*Coordination Chemistry Reviews*, 11 (1973) 343–402

# FIVE-COORDINATION IN IRON(II), COBALT(II) AND NICKEL(II) COMPLEXES

R. MORASSI, I. BERTINI and L. SACCONI*

*Istituto di Chimica Generale e Inorganica, Università di Firenze, Laboratorio CNR, 39 Via J. Nardi, 50132 Florence (Italy)*

(Received February 5th, 1973)

CONTENTS

## ABBREVIATIONS**

| | |
|---|---|
| B | monodentate ligand |
| L | organic ligand |
| R | alkyl or aryl group |
| X | coordinating anion (halide or pseudohalide unless otherwise specified) |
| Y | counterion |
| Z | substituent on aromatic ring |

---

[*] Author to whom correspondence should be addressed.

[**] Roman numerals in parentheses refer to the formulae shown in the text.

| | |
|---|---|
| abMe$_2$ | 2,2′-bis(*N*,*N*-dimethylamino)azobenzene |
| AP | diphenyl(*o*-diphenylarsinophenyl)phosphine |
| AsNAs | bis(2-diphenylarsinoethyl)amine |
| AsSAs | bis(2-diphenylarsinoethyl)sulphide |
| ASTP | tris(*o*-diphenylphosphinophenyl)arsine (LX) |
| atsc | acetonethiosemicarbazone |
| baphenMe$_2$ | *N*-(2′-*N*″,*N*″-dimethylaminophenyl)-2-*N*′,*N*′-dimethylaminobenzylideneimine |
| bdhe | *N*,*N*-bis(2-diethylaminoethyl)-2-hydroxyethylamine (XCII) |
| bdmp | 1,3-bis(dimethylphosphino)propane (XII) |
| BDPI | 2,3-butandionebis(2-diphenylphosphinoethyl)imine (LXXI) |
| bphen | *N*,*N*′-tetramethylenebis(5-chloro-2-hydroxybenzopheniminate) |
| btpy | 2,3-(dibenzothiazol-2-yl)pyridine |
| bza-R | benzoylacetone aryliminate |
| catec | *o*-dihydroxobenzene |
| CR | 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1] heptadeca-1(17),2,11,13,15-pentaene (LXXIV) |
| CRH | 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1] heptadeca-1(17),13,15-triene (LXXV) |
| 1,7-CT | 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene |
| 1,3,7,10-CT | 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14)3,7,10-tetraene |
| dabco$^+$ | 1,4-diazabicyclo[2.2.2] octonium |
| dacoDA | 1,5-diazacyclooctane *N*,*N*′-diacetate (XCIV) |
| DAP | bis(3-dimethylarsinopropyl)phenylphosphine |
| DAP-R$_2$ | 2,6-diacetylpyridinebis(alkylimine) (LIII) |
| das | *o*-phenylenebis(dimethylarsine) (XVII) |
| ddc | dimethyldithiocarbamate (XXIV) |
| ddta | 1,11-bis(dimethylamino)-3,9-dithia-6-azaundecane |
| DENB$_2$ | bis[2-(Z-benzylideneimino)ethyl] amine (XLIII) |
| DMMP | dimethyl methylphosphonate |
| dmp | 2,9-dimethyl-1,10-phenanthroline (XXXI) |
| DMS | 2,2′-dimercaptodiethylsulphide (XXXVIII) |
| dpb | 1,4-bis(diphenylphosphino)butane |
| dpe | 1,2-bis(diphenylphosphino)ethane (XV) |
| DPEA | bis[2-(2′-pyridyl)ethyl] amine (LV) |
| DPES | bis[2-(2′-pyridyl)ethyl] sulphide (LVI) |
| DPNB$_2$ | bis[2-(Z-benzylideneimino)propyl] amine (XLIV) |
| dpp | 1,3-bis(diphenylphosphino)propane |
| DSP | bis(*o*-methylthiophenyl)phenylphosphine |
| dthb | dithiobenzoate (XXII) |
| dthpa | dithiophenylacetate (XXIII) |
| edas | *cis*-1,2-bis(dimethylarsino)ethylene (XVIII) |
| EPNO | 4-ethoxypyridine *N*-oxide (VIII) |
| Et$_4$dien | bis(2-diethylaminoethyl)amine (XLII) |
| Etphos | 5-ethyl-5*H*-dibenzophosphole (VII) |
| Et$_6$tren | tris(2-diethylaminoethyl)amine (LXXIX) |
| fdma | ferrocene-1,1′-bis(dimethylarsine) (XX) |
| fdpa | ferrocene-1,1′-bis(diphenylarsine) (XIX) |
| H-nnpO | *N*-[2-(diphenylphosphine-oxide)ethyl]-*N*′,*N*′-diethylethylenediamine |
| FTP | bis[2-(diphenylphosphino)-3,4,5,6-tetrafluorophenyl] phenylphosphine |
| HPPH | 1,2-bis(phenylphosphino)ethane (XIII) |
| IAMP | (*N*-isopropyl-aminomethyl)pyridine-2 |
| LE | 1,2-di-(2′-pyridyl)ethane (XXIX) |
| LS | di-(2-pyridyl)disulphide (XXVIII) |
| lutox | 2,5-lutidine *N*-oxide (X) |
| π-ma | π-methallyl |

| | |
|---|---|
| MABen-NEt$_2$ | *N*-(2′-*N*″,*N*″-diethylaminoethyl)-2-*N*′-methylaminobenzylideneimine (L) |
| mbpt | 2-(6-methyl-2-pyridyl)benzothiazole |
| Me-dabco$^+$ | *N*-methyl-1,4-diazabicyclo[2.2.2] octonium |
| Me$_4$daeo | bis(2-dimethylaminoethyl)oxide (XLVII) |
| Me$_4$daes | bis(2-dimethylaminoethyl)sulphide (XLVIII) |
| Me$_5$dien | bis(2-dimethylaminoethyl)methylamine (XLI) |
| Me$_2$dpma | 6,6′-dimethyl-di-(2-pyridylmethyl)amine (LVII) |
| MeDPT | bis(3-aminopropyl)methylamine (XLIX) |
| Mephos | 5-methyl-5*H*-dibenzophosphole (VI) |
| mepic | 6-methyl-2-aminomethylpyridine |
| Me$_2$tpma | 2-pyridylmethyl-di-(6-methyl-2-pyridylmethyl)amine (LXXXII) |
| Me$_3$tpma | tri-(6-methyl-2-pyridylmethyl)amine (LXXXIII) |
| Me$_6$tpt | tris(3-dimethylaminopropyl)amine (LXXXI) |
| Me$_6$tren | tris(2-dimethylaminoethyl)amine (LXXVIII) |
| MOBen-NR$_2$ | *N*-(2′-*N*′,*N*′-dialkylaminoethyl)-2-methoxybenzylideneimine (LII) |
| MOBtn-NMe$_2$ | *N*-(3′-*N*′,*N*′-dimethylaminopropyl)-2-methoxybenzylideneimine |
| mpdc | α-*N*-methyl-*S*-methyl-β-*N*-(6-methylpyrid-2-yl)methylendithiocarbazate |
| mpdo | 1-(*o*-methoxyphenyl)-2,6-diazaoctane |
| mpq | 2-methyl-8-[(6-methyl-2-pyridyl)methyleneamino] quinoline |
| MSBen-NEt$_2$ | *N*-(2′-*N*′,*N*′-diethylaminoethyl)-2-methylthiobenzylideneimine (LI) |
| nas | 1,8-naphthalenebis(dimethylarsine) (XI) |
| NAs$_3$ | tris(2-diphenylarsinoethyl)amine |
| N$_3$As | *N*,*N*-bis(2-diethylaminoethyl)-2′-diphenylarsinoethylamine (LXXXV) |
| NNAs | *N*-(3′-diphenylarsinopropyl)-2-methylaminobenzylideneimine |
| NNP | *N*-(3′-diphenylphosphinopropyl)-2-methylaminobenzylideneimine |
| N-O$_3$ | tris(2-methoxyethyl)amine (XC) |
| N$_3$O | *N*,*N*-bis(2-diethylaminoethyl)-2′-methoxyethylamine (LXXXVI) |
| N$_2$O$_2$ | *N*,*N*-bis(2-methoxyethyl)-2′-diethylaminoethylamine (LXXXVIII) |
| NOAs$_2$ | *N*,*N*-bis(2-diphenylarsinoethyl)-2′-methoxyethylamine |
| NOP$_2$ | *N*,*N*-bis(2-diphenylphosphinoethyl)-2′-methoxyethylamine (LXV) |
| N$_2$OP | *N*-(2-diphenylphosphinoethyl)-*N*-(2-methoxyethyl)-*N*′,*N*′-diethylethylenediamine (LXVI) |
| NP$_3$ | tris(2-diphenylphosphinoethyl)amine (LVIII) |
| N$_3$P | *N*,*N*-bis(2-diethylaminoethyl)-2′-diphenylphosphinoethylamine (LXXXIV) |
| N$_2$P$_2$ | *N*,*N*-bis(2-diphenylphosphinoethyl)-2′-diethylaminoethylamine (LIX) |
| N$_2$S$_2$ | *N*,*N*-bis(2-methylthioethyl)-2′-diethylaminoethylamine (LXXXIX) |
| N$_3$S | *N*,*N*-bis(2-diethylaminoethyl)-2′-methylthioethylamine (LXXXVII) |
| NSN | 3-amino-1-(8′-quinolyl)-1-thiapropane |
| N$_2$SP | *N*-(2-diphenylphosphinoethyl)-*N*-(2-methylthioethyl)-*N*′,*N*′-diethylethylenediamine (LXVII) |
| NS$_3$-R | tris(2-alkylthioethyl)amine (XCI) |
| ONAs | *N*-(3′-diphenylarsinopropyl)-2-methoxybenzylideneimine |
| ONP | *N*-(3′-diphenylphosphinopropyl)-2-methoxybenzylideneimine |
| ONSMe | *N*-(2-methylthioethyl)salicylaldiminate (XL) |
| paenR$_2$ | *N*-(2′-*N*′,*N*′-dialkylaminoethyl)pyridinaldimine |
| 4PAP | 2-(diphenylphosphinoamino)-4-methylpyridine |
| paphenMe$_2$ | *N*-(2′-*N*′,*N*′-dimethylaminophenyl)pyridinaldimine |
| paphy | pyridine-2-aldehyde-2-pyridylhydrazone |
| phpin | 2-phenyl-isophosphindoline (III) |
| PhPMP | 2-(diphenylphosphinomethyl)pyridine |
| picox | 2-picoline *N*-oxide (IX) |
| pip | piperidine |
| pmp | 2,6-bis(diphenylphosphinomethyl)pyridine (CII) |
| PN | *o*-dimethylaminophenyl-diphenylphosphine (XXVII) |

| | |
|---|---|
| PNNP | *N*,*N'*-bis(2-diphenylphosphinoethyl)-*N*,*N'*-dimethylethylenediamine (LXX) |
| pnp | 2,6-bis(2-diphenylphosphinoethyl)pyridine (CI) |
| polyphos | 2,8,9-trioxa-1-phosphaadamantane |
| PSP | bis(2-diphenylphosphinoethyl)sulphide (XXXII) |
| PSSP | 1,3-bis(3-diphenylphosphinopropylthio)propane (LXIX) |
| PTAS | tris(*o*-diphenylarsinophenyl)phosphine (LX) |
| py | pyridine |
| pymp | 2-(diphenylphosphinomethyl)-6-methylpyridine (XXX) |
| pytz | 2,4-bis(2-pyridyl)thiazole |
| QAS | tris(*o*-diphenylarsinophenyl)arsine (LXII) |
| Qas | tris(*o*-dimethylarsinophenyl)arsine (LXIII) |
| qas | tris(3-dimethylarsinopropyl)arsine (LXIV) |
| qo | Z-2-nitrosophenoxide |
| QP | tris(*o*-diphenylphosphinophenyl)phosphine (LXVIII) |
| qp | tris(2-diphenylphosphinoethyl)phosphine |
| quin | quinoline |
| R$_2$dtp | *O*,*O'*-dialkyldithiophosphate |
| R$_2$dtpi | diaryldithiophosphinate, dialkyldithiophosphinate |
| R-imz | alkyl-imidazole, benzimidazole |
| R-nnp | *N*-alkyl-*N*-(2-diphenylphosphinoethyl)-*N'*,*N'*-dimethylethylenediamine (XLV, XLVI) |
| R-phenox | 10-alkyl-10-phenoxaphosphine |
| R-PNP | bis(2-diphenylphosphinoethyl)alkylamine (XXXIV) |
| sacsac | dithioacetylacetonate (XXV) |
| SALen | *N*,*N'*-ethylenebis(salicylideneiminate) (LXXII) |
| SAL-NR | *N*-alkyl-salicylideneiminate (XXVI) |
| SALoph | *N*,*N'*-bis(salicylidene)-*o*-phenylenediamine (CIII) |
| SALphen-NR$_2$ | *N*-(2-dialkylaminophenyl)salicylideneiminate |
| SAs$_3$ | bis(*o*-diphenylarsinophenyl)-*o*-methylthiophenylarsine |
| SBTAS | tris(*o*-diphenylarsinophenyl)stibine (LX) |
| sbtas | tris(3-dimethylarsinopropyl)stibine (LXI) |
| SBTP | tris(*o*-diphenylphosphinophenyl)stibine (LX) |
| SeP | diphenyl(*o*-methylselenophenyl)phosphine |
| SNAs | *N*-(3'-diphenylarsinopropyl)-2-methylthiobenzylideneimine |
| SNNMe | 6-methylpyrid-2-yl-*N*-(2'-methylthiophenyl)methyleneimine |
| SNP | *N*-(3'-diphenylphosphinopropyl)-2-methylthiobenzylideneimine |
| SNS | *N*-(2-methylthiophenyl)-2'-methylthiophenylmethyleneimine |
| SP | diphenyl(*o*-methylthiophenyl)phosphine |
| sp | ethyl(2-diethylphosphinoethyl)sulphide |
| stars | dimethyl(*o*-dimethylarsinophenyl)stibine |
| TAAB-LN | tetrabenzo-[*b*,*f*,*j*,*n*]-4,8,12,16,20-pentaaza-17,23-dioxa-20-methyl-bicyclo[7.7.7] tricosa-4,12-diene (XCVI) |
| TAAB-LS | tetrabenzo[*b*,*f*,*j*,*n*]-4,8,12,16-tetraaza-17,23-dioxa-20-thia-bicyclo[7.7.7] tricosa-4,12-diene (XCVII) |
| TACD | 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane |
| TAP | tris(3-dimethylarsinopropyl)phosphine (LXI) |
| TAS | bis(3-dimethylarsinopropyl)methylarsine (XXXV) |
| TDEH$_2$ | thiodiethanol |
| TDPME | 1,1,1-tris(diphenylphosphinomethyl)ethane (XXXVI) |
| TDPMM | tetrakis(diphenylphosphinomethyl)methane (XXXVII) |
| TEP | 1,2-bis(diethylphosphino)ethane (XIV) |
| terpy | 2,2',2''-terpyridyl (LIV) |
| tet | *N*,*N'*-bis(3-aminopropyl)piperazine (XCIII) |
| TIBP | tri-isobutyl-phosphate |
| TIB-R-DPT | bis[3-(2-mercaptobenzylideneimino)propyl] alkylamine (XCIX) |

| | |
|---|---|
| tmac | *trans*-2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadecane (LXXIII) |
| TMP | trimethylphosphate |
| tpen | *N*,*N*,*N*′-tris[2-(2′-pyridyl)ethyl] ethylenediamine (C) |
| TPH | bis(2-diphenylphosphinoethyl)phenylphosphine (XXXIII) |
| tpt | tris(3-aminopropyl)amine (LXXX) |
| tren | tris(2-aminoethyl)amine (LXXVII) |
| TSP | tris(*o*-methylthiophenyl)phosphine |
| TSeP | tris(*o*-methylselenophenyl)phosphine |
| ttas | bis(*o*-dimethylarsinophenyl)methylarsine (XXI) |
| TTP | 1,4,8,11-tetrathiacyclotetradecane (LXXVI) |
| tu | thiourea |
| VPP | *cis*-1,2-bis(diphenylphosphino)ethylene (XVI) |
| Z-SAL-DAES | bis[2-Z-salicylideneimino)ethyl] sulphide (XCV) |
| Z-SALen | *N*,*N*′-ethylenebis(Z-salicylideneiminate) (LXXII) |
| Z-SALen-NR$_2$ | *N*-(2′-*N*′,*N*′-dialkylaminoethyl)-Z-salicylideneiminate (XXXIX) |
| Z-SAL-NR | *N*-alkyl-Z-salicylideneiminate |
| Z-SAL-R-DPT | bis[3-(Z-salicylideneimino)propyl] alkylamine (XCVIII) |

## A. INTRODUCTION

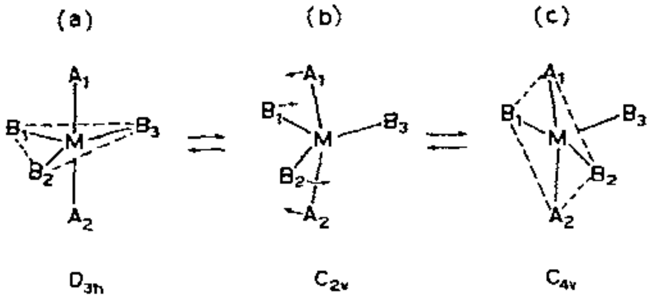
Both the experimental and theoretical aspects of five-coordinate complexes of iron(II), cobalt(II) and nickel(II) have undergone rapid development in recent years and some hundreds of contributions have been published in this field. Some review articles have sought to organize and rationalize the available information, paying most attention to such particular aspects of this type of coordination as its associated spectroscopic [1–2a], magnetic[2a–5] and structural[2a,6,7] properties.

The intent of this review is to collect together information on all the five-coordinate complexes of these metal ions thus far recognized, in order to ascertain the range (in terms of variety of metals and ligands) in which this type of coordination exists and to characterize the conditions and factors which determine whether a given ligand produces a five-coordinate complex. Particular attention will be paid to the spin-state of the complex, in the sense that high- and low-spin complexes have different stabilities, and different ranges of existence. Also, the spin-state is closely related to the properties of the donor groups and to the resulting geometry of the complex.

Data from polarized electronic spectra and magnetic anisotropy measurements form the basis for a more detailed discussion of the electronic structure of the complexes in the final section.

### *(i) Geometry of five-coordinate complexes*

The highest symmetry that a five-coordinate complex can possess is $D_{3h}$, that of a trigonal bipyramid (TBP). A variable parameter in this structure is the ratio of axial to equatorial bond lengths. Next highest is the square pyramid (SP) with symmetry $C_{4v}$ which has an additional structural parameter, the angle between the axial and equatorial bonds, de-



(I)

Fig.1. Geometrical distortion of five-coordinate complexes: (a) trigonal bipyramid ($D_{3h}$ symmetry); (b) intermediate geometry ($C_{2v}$ symmetry); (c) square pyramid ($C_{4v}$ symmetry).

signated the *apical angle*[8,9]. Both theoretical and experimental work indicate that a "standard" SP has an apical angle of ca. 100° (ref.5).

Usually the symmetry of this class of compounds is less high. A common distortion gives rise to a structure[3,7] which is intermediate between the trigonal bipyramidal and that of an idealized right square pyramid (Fig.1).

This type of distortion will be called *geometrical distortion* (type I), in that it is the bond angles which are principally affected. *Coordinative distortion* can be distinguished when one bond becomes longer than usual; in such cases one can apply the concept of "semicoordination" (ref.10). Two typical coordinative distortions are shown schematically in Fig.2: apical elongation (type II) and tetrahedral distortion (type III).

Obviously the steric characteristics of the ligands and their denticity will have a profound influence on the resulting stereochemistry. While monodentate ligands can in principle par-

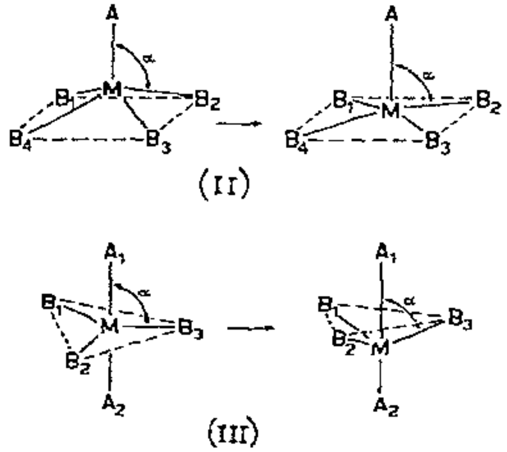


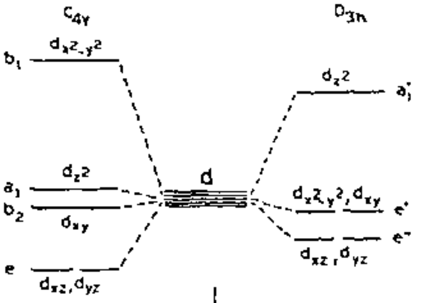
Fig.2. Typical coordinative distortions of five-coordinate complexes: (II) apical elongation in square pyramidal complexes; (III) tetrahedral distortion in trigonal bipyramidal complexes.

ticipate in any geometry whatsoever, polydentate ligands are subject to chelate effects. Bidentate and linear open-chain or cyclic tetradentate ligands tend to form SP complexes. Tridentate ligands generally give geometrically distorted complexes (type I), while tripod-like tetradentate ligands are by their nature well adapted to form complexes of TBP geometry.

### *(ii) Spin-state of five-coordinate complexes*

It is well known that five-coordinate complexes of iron(II), cobalt(II) and nickel(II) can be high- or low-spin in both TBP and SP geometries. For clarity, the electronic configurations of each ion in fields of $D_{3h}$ and $C_{4v}$ symmetry are shown in Fig.3.

It is clear that the strength of the ligand field, which determines the magnitude of the splitting, is important in determining spin-state. However, the nephelauxetic effect of the donor atoms is much more important since it can reduce the separation between the free ion terms by as much as 50%. As a result of this, the crossover point between high- and low-spin ground terms may occur at relatively small values of 10*Dq*. The nephelauxetic reduction is a function of the electronic delocalization on the ligand and the covalency of the metal—ligand bond, both properties related to the softness and π-bonding ability of the donor atoms. Thus, high-spin complexes are generally formed with hard donors (N, O, Cl, etc.) and low-spin complexes are formed with soft donors (P, As, I, etc.). A semi-empirical relationship has been found which relates the spin-state of five coordinate complexes of cobalt



| Ion | Configuration | Ground state | Configuration | Ground state |
|---|---|---|---|---|
| Fe | $(e)^4(b_2)^2$ | $^1A_1$ | $(e'')^4(e')^2$ | $^3A'_2$ |
| | $(e)^4(b_2)(a_1)$ | $^3B_2$ | $(e'')^3(e')^2(a'_1)$ | $^5E''$ |
| | $(e)^3(b_2)(a_1)(b_1)$ | $^5E$ | | |
| Co | $(e)^4(b_2)^2(a_1)$ | $^2A_1$ | $(e'')^4(e')^3$ | $^2E'$ |
| | $(e)^4(b_2)(a_1)(b_1)$ | $^4A_2$ | $(e'')^4(e')^2(a'_1)$ | $^4A'_2$ |
| Ni | $(e)^4(b_2)^2(a_1)^2$ | $^1A_1$ | $(e'')^4(e')^4$ | $^1A'_1$ |
| | $(e)^4(b_2)^2(a_1)(b_1)$ | $^3B_1$ | $(e'')^4(e')^3(a'_1)$ | $^2E'$ |

Fig.3. Splitting of 3*d* orbitals and electronic configurations for Fe$^{II}$ ($d^6$), Co$^{II}$ ($d^7$) and Ni$^{II}$ ($d^8$) in five-coordinate complexes with $C_{4v}$ and $D_{3h}$ symmetries.

(II) and nickel(II) with the "overall nucleophilicity" and "electronegativity" of the donor atoms[11].

Geometrical distortion of type I does not apparently influence the spin-state of cobalt (II) and nickel(II) complexes, but distortion involving bond length has a marked influence. Type II distortions generally favour the low-spin state, while distortions of type III, which are common among cobalt(II) complexes, favour the high-spin state[5].

## B. INCIDENCE OF FIVE-COORDINATE IRON(II), COBALT(II) AND NICKEL(II) COMPLEXES

In order to point out the range of existence and the factors determining the incidence of five-coordination, the complexes will be divided according to the denticity of the ligand and the spin-state. Some complexes showing spin-isomerism will be treated in a following section regardless of the denticity of the ligand. The characteristics of the known five-coordinate complexes of iron(II), cobalt(II) and nickel(II), are reported in Tables 1–6.

### *(i) Monodentate ligands*

The occurrence of five-coordination with monodentate ligands is of particular interest in that it is the result of a fine balance between the steric interactions among the various ligands and the specific tendency of the metal ion to achieve five-coordination. The lack of stabilization due to chelate effects and of a rigid ligand skeleton make it more difficult to characterize the factors which determine the formation of five-coordinate complexes. With a proper choice of the neutral ligand L and of the anions X, five-coordinate (high- and low-spin) complexes with the following stoichiometries have been isolated or identified in solution: $ML_3X_2$, $[ML_4X]^+$, $[ML_5]^{2+}$, $[ML_4L']^{2+}$ (where L and L′ are different ligands), $[MX_5]^{3-}$ and $[M_2Cl_8]^{4-}$. A selection of examples is given in Table 1.

TABLE 1

Five-coordinate iron(II), cobalt(II) and nickel(II) complexes with monodentate ligands

| Species[a] | Metal ion | Donor set | Physical state[b] and ref. | X-ray data[c] and ref. | Notes |
|---|---|---|---|---|---|
| *(i) Low-spin complexes* | | | | | |
| $M(PHPh_2)_3X_2$ | Co | $P_3X_2$ | c,s (12) | INT(13) | |
| | Ni | | c,s (14,15) | INT(13) | |
| $M(PMe_3)_3X_2$ | Ni | $P_3X_2$ | c,s (16–18) | | |
| $M(PRR'_2)_3(CN)_2$ | Co | $P_3C_2$ | c,s (19) | | $R \neq R' = Me, Et, Ph, OMe, OEt, OPh$ |
| | Ni | | c,s (20–23) | INT(24) | |
| $M(PPhEt_2)_3(C{\equiv}C{-}Ph)_2$ | Ni | $P_3C_2$ | c (25) | | |
| $M(PRR'_2)_3(NCS)_2$ | Co | $P_3N_2$ | c,s (26–28) | | $R = R' = Me, Pr$<br>$R \neq R' = Et, Ph$ |

TABLE 1 (continued)

| Species$^a$ | Metal ion | Donor set | Physical state$^b$ with ref. | X-ray data$^c$ with ref. | Notes |
|---|---|---|---|---|---|
| $M(PPhMe_2)_3X_2$ | Ni | $P_3X_2$ | c,s (29) | TBP(30) | |
| $[M(P(OMe)_3)_5]^{2+}$ | Ni | $P_5$ | c,s (31) | | |
| $[M(polyphos)_5]^{2+}$ | Ni | $P_5$ | c,s (32,33) | TBP(33) | |
| $M(phpin)_3X_2$ | Co | $P_3X_2$ | c,s (34) | | |
| | Ni | | c,s (35) | | |
| $M(Mephos)_3X_2$ | Co | $P_3X_2$ | c,(s) (36,37) | | |
| | Ni | | c,(s) (36,37) | INT,TBP(38,39) | |
| $M(Etphos)_3X_2$ | Co | $P_3X_2$ | c,(s) (36,37) | | |
| | Ni | | c,(s) (36,37) | TBP(38,39) | |
| $M(R{-}phenox)_3X_2$ | Ni | $P_3X_2$ | c (40) | | R = Me, Et |
| $M(PRR'_2)_3X_2$ | Co | $P_3X_2$ | c,s (41,42,42a) | | $R \neq R' = NMe_2$, F |
| $M(PHEt_2)_3X_2$ | Ni | $P_3X_2$ | c,s (43) | | |
| $[M(PHEt_2)_4X]^+$ | Ni | $P_4X$ | c,(s) (43) | | |
| $[M(PPh(OEt)_2)_4X]^+$ | Co | $P_4X$ | c,s (44) | | |
| $M(PPh(OEt)_2)_3(NCS)_2$ | Co | $P_3N_2$ | c,s (44) | | |
| $[M(CN)_5]^{3-}$ | Co | $C_5$ | c,s (45–48) | | |
| | Ni | | c,s (49–52) | INT and SP(53,54) | |
| $[M(PhNC)_5]^{2+}$ | Co | $C_5$ | (c) (54a,54b) | | |
| *(ii) High-spin complexes* | | | | | |
| $[M(Ph_2MeAsO)_4X]^+$ | Fe | $O_5$ | c,s (55) | (X) (55) | $X = ClO_4$, $NO_3$ |
| | Co | | c,s (55,56) | SP(57) | |
| | Ni | | c,s (55,56) | (X) (55) | |
| $[M(Ph_2MePO)_4X]^+$ | Fe | $O_5$ | c,s (55) | (X) (55) | $X = ClO_4$, $NO_3$ |
| | Co | | c,s (55) | (X) (55) | |
| | Ni | | c,s (55) | (X) (55) | |
| $[M(Ph_3AsO)_4X]^+$ | Fe | $O_5$ | c,s (55) | | $X = ClO_4$, $BF_4$, $ReO_4$ |
| | Co | | c,s (55) | | |
| | Ni | | c,s (55,58,59) | | |
| $[M(Ph_3PO)_4X]^+$ | Fe | $O_5$ | c,s (55) | | $X = ClO_4$, $BF_4$, NCS, I |
| | Co | | c,s (55) | | |
| | Ni | | c,s (55,58–60) | | |
| $[M(Me_3PO)_5]^{2+}$ | Co | $O_5$ | c (61) | (X) (61) | |
| | Ni | | c (61) | (X) (61) | |
| $[M(Me_3AsO)_5]^{2+}$ | Co | $O_5$ | c (61) | (X) (61) | |
| | Ni | | c,s (61) | SP(62) | |
| $[M(Me_3PO)_4ClO_4]^+$ | Fe | $O_5$ | c (61) | | |
| $[M(Me_3AsO)_4ClO_4]^+$ | Fe | | c (61) | | |
| | Ni | | c (61) | | |
| $[M(EPNO)_5]^{2+}$ | Co | $O_5$ | c,s (63) | | |
| | Ni | | c,s (63) | | |
| $M(EPNO)_3(NO_3)_2$ | Co | $O_5$ | c (64) | | |
| $[M(picox)_5]^{2+}$ | Co | $O_5$ | c,s (65) | TBP(66) | |
| $[M(picox)_4]_n^{2n+}$ | Ni | | c,s (67) | | (Polymeric) |
| $[M(lutox)_5]^{2+}$ | Co | $O_5$ | s (68,69)$^d$ | | |
| $[M(lutox)_4]_n^{2n+}$ | Ni | | c,s (67) | | (Polymeric) |
| $M(lutox)_2(NCS)_2$ | Co | $N_2O_2S$ | c (70) | | Bridging NCS |
| $[M(DMMP)_5]^{2+}$ | Fe | $O_5$ | c,s (71) | | |
| $[M(TMP)_5]^{2+}$ | Fe | $O_5$ | c,s (72) | | |

TABLE 1 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| | Co | | c (72) | | |
| | Ni | | s (72) | | |
| $[M(TIBP)_4(OH_2)]^{2+}$ | Co | $O_5$ | c,s (73) | | |
| | Ni | | c,s (73) | | |
| $[M_2Cl_8]^{4-}$ | Ni | $Cl_5$ | c (74) | SP(75) | |
| $[MCl_4(R-OH)]^{2-}$ | Ni | $OCl_4$ | c (74) | | R = Me, Et |
| $M(Me-dabco^+)(B)X_3$ | Fe | $N(B)X_3$ | c (76) | (X) (76) | $B = H_2O, NH_3$ |
| | Co | $N_2X_3$ | c (76) | | |
| | Ni | $N(B)X_3$ | c (76) | TBP(77) | |
| $[M(dabco^+)_2X_3]^+$ | Fe | $N_2X_3$ | c (78) | | X = Cl, Br |
| | Ni | | c (78) | | X = Cl, Br |

[a] The ligand notation is defined in the Abbreviations list.

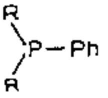
[b] c denotes crystals, s solution; parentheses denote uncertain assignment or, for solutions, equilibria with other species.

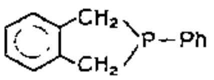
[c] Symbols for complete X-ray structures: TBP denotes trigonal bipyramid, SP square pyramid and INT intermediate structure. Indirect structural evidence (e.g. isomorphism with compounds of known structure) is indicated by (X).

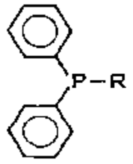
[d] The formation of $[M(lutox)_5]^{2+}$ species for M = Ni(II) has recently been reported[329].

### *(a) Low-spin complexes*

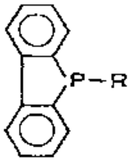
Among the low-spin complexes, the most common stoichiometries are $ML_3X_2$, $[ML_4X]^+$, $[ML_5]^{2+}$ and $[MX_5]^{3-}$. The $ML_3X_2$ complexes are derived from phosphorus-containing ligands (secondary or tertiary phosphines, phosphites, etc.). Since the occurrence of five-coordination is restricted to a narrow range where electronic and steric requirements of the ligands are properly balanced, phosphines and similar ligands are particularly suitable for the study of this phenomenon, because they can be synthesized with a wide range of steric and donor properties. Aromatic substituents decrease the donor power of the ligand but supposedly increase its π-backbonding capability. On the other hand aliphatic substituents have less effect on the π-backbonding capability, but increase the σ character of the coordination bonds and offer the best opportunity to vary the total bulkiness of the ligand. Quite bulky substituents favour the less strained planar or tetrahedral four-coordination. An example of such a balance is the observation that the ligand $Et_2PhP$ (I) (refs. 19, 21) does not form $ML_3X_2$ complexes (X = halogen) but the ligands $Me_2PhP$ (II) (refs. 29, 30) and phpin (III) (refs. 34, 35) do. Presumably the smaller size of $Me_2PhP$ and the smaller steric requirements of phpin with respect to $Et_2PhP$ are determining factors. Similarly $Ph_2MeP$ (IV) and $Ph_2EtP$ (V) do not form $ML_3X_2$ complexes (with X = halogen)[19,21,29] but the ligands


*(I)* R = Et
*(II)* R = Me


*(III)*



*(IV)* R=Me
*(V)* R=Et



*(VI)* R=Me
*(VII)* R=Et

Mephos (VI) and Etphos (VII), owing to their smaller steric requirements and probably to the different donor properties of the *sp*$^2$ phosphorus atom, do form such five-coordinate complexes[36–39]. The OR substituents on the phosphorus donor atom (organic phosphites, phosphonites, etc), although their role is not quite clear, particularly favour the formation of five-coordinate complexes, so that in some cases $[ML_5]^{2+}$ cationic complexes are also obtained[31–33].

Among the anions X, the $CN^-$ ion is particularly liable to induce five-coordination. Frequently a ligand L does not give rise to five-coordinate complexes when X = halide, but does when X = $CN^-$ (see Table 1). The capacity to stabilize five-coordinate complexes in general follows the order $CN^- \gg I^- > Br^- > Cl^- > NO_2^- > NCS^-$ although the $NCS^-$ ion has often been found to be effective in stabilizing low-spin five-coordinate cobalt(II) complexes[19,26–28]. Such an order cannot be explained in terms of ligand field strength but could be related to the polarizability and/or nephelauxetic effects of the donor groups. The only anion which appears capable of forming five-coordinate complexes by itself with cobalt(II) and nickel(II) is the $CN^-$ group: $[Ni(CN)_5]^{3-}$ complexes are easily formed even in aqueous solutions[49–51] and can be isolated using either counteranions of suitable bulkiness[53,54,79] or low-temperature techniques[52]; anionic $[Co(CN)_5]^{3-}$ species have been also identified in solution[45–47] and recently isolated[48].

It should be mentioned at this point that all the five-coordinate species here discussed are subject, in solution, to dissociation equilibria. Typical equilibria are those shown by the $ML_3X_2$ species.

$$ML_3X_2 \rightleftharpoons [ML_3X]^+ + X^- \qquad ML_3X_2 \rightleftharpoons ML_2X_2 + L$$

This instability in solution suggests that the choice of the solvent and of the synthesis conditions (temperature, ligand excess, etc.) is always of prime importance, whilst lattice forces, which can be tentatively controlled only in the case of ionic species, also play an important role in the isolation of these five-coordinate complexes.

### *(b) High-spin complexes*

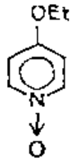
Most of the high-spin complexes have been obtained with the oxo-derivatives of the same ligands which form low-spin complexes. Tertiary phosphine oxides and arsine oxides as well as organic phosphates, readily give rise to high-spin five-coordinate complexes. Because of its high electronegativity, small *Dq* and low nucleophilicity, the introduction of oxygen into the ligand as donor atom does not greatly affect the steric characteristics but does allow for the formation of high-spin complexes. The presence of oxygen as donor atom is the main feature of the complexes of this type.

Some tertiary phosphine oxide and arsine oxide ligands capable of forming five-coordinate complexes are: $Ph_2MePO$ (ref. 55), $Ph_2MeAsO$ (refs. 55, 56), $Ph_3PO$ (refs. 55, 58–60) and $Ph_3AsO$ (refs. 55, 58, 59), which form $[ML_4X]^+$ complexes, where $X = ClO_4^-, NO_3^-, BF_4^-, NCS^-$ or $I^-$; also $Me_3PO$ (ref. 61) and $Me_3AsO$ (ref. 61), which can form either $[ML_4(ClO_4)]^+$ or $[ML_5]^{2+}$ complexes. The electronic properties of these ligands are presumably quite similar, whereas the steric requirements are expected to increase gradually on passing from the trimethyl to the triphenyl derivatives. The fact that all these ligands are able to form $[ML_4X]^+$ species can be accounted for by the particular geometry of the complexes, i.e. square pyramidal with the X atom in the apical position[57], and by the distance between the organic moieties and the metal ion. As a consequence, the steric balance of the ligands is less critical than it is for the analogous low-spin complexes. The effect on the steric crowding around the metal ion produced by the introduction of an oxygen donor atom between the phosphine and the metal ion is illustrated by the fact that the phosphines give rise to complexes with 1 : 2 (or 1 : 3 in the case of $Me_3P$) metal-to-ligand ratios, whereas the corresponding phosphine oxides can be bound to the metal with ratios up to 1 : 5.

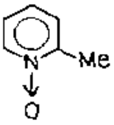
The occurrence of $[ML_5]^{2+}$ species with the least bulky trimethyl derivatives shows that the steric factors are important. The possibility of obtaining both $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^+$ species with these ligands, and the similar properties of these two types of complexes, suggest that the $ClO_4^-$ and L groups are similar in many respects, as is confirmed by X-ray structures[57,62]. On the other hand, the $[ML_4X]^+$ complexes obtained with the most bulky triphenyl derivatives owe most of their stability to packing effects since, depending on the counteranion, other species may be formed. With $BPh_4$, for instance, only tetrahedral $[ML_4]^{2+}$ complexes are obtained[55]. The compounds $ML_4(ClO_4)_2$ and $ML_4(BF_4)_2$ have been isolated as both the tetrahedral $[ML_4]^{2+}$ and five-coordinate $[ML_4(ClO_4)]^+$ or $[ML_4(BF_4)]^+$ isomers: the interconversion between the five-coordinate and four-coordinate isomer can also be performed in the solid state by heating[59,60].

With respect to their ability to give five-coordinate complexes, the phosphate, phosphonate and phosphinate ligands, which differ from the tertiary phosphine oxides in that one or more OR groups replace the R groups, are quite similar to the latter ligands. The effect of such a substitution is to decrease the donor power of the phosphoryl group, thus favouring an increase in the metal coordination number. In opposition to this, the bulkiness of the OR group tends to decrease the coordination number. The balance between these two factors leads to the formation of complexes with various coordination numbers, including the five-coordinate species $[ML_5]^{2+}$ and $[ML_4(OH_2)]^{2+}$ (refs. 71–73). These generally tend to increase their coordination number in solution by adding an extra ligand (ionic or neutral).

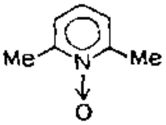
Although a large number of metal complexes with substituted pyridine *N*-oxides are known, only recently has the formation of five-coordinate complexes with such ligands been reported[63–70]. From the point of view of the coordination properties, pyridine *N*-oxide type ligands are quite versatile, in that metal complexes with several stoichiometries have been obtained depending on the anions, the reaction conditions and the type of metal ion. Although there is no apparent relationship between the nature of the substituent on the pyridine ring and the type of complex obtained, the substitution position does affect the coordination number: 3- and 4-substituted ligands tend to attain six-coordination whereas 2-substituted ligands favour four-coordination. Five-coordinate complexes have been obtained with both classes of substituted pyridine *N*-oxides. For example, EPNO (VIII) forms $[ML_5]^{2+}$ species in the solid state (M = Mn, Co, Ni and Zn) when the counteranion is $ClO_4^-$ and $[ML_6]^{2+}$ species (M = Co, Ni) when the counteranion is $NO_3^-$ (ref. 63). It is evident that the type of complex obtained depends on lattice forces only. The ligand picox (IX) forms $[ML_5]^{2+}$ species only with cobalt[65,66] whereas with nickel a polymeric, supposedly five-coordinate, complex $[(NiL_4)_n]^{2n+}$ has been obtained[67]. Finally, with the 2,6-disubstituted lutox ligand (X), tetrahedral $[ML_4]^{2+}$ complexes are obtained in the solid state which in solution add either another ligand molecule or solvent itself to form five-coordinate species[67–69].



*(VIII)*



*(IX)*



*(X)*

Recently, unusual five-coordinate complexes containing monoquaternized polyamines, either as ligands ($dabco^+$, Me-$dabco^+$) or as counteranions (Me-$dabco^+$), have been reported[74–78]. The use of such charged groups highlights the role of lattice energies[79] and the importance of a favourable hydrogen bond network in stabilizing such five-coordinate environments as $[Ni_2Cl_8]^{4-}$, $[NiCl_4(ROH)]^{2-}$, $M(Me\text{-}dabco^+)(B)X_3$ (B = $H_2O$, $NH_3$), $[M(dabco^+)_2X_3]^+$. In these instances it is difficult to establish any principles or even make intuitive predictions about the formation of five-coordinate complexes.

### *(ii) Bidentate ligands*

#### *(a) Low-spin complexes*

Bidentate ligands which give rise to five-coordinate low-spin complexes (Table 2) can be divided into two main groups: (1) neutral ligands containing phosphino and/or arsino groups, or containing one of these groups together with another donor moiety like SMe, SeMe or $SbMe_2$; (2) anionic thio ligands of the dithiocarboxylate and thioacetylacetonate type. With neutral ligands, five-coordinate $[ML_2X]^+$ species together with planar $[ML_2]^{2+}$ and $MLX_2$, and six-coordinate $ML_2X_2$ species can be obtained. The occurrence of five-coordination does not depend critically on the substituents at the donor atoms; in fact $[ML_2X]^+$ species have been obtained with hydrogen, alkyl or phenyl substituents. However, the size of the chelate ring is an important factor. Most of the five-coordinate complexes of this

TABLE 2

Five-coordinate iron(II), cobalt(II) and nickel(II) complexes with bidentate ligands

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| *(i) Low-spin complexes* | | | | | |
| $[M(das)_2X]^+$ | Ni | $As_4X$ | s (80) | | |
| $[M(nas)_2X]^+$ | Ni | $As_4X$ | c,s (81) | | |
| $[M(edas)_3]^{2+}$ | Ni | $As_5$ | c (82) | | |
| $[M(edas)_2X]^+$ | Co | $As_4X$ | s (83) | | |
| | Ni | | s (82) | | |
| $[M(dpe)_2X]^+$ | Co | $P_4X$ | c,s (84,85) | SP,TBP(85a,85b)[d] | |
| | Ni | | s (86) | | |
| $[M(bdmp)_2X]^+$ | Co | $P_4X$ | c,s (86a) | | |
| | Ni | | c,s (86a) | | |
| $[M(TEP)_2X]^+$ | Ni | $P_4X$ | c,s (87) | | |
| $[M(HPPH)_2X]^+$ | Ni | $P_4X$ | c,s (88) | | |
| $M(L)_{1.5}(CN)_2$ | Co | $P_3C_2$ | c,s (19) | | L = dpp, dpb, bdmp |
| | Ni | | c,s (86a,89,90) | | |
| $M(L)_{1.5}(NCS)_2$ | Co | $P_3N_2$ | c,s (19) | | L = dpp, dpb |
| $[M(VPP)_2X]^+$ | Ni | $P_4X$ | c,s (91) | | |
| $[M(AP)_2X]^+$ | Co | $As_2P_2X$ | c,s (92) | | |
| | Ni | | c,s (93) | | |
| $[M(SP)_2X]^+$ | Co | $S_2P_2X$ | c,s (92) | | |
| | Ni | | c,s (94) | | |
| $[M(SeP)_2X]^+$ | Co | $Se_2P_2X$ | c,s (92) | | |
| | Ni | | c,s (94) | | |
| $[M(sp)_2X]^+$ | Ni | $S_2P_2X$ | c,s (95) | | |
| $[M(stars)_2X]^+$ | Ni | $Sb_2As_2X$ | c,s (96) | | |
| $[M(das)(ttas)]^{2+}$ | Ni | $As_5$ | c,s (97–99) | SP(99) | |
| $M(dpe)(\pi\text{-}ma)Br$ | Ni | $P_2C_2Br$ | c (100,101) | SP(100,101) | |
| $M_3(dthb)_6$ | Ni | $S_5$ | c (102,103) | SP(103) | Trimeric |
| $M_2(dthpa)_4$ | Ni | $S_4Ni$ | c (104) | SP(104) | Dimeric, Ni–Ni bond |
| $M(ddc)_2NO$ | Co | $S_4(N)$ | c (105) | SP(105) | |
| $[M(PhPMP)_2X]^+$ | Co | $P_2N_2X$ | c (106) | | |
| | Ni | | c,s (106) | | |
| $M(4PAP)_2Cl_2$ | Co | ? | c (107) | | |
| $M(CO)(fdma)I_2$ | Ni | $As_2CI_2$ | c (108) | TBP(109) | |
| $M(CO)(fdpa)I_2$ | Ni | $As_2CI_2$ | c (108) | | |
| $M(sacsac)_2B$ | Co | $S_4(B)$ | c,s (110,111) | | B = $PPh_3$, $AsPh_3$, $SbPh_3$, py, pip |
| *(ii) High-spin complexes* | | | | | |
| $[M(SAL\text{–}NMe)_2]_2$ | Co | $N_2O_3$ | c,(s) (112) | TBP(113,114) | Dimeric |
| | Ni | | c (112) | (X) (113, 114) | (Solid soln. with the Zn complex) |
| $[M(Z\text{–}SALen\text{–}NEt_2)catec]_2$ | Co | $N_2O_3$ | c (118) | (X) (118) | Dimeric |
| | Ni | | c (118) | INT(118) | Dimeric |

TABLE 2 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| $M(Z\text{-}SAL\text{-}NR)_2py$ | Co | $N_3O_2$ | c,s (119,120) | | R = $(2,6\text{-}Me_2)C_6H_3$,<br>$(2,6\text{-}Et_2)C_6H_3$ |
| | Ni | | c,s (121) | | |
| $M(bza\text{-}R)_2py$ | Co | $N_3O_2$ | s (122) | | R = $(2,6\text{-}Me_2)C_6H_3$,<br>$(2,6\text{-}Et_2)C_6H_3$ |
| $[M(mepic)_2X]^+$ | Co | $N_4X$ | c,s (123) | | |
| | Ni | | c,s (124) | | |
| $[M(dmp)Cl_2]_2$ | Ni | $N_2Cl_3$ | c (125,126) | SP(126) | Dimeric |
| $[M(JAMP)_2X]^+$ | Co | $N_4X$ | c (127) | | X = Br, I |
| $[M(mbpt)(NCS)_2]_n$ | Co | ? | c (128) | | Polymeric |
| $[M(PN)X_2]_n$ | Ni | $(PNX_3)$ | c,s (129) | | Polymeric |
| $[M(LS)X_2]_{(2)}$ | Ni | $N_2X_3$ | c (130) | | (Dimeric) |
| $[M(LE)X_2]_{(2)}$ | Ni | $N_2X_3$ | c (130) | | (Dimeric) |
| $[M(qo)_2]_{(2)}$ | Ni | $N_2O_3$ | c,s (131) | | (Dimeric) |
| $[M(atsc)_2Cl]^+$ | Ni | $S_2N_2Cl$ | c (132) | INT(132)[e] | |
| $M(dmp)(R_2dtp)_2$ | Ni | $N_2S_3$ | c (133,134) | SP(133,134) | R = Me |
| $M(quin)(R_2dtpi)_2$ | Ni | $NS_4$ | c (134) | SP(134) | R = Et |
| $M(R_2dtp)_2B$ | Ni | $NS_4(PS_4)$ | c,(s) (135–141) | | R = alkyl; B =<br>amine, $PPh_3$ |
| $M(R_2dtpi)_2B$ | Ni | $NS_4$ | (s) (135,138) | | R = Ph; B = $Et_2NH$ |
| $[M(pymp)X_2]_{(2)}$ | Ni | $(PNX_3)$ | c (142) | | (dimeric)<br>X = Cl, Br, NCS |

[a] The ligand notation is defined in the Abbreviations list.

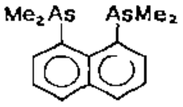
[b] c denotes crystals, s solution and (s) uncertain assignment or equilibria with other species.

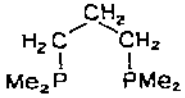
[c] Symbols for complete X-ray structures: TBP denotes trigonal bipyramid, SP square pyramid and INT intermediate structure. Indirect structural evidence (e.g. isomorphism with compounds of known structure) is indicated by (X).

[d] Further structural details of the isomers of $[Co(dpe)_2Cl]SnCl_3$ have recently been reported[330].

[e] Full structural details have recently been reported[331].

type so far isolated contain five-membered rings, the chelate chain being either saturated (ethylene bridge) or unsaturated (vinylene or *o*-phenylene bridge). Exceptions are the ligand nas, XI, which does form a six-membered chelate ring, but as a part of a naphthalenic

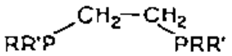

*(XI)*

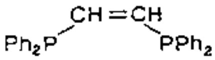

*(XII)*

ring and therefore of smaller size[81]; and the recently reported tetramethyl-substituted bdmp ligand XII[86a].

The formation of metal complexes with these neutral ligands can be considered to proceed by the following steps: (1) initial formation of a square planar moiety $[ML_2]^{2+}$, which can often be isolated by using non-coordinating anions; (2) formation of a monoadduct by adding a coordinating anion (halide or pseudohalide); (3) formation of a six-coordinated biadduct. The occurrence of step (2), which can be followed by spectrophotometric or conductometric measurements, is usual when five-membered chelate rings are present in the species $[ML_2]^{2+}$. The geometry of the five-coordinate species varies from TBP to SP as a function of the interligand and ligand–anion repulsions. The strain resulting from six-membered rings causes tetrahedral distortions which may inhibit step (2). If the anion is large and the ligand so bulky as to prevent the attainment of six-coordination, step (3) does not occur. It may also be found that only the $ML_2X_2$ complex can be isolated from a solution containing $[ML_2X]^+$ and $X^-$ species. Finally it should be observed that the situation may actually be more complicated if other equilibria occur in solution, e.g. dissociation equilibria giving rise to $MLX_2$ species[86].

Some examples will illustrate the influence of the factors mentioned in determining the resulting stereochemistry. Let us consider the coordinating properties of the following ligands: HPPH (XIII), TEP (XIV), dpe (XV) and VPP (XVI). The least hindered HPPH ligand gives rise to five-coordinate $[NiL_2X]^+$ (X = Br, I) and six-coordinate $NiL_2X_2$ (X = Cl, NCS)


(XIII) R = Ph, R′ = H
(XIV) R = R′ = Et
(XV) R = R′ = Ph


(XVI)

species, whereas only six-coordinate complexes are obtained with cobalt(II) (ref. 88). The TEP ligand forms only $[NiL_2X]^+$ species, which are also quite stable in solution[87]. The bulky dpe ligand, on the other hand, forms five-coordinate $[CoL_2X]^+$ (refs. 84, 85), and presumably six-coordinate tetragonal $NiL_2X_2$ complexes, the latter giving rise in solution to equilibria of the type[86]

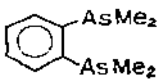
$$(NiL_2X_2) \rightleftharpoons [NiL_2X]^+ + X^- \rightleftharpoons NiLX_2 + L$$

The intrinsic steric hindrance of the dpe ligand is partially released when the ethylenic chain is replaced by a vinylenic chain (VPP ligand). In this case the species $[Ni(VPP)_2X]^+$ are more stable in solution, and can be isolated in the solid state[91].

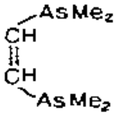
As we have pointed out, a long chain inhibits the formation of five-coordinate species; however, the ligands dpp and dpb form binuclear five-coordinate species with the metal cyanides of formula $M_2L_3(CN)_4$ where two bidentate ligands act as chelates and one as the bridging group[89,90]. Similar cyano derivatives, together with five-coordinate $[ML_2X]^+$ species (X = halide), are formed by the less hindered bdmp ligand XII[86a]. Presumably the achievement of the binuclear structure must be attributed, at least in part, to the special effect of the $CN^-$ ion in stabilizing five-coordination, mentioned above.

Among diarsines, the following ligands are known to form five-coordinate complexes: das (XVII), nas (XI), edas (XVIII), fdpa (XIX) and fdma (XX).

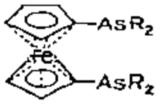
The first three ligands have the same substituents (methyl groups) at the arsenic atoms and similar rigid and unsaturated chains. Therefore the $[ML_2X]^+$ complexes have quite



(XVII)

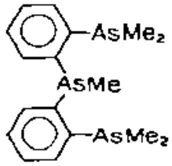


(XVIII)

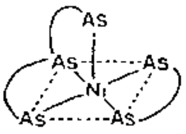


(XIX) R=Ph
(XX) R=Me

similar characteristics[80–83]. The ligands fdpa and fdma, on the other hand, only form unusual carbonyl complexes of formula $NiL(CO)I_2$ (refs. 108, 109). A characteristic of the ligands das and edas (and of tridentate triarsine ligands) is their capability to give rise to $NiAs_5$ chromophores. The arrangement of five $AsMe_2$ groups around the nickel ion appears to be a particularly stable structure. The $[Ni(edas)_3]^{2+}$ complex presumably occurs through the detachment of a donor atom[82], whereas in the precence of nickel, two das molecules rearranges to give the triarsine molecule (ttas. XXI) and the complex $[Ni(das)(ttas)]^{2+}$ is formed (see scheme 1)[97–99].

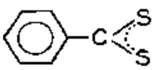


(XXI)

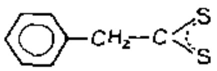


1

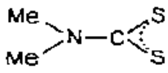
Some anionic sulphur-containing ligands reported to form five-coordinate complexes are dthb (XXII), dthpa (XXIII), ddc (XXIV) and sacsac (XXV). In these cases the extended



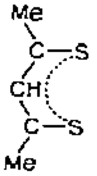
(XXII)



(XXIII)

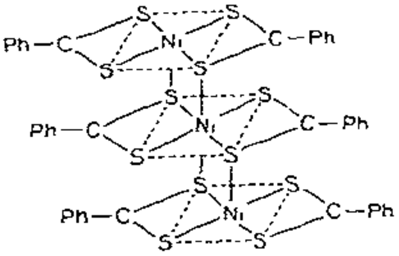


(XXIV)

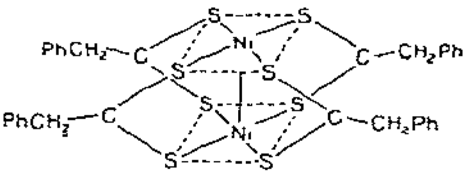


(XXV)

electron delocalization over the ligand is thought to be the main factor which determines the spin pairing. The complexes reported are of two types: (1) $ML_2L'$ complexes (L = ddc, sacsac), i.e. monoadducts with a neutral L′ ligand[105,110,111]; (2) polymeric $(ML_2)_n$ ($n$ = 2, 3) complexes which achieve five-coordination either through sulphur bridges (L = dthb) (refs. 102, 103) or through a metal–metal bond in a cage-like structure[104] (L = dthpa) (see schemes 2 and 3). The stabilization of the latter structures is largely due to packing effects in addition to the well known tendency of anionic thio donors to form multiple bridge bonds.



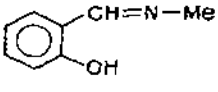
2



3

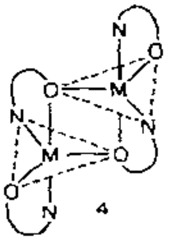
*(b) High spin complexes*

Ligands capable of forming this type of complex contain oxygen, sulphur (either in anionic or heterocyclic ligands) and nitrogen (heterocyclic bases) as the donor atoms. In contrast to the situation with low-spin complexes, cationic high-spin $[ML_2X]^+$ species are rather rare. The complexes isolated are mostly neutral with formulae $ML_2$, MLL′, $MLX_2$, $ML_2L''$ and MLL‴ (L, L′ = bidentate, L″ = monodentate, L‴ = *tridentate ligand*). Five-coordination in the $ML_2$, MLL′ and $MLX_2$ complexes is achieved through phenolic oxygen bridges or halogen or pseudohalogen bridges. This type of molecular association generally results from favourable packing effects, since in solution equilibria among various stereochemistries occur. A typical example of such bridging ligands is SAL-NMe (XXVI). The bis(*N*-methyl-salicylideneiminato)nickel(II) complex has been isolated both in a mono-



*(XXVI)*

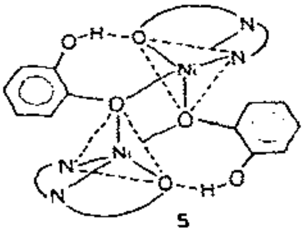
meric planar form[111a,111b] and in a polymeric six-coordinate form[111c]. However, when it forms solid solutions with the analogous zinc complex in a certain range of molar ratios, it assumes the dimeric five-coordinate structure of the latter complex (see scheme 4) (refs. 113, 114). In solution, equilibria between associated six-coordinate, planar and probably



4

five-coordinate species occur. In contrast the solid cobalt complex is obtained only in the dimeric five-coordinate form, which in solution partially transforms to a monomeric tetrahedral form[112]. It should be recalled here that SAL-NR ligands with bulkier imine substituents preferentially form four-coordinate complexes[115–117].

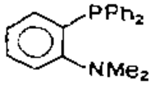
The stability of oxygen-bonded dimers is indicated by the structure of the complex $[M(Z\text{-}SALen\text{-}NEt_2)catec]_2$ (see scheme 5), where the achievement of five-coordination



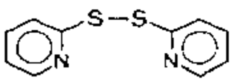
5

through an oxygen bridge is preferred to a monomeric structure with all the potential donor atoms singly coordinated[116].

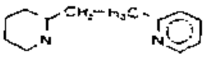
The occurrence of five-coordinate $MLX_2$ complexes as associated species through halide bridges depends on the use of sterically crowded ligands ( in order to prevent six-coordination) and anions particularly capable of forming bridges. These conditions are fulfilled, for example, with the ligands PN (XXVII)[129], LS (XXVIII)[130], LE (XXIX)[130], pymp (XXX)[142] and $NiX_2$ (X = Cl, Br, NCS). When X = I, however, tetrahedral $MLX_2$ complexes are obtained.



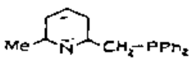
(XXVII)



(XXVIII)



(XXIX)



(XXX)

tained. Tetrahedral complexes are also obtained with cobalt(II) or iron(II) salts in agreement with the stronger tendency of these metal ions to give such stereochemistry. Finally the $Ni(dmp)Cl_2$ (dmp = XXXI) complex has been isolated in two isomeric forms, one

(XXXI)

pseudotetrahedral and the other dimeric five-coordinate[125,126].

The axial addition of a fifth ligand, either neutral or charged, to a planar metal chelate $[ML_2]^+$ to give a five-coordinate adduct is common, as seen above, when the resulting complex is low-spin, but it is uncommon when the resulting complex is high-spin. When the overall ligand field of the chelates and of the incoming group is sufficient to preserve the low-spin state, the structural perturbation caused by the fifth ligand is rather small and five-coordination may be preferred to six-coordination, which could require a change in spin-state. On the other hand, when the addition of a fifth ligand causes spin unpairing, the stability of the resulting complex is in general smaller than that of the six-coordinated biadduct unless the overall steric factors do not favour the latter coordination. For example, from planar bis[(*N*-2,6-dialkylphenyl)-Z-salicylideneiminato] nickel(II) and pyridine, either the six-coordinated biadduct or the five-coordinated monoadduct are isolated, or the unchanged starting complex is recovered, depending on the nature of the substituent Z[121]. Monoadducts have also been isolated with the analogous cobalt(II) complexes, which are themselves high-spin and therefore no change of spin-state occurs upon the formation of five-coordinate species[119,120].

High-spin five-coordinated adducts are obtained also from the planar bis-dithio chelates of nickel(II) (alkyl or aryl-substituted dithiophosphates or dithiophosphinates) and primary, secondary, and heterocyclic amines[135,137–141], or $\mathrm{Ph_3P}$ (ref. 136). In some cases, the thermodynamic functions of the planar ⇌ five-coordinate equilibria have been determined [140–141].

TABLE 3

Five-coordinate iron(II), cobalt(II) and nickel(II) complexes with tridentate ligands

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| *(i) Low-spin complexes* | | | | | |
| $\mathrm{M(TAS)X_2}$ | Ni | $\mathrm{As_3X_2}$ | c,s (143,146a) | SP(144) | |
| $\mathrm{[M(TAS)_2]^{2+}}$ | Ni | $\mathrm{As_5}$ | c,s (99,143,145) | | One unbonded donor |
| $\mathrm{M(ttas)X_2}$ | Ni | $\mathrm{As_3X_2}$ | c,s (145) | | |
| $\mathrm{[M(ttas)_2]^{2+}}$ | Ni | $\mathrm{As_5}$ | c,s (145) | | One unbonded donor |
| $\mathrm{M(AsNAs)X_2}$ | Ni | $\mathrm{As_2NX_2}$ | c,s (146) | | |
| $\mathrm{M(AsSAS)X_2}$ | Ni | $\mathrm{As_2SX_2}$ | c,s (146) | | |
| $\mathrm{M(DAP)X_2}$ | Ni | $\mathrm{As_2PX_2}$ | c,s (146a) | SP(146b) | |
| $\mathrm{M(PSP)X_2}$ | Co | $\mathrm{P_2SX_2}$ | c,s (147) | | |
| | Ni | | c (147,148) | | |
| $\mathrm{M(R\text{-}PNP)X_2}$ | Co | $\mathrm{NP_2X_2}$ | c,(s) (147) | (X) (147) | R = H, Me |
| | Ni | | c (147) | SP(149,150) | |
| $\mathrm{M(NNP)X_2}$ | Ni | $\mathrm{N_2PX_2}$ | c (151) | | X = I |
| $\mathrm{M(SNP)X_2}$ | Ni | $\mathrm{SNPX_2}$ | c,s (151) | | X = I |
| $\mathrm{M(FTP)X_2}$ | Ni | $\mathrm{P_3X_2}$ | c,s (151a) | | |
| $\mathrm{M(TPH)X_2}$ | Co | $\mathrm{P_3X_2}$ | c,(s) (152) | | |
| | Ni | | c (152a) | | |
| $\mathrm{M(DSP)X_2}$ | Ni | $\mathrm{S_2PX_2}$ | c,s (94) | SP(153) | |
| $\mathrm{M(TDPME)X_2}$ | Co | $\mathrm{P_3X_2}$ | c,(s) (154) | | |
| | Ni | | c,(s) (154) | | |
| $\mathrm{M(TDPMM)X_2}$ | Co | $\mathrm{P_3X_2}$ | c,s (155) | | |
| $\mathrm{[M_2(TAS)_3(OH_2)]^{2+}}$ | Ni | ? | c (156) | | (Dimeric) |
| $\mathrm{[M_2(DAP)_3(OH_2)]^{2+}}$ | Ni | ? | c (156) | | (Dimeric) |
| $\mathrm{M_2(DMS)_2}$ | Ni | $\mathrm{S_4Ni}$ | c (157,158) | SP(159,160) | Suggested Ni–Ni bond |

TABLE 3 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| $M(pnp)X_2$ | Ni | $P_2NX_2$ | c,s (161) | | X = Br, I |
| $M(pmp)X_2$ | Co | $P_2NX_2$ | c,s (162) | | X = I |
| | Ni | | c,s (162) | | X = Cl, Br, I |
| *(ii) High-spin complexes* | | | | | |
| $M(Z\text{-}SALen\text{-}NR_2)_2$ | Co | $N_3O_2$ | c,s (163) | (X) (163,165) | Z = H, 3-Cl, 5-Cl, 3-Me, 5-Me; R = Et, $-(CH_2)_4-$, $-(CH_2)_5-$ |
| | Ni | | c,s (164) | SP(165,166) | Z = 3-Cl, 5-Cl, 3, 4-benzo; R = Et. |
| $M(ONSMe)_2$ | Co | $N_2O_2S$ | c,s (167) | | |
| $\{M(SALphen\text{-}NR_2)X\}_2$ | Co | $N_2OX_2$ | c (168) | | Dimeric |
| $M(Me_5dien)X_2$ | Fe | $N_3X_2$ | c,s (169) | (X) (169) | |
| | Co | | c,s (169) | INT(170,171) | |
| | Ni | | c,s (169) | (X) (169) | |
| $M(Et_4dien)X_2$ | Co | $N_3X_2$ | c,s (172,173) | TBP(174) | |
| | Ni | | s (173,175) | | X = Cl, NCO |
| $M(Me_4daeo)X_2$ | Fe | $N_2OX_2$ | c,s (176) | | |
| | Co | | c,s (176) | | |
| | Ni | | c,s (176) | | |
| $M(Me_4daes)X_2$ | Co | $N_2SX_2$ | c,(s) (177) | | |
| | Ni | | c,(s) (177) | | |
| $M(MABen\text{-}NEt_2)X_2$ | Co | $N_3X_2$ | c,s (178) | | |
| | Ni | | c,(s) (178) | | |
| $M(MSBen\text{-}NEt_2)X_2$ | Co | $N_2SX_2$ | c,s (179) | | X = NCS |
| | Ni | | c,(s) (179) | | |
| $M(MOBen\text{-}NMe_2)X_2$ | Ni | $N_2OX_2$ | c,(s) (180) | | |
| $M(MOBtn\text{-}NMe_2)X_2$ | Ni | $N_2OX_2$ | c,(s) (180) | | |
| $M(mpdo)X_2$ | Ni | $N_2OX_2$ | c,s (180) | INT(181) | X = Br |
| $M(NNY)X_2$ | Ni | $N_2P(As)X_2$ | c,s (151) | | NNY = NNP, NNAs |
| $M(ONY)X_2$ | Ni | $ONP(As)X_2$ | c,s (151) | | ONY = ONP, ONAs |
| $M(SNY)X_2$ | Ni | $SNP(As)X_2$ | c,s (151) | | SNY = SNP, SNAs |
| $M(Z\text{-}SALen\text{-}NR_2)(Z'\text{-}SAL\text{-}NR')$ | Ni | $N_3O_2$ | s (182) | | Z = 5-Cl; R = Et; Z' = H, 3-Cl, 5-Cl; R' = Me, Et, iso-Pr, *n*-Pr, *n*-Bu |
| $M(paphy)X_2$ | Co | $N_3X_2$ | c,s (183) | SP(184,185) | |
| $M(paenR_2)X_2$ | Co | $N_3X_2$ | c,s (186) | | R = Me, Et |
| | Ni | | c,s (186) | | |
| $M(DAP\text{-}R_2)X_2$ | Co | $N_3X_2$ | c,s (187) | | R = Me, Et, *n*-Pr, iso-Pr, *sec*-Bu, Cy |
| | Ni | | c,s (187) | | |
| $M(terpy)X_2$ | Fe | $N_3X_2$ | c (188) | | |
| | Co | | c,s (183,188–191) | INT(192) | |
| | Ni | | c (183,189) | (X) (188) | |
| $M(DPEA)X_2$ | Fe | $N_3X_2$ | c (193) | | |
| | Co | | c,s (193) | | |
| | Ni | | c,s (194) | | |

TABLE 3 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| M(DPES)$X_2$ | Ni | $N_2SX_2$ | c,s (194) | | |
| M(SNNMe)$X_2$ | Fe | $N_2SX_2$ | c,s (195) | | |
| | Co | | c,s (195) | | |
| M($Me_2$dpma)$X_2$ | Ni | $N_3X_2$ | c,s (196) | INT(197) | |
| M(paphenMe$_2$)$X_2$ | Fe | $N_3X_2$ | c,s (198) | | |
| | Co | | c,s (198) | | |
| | Ni | | c,s (198) | | |
| M(baphenMe$_2$)$X_2$ | Fe | $N_3X_2$ | c,s (198) | | |
| | Co | | c,s (198) | | |
| | Ni | | c,s (198) | | |
| M(abMe$_2$)$X_2$ | Fe | $N_3X_2$ | c,s (198) | | |
| | Co | | c,s (198) | | |
| | Ni | | c,s (198) | | |
| M(SNS)$X_2$ | Co | $NS_2X_2$ | c,s (199) | | |
| M(MeDPT)$X_2$ | Ni | $N_3X_2$ | c,s (200) | | |
| M(DENB$_2$)$X_2$ | Ni | $N_3X_2$ | c,s (202) | | |
| M(DPNB$_2$)$X_2$ | Ni | $N_3X_2$ | c,s (202) | | |
| M(pytz)$X_2$ | Fe | $N_3X_2$ | c,s (203) | | |
| M(mpq)$X_2$ | Ni | $N_3X_2$ | c,s (204) | | |
| M(R-nnp)$X_2$ | Co | $N_2PX_2$ | c,(s) (205,206) | INT(207) | R = H, Me |
| M(H-nnpO)$X_2$ | Co | $N_2OX_2$ | c,s (206) | TBP(208) | X = NCS |
| M(btpy)$X_2$ | Fe | $NS_2X_2$ | c (209) | | |
| | Co | | c (209) | | |
| M(TDEH$_2$)$X_2$ | Co | $O_2SX_2$ | c,s (210) | | X = Cl |
| | Ni | | c,s (210) | | |
| M(mpdc)$X_2$ | Fe | $N_2SX_2$ | c (211) | | |
| | Ni | | c (211) | | |
| M(pnp)$X_2$ | Fe | $P_2NX_2$ | c,s (161) | | X = Cl, Br |
| | Co | | c,s (161) | | X = Cl |
| M(pmp)$X_2$ | Fe | $P_2NX_2$ | c,s (162) | | X = Cl, Br, I, NCS |
| | Co | | c,s (162) | | X = Cl |
| $[M(NSN)_2]^{2+}$ | Co | $N_3S_2$ | c (212) | | |

[a] The ligand notation is defined in the Abbreviations list.

[b] c denotes crystals, s solution and (s) uncertain assignment or equilibria with other species.

[c] Symbols for complete X-ray structure: TBP denotes trigonal bipyramid, SP square pyramid and INT intermediate structure. Indirect structural evidence (e.g. isomorphism with compounds of known structure) is indicated by (X).

### *(iii) Tridentate ligands*

#### *(a) Low-spin complexes*

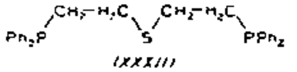
Among the ligands which give rise to five-coordinate complexes tridentate ligands (Table 3) are the most numerous. In fact the most common five-coordinate complexes are of the type $MLX_2$ where the neutralization of the charges may add further stability. Moreover, non-ionic species are favoured by the fact that five-coordinate complexes are generally obtained from organic solvents of low polarity. Low-spin complexes are obtained with ligands having As, P or S as donor atoms. The introduction of nitrogen into the donor set may result in a ligand field which stabilizes high-spin complexes.

The ligands used are either of the linear or the branched type. The linear ligands are the most common. The chains bridging the three donor atoms can be either aromatic or aliphatic. In the latter case, the resulting chelate rings can be five- or six-membered. In contrast to complexes with bidentate ligands, the complexes with six-membered chelate rings are more stable than the five-membered with respect to the dissociation into planar $[MLX]^+$ species.

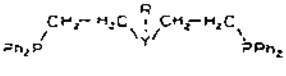
The mechanism of the formation of the five-coordinate complexes can be considered to proceed via the following steps: (1) formation of a planar species $[MLX]^+$ with the three ligand donors and the X donor nearly in the same plane; (2) addition of the second X donor in the apical position with neutralization of the charge and lowering of the basal X donor under the main basal plane because of X–X electrostatic repulsions.

From the available X-ray structures of these $MLX_2$ complexes, it appears that the interactions between the apical donor and the basal groups are quite strong[144,150]. Moreover the antibonding character of the $d_{z^2}$ orbital, which is filled for nickel(II) and half filled for cobalt(II), favours the apical elongation of the square pyramid. As a consequence of these factors the apical M–X bonds are in general longer than the basal M–X bonds[7].

Actually, planar $[MLX]^+$ species have been isolated only with nickel(II). Their relative stability with respect to the five-coordinate $MLX_2$ species and therefore the tendency of the latter form to dissociate in solution depends both on the overall steric requirements of the basal donors and on the specific tendency of the metal ion to give planar species. For cobalt complexes the above scheme is unrealistic in that, when the steric factors do not allow the formation of five-coordinate species, tetrahedral species are formed. For example with the ligands PSP (XXXII)[147,148], TPH (XXXIII)[152,152a] and R-PNP (XXXIV)[147] which differ in the central donor group, either five- or four-coordinate (planar with nickel and tetrahedral with cobalt) species have been reported. The first two ligands from solid five-coordinate $MLX_2$ complexes with both cobalt(II) and nickel(II). In solution, the nickel complexes (with the exception of $Ni(TPH)(CN)_2$ (ref. 152a)) dissociate completely to give planar $[NiLX]^+$ species. The R-PNP ligands deserve more comment in that they show the effects of the bulkiness of the R group. Both in the solid state and in solution the cobalt complexes with R = H are five-coordinate, whereas when R = Cy, pseudotetrahedral complexes with a $CoP_2X_2$ microsymmetry are obtained[147]. With R = Me, a five-coordinate ⇌ tetrahedral equilibrium exists in solution, while the solid complex is five-coordinate[147]. Analogously the $NiLX_2$ compounds (in the solid state) are five-coordinate when R = H or Me and planar when R = Cy, although the former complexes undergo essentially complete dissociation in solution[147] according to the equation



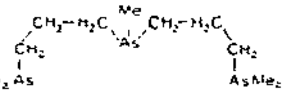
(XXXIII)



(XXXIII) Y = P, R = Ph
(XXXIV) Y = N, R = H, Me, Cy

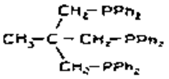
$$NiLX_2 \rightleftharpoons [NiLX]^+ + X^-$$

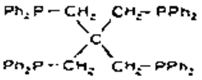
Among the ligands giving rise to six-membered chelate rings the ligands TAS (XXXV) and ttas (XXI) are among the more versatile, in that in addition to the $MLX_2$ species[143, 145, 146a] they also give five-coordinate $[NiL_2]^{2+}$ species with a free terminal donor group [143, 145] (with a structure similar to that of the $[Ni(das)(ttas)]^{2+}$ species reported among the bidentate ligands)[97–99]. The former also gives a binuclear complex $Ni_2L_3(H_2O)(ClO_4)_2$, probably containing two five-coordinate moieties bound by a ligand bridge[156].


(XXXV)

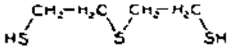
Unusual from a stereochemical point of view are the $Ni(DSP)X_2$ complexes[94], in that the apical position of the approximately square pyramid is occupied by a terminal thioether donor. This is presumably due to the particular rigidity of the ligand skeleton[153].

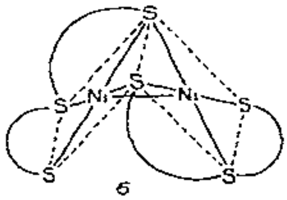
The branched tridentate ligands which may form low-spin five-coordinate complexes are TDPME (XXXVI)[154] and TDPMM (XXXVII)[155]. The geometry of these ligands is not suited to $MLX_2$ five-coordinated stereochemistry. However, together with four-coordinate $MLX_2$ species (planar with nickel and tetrahedral with cobalt), where the ligands behave as bidentate, five-coordinate structures with one phosphorus atom weakly bound have also been proposed[154, 155].


(XXXVI)


(XXXVII)

Finally the existence of a dimeric complex $Ni_2(DMS)_2$ (DMS shown as XXXVIII), consisting of two planar units sharing two sulphur atoms, should be mentioned. The dihedral angle of 82° brings the nickel atoms into an unusually close proximity, which may suggest the existence of the fifth bond (Ni–Ni) (refs. 157–160).


(XXXVIII)



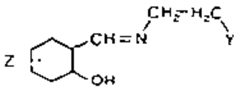
6

*(b) High-spin complexes*

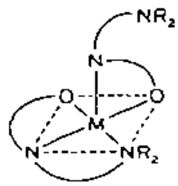
Five-coordinate high-spin complexes with tridentate ligands are mainly of two kinds:

(1) neutral $ML_2$ or cationic $[ML_2]^{2+}$ complexes in which one ligand L acts as tridentate and the other as bidentate; (2) neutral $MLX_2$ complexes where X is a halide or pseudohalide.

The neutral $ML_2$ complexes are the M(Z-SALen-$NR_2$) (M = Co, Ni), (protonated Z-SALen-$NR_2$ shown as XXXIX). The occurrence of five-coordination is due mainly to a favourable electronic and steric balance of the various substituents on the aromatic ring and on the β-nitrogen. In general, in solution there are four-coordinate (planar with nickel and tetrahedral with cobalt), five- and six-coordinate species in equilibrium, with the largest proportion of five-coordinate species occurring when the substituent at the salicylaldimine ring is 5-Cl and the substituents at the nitrogen are ethyl groups[163,164]. In this case, as well as with some other substituents, five-coordinate species with a free dialkylamino group are also obtained in the solid state (see scheme 7) (refs. 163–166). A similar situation occurs with the $M(ONSMe)_2$ (protonated ONSMe shown as XL) complexes where one of the two thioether groups is not bound[167].



(XXXIX) Y = $NR_2$
(XL) Y = SMe



7

The $MLX_2$ complexes are quite numerous (and often easily obtained). The steric and conformational requirements of the ligands capable of forming this type of complex are not so strict as in other cases previously mentioned. The chelate rings can be either five- or six-membered and the chains can be ethylenic, propylenic, o-phenylenic, etc. Similarly the ligand groups vary over a wide range from amines (aromatic and aliphatic), heterocyclic nitrogens and imines to thioethers and ethers. The most common donor set is $N_3X_2$, realized with several different nitrogen donor groups. The set $SN_2X_2$ is also rather common and some examples of donor sets $S_2NX_2$, $ON_2X_2$ and $ONSX_2$ are known. When a low-spin-inducing phosphorus or arsenic donor atom is present in the donor set together with nitrogen, oxygen or sulphur ("hybrid" ligands), the spin-state depends on the nature of the coordinated anion and on the lattice forces which may affect the geometry of the chromophore[5]. Some examples of complexes with intermediate magnetic properties will be given in Sect. B (*vi*).

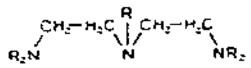
The high-spin $MLX_2$ complexes are in general more stable, with respect to the dissociation

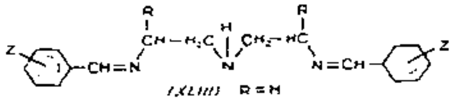
$$MLX_2 \text{ (five-coordinate)} \rightleftharpoons [MLX]^+ \text{ (planar)} + X^-$$

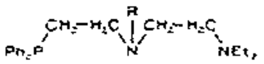
than the corresponding low-spin complexes. More frequently the following equilibrium occurs

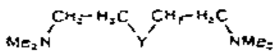
$MLX_2$ (five-coordinate) $\rightleftharpoons$ $MLX_2$ (tetrahedral)

involving the detachment of a donor group of the tridentate ligand. The type of equilibrium, if any, depends mainly on the metal ion. Cobalt complexes often give rise to the latter equilibrium, while for nickel the type of equilibrium depends on the strength of the donor atoms. When the coordinate bonds are largely covalent, i.e. with primary amines, P and As atoms, planar species are generally formed. With weaker and more bulky donor groups (generally tertiary amines), tetrahedral species can be obtained. The competition among all of these species, as well as six-coordinated species, is influenced by the substituents at the donor atoms, the nature of the X group and the specific tendency of the metal ion. Although it is difficult to account for the occurrence of five-coordination in every specific case in this class of complexes, by briefly surveying the numerous reported complexes it is possible to obtain an idea of the conditions necessary for it. As outlined above the preference of the metal ion for a five-coordinated structure with respect to a four-coordinated one depends on the geometry (planar or tetrahedral) of the alternative four-coordinate complex. When the alternative structure is six-coordinated, five-coordination is more favoured for cobalt than for nickel. For example, the $Me_5$dien ligand XLI is of the right size to form stable five-coordinate complexes with most of the first row transition metal salts (X = Cl, Br, I, NCS)[169]. The analogous $Et_4$dien (XLII), which has larger terminal donor groups and a less basic central nitrogen donor, forms five-coordinate complexes with cobalt[172–174] and planar with nickel[175], the latter giving rise to the $[MLX]^+ + X^- \rightleftharpoons MLX_2$ equilibrium in solution[175]. However the $Ni(Et_4dien)(NCS)_2$ complex is polymeric six-coordinate[173]. It appears therefore that bulkiness by itself is not the only factor determining the coordination number but that the overall properties of each donor group are also important. For example, the thiocyanate group has a strong tendency to act as a bridging ligand and therefore to form six-coordinate associated species. Stable five-coordinate nickel halide complexes, but polymeric six-coordinate thiocyanate complexes, are formed with the ligands $DENB_2$ (XLIII) and $DPNB_2$ (XLIV), which have the same skeleton as the $Et_4$dien and $Me_5$dien ligands[202]. The same basic skeleton is also present in the ligands H-nnp (XLV)[205,206], Me-nnp (XLVI)[205,206], $Me_5$daeo (XLVII)[176] and $Me_5$daes (XLVIII)[177], which also give rise to high-spin five-coordinate nickel, cobalt and iron complexes. The first two

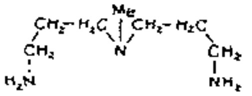

(XLI) R = R' = Me
(XLII) R = Et, R' = H


(XLIII) R = H
(XLIV) R = Me


(XLV) R = H
(XLVI) R = Me


(XLVII) Y = O
(XLVIII) Y = S

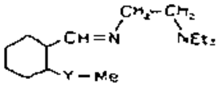
ligands give rise in solution to equilibria with tetrahedral species whose abundance increases with the bulkiness of the substituent ($H < CH_3$) on the central nitrogen donor[206]. A similar equilibrium is also shown by the $Me_5$daes complexes[177]. The ligand MeDPT (XLIX),


(XLIX)

containing two primary amino groups, also forms five-coordinate $NiLX_2$ complexes; the larger dimension of the chelate rings appears to provide the steric requirements necessary to limit the coordination number to five[200].

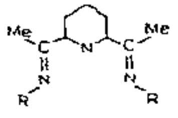
The corresponding Me-dien ligand (Me-dien denotes bis(2-aminoethyl)methylamine) forms $(MLX_2)_n$ six-coordinate polymeric complexes[201].

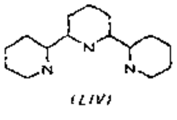
Another series of ligands of some interest from the point of view of coordination versatility is constituted by the Schiff bases formed from *N,N*-diethylethylenediamine and *o*-substituted benzaldehydes: MABen-$NEt_2$ (L), MSBen-$NEt_2$ (LI), and MOBen-$NEt_2$ (LII). The MAB and MSB derivatives form five-coordinate complexes with nickel halides[178,179],

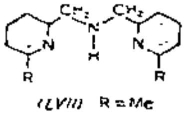

(L) Y = NH
(LI) Y = S
(LII) Y = O

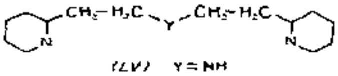
whereas cobalt halides give rise to five-coordinate complexes with the former ligand[178] and tetrahedral with the latter, the thioether group probably being non-coordinated[179]. This is consistent with the lower donor power of thioether sulphur compared with amine nitrogen. With the weak donor methoxy group only tetrahedral complexes are obtained[180]. However, when the bulkiness of the substituents on the β-nitrogen is decreased (methyl groups) or the aliphatic chain is made more flexible (trimethylenediamine either *N,N*-dimethyl or *N*-ethyl) even the MOB derivatives are able to form five-coordinate nickel complexes[180,181].

Several $MLX_2$ complexes are obtained with ligands containing one or more heterocyclic nitrogen atoms. The existence of extended π-systems adds further stability to the complexes. Typical ligands L are DAP-$R_2$ (LIII)[187], terpy (LIV)[183,188–191], DPEA (LV)[193,194], DPES (LVI)[194] and $Me_2$dpma (LVII)[196]. Comparison of DPEA, DPES and ($R_2$)dpma is interest-


(LIII)


(LIV)


(LVII) R = Me


(LV) Y = NH
(LVI) Y = S

ing. The former two ligands give rise to five-coordinate complexes, even without substituents on the pyridine ring[193,194], whereas the unsubstituted dpma ligand (R = H), owing to the small size of chelate rings, forms only six-coordinate $[NiL_2]^{2+}$ complexes[196]. However five-coordinate $MLX_2$ complexes are obtained when adequate hindrance is provided (e.g. by the *ortho* methyl groups in $Me_2$dpma)[196,197]. On the other hand, terpy, which can be considered the fully heterocyclic analogue of dpma, forms either the octahedral $[ML_2]^{2+}$ or the five-coordinate $MLX_2$ species (M = Fe, Co, Ni), depending on the synthesis conditions[188–192]. In solution, however, the latter complexes readily add a molecule of solvent or ligand thus becoming six-coordinated[189,191].

TABLE 4

Five-coordinate iron(II), cobalt(II) and nickel(II) complexes with tetradentate ligands

| Species$^a$ | Metal ion | Donor set | Physical state$^b$ with ref. | X-ray data$^c$ with ref. | Notes |
|---|---|---|---|---|---|
| *(i) Low-spin complexes* | | | | | |
| $[M(QP)X]^+$ | Fe | $P_4X$ | c,s (213,214) | | |
| | Co | | c,s (213,215) | INT(216) | |
| | Ni | | c,s (213,217) | | |
| $[M(QAS)X]^+$ | Ni | $As_4X$ | c,s (213,217) | | |
| $[M(qas)X]^+$ | Ni | $As_4X$ | c,s (218) | | |
| $[M(Qas)X]^+$ | Ni | $As_4X$ | c,s (219) | | |
| $[M(qp)X]^+$ | Co | $P_4X$ | c,s (220) | | |
| | Ni | | c,s (220) | | |
| $[M(TAP)X]^+$ | Ni | $PAs_3X$ | c,s (221) | TBP(222) | |
| $[M(TAP)(OH_2)]^{2+}$ | Ni | $PAs_3O$ | c,s (221) | | |
| $[M(TSP)X]^+$ | Ni | $PS_3X$ | c,s (223) | TBP(224) | |
| $[M(TSP)B]^{2+}$ | Ni | $PS_3(B)$ | c,s (223) | | B = $PPh_3$, $PMePh_2$, tu |
| $[M(TSeP)X]^+$ | Ni | $PSe_3X$ | c,s (225) | | |
| $[M(NP_3)X]^+$ | Co | $NP_3X$ | c,s (226) | SP(227,228) | X = NCS, (I, when Y = I, $BF_4$, $PF_6$) |
| | Ni | | c,s (226,229) | TBP(230,231) | |
| $[M(NAs_3)X]^+$ | Ni | $NAs_3X$ | c,s (146) | | |
| $[M(N_2P_2)X]^+$ | Ni | $N_2P_2X$ | c,s (232,233) | INT(234) | |
| $[M(NOP_2)X]^+$ | Co | $NOP_2X$ | c,s (235) | (X) (235) | X = NCS |
| | Ni | | c,s (235) | ESP(236,237) | |
| $[M(N_2OP)X]^+$ | Ni | $N_2OPX$ | c (238) | | X = I, NCS |
| $[M(NOAs_2)X]^+$ | Ni | $NOAs_2X$ | c,s (238) | | |
| $[M(SAs_3)X]^+$ | Ni | $As_3SX$ | c,s (239) | TBP(239) | |
| $[M(ASTP)X]^+$ | Ni | $AsP_3X$ | c,s (240,241) | | |
| $[M(SBTP)X]^+$ | Ni | $SbP_3X$ | c,s (240,241) | | |
| $[M(PTAS)X]^+$ | Ni | $PAs_3X$ | c,s (240,241) | | |
| $[M(SBTAS)X]^+$ | Ni | $SbAs_3X$ | c,s (241) | | |
| $[M(sbtas)X]^+$ | Ni | $SbAs_3X$ | c,s (242) | | |
| $[M(PSSP)X]^+$ | Co | $P_2S_2X$ | c,s (243) | | |
| | Ni | | c,s (148,243) | | |

TABLE 4 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| $[M(PNNP)X]^+$ | Co | $N_2P_2X$ | c,s (244) | ESP(245) | |
| | Ni | | c,s (244) | ESP(245) | |
| $[M(BDPI)X]^+$ | Ni | $N_2P_2X$ | c,s (246) | | |
| $[M(SALen)]_2$ | Co | $N_2O_3$ | c (247) | SP(248,249) | Dimeric |
| M(SALen)py | Co | $N_3O_2$ | c,s (247) | SP(250) | |
| $[M(tmac)X]^+$ | Ni | $N_4X$ | c,(s) (251) | | |
| $[M(CR)X]^+$ | Co | $N_4X$ | c,s (252) | | |
| | Ni | | c (253) | ESP(254) | X = Br |
| $[M(CRH)X]^+$ | Co | $N_4X$ | c,s (252) | | |
| | Ni | | c,(s) (255) | ESP(256) | $X = ClO_4$ |
| $[M(CR)B]^{2+}$ | Co | $N_4(B)$ | c,s (252) | | $B = NH_3, H_2O$, py |
| $[M(TTP)X]^+$ | Ni | $S_4X$ | s (257) | | X = I |
| *(ii) High-spin complexes* | | | | | |
| $[M(R_6tren)X]^+$ | Fe | $N_4X$ | c,s (258) | TBP(259) | R = Me, Et |
| | Co | | c,s (260,233) | TBP(261) | |
| | Ni | | c,s (260,233) | TBP(262,263) | |
| $[M(tren)X]^+$ | Co | $N_4X$ | c,s (264) | | X = I, NCS |
| $[M(Me_6tpt)X]^+$ | Co | $N_4X$ | c (265) | | |
| | Ni | | c,s (265) | | |
| $[M(tpt)X]^+$ | Co | $N_4X$ | c,s (266) | TBP(267) | |
| $[M(Me_ntpma)X]^+$ | Ni | $N_4X$ | c,s (196) | | $n = 2, 3$ |
| $[M(N_3P)X]^+$ | Co | $N_3PX$ | c,s (232,233) | TTBP(268) | |
| | Ni | | c,s (233,269) | (X) (233) | |
| $[M(N_3As)X]^+$ | Co | $N_3AsX$ | c,s (232,233) | | |
| | Ni | | c (232,233) | | X = I |
| $[M(N_2P_2)X]^+$ | Co | $N_2P_2X$ | c,s (232,233) | TTBP(234) | |
| $M(L)(NCS)_2$ | Co | $N_5$ | c,s (232,233) | | $L = N_3P, N_3As$ |
| | Ni | | c,s (232,233) | SP(271,272) | |
| $[M(N_3O)X]^+$ | Co | $N_3OX$ | c,s (273) | | |
| | Ni | | c,s (273) | | |
| $[M(N_3S)X]^+$ | Co | $N_3SX$ | c,s (273) | | |
| | Ni | | c,s (273) | | |
| $M(L)(NCS)_2$ | Co | $N_5$ | c,s (273) | TBP(274,275) | $L = N_3O, N_3S$, $Et_6tren$ |
| | Ni | | c,(s) (273) | (X) (273) | |
| $[M(N\text{-}O_3)X]^+$ | Co | $NO_3X$ | s (273) | | |
| $[M(N_2O_2)X]^+$ | Co | $N_2O_2X$ | c,s (273) | | |
| | Ni | | c,s (273) | | |
| $[M(N_2S_2)X]^+$ | Co | $N_2S_2X$ | c,s (273) | | |
| | Ni | | c,s (273) | | |
| $[M_2(bdhe)_2]^{2+}$ | Ni | $N_3O_2$ | c,s (276,277) | TBP(276,277) | Dimeric |
| $[M(NP_3)X]^+$ | Co | $NP_3X$ | c,s (226) | TTBP(278)[d] | X = Cl, Br, (I, when $Y = BPh_4$) |
| $[M(N_2OP)X]^+$ | Co | $N_2OPX$ | c,s (238) | | |
| $[M(N_2SP)X]^+$ | Co | $N_2SPX$ | c,s (238) | | |
| $[M(NOP_2)X]^+$ | Co | $NOP_2X$ | c,s (235) | TTBP(279) | X = Cl, Br, I |
| $[M(NS_3\text{-}R)X]^+$ | Co | $NS_3X$ | c,s (280, 281) | TBP (281) | R = Me, Et, iso-Pr, *tert.*-Bu |
| | Ni | | c,s (281) | | R = Et, iso-Pr, *tert.*-Bu |
| $M(Z\text{-}SALen)(OH_2)$ | Co | $N_2O_3$ | c (247) | | Z = 3-MeO |

TABLE 4 (continued)

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| $M(dacoDA)(OH_2)$ | Co | $N_2O_3$ | c,s (282,283) | (X) (283) | |
| | Ni | | c,s (282,283) | SP(284) | |
| $[M(tet)X]^+$ | Co | $N_4X$ | c,s (285,286) | (X) (286) | |
| | Ni | | c,s (285,286) | SP(285) | |
| $[M(1,7\text{-}CT)X]^+$ | Fe | $N_4X$ | c,s (287,287a) | | |
| $[M(1,3,7,10\text{-}CT)X]^+$ | Fe | $N_4X$ | c,s (287,287b) | | |
| $[M(CRH)X]^+$ | Fe | $N_4X$ | c,s (287) | | |
| $[M(TACD)X]^+$ | Ni | $N_4X$ | c,s (288) | | |
| $M(bphen)(OH_2)$ | Ni | $N_2O_2X$ | c,s (289) | | |

[a] The ligand notation is defined in the Abbreviations list.

[b] c denotes crystals, s solution and (s) uncertain assignment or equilibria with other species.

[c] Symbols for complete X-ray structures: TBP denotes trigonal bipyramid, SP square pyramid, INT intermediate structure, ESP elongated square pyramid and TTBP tetrahedrally distorted trigonal bipyramid. Indirect structural evidence (e.g. isomorphism with compounds of known structure) is indicated by (X).

[d] Full structural details were recently reported[332].

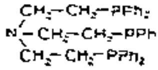
### *(iv) Tetradentate ligands*

#### *(a) Low-spin complexes*

The use of tetradentate ligands to facilitate the synthesis of five-coordinate complexes is quite widespread (see Table 4). Because of the presence of a large number of chelate rings the resulting complexes are generally quite stable. Moreover, tetradentate ligands can be made with such a geometry that, once they are coordinated to the metal ion, only one further coordination position is available.

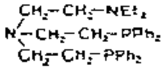
As outlined in the introduction, low-spin complexes may be obtained either with strong field donors (P and As), or, in the presence of weaker donors, when the resulting complex has an elongated square pyramidal structure. The latter stereochemistry is quite common with tetradentate open-chain and macrocyclic ligands. However, the most commonly used tetradentate ligands are tripod-shaped, since the tripod geometry is the most favourable for the formation of trigonal bipyramidal complexes in which the top (central) donor occupies one axial position and the three terminal donors the equatorial positions. If the bulkiness of the latter donor groups and the length of the chelate chains are properly chosen, only one further ligand, generally a halide or pseudohalide, can enter into the coordination sphere. The resulting cationic species $[MLX]^+$ are isolated either with the same X as counteranion, or more commonly with anions of low coordinating power such as $ClO_4^-$, $BF_4^-$, $PF_6^-$ or $BPh_4^-$.

Low-spin cobalt complexes of this type are not as common as those of nickel since they tend to distort towards a tetrahedron which stabilizes the high-spin state[5]. This is the case with the ligands $NP_3$ (LVIII) (refs. 226, 230, 231) and $N_2P_2$ (LIX) (refs. 232–234) which form low-spin trigonal bipyramidal nickel(II) complexes and usually, high-spin cobalt(II)



$$\mathrm{N}\left\langle\begin{array}{l}\mathrm{CH_2{-}CH_2{-}PPh_2}\\ \mathrm{CH_2{-}CH_2{-}PPh_2}\\ \mathrm{CH_2{-}CH_2{-}PPh_2}\end{array}\right.$$

(LVIII)

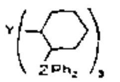


$$\mathrm{N}\left\langle\begin{array}{l}\mathrm{CH_2{-}CH_2{-}NEt_2}\\ \mathrm{CH_2{-}CH_2{-}PPh_2}\\ \mathrm{CH_2{-}CH_2{-}PPh_2}\end{array}\right.$$

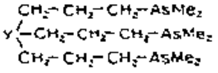
(LIX)

complexes. The exceptions are $[Co(NP_3)I]Y$ (where Y = I, $BF_4$ and $PF_6$) and $[Co(NP_3)NCS]BPh_4$, which are low-spin square pyramidal with an apical phosphorus atom[227,228]. For $[Co(NP_3)X]Y$ complexes see Sect. B (*vi*). Ligands containing multiple arsenic donor atoms have been found to bind to nickel(II), but not to iron(II) and cobalt(II).

The chains linking the donor groups are generally *o*-phenylenic, ethylenic or trimethylenic. Their length affects the geometry of the complex, in the sense that when the chelate rings are five-membered (*o*-phenylenic or ethylenic chains), the angles at the metal (L(apical)–M–L(equatorial)) are smaller than 90°, so that the metal is located below the equatorial plane of the resulting trigonal bipyramid. With trimethylenic chains the metal lies on the equatorial plane or even above it. The anomalous spectrochemical sequence (P > Sb > As) found for the apical donors in complexes with five-membered chelate rings (LX) has



(LX)
Y = P, As, Sb
Z = P, As

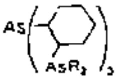


$$\mathrm{Y}\left\langle\begin{array}{l}\mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\\ \mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\\ \mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\end{array}\right.$$

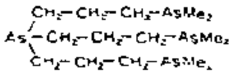
(LXI)
Y = P, As, Sb

been attributed to the "compression" of the apical donor towards the metal orbitals, which is greatest in the case of the large antimony atom[241]. The normal spectrochemical series (P > As > Sb) is found for analogous aliphatic ligands forming six-membered chelate rings (LXI) (refs. 218, 221, 242).

The electronic and steric requirements of the donor groups influence the stability of the complexes more than the chain length does. For example, although all three tripod ligands QAS (LXII)[217], Qas (LXIII)[219] and qas (LXIV)[218] with donor sets $As_4$ readily form stable $[NiLX]^+$ complexes, in solution the ligand Qas displaces QAS from its complexes, proba-



(LXII) R = Ph
(LXIII) R = Me

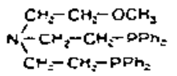


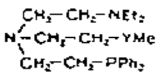
$$\mathrm{As}\left\langle\begin{array}{l}\mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\\ \mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\\ \mathrm{CH_2{-}CH_2{-}CH_2{-}AsMe_2}\end{array}\right.$$

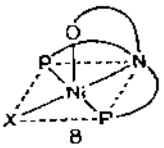
(LXIV)

bly on account of the greater donor power of the $AsMe_2$ groups compared with that of the $AsPh_2$ groups[219].

When the terminal donor groups are not equivalent (i.e. one donor group is different from the other two, or all three are different) a coordinative distortion or even a change in coordination number may occur depending on the nature of both the metal ion and the donor groups. For example, nickel complexes with the ligand $NOP_2$ (LXV)[235] have the oxygen donor weakly coordinated at the apex of an elongated square pyramid (see scheme 8)[236,237] whereas those of the $N_2OP$ (LXVI) and $N_2SP$ (LXVII) ligands are planar, the methoxy- and methylthio- groups respectively not being coordinated at all, except under particularly favourable solid state packing conditions[238]. On the other hand the complexes of co-


(LXV)

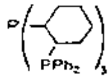

(LXVI) Y = O
(LXVII) Y = S



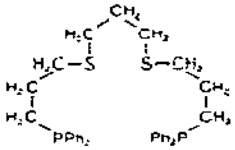
8

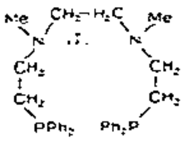
balt, which has a very low tendency towards planar stereochemistry, are trigonal bipyramidal with all these three ligands[235,238]. With this metal a geometrical distortion towards the tetrahedron is found[279], which is responsible for the high-spin state of its complexes.

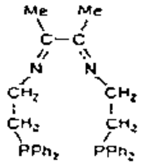
Finally, to illustrate the importance of the metal ion in determining the coordination number achieved with these ligands, it should be remembered that the QP ligand (LXVIII), which forms only five-coordinate complexes with nickel(II) and cobalt(II) under all conditions[215–217], will give six-coordinate complexes $M(QP)X_2$ with iron(II), when the coordinated anions are $CN^-$ and $NCS^-$[213,214].

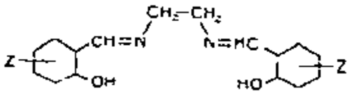

(LXVIII)

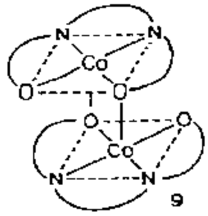
Typical linear open-chain tetradentate ligands which form five-coordinate complexes are PSSP (LXIX)[148,243], PNNP (LXX)[244,245] and BDPI (LXXI)[246]. With this type of ligand the planar structure $[ML]^{2+}$ is alternative to the five-coordinate $[MLX]^+$ – in fact $[NiL]^{2+}$ and sometimes also $[CoL]^{2+}$ complexes have been obtained[243–246]. Consistently, the planar ring-substituted CoSAlen complexes (Z-SALen shown as LXXII) have a strong tendency to increase their coordination number, as is shown by their well known oxygen-carrying ability[247]. A form of CoSALen, inactive towards oxygen absorption, has been found to be dimeric, five-coordinate, with bridging oxygens (see scheme 9)[248,249]. Also five-coor-


(LXIX)


(LXX)


(LXXI)

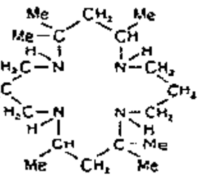

(LXXII)



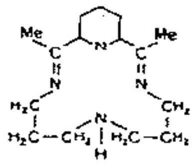
9

dinate are the monoadducts with pyridine[250], and some hydrate complexes[247]. The fact that most of these complexes are low-spin, even though the donor atoms are of the high-spin type, can be ascribed to apical elongation of the square pyramid in addition to the presence of a relatively strong field in the basal plane. Probably the anomalous magnetic behaviour of some of these complexes[306] is also related to these structural factors.

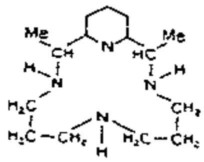
Macrocyclic ligands containing nitrogen (tmac, LXXIII[251], CR, LXXIV[252,253] and CRH, LXXV[252,255]) or sulphur (TTP, LXXVI[257]) as donor atoms may also form five-coordinate complexes. Again their low-spin state is ascribed to a strong apical elongation of the square pyramid; this has been confirmed by X-ray structures[254,256] of the complexes $[Ni(CR)X]^+$ and $[Ni(CRH)X]^+$. It should be noted that these macrocyclic ligands do not sterically hinder the achievement of six-coordination so that, together with five-coordinate $[MLX]^+$ species, six-coordinate tetragonal $MLX_2$ complexes have also been isolated[252–257].



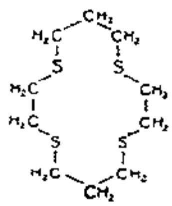
(LXXIII)



(LXXIV)



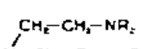
(LXXV)



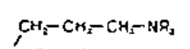
(LXXVI)

*(b) High-spin complexes*

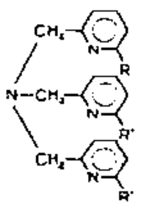
Tetradentate ligands with the same structural characteristics as have been discussed above, but with donor atoms such as oxygen and nitrogen, form high-spin five-coordinate complexes. The stereochemical influence of the skeletal geometry and of the size of the donor groups in tripod-shaped ligands is clearly exemplified by the characteristics of the metal complexes with the following ligands which have an $N_4$ donor set: tren (LXXVII), $Me_6$tren (LXXVIII), $Et_6$tren (LXXIX), tpt (LXXX), $Me_6$tpt (LXXXI), $Me_2$tpma (LXXXII) and $Me_3$tpma (LXXXIII).



(LXXVII) R=H
(LXXVIII) R=Me
(LXXIX) R=Et



(LXXX) R=H
(LXXXI) R=Me



(LXXXII) R=H, R'=Me
(LXXXIII) R=R'=Me

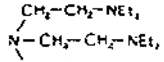
The first three ligands have identical chains (ethylenic), so their different coordination properties depend both on the bulkiness and the nucleophilicity of the donor groups. The

$Me_6$tren ligand forms five-coordinate $[MLX]^+$ complexes with all the bivalent *3d* ions[258–263], whereas the unsubstituted tren ligand (R = H) forms six-coordinate iron(II) and nickel(II), and five-coordinate cobalt(II), copper(II) and zinc(II) complexes, according to the specific preference of these metal ions for a given stereochemistry[264]. A further increase in the size of the donor groups, as in the ligand $Et_6$tren, does not introduce appreciable changes in the trigonal bipyramidal structure of the complexes[233]. However, the steric effects show up with the nickel thiocyanate complex $Ni(Et_6tren)(NCS)_2$ in that the ligand behaves as tridentate with one free arm, and both thiocyanate groups are bound to the metal[273]. Owing to the large coordinating power of the NCS ion, bulky or weak donor groups of tetradentate ligands are often prevented from bonding[233,235,272,273].

The ligands tpt and $Me_6$tpt possessing trimethylenic chains are more flexible than the corresponding tren derivatives with respect to the metal–ligand moiety[265–267]. For example, the N(apical)–Co–N(equatorial) angles of $[Co(tpt)X]^+$ are larger than 90° (ref. 267), whereas $[M(Me_6tpt)X]^+$ (M = Co, Ni) are presumably distorted towards a "capped" tetrahedron (N(apical)–M–N(equatorial) angles smaller than 90° (ref. 265)). In solution the $[Co(Me_6tpt)X]^+$ complexes become tetrahedral with the apical nitrogen not bound[265].

The $Me_2$tpma and $Me_3$tpma are pyridyl analogues of the tren series. In this case the increasing steric requirements of the ligands result from methyl groups substituted at the 2-position of the pyridine rings. Whereas the unsubstituted tpma ligand is reported to form six-coordinate nickel complexes, five-coordinate species are preferentially obtained as the number of methyl groups is increased[196]. However these ligands often behave as tridentate with a non-coordinating donor group, depending on the nature of the X anion[196].

The presence of different donor atoms in the donor set of these tetradentate ligands may give rise to either coordinative distortion or other stereochemistries depending on the donor groups involved, on the metal ion and on the X ion. For example, the $N_3P$ ligand LXXXIV gives rise to $[NiLX]^+$ complexes which have been isolated in two isomeric forms; one form being five-coordinate high-spin and the other planar and diamagnetic with one diethylamino group uncoordinated[233,269]. The latter isomer is predominant in solution and its proportion varies with the X ion in the order I ≪ Br < Cl (ref. 269). With the $N_3As$ ligand LXXXV only the iodo derivative is five-coordinate[233], the chloro, bromo and thiocyanato derivatives being planar with a free diphenylarsino group[233,270]. The distinctive behaviour of the iodo complex has been related to the soft character of the iodide ion which favours the coordination of the soft arsenic atom[233].

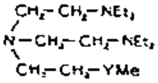


$$N(CH_2-CH_2-NEt_2)_2(CH_2-CH_2-YPh_2)$$

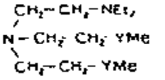
(LXXXIV) Y = P
(LXXXV) Y = As

With cobalt, however, trigonal bipyramidal complexes have been obtained with all the above ligands.

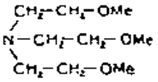
The ligands $N_3O$ (LXXXVI), $N_3S$ (LXXXVII), $N_2O_2$ (LXXXVIII), $N_2S_2$ (LXXXIX),


$N(CH_2{-}CH_2{-}NEt_2)_2(CH_2{-}CH_2{-}YMe)$

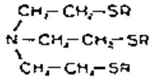
(LXXXVI) Y=O
(LXXXVII) Y=S


$N(CH_2{-}CH_2{-}NEt_2)(CH_2{-}CH_2{-}YMe)_2$

(LXXXVIII) Y=O
(LXXXIX) Y=S


$N(CH_2{-}CH_2{-}OMe)_3$

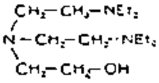
(XC)


$N(CH_2{-}CH_2{-}SR)_3$

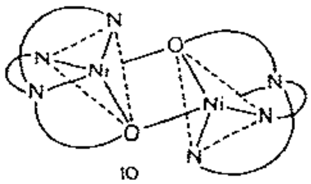
(XCI)
R=Me Et, i-Pr

$N{-}O_3$ (XC) and $NS_3{-}R$ (XCI) are able to form cobalt and nickel complexes with several stereochemistries[273,280,281], such as: (1) five-coordinate $[MLX]^+$ species; (2) five-coordinate $ML(NCS)_2$ species with the ligand acting as tridentate (in general, an ethereal or thioethereal group is not coordinated)[274,275]; (3) six-coordinate $MLX_2$ species (X = halogen, NCS); (4) polymeric six-coordinate $[(MLX)_n]^{n+}$ species. From this it can be concluded that the steric hindrance of the terminal donor group decreases in the order $Et_2N > SMe > OMe$, since the tendency to attain six-coordination as opposed to five-coordination increases in the order $(Et_6\,tren) < N_3S < N_3O < N_2S_2 < N_2O_2 < NS_3{-}Me < N{-}O_3$ (ref. 273); also, with the same ligand, six-coordinate nickel complexes and five-coordinate cobalt complexes are often obtained[273]. This is the case with the ligand $NS_3$-Me (ref. 280); however, if the size of the S–R group is increased (e.g. R = iso-Pr, *tert.*-Bu), five-coordinate nickel complexes are obtained[281].

Noteworthy is the behaviour[276,277] of the ligand bdhe (XCII), which undergoes deprotonation with nickel perchlorate, forming a complex with the empirical formula $Ni(L^-)ClO_4$. A structural analysis[276,277] has shown that five-coordination is achieved via dimerization through two oxygen bridges (see scheme 10). Such behaviour has also been encountered with bidentate ligands containing hydroxy groups (SAL-$NMe_2$, catec, qo).

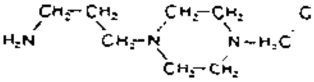

$N(CH_2{-}CH_2{-}NEt_2)_2(CH_2{-}CH_2{-}OH)$

(XCII)

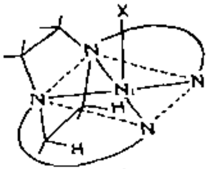


10

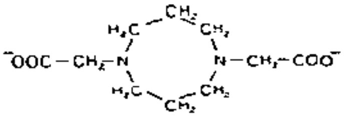
Passing now to open-chain ligands, particularly interesting is the behaviour of the ligands tet (XCIII)[285,286] and dacoDA (XCIV)[282–284]. Both form planar nickel complexes, $[NiL]^{2+}$ and NiL respectively, in which planarity is imposed by the conformation of the diaza-cyclohexane and diaza-cyclooctane rings. The axial addition of a fifth ligand is accompanied by



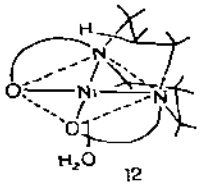
(XCIII)



11



(XCIV)



12

a twisting or folding of these rings in such a way that hydrogen atoms of the chain are forced into the opposite axial position, so preventing six-coordination (see schemes 11, 12) (refs. 282–286). The five-coordinate structure of these complexes with nickel and cobalt is thus determined by intrinsic geometric factors of the ligand. However, in the case of the tet derivative the NCS ion is able to form also six-coordinate $NiL(NCS)_2$, presumably because of its smaller effective radius and stronger bonding ability[285,286].

TABLE 5

Five-coordinate iron(II), cobalt(II) and nickel(II) complexes with pentadentate ligands

| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| *(i) Low-spin complexes* | | | | | |
| M(Z-SAL-DAES) | Ni | $O_2N_2S$ | c,s (291,292) | | Z = H, 5-Br, 3-Me, 3-MeO, 3-iso-Pr |
| M(TAAB-LN) | Ni | $N_5$ | c,s (293,294) | | |
| M(TAAB-LS) | Ni | $N_4S$ | c,s (293,294) | | |
| *(ii) High-spin complexes* | | | | | |
| M(Z-SAL-R-DPT) | Co | $N_3O_2$ | c,s (295) | (X) (295) | R = H, Me |
| | Ni | | c,s (295) | INT(296–298) | |
| M(TIB-R-DPT) | Co | $N_3S_2$ | c,s (299) | | R = H, Me |
| | Ni | | c,s (299) | | |
| $[M(tpen)]^{2+}$ | Ni | $N_5$ | c,s (300) | SP(301) | |
| $M(ddta)(OH_2)$ | Co | $N_3S_2$ | c (302) | | |
| | Ni | | c (302) | | |

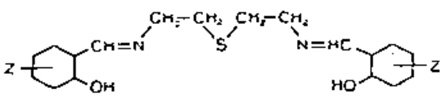
[a] The ligand notation is defined in the Abbreviations list.
[b] c denotes crystals, s solution.
[c] Symbols for complete X-ray structures: SP denotes square pyramid and INT intermediate structure. Indirect structural evidence (e.g. isomorphism with compounds of known structure) is indicated by (X).

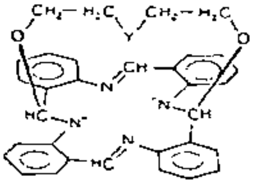
### *(v) Pentadentate ligands*

#### *(a) Low-spin complexes*

Although several types of ligand skeletons may be thought of for pentadenate ligands [290], their ability to form five-coordinate complexes (see Table 5) is restricted by the following conditions: (1) the intraligand repulsion effects must be low enough to allow coordination of all five donor groups to the central metal ion; (2) the crowding around the metal ion must be large enough to prevent a sixth donor group from bonding. Taking into account the difficulties in synthesizing such ligands, it can be well understood why five-coordinate complexes with pentadenate ligands are not numerous.

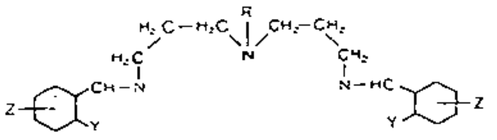
Low-spin five-coordinate structures have been proposed until now only for the complexes with Z-SAL-DAES (XCV) (refs. 291, 292), TAAB-LN (XCVI), and TAAB-LS (XCVII) ( refs. 293, 294) whose donor atoms are mostly of high-spin character. The low-spin state can therefore be accounted for by partial coordination of the apical donor atom of an approximate square pyramidal geometry. In the case of Ni(Z-SAL-DAES), however, some paramagnetism has been observed so that the possibility of spin-isomerism cannot be ruled out[292]. On the other hand the analogous Z-SAL-DIEN ligand, where sulphur is replaced by an NH group, forms only planar complexes with nickel, with the central nitrogen not bound [292]. The complexes Ni(TAAB-LN) and Ni(TAAB-LS) are obtained by alcoholysis of the imino groups of the planar complex Ni(TAAB) with the diols bis(2-hydroxyethyl)methylamine or bis(2-hydroxyethyl)sulphide[293,294]. Although the apical nitrogen or sulphur is presumably weakly coordinated, they are believed to be responsible for the template effect leading to the "basket-like" ligands[294].

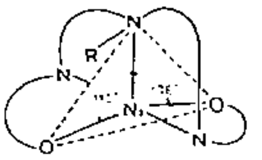

(XCV)


(XCVI) Y=N–Me
(XCVII) Y=S

## (b) High-spin complexes

Reaction of ring-substituted salicylaldehyde or 2-thiolbenzaldehyde with bis(3-aminopropyl)alkylamines yields the pentadentate ligands Z-SAL-R-DPT (XCVIII)[295–298] and TIB-R-DPT (XCIX)[299]. In these ligands, in contrast to the above-mentioned Z-SAL-DIEN, the flexibility of the trimethylene chains allows the central donor atom to coordinate easily in the axial position of a *trans* quasi-planar bis-salicylideneiminate-type moiety. As a result of this coordination, the R group may point towards either of the two aromatic rings (see scheme 13). The structure of Ni(SAL-Me-DPT) shows two different N(R)-Ni-O angles (106, 113°) so that the two aromatic groups are geometrically non-equivalent[296,297]. Two isomeric forms are thus obtained, differing in that the R group points towards either the first SAL group (angle of 106°) or the other SAL group[297]. In solution, two PMR signals for each aromatic position are observed[298a], which can be accounted for by either of two

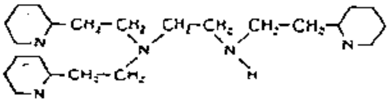

(XCVIII) Y=OH, R=H Me
(XCIX) Y=SH, R=H Me


13

alternative models: (1) two different N(R)-Ni-O angles but with the R group pointing towards one aromatic group only (if both isomers were present, four signals for each position would be expected): (2) equal (or averaged) N(R)-Ni-O angles, the non-equivalence of the SAL groups resulting from the fixed position of the R group (if this were averaged too, one signal for each position would be expected)[299].

Since the PMR spectrum of the analogous TIB derivatives shows only one signal for each aromatic position at higher temperature, it has been suggested that model (2) is the more probable, with a ligand conformational rearrangement which allows the two aromatic moieties to average their non equivalence during the PMR resonance time[299].

The ligand tpen (C) should also be mentioned since it is the only reported pentadentate



(C)

ligand which gives a cationic complex, $[Ni(tpen)]^{2+}$, with a square pyramidal structure[300, 301].

TABLE 6

Spin-isomeric five-coordinate iron(II), cobalt(II) and nickel(II) complexes

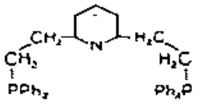
| Species[a] | Metal ion | Donor set | Physical state[b] with ref. | X-ray data[c] with ref. | Notes |
|---|---|---|---|---|---|
| $M(pnp)X_2$ | Fe | $P_2NX_2$ | c,s (161) | | X = I, NCS |
| | Co | | c,s (161,303) | | X = Br, I |
| | Ni | | c,s (161,304) | | X = Cl |
| $M(pmp)X_2$ | Co | $P_2NX_2$ | c,s (162) | | X = Br, NCS |
| | Ni | | c,s (162) | | X = NCS |
| $M(R\text{-}nnp)X_2$ | Co | $N_2PX_2$ | c (205,206) | SP(207) | R = H, X = NCS |
| M(SALoph)B | Co | $N_2O_2(B)$ | c,s (305,306) | | B = R-py, R-imz, $PPh_3$ |
| M(SALen)B | Co | $N_2O_2(B)$ | c,s (306) | | B = R-Py, R-imz |

[a] The ligand notation is defined in the Abbreviations list.
[b] c denotes crystals, s solution.
[c] SP denotes square pyramidal structure.

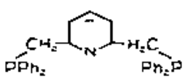
*(vi) Spin-isomeric complexes*

As outlined in the Introduction, the factors determining the spin state in five-coordinate complexes are the nature of the donor groups, and the geometrical or coordinative distortions, if any, of the chromophore[5]. When a proper balance of these two factors produces an energy gap of the order of magnitude of $kT$ between the lowest high- and low-spin levels, the population distribution over the two levels is temperature-dependent, and so are the magnetic properties. Under these conditions, the complexes are said to show spin-equilibrium, or spin-isomerism[307,308]. In order to locate the magnetic cross-over range between high- and low-spin complexes, and possibly to obtain spin-isomeric complexes, the donor groups in five-coordinate complexes have to be systematically varied. We have already seen that the semi-empirical parameters of the donor atoms, i.e. the overall electronegativity ($\Sigma\chi$) and the overall nucleophilicity ($\Sigma n^0$), correlate well with observed spin states[5,11]. However, it is not possible, at this time, to predict the distortions which may occur when the five-coordinate chromophore is formed and which have a direct effect on the spin state. Thus, even though a donor set having a $\Sigma\chi$ or $\Sigma n^0$ value close to the crossover range is chosen, the formation of a spin-isomeric complex is still a matter of chance. For example, the complex $[Co(NP_3)I]^+$ is low-spin when the counteranion is $I^-$, $BF_4^-$ or $PF_6^-$, but high-spin when the counteranion is $BPh_4^-$ (refs. 226–231). The former complexes have a definite square pyramidal geometry[227,228], whereas the latter is trigonal bipyramidal with a very large tetrahedral distortion (the Co–N(apical) distance is 2.74 Å and the N(apical)–Co–P angle is 74°) which accounts for the high-spin state[5,278,309]. A temperature-dependent configurational equilibrium between the two limiting geometries exists in solution, with which a change in spin-state is associated[226,308].

Ligands giving rise to five-coordinate complexes which are spin-isomeric in the solid state are the tridentate pnp (CI), pmp (CII), and H-nnp (XLV). Among the $M(pnp)X_2$ complexes, the spin state is determined by the nature of X. The nickel complexes are low-spin when X = Br, I, whereas the chloro derivative shows spin equilibrium[161,304]; the cobalt chloro derivative is high-spin whereas the bromo and iodo derivatives are spin-isomeric[161,303]; finally the iodo complex of iron shows spin equilibrium, whereas the chloro and bromo derivatives are high-spin[161]. Complexes of the pmp ligand show similar behaviour, although spin equilibrium does not necessarily occur in the same halo derivatives as those of pnp[162].



(CI)

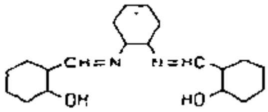


(CII)

Perhaps the most thoroughly investigated spin-isomeric complex is $Co(H\text{-}nnp)(NCS)_2$. It is essentially low-spin at 77°K and high-spin at 418°K (ref. 205). The continous variation of the magnetic properties is associated with changes in the visible and solid state infrared spectrum, the latter particularly in the $\nu$(N–H) and $\nu$(C≡N) regions[205,308]. Two separate sets of bands, whose relative intensities are temperature-dependent, are observed in each region. This suggests the presence of two molecular species (e.g. high- and low-spin species differing in bond distances) in equilibrium[205,206,308]. However, an X-ray structure of this complex at room temperature has shown only one kind of molecule with normal thermal parameters[207]. This apparent contradiction points out the lack of any completely satisfying model in this field, and indicates the need for further work to clarify the current debate on spin-isomeric complexes.

In contrast, the analogous Co(Me-nnp)$(NCS)_2$ complex is fully high-spin[206]. The major structural difference between these two complexes is that the latter complex is closer to a tetrahedrally distorted trigonal bipyramid, whereas the former one is closer to a slightly elongated square pyramid[207]. The influence of the geometry on the spin-state thus parallels that observed for the [Co($NP_3$)I] Y series[5].

It is quite difficult to rationalize, in terms of both structural and ligand field parameters, the behaviour of the five-coordinate monoadducts of Co(SALen) (SALen shown as LXXII) (ref. 306) and Co(SALoph) (SALoph shown as CIII)[305,306].



(CIII)

These complexes are found to be high-spin, low-spin, or spin-isomeric, depending on both the salycilaldimine substituent and the fifth (axial) donor group[305,306]. Probably the relation between the donor properties of the axial and planar donors, although not completely understood, accounts for the observed magnetic properties.

## C. RECENT ADVANCES IN SPECTROSCOPY AND MAGNETISM OF FIVE-COORDINATE NICKEL(II) AND COBALT(II) COMPLEXES

As soon as spectral data became available for five-coordinate complexes, ligand field calculations were performed in an attempt to assign the spectral bands and to account for the magnetic properties[310–315]. Since the complexes have a symmetry lower than cubic, two radial integral parameters ($B_2$ and $B_4$ in the crystal field model, or equivalent parameters in other models) are necessary to describe the effects of the ligand field, in addition to the usual nephelauxetic parameter[2]. The $B_4$ parameter can be related to the octahedral $Dq$ through the relation $Dq = \mu B_4/6$, and this value can be considered to be transferable to different symmetries for the same donors[2]. The $B_2$ integral must be parametrized, as the $B_2/B_4$ ratio is expected to vary in the range 1–5 (ref. 316).

Ligand field calculations on five-coordinate $Fe^{II}$, $Co^{II}$ and $Ni^{II}$ complexes were first performed by Ciampolini et al.[310–312] and Venanzi and co-workers[313,314], for high-spin and low-spin complexes respectively. Numerous contributions have been made to interpret more individual cases. They are reported in the excellent reviews by Furlani[1] and Ciampolini[2]. Recent papers by Gray and co-workers[317,318] and Ferraro et al.[319,320] discuss the temperature dependence and the pressure dependence of ligand field spectra of low-spin five-coordinate nickel(II) complexes.

Quite recently, single crystal spectral and magnetic measurements have been carried out on some representative high-spin nickel(II) and cobalt(II) complexes[263,321–328]. Since these experiments establish the validity of the ligand field model in this class of complexes and definitely confirm the assignments proposed, we shall discuss them in some detail.

*(i) High-spin nickel(II) complexes with square pyramidal geometry*

An energy level diagram for the triplet terms of the nickel(II) ion surrounded by five equivalent dipoles arranged in a square-pyramidal geometry is shown in Fig. 4, together with the effects on the energy levels of varying the $B_2/B_4$ radial integral ratio, the $Dq$(api-

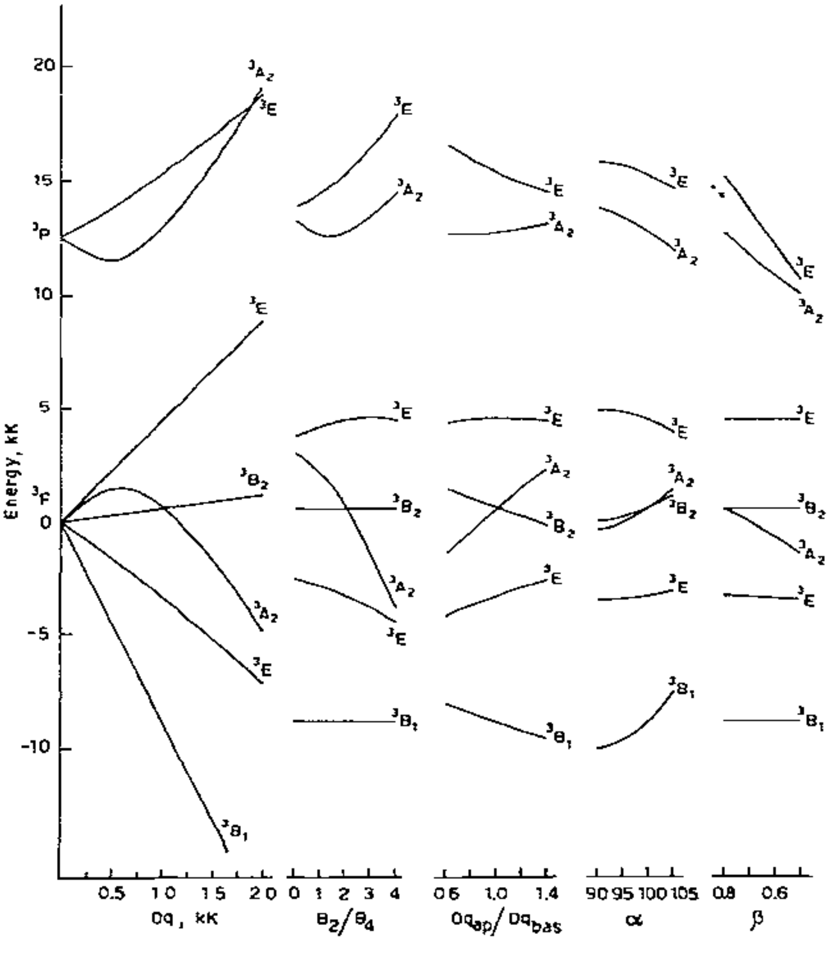


Fig.4. Energy level diagram for a nickel(II) ion in a ligand field of $C_{4v}$ symmetry ($B_2/B_4$ = 2, α = 100°, β = 0.80, $Dq_{ap} = Dq_{bas}$). From left to right, the effect of changing the $B_2/B_4$ ratio, the $Dq_{ap}/Dq_{bas}$ ratio, the apical angle α and the nephelauxetic parameter β (for $Dq_{bas}$ = 1.0 kK).

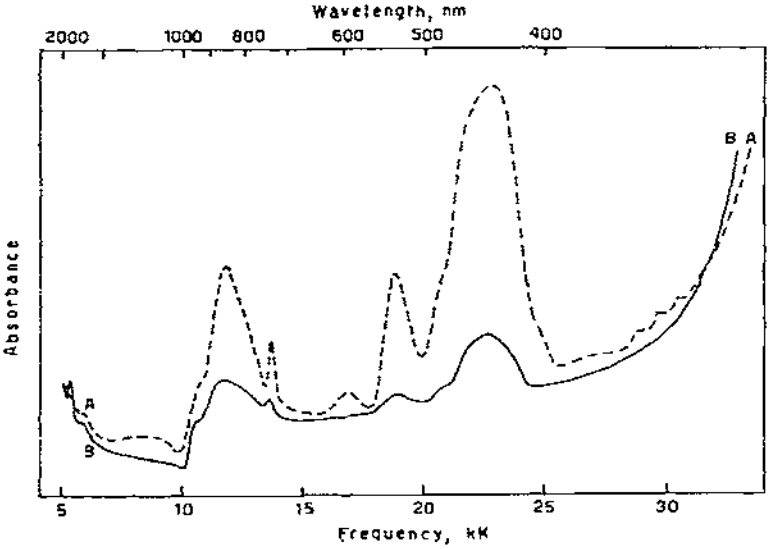


Fig.5. Single-crystal polarized electronic spectrum of the [Ni(Ph$_2$MeAsO)$_4$NO$_3$]NO$_3$ complex at 80°K. A, ⊥ polarized; B, ∥ polarized) (ref. 321).

cal)/$Dq$(basal) ratio, the apical angle $\alpha$ and the nephelauxetic parameter $\beta$ (ref.322). The ground state is an orbitally non-degenerate $^3B_1$ level which gives rise to transitions either not allowed or normally polarized (with respect to the $C_4$ axis).

TABLE 7

Observed and calculated band energies for [Ni(Ph$_2$MeAsO)$_4$NO$_3$]NO$_3$ (ref.[a])

| Assignment ($C_{4v}$) | | Polarization ($C_{4v}$) | Frequency (kK)<br>Observed | Calculated ($C_{4v}$) |
|---|---|---|---|---|
| $^3B_1$ → | $^3E(F)$ | Perpendicular | (< 5.5) | 3.89 |
| | $^3A_2(F)$ | Forbidden | 8.2 | 8.33 |
| | $^3B_2(F)$ | Forbidden | 9.3 | 9.14 |
| | $^3E(F)$ | Perpendicular | 11.9 | 11.57 |
| | $^3A_2(P)$ | Forbidden | 19.0 | 19.29 |
| | $^3E(P)$ | Perpendicular | 22.9 | 22.56 |

[a] Parameter values: $Dq_{\text{bas}}$ = 1.05 kK, $Cp/Dq$ = 3.0, $Dq_{\text{ap}}/Dq_{\text{bas}} = Cp_{\text{ap}}/Cp_{\text{bas}}$ = 0.8, $B$ = 0.85 kK, $\alpha$ = 105° (ref. 321).

Single-crystal polarized spectra of the [Ni(Ph$_2$MeAsO)$_4$NO$_3$]NO$_3$ complex are shown in Fig.5, and the proposed assignment is reported in Table 7 (ref. 321). The polarization properties agree satisfactorily with those expected. Because of the large number of parameters involved in the calculations, there are several combinations of parameter values which give a reasonable match between observed and calculated frequencies. However a critical examination of the dependence of the energies on the variation of parameters, and of the chemical significance of the parameters, may be of help in choosing the most reasonable parameter set. The energy fit reported in Table 7 has been obtained with the following set of parameters: $Dq(\text{basal}) = 1.05\ kK$; $\alpha = 105°$; $\beta = 0.82$; $B_2/B_4 = 1.75$; $Dq(\text{apical})/Dq(\text{basal}) = 0.8$. It should be noted that the apical angle has also been parametrized in that it may be different from that actually found by X-ray analysis owing to second-nearest-neighbour effects[321].

A $^3B_1$ ground level should produce a spin-only value for the magnetic moment. However, this level is mixed with the excited $E$ levels through spin–orbit coupling. A complete treatment inclusive of spin–orbit coupling was performed by Gerloch, Lewis, et al., to account for the magnetic anisotropy of the $[Ni(Ph_2MeAsO)_4NO_3]NO_3$ complex[321]. A partial energy level scheme resulting from successive spin–orbit and Zeeman perturbations is presented in Fig.6. According to this model[322], the molar susceptibility components (neglecting TIP contributions) are given by:

$$\chi_{\parallel} = \frac{N\beta^2}{kT}\,\frac{8e^{-\delta/kT}}{1 + 2e^{-\delta/kT}}$$

$$\chi_{\perp} = N\beta^2\,\frac{4A^2}{\delta}\,\frac{1 - e^{-\delta/kT}}{1 + 2e^{-\delta/kT}}$$

where

$$\delta = \left[\frac{(\sqrt{5}\,(c_1) + \sqrt{3}\,(c_2))^2}{\Delta_1} + \frac{(\sqrt{5}(c_2) + \sqrt{3}\,(c_1))^2}{\Delta_2}\right]\lambda^2$$

and

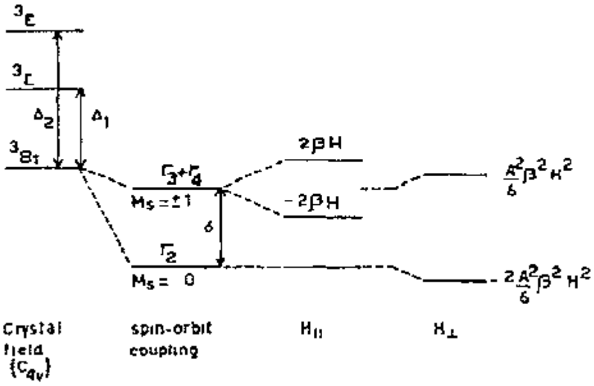


Fig.6. Splitting of the $^3B_1$ term under the effect of successive spin–orbit coupling and magnetic field perturbations[322].

$$A = \sqrt{2} - \frac{k\lambda}{\sqrt{2}}\left[\frac{(\sqrt{5}(c_1) + \sqrt{3}(c_2))^2}{\Delta_1} + \frac{5c_2{}^2 - 3c_1{}^2}{\Delta_2}\right]$$

($c_1$ and $c_2$ are diagonalization coefficients).

These formulae probably overestimate the second-order perturbation because of the proximity of the excited levels. However they show that a large orbital contribution is present, which may provide $\mu_{eff}$ values as large as 4.0 B.M. In fact the magnetic moments for square pyramidal nickel(II) magnetophores[56–62] range from 3.3 to 3.7 B.M.

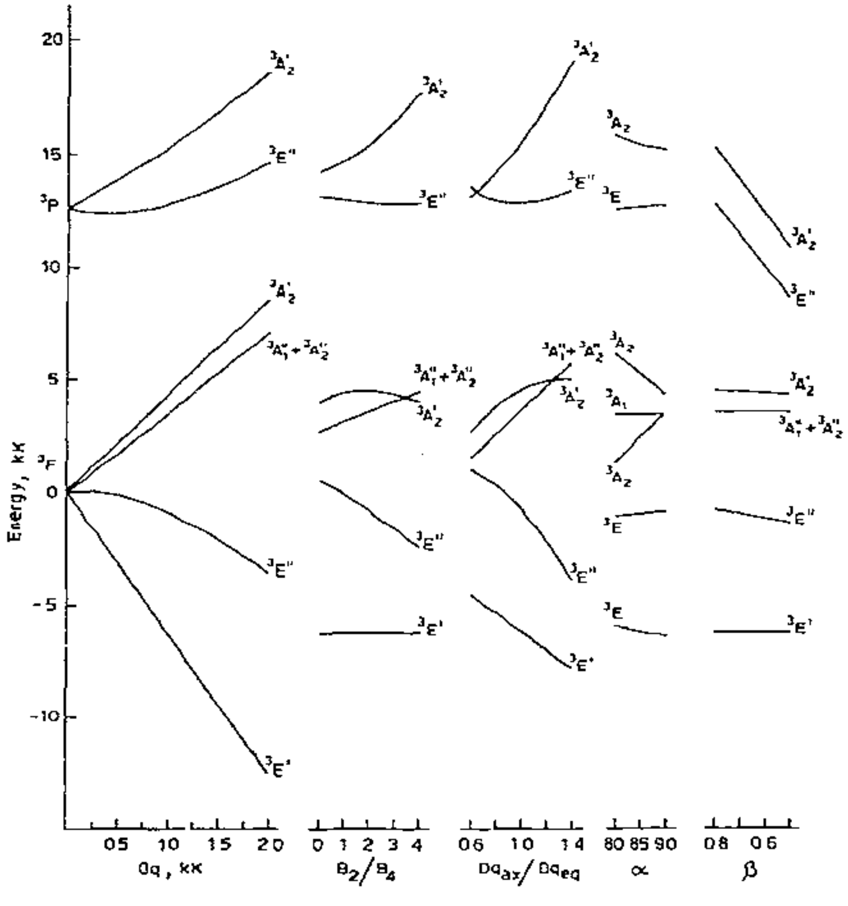


Fig.7. Energy level diagram for a nickel(II) ion in a ligand field of $D_{3h}$ symmetry ($B_2/B_4$ = 2, $\beta$ = 0.80, $Dq_{ax}$ = $Dq_{eq}$). From left to right, the effect of changing the $B_2/B_4$ ratio, the $Dq_{ax}/Dq_{eq}$ ratio, the apical angle α and the nephelauxetic parameter $\beta$ (for $Dq_{eq}$ = 1.0 kK).

### *(ii) High-spin nickel(II) complexes with trigonal bipyramidal geometry*

An energy level diagram[263] for the triplet terms of nickel(II) in $D_{3h}$ symmetry is given in Fig.7, together with the effects of varying: (a) the $B_2/B_4$ ratio; (b) the $Dq$(axial)/$Dq$ (equatorial) ratio; (c) the apical angle $\alpha$; and (d) the nephelauxetic parameter $\beta$. Spectra of chromophores with rigorous $D_{3h}$ symmetry have not yet been described. However, the [Ni(Me$_6$tren)X] X complexes exhibit a crystallographic $C_3$ symmetry, with an apical angle of 84° for the bromo derivative[252]. Such a symmetry requires a $^3E$ ground state. Unfortunately the halide complexes belong to a monometric crystallographic group[262], therefore anisotropic measurements cannot be performed on these complexes. In contrast, the crystals of [Ni(Me$_6$tren)NCS] NCS.aq are orthorhombic, and the chromophore may be regarded as having approximate $D_{3h}$ symmetry[263].

The single-crystal polarized spectra for this complex are reported in Fig.8, together with the proposed assignment[263], which agrees with the assignment previously proposed by Ciampolini et al.[311], and later by Wood[315]. For the $^3E$ ground level, under spin–orbit coupling and Zeeman effects (Fig.9) (ref. 323), the following susceptibility components are calculated[323], neglecting TIP contributions.

$$\chi_{\parallel} = \frac{N\beta^2}{3\kappa T} \frac{12(4e^{2\lambda/\kappa T} + 1)}{e^{2\lambda/\kappa T} + 1 + e^{-2\lambda/\kappa T}}$$

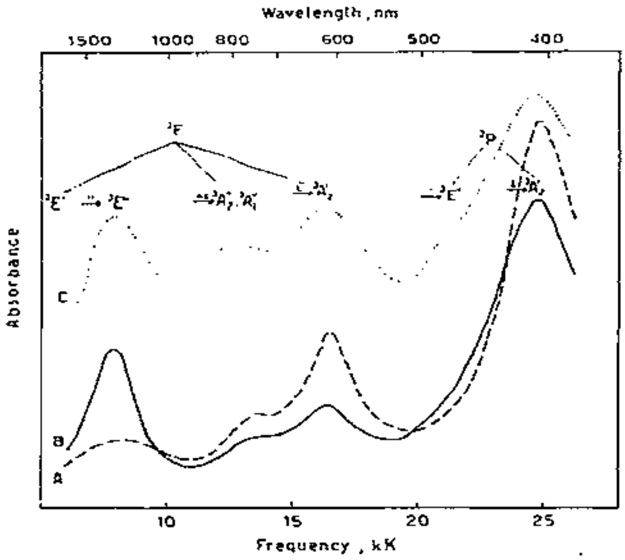


Fig.8. Single-crystal polarized electronic spectrum (A, mostly ⊥ polarized; B, mostly ∥ polarized) and diffuse reflectance spectrum (c) of the [Ni(Me$_6$tren)NCS] NCS.H$_2$O complex, with the proposed assignment in $D_{3h}$ symmetry (for $B_2/B_4$ = 1.5, $Dq_{ax}$ = $Dq_{eq}$ = 1.25 kK, $\beta$ = 0.75) (ref. 263).

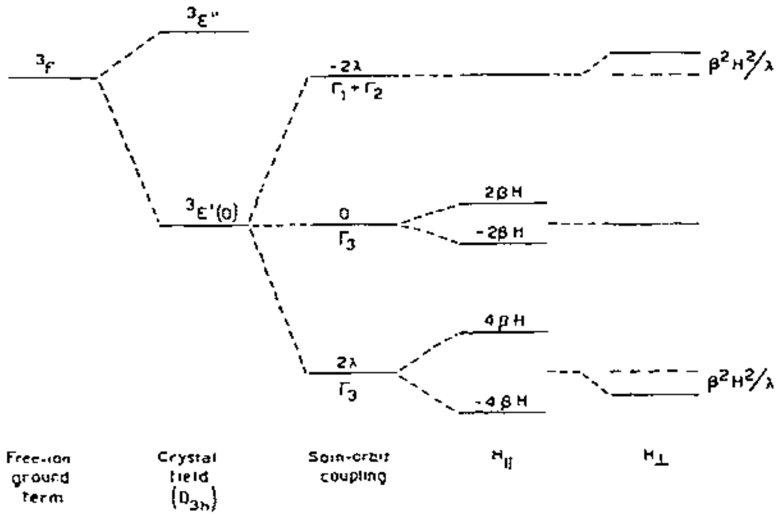


Fig.9. Splitting of the $^3E'$ term under the effect of successive spin–orbit coupling and magnetic field perturbations[324].

$$\chi_\perp = \frac{2N\beta^2}{\lambda}\,\frac{e^{2\lambda/\kappa T} - e^{-2\lambda/\kappa T}}{e^{2\lambda/\kappa T} + 1 + e^{-2\lambda/\kappa T}}$$

These formulae produce magnetic moments larger than observed. This has been attributed[323] to $E'$–$E''$ mixing under $C_{3v}$ symmetry, the states of $E''$ being eigenfunctions with $M_L = \pm 1$ while the ground state eigenfunctions have $M_L = \pm 2$. As an alternative, the $C_3$ symmetry of the halo complexes may be the result of a dynamical distortion which would allow for the ground state to be split[263].

### *(iii) High-spin nickel(II) complexes with intermediate geometry*

Chromophores with geometries intermediate between the TBP and the SP are quite numerous. Unfortunately they are difficult to handle owing to their low symmetry. An energy level diagram[324] for $C_{2v}$ symmetry is shown in Fig.10. The $N_3O_2$ chromophore of the NiSAL-MeDPT complex has an approximate $C_{2v}$ symmetry if the aliphatic chains and the salicylaldimine groups are neglected. The single-crystal polarized spectra of this complex[324] are shown in Fig. 11. The polarization properties are quite neat; however, they do not lead to a straightforward assignment. Table 8 reports an assignment based on the diagrams of Fig. 10 the values of the angles $\beta$ averaged to 110°*.

Magnetic moment values of this type of compound are ca. 3.3 B.M., i.e. generally lower that those found for complexes with higher symmetries.

---

* A paper discussing the spectral assignment of NiSAL-MeDPT has recently appeared[333]. A $^3B_2$ ground level in $C_{2v}$ symmetry has been proposed in order to account for the polarization properties. However, the correlation between $D_{3h}$ and $C_{4v}$ symmetries requires, by symmetry restrictions, an $A_1$ ground level (see Fig. 10).

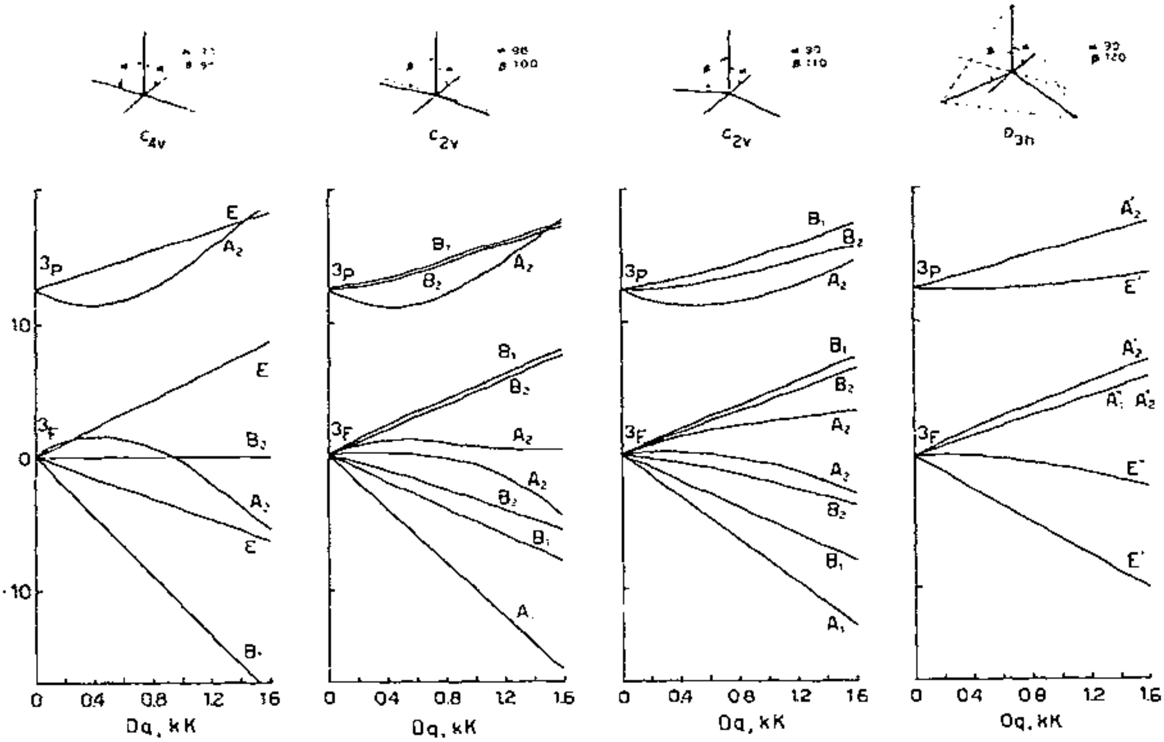


Fig.10. Electronic energy levels for the nickel(II) ion in $C_{4v}$ (left), $D_{3h}$ (right) and intermediate $C_{2v}$ symmetries, ($B_2/B_4$ = 2) (ref. 324).

## TABLE 8

Observed and calculated band energies for [NiSAL–MeDPT] (ref. [a])

| Assignment ($C_{2v}$) | | Frequency (kK) | |
|---|---|---|---|
| | | Observed | Calculated ($C_{2v}$) |
| $^3A_1$ → | $^3B_1(F)$ | (< 5.0) | 4.0 |
| | $^3B_2(F)$ | 8.4 | 7.6 |
| | $^3A_2(F)$ | 10.0 | 8.8 |
| | $^3A_2(F)$ | 12.0 | 13.4 |
| | $^3B_2(F)$ | 16.8 | 15.8 |
| | $^3B_1(F)$ | | 16.6 |
| | $^3A_2(P)$ | b | 23.8 |
| | $^3B_2(P)$ | | 25.2 |
| | $^3B_1(P)$ | | 26.6 |

[a] Parameter values: $Dq$ = 1.3 kK, $B_2/B_4$ = 2, $\beta$ = 110°.
[b] Masked by charge transfer[324].

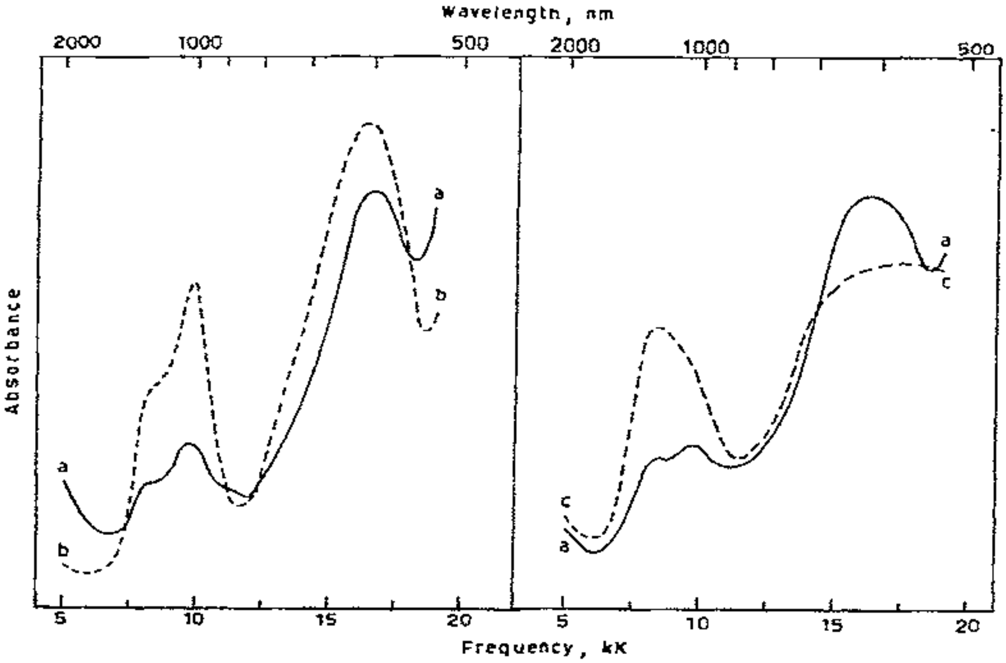


Fig. 11. Single-crystal polarized electronic spectrum of the NiSAL-MeDPT complex along *a*, *b*, and $c^*$ crystallographic directions corresponding to *y*, *z*, and *x* polarizations, respectively (ref. 324).

### *(iv) High-spin cobalt(II) complexes with square pyramidal geometry*

An energy level diagram for $C_{4v}$ cobalt complexes is shown in Fig.12, together with the effects of varying the ligand field parameters[322]. These diagrams show that there are several levels quite close to the ground level, which can be either the $^4A_2$ or the $^4E$. This situation renders more difficult the assignment of the spectra of square pyramidal complexes owing to the uncertainty of the ground level and to the mixing of these levels under the spin–orbit operator. A tentative assignment was first proposed for the $[Co(Ph_2MeAsO)_4ClO_4]ClO_4$ complex on the basis of the reflectance spectrum alone, assuming a $^4A_2$ ground level[312]. This assignment was eventually confirmed on the basis of single-crystal polarized spectra of $[Co(Ph_2MeAsO)_4NO_3]NO_3$ (ref. 325) (Fig.13). However, the polarization properties are not very marked, presumably because the *A* and *E* levels are very close, perhaps within 1 kK, and therefore strongly mixed via λ L.S.

Even the single-crystal anisotropic magnetic properties have been accounted for on the basis of a thermal population of the two levels. Reasonable parameters[325] which can describe the $CoO_5$ chromophore are: $Dq(\text{basal}) = 1.05\ kK$, $Dq(\text{apical})/Dq(\text{basal}) = 0.85$, $\beta = 0.87$, $\alpha = 106.5°$, $B_2/B_4 = 1.93$, $k = \lambda/\lambda_0 = 0.82$.

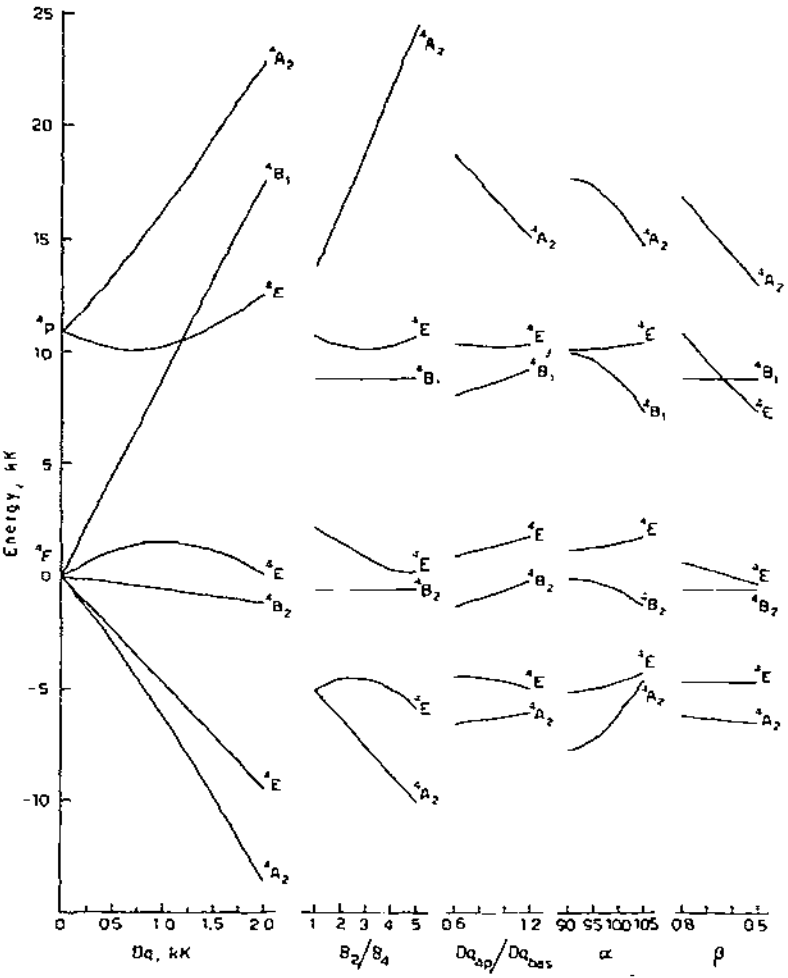


Fig.12. Energy level diagram for a cobalt(II) ion in a ligand field of $C_{4v}$ symmetry ($B_2/B_4 = 2$, $\alpha = 100°$, $\beta = 0.75$, $Dq_{ap} = Dq_{bas}$). From left to right, the effect of changing the $B_2/B_4$ ratio, the $Dq_{ap}/Dq_{bas}$ ratio, the apical angle $\alpha$ and the nephelauxetic parameter $\beta$ (for $Dq_{bas}$ = 1.0 kK) (ref. 322).

### *(v) High-spin cobalt(II) complexes with trigonal bipyramidal geometry*

An energy level diagram[326] for cobalt(II) in $D_{3h}$ symmetry is shown in Fig.14. Trigonal bipyramidal cobalt complexes of highest symmetry are the $Me_6$ tren halo derivatives, which, however, are crystallographically monometric[261]. The [Co($Me_6$tren)NCS] NCS.aq complex, isostructural with the analogous nickel complex, has been investigated using polarized light [326]. The polarized spectra shown in Fig.15 can be assigned on the basis of an effective $C_{3v}$ symmetry. In the present case the assignment is rather straightforward as shown in Table 9. Reasonable agreement has been obtained for $B_2/B_4$ ratios ranging from 1–1.7, $\beta$ = 0.65–

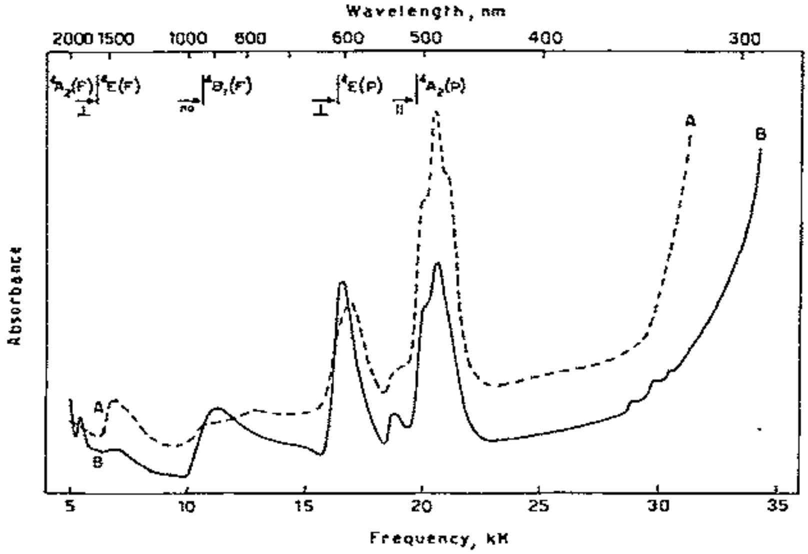


Fig.13. Single-crystal polarized electronic spectrum of the $[Co(Ph_2MeAsO)_4NO_3]NO_3$ complex at 80°K (A, ∥ polarized; B, ⊥ polarized), with the proposed assignment in $C_{4v}$ symmetry (for $Dq_{bas} = 1.05$ kK; $Dq_{ap}/Dq_{bas} = 0.9$; $B_2/B_4 = 1.75$; $\alpha = 108°$; $\beta = 0.87$) (ref. 325).

TABLE 9

Observed and calculated band energies for $[Co(Me_6tren)NCS]NCS.H_2O$[a]

| | | | Frequency (kK) | |
|---|---|---|---|---|
| Assignment ($C_{3v}$) | | Polarization ($C_{3v}$) | Observed | Calculated ($C_{3v}$) |
| $^4A_2$ → | $^4A_1(F)$ | Forbidden | (< 4.0) | 3.0 |
| | $^4A_2(F)$ | Parallel | (< 4.0) | 3.6 |
| | $^4E(F)$ | Perpendicular | 5.8 | 5.2 |
| | $^4E(F)$ | Perpendicular | 14.8 | 14.8 |
| | $^4A_2(P)$ | Parallel | 16.5 | 16.9 |
| | $^4E(P)$ | Perpendicular | 21.0 | 20.9 |

[a] Parameter values: $Dq_{eq} = 1.2$ kK, $B_2/B_4 = 1.0$, $Dq_{ax}/Dq_{eq} = 1.05$, $\alpha = 85°$, $\beta = 0.70$ (ref. 326).

0.75, $\alpha = 80$–$85°$; $Dq$(axial)/$Dq$(equatorial) = 0.95–1.05; $Dq$(equatorial) = 1.2–1.3 kK (ref. 326). The values of these parameters agree well with those of nickel and are quite consistent with those used for octahedral cobalt and nickel complexes with nitrogen donor atoms[326].

As mentioned earlier, high-spin trigonal bipyramidal cobalt complexes are often distorted towards the tetrahedron. The effect of such a distortion on the energy levels is shown on the right hand side of Fig.14. There is a general compression of the levels and the order

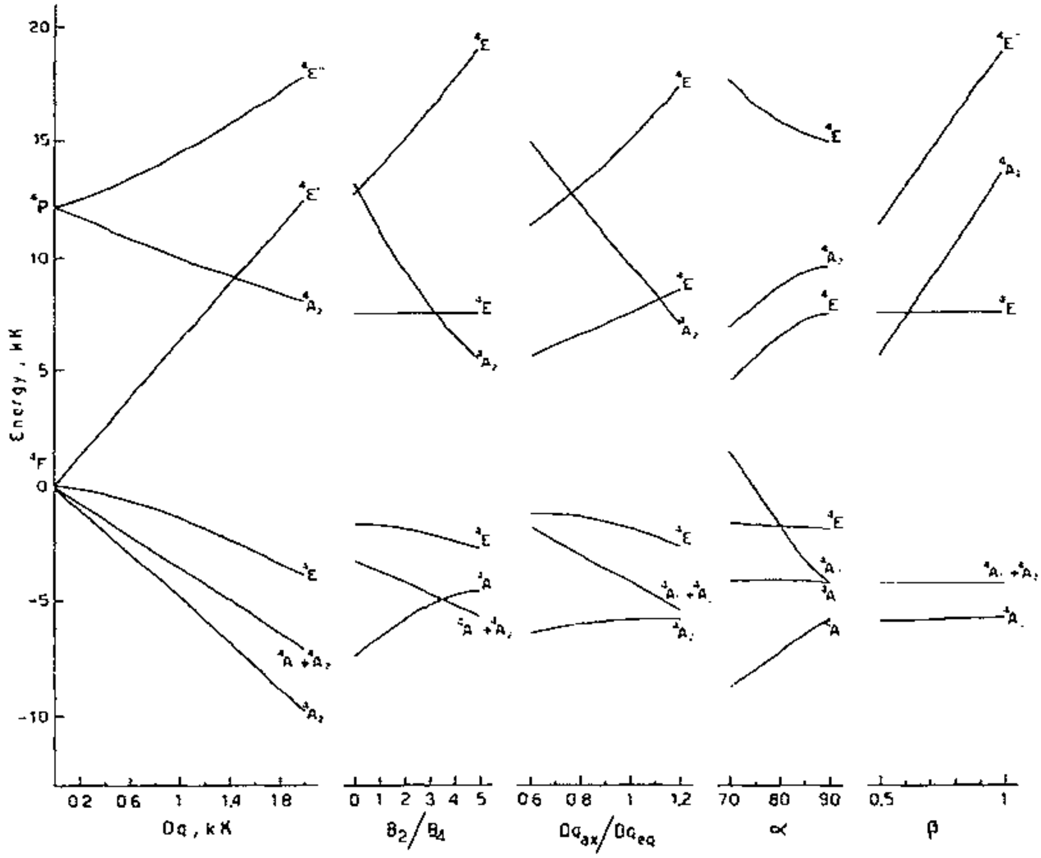


Fig.14. Energy level diagram for a cobalt(II) ion in a ligand field of $D_{3h}$ symmetry ($B_2/B_4 = 2$, $\beta = 0.75$, $Dq_{\mathrm{ax}} = Dq_{\mathrm{eq}}$). From left to right, the effect of changing the $B_2/B_4$ ratio, the $Dq_{\mathrm{ax}}/Dq_{\mathrm{eq}}$ ratio, the apical angle α and the nephelauxetic parameter β (for $Dq_{\mathrm{eq}} = 1.2$ kK) (ref. 326).

of some of them is inverted. This effect has been verified in the spectra of the $[\mathrm{Co(NP_3)Br}]\mathrm{PF_6}$ complex which is highly distorted towards the tetrahedron (Fig.16) (refs. 278, 327).

The effective magnetic moments of this class of complexes range between 4.3–4.6 B.M., owing to the orbital contribution of the excited $E$ levels[328]. A partial energy level scheme under spin–orbit and Zeeman operators is shown in Fig.17 (ref. 322). The main susceptibilities (neglecting TIP contribution) and $g$ values are given by

$$\chi_{\parallel} = \frac{N\beta^2}{\kappa T}\,\frac{1 + 9e^{-\delta/\kappa T}}{1 + e^{-\delta/\kappa T}} \qquad \left(\delta = \frac{12\lambda^2}{\Delta}\right)$$

$$\chi_{\perp} = N\beta^2\,\frac{\left(1 - \frac{6\kappa\lambda}{\Delta}\right)^2\left[\frac{4}{\kappa T} + \frac{6}{\delta}\left(1 - e^{-\delta/\kappa T}\right)\right]}{1 + e^{-\delta/\kappa T}}$$

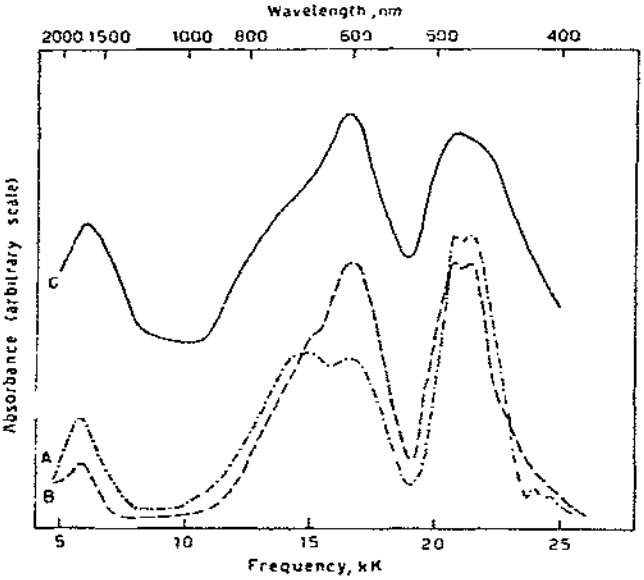


Fig.15. Single crystal polarized electronic spectrum (A, mostly ⊥ polarized; B, mostly ∥ polarized) and diffuse reflectance spectrum (C) of the [Co(Me$_6$tren)NCS]NCS.H$_2$O complex[326].

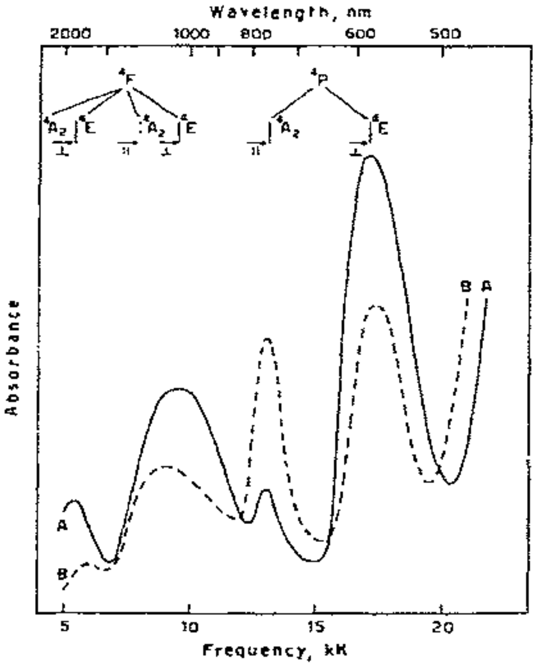


Fig.16. Single crystal polarized electronic spectrum of the [Co(NP$_3$)Br]PF$_6$ complex (A, mostly ⊥ polarized; B, mostly ∥ polarized) with the proposed assignment in $C_{3v}$ symmetry[327].

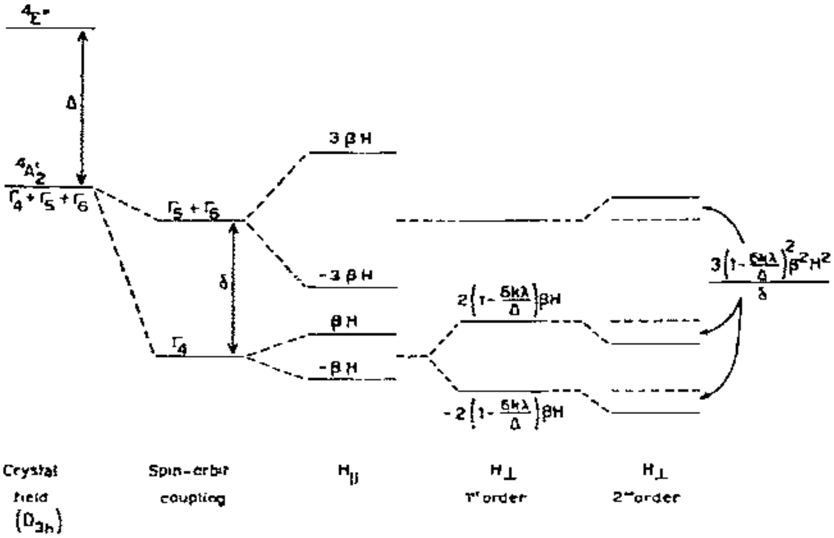


Fig.17. Splitting of the $^4A_2'$ term under the effect of successive spin–orbit coupling and magnetic field perturbations[322].

$$g_{\parallel} = 2$$
$$g_{\perp} = 2\left(1 - \frac{6\kappa\lambda}{\Delta}\right)$$

Since the energy separation between the ground level and the excited $E$ levels decreases with the axial donor strength, the $\mu_{\text{eff}}$ is expected to vary in the order I > Br > Cl for the $Me_6$tren complexes, as it has, in fact, been found to do.

## REFERENCES

1 C. Furlani, *Coord. Chem. Rev.*, 3 (1968) 141.
2 M. Ciampolini, *Struct. Bonding (Berlin)*, 6 (1969) 52.
2a J.S. Wood, *Progr. Inorg. Chem.* 16 (1972) 227.
3 L. Sacconi, *Pure Appl. Chem.*, 17 (1968) 95.
4 L. Sacconi, *Transition Metal Chem.*, 4 (1968) 199.
5 L. Sacconi, *Coord. Chem. Rev.*, 8 (1972) 351.
6 E.L. Muetterties and R.A. Schunn, *Quart. Rev., Chem. Soc.*, 20 (1966) 245.
7 P.L. Orioli, *Coord. Chem. Rev.*, 6 (1971) 285.
8 R.J. Gillespie, *J. Chem. Soc. London*, (1963) 4672.
9 J. Zemann, *Z. Anorg. Allg. Chem.*, 324 (1963) 241.
10 B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, 5 (1970) 143.
11 L. Sacconi, *J. Chem. Soc. A*, (1970) 248.
12 K. Issleib and E. Wenschuch, *Z. Anorg. Allg. Chem.*, 305 (1960) 15.
13 J.A. Bertrand and D.L. Plymale, *Inorg. Chem.*, 5 (1966) 879.
14 R.G. Hayter, *Inorg. Chem.*, 2 (1963) 932.

15 T.R. Dick and S.M. Nelson, *Inorg. Chem.*, 8 (1969) 1208.
16 K.A. Jensen and O. Dahl, *Acta Chem. Scand.*, 22 (1968) 1044.
17 B.B. Chastain, D.W. Meek, E. Billig, J.E. Hix, Jr. and H.B. Gray, *Inorg. Chem.*, 7 (1968) 2412.
18 O. Dahl, *Acta Chem. Scand.*, 23 (1969) 2342.
19 P. Rigo, M. Bressan and A. Turco, *Inorg. Chem.*, 7 (1968) 1460.
20 E.A. Rick and R.L. Pruett, *Chem. Commun.*,(1966) 697.
21 P. Rigo, C. Pecile and A. Turco, *Inorg. Chem.*, 6 (1967) 1636.
22 B.B. Chastain, E.A. Rick, R.L. Pruett and H.B. Gray, *J. Amer. Chem. Soc.*, 90 (1968) 3994.
23 K.J. Coskran, J.M. Jenkins and J.G. Verkade, *J. Amer. Chem. Soc.*, 90 (1968) 5437.
24 J.K. Stalick and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1084.
25 J. Chatt and B.L. Shaw, *J. Chem. Soc., London*, (1960) 1718.
26 M. Nicolini, C. Pecile and A. Turco, *J. Amer. Chem. Soc.*, 87 (1965) 2379.
27 M. Nicolini, C. Pecile and A. Turco, *Coord. Chem. Rev.*, 1 (1966) 133.
28 T. Boschi, M. Nicolini and A. Turco, *Coord. Chem. Rev.*, 1 (1966) 269.
29 E.C. Alyea and D.W. Meek, *J. Amer. Chem. Soc.*, 91 (1969) 5761.
30 J.K. Stalick and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1090.
31 K.J. Coskran, T.J. Huttemann and J.G. Verkade, *Advan. Chem. Ser.*, 62 (1967) 590.
32 T.J. Huttemann, B.M. Foxman, C.R. Sperati and J.G. Verkade, *Inorg. Chem.*, 4 (1965) 950.
33 E.F. Riedel and R.A. Jacobson, *Inorg. Chim. Acta*, 4 (1970) 407.
34 J.W. Collier and F.G. Mann, *J. Chem. Soc., London*, (1964) 1815.
35 J.W. Collier, F.G. Mann, D.G. Watson and H.R. Watson, *J. Chem. Soc., London*, (1964) 1803.
36 D.W. Allen, F.G. Mann and I.T. Millar, *Chem. Ind. (London)*, (1966) 2096.
37 D.W. Allen, I.T. Millar and F.G. Mann, *J. Chem. Soc. A*, (1969) 1101.
38 D.W. Allen, F.G. Mann, I.T. Millar, H.M. Powell and D.J. Watkin, *Chem. Commun.*, (1969) 1004.
39 H.M. Powell, D.J. Watkin and J.B. Wilford, *J. Chem. Soc. A*, (1971) 1803.
40 D.W. Allen, F.G. Mann and I.T. Millar, *J. Chem. Soc. C*, (1971) 3937.
41 T. Nowlin and K. Cohn, *Inorg. Chem.*, 10 (1971) 280.
42 T. Nowlin and K. Cohn, *Inorg. Chem.*, 11 (1972) 560.
42a T. Nowlin, S. Subramanian and K. Cohn, *Inorg. Chem.*, 11 (1972) 2907.
43 P. Rigo and M. Bressan, *Inorg. Chem.*, 11 (1972) 1314.
44 A. Bertacco, U. Mazzi and A.A. Orio, *Inorg. Chem.*, 11 (1972) 2547.
45 J.J. Alexander and H.B. Gray, *J. Amer. Chem. Soc.*, 89 (1967) 3356.
46 K.G. Caulton, *Inorg. Chem.*, 7 (1968) 392.
47 J.M. Pratt and R.J.P. Williams, *J. Chem. Soc. A*, (1967) 1291.
48 D.A. White, A.J. Solodar and M.M. Baizer, *Inorg. Chem.*, 11 (1972) 2160, and references therein.
49 R.L. McCullough, L.H. Jones and R.A. Penneman, *J. Inorg. Nucl. Chem.*, 13 (1960) 286.
50 J.S. Coleman, H. Petersen, Jr. and R.A. Penneman, *Inorg. Chem.*, 4 (1965) 135.
51 K.N. Raymond and F. Basolo, *Inorg. Chem.*, 5 (1966) 949.
52 W.C. Anderson and R.P. Harris, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 315.
53 K.N. Raymond, P.W. Corfield and J.A. Ibers, *Inorg. Chem.*, 7 (1968) 1362.
54 A. Terzis, K.N. Raymond and T.G. Spiro, *Inorg. Chem.*, 9 (1970) 2415.
54a J.M. Pratt and P.R. Silverman, *Chem. Commun.*, (1967) 117.
54b J.M. Pratt and P.R. Silverman, *J. Chem. Soc. A*, (1967) 1286.
55 S.H. Hunter, R.S. Nyholm and G.A. Rodley, *Inorg. Chim. Acta*, 3 (1969) 631.
56 J. Lewis, R.S. Nyholm and G.A. Rodley, *Nature (London)*, 207 (1965) 72.
57 P. Pauling, G.B. Robertson and G.A. Rodley, *Nature (London)*, 207 (1965) 73.
58 D.M.L. Goodgame, M. Goodgame and P.J. Hayward, *J. Chem. Soc. A*, (1970) 1352.
59 F. Mani, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 447.
60 M.W.G. de Bolster, I.E. Kortram and W.L. Groeneveld, *J. Inorg. Nucl. Chem.*, 34 (1972) 575.
61 A.M. Brodie, S.H. Hunter, G.A. Rodley and C.J. Wilkins, *Inorg. Chim. Acta*, 2 (1968) 195.
62 S.H. Hunter, G.A. Rodley and K. Emerson, *Chem. Commun.*, (1969) 1398.
63 N.M. Karayannis, J.V. Minkiewicz, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta*, 3 (1969) 129.
64 N.M. Karayannis, S.D. Sonsino, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta*, 4 (1970) 141.

65 W. Byers, A.B.P. Lever and R.V. Parish, *Inorg. Chem.*, 7 (1968) 1835.
66 B.A. Coyle and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 767.
67 N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *J. Inorg. Nucl. Chem.*, 33 (1971) 3185, and references therein.
68 N.M. Karayannis, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta*, 3 (1969) 415.
69 P.M. Enriquez, S.S. Zumdahl and L. Farshey, *Chem. Commun.*, (1970) 1527.
70 D.W. Herlocker, *Inorg. Chim. Acta*, 6 (1972) 211.
71 N.M. Karayannis, C. Owens, L.L. Pytlewski and M.M. Labes, *J. Inorg. Nucl. Chem.*, 31 (1969) 2767.
72 N.M. Karayannis, E.E. Bradshaw, L.L. Pytlewski and M.M. Labes, *J. Inorg. Nucl. Chem.*, 32 (1970) 1079.
73 N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *Inorg. Chim. Acta*, 4 (1970) 557.
74 V.L. Goedken, L.M. Vallarino and J.V. Quagliano, *J. Amer. Chem. Soc.*, 92 (1970) 303.
75 F.K. Ross and G.D. Stucky, *J. Amer. Chem. Soc.*, 92 (1970) 4538.
76 V.L. Goedken, J.V. Quagliano and L.M. Vallarino, *Inorg. Chem.*, 8 (1969) 2331.
77 F.K. Ross and G.D. Stucky, *Inorg. Chem.*, 8 (1969) 2734.
78 L.M. Vallarino, V.L. Goedken and J.V. Quagliano, *Inorg. Chem.*, 11 (1972) 1466.
79 F. Basolo, *Coord. Chem. Rev.*, 3 (1968) 213.
80 C.M. Harris, R.S. Nyholm and D.J. Phillips, *J. Chem. Soc., London*, (1960) 4379.
81 L. Di Sipio, L. Sindellari, E. Tondello, G. De Michelis and L. Oleari, *Coord. Chem. Rev.*, 2 (1967) 129.
82 M.A. Bennett and J.D. Wild, *J. Chem. Soc. A*, (1971) 536.
83 M.A. Bennett and J.D. Wild, *J. Chem. Soc. A*, (1971) 545.
84 A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, 93 (1963) 687.
85 W.D. Horrocks, Jr., G.R. Van Hecke and D.D. Hall, *Inorg. Chem.*, 6 (1967) 694.
85a J.K. Stalick, D.W. Meek, B.Y.K. Ho and J.J. Zuckerman, *J. Chem. Soc. Chem. Commun.*, (1972) 630.
85b J.K. Stalick, P.W.R. Corfield and D.W. Meek, *J. Amer. Chem. Soc.*, 94 (1972) 6194.
86 R. Morassi and A. Dei, *Inorg. Chim. Acta*, 6 (1972) 314.
86a J.C. Cloyd, Jr. and D.W. Meek, *Inorg. Chim. Acta*, 6 (1972) 480.
87 E.C. Alyea and D.W. Meek, *Inorg. Chem.*, 11 (1972) 1029.
88 K. Issleib and H. Weichmann, *Z. Anorg. Allg. Chem.*, 362 (1968) 33.
89 B. Corain, M. Bressan, P. Rigo and A. Turco, *Chem. Commun.*, (1968) 509.
90 P. Rigo, B. Corain and A. Turco, *Inorg. Chem.*, 7 (1968) 1623.
91 C.A. McAuliffe and D.W. Meek, *Inorg. Chem.*, 8 (1969) 904.
92 G. Dyer and D.W. Meek, *J. Amer. Chem. Soc.*, 89 (1967) 3983.
93 T.D. DuBois and D.W. Meek, *Inorg. Chem.*, 6 (1967) 1395.
94 M.O. Workman, G. Dyer and D.W. Meek, *Inorg. Chem.*, 6 (1967) 1543.
95 J.F. Sieckhaus and T. Layloff, *Inorg. Chem.*, 6 (1967) 2185.
96 B.R. Cook, C.A. McAuliffe and D.W. Meek, *Inorg. Chem.*, 10 (1971) 2676.
97 R.S. Nyholm, *J. Chem. Soc., London*, (1950) 2061.
98 B. Bosnich, R. Bramley, R.S. Nyholm and M.L. Tobe, *J. Amer. Chem. Soc.*, 88 (1966) 3926.
99 B. Bosnich, R.S. Nyholm, P.J. Pauling and M.L. Tobe, *J. Amer. Chem. Soc.*, 90 (1968) 4741.
100 M.R. Churchill and T.A. O'Brien, *Chem. Commun.*, (1968) 246.
101 M.R. Churchill and T.A. O'Brien, *J. Chem. Soc. A*, (1970) 206.
102 C. Furlani and M.L. Luciani, *Inorg. Chem.*, 7 (1968) 1586.
103 M. Bonamico, G. Dessy and V. Fares, *Chem. Commun.*, (1969) 324.
104 M. Bonamico, G. Dessy and V. Fares, *Chem. Commun.*, (1969) 1106.
105 P.R.H. Alderman, P.G. Owston and J.M. Rowe, *J. Chem. Soc. A*, (1962) 668.
106 E. Uhlig and M. Schäfer, *Z. Anorg. Allg. Chem.*, 359 (1968) 67.
107 E.W. Ainscough and L.K. Peterson, *Inorg. Chem.*, 9 (1970) 2699.
108 J.J. Bishop and A. Davison, *Inorg. Chem.*, 10 (1971) 832.
109 C.G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 11 (1972) 828.

110 J.F. White and M.F. Farona, *Inorg. Chem.*, 10 (1971) 1080.
111 K.M. Erck and B.B. Wayland, *Inorg. Chem.*, 11 (1972) 1141.
111a E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, 63 (1959) 1908.
111b J. Ferguson, *J. Chem. Phys.*, 34 (1961) 611.
111c L. Sacconi, P. Paoletti and R. Cini, *J. Inorg. Nucl. Chem.*, 8 (1958) 492; *J. Amer. Chem. Soc.*, 80 (1958) 3583.
112 L. Sacconi, M. Ciampolini and G.P. Speroni, *J. Amer. Chem. Soc.*, 87 (1965) 3102.
113 P.L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1965) 103.
114 P.L. Orioli, M. Di Vaira and L. Sacconi, *Inorg. Chem.*, 5 (1966) 400.
115 L. Sacconi, P. Paoletti and M. Ciampolini, *J. Amer. Chem. Soc.*, 85 (1963) 411.
116 L. Sacconi, *Essays Coord. Chem.*, 9 (1964) 148.
117 R.H. Holm and M.J. O'Connor, *Progr. Inorg. Chem.*, 14 (1971) 241.
118 L. Sacconi, P.L. Orioli and M. Di Vaira, *Chem. Commun.*, (1967) 849.
119 S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Jap.*, 38 (1965) 683.
120 S. Yamada and E. Yoshida, *Bull. Chem. Soc. Jap.*, 40 (1967) 1298.
121 P.A. Bone, E.D. McKenzie and K. Rowan, *Chem. Commun.*, (1970) 420.
122 S. Yamada and E. Yoshida, *Bull. Chem. Soc. Jap.*, 40 (1967) 1854.
123 S. Utsuno, *J. Inorg. Nucl. Chem.*, 32 (1970) 183.
124 S. Utsuno, *J. Inorg. Nucl. Chem.*, 32 (1970) 1631.
125 H.S. Preston and C.H.L. Kennard, *Chem. Commun.*, (1968) 819.
126 H.S. Preston and C.H.L. Kennard, *J. Chem. Soc. A*, (1969) 2682.
127 E. Uhlig, R. Krähmer and H. Wolf, *Z. Anorg. Allg. Chem.*, 361 (1968) 157.
128 P.S.K. Chia and S.E. Livingstone, *Inorg. Chim. Acta*, 2 (1968) 427.
129 R.E. Christopher, I.R. Gordon and L.M. Venanzi, *J. Chem. Soc. A*, (1968) 205.
130 M. Keeton and A.B.P. Lever, *Inorg. Chem.*, 10 (1971) 47.
131 J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A*, (1971) 602.
132 M. Mathew and G.J. Palenik, *J. Amer. Chem. Soc.*, 91 (1969) 4923.
133 P.S. Shetty, R.E. Ballard and Q. Fernando, *Chem. Commun.*, (1969) 717.
134 P.S. Shetty and Q. Fernando, *J. Amer. Chem. Soc.*, 92 (1970) 3964.
135 A. Sgamellotti, C. Furlani and F. Magrini, *J. Inorg. Nucl. Chem.*, 30 (1968) 2655.
136 N. Yoon, M.J. Incorvia and J.I. Zink, *J. Chem. Soc. Chem. Commun.*, (1972) 499.
137 J.R. Angus, G.M. Woltermann, W.R. Vincent and J.R. Wasson, *J. Inorg. Nucl. Chem.*, 33 (1971) 3041.
138 J.R. Angus, G.M. Woltermann and J.R. Wasson, *J. Inorg. Nucl. Chem.*, 33 (1971) 3967.
139 J.R. Angus and J.R. Wasson, *J. Coord. Chem.*, 1 (1971) 309.
139a H.E. Francis, G.L. Tincher, W.F. Wagner, J.R. Wasson and G.M. Woltermann, *Inorg. Chem.*, 10 (1971) 2620.
140 R.L. Carlin, J.S. Dubnoff and W.T. Huntress, *Proc. Chem. Soc.*, (1964) 228.
141 R.L. Carlin and D.B. Losee, *Inorg. Chem.*, 9 (1970) 2087.
142 W.V. Dahlhoff, T.R. Dick, G.H. Ford and S.M. Nelson, *J. Inorg. Nucl. Chem.*, 33 (1971) 1799.
143 G.A. Barclay, R.S. Nyholm and R.V. Parish, *J. Chem. Soc., London*, (1961) 4433.
144 G.A. Mair, H.M. Powell and D.E. Henn, *Proc. Chem. Soc.*, (1960) 415.
145 R.G. Cunninghame, R.S. Nyholm and M.L. Tobe, *J. Chem. Soc. Dalton*, (1972) 229.
146 L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, 7 (1968) 1417.
146a C.A. McAuliffe, M.O. Workman and D.W. Meek, *J. Coord. Chem.*, 2 (1972) 137.
146b G.J. Palenik and D.F. Rendle, unpublished results.
147 L. Sacconi and R. Morassi, *J. Chem. Soc. A*, (1968) 2997.
148 G. Degischer and G. Schwarzenbach, *Helv. Chim. Acta*, 49 (1966) 1927.
149 P.L. Orioli and L. Sacconi, *Chem. Commun.*, (1968) 1310.
150 P.L. Orioli and C. Ghilardi, *J. Chem. Soc. A*, (1970) 1511.
151 L. Sacconi, G.P. Speroni and R. Morassi, *Inorg. Chem.*, 7 (1968) 1521.
151a P.G. Eller and D.W. Meek, *Inorg. Chem.*, 11 (1972) 2518.
152 R.B. King, P.N. Kapoor and R.N. Kapoor, *Inorg. Chem.*, 10 (1971) 1841.

152a J.C. Cloyd, Jr. and D.W. Meek, *Inorg. Chim. Acta*, 6 (1972) 607.
153 D.W. Meek and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1915.
154 R. Davis and J.E. Fergusson, *Inorg. Chim. Acta*, 4 (1970) 23.
155 J. Ellermann and W.H. Gruber, *Z. Anorg. Allg. Chem.*, 364 (1970) 55.
156 C.A. McAuliffe, M.O. Workman and D.W. Meek, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 147.
157 G.A. Barclay, E.M. McPartlin and N.C. Stephenson, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 397.
158 G.A. Barclay, E.M. McPartlin and N.C. Stephenson, *Aust. J. Chem.*, 21 (1968) 2669.
159 G.A. Barclay, E.M. McPartlin and N.C. Stephenson, *Acta Crystallogr., Sect. B*, 25 (1969) 1262.
160 D.J. Baker, D.C. Goodall and D.S. Moss, *Chem. Commun.*, (1969) 325.
161 W.S.J. Kelly, G.H. Ford and S.M. Nelson, *J. Chem. Soc. A*, (1971) 388.
162 W.V. Dahlhoff and S.M. Nelson, *J. Chem. Soc. A*, (1971) 2184.
163 L. Sacconi, M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, 4 (1965) 1116.
164 L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, *Inorg. Chem.*, 4 (1965) 943.
165 L. Sacconi, P.L. Orioli and M. Di Vaira, *J. Amer. Chem. Soc.*, 87 (1965) 2059.
166 P.L. Orioli, M. Di Vaira and L. Sacconi, *J. Amer. Chem. Soc.*, 88 (1966) 4383.
167 E. Uhlig and B. Machelett, *Z. Chem.*, 9 (1969) 155.
168 P. Bamfield, *J. Chem. Soc. A*, (1968) 81.
169 M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, 5 (1966) 45.
170 M. Di Vaira and P.L. Orioli, *Chem. Commun.*, (1965) 590.
171 M. Di Vaira and P.L. Orioli, *Inorg. Chem.*, 8 (1969) 2729.
172 Z. Dori and H.B. Gray, *Inorg. Chem.*, 7 (1968) 889.
173 J.L. Burmeister, T.P. O'Sullivan and K.A. Johnson, *Inorg. Chem.*, 10 (1971) 1803.
174 Z. Dori, R. Eisenberg and H.B. Gray, *Inorg. Chem.*, 6 (1967) 483.
175 Z. Dori and H.B. Gray, *J. Amer. Chem. Soc.*, 88 (1966) 1394.
176 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 6 (1967) 445.
177 M. Ciampolini and J. Gelsomini, *Inorg. Chem.*, 6 (1967) 1821.
178 L. Sacconi, I. Bertini and R. Morassi, *Inorg. Chem.*, 6 (1967) 1548.
179 L. Sacconi and G.P. Speroni, *Inorg. Chem.*, 7 (1968) 295.
180 L. Sacconi and I. Bertini, *Inorg. Chem.*, 7 (1968) 1178.
181 P.L. Orioli and M. Di Vaira, *J. Chem. Soc. A*, (1968) 2079.
182 I. Bertini and F. Mani, *Inorg. Chem.*, 9 (1970) 248.
183 F. Lions, I.G. Dance and J. Lewis, *J. Chem. Soc. A*, (1967) 565.
184 I.G. Dance, M. Gerloch, J. Lewis, F.S. Stephens and F. Lions, *Nature (London)*, 210 (1966) 298.
185 M. Gerloch, *J. Chem. Soc., London*, (1966) 1317.
186 G. Zakrzewski and L. Sacconi, *Inorg. Chem.*, 7 (1968) 1034.
187 L. Sacconi, R. Morassi and S. Midollini, *J. Chem. Soc. A*, (1968) 1510.
188 J.S. Judge, W.M. Reiff, G.M. Intille, P. Ballway and W.A. Baker, Jr., *J. Inorg. Nucl. Chem.*, 29 (1967) 1711.
189 J.S. Judge and W.A. Baker, Jr., *Inorg. Chim. Acta*, 1 (1967) 239.
190 C.M. Harris, T.N. Lockyer and N.C. Stephenson, *Aust. J. Chem.*, 19 (1966) 1741.
191 C.M. Harris, T.N. Lockyer, R.L. Martin, H.R.H. Patil, E. Sinn and I.M. Stewart, *Aust. J. Chem.*, 22 (1969) 2105.
192 E. Goldschmied and N.C. Stephenson, *Acta Crystallogr., Sect. B*, 26 (1970) 1867.
193 D.P. Madden and S.M. Nelson, *J. Chem. Soc. A*, (1968) 2342.
194 S.M. Nelson and J. Rodgers, *Inorg. Chem.*, 6 (1967) 1390.
195 P.S.K. Chia and S.E. Livingstone, *Aust. J. Chem.*, 22 (1969) 1613.
196 M.M. Da Mota, J. Rodgers and S.M. Nelson, *J. Chem. Soc. A*, (1969) 2036.
197 J. Rodgers and R.A. Jacobson, *J. Chem. Soc. A*, (1970) 1826.
198 P. Bamfield, R. Price and R.G.J. Miller, *J. Chem. Soc. A*, (1969) 1447.
199 S.E. Livingstone and J.D. Nolan, *Aust. J. Chem.*, 22 (1969) 1817.
200 I. Bertini, D.L. Johnston and W. DeW. Horrocks, Jr., *Inorg. Chim. Acta*, 4 (1970) 79.
201 N.F. Curtis and H.K.J. Powell, *J. Chem. Soc. A*, (1968) 3069.
202 I. Bertini, D.L. Johnston and W. DeW. Horrocks, Jr., *Inorg. Chem.*, 9 (1970) 698.

203 H.A. Goodwin and R.N. Sylva, *Aust. J. Chem.*, 21 (1968) 2881.
204 M.R. Litzow, L.F. Power and A.M. Tait, *J. Chem. Soc. A*, (1970) 2907.
205 R. Morassi and L. Sacconi, *J. Amer. Chem. Soc.*, 92 (1970) 5241.
206 R. Morassi, F. Mani and L. Sacconi, *Inorg. Chem.*, 12 (1973) 1246.
207 A. Bianchi, C. Calabresi, C.A. Ghilardi, P.L. Orioli and L. Sacconi, *J. Chem. Soc. Dalton*, (1973) 1383.
208 C.A. Ghilardi and A. Bianchi Orlandini, *J. Chem. Soc. Dalton*, (1972) 1698.
209 S.E. Livingstone and J.D. Nolan, *J. Chem. Soc. Dalton*, (1972) 218.
210 B. Sen and D.A. Johnson, *J. Inorg. Nucl. Chem.*, 34 (1972) 609.
211 M. Akbar Ali, S.E. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, 6 (1972) 39.
212 D. StC. Black and I.A. McLean, *Aust. J. Chem.*, 24 (1971) 1377.
213 L.M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 3 (1964) 453.
214 M.T. Halfpenny, J.C. Hartley and L.M. Venanzi, *J. Chem. Soc. A*, (1967) 627.
215 J.C. Hartley, D.G.E. Kerfoot and L.M. Venanzi, *Inorg. Chim. Acta*, 1 (1967) 145.
216 T.L. Blundell, H.M. Powell and L.M. Venanzi, *Chem. Commun.*, (1967) 763.
217 G. Dyer, J.C. Hartley and L.M. Venanzi, *J. Chem. Soc., London*, (1965) 1293.
218 G.S. Benner and D.W. Meek, *Inorg. Chem.*, 6 (1967) 1399.
219 O.St.C. Headley, R.S. Nyholm, C.A. McAuliffe, L. Sindellari, M.L. Tobe and L.M. Venanzi, *Inorg. Chim. Acta*, 4 (1970) 93.
220 R.B. King, R.N. Kapoor, M.S. Saran and P.N. Kapoor, *Inorg. Chem.*, 10 (1971) 1851.
221 G.S. Benner, W.E. Hatfield and D.W. Meek, *Inorg. Chem.*, 3 (1964) 1544.
222 D.L. Stevenson and L.F. Dahl, *J. Amer. Chem. Soc.*, 89 (1967) 3424.
223 G. Dyer and D.W. Meek, *Inorg. Chem.*, 4 (1965) 1398.
224 L.P. Haugen and R. Eisenberg, *Inorg. Chem.*, 8 (1969) 1072.
225 G. Dyer and D.W. Meek, *Inorg. Chem.*, 6 (1967) 149.
226 L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 90 (1968) 5443.
227 P.L. Orioli and L. Sacconi, *Chem. Commun.*, (1969) 1012.
228 C. Mealli, P.L. Orioli and L. Sacconi, *J. Chem. Soc. A*, (1971) 2691.
229 L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 89 (1967) 2235.
230 P. Dapporto and L. Sacconi, *Chem. Commun.*, (1969) 1091.
231 P. Dapporto and L. Sacconi, *J. Chem. Soc. A*, (1970) 1804.
232 L. Sacconi and R. Morassi, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 449.
233 L. Sacconi and R. Morassi, *J. Chem. Soc. A*, (1969) 2904.
234 A. Bianchi, P. Dapporto, G. Fallani, C.A. Ghilardi and L. Sacconi, *J. Chem. Soc. Dalton*, (1973) 641.
235 R. Morassi and L. Sacconi, *J. Chem. Soc. A*, (1971) 492.
236 P. Dapporto, R. Morassi and L. Sacconi, *J. Chem. Soc. A*, (1970) 1298.
237 A. Bianchi and C.A. Ghilardi, *J. Chem. Soc. A*, (1971) 1096.
238 R. Morassi and L. Sacconi, *J. Chem. Soc. A*, (1971) 1487.
239 M. Mathew, G.J. Palenik, G. Dyer and D.W. Meek, *J. Chem. Soc. Chem. Commun.*, (1972) 379.
240 J.W. Dawson and L.M. Venanzi, *J. Amer. Chem. Soc.*, 90 (1968) 7229.
241 B.R. Higginson, C.A. McAuliffe and L.M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 37.
242 C.A. McAuliffe and D.W. Meek, *Inorg. Chim. Acta*, 5 (1971) 270.
243 T.D. DuBois and D.W. Meek, *Inorg. Chem.*, 8 (1969) 146.
244 L. Sacconi and A. Dei, *J. Coord. Chem.*, 1 (1971) 229.
245 A. Bianchi, C.A. Ghilardi, C. Mealli and L. Sacconi, *J. Chem. Soc. Chem. Commun.*, (1972) 651.
246 T.D. DuBois, *Inorg. Chem.*, 11 (1972) 718.
247 A. Earnshaw, P.C. Hewlett, E.A. King and L.F. Larkworthy, *J. Chem. Soc. A*, (1968) 241, and references therein.
248 S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Acta Crystallogr., Sect. B*, 25 (1969) 1671.
249 R. De Iasi, S.L. Holt and B. Post, *Inorg. Chem.*, 10 (1971) 1498.
250 M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc. A*, (1970) 2411.
251 E.K. Barefield and D.H. Busch, *Inorg. Chem.*, 10 (1971) 1216.
252 K.M. Long and D.H. Busch, *Inorg. Chem.*, 9 (1970) 505.

253 J.L. Karn and D.H. Busch, *Nature (London)*, 211 (1966) 160.
254 E.B. Fleischer and S.W. Hawkinson, *Inorg. Chem.*, 7 (1968) 2312.
255 J.L. Karn and D.H. Busch, *Inorg. Chem.*, 8 (1969) 1149.
256 R. Dewar and E.B. Fleischer, *Nature (London)*, 222 (1969) 372.
257 W. Rosen and D.H. Busch, *J. Amer. Chem. Soc.*, 91 (1969) 4694.
258 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5 (1966) 1150.
259 M. Di Vaira and P.L. Orioli, *Acta Crystallogr., Sect. B*, 24 (1968) 1269.
260 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5 (1966) 41.
261 M. Di Vaira and P.L. Orioli, *Inorg. Chem.*, 6 (1967) 955.
262 M. Di Vaira and P.L. Orioli, *Acta Crystallogr., Sect. B*, 24 (1968) 595.
263 I. Bertini, M. Ciampolini, P. Dapporto and D. Gatteschi, *Inorg. Chem.*, 11 (1972) 2254.
264 M. Ciampolini and P. Paoletti, *Inorg. Chem.*, 6 (1967) 1261.
265 A. Dei and R. Morassi, *J. Chem. Soc. A*, (1971) 2024.
266 L.V. Interrante and J.L. Shafer, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 411.
267 J.L. Shafer and K.N. Raymond, *Inorg. Chem.*, 10 (1971) 1799.
268 P. Dapporto and G. Fallani, *J. Chem. Soc. Dalton*, (1972) 1498.
269 I. Bertini, P. Dapporto, G. Fallani and L. Sacconi, *Inorg. Chem.*, 10 (1971) 1703.
270 M. Di Vaira and A. Bianchi Orlandini, *J. Chem. Soc. Dalton*, (1972) 1704.
271 M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1969) 10.
272 M. Di Vaira, *J. Chem. Soc. A*, (1971) 148.
273 L. Sacconi and R. Morassi, *J. Chem. Soc. A*, (1970) 575.
274 P. Dapporto, M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1969) 153.
275 P. Dapporto and M. Di Vaira, *J. Chem. Soc. A*, (1971) 1891.
276 P. Dapporto and L. Sacconi, *Chem. Commun.*, (1969) 329.
277 P. Dapporto and L. Sacconi, *J. Chem. Soc. A*, (1970) 618.
278 L. Sacconi, M. Di Vaira and A. Bianchi, *J. Amer. Chem. Soc.*, 92 (1970) 4465.
279 P. Dapporto, G. Fallani and L. Sacconi, *J. Coord. Chem.*, 1 (1971) 269.
280 M. Ciampolini, J. Gelsomini and N. Nardi, *Inorg. Chim. Acta*, 2 (1968) 343.
281 G. Fallani, R. Morassi, L. Sacconi and F. Zanobini, *Abstr. 6th. Nat. Meeting Ital. Assoc. Inorg. Chem., 1973*, B6 and unpublished results.
282 J.I. Legg, D.O. Nelson, D.L. Smith and M.L. Larson, *J. Amer. Chem. Soc.*, 90 (1968) 5030.
283 D.F. Averill, J.I. Legg and D.L. Smith, *Inorg. Chem.*, 11 (1972) 2344.
284 D.O. Nielson, M.L. Larsen, R.D. Willett and J.I. Legg, *J. Amer. Chem. Soc.*, 93 (1971) 5079.
285 N.A. Bailey, J.G. Gibson and E.D. McKenzie, *Chem. Commun.*, (1969) 741.
286 J.G. Gibson and E.D. McKenzie, *J. Chem. Soc. A*, (1971) 1029.
287 P.H. Merrell, V.L. Goedken, D.H. Busch and J.A. Stone, *J. Amer. Chem. Soc.*, 92 (1970) 7590.
287a V.L. Goedken, P.H. Merrell and D.H. Busch, *J. Amer. Chem. Soc.*, 94 (1972) 3397.
287b V.L. Goedken and D.H. Busch, *J. Amer. Chem. Soc.*, 94 (1972) 7355.
288 G.A. Kalligeros and E.L. Blinn, *Inorg. Chem.*, 11 (1972) 1145.
289 G.M. Mockler, G.W. Chaffey, E. Sinn and H. Wong, *Inorg. Chem.*, 11 (1972) 1308.
290 F. Lions, *Rev. Pure Appl. Chem.*, 19 (1969) 177.
291 L.T. Taylor and W.M. Coleman, *J. Amer. Chem. Soc.*, 92 (1970) 1449.
292 W.M. Coleman and L.T. Taylor, *J. Inorg. Nucl. Chem.*, 33 (1971) 3049.
293 V. Katovic, L.T. Taylor and D.H. Busch, *J. Amer. Chem. Soc.*, 91 (1969) 2122.
294 V. Katovic, L.T. Taylor and D.H. Busch, *Inorg. Chem.*, 10 (1971) 458.
295 L. Sacconi and I. Bertini, *J.Amer. Chem. Soc.*, 88 (1966) 5180.
296 P.L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1966) 300.
297 M. Di Vaira, P.L. Orioli and L. Sacconi, *Inorg. Chem.* 10 (1971) 553.
298 M. Seleborg, S.L. Holt and B. Post, *Inorg. Chem.*, 10 (1971) 1501.
298a G.N. La Mar and L. Sacconi, *J. Amer. Chem. Soc.*, 89 (1967) 2282.
299 I. Bertini, L. Sacconi and G.P. Speroni, *Inorg. Chem.*, 11 (1972) 1323.
300 A.T. Phillip, W. Mazurek and A.T. Casey, *Aust. J. Chem.*, 24 (1971) 501.
301 W. Mazurek, A.T. Phillip, B.F. Hoskins and F.D. Whillans, *Chem. Commun.*, (1970) 184.
302 D. StC. Black and I.A. McLean, *Aust. J. Chem.*, 24 (1971) 1391.

303 S.M. Nelson and W.S.J. Kelly, *Chem. Commun.*, (1969) 94.
304 S.M. Nelson and W.S.J. Kelly, *Chem. Commun.*, (1968) 436.
305 L.G. Marzilli, P.A. Marzilli and J. Halpern, *J. Amer. Chem. Soc.*, 93 (1971) 1374.
306 L.G. Marzilli and P.A. Marzilli, *Inorg. Chem.*, 11 (1972) 457.
307 E.K. Barefield, D.H. Busch and S.M. Nelson, *Quart. Rev., Chem. Soc.*, 22 (1968) 457.
308 L. Sacconi, *Pure Appl. Chem.*, 27 (1971) 161, and references therein.
309 M. Di Vaira, personal communication.
310 M. Ciampolini, *Inorg. Chem.*, 5 (1966) 35.
311 M. Ciampolini, N. Nardi and G.P. Speroni, *Coord. Chem. Rev.*, 1 (1966) 222.
312 M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, (1968) 2241.
313 M.J. Norgett, J.H.M. Thornley and L.M. Venanzi, *J. Chem. Soc. A*, (1967) 540; *Coord. Chem. Rev.*, 2 (1967) 99.
314 M.J. Norgett and L.M. Venanzi, *Inorg. Chim. Acta*, 2 (1968) 107.
315 J.S. Wood, *Inorg. Chem.*, 7 (1968) 852.
316 S.T. Spees, Jr., J.R. Perumareddi and A.W. Adamson, *J. Phys. Chem.*, 72 (1968) 1822.
317 J.R. Preer and H.B. Gray, *J. Amer. Chem. Soc.*, 92 (1970) 7306.
318 J.W. Dawson, L.M. Venanzi, J.R. Preer, J.E. Hix and H.B. Gray, *J. Amer. Chem. Soc.*, 93 (1971) 778.
319 J.R. Ferraro, D.W. Meek, E.C. Siwiec and A. Quattrochi, *J. Amer. Chem. Soc.*, 93 (1971) 3862.
320 J.R. Ferraro and K. Nakamoto, *Inorg. Chem.*, 11 (1972) 2290.
321 M. Gerloch, J. Kohl, J. Lewis and W. Urland, *J. Chem. Soc. A*, (1970) 3269.
322 D. Gatteschi and I. Bertini, *Abstr. Nat. Meet. Ital. Assoc. Inorg. Chem., 3rd, 1970*, C 34, and unpublished results.
323 J.S. Wood and P.T. Greene, *Inorg. Chem.*, 8 (1969) 491.
324 I. Bertini and D. Gatteschi, *J. Coord. Chem.*, 1 (1971) 285, and unpublished results.
325 M. Gerloch, J. Kohl, J. Lewis and W. Urland, *J. Chem. Soc. A*, (1970) 3283.
326 I. Bertini, M. Ciampolini and D. Gatteschi, *Inorg. Chem.*, 12 (1973) 693.
327 I. Bertini, M. Ciampolini and L. Sacconi, *J. Coord. Chem.*, 1 (1971) 73.
328 J.S. Wood, *J. Chem. Soc. A*, (1969) 1582.
329 P.M. Enriquez and S.S. Zumdahl, *Inorg. Chem.*, 12 (1973) 2475.
330 J.K. Stalick, P.W.R. Corfield and D.W. Meek, *Inorg. Chem.*, 12 (1973) 1668.
331 M. Mathew, G.J. Palenik and G.R. Clark, *Inorg. Chem.*, 12 (1973) 446.
332 M. Di Vaira and A. Bianchi Orlandini, *Inorg. Chem.*, 12 (1973) 1292.
333 M. Nemiroff and S.L. Holt, *Inorg. Chem.*, 12 (1973) 2032.