The Co-ordination of Ambidentate Ligands

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1 Introduction

Early in the development of co-ordination chemistry Jorgensen[1] prepared two isomers of the molecular formula $[Co(NH_3)_5NO_2]Cl_2$ which differed only in the mode of attachment of the NO_2-group to the cobalt atom. He believed that the unstable red form contained the nitrito-(Co—ONO) and the stable yellow form, the nitro-($Co—NO_2$) linkage. This view has been confirmed by recent spectroscopic studies.[2] Werner[3] recognised that this was an example of a general type of isomerism which he termed 'salt isomerism'. The almost equivalent terms, 'structural isomerism'[4] and 'linkage isomerism'[5] are currently more fashionable. Linkage isomers differ only in the actual atom (of a polyatomic ligand) attached to the central metal ion, all other attached groups, the geometrical configurations and the conformations of the isomeric molecules being the same. Some common ligands known to form linkage isomers are CN^-, NO_2^-, NCS^-, $NCSe^-$, and SO_3^{2-}: the subject has been reviewed recently.[6]

Kornblum[7] wrote, when describing a particular class of organic reactions: 'It is desirable to have a simple name for anions which possess two different reactive positions. Among such ions are NO_2^-, CN^-, SCN^-, diazotate ions, enolate ions and the anions obtained from α-hydroxypyridine, nitroparaffins, acid amides, thio-amides, *etc.* Since these anions undergo covalence formation at one or the other of two available positions the term ambident is proposed.' The same term has been applied to inorganic chemistry, especially in the sense that ambidentate ligands may form linkage isomers, but also to describe those ligands which are potentially capable of co-ordinating through more than one site, even though no linkage isomers are known: in many cases one form of co-ordination is favoured by one metal while a different metal attracts the alternative donor site of the ligand. This approach results in the number and

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[1] S M. Jorgensen, *Z. anorg. Chem.*, 1894, **5**, 147.

[2] R. B. Penland, T J. Lane, and J V. Quagliano, *J. Amer. Chem. Soc.*, 1956, **78**, 887.

[3] A. Werner, *Ber.*, 1907, **40**, 765.

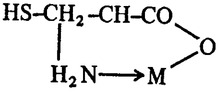
[4] R. G. Wilkins and M. G. J. Williams 'Modern Co-ordination Chemistry', ed. J. Lewis and R. Wilkins, Interscience, New York, 1960, p. 175.

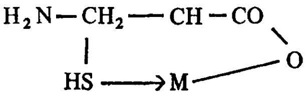
[5] F Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', John Wiley, New York, 2nd edn., 1967, p. 13.

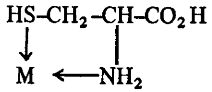
[6] R. T. M. Fraser, 'Werner Centennial', Advances in Chemistry Series no. 62, American Chemical Society, 1967, p. 296; J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205; 1968, **3**, 225; Ref. 5, p. 291.

[7] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

variety of ligands falling under the heading ambidentate being very large. For example, a diatomic group AB may form complexes with the following types of linkage: M—AB, M—BA, M—A(B)—M, M—B(A)—M, or M—AB—M. The acetylacetonate anion is known to co-ordinate to platinum either through the γ-carbon atom or through both oxygen atoms,[8] and acetylacetone can co-ordinate through the C=C bond in addition.[9] Cysteine may form chelates in any one of the three following ways:







This is not to suggest that all these structures are of equal probability but to establish that the more varied acceptor properties of metal ions relative to carbon* extend the number of ambidentate ligands considerably. Similarly π-donors with another co-ordination site, *e.g.* allylamine, alkylvinylketones, and related compounds have been reviewed recently.[10] However, there are clear distinctions between these examples, and the following definition is proposed to clarify the situation:

Ambidentate ligand – a ligand containing two or more different types of potential sigma donor sites, only one of which sites is involved in co-ordination at any one time.

This definition is very similar to Kornblum's. It excludes bridging systems and flexidentate ligands having more than one co-ordination site on different atoms of the same element, such as SO_4^{2-} or ethylenediamine, without excluding such compounds as 4-aminopyridine containing two chemically different nitrogen atoms. It restricts possible chelates to situations in which they act as unidentate ligands only. The subdivisions of this definition, *i.e.* chelating ambidentate ligands and σ–π ambidentate ligands, follow without needing further explanation. In practice, it is found that one of the various possible modes of linkage of an ambidentate ligand is more common than the others although these alternative structures can be assumed under special circumstances. The chemistry of ambidentate ligands, therefore, presents interesting opportunities in synthetic inorganic chemistry and a study of the factors favouring different modes of co-ordination of the ambidentate ligands is of potential theoretical interest. In this Review we shall discuss the ambidentate behaviour or potential ambidentate behaviour of a number of ligands. Emphasis will be placed on sigma donors, and examples of bridging behaviour or chelation will be included only when relevant to the main discussion. To facilitate the survey, the following classification, based on the complexity of the ligand molecules, will be adopted:

(*i*) Diatomic ambidentate ligands.

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*Aspects of ambidentate behaviour in organic chemistry have been discussed recently by Hünig, *Angew. Chem. Internat. Edn.*, 1964, **3**, 548; Gompper *ibid.*, 1964, **3**, 560.

[8] K. Kite and M. R. Truter, *J. Chem. Soc.*, (*A*), 1968, 934.

[9] G. Allen, J. Lewis, R. G. Long, and C. Oldham, *Nature*, 1964, **202**, 580.

[10] J. A. McGinnety and M. J. Mays, *Ann. Reports* (*A*), 1967, **64**, 352; 1968, **65**, 383.

(*ii*) Polyatomic ligands in which the two different donor atoms are directly linked.

(*iii*) Polyatomic ligands in which the two different donor atoms are separated by a non-donor atom.

(*iv*) Miscellaneous ambidentate ligands.

Ligands containing two different donor atoms separated by two or three non-donor atoms will not be considered generally as these are potential chelates.

2 Diatomic Ambidentate Ligands

Considering C, N, O, F, P, S, Cl, As, Se, Br, Sb, Te, and I as the common donor atoms, seventy-eight (*i.e.* the number of ways of choosing two from thirteen) diatomic ligands are theoretically possible. However, only the hypohalite and cyanide ions, CO, CS, and NO are known as possible ligands, although the fact that CS has no long-term chemical existence in the non-complexed state suggests that further diatomic ligands may be discovered.

A. Cyanide Complexes.—The chemistry of the cyanide ion has been reviewed generally[11] and with special reference to its ambidentate nature.[11c] Normally anionic complexes of the type $[M^{m}(CN)_n]^{m-n}$ are obtained. There are, however, a number of well-substantiated examples in which the nitrogen is involved in co-ordination as well as the carbon [there do not seem to be any examples of M—C(N)—M bridging]. Thus, a number of metal cyanide complexes form adducts with BF_3, in which a $M—C{\equiv}N—BF_3$ system exists.[12] In a similar fashion, the irradiation of a solution of $M(CO)_6$ (M = Cr or W) and subsequent treatment with HCN gave $(CO)_5MNCH$ which isomerised under suitable conditions to give $(CO)_5MCNH$.[13] Such behaviour is reminiscent of polymeric cyanide complexes many of which have the face-centred-cubic lattice of Prussian Blue. This structure has three types of site for the metal ion, two of which are octahedral holes surrounded by six carbon or nitrogen atoms respectively and the third type is a large interstitial hole.[14] Table 1 shows whether or not metal ions are in one or the other of the octahedral holes in a number of these compounds, (no attention is paid to whether or not the interstitial site is occupied) and is in good general agreement with predictions based on crystal field stabilisation energies.[15] However, the calculations predicted that $KCr^{III}—(CN)_6-Fe^{II}$ should be less stable than $KFe^{II}—(CN)_6—Cr^{III}$ and since $[Cr(CN)_6]^{3-}$ is kinetically rather inert there appeared to be the possibility of linkage isomerism. This proved to be the case, and the addition of an iron(II) solution to a solution of $K_3Cr(CN)_6$ gave a brick-red precipitate which converts to the dark green

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[11] *a* B. M. Chadwick and A. G. Sharpe, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 84; *b* D. Britton, *Perspectives in Structural Chem.*, 1967, **1**, 109; *c* D. F. Shriver, *Structure and Bonding*, 1966, **1**, 32.

[12] D. F. Shriver, *J. Amer. Chem. Soc.*, 1963, **85**, 1405 and refs. in 11(c).

[13] J. F. Guttenberger, *Chem. Ber.*, 1968, **101**, 403.

[14] H. B Weiser, W. O. Milligan, and J. B. Bates, *J. Chem. Phys.*, 1942, **46**, 99.

[15] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

Table 1 *The structures of some Prussian Blue analogues**

Metal in: *N hole*	*C hole*	*Reference*
Mn^{2+}	Fe^{3+}	*a*
Ni^{2+}	Fe^{3+}	*a*
Cu^{2+}	Fe^{3+}	*a*
Zn^{2+}	Fe^{3+}	*a*
Fe^{3+}	Fe^{2+}	*a*
Mn^{2+}	Co^{3+}	*a*
Fe^{2+}	Co^{3+}	*a*
Co^{2+}	Co^{3+}	*a, b*
Ni^{2+}	Co^{3+}	*a*
Cu^{2+}	Co^{3+}	*a*
Zn^{2+}	Co^{3+}	*a*
Ni^{2+}	Cr^{3+}	*a*
Zn^{2+}	Cr^{3+}	*a*
Cr^{3+}	Fe^{2+}	*a*†
Mn^{2+} or Fe^{3+}	Fe^{2+}	*c*†

*The compounds are not always accurately stoicheiometric and may range between the limiting compositions $KM^{II}M^{III}(CN_6)$and $M^{II}_3M^{III}_2(CN)_{12}$. In general, the N holes contain high spin ions and the C holes low spin ions as is strikingly shown in K_2 $Mn^{II}_2(CN)_6$ which has one of each.[d]

†See text.

[a] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725 and refs. therein; [b] D. F. Shriver and D. B. Brown, *Inorg. Chem.*, 1969, **8**, 42; [c] D. B. Brown and D. F. Shriver, *Inorg. Chem.*, 1969, **8**, 37; [d] A. M. Qureshi and A. G. Sharpe, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2269.

isomer at 100°. Physical measurements confirmed this to be a $Cr^{III}—C{\equiv}N—Fe^{II}$ to $Fe^{II}—C{\equiv}N—Cr^{III}$ isomerisation. It was also shown[16] that $Fe_3[Mn(CN)_6]_2$ initially contained Fe—N and Mn—C bonds which rearrange to give a material containing Fe—C bonds, and that a compound of approximate composition $Co_3[Cr(CN)_6]_2$ appeared to undergo isomerisation on heating in an inert atmosphere to give a product containing $Co^{II}—C$ bonds; subsequent air oxidation led to the presence of $Cr^{III}—N$ and $Co^{III}—C$ bonds.

Isocyano-compounds are not well established. They have been a subject for debate in the chemistry of the non-metals (with the exception of carbon), and have been postulated as intermediates in a number of reactions.[11c,17] However, convincing evidence has been put forward to support the presence of small amounts (0·2%) of Me_3SiNC in the isomeric cyanide.[18] Transition-metal isocyanides, $[Co(CN)_5NC]^{3-}$ and $[Cr(H_2O)_5NC]^{2+}$ have been detected during studies of the kinetics of a number of redox reactions of $[Co(CN)_5]^{3-}$ with

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[16] D. B. Brown and D F. Shriver, *Inorg. Chem.*, 1969, **8**, 37.

[17] J. S. Thayer, *Inorg. Chem.*, 1968, **7**, 2599.

[18] M. R. Booth and S. G. Frankiss, *Chem. Comm.*, 1968, 1347.

various substituted cobalt(III)[19] and chromium(III)[20] species; the latter intermediate was also observed in exchange reactions involving $[Cr(H_2O)_6]^{3+}$ and some aquo-cyano-complexes of chromium(III).[21] The oxidation of $[Co(NH_3)_5NCS]^{2+}$ to $[Co(NH_3)_5CN]^{2+}$ seems likely to involve the same type of intermediate, but the similar conversion of [Pd L(NCS)]$^+$ to [Pd L(CN)]$^+$ (L = tetraethyldiethylene triamine) is believed to take place *via* the re-entry of a free cyanide ion to the co-ordination sphere.[22] The close similarity of these transient intermediates to complexes containing bridging cyanides is emphasised by the preparation of $Co(NH_3)_5{\cdot}NC{\cdot}Co(CN)_5$.[23]

Recently Kuroda and Gentile[24] have claimed the existence of discrete isocyano-complexes of the type [Co trien $(NC)_2]ClO_4$ on the basis of electronic and vibrational spectra. However, the interpretation of the former has been challenged,[25] and Burmeister[6] has questioned both the latter and the absence of any rationale for the formation and stability of these compounds, although Espenson[21] has estimated that the isomerisation energy for $[(Cr(H_2O)_5NC]^{2+}$ is small. In the absence of further evidence the existence of stable isocyano-complexes must remain a matter for further experimental work.

The co-ordination behaviour of the cyanide ion and the preponderance of metal—carbon bonds have been explained[26] on the basis of the localisation of the highest filled molecular orbital with σ symmetry on the carbon atom, as shown by LCAO–MO–SCF calculations. Similar LCAO–MO calculations by Purcell[27] show that the nitrogen lone pair of electrons is more basic in the Lewis sense for HCN and CH_3CN than for CN^-: a similar increase in basicity on co-ordination would account for the many bridged compounds of the type M—CN—M′. The formation of unstable isocyano intermediates is then a consequence of this bridging mode, and the isolation of such compounds may depend largely on kinetic factors.

B. Complexes Containing Carbon Monoxide.—Carbon monoxide normally acts as a unidentate ligand through the carbon atom. It is also known as a bridging group where, unlike the isoelectronic cyanide ion, it co-ordinates through the carbon only, in either a ketonic or triply bridging fashion.[28] Isocarbonyl complexes have been postulated as intermediates in some decarbonylation reactions, for example:[29]

[19] J. L. Burmeister and D. Sutherland, *Chem. Comm.*, 1965, 175; J. Halpern and S. Nakamura, *J. Amer. Chem. Soc.*, 1965, **87**, 3002; J. P. Birk and J. Halpern, *ibid.*, 1968, **90**, 305.

[20] J. H. Espenson and J. P. Birk, *J. Amer. Chem. Soc.*, 1965, **87**, 3280; J. P. Birk and J. H. Espenson, *ibid.*, 1968, **90**, 1153.

[21] J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, 1968, **90**, 2266.

[22] K. Schug, B. Miniatas, A. J. Sadowski, T. Yano, and K. Ueno, *Inorg. Chem.*, 1968, **7**, 1669.

[23] R. A. de Castello, C. P. Mac-Coll, N. B. Egen, and A. Haim, *Inorg. Chem.*, 1969, **8**, 699.

[24] K. Kuroda and P. S. Gentile, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 151.

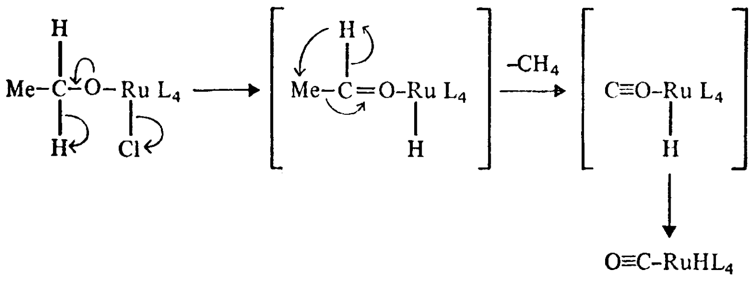
[25] K. Konya, H. Nishikawa, and M. Shibita, *Inorg. Chem.*, 1968, **7**, 1165.

[26] D. F. Shiver and J. Posner, *J. Amer. Chem. Soc.*, 1966, **88**, 1672.

[27] K. F. Purcell, *J. Amer. Chem. Soc.*, 1967, **89**, 247.

[28] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 2nd edn., John Wiley, London, 1966.

[29] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.



Nyholm[30] has suggested the possibility of co-ordination through the oxygen atom in AuCOCl but this has not been confirmed. Some 1 : 2 adducts between arene metal tricarbonyls and mercury(II) halides may be formulated as compounds with the mercury(II) halide co-ordinated to the oxygen of the carbonyl group.[31] These few examples involving oxygen co-ordination, in contrast to the very many carbon-bonded carbonyls, may be explained in terms of the molecular orbital description of carbon monoxide.[32] The lone pair of electrons on the carbon atom is strongly directed away from the C—O bond and hence most readily available for co-ordination while the greater electronegativity of the oxygen atom causes the electron cloud to be very tightly held by this atom and so less available for co-ordination. Factors favouring the ketonic linkage of carbon monoxide are not clear. In general, a polymeric structure is favoured for a complex of the empirical formula $M(CO)_n$ if n is such that the available orbitals on the metal atom are not fully occupied. However, the polymerisation does not necessarily involve ketonic bridging; it can also be effected through metal—metal bonding.

C. Complexes Containing the Thiocarbonyl Group.—The diatomic entity CS is not known to exist as a stable species. It is, therefore, remarkable that a few stable complexes containing the thiocarbonyl group as a ligand are known. $[Rh(Ph_3P)_2(CS)Cl]$ is obtained by refluxing tris-(triphenylphosphine)chlororhodium(I) with carbon disulphide in the presence of methanol when the CS group is abstracted to give the thiocarbonyl complex.[33] On oxidation with chlorine the rhodium(III) complex $[Rh(Ph_3P)_2(CS)Cl_3]$ is obtained. The corresponding bromo-complexes have also been prepared.[33] The observed[33] ratio (1·5:1) of the C—O and C—S stretching frequencies in the corresponding carbonyl and thiocarbonyl complexes is in agreement with that expected from a consideration of the masses of the two groups if the mode of linkage is assumed

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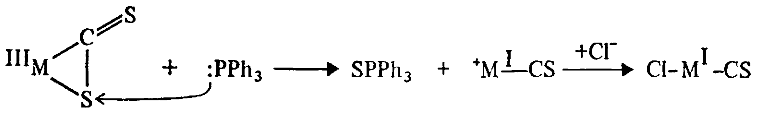
[30] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273.
[31] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 2851.
[32] C. A. Coulson, 'Valence', 2nd edn., Oxford University Press, 1961.
[33] M. C. Baird and G. Wilkinson, *Chem. Comm.*, 1966, 267; M. C. Baird, G. Hartwell, jun., and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 2037.

to be similar in the two. The formation of a linear metal—carbon—sulphur bond has been confirmed, by *X*-ray analysis of $Rh(Ph_3P)_2(CS)Cl$.[34]

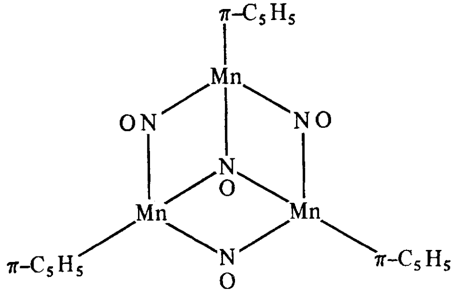
The corresponding iridium complex is also known and has been prepared from $[IrCO(\pi\text{-}CS_2)\,(PPh_3)_3]^+$ which was isolated as the tetraphenylborate.[35] Such cationic species are believed to be involved in the formation of the thiocarbonyl complexes and the following reaction scheme has been suggested:[35]



Thiocarbonyl complexes of other metals have since been reported.[36]

If the arguments advanced to explain the mode of co-ordination of CN^- and CO are valid, the similar calculation for CS suggests that thiocarbonyl complexes should be more stable than carbonyls,[37] and that CS is more likely to form normal and iso-complexes.

D. Complexes Containing Nitric Oxide.—Nitrosyl complexes have been reviewed recently.[38] In all the known monomeric nitrosyl complexes the ligand is bonded through the nitrogen atom, which is also involved in both double and triple bridging as in $(\pi\text{-}C_5H_5)_3\,Mn_3(NO)_4$:[39]



Nitric oxide is an odd-electron molecule and may fairly easily lose one electron to give the nitrosonium ion NO^+. The extent to which this happens in complexes

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[34] J. C. de Boer, D. Rodgers, A. C. Skapski, and P. G. H. Troughton, *Chem. Comm.*, 1966, 756.

[35] M. P. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2813.

[36] J. D. Gilbert, M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2198; L. Busetto and R. J. Angelici, *J. Amer. Chem. Soc.*, 1968, **90**, 3283; E. Klumpp, G. Bor, and L. Marko, *J. Organometal Chem.*, 1968, **11**, 207

[37] W. G. Richards, *Trans. Faraday Soc.*, 1967, **63**, 257.

[38] B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, 1966, **7**, 277; W. P. Griffiths, *Adv. Organometal Chem.*, 1968, **7**, 211; M. J. Cleare, *Platinum Metals Rev.*, 1968, **12**, 131.

[39] R. C. Elder, F. A. Cotton, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1967, **89**, 3645.

is the subject of some speculation, but it seems that a discussion of metal–nitrosyl bonding in terms of NO or NO^+ is very much over-simplified. Some of this speculation will have been resolved by *X*-ray measurements which have shown that the black isomer of $[Co(NH_3)_5NO]^{2+}$ has a Co—N—O moiety with a significantly greater N—O distance (1·26, or 1·41 Å)[40a,b] than usual (1·1—1·2 Å)[41] whereas the red isomer is dimeric with a bridging hyponitrite ion.[42] The structure of $Ir(NO)(CO)(PPh_3)_2Cl$ has been shown to have a 'bent' nitrosyl group ($\widehat{\mathrm{Ir{-}N{-}O}} = 124^{\circ}$):[41] the first time that this species has been unequivocally established. It was suggested that the bent structure arose because the nitrosyl group here accepts electrons from the metal.

As with CN^- and CO, the lone pair of electrons is more available on one atom than the other.[43] For NO, nitrogen is the favoured atom, and it is nitrogen through which metal—nitrosyl bonds are formed.

E. Hypohalito-complexes.—The strong oxidising properties of the hypohalous acids and their tendency to disproportionate probably account for the lack of information on the co-ordination of their ions. If any hypohalite complexes are prepared it is to be expected that they are of the form M—OX, though M—XO complexes may perhaps occur for the less electronegative halogens.

3 Polyatomic Ambidentate Ligands with Adjacent Donor Atoms

This class is represented by various ligands with nitrogen and oxygen, sulphur and oxygen *etc.*, as the donor atoms. These alternatives provide convenient sub-headings.

A. Nitrogen *versus* Oxygen.—The nitrite ion is the most widely studied of these ligands. It can form nitro-($M—NO_2$) or nitrito-(—ONO) complexes and it also has a number of bridging (through O and N or O) or chelating (through O and O) modes. For those complexes where the nitrite ion is the only ligand it seems that nitro-complexes are formed predominantly as long as the central metal is co-ordinatively saturated, as in the four-co-ordinate $K_2[Pt(NO_2)_4]$.[44] When this is not so, as in $[M(NO_2)_4]^{2-}$ (M = Mn, Co, or Cd), chelating or bridging groups are formed to satisfy the hexaco-ordination of the metal.[45] In a series of octahedral complexes $K_2M'[M''(NO_2)_6]$, where M′ = Pb^{II} or Ba^{II} and M″ = Fe^{II}, Co^{II}, Ni^{II}, or Cu^{II}, the central metal was shown by spectroscopic methods to be surrounded by six nitro-groups.[46] Neutron diffraction confirmed this result for $K_2Pb[Cu(NO_2)_6]$.[47] A mixed structure has been proposed for $K_4[Ni(NO_2)_4$-

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[40] *a* D. A. Hall and A. A. Taggart, *J. Chem. Soc.*, 1965, 1359; *b* D. H. Dale and D. C. Hodgkin, *ibid.*, 1965, 1364.

[41] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.

[42] B. F. Hoskins, F. D. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Comm.*, 1969, 69.

[43] H. Brion, C. Moser, and M. Yamazaki, *J. Chem. Phys.*, 1959, **30**, 673.

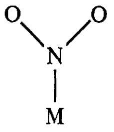
[44] K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

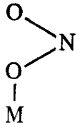
[45] D. M. L. Goodgame and M. A. Hitchman, *J. Chem. Soc.* (*A*), 1967, 612.

[46] H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, 1966, **5**, 669.

[47] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1969, 386.

$(ONO)_2]$ and explained on the basis of the greater steric requirements of the nitro- than the nitrito-group:[48]





The nature of the other cation may have some bearing on the preferred co-ordination of the group, and weak bridges may be involved. However, the previous discussion oversimplifies the results since some nitrito-complexes have been reported,[45] as in $[M(ONO)_4]^{2-}$, ($M = Cu^{II}$ or Zn^{II}): $K_3[Cu(NO_2)_5]$ has been suggested[49] but the spectra have been reinterpreted to show nitrito-linkages.[50]

The influence of steric effects is seen more clearly in some mixed ligand complexes, $NiL_x(NO_2)_2$. Nitro-complexes are formed when L_x is made up of four ammonia,[50] or two ethylenediamine,[50] *N*-alkylethylenediamine,[50] 2,2′-bipyridine,[51] 2-aminomethylpiperidine[51] or 2-aminomethylpyridine[51] groups. If the number of substituents on the ligand is increased (*e.g.* to *NN*-dialkylethylenediamine,[50] by adding a methyl group to the nitrogen or ring of the piperidine or pyridine ligands,[51] or by replacing the planar bis bipyridine with the non-planar tetrakis pyridine[50] system) then nitrito-complexes are formed. Unsubstituted polymethylenediamines give nitro-complexes.[52] Steric effects are further demonstrated by the fact that [Ni(*rac*-stieen)$_2$ $(NO_2)_2$],* having equatorial benzene rings, is a nitro-complex[53] while [Ni(*meso*-stieen)$_2$ $(NO_2)_2$], having axially directed rings and consequently exerting greater repulsion on the NO_2-group, contains the nitrito-linkage.[50]

The nitrite group also shows a strong tendency to chelate and this has been observed in cobalt(II) and nickel(II) complexes of the form $ML_2(NO_2)_2$ where L is a unidentate or $\frac{1}{2}$ bidentate ligand.[54]

In view of the foregoing, it is not surprising that examples can be found where the nitrito—nitro equilibrium lies strongly neither to the left nor right, and where linkage isomerism has been found. Thus, [Ni(*NN*-dimethylethylenediamine)$_2$-$(ONO)_2$] and [Ni(*NN*′-diethylethylenediamine) $(ONO)_2$] exist in nitro–nitrito equilibria in chloroform,[53] and a number of compounds $[M(NH_3)_5\ (NO_2)]^{n+}$

*Stieen = 1,2-diphenylethylenediamine.

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[48] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1967, **6**, 813.
[49] R D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 5399.
[50] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1964, **3**, 1389.
[51] L. El-Sayed and R. O. Ragsdale, *Inorg. Chem.*, 1967, **6**, 1638.
[52] A. Takeuchi, K. Sato, K. Sone, S. Yamada, and K. Yamasaki, *Inorg. Ch'm. Acta*, 1967, **1**, 399.
[53] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1966, **5**, 1303.
[54] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1965, **4**, 721; L. El-Sayed and R. O. Ragsdale, *ibid.*, 1967, **6**, 1644.

(M = Co^{III}, Rh^{III}, Ir^{III}, and Pt^{IV}) are prepared from their nitrito-isomers, formed initially as unstable intermediates.[1,55] (See ref. 6 for complete list.) If these nitrito-intermediates are isolable as a consequence of kinetic control arising in less labile d^6 systems, chromium(III) offers an interesting comparison since the known complexes are all nitrito and show no tendency to isomerise.[56]

In contrast to the rich and varied chemistry of the nitro-group, little is known about other ligands having nitrogen and oxygen as their donor atoms. Co-ordination compounds of hydroxylamine with cobalt, nickel, palladium, and platinum are known and their i.r. spectra indicate that the ligand is co-ordinated through the nitrogen atom.[57] Vanadium(V) complexes with *N*-benzoyl-*N*-phenylhydroxylamine and its analogues have been reported but no structural information is available;[58] chelation seems likely.

B. Sulphur *versus* Oxygen.—The sulphite ion is known to form complexes with a number of elements.[59] In many cases it acts as a unidentate ligand, but bridging and chelating behaviour is also possible. In the former case, bonding through sulphur appears to be preferred, for example in complexes of cobalt(III),[60,61] iridium(III),[62] palladium(II),[63] and platinum(II).[64] $Tl_2[Cu(SO_3)_2]$ is believed to contain the oxygen-bonded sulphite group from its i.r. spectra, although it was impossible to obtain an analytically pure sample:[65] the oxidation state of the copper [initially (II)] is not specified, and it is interesting to note that the compound $Cu_2SO_3{\cdot}CuSO_3,2H_2O$ has the sulphur atoms co-ordinated to a tetrahedral copper(I) while the oxygen co-ordinates to the same atom and to an octahedral copper(II) giving a three-dimensional network of linked octahedra and tetrahedra.[66] Linkage isomerism in sulphite complexes was incorrectly[67] quoted[68] as occurring after the addition of sulphur dioxide or sodium sulphite solutions to a solution of $[Co(NH_3)_5H_2O]^{2+}$ at low temperature and pH. An unstable pink intermediate, supposedly O-bonded $[Co(NH_3)_5OSO_2]^+$, was reported as appearing. In fact, only the stable yellow-brown S-bonded $[Co(NH_3)_5SO_3]^+$ is known.[60]

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[55] F. Basolo and G. S. Hammaker, *J. Amer. Chem. Soc.*, 1960, **82**, 1001; F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1.

[56] W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, 1967, **6**, 87.

[57] Yu. Ya. Kharitonov, M. A. Sarukhanov, and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, 1967, **12**, 82; 1966, **11**, 1359.

[58] A. K. Majumdar, B. C. Bhattacharyya, and G Das, *J. Indian Chem. Soc.*, 1968, **45**, 964.

[59] S. E. Livingstone, *Quart. Rev.*, 1965, **19**, 386.

[60] H. Siebert, *Z. anorg. Chem.*, 1959, **298**, 51.

[61] S. Baggio and L. N. Becka, *Chem. Comm.*, 1967, 506.

[62] A. V. Babaeva, Yu Ya Kharitonov, and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem.*, 1961, **6**, 115; I. B. Baronovskii and A. V. Babaeva, *ibid.*, 1968, **13**, 721.

[63] M. A. Spinnler and L. N. Becka, *J. Chem. Soc.* (*A*), 1967, 1194; M. V. Capparelli and L. N. Becka, *ibid.*, 1969, 260.

[64] A. V. Babaeva, Yu Ya Kharitonov, and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem.*, 1961, **6**, 1159.

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

[66] P. Kierkegaard and B. Nyberg, *Acta Chem. Scand.*, 1965, **19**, 2189.

[67] See Note 3 in J. L. Burmeister, H. J. Gysling, and J. C. Lim, *J. Amer. Chem. Soc.*, 1969, **91**, 44.

[68] D. R. Stranks quoted by R. T. M. Fraser, ref. 6a.

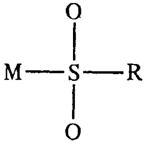
Co-ordination compounds containing sulphur dioxide were first prepared by Gleu,[69] by the action of halo-acids on the sulphitoammines of ruthenium. Complexes of other platinum metals (except osmium),[70,71] iron,[70] cobalt,[72] manganese,[70] molybdenum,[73] and tungsten[73] have been obtained recently. Sulphur dioxide generally acts as a unidentate ligand when it is co-ordinated through the sulphur atom.

Vlcek and Basolo[72] have reported a cobalt complex, $Co_2(CN)_{10}SO_2$, in which the ligand is considered to act as a bidentate bridging group; the bridging is supposed to take place only through the sulphur atom. *X*-Ray analyses of some of the complexes containing unidentate sulphur dioxide have confirmed M—S bonding,[74] although it has been suggested that in the compound $IrCl(CO)(PPh_3)_2(SO_2)$ electrons are donated by the metal to an empty orbital on the sulphur (*cf.* the corresponding nitrosyl compound).[41] Nucleophilic attack on SO_2 was also postulated as the first stage in the preparation of a rhodium(I) adduct.[71]

Sulphur dioxide will also react in a rather different fashion with some transition-metal compounds, especially organometallics with which it can undergo insertion reactions:[75]

$$Mn(CO)_5R + SO_2 \longrightarrow Mn(CO)_5\,SO_2R$$

Wojcicki and his co-workers[76] have established that a structure (I) involving M—S bonding, analogous to a sulphone, applies in substituted carbonyl complexes involving molybdenum, manganese, rhenium, and iron.



$$\mathrm{M{-}\underset{\underset{\textstyle O}{|}}{\overset{\overset{\textstyle O}{|}}{S}}{-}R}$$

(I)

Sulphinates can also be prepared by the oxidative addition of sulphonyl chlorides to square planar iridium(I) compounds.

$$(Ph_3P)_2Ir(CO)Cl + RSO_2Cl \longrightarrow (Ph_3P)_2Ir(CO)Cl_2SO_2R$$

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[69] K. Gleu, W. Breucl and W. Rehm, *Z. anorg. Chem.*, 1936, **227**, 237.

[70] L. Vaska and S. S. Bath, *J. Amer. Chem. Soc.*, 1966, **88**, 1333; L. Vaska and L. Catone, *J. Amer. Chem. Soc.*, 1966, **88**, 5324; J. J. Levison and S. D. Robinson, *Chem. Comm.*, 1967, 199; *Inorg. Nuclear Chem. Letters*, 1968, **4**, 407.

[71] R. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 5377.

[72] A. A. Vlček and F. Basolo, *Inorg. Chem.*, 1966, **5**, 156.

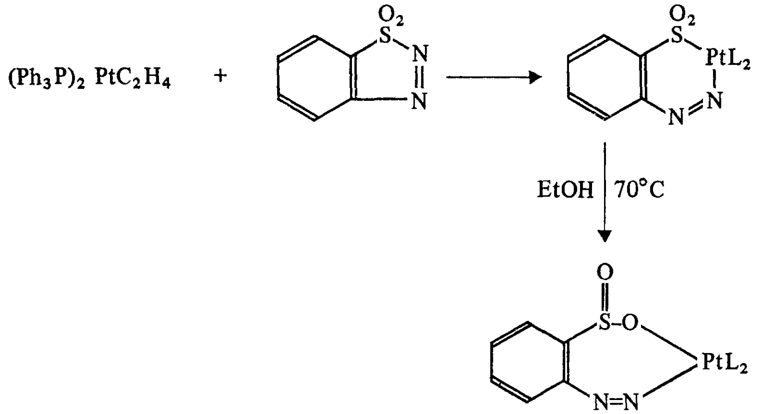
[73] C. G. Hull and M. H. B Stiddard, *J. Chem. Soc.* (*A*), 1968, 710.

[74] L. H. Vogt, jun., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, 1965, **4**, 1157; S. J. La Place and J. A. Ibers, *ibid.*, 1966, **5**, 405.

[75] See, for example, in E. W. Abel and B. C. Grosse, *Organometallic Chem. Rev.*, 1967, **2**, 443.

[76] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 1964, **86**, 5051; 1966, **88**, 4862; *Inorg. Chem.*, 1966, **5**, 889; F. A. Hartman and A. Wojcicki, *J. Amer. Chem. Soc.*, 1966, **88**, 844; 1967, **89**, 2493; *Inorg. Nuclear Chem. Letters*, 1966, **2**, 303.

The structure of these compounds also involves M—S bonding and while many of the alkyl derivatives appear quite stable, when R = *p*-tolyl heating to 110° leads to the evolution of SO_2 and the formation of an Ir—C bond, the reverse of the insertion reactions above.[77] Cobalt compounds of this type have been prepared by both SO_2 insertion[78] and oxidative addition.[79] Main-group alkyls and aryls undergo insertion reactions and polymeric complexes with M—O(SR)O—M bridges have been proposed for aluminium,[80] gallium,[80] and lead.[81] Mercury forms a similar type of polymer $PhHgO_2SPh$ which demonstrates linkage isomerism to give a monomeric Hg—S compound.[82] Thus far, reactions concerning the formation of sulphinates by indirect means have been considered, but some workers have prepared sulphinato-complexes of divalent transition metals by reaction of hydrated halide with sodium aryl sulphinate in water.[83] *X*-Ray analysis shows that bis(toluene-*p*-sulphinato)copper(II) tetrahydrate contains monodentate O-bonded sulphinate groups,[84] and it is thought that the compounds $M(C_6H_5SO_2)_2(H_2O)_2$ (M^{II} = Mn, Fe, Co, Ni, Cu) have bridging or chelating structures with only oxygen co-ordinated.[83] Some mixed ligand complexes of palladium(II) show Pd—S bonding.[85] An interesting example of sulphinate linkage isomerism, which involves chelation and is therefore strictly outside the scope of this Review is:[86]



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[77] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 180.

[78] K. S. Murray, R. J. Cozens, G. B. Deacon, P. W. Felder, and B. O. West, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 705.

[79] K. Yamamoto, T. Shono, and K. Shinra, *Nippon Kagaku Zasshi*, 1967, **88**, 958 (*Chem. Abs.*, 1968, **68**, 92568w).

[80] G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1964, 1295.

[81] R. Gelius, *Z. anorg. Chem.*, 1967, **349**, 22; Von F. Huber and F.-J. Padberg, *ibid.*, 1967, **351**, 1.

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[83] C. W. Dudley and C. Oldham, *Inorg. Chim. Acta*, 1968, **2**, 199.

[84] D. A. Langs and C. R. Hare, *Chem. Comm.*, 1967, 853.

[85] B. Chiswell and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1246; C. W. Dudley and C. Oldham, *Inorg. Chim. Acta*, 1969, **3**, 3.

[86] C. D. Cook and J. S. Jauhal, *J. Amer. Chem. Soc.*, 1968, **90**, 1464.

Sulphoxides have been widely studied as ligands and their co-ordination behaviour reviewed.[87] Dimethyl sulphoxide co-ordinates through oxygen to the lanthanides and yttrium,[88] and to the first-row transition elements,[89–91] and through sulphur to platinum(II),[90] palladium(II),[90–92] iridium(III),[93a] and rhodium(II),[93b] there being *X*-ray confirmation of the i.r. diagnosis for both types of bonding.[91–93] A number of metal carbonyl compounds with dimethyl sulphoxide have been collated[75] and form metal—oxygen bonds.[87] Both S- and O-bonded ligands appear to be present in $Pd(Me_2SO)_4^{2+}$.[94] A similar possibility exists in UCl_4,5DMSO but adducts with other actinide tetrahalides are clearly O-bonded.[95] The use of other sulphoxides—tetramethylene,[96] alkyl,[97] or phenyl[97,98]—does not alter the pattern of co-ordination behaviour described above. The co-ordinating properties of these ligands have been compared with similar oxide ligands.[99] A few complexes of thionyl chloride have been prepared,[100] but structural information is sparse. $AlCl_3 \cdot SOCl_2$ is thought to have an Al—O bond.[101]

C. Selenium *versus* **Oxygen.**—There is little information on adducts with selenium–oxygen ligands. Selenito-complexes of cobalt, nickel, and copper are known, but their structures do not appear to have been studied.[102] Dimethyl selenoxide forms O-bonded adducts with some transition-metal chlorides[103] and with tin(IV):[104] it forms a series of O-bonded hexakis complexes with transi-

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[88] S. K. Ramalingam and S. Soundararajan, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1763.

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[90] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2968; J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nuclear Chem.*, 1961, **16**, 219.

[91] M. J. Bennett, F. A. Cotton and D. L. Weaver, *Nature*, 1966, **212**, 286; M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Cryst.*, 1967, **23**, 788.

[92] D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Comm.*, 1967, 1080.

[93] *a* M. C. McPartlin and R. Mason, *Chem. Comm.*, 1967, 545; *b* S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, 1963, **2**, 960.

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[99] R. S. Drago and D. W. Meek, *J. Phys. Chem.*, 1961, **65**, 1446.

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[101] D. A. Long and R. T. Bailey, *Trans. Faraday Soc.*, 1963, **59**, 594.

[102] H. L. Riley, *J. Chem. Soc.*, 1928, 2985; P. Ray and A. N. Ghosh, *J. Indian. Chem. Soc.*, 1936, **13**, 494.

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[104] T. Tanaka and T. Kamitani, *Inorg. Chim. Acta*, 1968, **2**, 175.

tion-metal perchlorates.[105] Diphenylselenoxide forms O-bonded adducts with the chlorides of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Hg^{II}, Zr^{IV}, and Sn^{IV}.[106]

D. Nitrogen *versus* **Phosphorus.**—The chemistry of amino-fluorophosphines has been reviewed.[107] There is a tendency for oxidising species ($CuCl_2$) to oxidise Me_2NPF_2 to the phosphorane $Me_2NPF_2Cl_2$; this ligand forms complexes with CuCl *via* the phosphorus.[108] P-Bonded adducts are formed between various ligands of this type and a number of carbonyl complexes.[107,109] Some *X*-ray studies have been made on nickel tetrakis piperidine-*N*-difluorophosphine.[110] Similarly, some P—P bonds have been formed by reactions of $(Me)_{3-n}\,(Me_2N)_nP$ (n = 0—3), with PF_5.[111]

E. Nitrogen *versus* **Sulphur.**—Tetrasulphur tetranitride is known to form adducts with Lewis acids.[112,113] The molecular structure of two of these compounds, S_4N_4, $SbCl_5$ and S_4N_4,BF_3 shows that co-ordination takes place *via* one nitrogen atom.[114] In other situations the metal may be chelated by sulphur–nitrogen systems of varying sizes.[113] Reactions of S_4N_4 with metal carbonyls lead to 'thionitrosyls', but such structural information as is available suggests that these also are chelates.[115] Thionitroso-complexes $(RNS)Fe_2(CO)_6$ have been reported but these are believed to involve a complicated Fe—N—S—Fe bridging structure.[116]

4 Polyatomic Ambidentate Ligands with One Central Atom Separating the Donor Atoms

The presence of a central atom especially one of the second or subsequent rows, means that the possibility of chelation is increased over the ligands of the previous section. The examples cited consist largely of cases where the ligand is unidentate.

A. Nitrogen *versus* **Sulphur.**—The widely studied thiocyanate ion is considered first. It forms compounds with most of the elements in the periodic table and its mode of co-ordination may be determined conveniently using i.r. spectroscopy, providing the results are interpreted with caution. The three fundamental

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[105] R. Paetzold and G. Bochmann, *Z. Chem.*, 1968, **8**, 308.
[106] R. Paetzold and P. Vordank, *Z. anorg. Chem.*, 1966, **347**, 294.
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[110] B. Greenberg, A. Amendola, and R. Schmutzler, *Naturwiss.*, 1963, **50**, 518.
[111] D. H. Brown, K D. Crosbie, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1969, 551.
[112] K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, 1967, **6**, 107.
[113] A. J. Bannister and J. S. Padley, *J. Chem. Soc.* (*A*), 1969, 658.
[114] D. Neubauer and J. Weiss, *Z. anorg. Chem.*, 1960, **303**, 28; H. G. B. Drew, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1967, **6**, 1906.
[115] M. Goehring and A. Debo, *Z. anorg. Chem.*, 1953, **273**, 319; T. S. Piper, *J. Amer. Chem. Soc.*, 1958, **80**, 30.
[116] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1968, **7**, 1833.

frequencies of thiocyanate group lie in the range: ν_1 2040—2080; ν_2 465—480; and ν_3 780—860 cm^{-1} for an N-bonded group, whereas for an S-bonded group the ranges are: ν_1 2080—2120, ν_2 410—470, and ν_3 690—720 cm^{-1}: the frequencies may be described approximately as C—N stretch, N—C—S bend and C—S stretch respectively.[117] There are known, however, linkage isomers where ν_1 is greater for the S-bonded than for the N-bonded isomer.[118,119] Furthermore, the first overtone of ν_2 has an intensity comparable to ν_3, and a band in the 880—800 cm^{-1} region may be assigned to either $2\nu_2$ for an S-bonded or ν_3 for an N-bonded compound.[120] By consideration of all three fundamentals one can often determine the mode of co-ordination from the positions of observed bands, but in a complicated spectrum this is not always possible. In such circumstances, it is preferable to measure the integrated intensity of ν_1 when values greater or less than the free ion value suggest N-bonded or S-bonded thiocyanate groups respectively:[121] this procedure has been rationalised.[122]

Table 2 shows some thiocyanate complexes of the transition elements (mixed ligand complexes will be discussed shortly) and it is not surprising in view of the above, that different conclusions have been reached by different authors on the structure of the rhenium(IV) complex. Table 2 shows that the mode of bonding varies from metal to metal and that, using the Ahrland–Chatt–Davies classification,[123] class 'b' metals form thiocyanato- and class 'a' isothiocyanato-complexes. This pattern is amplified by consideration of further compounds. The lanthanides (except Ce^{III}, Pm^{III}, Tm^{III}, and Lu^{III}) form $M(NCS)_6^{3-}$,[124] and some mixed ligand isothiocyanates.[125] Scandium(III) forms isothiocyanato-complexes in the presence of a variety of nitrogen and oxygen donors.[126] Octaisothiocyanato-complexes are formed by thorium(IV)[127] and uranium(IV),[127,128] and the uranyl group forms several isothiocyanato-complexes,[128,129] Isothiocyanates also predominate amongst the main group elements.[130] Complexes of gallium(III)[131]

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[117] 'Spectroscopic Properties of Inorganic and Organometallic Compounds', Chemical Society, London, 1968, vol. 1, p. 196.

[118] H.-H. Schmidtke, *J. Amer. Chem. Soc.*, 1965, **87**, 2522; *Z. phys. Chem. (Frankfurt)*, 1965, **45**, 305.

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[125] F. A. Hart and F. P. Laming, *J. Inorg. Nuclear Chem.*, 1964, **26**, 579; D. R. Cousins and F. A. Hart, *ibid.*, 1968, **30**, 3009; A. M. Colub and Au Van Luong, *Russ J. Inorg. Chem.*, 1968, **13**, 1737; 1969, **14**, 47.

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[131] S. J. Patel and D. G. Tuck, *Canad. J. Chem.*, 1969, **47**, 229.

Table 2 *Some thiocyanate complexes of the transition elements*

$Ti(NCS)_6^{3-}$ [a]	$V(NCS)_6^{3-}$ [b]	$Cr(NCS)_6^{3-}$ [c]	$Mn(NCS)_4^{2-}$ [d]	$Fe(NCS)_4^{2-}$ [d]	$Co(NCS)_4^{2-}$ [c, d]	$Ni(NCS)_4^{2-}$ [c, d]	$Cu(NCS)_4^{2-}$ [c, d]	$Zn(NCS)_4^{2-}$ [c, d, e]
			$Mn(NCS)_6^{4-}$ [f]	$Fe(NCS)_6^{3-}$ [f]		$Ni(NCS)_6^{4-}$ [d]		
$Zr(CNS)_8^{4-}$ [g]	* $Nb(NCS)_6^{2-}$ [h, i, j]	$Mo(NCS)_6^{3-}$ [b]	$Tc(NCS)_6^{-}$ [k]	$Ru(NCS)_6^{3-}$ [c]	$Rh(SCN)_6^{3-}$ [c]	$Pd(SCN)_4^{2-}$ [c]	$[(AgSCN)(SCN)]^{-}$ [l]	$Cd(NCS)_2(SCN)_2^{2-}$ [e]
$Hf(CNS)_8^{4-}$ [g]	* $Ta(NCS)_6^{-}$ [h]	$W(CNS)_6$ [m]	$Re(NCS)_6^{2-}$ [n]	$Os(NCS)_6^{3-}$ [c]	$Ir(SCN)_6^{3-}$ [c]	$Pt(SCN)_4^{2-}$ [c]	$Au(SCN)_4^{-}$ [c]	$Hg(SCN)_4^{2-}$ [e]
			$Re(SCN)_6^{-}$ [o]			$Pt(SCN)_6^{2-}$ [c]		
			$Re(SCN)_6^{2-}$ [o]					

Isothiocyanato – complexes M–NCS. Thiocyanato – complexes M–SCN. Structure unknown M–CNS.
Borderline class 'a'/class 'b' metals enclosed in ………… Class 'a' metals on the left (plus Zn). Class 'b' metals – bottom right.
*In solution only.

[a] W. Lenz, H. L. Schlaefer, and A. Ludi, *Z. anorg. Chem.*, 1969, **365**, 55; [b] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590; [c] H.-H. Schmidtke, *Ber. Bunsengesellschaft physik. Chem.*, 1967, **71**, 1138 and refs. therein; [d] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 715; [e] K. A. Taylor, T. V. Long, and R. A. Plane, *J. Chem. Phys.*, 1967, **47**, 138; [f] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 268; [g] A. M. Golub and V. N. Sergunkin, *Russ. J. Inorg. Chem.* 1966, **11**, 419; [h] T. M. Brown and G. F. Knox, *J. Amer. Chem. Soc.*, 1967, **89**, 5296; [i] H. Boehland, E. Tiede, and E. Zenker, *J. Less Common Metals*, 1968, **15**, 89; [j] G. F. Knox and T. M. Brown, *Inorg Chem.*, 1969, **8**, 1401; [k] K. Schwochau and H. H. Pieper, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 711; [l] I. Lindquist and B. Strandberg, *Acta Cryst.* 1957, **10**, 173; [m] H. Funk and H. Böhland, *Z. anorg. Chem.*, 1963, **324**, 168; [n] F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, 1967, **6**, 929; [o] R. A. Bailey and S. L. Kozak, *Inorg. Chem.*, 1967, **6**, 419; 2155.

and indium(III)[132] form isothiocyanates although the cyclic trimers $(Et_2MSCN)_3$, (M = Al, Ga, or In) have M—S—M bridges.[133] Tin(II) forms N-bonded thiocyanates.[134]

Table 3 shows the effect of other ligands on the preferred linkage of the thiocyanato-group to palladium(II) and cobalt(III). It is apparent that ligands with a tendency to back-bond with the metals, *i.e.* to accept some electron density from the metal into empty orbitals, encourage the formation of Pd—NCS and Co—SCN bonds respectively. Thus, any explanation involving π-bonding for the behaviour of palladium[135] (*e.g.* that the decreased electron density result-

Table 3 *Effect of* L *on the equilibrium* L—M—SCN $\rightleftharpoons$ L—M—NCS

Pd $(SCN)_4^{2-}$	*a*	$Co(NH_3)_5(NCS)^{2+}$	*h*
		$Co(NH_3)_4(NCS)_2^+$	*h*
Pd $(NH_3)_2(SCN)_2$	*a*	Co en_2 L $(NCS)^+$	*h*
Pd $(PEt_3)_2(NCS)_2$	*a*	L = Cl^- or NCS^-	
		Co(tet a) $(NCS)_2^+$	*i*
*Pd bipy$(NCS)_2$	*b, c*	Co(tet b) $(NCS)_2^+$	*i*
Pd (4,4'-Me_2bipy) (NCS)		$Co(C_{16}H_{32}N_4)$ $(NCS)_2^+$	*j*
(SCN)	*d*	*$Co(DH)_2$ L (NCS)	*k*
Pd phen$(SCN)_2$	*d*	L = NO_2^-, various	
Pd (5,NO_2-phen) $(NCS)_2$	*d*	pyridines and anilines	
Pd $(PPh_3)_2$ $(NCS)_2$	*c*	*$Co(CN)_5(SCN)^{3-}$	*l*
*Pd $(AsPh_3)_2(NCS)_2$	*b, c*	Co $bipy_2$ $(SCN)_2^+$	*m, n*
Pd $(SbPh_3)_2(SCN)_2$	*c*	Co $phen_2$ $(SCN)_2^+$	*m*
		Cobalamin-SCN	*o*
Pd dien $(SCN)^+$	*e*	$Co(DH)_2$ L (SCN)	*k*
Pd Et_4 dien$(NCS)^+$ SCN^-	*e, f*	L = Cl^-, Br^-, SCN^-, H_2O,	
Pd Et_4 dien$(SCN)^+$ PBh_4	*g*	NH_3, PPh_3	

*Stable linkage isomer.

Abbreviations: bipy = 2,2'bipyridyl; phen = o-phenanthroline; dien = diethylenetriamine; tet a and tet b = *trans*- and *cis*-hexamethyl-1,4,8,11-tetra-azacyclotetradecane; $C_{16}H_{32}N_4$ = hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene; DH = dimethylglyoximato; cobalamin = Vit B_{12a} with H_2O replaced.

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[133] K. Dehnicke, *Angew. Chem. Internat. Edn.*, 1967, **6**, 947.

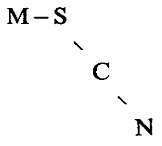
[134] B. R. Chamberlain and W. Moser, *J. Chem. Soc. (A)*, 1969, 354.

ing from back-bonding increases the effective positive charge on the metal or makes it 'harder',[136] and favours the formation of the more ionic Pd—N bond)[135] is contradicted by the cobalt compounds. Similarly, the concept of symbiosis,[137] which accounts for the latter, is not consistent with the changes in the palladium compounds. Rhodium(I) forms square planar isothiocyanato-complexes with π-acceptor type ligands in general agreement with the palladium compounds,[138] whereas rhodium(III) is similar to cobalt(III) and iridium(III) in forming $[M(NH_3)_5NCS]^+$.[118] Further, although the stable isomer of $Mn(CO)_5SCN$ is S-bonded, and this is maintained where only one CO group is substituted, the replacement of two CO groups by weaker π-bonding ligands, or by anilines which cannot take part in π-bonding, results in the formation of isothiocyanates.[139] The behaviour of these manganese compounds is in contrast to that of palladium, but is in general agreement with that of cobalt.

It seems therefore, that the co-ordination of the thiocyanate group towards certain metals may be modified by the presence of other ligands. This does not occur for every metal, *cf.* scandium and the lanthanides,[124–126] but if the metal belongs to class 'b' or shows characteristics intermediate between class 'a' and class 'b', then the effect of other ligands may be important in determining its behaviour. The fact that neither $[Cr(CO)_5NCS]^-$ [140] nor $(\pi\text{-}C_5H_5)Cr(NO)_2NCS$[141] form thiocyanato-linkages whereas the similar compounds $Mn(CO)_5SCN$,[139] $(\pi\text{-}C_5H_5)Fe(CO)_2SCN$,[141] $(\pi\text{-}C_5H_5)M(CO)_3SCN$,[141] and $[M(CO)_5SCN]^-$,[140] (where M = Mo or W) all do, perhaps is because chromium(0) is closer to class 'a' than the remainder, and is too close to be modified by the five carbonyl groups.

The precise nature of the ligand effect is not apparent, although it must be electronic in origin. It acts in one way towards the group of compounds exemplified by palladium, and in the opposite way to the cobalt compounds. It is not clear whether the existence of two groups of compounds relates to class 'b' and borderline cases, to square planar and octahedral cases, to d^8 and d^6 cases or to some other description more fundamental than 'the palladium and cobalt groups'.

However, it is not surprising to find borderline situations in which the factors just discussed appear to be in approximate balance. Under these circumstances linkage isomers may be found,[6,119] or other effects may be recognised as tilting the equilibrium position one way or the other. Thus, the differing steric requirements of the M–S over the M–N–C–S linkage have been used to



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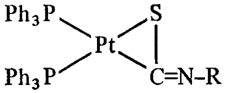
[135] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.
[136] R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533.
[137] C. K. Jorgenson, *Inorg. Chem.*, 1964, **3**, 1201.
[138] M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, 1967, **6**, 1854.
[139] *a* M. F. Farona and A. Wojcicki, *Inorg. Chem.*, 1965, **4**, 857; *b* 1965, **4**, 1402.
[140] A. Wojcicki and M. F. Farona, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2289.
[141] T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1268.

explain the formation of [Pd Et_4 dienNCS]$^+$ (see Table 3) and of *cis*-$Mn(CO)_3L_2SCN$ (where L = Ph_3As or Ph_3Sb), when the *trans*-isomer is an isothiocyanate.[139b] The nature of the solvent can change the mode of linkage in solution,[139,141–3] as can the counter-ion used.[144] The complexity and versatility of the thiocyanate group are well illustrated by the isolation and characterisation of the three possible linkage isomers in the system, bisthiocyanato-tri-(2-pyridyl)-aminecopper(II).[145]

In contrast, there are few examples in which organic thiocyanates or isothiocyanates act as ligands. Ethyl thiocyanate forms bis-adducts with $TiCl_4$, $TiBr_4$, and $SnCl_4$ in which M—S bonds are believed to be present.[146] Ethyl isothiocyanate forms a 1:1 adduct with $TiCl_4$ which is a liquid at room temperature.[146] No structural assignments are made by the authors, but the adduct shows an i.r. band at 1605 cm^{-1} [146] which is similar to that observed in the compounds [$Pt(Ph_3P)_2(RNCS)$] where R = methyl or phenyl.[147] These latter compounds have been assigned the structure:



A similar structure is proposed for [$Rh(Ph_3P)_2(PhNCS)_2$] with the extra phenyl isothiocyanate acting as a unidentate ligand through sulphur.[147] It is thought that the analogous platinum compound with allyl isothiocyanate contains the allyl radical and the thiocyanate group co-ordinated separately. A similar process is suggested for the reaction of allyl isothiocyanate with palladium(II) chloride but the ligand remains intact and co-ordinates to cobalt(II) and chromium(III) through nitrogen.[148]

There appears to be relatively little structural information concerning the co-ordination of thioamides. *NN*-Dimethyl thioacetamide co-ordinates to cobalt(II) through sulphur.[149] On the other hand, there is a wealth of information on the co-ordination of thiourea. It frequently acts as a unidentate ligand, when it co-ordinates through sulphur to palladium(II), platinum(II) and several 3*d* elements.[150] S-Bonded compounds [$Re\,tu_3X_3$] are known.[151] (tu = thiourea.)

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[142] A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, unpublished results.

[143] F. Basolo, W. H. Baddley, and K. J. Wiedenbaum, *J. Amer. Chem. Soc.*, 1966, **88**, 1576.

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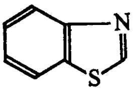
[150] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527; D. C. Flint and M. Goodgame, *J. Chem. Soc.* (*A*), 1966, 744; D. M. Adams and J. B. Cornell, *ibid.*, 1967, 884.

[151] F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, 1967, **6**, 214.

In the compounds M $tu_2(NCS)_2$, (M = Mn, Co, Ni, or Cd), thiourea forms a bidentate bridge through the sulphur atom.[152] The only example of a unidentate N-bonded thiourea (or thioamide) appears to be in the compound Ti tu_2Cl_4.[153] The ligand thiocarbohydrazide, $(H_2N{\cdot}NH)_2CS$, frequently acts as a chelate but as a unidentate ligand it co-ordinates through sulphur to Zn^{II}, Cd^{II} and Hg^{II} and to some 3*d* elements.[154]

Benzothiazole (II) has been shown to form complexes with iron(II),[155] cobalt(II),[155-7] nickel(II),[155,156] copper(II),[157] and zinc(II)[156] and with a number of different anions. Co-ordination occurs *via* the nitrogen atom,[156,157] except when the ligand has a bridging rôle in which case both heteroatoms are involved.[156] 2-Methylbenzothiazole behaves in a similar fashion.[158]



(II)

Unidentate dithiocarbate complexes of rhodium and iron have been reported in which metal—sulphur bonds are formed.[159] Similar bonding occurs with some quadrivalent actinides.[160] Dithio-oxamide chelates to $TiBr_4$ and $SnCl_4$ through the nitrogen atoms.[161]

B. Nitrogen *versus* Oxygen.—The cyanate ion is known to form complexes with a wide number of metals, although its co-ordination behaviour has not been studied as widely as that of the thiocyanate ion. Anionic isocyanato-complexes $[M^{m}(NCO)_n]^{m-n}$ have been reported[162] for M = Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Pd^{II}, and Sn^{IV}. Varying the σ- and π-donor properties of the ligands in some complexes of the type $[ML_2(NCO)_2]$, where M = Pd^{II} or Pt^{II}, does not alter the mode of co-ordination of the cyanate group.[163] Isocyanato-complexes are generally formed in mixed ligand complexes of

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[152] M. Nardelli, A. Braibanti, and G. Fava, *Gazzetta*, 1957, **87**, 1209.
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[155] N. N. Y. Chan, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.* (*A*), 1968, 2499.
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[157] R. A. Ford, G. Halkyard, and A. E. Underhill, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 507.
[158] E. J. Duff, M. N. Hughes, and K. J. Rutt, *J. Chem. Soc.* (*A*), 1969, 2126.
[159] C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 84.
[160] J. P. Bibler and D. G. Karraker, U.S. At. Energy Comm., DP-MS-66-82 (*Chem. Abs.*, 1968, **68**, 8892s).
[161] S. C. Jain and R. Rivest, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2787.
[162] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 262; 1268.
[163] A. H. Norbury and A. I. P. Sinha, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 355; *J. Chem. Soc.* (*A*), 1968, 1598.

cobalt,[164,165] nickel,[166] palladium,[167] and platinum.[167,168] It was originally suggested that bridging of the type M—NCO—M occurred in the octahedral complex $[Co(4\text{-}NC{\cdot}C_5H_5N)_2(NCO)_2]$,[165] but subsequent research established that the bridging was of the type M—N(CO)—M in this and a number of related complexes.[169] N.m.r. evidence indicated that linkage isomerism of the cyanate group took place in solutions of $[Pt(Et_3P)_2(NCO)H]$, but only the isocyanate was isolated as a solid.[170] The oxygen atom is believed to be the donor atom to chromium(II) in melts of $CrCl_3$ in KNCS, but again no solid cyanates have been isolated.[171]

The bis(cyclopentadienyl)titanium(IV) species forms a bis-cyanate complex which has been reported as N-bonded[172] or O-bonded[173] by different authors. $(\pi\text{-}C_5H_5)_2\,Ti(NCO)$[174] and $(\pi\text{-}C_5H_5)_2\,V(NCO)_2$[175] both form N-bonded complexes. If $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$ is the correct formulation, it joins the complex hexacyanates of rhenium(IV), rhenium(V) and molybdenum(III)[176] as the only isolated O-bonded inorganic cyanates.

A number of organic cyanates are known,[177] but their co-ordination behaviour has yet to be investigated. There are no examples of unidentate co-ordination of organic isocyanates, although some instances have been cited of bridging in complexes by these molecules.[146,178]

Amides have been extensively studied as ligands. Their uses as non-aqueous solvents have been reviewed.[179] Primary amides co-ordinate through oxygen to a number of conventional Lewis acids,[180] to the later 3*d* elements[181,182] and

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

[165] H. C. A. King, E. Körös, and S. M. Nelson, *Nature*, 1962, **196**, 572.

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[175] G. Doyle and R. S. Stuart, *Inorg. Chem.*, 1968, **7**, 2479.

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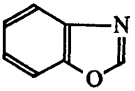
[180] J. Archambault and R. Rivest, *Canad. J. Chem.*, 1958, **36**, 1461; W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 1960, 2144; A. Clearfield, and E. Malkiewich, *J. Inorg. Nuclear Chem.*, 1963, **25**, 237; R. C. Paul, B. R. Sreenathan, and S. L. Chadha, *ibid.*, 1966, **28**, 1225.

[181] C. R. Rollinson and R. C. White, *Inorg. Chem.*, 1962, **1**, 281; W. E. Bull, S. K. Madan and J. E. Willis, *ibid.*, 1963, **2**, 303; S. K. Madan and H. H. Denk, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1049.

[182] R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, 1963, **2**, 124; M. B. Welch, R. S. Stephens, and R. O. Ragsdale, *Inorg. Chim. Acta*, 1968, **2**, 367.

to palladium(II) and platinum.[183] The donor properties are modified on varying the amide substituents[182] but there is no evidence to suggest that the mode of co-ordination is affected. Bridging may involve both N and O,[184] although there are no unequivocal examples to confirm this. Urea and substituted ureas act as unidentate ligands. Urea is N-bonded in its complexes with palladium(II) and platinum(II)[185] and in $[Sn(urea)_2Cl_4]$[186] but is O-bonded in complexes with chromium(III), iron(III), copper(II), zinc(II),[185] and even in $[Sn(urea)_2Br_4]$.[186] Substituted ureas also co-ordinate through oxygen.[187]

Benzoxazole (III) forms complexes with cobalt(II), nickel(II), copper(II), and zinc(II) which are N-bonded,[188] but 2-methylbenzoxazole co-ordinates to the same metals through oxygen.[189]



(III)

C. Nitrogen *versus* Selenium.—Selenocyanate complexes have been reviewed.[190] The co-ordination behaviour of the selenocyanate ion is similar to that of the thiocyanate ion, in that it normally co-ordinates with class 'a' metals through nitrogen, and with class 'b' metals through selenium.[6,191] Although some selenocyanato–vanadium(III) complexes have recently been reported,[192]* in contradiction to earlier work,[193] the mode of co-ordination appears to be less sensitive to the electronic influence of other ligands in the complex. Thus, unlike the change from Pd—S to Pd—N bonding in $[PdL_2(SCN)_2]$ complexes

*The existence of selenocyanato-vanadium(III) complexes was reported in *Chem. Abs.*, 1969, **70**, 102599q/192. The abstract is incorrect. The original paper confims that the compounds contain the N-bonded isoselenocyanato-grouping.

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when L is changed from a σ-bonding ligand to a π-bonding ligand, in all the corresponding palladium–selenocyanate complexes except [Pd(n-$Bu_3P)_2(NCSe)_2$], palladium–selenium bonds are formed.[194] Steric effects, on the other hand, can modify the mode of bonding and have been used to implement the synthesis of linkage isomers:[144a] the counterion can also be important as was noted for the thiocyanate ion.[144]

There is little information on other ligands of this type (N—X—Se). Some *NN'*-disubstituted selenoureas act as unidentate ligands through selenium towards palladium(II) and platinum(III).[195]

D. Sulphur *versus* Oxygen.—The thiosulphate ion, like the sulphite ion, co-ordinates most readily through sulphur to the 3*d* elements[196–8] and to palladium(II) and platinum(II)[198,199] Chromate oxidation of the thiosulphate ion probably results in the formation of $[O_3CrS_2O_3]^{2-}$.[200] Chelation through sulphur and one oxygen has been confirmed by *X*-ray crystallography.[201] Linkage isomerism has been suggested for the ion $[Co(CN)_5S_2O_3]^{4-}$ on chemical evidence,[202] but this is unconfirmed by any modern physical techniques. There is kinetic evidence for linkage isomerism in the complex ion $[Co(NH_3)_5S_2O_3]^+$.[203]

The thiophosphate ion, SPO_3^{3-}, forms Co—S bonds in some ammine complexes of cobalt(III).[197]

5 Miscellaneous Ambidentate Ligands

There are some ligands which do not fit conveniently into any of the previous sections and yet which merit a brief mention. Thus, sulphinamides $MeS(O)NR_2$, like dimethylsulphoxide, co-ordinate to 3*d* elements through oxygen.[204] The nitrosodicyanomethanide ion $[ONC(CN)_2]^-$ forms tetrakispyridine complexes with cobalt(II), nickel(II) and copper(II) through the nitrosyl nitrogen,[205] whereas [Ni $py_4(ONO)_3$] contains the nitrito-linkage.[50] When 2-(diphenyl-arsinomethyl) pyridine does act as a unidentate ligand towards cobalt(II), it is through nitrogen that it co-ordinates.[206]

1,4-Thioxan forms S-bonded complexes with copper, silver, palladium,

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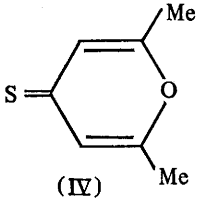
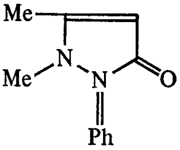
platinum, rhodium, cadmium, and mercury,[207,208] and recent studies show that the same bonding applies with titanium(IV), niobium(V), tantalum(V), tin(IV), aluminium(III), and molybdenum(IV).[209] The ligand selenoxan bonds through the selenium atom in its complexes with titanium(IV), tin(IV), and niobium(V).[209] In the complex $BF_3 \cdot C_4H_8OS$, however, i.r. evidence indicates co-ordination of the ligand through the oxygen atom.[209] Co-ordination through both oxygen and sulphur atoms, has been suggested[210] for the polymeric complex $[TiCl_3 \cdot C_4H_8OS]_n$. Similarly, 2,6-dimethyl-4-thiopyrone (IV) forms S-bonded complexes with Cu^I, Ag^I, Fe^{II}, Co^{II}, Ni^{II}, Pd^{II}, Pt^{II}, Hg^{II}, Sb^{III}, and Bi^{III}.[211]



(IV)

The corresponding pyrone co-ordinates to a number of Lewis acids through the keto-oxygen,[212] as is the case when xanthone[213] or 4-pyridone[214] are the donors. Antipyrine (V) also co-ordinates through oxygen.[215]



(V)

The heterocyclic nitrogen is the preferred donor atom in some cyanopyridines[216] and in 4-aminopyridine.[217] Imidazole probably co-ordinates through the tertiary nitrogen also.[218]

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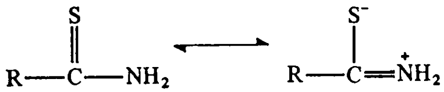
6 Conclusions

Any conclusions that can be drawn from this survey are, at best, tentative since many of the ligands included have had their co-ordination behaviour towards only cobalt, nickel, and copper studied. This consequence of the recent interest in crystal field theory has as its corollary the fact that the co-ordination chemistry of the titanium and vanadium sub-groups has been somewhat neglected. However, some of the results pertaining to these two latter sub-groups suggest that their allocation to 'class a' should be changed and that, in many aspects of their chemistry, they should be classified as 'borderline' (see Section 5—thioxan). The transition elements as a whole are, therefore, either 'borderline' or 'class b' and, as originally stated,[123] their characters may change as their oxidation or magnetic states are altered, or, as Pearson[136] later noted, as the nature of the surrounding ligands is modified.

If the above supposition is correct, it is no longer useful to explain the behaviour of a particular ambidentate ligand, dimethyl sulphoxide for example, as arising from the preference of 'class b' metals for sulphur and of 'class a' for oxygen, even though the description is apposite in this case. If other similar ligands are considered then $S_2O_3^{2-}$, SO_3^{2-}, SO_2, and RSO_2^- all prefer to co-ordinate through sulphur, and only in the case of the sulphinate group is there any pronounced tendency to form M—O bonds (see sections 3B and 4D).

Thus, the preferred mode of co-ordination of an ambidentate ligand is determined by the nature of the respective donor sites as well as that of the acceptor. This is particularly apparent when the ligands reviewed in Section 2 (CO, CN^-, NO^+, and CS) are considered. Calculations suggest that in every case the mode of bonding can be correlated with the availability of a large, correctly orientated pair of electrons on the bonding atom. The interesting change then, in considering the sulphur–oxygen ligands of the previous paragraph, is that which takes place in the distribution of electrons within the S—O bond in X_2SO as X changes from O^- to Me. As a consequence of this change, the differing ligands have varying abilities to differentiate between the acceptor systems.

There are no other comparable systems of ambidentate ligands in which the two donor atoms belong to the same periodic group. It is even less satisfactory to use the 'a/b' classification to account for the behaviour of a ligand containing donor atoms from different groups as well as different rows of the periodic table. However, this is done for the archetypal ambidentate ligand, the thiocyanate ion, and, as was seen in Table 2, done with remarkable success. The overriding importance of charge distribution is seen when the thiocyanate ion is compared with thioamides having the same N—C—S framework. The electron distribution in thioamides is indicated by the canonical forms:



and co-ordination accordingly takes place through sulphur.

When ligands containing donor atoms of the same row are considered, the same effects are seen to predominate. NCO^-, with its electronic charge concentrated on the nitrogen, co-ordinates largely through nitrogen while amides, with similar canonical forms to thioamides, co-ordinate through oxygen. In the case of NO_2^- it is apparent that steric effects can stabilise nitrito-compounds which would normally be thermodynamically less stable than the nitro-compounds. Kinetic results show how the nitrito-group can readily isomerise by an intramolecular process. However it is not clear why nitro-complexes should be thus preferred.

The few results available for ligands with the same donor atoms in different states of hybridisation indicate that co-ordination occurs more readily through an atom with its lone pair of electrons in an sp^2 rather than an sp^3 orbital, but that the necessarily greater double-bonding associated with atoms in *sp* hybridisation reduces or counteracts the greater extension of the *sp* hybrid orbital (see Section 5).

The varied behaviour of the thiocyanate ion, and the interest and activity in its study, are consequences of its equitable electron distribution. It is therefore more likely to be sensitive to relatively small changes in the acceptor, and is thus a useful probe into the electronic nature of the acceptor. It is anticipated that the most promising developments in the chemistry of ambidentate ligands will come from the search for other ligands with similarly equitable electron distributions for the study of borderline acceptors, or alternatively, in the search for ligands which are ambidentate towards a particular group of metals, the titanium sub-group for example, and which may therefore be used to probe the nature of these metals in their complexes. In either case, ligands which can have their own character modified by changing substituents are to be preferred.