Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

THE STEREOCHEMISTRY OF FIVE-COORDINATE NICKEL(II) AND COBALT(II) COMPLEXES

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(Received August 20th, 1970)

CONTENTS

ABBREVIATIONS

atsc	acetonethiosemicarbazone
bda	bis (2-diphenylphosphinoethyl) amine
bddae	*N*, *N*-bis (2-diethylaminoethyl)-2-diphenylarsinoethylamine
bdhe	*N*, *N*-bis (2-diethylaminoethyl)-2-hydroxethylamine
bdme	*N*, *N*-bis (2-diethylaminoethyl)-2-methylthioethylamine
catec	*o*-dihydroxobenzene
CR	2, 12-dimethyl-3, 7, 11, 17-tetraazabicyclo[11.3.1] heptadeca-1(17), 2, 11, 13, 15-pentaene
dacoDA	1, 5-diazacyclooctane-*N*, *N*′-diacetate
ddc	dimethyldithiocarbamate
diars	*o*-phenylenebis (dimethylarsine)
diphos	bis(1, 2-(diphenylphosphino) ethane)
dmp	2, 9-dimethyl-1, 10-phenanthroline
DSP	bis (*o*-methylthiophenyl) phenylphosphine
dtb	dithiobenzoate
dtpa	dithiophenylacetate
Et_4dien	bis (2-diethylaminoethyl) amine

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Etphos	9-ethyl-9-phosphafluorene
π-ma	π-methallyl
Medabco	*N*-methyl-1, 4-diazabicyclo[2.2.2] octonium ion
Me$_5$dien	bis(2-dimethylaminoethyl) methylamine
Me$_2$dpma	6, 6'-dimethyldi-(2-pyridylmethyl) amine
Me$_2$dtp	bis (*o*, *o*'-dimethyl-dithiophosphate)
Mephos	9-methyl-9-phosphafluorene
Me$_6$tren	tris (2-dimethylaminoethyl) amine
mpdo	1-(*o*-methoxyphenyl)-2, 6-diazaoctane
NOP$_2$	*N*, *N*-bis (2-diphenylphosphinoethyl)-2-methoxyethylamine
paphy	pyridine-2-aldehyde-2-pyridylhydrazone
picox	2-picoline-*N*-oxide
QP	tris (*o*-diphenylphosphinophenyl) phosphine
Salen	*N*, *N*'-ethylene-bis (salicylaldimine)
SalenNEt$_2$	*N*-β-diethylaminoethyl-salicylaldimine
SalMedpt	bis (salicylidene-γ-iminopropyl) methylamine
TAP	tris (3-dimethylarsinopropyl) phosphine
tas	bis (3-dimethylarsinopropyl) methylarsine
tcbt	1, 2, 3, 4-tetrachlorobenzene-5, 6-dithiolate
tda	tris (2-diphenylphosphinoethyl) amine
2, 3, 2-tet	*N*, *N*'-di-(3-aminopropyl) piperazine
tfet	1, 2-bis (trifluoromethyl) ethylene-1, 2-dithiolate
tpen	*N*, *N*, *N*'-tris[2-(2'-pyridyl) ethyl] ethylenediamine
triars	bis (*o*-dimethylarsinophenyl) methylarsine
TSP	tris (*o*-methylthiophenyl) phosphine

A. INTRODUCTION

The subject of five-coordination in transition metals has been extensively treated both from the spectroscopic [1,2,3] and the stereochemical [4,5] point of view, but a large amount of X-ray structural work has been done recently in this field. A survey of the recent literature shows that most of the X-ray work has been done with 3*d* transition metal complexes. Apart from copper(II), for which the number of structures of five-coordinate complexes reported is close to eighty or so, it appears that nickel(II) and cobalt(II) are the metals most largely studied, particularly due to the impulse of Sacconi's and Ibers' schools. In fact, not less than thirty-five complete X-ray structures of five-coordinate nickel(II) complexes and fourteen of cobalt(II) complexes have been reported.

From the large amount of material available it appears now possible to make some detailed considerations on the stereochemistry and the bonding in these complexes. Unfortunately, with few exceptions, the cobalt(II) and nickel(II) complexes whose structures have been determined by X-ray analysis, are formed with polydentate ligands, or, less often, with bulky monodentate ligands. In these complexes the steric requirements of the ligand molecule play an important role in determining both the type of geometry for the coordination polyhedron and the values of the bond lengths and angles about the metal atom. This shows of course that in spite of the large number of structures of five-coordinate complexes available, five-coordination for cobalt(II) and nickel(II) must be considered unusual and is favoured by the use of bulky and polydentate ligands which prevent six-coordination around the metal.

In spite of these limitations, a detailed comparison of bond lengths and angles in related structures allows one to draw interesting conclusions about the electronic structures of the atoms and the nature of the metal–ligand bond.

B. THE RELATIVE STABILITY OF FIVE-COORDINATE GEOMETRIES

Although the stability of five-coordinate geometries has been discussed by several authors[1,6,7] a short survey of the results is obviously necessary before a discussion of the stereochemistry of five-coordinate complexes.

On the basis of charge repulsion considerations, Zemann[7] has shown that the most stable arrangement for five ligands ML_5 at equal distances from M is the trigonal bipyramid (D_{3h} symmetry) (Fig. 1(a)). Only slightly less stable is a square pyramid (C_{4v} symmetry) (Fig. 1(c)) with the central atom M above the basal plane. For bivalent L^{2-} ions and an M–L distance of 2.0 Å, the trigonal bipyramid is 5.96 $\text{kcal} \cdot \text{mol}^{-1}$ more stable than the square pyramid. Zemann's results are summarized in Table 1.

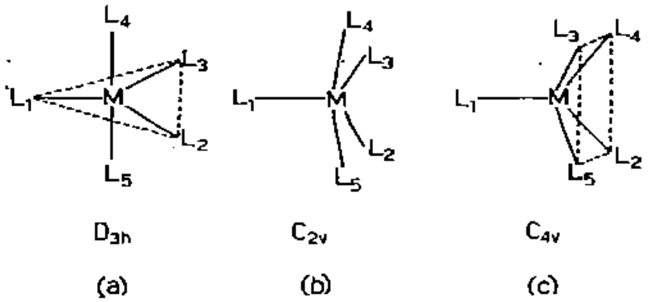


Fig. 1. Interconversion between the two idealized five-coordinate geometries; (a) trigonal bipyramid (D_{3h} symmetry); (b) intermediate geometry (C_{2v} symmetry); (c) square pyramid (C_{4v} symmetry).

TABLE 1

Angular values of the idealized five-coordinate geometries[a,b] (°)

Angle	*Square pyramid (C_{4v} symmetry)*	*Trigonal bipyramid (D_{3h} symmetry)*
L_1–M–L_2	104.1	120
L_1–M–L_3	104.1	120
L_1–M–L_4	104.1	90
L_1–M–L_5	104.1	90
L_2–M–L_3	151.9	120
L_4–M–L_5	151.9	180
L_2–M–L_4	86.6	90
L_4–M–L_3	86.6	90
L_3–M–L_5	86.6	90
L_5–M–L_2	86.6	90

[a] Charge repulsion model[7]. [b] See Fig. 1 for labeling.

Although the above considerations strictly apply to ionic complexes, Gillespie [6] has shown that analogous results are obtained considering the repulsions of five valence shell electron pairs at the same average distance from the nucleus.

An interesting result of Zemann's treatment is that the potential energy maximum between the two minima is rather flat, indicating that intermediate configurations are not energetically unfavourable. As shown in Fig. 1 it is possible to pass from D_{3h} to C_{4v} via a structure of C_{2v} symmetry, by opening the L_2-M-L_3 angle and closing the L_4-M-L_5 angle. This process of interconversion must be kept in mind whenever examining the stereochemistry of five-coordinate complexes. Many coordination polyhedra are in fact intermediate between the two idealized models and their geometry can be referred to Fig. 1(b), the values of the angles being determined in each case by a number of factors discussed below. The L_4-M-L_5 angle may not be involved in the interconversion process, particularly when the resultant square pyramid would have the metal atom coplanar with the basal ligands (see below) or when the geometric constraints of the ligand molecule do not allow bending of the $M-L_4$ and $M-L_5$ bonds.

For d^1 to d^9 electronic configurations the crystal field stabilization energy (C.F.S.E.) favours a square pyramidal model in all cases. Table 2 reports data for d^7 and d^8 configurations [8]. However, it has been shown [9] that the stabilization due to crystal field energy decreases for models in which the $L_{ap}-M-L_{bas}$ angle deviates from 90°, so that for values of 105° a trigonal bipyramidal configuration may be more stable in some cases. As a result of these considerations square pyramidal coordination polyhedra of 3*d* complexes with essentially ionic binding show $L_{ap}-M-L_{bas}$ angles of about 100°, somewhat smaller than the value calculated on the basis of the charge repulsion model (Table 1). For an M–L distance of 2.0 Å this corresponds to a displacement of the metal atom of 0.34 Å above the basal plane, compared with the value of 0.48 Å calculated for Zemann's model.

TABLE 2

Crystal field stabilization energies (in *Dq*) for d^7 and d^8 configurations [a]

	Strong field		*Weak field*	
	Sq. pyr.	*Trig. bip.*	*Sq. pyr.*	*Trig. bip.*
d^7	−19.14	−13.34	− 9.14	−5.45
d^8	−18.28	−14.16	−10.00	−6.27

[a] From Ref. 8.

The nature of the metal ligand bonding should also be considered in discussing the stability of five-coordinate geometries and in particular the possibility of π-bonding. This subject has been discussed in detail by Furlani [2]. According to this author, the total possibility of π-bond formation in a square pyramid is more effective than in a trigonal bipyramid, essentially because the d_{xy}, d_{xz} and d_{yz} metal orbitals have full π-function, whereas in the trigonal bipyramid only d_{xz} and d_{yz} have full π-function, since d_{xy} and $d_{x^2-y^2}$ are partially σ-antibonding. Coplanarity of the metal atom with the basal ligands makes π-bonding more efficient, especially with chelating ligands having a system of organic type π-orbitals.

Other factors affecting the stability of five-coordinate geometries are the shape of the ligand molecule and packing effects.

The steric requirements of the ligand molecule can obviously influence the type of coordination geometry around the metal atom, but some recent structural determinations have shown that the flexibility of polydentate ligand molecules is greater than one might think.

Packing effects can act through formation of dimers, hydrogen bonding and influence of counterions of particular shape, but it is very hard to make an a priori evaluation of these effects.

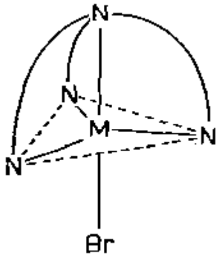
C. FACTORS CAUSING DISTORTIONS FROM THE IDEALIZED MODELS

The two idealized polyhedra described in the previous chapter are very seldom met in practice because several types of distortions can be caused by a number of factors which will be discussed briefly.

(i) Stereochemical activity of the d electrons

The effect of the non-uniform distribution of the *d* electrons on bond lengths in five-coordinate complexes was first discussed by Gillespie [6], who simply considered the *d* shell as having an ellipsoidal rather than spherical shape. Recently with the increasing accuracy of X-ray diffraction methods, the effect of this non-uniform distribution has been demonstrated.

The series of high spin five-coordinate complexes $[M^{II}(Me_6tren)Br]Br$, (M^{II} = Mn, Fe, Co, Ni, Cu, Zn) provides a good example of stereochemical activity of the *d* electrons in five-coordinate complexes. Crystals of the compounds are isomorphous, space group $P2_13$. The structure consists of trigonal bipyramidal $[M(Me_6tren)Br]^+$ cations and Br^- anions, arranged in a distorted NaCl type of lattice [10–13], [I].



I

Figure 2 shows a plot of the M—N and M—Br distances against the atomic number. The distances do not decrease monotonically as one would expect by considering the regular increase of the effective nuclear charge and moreover equatorial and apical distances do not behave in the same manner. This behaviour can be easily explained by considering the

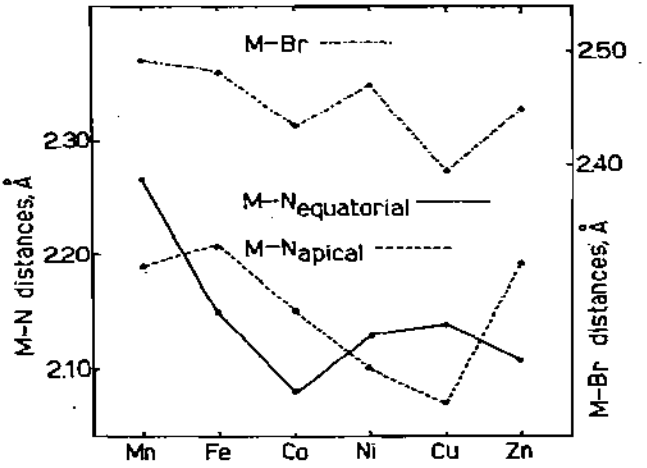


Fig. 2. Plot of the M—N and M—Br distances vs. the atomic number in the series of complexes $[M^{II}(Me_6tren)Br]Br$, (M^{II} = Mn, Fe, Co, Ni, Cu, Zn). Standard deviations are about 0.015 and 0.005 Å for M—N and M—Br bond lengths respectively (thoughout the paper standard deviations on bond lengths and angles are given as numbers in parentheses on the last significant digit).

one-electron splitting scheme of the d orbitals in a field of C_{3v} symmetry (the symmetry of the coordination polyhedron) (Fig. 3).

The equatorial M—N distances in fact, show an increase for nickel and copper (d^8 and d^9), when the $d_{x^2-y^2}$ and d_{xy} orbitals, lying in the equatorial plane, are being filled. The large increase of the apical M—N distance for zinc (d^{10}) can be accounted for by the filling of the d_{z^2} orbital, which points towards the nitrogen atom.

The apical Mn—N distance is shorter than expected, since for a d^5 ion, with a spherical

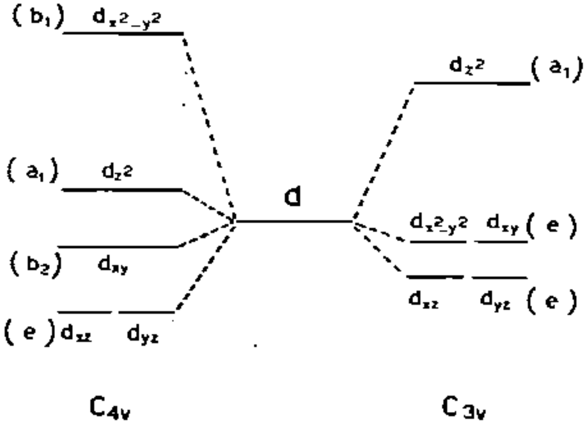


Fig. 3. Splitting of the d orbitals in C_{4v} and C_{3v} fields.

distribution of the *d* electron density, ligand–ligand repulsions should make the apical distance slightly longer than the equatorial distances (see below). The observed value of 2.19(3) Å is probably imposed by the geometric constraints of the tripod-like ligand. This is supported by the value of the N–N "bite" distance in this complex, which is the largest of all the N–N distances in the series [13].

The M–Br distances behave similarly to the apical M–N distances, except for the Ni–Br distance, which is longer than expected. However, in the nickel complex one of the bromine contacts with a methyl group is only 3.41 Å (sum of Van der Waals radii about 3.90 Å), so that steric repulsions prevent a closer approach of the bromine atom. In the copper complex, with a shorter M–Br distance this same contact remains at 3.41 Å, which is made possible by a slight rotation of the methyl groups around the equatorial M–N bond.

(ii) Other factors

Zemann's treatment considers the five ligands at equal distances from the central metal atom, but ligand–ligand repulsions alone favour axial lengthening both in the trigonal bipyramid and in the square pyramid [4].

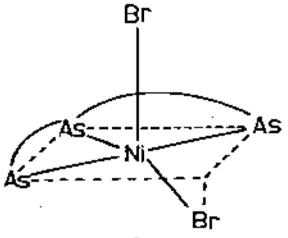
Jahn–Teller effects can also cause distortions from the idealized models in five-coordinate complexes. It is well known [14] that any non-linear molecule in a degenerate electronic state, will distort to remove the degeneracy, providing then some additional stabilization energy to the system. Several examples of this type of distortion occur in five-coordinate 3*d* metal complexes and some of them concerning nickel(II) and cobalt(II) complexes will be mentioned later.

Finally two other causes of deviation from regularity are intermolecular forces and steric constraints of the ligand molecule in complexes formed with bulky or polydentate ligands.

D. NICKEL(II) COMPLEXES

(i) General remarks

The first five-coordinate nickel(II) complex whose structure was determined by X-ray analysis was Ni(tas)Br_2 [15] in 1960. The coordination polyhedron about the metal atom was described as a distorted square pyramid with one bromine atom depressed below the basal plane [II]. It was five years later that the second structure of a five-coordinate



II

nickel(II) complex was described by X-ray analysis [16,17], so that most of the X-ray work in this field has been done in the last five years.

A short review on five-coordinate nickel(II) complexes with particular emphasis on visible spectra has appeared as part of an extensive article on the electronic structure and stereochemistry of nickel(II) [18].

Most of the complexes for which structural data are available, are formed by polydentate ligands such as polyamines, salicylaldimines, polyarsines and polyphosphines. In the few cases where five monodentate ligands are bound to the metal atom, except for the $Ni(CN)_5^{3-}$ ion, bulky ligands have been employed, such as phosphines, $(CH_3)_3AsO$ or Medabco.

On the basis of their magnetic properties five-coordinate nickel(II) complexes can be low-spin diamagnetic or high-spin with two unpaired electrons. Low-spin complexes are formed with low electronegative donor atoms such as C, S, P and As, which are often involved in strong π-bond formation. The high-spin complexes are formed with highly electronegative elements such as N and O capable of forming strong σ-bonds with the metal. However, in some cases it is possible to have low-spin complexes with a set of donor atoms typical of the high-spin complexes, if the geometric requirements of the ligand molecule are such to bring four coplanar donor atoms close to the central metal atom [19]. In these conditions the field strength may be large enough to promote spin pairing on the central metal atom. The coordination polyhedron is completed by a fifth ligand at the apex of a square pyramid, forming a long bond with the metal.

The distinction between low- and high-spin complexes must be kept in mind on discussing the stereochemistry of five-coordinate nickel(II) complexes, since stereochemistry and spin state of the metal atom are strictly correlated as will be shown later.

A survey of the available structural data (Table 3) shows that eighteen out of thirty-five coordination polyhedra can be described as more or less distorted square pyramids, eight as trigonal bipyramids and nine show a geometry intermediate between the two limiting models. Furthermore, of the eight complexes showing a trigonal bipyramidal geometry, six are formed by ligands whose trigonal symmetry is certainly an important factor for the stereochemistry of the complex.

The prevalence of square pyramidal stereochemistries for five-coordinate nickel(II) complexes is in agreement with the predictions of C.F.S.E. (Table 2). Although C.F.S.E. is only a small portion of the total binding energy of a complex, the energy difference between the square pyramidal and the trigonal bipyramidal configuration is small [7]. C.F.S.E. can then provide the extra energy to stabilize the square pyramidal configuration. In low-spin complexes an additional stabilization factor should be considered, namely π-bonding between the metal and the donor atoms. This is more effective in square pyramidal arrangements, particularly when delocalized systems of bonds are formed [2]. Of course, it would be interesting to see how many square pyramidal stereochemistries are imposed by the shape of the ligand molecule, but this is not so immediate to establish as for trigonal bipyramidal complexes. However it should be pointed out that complexes with five equal monodentate ligands show a square pyramidal [34,43] or an intermediate [43] structure, and that square pyramidal structures are also formed with tripod ligands [31,53].

TABLE 3

Stereochemistry of five-coordinate nickel(II) complexes

Trigonal bipyramidal [a]		*Intermediate* [b]		*Square pyramidal* [a]	
Complex	*Ref.*	*Complex*	*Ref.*	*Complex*	*Ref.*
High-spin complexes					
$[Ni(Me_6tren)Br]Br$	11	$Ni(SalMedpt)$	23	$Ni(5\text{-}Cl\text{-}SalenNEt_2)_2$	16,17
$[Ni_2(bdhe)_2](ClO_4)_2$	20,21	$Ni_2(SalenNEt_2)_2(catec)_2$	24	$[Ni(dmp)Cl_2]_2 \cdot 2CHCl_3$	28,29
$Ni(Medabco)Cl_3 \cdot H_2O$	22	$Ni(mpdo)Br_2$	25	$[Ni(dacoDA)(H_2O)] \cdot 2H_2O$	30
		$[Ni(atsc)_2Cl]Cl \cdot H_2O$	26	$Ni(bddae)(NCS)_2$	31
		$Ni(Me_2dpma)Br_2$	27	$[Ni(2,3,2\text{-}tet)Cl]Cl$	32
				$Ni(dmp)(Me_2dtp)_2$	33
				$[Ni(OAs(CH_3)_3)_5](ClO_4)_2$	34
				$[Ni(tpen)](ClO_4)_2 \cdot MeNO_2$	35
Low-spin complexes					
$[Ni(TAP)CN]ClO_4$	36	$Ni(PH(C_6H_5)_2)_3I_2$	42	$Ni(tas)Br_2$	15
$[Ni(tda)I]I$	37,38	${}^{c}Ni(CN)_5^{3-}$	43	$[Ni(CR)Br]Br \cdot H_2O$	19
$[Ni(TSP)Cl]ClO_4$	39	$Ni(Mephos)_3(CN)_2$	41	$Ni(bda)Br_2$	45,46
$Ni(P(C_6H_5)(CH_3)_2)_3(CN)_2$	40	$Ni(P(C_6H_5)(OC_2H_5)_2)_3(CN)_2$	44	${}^{c}Ni(CN)_5^{3-}$	43
$Ni(Etphos)_3(CN)_2$	41			$[Ni(diars)(triars)](ClO_4)_2$	47
				$Ni(\pi\text{-}ma)(diphos)Br$	48,49
				$Ni(DSP)I_2$	50
				$Ni_2(dtpa)_4$	51
				$Ni_3(dtb)_6$	52
				$[Ni(NOP_2)I]I$	53

[a] Rigorously, the terms triangular bipyramid and quadrangular pyramid should be used for most coordination polyhedra, leaving the terms trigonal bipyramid and square pyramid only for bipyramids with C_{3v} symmetry and pyramids with C_{4v} symmetry respectively. [b] On the basis of the interconversion process described in Fig. 1(a) a coordination polyhedron has been defined intermediate when the L_2-M-L_3 angle is in the range 130–150°. [c] The structure of $[Cr(en)_3]Ni(CN)_5 \cdot 1.5\ H_2O$ contains two types of $Ni(CN)_5^{3-}$ ions: one having a stereochemistry intermediate between a trigonal bipyramid and a square pyramid and the other with an almost regular square pyramidal stereochemistry.

(ii) High-spin species

Ni(5-Cl-SalenNEt$_2$)$_2$ was the first high-spin five-coordinate nickel(II) complex whose structure was determined by X-ray analysis [16,17]. The coordination polyhedron about the metal atom can be described as a distorted square pyramid with the nickel atom 0.36 Å above the basal plane (Fig. 4). It should be noted that the basal Ni—N(2) and the apical Ni—N(1) distances are about the same, within their standard deviations.

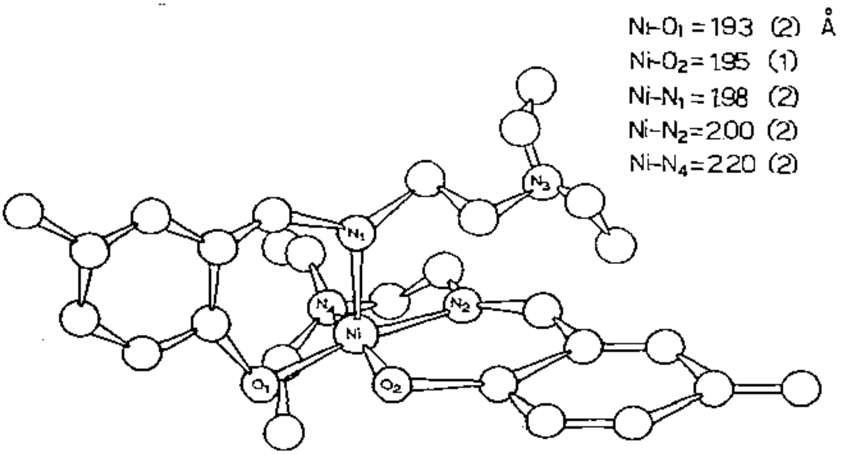


Fig. 4. The stereochemistry of Ni(5-Cl-SalenNEt$_2$)$_2$ (from Ref. 17).

Apart from distortions imposed by the steric requirements of the various ligand molecules, these stereochemical features appear to be common to all the high-spin square pyramidal nickel(II) complexes. Displacements of the nickel atom above the basal plane range in fact between 0.3 and 0.4 Å and no significant elongation of the apical bond is noted in all the complexes (Table 4). As it will be seen later, low-spin square pyramidal nickel(II) complexes show a somehwat different stereochemistry.

A careful study of the intramolecular contacts in Ni(5-Cl-SalenNEt$_2$)$_2$ shows that, assuming a C—H distance of 1.05 Å, a hydrogen atom from a methyl group is found at about 2.60 Å from the nickel atom in the proximity of the unused octahedral position. The presence of a hydrogen atom occupying the vacant octahedral site, has been pointed out in several square pyramidal structures of both low and high spin transition metal complexes [30,46,54–56].

In all these cases the metal—hydrogen distance is about what should be expected on the basis of Van der Waals radii. Whether in these complexes the metal atom has to be considered truly five-coordinate with steric hindrance in the sixth position or six-coordinate with a weak metal—hydrogen interaction, cannot be decided without the aid of other evidence, such as spectroscopic techniques. However, the presence of these hydrogen atoms contributes undoubtedly to the stability of several square pyramidal complexes. The ability of the dacoDA ligand to form square pyramidal complexes has been attributed

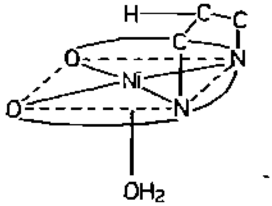
TABLE 4

Some geometrical parameters in square pyramidal nickel(II) complexes

Complex	*M–L*	*Basal dist.* [a] (Å)	*Apical dist.* (Å)	*Displacement from basal plane* (Å)
High-spin complexes				
$Ni(5\text{-}Cl\text{-}SalenNEt_2)_2$	Ni–N	2.00(2)	1.98(2)	0.36
$[Ni(dmp)Cl_2]_2 \cdot 2CHCl_3$	Ni–N	2.07(1)	2.06(1)	0.39
$[Ni(dacoDA)(H_2O)] \cdot 2H_2O$	$Ni–O(H_2O)$		2.01	~0.34
$Ni(bddae)(NCS)_2$	Ni–N(NCS)	1.97(1)	1.95(1)	0.34
[Ni(2,3,2-tet)Cl] Cl	Ni–Cl		2.33	0.34
$Ni(dmp)(Me_2dtp)_2$	Ni–N	2.00(1)	1.99(1)	*b*
$[Ni(OAs(CH_3)_3)_5](ClO_4)_2$	Ni–O	*c*	*c*	~0.30
$[Ni(tpen)](ClO_4)_2 \cdot MeNO_2$	Ni–N	2.10(1)	2.01(1)	0.32
Low-spin complexes				
$Ni(tas)Br_2$	Ni–Br	2.37	2.69	*b*
$[Ni(CR)Br]Br \cdot H_2O$	Ni–Br		2.791(4)	0.17
$Ni(bda)Br_2$	Ni–Br	2.33(1)	2.70(1)	0.16
$Ni(CN)_5^{3-}$	Ni–C	1.85(1)	2.17(1)	0.34
$[Ni(diars)(triars)](ClO_4)_2$	Ni–As	2.29	2.39	not reported
Ni(π-ma)(diphos)Br	Ni–Br		2.671(2)	0.34 [d]
$Ni(DSP)I_2$	Ni–S	2.19(1)	2.79(1)	0.09
$Ni_2(dtpa)_4$	Ni–Ni		2.560(5)	0.13
$Ni_3(dtc)_6$	Ni–S	2.219(2)	2.774(5)	not reported
$[Ni(NOP_2)I]I$	Ni–O		2.62(2)	0.12

[a] Distances have been averaged in case of more than one chemically equivalent bond. [b] Distortions preclude defining a plane containing the four basal ligands. [c] The individual Ni–O distances are not reported, but the authors say that they range from 1.95 to 2.02 Å, and the axial oxygen does not seem to be significantly different from the basal four. [d] The basal plane has been arbitrarily defined as passing through the phosphorus atoms and a third point two-thirds the way along from the central to the terminal atoms of the π-allyl ligand.

in fact to the possibility that one of the β-methylene protons, through the folding of one half of the chelated eight-membered ring towards the metal ion, could block the unused sixth position. The X-ray structural investigation [30] has confirmed these predictions [III].



III

Only three structures of high-spin trigonal bipyramidal nickel(II) complexes have been so far reported and all are formed by ligands having trigonal symmetry: two by tetradentate tripod-like ligands [11,20,21] and one by the monodentate ligand ion Medabco [22].

It should be pointed out that nickel(II) in a weak field of C_{3v} symmetry has an electronic degenerate ground state ^3E. Distortion of the trigonal symmetry should take place in order to remove the degeneracy. In agreement with this prediction the coordination polyhedron of Ni(Medabco)$Cl_3 \cdot H_2O$ shows distortions of this type, the three equatorial angles in the bipyramid being significantly different from 120° [22]. The above considerations do not apparently hold for $[Ni(Me_6tren)Br]^+$, which possesses rigorous C_3 crystallographic symmetry, the three-fold axis passing through the apical bromine, metal and tertiary nitrogen atoms [11]. On the other hand it has been shown [57] that spin–orbit coupling does not remove completely the degeneracy in this case. Also the possibility of a dynamical effect seems to be excluded by inspection of the temperature factors of the atoms in the coordination polyhedron. Most likely the small gain in energy due to the Jahn–Teller distortion would be overriden by the packing energy loss caused by the removal of the cubic symmetry of the crystal.

A few complexes can be described as having an intermediate structure, on the basis of the interconversion process between trigonal bipyramid and square pyramid already mentioned. Ni(SalMedpt) provides a good example of this type of stereochemistry [23]. The coordination polyhedron can be described in terms of a highly distorted trigonal bipyramid, with O(1), O(2) and N(3) in the equatorial plane and N(1) and N(2) in the axial positions (Fig. 5). The N(1)–Ni–N(2) angle is not involved in the interconversion process, presumably due to the steric constraints of the ligand molecule. The stereochemistry of this complex appears in fact largely affected by the geometry of the ligand molecule. Ni(SalMedpt) and $[Ni(tpen)](ClO_4)_2 \cdot MeNO_2$, which has a square pyramidal structure [35], form the known two cases of pentacoordinated complexes formed by pentadentate ligands.

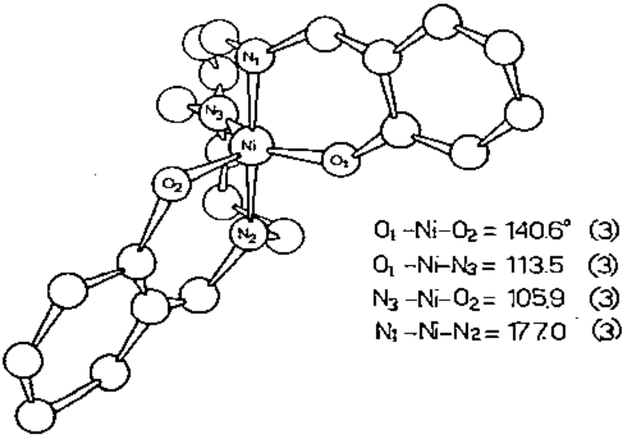


Fig. 5. The stereochemistry of Ni(SalMedpt) (from Ref. 23).

(iii) Low-spin species

Low-spin five-coordinate nickel(II) complexes have also been found to show square pyramidal, trigonal bipyramidal and intermediate stereochemistries.

As anticipated before, the stereochemistry of low-spin square pyramidal nickel(II) complexes is somewhat different from that of the high-spin complexes. An inspection of Table 4 shows that (*a*) the apical nickel—ligand distance is significantly longer than the analogous basal distances; (*b*) the displacement of the nickel atom from the basal plane is usually small; (*c*) the basal nickel—ligand distances are shorter than expected for five-coordinate complexes and are comparable with analogous distances of square planar nickel(II) complexes. These features appear to be common to other square pyramidal diamagnetic d^8 complexes [55,56,58,59].

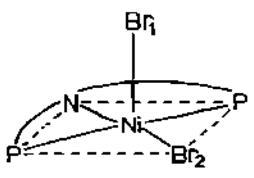
Several authors have discussed the elongation of the apical bond in these complexes, attributing it to the stereochemical activity of the *d* electrons [45,46,48–50,59]. In d^8 systems in strong fields of C_{4v} symmetry the $d_{x^2-y^2}$ orbital is empty and the d_{z^2} orbital which points at the apical ligand, contains two electrons.

One should therefore expect that the screening effect of the electron pair would cause a weakening of the apical bond. This effect is expected to be most pronounced for ionic ligands, especially halide ions. In the high-spin complexes, on the contrary, both the $d_{x^2-y^2}$ and d_{z^2} orbitals contain one electron each, so that the stereochemical activity of the *d* electrons will be greatly reduced. This will then lead to the formation of five strong bonds between the metal atom and the ligands.

Coplanarity of the metal atom with the basal ligands in low-spin complexes is favoured by ligand field stabilization energy and metal—ligand π-bonding which cannot be neglected in these complexes. Both effects have been briefly discussed in the first part of this article.

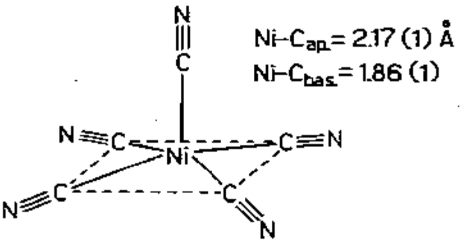
The shortening of the basal bonds and the smaller displacements of the nickel atom from the basal plane observed in these complexes should be seen as a tendency of the nickel atom towards the square planar coordination, which is the preferred coordination for diamagnetic d^8 ions. This would be the limiting configuration when the perturbation of the fifth ligand would vanish.

The structure of Ni(bda)Br_2 [45,46] is typical of most low-spin square pyramidal nickel(II) complexes [IV]. The apical Ni—Br distance is 0.37 Å longer than the basal one and the nickel atom is only 0.16 Å above the basal plane. The molecule possesses a crystallographic plane of symmetry passing through the bromine, nitrogen and nickel atoms.



Ni–Br_1 = 2.698 (7) Å
Ni–Br_2 = 2.333 (7)
Ni–P = 2.172 (5)
Ni–N = 2.006 (30)

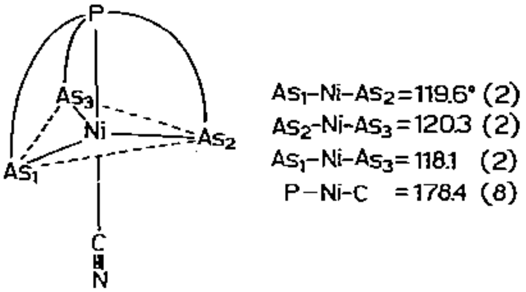
IV



V

A somewhat different stereochemistry has been found when all the five donor atoms are chemically equivalent and capable of forming strong covalent bonds, such as in the square pyramidal $Ni(CN)_5^{3-}$ anion [43] [V]. Again the apical Ni–C distance is about 0.3 Å longer than the basal ones but the nickel atom is well above the basal plane by 0.34 Å. It is reasonable to assume that in this structure, with essentially covalent character of the bonds, repulsions between bonding electron pairs would predominate over the other factors, leading then, according to Gillespie's arguments, to a square pyramidal arrangement with the metal atom above the basal plane.

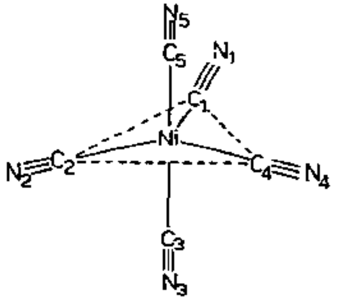
Structures of regular trigonal bipyramidal low-spin nickel(II) complexes have been determined, either possessing rigorous C_3 crystallographic symmetry [37,38] or only approximate three-fold symmetry [36]. Although the highly stable rhombohedral packing of the ions in [Ni(tda)I] I (space group $R3$) could be in part responsible for the lack of distortion of the complex cation, the structure of [Ni(TAP)CN] ClO_4 [VI] shows that



VI

Jahn–Teller distortions are inactive in trigonal bipyramidal low-spin nickel(II) complexes. This is in agreement with the non-degenerate electronic ground state (^1A) of the low-spin nickel(II) complexes in fields of C_{3v} symmetry. The slight distortions from trigonal symmetry shown by the other complexes [39,40,41] should therefore be attributed to packing effects or non-bonding repulsions.

Considerations on the stereochemical activity of the d electrons of the metal in these complexes predict a contraction of the axial bond lengths vs. equatorial bond lengths. In fact, using Gillespie's terminology, for a low-spin d^8 ion in a field of C_{3v} symmetry, the d electron density distribution is an oblate ellipsoid, since the d_{z^2} orbital is empty. Unfortunately structures of low-spin trigonal bipyramidal nickel(II) complexes with chemically equivalent apical and equatorial ligands are not known. However in the $Ni(CN)_5^{3-}$ ion with an intermediate stereochemistry [43] [VII], the equatorial Ni–C distances average 1.94(1) Å whereas the apical distances average 1.84(1) Å. The stereochemistry of this ion is typical of a group of low-spin nickel(II) complexes whose coordination polyhedron appears to be intermediate between the trigonal bipyramid and the square pyramid. As in the high-spin complexes with intermediate structure, one of the equatorial angles in the trigonal bipyramid is larger than the other two angles, but in these complexes an additional type of distortion is present, namely the lenghtening of the metal–ligand bond opposite to the large angle (Table 5). It can be noted that the larger the equatorial angle, the longer is the bond opposite to it vs. the two other metal–ligand equatorial bonds. The effect is particularly large for ionic ligands. This behaviour is in agreement with the increasing square pyramidal character of the coordination polyhedron.



$Ni{-}C_1 = 1.99\ (1)$ Å
$Ni{-}C_2 = 1.91\ (1)$
$Ni{-}C_3 = 1.83\ (1)$
$Ni{-}C_4 = 1.90\ (1)$
$Ni{-}C_5 = 1.85\ (1)$

$C_1{-}Ni{-}C_2 = 107.3°\ (5)$
$C_2{-}Ni{-}C_4 = 141.2\ (5)$
$C_4{-}Ni{-}C_1 = 111.5\ (5)$
$C_5{-}Ni{-}C_3 = 172.8\ (5)$

VII

A further point of interest in trigonal bipyramidal nickel(II) complexes with tripod ligands is the deviation of the metal atom from the equatorial plane of the bipyramid. A survey of the available data for both low- and high-spin complexes shows that the direction of displacement is mainly controlled by steric considerations [39]. When six-membered chelate rings are formed, the displacement is towards the apical atom of the tripod ligand, whereas with five-membered chelate rings the displacement is in the opposite direction.

E. COBALT(II) COMPLEXES

(i) General remarks

Table 6 reports the structures of five-coordinate cobalt(II) complexes so far determined by X-ray analysis.

$Co(ddc)_2NO$ was the first five-coordinate cobalt(II) complex whose structure was described by X-ray analysis [69]. The coordination around the cobalt atom is square pyramidal, the metal atom being 0.54 Å above the basal plane [VIII]. The bonding of the nitrosyl group in this complex has been the subject of several disputes, but unfortunately

TABLE 5

Some geometrical parameters in low-spin nickel(II) complexes illustrating the progressive distortion from the trigonal bipyramid towards the square pyramid

Complex	*Equat. angles* (°)	*M–L*	*Equat. dist.* (Å)	Δ (Å) [a]
[b][Ni(TAP)CN]ClO$_4$	119.6(2) 120.3(2) 118.1(2)	Ni–As	2.338(6) 2.317(6) 2.313(5)	−0.01
Ni(P(C$_6$H$_5$)(CH$_3$)$_2$)$_3$(CN)$_2$	116.7(1) 127.0(1) 116.2(1)	Ni–P	2.223(3) 2.261(3) 2.223(3)	+0.04
Ni(PH(C$_6$H$_5$)$_2$)$_3$I$_2$	105(1) 133(1) 123(1)	Ni–I	2.49(2) 2.80(2) c	+0.31
Ni(P(C$_6$H$_5$)(OC$_2$H$_5$)$_2$)$_3$(CN)$_2$	113.0(2) 133.5(2) 113.0(2)	Ni–P	2.189(6) 2.289(5) 2.205(6)	+0.09
Ni(Mephos)$_3$(CN)$_2$	107.7 140.2 112.0	Ni–P	d 2.32 d	
Ni(CN)$_5^{3-}$	107.3(5) 141.2(5) 111.5(5)	Ni–C	1.90(1) 1.99(1) 1.91(1)	+0.09
[e] Ni(CN)$_5^{3-}$	96.8(5) 159.3(5) 103.9(5)	Ni–C	1.84(1) 2.17(1) 1.87(1)	+0.31

[a] Δ is the difference between the bond length opposite to the large angle and the average value of the other two. [b] Almost regular trigonal bipyramid. [c] The third bond is Ni–P. [d] The two other bonds are Ni–C. [e] Almost regular square pyramid.

only two-dimensional data were used in the analysis owing to the difficulty of finding untwinned crystals.

Five-coordinate cobalt(II) complexes can be low-spin with one unpaired electron or high-spin with three unpaired electrons. The same considerations about the nature of the donor atoms causing low- or high-spin states for nickel(II), also hold true for cobalt(II), although it has been shown that spin pairing is achieved at higher field strength than for nickel(II) [75].

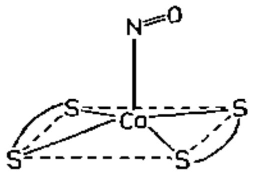
Although the number of structures available is too small to draw any conclusion, it appears that trigonal bipyramidal stereochemistries prevail in high-spin complexes, and square pyramidal ones in the low-spin case. Furthermore, the high-spin complex [Co(picox)$_5$](ClO$_4$)$_2$ with five identical monodentate ligands [62] has a trigonal bipyrami-

TABLE 6

Stereochemistry of five-coordinate cobalt(II) complexes

Trigonal bipyramidal [a]		*Intermediate* [a]		*Square pyramidal* [a]	
Complex	*Ref.*	*Complex*	*Ref.*	*Complex*	*Ref.*
High-spin complexes					
$Co(Et_4dien)Cl_2$	60	$Co(Me_5dien)Cl_2$	63,64	$Co(paphy)Cl_2$	65,66
$[Co(Me_6tren)Br]Br$	10			$[Co(OAs(C_6H_5)_2(CH_3))_4ClO_4]ClO_4$	67
$Co(bdme)(NCS)_2$	61				
$[Co(picox)_5](ClO_4)_2$	62				
Low-spin complexes					
		$Co(PH(C_6H_5)_2)_3Br_2$	42	$Co(ddc)_2NO$	69
		$[Co(QP)Cl]BPh_4$	68	[b] $Co_2(tfet)_4$	70
				[b] $[Co_2(tcbt)_4](N\text{-}Bu_4)_2$	71
				$[Co(tda)I]I$	73
				$Co_2(Salen)_2$	74

[a] See comments on Table 3. [b] These two compounds have been considered cobalt(II) complexes although there is no general agreement about the oxidation state of the metal in these complexes [72].

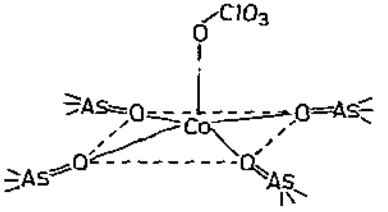


VIII

dal structure, and the low-spin complex [Co(tda)I] I formed by a tripod ligand [73] has a square pyramidal structure. In this connection it is interesting to point out that for high-spin square pyramidal cobalt(II) the stabilization due to crystal field energy decreases more rapidly than for nickel(II), when the L_{ap}—M—L_{bas} angle becomes greater [1] than 90°.

(ii) High-spin species

$[Co(OAs(C_6H_5)_2(CH_3))_4(ClO_4)]ClO_4$ was the first high-spin five-coordinate cobalt(II) complex described by X-ray analysis [67]. The coordination polyhedron is a regular square pyramid with C_4 crystallographic symmetry [IX]. The cobalt atom, which lies on the



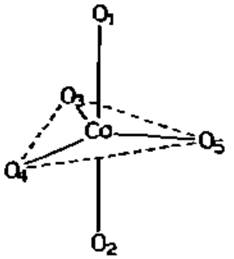
IX

fourfold axis, is 0.32 Å above the basal plane. The ClO_4-group in the apical position shows rotational disorder among four equivalent orientations, preserving in this way the fourfold symmetry. The basal and apical Co—O distances do not appear significantly different.

The structure of $[Co(picox)_5](ClO_4)_2$ is the single example of a five-coordinate cobalt(II) complex with five identical monodentate ligands [62]. The coordination polyhedron is a distorted trigonal bipyramid, one of the equatorial angles being larger than the other two [X], but the distortions cannot be easily related to packing effects or non-bonding repulsions [62]. Anyway the distortions are again towards a square pyramidal structure.

The axial Co—O bond lengths are about 0.1 Å longer than the equatorial ones, which is in agreement with the stereochemical activity of the *d* electrons (see Fig. 2).

The remaining high-spin cobalt(II) complexes whose structures have been described by X-ray methods, are formed by tridentate or tetradentate polyamines. The coordination



Co–O_1 = 2.10 (1) Å
Co–O_2 = 2.09 (1)
Co–O_3 = 1.99 (1)
Co–O_4 = 1.97 (1)
Co–O_5 = 1.97 (1)

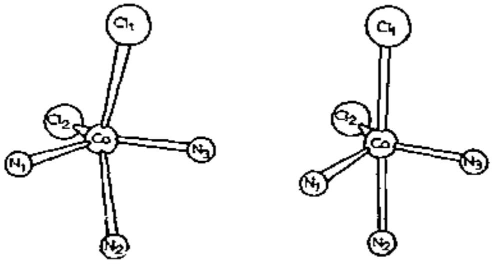
O_1–Co–O_2 = 173.4° (4)
O_3–Co–O_4 = 115.4 (5)
O_4–Co–O_5 = 129.8 (8)
O_3–Co–O_5 = 113.7 (8)

X

around the cobalt atom is completed by halide or thiocyanate ions. Owing to the steric constraints and bulkiness of the ligands, all these complexes show very distorted coordination polyhedra, except [Co(Me_6tren)Br] Br, formed by a symmetrical tripod ligand. The structure of this complex was described in the first part of this article.

The structures of Co(Me_5dien)Cl_2 and Co(Et_4dien)Cl_2 provide an interesting example of the effect of non-bonding repulsions on the stereochemistry of five-coordinate complexes [60,63,64].

Co(Et_4dien)Cl_2 and Co(Me_5dien)Cl_2 differ only in the nature of the alkyl substituents at the nitrogen atoms of the amine ligand. This means that the differences between the geometries of the two coordination polyhedra must be essentially attributed to intramolecular crowding. Although the coordination polyhedron of Co(Et_4dien)Cl_2 can be described as a distorted trigonal bipyramid, that of Co(Me_5dien)Cl_2 cannot be easily described in terms of either geometry (Fig. 6). An inspection of the intramolecular contacts shows that non-bonding repulsions are greater in Co(Me_5dien)Cl_2 than in Co(Et_4dien)Cl_2 [64]. In particular the presence of a short contact between Cl(2) and the carbon atom of the central methyl group (3.22 Å against ~ 3.80 Å sum of Van der Waals



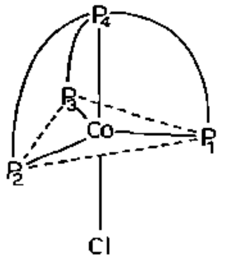
Cl_1–Co–N_2 =	162.1°	(4)	173.4°	(4)
N_1–Co–N_3 =	135.4	(5)	120.4	(4)
N_3–Co–Cl_2 =	112.4	(4)	105.9	(2)
Cl_2–Co–N_1 =	107.7	(4)	126.8	(2)

Fig. 6. The coordination polyhedra of Co(Me_5dien)Cl_2 (left) and of Co(Et_4dien)Cl_2 (right) (from Ref. 64).

radii) appears to be responsible for several distortions in the coordination polyhedron of Co(Me$_5$dien)Cl$_2$: (*a*) the decrease of the Cl(1)–Co–N(2) angle from 173.4(4) to 162.1(4)°, N(2) being pushed away from Cl(2); (*b*) the increase of the N(1)–Co–N(3) angle from 120.4(4) to 135.4(5)°; (*c*) the lengthening of the Co–N(2) bond [2.29(1) Å against the 2.11(1) Å (average) of Co–N(1) and Co–N(3)]. It appears therefore that non-bonding repulsions have forced the coordination polyhedron of Co(Me$_5$dien)Cl$_2$ in the direction of a square pyramidal geometry.

(iii) Low-spin species

An interesting aspect of Table 6 is the absence of structures of low-spin complexes having regular or slightly distorted trigonal bipyramidal stereochemistry, although complexes formed with tripod ligands have been described by X-ray analysis [68,73]. This may obviously be a consequence of the small number of structures of these complexes so far determined by X-ray analysis, but it is also in keeping with the fact that low-spin d^7 systems in fields of C_{3v} symmetry have an orbitally degenerate ground state (^2E) and are therefore subject to Jahn–Teller distortion. It is expected that in these complexes the distortion removing the trigonal symmetry would be particularly large as the odd electron is in antibonding levels, where the splitting should be greater than that of non-bonding levels [76]. In agreement with these arguments the complex [Co(QP)Cl] BPh$_4$ [68], formed by a symmetrical tripod ligand, shows one of the equatorial angles much larger than the other two, so that its stereochemistry can be described as intermediate between the square pyramid and the trigonal bipyramid [XI]. A further point of interest in the structure of [Co(QP)Cl] BPh$_4$ is the exceptionally short apical Co–P bond length of 2.02(1) Å. Although a small contraction of the apical bond should be expected on the basis of the slightly oblate shape of the *d* electron density distribution ellipsoid, the shortening of this bond seems too great to be explained on this basis. The fact that a very short apical Ni–P bond of 2.11(1) Å is found also in the nickel(II) complex with the similar ligand TSP, suggests that the explanation must be found in the rigid geometric requirements of the organic ligand. In agreement with this, a Ni–P distance of 2.21(1) Å is found in [Ni(TAP)CN] ClO$_4$ [36], where six-membered chelate rings are formed by the more flexible TAP ligand. Once again one must be very careful in drawing conclusions from the stereochemistry of complexes formed by polydentate ligands.

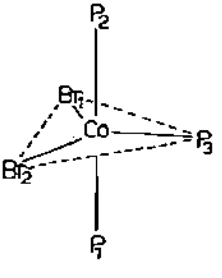


Co–P$_1$ = 2.26 (1) Å
Co–P$_2$ = 2.32 (1)
Co–P$_3$ = 2.27 (1)
Co–P$_4$ = 2.02 (1)

P$_4$–Co–Cl = 171.2°
P$_1$–Co–P$_3$ = 112.7
P$_3$–Co–P$_2$ = 137.6
P$_2$–Co–P$_1$ = 108.7

XI

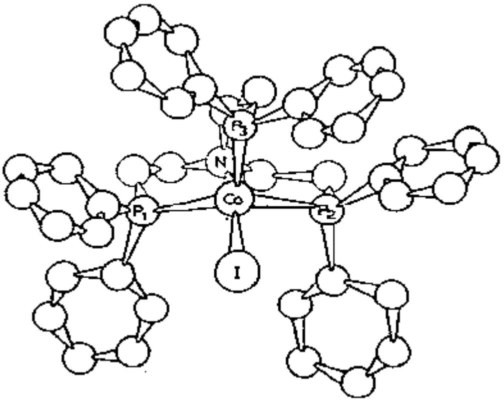
A structure similar to that of [Co(QP)Cl] BPh_4 is also shown by $Co(PH(C_6H_5)_2)_3Br_2$ [42]. In this complex, moreover, the Co—Br bond opposite to the large equatorial angle is longer than the other Co—Br bond [XII]. This effect has been noted also in the analogous nickel(II) complexes with intermediate stereochemistry (Table 5) and attributed to the stereochemical activity of the *d* electrons of the metal, in relation to the increasing square pyramidal character of the coordination polyhedron. However, for low-spin cobalt(II), with only one electron in the d_{z^2} orbital, the *d* electron density distribution in a field of C_{4v} symmetry is an ellipsoid less prolate than for nickel(II) and therefore the effect should be less pronounced. It is probably evident in this complex owing to the ionic nature of the ligand involved.



XII

Co–Br_1 = 2.54 (1) Å
Co–Br_2 = 2.33 (1)
Br_1–Co–Br_2 = 125.6° (2)
Br_2–Co–P_3 = 136.3 (3)
Br_1–Co–P_3 = 98.1 (3)
P_2–Co–P_1 = 175.9 (4)

The other low-spin cobalt(II) complex formed by a tripod ligand, [Co(tda)I] I, has a square pyramidal structure [73]. The four basal atoms are coplanar within 0.04 Å and the metal atom is 0.34 Å above the basal plane (Fig. 7). This was the first square pyramidal stereochemistry formed by a tripod ligand acting as tetradentate ligand. This structure appears even more unusual if we consider that the analogous nickel(II) complex has a trigonal bipyramidal stereochemistry with C_3 crystallographic symmetry [37,38]. Besides ligand field stabilization energy, other factors contributing to the stability of the

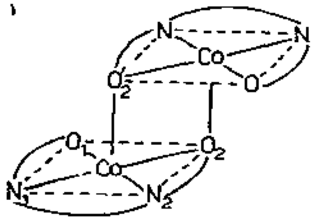


Co–N = 2.12 (1) Å
Co–P_1 = 2.23 (1)
Co–I = 2.58 (1)
Co–P_2 = 2.26 (1)
Co–P_3 = 2.28 (1)

Fig. 7. The stereochemistry of [Co(tda)I] I (from Ref. 73).

cobalt(II) complex can be found by an 'a posteriori' examination of the structure: interactions between phenyl groups of the ligand and presence of a hydrogen atom from a benzene ring blocking the sixth unused position. However, most likely, the primary driving force of the unusual structure of this complex is the distortion from the trigonal symmetry due to the Jahn–Teller effect.

A few other low-spin cobalt(II) complexes have a dimeric structure with sulphur or oxygen bridges [70,71,74]. In these structures the cobalt atom shows a distorted square pyramidal coordination with short metal–ligand basal distances and a long apical bond with the bridging donor atom. An interesting example of these structures is provided by $Co_2(Salen)_2$ [74] [XIII]. In this complex the set of donor atoms is more typical of a high-spin than of a low-spin complex. However, as already pointed out for nickel(II), the strict geometric requirements of the ligand molecule lead to the formation of four short metal–ligand basal bonds. The dimers possess a center of symmetry half-way between the cobalt atoms.



$Co–O_1 = 1.88\ (1)$ Å
$Co–N_1 = 1.88\ (1)$
$Co–N_2 = 1.88\ (1)$
$Co–O_2 = 1.95\ (1)$
$Co–O'_2 = 2.25\ (1)$

XIII

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the many stimulating discussions I have had with my colleagues Dr. M. Ciampolini and Dr. M. Di Vaira.

REFERENCES

1. L. Sacconi, *Pure Appl. Chem.*, 17 (1968) 95.
2. C. Furlani, *Coord. Chem. Rev.*, 3 (1968) 141.
3. M. Ciampolini, *Struct. Bond.*, 6 (1969) 52.
4. E.L. Muetterties and R.A. Schunn, *Quart. Rev.*, 20 (1966) 245.
5. J.S. Wood, *Coord. Chem. Rev.*, 2 (1967) 403.
6. R.J. Gillespie, *J. Chem. Soc.*, (1963) 4672.
7. J. Zemann, *Z. Anorg. Allgem. Chem.*, 324 (1963) 241.
8. F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958, p. 55.
9. M. Ciampolini, *Inorg. Chem.*, 5 (1966) 35.
10. M. Di Vaira and P.L. Orioli, *Inorg. Chem.*, 6 (1967) 955.
11. M. Di Vaira and P.L. Orioli, *Acta Cryst.*, B24 (1968) 595.
12. M. Di Vaira and P.L. Orioli, *Acta Cryst.*, B24 (1968) 1269.
13. M. Ciampolini, M. Di Vaira and P.L. Orioli, *Proc. XI I.C.C.C., Haifa and Jerusalem, 1968*, p. 217.
14. H.A. Jahn and E. Teller, *Proc. Roy. Soc. (London), Ser. A*, 164 (1937) 220.

15. G.A. Mair, H.M. Powell and D.E. Henn, *Proc. Chem. Soc.*, (1960) 415.
16. L. Sacconi, P.L. Orioli and M. Di Vaira, *J. Amer. Chem. Soc.*, 87 (1965) 2059.
17. P.L. Orioli, M. Di Vaira and L. Sacconi, *J. Amer. Chem. Soc.*, 88 (1966) 4385.
18. L. Sacconi, in *Transition Metal Chemistry*, R.L. Carlin (Ed.), Dekker, New York, 1968, Vol. IV, p. 199.
19. E.B. Fleischer and S.W. Hawkinson, *Inorg. Chem.*, 7 (1968) 2312.
20. P. Dapporto and L. Sacconi, *Chem. Commun.*, (1969) 329.
21. P. Dapporto and L. Sacconi, *J. Chem. Soc. (A)*, (1970) 618.
22. F.K. Ross and G.D. Stucky, *Inorg. Chem.*, 8 (1969) 2734.
23. P.L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1966) 300.
24. L. Sacconi, P.L. Orioli and M. Di Vaira, *Chem. Commun.*, (1967) 849.
25. P.L. Orioli and M. Di Vaira, *J. Chem. Soc. (A)*, (1968) 2078.
26. M. Mathew and G.J. Palenik, *J. Amer. Chem. Soc.*, 91 (1969) 4923.
27. J. Rodgers and R.A. Jacobson, *J. Chem. Soc. (A)*, (1970) 1826.
28. H.S. Preston and C.H.L. Kennard, *Chem. Commun.*, (1968) 819.
29. H.S. Preston and C.H.L. Kennard, *J. Chem. Soc. (A)*, (1969) 2682.
30. J.I. Legg, D.O. Nielson, D.L. Smith and M.L. Larson, *J. Amer. Chem. Soc.*, 90 (1968) 5030.
31. M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1969) 10.
32. N.A. Bailey, J.G. Gibson and E.D. McKenzie, *Chem. Commun.*, (1969) 741.
33. P.S. Shetty, R.E. Ballard and Q. Fernando, *Chem. Commun.*, (1969) 717.
34. S.H. Hunter, K. Emerson and G.A. Rodley, *Chem. Commun.*, (1969) 1398.
35. W. Mazurek, A.T. Phillip, B.F. Hoskins and F.D. Whillans, *Chem. Commun.*, (1970) 184.
36. D.L. Stevenson and L.F. Dahl, *J. Amer. Chem. Soc.*, 89 (1967) 3424.
37. P. Dapporto and L. Sacconi, *Chem. Commun.*, (1969) 1091.
38. P. Dapporto and L. Sacconi, *J. Chem. Soc. (A)*, (1970) 1804.
39. L.P. Haugen and R. Eisenberg, *Inorg. Chem.*, 8 (1969) 1072.
40. J.K. Stalick and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1090.
41. D.W. Allen, F.G. Mann, I.T. Millar, H.M. Powell and D. Watkin, *Chem. Commun.*, (1969) 1004.
42. J.A. Bertrand and D.L. Plymale, *Inorg. Chem.*, 5 (1966) 879.
43. K.N. Raymond, P.W.R. Corfield and J.A. Ibers, *Inorg. Chem.*, 7 (1968) 1362.
44. J.K. Stalick and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1084.
45. P.L. Orioli and L. Sacconi, *Chem. Commun.*, (1968) 1310.
46. P.L. Orioli and C.A. Ghilardi, *J. Chem. Soc. (A)*, (1970) 1511.
47. B. Bosnich, R.S. Nyholm, P.J. Pauling and M.L. Tobe, *J. Amer. Chem. Soc.*, 90 (1968) 4740.
48. M.R. Churchill and T.A. O'Brien, *Chem. Commun.*, (1968) 246.
49. M.R. Churchill and T.A. O'Brien, *J. Chem. Soc. (A)*, (1970) 206.
50. D.W. Meek and J.A. Ibers, *Inorg. Chem.*, 8 (1969) 1915.
51. M. Bonamico, G. Dessy and V. Fares, *Chem. Commun.*, (1969) 1106.
52. M. Bonamico, G. Dessy and V. Fares, *Chem. Commun.*, (1969) 324.
53. P. Dapporto, R. Morassi and L. Sacconi, *J. Chem. Soc. (A)*, (1970) 1298.
54. S.J. La Placa and J.A. Ibers, *Inorg. Chem.*, 4 (1965) 778.
55. N.A. Bailey, J.M. Jenkins, R. Mason and B.L. Shaw, *Chem. Commun.*, (1965) 237.
56. N.A. Bailey and R. Mason, *J. Chem. Soc. (A)*, (1968) 2594.
57. J.S. Wood and P.T. Greene, *Inorg. Chem.*, 8 (1969) 491.
58. J.W. Collier, F.G. Mann, D.G. Watson and H.R. Watson, *J. Chem. Soc.*, (1964) 1803.
59. T.L. Blundell and H.M. Powell, *J. Chem. Soc. (A)*, (1967) 1650.
60. Z. Dori, R. Eisenberg and H.B. Gray, *Inorg. Chem.*, 6 (1967) 483.
61. P. Dapporto, M. Di Vaira and L. Sacconi, *Chem. Commun.*, (1969) 153.
62. B.A. Coyle and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 767.
63. M. Di Vaira and P.L. Orioli, *Chem. Commun.*, (1965) 590.
64. M. Di Vaira and P.L. Orioli, *Inorg. Chem.*, 8 (1969) 2729.
65. I.G. Dance, M. Gerloch, J. Lewis, F.S. Stephens and F. Lions, *Nature*, 210 (1966) 298.
66. M. Gerloch, *J. Chem. Soc. (A)*, (1966) 1317.

67. P. Pauling, G.B. Robertson and G.A. Rodley, *Nature*, 207 (1965) 53.
68. T.L. Blundell, H.M. Powell and L.M. Venanzi, *Chem. Commun.*, (1967) 763.
69. P.R.H. Alderman, P.G. Owston and J.M. Rowe, *J. Chem. Soc.*, (1962) 668.
70. J.H. Enemark and W.N. Lipscomb, *Inorg. Chem.*, 4 (1965) 1729.
71. M.J. Baker-Hawkes, Z. Dori, R. Eisenberg and H.B. Gray, *J. Amer. Chem. Soc.*, 90 (1968) 4253.
72. J.A. McCleverty, in *Progress in Inorganic Chemistry*, F.A. Cotton (Ed.), Wiley, New York, 1968, Vol. X, p. 121.
73. P.L. Orioli and L. Sacconi, *Chem. Commun.*, (1969) 1012.
74. S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Acta Cryst.*, B25 (1969) 1671.
75. L. Sacconi, *J. Chem. Soc. (A)*, (1970) 248.
76. M.J. Norgett and L.M. Venanzi, *Inorg. Chim. Acta*, 2 (1968) 107.