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Organodisulphide complexes

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CONTENTS

ABBREVIATIONS

AED	[2-aminoethyl(ethyl)]disulphide: $NH_2CH_2CH_2SSCH_2CH_3$
APD	bis(2-aminophenyl)disulphide; 2,2′-dithiodianiline: $[NH_2C_6H_4S{-}]_2$
BTEA	benzyltriethylammonium: $[BzEt_3N]^+$
CT	charge transfer
Cp	cyclopentadienyl: $[C_5H_5]^-$

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Cp*	pentamethylcyclopentadienyl: $[C_5Me_5]^-$
CYST	cystine: $[HO_2CCH(NH_2)CH_2S-]_2$
CYSTAM	cystamine; bis(2-aminoethyl)disulphide: $[NH_2CH_2CH_2S-]_2$
DAD	bis[*N*(*N*,*N*-dimethylaminoethyl)aminoethyl]disulphide: $[Me_2NCH_2CH_2NHCH_2CH_2S-]_2$
DAT	*N*(*N*,*N*-dimethylaminoethyl)aminoethanethiolate: $[Me_2NCH_2CH_2NHCH_2CH_2S]^-$
DED	bis[2-(*N*,*N*-dimethylamino)ethyl]disulphide: $[Me_2NCH_2CH_2S-]_2$
DMAD	bis(2,2-dimethylacetato)disulphide: $[O_2CC(CH_3)_2S-]_2^{2-}$
DMF	*N*,*N*-dimethylformamide
DTPP	α,α′-[dithiobis(*o*-phenylenenitrile)]di-2-picoline; bis[2-{(2-pyridylmethyl)imino}phenyl]disulphide; 2,2′-di(pyrid-2-ylmethyleneimine)diphenyldisulphide: $[(C_5H_4N)CH{=}NC_6H_4S-]_2$
en	ethylenediamine
EtOH	ethanol
ESR	electron spin resonance
G_2S_2	glutathionedisulphide; glutathione oxidized; violet glutathione: $[HO_2CCH(NH_2)CH_2CH_2CONHCH(CONHCH_2CO_2H)CH_2S-]_2$
H_2SALES	*N*,*N*′-[1,1′-dithiobis(ethylene)]bis(salicylideneimine): $[HOC_6H_4CH{=}NCH_2CH_2S-]_2$
H_2SALPS	*N*,*N*′-[1,1′-dithiobis(phenylene)]bis(salicylideneimine): $[HOC_6H_4CH{=}NC_6H_4S-]_2$
IMAD	bis[2-(imidazolylmethyl)aminoethyl]disulphide: $[(C_3H_3N_2)CH_2NHCH_2CH_2S-]_2$
IR	infrared
M	metal centre
MAMI	5-(1,2,5-dithiazepan-5-ylmethylene)-4-methyl-2-ethylimidazole: $[(C_5H_8S_2)CH_2(C_3H_3N_2)]$
MeCN	acetonitrile
MeOH	methanol
MS	mass spectrometry
NMR	nuclear magnetic resonance
PDS	D-penicillaminedisulphide; 3,3,3′,3′-tetramethyl-D-cystine: $[HO_2CCH(NH_2)C(CH_3)_2S-]_2$
PED	bis(2-pyridylethyl)disulphide; (2,2′-dithiodiethylene) dipyridine: $[(C_5H_4N)CH_2CH_2S-]_2$
Pm	pyrimidyl
PMS	bis[2-{(pyridylmethyl)amino}ethyl]disulphide: $[(C_5H_4N)CH_2NHCH_2CH_2S-]_2$
Pm_2S_2	bis(2-pyrimidyl)disulphide: $[(C_4H_3N_2)S-]_2$
PTT	propane-1,2,3-trithiolate: $[SCH_2CH(S)CH_2S]^{3-}$
Py	pyridyl

Py_2S_2	bis(2-pyridyl)disulphide: $[C_5H_4N)S-]_2$
R	alkyl or aryl group: Me = methyl; Et = ethyl; i-Pr = iso-propyl; *n*-Bu = *n*-butyl; *t*-Bu = *tert*-butyl; *i*-Bu = iso-butyl; Ph = phenyl; Bz = benzyl
THF	tetrahydrofuran
TTD	bis(propane-1,2-dithiolate)disulphide; 1,2,7,8-tetrathiolate-4,5-dithia-octane: $[SCH_2CH(S)CH_2S-]_2^{4-}$
UV-V	ultraviolet–visible

A. INTRODUCTION

(i) *Background*

A number of organic ligands containing a disulphide group, RSSR, are reduced, via oxidative addition, by reaction with metal ions in low oxidation states incorporating the thiolate group, RS^-, as bridging [1] or terminal [2] ligands.

Similarly, in most other cases, organic disulphide ligands cleave by action of an electrophile, E^+, such as metal ion, assisted by a nucleophile, Nu^-. The mechanism of this metal-catalysed cleavage can involve an initial coordination of the electrophile at one sulphur atom followed by nucleophilic attack at the second sulphur atom [3,4]:

$$RSSR \xrightarrow{E^+} R\overset{+}{S}(-E)SR \xrightarrow{Nu^-} RSE + RSNu$$

A further redox process may occur in the RSE species, i.e. $[RSCu]^+$ undergoes a one-electron reductive elimination to give Cu(I) and a mercapto radical, $RS\cdot$, which by recombination regenerates half of the initial disulphide ligand [5]. Cu(I) may also form a stable complex if an excess of the disulphide ligand is present [6]. On the other hand, if the metal ion is not reduced, RSE may be isolated as a stable complex [7].

The susceptibility of coordinated disulphide ligands to cleave via oxidative addition or nucleophilic attack is a difficulty inherent to the preparation and isolation of metal disulphide complexes. However, since the first crystal structure determination of an organic disulphide ligand coordinated to a metal ion by Brändén in 1967 [8], the syntheses of nearly 100 metal disulphide complexes have been reported, one fourth of which have been authenticated by X-ray diffraction analysis.

Several synthetic routes to coordinated disulphides involve direct combination of metal ions with chelating disulphides or ligand substitution by simple alkyl- or aryldisulphides. In both cases, symmetrical ligands are generally used. Other more specific routes involve oxidation of coordinated thiolato ligands, chemical or electrochemical oxidative cyclization of coordinated dithiols, induced electron transfer, and electrophilic addition of RS^+ groups to coordinated thiolato ligands.

This review is concerned with the synthesis and structural aspects of organodisulphide–metal complexes and with some spectral properties of the S—S group bound to metal centres. The literature up to 1990 is covered. Two earlier reviews on the reactivity of metal ion–sulphur bonds [9] and the structural chemistry of metal thiolate complexes [10] also include a brief reference to organic disulphide–metal complexes.

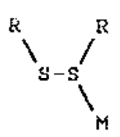
(ii) Biochemical implications

In recent years, the synthesis and study of new compounds exhibiting an M—S (disulphide) bond has been encouraged due to their probable relevancy with certain redox processes in biological systems. For example, it has been postulated that the oxidized form of two-electron copper oxidase ceruloplasmin contains in the two-copper site the $RSSR[Cu(I)]_2$ unit [11]. Similarly, in stellacyanin (a type I blue copper protein), a disulphide sulphur atom has been postulated as a probable ligand in the fourth coordination site of the copper ion [12]. This suggestion has recently been reinforced [13,14]. On the other hand, in certain model complexes related to molybdenum enzymes, a partial bond formation between two coordinated RS^- ligands at a molybdenum(VI) centre has been observed [15].

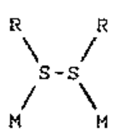
These examples show, in general, the importance of the chemistry of the thiol–disulphide couple in essential processes, and it is likely that the interest in this field will grow in the next few years.

(iii) Coordination modes of the disulphide group

Organic disulphide ligands are able to function in two different coordination modes: as monodentate ligands (terminal or end-on coordination) by using only one of the sulphur atoms (A), and as bidentate ligands (bridging or cis end-on coordination) by using both sulphur atoms (B).



A



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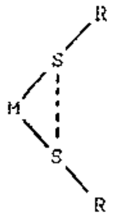

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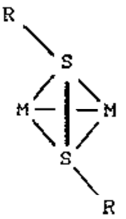


D

A different coordination mode, i.e. a side-on coordination, where both disulphide sulphur atoms coordinate a metal centre, has not been reported in the literature.

The distance between the metal centre and the more distant disulphide sulphur atom is normally too long (>3.7 Å) to be considered as a weak interaction. However, in several complexes containing two coordinated thiolate ligands, a partial bond formation, RS ··· SR, has been observed (C) [15]. On the other hand, a double bridge or double side-on coordination (D) has been suggested for the complex $[Co_2(CO)_6\{(C_6F_5)_2S_2\}]$ [16] in which both sulphur atoms of the disulphide ligand are bound to each of two cobalt atoms. To our knowledge this complex would be the first example reported having such a type of coordination. Unfortunately, its structure has so far not been confirmed by diffraction methods.

In the disulphide complexes reviewed in this article whose structures have been authenticated by X-ray structural analysis, the disulphide groups adopt either type A, type B, or both types of coordination. In some cases, the M–S bond does not exist. In a surprising copper(I) complex, both monomeric and polymeric units are observed. In each case, the metal centre is similarly coordinated by a ligand molecule through an N, S donor set. However, in the monomeric unit, the second ligand coordinates through an N,N donor set, whereas in the polymeric unit, two halves of two different ligand molecules also coordinate through their N atoms.

A great diversity of structural types, i.e. monomeric, dimeric, and polymeric, with metal centres having tetrahedral, trigonal bipyramidal, square pyramidal and octahedral symmetry have been observed.

B. DISULPHIDE COMPLEXES. STRUCTURAL ASPECTS

(i) Dialkyl- and diaryldisulphides

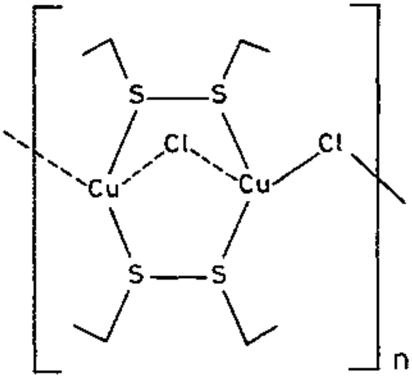
Certain simple organic disulphide ligands such as Me_2S_2, Et_2S_2, Ph_2S_2, and some of their derivatives are able to form stable complexes with metal ions in low oxidation states, i.e. Cu(I), Re(I), Co(0), etc. The stability of these complexes must be considered within certain restrictions since, in some cases, a complex can be air stable but sensitive towards daylight and/or moisture.

In general, these ligands (one or two per complex molecule) adopt a type B coordination. However, in an exceptional case, diphenyldisulphide has been shown to function as a terminal as well as a bridging ligand within the same complex molecule.

(a) Copper(I) complexes

The structures of two polymeric copper complexes containing Et_2S_2 as ligand have been described: $CuCl \cdot Et_2S_2$ [8] and $2CuI \cdot Et_2S_2$ [18]. The crystal structures of these complexes show some important differences. For example, the stoichiometry of the chloro analogue shows a 1:1 molar ratio between copper and ligand molecule, whereas CuI forms a complex where this molar ratio is 2:1.

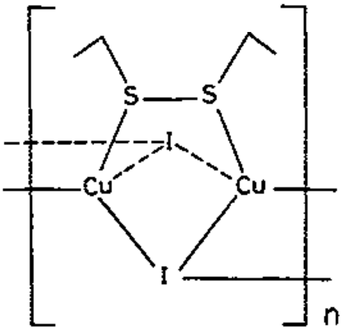
$CuCl \cdot Et_2S_2$, **I**, was the first example authenticated by X-ray structural analysis



I

in which a disulphide sulphur atom coordinated to a metal ion was demonstrated [8]. The complex was prepared by dissolving freshly purified CuCl in an excess of Et_2S_2. The complex loses Et_2S_2 and is air sensitive.

The structure of the chloro complex, **I**, has a continuous —Cl—Cu—Cl—Cu—Cl— chain with alternative pairs of Cu(I) ions bridged by two Et_2S_2 molecules. Thus, every Cu(I) ion is approximately tetrahedrally coordinated by two chloride ions and two sulphur atoms. Paired copper(I) ions are at a non-bonding distance of 3.22 Å, whereas those linked only by a μ-chloro bridge are at 3.68 Å.



II

The iodo-complex, $2CuI \cdot Et_2S_2$, **II**, has been synthesized as described above [18]. In its structure, each iodide ion coordinates to three Cu(I) ions, and each Cu(I) ion has an approximately tetrahedral coordination consisting of three iodide ions and one sulphur atom. Those pairs bridged by disulphide are separated by 2.756(3) Å, whereas contacts between adjacent symmetry-related Cu(I) ions bridged only by two iodide ions are separated by 2.612(3) Å. Surprisingly, the shortest bond length is between diiodide-bridged Cu(I) ions rather than pairs of Cu(I) ions bridged by a disulphide molecule and two iodide ions. Obviously, the increase of the copper–

copper bond length is induced by the presence of the disulphide bridge. The Cu(I) ions are much closer to one another in the iodo complex than in the chloro complex. Thus, while in the first case there are two iodide bridges between a pair of Cu(I) ions, in the second case there exists only one chloride bridge.

In spite of the fact that complexes **I** and **II** are very different, a comparison of the geometry of the Et_2S_2 ligand in both complexes shows remarkable structural similarities [8,18]: (1) the C–S–S–C dihedral angles are 97.7 and 95.6(10)°, respectively, and can be considered as normal having in mind the preference for disulphides to adopt a conformation with dihedral angles close to 90°. In this manner, the interelectronic repulsion between two lone pairs of electrons contained in p orbitals on the adjacent sulphur atoms is minimized; (2) the average values of Cu–S–S angles are 99.7(6) and 94.8(2)° being, for **II**, 5° lower than for **I** as a consequence of the shorter copper–copper bond length; (3) the average values of Cu–S bond lengths, 2.37(1) and 2.335(4) Å, respectively, are surprisingly short, indicating strong Cu–S interaction.

The average values of the S–S bond lengths in complexes **I** and **II** are 2.04(2) and 2.063(5) Å, respectively, and represent a lengthening by ca. 0.03 and 0.053 Å with respect to the uncoordinated Et_2S_2 molecule.

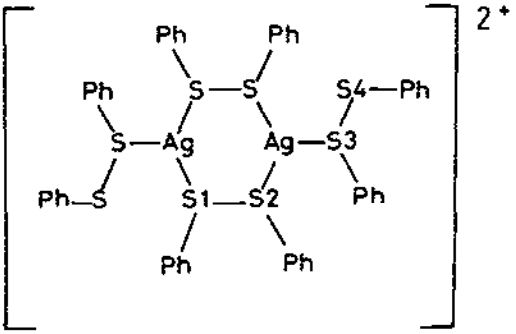
The Raman spectra for both complexes **I** and **II**, and for the uncoordinated Et_2S_2 ligand exhibit bands at 494, 486 and 508 cm^{-1}, respectively. These values indicate minimal changes in the geometry of the coordinated and uncoordinated Et_2S_2 ligand [18].

Similar complexes, such as $CuCl \cdot Me_2S_2$, $CuBr \cdot Me_2S_2$, $nCuI \cdot Me_2S_2$, and $CuBr \cdot Et_2S_2$, have also been reported [18] although, in most cases, they have been shown to be unstable, losing the disulphide ligand upon standing. They are also sensitive towards moist air.

(b) Silver(I) complexes

Ph_2S_2 reacts with $AgAsF_6$ in liquid SO_2 affording the complex formulated as $[Ag_2(Ph_2S_2)_4][AsF_6]_2$ (**III**) [19]. The structure consists of a six-membered Ag_2S_4 ring in a chair conformation where two independent Ph_2S_2 molecules bridge two Ag(I) ions; furthermore, each Ag(I) ion is coordinated in an exocyclic manner by a disulphide molecule through only one sulphur atom, completing an irregular three-coordination. Thus, the same ligand adopts a terminal type A coordination and a bridging type B coordination, this being the first case reported in the literature with these surprising characteristics. Additionally, above and below the Ag_2S_4 hexagonal ring, an AsF_6^- counter ion coordinates weakly to different silver(I) ions through two fluorine atoms.

The S–S bond length in the exocyclic ligand (2.080(3) Å) is longer than the bond length for the bidentate counterpart in the hexagonal ring (2.065(2) Å) and both are significantly longer than that of the uncoordinated ligand (2.023 Å) [20]. Similarly, the C–S(1)–S(2)–C and C–S(3)–S(4)–C dihedral angles are 74 and 70°,



III

respectively, and are significantly smaller than in the uncoordinated ligand (85.0°) [20]. In both cases, the angles were calculated from the experimental data given in refs. 19 and 20. The Ag—S(1), Ag—S(2), and Ag—S(3) bond lengths are 2.503(2), 2.638(2) and 2.534(2) Å, respectively. The significant difference of 0.135 Å in the S—S bond lengths in the cyclic ring was not discussed.

The strong Raman bands at 512 and 458 cm^{-1} [19] (not assigned) would correspond to ν(S—S) modes of the terminal and bridging Ph_2S_2 ligands, respectively.

(c) Palladium(II) complex

Ph_2S_2, in slight excess, reacts with *trans*-$[Pd(MeCN)_2Cl_2]$ in benzene solution affording a crystalline compound of formula $[Pd_2Cl_4(Ph_2S_2)_2]$ [21]. On the basis of molecular weight measurements and infrared data, a structure with two $PdCl_2$ moieties bridged by two molecules of Ph_2S_2 has been suggested. This complex, stable in the solid state (m.p. 182° dec.), undergoes complete decomposition when heated in benzene, giving metallic palladium and probably PhSCl. However, the reaction of Ph_2S_2 on $Na_2[PdCl_4]$ in MeOH yields a polymeric compound of formula $[Pd(SPh)Cl]_n$.

(d) Platinum(IV) complexes

Trimethylplatinum(IV) halides react with Me_2S_2 (1:1) in refluxing $CHCl_3$, giving crystalline binuclear complexes of formula $[Pt_2X_2(Me)_6(Me_2S_2)]$ (X = Cl, Br, I) [22]. These complexes are stable both in air and in solution. The structural assignments for these complexes have been based on ^{1}H-NMR solution studies. The suggested structures consist in two fac-trimethylplatinum(IV) cations bridged by two halide ions and one disulphide molecule. The structure of the isostructural complex $[\{Pt(Me)_3\}_2Br_2(Me_2Se_2)]$ has been confirmed by X-ray crystallography [23].

(e) Cobalt(0) complexes

A crystalline, diamagnetic, soluble in organic solvents, and very air-stable complex has been obtained by the reaction of $(C_6F_5)_2S_2$ on $Co_2(CO)_8$ (1:1) in hexane under N_2 [16]. This complex, characterized by IR and MS, has been formulated as $[Co_2(CO)_6\{(C_6F_5)_2S_2\}]$. In most other cases, the usual reactivity path is that corresponding to the oxidative addition of the transition metal across the S–S bond [1,2].

In the structure suggested, both sulphur atoms of the disulphide ligand are bound to each of two metal atoms of the Co–Co centres, giving a tetrahedral geometry. Such a coordination mode can be described as doubly bridged or double side-on coordination (see Sect. A.(iii), structure D). In this manner, each cobalt atom has formally 18 electrons and each sulphur atom functions as a two-electron donor ("two-unpaired-electron donor") having formally 10 electrons in their valence shell (sp^3d hybridation). Unfortunately, the structure of this complex has not yet been confirmed by X-ray diffraction analysis.

A complex with similar properties containing $(C_6Cl_5)S_2$ as the disulphide ligand was also formulated as $[Co_2(CO)_6\{(C_6Cl_5)_2S_2\}]$, but this complex is much less stable [16].

(f) Iron(I) complexes

Several stable organoiron-disulphide complexes have been reported and characterized by IR, and ^{13}C- and ^{1}H-NMR spectroscopy. Three procedures have been used for the synthesis of the following complexes.

Substitution of the THF ligand in $[CpFe(CO)_2(THF)]BF_4$ by RSSR. When $[CpFe(CO)_2(THF)]BF_4$ and RSSR (R = Me, *n*-Bu, *t*-Bu, Ph) are allowed to react in equimolar amounts in CH_2Cl_2 under mild conditions (25°C), a product of the stoichiometry $[CpFe(CO)_2(R_2S_2)]BF_4$ is obtained [2,24]. For these complexes, a type A coordination of the disulphide ligand has been suggested. However, if a 2:1 molar ratio is used (R = Ph), the resulting product is the binuclear complex $[\{CpFe(CO)_2\}_2(Ph_2S_2)]BF_4$, where the disulphide ligand adopts a type B coordination. The latter complex can be converted to the corresponding mononuclear species $[CpFe(CO)_2(Ph_2S_2)]BF_4$ on dissolution in MeCN.

Oxidation of the thiolate ligand in $[(C_5R_5)Fe(CO)_2(SPh)]$ species (R = H, Me). $[\{CpFe(CO)_2\}_2(Ph_2S_2)](PF_6)_2$ and $[\{Cp^*Fe(CO)_2\}_2(Ph_2S_2)](PF_6)_2$ have been prepared by the reaction of $[CpFe(CO)_2(SPh)]$ and $[Cp^*Fe(CO)_2(SPh)]$ with $NOPF_6$ and $AgPF_6$ as oxidizing agents, respectively [2]. The formation of these complexes, where the Ph_2S_2 adopts a type B coordination, probably involves the loss of a non-bonding electron from the thiolate ligand followed by coupling of the resulting ligand-centred radical species.

Addition of the electrophilic RS^+ group to metal thiolate complexes. Reactions of $[Me_2SSMe]BF_4$ with metal thiolate complexes such as $[CpFe(CO)L(SPh)]$ (L = CO, PPh_3, $P(OPh)_3$, PPh_2Me, $PPh_2(OMe)$) in CH_2Cl_2 give new stable crystalline species with asymmetrical disulphide ligands: $[CpFe(CO)L(PhSSMe)]BF_4$ [25]. In these complexes, a type A coordination has been suggested.

Although ν(CO) values for $[CpFe(CO)_2(RSSMe)]BF_4$ (R = Ph, Me) are essentially the same (2065, 2028 cm^{-1} vs. 2071, 2025 cm^{-1}), the ^{1}H-NMR spectra allow one to distinguish between these two species. The protons for the uncoordinated CH_3S group are shifted downfield, from δ 2.33 in the free ligand to values between δ 2.49 and 2.55. This shift is smaller than that found when Me_2S_2 (δ 2.39) undergoes complexation in $[CpFe(CO)_2(Me_2S_2)]BF_4$ (δ 2.80, 2.98) [24].

The same type of reaction has been applied to the synthesis of $[CpW(CO)_3(Me_2S_2)]BF_4$ and the unstable analogue $[CpMo(CO)_3(Me_2S_2)]BF_4$ [25].

(g) Ruthenium(II) complexes

Pentammine(1,2-dithiane)ruthenium(II) hexafluorophosphate complex $[(NH_3)_5Ru(\overline{SSCH_2CH_2CH_2CH_2})](PF_6)_2$ can be prepared by direct substitution of a water molecule on $[(NH_3)_5Ru(OH_2)]^{2+}$ by 1,2-dithiane in petroleum ether/acetone [26]. However, with the analogous five-membered ligand, preparation by this route is not successful. By an alternative method starting with the same aquo complex and 1,4-butanedithiol, the disulphide complex can also be synthesized via oxidative cyclization of the coordinated dithiol, $[(NH_3)_5Ru(S(H)CH_2CH_2CH_2CH_2SH)]^{2+}$ [26]. This product undergoes one-electron oxidation to the Ru(III) thiol state and, on further one-electron oxidation produces the cyclic disulphide coordinated to Ru(II). The use of Ce(IV), but not Fe(III) or Ru(III)bis(nitrile) complex, leads to a cyclized product. The analogous product containing $\overline{SSCH_2CH_2CH_2}$ was synthesized using this procedure. A type A coordination is assumed in both cases.

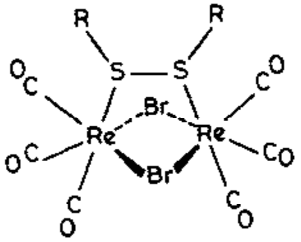
The Ru(II)–disulphide complex can be further oxidized by Ce(IV) to give $[(NH_3)_5Ru(\overline{SSCH_2CH_2CH_2CH_2})]^{3+}$ and then reduced with Zn/Mg [26].

The reversible oxidation of the Ru(II)–disulphide complex is also observed by cyclic voltammetry; E_f for the one-electron couple was measured as 630 mV vs. NHE at 25°C [26].

The visible absorption bands at 618 and 768 nm observed in the Ru(III) complexes containing six- and five-membered disulphide ligands, respectively, have been attributed to CT from the antibonding level arising from the sulphur lone-pair interaction on the disulphide group [26].

(h) Rhenium(I) complexes

Two similar dimeric Re(I) complexes containing Me_2S_2 and Ph_2S_2 as ligands have been characterized by X-ray structural methods: $[Re_2Br_2(CO)_6(Me_2S_2)]$ (**IV**) [27] and $[Re_2Br_2(CO)_6(Ph_2S_2)]$ (**V**) [28]. Similarly, complexes formulated as $[Re_2Br_2(CO)_6\{(C_6H_4\text{-}p\text{-}Me)_2S_2\}]$ [28] and $[Re_2X_2(CO)_6\{(RCH_2)_2S_2\}]$, (X = Cl, Br; R = Ph, Me_3Si) [29] have been characterized by spectroscopic methods.



IV , R = Me

V , R = Ph

The structure of **IV** consists of two Re(I) ions bridged by two bromide ions, and each is bound to three carbonyl groups in a fac arrangement with one occupying an axial position and two occupying equatorial positions. The other axial positions of the dimer are occupied by two sulphur atoms of the bridging Me_2S_2 ligand. The $(OC)_2ReBr_2Re(CO)_2$ fragment is not planar; instead, there is a folding of the molecule along the Br–Br′ vector such that the two $ReBr_2$ fragments make an angle of 28.0°. The two Re(I) ions are at a non-bonding distance of 3.790(2) Å [27].

The S–S bond length (2.111(13) Å) is much longer than that of the parent uncoordinated molecule (2.022(3) Å) [30]. Likewise, the C–S–S–C dihedral angle has increased from 83.9(9)° in the free molecule [30] to 121.2° in the dimeric complex. The average value of the Re–S bond lengths (2.485(9) Å) is similar to the mean of several Re–S bond lengths given in the literature (2.470 ± 0.052 Å) [28].

Complex **V** is isostructural with **IV**. The crystallographic results indicate that the structural parameters are very similar. For example, the Re ⋯ Re non-bonding distance is 3.782(2) Å, and the Re–S bond length is 2.487(6) Å [28], nearly identical to that found for the corresponding Me_2S_2 complex [27]. Only in the coordinated Ph_2S_2 ligand have some changes been observed. The S–S bond length and the C–S–S–C dihedral angle are 2.140(9) Å and 116.9°, respectively. For the uncoordinated Ph_2S_2, these parameters are 2.023(1) Å and 85° [20].

On the other hand, the complexes formulated as $[Re_2X_2(CO)_6\{(RCH_2)_2S_2\}]$ have been synthesized by reaction of $(PhCH_2)_2S_2$ or $(Me_3SiCH_2)_2S_2$ on a suspension of $[Re_2X_2(CO)_6(THF)_2]$ (or directly on $[Re_2(CO)_8X_2]$) in toluene [29]. These complexes are stable crystalline compounds. Although their structures have not been characterized by X-ray structural analysis, it is possible to assume for these complexes a similar geometry to that of the analogous complex $[Re_2(CO)_6Br_2\{(PhCH_2)_2Se_2\}]$ [29] or similar to **IV** and **V** as described above.

(ii) Aminedisulphides

Organic disulphides containing amine, pyridine, or pyrimidine groups have been studied as potential ligands. These symmetrical nitrogenated disulphides have been shown to coordinate metal ions through NN, NS, NSN and NSSN donor sets. The hard and soft acid character of each metal ion is probably a determinant factor in its coordination pattern. From this point of view, it is possible to understand why the Co(II) ion prefers to be coordinated by the two nitrogen atoms of Py_2S_2 [31] instead of one nitrogen atom and one disulphide sulphur atom, or why two Py_2S_2 molecules coordinate to the Cu(I) ion using two different donor sets, i.e. NS and NN [17].

On the other hand, the reactivity of the amine group of bis(2-aminoethyl)disulphide (cystamine), or the analogue bis(2-aminophenyl)disulphide, has allowed the synthesis of Schiff base ligands by reaction with salicylaldehyde or pyridinecarboxaldehyde. The new derivatives contain $O_2N_2S_2$ and N_4S_2 donor sets, respectively (vide infra). Other derivatives of cystamine are also possible.

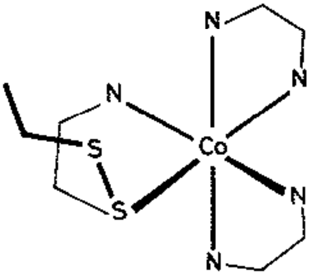
Due to the great diversity of metal complexes described in the literature, this section has been organized according to the nature of the disulphide ligands instead of the type of metal ion.

(a) 2-Aminoethyl-alkyldisulphides and related compounds

The reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with one equivalent of an oxidizing agent, Np(VI) or Co(III), in aqueous $HClO_4$ gives $[(en)_2Co\{S(SCH_2CH_2NH_2)CH_2CH_2NH_2\}]^{3+}$ [32]. This reaction has been described as induced electron transfer and has been applied in the synthesis of complexes containing symmetrical disulphides [26,32,33]. On the other hand, complexes of the general formula $[(en)_2Co\{S(SR)CH_2CH_2NH_2\}]^{3+}$, where R = Me, Et, i-Pr, *t*-Bu, Ph, have been prepared by reaction of the aminothiolate complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with *N*-(alkylthio)- or (arylthio)phthalimides in DMF [34]. The complexes containing a functionalized group ($R = C(CH_3)_2COOH$, CH_2CH_2OH, $CH_2C(O)OCH_3$) have been obtained by reaction of the aminothiolate complex with an RS^+ donor, i.e. $CH_3OC(O)SSR$ in DMF [33]. In this way, it has been possible to synthesize coordinated unsymmetrical disulphides.

As a model for the great variety of compounds formed, the structure of $[(en)_2Co(AEED)]^{3+}$ (**VI**) [34] has been determined by X-ray diffraction analysis. The structure consists of a central Co(III) ion octahedrally coordinated by four amine nitrogen atoms of two ethylenediamine ligands, and one nitrogen atom and one sulphur atom of the aminodisulphide ligand derived from the aminoethanethiolato ligand of the parent complex. The Co–S and S–S bond lengths are 2.272(3) and 2.033(3) Å, respectively, and the C–S–S–C dihedral angle is 103°.

The Raman spectrum of this complex exhibits a band at 508 cm^{-1} assigned to the S–S linkage of the coordinated disulphide. The electronic spectra of all the disulphide complexes $[(en)_2Co\{S(SR)CH_2CH_2NH_2\}]^{3+}$ exhibit a band at ca. 340 nm, which is not present in the spectrum of the parent thiolato complex and is assigned to a probable CT transition in the CoS(SR)R chromophore [34].



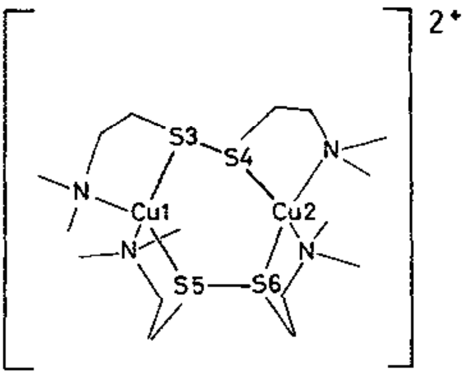
VI

(b) Cystamine or bis(2-aminoethyl)disulphide and its derivatives

Cystamine. The addition of cystamine to Ni(II) or Cu(II) chlorides or perchlorates in EtOH at room temperature using a molar ratio of 5:1 results in the precipitation of $[Ni(CYSTAM)_2]X_2$ and $[Cu(CYSTAM)_2]X_2$, $X = Cl, ClO_4$ [7]. On the basis of the IR, Raman and reflectance spectra, a distorted octahedral symmetry has been suggested for the Ni(II) complex. However, the Ni–S interaction must not significantly alter the disulphide bond since the S–S Raman stretch frequency (502 cm^{-1}) is only slightly lowered compared with that of the free ligand (511 cm^{-1}). In the case of the Cu(II) complex, the absence of any intense visible band at ca. 20.000 cm^{-1}, where a $S(\sigma) \rightarrow Cu(II)$ CT band is expected, indicates that the Cu(II)–S interaction is, at best, weak.

Bis(cystamine)nickel(II) and copper(II) complexes are unstable in the presence of water. The Ni(II) complex in aqueous solution deposits, within a few days, a crystalline compound which proved to be the *trans*-bis(β-mercaptoethylamine)-nickel(II) complex [7]. In the case of the Cu(II) complex, a partial reduction of the metal centre occurs. On the other hand, the insolubility of these disulphide complexes in organic solvents has prevented the preparation of crystals for X-ray structural determinations.

Alkyl derivatives of cystamine. The *N,N,N′,N′*-tetramethylated derivative of cystamine, DED, reacts with $[Cu(H_2O)_6](BF_4)_2$ in MeOH (molar ratio 2:1) affording a dimeric cyclic complex formulated as $[Cu_2(DED)_2](BF_4)_2$ (**VII**) [6]. An identical complex was also obtained by adding the ligand to $[Cu(CH_3CN)_4]BF_4$ suspended in MeOH (molar ratio 1:1) [6]. This complex is relatively unstable and, after several days, the crystals begin to darken and to lose mercaptan. Excessive heating of the MeOH solutions also results in ligand decomposition. The structure reported consists of a central six-membered $\overline{CuSSCuSS}$ ring in a twisted-boat conformation, where each disulphide sulphur atom per ligand coordinates a different Cu(I) ion. Moreover, four strained $\overline{CuSCCN}$ rings share an edge with the central ring, resulting in a distorted tetrahedral coordination geometry for Cu(I).



VII

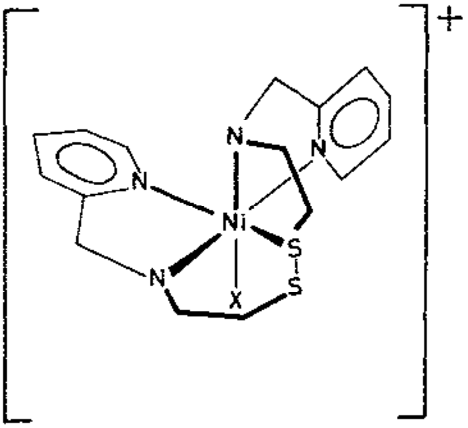
The S(3)–S(4) and S(5)–S(6) bond lengths are 2.084(9) and 2.068(8) Å, and the Cu(11)–S(3)–S(4)–C(15) and C(19)–S(5)–S(6)–C(23) dihedral angles are 105.9(13) and 106.7(13)°, respectively. These bond lengths are significantly longer, and the dihedral angles larger than the corresponding values of 2.037(1) Å and 82.4(4)° observed in the crystal structure of the uncoordinated ligand as dichlorhydrate salt [35].

The four Cu–S bond lengths Cu(1)–S(3) = 2.288(6), Cu(1)–S(5) = 2.302(7), Cu(2)–S(4) = 2.283(7), and Cu(2)–S(6) = 2.326(6) Å, are lower than the bond lengths found in the binuclear complexes **I**: 2.34(1) and 2.40(1) Å [8], and **II**: 2.333(4) and 2.338(4) Å [8].

The Raman spectrum of complex **VII** shows a strong band at 463 cm^{-1}, which represents a lowering of 43 cm^{-1} compared with those of the free ligand chlorhydrate. This observation is consistent with the lengthening of the S–S bond distances (0.047 and 0.031 Å), and with the incorporation of the S–S and C–S moieties into the strained-ring systems of the complex.

Pyridylmethyl derivative of cystamine. A pyridylmethyl derivative of cystamine, PMS, reacts with $NiBr_2$ or $NiCl_2$ in ethanol/water solution affording, in the presence of $LiClO_4$, complexes of the formula $[Ni(PMS)X]ClO_4$, X = Cl, **VIII** [36]; Br, **IX** [37]. The structures of both complexes have been reported and indicate that they are isostructural.

The PMS ligand functions as a neutral pentadentate chelating agent, coordinating to the Ni(II) ion through the two cis pyridyl nitrogen atoms, the two cis amino nitrogen atoms, and only one disulphide sulphur atom. The sixth coordination site is occupied by a halide ion. The occupancy of the three consecutive equatorial coordination sites, forming five- and six-membered chelate rings, is accomplished by the RSS– fragment of the ligand. The other fragment forms two additional five-membered rings occupying an axial and the remaining equatorial sites. The sixth coordination site is occupied by a chloride or bromide ion.



VIII (X = Cl)
IX (X = Br)

In complexes **VIII** and **IX**, the S–S bond lengths (2.039(7) and 2.040(3) Å) and the C—S—S—C dihedral angles (86 to 85°) indicate that the geometry of the disulphide group has not been altered by the coordination of the two different halide ions. The Ni–S bond lengths (2.472(5) and 2.456(2) Å) are comparable with the sum of the corresponding Pauling covalent radii [38] (2.43 Å), indicating strong interactions.

More recently, the isolation of the crystalline binuclear complex $[Cu_2(PMS)]Cl_4$ has been reported [39]. This product has been obtained by the reaction of $PMS \cdot 4HCl \cdot H_2O$ on $CuCl_2 \cdot 2H_2O$ in EtOH in a molar ratio of 1:2. Unfortunately, no structural information has been reported on this interesting compound. However, comparison of the electronic absorption and ESR spectral data for the 1:1 Cu(II)–PMS compound suggests the formation of CuN_4S species where the Cu(II) ion is coordinated in a square pyramidal geometry to a disulphide sulphur atom in an equatorial position.

Imidazolylmethyl derivative of cystamine. An imidazolylmethyl derivative of cystamine, $IMAD \cdot 3HCl \cdot H_2O$, reacts with $Cu(ClO_4)_2 \cdot 6H_2O$ in equimolar amounts in water solution to give $[Cu(IMAD)](ClO_4)_2 \cdot H_2O$ as a crystalline solid [39]. The stable compound was recrystallized from water. The visible and ESR spectra indicate that the 1:1 Cu(II)–IMAD species has a planar CuN_4 coordination structure with negligible Cu(II)–S interaction. The stability of this complex towards disulphide bond cleavage has been attributed to that peculiarity. Moreover, the absence of a S → Cu(II) CT band at ca. 330 nm supports this observation.

Schiff base derivative of cystamine. The Schiff base derivative of cystamine and salicylaldehyde, H_2SALES, reacts with $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ in MeOH (1:1) affording the neutral complex [Ni(SALES)] [40]. The spectral and magnetic properties of this sparingly soluble complex suggest a square pyramidal structure with a weak Ni—S bond. A weak band at 325 cm^{-1} has been tentatively assigned to a Ni—S stretch. The coordination of a disulphide sulphur atom is expected to shift the S—S Raman stretching band which is observed at 505 cm^{-1} in the free ligand. Unfortunately, the Raman spectrum of [Ni(SALES)] could not be recorded due to a strong absorption of the 632.8 nm laser line by the green complex.

(c) Bis(2-aminophenyl)disulphide and its derivatives

Bis(2-aminophenyl)disulphide. Bis(2-aminophenyl)disulphide, APD, reacts with $NiCl_2$ and $NiBr_2$ in hot EtOH giving the crystalline paramagnetic complexes Ni(APD)Cl_2 and Ni(APD)Br_2, respectively [41]. These complexes have been well characterized by spectroscopic methods (IR and UV-V). The principal IR stretching bands of both complexes are very similar, indicating their probable isostructural character. The band at 326–328 cm^{-1} has been attributed to a ν(M—S) mode.

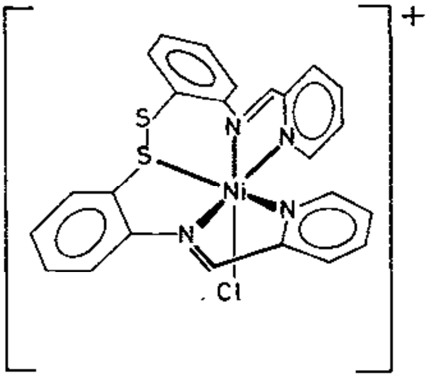
The structure suggested involves coordination through two amine nitrogen atoms and one disulphide sulphur atom. The Ni(II) ion probably achieves six-coordination via a polymeric structure involving halide bridges.

Schiff base derivatives of bis(2-aminophenyl)disulphide. Condensation reactions of APD with 2-pyridinecarboxaldehyde and salicylaldehyde give the two Schiff bases DTPP and H_2SALPS, respectively (vide infra). DTPP and H_2SALPS Schiff bases are polydentate ligands containing N_4S_2 and $O_2N_2S_2$ donor sets. However, only one of the two sulphur atoms is able to coordinate metal ions. In this manner, these Schiff bases are able to function as pentadentate ligands, with DTPP as a neutral chelating agent, and H_2SALPS as a dianionic chelating agent.

DTPP-complexes. DTPP reacts with nickel(II) and manganese(II) in alcohol to give the complexes [M(DTPP)X]X · $n$$H_2O$ (M = Mn,Ni; X = Cl,Br), [Ni(DTPP)Cl]-ClO_4, [Ni(DTPP)X]BF_4 (X = Cl, Br), and [Mn(DTPP)I]ClO_4. The complex [Ni(DTPP)Br]Br · H_2O was obtained by reaction of Ni(APD)Cl_2 on 2-pyridinecarboxaldehyde [41]. These complexes have been characterized by elementary analysis, spectral methods (IR and visible–near infrared), magnetic moments and conductivity measurements. An IR band at about 320 cm^{-1} in the spectra of these complexes has been assigned to a ν(M—S) vibrational mode.

The evidence indicates that the DTPP ligand functions as a pentadentate chelating agent in these complexes and that one of the sulphur atoms of the disulphide group is coordinated. The sixth coordination site is occupied by the halide ion.

The structure of [Ni(DTPP)Cl]ClO_4, X, has been characterized by X-ray diffraction analysis [42]. In this structure, the Ni(II) ion resides in a six-coordinate environment consisting of two cis pyridyl nitrogen atoms, two cis imine nitrogen atoms, one disulphide sulphur atom, and a chloride ion. One half of the organic disulphide, RS—, occupies three consecutive equatorial octahedral sites, forming two five-membered chelate rings. The other fragment forms six- and five-membered chelate rings with one sulphur atom uncoordinated.



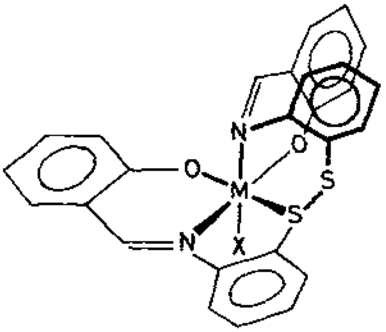
X

On the other hand, the S—S and C—S bond length values (2.089(8) and 1.76(2) Å, respectively) and the C—S—S—C dihedral angle value of 55.4(10)° are a consequence of a significant alteration due to intraligand electronic factors and to the stereochemical requirements of the coordination environment about the Ni(II) ion [42]. The C—S—S—C dihedral angle is appreciably smaller than 90° where long pair–lone pair repulsions between the sulphur atoms would be minimized and a favourable π overlap would be maximized. Nevertheless, this small angle, apparently required of the ligand upon coordination, would be expected to lead to a 0.04 Å increase, or somewhat less in the S—S bond length [43]. Nevertheless, the Ni—S bond length of 2.470(5) Å is considered as a normal strong bond, in excellent agreement with similar complexes.

SALPS complexes. The structure of three monomeric complexes having the general formula [M(SALPS)X], where M = Fe(III) (**XI**) [44], M = Mn(II) (**XII**) [45] and M = Ni(II) (**XIII**) [40], have been reported in the literature.

In these structures, SALPS coordinates to the metal ions through the two cis phenolate oxygen atoms, the two cis imine nitrogen atoms, and only one disulphide sulphur atom. In **XI**, the sixth coordination site is occupied by a chloride ion, whereas in **XII** and **XIII**, this site is occupied by a MeOH molecule. In addition, the last two complexes contain a molecule of MeOH and are isostructural compounds.

As in the DTPP complex, one half of the SALPS ligand, the RS— fragment, occupies three consecutive equatorial coordination sites forming six- and five-membered chelate rings. The other fragment of the disulphide ligand forms two additional six-membered rings occupying an axial site and the remaining equatorial site. It is possible to describe the coordination configuration or "wrap" of SALPS and DTPP ligands as a successive "equatorial" and "facial" coordination. The structures of **XI**–**XIII** are nearly mirror images of that corresponding to **X**.



XI (M = Fe(III); X = Cl$^-$)

XII (M = Mn(II), X = MeOH)

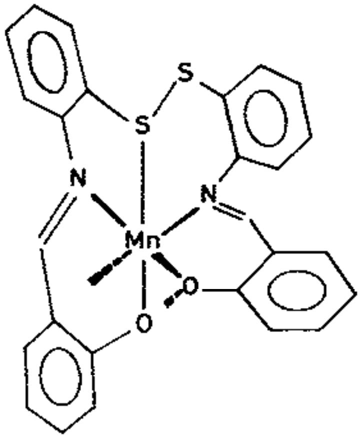
XIII (M = Ni(II), X = MeOH)

The S–S bond lengths in **XII** and **XIII** (2.065(1) and 2.066(1) Å) are slightly longer than that of **XI** (2.046(5) Å). The isostructural character of the former compounds may explain their essentially identical bond lengths.

On the other hand, the M–S bond lengths for complexes **XI**–**XIII** are 2.536(4), 2.769(1) and 2.531(1) Å, respectively. While the last two values can be considered as normal, the bond length corresponding to the Fe–S bond seems abnormally long considering the oxidation state of the iron ion. Similarly, since the Ni(II)–S and Fe(III)–S bond lengths are essentially the same, the C–S–S–C dihedral angles of **XI** and **XIII** (133.5 and 71.6°, respectively) can be attributed to the difference of 0.020 Å between the two S–S bond lengths.

A type B coordination of the S–S group is ruled out due to the long distances between M and the more distant sulphur atom: 3.79 Å (**XI**), 3.914(2) Å (**XII**) and 3.76 Å (**XIII**).

When complex **XII** is dissolved in MeCN, the coordinated MeOH is displaced giving the dimeric complex [Mn(SALPS)]$_2$, **XIV** [45]. For simplicity, **XIV** has been drawn as a hemi-molecule. In this dimer, Mn(II) ions are bridged by two phenolato oxygen atoms, giving a binuclear edge-sharing bioctahedral molecule. The dimer has been formed so as to orient both disulphide groups on the same side of the molecule. The S–S bond lengths, 2.064(3) and 2.052(2) Å, show an inappreciable shortening with respect to the monomeric complex. On the other hand, the Mn ··· Mn distance is 3.300(1) Å. In this case, the distances between Mn(II) and the more distant sulphur atom are 3.929(3) and 3.887(3) Å, indicating the absence of Mn–S bonding and confirming a type A coordination.



XIV

(d) Pyridyldisulphides

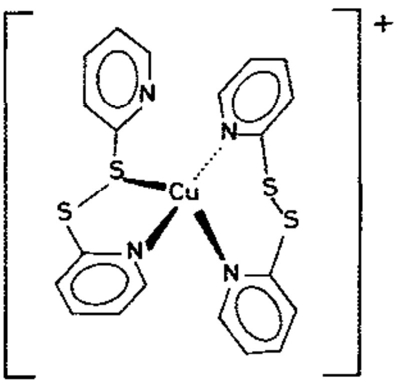
Bis(2-pyridyl)disulphide. This interesting ligand has been shown to coordinate in at least three different modes: as NN– and NS– bidentate ligands, and as an NN–bridging ligand.

The first complexes containing Py_2S_2 were obtained by reaction of this ligand on the corresponding MX_2 salt in EtOH (1:1). These complexes were formulated as $M(Py_2S_2)X_2$, where M = Ni, and X = Cl, Br, CNS; M = Co, and X = Cl, Br, I; M = Hg, Zn, and X = Cl [46]. All complexes were structurally characterized by using electronic and vibrational spectra, and magnetic measurements. The Co(II) ion forms tetrahedral complexes, while the Ni(II) ion forms tetrahedral, square planar and five-coordinate complexes, and the Zn(II) ion probably forms polymeric complexes. It was observed that the sulphur atoms are not involved in the coordination. In the case of the Hg(II) complex, a linear Cl–Hg–Cl molecule linked by Py_2S_2 through long and weak Hg ··· S bonds was suggested [46].

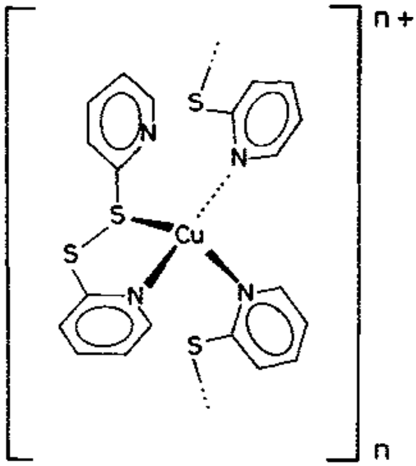
The $[Co(Py_2S_2)Cl_2]$ and $[Hg(Py_2S_2)Cl_2]$ complexes have been studied by X-ray crystallographic methods. In the first case, the tetrahedral structure, where the sulphur atoms are not coordinated, was confirmed [31], and in the second case, the absence of Hg ··· S bonding was demonstrated [47] (see Sect. D).

$[Cu(Py_2S_2)_2]ClO_4$ is the only known complex in which the Py_2S_2 ligand binds to a metal ion through a disulphide sulphur atom [17]. The crystalline complex has been prepared by a redox reaction adding copper(II) perchlorate on Py_2S_2 in MeOH (1:3).

The structure of this complex consists of two different cationic species: the mononuclear cation, $[Cu(Py_2S_2)_2]^+$, **XVa**, and the polymeric cation, $[Cu(Py_2S_2)(PyS-)_2,]_n^{n+}$, **XVb**. In each case, the Cu(I) ion is tetrahedrally coordinated. In the mononuclear species, one ligand coordinates through its two pyridyl nitrogen atoms to form a seven-membered $\overline{\text{SCNCuNCS}}$ chelated ring and the other ligand coordinates through one pyridyl nitrogen atom and the more distant sulphur atom, forming a five-membered $\overline{\text{CNCuSS}}$ chelate ring. In the polymeric cation, two pyridyl nitrogen atoms of two different bridging ligands coordinate to Cu(I) ion, and a third ligand adopts the same coordination mode through the N,S atoms forming a similar five-membered chelate ring.



XV a



XV b

In **XVa**, the S—S bond lengths and the C—S—S—C dihedral angles for NS— and NN— ligands are 2.032(4) and 2.047(5) Å, and 92.4 and 93.3°, respectively. Similarly, in **XVb** these parameters for the NS— and bridging N— ligands are 2.025(4) and 2.026(4) Å, and 91.1 and 88.7°, respectively. On the other hand, the Cu—S bond lengths in **XVa** and **XVb** are 2.396(3) and 2.439(3) Å.

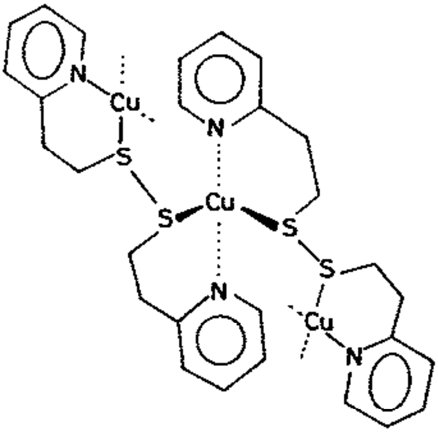
These values clearly show the non-equivalence of the ligand molecules. Moreover, the S—S and Cu—S bond lengths and the C—S—S—C dihedral angles of the five-membered $\overline{\text{CNCuSS}}$ rings in both cationic species are different. Likewise, it can be seen that the S–S bond lengths in the NS— and N— ligands in **XVb** are the same, that is they do not depend upon whether coordination to Cu(I) ion has occurred. The C—S—S—C dihedral angle in the uncoordinated ligand, Py_2S_2, is 87.10°, similar to those observed in **XVa** and **XVb**. On the other hand, the S—S bond length, 2.016(5) Å [48] is, as expected, smaller than the values observed in the coordinated ligands.

Finally, the S–S bond length in the NN— ligand of **XVa** (2.047(5) Å) is similar to that of 2.040(2) Å observed in the $[Co(Py_2S_2)Cl_2]$ complex [31] where it exists in a similar coordination mode.

The more relevant spectroscopic properties exhibited by this complex are the strong band observed at 536 cm^{-1} with a shoulder of medium intensity at 530 cm^{-1} in the Raman spectrum, and the shoulder centred at 335 nm observed in the electronic absorption spectrum. In the first case, the band, shifted by 17–22 cm^{-1} to lower energy relative to the free ligand, has been associated with the coordination of the disulphide group and its incorporation into the chelate ring. In the second case, the absorption band has been attributed either to a CT between the Cu(I) ion and the disulphide group or to a significantly red-shifted disulphide absorption [17].

Bis(2-pyridylethyl)disulphide. The reaction of hydrated $Cu(ClO_4)_2$ with the PED ligand in MeOH solution (1:3) affords a compound formulated as $[Cu(PED)]ClO_4$ [49]. In this redox reaction, the organic disulphide reduces Cu(II) to Cu(I) which forms, with an excess of disulphide, the Cu(I) complex.

The cationic complex $[Cu(PED)]_n^{n+}$, **XVI**, consists of Cu(I) ions coordinated by two RS— fragments of two different molecules. The other two RS— fragments are associated with two different Cu(I) ions, forming a cationic polymeric chain. Each Cu(I) ion is approximately tetrahedrally coordinated through two pyridyl nitrogen atoms and two disulphide sulphur atoms forming two six-membered $\overline{\text{CuSCCCN}}$ chelate rings. The ligand obviously adopts a type B coordination.



XVI

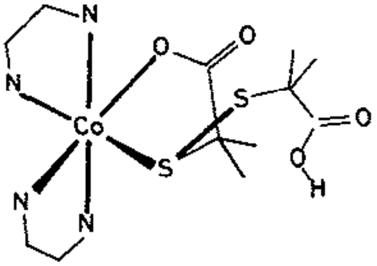
The S—S bond length and C—S—S—C dihedral angle are 2.081(1) Å and 59.73(13)°, whereas the Cu—S bond lengths are 2.318(1) and 2.325(1) Å. It is probable that the small dihedral angle is principally a consequence of the steric requirements imposed by the binucleating character of the ligand and the strain of the chelate ring systems.

The Raman spectrum shows a strong band at 484 cm^{-1}. This band, assigned to ν(S—S), is observed about 25 cm^{-1} lower than that of the uncoordinated ligand. This fact correlates qualitatively with the observed coordination of the disulphide moiety, the closing of the C–S–S–C dihedral angle and the lengthening of the S–S bond.

(iii) Alkylcarboxylate- and dicarboxylatedisulphides

The syntheses of a series of Co(II) complexes containing unsymmetrical and symmetrical alkylcarboxylate- and carboxylic carboxylate ligands have been reported [34]. Complexes characterized as $[(en)_2Co\{S(SC(CH_3)_3)XCOO\}]^{2+}$, where $X = CH_2$, $CH(CH_3)$ and $C(CH_3)_2$, have been obtained by reaction of a particular mercaptocarboxylate complex $[(en)_2Co(SXCOO)]^+$ with a $[RS]^+$ donor group, i.e. *tert*-butylsulphenyl iodide, *tert*-BuSI, in DMF [34]. Other types of complexes, $[(en)_2Co\{S(SXCOOH)YCOO\}]^{2+}$, where $X = Y = CH_2$, $CH(CH_3)$, $C(CH_3)_2$, have been prepared via induced electron transfer [34] initiated by a one-equivalent oxidation of the respective thiolate complex, $[(en)_2Co(SCH_2COO)]^+$, $[(en)_2Co\{SCH(CH_3)COO\}]^+$ and $[(en)_2Co\{SC(CH_3)_2COO\}]^+$ with $[Co(aq)]^{3+}$.

As a representative of this group of compounds, the structure of $[(en)_2Co(DMAD)]^{2+}$, **XVII** [34], has been determined by X-ray diffraction analysis. The structure is similar to **VI**. The ligand bis(2,2-dimethylacetato)disulphide coordinates to the Co(III) ion by a carboxylate oxygen atom and a sulphur atom of the disulphide ligand. The carboxylic group present in the pendant segment remains uncoordinated.



XVII

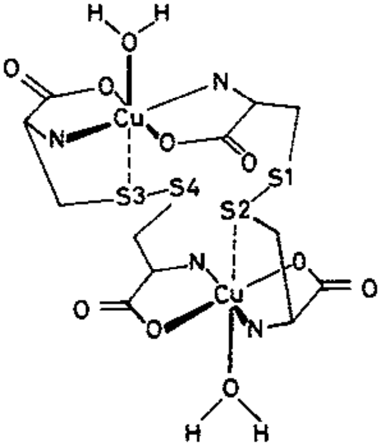
The Co–S and S–S bond lengths are 2.260(3) and 2.052(3) Å, respectively, and the C–S–S–C dihedral angle is 121.3°. While the Co–S bond length is essentially the same as that observed in **VI**, significant differences are observed in the S–S bond lengths (0.019 Å) and in the C–S–S–C dihedral angles (18.3°).

On the other hand, the electronic spectra of all complexes reported exhibit a similar band at 340 nm, similar to that reported for **VI** and its analogues, which has been attributed to the CoS(SR)R chromophore.

C. DISULPHIDE COMPLEXES WITH WEAK METAL–SULPHUR BONDING

Two Cu(II) complexes containing D-penicillamine disulphide, PDS, and glutathione disulphide, G_2S_2, a typical ligand of biological origin, and one Cd(II) complex containing an imidazolic derivative of dithiazepan, MAMI, in which the M–S bonds are weak, have been described [50–52].

$[Cu(PDS)]_2 \cdot 9H_2O$, **XVIII**, was obtained from D-PDS and $CuCl_2 \cdot 2H_2O$ (1:1) in water solution [50]. PDS is neutralized by $NaHCO_3$ in water solution and, after the elimination of the CO_2, the solution is diluted with water and i-PrOH.



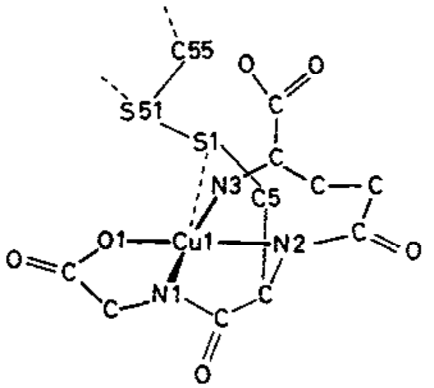
XVIII

The structure of **XVIII** ($R = 0.077$; $R_w = 0.091$) consists of dimeric units in which two crystallographically non-equivalent copper ions are bridged by two penicillamine disulphide ligands. The Cu ··· Cu distance (6.399(5) Å) indicates the independent character of both Cu(II) ions. Two nitrogen and two oxygen atoms appertaining to the terminal aminoacid moieties are bound to each copper ion in an approximately trans square-planar geometry. In each case, the fifth coordination site is occupied by a water molecule, while one disulphide unit occupies the sixth coordination site.

The Cu–S(2) and Cu–S(3) bond lengths (3.138(9) and 3.057(10) Å, respectively) suggest that the sulphur atoms are weakly bound to copper(II) ions. The disulphide units exhibit typical S–S bond lengths (S(1)–S(2) = 2.03(1) and S(3)–S(4) = 2.05(1) Å) and are located in the interior of the dimer. On the other hand, the C–S(1)–S(2)–C and C–S(3)–S(4)–C dihedral angles (103(1) and 101(1)°, respectively) are equivalent experimentally.

The S–S bond length and C–S–S–C dihedral angle of the uncoordinated PDS are 2.049(3) Å and 115°, respectively [53]. The decrease of the dihedral angle may be explained by the binucleating character of the ligands. Probably, in a monomeric complex, the dihedral angle may be smaller.

The second complex, $[Cu_2(G_2S_2)]Na_4 \cdot 6H_2O$, **XIX**, [51] was obtained from a 1:1 reduced glutathione–Cu(II) reaction mixture neutralized with carbonate under a nitrogen atmosphere. The solid was recrystallized from water–EtOH(1:3) solution.



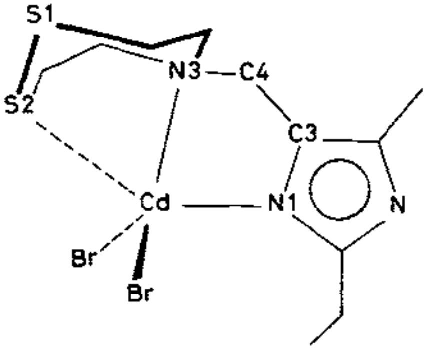
XIX

In the structure of **XIX** ($R = 0.17$), the glutathione disulphide molecule functions as a binucleating ligand coordinating two copper ions with two symmetrical peptide groups. For simplicity, **XIX**, has been drawn as a hemi-molecule. As in the last case, the long Cu ⋯ Cu distance (5.21 Å) indicates a negligible internuclear interaction. The magnetic susceptibility and ESR features of this complex also support this result [51].

Each Cu(II) ion is coordinated through two deprotonated peptide nitrogen atoms, the glutamic amine nitrogen atom and the glycinyl terminal carboxylate oxygen atom, in a near-planar geometry, whereas the cysteinyl sulphur atoms, S(1) and S(51), are bonded apically to form the respective square pyramids. The Cu(1)–S(1) and Cu(51)–S(51) bond lengths (3.16(1) and 3.28(1) Å) are similar to the sum of the square dsp^2 radius for Cu(II) ion of ca. 1.30 Å and the sulphur van der Waals radius of 1.85 Å, indicating a weak bonding interaction. The S–S bond length (2.06(1) Å) and the C–S(1)–S(51)–C dihedral angle (108.5°) are nearly comparable with those of **XVIII**.

$[Cd(MAMI)Br_2]$, **XX**, [52] is obtained by reaction of MAMI ligand on $CdBr_2$ (1:1) in MeOH–water solution. The structure of **XX** consists of a central Cd(II) ion coordinated to a pair of bromide ions, an imidazole nitrogen atom, an amine nitrogen atom, and a disulphide sulphur atom. The geometry about the cadmium centre may be described as highly distorted trigonal bipyramidal, where an imidazole nitrogen atom and a disulphide sulphur atom occupy the axial sites. The coordination of the

MAMI ligand to the Cd(II) ion generates three chelate rings: the five-membered Cd–N(1)–C(3)–C(4)–N(3) and Cd–S(2)–C(22)–C(21)–N(3) rings assume asymmetric envelope conformations; the six-membered Cd–S(2)–S(1)–C(12)–C(11)–N(3) ring displays an asymmetric boat conformation.



XX

The Cd–S bond length (2.938(2) Å) indicates, as in the case described above, a weak interaction. The folding of the dithiazepane ring so as to direct the lone pairs of the S(2) and N(3) atoms towards the Cd(II) centre (N(3)–C(4)–C(3) = 112.1° vs. N(1)–C(3)–C(4) = 119.5°) provides strong evidence for Cd–S covalent bonding. The S–S bond length is 2.042(3) Å, and the C(12)–S(1)–S(2)–C(22) dihedral angle is 76.8°.

The analogue complex [Cd(MAMI)Cl_2] has also been synthesized and characterized [52].

Finally, a series of complexes of Cu(II), Ni(II), Zn(II), Pb(II), and Co(II) with L-cystine having the formula [M(CYST)]·H_2O have been described and characterized by IR and Raman spectroscopy [54].

The Raman spectra of the Cu(II) complex synthesized at low temperature (25°C) show a ν(S–S) band at 497 cm^{-1} similar to that observed in L-cystine. The spectra for complexes with Cu(II) (prepared at 100°C), Ni(II), Zn(II), and Co(II) are similar and contain a relatively weak and broad S–S stretching band at 510–514 cm^{-1}. For the Pb(II) complex, a band at lower energy has been observed. No consideration of a possible M–S interaction was discussed.

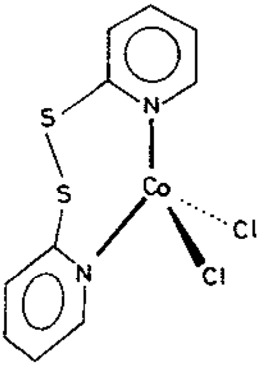
D. DISULPHIDE COMPLEXES WITH NON-METAL–SULPHUR INTERACTION

Although the aim of this article is to review the structural aspects of metal–disulphide complexes, where strong or weak bonding exists, it is also interesting to consider a few examples reported in the literature where this interaction is hindered or it has not been preferred.

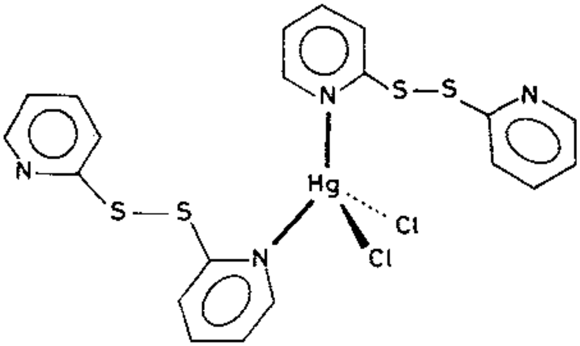
Two representative examples of unexpected complexes have been reported: the binuclear complex $(BTEA)_2[Mn(DTT)_2]$ [55] and the tetranuclear complex

$[Mo_4O_{12}(DAD)_2(DMF)_2]$ [56]. In both cases, the disulphide group was formed by oxidation of terminal thiolate groups during the synthesis and recrystallization processes, respectively. In these complexes, the disulphide groups are too distant from the metal centre to interact with it.

On the other hand, in $[Co(Py_2S_2)Cl]$ (**XXI**) [31], $[Hg(Py_2S_2)Cl_2]$ (**XXII**) [47], and $[Cu(Pm_2S_2)Cl] \cdot H_2O$ (**XXIII**) [57], complexes in which M—S bonding might be expected, the structures studied by X-ray crystallography indicate that the metal ions prefer NN-coordination through the two pyridyl nitrogen atoms instead of NS-coordination of the same ligand molecule, i.e. the Co(II) complex, **XXI**, or one pyridyl or pyrimidyl nitrogen atom from each of two different ligand molecules, i.e. the complexes **XXII** and **XXIII**. While **XXI** is monomeric, **XXII** and **XXIII** are polymeric compounds.

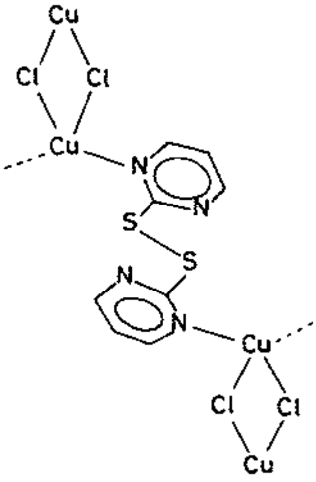


XXI



XXII

The S—S bond lengths and C—S—S—C dihedral angles are as follows: 2.040(2) Å and 102.2(3)° for **XXI**, 2.030(2) Å and 93.7° for **XXII**, and 2.113(1) Å and 180.0° for



XXIII

XXIII. This complex represents the first example where an organic disulphide exhibits the longer S—S bond length and the larger C—S—S—C dihedral angle [57].

In complex **XXI**, a ν(S—S) Raman band at 522 cm^{-1} has been observed, representing a significant shift of 25 cm^{-1} to lower energy relative to that of the uncoordinated ligand. This result correlates with the observed increase in the S—S bond length from 2.016(2) Å in the uncoordinated ligand [58] to 2.040(2) Å in the complex.

In complex **XXIII**, a ν(S—S) band of medium intensity occurs at 548 cm^{-1}, which is nearly the same (only 1 cm^{-1} higher) in energy as the corresponding band in the free ligand. This result could lead to the conclusion that the S—S bond length remains unmodified upon complexation. However, the difference observed in the S—S bond lengths is 0.014 Å. This example requires further analysis.

Raman information relative to complex **XXIII** has not been reported.

E. EMPIRICAL RELATIONS BETWEEN S—S BOND LENGTHS AND C—S—S—C DIHEDRAL ANGLES

As has been shown, the S—S bond length in an organic disulphide molecule is dependent on the value of the C—S—S—C dihedral angle, probably because of variations in the lone pair repulsions [43,59]. These repulsions are largest when the dihedral angle is 0° (largest bond length) and minimal when it is 90° (smallest bond length). A curve drawn through "average" points indicates that a C—S—S—C dihedral angle of about 90° corresponds to an S—S bond length of about 2.03 Å, whereas for an angle of about 0°, the bond length is about 2.10 Å [43].

By applying the same methodology described in ref. 43 to the complexes containing disulphide ligands with a type A coordination, a similar curve has been obtained (Fig. 1). In this case, the average points have been calculated for the groups 40–60°, 60–80°, 80–100°, 100–120°, and 120–140°. It can be seen that the slope of the curve between 0 and 90° is higher than that corresponding to 90–140°. It seems likely that the shortening of the S—S bond lengths for dihedral angles of about 90° could also be caused, as in uncoordinated organic disulphides [43], by π bonding arising from overlap of the pπ electron pair of the free sulphur atom with a 3d orbital of the coordinated sulphur atom. On the other hand, the maximum repulsion at 0° could be due to the lone pair–bonding pair(R) and bonding pair(R)–bonding pair(R) repulsions, while at 180°, only the lone pair–bonding pair(R) repulsion would apparently be acting.

Unfortunately, disulphide–metal complexes with type A coordination exhibiting dihedral angles smaller than 50° and greater than 140° have not been reported.

The curve of Fig. 1 indicates that, between 0 and 90°, the greater the dihedral angle, the shorter is the S—S bond length. By contrast, between 90 and 180°, the greater the dihedral angle, the longer is the S—S bond length.

Table 1 contains M—S, S—S, and C—S—S—C parameters of all the complexes described in this article, while Table 2 contains the S—S and C—S—S—C parameters related to uncoordinated disulphide ligands, some of which form complexes whose structures have been authenticated by X-ray diffraction studies. Comparison of both

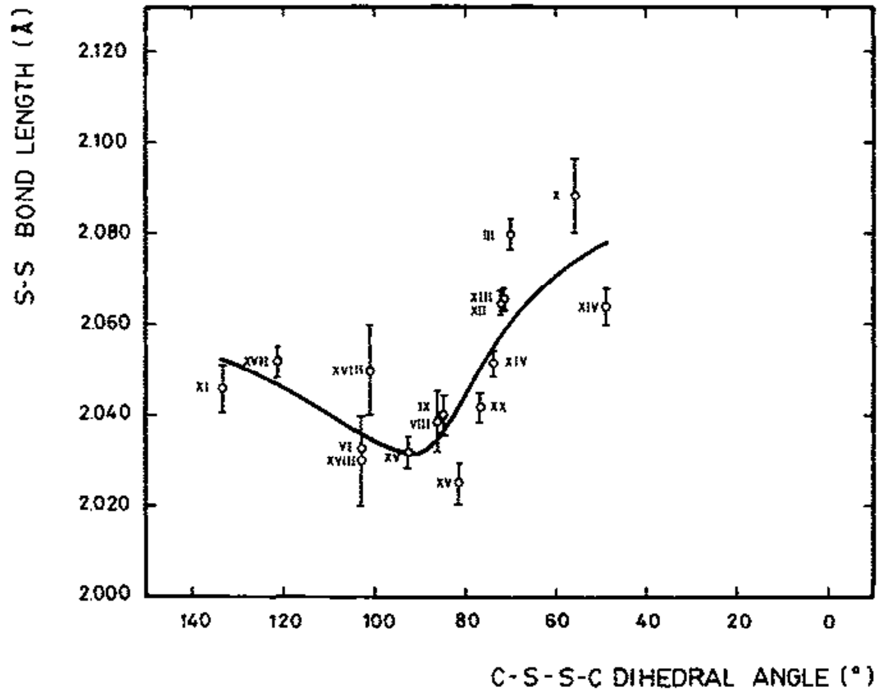


Fig. 1. Variation of the S—S bond lengths vs. C—S—S—C dihedral angles in organodisulphide complexes with type A coordination.

TABLE 1

M–S and S–S bond lengths and C–S–S–C dihedral angles in organosulphide complexes

No.	Compound	Bond length (Å)		Dihedral angle (°)	Ref.
		M–S	S–S	C–S–S–C	
I	$[Cu_2Cl_2(Et_2S_2)_2]_n$	2.34(1)	2.04(2)	97.7	8
		2.40(1)			
II	$[Cu_2I_2(Et_2S_2)]_n$	2.333(4)	2.063(5)	95.6(10)	18
		2.338(4)			
III	$[Ag_2(Ph_2S_2)_4](AsF_6)_2$	2.503(2)	2.065(2)	74[a]	19
		2.638(2)			
		2.534(2)	2.080(3)	70[a]	
IV	$[Re_2Br_2(CO)_6(Me_2S_2)]$	2.492(9)	2.111(13)	121.2	27
V	$[Re_2Br_2(CO)_6(Ph_2S_2)]$	2.487(6)	2.140(9)	116.9	28
VI	$[(en)_2Co(AED)](ClO_4)_3$	2.272(2)	2.033(3)	103.0	34
VII	$[Cu(DED)]_2(BF_4)_2$	2.288(6)	2.084(9)	105.9(13)	6
		2.302(7)			
		2.283(7)	2.068(8)	106.7(13)	
		2.326(6)			
VIII	$[Ni(PMS)Cl]ClO_4$	2.472(5)	2.039(7)	86	36
IX	$[Ni(PMS)Br]ClO_4$	2.456(2)	2.040(3)	85	37
X	$[Ni(DTPP)Cl]ClO_4$	2.470(5)	2.089(8)	55.4	42
XI	$[Fe(SALPS)Cl]$	2.536(4)	2.046(5)	133.5[a]	44
XII	$[Mn(SALPS)MeOH]MeOH$	2.769(1)	2.065(1)	71.9	45
XIII	$[Ni(SALPS)MeOH]MeOH$	2.531(1)	2.066(1)	71.6	40
XIV	$[Mn(SALPS)]_2 \cdot 2AN$	2.757(2)	2.064(3)	48.9[a]	45
		2.707(2)	2.052(2)	73.6[a]	
XVa	$[Cu(Py_2S_2)_2]ClO_4$	2.439(3)	2.025(4)	81.1[b]	17
		–	2.026(4)	88.7[b]	
XVb	$[Cu(Py_2S_2)(PyS)_2]_n(ClO_4)_n$	2.396(3)	2.032(4)	92.4[c]	
		–	2.047(5)	93.3[c]	
XVI	$[Cu(PED)]_n(ClO_4)_n$	2.318(1)	2.081(1)	59.73(13)	48
		2.325(1)			
XVII	$[(en)_2Co(DMAD)](ClO_4)_2 \cdot 2H_2O$	2.260(3)	2.052(3)	121.3	33
XVIII	$[Cu(PDS)]_2$	3.057(10)	2.03(1)	103(1)	49
		3.138(9)	2.05(1)	101(1)	
XIX	$[Cu_2(G_2S_2)]Na_4 \cdot 6H_2O$	3.16(1)	2.06(1)	108.5	50
XX	$[Cd(MAMI)Br_2]$	2.938(2)	2.042(3)	76.8	51
XXI	$[Co(Py_2S_2)Cl_2]$	–	2.040(2)	102.2	31
XXII	$[Hg(Py_2S_2)Cl_2]_n$	–	2.030(2)	93.7	47
XXIII	$[Cu(Pm_2S_2)Cl]_n \cdot (H_2O)_n$	–	2.113(1)	180.0	55

[a] Values calculated from the data reported in the reference.

[b] Monomeric unit.

[c] Polymeric unit.

TABLE 2

S–S bond lengths and C–S–S–C dihedral angles in organodisulphide ligands

Ligand	Bond length (Å)	Dihedral angle (°)	Ref.
	S–S	C–S–S–C	
Dimethyldisulphide	2.022(3)	83.9(9)	30
Diphenyldisulphide	2.023(1)	85.0[a]	20
Dipentafluorophenyldisulphide	2.059(4)	76.5	61
Dibenzyldisulphide	2.02	92	62
Bis(2-pyridyl)disulphide	2.016(2)	87.1	48
Bis(2-pyrimidyl)disulphide	2.017(2)	83.9[b]	57
	2.020(2)	85.4[b]	
Bis(2-aminophenyl)disulphide	2.060(3)	90.5	63
Bis[2-(*N*,*N*-dimethylamino)ethyl] disulphide dihydrochloride	2.037(1)	82.4(2)	35
D-Penicillamine disulphide dihydrochloride(3,3,3′,3′-tetramethyl-D-cystine)	2.049(3)	115	53
L-Cystine dihydrochloride	2.038(6)	81.7(2)	64
M-Penicillamine disulphide dihydrate (3,3,3′,3′-tetramethyl-M-cystine)	2.032(3)	119.4(4)	65
L-Cystine	2.032(4)	74(1)	66

[a] Calculated from the experimental data given in ref. 20.

[b] Two independent molecules are present in the structure.

tables indicates that, in general, coordination causes the S–S bond lengths and C–S–S–C dihedral angles of the organic disulphide ligands to become longer and larger, respectively.

A different empirical relation between S–S bond lengths and (N or C)–C–S–S dihedral angles, was reported for organic disulphides and 11 transition metal complexes [60].

Because of the limited number of disulphide–metal complexes in which the ligand adopts a type B coordination, a correlation similar to that described above has not been attempted, but it seems likely that this family of binuclear disulphide–metal complexes follows a comparable but different behaviour.

This type of correlation is of interest considering the relation between the conformation about the S–S bond and the Raman stretching frequencies [67,68].

F. FINAL COMMENTS

Through the different examples presented here, it is possible to understand some of the more pronounced aspects of the nature of the M–S(disulphide) bond. It is also possible to establish a similarity between the complexing behaviour of disulphide sulphur atoms and that of thioether sulphur atoms since both exhibit uncharged sulphur atoms. For example, the complexes having only disulphide ligands (Sect. B) involve the same metal ions that are commonly associated with thioether sulphur coordination: Cu, Ag, Pd, Ru, and Pt, as well as other metal ions in low oxidation states [9]. In view of this similarity in behaviour, it must be assumed that both Au and Hg would also form disulphide complexes, since both react with thioethers.

Although the structures of many complexes mentioned in this article have been well documented on the basis of spectroscopic data, some deserve to be studied by X-ray diffraction methods in order to increase the volume of structural information. Similarly, Raman spectroscopy is, in general, a valuable tool for determining the existence of an M—S(disulphide) bond. However, the number of articles including this type of information is, at the moment, too scarce. On this basis, it would be possible to establish better structural and spectroscopic correlations.

Finally, because of the unquestionable relevancy of the disulphide group in biological processes, it is hoped that greater activity will be generated in the field of inorganic models of specific sites pertaining to copper, iron and molybdenum proteins.

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