

Electrochemical synthesis of metallic complexes of bidentate thiolates containing nitrogen as an additional donor atom

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Abstract

In this work, we describe the results obtained by our group on the synthesis of metallic thiolato complexes by the electrochemical oxidation of a sacrificial anode in a non-aqueous solution of the precursor ligand. In addition to its simplicity and high yield, the electrochemical method is both quick and selective, and provides a pathway to new compounds. The procedure has proven to be quite effective in obtaining mixed complexes in a single step by simply adding a second ligand to the cell. Our report is restricted to the synthesis and

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structural characterization of metallic compounds with heterocyclic thiones with diverse degrees of steric hindrance and containing, apart from sulfur, nitrogen atoms as donor atoms. The synthesis and structures of mixed complexes containing additional coligands such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe), are also described. A main part of the discussion is related to the influence of the steric hindrance and the presence of additional coligands on the degree of association of the metallic thiolates. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemical synthesis; Metallic thiolates; Heterocyclic thiones

Nomenclature

acac	acetylacetonate
hFacac	hexafluoracetylacetonate
py	pyridine
bipy	2,2'-bipyridine
phen	1,10-phenanthroline
dppm	bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dmp	2,9-dimethyl-1,10-phenanthroline
pySH	pyridine-2-thione
RpyS	pyridine-2-thione derivative
3-CF ₃ pySH	3-trifluoromethylpyridine-2-thione
3-Me ₃ SipySH	3-trimethylsilylpyridine-2-thione
6-TexMe ₂ SipySH	6-texyldimethylsilylpyridine-2-thione
3,6-(TexMe ₂ Si) ₂ pySH	3,6-bistexyldimethylsilylpyridine-2-thione
3-'BuMe ₂ SipySH	3- <i>tert</i> -butyldimethylsilylpyridine-2-thione
6-'BuMe ₂ SipySH	6- <i>tert</i> -butyldimethylsilylpyridine-2-thione
3,6-(^t BuMe ₂ Si) ₂ pySH	3,6-bis- <i>tert</i> -butyldimethylsilylpyridine-2-thione
pymSH	pyrimidine-2-thione
4,6-Me ₂ pymSH	4,6-dimethylpyrimidine-2-thione
4,6-MeCF ₃ pymSH	4-methyl-6-trifluoromethylpyrimidine-2-thione
5-Et-4,6-Me ₂ pymSH	5-ethyl-4,6-dimethylpyrimidine-2-thione
bzSH	benzothiazole-2-thione
MeImSH	1-methylimidazole-2-thione
imid	imidazole
1-Meimid	1-methylimidazole
HPT	1-hydroxypyridine-2-thione
TTFTCH	1,3,5-tris(trifluoromethyl)-1,3,5-trioxycyclohexane
oct	octahedral
sp	square planar
tbp	trigonal bipyramidal
tet	tetrahedral

1. Introduction

Although metal thiolates have been known since the beginning of co-ordination chemistry, in the last two decades an increasing interest in the study of these species has ensued as a result of a diversity of factors [1–7]:

1. From a bioinorganic point of view, thiolate complexes are of great importance, mainly due to the presence of thiolate donors in the co-ordination sphere of many metal ions in very diverse metalloproteins [8,9].
2. The growth in the utilization of metal thiolates in medicine. Particularly important are gold thiolates in the treatment of arthritis or as antitumor agents [1,9].
3. The use of volatile molecular thiolates as starting materials for chemical surface deposition of layers of metals or sulfides from vapor phase, (CVD) [1,10]. This requires the presence of low molecular weight species that are easily volatilized, at least to low pressure and that are thermally stable to sublime without decomposition.

Apart from their biological importance and the numerous potential applications, metallic complexes containing thiolate ligands are interesting from a structural point of view in their own right [2,5–7] since they adopt geometries of variable nuclearities with great structural complexity, as a result of their tendency to form metal bridges. This tendency towards polymerization can be modulated by manipulation of the nature of the R group bonded to the sulfur atom. An increase in the R volume is associated with a lower degree of polymerization as a result of steric hindrance.

Thus, the structure of compounds $[\text{Zn}(\text{SPh})_2]$ and $[\text{Cd}(\text{SPh})_2]$ [11] that can be considered as prototypes of the less sterically hindered thiolates, are polymers with an adamantane-like structure (Fig. 1). However, the presence of a methyl group *ortho* to the sulfur atom in the phenyl ring yields a macrocyclic structure containing seven cadmium atoms [12] (Fig. 2). The presence of three *tert*-butyl groups on the ring makes the compounds $[\text{M}(\text{S}-t\text{Bu}_3\text{C}_6\text{H}_2-2,4,6)_2]$ ($\text{M} = \text{Zn}$ ([13], Fig. 3) or Cd ([14], Fig. 4) have a dimeric structure. In both cases, two of the ligands have terminal sulfur atoms whilst another two sulfur atoms act as bridges between cadmium atoms; each metal possesses an unusual co-ordination number of three.

Analogous studies have been carried out with silver complexes [15]. With a slightly hindered thiolate ligand like $(\text{Me}_3\text{Si})\text{CH}_2\text{S}^-$, the compound $[\text{Ag}\{\text{SCH}_2(\text{SiMe}_3)_3\}_n]^-$ exists as a polymeric chain structure (Fig. 5). When another trimethylsilyl group is introduced, the resulting more bulky ligand, $(\text{Me}_3\text{Si})_2\text{CHS}^-$, gives rise to an octanuclear structure $[\text{Ag}\{\text{SCH}(\text{SiMe}_3)_2\}_8]$ (Fig. 6). Further degrees of steric hindrance on the sulfur atom, as with $(\text{Me}_3\text{Si})_3\text{CS}^-$ or $(\text{Me}_2\text{PhSi})_3\text{CS}^-$ substituents, leads to the formation of tetrameric $[\text{Ag}\{\text{SC}(\text{SiMe}_3)_3\}_4]$ (Fig. 7) and the trimeric species $[\text{Ag}\{\text{SC}(\text{SiMe}_2\text{Ph})_3\}_3]$ (Fig. 8), respectively.

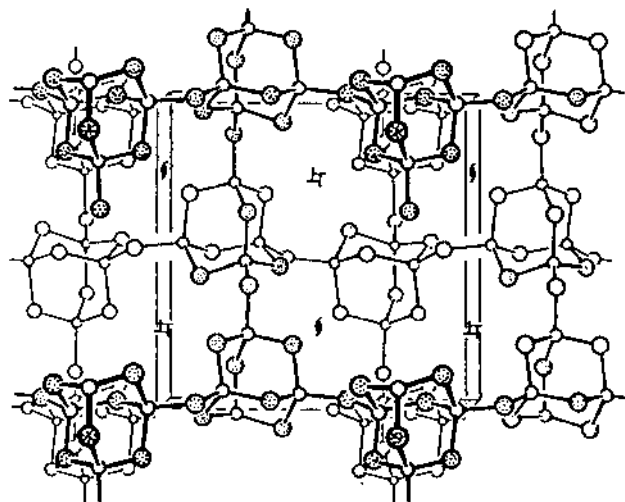


Fig. 1. Molecular structure of [Cd(SPh)₂] (adapted from Ref. [11]).

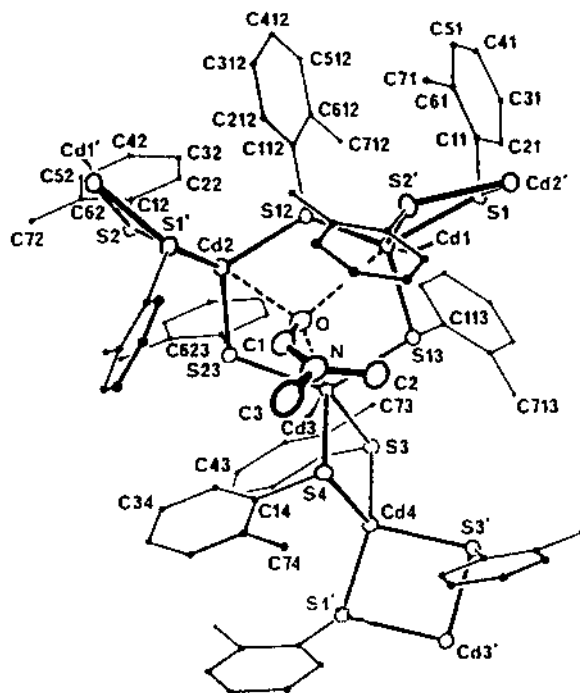


Fig. 2. Molecular structure of [Cd(SPh-2-Me)₂] (adapted from Ref. [12]).

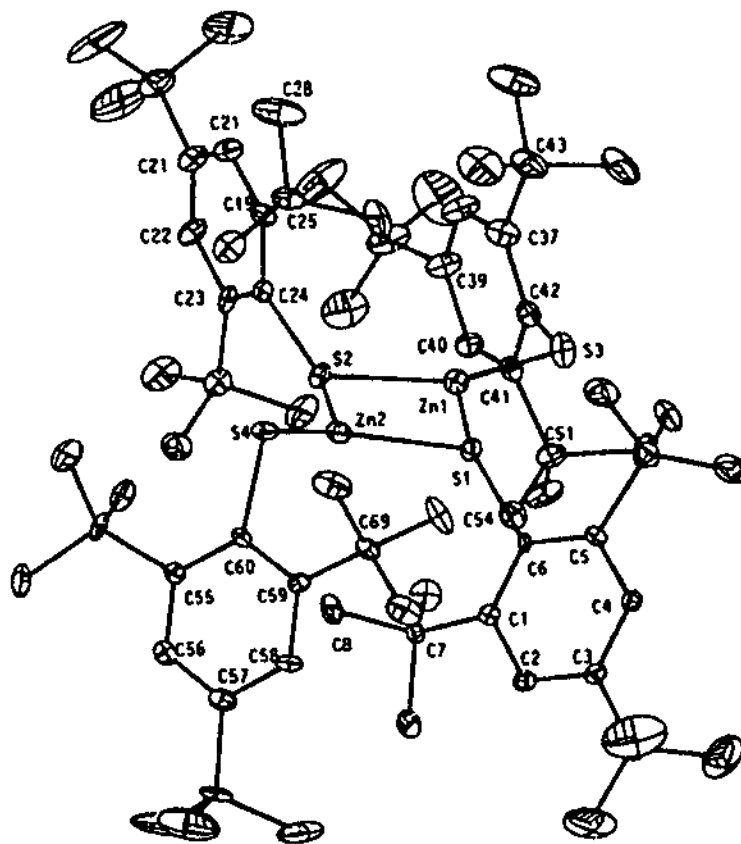


Fig. 3. Molecular structure of $[\text{Zn}(\text{S-Bu}_3\text{C}_6\text{H}_2-2,4,6)_2]$ (adapted from Ref. [13]).

The same type of behavior is also observed for Cu(I), although a structural parallelism does not always exist between the Cu(I) and Ag(I) derivatives. Thus, while Cu(I) [16] forms a dodecametallic cluster with the $2-(\text{SiMe}_3)-\text{C}_6\text{H}_4\text{S}^-$ ligand, with linear and planar trigonal environments for the copper atoms (Fig. 9), Ag(I) [17] yields a bicyclic structure (Fig. 10). The tetranuclear structure of the Cu(I) complex (Fig. 11) with the $2,6-(\text{SiMe}_3)_2-\text{C}_6\text{H}_3\text{S}^-$ ligand is another example of the influence steric hindrance has on the nuclearity [18].

In the examples discussed, the higher the steric requirements of the ligands the lower the degree of association. This reduction in the degree of association can also be achieved by simultaneous co-ordination of the metal to other donor atoms, either by introduction of an additional neutral ligand apart from the thiol, or by use of chelating ligands containing other donor groups along with the thiolate sulfur atom.

In this review, the results obtained by our group on the electrochemical synthesis of metallic complexes of chelating thiolates with diverse degrees of steric hindrance and containing, apart from sulfur, nitrogen atoms as donor atoms are described.

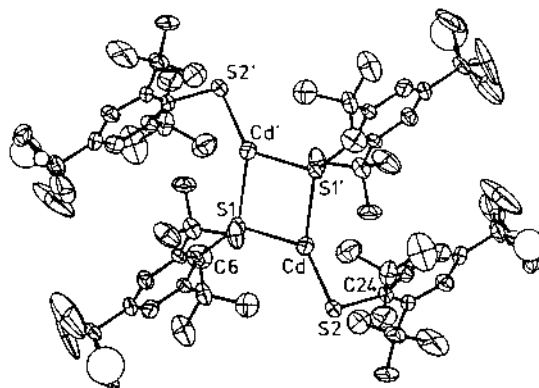


Fig. 4. Molecular structure of $[\text{Cd}(\text{S}'\text{-Bu}_3\text{C}_6\text{H}_2\text{-2,4,6})_2]$ (adapted from Ref. [14]).

2. Electrochemical synthesis of co-ordination compounds

In the last few years, a good deal of work has been dedicated to the development of synthetic methods for the preparation of co-ordination compounds using metals as the precursors. Several reviews have been published on this topic [19–23]. One of the processes involves the electrolytic oxidation of a metallic anode of an electrochemical cell containing a ligand in a suitable solvent.

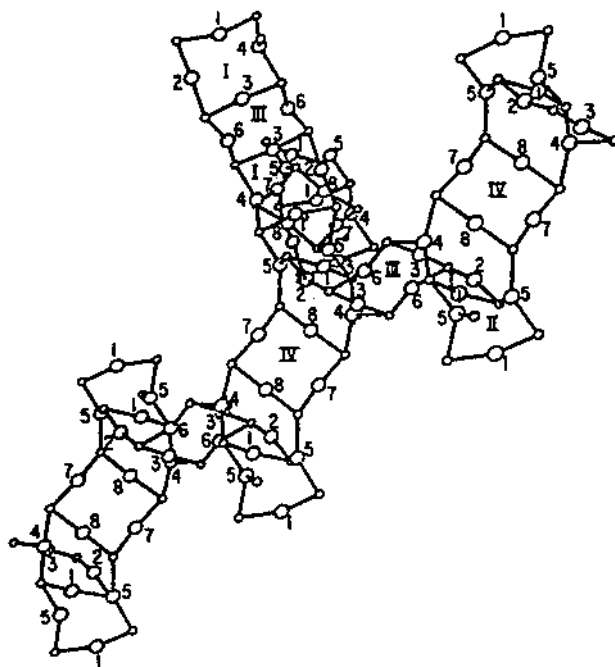


Fig. 5. Molecular structure of $[\text{Ag}_4\{\text{SCH}_2(\text{SiMe}_3)_3\}]_n^-$ (adapted from Ref. [15]).

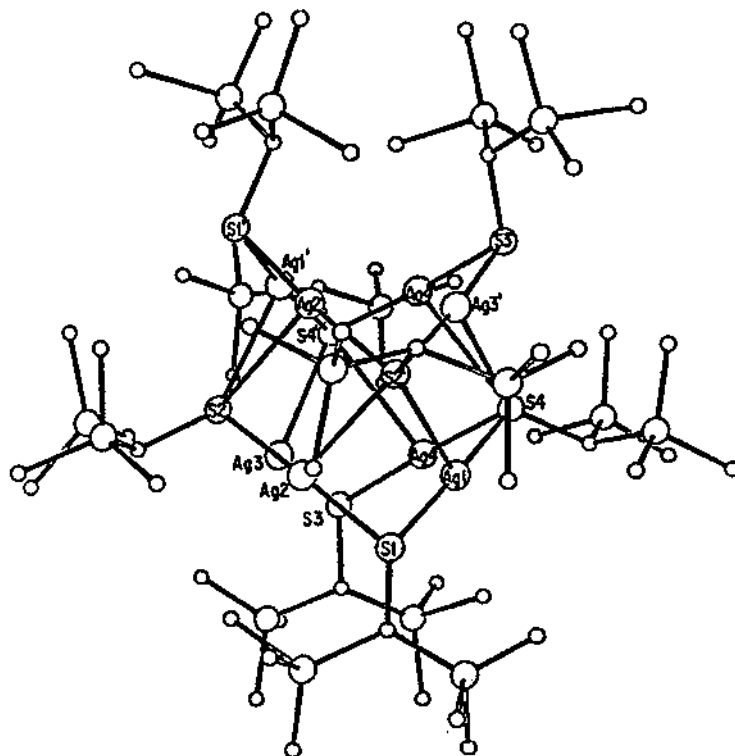


Fig. 6. Molecular structure of $[\text{Ag}\{\text{SCH}(\text{SiMe}_3)_2\}]_8$ (adapted from Ref. [15]).

The method was developed mainly by D.G. Tuck not just for the synthesis of co-ordination compounds, but also for organometallic compounds. Several reviews dealing with the possibilities of the method have appeared recently [19–23].

Experimentally, the technique is extremely simple. The experimental conditions of the synthesis are usually gentle, taking place at atmospheric pressure and room temperature. This contrasts with other procedures that also start with the metal, but that normally demand more drastic conditions, such as the use of metal vapors or of autoclaves to carry out processes at high pressures.

In addition, the procedure has other advantages which include the fact that the redox reactions involved do not require the use of oxidizing or reducing agents. In many cases, this is very useful as the presence of anionic species coming either from the metallic precursor or from the oxidizers can be avoided. Consequently, the solution does not contain potential competitors of the ligand in study. Moreover, the metallic sheets required are now readily available in high purity. In the cases in which the metal is not readily available, it can be deposited on platinum sheets using an electrolytic process and subsequently used as an anode in the synthetic process.

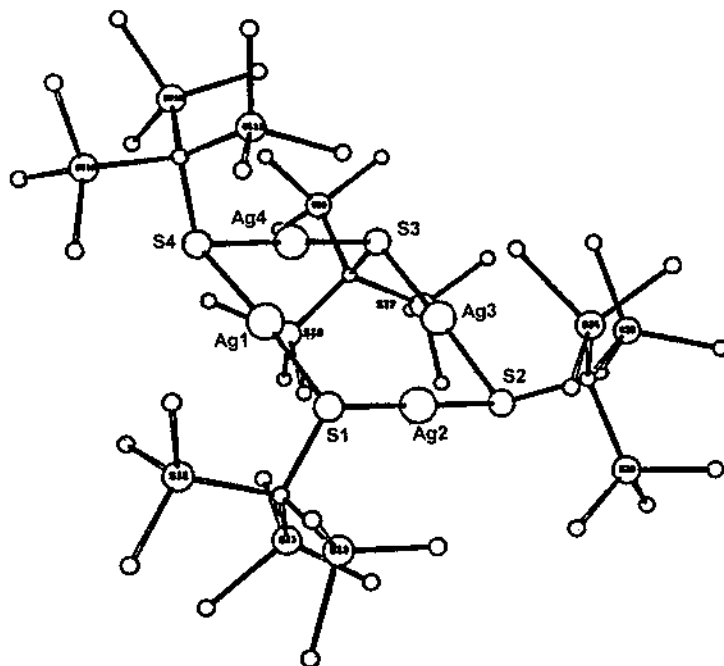


Fig. 7. Molecular structure of $[\text{Ag}\{\text{SC}(\text{SiMe}_3)_3\}]_4$ (adapted from Ref. [15]).

During the synthesis, the compound can be produced as slowly as desired merely by regulating the intensity of the electrical current passing through the cell. For this reason, in a good number of cases, well crystallized species can be obtained, allowing, in many cases, the isolation of monocrystals suitable for X-ray diffraction, without the need for subsequent recrystallizations.

The reaction pathway can be determined measuring the ‘electrochemical efficiency’, defined as the ratio of the number of moles of metal that react to the number of moles of electrons that travel through the cell. This magnitude is indicative of the anodic process that takes place. It is an experimental fact that in practically all cases in which the metal presents different well defined oxidation states, the anodic oxidation initially takes the metal to its lowest oxidation state. This is quite interesting if the aim is to obtain compounds in low oxidation states. In this case, the strategy implies to perform the experiment in such a way that the species originally formed do not suffer an additional oxidation in solution.

Lastly, the procedure has proven to be quite effective in obtaining mixed complexes in a single step by simply adding a second ligand to the cell.

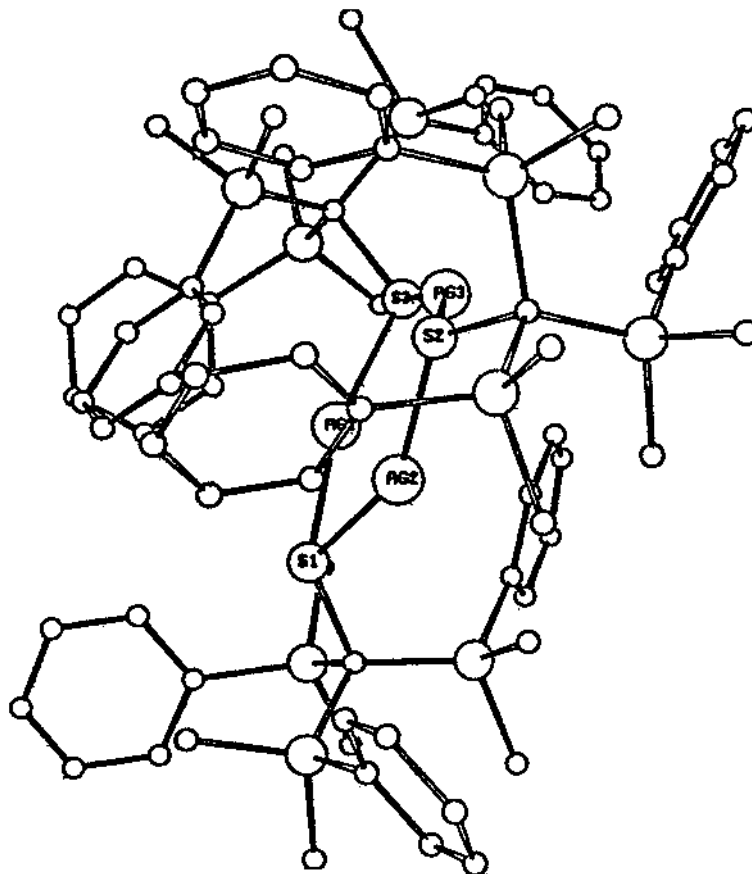


Fig. 8. Molecular structure of $[\text{Ag}\{\text{SC}(\text{SiMe}_2\text{Ph})_3\}]_3$ (adapted from Ref. [15]).

3. Cobalt complexes

The anodic oxidation of cobalt in an electrochemical cell containing an acetonitrile solution of different ligands, leads to the formation of complexes with analytical data in agreement with the general stoichiometries $[\text{Co}(\text{RpyS})_2]$ or $[\text{Co}(\text{RpyS})_3]$, depending on the nature of the ligand; RpyS, in all cases, represents the anion of the corresponding heterocyclic thione. Thus, when no, or just one, substituent is present on the pyridine ring of the ligand, Co(III) compounds with stoichiometry $[\text{Co}(\text{RpyS})_3]$ are obtained, while when the ligands possess two substituents, $[\text{Co}(\text{RpyS})_2]$ compounds are obtained. This is probably due to the greater steric hindrance produced by the two substituents on the ligand in positions close to the donor atoms.

The presence of additional nitrogen ligands in the electrochemical cell, for example 2,2'-bipyridine or 1,10-phenanthroline, does not lead toward the formation

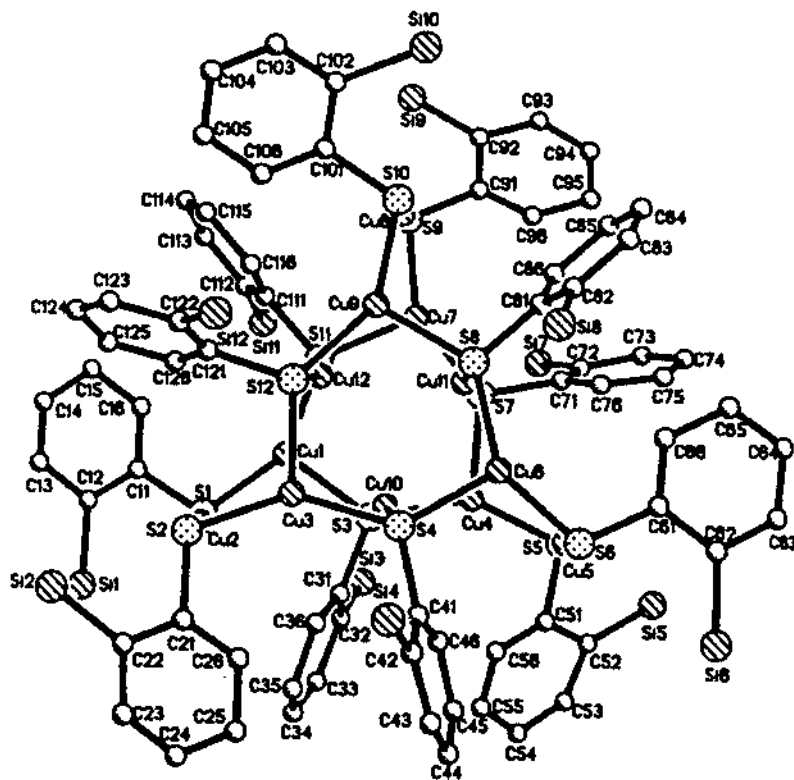


Fig. 9. Molecular structure of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-2-SiMe}_3)]_{12}$ (adapted from Ref. [16]).

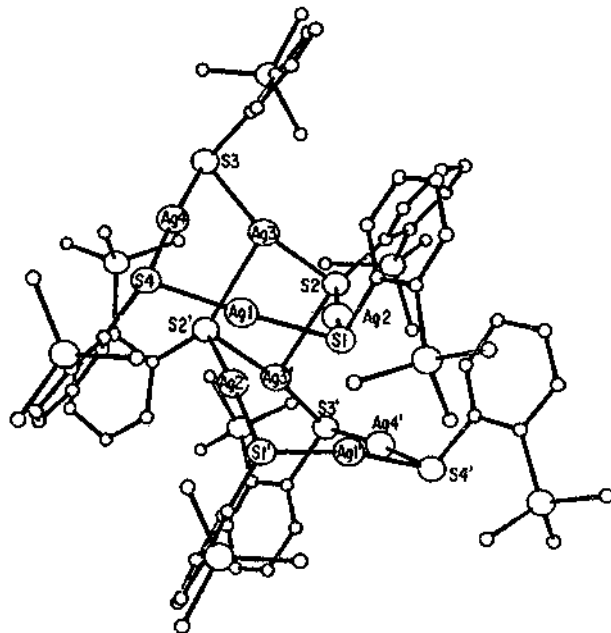
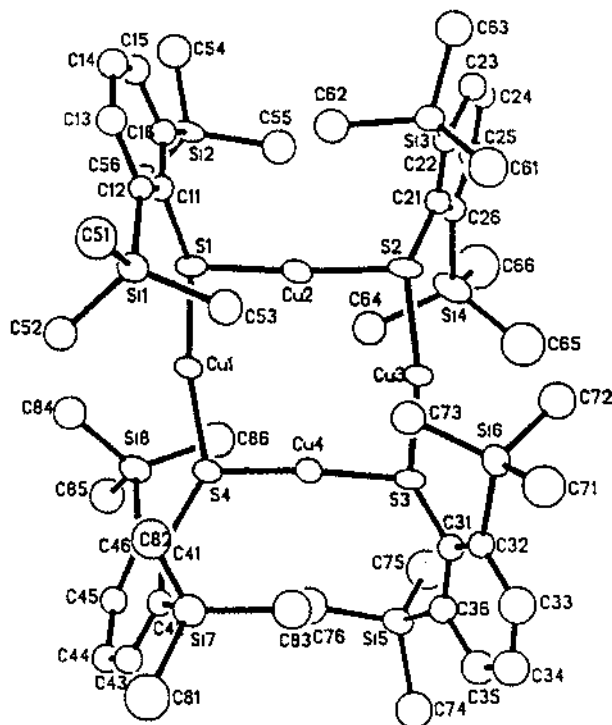
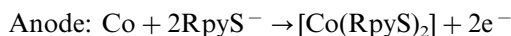
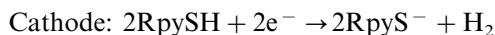


Fig. 10. Molecular structure of $[\{\text{Ag}(\text{SC}_6\text{H}_4\text{-2-SiMe}_3)\}_4]_2$ (adapted from Ref. [17]).



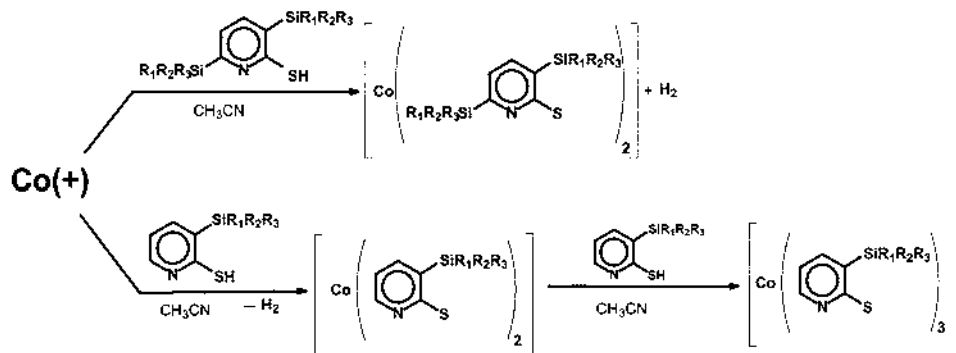
of mixed complexes. In all cases, the compounds obtained have either $[\text{Co}(\text{RpyS})_3]$ or $[\text{Co}(\text{RpyS})_2]$ stoichiometries [24].

The electrochemical efficiency values are in all cases are close to 0.5 mol F⁻¹, independently of whether the final compound corresponds with the metal in II or III oxidation state. This indicates that anodic oxidation results in the formation of Co(II) species. These data, and the hydrogen formation at the cathode in all cases, are in accord with the following reaction mechanism:



In those cases where the final product is a Co(III) compound, this originates from subsequent oxidation in solution of the Co(II) compound initially formed. This behavior has already been observed during the synthesis of cobalt compounds with other ligands (Scheme 1, [25]).

The spectroscopic data obtained for the Co(III) complexes are in accordance with an octahedral environment for the metal. The diamagnetic character of these complexes confirms the presence of a low spin d^6 system. The ^1H - and ^{13}C -NMR spectra show that the three ligands are equivalent, hence the compound structure in solution is that of the *facial* isomer.



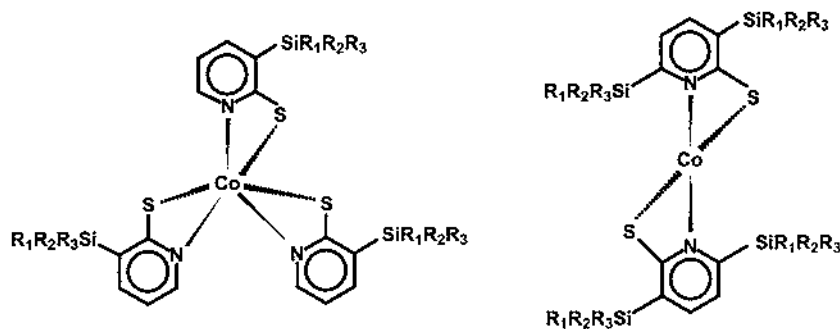
Scheme 1.

These solution structures differ from those found in cobalt complexes with less hindered pyridine-2-thione derivatives, such as [Co(pyS)₃] and [Co(3-Me₃SipyS)₃] complexes [26]. In solid state a distorted octahedral structure is observed with the ligands in a *mer* disposition. In addition, in the case of [Co(pyS)₃] the *mer* disposition is maintained in solution. Although some explanations have been put forward to clarify these facts, the problem is still far from resolved and much more experimental data are required to ascertain what factors, electronic and/or steric for the ligands, and electronic for the metal, determine the relative stabilities of the *mer* and *fac* isomers (Scheme 2).

In the case of Co(II) compounds, the spectroscopic data are in accord with a tetrahedral structure.

4. Nickel complexes

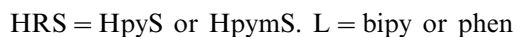
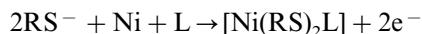
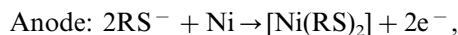
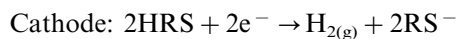
Anodic oxidation of nickel in acetonitrile solutions of pyridine-2-thione, pyrimidine-2-thione derivatives and of benzimidazole-2-thione leads to the isolation of a series of complexes with analytical data in accordance with an [Ni(RS)₂] stoichiometry, where RS stands for the anion of the appropriately substituted thiones.



Scheme 2.

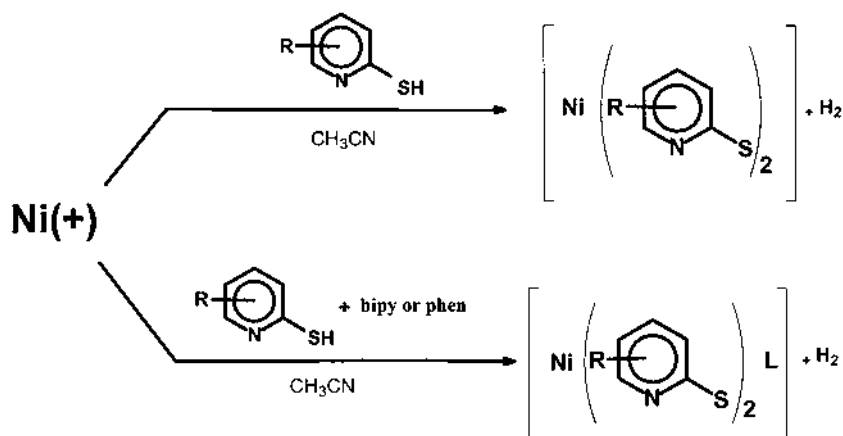
When additional ligands such as 2,2'-bipyridine or 1,10 phenanthroline are added to the solution, the result is the production of mixed complexes with analytical data corresponding to the formulae $[\text{Ni}(\text{RS})_2\text{L}]$, where now L represents the additional bidentate ligand [24,27].

The electrochemical efficiency values are close to 0.5 mol F^{-1} , which are in accord with the following reaction mechanism:



Complexes in which the ligands have a single substituent on the ring are diamagnetic (Scheme 3). Hence, a square planar structure is proposed, a conclusion which is supported by their diffuse reflectance spectra. The structure of the $[\text{Ni}(\text{3-Me}_3\text{SipyS})_2]$ [28] complex has been determined by X-ray diffraction (Fig. 12) and consists of discrete molecules with the nickel atom in a $[\text{NiN}_2\text{S}_2]$ square planar environment. The disposition of the ligands corresponds to that of the *trans* isomer. The nickel atom environment is planar with a deviation of no greater than $0.003 \text{ \AA}$ out of the best plane formed by the metallic atom and the donor atoms. The four-membered chelating rings are also planar, with dihedral angles between the planes of only 2° . The N–Ni–S bond angles are very different from those expected for this geometry, but the N–Ni–N and S–Ni–S angles are all 180° .

The Ni–S bond distance, $2.2281(8) \text{ \AA}$, is somewhat greater than that found in other square planar nickel complexes, e.g. bis(pyridine-*N*-oxide-2-thiolate)-nickel(II), $2.138(2) \text{ \AA}$ [29], and bis(methylthiohydroxamate)nickel(II), $2.18(2) \text{ \AA}$ [30], the latter also having *trans* sulfur atoms (Table 1). This can be attributed to the fact that in these cases the chelate ring is five-membered.



Scheme 3.

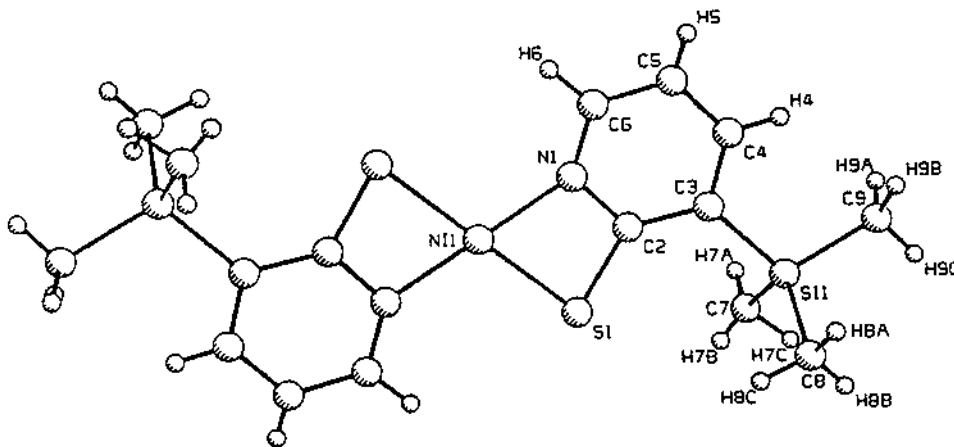


Fig. 12. Molecular structure of $[\text{Ni}(\text{3-Me}_3\text{SipyS})_2]$ (adapted from Ref. [28]).

The Ni–N distance of 1.873(2) Å, is very similar to that found in other nickel complexes having a square planar structure, e.g. in bis(cyclohexane-1,2-bis-2'-pyridylhydrazonato)dinickel(II) (1.89) Å [31].

In the pyridine-2-thionate ligand, the geometric parameters are close to those reported for the complexes previously mentioned, and correspond to those of the co-ordinated ligand preferably in the thiolate form.

The structure of this complex contrasts with that of the complex with the ligand having no substituents. Spectroscopic data suggests that this last compound possesses a polymeric octahedral structure, probably via sulfur bridges [32].

Thus, while $[\text{Ni}(\text{3-Me}_3\text{SipyS})_2]$ is diamagnetic, the compound with the same empirical formula but having no substituents has a magnetic moment of 3.37 MB, in accord with a d^8 high spin configuration in an octahedral environment. The electronic spectrum of the compound also supports this interpretation [32].

This is a clear example of how the different steric effects produced by the substituents on the ring can condition not only the degree of aggregation but also the stereochemistry of the compound.

Table 1

Selected Ni–S and Ni–N bond distances (Å) for square planar nickel(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
$[\text{Ni}(\text{3-Me}_3\text{SipyS})_2]$	Ni–S = 2.2281 (8) Å			[28]
$[\text{Ni}(\text{PT})_2]$	sp	NiO_2S_2	2.138	[29]
$[\text{Ni}(\text{SMcC=NOH})_2]$	sp	NiO_2S_2	2.18	[30]
$[\text{Ni}(\text{3-Me}_3\text{SipyS})_2]$	Ni–N = 1.873 (2) Å			[28]
$[\text{Ni}(\text{py-N=NCHR-})_2]$	sp	NiN_4	1.89	[31]

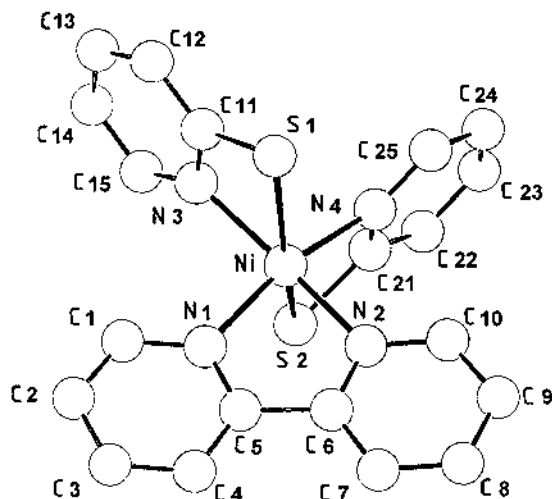


Fig. 13. Molecular structure of $[\text{Ni}(\text{pyS})_2(\text{bipy})]$ (Ref. [32]).

This effect is further exemplified in the complexes in which the ligand has two substituents, for example $[\text{Ni}(3,6\text{-}(\text{TexMe}_2\text{SipyS})_2)]$ and $[\text{Ni}(3,6\text{-}'\text{BuMe}_2\text{SipyS})_2]$. The complexes are paramagnetic (2.85 and 2.80 MB) and have visible spectra in accordance with tetrahedral environment around the metal atom. In this case, the strong steric hindrance not only precluded the polymerization but in addition, has impeded the formation of square planar compounds [24].

The presence of additional nitrogen ligands, 2,2'-bipyridine or 1,10-phenanthroline, in the electrochemical cell gives mixed complexes of type $[\text{Ni}(\text{RS})_2(\text{bipy})]$ or $[\text{Ni}(\text{RS})_2(\text{phen})]$. This shows that the method is very adequate for obtaining neutral octahedral monomeric complexes of nickel with bidentate thionate ligands. These are the first nickel complexes prepared with these characteristics. The structures of bipyridine bis(pyridine-2-thionate)nickel (II) ([32], Fig. 13) and of the pyrimidine-2-thionate analogue ([33], Fig. 14) have been determined by X-ray diffraction.

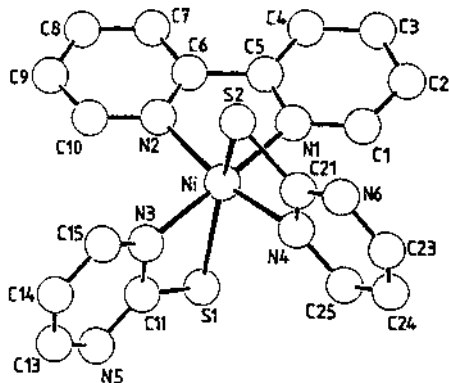


Fig. 14. Molecular structure of $[\text{Ni}(\text{pymS})_2(\text{bipy})]$ (Ref. [33]).

The structures of both compounds are very similar. The nickel atom is in very distorted $[\text{NiN}_4\text{S}_2]$ octahedral environments, and co-ordinated to a bidentate bipyridine ligand and to two pyridine-2-thionate or pyrimidine-2-thionate ligands which act as chelates through the sulfur and nitrogen atoms. The sulfur atoms are in *trans* positions, although the S–Ni–S angles differ significantly from 180° . Also, the 2,2'-bipyridine bis-(3- CF_3 -pyridine-2-thionate)nickel(II) complex shows the nickel atom to be in a distorted octahedral environment with bidentate thione ligands, and the sulfur atoms in *trans* disposition (Fig. 15). The co-ordination sphere is completed by two nitrogen atoms from the phenanthroline [34].

The spectroscopic and magnetic data of the remaining compounds, whose structure has not been possible to determine by X-ray diffraction are concordant with the octahedral environment for the nickel atom.

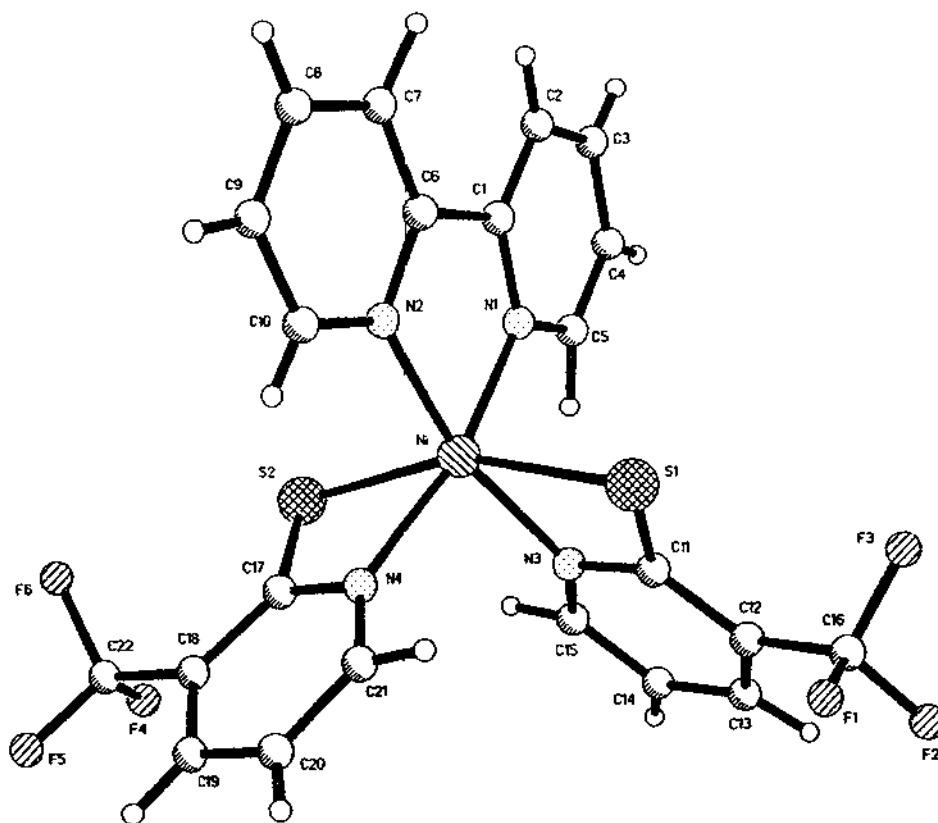
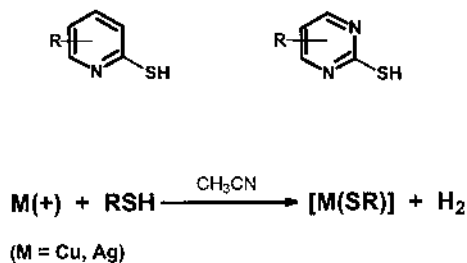


Fig. 15. Molecular structure of $[\text{Ni}(\text{3-CF}_3\text{pyS})_2(\text{bipy})]$ (Ref. [34]).

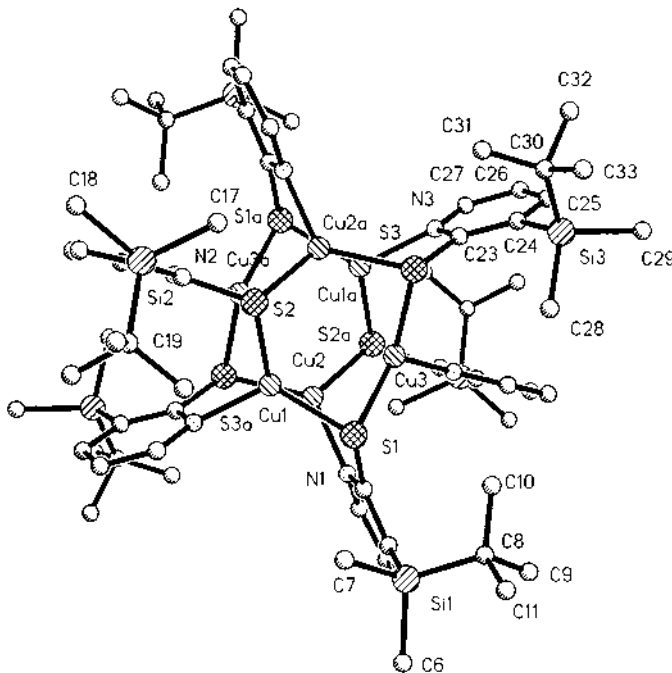


Scheme 4.

5. Copper and silver complexes

In all cases, the complexes of copper and silver with heterocyclic thiones obtained by anodic oxidation of copper or silver have a $[\text{Cu}(\text{SR})]$ and $[\text{Ag}(\text{SR})]$ formulation, where SR stands for the anionic form of the heterocyclic base (Scheme 4).

The crystal structure of $[\text{Cu}_6(3\text{'-BuMe}_2\text{SipyS})_6]$ [24] is hexanuclear with six copper atoms at the vertices of a highly distorted octahedron (Fig. 16). The distances between the different copper atoms are much greater than those found in metal copper, which clearly suggests the absence of a bond between metallic atoms within the molecule.

Fig. 16. Molecular structure of $[\text{Cu}_6(3\text{'-BuMe}_2\text{SipyS})_6]$ (Ref. [24]).

Each of the pyridine-2-thiolate ligands acts as a $\mu^3(\text{N-S})$ triple bridge, and it is bound to the three different metallic atoms that define one of the faces of the octahedron. The nitrogen and sulfur atoms act as a bridge between two metallic atoms. Each copper atom is in a distorted trigonal geometry environment and is bound to the sulfur atoms of two ligands and to the nitrogen atom of another ligand.

The structure of $[\text{Cu}_6(6\text{-TexMe}_2\text{SipyS})_6]$ ([24], Fig. 17), is similar to that of $[\text{Cu}_6(3\text{-}^i\text{BuMe}_2\text{SipyS})_6]$, although the coordination polyhedron is more distorted.

Hexanuclear structures similar to these were observed for $[\text{Cu}(\text{pyS})_6]$ ([35], Fig. 18) and $[\text{Cu}(4,6\text{-Me}_2\text{pymS})_6]$ ([36], Fig. 19), and for $[\text{Cu}(3\text{-Me}_3\text{SipyS})_6]$ ([37], Fig. 20); the last compound was obtained by reacting $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ with a methanolic solution of the ligand. However, electrochemical synthesis of this compound gives a complex with the same stoichiometry, but with a tetranuclear structure, $[\text{Cu}(3\text{-Me}_3\text{SipyS})_4]$ ([38], Fig. 21). In this structure, the copper atoms are arranged at the vertices of a tetrahedron. Each ligand is bonded to the three copper atoms defining one of the faces of the tetrahedron; each copper atom is bonded to three ligands: to two through the sulfur atom and to the other through the nitrogen atom. This is a clear example of how different methods of synthesis produce different degrees of polymerization for a compound of identical stoichiometry (Scheme 5).

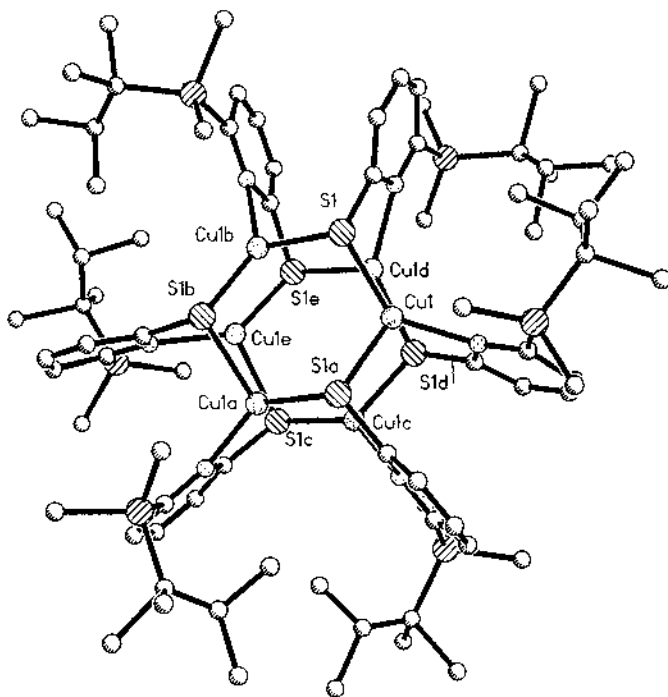


Fig. 17. Molecular structure of $[\text{Cu}_6(6\text{-TexMe}_2\text{SipyS})_6]$ (Ref. [24]).

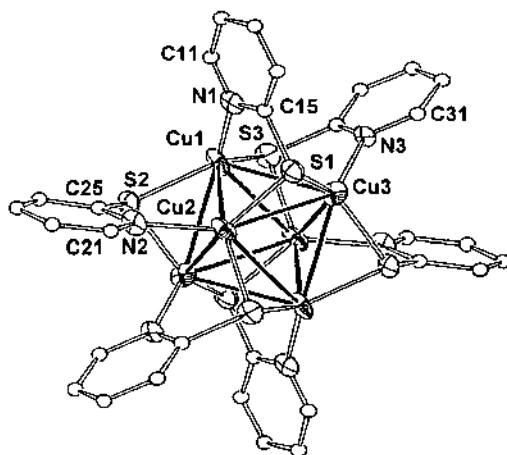


Fig. 18. Molecular structure of $[\text{Cu}(\text{pyS})]_6$ (adapted from Ref. [35]).

In the case of silver, the complex $[\text{Ag}_6(6\text{'BuMe}_2\text{SipyS})_6]$ [39] was studied by X-ray diffraction which reveals a hexanuclear structure of silver atoms (Fig. 22).

The intermetallic distances demonstrate that there is no interaction between the silver atoms.

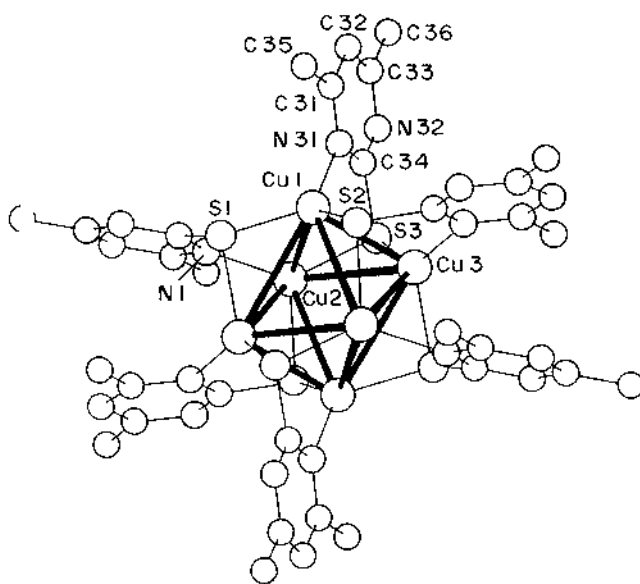


Fig. 19. Molecular structure of $[\text{Cu}(4,6\text{-Me}_2\text{pymS})]_6$ (adapted from Ref. [36]).

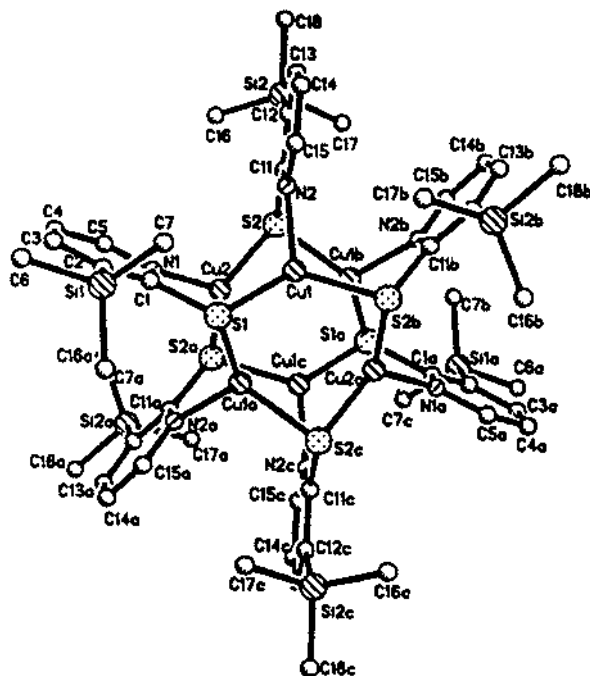


Fig. 20. Molecular structure of $[\text{Cu}(\text{3-Me}_3\text{SipyS})]_6$ (adapted from Ref. [37]).

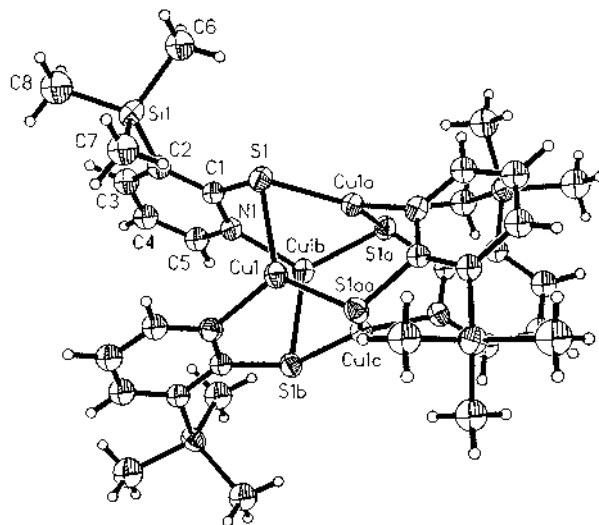
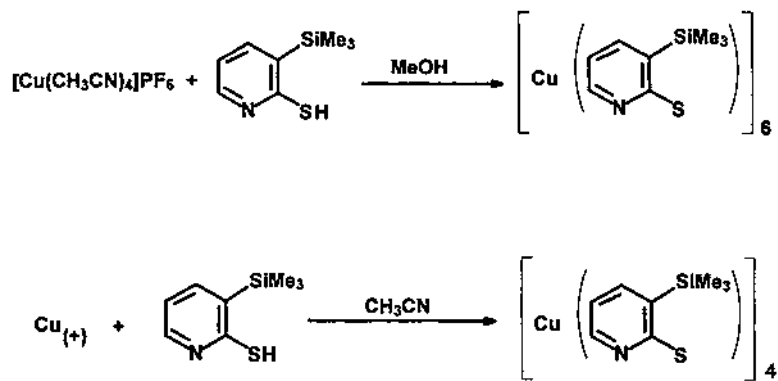
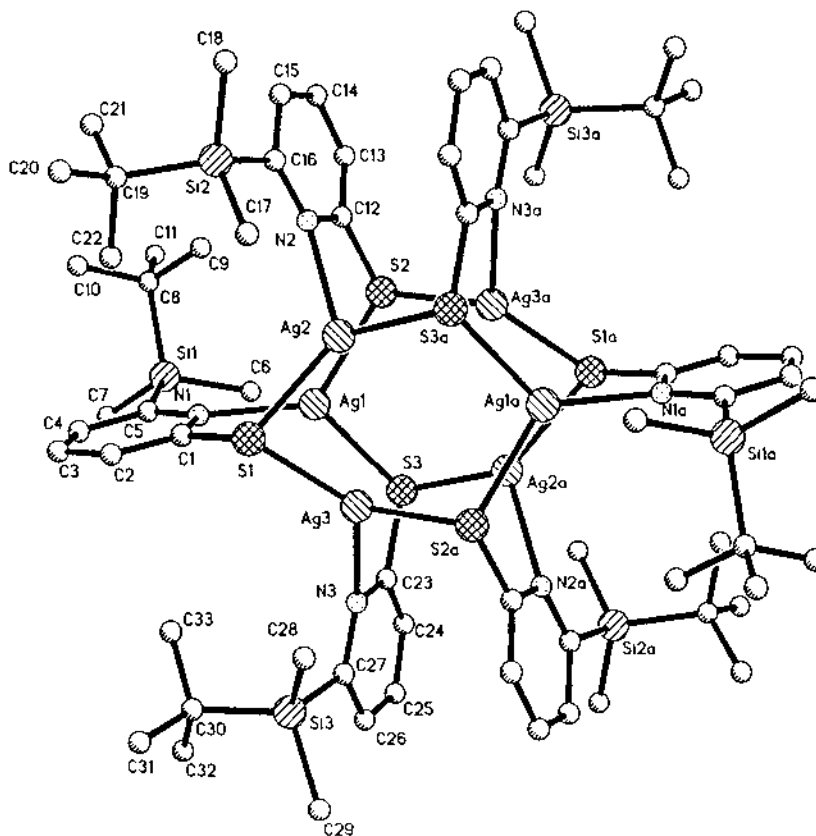


Fig. 21. Molecular structure of $[\text{Cu}(\text{3-Me}_3\text{SipyS})]_4$ (adapted from Ref. [38]).



Scheme 5.

Fig. 22. Molecular structure of $[\text{Ag}_6(6\text{-}t\text{BuMe}_2\text{SipyS})_6]$ (adapted from Ref. [39]).

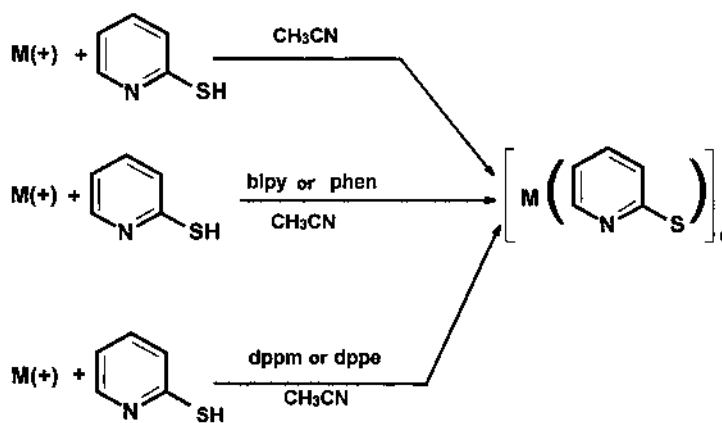
A way to describe this structure is to consider the molecular complex as a paddlewheel, in which the hub is formed by two Ag_3S_3 rings and the six paddles are the fragments $\text{C}_5\text{H}_3\text{N}(\text{SiMe}_2\text{Bu})$. The ligands act as bridges between two Ag_3S_3 rings, in such a way that three nitrogen atoms are in each ring. The sulfur atoms act as bridges between adjacent metallic atoms in an Ag_3S_3 ring. The trigonal geometry around each silver atom is completed by nitrogen atoms.

All the copper and silver complexes that have been synthesized have similar spectroscopic data. Therefore, analogous structures to that determined by X-ray diffraction can be proposed for all of them, with the metal atoms in trigonal environments and the ligands acting as triple bridges.

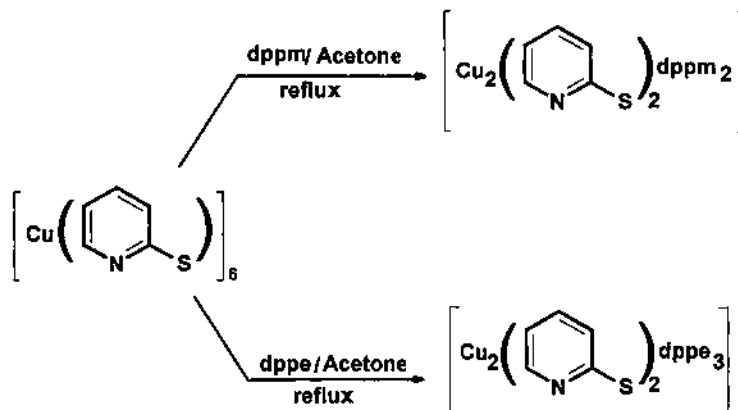
In order to reduce the nuclearity of the compounds, the synthesis of mixed compounds of copper and silver has been undertaken. However, neither phenanthroline nor bipyridine could be incorporated to the metal coordination sphere through electrochemical experiments. The same negative result is produced when bidentate phosphines as bis(diphenylphosphine)methane (dppm) and 1,2-bis(diphenylphosphine) ethane (dppe) are added to the cell (Scheme 6).

For this reason, the synthesis of these mixed complexes was attempted by reacting the phosphine ligand with the previously electrochemically synthesized homoleptic complex. The results depend on the nature of the metal. Thus, in the case of copper it has been possible to isolate some compounds having analytical data in agreement with $[\text{Cu}(\text{RpyS})(\text{dppm})]$ and $[\text{Cu}_2(\text{RpyS})_2(\text{dppe})_3]$ formulations (Scheme 7).

The compound $[\text{Cu}_2(6\text{'BuMe}_2\text{SipyS})_2(\text{dppm})_2]$ ([40], Fig. 23) shows a dinuclear structure, with different environments for each copper atom. Thus, the Cu(1) atom is trigonally coordinated to a phosphorus atom of a dppm molecule, to a nitrogen of a pyridine-2-thione $\mu(\text{N}-\text{S})$ ligand and to a sulfur atom of another pyridine-2-



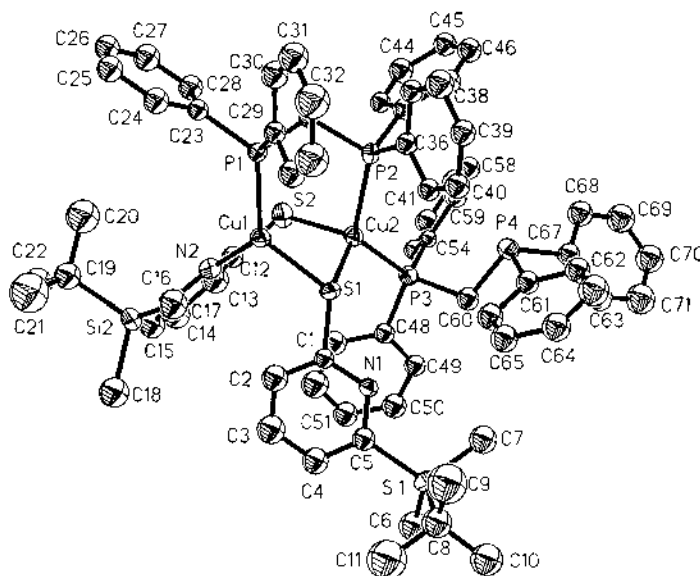
Scheme 6.



Scheme 7.

thione ligand. The other metallic atom is tetrahedrally coordinated by two phosphorus atoms, each from a different dppm ligand, and to two sulfur atoms, each belonging to a pyridine-2-thione ligand.

In addition to the copper atoms are in different environments, the two dppm ligands are non-equivalent. One of the dppm ligands acts as a monodentate terminal ligand while the other behaves as a bidentate bridge between the two copper atoms. The two thiolate ligands are also non-equivalent. Thus, one of the

Fig. 23. Molecular structure of $[\text{Cu}_2(6\text{-}^t\text{BuMe}_2\text{SipyS})_2(\text{dppm})_2]$ (adapted from Ref. [40]).

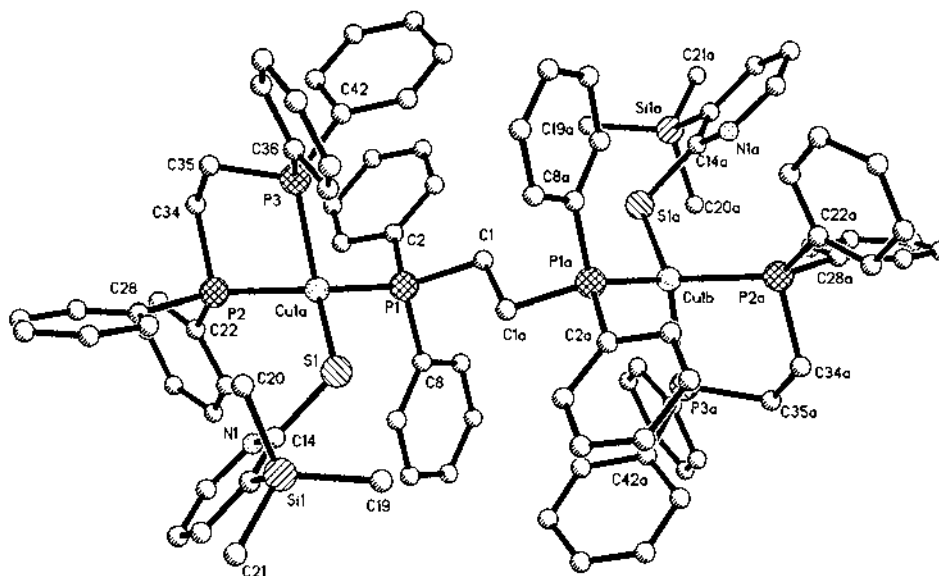
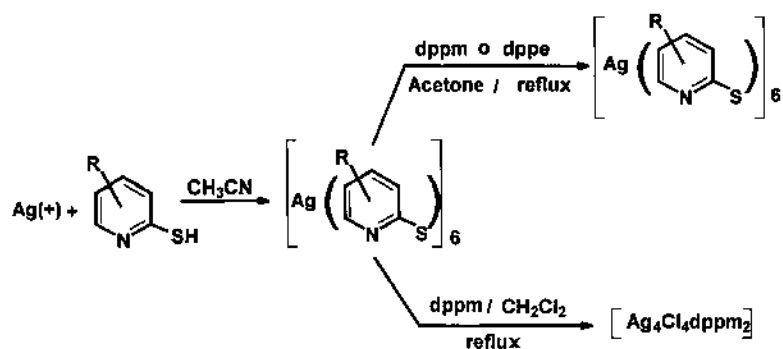


Fig. 24. Molecular structure of $[\text{Cu}_2(3\text{-Me}_3\text{SipyS})_2(\text{dppe})_3]$ (adapted from Ref. [41]).

pyridine-2-thiolate ligands acts as a monodentate $\mu_2\text{-S}$ bridge whilst the other as a bidentate $\mu(\text{N},\text{S})$ bridge.

The structure of $[\text{Cu}_2(3\text{-Me}_3\text{SipyS})_2(\text{dppe})_3]$ (Fig. 24, [41]) is different, probably because of the greater chelating bite angle of dppe. Thus, the compound is a dimer in which one of the dppe molecules acts as a bridge between both copper atoms and each of the other two phosphines chelates a copper atom. The distorted tetrahedral coordination around the metal is achieved when a molecule of the thione ligand acts as monodentate terminal ligand through the sulfur atom only.



Scheme 8.

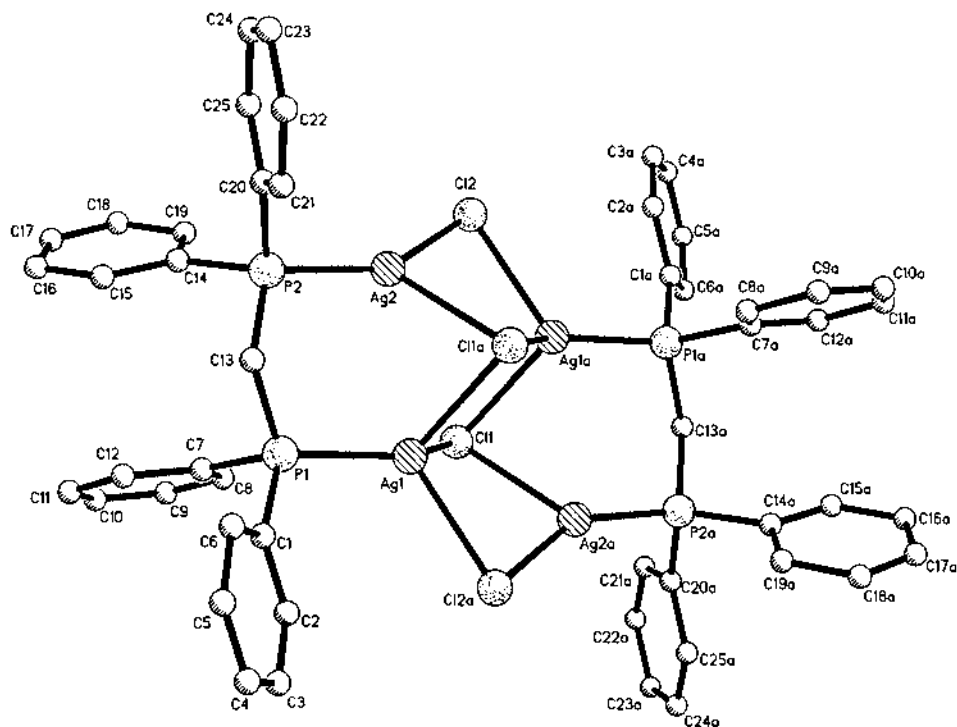


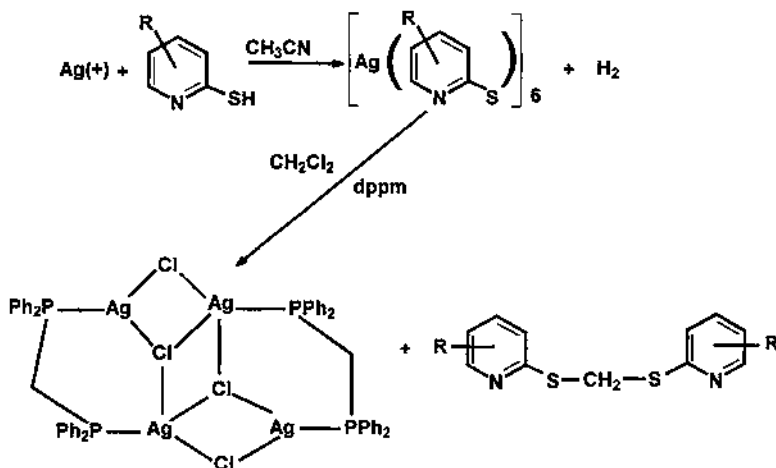
Fig. 25. Molecular structure of $[\text{Ag}_4\text{Cl}_4(\text{dppm})_2]$ (adapted from Ref. [39]).

For silver, the data show that in all cases the phosphine does not coordinate to the metal, as the compounds obtained all have the same $[\text{Ag}(\text{RpyS})]$ stoichiometry (Scheme 8).

In an attempt to prepare mixed complexes of silver, a mixture of the homoleptic compound and phosphine was refluxed in a mixture of acetonitrile and dichloromethane. X-ray diffraction of the products of this reaction demonstrated that the compound had an $[\text{Ag}_4\text{Cl}_4(\text{dppm})_2]$ formulation (Fig. 25).

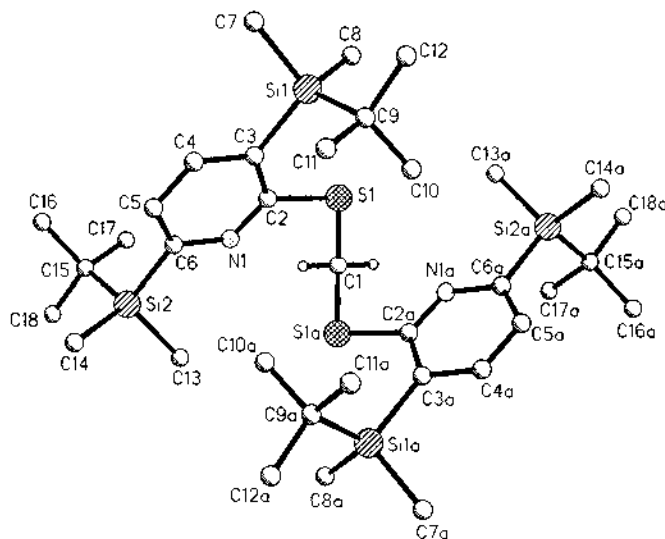
The structure of $[\text{Ag}_4\text{Cl}_4(\text{dppm})_2]$ [39] shows a tetranuclear arrangement of silver atoms, with two of these atoms trigonally coordinated by a doubly bridging chlorine atom, a triply bridging chlorine atom and a phosphorus atom of a dppm ligand that acts as a bridge between two metallic atoms. Each of the other silver atoms are in a tetrahedral environment. Each of these silver atoms is bonded to the other phosphorus atom of the dppm bridge ligand, to a doubly bridging chlorine atom, to two triply bridging chlorine atoms. This compound is probably formed by an electrophilic attack of the silver atom of the original complex on the chlorine atom of the dichloromethane molecule used as solvent (Scheme 9).

The reaction also leads the formation of a ligand in which two heterocyclic thione groups are joined by a methylene group.



Scheme 9.

Although it has not been possible to isolate the dimer indicated in the scheme, the compound 3,6- t -BuMe₂SipyS-CH₂-SpySiMe₂Bu-3,6 [39], produced during the analogous reaction between $[\text{Ag}(3,6\text{-}t\text{-BuMe}_2\text{SipyS})]$ and dppm in an acetonitrile–dichloromethane mixture, has been isolated and characterized by X-ray diffraction (Fig. 26). Its formation supports the proposed reaction mechanism.



5.1. IR spectroscopy

A weak band corresponding to the $\nu(\text{N-H})$ vibration was not observed in the IR spectra of the complexes. This was to be expected in view of the molecular structure of the complexes and is indicative of the deprotonation of the ligand during the electrochemical synthesis.

For the mixed complex of copper with 1,2-bis(diphenylphosphino)ethane or bis(diphenylphosphino)methane, bands corresponding to the coordinated diphosphine are also observed.

5.2. ^1H - and ^{13}C -NMR

The ^1H -NMR spectra of the complexes show the signal due to the NH proton is absent. This is indicative, once more, of deprotonation of the ligands and their coordination to the metallic atom in the thiolate form.

In the ^{13}C -NMR spectra of the complexes, an upfield shift of the signal corresponding to the C_2 carbon atom was observed. This is probably due to a reduction in the $\text{C}=\text{S}$ bond order. This observation can be taken as an additional proof that the thiolate form is the predominating ligand form in the complex.

The ^{31}P -NMR spectrum of $[\text{Cu}_2(3\text{-Me}_3\text{SipyS})_2(\text{dppe})_3]$ shows a broad signal at -10.86 ppm. As in homologous pyS^- complex, has undergone a downfield shift with respect to the free ligand. Such a shift is characteristic of dppe as a bridge ligand. Therefore its structure can be anticipated to be similar to the pyS^- analogue: a $[\text{Cu}_2(3\text{-Me}_3\text{SipyS})_2(\text{dppe})_3]$ dimer with the three diphosphine ligands acting as bridges between the metallic atoms.

6. Zinc and cadmium complexes

The electrochemical synthetic methodology has also been very useful in the preparation of complexes of zinc and cadmium with heterocyclic thiones, as well as of mixed compounds with bipyridine, phenanthroline and pyridine.

The structures of the homoleptic complexes $[\text{Cd}(4,6\text{-Me}_2\text{pymS}_2)]$ and $[\text{Cd}(3\text{-Me}_3\text{SipyS})_2]$ and of the mixed compounds $[\text{Zn}(\text{pyS})_2(\text{phen})]$, $[\text{Zn}(3\text{-CF}_3\text{pyS})_2(\text{phen})]$, $[\text{Zn}(4,6\text{-Me}_2\text{pymS})_2(\text{py})]$, $[\text{Zn}(\text{bzS})_2(\text{phen})]$, $[\text{Cd}(\text{pymS})_2(\text{phen})]$ and $[\text{Cd}(3\text{-CF}_3\text{pyS})_2(\text{bipy})]$ have been determined by X-ray diffraction.

In the case of zinc, homoleptic complexes in which the ligands do not possess substituents or if the substituents are of small volume, are very insoluble, making it impossible to determine their structures by X-ray diffraction. This high insolubility suggests that they are probably polymers. Once again, the presence of bulky substituents like 3-trimethylsilyl groups in position 3 reduces the degree of polymerization and yields a binuclear compound $[\text{Zn}_2(3\text{-Me}_3\text{SipyS})_4]$ (Fig. 27, [42]). Each metallic atom is tetrahedrally coordinated to the sulfur and nitrogen

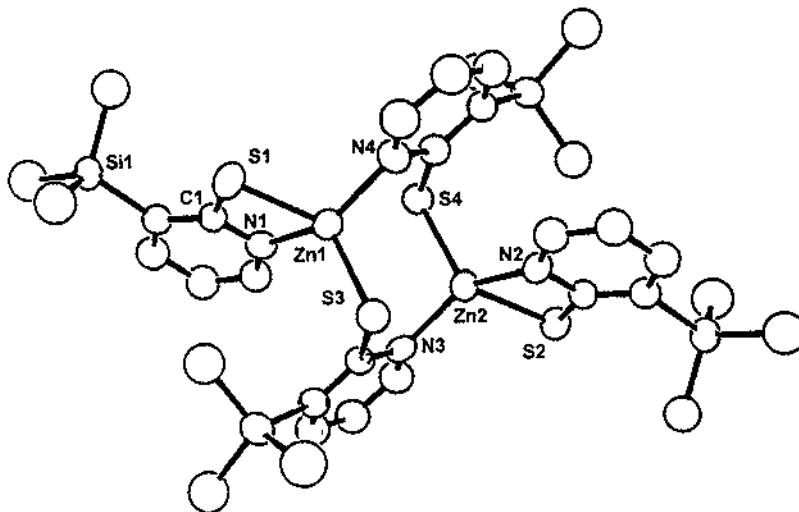


Fig. 27. Molecular structure of $[\text{Zn}_2(3\text{-Me}_3\text{SipyS})_4]$ (adapted from Ref. [42]).

atoms of a terminal ligand, a bridging sulfur atom and the nitrogen of the other ligand, which acts as a three electron donor.

In the case of cadmium, the compound is also binuclear [43], $[\text{Cd}_2(3\text{-Me}_3\text{SipyS})_4]$ (Fig. 28), but now the metal is pentacoordinated possibly due to the greater size of the cadmium atom. In this case, the bridging ligands act as $[\text{N}, -(\mu\text{-S})_2]$ five electron donors.

The dimeric molecules possess a crystallographic symmetry center. The two cadmium atoms and the two sulfur bridge atoms (Cd_2S_2) are strictly coplanar, with two longer Cd–S bonds (2.667(2) Å) and two shorter ones (2.597(2) Å). Each cadmium atom is coordinated to a sulfur and nitrogen atom of a bidentate terminal 3-trimethylsilyl-pyridine-2-thiolate ligand and to two sulfur atoms, proceeding from two double bridge five electron donor ligands. The fifth donor atom is a nitrogen atom belonging to one of these bridging ligands.

The geometry around the cadmium atom can be described as a severely distorted trigonal bipyramid, with two nitrogen atoms in apical positions. This distortion is produced by the small size of the chelating angles. The S(1)–Cd–N(1) and S(2)–Cd–N(2), angles are 62.06(9) and 64.84(9)°, respectively, very different from the expected 90° for a regular trigonal bipyramidal structure. Likewise, the N(1)–Cd–N(2) angle of 158.1(1)° is also very different from the ideal value of 180°.

The Cd–S distances are significantly different, those involving sulfur bridging atoms being slightly longer (2.597(2) and 2.667(2) Å) than those corresponding to terminal sulfur atoms (2.495(1) Å). The same situation is also observed in other systems having both terminal and bridging types of sulfur atoms. The

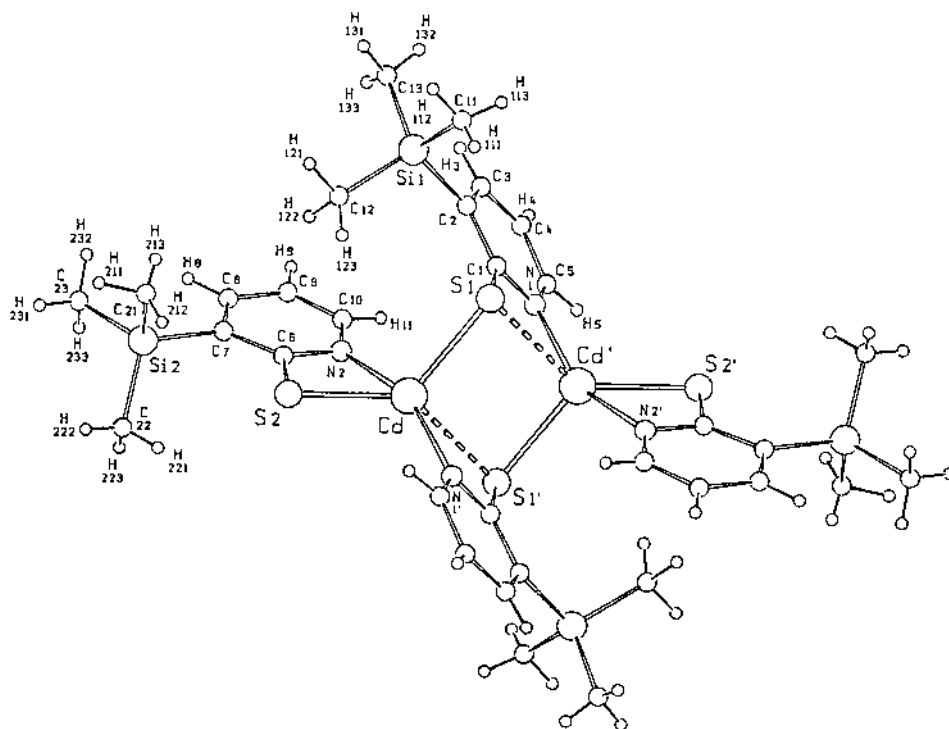


Fig. 28. Molecular structure of $[\text{Cd}_2(3\text{-Me}_3\text{SipyS})_4]$ (adapted from Ref. [43]).

Cd–S bond lengths found in this compound are considerably shorter than those observed in other pentacoordinate dimeric complexes (Table 2), as in $\{\text{Cd}_2[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_4\}$ [44] and $\{\text{Cd}_2[\text{S}_2\text{CN}(\text{CH}_2)_6]_4\}$ [45], where the Cd–S bridging and terminal bond lengths are in the range of 2.80–2.87 and 2.53–2.64 Å, respectively, suggesting that the Cd–S_{bridging} and Cd–S_{terminal} bonds in this complex are relatively strong.

All Cd–N distances are very similar, 2.381(4) Å, independent of the nitrogen containing ligand, and slightly greater than those observed in octahedral com-

Table 2
Selected Cd–S bond distances for cadmium(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
$[\text{Cd}_2(3\text{-Me}_3\text{SipyS})_4]$	$\text{Cd-S}_{\text{terminal}} = 2.495(1)$ Å			[43]
$[\text{Cd}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_4]$	tbp	CdS_5	2.536–2.594	[44]
$[\text{Cd}_2(\text{S}_2\text{CN}(\text{CH}_2)_6)_4]$	tbp	CdS_5	2.539–2.631	[45]
$[\text{Cd}_2(3\text{-Me}_3\text{SipyS})_4]$	$\text{Cd-S}_{\text{bridging}} = 2.632(2)$ Å			[43]
$[\text{Cd}_2(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)_4]$	tbp	CdS_5	2.644, 2.800	[44]
$[\text{Cd}_2(\text{S}_2\text{CN}(\text{CH}_2)_6)_4]$	tbp	CdS_5	2.87	[45]

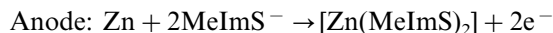
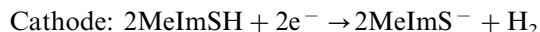
Table 3
Selected Cd–N bond distances for cadmium(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
[Cd ₂ (3-Me ₃ SipyS) ₄]	Cd–N _{py} = 2.381(4) Å			[43]
[Cd(C ₆ H ₄ NO ₂)(H ₂ O) ₄]	oct	CdN ₂ O ₄	2.310(3)	[46]
[Cd(HCOO) ₂ (C ₆ H ₄ NCONH ₂)(H ₂ O) ₂]	oct	CdN ₂ O ₄	2.336(5)	[47]
[CdCl ₂ (py) ₂]	oct	CdCl ₄ N ₂	2.35	[48]
[Cd(C ₅ H ₄ NCOO) ₂]	oct	CdN ₂ O ₄	2.23	[49]

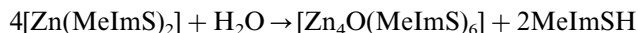
plexes of cadmium (II) with nitrogen donors of heterocyclic ligands (Table 3), e.g. 2.310(3) Å in bis(*N*-isonicotinato)tetraaquo cadmium(II) [46], 2.336(5) Å in diformatodiaquobis (nicotinamide) cadmium(II) [47], 2.35 Å in [CdCl₂(py)₂] [48] and 2.23 Å in pyridine-2-carboxylate cadmium(II) [49].

The mean value of the S–C distance, of 1.760(4) Å, is much longer than that found in the pyridine-2-thione free ligand, 1.68 Å [50]. This suggests, therefore, that the ligands bind to the metal mainly in the thiolate form.

A very interesting case occurs in the electrochemical oxidation of zinc in the presence of 1-methylimidazole-2-thione (MeImSH), which gives a solution that after evaporation, treatment with chloroform and recrystallization from ethanol, gives rise to a complex formulated as [Zn₄O(MeImS)₆] [51]. This complex is probably formed by reaction of the compound [Zn(MeImS)₂] formed at the anode according to the process:



with water present in the solvent.



The compound has an unusual structure with a central oxygen atom tetrahedrally surrounded by four zinc atoms (Fig. 29). Each zinc atom is four coordinate; three of the zinc atoms are bonded to the oxygen atom and to three 1-methylimidazoline-2-thionate ligands (to two via nitrogen atoms and to one via the sulfur atom). The other Zn atom is four coordinated with bonds with the oxygen atom and three sulfur atoms from three different bridging ligands. Therefore, each ligand acts as (N,S)-bridging three electron donor ligand. Each anion of the 1-methylimidazole-2-thione ligand bridges pairs of zinc atoms along the edges of the tetrahedron, and lies out the plane containing the central oxygen atom and one edge of the Zn-tetrahedron, as in the complex [Be₄O(CH₃COO)₆] [52].

The complex of cadmium with 4,6-Me₂pymSH gives a hexanuclear structure with the six cadmium atoms forming a regular planar hexagon ([53], Fig. 30). The metallic atoms are joined by twelve sulfur bridging atoms, six above and six below the plane formed by the cadmium atoms (Fig. 31). Each metal is coordinated to one

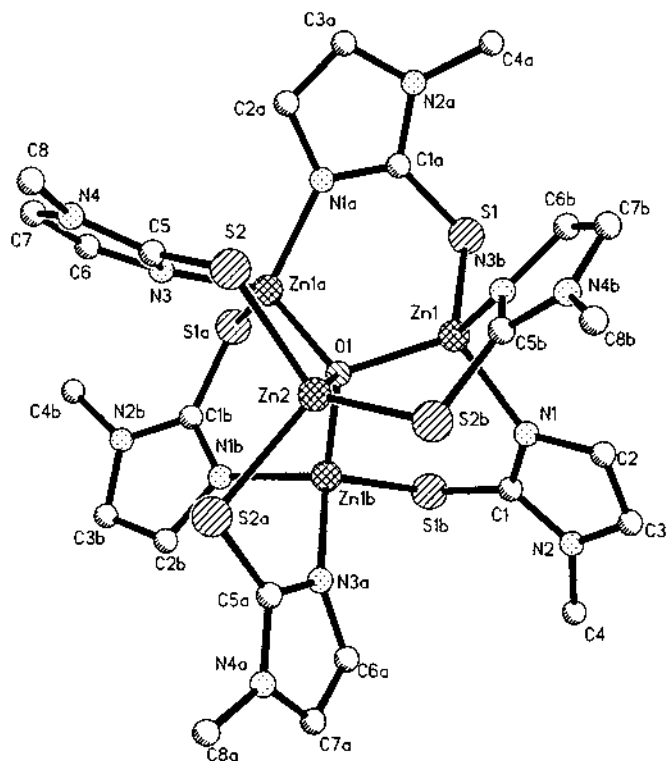


Fig. 29. Perspective view of the $[\text{Zn}_4\text{O}(\text{MeImS})_6]$ molecule (adapted from Ref. [51]).

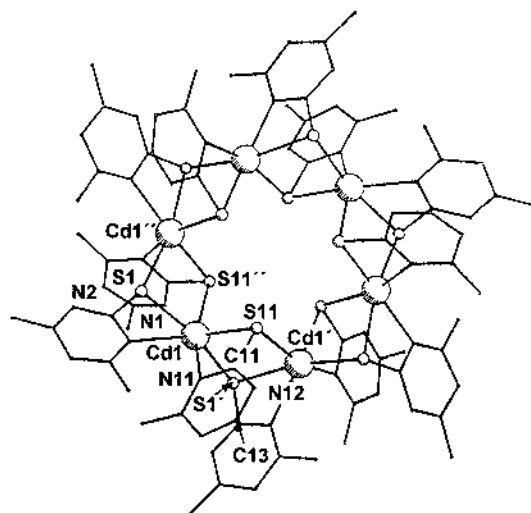


Fig. 30. Perspective view of the structure of $[\{\text{Cd}(\text{4,6-Me}_2\text{pymS})_2\}_6]$ (adapted from Ref. [53]).

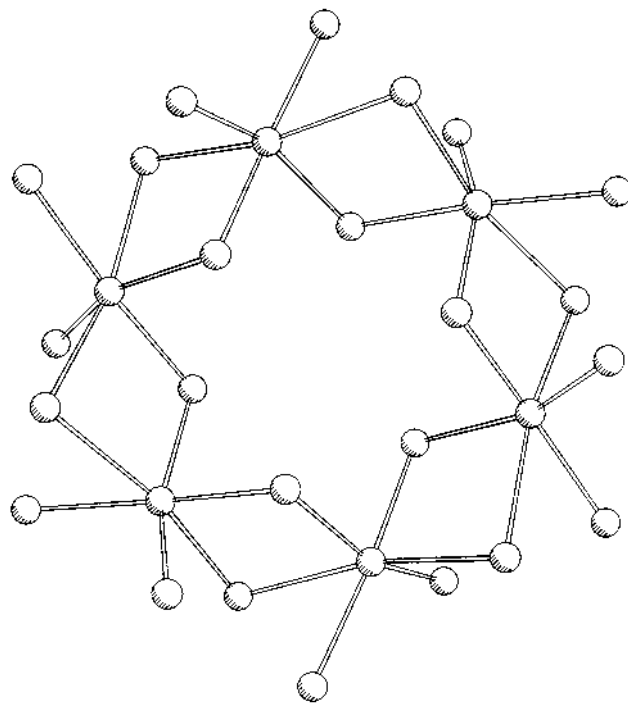


Fig. 31. Perspective view of the co-ordination sphere of the metals in $[Cd(4,6-Me_2pymS)_2]_6$ (adapted from Ref. [53]).

nitrogen atom and the bridging sulfur atom of two 4,6-dimethylpyrimidine-2-thiolate ligands, and to two other bridging sulfur atoms from two ligands bound to other cadmium atoms. Therefore, each ligand acts as a bridging $[N,(\mu-S)_2]$ five electron donor ligand.

The Cd–S (2.638(8)–2.666(8)) and Cd–N (2.36(2) and 2.38(2)) distances are analogous to those found in other complexes (Table 4) and very similar to those observed in $[Cd_2(3-Me_3SipyS)_4]$ [43], vide infra.

Table 4
Selected Cd–S and Cd–N bond distances for cadmium(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
$[Cd(4,6-Me_2pymS)_2]_6$	$Cd-S_{\text{bridging}} = 2.638(8)–2.666(8)$ Å			[53]
$[Cd(pyS)_2]_n$	oct	CdS_4N_2	2.809(4)–3.038(4) 2.543(5)–2.649(4)	[54]
$[Cd(bzS)_2]_n$	oct	CdS_4N_2	3.061(8)–3.129(4) 2.547(4)–2.606(4)	[54]
$[Cd(4,6-Me_2pymS)_2]_6$	Cd–N = 2.36(2), 2.38(2) Å			[53]
$[Cd(pyS)_2]_n$	oct	CdS_4N_2	2.343(4)	[54]
$[Cd(bzS)_2]_n$	oct	CdS_4N_2	2.306(4)	[54]

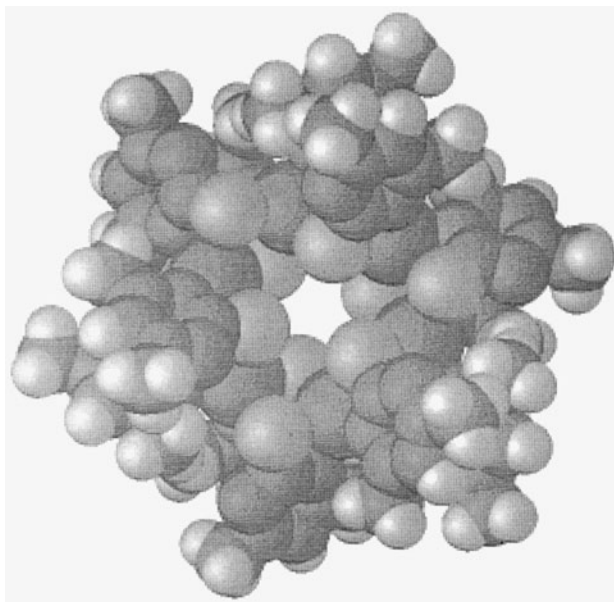


Fig. 32. Space-filling representation of the crystal structure of $[\{\text{Cd}(\text{4,6-Me}_2\text{pymS})_2\}_6]$ (adapted from Ref. [53]).

A very significant fact about this compound $[\{\text{Cd}(\text{4,6-Me}_2\text{pymS})_2\}_6]$ is that its molecules arrange themselves in such a way that holes large enough to accommodate small molecules as acetylene, CO or I_2 appear in the crystal lattice (Fig. 32).

This structure differs totally from that of the complex of cadmium with pyridine-2-thione [54], which shows a polymeric structure with the metallic atom hexacoordi-

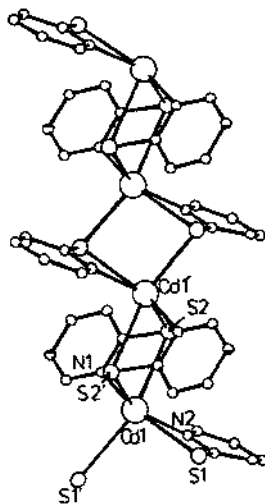


Fig. 33. Molecular structure of $[\text{Cd}(\text{pyS})_2]$ (adapted from Ref. [54]).

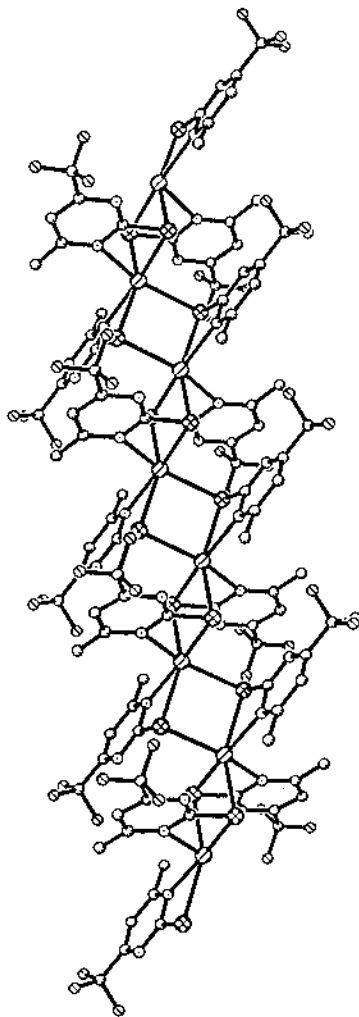


Fig. 34. The structure of the complex $[\text{Cd}(4,6\text{-MeCF}_3\text{pymS})_2]$ (adapted from Ref. [55]).

nated by two nitrogen and four sulfur atoms in a distorted octahedral environment (Fig. 33). Each pair of cadmium atoms bridged by the sulfur atoms of two ligands. These ligand pairs alternate in perpendicular and parallel positions to the chain.

The steric hindrance produced by the presence of the methyl groups in the cadmium complex is probably responsible for the difference in the degree of polymerization in both compounds.

A comparison of the structures of the complexes of cadmium with pyridine-2-thione (Fig. 33), 4,6-dimethylpyrimidine-2-thione (Fig. 30) and 3-trimethylsilylpyridine-2-thione (Fig. 27) shows how an increase in the steric hindrance produced by the substituents on the ligand can drastically modify the structure of the resultant compound.

Although these results clearly show that steric hindrance influences the degree of polymerization and the structure of the metal thiolates, this is not the only factor controlling the outcome of the reaction. Factors such as reaction conditions, charge, solvent, etc. can also play a crucial role in determining the degree of association. An illustrative example is the complex of $[\text{Cd}(4,6\text{-MeCF}_3\text{pymS})_2]$ [55], whose structure differs totally from that of the hexanuclear complex of Cd with 4,6-dimethylpyrimidine-2-thiolate, described previously. Despite the presence of a CF_3 group that is bulkier than the CH_3 group, the compound has a polymeric chain structure (Fig. 34) in which the metallic atom is hexacoordinated by two nitrogen atoms and four sulfur atoms in a distorted octahedral $[\text{CdN}_2\text{S}_4]$ environment (Fig. 35). Each ligand is joined by the nitrogen to a cadmium atom and acts as a bridge through the sulfur atom between this metallic atom and the other adjacent cadmium atom. The second ligand, almost perpendicular to the first is joined to that cadmium by the nitrogen and bridges the previous adjacent atom on the chain. Thus the thione acts as a five electron donor $[\text{N},(\mu\text{-S})_2]$ bridging ligand.

It appears that the complex initially formed may not be the most thermodynamically stable. The isolated product will be the kinetically formed compound, if this is insoluble. This is the case of the hexanuclear crystal compound $[\text{Cd}(4,6\text{-}$

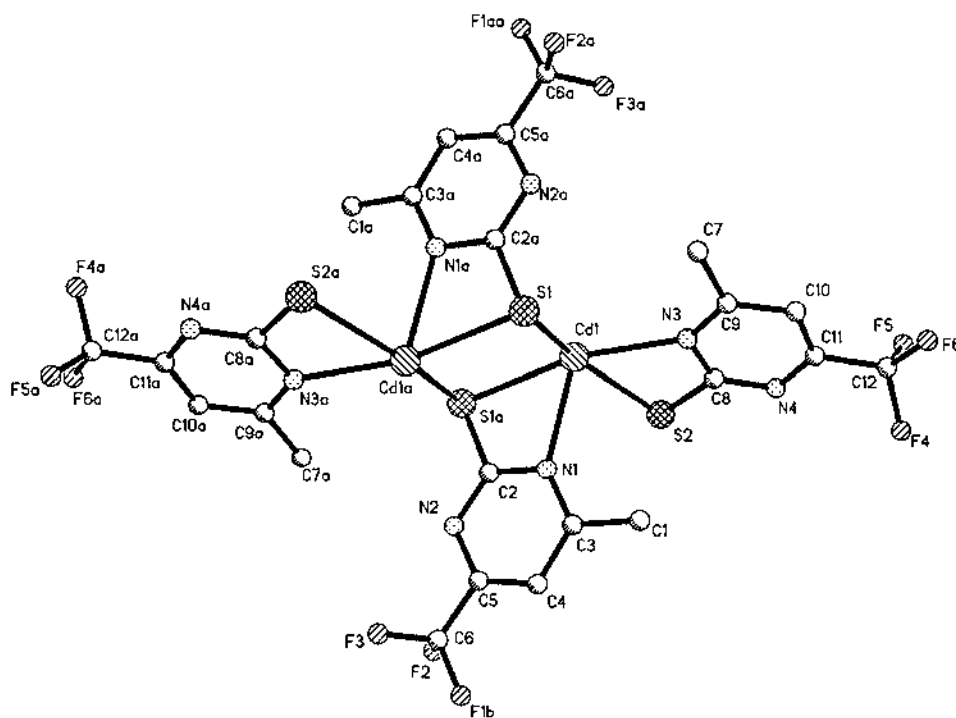


Fig. 35. A view of the coordination sphere of the metal in the complex $[\text{Cd}(4,6\text{-MeCF}_3\text{pymS})_2]$ (adapted from Ref. [55]).

Me_2pymS_2][53], which changes with time to yield a highly insoluble polymeric and non recrystallizable product. If the kinetically stable product is soluble, it will change slowly in solution to yield the thermodynamically stable polymeric product which can be obtained as a crystalline compound, as in the case of the complex $[\text{Cd}(4,6\text{-MeCF}_3\text{pymS})_2]$ [55].

The conclusion is that a compound can exist in different structures, making it interesting to try to prepare these metastable forms under gentle reaction conditions.

In the case of mixed complexes, the inclusion of an additional neutral ligand such as pyridine, phenanthroline or bipyridine in the coordination sphere of the metal yields monomeric compounds that in the case of $[\text{Zn}(\text{pyS})_2(\text{phen})]$ [56], $[\text{Zn}(4,6\text{-Me}_2\text{pymS})_2(\text{py})]$ [57], and $[\text{Zn}(\text{bzS})_2(\text{bipy})]$ [58] and $[\text{Cd}(\text{pymS})_2(\text{phen})]$ [59] have been characterized by X-ray diffraction.

The crystal structure of $[\text{Zn}(\text{pyS})_2(\text{phen})]$ shows the zinc atom bonded to two bidentate pyridine-2-thionate ligands through the nitrogen and sulfur atoms and to the two nitrogen atoms of the phenanthroline (Fig. 36). The zinc atom environment is a distorted octahedron with the sulfur atoms in *trans* positions, although the S1-Zn-S2 angle, $160.3(9)^\circ$, is very different from 180° . The $\text{Zn-N}_{\text{phen}}$ bond distances are similar to those found in other octahedral complexes (Table 5), for example $[\text{Zn}(\text{O}_2\text{C}_6\text{H}_4)(\text{phen})_2]$ [60], but slightly greater than those present in the tetrahedral complex $[\text{ZnCl}_2(\text{phen})]$ [61].

The Zn-N_{pys} bond distances are considerably longer than those found in tetrahedral complexes of zinc with pyridine [62–64] and even greater than those of octahedral compounds dinitrito-bis(pyridine)zinc(II) and dinitrito-bis(2-methylpyridine) zinc(II) [66] (Table 5). This longer Zn-N_{pys} distance is probably due to the steric hindrance created by the four-member chelate rings. On the other hand, the Zn-S distances are significantly longer than those found in distorted tetrahedral thiolates of type $[\text{ZnS}_4]$ that show bond lengths in the range $2.25\text{--}2.36\text{ \AA}$ [67–70]. To date, no Zn-S bond distance data in octahedral complexes have

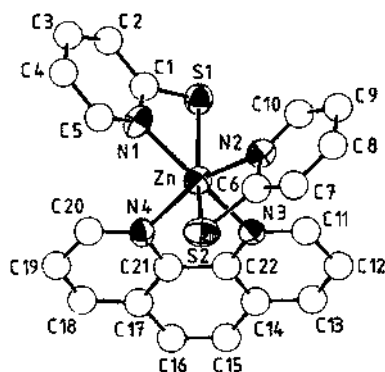


Fig. 36. Molecular structure of $[\text{Zn}(\text{pyS})_2(\text{phen})]$ (adapted from Ref. [56]).

Table 5
Selected Zn–N and Zn–S bond distances for zinc(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
[Zn(pyS) ₂ (phen)]		Zn–N _{phen} = 2.182 (6) Å		[56]
[Zn(O ₂ C ₆ H ₄)(phen)]	oct	ZnO ₂ N ₄	2.189	[60]
[Zn(phen)Cl ₂]	tet	ZnCl ₂ N ₂	2.061	[61]
[Zn(pyS) ₂ (phen)]		Zn–N _{pyS} = 2.106 (6) Å		[56]
[Zn(4-R-py) ₂ Cl ₂]	tet	ZnCl ₂ N ₂	2.040–2.060	[62–64]
R = H, methyl, vinyl, acetyl, cyano				
[Zn(imid) ₄](ClO ₄) ₂	tet	ZnN ₄	2.000	[65]
[Zn(py) ₂ (ONO) ₂]	oct	ZnO ₂ N ₂	2.063	[66]
[Zn(2-Mepy) ₂ (ONO) ₂]	oct	ZnO ₄ N ₂	2.068	[66]
[Zn(pyS) ₂ (phen)]		Zn–S = 2.627(2)–2.546(3) Å		[56]
[Zn(SC ₆ H ₅) ₄][Ph ₄ P] ₂	tet	ZnS ₄	2.33–2.36	[67]
[Zn(SPh) ₄][NMe ₄] ₂	tet	ZnS ₄	2.34–2.38	[68]
[Zn(S-ptolyl) ₂ (phen)]	tet	ZnS ₂ N ₂	2.261	[69]
[Zn(S-2,4,6- <i>i</i> Pr ₃ C ₆ H ₂) ₂ (bipy)]	tet	ZnS ₂ N ₂	2.256	[70]
[Zn(S-Me ₄ C ₆ H) ₂ (1-Me-imid) ₂]	tet	ZnS ₂ N ₂	2.300	[70]

been reported, the [Zn(pyS)₂(phen)] is the first example of an octahedral complex of Zn with a thiolate ligand.

In the case of [Zn(4,6-Me₂pymS)₂(py)] [57], the inclusion of pyridine as an additional ligand yields a monomeric compound where the zinc atom is coordinated to a nitrogen atom of a pyridine molecule, a sulfur atom and to one of the nitrogen atoms of each of the two bidentate ligands, 4,6-dimethyl-pyrimidine-2-thione (Fig. 37). The coordination number of zinc is five and the coordination polyhedron can

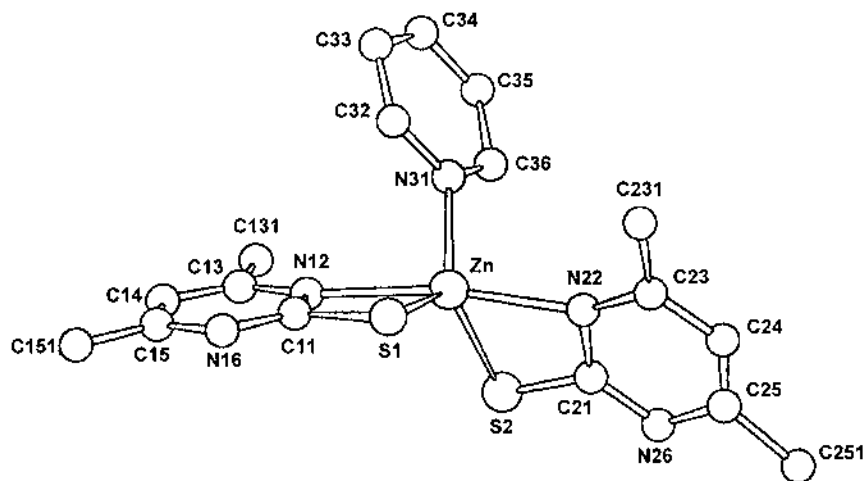


Fig. 37. Molecular structure of [Zn(4,6-Me₂pymS)₂(py)] (adapted from Ref. [57]).

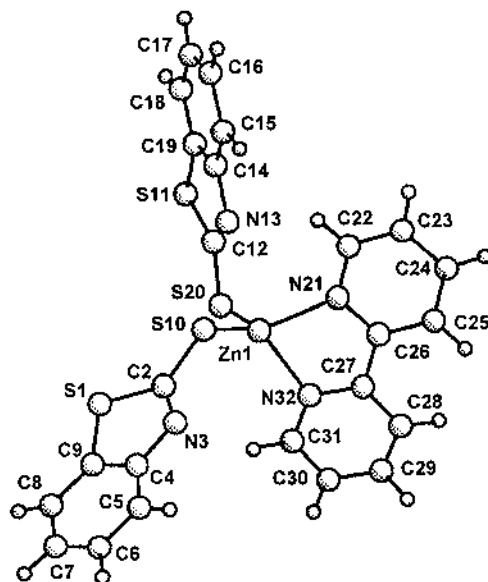


Fig. 38. Molecular structure of $[\text{Zn}(\text{bzS})_2(\text{bipy})]$ (adapted from Ref. [58]).

be described as a distorted trigonal bipyramid. The equatorial plane is defined by the sulfur and nitrogen of the pyridine and the apical positions are occupied by the two nitrogen atoms proceeding from the two 4,6-dimethyl-pyrimidine-2-thione ligands.

The $\text{N}(12)\text{--Zn--N}(22)$ angle between the nitrogen atoms in the apical position, $168.1(2)^\circ$, and the $\text{S}(1)\text{--Zn--N}(12)$ and $\text{S}(2)\text{--Zn--N}(22)$ chelate angles, $68.2(2)$ and $68.6(2)^\circ$ respectively, are however, far from the theoretical values for regular geometry.

The $\text{Zn--N}_{\text{pymS}}$ distances, $2.264(5)$ and $2.219(5)$ Å, are appreciably longer than those found in $[\text{Zn}(\text{pyS})_2(\text{phen})]$ ($2.085(6)$ and $2.128(7)$ Å) [56] and much longer than those in other pyridine complexes with a tetrahedral geometry [62–64], $2.040\text{--}2.060$ Å, or with an octahedral geometry, $2.063\text{--}2.068$ Å ([66], Table 5). This suggests that the $\text{Zn--N}_{\text{pymS}}$ bonds are relatively weak in this compound.

The Zn--N_{py} distance $2.057(4)$ Å is very similar to those found in the pyridine complexes already mentioned.

The Zn--S distances, $2.347(2)$ and $2.369(2)$ Å, are intermediate between the distances found in octahedral complexes, for example, $2.627\text{--}2.546$ Å in $[\text{Zn}(\text{pyS})_2(\text{phen})]$ [56], and in tetrahedral thiolates, $2.263(1)$ Å in $[\text{bis}(2\text{-(pyrrol-2-yl)methyleneamine)}\text{thiophenolate}]\text{zinc(II)}$ [71] and 2.286 Å in $[\text{Zn}_4(\text{SC}_6\text{H}_5)_{10}]^{2-}$ [72]. This is not surprising since the coordination number of the metal in this compound is between four and six.

In the previous cases, the thione ligand behaved as a bidentate ligand through the sulfur and the nitrogen atoms. However, in the case of the complex $[\text{Zn}(\text{bzS})_2(\text{bipy})]$ [58], the situation is different.

The crystalline structure of the complex is formed by monomeric units with the zinc atom coordinated by the exocyclic sulfur atom of each of the two thiolate monodentate ligands and by the two nitrogen atoms of the bipyridine (Fig. 38). The zinc atom is in a distorted tetrahedral $[\text{ZnS}_2\text{N}_2]$ environment.

This distortion is a reflection of the small bite angle of the bidentate bipyridine (ca. 79°). The other angles, 104 – 121° , also deviate from the theoretical tetrahedral value.

The $\text{Zn}-\text{N}_{\text{bipy}}$ bond distances, $2.100(8)$ and $2.088(7)$ Å, are very similar to those found in another tetrahedral complex of zinc and bipyridine $[\text{Zn}(\text{S}-2,4,6\text{-iPr}_3\text{C}_6\text{H}_2)_2(\text{bipy})]$ [70]. On the other hand, the $\text{Zn}-\text{S}$ distances of $2.294(5)$ and $2.321(4)$ Å are analogous to those observed in other distorted tetrahedral thiolates (Table 5), which show bond distances in the range of 2.25 – 2.36 Å [67–70]. In addition, the $\text{Zn}-\text{N}$ distance, as well as the $\text{Zn}-\text{S}$ distance, are very similar to those of the complex $[\text{Zn}(\text{S}-p\text{-tolyl})_2(\text{phen})]$ [69] that was used recently as a model compound in an EXAFS study of the Zn center in TFIIIA ([73], Fig. 39). Consequently, $[\text{Zn}(\text{bzS})_2(\text{bipy})]$ can be considered as a mimic model of the zinc atom environment in that protein.

Although the structure of the homoleptic compound of Zn with 2-mercaptobenzothiazole is not known, the structure of the cadmium derivative is [54]. In this compound (Fig. 40), the benzothiazole-2-thiolate ligand acts as a double bidentate bridge giving rise to a polymeric structure in which each cadmium atom exists in a distorted octahedral environment. It is very probable that the zinc compound with 2-mercaptobenzothiazole has a similar structure. Once again the inclusion of an

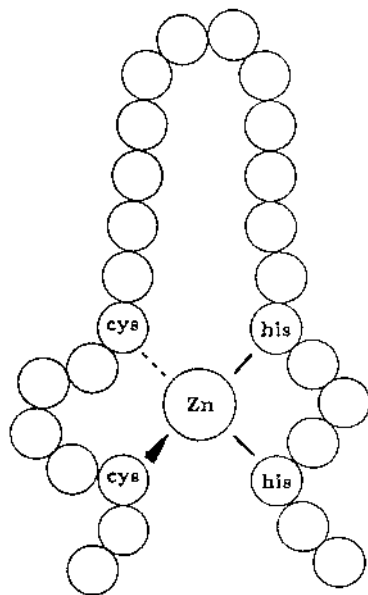


Fig. 39. The 'zinc finger' structure proposed for transcription factor IIIA.

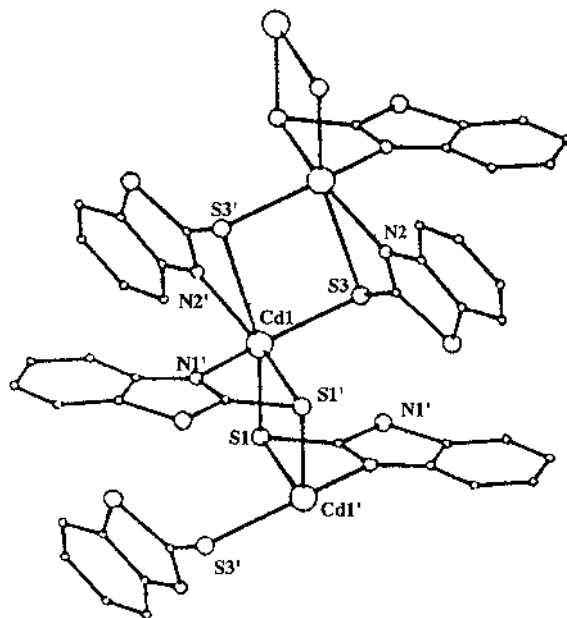


Fig. 40. Molecular structure of $[\text{Cd}(\text{bzS})_2]$ (adapted from Ref. [54]).

additional neutral ligand in the zinc compound, such as bipyridine, gives rise to a complex of lower nuclearity.

In the same way, the presence of phenanthroline in the cadmium coordination sphere in $[\text{Cd}(\text{pymS})_2(\text{phen})]$ [59] yields a monomeric compound with the cadmium atom in a distorted octahedral $[\text{CdN}_4\text{S}_2]$ environment (Fig. 41).

A remarkable characteristic of this compound is that the sulfur atoms are arranged in *cis* position. This differs from that found in other known octahedral complexes with two chelate ligands, either pyridine-2-thionates, pyrimidine-2-thionates or benzothiazole-2-thionates [32,33,59,74–80], in which the sulfur atoms find themselves in *trans* positions (Table 6).

The Cd–S bond distances are slightly shorter than those found in other octahedral complexes of cadmium [81–83] (Table 7), but almost equal to those observed in pentacoordinate [44,45] and $[\text{Cd}(\text{SR})_4]^{2-}$ distorted tetrahedral compounds [67,68,84]. This distance is even slightly shorter than the Zn–S distance found in $[\text{Zn}(\text{pyS})_2(\text{phen})]$ [56]. The aforementioned facts contrast with the observation that analogous complexes of the same metal either with bidentate pyS or pymS have very similar M–S distances ([85,86], Table 8). Therefore, it would be expected that the Cd–S distances in $[\text{Cd}(\text{pymS})_2(\text{phen})]$ should be very similar to those of $[\text{Cd}(\text{pyS})_2(\text{phen})]$, and 0.2 Å (the difference between the van der Waals radii of Zn and Cd) shorter than those of $[\text{Zn}(\text{pyS})_2(\text{phen})]$ [56]. This tendency has been observed in the case of $[\text{M}(\text{SR})_4]^{2-}$ complexes of zinc and cadmium ([67,68,84], Table 9).

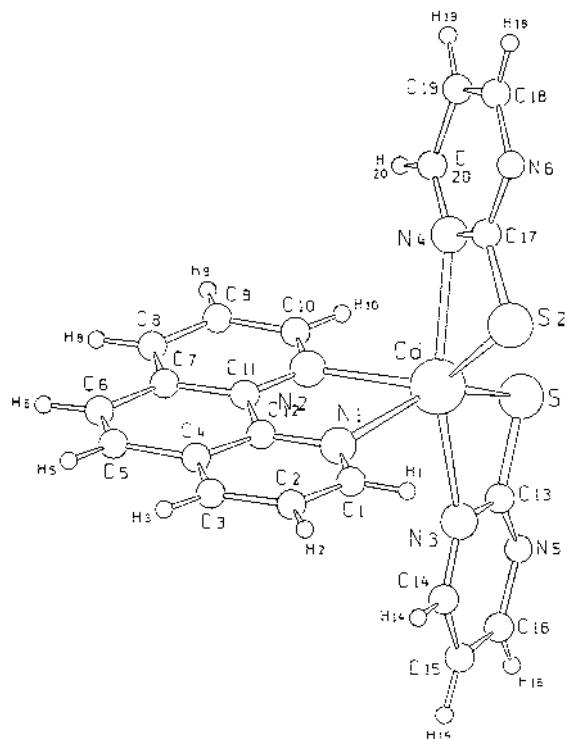


Fig. 41. Perspective view of $[\text{Cd}(\text{pymS})_2(\text{phen})]$ (adapted from Ref. [59]).

Table 6

S–M–S bond angles (°) for mixed-ligand hexacoordinate complexes with two heterocyclic thiolate ligands

Complex	Angle S–M–S	Ref.
$[\text{Cd}(\text{pymS})_2(\text{phen})]$	116.2(2)	[59]
$[\text{Ru}(\text{pyS})_2(\text{PPh}_3)_2]$	154.7(1)	[74]
$[\text{Sn}(\text{pyS})_2\text{Cl}_2]$	154.2(1)	[75]
$[\text{Ru}(\text{pyS})_2(\text{CO})(\text{PPh}_3)]$	157.96(3)	[76]
$[\text{Os}(\text{pyS})_2(\text{CO})_2]$	152.6	[77]
$[\text{Cd}(\text{pyS})_2(\text{py})_2]$	163.9(1)	[78]
	161.8(1)	
$[\text{Ru}(\text{pyS})_2(\text{dppe})]$	155.0(1)	[79]
$[\text{Ni}(\text{bzS})_2(\text{dmp})]$	167.5(1)	[80]
$[\text{Ni}(\text{pyS})_2(\text{bipy})]$	155.96(3)	[32]
$[\text{Ni}(\text{pymS})_2(\text{bipy})]$	154.26(7)	[33]
$[\text{Zn}(\text{pyS})_2(\text{phen})]$	160.7(1)	[56]

Table 7

Selected Cd–S bond distances for cadmium(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
[Cd(pymS) ₂ (phen)]		Cd–S = 2.588(3), 2.549(3) Å		[59]
[Cd(S ₂ COC ₂ H ₅) ₂ (phen)]	oct	CdS ₄ N ₂	2.647, 2.727	[81]
[Cd(S ₂ CN(C ₂ H ₅) ₂) ₃] [–]	oct	CdS ₆	2.657–2.755	[82]
{Cd[(S ₂ P(OC ₃ H ₇) ₂) ₃]} [–]	oct	CdS ₆	2.664–2.704	[82]
[Cd(S ₂ CSC ₄ H ₉ - <i>n</i>) ₂ (bipy)]	oct	CdS ₄ N ₂	2.66–2.70	[83]
[Cd(C ₇ H ₄ NS ₂) ₃] [–]	oct	CdS ₂ N ₄	2.667	[82]
[Cd ₂ (S ₂ CN(C ₂ H ₅) ₂) ₄]	tbp	CdS ₅	2.536–2.594	[44]
[Cd ₂ (S ₂ CN(CH ₂) ₆) ₄]	tbp	CdS ₅	2.539–2.631	[45]
[Cd(SR) ₄] ^{2–}	tet	CdS ₄	2.53–2.56	[67,68,84]
[Cd(SR–Ph) ₂ (1-Meimid) ₂]	tet	CdS ₂ N ₂	2.462	[84]

Table 8

M–S bond distances for pyridin and pyrimidin-2-thiolate complexes

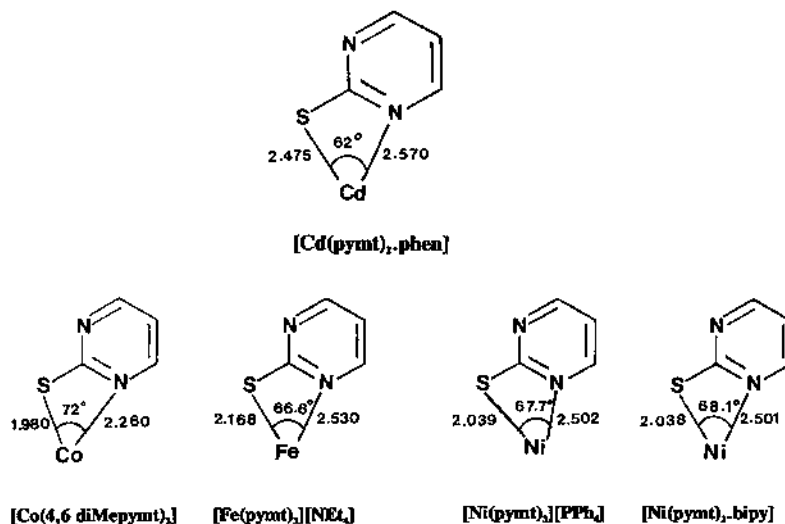
Ligand (L)					
Metal	Formula	pyS	Ref.	pymS	Ref.
Ni	[NiL ₃] [–]	2.518–2.541	[85]	2.460–2.545	[85]
Fe	[FeL ₃] [–]	2.568–2.589	[86]	2.523–2.537	[87,88]
Ni	[NiL ₂ (bipy)]	2.475–2.495	[32]	2.480–2.523	[33]
Zn	[ZnL ₂ (phen)]	2.627–2.551	[56]	–	
Cd	[CdL ₂ (phen)]	–		2.588, 2.549	[59]

Table 9

Comparison of M–S bond distance (Å) for tetracoordinated zinc(II) and cadmium(II) thiolate complexes

Cd = 1.58 Å, Zn = 1.39 Å			
Complex	Zinc	Cadmium	Difference
[M(SR) ₄]	[Zn(SPh) ₄][NMe ₄] ₂ 2.353 [68]	[Cd(SPh) ₄][NMe ₄] ₂ 2.535 [68]	0.18
	[Zn(SPh) ₄][PPh ₄] ₂ 2.33–2.36 [67]	[Cd(SPh) ₄][PPh ₄] ₂ 2.52–2.54 [67]	0.19
[M(SR) ₂ (N) ₂]	[Zn(S–Me ₄ C ₆ H) ₂ (1-Meimid) ₂] 2.300 [70]	[Cd(S–RC ₆ H ₂) ₂ (1-Meimid) ₂] 2.462 [84]	0.16

The Cd–N_{pymS} bond distances, 2.42(2) and 2.53(2) Å, are also considerably greater than those found in the tetrahedral [Cd(thiamine)Cl₃] · 0.6H₂O [89] and even slightly longer than those observed in other octahedral complexes of cadmium(II) with nitrogen-donor heterocyclic ligands [46–49] as for example 2.310(3) Å in



Scheme 10.

bis-(*N*-isonicotinato)tetraaquocadmium(II) [46]; 2.336(5) in diformatodiaquobis(nicotinamide) cadmium(II) [47]; 2.35 Å in $\text{CdCl}_2 \cdot 2\text{py}$ [48] and 2.23(2) Å in pyridine-2-carboxylate cadmium(II) [49].

On the other hand, Cd–S and Cd–N_{pymS} bond lengths on the chelate rings are significantly greater, and the S–Cd–N_{pymS} chelate angle is shorter than the corresponding parameters of other octahedral metallic complexes containing this ligand (Scheme 10, [33,59,85,87,88,90]).

The Cd–N_{phen} bond distances are very similar to those observed in $[\text{Cd}(\text{acac})_2(\text{phen})]$ and $[\text{Cd}(\text{CF}_3\text{COCHCOC}_6\text{H}_5)_2(\text{phen})]$ [60] (Table 10).

The structural data discussed, *vide supra*, show that in the pyrimidine-2-thionate complexes, each pyrimidine-2-thionate ligand possesses a non-coordinated nitrogen atom. To check whether the basicity of this nitrogen atom was sufficient to react with Lewis acids to produce heteropolynuclear compounds, $[\text{Cd}(\text{pymS})_2(\text{phen})]$ was reacted with bis(hexafluoroacetylacetonate) of copper(II) in acetonitrile as solvent.

Table 10
Selected Cd–N bond distances for cadmium(II) complexes

Complex	Approximate geometry	Coordination sphere	Bond distance (Å)	Ref.
Cd–N _{phen} = 2.349, 2.36 Å				
$[\text{Cd}(\text{acac})_2(\text{phen})]$	oct	CdO_4N_2	2.368(2)	[60]
$[\text{Cd}(\text{CF}_3\text{COCHCOPh})_2(\text{phen})]$	oct	CdO_4N_2	2.32(3)	[60]
$[\text{Cd}(\text{S}_2\text{COC}_2\text{H}_5)_2(\text{phen})]$	oct	CdS_4N_2	2.386	[81]

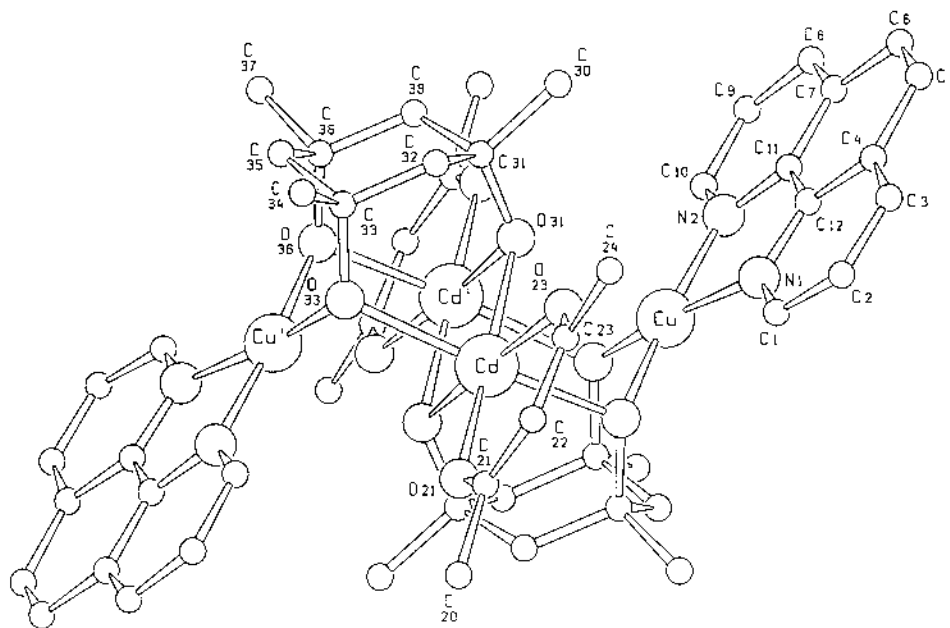


Fig. 42. Perspective view of the structure of $[\text{Cu}_2(\text{phen})_2(\mu^3\text{-TTFTCH})_2\text{Cd}_2(\text{hFacac})_2]$ (adapted from Ref. [91]).

The crystal structure of the compound $[\text{Cu}_2(\text{phen})_2(\mu^3\text{-TTFTCH})_2\text{Cd}_2(\text{hFacac})_2]$ [91] formed in this reaction is shown in Fig. 42.

In this compound, the pyrimidine-2-thione ligands of the precursor have disappeared, the phenanthroline molecules have moved from the coordination sphere of the cadmium atoms to the coordination sphere of the copper atoms, and in addition, a new cyclic tridentate trianionic ligand appears.

The compound is a heteronuclear complex that contains two copper and two cadmium coplanar atoms per molecule (Fig. 43). The new cyclic tridentate ligands, two per molecule, one above the metallic plane and the other below, show two of the oxygens acting as bridges between the Cu and Cd atoms, and the third between the two cadmium atoms. Each copper atom is tetracoordinated by two phenanthroline nitrogen atoms and two oxygen bridge atoms, one from each new ligand, and each Cd atom is hexacoordinated by the oxygen atoms of the hexafluoroacetylacetonate ion and four oxygen bridges of the new ligands. (1,3,5 tris(trifluoromethyl)-1,3,5-trioxycyclohexane trianion, TTFTCH) (Fig. 44).

The complexes have also been characterized by IR and NMR spectroscopy. The IR spectra of the complexes show the absence of the $\nu(\text{NH})$ band of the free heterocyclic ligand, demonstrating deprotonization of the ligand during the electrochemical process. The spectra of the mixed complexes show the presence of bands attributed to coordinated bipyridine and phenanthroline ligands. In the ^1H -NMR spectra, the signal due to the NH group is again absent and the ^{13}C -NMR show

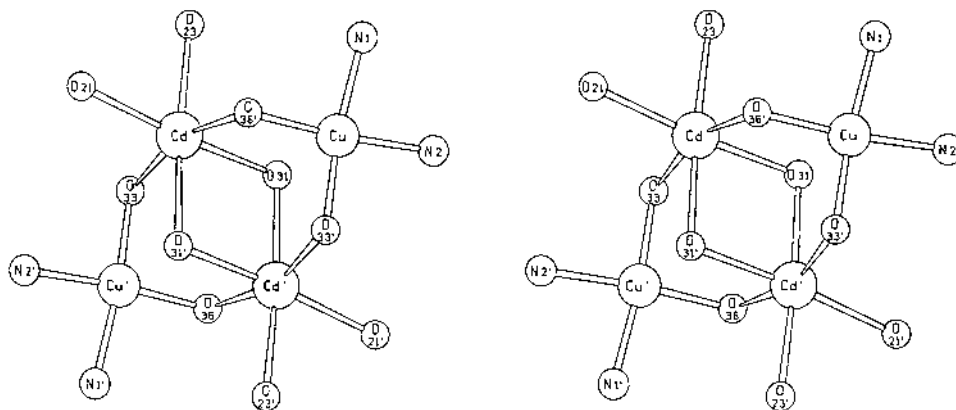


Fig. 43. A stereoscopic view of the coordination sphere of the metals in the $[\text{Cu}_2(\text{phen})_2(\mu^3\text{-TTFTCH})_2\text{Cd}_2(\text{hFacac})_2]$ complex (adapted from Ref. [91]).

that in all cases, the signal due to C_2 undergoes an upfield shift with respect to the free ligand. This can be attributed to a decrease in the $\text{C}=\text{S}$ bond order and therefore, a greater thiolate character for the ligand in the complex than in the free ligand. In addition, in the 4,6-Me₂pymS complexes, the ^1H spectra show two signals due to the pyrimidine ligand: a singlet between 6.75 and 6.56 ppm, corresponding to the H_5 proton and a singlet between 2.21 and 2.00 ppm due to the protons of the

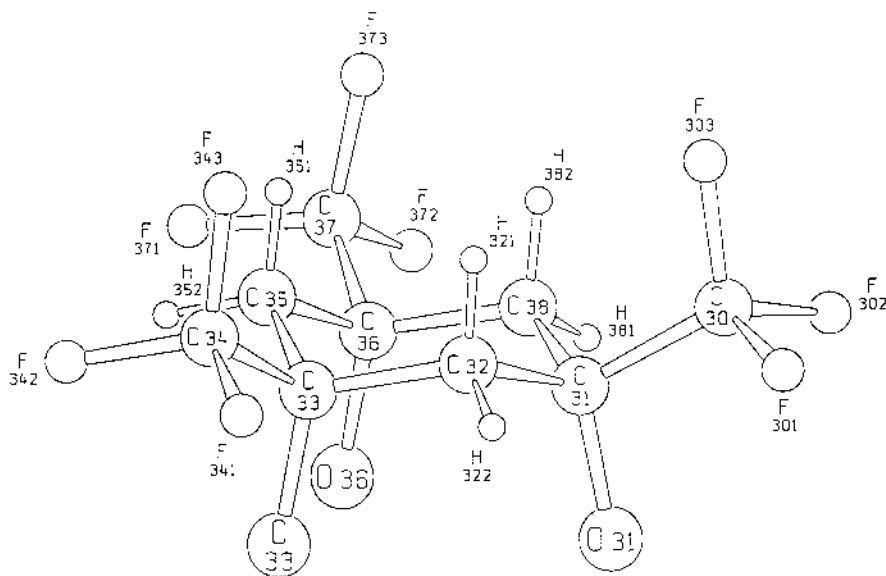


Fig. 44. A view of the structure of the (1,3,5 tris(trifluoromethyl)-1,3,5-trioxycyclohexane (adapted from Ref. [91]).

methyl groups that are chemically equivalent. This equivalency is also seen in the ^{13}C -NMR spectra, where only one signal around 22.5 ppm for the carbon atoms of the two methyl groups is observed.

If the complexes in solution had been able to maintain the same structure as in the solid state, with bidentate pyrimidine ligands through the sulfur and one of the nitrogen atoms, as in the case of $[\text{Zn}(4,6\text{-Me}_2\text{pymS})_2(\text{py})]$ [57], the ^1H -NMR spectra should present two signals, one for each of the non-equivalent methyl groups. To test this hypothesis, the spectra were measured at variable temperature from 300 to 218 K; at 218 K the protons of the methyl groups give two different signals, indicating that at that temperature the rate of the exchange process is reduced to the point where the non-equivalency of the hydrogens is detected.

Both ^1H and ^{13}C spectra also contain signals corresponding to the coordinated bipyridine, phenanthroline or pyridine ligands.

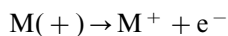
These results are compatible with a monomeric structure and an octahedral geometry around the metallic atoms in solution for mixed complexes of zinc and cadmium with bipyridine or phenanthroline, similar to that found in the solid state for $[\text{Zn}(\text{pyS})_2(\text{phen})]$ and $[\text{Cd}(\text{pymS})_2(\text{phen})]$.

7. Gallium, indium and thallium complexes

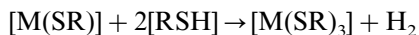
The coordination chemistry of these elements with thiolate ligand has seldom been studied and few compounds have been structurally characterized. The importance of these compounds as possible precursors in the preparation of thin films of metallic sulfides using deposition techniques of metallic vapors, has recently encouraged research to obtain low nuclearity compounds of these elements. This can be achieved by using sterically hindered thiolate ligands [92,93]. On the other hand, it has been demonstrated that indium complexes of heterocyclic thiones are adequate sources of ^{111}In and ^{113}In gamma emitters for medicinal imaging [94,95].

The electrochemical oxidation of gallium, indium and thallium in the presence of heterocyclic thiones as ligands has been shown to be an effective method for the synthesis of complexes containing these metals. The compounds obtained are generally of general stoichiometries $[\text{Ga}(\text{SR})_3]$, $[\text{In}(\text{SR})_3]$ and $[\text{Tl}(\text{SR})]$. Only in some cases has it been possible to isolate the $\text{In}(\text{I})$ species [96].

The electrochemical efficiency values found in the synthesis process of these compounds have always been close to 1 mol F^{-1} , indicating anodic processes in which the M^+ species are initially formed according to:



In view of these data, a second oxidation step in solution can be postulated, at least in the case of gallium and indium complexes:



In these compounds, the monoanionic ligands are of bidentate character, resulting in monomeric complexes with the metal in a $[\text{MN}_3\text{S}_3]$ distorted octahedral

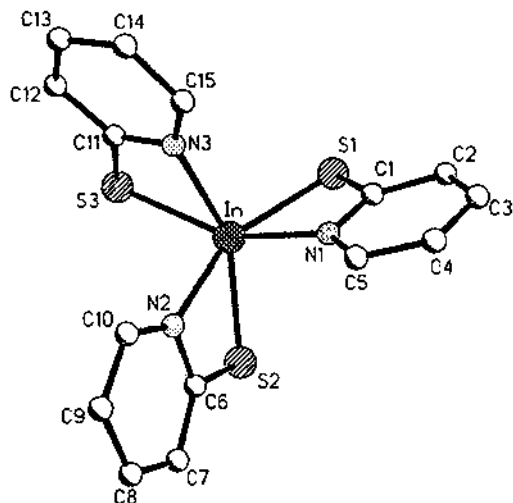


Fig. 45. Molecular structure of [In(pyS)₃] (adapted from Ref. [94]).

environment. This environment has been found in [In(pyS)₃] (Fig. 45, [94]) and in [In(3-CF₃pyS)₃] (Fig. 46, [97]). Fig. 45 shows the indium atom coordinated by three monoanionic pyridine-2-thionate ligands, with its nitrogen and sulfur atoms giving rise to the formation of four-member chelate rings with small chelate angle values around the metal. As a consequence, the octahedral environment around the

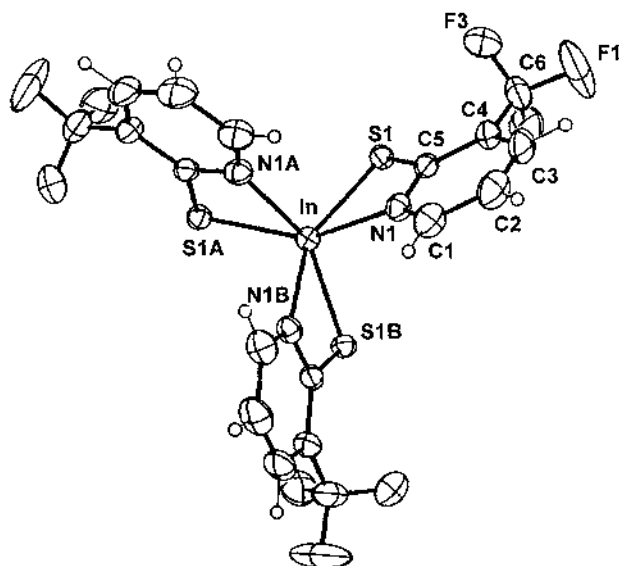


Fig. 46. Molecular structure of [In(3-CF₃pyS)₃] (adapted from Ref. [97]).

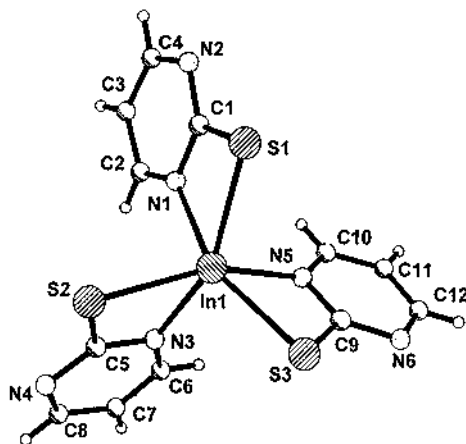


Fig. 47. Molecular structure of $[\text{In}(\text{pmyS})_3]$ (adapted from Ref. [98]).

indium is highly distorted. The arrangement of the donor atoms around the metal gives rise to the *facial* isomer. The same disposition has been found in $[\text{In}(\text{3-Me}_3\text{SipyS})_3]$ [94].

The pyrimidine-2-thione indium, $[\text{In}(\text{RpymS})_3]$ ($\text{R} = \text{H}$, 4,6- Me_2 , 5-Et-4,6- Me_2 and 4,6-(Me, CF_3)) are similar, [98]. The crystal structure of two of them demonstrate that in these compounds, the ligand behaves analogously to the way observed in the case of pyridine-2-thione, the indium atom coordinating the sulfur atom and one of the heterocyclic nitrogen atoms of each ligand; the other nitrogen atom remaining uncoordinated. Figs. 47 and 48 show the structures of $[\text{In}(\text{pymS})_3]$ and $[\text{In}(\text{5-Et-4,6-Me}_2\text{pymS})_3]$.

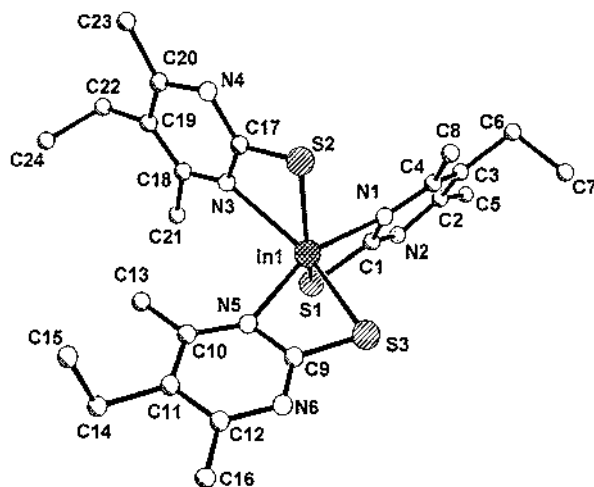


Fig. 48. Molecular structure of $[\text{In}(\text{5-Et-4,6-Me}_2\text{pmyS})_3]$ (adapted from Ref. [98]).

Again the metallic atom environment is a distorted octahedron. The structural parameters for both complexes are similar and fall in the range for octahedral compounds of In(III) containing this type of donor atom. Therefore, the presence of substituents on the ligand in the compound $[\text{In}(\text{5-Et-4,6-Me}_2\text{pymS})_3]$ does not produce significant modifications in the values of these parameters, although, their presence increase its solubility and facilitates its studies in solution. However, the arrangement of donor atoms around the metallic atom depends on the nature of the substituents. So, while in the case of $[\text{In}(\text{pymS})_3]$, the observed isomer is *facial*, the disposition is *meridional* in $[\text{In}(\text{5-Et-4,6-Me}_2\text{pymS})_3]$. It is worth noting that solution studies by means of ^1H -, ^{13}C - and ^{19}F -NMR show that in the four compounds studied, the ligands are equivalent and that therefore the structures in solution for these compounds correspond to the *facial* isomer. These NMR studies in solution also show an equivalency between H_6 and H_4 in $[\text{In}(\text{pymS})_3]$ as well as between both methyl groups in $[\text{In}(\text{5-Et-4,6-Me}_2\text{pymS})_3]$.

These studies have been expanded to include the synthesis of compounds with ligands that can be considered as related to those previously indicated. Compounds of these metals with pyridine-2-selenol have been synthesized [99]. The structural determination of the indium compound again shows that the metal is in an octahedral environment and coordinated to three nitrogen atoms and three selenium atoms of three anionic ligands (Fig. 49).

As it happens in most of the cases discussed, the arrangement of the ligands corresponds to the *facial* isomer, a structure which is maintained in solution as can be deduced from the presence of a single signal at 399 ppm in the ^{77}Se spectrum.

The electrochemical oxidation of Ga, In and Tl in the presence of the ligand 1-hydroxypyridine-2-thione (HPT) has allowed for the synthesis of $[\text{Ga}(\text{PT})_3]$, $[\text{In}(\text{PT})_3]$, $[\text{Tl}(\text{PT})_3]$ and $[\text{Tl}(\text{PT})]$ [100] to be effected. The gallium and indium are the only produced products during the electrochemical procedure. However, in the case of thallium, the electrolysis produced initially an insoluble solid with a $[\text{Tl}(\text{PT})]$ formulation. Without any doubt, its high insolubility in acetonitrile facilitates its isolation. Air concentration of the mother solution allows the isolation of some crystals of $[\text{Tl}(\text{PT})_3]$ which it has been produced by the aerial oxidation of the thallium compound that remains in solution. This was proven by passing a stream of oxygen through a $[\text{Tl}(\text{PT})]$ suspension, when observed transformation of the Tl(I) compound into the Tl(III) was observed.

The structures of the compounds $[\text{In}(\text{PT})_3]$ and $[\text{Tl}(\text{PT})_3]$ have been studied by X-ray diffraction; their structures are shown in Figs. 50 and 51.

Both structures are very similar, having the metal coordinated to three sulfur atoms and three oxygens of three monoanionic bidentate ligands with the metal in a distorted octahedral environment. In both cases, the arrangement of the ligands corresponds to the *meridional* isomer. This disposition is not retained in chloroform solution. The ^1H - and ^{13}C -NMR spectra show that the ligands in these complexes are equivalent, as expected for a *facial* arrangement of the ligands. To check that the equivalence was not due to any scrambling process of the ligands, the spectra

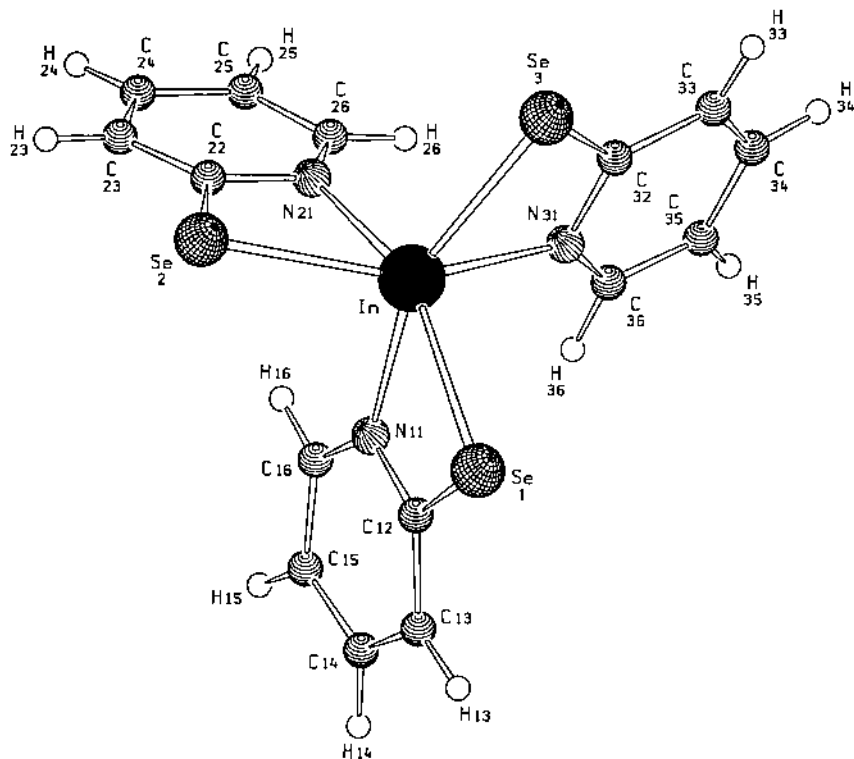


Fig. 49. Molecular structure of $[\text{In}(\text{pySe})_3]$ (adapted from Ref. [99]).

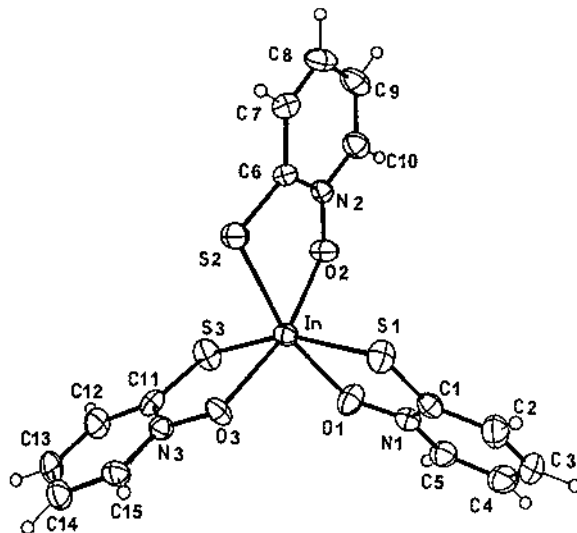


Fig. 50. Molecular structure of $[\text{In}(\text{PT})_3]$ (adapted from Ref. [100]).

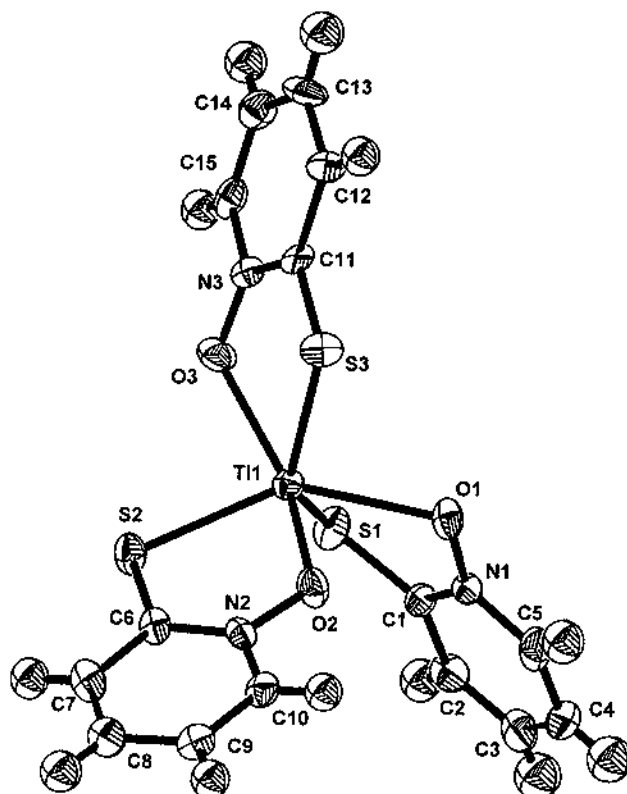


Fig. 51. Molecular structure of $[\text{Tl}(\text{PT})_3]$ (adapted from Ref. [100]).

were obtained at 218 K, the lowest temperature compatible with the use of chloroform as a solvent. The spectra are not temperature dependent. This suggests that the scrambling process is either non-existent or too fast to be detected, even at 218 K. This structural change, from *meridional* to *facial* in going from the solid state to the solution, was discussed in the case of cobalt and indium pyridine-2-thionates (*vide supra*), and is an additional proof that other factors, apart from steric hindrance, are important in determining the compound structure in solid state and in solution.

The ^{205}Tl spectrum of the compound $[\text{Tl}(\text{PT})_3]$ shows a single signal at 2968.4 ppm, characteristic of Tl(III) in octahedral environments (Fig. 52). However, the complex $[\text{Tl}(\text{PT})]$, exhibits a signal, at 2696.7 ppm, which is typical of Tl(I) complexes. A lower intensity signal is also observed at 2967.90 ppm as a consequence of the presence of trace amounts of a Tl(III) compound.

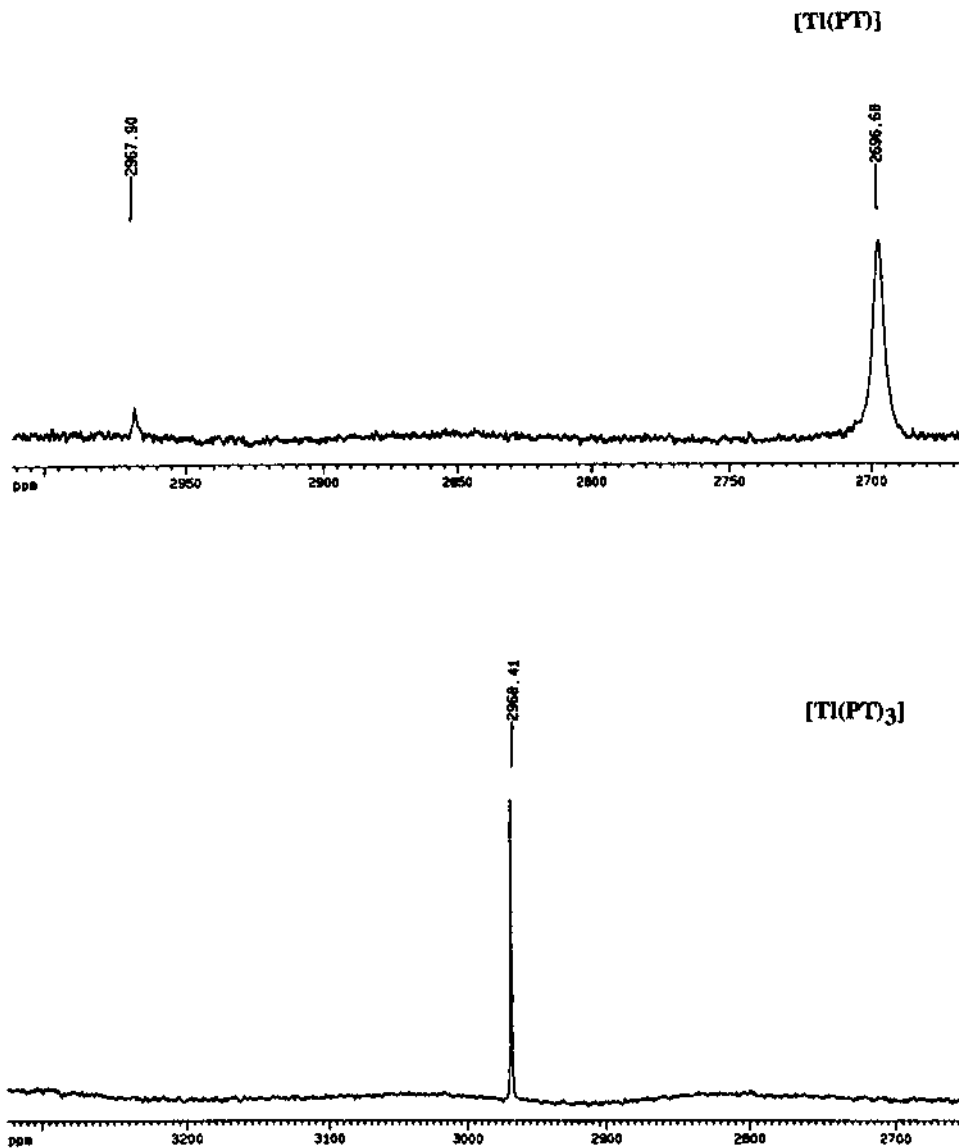


Fig. 52. ^{205}Tl -NMR spectra of (a) $[\text{Ti}(\text{PT})]$ and (b) $[\text{Ti}(\text{PT})_3]$ in CDCl_3 (adapted from Ref. [100]).

Acknowledgements

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