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Recent studies in the coordination chemistry of heterocyclic thiones and thionates

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Contents

Abbreviations: Acac, acetylacetonate; bimtH, benzimidazoline-2-thione; boztH, benzoxazoline-2-thione; Bpy, 2,2,-bipyridine; btztH, benzthiazoline-2-thione; DMF, dimethylformamide; DMSO, dimethylsulfoxide; Dppe, bis(diphenylphosphino)ethane; Dppm, bis(diphenylphosphino)methane; EDTA, ethylenediaminotetraacetate(4-); imH, imidazole; imtH, imidazoline-2-thione; oztH, oxazoline-2-thione; pymtH, pyrimidine-2-thione; pytH, pyridine-2-thione; THF, tetrahydrofuran; tztH, thiazoline-2-thione.

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Abstract

Heterocyclic thioamides usually occurring in their thioketo form are referred to as 'thiones' and their corresponding anions as 'thionates'. The coordination chemistry of this group of ligands is rich due to their versatility in adopting monodentate, bridging and chelating modes of coordination. The recent advances made in this field of coordination chemistry are reported covering the period from 1996 to 1999, i.e. from the last review published on the subject by the late Eric Raper until about a year after his decease. The coverage is aimed at being brief indicating the main points in every publication presented. Thiones and thionates are classified as five-, six- and higher member rings and condensed rings and their coordination to transition and non-transition metals are discussed separately.

Keywords: Heterocyclic thioamides; Thiones; Thionates; Coordination compounds; Metal complexes

1. Introduction

Among the interesting features of modern science the persistent increase in the rate of appearance of new journals and the concomitant rate of publication of papers are the most noticeable. The field of study of the coordination potential of heterocyclic thiones especially those possessing an α-N-heteroatom as well as their corresponding anions, referred to as thionates, could not be an exception. There is indeed a considerable versatility in the coordination modes of these molecules which may include monodentate binding through S(I) or through N(II), bridging through a single S(III), bridging through both S and N(IV) or chelating via the S-to-N backbone (VI) (Fig. 1).

All these modes either alone or in combinations (V, VII) have been observed and assigned on the basis of congruent evidence of spectroscopic characterizations or crystal structure determination of both homo- and hetero-leptic metal complexes.

The first complete treatment of this body of information appeared about 15 years ago [1] and considered the sum of the relevant literature. The author of that work was the late Eric Raper, who was a major contributor in the expansion and exploitation of the field and he continued by publishing three more reviews concerning the advances in the thione [2] and thionate [3,4] coordination chemistry, respectively. This is an attempt to carry on his coverage of the thione–thionate coordination versatility, including the studies published in the mainstream literature since 1996 when Eric's last review as well as a extensive one describing thione

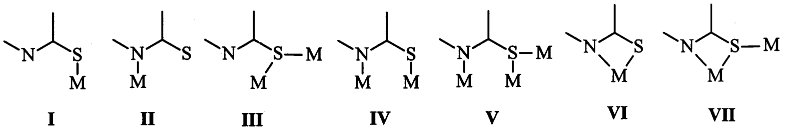


Fig. 1.

complexes of group 11 metals appeared [5] until about the middle of 1999, just a year after his transition to eternity. This is not an attempt to review Eric's work as other authors in other papers will undoubtedly do so but it has both the honor and the regret to include his last contributions in the field.

Heterocyclic thiones forming the backbone of more complicated organic ligands which use other sites for their attachment to the metal will not be treated along with specific types of molecules having a thioketo group like 1,3-dithiole-2-thiones which form a vast and expanding field of research with technological applications and have the merit for separate treatment in their own.

Unfortunately in describing the coordination of such an extended group of compounds possessing such a variety in coordination modes it is difficult to follow strictly a specific plan of presentation. However, thione complexes will be discussed separately from thionate complexes as far as this will be possible. Although the vast majority of complexes refer to group 8–11 transition metals the classification will follow the general division between thiones possessing five- six- and higher-membered heterocyclic rings. In this respect, quinolinethiones and thiopurines will be classified as condensed systems since the thioketo group, which is mainly responsible for their coordination is situated on a six-membered ring. Usually N chelation is also present in their complexes. Transition and non-transition metal compounds will be considered separately within the same group of thiones. In every case the main points of interest described in the published paper will be presented whether they are related to the synthetic method or spectroscopic study or reactivity of the compounds synthesized avoiding as much as possible extensive tabulation of physicochemical data and parameters. It has also been verified in many cases that the stoicheiometry of thione and thionate oligomers depends greatly on the reaction, isolation or crystallization procedure applied. In this respect only the compounds reported during the above period will be discussed and their structural data will not be related to those of previous studies, since these may be obtained from the reviews of Eric Raper.

Effort has been made to keep drawings to a minimum and in this respect original crystal structures are not represented. Furthermore, in the few complex structures drawn only the metal environment is presented. Extensive tabulation of structural information was also avoided and the essential structural information has been combined in two tables dealing with thiones and thionates, respectively (Tables 1 and 2).

2. Thione complexes

The term is applicable since most of the compounds, especially the heterocyclic thioamides considered, have been shown to occur in the thione rather than the thiol form both in the solid state and in most of the common solvents [6], with only occasional striking exceptions.

Table 1
Relevant bond distances (Å) for a series of thione complexes[a]

M–S bond	M–N bond	S–C bond	Reference
Five-membered ring thiones			
Co–S 2.349 (1)			[51]
Co–S 2.322 (3) 2.317 (2)		S–C 1.604 (11) 1.623 (9)	[51]
Co–S 2.308 (3)-2.337 (3)			[51]
Ni–S 2.411 (1)		S–C 1.686 (4)	[7]
Cu–S 2.4908 (18)		S–C 1.681 (7)	[13]
Cu–S 2.304 (3)		S–C 1.678 (8)	[14]
Cu–S 2.234 (1)		S–C 1.652 (4)	[17]
Cu–S 2.418 (5)		S–C 1.677 (8)	[18]
Cu–S 2.3821 (13)			[19]
Cu–S 2.335 (1) 2.514 (1)			[20]
Cu–S 2.340 (2)	Cu–N 2.022 (2)	S–C 1.692 (3)	[21]
Cu–S 2.347 (1)	Cu–N 1.921 (3)	S–C 1.688 (3)	[21]
Cu–S 2.293 (2) 2.280 (1)		S–C 1.665 (5)	[22]
Cu–S$_{brid}$ 2.432 (2)			[22]
Cu–S 2.2089 (12) 2.2274 (12)		S–C 1.712 (4) 1.716 (4)	[26]
Cu–S 2.309 (1)-2.593 (1)			[51]
Cu–S 2.296 (1) 2.314 (1)			[51]
Zn–S 2.358 (2) 2.390 (2)			[51]
Pd–S 2.32 (2)-2.32 (9)		S–C 1.71 (4)	[9]
Cd–S 2.525 (2) 2.535 (2)		S–C 1.710 (6) 1.721 (6)	[32]
Sn–S 2.572 (6) 2.601 (10)		S–C 1.74 (3) 1.74 (4)	[23]
Pt–S 2.317 (4) 2.334 (4)		S–C 1.70 (2) 1.82 (2)	[11]
Au–S 2.326 (3) 2.331 (3)		S–C 1.709 (5) 1.714 (5)	[27]
Au–S 2.318 (2)-2.409 (2)		S–C 1.723 (7)-1.732 (7)	[27]
Hg–S 2.405 (4)-2.419 (4)		S–C 1.73 (2)-1.744 (14)	[29]
Hg–S 2.467 (2)		S–C 1.702 (7)	[31]
Six-membered ring thiones			
Cu–S 2.393 (4) 2.425 (4)		S–C 1.690	[37]
Cu–S 2.331 (1)-2.379 (2)		S–C 1.693 (3)-1.703 (4)	[38]
Cu–S 2.602 (1) 2.632 (1)		S–C 1.693 (4) 1.711 (4)	[39]
Cu–S$_{mono}$ 2.284 (2)-2.298 (2)		S–C 1.699 (8) 1.708 (8)	[41]
Cu–S$_{brid}$ 2.377 (2)-2.443 (2)			[41]
Cu–S 2.215 (4)		S–C 1.72 (1)	[42]
Cu–S 2.363 (3)			[43]
Cu–S 2.348 (2)		S–C 1.703 (6)	[44]
Cu–S$_{term}$ 2.304 (1) 2.307 (1)		S–C 1.698 (4) 1.710 (3)	[88]
Cu–S$_{brid}$ 2.403 (1) 2.406 (1)		S–C 1.717 (3)	[88]
Pd–S 2.399 (2)-2.407 (2)		S–C 1.696 (8) 1.703 (7)	[36]
Ag–S 2.638 (2) 2.699 (2)		S–C 1.648 (7) 1.655 (7)	[15]
Ag–S 2.557 (1)-2.592 (1)		S–C 1.695 (5)-1.701 (5)	[38]
Au–S 2.337 (3) 2.334 (3)		S–C 1.735 (12) 1.741 (12)	[27]
Higher ring thiones			
Hg–S 2.496 (5)		S–C 1.688 (8)	[45]
Condensed ring thiones			
Au–S 2.354 (4)	Au–N 2.124 (7)	S–C 1.722 (4)	[27]

[a] S.D., when available are given in parenthesis following the bond distance value. In clusters or in asymmetric molecules where a variety of bond distances are reported, their range rather than several discrete values are presented.

2.1. Five-membered ring thiones

2.1.1. Complexes with transition metals

The reaction of $Ni(NO_3)_2$ with two equivalents of 4-amino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazole-5-thione in ethanol produced diaquabis(LH-κ^2N,S) nickel(II) nitrate the structural determination of which verified the chelating coordination of the thione ligand and the formation of an octahedral nickel complex with the S atoms *trans* and the amino N donors in *cis* equatorial positions [7].

The formation of $[(\mu\text{-MeimtH})Au_2(PP)](ClO_4)_2$ complexes upon reaction of 1-methyl-imidazoline-2-thione with the $[Au_2(PP)](ClO_4)_2$ complexes where PP, bis-(diphenylphosphino)methane (dppm); bis(diphenylphosphino)ethane (dppe); or dppp was verified through the existence of two distinct signals in the ^{31}P-NMR spectra recorded in acetone. The spectrum of the dppp complex revealed no PP coupling. Deprotonation of the thione ligand was achieved by treatment of a tetrahydrofuran (THF) solution of the dppm complex with Na_2CO_3 [8]. The same thione was reacted with K_2PdCl_4 and the product studied by infrared (IR) spectroscopy and magnetic measurements. The crystal structure determination of the product confirmed its formula as $[Pd(LH\text{-}\kappa^1S)]Cl_2 \cdot 2H_2O$ where the chloride anions are doubly bridged by hydrogen bonds to two adjacent thione ligands and Pd is located in a square planar environment [9]. The thermal stability of a series of analogous compounds with both Pd and Pt and a variety of counteranions was also investigated by simultaneous TG, DTA and DTG recording. All Pt complexes decomposed along with their melting. The most thermally stable compound proved to be $Pd(LH)_4Br_2$ [10]. The reaction of K_2PtCl_4 with 1,3-dimethylimidazoline-2-thione in warm water yielded the homoleptic $[Pt(LH)_4]Cl_2 \cdot 4H_2O$ complex. Single crystals of the complex were irradiated both at room temperature and at 77 K and the radiation defects investigated by EPR in a range of temperatures between 77 and 298 K. The simulation of the signals observed following their temperature and angular dependence proved that irradiation gives rise to at least four species which have undergone electron transfer being identified as Pt(I) or Pt(III) compounds [11].

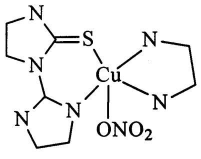
Refluxing of K_2PtCl_4 with two equivalents of thiazoline-2-thione (tztH) in water produced a 1:2 mixture of the complexes $Pt(LH)_2Cl_2$ and $[Pt(LH)_3Cl]Cl$. Heating of this mixture above its decomposition temperature under dinitrogen for 15 min resulted in the formation of trinuclear complex of formula $[Pt_3(LH)_8]Cl_2$. The structure of the final product was identified by X-ray photoelectron spectroscopy and by large angle X-ray scattering, revealing the existence of four bridging and four terminal thione ligands [12]. A sacrificial Cu anode was used in the electrolysis of tztH in toluene with NBu_4BF_4 as supporting electrolyte. The polymeric solvated complex $[Cu_4(tzt)_4 \cdot \text{toluene}]_n$ was isolated along with a small amount of cyclo(tetrakis-μ_3(η^2-S,η^1-N-tzt)-bis(η^1-S-tztH) tetracopper [13]. Assignment of the existence of both neutral and deprotonated thione ligand as well as of the coordination mode of both forms was carried out by vibrational and ^{1}H-NMR studies in a variety of solvents and in a range of temperatures. The structure of bis{μ-chloro-[2(3H)-benzothiazolethione](triphenylphosphine)copper(I)} dihydrate was solved and the tetrahedral environment of each of the copper atoms verified. The intramolecular

Cu···Cu separation was observed as 3.400 (2) Å [14]. The reaction of $AgNO_3$ with triphenylphosphine and imidazoline-2-thione, oxazoline-2-thione and their benzo analogues in a 1:2:2 ratio in EtOH or EtOH–$CHCl_3$ in room temperature yielded mononuclear complexes of the formula $[Ag(PPh_3)_2(\eta^1\text{-S-LH})_2]NO_3$. Variable temperature ^{31}P-NMR studies in dichloromethane solution verified the lability of the coordinated phosphine and the possible participation of nitrate anions in the coordination [15].

The reaction of $AuCl(PMe_3)$ with imidazolidine-2-thione or 1,3-diazinanethione in refluxing MeOH produced crystalline solids which upon recrystallization from aqueous methanol yielded complexes of the formula $[Au(PMe_3)(\eta^1\text{-S-LH})]Cl$. The characterization of the complexes was based upon their IR, ^{13}C-{^{1}H} and ^{31}P-NMR studies carried out in CD_3OD [16].

A 4-fold excess of the ligand 2-*S*-methyl-5,5-dimethylimidazoline-4-thione reduced $CuCl_2 \cdot 2H_2O$ in MeCN solution under an inert atmosphere to produce catena-chloro(μ-N,S-LH) copper(I) which owes its conformation to the strong intramolecular hydrogen bonding between the chloride and the imino proton of the ligand as well as to the interchain Cu···S interaction of 2.898 (2) Å between the metal and the thioether S atom [17]. The almost trigonal copper environment is a CuClNS one due to the bridging coordination mode of the thione. The reaction of tztH with $CuCl(PPh_3)_3$ in EtOH produced the monomeric tetrahedral complex $CuCl(LH)(PPh_3)_2$ the crystal structure of which was determined [18]. A series of analogous complexes with imtH, bimtH, btztH, and substituted benzimidazoline-2-thione were prepared and studied by IR and UV–vis spectroscopy. Their photolysis resulted in the elimination of phosphine and precipitation of solid compounds with the stoicheiometry $CuCl(LH)_2$ [18]. The reaction of cuprous halides with phosphine and thione ligands is still used for the synthesis of mixed ligand complexes and in such a reaction scheme in acetone complexes of the general formula $CuX(PAr_3)_2$(benz-1,3-thiazolidine-2-thione) were prepared with X, Cl or Br; and Ar, phenyl, *m*- or *p*-tolyl groups. Diphenyl-*p*-tolyl phosphine has also been used. The structure of the $CuCl(PPh_3)_2(LH)$ complex was determined and verified the well-known tendency of copper to adopt a distorted tetrahedral coordination [19]. A variation of the above procedure was adopted in the reaction of CuBr with triphenylphosphine and benz-1,3-thiazolidine-2-thione in 1:1:1 molar ratio which was carried out in the solid state at 125°C for 8 h. Extraction of the product with dimethylformamide (DMF) yielded the dimer complex $[\{CuBr(PPh_3)\}_2(\mu\text{-LH})_2]$ which was shown to possess a planar Cu_2S_2 core with acute Cu–S–Cu angles of 74.2° [20].

Reaction of 4-amino-1,2,4-triazole-5-thione with $Cu(NO_3)_2$ in the presence of 2,2-bipyridine (bpy) resulted in the formation of the complex $[Cu(bpy)(HL)(OH_2)](NO_3)_2$ the crystal structure of which was determined and proved the chelation of the ligand through its sulfur and amino-nitrogen atoms and the distorted square pyramidal geometry of the chromophore. Under analogous conditions but in the presence of LiOH, imidazolidine-2-thione gave the compound $[Cu(bpy)(L)(NO_3)](NO_3)$ (VIII) where the 1-(1′-imidazolin-2′-yl)-imidazolidine-2-thione ligand was prepared in situ. This ligand is chelating through the sulfur and one heterocyclic nitrogen giving rise to a trigonal pyramidal environment around copper [21].



Structure VIII

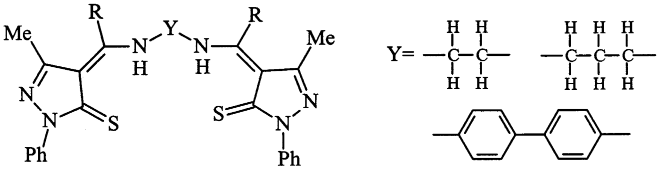
The reaction of 4,5-ethylenedithio-1,3-dithiole-2-thione with CuI in a 2:1 molar ratio in MeCN resulted in the formation of polymeric $[Cu_4I_4(LH)_4]$ in the stepped formation. The copper atoms are all tetrahedral but occur in two different environments, namely CuI_2SS and CuI_3S. Slow interaction with iodine resulted in partial oxidation to $[Cu_4I_4(LH)_4] \cdot I_x$ [22].

The bis diiodine complex of 1,1′-bis(3-methyl-4-imidazoline-2-thione)methane reacted with elemental tin in ether at room temperature affording after a period of 10 days a complex of the stoicheiometry $[Sn(L)_2](I_3)_2 \cdot 2/3I_2$ which was investigated by IR, Raman spectroscopy and X-ray structure determination and revealed a local octahedral tin environment with *trans*-iodides and chelating thione ligands [23].

Dioxane solutions of Mn(II), Co(II), Ni(II) and Zn(II) acetates reacted with ethyl *S*-(2-benzothiazolyl)mercaptoacetate to produce complexes of the formula $[Mn(n^1\text{-}N,L)_2(OAc)_2]$ and $[M(L)_2](OAc)_2$ for the rest of the metals. The formulation of the complexes was based upon conductance, magnetic measurements, thermal and UV–vis and X-ray photoelectron spectroscopy measurements [24]. The ligand in the complexes is chelating utilizing both S and N for Co and Ni and N and O for the Zn compounds, respectively.

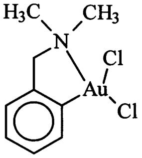
The potassium salt of the tridentate hydrotris(3-methyl-2-thioxo-1-imidazolyl)borate produced both polymeric Ag_2L_2 and $Ag(L)(PPh_3)$ depending on the reaction conditions. Comparative study of the IR, far-IR and ^{31}P-NMR spectra of the compounds with those of analogous complexes confirmed the *S*-coordination of the ligand in both cases and helped in the proposal of a trigonal AgS_2P and tetrahedral AgS_4 environment for the metal in the two complexes, respectively [25].

The Schiff bases IX derived from 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-thione and a series of diamines served as polyfunctional ligands which promptly reacted with bivalent metal acetates in refluxing EtOH to yield tetracoordinated $M(L^{2-})$ complexes. Study of the UV–vis spectra of the nickel complexes revealed the existence of both conformational isomers in solution while EPR studies of the copper complexes determined that the electronic effect of the biphenyl ring dominates in the determination of the structure over the steric effects [26].



Structure IX

The organogold complex X reacted with tztH to give a complex where the alkylamino site of the aryl was protonated. The crystal structure of the complex $[Au(LH)Cl(tztH)_2]Cl_2$ was determined confirming the monodentate character of the thione and the planar environment around the metal centre [27].



Structure X

2.1.2. Complexes with non-transition metals

Several adducts of imidazoline-2-thione and its 1-methyl analogue were formed upon refluxing in dichloromethane of the thiones with organotin compounds or tetrahalogenotin(IV). The IR and ^{1}H- and ^{13}C-NMR spectra of the complexes revealed that both in the solid state and in solution the thiones appear in their thione form while Mössbauer studies helped in the determination of the environment of tin as trigonal bipyramidal in $SnPh_3Cl$(MeimtH) and octahedral in the rest of the complexes therefore suggesting double chloride bridging in the complexes $[SnMeCl_3(MeimtH)]_2$, $\{SnMeCl_3(imtH)]_2$ and $[SnBuCl_3(MeimtH)]_2$. The ^{119}Sn-NMR spectra obtained were also indicative of the complete dissociation of the $SnPh_3Cl$(MeimtH) compound and the partial hydrolysis of $[SnBuCl_3(MeimtH)]_2$ in D_2O [28].

The halogeno complexes of Hg(II) with 1-methyl-imidazoline-2-thione with the general stoicheiometry $HgX_2(\eta^1\text{-S-LH})_2$ were prepared in aqueous ethanol and were characterized by IR, ^{13}C-NMR measurements and DCS studies. The crystal structure for the bromo complex revealed its dinuclear nature with bridging bromines *trans* to the terminal ones. The latter were found to act as links of adjacent dimers through a Hg…Br interaction ranging between 3.587 and 3.791 Å [29]. ^{1}H-, ^{13}C- and ^{198}Hg-NMR studies of $Hg(LH)_2X_2$ complexes where LH, imztH; and its *N*-methyl, *N*-ethyl, *N*-propyl or *N*,*N*′-dimethyl derivatives were in support of S-monodentate coordination of the ligands and formation of a single species in solution although there was, in a number of cases, an indication of exchange line broadening in the Hg spectra [30]. The complex of 4,5-ethylenedithio-1,3-dithiole-2-thione with $HgCl_2$ is dimeric in nature with a double chloro bridge and furthermore is found to form a one-dimensional ribbon through intermolecular S···S and S···terminal Cl interactions [31].

Refluxing of $CdCl_2$ with two equivalents of tztH in aqueous methanol for 2 h and subsequent evaporation of the solvent produced the mononuclear dichlorobis(η^1-S-tztH)cadmium(II) the structure of which was determined by X-ray diffraction [32].

The data collected from ^{13}C-MAS measurements reveal a deshielding of the keto and thioketo C atoms of 5,5,-dimethyl-4-oxoimidazolidine-2-thione ligand in its polymeric [Cs(LH)(OH)] complex which appears in a layer form with approximately van der Waals separations between the layers [33]. The data concerning Cs indicate the existence, in solution of discrete Cs^+ ions.

2.2. Six-membered ring thiones

Two routes have been exploited for the formation of manganese complexes with pyridine-2-thione with the stoicheiometry $MnX_2(pytH)_2$. Exposure of $MnCl_2(pytH)_4$ to vacuum resulted in the formation of $MnCl_2(pytH)_2$ while evaporation of an ethanolic solution of the ligand with $MnBr_2 \cdot 4H_2O$ gave the corresponding bromide [34]. Under these conditions $MnBr_2(pytH)_4$ was not isolated.

Reacting pytH with $FeCl_2$ and $FeCl_3$ in aqueous EtOH yielded products after 3 days with the stoicheiometries $FeCl_2(pytH)$ and $FeCl_4$(pyridine-2-thione disulfide). Mössbauer spectroscopic data confirmed the existence of Fe(II) and Fe(III) centres, respectively, and furthermore indicated that in the latter compound the monoprotonated form of the disulfide is present as a countercation to the $FeCl_4$ anion [35].

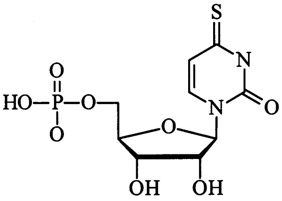
Spectroscopic and structural information has been published on the bis(pyridine-2-thione)bis(diphenylphosphinomethane)dipalladium(II) perchlorate which was produced by the addition of pyridine-2-thione to $[Pd_2(\mu\text{-dppm})_2][ClO_4]_2$ in methanol. The complex is a doubly bridged dimer with a monodentate thione ligand coordinated to each metal atom and a short Pd···Pd distance of 2.6645 (6) Å indicating a Pd–Pd bond. On the grounds of solid state and solution spectra it is concluded that in both states the structure of the complex remains unchanged [36].

A series of $CuCl(\eta^1\text{-S-LH})(PPh_3)_2$ complexes with pytH, pymtH, 4,6-dimethyl-pyrimidine-2-thione and 4-hydroxy-5-methyl-pyrimidine-2-thione were prepared and studied by IR and UV–vis spectroscopy. Their photolysis was carried out under aerobic conditions proceeding through phosphine elimination and subsequent oxidation to the corresponding phosphinoxide and precipitation of solid compounds with the stoicheiometry $CuCl(LH)_2$ [18]. Refluxing of cuprous halides with a tertiary phosphine and pyridine-2-thione in a molar ratio of 1:2:1 in chloroform results in the formation of dimeric complexes of the formula $[\{CuX(PAr_3)\}_2(\mu\text{-pytH})_2]$ where Ar, *p*-tolyl (X, Cl; Br) or *m*-tolyl (X, Br; I). The complexes were investigated by UV–vis, ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy in chloroform solutions and the crystal structure of the thione-bridged dimer $[CuI(P\{p\text{-tol}\}_3)(pytH)]_2$ was determined revealing a distorted tetrahedral environment around each metal centre [37]. The synthesis and crystal structure determination of the mononuclear homoleptic tetrafluoroborate complexes of copper(I) and silver(I) with 1-methyl-2-(1H)-pyridine-2-thione have been reported. The existence of a distorted tetrahedral environment around the metals was verified [38].

The reaction of $AgNO_3$ with triphenylphosphine and heterocyclic thiones in a 1:2:2 ratio in EtOH or EtOH–$CHCl_3$ in room temperature yielded mononuclear complexes of the formula $[Ag(PPh_3)_2(\eta^1\text{-S-LH})_2]NO_3$ with the notable exception of pymtH for which $[Ag(PPh_3)_2(\eta^1\text{-S},\eta^1\text{-N-pymtH})]NO_3$ was obtained due to the chelating ability of the ligand which is observed in the form of a Ag···N separation of 2.748 (3) Å [39]. The crystal structure of the pyridine-2-thione complex was also solved. In both cases, the nitrate anions are not coordinated but are bridging adjacent units through strong hydrogen bonds mainly to the imino protons of the thione ligands. The crystal structure of the analogous complex with benzoxazoline-2-thione has also been reported [15]. Furthermore ^{31}P-NMR studies of a series of the above complexes studied in dichloromethane solution in a range of temperatures verified the lability of the coordinated phosphine and the possible participation of nitrate anions in the coordination.

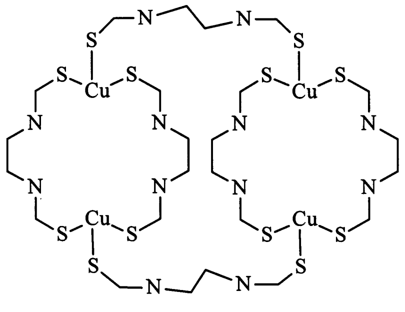
The organogold complex $AuCl_2$(2-(dimethylaminoethyl)phenyl) reacted with pyridine-2-thione to give several complexes where protonation the dimethylamino group of the coordinated aryl and subsequent cleavage of the Au–N bond. The crystal structure of $[Au(LNH)Cl(pytH)_2]Cl_2$ was determined confirming the existence of the gold atom in a distorted planar environment [27].

The tendency of Au(III) complexes to interact with 4-thiouridine-5′-monophosphate has been studied as a model of gold drug interaction with nucleobases. For this purpose, the kinetic and activation parameters of the insertion of the ligand to *trans*-$[AuCl_2(NH_3)_2]^+$ and *trans*-$[AuCl_2(CN)_2]^-$ has been investigated in the range of $2.9 \leq pH \leq 7.0$ with the main body of information derived at a pH value of 4.0. Protonation equilibria had to be taken into consideration and consequently it was observed that electrostatic interactions between the ligand and the metal centre and the steric blocking of the thioketo binding site have to be opposing in order for the insertion to proceed at a reasonable speed [40].



Structure XI

The reaction of *N*,*N*′-ethylenebis(pyridine-2-thione) with $[Cu(NCMe)_4]PF_6$ in mixed EtOH–MeCN medium produced the polymeric complex XII with the formula $\{[Cu_2(L)_3(PF_6)_2]_2\}_\infty$. Each of the units is connected to the next through one monodentate thione therefore giving rise to a tetramer with two 18- and one 36-membered rings. The tetrahedral copper environment is completed through interaction with S atoms from neighboring units [41].



Structure XII

Tetrahydropyrimidine-2-thione reacted promptly with CuBr to form a monomeric $Cu(LH)_2Br$ compound, which further reacted with several phosphines and triphenylarsine to give the corresponding tetrahedral complexes. The crystal structure of the initial complex was determined and ^1H-, ^{13}C- and ^{31}P-NMR studies verified the structure of the final products [42]. Excess of the above ligand reacted with the trinuclear $(PPh_3)_3WS_4Cu_2$ $0.8CH_2Cl_2$ in CH_2Cl_2 produced a solid product which upon recrystallization from propanol yielded the linear trinuclear complex of the formula $[\{Cu(PPh_3)(thpymtH)\}_2(\mu\text{-}WS_4)]$ where the environment around each copper is pseudotetrahedral [43] consisting of two sulfido bridges to tungsten, one thioketo atom from the thione and one phosphorus atom. An analogous reaction using tetrathiomolybdate and pyridine-2-thione yielded a similar linear cluster of the formula $[\{Cu(PPh_3)(\eta^1\text{-S-pytH})\}_2(\mu\text{-}MoS_4)]$ with similar characteristics regarding the thione coordination mode and the copper environment [44].

2.3. Higher ring thiones

Refluxing of $AuCl(PMe_3)$ in MeOH for 6 h with 1,3-diazepinethione produced $[Au(PMe_3)(\eta^1\text{-S-LH})]Cl$ which was characterized by IR, ^{13}C-$\{^1H\}$ and ^{31}P-NMR studies carried out in CD_3OD [16].

1-Azacycloheptane-2-thione reacted at room temperature with $HgCl_2$ to form a solid product, which upon recrystallization from acetone produced crystals of the formula $HgCl_2(\eta^1\text{-S-LH})_2$ possessing a tetrahedral environment around Hg(II) [45]. Multinuclear NMR studies of $HgX_2(LH)_2$ with LH, 1,3-diazinane-2-thione and 1,3-diazepine-2-thione confirmed the n^1-*S* coordination mode of the ligands and the formation of a single species in solution [30].

2.4. Condensed ring thiones

The reaction of $RuCl_2(PPh_3)_2$ in EtOH under dinitrogen with various purine-6-thiones has been investigated and the final products were identified to contain neutral ligands chelating to the metal centre giving rise to an overall pseudo octahedral Ru environment. The complexes isolated were $[Ru(H_2L\text{-}\kappa^2N,S)_2(PPh_3)_2][CF_3SO_3]_2$ and the corresponding chloride for 2-amino-purine-6-thione, $[Ru(H_2L\ L\text{-}\kappa^2N,S)_2(PPh_3)_2]Cl_2$ for 2′,3′,5′-tri-*O*-acetylriboside-purine-6-thione and $[Ru(H_2L\ L\text{-}\kappa^2N,S)_2(PPh_3)_2][CF_3SO_3]_2$ for purine-6-thione [46]. Electrochemical study of the latter revealed one monoelectronic oxidation at 1.02 V. Reaction of $RuCl_3(AsPh_3)_2(MeOH)$ with excess purine-6-thione in refluxing methanol produced $[Ru(H_2L)_2(AsPh_3)_2(MeOH)]Cl_2$.

Extensive studies have been reported for the interaction of 6-mercaptopurine with divalent copper salts in water under carefully controlled pH conditions and in metal–ligand ratios 1:1, 1:2 and 1:3. On the basis of IR, UV–vis, EPR spectra obtained and on magnetic measurements it was concluded that a polymer of the bisanionic form of the ligand is formed which gives rise to a local tetragonal copper environment and which appears to be thermally and kinetically stable [47]. The complex CuCl(η^1-S-quinoline-2-thione)(PPh_3)$_2$ was prepared and studied by IR and UV–vis spectroscopy. Its photolysis revealed phosphine elimination and formation of CuCl(LH)$_2$ [18].

The synthesis of a series of complexes with 1-(2′-pyridyl)benzothiazole-2-thione has been reported by its reaction in ethanolic solution with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Ru(III), Rh(III), Pt(IV) and Au(III). The ligand is assumed to coordinate through its thioketo group and the pyridine heteroatom on the basis of IR, UV–vis, ^{1}H-NMR spectroscopic evidence and molecular conductance measurements carried out in dimethylsulfoxide (DMSO). Octahedral environment was suggested for all the metals except Au for which trigonal bipyramidal was proposed as more plausible. In this respect, the Cr, Fe, Ru and Rh complexes are formulated as dimers with a double chloride bridge between the two metal centres [48]. The ligands 1-(2′-benzoxazolyl)pyridine-2-thione and its 2′-benzothiazolyl analogue were also used as bidentate ligands towards the same group of metals and their coordination suggested to involve both the thione moiety and the N heteroatom of the five-membered heterocycle. Magnetic measurements are in accordance with the proposed octahedral coordination of the metal centres and in support of the rest of the spectroscopic evidence [49]. In an analogous study the more extended 1,1-(2,6-pyrimidyl)bisbenzothiazole-2-thione ligand was utilized and the resulting complexes were studied by the same methods as above providing evidence for the octahedral coordination environment for the metals and the chelating ability of the ligand used. The Cr, Fe, Ru and Rh complexes were formulated as dimers with double chloride bridges between the metal centres [50].

A wide variety of metal salts reacted with *N*,*N*′-ethylenebis(pyrrolidine-2-thione) to give complexes of the general formula $MY_2(L)_2$, where M, Co; Ni; Cu; Zn; Cd and Y, Cl; Br; I; NCS; NO_3;or ClO_4. The crystal structures of $[CoCl_2(L)]_2$, $[Co(NCS)_2(L)]_n$, $[ZnBr_2(L)]_n$ and $[CuCl(L)]_n$ were reported [51]. Analogous reactions and products were also reported for the closely related *N*,*N*′-*p*-phenylenedimethylenebis(pyrrolidine-2-thione).

3. Thionate complexes

The term ‘thionate’ is being used in accordance with the proposal of Raper and is suitable in distinguishing the anions of heterocyclic thiones from other ‘thiolates’ e.g. anions of thiols in general which might be either alkyl or aryl thiols. Among the methods for obtaining thionate complexes the electrochemical anodic oxidation of the desired metal by neutral ligand solutions in aprotic solvents is gaining importance and a review of the technique and the structural determination of a wide variety of products has appeared [52].

Table 2
Relevant bond distances (Å) for a series of thionate complexes[a]

M–S bond	M–N bond	S–C bond	Reference
Five-membered ring thionates			
Co–S 2.682 (1) 2.470 (1)	Co–N 2.000 (2) 2.024 (2)		[56]
	Co–N 1.938 (2)		[56]
Cu–S 2.225 (2)-2.362 (2)	Cu–N 1.996 (7)-2.017 (5)	S–C 1.726 (7) 1.727 (8)	[13]
Cu–S 2.358 (1) 2.360 (1)	Li–N 2.030 (5) 2.035 (5)	S–C 1.704 (4) 1.708 (4)	[59]
Cu–S 2.345 (1)-2.409 (1)	Cu–N 1.298 (6)	S–C 1.715 (8) 1.727 (8)	[59]
Cu(II)–S 2.295 (2)		S–C 1.696 (9)	[63]
Cu–S 2.387 (1) 2.397 (2)	Cu–N 2.029-2.074 (5)	S–C 1.717 (7)	[70]
Cu–S 2.231(2)-2.286 (2)	Cu–N 2.007(6)	S–C 1.776 (7)	[89]
Zn–S 2.372 (4)		S–C 1.72	[73]
Zn–S 2.323 (5)-2.266 (5)	Zn–N 2.031 (1)-2.13 (2)	S–C 1.68 (2)-1.740 (4)	[75]
Zn–S 2.293 (2)	Zn–N 2.039 (3)	S–C 1.719 (4)	[75]
Pd–S 2.352 (4) 2.374 (12)	Pd–N 2.071 (9) 2.050 (9)		[61]
Pd–S 2.332 (1) 2.339 (1)		S–C 1.727 (4) 1.735 (4)	[70]
Ag–S 2.530 (1)		S–C 1.698 (5)	[70]
Sn–S 2.437 (1)	Sn–N 2.9203	S–C 1.746 (4)	[72]
Sn–S 2.481 (2)	Sn–N 2.947 (4)	S–C 1.719 (5)	[80]
Sn–S 2.772 (1)	Sn–N 2.463 (4)- 2.261 (3)	S–C 1.669 (5)- 1.718 (5)	[81]
Ru–S 2.424 (1)-2.438 (1)	Ru–N 2.051 (1) 2.069 (3)	S–C 1.763 (3) 1.770 (3)	[57]
Ru–S 2.450 (2)		S–C 1.702 (8)	[57]
Ru–S 2.503 (2)	Ru–N 2.242 (6)	S–C 1.714 (8)	[58]
Rh–S 2.452 (3)	Ru–N 2.149 (9)		[54]
Rh–S 2.392 (9) 2.432 (8)	Rh–N 2.07 (3) 2.10 (2)		[54]
Pt–S 2.329 (4)			[12]
Au–S 2.325 (1)		S–C 1.740 (4)	[70]
Au–S 2.356 (1)-2.358 (1)		S–C 1.743 (6) 1.735 (0)	[70]
Au–S 2.304 (2)		S–C 1.733 (7)	[70]
Au–S 2.279 (2) 2.288 (2)		S–C 1.725 (7) 1.748 (7)	[70]
Hg–S 2.566 (3)		S–C 1.716 (5)	[70]
Hg–S 2.507 (2) 2.595 (3)		S–C 1.73 (1)	[70]
Hg–S 2.431 (2)		S–C 1.737 (7)	[78]
Tl–S 3.200 (3) 3.530 (2)	Tl–N 2.540 (5)		[74]
Tl–S 2.986 (4) 3.038 (4) 3.406 (4)			[74]
Six-membered ring thionates			
V–S 2.389 (3) 2.396 (3)		S–C 1.699 (9)	[98]
Mn–S 2.503 (2)- 2.890 (2)	Mn–N 2.214 (5) 2.231 (5)	S–C 1.751 (6)	[34]
Co(III)–S 2.284 (3) 2.286 (3)	Co–N 1.936 (7) 1.955 (7)	S–C 1.708 (9) 1.724 (10)	[84]
Co(III)–S 2.277 (2) 2.2860 (2)	Co–N 1.956 (4) 1.933 (4)	S–C 1.712 (5) 1.733 (5)	[84]
Co–S 2.321 (2)-2.580 (3)	Co–N 2.138 (7)-2.266 (7)	S–C 1.666 (7)-1.84 (1)	[85]
Co–S 2.299 (1) 2.300 (1)	Co–N 1.917 (4) 1.925 (4)		[96]
Co–S 2.273 (3)	Co–N 1.919 (4)		[96]
Cu–S 2.320 (3)		S–C 1.758 (12)	[90]
Cu–S 2.239 (2)-2.264 (2)		S–C 1.753 (6)-1.776 (6)	[91]
Mo–S 2.344 (2)-2.564 (2)	Mo–N 2.177(6)-2.337(6)	S–C 1.771(8)-1.804 (8)	[82]
Mo–S 2.460 (1) 2.497 (2)	Mo–N 2.261 (5)	S–C 1.772 (6)	[82]
Ru–S 2.430 (5)-2.458 (5)	Ru–N 2.05 (2) 2.10 (2)	S–C 1.74 (2) 1.76 (2)	[57]
Ru–S 2.431 (4) 2.444 (4)	Ru–N 2.11 (1)	S–C 1.70 (1) 1.73 (1)	[57]
Ru–S 2.488 (2) 2.451 (2)	Ru–N 2.142 (7)		[58]

Table 2 (*Continued*)

M–S bond	M–N bond	S–C bond	Reference
Ru–S 2.457 (6) 2.480 (6)	Ru–N 2.155(4) 2.21(2)		[58]
Ru–S 2.408 (2)	Ru–N 2.103 (6)	S–C 1.711 (8)	[95]
Ag–S 2.479 (4)-2.529 (4)	Ag–N 2.271 (11)-2.363 (11)	S–C 1.771 (14)-1.733 (15)	[92]
Cd–S 2.668 (4)-2.750 (4)	Cd–N 2.398 (10) 2.479 (11)	S–C 1.754 (13) 1.755(14)	[102]
Sn–S 2.46 (3)	Sn–N 2.488 (9)	S–C 1.75 (1)	[103]
Sn–S 2.473 (2)	Sn–N 2.426 (4)	S–C 1.750 (5)	[103]
Re–S 2.372 (2)-2.393 (2)	Re–N 2.090 (5)-2.165 (5)		[83]
Os–S 2.410 (3) 2.433 (3)		S–C 1.79 (1)	[99]
Os–S 2.444 (3) 2.465 (4)		S–C 1.77 (1)	[99]
Au–S 2.256 (3)		S–C 1.76 (1)	[93]
Higher ring thionates			
In–S 2.517 (2)-2.546 (2)		S–C 1.722	[105]
Tl–S 2.351 (3)-2.546 (3)		S–C 1.716-1.733	[105]
Condensed ring thionates			
Co–S 2.331 (1)	Co–N 1.953 (3)	S–C 1.732 (4)	[110]
Rh–S 2.403 (2)		S–C 1.685 (8)	[111]
Pd–S 2.343 (3)	Pd–N 2.052 (9)		[112]
Re–S 2.455 (2) 2.533 (2)	Re–N 2.166 96) 2.191 (6)		[106]
Pt–S 2.356 (9) 2.349 93)			[112]
Pt–S 2.349 (3)	Pt–N 2.090 (10)		[112]
Au–S 2.296 (8)			[108]
Au–S 2.342 (3) 2.343 (3)			[108]

[a] S.D., when available are given in parenthesis following the bond distance value. In clusters or in asymmetric molecules where a variety of bond distances are reported, their range rather than several discrete values are presented.

3.1. Five-membered ring thionates

3.1.1. Complexes with transition metals

Reaction of thiazolidine-2-thione with K_2PtCl_4 in aqueous solution in a molar ratio of 2:1 or heating of the solid platinum complexes PtL_2Cl_2 and $[PtL_3Cl]Cl$ at 150°C produced the solid amorphous trinuclear complex $[Pt_3(L)_4(\mu\text{-}L)_4]Cl_6$ the large angle X-ray scattering study of which verified the coordinating scheme of the thionate ligands and the participation of the chloride anions in a hydrogen bond network to the amino groups of the thionates. The best fit of the results was achieved by assuming a Pt–S distance of 2.392 (4) Å for both bridging and terminal thionates [12].

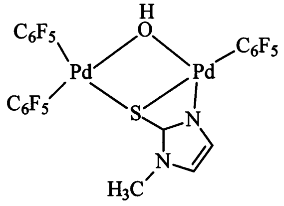
Reaction of (acetylacetonato)(2-(dimethylaminomethyl)phenyl-C-1,N)palladium-(II) with 2.3 equivalents of btztH in CH_2Cl_2 at room temperature resulted in the formation of the homoleptic dimeric bisthionato complexes. The same reaction with bimtH, tztH afforded protonation and subsequent elimination of the acetylacetone and formation of dimeric heteroleptic thione-bridged complexes. Analogous bridged compounds were obtained when (acetylacetonato)-(8-methylquinolyl-C,N)palladium(II) was used as starting material [53]. The compounds were characterized by IR and ^{1}H-NMR spectroscopy and it was verified that in solution only one isomer is present with C *trans*- to N and a head-to-tail arrangement for the thionate ligands. The complexes obtained by the reaction of imidazolidine-2-thione and 1-methyl-imidazoline-2-thione with $[RhCl_3(CH_3C(CH_2PPh_2)_3)]$ had the stoicheiometry $RhCl(L)(CH_3C(CH_2PPh_2)_3)]Cl$ and were studied by ^{31}P-NMR spectroscopy and appeared to be rigid. However, the reaction of the above thiones and benzimidazoline-2-thione with $[Rh(MeCN)_3(CH_3C(CH_2PPh_2)_3)]^{3+}$ produced complexes with the stoicheiometry $[Rh(L)_2(CH_3C\{CH_2PPh_2\}_2CH_2P(=O)Ph_2)]^+$ indicating that in the process the tripodal phosphine has removed one of its arms from the metal vicinity rendering the diphenylphosphino group amenable to oxidation [54]. The crystal structures of $[RhCl(imt)(CH_3C(CH_2PPh_2)_3)]Cl$ and $[Rh(Meimt)_2(CH_3C\{CH_2PPh_2\}_2CH_2P(=O)Ph_2)](CF_3SO_3)$ were also reported verifying the chelating coordination of the thionates.

An interesting competition between SCN^- and Cl^- depending on the pH was observed in the reaction of an equimolar mixture of KSCN and benzimidazole-2-thione or benzoxazole-2-thione with $[ReOCl_5]^{2-}$ in aqueous media. The resulting complexes are of the formula $[ReO(\eta^1\text{-S-LH})(OH_2)(SCN)_nCl_{3-n}]$ where $n = 2$ when the reaction is carried out in 6 N HCl and drops to $n = 1$ when 9 N HCl is used. Relevant IR, UV–vis spectra and magnetic measurements support an octahedral Re environment thus suggesting monodentate coordination of the thione ligands [55].

Benz-1,3-thiazolidine-2-thione reacted in methanol under dinitrogen atmosphere with $CoCl_2$ in the presence of phosphines to yield complexes $Co(\eta^1\text{-N-L})_2(PBu^n_3)_2$ with cobalt in a square environment and $Co(\eta^1\text{-N},\eta^1\text{-S-L})_2(dppe)$ which was shown to be octahedral [56]. The complexes were investigated by EPR and magnetic measurements over a range of temperatures and by cyclic voltammetry in DMF and MeCN revealing that they are at least partly solvated. The above thione yielded half-sandwich compounds incorporating the fragment $[Ru(9aneS_3)]$, where $[9]aneS_3$ represents 1,4,7-trithiacyclononane. Its reaction with $[Ru([9]aneS_3)(MeCN)_3]^{2+}$ produced the dinuclear complexes $[\{Ru([9]aneS_3)\}_2(\mu\text{-L})_2]^{2+}$ with μ-1κS:2κ^2N,S bridging ligands, which upon crystallization from MeCN yielded $[\{Ru(MeCN)([9]aneS_3)\}_2(\mu\text{-L})_2]^{2+}$ where the thionate is S-bridging. Analogous reactions were carried out with imidazoline-2-thione and related precursors, e.g. $[Ru([9]aneS_3)Cl_2(PPh_3)]$ or $[Ru([9]aneS_3)(MeCN)_2(PPh_3)]^{2+}$. In the former case $[RuCl(imtH)([9]aneS_3)]Cl$ was isolated while in the latter, depending on the metal–thione ratio used either $[Ru(imtH)(MeCN)(PPh_3)([9]aneS_3)]^{2+}$ or $[Ru(imtH)_2(PPh_3)([9]aneS_3)]^{2+}$ were obtained [57]. The octahedral environment of Ru(II) in $[Ru(MeCN)(btzt)(triphos)]^+$ where triphos represents the tridentate phosphine $CH_3C(CH_2PPh_2)_3$ was verified by its crystal structure determination and the dissociation of MeCN observed by ^{31}P-NMR measurements in a wide range of temperatures [58].

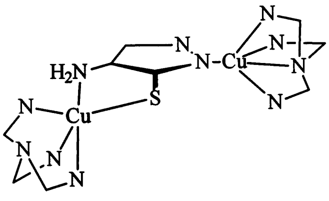
Treatment of $[Cu(Cp)(PPh_3)]$ in THF with the lithium salt of botzH yielded the complex $[\{Cu(PPh_3)\}(\mu\text{-L})\{Li(THF)_2\}]$ which upon treatment with $CuCl_2$ in THF underwent ligand transfer to afford $Cu(L)_2(PPh_3)_2$ and $[Cu(L)(PPh_3)]_4$. The crystal structures of both the intermediate and the final Cu(I) complexes were determined at low temperature. In the first case, the thionate ligand is bridging two different metals coordinating to copper through its S and to lithium through its N atom. The tetrameric cluster contained three bridging and one μ_3-S bridging thionates and its electrochemical oxidation was realized in a single irreversible step, whereas the first complex revealed a complicated behavior indicating formation of by-products most probably due to the lability of the phosphine and not to Li^+ dissociation as a series of treatments revealed [59]. Both benzoxazoline-2-thione and its anionic bis complex with Au(I) reacted with $AgClO_4$ to yield the homo- and hetero-binuclear compounds $[Ag_2(\mu\text{-L})_2]^{2+}$ and $[AgAu(\mu\text{-L})_2$, respectively. For the latter linear AgN_2 and AuS_2 environments were proposed [60].

The reaction of the anionic complexes of the formula $[\{M(C_6X_5)_2\}_2(\mu\text{-OH})_2]^{2-}$ with two equivalents of 2,6-dimethyl-5-*oxo*-1,2,4-triazine-3-thione and 6-methyl-5-*oxo*-1,2,4-triazine-3-thione in acetone or dichloromethane has been shown to split the dimers and cleave the hydroxyl bridges yielding monomeric complexes of the formula $[M(C_6X_5)_2(\eta^2\text{-thionate})]^-$ (X, F; Cl; M, Pd; Pt) [61]. The corresponding pentafluorophenyl complexes with 1-methyl-imidazoline-2-thione proved to be in dynamic equilibrium in solution as NMR studies revealed but in the solid state appeared similar to the above described complexes. However, slow crystallization in the presence of traces of water produced the dimeric compound XIII.



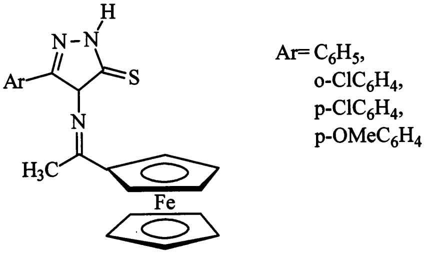
Structure XIII

Reaction of 5-amino-1,3,4-thiadiazole-2-thiol with divalent copper salts in warm alcoholic media yielded two green Cu(II) complexes of the formula $[Cu(\kappa^2\text{-}N,N'\text{-}L)_2(OH_2)]$ and $[Cu(imH)_2(LH)(SO_4)]$, respectively, both of which appear to be non-electrolytes in DMSO. The compounds were studied by IR and Raman and in view of the corresponding spectra of the ligands their assignment has been carried out indicating that the thione ligand is chelated to the metal through the amino group and the closest N heteroatom [62]. The closely related 4-amino-1,2,4-triazole-5-thione upon reaction with (*tris*((benzimidazol-2-yl)methyl)amino)(nitrato)copper-(II) nitrate in aqueous ethanol yielded a dimeric compound XIV with bridging thionate which was characterized by its IR and UV–vis spectra. The crystal structure determination of the compound revealed two distinct copper sites, with one copper coordinated to the N1 of the thione ring and the polyamino ligand and the other chelated to the exocyclic sulfur and the 4-amino group thus forming a distorted square pyramidal environment [63].



Structure XIV

The ligands XV reacted with bis(cyclopentadienyl)bischloro titanium and zirconium in refluxing THF to afford compounds of the stoicheiometries $(Cp)_2MCl(L)$ or $(Cp)MCl(L)_2$. The reaction with $(Cp)TiCl_3$ produced $(Cp)TiCl_2(L)$ and $(Cp)TiCl(L)_2$, respectively. All the complexes were studied by IR, UV–vis, ^{1}H- and ^{13}C-NMR and in every case confirmation of the chelation of the ligand through the thioketo group and the exocyclic imino N atom [64].



Structure XV

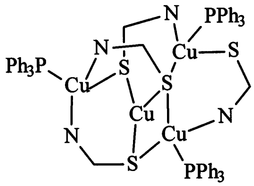
The reaction of 2-amino-5-mercapto-1,3,4-thiadiazole with divalent copper salts produced complexes which were formulated as $[Cu_2(\mu\text{-}Cl)_2(\mu\text{-}L)_2]$, $[\{Cu(OAc)\}_4(\mu\text{-}OAc)_4(\mu\text{-}L)_2]$ and $[\{Cu(LH)(L)\}_2(\mu\text{-}Cl)_2]$, respectively, in view of their thermal decomposition studies [65].

The insoluble silver complexes of 3-amino-5-mercapto-1,2,4-triazole and its *S*-methylated analogue were produced in aqueous ethanol and characterized by IR-, far-IR and X-ray powder spectroscopy the data of which suggest a 1κN; 1κ^{2}N,S bonding for the ligands [66]. The corresponding 4-amino-5-mercapto-1,2,4-triazole and its 3-methyl, ethyl and isopropyl derivatives formed Schiff bases with furfuraldehyde which upon reaction with divalent metal acetates formed compounds of the formula $M(L)(OAc)\cdot nH_2O$ or $M(L)_2\cdot nH_2O$ (M, Co; Ni; or Cu) depending upon the ratio of the reactants. The UV–vis, ^{1}H-NMR, EPR studies and magnetic measurements of the complexes suggest their formulation as octahedral with water molecules participating in the formation of the coordination environment [67]. The 3-phenyl- derivative of the above triazolethione and the corresponding oxadiazole were reacted with $FeSO_4$ and $FeCl_3$ in aqueous ethanol in the presence of pyridine or 8-hydroxyquinoline in slightly alkaline conditions and the products obtained were studied by IR, UV–vis, Mössbauer spectroscopy as well as with conductance and magnetic measurements which confirmed the bidentate character of the thionate ligands. The octahedral environment deduced for the complexes suggests the existence of a double hydroxo- bridge in the complexes $[\{Fe(L)(OH)(py)\}_2(\mu\text{-}OH)_2]$

and [{Fe(8-hydroxyquinolinate)(L)}$_2$(μ-OH)$_2$]. The antifungal activity of the compounds was tested and proved to be inferior to that of 8-hydroxyquinoline [68]. Trivalent iron reacted also with benzimidazoline-2-thione and benzoxazoline-2-thione in anhydrous methanol in the presence of NaSH to form doubly bridged sulfido dimers of the formula [{Fe(L)}$_2$(μ-S)$_2$]. IR, ^{1}H-NMR spectroscopy and magnetic measurements suggested a tetrahedral environment around the Fe(III) centres. The nitrate reductase activity of the complexes was determined both in phosphate buffered solution and in DMSO. In DMSO the complexes appeared to have better activity than the ferric salts and the free ligands whereas the opposite was observed in the buffered solution [69].

Reaction of AuCl$_2$(2-(dimethylaminoethyl)phenyl) 1-methylemercaptotetrazole yielded [Au(LH)(1-methylmercaptotetrazolate)$_3$] the crystal structure of which has been determined. The compound is further transformed to the corresponding Au(I) complex [Au(HL)$_2$]$^+$. The thione ligands are monodentate and only purine is chelating. Furthermore the reaction of the tetrazole sodium salt with NaAuCl$_4$ produced the homoleptic anionic structurally characterized [Au(L)$_4$]$^-$ complex [27].

The systematics in the coordination of 2-methyl- and 2-phenyl-1,2,3,4-tetrazole-5-thionate (MeL and PhL, respectively, in the following) were investigated towards heavy metals especially Pd, Hg and group 11 metals. In all cases, the S-monodentate coordination was verified by X-ray structural analysis [70]. The complexes Au(PPh$_3$)(MeL) Au(PPh$_3$)(PhL) and [Au(PhL)$_2$]$^-$ appeared to be almost linear with P–Au–S or S–Au–S angles between 170.11 (3) and 175.15 (7)°, the homoleptic [Au(MeL)$_4$]$^-$ and [Pd(MeL)$_4$]$^{2-}$ were prove to be square planar. The environment of monomeric Ag(PPh$_3$)$_2$(PhL) was trigonal planar while for the corresponding Au(PPh$_3$)(MeL) a dimeric structure was realized due to intermolecular Au...S interactions. The mercury complexes Hg(PPh$_3$)$_2$(PhL)$_2$ and [Hg(PhL)$_4$]$^{2-}$ possess a metal atom in a distorted tetrahedral environment while the crystal structure of the supposed [Cu(PPh$_3$)(MeL)]$_4$ tetramer XVI proved to contain units of the stoicheiometry Cu$_4$(PPh$_3$)$_3$(MeL)$_4$ with three metal atoms in a distorted trigonal pyramidal environment and the fourth one in a three-coordinate one.



Structure XVI

Mössbauer spectroscopy has revealed that the reaction product of 1,3,4-thiadiazole-2,5-dithiol with FeCl$_2$ in aqueous ethanol consists of Fe(L)$_2$ units where the monoanion of the thiol is present [35].

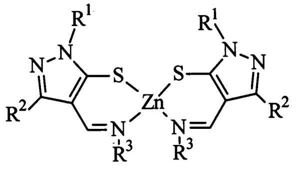
3.1.2. Complexes with non-transition metals

Analytical applications of thioamide ligands have appeared recently, especially when binding to heavy metals is desired. In such an effort modification of polished glassy carbon electrodes was performed by anodic polymerization of bimtH and boxtH which proved to form a surface coat of the corresponding disulfides. The modified electrode binds Hg^{2+} from solution in a selective manner, providing also good sensitivity, substantial stability over a period of time and effective regeneration [71].

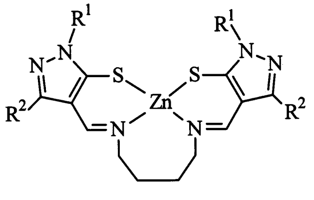
Triphenyl(2-mercapto-1-methylimidazolato)tin(IV) was obtained from the reaction of the thione ligand with Ph_3SnOH. The compound revealed a tetrahedral Sn environment with a slight distortion due to a Sn···N interaction at 2.920 Å in the solid state but in solution ^{119}Sn-NMR studies in a range of temperatures support. The existence of a hydrolytic equilibrium with the starting materials [72]. A tetrahedral zinc environment was observed in dichlorobis[1-methyl-3(prop-2-enyl)imidazole-2(3*H*)-thione-S]zinc(II) [73].

Both bridging and chelating thionates were observed in the complexes $Me_2Tl(L)$ prepared by the reaction of Me_2TlOH with 5-(2-pyridinylmethylene)rhodanine and 5-(2-pyridinylmethylene)-2-thiohydantoin. In the former Tl is located in a distorted octahedron with a chelating thionate ligand while it is also bridged to an O and a S atoms of adjacent units. The latter complex is among the few examples where a ligand is present in various tautomeric forms, as both N1 and N3 deprotonated thionates occur. Furthermore two bonding modes are presented in one of which the pyridine N is the second chelation point. The thione S of this molecule is bridging two adjacent Tl centres and the whole structure is tetrameric [74]. In DMSO solution both compounds behave however as partly ionic and the thiohydantoin complex reveals broadening of the NH protons due to exchange.

Pseudotetrahedral coordination around zinc with a slight distortion towards *trans*-planar was observed for two complexes of the formula ZnL_2 where L, 4-(2,6-dimethylphenyliminomethyl)-1-methyl-3-phenylpyrazole-5-thiolate or 4-isopropyliminomethyl-3-methyl-1-phenylpyrazole-5-thiolate [75]. The compounds were synthesized by reacting the neutral ligand with $Zn(MeCO_2)_2$ at room temperature in the presence of NaOMe and their structure resembles that of the zinc centre in horse liver alcohol dehydrogenase. Their electrochemical oxidation was quasi-reversible and their racemization kinetics and energetics for the bis chelate complexes (XVII a) were studied by ^{1}H-NMR measurements. The closely related complexes (XVII b) presented high redox potentials and water insolubility therefore precluding their utilization as models for enzymic sites [76].



(a)



(b)

The reaction of 4-amino-3-(*o*-tolyloxymethyl)-1,2,4triazole-5-thione with a variety of metals including Zn(II), Hg(II), Pb(II) and Tl(I) and their study by IR, UV–vis spectroscopy and magnetic measurements has been reported [77].

The coordination of 3-amino-5-mercapto-1,2,4-triazole towards mercury is κ^1S as the crystal structure of $HgBr_2(LH)_2$ confirmed [78]. Arylmercurial complexes of the formula ArHgL where Ar, C_6H_5, 4-MeC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4 and 4-$OMeC_6H_4$ and L, 2-mercapto-5-methyl-1,3,4-thiadiazolate or 3-mercapto-5-[4′-methylquinolinyl-2-oxomethyl]-1,3,4-oxadiazolate were obtained by microwave irradiation of a DMF solution of the thione, the corresponding arylmercury chloride and K_2CO_3 at 2.45 GHz [79].

The coordination modes of the monoanion of 1-phenyl-1H-tetrazole-5-thione towards tin(IV) are discussed in view of previous crystallographic studies of organotin complexes of this ligand of the formula SnR_3L or SnR_2L_2 correlated with the structure of $SnMe_2L_2$ where the tin environment may be viewed as distorted trapezoidal bipyramid. The ligand is monodentate and there exists a distant Sn···N interaction at 2.947(4) Å, which is between the sum of the covalent and the van der Waals radii of the atoms under consideration [80]. Reaction of the above thione with phenanthroline and $SnMe_2O$ in refluxing methanol produced the compound $[SnMe_2(phen)(L)_2]$ the crystal structure determination of which presented two distinctively different molecules in the unit cell with SnN_4C_2 and SnN_3SC_2 environments, respectively, the two methyl groups occupying the apical positions in the coordination sphere [81]. Study of the ^1H-, ^{13}C-and ^{119}Sn-NMR signals obtained in $CDCl_3$ revealed that the two forms are rapidly exchanging in solution.

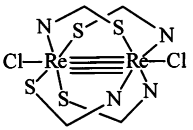
3.2. Six-membered ring thionates

3.2.1. Complexes with transition metals

Reaction of $Mn(MeCO_2)_2 \cdot 4H_2O$ with pyridine-2-thione in ethanolic solution for 2 h resulted in the formation of the polymeric compound $[Mn(pyt)]_n$ where octahedral Mn environment was shown by X-ray crystallography. The ligand anion is chelating while S bridges are formed between adjacent units [34].

The reaction of $Mo(CO)_3(MeCN)_3$ with pyridine-2-thione and triphenylphosphine in THF at 50°C produced a mixture which upon chromatographic separation yielded $[Mo_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2]$ along with small amounts of $[Mo_3(\mu\text{-}L)_2(\mu_3\text{-}L)_2(CO)_6]$. Upon reduction of the elute volume a more soluble compound with the stoicheiometry $[Mo_2(\mu\text{-}L)_2(CO)_5(PPh_3)]$ was also obtained. The crystal structure determination of the first two complexes revealed the existence of bridging thionates as well as Mo–Mo bonds [82].

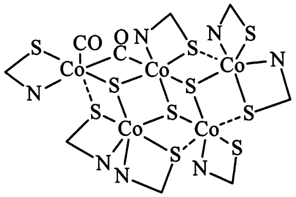
Substitution of halide ions from $[Re_2X_8]^{2-}$ occurred upon refluxing in MeCN with pytH, producing complexes of the formula $\{ReX]_2(\mu\text{-}L)_4$ with X, Cl or Br (XVIII). The same final products were prepared upon reaction of *cis*-$Re_2(OAc)_2X_4(OH_2)_2$ with a 4-fold excess of the ligand in refluxing ethanol. The non-symmetrical distribution of the bridging thionate ligands was suggested by the complexity of the ^1H-NMR spectra of the products and was verified by X-ray structural analysis of the chloro complex [83].



Structure XVIII

Reaction of pyridine-2-thione with $[Ru(MeCN)_3(1,4,7\text{-trithiacyclononane})]^{2+}$ in methanol afforded the complex $[\{Ru(L)\}_2(\mu\text{-pyt})_2]^{2+}$ the crystal structure determination of which proved the bridging character of the thionate in the μ-1κS:2κ^{2}N,S mode. An analogous reaction between dithiuracil and $[Ru(MeCN)_2(1,4,7\text{-trithiacyclononane})(PPh_3)]^{2+}$ yielded the dinuclear complexes of the formula $[\{Ru(L)(PPh_3)\}_2(\mu\text{-dtur})]^{2+}$ and $[\{RuCl(L)(PPh_3)\}(\mu\text{-dtur})\{Ru(L)(PPh_3)\}]^{+}$, respectively. The X-ray structural study of the latter revealed the unique bridging mode of dithiuracilate which is N,S chelating to one of the metal centres and S-monodentate to the second one [57]. The complex $[Ru(triphos)(MeCN)(pymt)]^{+}$ where triphos, $CH_3C(CH_2PPh_2)_3$ was assigned an octahedral environment on the basis of its spectral data and the structural information of analogous compounds. The coordinated MeCN molecule seems however to be labile as variable temperature ^{31}P-NMR measurements and the characterization of products of the formula $[Ru(triphos)(pymt)_2]$ and $[Ru(triphosO)(pymt)_2]$ revealed. The former of the last two complexes includes one chelating and one S-monodentate thionate anion while the latter, due to the oxidation of the temporarily de-coordinated phosphine arm, possesses two chelating pyrimidine-2-thionates [58]. The ligand pyridine-2-thione is analogous although in that case it was not possible to verify the results in the form of a crystal structure determination.

Two complexes of the general formula $[Co(P^nBu_3)_2(L)_2](BF_4)$ (L, pyridine-2-thionate or pyrimidine-2-thionate) were prepared by reacting $CoCl_2$ with the appropriate thione ligand in ethanol in the presence of MeONa. The compounds are octahedral with *trans*-phosphine ligands and *cis* orientation of the heterocyclic thionate chelates [84]. The reaction of pyridine-2-thione with $[Co(CO)_4]^-$ in THF at 40°C for 2 h in the presence of NEt_4Cl produced after recrystallization from ethanol the pentanuclear cluster with the formula $Co_5(\mu_3\text{-}S)_3(CO)_2(pyt)_7$. The cluster XIX includes three chelating and four bridging thionate units and can be viewed as an edge sharing of two distinct cubane-like clusters with Co_3S_4 and Co_3S_3C cores, respectively [85]. Reinvestigation of the structure of the homoleptic $Co(pyt)_3$ and $Co(pymt)_3$ complexes has been carried out utilizing one and two-dimensional ^{1}H- and ^{13}C-NMR measurements in $CDCl_3$ solution over a range of temperatures. The *mer*-isomers exist in solution as also shown to exist in the solid state for the former compound, with the three chelating ligands differing in their degree of thiolate or thionate character. The variable temperature dependence of the line shape of the two 6-H appearing around 8.08 ppm was ascribed to an intramolecular tautomerization of the coordinated ligand anions [86].



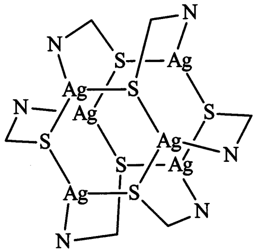
Structure XIX

Anodic electrooxidation of nickel with an acetonitrile solution of 6-*tert*-butyldimethylsilylpyridine-2-thione yielded the mononuclear $Ni(L)_2$ complex. When added in the electrolytic cell, 2,2′-bipyridine inserted into the complex to form $Ni(L)_2(bpy)$. The stoicheiometries of the complexes and the chelation of the thione ligand were derived from vibrational and nuclear magnetic resonance data in solution [87].

The reaction of the anionic complexes of the formula $[\{M(C_6X_5)_2\}_2(\mu\text{-}OH)_2]^{2-}$ with two equivalents of pyridine-2-thione or pyrimidine-2-thione in acetone or dichloromethane yielded monomeric complexes of the formula $[M(C_6X_5)_2(\eta^2\text{-thionate})]^-$ (X, F; Cl; M, Pd; Pt) [61]. The organopalladium complex (acac)(2-(dimethylaminomethyl)phenyl-C-1,N)Pd(II) with 2.3 equivalents of pytH or pymtH at room temperature resulted in the formation of the homoleptic dimeric bisthionato complexes [53]. The compounds were characterized by IR and ^{1}H-NMR spectroscopy. In solution only one isomer is present with C *trans* to N and a head-to-tail arrangement for the thionate ligands.

Pyridine-2-thione is known to react with copper salts to afford various complexes depending upon the salt and the solvent used. Addition of the ligand in 4-fold excess to an aqueous slurry of CuO in the presence of toluene-*p*-sulfonic acid produced the sulfonate complex $[\{Cu(pytH)_2\}_2(\mu\text{-}pytH)_2]^{2+}$ which on the basis of solution NMR studies [88] appears either to dissociate in solution or to undergo rapid exchange of its ligands. Reaction of pyridine-2-thione with $CuSO_4$ and $Cu(NO_3)_2$ in the presence of the conjugate acid yielded the compounds $[Cu_2(pytH)_2(SO_4)]$ and $[Cu(pytH)_2(NO_3)]$, respectively, which upon treatment with hydrohalogens gave the well-known polymeric $[CuX(pytH)]_n$ complexes. An interesting route to the synthesis of the well-known six-membered cluster $[Cu_6(pyt)_6]$ has been achieved through the reaction of 1,3-bis(2-pyridyl)-1-thiopropane with $CuSO_4$ in boiling aqueous methanol, 2-pyridyldisulfide and 2-vinylpyridine being among the products occurring after the cleavage of the ligand [88]. Reaction of the same ligand with monovalent copper salts in non-aqueous solvents yielded complexes with stoicheiometries depending on the solvent, i.e. $[Cu_2L_3]^{2+}$ in MeCN or $[Cu_2(L)(pyt)]^+$ in THF. The extremely bulky 6-*tert*-butyldimethylsilylpyridine-2-thione ligand when subjected to electrolysis in MeCN solution reacted with the sacrificial electrodes to afford complexes of the formula $[ML]_n$ where M, Cu or Ag. The copper complex further reacts with dppe and dppm to yield insertion products of the formula $[\{Cu(dppe)(L)\}_2(\mu\text{-}dppe)]$ and $[\{Cu(dppm)\}_2(\mu\text{-}dppm)(\mu\text{-}L)_2]$. The stoicheiometry of the complexes and the ligand coordination modes have been assigned by IR, ^{1}H- and ^{13}C-NMR studies [13]. The closely related 3-trimethylsilylpyridine-2-thione formed the corresponding thionate tetramer [89] which upon reaction with dppe in a 2:3 molar ratio in Me_2CO produced the dimeric compound $[\{Cu(dppe)\}_2(\mu\text{-}dppe)]$ the crystal structure of which was determined and discussed in relation to analogous complexes [90]. In analogy with the hexanuclear cluster of copper(I) with pyrimidine-2-thionate the corresponding one with the 4,6-dimethyl substituted ligand was prepared and the structure of the resulting hexacis[(μ_3-4,6-dimethylpyrimidine-2-thionato-N:S:S) copper(I)] dihydrate was determined revealing again that the copper atoms are in a square pyramidal environment with unequal Cu–S distances [91]. Both pyridine-2-thione and its *S*-methyl derivative as well as $[Au(pyt)_2]$- reacted with $AgClO_4$ to yield the homo- and hetero-binuclear compounds $[Ag_2(\mu\text{-}L)_2]^{2+}$ and $[AgAu(\mu\text{-}L)_2$, respectively. For the latter linear AgN_2 and AuS_2 environments were proposed [60].

Anodic deposition of the bulky 6-(*tert*-butyldimethylsilyl)pyridine-2-thione and 3,6-di(*tert*-butyldimethylsilyl)pyridine-2-thione on silver in acetonitrile solution yielded the corresponding hexameric thionate complexes. Reaction of both complexes with dppm in a mixture of $MeCN-CH_2Cl_2$ yielded $Ag_4Cl_4(dppm)_2$ in the first case and bis[3,6-bis(*tert*-butyldimethylsilyl)-2-pyridyl-sulfanyl]methane in the second case. The crystal structure determination of the hexameric cluster of the monosubstituted thionate XX revealed distorted trigonal silver environments with varying Ag···Ag interactions the smaller of which is 2.882 (2) Å and is considered as non-bonding [92].

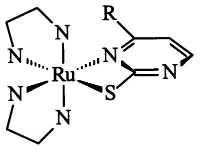


Structure XX

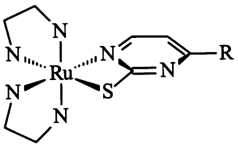
The 1:1 complex of methyl-4,6-*O*-benzylidene-*n*-deoxy-*n*-(diphenylphosphino)-α-D-altopyranoside (where $n = 2$ or 3) with AuCl reacted with pytH or pymtH in methanol in the presence of NaOMe and substituted the corresponding thionate for the chloride ion. The compounds were identified on the basis of their IR. ^{31}P- and two-dimensional ^{1}H- ^{13}C- correlated spectra. The structure of the pyrimidinethionato complex revealed its S-coordination to the metal centre [93].

Refluxing of $ReOX_2(OEt)(PPh_3)_2$ with 4,6-dimethylpyrimidine-2-thione in equimolar amounts in Me_2CO afforded $ReOX_2(L)(PPh_3)$ (X, Cl; Br; I) regardless of the duration of the reflux. The identity of the electronic spectra both in chloroform solution and in the solid state argue in favor of retention of the highly distorted octahedral environment, which was ascribed on the grounds of the magnetic measurements carried out [94]. Upon standing small amounts of $ReX_2(L)(PPh_3)_2$ were obtained which upon oxidation by atmospheric oxygen afforded $ReOX_2(L)$-(PPh_3) again as NIR and ^{1}H-NMR studies revealed.

Several substituted pyrimidine-2-thiones and thiouracils reacted with $RuCl_2(bpy)_2$ in aqueous methanol and afforded complexes of the formula $[Ru(L\text{-}N,S)(bpy)_2](ClO_4)$. The verification of the adjacent–remote linkage isomerism (XXI) in these complexes was studied by means of NMR measurements focusing on the C4 substituent signals providing grounds for the suggestion that a cooperation between steric repulsion and interactions between the alkyl substituents with the aromatic system of the bipyridine ligands is determining the adjacent–remote ratio in each case. Careful crystallization of the 4-methylpyrimidine-2-thionate complex yielded the pure adjacent form the crystal structure of which was determined [95].



adjacent



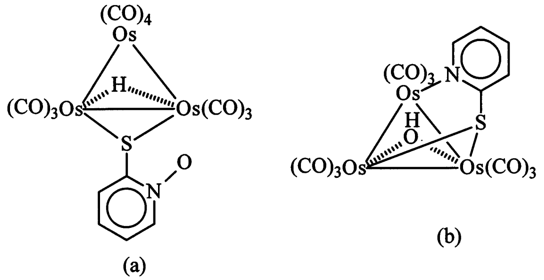
remote

The Rh(III) complex of the tripodal phosphine triphos ($CH_3C(CH_2PPh_2)_3$) $RhCl_3$(triphos) reacted with pyrimidine-2-thione to produce the complex [RhCl(L)(triphos)]Cl while the analogous $Rh(MeCN)_3$(triphos)]$(CF_3SO_3)_3$ produced $[Rh(L)_2$(triphos)](CF_3SO_3). ^{31}P-NMR investigation of the former complex in acetonitrile revealed lability of the tripodal phosphine and formation of the complex [Rh(L)(MeCN)(triphos)]$(CF_3SO_3)_2$. The evidence accounts for an equilibrium between the κ^3P and κ^2P forms of the phosphine ligand [54].

Under strong alkaline conditions and at 70°C *trans*-$[Co(en)_2Cl_2]$ reacted with 6-amino-thiouracil to produce both $[Co(en)_3]^{3+}$ and $[Co(en)_2(L)]Cl$ which upon treatment with perchlorate ions gave rise to $[Co(en)_2(L)]ClO_4$ and the corresponding complex with the protonated sulfide. The structures of both complexes was determined the latter being present as a dimer due to intramolecular hydrogen bonding [96]. Identical products were obtained by the photochemical reaction of $[Co(en)_3]Cl_3$ with stoicheiometric amount of the thione under alkaline conditions.

Ab initio studies at the Hartree-Fock-SCF level using effective core potentials have been applied in the investigation of the reactivity of 2-thiouracil towards triethylphosphine gold(I) cations. The 1:1 interaction proved the linear $Au(PEt_3)(L)$ complex to be the more stable with internal parameters quite similar to those observed crystallographically while the 2:1 interaction of the ligand bisanion predicted the bridging N,S mode of the ligand as the more stable leading to two almost linear P–Au–S and P–Au–N environments, respectively [97].

Reaction of VCl_3 with 3-hydroxy-pyridine-2-thione (LH_2) in the presence of NaOMe yielded a square pyramidal complex with the stoicheiometry $VO(\eta^1\text{-O},\eta^1\text{-S-LH})_2$ and in the form of infinite two-dimensional network due to intermolecular hydrogen bonds of the thioamido proton. The ligand anion coordinates in a chelating fashion as IR and EPR spectroscopic measurements verified [98]. When the ligand reacted with $Os_3(CO)_{11}(NCMe)$ in CH_2Cl_2 resulted in the formation of several products, mainly $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S})$ (XXII a), $Os_3(CO)_{10}(\mu\text{-H})(\eta^2\text{-L})$ and $Os_3(CO)_9(\mu\text{-H})(\mu\text{-}\eta^2\text{:}\eta^1\text{-L})$. The two first complexes yield the third one upon treatment with Me_3NO. Thermolysis of the first and third complexes at 80°C resulted in the formation of clusters with pyridine-2-thionate, namely $Os_3(CO)_9(\mu\text{-H})(\mu_3\text{-pytH})$ and $Os_3(CO)_9(\mu\text{-OH})(\mu_3\text{-pytH})$ (XXII b). The crystal structures of the depicted clusters have been solved and reported [99].



(a)
(b)

Structures XXII

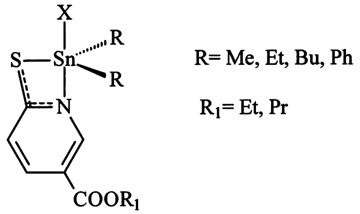
The stoicheiometric reaction of 2-mercaptonicotinic acid (H_2L) with [Ru(HEDTA)-(OH_2)] in aqueous media proved to yield at pH 4 the red complex $[(HL)Ru(EDTA)]^{2-}$ where n^1-S coordination of the ligand is proposed and at pH 6 the blue $[(L)Ru(EDTA)]^{3-}$ complex where the ligand is chelating to the metal. Stopped flow kinetic measurements of the formation of the former and of its transformation to the latter complex have been carried out. Furthermore, spectroelectrochemical study of the reaction of the ligand towards $[Ru(EDTA)]^-$ in a 1:2 molar ratio was carried out and the results obtained were in accordance with ZINDO calculations which predicted the formation of a stable $[\{Ru(EDTA)\}_2(\mu\text{-}n^1\text{-}N,n^1\text{-}S;n^1\text{-}S,n^1\text{-}O\text{-}L)]$ [100].

3.2.2. Complexes with non-transition metals

The monohalogeno tin complexes $Me_2SnCl(L)$ where L, pyridine-2-thionate or pyrimidine-2-thionate were found to bind to DNA fragments in contrast with their bisthionato counterparts. The compounds formed are suggested to be of the stoicheiometry $Me_2Sn(L)$(DNA monomer) and the environment around tin is either trigonal bipyramidal or octahedral depending on the assumptions in the utilization of the point-charge model treatment of the Mössbauer spectra obtained. Variable temperature Mössbauer spectroscopy also gave evidence for dynamic behavior of the above complexes and subsequent formation of compounds $Me_2Sn(\text{DNA monomer})_2$ [101].

Electrolysis of a MeCN solution of 4-methyl-6-trifluoromethyl-pyrimidine-2-thione with a Cd anode produced a polymeric complex with the stoicheiometry CdL_2 the crystal structure of which revealed its constitution of dimer units with two chelating and two bridging thionate ligands [102].

Reaction of the ethyl and propyl pyridine-2-thione-5-carboxylate with organotin compounds in ethanol in the presence of triethylamine produced complexes of the formula $R_2SnX(L)$ where R, Me; Et; Bu or Ph and X, Cl or Br (XXIII). The crystal structure determination of the bisetylbromo and the bismethyl chloro compounds revealed strongly distorted trigonal bipyramidal environment for the tin atom with chelating thionate and the halogen and the thione N-atoms occupying the apical positions. Resemblances of the Mössbauer spectra of the rest of the compounds indicated analogous structures for them also [103].



Structure XXIII

3.3. Higher ring thionates

Refluxing in a mixture of EtOH and CH_2Cl_2 of $[M(CO)_3(PPh_3)_2Cl]$ with 7-chloro-1,3-dihydro-5-phenyl-2H-1,4-benzodiazepin-4-thio-2-thione or its 2-chlorophenyl counterpart produced the complexes $[M(CO)_2(PPh_3)_2(L)]$ (M, Re; Tc) complexes. They were characterized by IR, ^{1}H- and ^{31}P-NMR studies and the coordination of the ligands was verified to be N,S-chelating in accordance with the corresponding *oxo* complexes for which structural evidence exist [104]. The metal environment is therefore supposed to be octahedral with apical phosphines and *cis* carbonyl groups.

Electrochemical oxidation of anodic Ga, In and Tl was performed using MeCN solutions of 1-hydroxypyridine-2-thione with NEt_4ClO_4 as supporting electrolyte. The compounds formed were studied by IR, ^{1}H- and ^{13}C-NMR spectroscopy and were identified as monomeric with the formula $M(\eta^2\text{-O,S-thionate})_3$. Interestingly enough NMR studies predict the *fac* structure as prevailing in solution while crystal structure determination for the In and Tl complexes showed that the solids adopt the *mer* conformation [105]. The corresponding Tl(I) thionate complex was isolated as well and according to ^{205}Tl-NMR studies in solution it appeared to form traces of its Tl(III) counterpart.

3.4. Condensed ring thionates

Quinoline-2-thione proved once again its tendency to form chelate coordination compounds. Refluxing of excess of the thione with $ReH_7(dppe)$ in benzene produced $ReH(\eta^1\text{-S},\eta^1\text{-N-L})(PPh_3)_2$ the crystal structure of which was determined [106]. The reaction was carried out in a variety of solvents under stoicheiometric conditions leading initially to the formation of $ReH_4(L)(PPh_3)_2$ which appeared to decompose upon prolonged refluxing. Addition of a second equivalent of the thione and further refluxing yielded a small amount of the $ReH(L)_2(PPh_3)_2$ as the coupling of ^{1}H-NMR spectra of the products revealed the Re–H resonance pattern expected.

The NMR study of $OsH(CO)(PPh_3)_2$(8-quinolinthionate) by utilizing NOE measurements at 193 K provided evidence for the existence of both *cis* and *trans* isomers of hydride relative to the sulfur of the thionate ligand in a ratio of 1:3. Reaction of this mixture with $HBF_4 \cdot Et_2O$ under Ar produced a mixture of the corresponding η^2-dihydrogen complexes as well as complexes with η^1-H and S protonated thione [107]. The structures of the 8-quinolinethionate gold complexes with the formulas $[Au(PPh_3)(L)]BF_4$ and $[\{Au(PPh_3)\}_2(L)]BF_4$ were determined. In the former a weak Au···N interaction may account for the deviation from linearity (P–Au–S angle observed to be 163.7 (3)°) while in the latter the bridging nature of the thionate brings the two metal centres in proximity and gives rise to a UV–vis absorption spectrum dependent on the solvent as well as to an emission spectrum with a characteristic band at 640 nm with a lifetime of 26 μs [108].

The interaction of 9H-purine-6(1H)-thione, 2-amino-purine-6(1*H*)-thione and 3,6-dihydro-6-thioxo-3-purine-2(1*H*)-one towards *fac*-$[CoCl_3$(triazacyclononane)] in alkaline media has been investigated. After successive evaporations of the products their chromatographic separation revealed the existence of both trimeric and tetrameric compounds of the formula $[Co_3L_3(\text{triazacyclononane})_3]^{3+}$ and $[Co_4L_4(\text{triazacyclononane})_4]^{4+}$. The nuclearity of the complexes was identified utilizing ESI mass spectrometry results and the geometrical isomers present were identified by NMR studies in solution [109]. The reaction of either *rac*-$\{Co(en)_3]Cl_3$ or *trans*-$\{CoCl_2(en)_2]Cl$ with 9H-purine-6(1*H*)-thione, its 2-amino and 2-hydroxy substituted analogues as well as with 2,3-dihydro-2-thioxo-9H-purin-6(1*H*)-one and 1H-pyrazolo[3,4-d]-pyrimidine-4(5*H*)-thione yielded after chromatographic separation, complexes of the formula $[Co(L^-)(en)_2]^{2+}$ or $[Co(L^{2-})(en)_2]^+$. The linkage isomerism expected in these complexes was studied by ^{1}H-, ^{13}C-NMR and ^{1}H–^{13}C COSY measurements. The crystal structure of the purinethionate complex $[Co(L)(en)_2]Cl$ was determined crystallographically and the thionate was verified to chelate to the metal through S6 and N7. An interesting stacking of the purine rings of adjacent molecules was also present in the unit cell of the compound [110].

When a 3-fold excess of purinethione was refluxed for 3 h with $RhCl_2Ph(SbPh_3)$ in ethanol the product obtained was of the formula $RhCl_2Ph(LH)(SbPh_3)\cdot EtOH$. The crystal structure determination revealed the existence of two types of molecules differing in the orientation of the phenyl substituent. The pseudooctahedral environment around the metal is determined by *trans* chlorine orientation and chelating thione with the heterocyclic N being *trans* to the phenyl substituent [111].

The reaction of 8-thiotheophylline with Pd and Pt in the presence of dppm resulted in the formation of compounds with the stoicheiometries $M(LH)_2$(dppm), $[M(\mu\text{-}L)(dppm)]_2$, and $[M_2(\mu\text{-}L)_2(dppm)]$. Reaction of the MCl_2(dppm) complexes with the ligand resulted in the formation of $[M_2(\mu\text{-}L)_2(dppm)(bpy)]$. The binuclear complexes are obtained both as single or mixed metal compounds in accordance with the IR and ^{31}P-NMR studies which revealed almost identical environments in Pd and Pt complexes indicating the possibility of metal substitution without significant alterations in the coordination environment [112]. The crsytal structures of $[Pt(\mu\text{-}L)(dppm)]_2\cdot 2DMSO$ and $[PdPt(\mu\text{-}L)_2(dppm)_2]\cdot 7H_2O$ were determined revealing a head-to-tail bridging mode of the thioamide.

The organogold complex $AuCl_2$(2-(dimethylaminoethyl)phenyl) reacted with 6-mercaptopurine to give a complexes of the thionato ligand and the N-protonated aryl. The crystal structures of the complex [Au(LH)Cl(6-mercaptopurinato)]Cl was determined confirming the chelating character of the purine and the planar environment around the metal centre [27].

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