METAL COMPLEXES OF LIGANDS CONTAINING SULPHUR, SELENIUM, OR TELLURIUM AS DONOR ATOMS

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1. Introduction

By far the most studied ligands are the halide ions, cyanide ion, and ligands having oxygen or nitrogen as the donor atom. Ligands having sulphur, selenium, or tellurium as donor atoms have been less extensively studied, although in recent years there has been a considerable interest shown in sulphur-ligands. There appears to have been no recent review devoted entirely to metal complexes of ligands with sulphur, selenium, and tellurium as donor atoms but certain aspects of sulphur-containing ligands have been discussed in recent books.[1,2] This Review outlines the types of metal complexes formed by various ligands containing sulphur, selenium, and tellurium and, where possible, compares the properties of these complexes with those of complexes of analogous oxygen-containing ligands. Greater attention has been given to the more recent work, especially that dealing with structure and the nature of the bonding.

2. General Considerations

The electronegativities of atoms which can act as donors fall in the series: $F > O > N > Cl > Br > I \sim S \sim Se \sim C > Te > P > As > Sb$. However, the effective electronegativity will be influenced by the other atoms or groups attached to the donor atom. From a consideration of an electrostatic model, it can be said that, for a unidentate ligand, the co-ordinating ability will depend not only on the electronegativity but on the total dipole moment (μ) of the ligand:

$$\mu = P + p^1 = P + \alpha E \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where P = the permanent dipole moment, p^1 = the induced dipole moment, α = the polarisability, and E = the inducing electrostatic field.

Thus, although the permanent dipole moment of NH_3 is less than that of H_2O, the total dipole moment of NH_3 may be greater in the presence of a cation with a high polarising power. The larger size and smaller permanent dipole moment of H_2S ($\mu_{H_2S} \sim 1{\cdot}1$ D; μ_{H_2O}, $1{\cdot}9$ D) reduce its co-ordinating ability below that of water for ions of low field-strength. However, H_2S is more polarisable than water (molar refractivity of donor atoms: H_2O, 3·7 c.c.; H_2S, 9·5 c.c.) and with ions of high field-strength (*e.g.*, Hg^{2+},

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[1] C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, 1963, p. 131.

[2] C. M. Harris and S. E. Livingstone, "Bidentate Chelates" in "Chelating Agents and Metal Chelates," ed. F. P. Dwyer and D. P. Mellor, Academic Press, New York, 1964, p. 95.

Ag^+) H_2S co-ordinates strongly and protons are forced off to give insoluble sulphides. An analogous situation occurs with water: Fe^{3+} forms $[Fe(H_2O)_6]^{3+}$ which has a strong tendency to lose a proton:

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5\,OH]^{2+} + H^+$$

Such is the tendency for $[Pt(en)_2(H_2O)_2]^{4+}$ to lose protons to give the dihydroxo-complex $[Pt(en)_2(OH)_2]^{2+}$ that it is a strong acid.

Whereas both the permanent dipole moment and co-ordinating ability decrease in the series: $H_2O > ROH > R_2O$, the reverse order holds for sulphur, both dipole moment and co-ordinating ability increasing in the order: $H_2S < RSH < R_2S$. Moreover, although the polarisability is decreased by alkyl substitution, the decrease is much less (5%) in going from H_2S to R_2S than the decrease (24%) in going from H_2O to R_2O.[3]

If we consider the formation of a complex between a metal ion M^+ and a negatively charged ligand L^-, on an electrostatic model the bond strength ($-\Delta H$) will be given by:

$$-\Delta H = \frac{Ze \times e}{r_{M^+} + r_{L^-}} \quad \ldots\ldots\ldots\ldots \quad (2)$$

where Ze = effective nuclear charge on M, e = electronic charge, and r = ionic radius. Accordingly we should expect that for any metal ion RO^- would co-ordinate more strongly than RS^-, because of the greater size of the sulphur atom; hence $\Delta H(RO^-) > \Delta H(RS^-)$. If, on the other hand, we consider the M–L bond to be covalent, then:

$$-\Delta H = I_M - E_L + f(\chi_M \times \chi_L) \quad \ldots\ldots \quad (3)$$

where I_M = ionisation potential of M, E_L = electron affinity of L, and $f(\chi_M \times \chi_L)$ = a function of the electronegativities (χ) of M and L. Here again, since oxygen is considerably more electronegative than sulphur, we would expect $RO^- \gg RS^-$.

Now let us consider an uncharged ligand L; on an electrostatic model the induced dipole of L will be oriented towards M^+ to form a complex $M^+ \ldots\ldots \delta^-L$

$$-\Delta H = \frac{Ze \times (P + p^1)}{r_1^2} \quad \ldots\ldots\ldots\ldots \quad (4)$$

where r_1 = distance between centre of M^+ and centre of dipole. The larger value of r_1 and the smaller value of P for sulphur than for oxygen probably outweigh the effect of the larger value of p^1 and we would expect $R_2O > R_2S$. On a covalent model, if the lone pair is equally shared between M^+ and L, the complex will be represented by $M \div L^+$. The bond strength will be given by (5).

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[3] R. W. Parry and R. N. Keller, "Electrostatic Theory of Co-ordination Compounds" in "Chemistry of the Co-ordination Compounds," ed. J. C. Bailar, Reinhold, New York, 1956, p. 119.

$$-\Delta H = I_M - I_L + f^1 (\chi_M \times \chi_{L^+}) \quad \ldots\ldots \quad (5)$$

However, the system $M \div L^+$ represents the extreme of covalency: the positive charge on M will not be transferred completely to L and the terms I_L and χ_{L^+} will not be as important as indicated by (5); the true picture will be somewhat intermediate between (3) and (5). Nevertheless, for an uncharged ligand, on both the electrostatic and covalent models, we would expect $R_2O > R_2S > R_2Se > R_2Te$. However, in the covalent models we have ignored any contribution made by π-bonding.

Except in special instances[4] (*e.g.*, NO_2^-, 2,2′-bipyridyl, dimethylglyoxime), oxygen and nitrogen have no orbitals available to accept electrons from suitably placed filled *d* orbitals on the metal atom. On the other hand, sulphur and phosphorus have vacant *d* orbitals which can be used for d_π–d_π bonding such as can occur with the later transition metals in their normal oxidation states and with the early transition metals in unusually low oxidation states. The extent to which such π-bonding occurs is difficult to assess but the available evidence suggests that in favourable circumstances it does occur with ligands containing sulphur, selenium, and tellurium, but to a lesser extent than with R_3P, R_3As, CN^-, and CO. Consequently, if π-bonding can occur we might expect it to cause a reversal of the order to $RS^- > RO^-$ and $R_2S > R_2O$. The conditions for π-bonding are most favourable with the later members of the second and third transition series [*e.g.*, Pd^{II}, Pt^{II}, Hg^{II}] and with the early transition metals in low oxidation states [*e.g.*, Mo^0, W^0, Re^I].

The polarisabilities of sulphur ligands decrease in the order $S^{2-} > RS^- > R_2S$. Therefore in any consideration of the bonding properties of sulphur ligands, the distinction between sulphide ion, mercaptide ion, and thioethers should be borne in mind. Not only the polarisabilities but the number of lone pairs also decrease. Williams[5] has suggested that the principal difference between thiols and thioethers as ligands is that the former are more highly polarisable but not as effective d_π electron acceptors as the latter.

In complexes containing charged sulphur ligands such as RS^-, $(EtO)_2PS_2^-$, and $ROCS_2^-$, the sulphur atom is bicovalent and has a V-shaped configuration, whereas in complexes of R_2S it is tricovalent and trigonal pyramidal. When the thio-group acts as a bridge the sulphur atom is tricovalent and pyramidal.

Coates[6] observed that the strength of co-ordination of XMe_2 (X = O, S, Se, Te) to $AlMe_3$ is in the order O > S > Se > Te but whereas dialkyl sulphides, selenides, and tellurides co-ordinate to Pd^{II}, Pt^{II}, and Hg^{II}, ethers do not. A more extensive survey of the relative affinities of ligand atoms for metal ions was made by Ahrland, Chatt, and Davies[7]

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[4] R. S. Nyholm, *Rev. Pure and Appl. Chem.*, 1954, **4**, 15; D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 332.

[5] R. J. P. Williams, *Ann. Reports Progr. Chem.*, 1959, **56**, 87.

[6] G. E. Coates, *J.*, 1951, 2003.

[7] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

who divided metals into two classes: (*a*) those which form the most stable complexes with the first ligand atom of each group; (*b*) those which form the most stable complexes with the second or subsequent ligand atom. For class (*a*) metals $O \gg S > Se > Te$; for class (*b*) metals $S \gg O$ but almost any sequence of S, Se, and Te may occur. Class (*b*) metals form a triangular area, with a somewhat diffuse border, in the centre of the Periodic Table. Metals of pronounced (*b*) character are in the centre of this area. Co-ordination of C_2H_4, CO, and CNR occurs only with metals of pronounced (*b*) character. The oxidation state of the metal affects the degree of (*b*) character, which is strongest for transition metals in low oxidation states: *i.e.*, metals having non-bonding *d* electrons and thus capable of forming d_π–p_π and d_π–d_π bonds by donating a pair of electrons to the ligand. Using a simple model and taking into account the ionisation potential of the metal and the electrostatic energy involved when the ions M^{n+} and X^- are brought together from infinity, Craig and Nyholm[8] have given a semi-quantitative explanation of class (*a*) and (*b*) behaviour toward halide ions.

Pearson[9] has classified metal ions and ligands into "hard" and "soft" Lewis acids and bases and he has suggested a general rule that hard acids bind strongly to hard bases and soft acids to soft bases. Hard acids are those that bind to bases which bind strongly to the proton, *i.e.*, basic in the usual sense, while soft acids bind strongly to highly polarisable or unsaturated bases which often have negligible proton basicity, *e.g.*, R_2S. Yet it is possible for a base to be soft and strongly binding to the proton—such a case is the highly polarisable S^{2-} ion. Pearson's hard and soft acids correspond roughly to (*a*) and (*b*) metals, respectively.

Jørgensen[10] has pointed out that class (*b*) contains three rather disparate categories: (i) metals with unusually low oxidation numbers; (ii) metals with certain high oxidation numbers; (iii) the s^2 family Sn^{II}, Sb^{III}, Tl^{I}, Pb^{II}, Bi^{III}, showing (*b*) character to heavy halides and chalcogenides but (*a*) aversion to CN^-. Jørgensen also suggested that some metals may have (*b*) character in a low and a high oxidation state yet (*a*) character in an intermediate oxidation state.

The spectrochemical series of ligands is arranged according to the spectroscopic splitting parameter Δ, as given by the frequency of the lowest ligand-field absorption band in a transition metal complex. The series is:[11] $I^- < Br^- < SCN^- \sim Cl^- < (EtO)_2PSe_2^- \sim S^{2-} \sim (EtO)_2PS_2^- < F^- < Et_2NCS_2^- <$ urea $\sim OH^- < C_2O_4^{2-} \sim O^{2-} \sim H_2O < NCS^- <$ glycine $<$ py $\sim NH_3 <$ en $\sim SO_3^{2-} < NO_2^- \sim$ phen $\sim$ bipy $< H^- < CH_3^- < CN^- < CO$ (py = pyridine; en = ethylendiamine; bipy = 2,2′-bipyridyl;

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[8] D. P. Craig and R. S. Nyholm, "The Nature of the Metal–Ligand Bond" in "Chelating Agents and Metal Chelates," ed. F. P. Dwyer and D. P. Mellor, Academic Press, New York, 1964, p. 51.

[9] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[10] C. K. Jørgensen, *Inorg. Chem.*, 1964, 3, 1201.

[11] C. K. Jørgensen, *Ricerca sci.*, 1964, **34**, 3.

phen = 1,10-phenanthroline). The position of sulphur ligands is not clear, as relatively few complexes of sulphur ligands have been studied spectrophotometrically. However, although some sulphur ligands are near Cl^-, sulphur appears to have a wide range, as SO_3^{2-} when bound through sulphur has a late position in the series near NO_2^-. R_2S probably occurs between H_2O and NCS^-;[12] the position of RS^- has not been established. The series roughly follows the order of decreasing radii of the ligand atom, *i.e.*: $I > Br > Cl > S > F > O > N > C$. The parameter Δ is dependent on (i) electrostatic attraction; (ii) the effect of the lone pairs on the ligand; (iii) M→L d_π–p_π or d_π–d_π bonding; (iv) L→M p_π–d_π bonding; (i), (ii), and (iii) increase Δ whereas (iv) decreases it.[13]

The nephelauxetic series[14,15] is a measure of the "covalent" tendency of the ligands. The repulsions between the *d* electrons are decreased by complex formation by from 5 to 40% for 3*d* complexes.[13] β (= B'/B) is the ratio of the electronic repulsion parameters for the complex (B') and for the free gaseous ion (B). The nephelauxetic series of ligands is arranged according to increasing values of $(1 - \beta)$: $F^- < H_2O <$ urea $< NH_3 <$ en $\sim C_2O_4^{2-} < NCS^- < Cl^- \sim CN^- < Br^- < S^{2-} \sim (EtO)_2PS_2^- \sim I^- < (EtO)_2PSe_2^-$. This order roughly follows the order of decreasing electronegativities: $F > O > N > Cl > Br > S \sim I > Se$.[11,15] Because of insufficient data it is far from certain that all sulphur ligands have a high nephelauxetic effect.

Optical electronegativity (x_{opt}) is derived from the observation that the electron transfer bands of a chromophore MX_6 shift as X varies.[16] The optical electronegativity of a ligand is closely related to the electronegativity of the donor atom and the values of x_{opt} for sulphur ligands are those expected on the basis of the electronegativity of the sulphur atom,[17] whereas the situation with oxygen-ligands is much more complicated.[18]

The free-energy change ΔG is related to the corresponding equilibrium constant:

$$\Delta G = \Delta H - T\Delta S = -RT\ln K$$

Thus the relative stability of a metal complex is related to the ligational free-energy change ΔG. For many reactions both heat and entropy changes favour complex formation but ΔS can vary widely, being either positive or negative. Ligational enthalpy in aqueous solution is the small heat change which accompanies the replacement of water by other ligands and is the resultant of several, often large, heat terms related not only to the

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[12] C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.

[13] T. M. Dunn, "Visible and Ultraviolet Spectra of Complex Compounds," in "Modern Co-ordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 229.

[14] C. K. Jørgensen and C. E. Schaffer, *J. Inorg. Nuclear Chem.*, 1958, **8**, 143.

[15] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962, p. 134.

[16] C. K. Jørgensen, *Adv. Chem. Phys.*, 1963, **5**, 33; ref. 1 p. 5.

[17] C. K. Jørgensen, *Acta Chem. Scand.*, 1962, **16**, 2017.

[18] A. Carrington and C. K. Jørgensen, *Mol. Phys.*, 1961, **4**, 395.

strength of the metal–ligand bond but also to the solvation energies of the ions. The stepwise ligational enthalpies ΔH_n for ionic ligands in aqueous solution are usually between -5 and $+5$ kcal.mole^{-1} but may be as large as -10 kcal. for Ag^{I} and Hg^{II} with CN^- or I^-. The values for neutral unidentate ligands are usually between 0 and -5 kcal.mole^{-1}.[19] For similar ligands the ligational entropy changes (ΔS_n) for the formation of metal complexes in the series Mn^{II} to Cu^{II} are approximately equal, so that the free-energy sequence, as determined by measurements of stability constants, is the enthalpy sequence.[19] For halide complexes, when the entropy term predominates, the free-energy sequence is $F > Cl > Br > I$ but the sequence is reversed when the enthalpy term is more important.[20] The latter occurs when the bonding is essentially covalent rather than electrostatic, *i.e.*, with class (*b*) metals. Although the entropy changes for the formation of $[Hg(SCN)_4]^{2-}$ and $[Hg(SeCN)_4]^{2-}$ are roughly equal, the enthalpy change is considerably more exothermic for the latter.[21]

Low-spin d^8 ions, Pd^{II}, Pt^{II}, and Au^{III}, and d^{10} ions, Cu^{I}, Ag^{I}, Au^{I}, and Hg^{II} have the highest formation constants with the heavy halides and with sulphur ligands. Being typically (*b*), they form strong σ bonds with soft ligands and also d_π–d_π bonds by donation of a pair of electrons to the ligand. In general, donor atoms which give large ligand-field splittings form their strongest complexes with metals which are particularly sensitive to ligand-field stabilisation (class *b*), whereas donor atoms which produce small ligand-fields tend to form more stable complexes with cations which are insensitive to ligand-field stabilisation (class *a*).[22] Stability-constant measurements on complexes of some S–O$^-$ chelate ligands showed[23] that for these ligands the "natural order" for log K_1: $Co < Ni < Cu > Zn$ is maintained but Cd and Pb fall out of line in the Mellor–Maley series[24a] ($Mg < Mn < Fe < Cd < Zn < Co < Pb < Ni < Cu < Pd$) which holds for oxygen- and nitrogen-ligands.

The "natural order" for the first-row transition metals is a direct consequence of their ionisation potentials and ionic radii,[24b] with the added factor of Jahn–Teller stabilisation in the case of Cr^{II} and Cu^{II}; on the other hand, Cd and Pb, not being in the first-row transition series, behave differently towards sulphur. For these two metals the possibility of some degree of L → M π-bonding in the complexes studied by Irving and Fernelius[23] cannot be excluded.

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[19] F. J. C. Rossotti, "The Thermodynamics of Metal Ion Complex Formation in Solution," in "Modern Co-ordination Chemistry," ed. J. Lewis and R. J. Wilkins, Interscience, New York, 1960, p. 1.

[20] A. A. Grinberg and K. B. Yatsimirskii, *Bull. Acad. Sci. U.R.S.S. Div. Chem. Sci.*, 1952, 239; R. J. P. Williams, *J. Phys. Chem.*, 1954, **58**, 121; E. L. King, *J. Chem. Educ.*, 1953, **30**, 71; A. J. Poë and M. S. Vaidya, *Nature*, 1959, **184**, 1139.

[21] V. T. Toropova, *Zhur. neorg. Khim.*, 1956, **1**, 243.

[22] L. E. Orgel, 10e Conseil de l'Institut international de Chemie Solvay, Stoops, Brussels, 1956, p. 289.

[23] R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, 1956, **60**, 1427.

[24] (*a*) D. P. Mellor and L. Maley, *Nature*, 1948, **159**, 370; (*b*) H. Irving and R. J. P. Williams, *J.*, 1953, 3192.

The stability constants of complexes of a considerable number of sulphur-ligands have been measured[25] but unfortunately in most instances the data are not available for the same metals with the oxygen analogues. It is hoped that in the future measurements will be made so that for borderline metals a comparison can be drawn between the stabilities of complexes of analogous oxygen and sulphur ligands.

Thiols but not thioethers cause spin-pairing in complexes of Co^{II} and Ni^{II}.[26] The ability to cause spin-pairing in complexes of Co^{II} and Ni^{II} is confined to "soft" bases which are relatively strong π-acceptors. However, the polarisability of the ligand atom is the more decisive factor.

The *trans*-effect which is dependent on the permanent dipole moment, the induced dipole moment, the polarisability, the charge and the size of the ligand, and on the degree of π-bonding, is very strong in sulphur-ligands.[3,27] Although a relative order of the strength of the *trans*-effect among a number of ligands has been suggested,[28] many of the data are based on relative yields obtained under different sets of conditions. Hence the positions of sulphur-ligands compared with other ligands having a strong *trans*-directing influence may vary considerably according to the particular system being studied.

3. Complexes of Sulphide and Selenide Ion

The simplest sulphur ligand is the sulphide ion. Many metal sulphides are extremely insoluble in water, Selenides are similar but are soon oxidised by air with the separation of selenium, while tellurides are usually even less stable to air. Quite a few metal sulphides are soluble in solutions of ammonium or potassium sulphide to give soluble complex sulphides and use was made of this complexing power of the sulphide ion in qualitative analysis. Hg^{II}, Ge^{IV}, Sn^{IV}, As^{III}, As^{V}, Sb^{V}, Mo^{VI}, W^{VI}, and Re^{VII} form soluble complex sulphides.

The thio-salts Na_2SnS_3,aq. and Na_4SnS_4,aq. are readily hydrolysed and are decomposed by dilute acid.[29] Stannic selenide $SnSe_2$ dissolves in a solution of potassium selenide from which crystals of $K_2SnSe_3,3H_2O$ can be obtained.[30] Potassium thioarsenite K_3AsS_3 and thioantimonite K_3SbS_3 and sodium thioantimonate $Na_3SbS_4,9H_2O$ can be isolated. The esters $As(SPh)_3$ and $Sb(SPh)_3$ are known; they can be oxidised by sulphur to $S.As(SPh)_3$ and $S.Sb(SPh)_3$.[31] Thiostannate esters $Sn(SR)_4$ have been

[25] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-ion Complexes," *Chem. Soc. Special Publ.*, No. 17, 1964.

[26] (*a*) S. E. Livingstone, *J.*, 1956, 1042; (*b*) R. S. Nyholm, *Chem. Rev.*, 1953, **53**, 263.

[27] (*a*) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 172; (*b*) J. V. Quagliano and L. Schubert, *Chem. Rev.*, 1952, **50**, 201.

[28] J. Chatt and A. A. Williams, *J.*, 1951, 3061; J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J.*, 1955, 4456.

[29] G. Spacu and A. Pop, *Bull. Acad. Sci. Roumanie*, 1939, **21**, 52.

[30] A. Ditte, *Compt. rend.*, 1882, **95**, 641.

[31] R. Klement and R. Reuber *Ber.*, 1935, **68**, 1761; H. J. Backer and J. Kramer, *Rec. Trav. chim.*, 1933, **52**, 916.

prepared from $SnCl_4$ and NaSR; they are volatile at low pressures.[31]

Molybdenum(VI) gives a series of thiomolybdates: $K_2[MoO_3S]$, $K_2[MoO_2S_2]$, $K_2[MoOS_3]$, and $K_2[MoS_4]$. A similar series is known with tungsten(VI), and the selenium analogues $(NH_4)_2[WO_2Se_2]$ and $(NH_4)_2[WSe_4]$ have been obtained.[32]

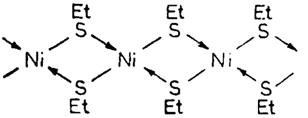
Cu^I and Au^I give polysulphide complexes $[CuS_4]^-$ and $[AuS_3]^-$, containing S–S links. Other polysulphides of Cu^I have been studied.[33]

The spectra of solutions of complex sulphides have been but little investigated, although the spectra of solid $M^{II}S_4$ chromophores (M = Fe, Co, Ni, Cu) indicate that Δ is larger than for $M^{II}Cl_4$ and that the nephelauxetic effect is also greater.[1]

4. Complexes of Negatively Charged Unidentate Ligands

4.1. Thiols—Mercaptide ions RS^-, being highly polarisable, form strong bonds with typical class (*b*) metal ions. The avidity of thiols for Hg^{II} has long been known, hence the name "mercaptan". The mercaptides $Hg(SR)_2$ (where R is an alkyl radical from ethyl to n-octyl) are monomeric in benzene.[34] Mercury compounds have been used for analytical reagents for thiols and disulphides. The desirable properties for such a reagent are rather restrictive and only $HgCl_2$ and MeHgI, especially the latter, adequately fulfil all the requirements.[35]

With Ni^{II} ethyl mercaptan forms the diamagnetic complex $Ni(SEt)_2$ for which the polymeric structure (I) was suggested.[36] The Pd^{II} mercaptides $Pd(SR)_2$ (R = Et, Pr^n, Bu^n, Am^n) are associated in ethylene dibromide and chloroform and probably have a similar polymeric structure.[34] Thiophenol gives an intense colour with Pd^{II} [$Pd(SPh)_2$ is bright vermilion] yet no similar colour is developed with compounds of Ag, Au, Rh, Ir, or Pt.[34] The square-planar monomeric complexes $[Ni(SPh)_2L_2]$ and $[Pd(SPh)_2L_2]$ (L = Et_3P, $PhEt_2P$; 2L = $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$) have been recently described.[37]



(I)

Whereas halogen-bridged dimeric complexes of Pd^{II} and Pt^{II} are readily split by *p*-toluidine and other unidentate ligands, the corresponding alkylthio-bridged complexes are not.[38] *cis* and *trans* Isomers of the Pt^{II} com-

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[32] J. W. Retgers, *Z. phys. Chem.*, 1892, **10**, 548; V. Lenher and A. G. Fruehan, *J. Amer. Chem. Soc.*, 1927, **49**, 3076.

[33] G. Peyronel, D. de Filippo, and G. Marotrigiano, *Gazzetta*, 1961, **91**, 1190, 1196.

[34] F. G. Mann and D. Purdie, *J.*, 1935, 1549.

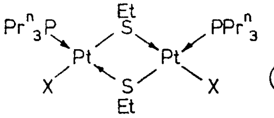
[35] S. J. Leach, *Austral. J. Chem.*, 1960, **13**, 520.

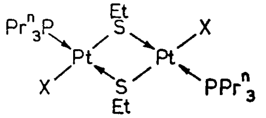
[36] K. A. Jensen, *Z. anorg. Chem.*, 1944, **252**, 227.

[37] R. G. Hayter and F. S. Humiec, *J. Inorg. Nuclear Chem.*, 1964, **26**, 807.

[38] J. Chatt and F. G. Mann, *J.*, 1938, 1949; J. Chatt, F. G. Mann, and A. F. Wells, *J.*, 1938, 2086; J. Chatt, *J.*, 1950, 2301.

plexes $[\text{Pt}(\text{PPr}_3{}^{\text{n}})(\text{EtS})\text{X}]_2$ (X = Cl, SEt) (II) and (III) have been prepared; the *cis*-Pd^{II} analogue (X = Cl) was isolated but not the *trans*.[39,40] Another type of isomerism involving the bridging thiol, has been reported to occur


(II)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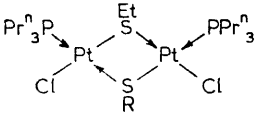
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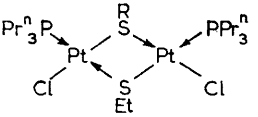
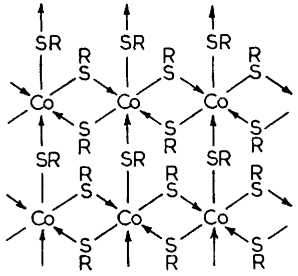

(V)

in alkylthio-bridged Pt^{II} complexes, containing two different alkylmercaptans;[40] the isomers are shown (IV and V). Hexanethiol forms a Co^{III} complex $\text{Co}(\text{C}_6\text{H}_{13}\text{S})_3$ for which the polymeric structure (VI) has been suggested as a possibility.[41] The reaction of cobalamin with thiols has been examined.[42]


(VI)

The phenylthio-Sn^{IV} complex $\text{Ph}_2\text{Sn}(\text{SPh})_2$ was prepared under anhydrous conditions;[43] however, the complexes $\text{R}_3\text{SnSR}'$, $\text{R}_2\text{Sn}(\text{SR}')_2$, and $\text{RSn}(\text{SR}')_3$ (R = Me, Et; R′ = alkyl or Ph) can be obtained from aqueous solution. The Sn–S bond in $\text{Me}_3\text{SnSR}'$ is cleaved by PCl_3 to yield $(\text{R}'\text{S})_3$ P and Me_3SnCl and by Br_2 to yield R′S.SR′ and Me_3SnBr.[44]

4.2. Sulphite Ion.—The sulphite ion is said to form complexes with Be, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, and Hg,[45] although some are probably double salts rather than true complexes (see below). Most of the metals listed are class (*b*) metals and with these strong complexes are formed.

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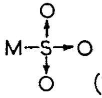
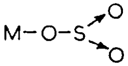
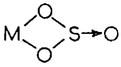
[39] J. Chatt and F. A. Hart, *J.*, 1953, 2363.
[40] J. Chatt and F. A. Hart, *J.*, 1960, 2807.
[41] B. J. McCormick and G. Gorin, *Inorg. Chem.*, 1963, **2**, 928.
[42] D. H. Dolphin and A. W. Johnson, *Proc. Chem. Soc.*, 1963, 311.
[43] H. J. Backer and J. Kramer, *Rec. Trav. chim.*, 1934, **53**, 1101.
[44] E. W. Abel and D. B. Brady, *J.*, 1965, 1192.
[45] A. Werner, "Neure Anschauunger auf dem Gebiete der anorganischen Chemie," 5th edn. Vieweg, Braunschweig, 1923, p. 120.

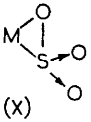
In many complexes the sulphite ion is unidentate but in others it occupies two co-ordination positions. There appears to be no easy way of converting unidentate into bidentate complexes.[46] Aquo-Pd^{II} complexes such as $[Pd(SO_3)(H_2O)_3]$ cannot be dehydrated to give bidentate complexes,[47] as has been done with sulphato-complexes.[48]

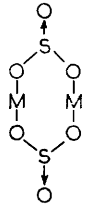
The values of the stability constants for Hg^{II} ($\log_{10}\beta_2$, 22·9) and Tl^{III} ($\log_{10}\beta_4$, 34) are remarkably high.[25] The exceptional stability of the Hg^{II} complex (mercury usually forms weak links with oxygen) and the fact that strong complexes are formed by Ir^{III}, Pd^{II}, and Pt^{II} suggests that the ligand is S-bonded as in (VII) when unidentate. The SO_3^{2-} ion has C_{3v} symmetry, which would be effectively unchanged if the ligand is S-bonded, whereas O-bonding (VIII) would lower the symmetry to C_s. If S-bonding occurs, the S–O stretching frequency would be expected to be higher than in the free SO_3^{2-} ion but if O bonding is present, both higher and lower frequencies would be expected because of the lowering of the symmetry from C_{3v} to C_s. The infrared spectra of a number of unidentate sulphito-complexes of Co^{III}, Rh^{III}, Ir^{III}, Pd^{II}, and Pt^{II} are similar to the spectrum of $(NH_4)_2[Hg(SO_3)_2]$ and are in accordance with S-bonding of the ligand.[46,49,50] However, $Tl_2[Cu(SO_3)_2]$ appears to be O-bonded, while the compounds $(NH_4)_2M^{II}(SO_3)_2$ (M^{II} = Mg, Mn, Fe, Co, Ni, Zn, and Cd) and NH_4CuSO_3 are double salts, since their spectra are similar to that of Na_2SO_3.[50] Several sulphito-complexes of Os^{IV} and Os^{VI} are known.[51] As osmium has a low affinity for sulphur-ligands, the SO_3^{2-} group may be O-bonded in these complexes.

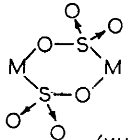

(VII)


(VIII)


(IX)


(X)


(XI)


(XII)

When occupying two co-ordination positions the sulphito-group may be bidentate as in (IX) or (X) or it may be bridging as in (XI) or (XII). The sulphito-group in (IX) and (XI) has C_{3v} symmetry but it has been

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[46] M. E. Baldwin, *J.*, 1961, 3123.

[47] G. A. Earwicker, *J.* 1960, 2620.

[48] C. G. Barraclough and M. L. Tobe, *J.*, 1961, 1993.

[49] A. V. Babaeva, Yu. Ya. Kharitonov, and Z. M. Novozhenyuk, *Zhur. neorg. Khim.*, 1961, **6**, 2263, 2281; A. V. Babaeva, Yu. Ya. Kharitonov, and I. B. Baranovskii, *ibid.*, 1962, **7**, 1247; A. V. Babaeva, Yu. Ya. Kharitonov, and E. V. Shenderetskaya, *ibid.*, p. 1530.

[50] G. Newman and D. B. Powell, *Spectrochim. Acta*, 1963, **19**, 213.

[51] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p. 1496.

suggested that it is doubtful if infrared data can distinguish between (IX), (XI), and (XII).[50] As (X) involves a 3-membered ring which might be easily ruptured and as $[Co(en)_2SO_3]^+$ is stable in water, it has been inferred from this and the infrared spectrum that the sulphito-group is bound as in (IX).[46] The infrared spectra of $[Co(SO_3)_3]^{3-}$ and $[Rh(SO_3)_3]^{3-}$ have been interpreted as indicating that the sulphito-groups are bridging as in (XI) or (XII).[52] It is unlikely that the structures (X) and (XII) occur.

The sulphito-group has a marked *trans*-effect which is greater than that of the nitro-group in Pt^{II}, Co^{III}, and Ir^{III} complexes.[53] Sulphitocobalamin has been recently reported;[54] in this compound SO_3^{2-} has replaced the CN^- group attached to the cobalt atom in vitamin B_{12}.[54] The fact that amine-sulphito-complexes of Co^{III} are yellow and those of Rh^{III}, Ir^{III}, Pd^{II}, and Pt^{II} are colourless indicates that SO_3^{2-} has a high position in the spectrochemical series, comparable with that of NH_3.[1]

4.3. Thiosulphate Ion.—Alkaline thiosulphate will dissolve many insoluble salts of Pb^{II}, Hg^{II}, Cu^I, and Ag^I. Strong complexes are formed with Cu^I, Ag^I, and Au^I; bivalent copper is reduced by $S_2O_3^{2-}$ to the Cu^I complex. As with sulphite ion, the stability constants for Hg^{II} ($\log_{10}\beta_2$, 29·9) and Tl^{III} ($\log_{10}\beta_4$, 41) are remarkably high.[25]

The thiosulphate ion is usually unidentate, as it undoubtedly is in $[Hg(S_2O_3)_2]^{2-}$ but it may well be bidentate in $[Bi(S_2O_3)_3]$.[3-] When unidentate, it is almost certainly S-bonded through the central sulphur atom as is sulphite ion. The reactivity of co-ordinated $S_2O_3^{2-}$ in Co^{III} complexes is lower than that of NO_2^- and it is not displaced by H_2O in solution.[55]

Bivalent platinum forms the very stable complexes $[Pt(S_2O_3)Cl_2]^{2-}$ and $[Pt(S_2O_3)_2]^{2-}$ in which the ligand is almost certainly chelated; the complexes $[Pt(S_2O_3)_3]^{4-}$ and $[Pt(S_2O_3)_4]^{6-}$ are also known.[56] In the chelate complexes the ligand is bound through one sulphur and one oxygen atom, as *cis* and *trans* isomers of $[Pt(S_2O_3)_2]^{2-}$ have been prepared.[57] However, only one isomer is known with Pd^{II}. The group *trans* to $S_2O_3^{2-}$ is labilised in the same way as in thiourea complexes of Pt^{II};[25b] this is a further indication that the ligand is bound through sulphur.

4.4. Thiocyanate and Selenocyanate Ion.—The standard free energies of formation of XCN^- (X = O, S, Se) increase linearly with the ionic radius of X.[58]

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[52] A. V. Babaeva and Yu. Ya. Kharitonov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **144**, 559.

[53] A. V. Ablov and G. P. Syrtsova, *Zhur. neorg. Khim.*, 1960, **5**, 1221; A. V. Babaeva and I. B. Baranovskii, *ibid.*, 1962, **7**, 783; I. I. Charnyaev and Z. M. Novozhenyuk, *ibid.*, 1961, **6**, 2462.

[54] D. H. Dolphin, W. A. Johnson, and N. Shaw, *Nature*, 1963, **199**, 170.

[55] A. V. Babaeva, I. B. Baranovskii, and Yu. Ya. Kharatonov, *Zhur. neorg. Khim.*, 1963, **8**, 604.

[56] P. Shottlander, *Annalen*, 1866, **140**, 200; D. I. Ryabchikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **27**, 349; **28**, 231; 1944, **44**, 277.

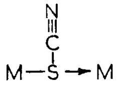
[57] D. I. Ryabchikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **41**, 208.

[58] S. Hamada, *Nippon Kagaku Zasshi*, 1961, **82**, 1327.

The only transition-metal cyanato-complexes which had been reported prior to 1964 were $K_2[Co(NCO)_4]$,[59] $K[M(NCO)_3]$ (M = Cu, Cd) and $[M\{(CH_2)_6N_4\}_2(H_2O)_4]$ $[M(NCO)_4]$ (M = Co, Ni, Cu).[60] Recently the compounds $[NEt_4]_2[M(NCO)_4]$ (M = Mn, Fe, Co, Ni, Cu, Zn, and Cd) and $[NEt_4]$ $[Fe^{III}(NCO)_4]$ were reported; in these tetrahedral complexes the cyanato-group is considered to be bonded to the metal through the nitrogen atom: thus, strictly speaking, they are isocyanato-complexes.[61]

On the other hand, the thiocyanate ion forms complexes with most transition metals, although those of thorium and niobium have only recently been reported.[62,63] Some of these complexes, such as the high-spin iron(III) complex $[NEt_4]_3[Fe(NCS)_6]$[64] and the molybdenum(V) complex $[pyH]_4[Mo_2O_4(NCS)_6]$,[65] are deeply coloured. Except in ionic compounds such as KSCN, the thiocyanate group can be co-ordinated in at least four ways as shown in (XIII)—(XVI).

$M{-}S{-}C{\equiv}N$ (XIII) $M{-}N{=}C{=}S$ (XIV) $M{-}S{-}C{\equiv}N{\rightarrow}M$ (XV)



$M{-}\overset{\overset{\overset{N}{|||}}{C}}{\underset{|}{S}}{\rightarrow}M$

(XVI)

The structures represented by (XIII), (XIV), and (XV) only have been established by crystal structure determinations, although in $AgSCN,PPr_3^n$ the SCN group links three silver atoms, two through sulphur and one through nitrogen.[66]

The deep blue insoluble $CoHg(SCN)_4$ has a polymeric structure in which each cobalt atom is tetrahedrally surrounded by four nitrogen atoms of the thiocyanato-group while the sulphur atoms are bound to four different mercury atoms, which are tetrahedrally surrounded by sulphur atoms.[67] The electronic spectra of $HgM(NCS)_4$ (M = Mn, Fe) indicate an essentially tetrahedral environment of the nitrogen atoms about Mn and Fe;[68] the SCN^- group is probably S-bonded to Hg. The SCN^- group also acts as a bridge in the octahedrally co-ordinated $Ni(NH_3)_2(NCS)_2$,[69] $Co(py)_2(NCS)_2$,[70] $Cu(py)_2(NCS)_2$,[70] $Cd(etu)_2(SCN)_2$ (etu = ethylenethiourea),[71] in AgSCN,[72] and in the dimeric $AgSCN,PEt_3$;[73] in $Cu(NCS)_2(py)_2$ the

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[59] C. W. Blomstrand, *J. prakt. Chem.*, 1871, (2) **3**, 221.

[60] R. Ripan, *Chem. Zentral.*, 1930, **12**, i, 967.

[61] D. Forster and D. M. L. Goodgame, *J.*, 1964, 2790; 1965, 262.

[62] A. K. Molodkin and G. A. Skotnickova, *Zhur. neorg. Khim.*, 1964, **9**, 1548.

[63] A. M. Golub and A. M. Sych, *Zhur. neorg. Khim.*, 1964, **9**, 1085.

[64] S. E. Livingstone and T. N. Lockyer, unpublished work.

[65] R. G. James and W. Wardlaw, *J.*, 1928, 2726; P. C. H. Mitchell and R. J. P. Williams, *J.*, 1962, 4570.

[66] A. Turco, C. Panattoni, and E. Frasson, *Nature*, 1960, **187**, 772.

[67] J. W. Jeffrey, *Nature*, 1947, **159**, 610.

[68] D. Forster and D. M. L. Goodgame, *J.*, 1965, 268.

[69] M. A. Porai-Koshits, E. K. Iukno, A. S. Antsyshkina, and E. Dikareva, *Soviet Phys.-Cryst.*, 1957, **2**, 366.

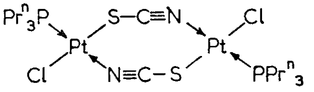
[70] M. A. Porai-Koshits and G. N. Tishchenko, *Soviet Phys.-Cryst.*, 1960, **4**, 216.

[71] L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, 1960, **13**, 125.

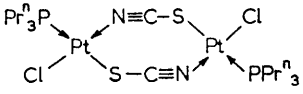
[72] I. Lindqvist, *Acta Cryst.*, 1957, **10**, 29.

[73] A. Turco, C. Panattoni, and E. Frasson, *Ricerca sci.*, 1960, **30**, 1071.

Cu–S distances are longer than the Co–S distance in the Co^{II} compound owing to Jahn–Teller distortion.[70] Bridging occurs in $Pt_2(PPr^n_3)_2Cl_2(SCN)_2$ which has been isolated in two isomeric forms (XVII) and (XVIII).[74]



(XVII)



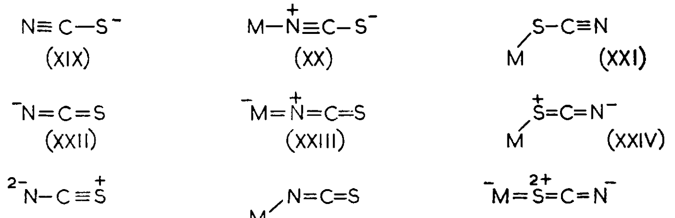
(XVIII)

The C≡N stretching frequency in a bridging thiocyanato-group is higher than in a terminal thiocyanato-group.[75]

In general the thiocyanate ion co-ordinates to (*a*) class metals through nitrogen and to (*b*) class metals through sulphur but it is known from *X*-ray analysis that with thiocyanate ion the first-row transition metals Cr, Mn, Co, Ni, Cu, and Zn form M–N bonds.[76,77,78] However, the oxidation state of the metal, the nature of the other ligands in the complex, and steric factors may determine the way in which the thiocyanato-group is bound. In $Cu(en)_2(SCN)_2$ the non-linear thiocyanato-groups are S-bonded in a tetragonally distorted octahedral configuration.[79]

The C≡N stretching frequency has been used[80] to distinguish between S- and N-bonding, since among complexes of known structure those which are S-bonded have generally high values for the C≡N stretching frequency but some overlap occurs. It has been found that the C–S stretching frequency is more diagnostic, as in S-bonded complexes it occurs at 690—720 cm.$^{-1}$ and in N-bonded complexes at 780—860 cm.$^{-1}$.[81,82] The M–SCN linkage is always angular but the M–NCS linkage can be collinear or angular with the M–N–C angle as low as 140°.[81,78] Various canonical structures can be written for the thiocyanato-group:

Free ion M–N bonding M–S bonding



(XIX) (XX) (XXI)

(XXII) (XXIII) (XXIV)

(XXV) (XXVI) (XXVII)

[74] J. Chatt and F. A. Hart, *Nature*, 1952, **169**, 673; J. Chatt, L. A. Duncanson, F. A. Hart, and P. G. Owston, *ibid.*, 1958, **181**, 43; P. G. Owston and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 253; J. Chatt and F. A. Hart, *J.*, 1961, 1416.

[75] J. Chatt and L. A. Duncanson, *Nature*, 1956, **178**, 997.

[76] G. S. Zhdanov and Z. V. Zvonkova, *Zhur. fiz. Khim. U.S.S.R.*, 1950, **24**, 1339.

[77] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66 and references therein.

[78] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1963, **16**, 753.

[79] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 254.

[80] B. C. H. Mitchell and R. J. P. Williams, *J.*, 1960, 1912.

[81] J. Lewis, R. S. Nyholm, and P. W. Smith, *J.*, 1961, 4590.

[82] A. Tramer, *J. Chim. phys.*, 1962, **59**, 232.

It has been suggested that (XIX) predominates in KSCN[83] and (XXVI) or (XX) predominates in N-bonded complexes while for S-bonded complexes (XXI) is important.[81] On the assumptions that (*a*) the lone pairs on the sulphur atom are more easily polarised and (*b*) the permanent lone-pair dipole on the nitrogen atom is larger than on the sulphur atom, Lewis, Nyholm, and Smith[81] suggest that, when thiocyanate ion is the only ligand, the way in which the group is bound is decided by the relative bond energies of a covalent M–S bond and the more ionic M–N bond.

Nuclear magnetic resonance (NMR) spectroscopy has been used to distinguish between N- and S-bonded thiocyanate. In known S-bonded complexes the ^{14}N resonance is shifted slightly downfield compared with the free SCN^- ion and in N-bonded complexes it is shifted upfield by a comparatively large amount. It has been suggested that N-bonding lowers the energy of the non-bonding orbital and shifts the ^{14}N resonance upfield and that S-bonding, while not affecting the non-bonding orbital, lowers the energy of the delocalized anti-bonding orbital by mixing in its own stabilized *d*-orbitals, thus causing a small low-field shift of the resonance.[84]

Infrared spectral data indicate S-bonding in $[M(SCN)_4]^{2-}$ and in $[M(NH_3)_2(SCN)_2]$ (M = Pd, Pt) but N-bonding in $[M(PR_3)_2(SCN)_2]$. The change from M–S to M–N bonding in these complexes of class (*b*) metals has been explained on the basis that strong π-electron acceptors, such as tertiary phosphines, can make the $d\epsilon$ orbitals of the metal less available for binding with the π-orbitals of the sulphur atom.[77] The compounds *cis*-$Mn(CO)_3(am)_2NCS$ (am = py, *p*-toluidine, ½bipy) and *trans*-$Mn(CO)_3(PEt_3)_2NCS$ are N-bonded but *cis*-$Mn(CO)_3(SbPh_3)_2SCN$ is S-bonded.[85] It appears that in the presence of strongly π-bonding ligands the effective charge on the metal plays an important rôle; thus complexes with bases weaker than PPh_3 (*e.g.*, CO, $SbPh_3$) are S-bonded, whereas complexes containing stronger bases such as amines are N-bonded.[85] Most first-row transition metals are N-bonded, but $Co(SCN)_2(PPh_3)_2$ and $Cu(SCN)_2(PPh_3)_2$ are S-bonded.[86] Whereas $Mn(CO)_5SCN$ is S-bonded, the isoelectronic $[Cr(CO)_5NCS]^-$ is N-bonded; the decrease in charge on the metal atom causes a change from S- to N-bonding.[87]

It has been shown[88] that steric factors influence the manner of attachment of the thiocyanato-group in the complexes $ML_2(SCN)_2$ (M = Pd, Pt; L = amine, ½diamine, PR_3, SbR_3) some of which are S-bonded and others are N-bonded. The steric requirements for M–SCN are greater than for the linear M–NCS. Since Pd(α-picoline)$_2$(SCN)$_2$ is S-bonded and

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[83] L. H. Jones, *J. Chem. Phys.*, 1956, **25**, 1069; 1958, **28**, 1234.

[84] O. W. Haworth, R. E. Richards, and L. M. Venanzi, *J.*, 1964, 3335.

[85] A. Wojcicki and M. F. Farona, *Inorg. Chem.*, 1964, **3**, 151.

[86] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157; M. A. Poraj-Kosic, *Acta Cryst. Suppl.*, 1963, A **42**, abstract 4.72.

[87] A. Wojcicki and M. F. Farcna, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2289.

[88] F. Basolo, W. H. Baddeley, and J. L. Burmeister, *Inorg. Chem.*, 1964, **3**, 1202.

$Pd(py)_2(NCS)_2$ is N-bonded, it seems that electronic effects are also important.[88]

Although selenocyanato-complexes of platinum[89] and mercury[90] have long been known, very little has been reported on selenocyanato-complexes until the past few years. The manner of co-ordination of selenocyanate ion can be established by infrared spectroscopy: the C–Se stretching frequency, which occurs at 558 cm.$^{-1}$ in KSeCN,[91] occurs in the range 520—543 cm.$^{-1}$ for Se-bonded complexes and at 639—672 cm.$^{-1}$ for N-bonded complexes.[92] The complexes $[Pt(SeCN)_6]^{2-}$ and $[Hg(SeCN)_4]^{2-}$ are Se-bonded while $[Co(NCSe)_4]^{2-}$ and $[Cr(NCSe)_6]^{3-}$ are N-bonded.[92,93,94] *X*-Ray investigation has established the presence of Co–NCSe–Hg bridges in $CoHg(SeCN)_4$ which is isomorphous with $CoHg(SCN)_4$.[95] Selenocyanato-bridges are also present in $Co(py)_2(NCSe)_2$.[96] The tetrahedral complexes $Co(quinoline)_2(NCSe)_2$ and $Co(Ph_3PO)_2(NCSe)_2$ and the *trans*-octahedral complex $Co(py)_4(NCSe)_2$ are N-bonded and isomorphous with their thiocyanato-analogues.[94] The magnetic moment of $Co(Ph_3P)_2(NCSe)_2$ is 3·4 B.M.; it has been suggested that this compound contains equal numbers of octahedral low-spin cobalt(II) and tetrahedral high-spin cobalt(II) ions.[94] An *X*-ray structural determination of $NH_4[Co(SeCN)_2(DH)_2],3H_2O$ (DH_2 = dimethylglyoxime) shows that this complex has a *trans* configuration and that the $SeCN^-$ group is bound through Se.[97] The selenocyanate complexes of Ag^I, Cd^{II}, and Hg^{II} are more stable than the corresponding thiocyanates.[21]

As might be expected, the position of the thiocyanate ion in the spectrochemical series depends on whether it is S- or N-bonded. When S-bonded it occupies a position approximately equal to Cl^- but when N-bonded it lies between H_2O and NH_3.[98,99] The value of Δ (18,000 cm.$^{-1}$) obtained for $[Cr(NCSe)_6]^{3-}$ shows that N-bonded selenocyanate creates a slightly stronger field than N-bonded thiocyanate (17,800 cm.$^{-1}$).[93]

5. Complexes of Neutral Unidentate Ligands

5.1. Thioethers, Selenoethers, and Telluroethers.—Thioethers do not co-ordinate very strongly to metals apart from Pt^{II}, Pd^{II}, Rh^{III}, Ir^{III}, and

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[89] A. Werner and A. Miolati, *Z. phys. Chem.*, 1894, **14**, 507.

[90] A. Rosenheim and M. Pritze, *Z. anorg. Chem.*, 1909, **63**, 275.

[91] H. W. Morgan, *J. Inorg. Nuclear Chem.*, 1961, **16**, 367.

[92] C. Pecile, A. Turco, and G. Pizzolotto, *Ricerca sci.*, 1961, **31**, 2A, 247; A. Turco, C. Pecile, and M. Niccolini, *J.*, 1962, 3008.

[93] K. Michelson, *Acta Chem. Scand.*, 1963, **17**, 1811.

[94] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, 1962, **1**, 565.

[95] E. Frasson, A. Turco, and C. Panattoni, *Gazzetta*, 1961, **91**, 750.

[96] S. M. Nelson, *Proc. Chem. Soc.*, 1961, 372.

[97] A. V. Ablov and V. N. Shafranskii, *Zhur. neorg. Khim.*, 1964, **9**, 585.

[98] C. E. Schäffer, Internat. Conf. on Co-ordination Chem., London, *Chem. Soc. Special Publ.*, No. 13, 1959, p. 153.

[99] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962, p. 109.

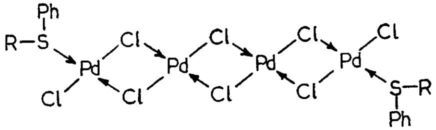
Hg^{II}. Dimethyl sulphide forms three isomeric compounds of general formula $PtCl_2(Me_2S)_2$.[100] The γ-isomer is $[Pt(Me_2S)_4]\ [PtCl_4]$. The complexes $Pt(R_2S)_2Cl_2$ (R = Et, Pr^n, Bu^n) were among the first metal complexes to be investigated by dipole moment measurements; the α-isomers have dipole moments of approximately 2·4 D, while the β-isomers have moments in the range 9·0—9·5 D.[101] These results show that the α-isomers are *trans* and the β-isomers are *cis*. The *trans* structure was confirmed by an *X*-ray investigation.[102] Sulphur has a much lower affinity for Pt^{IV} than for $^-Pt^{II}$ and various attempts to prepare Pt^{IV} complexes of thioethers have been unsuccessful.

The complexes of selenoethers resemble closely the analogous thioether complexes. The compounds $Pt(R_2Se)_2Cl_2$ (R = Me, Et, Pr^n, $Me_2CH_2{\cdot}CH_2{\cdot}CH_2$, Ph) occur in α, β, and γ-isomeric forms. The α- and β-isomers are monomeric and the values for their dipole moments are similar to those of their sulphur-analogues.[103]

The corresponding complexes of telluroethers are much less stable. The best characterised compound is $Pt\{(Ph{\cdot}CH_2)_2Te\}_2Cl_2$ which probably has the *trans* configuration, as it is soluble in chloroform. It is stable in the solid state but rapidly decomposes in solution to platinum, tellurium, and bibenzyl; no isomers are known.[104]

The Pd^{II} complexes $Pd(R_2S)_2Cl_2$ can be readily prepared but in the α-form only;[105] $Pd(Me_2S)_2Cl_2$ is completely isomorphous with *trans*-$Pt(Me_2S)_2Cl_2$.[102] The Pd^{II} complexes of RSPh (R = alkyl) have been used to identify the alkyl phenyl sulphides, as, unlike dialkyl sulphides, these alkyl phenyl sulphides do not co-ordinate readily with mercury. With $PdCl_2$ yellow monomeric complexes $Pd(PhSR)_2Cl_2$ are usually formed but when R = Bu^t or Me_2EtC the red complexes $PhSR,2PdCl_2$ are formed.[106] These complexes probably have the tetrameric structure (XXVIII); if so, they are the only known Pd^{II} complexes of this type. Dialkyl and diaryl selenides form stable complexes $Pd(R_2Se)_2X_2$ (R = Me, Et, Bu^n, Ph; X = Cl, Br, I).[104]

Chloro-bridged Pt^{II} compounds of general formula $L_2Pt_2Cl_4$ (L = R_2S,



(XXVIII)

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[100] L. A. Tschugaev and W. Subbotin, *Ber.*, 1910, **43**, 1200.

[101] K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 97, 115.

[102] E. G. Cox, H. Saenger, and W. Wardlaw, *J.*, 1934, 182.

[103] E. Fritzmann, *Z. anorg. Chem.*, 1911, **73**, 239; E. Fritzmann and V. V. Krinitzki, *J. Appl. Chem. Rus.*, 1939, **11**, 1610.

[104] E. Fritzmann, *J. Russ. Chem. Soc.*, 1915, **47**, 588; *Z. anorg. Chem.*, 1924, **133** 119, 133.

[105] L. Tschugaev, *Z. anorg. Chem.*, 1924, **134**, 277; L. Tschugaev, and C. Ivanov, *ibid.*, 1924, **135**, 153; F. G. Mann and D. Purdie, *J.*, 1935, 1549.

[106] V. N. Ipatiev and B. S. Friedman, *J. Amer. Chem. Soc.*, 1939, **61**, 684.

R_2Se, R_2Te; R = alkyl) have been prepared; the selenide and telluride complexes are brownish-orange and more soluble than the yellow sulphide complexes. The stability of these complexes and those of Group V ligands falls in the order $R_3P \sim R_2S > R_3As >$ amine $> R_2Te > R_3Sb > R_2Se$.[107] The analogous Pd^{II} complexes $L_2Pd_2Cl_4$ are more soluble and less stable than the Pt complexes but, when $L = R_2Se$, they are more stable. The stability sequence of the Pd complexes is: $R_3P > R_3As \sim R_2S > R_2Se > R_2Te > R_3Sb$. The reverse order of stability for the R_2Te and R_2Se complexes of Pd may be due to the relative sizes of the orbitals used for σ-bonds, Se being comparable with Pd and Te with Pt.[108] A study of the N–H stretching frequencies of the series *trans*-[L,amPtCl$_2$] [am = RNH_2 or R_2NH; L = piperidine, γ-picoline, R_3P, R_3As, R_3Sb, R_2S, R_2Se, R_2Te, $P(OR)_3$, or C_2H_4] shows the increasing inductive effect transmitted across the Pt atom from the ligand donor atom to the N–H bond when the ligands are arranged in the series: γ-picoline < piperidine $< R_2S < R_2Se < R_2Te < R_3As < R_3P < R_3Sb < P(OR)_3 < C_2H_4$.[109]

The ligand-field splittings inferred from the energies of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in the complexes *trans*-[L,piperidinePtCl$_2$] decrease when L is arranged in the sequence: $P(OMe)_3 > Pr_3P >$ piperidine $> Pr_3As > Et_2S > Et_2Se > Et_2Te$. The range of energies is small, varying from 33,400 cm.$^{-1}$ when $L = P(OMe)_3$ to 29,400 cm.$^{-1}$ when $L = Et_2Te$.[110]

Rhodium(III) gives complexes of the type $Rh(SEt_2)_3X_3$ (X = Cl, Br, I).[111] The corresponding Ir^{III} chloro-complex was reported in *cis* and *trans* isomeric forms.[112] The yellow *cis*-isomer is soluble in polar solvents yet the "*trans*" isomer is soluble in chloroform and nitrobenzene but not in most non-polar solvents. A recent reinvestigation of these isomeric complexes by means of a number of physical techniques has shown that the yellow is indeed *cis*-$[Ir(Et_2S)_3Cl_3]$ but the red isomer is in fact the salt *trans*-$[Ir(Et_2S)_4Cl_2]$ *trans*-$[Ir(Et_2S)_2Cl_4]$. An Ir^{IV} complex $[Ir(Et_2S)_2Cl_4]$ was also reported.[113]

The monomeric Au^{I} complex $Au(Et_2S)Cl$ is unstable.[114]

Thioethers form at least three types of Hg^{II} halogen complex: (*a*) monomeric $(R_2S)_2HgX_2$; (*b*) halogen-bridged dimeric $[R_2SHgX_2]_2$ (XXIX); (*c*) complexes $R_2S,2HgX_2$ of uncertain structure.[115]

The co-ordinating ability of bischloroethyl sulphide $(ClC_2H_4)_2S$ is weaker than that of diethyl sulphide; bis-complexes $Pt\{(ClC_2H_4)_2S\}_2X_2$ (X = Cl,NO_2) are formed but this ligand, unlike Et_2S, will not replace

[107] J. Chatt and L. M. Venanzi, *J.*, 1955, 2787.

[108] J. Chatt and L. M. Venanzi, *J.*, 1957, 2351.

[109] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J.*, 1955, 4461.

[110] J. Chatt, G. Gamlen, and L. E. Orgel, *J.*, 1959, 1047.

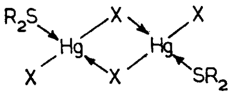
[111] F. P. Dwyer and R. S. Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 67.

[112] P. C. Rây, N. Adhikari, and R. Ghosh, *J. Indian Chem. Soc.*, 1933, **10**, 275.

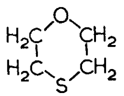
[113] G. B. Kauffman, J. Hwa-San Tsai, R. C. Fay, and C. K. Jørgensen, *Inorg. Chem.*, 1963. **2**, 1233.

[114] F. G. Mann, A. F. Wells, and D. Purdie, *J.*, 1937, 1828.

[115] S. Smiles, *J.*, 1900, **77**, 163; W. F. Faragher, J. C. Morell, and S. Comay, *J. Amer. Chem. Soc.*, 1929, **51**, 2774.



(XXIX)



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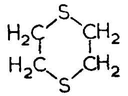


(XXXI)

NH_3 or RNH_2 from Pt^{II} complexes. As a result of the increased *trans*-effect compared with Et_2S, one ligand is extremely labile.[116]

Although Ti^{IV} is regarded as having class (*a*) behaviour, $TiCl_4$ and $TiBr_4$ form ill-defined complexes with dialkyl ethers but the compounds $TiX_4(R_2S)_2$ ($R = Me,Et$) are stable and crystalline. However, thioether complexes of Ti^{III} are unstable and less well defined. Thioethers do not replace NMe_3 completely from $TiCl_3(NMe_3)_2$, although the amine is readily replaced by oxygen-ligands. Thus for Ti^{IV}: S > O but for Ti^{III}: O > S.[117] Thioxan (XXX) and dithian (XXXI) give 2:1 adducts with $TiCl_4$ and $TiBr_4$; thioxan is S-bonded in these complexes.[118] With V^{III} dialkyl sulphides form $VCl_3(R_2S)_2$ ($R = Me,Et$); these complexes are monomeric with a dipole moment of 2·5 D; their spectra are interpreted as indicating a *trans*-trigonal bipyramidal configuration.[118]

Complexes of Nb^V and Ta^V have been isolated: MX_5,R_2S ($M = Nb, Ta$; $X = F, Cl, Br$; $R = Et, Me$) and TaI_5, R_2S are thermally more stable than the corresponding ether complexes.[119] The ether can be replaced by the corresponding thioether in MCl_5,Et_2O and in $NbCl_5,Pr^n{}_2O$. These results suggest that the bond energy of the M–S bond is greater than that of the M–O bond in these complexes. This is surprising in view of the avidity of these metals for oxygen. However, Me_2O is not displaced by Me_2S from MCl_5,Me_2O, nor yet is Me_2S displaced by Me_2O from $TaCl_5,Me_2S$.[120] The authors state that one cannot accept the explanation of simple back-co-ordination of unshared *d* electrons from a penultimate shell, since there are none. They suggest three factors: (i) a steric effect; (ii) the dipole moment of the ligand; (iii) the polarisabilities of sulphur and oxygen. The first factor is responsible for the greater stability of the methyl adducts. The second and third factors are responsible for the greater stability of the thioether adducts, since the dipole moment of Et_2S (1·58 D) is greater than that of Et_2O (1·15 D) while the polarisability of sulphur in Et_2S is much greater than that of oxygen in Et_2O. Mo^V gives the complexes $MoOCl_3,R_2S$ ($R = Me,Et,Pr^n$).[121]

[116] A. V. Babaeva, V. A. Golovnya, and L. A. Nazarova, *Zhur. neorg. Khim.*, 1959, **4**, 1741.

[117] K. Baker and G. W. A. Fowles, *Proc. Chem. Soc.*, 1964, 362.

[118] G. W. A. Fowles, Proc. VIIIth Internat. Conf. on Co-ordination Chem., Springer Verlag, Vienna, 1964, p. 208.

[119] F. Fairbrother and J. F. Nixon, *J.*, 1962, 150; F. Fairbrother, K. H. Grundy, and A. Thompson, *J.*, *1965*, *765*.

[120] D. B. Copley, F. Fairbrother, and A. Thompson, *J.*, 1964, 315.

[121] K. Feenan and G. W. A Fowles, *Inorg. Chem.*, 1965, **4**, 310.

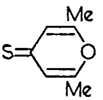
A thermochemical study of the relative donor strengths of some oxygen and sulphur ligands towards $SnCl_4$ and $SbCl_5$ has shown that Et_2S is co-ordinated more strongly than Et_2O, indicating that Sn^{IV} and Sb^{V} should be regarded as borderline rather than class (*a*) metals.[122]

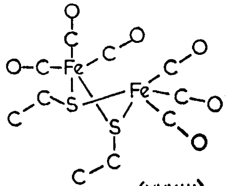
Diethyl sulphide and tetrahydrothiophen form weak complexes $Et_2S.BH_3$, $Et_2S.BF_3$, $(CH_2)_4S.BH_3$, and $(CH_2)_4S.BF_3$; BH_3 forms more stable adducts than BF_3 with R_2S but the reverse is true for R_2O.[123] Stable 1:1 and 1:2 complexes are formed by $SnCl_4$ with dialkyl sulphides and saturated heterocycles such as tetrahydrothiophen but the unstable thiophen adduct is not bonded through sulphur but is considered to be a π-electron complex.[124]

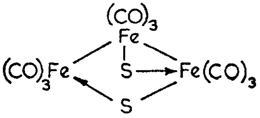
Dimethyl telluride forms the unstable complexes $AgI(Me_2Te)_2$ and $Me_2Te(AgI)_2$; the selenium complex $Me_2Se(AgI)_2$ is very unstable but Me_2S and Me_2O show no sign of co-ordinating to AgI.[6] The stability order towards Hg^{II} halides is also: Te > Se > S.[6]

The infrared spectra of the 1,4-dithian (XXXI) complexes $M(C_4H_8S_2)Cl_2$ (M = Pt, Cu, Cd, Hg) and $Au(C_4H_8S_2)Cl_3$ have been interpreted as denoting that in these compounds the ligand is in the chair configuration, as in 1,4-dithian itself, and that the complexes are most likely polymeric, with each sulphur atom of the ligand bound to a different metal atom. On the other hand, the thioxan (XXX) complexes $M(C_4H_8OS)_2$ (M = Pt, Cu, Hg) are monomeric with the ligand bound through the sulphur atom only.[125]

2,6-Dimethyl-4-thiopyrone (DMPT;XXXII) forms compounds $M(DMTP)_2Cl$ (M = Cu,Ag), $M(DMTP)_2Cl_2$ (M = Fe,Co,Ni,Pd,Pt,Hg), and $M(DMTP)_2Cl_3$ (M = Sb, Bi). It is claimed that the infrared spectra indicate that the ligand is S-bonded.[126] The ligand is a poor donor, as it is readily displaced by water, pyridine, or halide ion.


(XXXII)


(XXXIII)


(XXXIV)

5.2. Sulpho-, Seleno-, and Telluro-derivatives of Metal Carbonyls and Cyclopentadienyls.—Many examples are known of metal carbonyl

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[122] I. Lindqvist and M. Zachrisson, *Acta Chem. Scand.*, 1960, **14**, 453.

[123] T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1959, **81**, 2989.

[124] I. P. Gol'dshtein, E. N. Gur'yanova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **144**, 569, 788.

[125] P. Hendra and D. B. Powell *J.*, 1960, 5105.

[126] H. B. Gray, E. Billig, R. Hall, and L. C. King, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1089.

complexes which contain sulphur-ligands; there are also a few carbonyl complexes known with selenium-ligands. The complex $[Fe(CO)_3SEt]_2$ is dimeric[127] and is similar to the isoelectronic nitrosyl sulphide $[Fe(NO)_2SEt]_2$.[128] An *X*-ray investigation of $[Fe(CO)_3SEt]_2$ shows that the structure is that of two distorted tetragonal pyramids joined together as shown in (XXXIII).[129] The Fe–S distance (2·26 Å) is the same as in $[Fe(NO)_2SEt]_2$, while the Fe–Fe distance is 2·54 Å compared with 2·72 Å in the nitrosyl complex.[130] The geometry gives an explanation of the existence of two isomers of the analogous SMe complex,[131] because the alkyl groups can be *syn* or *anti*. Data obtained from infrared and proton resonance spectra and from magnetic and dipole moment measurements indicate that the compounds $[Fe(CO)_3L]_2$ (L = S, Se, SPh, and SeEt) have two bridging S or Se atoms which do not form a plane with the Fe atoms.[132] The structure of these compounds is, no doubt, similar to that of $[Fe(CO)_3SEt]_2$ (XXXIII). Infrared spectral measurements on the trisubstituted molybdenum carbonyls $Mo(CO)_3L_3$ [L = Me_2S, Et_2S, $(CH_2)_4S$, $(NH_2)_2C{=}S$, $MeC({=}S)NH_2$] show that all the ligands are bonded through sulphur. The thiourea and thioacetamide complexes are the most stable. A comparison of the C–O stretching frequencies indicates that the thioethers have a substantial tendency to function as π-acceptors, though not to the same extent as tertiary phosphines and arsines, while thiourea and thioacetamide have only a small, though definite, tendency to do so.[133] Some of the carbonyl groups in $Ni(CO)_4$ and $Mo(CO)_6$ can be directly substituted by dialkyl sulphides to yield $Ni(CO)_{4-n}(R_2S)_n$ and $Mo(CO)_{6-n}(R_2S)_n$ (n = 1 or 2). The force constant of the C–O stretching mode decreases with increase of sustitution, indicating some degree of π-bonding by the thioether.[134]

The reaction of 2,5-dithiahexane (S–S) and 3,6,9-trithiaundecane (S–S–S) with the hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) yields complexes $M(S{-}S)(CO)_4$ (M = Cr,Mo,W) and $M(S{-}S{-}S)(CO)_3$ (M = Cr, Mo but not W). The reaction of $M(S{-}S)(CO)_4$ with I_2 yields the seven-co-ordinate complexes $M(S{-}S)(CO)_3I_2$ (M = Mo, W). On the other hand, the compound $Mn(S{-}S{-}S)(CO)_3Br$ is probably six-co-ordinate, as it gives a sulphonium salt with methyl iodide, suggesting that in this complex the ligand is co-ordinated through only two of the sulphur atoms.[135]

A thio-bridged rhenium complex $[Re(CO)_4SPh]_2$ is known[136] and thio-

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[127] H. Reihlen, A. von Friedolsheim, and W. Oswald, *Annalen*, 1928, **465**, 72.

[128] K. A. Hofmann and O. F. Wiede, *Z. anorg. Chem.*, 1895, **9**, 300.

[129] L. F. Dahl and Chin-Hsuan Wei, *Inorg. Chem.*, 1963, **2**, 328.

[130] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, 1958, **11**, 599.

[131] R. B. King, *J. Amer. Chem. Soc.*, 1962, **84**, 2460.

[132] W. Hieber and W. Beck, *Z. anorg. Chem.*, 1960, **305**, 265; S. F. A. Kettle and L. E. Orgel, *J.*, 1960, 3890; Chin Hsuan Wei and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 493.

[133] F. A. Cotton and F. Zingales, *Chem. and Ind.*, 1960, 1219; *Inorg. Chem.*, 1962, **1**, 145.

[134] G. Bouquet and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 433.

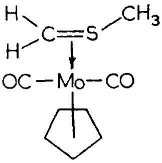
[135] H. C. E. Mannerskantz and G. Wilkinson, *J.*, 1962, 4454.

[136] W. Hieber and L. Schuster, *Z. anorg. Chem.*, 1956, **285**, 205.

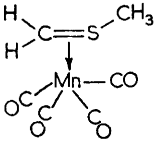
bridged iron complexes have been studied by King.[131,137] Infrared spectral measurements confirm that these compounds do not have bridging carbonyl groups. The structure of the diamagnetic volatile complex $Fe_3(CO)_9S_2$ is probably that shown in (XXXIV).

The reaction of sulphur with $Co_2(CO)_8$ yields a mixture of several sulphur-containing cobalt carbonyl complexes.[138] Other sulphur-containing cobalt carbonyls have also been reported[139] but their structures have not been elucidated.

Cyclopentadienyl complexes $[(C_5H_5)Fe(CO)SMe]_2$, $[(C_5H_5)CoSMe]_2$, $[(C_5H_5)Cr_2(MeS)_3]$, $[(C_5H_5)Mo(MeS)_2]_2$, and $[(C_5H_5)V(MeS)_2]_2$ have been prepared.[140] The iron and cobalt complexes apparently contain two, the chromium complex three, and the molybdenum and vanadium complexes four, sulphur-bridges. Similar nickelocene derivatives $[(C_5H_5)NiSR]_2$ (R = Me,Et,Ph) are known.[141] King and Bisnette[142] recently reported a new type of complex with a sulphur-containing ligand coordinated through a C=S bond; the postulated structures of two of these complexes are shown in (XXXV) and (XXXVI).



(XXXV)



(XXXVI)

Several organotellurium-containing metal carbonyls are known:[143] $(Ph_2Te)Fe(CO)_3Br_2$, $(Ph_2Te)_2Mn(CO)_3X$ (X = Cl, Br, I), and the dimeric complex $[(p\text{-}MeO{\cdot}C_6H_4{\cdot}Te)Fe(CO)_3]_2$; the last compound must contain two tellurium bridges and is similar to the sulphur-bridged complexes described above.

5.3. Complexes of Thiourea and its Derivatives.—Thiourea acts as a unidentate ligand forming strong complexes with (*b*) class metal ions, in particular Cu^I, Ag^I, Au^I, and Hg^{II}. It is noteworthy that Ag^I is complexed more strongly than Cd^{II} and Pb^{II}.[25] Thiourea reduces Cu^{II} to Cu^I, Au^{III} to Au^I, Pt^{IV} to Pt^{II}, and Te^{IV} to Te^{II} and forms complexes with the metal

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[137] R. B. King, *Inorg. Chem.*, 1963, **2**, 641; *J. Amer. Chem. Soc.*, 1963, **85**, 1584.

[138] L. Markó, G. Bor, E. Klumpp, B. Markó, and G. Almasy, *Chem. Ber.*, 1963, **96**, 955.

[139] L. Markó, G. Bor, and E. Klumpp, *Angew. Chem.*, 1963, **75**, 248; E. Klumpp, L. Markó, and G. Bor, *Chem. Ber.*, 1964, **97**, 926; S. A. Khatlob, L. Markó, G. Bor, and B. Markó, *J. Organometallic Chem.*, 1964, **1**, 373.

[140] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600; R. B. King, *ibid.*, 1963, **85**, 1587; R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, 1963, **2**, 219.

[141] W. K. Schropp, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1688.

[142] R. B. King and M. B. Bisnette, *J. Amer. Chem. Soc.*, 1964, **86**, 1267.

[143] W. Hieber and J. Kruck, *Chem. Ber.*, 1962, **95**, 2027.

in the lower oxidation state; hence the claim that thiourea stabilises Rh^{IV} in solution[144] is surprising.

Infrared studies have shown that urea co-ordinates through nitrogen in its complexes with Pd^{II} and Pt^{II} and in $Sn(urea)_2Cl_4$ but through oxygen in its complexes with Cr^{III}, Fe^{III}, Cu^{II}, and Zn^{II} and in $Sn(urea)_2Br_4$.[145,146] On the other hand, thiourea co-ordinates through sulphur, not only with class (*b*) metals,[147] but with Sn^{IV},[146] Pb^{II},[148] and Te^{II};[149] however, infrared spectral measurements indicate that the ligand is co-ordinated through nitrogen in $Ti(tu)_2Cl_4$ (tu = thiourea).[150]

The structures of a number of thiourea complexes have been determined by *X*-ray analysis. The nickel atom in $[Ni(tu)_4Cl_2]$ is surrounded by four sulphur atoms at 2·45 Å and the two chlorine atoms are at 2·40 Å in the *trans*-octahedral sites.[151] Lopez-Castro and Truter[152] also determined the structure of this *high-spin* compound and commented that in diamagnetic Ni^{II} complexes the Ni–S distance is 2·1—2·3 Å, whereas in six-co-ordinate complexes it is 2·4—2·6 Å; this is in accordance with ligand-field theory which predicts that the stronger field produced by the ligands closer to nickel will cause the $d\gamma$ electrons to pair in the d_{z^2} orbitals, so producing a diamagnetic complex with no close neighbours in the *z* direction.

The compound $Ni(tu)_2(NCS)_2$ is octahedral and polymeric; the sulphur atom of each thiourea molecule is bound to two nickel atoms. Each nickel atom is bound to four sulphur atoms at a distance of 2·54 Å and to two nitrogen atoms (at 1·99 Å) from the thiocyanate groups.[153] The S–C distance is abnormally long (1·77 Å) compared with 1·64 Å in thiourea itself[154] and in $Ni(tu)_4Cl_2$.[155,151] The compounds $M(tu)_2(NCS)_2$ (M = Mn,Co,Cd) are isostructural with $Ni(tu)_2(NCS)_2$ but $Zn(tu)_2(NCS)_2$ is not.[151] In the compound $[Ni(py)_2(tu)_2Cl_4]$ (py = pyridine) the sulphur atoms of two of the four thiourea molecules are probably bridging in a similar manner.[156]

The complex $Cd(tu)_2Cl_2$ is tetrahedral but $Pb(tu)_2Cl_2$ has a polymeric structure in which the lead atom is seven-co-ordinate, being surrounded by four bridging sulphur atoms at 2·9—3·1 Å and two bridging chlorine atoms at 3·2 Å, while the non-bridging chlorine is at a distance of 2·75 Å

[144] F. Pantani and P. G. Desideri, *Talanta*, 1960, **5**, 69.

[145] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 1575.

[146] D. S. Bystrov, T. N. Sumarokova, and V. N. Filiminov, *Optics and Spectroscopy*, 1960, **9**, 239.

[147] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527.

[148] M. Nardelli, L. Cavalca, and A. Braibanti, *Gazzetta*, 1956, **86**, 867, 1037.

[149] O. Foss and S. Hauge, *Acta Chem. Scand.*, 1959, **13**, 1252.

[150] R. Rivest, *Canad. J. Chem.*, 1962, **40**, 2234.

[151] M. Nardelli, *Gazzetta*, 1959, **89**, 1616.

[152] A. Lopez-Castro and M. R. Truter, *J.*, 1963, 1309.

[153] M. Nardelli, A. Braibanti, and G. Fava, *Gazzetta*, 1957, **87**, 1209.

[154] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, 1931, **81**, 386.

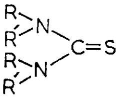
[155] L. Cavalca, M. Nardelli, and A. Braiban , *Gazetta*, 1956, **86**, 942.

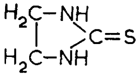
[156] A. V. Babaeva and Yan Vei-da, *Zhur. neorg. Khim.*, 1960, **5**, 2735.

from the central metal atom.[151] In $[\mathrm{Te(tu)_4}]\mathrm{Cl_2}$ each tellurium atom has a square-planar arrangement of four sulphur atoms.[157]

The complex $[\mathrm{Mo(tu)_3Cl_3}]$ has a magnetic moment of 3·71 B.M.,[158] within the range 3·66—3·88 B.M. found for most $\mathrm{Mo^{III}}$ compounds,[159] but the complex $[\mathrm{Mo_2(tu)_3Cl_6}]$ has a moment of 0·59 B.M. In the latter complex the two molybdenum octahedra are bridged by either three chlorine or three sulphur atoms (from the thiourea groups) and the low value of the magnetic moment is ascribed to spin–orbit coupling due to metal–metal interaction, either directly or *via* the bridging atoms.[158,160]

Complexes of *NN'*-substituted thioureas (XXXVII); R = alkyl or aryl, R' = alkyl, aryl, or H have been extensively studied. Ethylenethiourea


(XXXVII)


(XXXVIII)

(etu; XXXVIII) with $\mathrm{Cu^{I}}$ and $\mathrm{Ag^{I}}$ gives complexes containing 1, 2, 3, or 4 molecules of ligand, whereas with $\mathrm{Au^{I}}$ complexes with 1 or 2 ligand molecules only are formed.[161] Complexes of ethylenethiourea with $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$, and $\mathrm{Ni^{II}}$ have also been investigated.[162,163] $\mathrm{Cu^{I}}$ and $\mathrm{Ag^{I}}$ complexes with other substituted thioureas are known; their structures are often complex.[164] $\mathrm{Te^{II}}$ and $\mathrm{Te^{IV}}$ complexes of several substituted thioureas have been reported.[165]

The complexes $[\mathrm{Ni(ntu)_2X_2}]$ [X = Cl,Br; ntu = 1-(1-naphthyl)- 2-thiourea] are tetrahedral; the paramagnetic compounds $\mathrm{Ni(etu)_4X_2}$ (X = Cl,Br) are octahedral and have been isolated in *cis* and *trans* forms but the iodo-complex $\mathrm{Ni(etu)_4I_2}$ is six-co-ordinate[166] and is a rare example of a tetragonal diamagnetic $\mathrm{Ni^{II}}$ complex,[167] while the perchlorate $[\mathrm{Ni(etu)_4}](\mathrm{ClO_4})_2$ is diamagnetic and square-planar. Holt and Carlin[166] have pointed out that systems in which $\mathrm{Ni^{II}}$ attains a variety of stereochemical environments with the one donor atom are rare, yet with 1-(1-naphthyl)-2-thiourea $\mathrm{Ni^{II}}$ gives tetrahedral, and with ethylenethiourea paramagnetic octahedral, diamagnetic tetragonal, and diamagnetic square-

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[157] O. Foss and S. Hauge, *Acta Chem. Scand.*, 1961, **15**, 1616.

[158] V. B. Evdokmov, V. V. Zelenstov, I. D. Kolli, Wen-Hsia T'ang, and V. I. Spitsyn, *Doklady Akad. Nauk S.S.S.R.*, 1962, **145**, 1282.

[159] B. N. Figgis, and J. Lewis in "Modern Co-ordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 425.

[160] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, 1965, **18**, in the press.

[161] G. T. Morgan and F. H. Burstall, *J.*, 1928, 143.

[162] M. Nardelli, I. Chierici, and A. Braibanti, *Gazzetta*, 1958, **88**, 37.

[163] R. L. Carlin and S. L. Holt, *Inorg. Chem.*, 1963, **2**, 849.

[164] S. N. Banerjee and A. C. Sukthankar, *J. Indian Chem. Soc.*, 1963, **40**, 387.

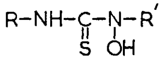
[165] O. Foss and W. Johannessen, *Acta Chem. Scand.*, 1961, **15**, 1939, 1947, and references therein.

[166] S. L. Holt and R. L. Carlin, *J. Amer. Chem. Soc.*, 1964, **86**, 3017.

[167] C. M. Harris and S. E. Livingstone, *Rev. Pure and Appl. Chem.* (*Australia*), **1962, 12,** 16.

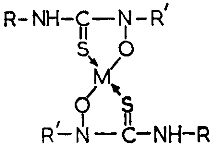
planar complexes, in addition to what appear to be the first isolated geometrical isomers of octahedral Ni^{II}.

NN'-Diethylthiourea, *NN'*-diphenylthiourea, and *NN*-diphenylthiourea behave as bidentate chelating agents, being bonded through both nitrogen atoms, in the complexes $2TiCl_4,L$ (L = substituted thiourea).[150] *S*-Acetylthiourea (satu) forms with Cu^I only a 1:1 complex Cu(satu)Cl;[168] it would be interesting to know if the ligand is N- or S-bonded in this compound. Bis-chelated complexes of Co^{II}, Ni^{II}, and Cu^{II} are formed by a number of *NN'*-diaryl-*N*-hydroxothioureas (XXXIX); the hydrogen of the OH group is replaced and the ligand is most probably co-ordinated through sulphur and oxygen as in (XL).[169]



$R{-}NH{-}\underset{\underset{S}{\|}}{C}{-}\underset{\underset{OH}{|}}{N}{-}R'$

(XXXIX)



(XL)

Data obtained from an investigation of Co^{II} complexes indicate that ethylenethiourea is higher in the spectrochemical series than R_2S, lying between N_3^- and Ph_3PO. B' is 66% of the value for the free ion, suggesting appreciable orbital overlap, which is to be expected for the large polarisable sulphur atom; the position of etu is thus at the low end of the nephelauxetic series, approximately equal to that of iodide ion.[163]

5.4. Selenourea Complexes.—Selenourea (su) gives precipitates which are soluble in the presence of excess of the ligand with Pd,Cu,Ag,Au,Hg, Sn, As, Sb, and Bi and a Pb complex which is insoluble in excess. Bi^{III} forms a yellow complex with a Bi:su ratio of 1:9 and a red 1:12 complex:[170] their structures are unknown but they are more stable than $[Bi(tu)_6]^{3+}$.[171] Whereas Os^{III} forms a 6:1 complex with thiourea $[Os(tu)_6]$,$^{3+}$ with selenourea an 8:1 complex $[Os(su)_8]^{3+}$ is formed; apparently the latter is a genuine eight-co-ordinate complex, as the bluish-green colour is not produced in solution until the eighth mol. of ligand has been added.[172]

5.5. Thioacetamide and Thiobenzamide Complexes.—Thioacetamide, $CH_3{\cdot}CS{\cdot}NH_2$ (tam) gives complexes $[M(tam)_4]^+$ (M = Cu, Ag) which are S-bonded and tetrahedral.[173] On the other hand, Au^I forms a two-covalent complex $[Au(tam)_2]Br$.[174] With bivalent metals tetrahedral

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[168] S. K. Siddhanta and S. N. Banerjee, *J. Indian Chem. Soc.*, 1961, **38**, 747.
[169] B. Hirsch, *J. prakt. Chem.*, 1961, **12**, 264.
[170] A. T. Pilipenko and I. P. Sereda, *Zhur. analit. Khim.*, 1958, **13**, 3.
[171] S. I. Gusev and L. A. Ketova, *Zhur neorg. Khim.*, 1961, **6**, 1881.
[172] A. T. Pilipenko and I. P. Serada, *Zhur. neorg. Khim.*, 1961, **6**, 413.
[173] N. S. Kurkaskov, *Zhur. Russ. Fiz.-Khim. Obshch.*, 1893, **25**, 693; *J. prakt. Chem.*, 1895, [2], **51**, 234; E. G. Cox, W. Wardlaw, and K. C. Webster, *J.*, 1936, 775; D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1960, **82**, 4169.
[174] F. H. Brain and C. S. Gibson, *Brit. Assoc. Advance Sci. Report*, 1938, p. 37.

complexes [M(tam)$_2$Cl$_2$] (M = Fe,Co,Zn,Cd) and octahedral complexes [M(tam)$_4$Cl$_2$] (M = Ni,Cd) are known.[175] Dioximato-complexes of Co^{III} containing one or two molecules of thiocetamide have been recently reported, *viz.*, [Co(DH)$_2$(tam)X] and [Co(DH)$_2$(tam)$_2$]$^+$; similar complexes are known with other unidentate sulphur ligands such as thiourea and thiosemicarbazide.[97] Thiobenzamide behaves similarly to thioacetamide and forms complexes with class (*b*) metal ions.[176]

5.6. Triphenylphosphine Sulphide and Selenide.—Whereas triphenylphosphine oxide, Ph$_3$PO, forms a variety of interesting complexes with first-row transition elements,[177] the donor properties of Ph$_3$PS and Ph$_3$PSe appear to be rather weak; however, the insoluble complexes Pd(Ph$_3$PS)$_2$ Cl$_2$, Pd(Ph$_3$PSe)$_2$Cl$_2$, and Sn(Ph$_3$PSe)$_2$Cl$_4$ have been reported.[178]

5.7. Dimethyl Sulphoxide Complexes.—Dimethyl sulphoxide, Me$_2$SO, forms complexes with transition metal ions. The ligand is bound through oxygen except in the Pd^{II} and Pt^{II} complexes where it is S-bonded.[179]

6. Complexes of Chelate Ligands

6.1. Chelate Ligands with Thioether or Selenoether Groups.—Chelate ligands with two thioether groups give similar complexes to those formed by unidentate thioethers. 1,2-Dialkyl- and diaryl-dithioethanes RS·CH$_2$·CH$_2$·SR form stable complexes with most (*b*) class metals and some borderline metals such as Bi^{III} and Sn^{IV}.[100,180,181,182] The diselenoether EtSe·CH$_2$·CH$_2$·CH$_2$·SeEt forms a 1:1 complex with PtCl$_2$ similar to the dithioethers.[103] Spectral data obtained from Ni^{II} complexes shows that 1,2-dialkyldithioethanes have a ligand-field stronger than ethylenethiourea and almost as strong as NH$_3$.[183] For organometallic derivatives of transition metals to be stable it is necessary to have present in the complex other ligands, such as tertiary phosphines, capable of accepting d_π electrons from the metal atom; 1,2-dimethyldithioethane has a sufficiently strong ligand-field to stabilise the Pt–Me bonds in (EtS·CH$_2$·CH$_2$·SEt)PtMe$_2$.[184] Titanium(IV) forms the complexes (RS·CH$_2$·CH$_2$·SR)TiX$_4$ (R = Ph,Me; X = Cl,Br).[117] Although aliphatic dithioethers form octahedral Ni^{II}

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[175] M. Nardelli and I. Chierici, *Gazzetta*, 1957, **87**, 1478.

[176] F. Kašpárek and J. Mollin, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2919.

[177] E. Bannister and F. A. Cotton, *J.*, 1960, 1873, 1878.

[178] E. Bannister and F. A. Cotton, *J.*, 1960, 1959.

[179] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986; F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534; D. W. Meek, D. K. Straub, and R. S. Drago, *J. Amer. Chem. Soc.*, 1960, **82**, 6013; J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nuclear Chem.*, 1961, **16**, 219.

[180] L. Tschugaeff, *Ber.*, 1908, **41**, 222.

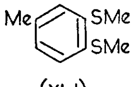
[181] Z. Tschougaeff and D. Fraenkel, *Compt. rend. Acad. Sci.*, 1912, **154**, 33; L. Tschugaeff and A. Kobljanski, *Z. anorg. Chem.*, 1913, **83**, 8.

[182] G. M. Bennett, A. N. Moses, and F. S. Statham, *J.*, 1930, 1668.

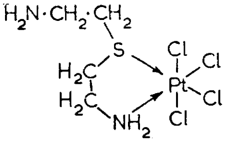
[183] R. L. Carlin and E. Weissberger, *Inorg. Chem.*, 1964, **3**, 611.

[184] J. Chatt and B. L. Shaw, *J.*, 1959, 705.

complexes, 4-methylthioveratrole (XLI) shows little tendency to co-ordinate to Ni^{II}.[180,185]



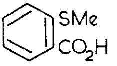
(XLI)



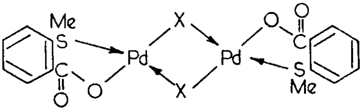
(XLII)

Chelate ligands having a thioether sulphur and another donor atom often co-ordinate more strongly than dithioethers. The co-ordinating ability of some β-aminothioethers $RS{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ has been investigated.[186] The free NH_2 group in the Pt^{IV} complex (XLII) is capable of forming salts and the complex was optically resolved showing that the asymmetry is due to the tercovalent sulphur atom.[187]

o-Methylmercaptobenzoic acid (XLIII) forms inner complexes with Pd^{II}, Cu^{II}, Cd^{II}, and Hg^{II} but not with Pt^{II} which has a low affinity for oxygen-ligands.[188,189] This and other *o*-alkylmercaptobenzoic acids form halogen-bridged dinuclear complexes (XLIV; M = Pd, Cu, Hg; X = Cl or Br).[189,190,191]



(XLIII)



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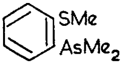

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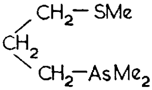

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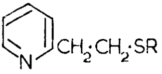
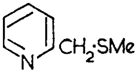
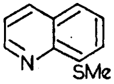


(XLVII)



(XLVIII)



(XLIX)

Dimethyl-*o*-methylthiophenylarsine (XLV) forms strong complexes with Co^{II}, Rh^{III}, Ir^{III}, Ni^{II}, Pd^{II}, Pt^{II}, Cu^{I}, Ag^{I}, and Au^{I}.[192,193,194] This ligand forms complexes of Pd^{II} and Pt^{II} having co-ordination numbers

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[185] R. Backhouse, M. E. Foss, and R. S. Nyholm, *J.*, 1957, 1714.

[186] E. Gonick, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1954, **76,** 4671.

[187] F. G. Mann, *J.*, 1930, 1745.

[188] S. E. Livingstone, R. A. Plowman, and J. Sorenson, *J. Proc. Roy. Soc. New South Wales*, 1950, **84,** 28.

[189] S. E. Livingstone and R. A. Plowman, *J. Proc. Roy. Soc. New South Wales*, 1951, **85,** 116.

[190] S. E. Livingstone and R. A. Plowman, *J. Proc. Roy. Soc. New South Wales*, 1950, **84,** 188.

[191] S. E. Livingstone, *J.*, 1956, 1989.

[192] S. E. Livingstone, *Chem. and Ind.*, 1957, 143; *J.*, 1958, 4222.

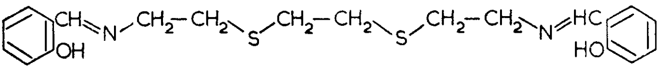
[193] B. Chiswell and S. E. Livingstone, *J.*, 1959, 2931; 1960, **97,** 3181.

[194] B. Chiswell and S. E. Livingstone, *J.*, 1960, 1071.

greater than the usual value of four.[167,194,195] On the other hand, dimethyl-3-methylthiopropylarsine (XLVI) forms stable complexes with Pd$^{\text{II}}$, Pt$^{\text{II}}$, and Cu$^{\text{I}}$ only, unstable products being formed with other (*b*) class metals.[196]

2-(2-Methylthioethyl)pyridine (XLVII; R = Me) gives stable chelates with typically (*b*) metals.[197] Measurements of stability constants indicate that 2-(2-methylthiomethyl)pyridine (XLVIII) also acts as a chelate group.[198] 8-Methylthioquinoline (XLIX; N—S) appears to give only 1:1 complexes of the type $M(N\text{–}S)X_2$ with Pd$^{\text{II}}$, Pt$^{\text{II}}$, and Hg$^{\text{II}}$ but the 2:1 complex $[Cu(N\text{–}S)_2](ClO_4)_2$ can be readily isolated.[199]

Schiff bases derived from 1,8-diamino-3,6-dithiaoctane, by the loss of two protons, function as sexadentates; the bond angles about the sulphur atoms are such that the molecule can fit almost strainlessly around the six octahedral positions of a metal ion. The Co$^{\text{III}}$ complex, of 1,8-bis(salicylideneamino)-3,6-dithiaoctane (L) was resolved and found to have a high value for the molecular rotation.[200] The Schiff bases derived from pyridine-2-aldehyde and acetylacetone also function as sexadentates.[201] Schiff bases formed by the condensation of salicyaldehyde with α,ω-diamines of general formula $H_2N{\cdot}[CH_2]_x{\cdot}S{\cdot}[CH_2]_y{\cdot}S{\cdot}[CH_2]_z{\cdot}NH_2$ (x, y, z = 2 or 3) form Co$^{\text{III}}$ complexes with very high values for $[M]^{\mathrm{D}}$.[202]



(L)

6.2. Chelate Ligands containing One Thiol Group.—The stability constants have been measured for some metal complexes of the following ligands:[25] thioglycollic acid, $HS{\cdot}CH_2{\cdot}CO_2H$; β-mercaptopropionic acid, $HS{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$; 2-aminoethanethiol, $HS{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$; cysteine, $HS{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$; mercaptosuccinic acid, $HO_2C{\cdot}CH(SH){\cdot}CH_2{\cdot}CO_2H$. However, the available data do not usually allow comparisons to be made between complexes of analogous sulphur- and oxygen-ligands. It is noteworthy that cysteine forms extremely stable complexes with Hg$^{\text{II}}$ and Fe$^{\text{III}}$. The stabilities of UO_2^{2+} chelates of hydroxy-, mercapto-, and amino-derivatives of acetic, propionic, and succinic acids fall in the series: $NH_2 > OH > SH$[203] and Am$^{\text{IV}}$ forms a stronger complex with glycollate

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[195] S. E. Livingstone and B. Wheelahan, *Austral. J. Chem.*, 1964, **17**, 219.

[196] B. Chiswell and S. E. Livingstone, *J. Inorg. Nuclear Chem.*, 1961, **23**, 37.

[197] P. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, unpublished work.

[198] K. Kahmann, H. Sigel, and H. Erlenmeyer, *Helv. Chim. Acta*, 1964, **47**, 1754.

[199] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, unpublished work.

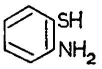
[200] F. P. Dwyer and F. Lions, *J. Amer. Chem. Soc.*, 1947, **69**, 2917.

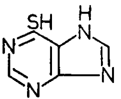
[201] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, 1957, **79**, 1269; F. Lions and K. V. Martin, *ibid.*, 1958, **80**, 3858.

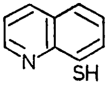
[202] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, 1952, **74**, 4188.

[203] M. Cefola, R. C. Taylor, P. S. Gentile, and A. V. Celiano, *J. Phys. Chem.*, 1962, **66**, 790.

than with thioglycollate ion;[204] these results indicate the (*a*) class behaviour of UO_2^{2+} and Am^{IV}. The stabilities of complexes of Co^{II}, Ni^{II}, Ag^{I}, Zn^{II}, and Hg^{II} with mercaptosuccinic acid are higher than for the nitrogen- and oxygen-analogues, aspartic and malic acids.[205] The chelating tendencies of some α-mercaptoacetamides $RNH{\cdot}CO{\cdot}CH_2SH$ (R = aryl) have been examined; for these ligands $UO_2 > Be > Ni > Mn$.[206] The chelates of Zn^{II} and Pb^{II} with *o*-aminobenzenethiol (LI) and 6-mercaptopurine (LII) are more stable than the corresponding oxygen-chelates.[207]


(LI)

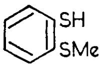

(LII)

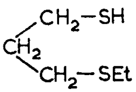

(LIII)

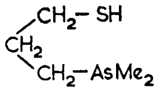
o-Aminobenzenethiol forms low-spin inner complexes with Co^{II} and Ni^{II}.[26a,208] The yellowish-buff Ni^{II} complex can be converted in strongly alkaline medium into a deep blue compound which is said to contain Ni^{IV}.[208]

8-Mercaptoquinoline (LIII) forms strong chelates with class (*b*) metals.[209,210,211] There is a considerable bathochromic shift in the long-wave absorption maxima of the chelates of Ru^{III}, Os^{III}, Rh^{III}, Ir^{III}, Pd^{II}, and Pt^{II}; this shift is ascribed to the high strength of the M–N bond.[211] The chelates of the platinum metals with 5-chloro-8-mercaptoquinoline and 5-bromo-8-mercaptoquinoline are more stable than those of (LIII). The stability of the chelates of 5-chloro-8-mercaptoquinoline is in the order $Pd > Pt > Rh > Ir > Ru > Os$.[212]

o-Methylthiobenzenethiol (LIV), 3-ethylthiopropane-1-thiol (LV) and


(LIV)


(LV)


(LVI)

3-dimethylarsinopropane-1-thiol (LVI) form square-planar inner complexes with Ni^{II}, Pd^{II}, and Pt^{II}.[26a,213] With Pd^{II} these ligands form thiolo-

[204] I. Grenthe, *Acta Chem. Scand.*, 1962, **16**, 1695.

[205] G. R. Lenz and A. E. Martell, *Inorg. Chem.*, 1965, **4**, 378.

[206] D. F. Martin, *J. Amer. Chem. Soc.*, 1961, **83**, 1076.

[207] R. G. Charles and H. Freiser, *J. Amer. Chem. Soc.*, 1952, **74**, 1385; G. E. Cheney, H. Freiser, and Q. Fernando, *ibid.*, 1959, **81**, 2611.

[208] W. Hieber and R. Brück, *Naturwiss.*, 1949, **36**, 312; *Z. anorg. Chem.*, 1952, **269**, 13.

[209] J. Bankovskis, A. Ievinš, and Z. Lepina, *Zhur. analit. Khim.*, 1960, **15**, 4; Yu.I. Usatenko and V. I. Suprunovich, *Latvijas P.S.R. Zinatnu Akad. Vestis, Kim. Ser.*, 1963, 181; A. Corsini, Q. Fernando, and H. Freiser, *Talanta*, 1963, **11**, 63.

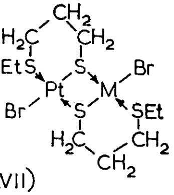
[210] E. V. Vasil'eva, T. K. Nedopekin, and V. E. Petrun'kin, *Ukrain khim. Zhur.*, 1962, **28**, 773.

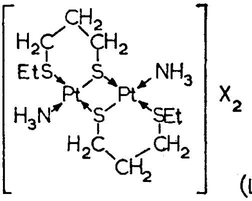
[211] J. Bankovskis, G. Mezarups, and A. levinš, *Zhur. analit. Khim.*, 1962, **17** 721.

[212] J. Bankovskis, G. Mezarups, and A. Ievinš, *Latvijas P.S.R. Zinatnu Akad.,Vestis, Kim. Ser.*, 1962, 323; J. Cirule, J. Bankovskis, A. Ievinš, and J. Asaks, *ibid.*, 1964, 135.

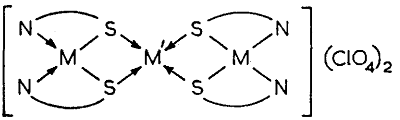
[213] S. E. Livingstone, *J.*, 1956, 437.

bridged compounds which are more stable than halogen-bridged complexes. The ligand (LV) gives similar Pt^{II} bridged complexes and also binuclear complexes containing another metal atom in addition to Pt (LVII; M = Hg, Pd). The cationic bridged complex (LVIII; X = Cl, ClO_4) was also isolated.[214]


(LVII)


(LVIII)

With Ni^{II} mercaptoacetic acid forms the monomeric complex $[Ni(SCH_2CO_2)_2]^{2-}$ and the multinuclear thiolo-bridged species $[Ni_4(SCH_2CO_2)_6]^{4-}$.[215] 2-Aminoethanethiol gives a trinuclear cationic complex (LIX; M = M′ = Ni).[216] 2-(2-Mercaptoethyl)pyridine (XLVII; R = H) gives inner complexes and binuclear bridged complexes with Ni^{II}, Pd^{II}, and Pt^{II} and also trinuclear complexes (LIX; M = Ni and M′ = Ni, Pd).[217] Square-planar Ni^{II} complexes of some chelating thiols have been used in template reactions to produce macrocyclic ligands *in situ*.[218] Template syntheses—a fascinating new development in co-ordination chemistry—involving sulphur ligands have been used to prepare quadridentate complexes of Zn^{II}, Cd^{II}, and Hg^{II}.[219]


(LIX)

Thioamidopyridine (LX) forms high-spin complexes $[M(C_6H_6N_2S)_3](ClO_4)_2$ (M = Fe, Co, Ni); complexes of Co^{III}, Cu^{I}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II} are also known.[220] *N*-2-Mercaptophenylene-2′-pyridylmethyleneimine (LXI) acts as a terdentate and forms binuclear complexes containing eight-

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[214] S. E. Livingstone, *J.*, 1956, 1994.

[215] D. L. Leussing, R. E. Laramy, and G. S. Alberts, *J. Amer. Chem. Soc.*, 1960, **82**, 4826.

[216] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, 1962, **1**, 872, 878.

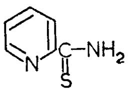
[217] J. W. Wrathall and D. H. Busch, *Inorg. Chem.*, 1963, **2**, 1182.

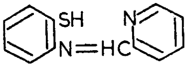
[218] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 1962, **84**, 1762; D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *ibid.*, 1964, **86**, 3651.

[219] H. Jadamus, Q. Fernando, and H. Freiser, *J. Amer. Chem. Soc.*, 1964, **86**, 3056.

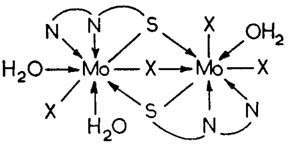
[220] G. J. Sutton, *Austral. J. Chem.*, 1963, **16**, 371, 1137; 1964, **17**, 1360.

(LX)

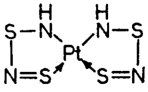




(LXI)



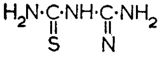
(LXII)



(LXIII)

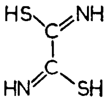
co-ordinate Mo^{III} (LXII; X = Cl,Br). Similar Mo^{III} complexes are formed by a number of other chelating thiols; all have anomalously low magnetic moments due to metal–metal interaction.[160]

The thionitrosyl complex $Pt(S_2N_2H)_2$ has the *cis*-planar configuration (LXIII)[221] but the Ni^{II} complex of the mono-*N*-methyl derivative, *viz.*, $Ni(S_2N_2Me)_2$, is *trans*-planar.[222] Complexes of neutral and deprotonated guanylthiourea (LXIV) are known.[223] The crystal structure of dithio-oxamide (rubeanic acid; LXV) has been recently determined;[224] this ligand



$H_2N{\cdot}C(=S){\cdot}NH{\cdot}C(=N){\cdot}NH_2$

(LXIV)



(LXV)

forms insoluble complexes which are probably polymeric.[225] Its use as an analytical reagent has been reviewed[226] and the structures of its metal complexes and those of *NN'*-disubstituted dithio-oxamides have been discussed.[227]

Thiosemicarbazide exists in tautomeric forms (LXVI) and (LXVII) and can act as a neutral or a charged chelate group. The inner complexes of Ni^{II}, Pd^{II}, and Pt^{II} were each obtained in two forms which were assumed to be *cis–trans* isomers.[228] However, a structure determination of the red form of $Ni(CH_4N_3S)_2$ shows it to be *trans* square-planar with nearly complete localisation of the double bond between the nitrogen and carbon

[221] I. Lindqvist and J. Weiss, *J. Inorg. Nuclear Chem.*, 1958, **6**, 184; I. Lindqvist and R. Rosenstein, *ibid.*, 1958, **7**, 421.

[222] J. Weiss and M. Ziegler, *Z. anorg Chem.*, 1963, **322**, 184.

[223] P. Rây, *Chem. Rev.*, 1961, **61**, 313.

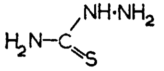
[224] P. J. Wheatley, *J.*, 1965, 396.

[225] K. A. Jensen, *Z. anorg Chem.*, 1944, **252**, 227; R. V. G. Ewens and C. S. Gibson, *J.*, 1949, 3308.

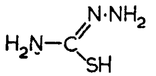
[226] R. Rây and J. Xavier, *J. Indian Chem. Soc.*, 1961, **38**, 535.

[227] R. N. Hurd, G. de la Mater, G. C. McElheny, and L. V. Peiffer, *J. Amer. Chem. Soc.*, 1960, **82**, 4454; R. N. Hurd, G. de la Mater, G. C. McElheny, and J. P. McDermott, in, "Advances in the Chemistry of the Co-ordination Compounds," ed. S. Kirchner, Macmillan, New York, 1961, p. 350.

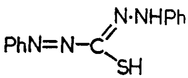
[228] K. A. Jensen and E. Raneke-Madsen, *Z. anorg. Chem.*, 1934, **219**, 243; K. A. Jensen, *ibid.*, 1934, **221**, 6, 11.



(LXVI)



(LXVII)

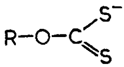


(LXVIII)

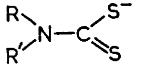
atoms. Although both forms are diamagnetic, it seems doubtful if the grey form is the *cis*-isomer but a structure determination was not possible.[229] Two isomeric forms of the inner complex of Co^{III} have been isolated; their colours suggest that they are *cis–trans* isomers.[230] Complexes of Schiff bases of thiosemicarbazide have been recently reported.[231]

3-Mercapto-1,5-diphenylformazan (dithizone = HDz; LXVIII) forms highly coloured inner complexes with most (*b*) class and several borderline metals; it forms Et_3SnDz, Et_2SnDz, and Et_3PbDz.[232] A crystal structure determination of Hg Dz_2,2py shows that the mercury atom is bound to the sulphur atoms of each dithizone but the nitrogen atom of the azo-group is weakly co-ordinated at a distance of 0·4—0·5 Å greater than expected for a covalent bond, giving the molecule a distorted tetrahedral arrangement.[233] However, in $CuDz_2$ the copper atom is square-planar and the ligand is bidentate.[234]

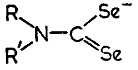
6.3. Alkyl Xanthates, Dialkyl-dithiocarbamates, -diselenocarbamates, -dithiophosphates, and -diselenophosphates.—Four membered chelate rings are formed by alkyl xanthates (LXIX), dialkyl-dithiocarbamates (LXX), -diselenocarbamates (LXXI), -dithiophosphates (LXXII), and -diselenophosphates (LXXIII). These ligands form inner complexes with class (*b*) bi- and ter-valent metals. The xanthate complexes are less stable than



(LXIX)

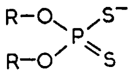


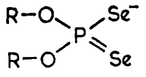
(LXX)



(LXXI)

(LXXII)





(LXXIII)

those of dithiocarbamates.[235] The Ni^{II} complexes of (LXIX), (LXX), and (LXXII) are spin-paired.[235,236,237] As might be expected, the Hg^{II} complex of diethyldithiocarbamate has a high stability constant.[238] Reviews have

[229] M. Nardelli and P. Boldrini, *Gazzetta*, 1961, **91**, 280; L. Cavalca, M. Nardelli, G. Fava, *Acta Cryst.*, 1962, **15**, 1139.

[230] N. M. Samus, *Zhur. neorg. Khim.*, 1963, **8**, 72.

[231] A. V. Ablov and N. I. Belichuk, *Zhur. neorg. Khim.*, 1963, **8**, 77, 612; A. V. Ablov and N. V. Gerbeleu, *ibid.*, 1964, **9**, 85.

[232] H. Irving and C. F. Bell, *J.*, 1954, 4253; H. Irving and J. J. Cox, *J.*, 1961, 1470, and references therein.

[233] M. M. Harding, *J.*, 1958, 4136.

[234] R. F. Bryan and P. M. Knopf, *Proc. Chem. Soc.*, 1961, 203.

[235] L. Malatesta, *Gazzetta*, 1940, **70**, 541, 553.

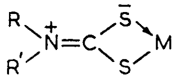
[236] L. Cambi and L. Szego, *Ber.*, 1931, **64**, 2591; 1933, **66**, 656.

[237] L. Malatesta and R. Pizzotti, *Chimica e industria*, 1945, **27**, 6.

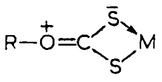
[238] W. Kemula, A. Hulanicki, and W. Nawrot, *Roczniki Chem.*, 1962, **36**, 1717.

been written on metal complexes of dithiocarbamates[239,240] and dithiophosphates[241] while the visible–ultraviolet spectra of the transition-metal complexes of these ligands have been discussed.[1,12,242]

The infrared spectra of dithiocarbamate complexes show that there is considerable double-bond character in the C–N bond (LXXIV) but in the xanthate complexes the canonical form (LXXV) contributes little to the structure.[243] The P–S bond has little double-bond character in the diethyldithiophosphate complexes.[1] A structure analysis of Ni^{II} *NN*-diethyldithiocarbamate shows square-co-ordination of the four sulphur atoms about the nickel and the C = S double bond is delocalised in the chelate ring while the C–N and C–S distances are shorter than expected for single bonds.[244]



(LXXIV)



(LXXV)

In Cu^{II} *NN*-diethyldithiocarbamate the copper atom is at the apex of a pyramid with four sulphur atoms at the base.[245] In the di-n-propyl homologue the copper atom is five-co-ordinate and 0·4 Å above the plane of the square containing the four sulphur atoms; there are four short (2·32 Å) and one long intermolecular (2·71 Å) Cu–S bonds.[246] Although readily soluble in organic solvents, *NN*-diethyldithiocarbamate complexes of Cu^{I}, Ag^{I}, and Au^{I} are polymeric, the degree of polymerisation being 2 for Au, 4 for Cu, and 6 for Ag; the Au atom is two-covalent while Cu and Ag are tri-co-ordinate. The ligands are not chelated but bound through both sulphur atoms to different metal atoms. All the complexes have short metal–metal distances, that for the Au complex (2·76 Å) being shorter than in the metal. The dimethyl homologues are practically insoluble in organic solvents and are probably highly polymeric. It seems that the steric requirement of the ligand is the important factor in deciding the co-ordination number of the metal and the configuration of the complex.[247]

The diamagnetic complex $[Co(Me_2NCS_2)_2NO]$ has a rectangular pyramidal configuration with NO at the apex and the Co atom lying 0·54 Å above the basal plane.[248] The Mo^{V} xanthate complex $[(EtOCS_2)_2$

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[239] K. Gleu and R. Schwab, *Angew. Chem.*, 1950, **62**, 320.

[240] M. Delépine, *Bull. Soc. chim. France*, 1958, **5**.

[241] A. I. Busev and M. L. Ivanyutin, *Trudy Komisii Anal. Khim. Akad. Nauk S.S.S.R., Inst. Geokhim. i anala. Khim.*, 1960, **11**, 172.

[242] S. Kida and H. Yoneda, *J. Chem. Soc. Japan*, 1955, **76**, 1059.

[243] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemi*, 1956, **29**, 75.

[244] E. A. Shugam and V. M. Levina, *Kristallografiya*, 1960, **5**, 32.

[245] R. Bally, *Compt. rend.*, 1963, **257**, 425.

[246] G. Peyronel and A. Pignedou, *Ricerca sci.*, 1959, **29**, 1505; *Gazzetta*, 1962, **92**, 745.

[247] R. Hesse, "Advances in the Chemistry of the Co-ordination Compounds" (Proc. 6 ICCC, Detroit), ed. S. Kirchner, MacMillan, New York, 1961, p. 314; *Arkiv. Kemi*, 1963, **20**, 481.

[248] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J.*, 1962, 668.

MoO]$_2$O, first reported by Malatesta,[249] has a configuration consisting of two distorted molybdenum octahedra sharing a bridging oxygen atom; the metal–metal interaction occurs *via* the bridging oxygen, as the Mo–Mo distance is 3·72 Å.[250] In the monomeric diamagnetic complex ReCl$_2$(Et$_2$NCS$_2$) the Re$^{\text{III}}$ atom is said to be tetrahedral with d^3s hybridisation.[251]

The infrared spectrum of the Pt$^{\text{II}}$ complex of *NN*-diethyldithiocarbamate indicates single bond-order in the C–S bond, while the Pt–S stretching mode occurs at 375 cm.$^{-1}$.[252] The M–S stretching frequencies of the Ni$^{\text{II}}$, Pd$^{\text{II}}$, Co$^{\text{III}}$, and Cr$^{\text{III}}$ chelates of diethyldithiophosphate occur in the range 308—358 cm.$^{-1}$.[253]

Whereas Fe$^{\text{III}}$ complexes of xanthates are spin-paired and those of monoalkylcarbamates RNH·CS$_2^-$ are spin-free, the magnetic moments of the complexes Fe(RR′N·CS$_2$)$_3$ are temperature-dependent and lie between the values expected for one and five unpaired electrons. The ligand-field in these complexes is close to the critical value which determines the transition $3d\epsilon^5 \rightarrow 3d\epsilon^3\ 3d\gamma^2$.[2,236]

Complexes of dialkyl-diselenocarbamates and -diselenophosphates have been reported.[254,255] Although most of the known complexes of the ligands described in this section contain class (*b*) or borderline metals, Se$^{\text{II}}$ complexes have been reported with dialkyldiselenocarbamates[256] and diethyldithiophosphate.[257] Amines give 1:1 adducts with Zn and Cd *NN′*-diethyldithiocarbamate; the latter is the first reported example of five-co-ordinate Cd$^{\text{II}}$.[258] Dioximato-complexes of Co$^{\text{III}}$ are known with 1 and 2 molecules of dialkyldithiocarbamate, which is displaced by halide ion.[259] The infrared spectra of the carbonyl complexes Mn(CO)$_4$(Et$_2$NCS$_2$), Fe(CO)$_2$(Me$_2$NCS$_2$)$_2$, and Rh(CO)$_2$(Me$_2$NCS$_2$) show partial double-bond character in the C–N bond while the sulphur-ligands have no marked effect on the M–CO multiple bonding.[260] The Ni$^{\text{II}}$ complexes of ethyl xanthate and diethyldithiophosphate form green 2:1 pyridine adducts which are octahedral and paramagnetic.[12] The spectra of solutions of Ni$^{\text{II}}$ diethyldithiophosphate containing secondary or heterocyclic amines have been interpreted as indicating distorted five-co-ordination.[261]

Ethyl xanthate, diethyldithiophosphate, and diethyldiselenophosphate

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[249] L. Malatesta, *Gazzetta*, 1939, **69**, 408.

[250] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024.

[251] R. Colton, R. Levitus, and G. Wilkinson, *J.*, 1960, 5275.

[252] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, 1963, **39**, 423.

[253] S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Austral. J. Chem.*, 1965, **18**. 673.

[254] D. Barnard and D. T. Woodbridge, *J.*, 1961, 2922.

[255] C. K. Jørgensen, *Mol. Phys.*, 1962, **5**, 485.

[256] A. Rosenbaum, H. Kirchberg, and E. Leibnitz, *J. prakt. Chem.*, 1963, **19**, 1.

[257] A. I. Busev and Khoang Min Tyau, *Zhur. neorg. Khim.*, 1962, **7**, 88.

[258] G. M. C. Higgins and B. Saville, *J.*, 1963, 2812.

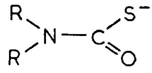
[259] A. V. Ablov and V. N. Shafranskii, *Zhur. neorg. Khim.*, 1961, **6**, 1781.

[260] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1964, **3**, 1398.

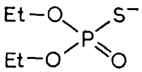
[261] C. K. Jørgensen, *Acta Chem. Scand.*, 1963, **17**, 533.

occupy an early position (between Cl^- and F^-) in the spectrochemical series and a late position in the nephelauxetic series, the last-named ligand coming after I^-.[11,255,262]

The monothio-ligand, dialkylthiocarbamate (LXXVI) forms polymeric complexes with Cu^I, Ag^I, and Au^I.[263] Diethylthiophosphate (LXXVII) acts as a unidentate sulphur-ligand in the Ag^I and Hg^{II} complexes which are more stable than the thiocyanate but less stable than the thiourea complexes of these metals.[264] Monothiophosphate SPO_3^- can act as a uni- or bi-dentate ligand in Co^{III} complexes.[265]

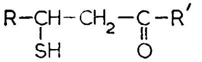


(LXXVI)

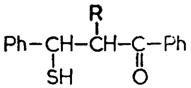


(LXXVII)

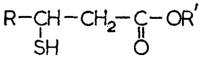
6.4. Thio-derivatives of β-Diketones and β-Keto-esters.—Tanaka and Yokoyama have prepared a large number of β-mercaptoketones and β-mercaptoesters and investigated their co-ordinating ability. β-Mercaptoketones (LXXVIII; when R′ = Ph, R = Ph, *m*-tolyl, *p*-chlorophenyl, 1-naphthyl, 2-thienyl, 2-furyl; when R′ = 2-thienyl, R = Ph, 2-furyl) and α-C-substituted β-mercaptoketones (LXXIX; R = Me, Ph) react with Cu^{2+} ion to give yellow Cu^I complexes but do not yield Ni^{II} complexes.[266] The authors suggest that the ligand is chelated in these complexes but this seems unlikely. On the other hand, β-mercaptohydrocinnamic acid esters (LXXX; R = Ph, R′ = alkyl, Ph), substituted β-mercaptohydrocinnamic acid esters (LXXX; when R = *p*-chlorophenyl, R′ = alkyl; when R = *p*-methoxyphenyl, 1-naphthyl, 2-furyl; R′ = Et), and *S*-esters of β-mercaptothiohydrocinnamic acid (LXXXI; R = alkyl, Ph, benzyl) form


$\mathrm{R{-}\underset{SH}{\underset{|}{CH}}{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}R'}$

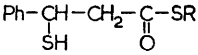
(LXXVIII)


$\mathrm{Ph{-}\underset{SH}{\underset{|}{CH}}{-}\overset{R}{\overset{|}{CH}}{-}\underset{O}{\underset{\|}{C}}{-}Ph}$

(LXXIX)


$\mathrm{R{-}\underset{SH}{\underset{|}{CH}}{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}OR'}$

(LXXX)


$\mathrm{Ph{-}\underset{SH}{\underset{|}{CH}}{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}SR}$

(LXXXI)

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[262] C. K. Jørgensen, *Acta Chem. Scand.*, 1962, **16**, 2017.

[263] S. Åkerstrom, *Acta Chem. Scand.*, 1963, **17**, 1187.

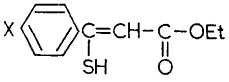
[264] V. F. Toropova, M. K. Saikina, and N. K. Lutskaya, *Zhur. neorg. Khim.*, 1961, **6**, 2086.

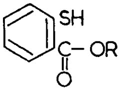
[265] J. Hidaka, J. Fujita, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1959, **32**, 1317.

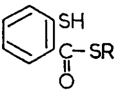
[266] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (*Tokyo*), 1960, **8**, 275, 280, 1008, 1012.

stable brick red 2:1 Ni^{II} complexes in addition to yellow Cu^{I} complexes.[267]

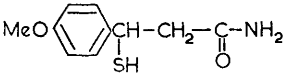
α,β-Unsaturated β-mercapto-acid esters (LXXII; X = H, NO_2, Cl, OMe) give stable Ni^{II}, Co^{III}, and Fe^{III} complexes; the 3:1 M^{III} complexes are obtained from Co^{2+} and Fe^{2+} salts.[268]

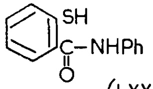

(LXXXII)


(LXXXIII)


(LXXXIV)

Esters of *o*-mercaptobenzoic acid (LXXXIII; R = Et, Pr^i, isopentyl) and *S*-esters of *o*-mercaptobenzoic acid (LXXXIV; R = Et, Pr^i, isopentyl) give orange-red Ni^{II} and green Co^{III} complexes. The C=O stretching frequency occurs at 1700 cm.$^{-1}$ in the *O*-esters (LXXXIII) and at 1610—1620 cm.$^{-1}$ in their Ni^{II} and Co^{III} complexes; it occurs at 1680 cm.$^{-1}$ in the *S*-esters and at 1575—1580 cm.$^{-1}$ in the Ni^{II} and Co^{III} complexes but at 1680 cm.$^{-1}$ in the Cu^{I} complexes.[269] This indicates that the ligands are bidentate, being bound through sulphur and oxygen atoms, in the Ni^{II} and Co^{III} complexes, whereas the carbonyl group is not co-ordinated in the Cu^{I} complex. The extra stability of the Ni^{II} and Co^{III} complexes of the ligands (LXXXII), (LXXXIII), and (LXXXIV) is apparently due to the existence in the chelate ring of a conjugated double-bond system which allows some electron delocalisation.


(LXXXV)


(LXXXVI)

Nickel(II) complexes are formed by β-mercapto-*p*-hydrocinnamaniside (LXXXV) and *o*-mercaptobenzanilide (LXXXVI). As the frequencies of the two infrared bands associated with the amide group do not alter on co-ordination, it has been inferred that the ligands are (S–O) rather than (S–N) chelated.[270]

A number of monothio-β-diketones (LXXXVII; where R = Me, R′ = Me,Ph,CF_3,OEt; where R = Ph, R′ = Ph,OEt; where R = 2-thienyl, R′ = CF_3; R = R′ = CMe_3) have been prepared. Evidence obtained from infrared, NMR, and mass spectrometry shows that these compounds exist almost entirely in the enethiol form; the absence of a sharp SH absorption at *ca.* 2570 cm.$^{-1}$ in their spectra indicates that the thiol hydrogen is strongly chelated between the sulphur and oxygen atoms as in

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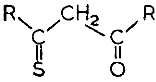
[267] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (*Tokyo*), 1961, **9**, 66, 110; 1962, **10**, 13.

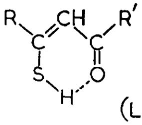
[268] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (*Tokyo*), 1962, **10**, 19.

[269] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (*Tokyo*), 1962, **10**, 25.

[270] H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull.* (*Tokyo*), 1962, **10**, 556.



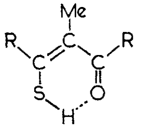
(LXXXVII)



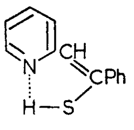
(LXXXVIII)

(LXXXVIII).[271,253] All these ligands form strong diamagnetic square-planar Ni^{II} inner complexes which are readily soluble in organic solvents. It is significant that the replacement of one oxygen atom in β-diketones by sulphur causes a change in bond-type of the Ni^{II} complexes from high-spin to low-spin. The infrared spectra of the ligands and of their Ni^{II} chelates display a strong band in the range 1260—1190 cm.$^{-1}$; this band alters little on co-ordination and has been assigned to the $C = S$ stretch possibly coupled with the $C = O$ or $C = C$ stretching modes.[253] The lowest frequency band in the visible spectra of the Ni^{II} chelates occurs in the range 675—620 mμ (14·8—16·13 kK); accordingly these ligands fall between diethyldithiocarbamate and diethyldithiophosphate in the spectrochemical series.[272] Mass spectrometry has shown that the Ni–S bond is stronger than the Ni–O bond in these complexes, as the latter is always ruptured first.[273] The Ni^{II} complexes of the β-mercapto-esters (LXXXVIII; $R = Me,Ph$, $R' = OEt$) form paramagnetic octahedral bis-pyridine adducts, but such is the preference of the Ni atom to retain a square-planar configuration in the complexes of β-mercaptoketones (LXXXVII; $R' \neq OEt$) that pyridine adducts are not formed, although a very unstable yellow adduct of γ-picoline was isolated.[253] The β-mercaptoketones form stable complexes with a number of class (*b*) and borderline metals; the green Fe^{III} complexes are high-spin.[274]

Ni^{II} chelates were obtained with the α-methyl-substituted ligands (LXXXIX; $R = Me$, Ph) but no Pd^{II} or Pt^{II} complexes could be obtained, whereas the non-α-substituted β-mercaptoketones (LXXXVIII) readily yield complexes with Pd^{II} and Pt^{II}.[275] It is difficult to explain these results but steric hindrance by the α-Me group apparently lowers the chelating ability of these ligands.



(LXXXIX)



(XC)

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[271] S. H. H. Chaston and S. E. Livingstone, *Proc. Chem. Soc.*, 1964, 111; Proc. VIII International Conference on Co-ordination Chemistry, Verlag, Vienna, 1964, p. 370.

[272] S. H. H. Chaston and S. E. Livingstone, unpublished work.

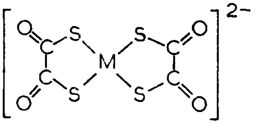
[273] S. E. Livingstone and J. S. Shannon, unpublished work.

[274] S. H. H. Chaston, R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, unpublished work.

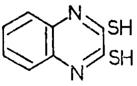
[275] R. K. Y. Ho, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, in the press.

2-Picolylphenylthioketone (XC) forms stable chelates with Co^{III}, Ni^{II}, Pd^{II}, Cu^{II}, and Zn^{II}; these complexes resemble those of 3-mercapto-1,3-diphenylprop-2-en-1-one (LXXXVIII; R = R′ = Ph).[276]

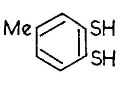
6.5. α-Dithiols.—The dithio-oxalate ion forms anionic metal chelates $[M(C_2O_2S_2)_2]^{2-}$ (M = Ni, Pd, Pt) and $[M(C_2O_2S_2)_3]^{3-}$ (M = Cr, Co, Rh) which are intensely coloured and very stable;[277] the former are square-planar with the structure (XCI)[278] and the latter have been resolved.[279] Measurements of formation constants show that for Ni^{II}: dithio-oxalate > dithiomalonate > thiocarbonate, CS_3^{2-}; the Ni^{II} chelates of these ligands are much more stable than those of their oxygen analogues.[280]



(XCI)



(XCII)



(XCIII)

Several α-dithiols of general formula $HS{\cdot}CH_2(SH){\cdot}CH_2{\cdot}CH_2Y$ form strong complexes with Fe^{III}, Sn^{II}, Pb^{II}, As^{III}, and Bi^{III} as well as with typically (*b*) class metals; the stabilities of the complexes of Zn^{II}, Cd^{II}, Hg^{II}, and Pb^{II} with a number of α-dithiols have been compared.[211,281] Ethanedithiol, $HS{\cdot}CH_2{\cdot}CH_2{\cdot}SH$ (esH_2), gives the very stable complexes $[Ni(es)_2]^{2-}$ and $[Ni_2(es)_3]^{2-}$ and the complex formation between 2,3-dimercapto-1-propanol and Mn^{II}, Fe^{III}, Ni^{II}, and Zn^{II} has been investigated.[282] Quinoxaline-2,3-dithiol (XCII) has been used for the colorimetric estimation of cobalt and nickel.[283] Complexes of toulene-3,4-dithiol (XCIII; $TDTH_2$) with zinc and molybdenum have been reported.[284]

In 1962 Schrauzer and Mayweg[285] reported the first example of a very interesting series of metal chelates formed by α-dithiols: by heating nickel sulphide and diphenylacetylene together in toluene in a sealed tube they obtained the diamagnetic complex $Ni(Ph_2C_2S_2)_2$. Shortly afterwards Gray *et al.*[286] reported complexes of maleonitriledithiolate (MNT^{2-}) of

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[276] Von E. Uhlemann, G. Klose, and H. Muller, *Z. Naturforsch.*, 1964, **19b**, 962.

[277] H. O. Jones and H. S. Tasker, *J.*, 1909, **95**, 1904; C. S. Robinson and H. O. Jones, 1912, **101**, 62.

[278] E. G. Cox, W. Wardlaw, and K. C. Webster, *J.*, 1935, 1475.

[279] F. P. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1959, **81**, 2335.

[280] W. A. Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 5680.

[281] E. V. Vasil'eva and T. K. Nedopekin, *Tiolovye Soedinen, v. Med., Ukrain. Nauch-Issledovatel. Sanit. Khim. Inst., Trudy Nauch. Konf., Kiev*, 1957, p. 36.

[282] D. L. Leussing, *J. Amer. Chem. Soc.*, 1959, **81**, 4208; D. L. Leussing and G. S. Alberts, *ibid.*, 1960, **82**, 4458; D. L. Leussing and T. N. Tischer, *ibid.*, 1961, **83**, 65; D. L. Leussing and J. P. Mislan, *J. Phys. Chem.*, 1960, **64**, 1908.

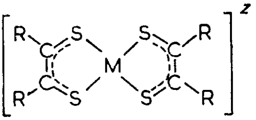
[283] R. W. Burke and J. H. Yoe, *Analyt. Chim.*, 1962, **34**, 1378; G. H. Ayres and R. R. Annand, *ibid.*, 1963, **35**, 33.

[284] K. Wallenfels and H. Sund, *Biochem. Z.*, 1957, **329**, 17; T. W. Gilbert and E. B. Sandell, *J. Amer. Chem. Soc.*, 1960, **82**, 1087.

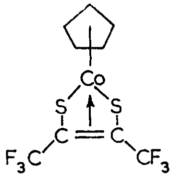
[285] G. N. Schrauzer and V. Mayweg, *J. Amer. Chem. Soc.*, 1962, **84**, 3221.

[286] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962. **84**, 3596.

general formula $[NBu^n_4]_2[M(MNT)_2]$ (M = Co, Ni, Pd, Pt, Cu, Zn). Davison *et al.*[287] recognised the relationship between the Ni complex of Schrauzer and the MNT complexes and they reported three series of complexes, related by electron-transfer reactions, and of general formula (XCIV; when R = Ph, CF_3, M = Ni, $z = 0, -1, -2$; when R = CN, M = Co, Ni, Pd, Pt, Cu, Au, $z = -1$).



(XCIV)



(XCV)

Toluene-3,4-dithiol forms complexes $[Ph_3AsMe][M(TDT)_2]$ (M = Fe, Co, Ni, Cu); the values of μ_{eff}(B.M.) are Fe, 4·39; Co, 3·27; Ni, 1·89, Cu, 0. The spectra were interpreted as indicating that these complexes are square-planar and contain the metal in the +1 oxidation state; the authors suggested that the unpaired electron which each radicle anion would possess must be paired with its partner in one of the π-orbitals of the complex. Thus $[Co(TDT)_2]^-$ was regarded as the first example of a high-spin square d^8 complex.[288] However, the complex $[Co(MNT)_2]^{2-}$ was shown to be low-spin,[289] although it had been previously reported as high-spin;[286] $[NBu^n_4][Co(MNT)_2]$ is diamagnetic in the solid state and in cyclohexanone solution but has a moment of 2·81 B.M. in dimethyl sulphoxide.[290]

A structure determination of $[NMe_4]_2[Ni(MNT)_2]$ shows that the nickel atom is square-planar with nearest Ni–Ni distance of 8·05 Å and a C–C distance (1·30 Å) indicating an order of 2·1 for the bond between the two carbon atoms linked to sulphur and CN.[291] The complex $[NBu^n_4]_2$-$[Rh(MNT)_2]$ (μ_{eff}, 1·91 B.M.) apparently contains square-planar Rh^{II}.[292] The four-, five-, and six-co-ordinate diamagnetic complexes $[NBu^n_4]$-$[Co(MNT)_2]$, $[NBu^n_4][Co(MNT)_2L]$ (L = pyridine, 1,10-phenanthroline, diarsine), $[NBu^n_4]_3[Co(MNT)_3]$ formally contain Co^{III} but certain characteristics of these complexes are not compatible with what is expected for Co^{III}. These are: (i) the existence of stable four- and five-co-ordinate species; (ii) the ready interconvertibility among four-, five-, and six-co-ordination; (iii) the ligand-affinity order $P > N$ (soft-acid behaviour) is

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[287] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1963, **85**, 2029; *Inorg. Chem.*, 1963, **2**, 1227.

[288] H. B. Gray and E. Billig, *J. Amer. Chem. Soc.*, 1963, **85**, 2019.

[289] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1963, **85**, 3049.

[290] E. Billig, H. B. Gray, S. I. Shupack, J. H. Waters, and R. Williams, *Proc. Chem. Soc.*, 1964, 110.

[291] R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 113.

[292] E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 926.

consistent with d^8 systems. Consequently, the bond-pair is considered as more nearly localised on the metal atom than on the ligands.[293] The complexes $[M(MNT)_2]^-$ (M = Fe, Ni, Pd, Pt) exhibit singlet–triplet magnetic behaviour which, on the assumption that these complexes are square-planar and contain formally M^{III}, is attributed to spin interactions between pairs of metal ions through the sulphur atoms of adjacent ligands.[294]

Shupack *et al.*[295] observed that one way to stabilise square-planar geometry is to involve the d_{xy}, d_{yz}, and p_z valence orbitals of the metal in an extensive π-orbital network spanning the entire complex, thus allowing as much delocalisation as possible. Two ligands with good donor atoms and considerably delocalised π-orbital systems are MNT^{2-} and TDT^{2-}. The following square-planar complexes have been reported:

(1) $S = 1$ $[Co(TDT)_2]^-$
(2) $S = \frac{1}{2}$ $[Rh(MNT)_2]^{2-}$
(3) $S = 0$ $[Cu(TDT)_2]^-$ and $[Cu(MNT)_2]^-$
(4) $S = \frac{1}{2}$ $[M(TDT)_2]^-$ and $[M(MNT)_2]^-$ (M = Ni,Pd,Pt)
(5) $S = \frac{1}{2}$ and 3/2 $[Fe(TDT)_2]^-$ and $[Fe(MNT)_2]^-$

The complexes $[Ni(S_2C_2MeR)_2]$ (R = Me, Ph) are also known.[296] Shupack *et al.*[295] report that electron spin resonance (e.s.r.) measurements indicate that the unpaired electron in these square-planar complexes is in an orbital which is localised over metal and ligand but is predominantly ligand. They are of the opinion that a general molecular orbital formulation of the ground state is preferable to an assignment of a definite oxidation state to the metal.

Although MNT^{2-} produces a weak ligand field comparable with Br^-, the d^8 complexes are unusually stable and are inert to substitution by most ligands; MNT^{2-} also appears to have a strong *trans*-effect.[297] All, including the Cu complex, remain truly square-planar in strongly co-ordinating solvents, showing a lack of axial perturbation by solvent molecules. This unusual stability of the square-planar configuration is regarded as evidence of the involvement of the $4p_z$ orbital in π-bonding, giving added stability to the electronic delocalisation throughout the system.[297]

The six-co-ordinate complexes $[M(S_2C_2R_2)_3]^z$ (when R = CF_3, M = Cr, Mo, W, $z = 0, -1, -2$; when R = CN, M = Cr, V, $z = -2$, M = Cr, $z = -3$) are similar to the bis-complexes in that they contain metals stabilised in several oxidation states and are interconvertible by oxidation–reduction reactions. The most obvious assignments of the three iso-

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[293] C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 2958.

[294] J. F. Weicher, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 4329

[295] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, 1964, **86**, 4594.

[296] G. N. Schrauzer and V. Mayweg, *Z. Naturforsch.*, 1964, **19b**, 192.

[297] E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, 1964, **3**, 663.

electronic series M = Cr, Mo, W; R = CF_3; $z = 0, -1, -2$) as d^0, d^1, and d^2 are not at all rationalised with data obtained from e.s.r.[298] Similarly the assignment of an oxidation state of +6 (*i.e.*, $3p^5$) for vanadium in $[V(S_2C_2Ph_2)_3]$ seems unreasonable.[299] The complexes $[M(S_2C_2Ph_2)_3]$ (M = Cr, Mo, W) are also known.[300] In the series $[V(S_2C_2R_2)_3]^z$ (R = CF_3, $z = -1, -2$; R = Ph, $z = 0, -1, -2$) when $z = -1$ the compounds are diamagnetic but when $z = 0, -2$, and for $[V(TDT)_3]^{2-}$, μ_{eff} = 1·73—1·90 B.M. Proton resonance studies show that in the paramagnetic compounds the electron is strongly localised on the ligands.[301]

Carbonyl compounds containing bridging α-dithiols—*viz.*, $[(CO)_6Fe_2(TDT)]$ and $[(C_5H_5)_2M_2\{S_2C_2(CF_3)_2\}_2]$ (M = V, Cr, Mo)—have been reported by King[137] who suggested the structure (XCV) for the monomeric Co^{III} complex. The existence of the monomeric complex $[PhC{:}S(S)Mn(CO)_4]$, in which the dithiobenzoate ion is bidentate, suggests the involvement of the metal in the aromatic system through π-bonding between the metal and sulphur atoms.[302] The CO and NO stretching frequencies of $[Ph_3PMe][Mn(CO)_4MNT]$ and $[Ph_4P]_2$ $[Mo(NO)_2(MNT)_2]$ suggest that MNT^{2-} is functioning as a π-acceptor from the metal which is in a low oxidation state.[303]

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