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REACTIONS INVOLVING METAL COMPLEXES OF SULPHUR LIGANDS

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CONTENTS

A. INTRODUCTION

The reactions of metal chelates have been studied since Werner's time; however, it is only in recent years that extensive work has been carried out in many areas of this field[1–9]. These reactions are of intrinsic interest but their investigation has been stimulated by the implications for chemical synthesis, catalysis or biology which often arise from their study. Very recently much interest has been shown in the reactions of sulphur chelates and it is within this particular area that very significant advances have been made.

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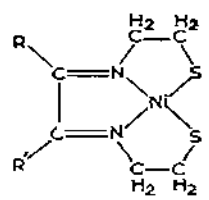
The scope of this review has been restricted to a general coverage of the main reactions involving metal complexes of sulphur ligands.

B. METAL-ION INDUCED REARRANGEMENTS AND RELATED REACTIONS

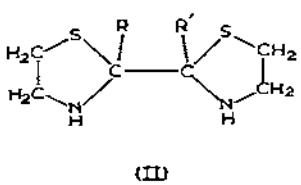
(i) The influence of metal ions on the formation of certain sulphur-containing Schiff bases.—There are several reactions in which a metal ion induces a structural change in a sulphur-containing organic molecule to yield a form more suitable for coordination.

Condensation of 2-aminoethanethiol with an aldehyde does not usually lead to isolation of the corresponding Schiff base but instead generally yields a thiazolidine. Similarly 2-aminobenzenethiol normally forms a benzothiazoline. However, in both cases the corresponding oxidized products can be sometimes isolated[10–14]. Nevertheless alcohol solutions of various α-diketones react with 2-aminoethanethiol in the presence of nickel ions to yield nickel complexes (I) of the corresponding Schiff base in good yields[15]. The planar structure of one such product (I, $R = R' = CH_3$) has been confirmed by an X-ray investigation[16]. Repetition of these experiments[15] in the absence of the nickel ions yields the bis-thiazolidinyl (II) as the main product, although small amounts of the tautomeric Schiff base



(I)

(III) are also formed. It was concluded that the metal ion acts as a template which favours formation of the Schiff base. A similar nickel complex is claimed to be formed by reaction of the nickel ion directly with a solution of (II; $R = R' = H$)[17]. Since solutions of thiazolidines are known to give positive tests for the presence of free mercapto groups[18,19], it has been suggested[17,20] that the bis-thiazolidinyl (II) may exist in solution in equilibrium with small amounts of both the Schiff base and the initial reactants. The complexation of the small amount of Schiff base



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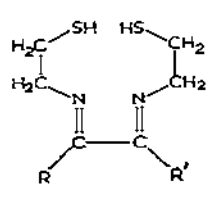
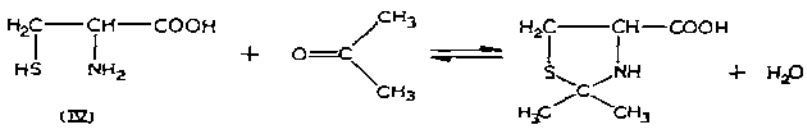


(III)

will thus eventually lead to formation of the complex in high yield (provided the latter is only slightly dissociated). Such a reaction provides an example of what has been termed the thermodynamic template effect[20].

Condensation of cysteine (IV) with acetone yields 2,2-dimethylthiazolidine-4-carhoxylic acid (V)[21,22] which has been used successfully for the treatment of Wilson's disease[23]. Associated with this disease are high copper contents in certain organs of the body such as the liver and brain. It has been assumed that (V) chelates the copper and thus facilitates its removal from the body[4]. However, by analogy with the metal-ion induced rearrangements of thiazolidines just discussed, it is possible that a similar rearrangement may occur to produce a thiolo complex when (V) reacts with copper. In cysteine–acetone–water solutions an equilibrium of the type shown in Scheme I is known to occur[21] and in the treatment of Wilson's disease, complexation of the copper directly with cysteine would also appear to be

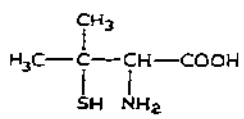


(IV) (V)

SCHEME 1

likely. In this regard it is perhaps significant that the closely related amino-acid pencillamine (VI) is also commonly used for the treatment of Wilson's disease[4].

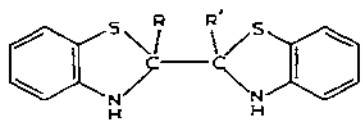
Condensation of 2-aminobenzenethiol with an α-diketone results in isolation of what is probably the bis-benzothiazolinyl compound (VII)[17,24–26], although



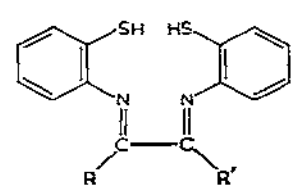
(VI)

the absolute structure of this condensation product has not yet been determined[26]. In solution this condensation product undoubtedly exists in equilibrium with small amounts of the tautomeric Schiff base (VIII)[17,24–26].

Tbe formation of tbe Schiff base (VIII) in solution is known to be influenced firstly by the *p*H and secondly by the presence of certain metal ions. Basic conditions favour the formation to the coloured dianionic form of (VIII). Highly col-



(VII)



(VIII)

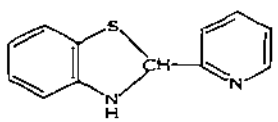
oured crystalline metal complexes of this dianion with mercury, silver, gold, zinc, cadmium, and nickel have been reported[17,24–28].

The inherent specificity of this rearrangement reaction towards certain metal ions and its dependence on *pH* provide a versatile set of conditions for effecting the selective separation of metal-ion mixtures from solution. Some investigations of this type have been undertaken in order to effect the extraction of metals from sea water[28].

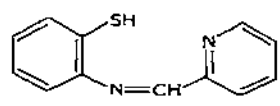
The rates of formation, in dimethylformamide, of the zinc(II) and cadmium (II) complexes have been studied spectrophotometrically[17,24]. The rate determining step in the formation of the zinc complex is probably the conversion of (VII; R = R′ = H) to the Schiff base tautomer (VIII; R = R′ = H), whereas with cadmium the reaction has been postulated to proceed via a direct attack on the bis-henzothiazolinyl by the metal ion; tbe course of the reaction is thus metal-ion dependent.

The analogous metal-ion induced rearrangements of similar bis-benzoxazolines have also been studied[28].

Condensation of 2-aminobenzenethiol with pyridine-2-aldehyde yields 2-(2-pyridyl) benzothiazoline (IX) which is readily converted to the tautomeric Schiff base, *N*-2-mercaptophenyl-2′-pyridylmethyleneimine (X) by alkali or certain metal ions[29].



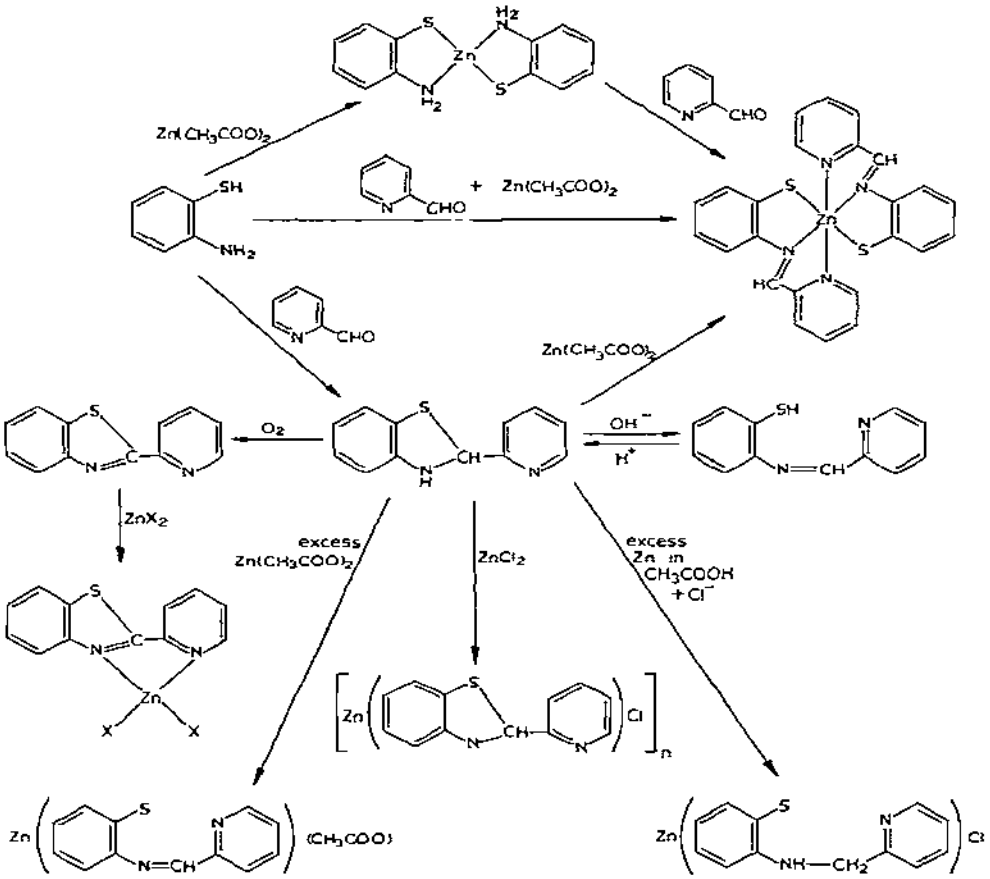
(IX)



(X)

Two moles of (IX) react with one mole of zinc acetate to yield a reddisb-black, bis-ligand complex of (X). This complex can also be obtained from the reaction of bis(2-aminobenzenethiolo)zinc(II) with pyridine-2-aldehyde. Reaction of zinc chloride with (IX) yields a mono-ligand complex; its yellow colour suggests that the deprotonated form of the non-rearranged ligand (IX) may be acting as a bidentate[29]. Nevertheless, confirmation of the true nature of this compound must await the results of an X-ray structure determination. These and other related reactions of zinc chelates are summarized[29,30] in Scheme II.

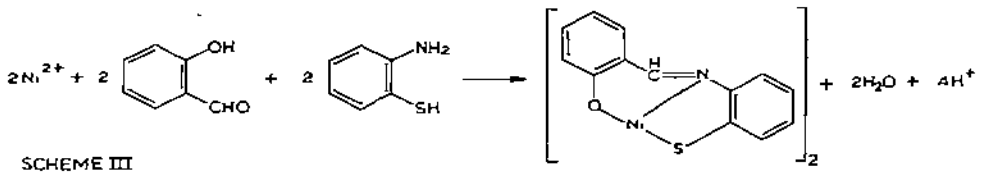
Cadmium acetate[29], nickel acetate[31] and copper(II) chloride[30] also induce rearrangement of (IX) to yield coloured complexes. The intense colours of these complexes are undoubtedly associated with the high degree of conjugation and electron delocalization in the coordinated Schiff base (X). In addition, each of these complexes incorporates the α-diimine grouping in its structure and many other complexes which contain this linkage are also intensely coloured[32]. The ease with which *S*-methylation of the bis-ligand nickel complex of (X) occurs[31] to yield the corresponding known[33] thioether complex indicates that the sulpbur donors in this complex are not bridging (*cf.* C(i)).



SCHEME II

The interaction of 2-(6-methyl-2-pyridyl)benzothiazoline with these metal ions has also been studied and in some instances similar rearrangement reactions have been observed[34]. Although it has definitely been established that these rearrangements of thiazolidines and benzothiazolines to their Schiff base tautomers are both metal ion and pH dependent, it is also apparent that they are influenced by other factors such as the solvent used and the relative solubilities of the various species formed in solution.

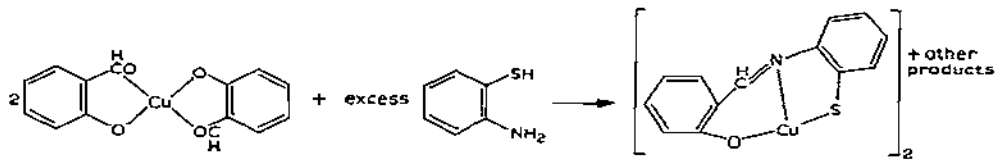
It has already been noted that in certain cases it is possible to obtain these compounds by the condensation *in situ* of their components and a further reaction of this type is shown[35] in Scheme III. In this reaction the orienting influence of the metal ion may facilitate the condensation reaction (kinetic template effect[20]); however, kinetic studies have revealed that in several other related reactions the kinetic template mechanism does not operate and the rate of condensation is found to be independent of the metal-ion concentration in these cases[36]. The product(XI) of this reaction is presumably a sulphur-bridged dimer.



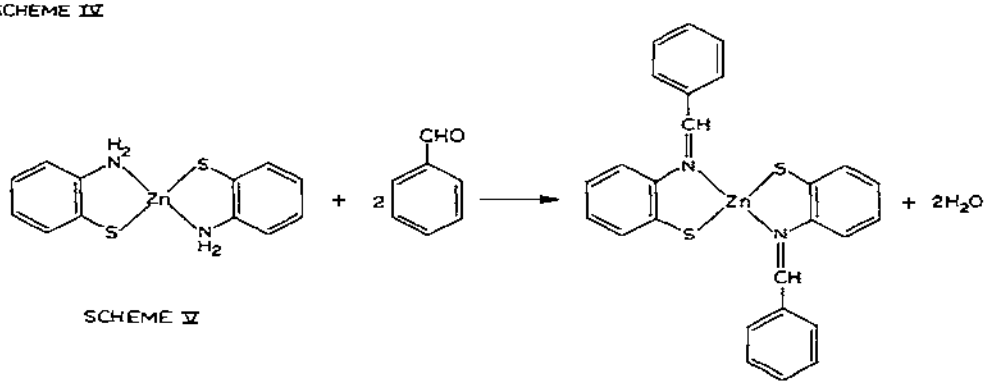
SCHEME III

(XI)

There are two modifications of this general method and both involve prior coordination of one of the components (*i.e.* aldehyde or amine) of the Schiff base before the condensation occurs. One example of each is given by Scheme IV[37] and Scheme V[38].

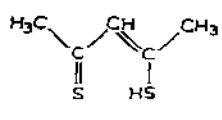


SCHEME IV

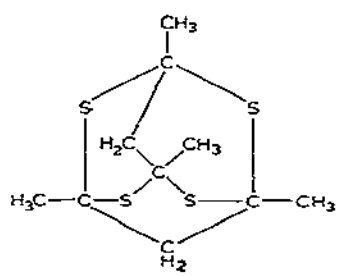


SCHEME V

It is pointed out that owing to the masking of the nucleophilicity of the coordinated[20] amine, reactions of the type illustrated by Scheme V are often difficult and in fact there is little evidence that amine ligands will undergo Schiff base condensation whilst coordinated[20]. Hence in many cases the reaction may depend upon the prior displacement of the ligand (or amine group) before condensation occurs[29,31].



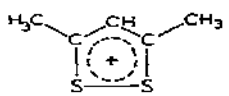
(XII)



(XIII)

(*ii*) *The role of the metal ion in the formation of complexes of dithioacetylacetone.* — By treatment of many β-diketones in ethanol with hydrogen sulphide and hydrogen chloride it has been possible to isolate the corresponding monothio-β-diketones[39–42]. Attempts to obtain dithioacetylacetone (XII) by a modification of this method have been unsuccessful and have resulted instead in the formation of a dimer of structure (XIII)[43,44]. However, if the reaction is carried out in the presence of certain metal ions, then complexes of dithioacetylacetone can be isolated from the reaction mixture. Complexes of (XII) with cobalt (II), nickel (II), palladium (II), and platinum (II) have been prepared in this manner[44] and thus in each case the stabilization, by complex formation, of a normally unattainable organic product (XII) has occured. The square-planar structure of the cobalt (II) complex has been confirmed by X-ray analysis[45] and the infrared spectrum of the nickel complex has been investigated[46]. All attempts to convert the dimer (XIII) to dithioacetylacetone by reaction with metal ions have been unsuccessful.

Similar procedures using iron(II), manganese(II) or mercury(II) have resulted in isolation of metal complexes in which the dithiolium ion (XIV) appears to be



(XIV)

acting as a ligand[47]. In each of these reactions the presence of the metal ion effectively prevents the formation of the normal organic product (XIII) and yields instead metal chelates of new organic ligands. In contrast, the metal-ion induced rearrangements dicussed in B(i) involve, *inter alia*, the perturbation of an existing equilibrium with the concomitant conversion of the main product of the organic reaction to a form more suitable for coordination.

C. REACTIONS WHICH DIRECTLY INVOLVE THE SITE OF COORDINATION OF THE SULPHUR ATOM

(*i*) *S-Alkylation and S-dealkylation reactions.* — The *S*-alkylation of coordinated thiolo groups has been observed to occur when certain metal complexes of thiols are treated with alkyl halides. Typical of this type of reaction is the alkylation of the methane- or ethane-thiol complexes of platinum[48] as shown in (1)

$$Pt(SR)_2 + 2RI \rightarrow Pt(SR_2)_2I_2 \quad (1)$$

$$R = CH_3, C_2H_5$$

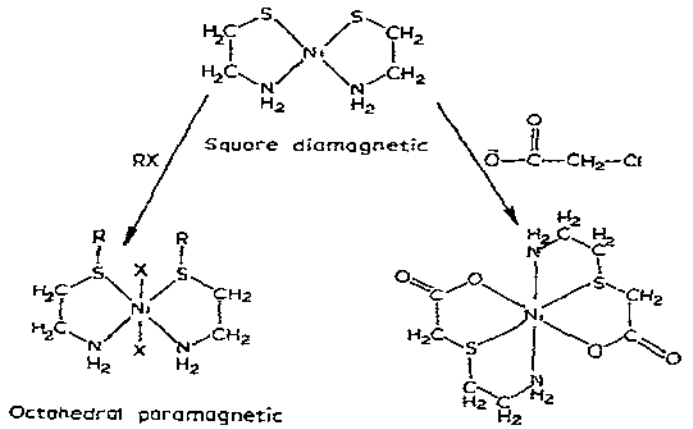
Similar alkylation reactions of the thiolo complexes of mercury(II) and copper(II) have been reported[49–54]; however, in some cases the resultant (uncoordinated) thioether ligands were isolated directly and not in the form of their metal complexes.

Equation (2) illustrates one such reaction in which the weaker bonding ability of the thioether sulphur donor compared to its thiolo precursor leads to ligand displacement after *S*-alkylation[54].

$$C_6H_5HgSC_6H_5 + C_6H_5CH_2Cl \rightarrow C_6H_5HgCl + C_6H_5SCH_2C_6H_5 \ldots . \quad (2)$$

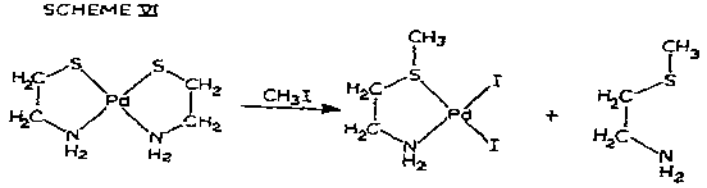
Ewens and Gibson[55] investigated the reactivity of the coordinated sulphur atom in (2-aminoethanethiolo)diethylgold(III) and showed that it undergoes reactions which are typical of thiols. The isolation of a crystalline sulphilimine derivative of this compound was found to be possible. Reaction with ethyl bromide in alcohol resulted in *S*-alkylation and the corresponding thioether complex was isolated as its picrate salt.

In the course of a detailed study of this type of reaction, Busch and his coworkers[56–58] have investigated the *S*-alkylation of the nickel(II) and palladium(II) complexes of 2-aminoethanethiol. In Schemes VI and VII some typical reactions are shown.



R = CH_3; X = I
R = $CH_2C_6H_5$; X = Cl, Br, or I.

SCHEME VI

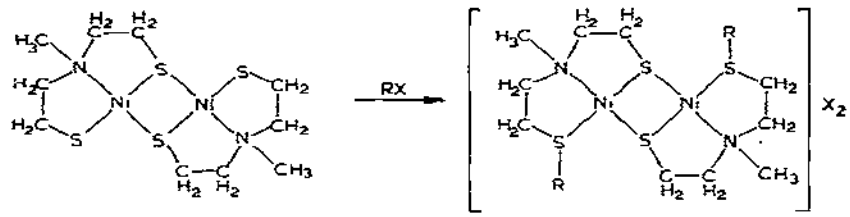


SCHEME VII

In both reactions illustrated in Scheme VI *S*-alkylation of the square-planar, diamagnetic nickel(II) complex is accompanied by an increase in the coordination number and yields high-spin complexes. These changes emphasize the difference in ligand-field strength of thioether donors compared to thiolo donors.

It is noteworthy that *S*-alkylation occurs more readily with nickel chelates

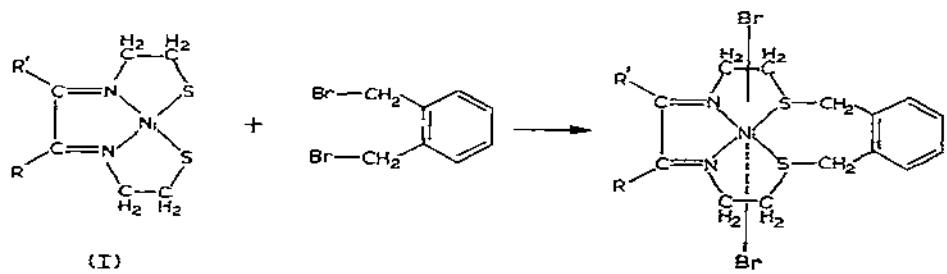
than with their palladium analogues. Furthermore it has been shown that under normal conditions *S*-alkylation will only occur at sulphur atoms which are terminal (and therefore two coordinate). This latter fact is illustrated by the behaviour of an excess of alkyl halide with bis(methyl-2,2[1]-dimercaptodiethylamine)dinickel(II) which contains both terminal and bridging (3-coordinate) sulphur atoms. In this case, *S*-alkylation occurs only at the terminal sulphur atoms[56,57] (Scheme VIII).



RX = CH_3I or $C_6H_5CH_2Br$

SCHEME VIII

Kinetic studies have indicated that the sulphur atom remains coordinated during the *S*-alkylation reaction[56] and Busch *et al.* have reacted α,α′-dibromo-*o*-xylene with nickel complexes of the quadridentate Schiff bases derived from the condensation of α-diketones with 2-aminoethanethiol[56,59,60]. In these reactions the nickel atom serves as a template for ring closure. The reaction is illustrated by Scheme IX.



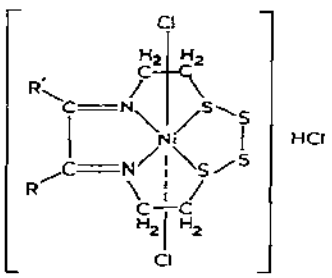
(I) (XV)

SCHEME IX

Kinetic studies[60] of the reaction of (I) with benzyl bromide and α,α′-dibromo-*o*-xylene, respectively, indicate that a sterically directed mechanism occurs in the latter case. In the former reaction, the alkylation of the sulphurs occurs consecutively and it is possible to obtain second-order rate constants for each step. The reaction of α,α′-dibromo-*o*-xylene with (I) also was shown to proceed by an initial slow step but the second condensation occurred so rapidly that it could not be followed.

The magnetic properties of (XV, R = R′ = CH_3) have been found to vary in different solvents and the factors influencing these changes have recently been

discussed[61]. Although 1,2-dibromoethane fails to act as a ring-closing agent when reacted with (I), the 1,3- or 1,4-dibromo compounds do yield macrocycles[59,62] and this is a reflection of the comparatively large distance between the sulphur atoms in (I). An X-ray structure determination of (I, R = R′ = CH_3) has confirmed that this is the case[16]. Recently in a preliminary publication it has been reported that ring closure of (I) in chloroform can be effected by sulphur monochloride to yield[63] the macrocycle (XVI). This is the first example of polysulphide bridge formation involving coordinated and uncoordinated sulphur atoms and will probably be the precursor of a whole series of similar ligand reactions.



(XVI)

The *S*-alkylation of coordinated thiolo donors implies that the sulphur atoms retain some of the nucleophilic character present in the corresponding free mercaptide ion[57]. The readiness of terminal thiolo groups to donate to a second metal ion and form *S*-bridges[64] also reflects their nucleophilic character. The formation of *S*-bridges will be discussed in C(iii).

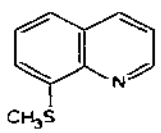
Lindoy and Livingstone[31] have effected *S*-methylation of nickel chelates of 2-aminobenzenethiol and some of its derivatives. It has been demonstrated that these *S*-methylation reactions can be used with other reactions of these metal chelates in such a manner that many interconversions are possible. The resulting system of reactions and interconversions provides a novel method of studying the coordination chemistry of the range of related nickel chelates produced. Bis(2-aminobenzenethiolo)nickel(II) readily reacts with methyl iodide to yield the corresponding thioether complex and this reaction confirms the postulate[65] that the sulphur donors in the thiolo compound are terminal. Previously a thiolobridged structure had been assigned to this compound[66].

Reaction of this compound (or its palladium analogue) with potassium amide in liquid ammonia results in deprotonation of the coordinated amines to yield the potassium salt of the corresponding anionic complex[67]. Both the nickel and the palladium anions react with water to regenerate the original complexes or with methyl iodide to form *S*- and *N*-methylated derivatives. The reaction of methyl iodide with the palladium salt is given by (3).

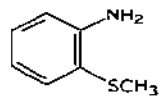
$$K_2[Pd(HNC_6H_4S)_2] + CH_3I(\text{excess}) \rightarrow Pd(H_3CHNC_6H_4SCH_3)I_2 \ldots\ldots \quad (3)$$

The cleavage of ethers by acidic reagents has long been a standard reaction in organic synthesis and the *O*-dealkylation of two copper(II) chelates of ether ligands has recently been reported[68]. The cleavage of thioethers is generally more difficult than the cleavage of ethers[69]. Nevertheless, under forcing conditions reagents such as hydrogen bromide or aluminium chloride will often effect cleavage of thioethers[70].

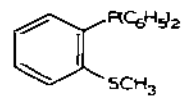
Although over eighty years ago it was reported that *S*-demethylation of dimethyl sulphide occurs in the presence of platinum(II) chloride[71], it was not until recently[72–76] that many thioether chelates of d^8 metal ions were shown to undergo *S*-dealkylation reactions to yield metal chelates of the corresponding thiols. *S*-Demethylation of the ligands (XVII)–(XX) has been observed to occur when these ligands are bound to certain (*b*) class metals, *viz*: (XVII) to palladium (II), platinum(II) or gold(III)[73,76]; (XVIII) to palladium(II) or platinum(II)[75], (XIX) to nickel(II) or palladium(II)[74]; and (XX) to palladium(II) or platinum (II)[72,76]



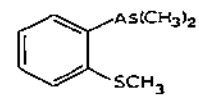
(XVII)



(XVIII)



(XIX; MeS–P)



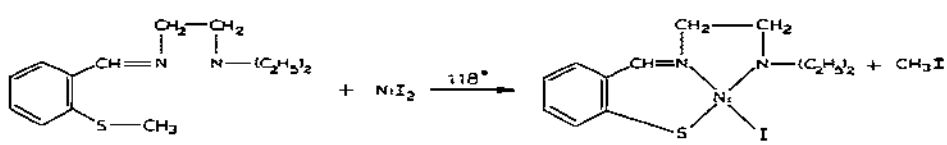
(XX; MeS–As)

The ease with which *S*-demethylation occurs is found to vary. The diamagnetic complex, $[Ni(MeS\text{-}P)_2](ClO_4)_2$, readily undergoes *S*-demethylation on being heated for a short period in an alcohol–dimethylformamide (DMF) mixture[74]. The n.m.r. spectrum of the product, $Ni(S\text{-}P)_2$, confirms the absence of methyl protons. In contrast, the *S*-demethylation of the palladium(II) and platinum(II) complexes of (XX) was only effected after they were heated in dimethylformamide at *ca.* 150° for several hours[76].

Attempts to effect *S*-dealkylation of the platinum(II) complex of thioanisole in boiling dimethylformamide or boiling n-butanol resulted in decomposition[77] and it is apparent that the ease of *S*-dealkylation of thioether chelates depends upon both the nature of other donor atoms and the central metal ion. *S*-Demethylation of $Pd(MeS\text{-}As)Br_2$ can also be effected by heating this complex in cyclohexanone at the reflux[76].

By a related procedure using boiling n-butanol, Sacconi and Speroni[78] have carried out the *S*-demethylation reaction illustrated in Scheme X.

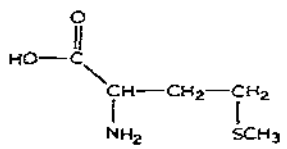
It is possible that the mechanism of the *S*-dealkylation reaction is similar to



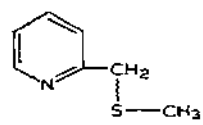
SCHEME X

that postulated for the Zeisel cleavage of an ether by hydrogen halide. However, in the dealkylation of a thioether complex, the role of the proton is undertaken instead by the metal ion. Confirmation of the exact mechanism must await the results of kinetic studies.

The *S*-demethylation *in vivo* of the amino-acid methionine (XXI) occurs via a sulphonium salt[79] and treatment with boiling 18N sulphuric acid also causes *S*-demethylation[80]. The palladium(II) and platinum(II) complexes of (XXI) have this ligand coordinated via its $-NH_2$ and $-SCH_3$ groups[81–83]. Attempts to induce *S*-demethylation of these complexes in dimethylformamide led to decomposition[77]. An attempt to effect *S*-demethylation of the palladium complex of (XXII) was also unsuccessful[77]. In contrast to the other ligands whose palladium chelates have



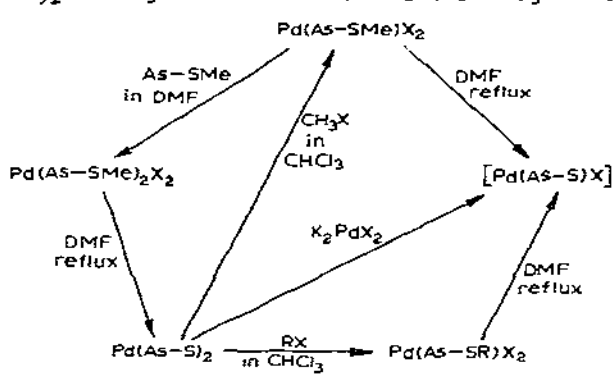
(XXI)



(XXII)

been observed to undergo *S*-demethylation, both of these ligands have the $-SCH_3$ group attached directly to an aliphatic chain and it seems that this type of thioether may be more difficult to cleave. However, the situation is complicated by the need for the metal complex to resist decomposition during the often severe reaction conditions needed to effect *S*-dealkylation.

The *S*-dealkylation reaction provides a method of preparation for metal chelates of thiols which may be difficult to prepare otherwise; for example, previous attempts to synthesise dimethyl-*o*-mercaptophenylarsine were unsuccessful[76]. Together with the *S*-alkylation reaction, the *S*-dealkylation reaction provides a method of effecting alkyl exchange of thioethers. Some of the reactions of the palladium(II) complexes of dimethyl-*o*-methylthiophenylarsine (XX, MeS-As) and its derivatives are summarised in Scheme XI. Although the sulphur atoms in $Pd(As–S)_2$ readily react with a number of alkyl halides, they failed to yield a



SCHEME XI

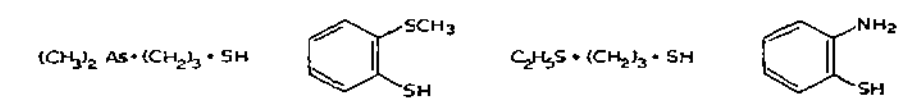
definite product with α,α′-dibromo-*o*-xylene which has been shown to condense with two such sulphur donors when they are mutually *cis*[59]. These observations suggested that in $Pd(As–S)_2$ both sulphur atoms are terminal and mutually *trans*. A recent X-ray structure determination on this compounds has confirmed that this is the case[84].

(*ii*) *Cleavage of thioesters.*—Mercury(II) ions readily cleave a number of thioesters to yield thiolo-mercury(II) complexes among other products[85–88]. Several biologically important thioesters have been cleaved in this manner. Silver(I) ions also promote similar reactions[89,90] and it has been suggested that coordination (but not necessarily chelation) of the sulphur atom to the metal ion is sufficiently strong to initiate cleavage by a mechanism involving nucleophilic attack[88].

(*iii*) *Formation of sulphur bridges.*—A feature of many coordinated thiolo-sulphur atoms is their tendency to form bridges to adjacent metal ions and such bridged structures are reflected by the well known insolubility of many thiolo complexes[64,91]. Sulphur bridges are usually very resistant to cleavage; for example, *p*-toluidine and other unidentate ligands readily split halogeno-bridged dimeric complexes of palladium(II) and platinum(II), whereas the corresponding alkylthiolo-bridged complexes are not cleaved even under more rigorous reaction conditions[92]. Nevertheless, the strength of any *S*-bridge depends on a number of variables and it has recently been demonstrated[93] that Lewis bases of the type Ph_3X(X = P, As, Sb, O_3P) will cleave the *S*-bridges in certain polymeric complexes of α-dithiols to yield the corresponding monomeric base adducts.

Most *S*-bridges form spontaneously during the preparation of the metal complexes. However, it is particularly appropriate to consider here those bridging reactions in which the initial complex (containing terminal sulphur atoms) can be isolated before *S*-bridges are induced to form.

Dimeric, thiolo-bridged complexes of palladium(II) with the ligands (XXIII) to (XXVI) have been prepared by reaction of the corresponding bis-ligand chelates in acetone with aqueous solutions of potassium tetrahalogenopalladate(II)[94].



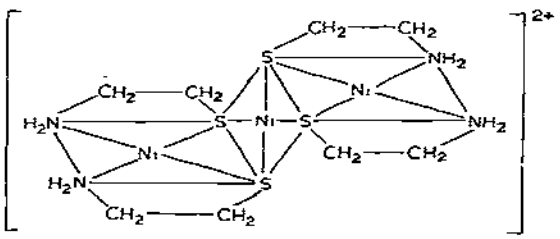
(XXIII) (XXIV) (XXV) (XXVI)

Direct reaction of the bis-ligand platinum(II) complexes of (XXIII) and (XXV) with platinous chloride at *ca.* 150° yields similar thiolo-bridged dimers[95].

Modification of the latter reaction has produced mixed-metal dimers of (XXV) containing both platinum(II) and mercury(II) and also platinum(II) and palladium(II)[95].

Busch *et al.* have made a detailed study of the complexes of 2-aminoethanethiol[96–98]. The green, bis-ligand nickel complex was assigned a square-planar arrangement of its donor atoms. It was predicted that this complex would itself act

as a chelating agent and indeed reaction with a nickel salt yielded the trimeric complex (XXVII)[96] whose structure has been confirmed by X-ray diffraction[99]. This compound can also be prepared by the direct reaction of the ligand with the nickel salt in the required stoicheiometric ratio[96].



(XXVII)

Reaction of the tetrachloropalladate(II) ion with the bis-ligand palladium(II) complex also yields an analogous trimer[96]. A range of similar mixed-metal trimers has also been prepared and equation (4) illustrates some typical reactions[97].

$$2[M'(NH_2CH_2CH_2S)_2] + M^{n+} \rightarrow \{M[M'(NH_2CH_2CH_2S)_2]_2\}^{n+} \ldots . \quad (4)$$

$M' = Ni^{II}$; $M = Pd^{II}$, Pt^{II}, Cu^{I}, Cu^{II} and Cd^{II}.

$M' = Pd^{II}$; $M = Ni^{II}$.

Tris(2-aminoethanethiolo)cobalt(III), also reacts with cobalt(III) ions to yield the trinuclear complex, $[Co(CoL_3)_2]Br_3$ in which the central cobalt ion is bound to each CoL_3 unit by three sulphur bridges[98]. This compound has been resolved into its optical isomers by ion exchange chromatography[100].

Complexes of a number of *N*-substituted 2-aminoethanethiols have been prepared[101–103]. In most cases the complexes are postulated to be square planar and *trans*[103] and the *trans* structure of the *N,N*-dimethyl derivative has been confirmed by X-ray diffraction[104]. The nickel complexes of the ligands with limited steric requirements react with nickel ions to yield trimeric complexes[103] similar to (XXVII).

Complexes of 2-(2-mercaptoethyl)pyridine with nickel(II), palladium(II), platinum(II), and cobalt(II) have been investigated and by similar procedures to those used in the preparation of the 2-aminoethanethiol complexes, compounds of the type ML_2 and $M_3L_4X_2$ were obtained[105]. However, the trinuclear complexes can only be isolated if the anion is one of low coordinating power, such as nitrate or perchlorate. In the presence of halide ions *S*-bridged neutral complexes of the type $M_2L_2X_2$ are obtained[105,106].

A study of the reaction between nickel ions and mercaptoacetate ions has shown that polymeric species, related to those just discussed, are formed in solution[107].

(*iv*) *Disulphide cleavage.*—The cleavage of organic disulphides to yield thiols is a well known organic reaction[108–110] and can be effected by almost any of the common reducing agents[111]. A recent investigation has shown that certain disul-

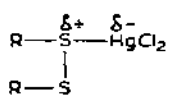
phides are slowly cleaved when reacted with hydrogen chloride and mercury in sealed tubes[112]. The reaction is as in (5).

$$R-S-S-R+Hg+2HCl \rightarrow 2RSH+HgCl_2 \ldots\ldots \quad (5)$$

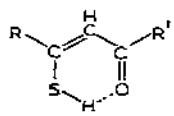
In contrast, aqueous mercuric chloride or acetate also cleave certain disulphides to yield the corresponding thiolo-mercury(II) complexes[111,113,114]. Although the stoicheiometry of the mercury complex depends upon the particular disulphide used, the reaction shown in (6) is typical.

$$R-S-S-R+HgCl_2 \rightarrow R-S-HgCl\downarrow +R-S-Cl \ldots \quad (6)$$

The free thiol can be obtained by treatment of the mercury complex with acid. It has been postulated[111] that the initial stage of the reaction is the formation of the species (XXVIII) which then undergoes fission – presumably as a result of nucleophilic attack.



(XXVIII)



(XXIX)

Oxidation of the monothio-β-diketones (XXIX; R = C_6H_5, R′ = C_6H_5 or CH_3; R = CH_3, R′ = CF_3) yields the corresponding disulphides. Reaction of each of these disulphides in alcohol with nickel acetate and aqueous sodium hydroxide results in cleavage of the S-S bond and bis-ligand chelates of the corresponding monothio-β-diketone are obtained[42,115]. Although cleavage of the disulphide could involve reduction, with alcohol as the reducing agent, it seems quite likely that a mechanism related to that postulated for the cleavage of disulphides in the presence of mercuric chloride may occur.

Di-8-quinolyl disulphide is cleaved by a number of metal ions and the specificity of the reaction has been utilized in analytical procedures for the detection of palladium and platinum[116].

Examples of the cleavage of organic disulphides during the synthesis of carbonyl(organothio)metal complexes are quite common[117–119]. Several reactions which give rise to complete (oxidative) decarboxylation of the reacting metal carbonyl are also known[120]. Typical reactions are given by (7)[121], (8)[122] and (9)[123,124].

$$[\pi\text{–}C_5H_5Fe(CO)_2]_2+(CH_3)_2S_2 \rightarrow [\pi\text{–}C_5H_5Fe(CO)SCH_3]_2 \ldots \quad (7)$$

$$\pi\text{–}C_5H_5V(CO)_4+(CH_3)_2S_2 \rightarrow [\pi\text{–}C_5H_5V(SCH_3)_2]_2 \ldots\ldots \quad (8)$$

$$Ni(CO)_4+(C_2H_5)_2S_2 \rightarrow [Ni(SC_2H_5)_2]_6 \ldots\ldots\ldots \quad (9)$$

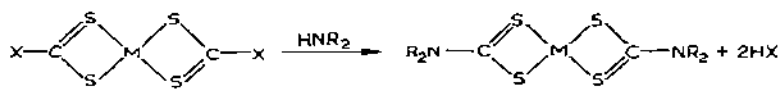
D. OTHER REACTIONS

(*i*) *Disulphide formation.*—A common organic reaction of thiols is their oxidation to disulphides[125–127]. Metal-ion catalyzed autoxidation of thiols was

first studied in 1881 when it was demonstrated that the presence of iron greatly accelerates the rate of aerial oxidation of mercaptoacetic acid[128]. This reaction has since been studied by several investigators[129–133] and similar studies of the iron-cysteine and cobalt-cysteine systems have been reported[134–136]. It is apparent that, although complex formation is invariably involved, the mechanisms of these oxidations are often complicated and also quite dependent upon the reaction conditions.

Other examples of oxidation of thiols to their disulphides in the presence of copper(II)[137], manganese(II)[136], manganese(III)[138], iron(III)[41,138], cobalt(II)[138] and molybdenum(V)[139] have been reported.

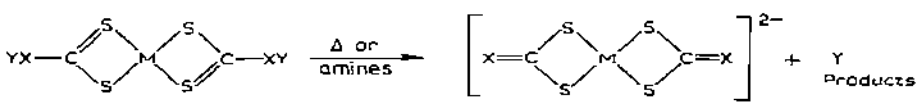
(*ii*) *Reactions involving xanthates, dithiocarbamates and related ligands.*— Fackler *et al.*[140] have recently described some nucleophilic substitution reactions of coordinated xanthates and dithiocarbamates. The general reaction is illustrated



$M = Ni^{II}$, Pd^{II}, Pt^{II}.
$X = NH_2$, NHR, $OCH_2C_6H_5$.

SCHEME XII

by Scheme XII. Evidence suggests that the reaction occurs without rupture of the metal-sulphur bonds and a direct nucleophilic attack mechanism is proposed for the reaction. These workers[140] have also reported the related reaction illustrated by Scheme XIII.

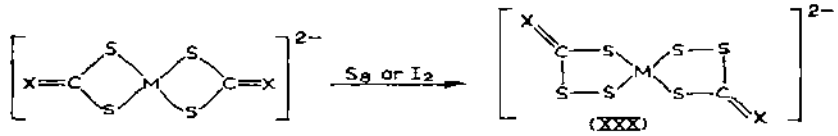


M = transition metal ions
X = O, S; Y = R.

SCHEME XIII

Coucouvanis and Fackler[141] have shown that other related 1,1-dithiolate metal complexes react with elemental sulphur or oxidizing agents to form new complexes containing one additional sulphur atom per ligand molecule (Scheme XIV).

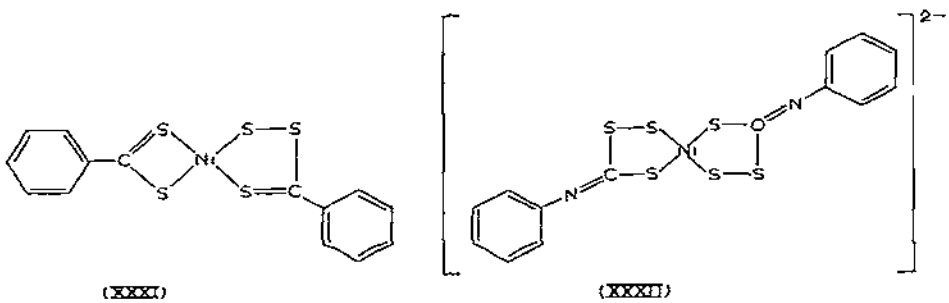
The new species (XXX) react with triphenylphosphine to yield the original 1,1-dithiolate complexes and triphenylphosphine sulphide. The abstraction of sulphur from these compounds has been investigated by means of radioactive sulphur-35 tracer studies and it has been demonstrated that the sulphur atom removed by the triphenylphosphine is the same one which was previously added.



M = Ni^{II}, Pd^{II}, Pt^{II}
X = S, NR, CR_2

SCHEME XIV

Using the above investigation as a guide, these authors were able to demonstrate[142] that the often quoted[143] compounds which result from the oxidation of nickel(II) dithiobenzoate or nickel(II) *N*-phenyldithiocarbamate are not dimeric sulphur-bridged nickel(IV) species as originally proposed[144] but rather nickel(II) compounds with structures (XXXI) and (XXXII), respectively.



(XXXI) (XXXII)

Other similar sulphur addition and abstraction reactions are known and the presence of a sulphur-rich, five-membered ring in $Fe(S_2CC_6H_5)_2(S_3CC_6H_5)$ has recently been confirmed by X-ray diffraction[145].

A number of metal complexes are known to undergo carbon disulphide insertion reactions to yield dithiocarbamate, xanthate or alkyltrithiocarbonate complexes[146]. Equation (10) illustrates a typical reaction.

$$(\pi\text{–}C_5H_5NiSR)_2 + CS_2 \rightarrow \pi\text{–}C_5H_5NiS_2CSR \ldots\ldots \quad (10)$$

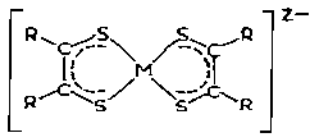
Finally it is noted that reaction of the molybdenum(V) ethylxanthate complex, $Mo_2O_3(xan)_4$, with thiols results in formation of the interesting molybdenum (IV) complex, MoS(SR)(xan)[139]. Although it appears to be polymeric, no structure has been postulated for this compound.

(*iii*) *Reactions of α-dithiolate complexes.*—One of the more recent advances in coordination chemistry has been the discovery and investigation of novel redox reactions of many metal complexes of α-dithiols and other related ligands. These reactions have been reviewed elsewhere[64,147,148] and more emphasis will be given here to those aspects which are appropriate to a general discussion of the reactions of sulphur complexes.

Several α-dithiol ligands have been shown to have the unique property of

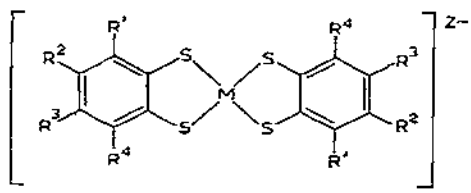
stabilizing a number of complexes of a particular metal such that any complex is formally convertable to another in the series by a redox reaction.

Many reactions involving the metal chelates of a variety of *cis*-1,2-disubstituted ethylene-1,2-dithiolate anions have been reported. These, together with the similar reactions of various substituted 1,2-dimercaptobenzene complexes, provide the most thoroughly studied reactions of this type. Accordingly both series of reactions are discussed here in reasonable detail as being representative of the overall general class of reactions. The bis-ligand complexes obtained with these two ligand types are summarised by (XXXIII) and (XXXIV).



(XXXIII)

z = 0, 1, 2
M = Fe, Co, Ni, Pd, Pt, Cu, Zn, Rh, Re, Au.
R = H, C_6H_5, CH_3, CF_3, CN

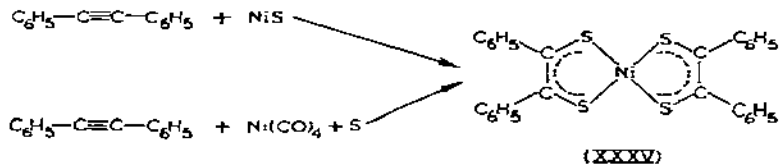


(XXXIV)

z = 0, 1, 2.
M = Fe, Co, Ni, Pt, Cu, Au, Sn.
R^1, R^2, R^3, R^4 = H, CH_3, Cl.

The first member of the series of complexes of type (I) was reported by Schrauzer and Mayweg[149]. These authors prepared the diamagnetic nickel complex (XXXV) which was obtained as nearly black crystals from the reaction at 120° of technical grade nickel sulphide with diphenylacetylene in toluene (Scheme XV). Alternatively, the complex can be prepared in low yield by refluxing nickel carbonyl (or finely divided nickel metal) with diphenylacetylene and sulphur in toluene (Scheme XV). A crystal structure determination of (XXXV) has since shown that it has a square planar stereochemistry[150].

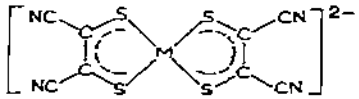
Gray *et al.*[151] reported the preparation of some bis-ligand complexes of the



(XXXV)

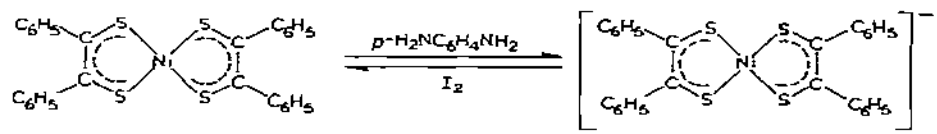
SCHEME XV

dinegative *cis*-1,2-dicyanoethylene-1,2-dithiolate anion (MNT^{2-})[152] of type (XXXVI; M = Co, Ni, Pd, Pt, Cu, Zn).



(XXXVI)

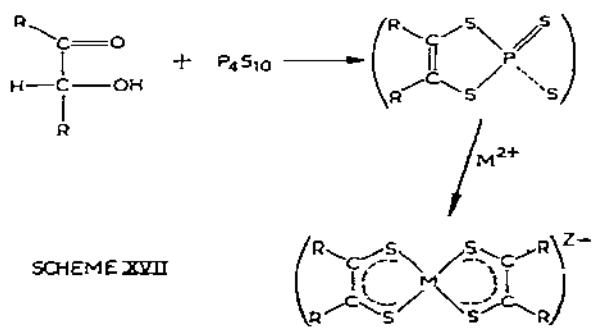
Davison *et al.*[153,154] observed that the easy isolation of the complexes (XXXV) and (XXXVI; M = Ni) suggests that reasonable stabilities may be associated with both electronic arrangements and that it might be possible to reduce complexes similar to (XXXV) to yield mono- and/or dinegative species, whereas complexes of type (XXXVI) might be capable of oxidation to yield mononegative or neutral species. Accordingly these authors used a series of electron transfer reactions to prepare a range of complexes of the type (XXXIII). Typical of these reactions is the interconversion of (XXXV), and its mononegative anion (XXXVII)[154]. Treatment of (XXXV) in dimethylsulphoxide with *p*-phenylenediamine produces the anion (XXXVII; Scheme XVI). The tetraphenylarsonium and tetraethylammonium salts of this anion can be isolated and have magnetic moments of 1.86 and 1.82 B.M., respectively. Oxidation with iodine in dichloromethane readily converts the anionic species to the neutral complex (XXXV; Scheme XVI).



(XXXV) (XXXVII)

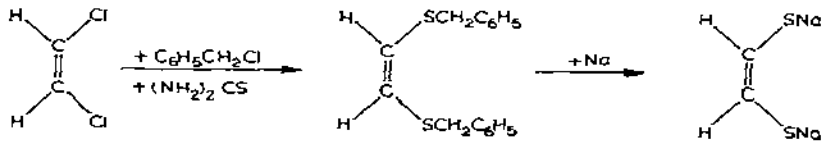
SCHEME XVI

A general method for the syntheses of complexes of type (XXXIII) (R = phenyl, substituted phenyl or alkyl) has been devised[155–158] and has considerably aided the preparation of new complexes. The method involves the treatment of the easily accessible acyloins with excess P_4S_{10}. The resulting solutions contain thioesters of the corresponding dithiols and treatment of these solutions with certain metal salts yields the required metal complexes (Scheme XVII).



SCHEME XVII

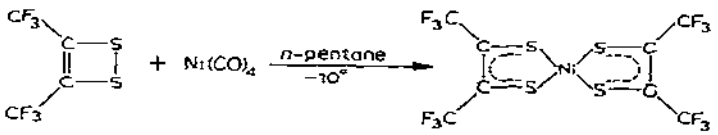
Attempts to prepare the corresponding unsubstituted complexes by the above general method have been unsuccessful[159]. However the nickel complex[159–161] has since been prepared directly from the disodium salt of cis–dimercaptoethylene which was obtained[162] by the *S*-dealkylation reaction illustrated in Scheme XVIII.



SCHEME XVIII

The method of preparation of this complex suggests that metal-ion induced *S*-dealkylation reactions of the type discussed in C(i) could well provide fruitful synthetic pathways for other dithiolate complexes which are difficult to prepare by the normal procedures.

The purplish-black, air stable complex (XXXIX) was first produced[154] from bis-(trifluoromethyl)-1,2-dithietene (XXXVIII) by the interesting reaction illustrated in Scheme XIX.



(XXXVIII) (XXXIX)

SCHEME XIX

More recently, Davison *et al.*[163] have devised a more convenient synthetic method for preparation of (XXXIX) and related complexes. These authors found that halotriphenylphosphine complexes react directly with bis-(trifluoromethyl)-1,2-dithietene in benzene or dichloromethane to yield the bis-dithiolato complexes. Complexes of cobalt, nickel, palladium, platinum, copper and gold have been prepared by this procedure.

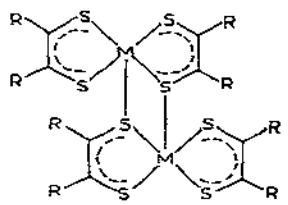
The diamagnetic nickel complex (XXXIX) readily abstracts electrons from basic solvents; for example, dissolution in acetone yields the anion (XXXIII; R = CF_3, M = Ni, z = 1) which can be isolated as its tetraethylammonium salt.

The mono-and di-charged anionic complexes of the maleonitriledithiolate anion with copper, cobalt, nickel, palladium, platinum, rhodium, rhenium and gold have been intensively studied[151,154,164–169]. X-ray structure determinations[170–172] on complexes containing the $[Ni(MNT)_2]^{2-}$, $[Co(MNT)_2]^{2-}$ and $[Cu(MNT)_2]^{-}$ ions have confirmed that all have square-planar stereochemistry and in each case the point group symmetry of the anions is very nearly D_{2h}. The anions $[M(MNT)_2]^{2-}$ (M = Rh, Pt, Cu) are isomorphous with the other square planar complexes[173,174].

The stability of $[Ni(MNT)_2]^{2-}$ towards adduct formation is exemplified by

the constancy of the electronic spectrum of this ion in a wide range of coordinating solvents and even treatment with the strong chelating ligand, 1,10-phenanthroline, does not lead to an expansion of the coordination number[148,166]. The esr spectrum of $[Cu(MNT)_2]^{2-}$ in a similar range of solvents is also virtually constant and indicates that this complex is also resistant to axial perturbations[173]. In contrast however, other complexes of types (XXXIII) and (XXXIV) are now known to be sulphur-bridged dimers. In many cases Lewis bases also react with the basic square planar structure to yield monomeric base adducts. The preparations, reactions and structures of both types of five coordinate species will now be discussed.

The species $[Ni(MNT)_2]^-$ has been shown to have a co-planar arrangement of the ligands and metal ion but in this case weak dimerisation of the type shown in (XL) occurs between neighbouring anions[175]. This complex exhibits singlet-triplet magnetic behaviour which is attributed to spin interactions between pairs of metal



(XL)

ions via the bridging sulphur atoms[176]. The analogous iron, palladium and platinum complexes behave similarly[176] and the dimeric, square-pyramidal structure of $(Fe(MNT)_2]^-$ has been confirmed by X-ray analysis[177,178]. A similar dimeric structure[163] has been postulated for $[Co(MNT)_2]^-$ and this species has been demonstrated to react with a range of Lewis bases to yield adducts[179,180].

The complexes $M[S_2C_2(CF_3)_2]_2$ (M = Fe, Co) are also dimeric[181,182] and both undergo discrete one-electron transfer reactions in dichloromethane without disruption of their dimeric structures[183]. Synthetic and polarographic studies[184] have revealed that all these iron and cobalt complexes are best considered as part of the general series: $[M-S_4]_2^0$, $[M-S_4]_2^-$, $[M-S_4]_2^{2-}$ and $[M-S_4]^{2-}$. All members of the series $[CoS_4C_4(CF_3)_4]_2^0$, $[CoS_4C_4(CF_3)_4]^2$, $[CoS_4C_4(CF_3)_4]_2^{2-}$ and $[CoS_4C_4(CF_3)_4]^{2-}$ have been isolated.

In many cases the structures of complexes of type XXXIV are similar to the corresponding complexes of type XXXIII. One exception is the cobalt anionic complex of toluene-3,4-dithiol, $[Co(tdt)_2]^-$ which is not a five coordinate dimer but rather has a monomeric square-planar structure[185]. Nevertheless the tetra-*n*-butylammonium bis(1,2,3,4-tetrachlorobenzene-5,6-dithiolato)cobaltate salt does contain the usual dimeric anion[186]. A comparison of the magnetic and structural properties of these two complexes has given information on the nature of the factors influencing dimer formation[186–189]. In the second complex the electronega-

tive chlorine substituents remove electron density from the central metal atom, particularly that associated with the $4p_z$ orbital, thus making this orbital more available for forming axial σ bonds with Lewis bases[186]. The complexes $M[S_2C_2(C_6H_5)_2]_2^z$ (M=Fe, Co; z=O, −1) are also believed to contain sulphur bridges[182,184,190]. Reaction of the neutral species with monodentate phosphine ligands yields 1:1 adducts[182] which have been shown by esr measurements to be square pyramidal[191]. Synthetic and polarographic studies[93] incidate that $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$ and $(C_6H_5O)_3P$ also cleave the dimeric complexes $[M(S_2C_2R_2)_2]_2^z$ (M=Co, Fe, R=CF_3, z=O,−1,−2; R=CN, z=−2) to yield monomeric, five-coordinate 1:1 adducts. Polarographic studies of these adducts indicate the existence of three complexes (z=+1,0,−1) for M=Co and R=CF_3 and at least two (z=0,−1) for M=Co (R=CN) and for M=Fe (R=CF_3 or CN). If $Fe[S_2C_2(C_6H_5)_2]_2$ is suspended in toluene and heated to 190–200° in a sealed tube then partial degradation occurs[182] with the formation of a new sulphur-bridged dimer of composition $Fe_2S_2[S_2C_2(C_6H_5)_2]_2$ (Scheme XX). This compound is also formed when metallic iron or iron carbonyl are heated with sulphur

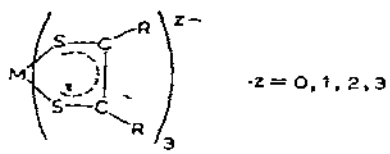
$$\{Fe[S_2C_2(C_6H_5)_2]_2\}_2 \xrightarrow[\text{toluene}]{190\text{–}200^\circ} Fe_2S_2[S_2C_2(C_6H_5)_2]_2 + \text{other products}$$

Scheme (XX)

and diphenylacetylene under similar conditions to those used in the original preparation of $Ni[S_2C_2(C_6H_5)_2]_2$.

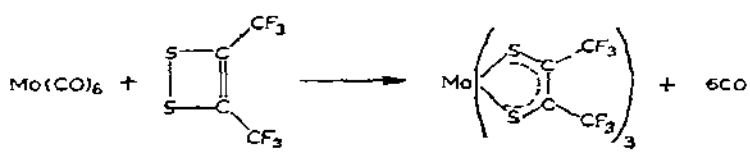
Reaction of triphenylphosphinegold chloride with bis (trifluoromethyl)−1,2-dithietene under aprotic conditions yields the novel gold complex, $\{(C_6H_5)_3PAu[S_2C_2(CF_3)_2]_2\}Cl$ which has also been postulated to be five-coordinate[163].

Tris-ligand complexes of type (XLI) are also known.



(XLI)

One of the first of such complexes to be isolated was obtained by the reaction illustrated[192] in Scheme XXI. Since this initial report a number of related complexes with a variety of metals have been prepared[156,180,193–195].



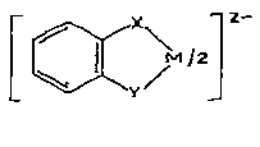
SCHEME XXI

An X-ray structural investigation[196,197] of $Re[S_2C_2(C_6H_5)_2]_3$ has shown that trigonal prismatic coordination occurs in this compound. Similar studies have revealed that related vanadium[198] and molybdenum[199] complexes also have this stereochemistry and powder diffraction evidence suggests that other tungsten, molybdenum and chromium complexes are also trigonal prismatic[198–200]. Details of the structures of these complexes are given in recent reviews[148,201].

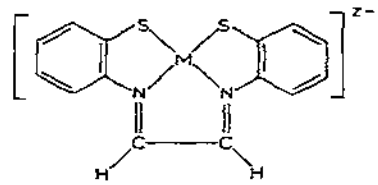
It has been postulated[148] that the constancy of the closest interligand sulphur–sulphur distance in the various analogous trigonal prismatic complexes of different metals is due to the occurrence of considerable bonding interaction between these particular sulphur atoms. This is considered to be a major factor in the stabilization of this unusual stereochemistry.

Nevertheless the structure of the $[V(MNT)_3]^{2-}$ ion is intermediate between an octahedron and a trigonal prism[202] and is in accord with the prediction[148] that the anionic species will have more tendency towards octahedral coordination than the corresponding neutral species.

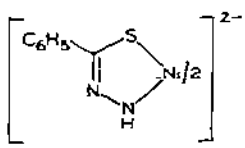
As is the case with the bis-ligand complexes, these tris-ligand complexes of the various *cis*-1,2-disubstituted ethylene-1,2-dithiolate and substituted 1,2-dimercaptobenzene ligands have been intensively studied[203]. In many cases the complexes of a particular metal with z=0, 1, 2 or 3 are interconvertible by chemical or electrochemical one-electron transfer reactions[193–195,200,203,204].



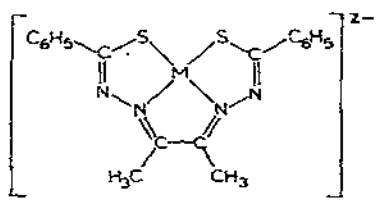
(XLII)



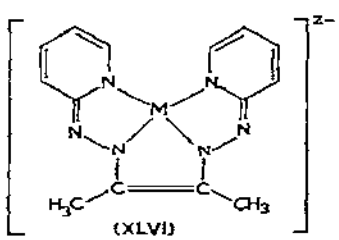
(XLIII)



(XLIV)



(XLV)



(XLVI)

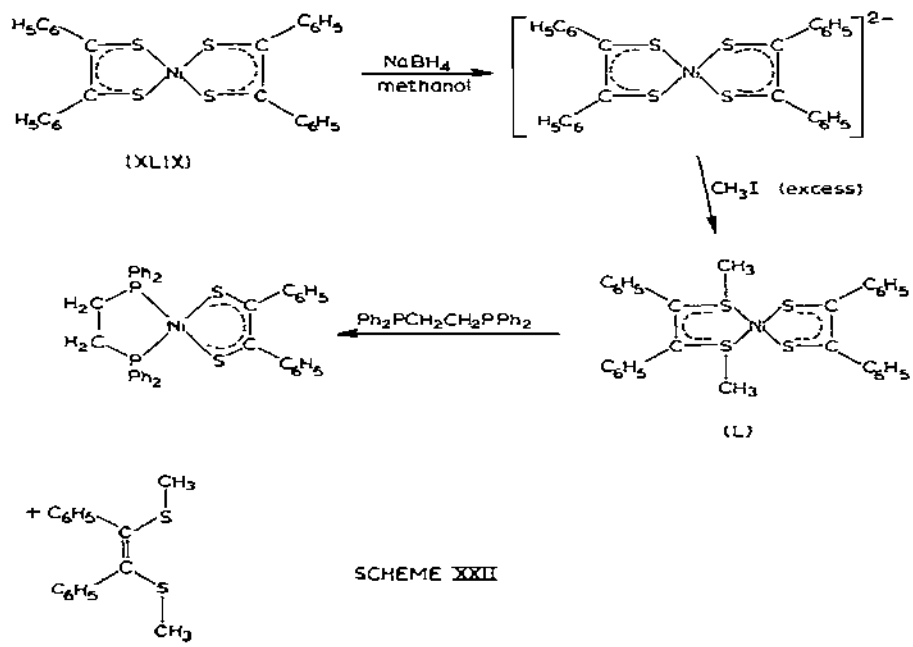
Recent work has shown that other complexes apart from those with a S_4 (orS_6) coordination sphere can also undergo electron transfer reactions. Investigations on each of the series represented by (XLII) (X=Y=O[205]; X=Y=NH[206,207]; X=O, Y=S[207]; X=NH, Y=S[207,208]), XLIII[27,208–210] XLIV[208,211], XLV[208,212], and XLVI[213] have been carried out.

There has been much controversy about the nature of the bonding and the true oxidation states of the metals in many of the complexes so far described[27,165,166,204,208–210]. The ligands in the complexes of type (XXXIII) have been postulated to be either olefin dithiolate anions (XLVII) or dithiodiketones (XLVIII). Alternatively the complexes can be considered to be intermediate between these extremes. Many of these compounds have also been described as

(XLVII) (XLVIII)

containing cation-stabilized free radicals. Although it is now widely accepted that these compounds defy description in terms of formal oxidation states of the central metals, it appears that no generally-accepted comprehensive description of their nature has yet been put forward.

Examination of the various ligand bond distances in several complexes has been carried out[201] and at least in the cases of the dianionic species, $[M(MNT)_2]^{2-}$ (M=Co, Ni), the ligands can be considered to approach true dithiolates. Using



(XLIX) (L)

SCHEME XXII

MO calculations and group theoretical considerations[214], the charge distributions in the species $[Ni(S_2C_2R_2)]_2^z$ (z=0,−1,−2) have been obtained. In the dianion, localization of negative charge on the four sulphur donors is shown to occur and the nucleophilicity of these atoms has been demonstrated chemically. Alkylating agents react with the complexes $[M(S_2C_2R_2)_2]^{2-}$ (M=Ni, Pt, Pd) to yield the dialkylated derivatives (L; Scheme XXII). The greater lability of the dialkylated ligand compared to the parent dithiolate ion is indicated by the ease with which it is replaced by strong chelating ligands such as ethylenebis-diphenylphosphine or 2,2′-dipyridyl (Scheme XXII).

It has been suggested[214] that the initial alkylation of one sulphur donor in (XLIX) is responsible for an increase in the nucleophilicity of the other sulphur in the same chelate ring and thus the second alkylation occurs at this donor.

Preliminary investigations[214] indicate that the tris-complexes, $\{M[S_2C_2(C_6H_5)_2]_3\}^{2-}$ (M=V, Mo, W), also undergo similar *S*-alkylations, but the reactions are complicated in these cases by the subsequent decomposition of the products.

A number of interesting reactions involving metal carbonyls or their derivatives and α-dithiolate ligands are known. Aspects of these reactions have been discussed in recent reviews[118,119].

Reactions of bis(trifluoromethyl)dithietene and cyclopentadienyl metal carbonyls have produced a range of complexes of the type $[C_5H_5MS_2C_2(CF_3)_2]_n$ (M=V, Cr or Mo, n=2; M=Co or Ni, n=1; M=Rh, n=1)[215,216]. A similar iridium compound (n=1) is obtained from $C_5H_5IrC_8H_{12}$ and bis(trifluoromethyl)dithietene[216]. Crystal structure determinations on the molybdenum[217] and chromium[218] complexes have shown them to be *S*-bridged dimers.

Some reactions of the dithietene with other carbonyl derivatives are illustrated by equations (11) (14)[215,216] and related reactions with carbonyl derivatives of vanadium [195] and iron[219] have also been studied.

$$[C_5H_5Cr(CO)_3]_2Hg+(CF_3)_2C_2S_2 \rightarrow [C_5H_5CrS_2C_2(CF_3)_2]_2 \quad (11)$$

$$[C_5H_5Mo(CO)_2NO]+(CF_3)_2C_2S_2 \rightarrow [C_5H_5Mo(NO)S_2C_2(CF_3)_2]_2 \quad (12)$$

$$[C_5H_5W(CO)_2NO]+(CF_3)_2C_2S_2 \rightarrow C_5H_5W[S_2C_2(CF_3)_2]_2 \quad (13)$$

$$[C_5H_5Mn(CO)NO]_2+(CF_3)_2C_2S_2 \rightarrow C_5H_5Mn(NO)S_2C_2(CF_3)_2 \quad (14)$$

Reduction of some of these π-cyclopentadienyl compounds to anions can be effected by treatment with alcoholic hydrazine[216]. In this manner the square planar species $\{M[S_2C_2(CF_3)_2]_2\}^{z-}$ (M=Fe, z=1; M=Co, z=2; M=Ni, z=2) have been prepared as well as the previously unreported species $\{C_5H_5W[S_2C_2(CF_3)_2]_2\}^-$ and $\{[(CF_3)_2C_2S_2]_2MnNO\}^{2-}$. All these anionic complexes can be isolated as their tetraethylammonium salts. Oxidation of $[CH_3SFeCOC_5H_5]_2$ with $AgSbF_6$ yields $[CH_3SFeCOC_5H_5]_2[SbF_6]$[216].

Although a large number of synthetic reactions between other α-dithiolate ligands and metal carbonyls or their derivatives are known[118,221–223], it appears

that the hexafluorobut-2-ene dithiolate complexes discussed above are the only examples in which their electron transfer properties have been investigated.

E. CONCLUDING REMARKS

In the preceding discussion an attempt has been made to indicate the wide variety of reaction types which involve sulphur chelates. Many of the reactions illustrate the observation that the reactions of metal complexes can often provide more information about the complexes involved than would be the case in the traditional type of synthetic coordination chemistry. This aspect of the reactions of metal complexes will very likely receive more attention in the future. Moreover, many of the reactions of sulphur chelates have implications in biosynthesis and this will undoubtedly be another impetus for their future study.

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