siddiqi, J. Inorg. Nucl. Chem., 39 (1977) 581.
282 M.M. Osman, M.A. Makhyoun and T.B. Tadros, Bull. Soc. Chim. Fr., 11–12 (1980) 451.
283 S.A.A. Zaidi and D.K. Varshney, J. Inorg. Nucl. Chem., 37 (1975) 1804.
284 A.K. Majumdar and B.R. Singh, Fresenius Z. Anal. Chem., 193 (1963) 33.
285 G.D. Thorn, Can. J. Chem., 38 (1960) 1439.
286 A.C. Fabretti, G.C. Franchini and G. Peyronel, Transition Met. Chem., 7 (1982) 105.
287 A.C. Fabretti, G.C. Franchini and G. Peyronel, Spectrochim. Acta, Part A, 36 (1980) 517.
288 A.C. Fabretti, G.C. Franchini and G. Peyronel and M. Bellei, Spectrochim. Acta, Part A, 37 (1981) 587.
289 M.R. Gajendragad and U. Agarwala, J. Inorg. Nucl. Chem., 37 (1975) 249.
290 M.R. Gajendragad and U. Agarwala, Bull. Chem. Soc. Jpn., 48 (1975) 1024.
291 M.R. Gajendragad and U. Agarwala, Indian J. Chem., 13 (1975) 1331.
292 T.C. Downie, W. Harrison, E.S. Raper and M.A. Hepworth, Acta Crystallogr., Sect. B, 28 (1972) 1584.
293 M.A. Ali, S.E. Livingstone and D.J. Phillips, Inorg. Chim. Acta, 7 (1973) 533.
294 F.A. Devillanova and G. Verani, J. Coord. Chem., 7 (1978) 177.

295 F. Cristiani, F.A. Devillanova, A. Diaz and G. Verani, Spectrochim. Acta, Part A, 38 (1982) 1303.
296 P. Groth, K. Davidkov and D. Simov, Acta Chem. Scand., 26 (1972) 1931.
297 C. Preti and G. Tosi, Can. J. Chem., 54 (1976) 85.
298 C. Preti and G. Tosi, J. Inorg. Nucl. Chem., 38 (1976) 1125.
299 C. Preti and G. Tosi, J. Coord. Chem., 7 (1977) 35.
300 C. Preti and G. Tosi, J. Coord. Chem., 8 (1978) 15.
301 C. Preti and G. Tosi, Can. J. Chem., 55 (1977) 1409.
302 D. Harrison and J.T. Ralph, J. Chem. Soc. B, (1967) 14.
303 S.P. Agrawal and R.A. Rai, Transition Met. Chem., 1 (1976) 238.
304 R.A. Rai, U. Agarwala and L. Agarwala, Indian J. Chem., 18A (1979) 426.
305 G. Steimecke, J. Sieler, R. Kirmse and E. Hoyer, Phosphorus Sulphur, 7 (1979) 49.
306 L. Sjölin, O. Lindqvist, J. Sieler, G. Steimecke and E. Hoyer, Acta Chem. Scand., Ser. A, 33 (1979) 445.
307 G. Steimecke, R. Kirmse, W. Dietsch, E. Fanghärel and E. Hoyer, Proc. Conf. Coord. Chem., 7 (1978) 229.
308 O. Lindqvist, L. Sjölin, J. Sieler, G. Steimecke and E. Hoyer, Acta Chem. Scand., Ser. A, 36 (1982) 853.
309 O. Lindqvist, L. Andersen, J. Sieler, G. Steimecke and E. Hoyer, Acta Chem. Scand., A36 (1982) 855.
310 F. Petillon and J.E. Guerchais, Bull. Soc. Chim. Fr., 7 (1971) 2455.