

FIVE-COORDINATION IN 3d METAL COMPLEXES

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INTRODUCTION

In recent years a good number of five-coordinate complexes of metals of the first transition row have been described, so that now this type of coordination is no longer exceptional¹. We are going to discuss the properties of these complexes, paying particular attention to their thermodynamic, magnetic and spectroscopic aspects. In this contribution five-coordinate complexes of 3d metals with zero or negative oxidation states and compounds which have been known for a long time are not considered.

GEOMETRY

All the observed five-coordinate structures can be referred back to the two most symmetrical configurations, square pyramidal (C_{4v} symmetry) and trigonal bipyramidal (D_{3h} symmetry). These idealized structures are rarely met with in practice (*Figure 1*). They can be interconverted by means of simple angular distortions, such as increasing the angle B_1-M-B_2 until A_1, B_1, B_2 and A_2 are coplanar and *vice versa*. The metal atom need not lie in the square pyramids basal plane, and if it does not, the bonds A_1-M-A_2 are also involved in the interconversion.

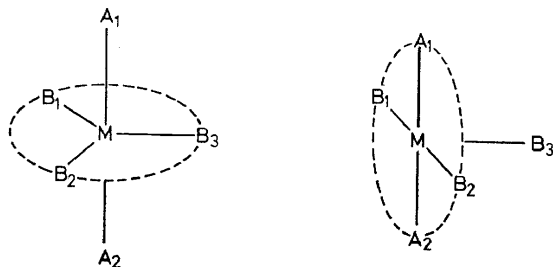


Figure 1. Interconversion between the trigonal bipyramid and square pyramid

The principal factors that determine the configuration are: electrostatic repulsion between ligands; the nature of the metal-ligand bonds; the crystal field stabilization energy; the shape of the ligand molecules and crystal packing effects.

With regard to the ligand-ligand repulsion factor, it has been shown that the trigonal bipyramid is the more stable regular structure² (*Figure 2*). However, a distorted square pyramidal structure may be only slightly less stable, as for example when the apical angle is a little more than 100° . (The apical angle is the angle between apical bond and the four equatorial bonds.)

Gillespie's analysis in terms of valence shell electron pair repulsions leads towards the same conclusion³. In this treatment, a square pyramid distorted in the manner just described is only 8 per cent less stable than the trigonal bipyramid. In covalent complexes where presumably the interactions between bonded pairs of electrons are more important than bonded-nonbonded electron pair interactions, the trigonal bipyramidal configuration is

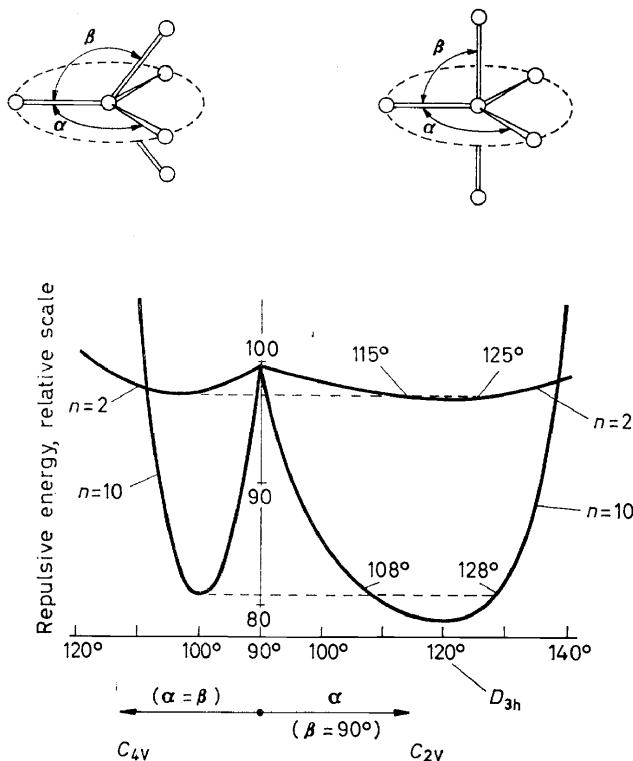


Figure 2. Behaviour of the repulsive energies of the type $F \propto R^{-n}$. Coulomb repulsions, $n = 2$; Born repulsions, $n = 10$. Five ligands arranged according to the C_{4v} point group (left side) and C_{2v} point group (right side). The trigonal bipyramid occurs for $\alpha = 120^\circ$ and $\beta = 90^\circ$ ⁴

favoured³. On the other hand, it is essentially the ionic compounds in which the interaction between bonding electron pairs and the d -shell predominates and in which a square pyramidal configuration is to be expected³. But, we shall see that the other factors such as ligand geometries and lattice forces often determine the geometry of the complex so that a direct correlation between bond type and stereochemistry would not appear to exist.

Table 1 shows the CFSE for various electronic configurations⁴. One sees that the square pyramid configuration is always more stabilized by crystal field splittings than the bipyramidal when the apical angle is 90° , but when the apical angle ranges from 100 – 105° the energy difference between the two configurations is very small and the bipyramidal may even be the more stable, as with d^4 , d^9 and low-spin d^8 . If the ligand is polydentate, the steric

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restrictions imposed by its geometry determine, in the final analysis, the stereochemistry adopted by the complex.

Structural data for five-coordinate complexes of the 3d elements have become fairly numerous. In square pyramidal structures the apical angle found is usually between 100° and 106°, as shown in *Table 2*. The only

Table 1. CFSE for five-coordinated 3d metal complexes⁴

d^n	S	Square Pyr.		Trig. Bipy.
		$\beta = 90^\circ$	$\beta = 105^\circ$	
LOW-SPIN				
d^5	3/2	0.894	0.628	0.624
d^6	1	1.192	0.812	0.792
d^7	1/2	1.131	0.920	0.852
d^8	0	1.192	0.888	0.912
HIGH-SPIN				
d^1, d^6		0.298	0.184	0.168
d^2, d^7		0.596	0.368	0.337
d^3, d^8		0.635	0.476	0.397
d^4, d^9		0.596	0.444	0.456

Table 2. Apical angles of square pyramidal structures

Complex	β	Ref.
[Co(ClO ₄)(OAsMePh ₂) ₄]ClO ₄	100°	5
[Cr(en) ₃][Ni(CN) ₅].1.5 H ₂ O	100°	6
α -Chlorohaemiferon(III)	102°	7
Methoxyiron(III)mesoporphyrin	103°	8
Co(S ₂ CNMe ₂) ₂ (NO)	103°	9
VO(acac) ₂	106°	10

regular trigonal bipyramidal structure occurs in the complex [Cr(NH₃)₆] [CuCl₅]¹¹ (*Figure 3*). However, the complexes [MBr(Me₆tren)] Br¹² [Me₆tren = tris(2-dimethylaminoethyl)amine; M = Mn to Zn] retain the three-fold symmetry axis, with the angle $\beta \approx 82^\circ$ ranging from 81° to 84°,¹³ and C₃ symmetry is also retained in the cluster compounds Cu₄OCl₆(OPPh₃)₄¹⁴ (*Figure 3*) and Cu₄OCl₆(py)₄¹⁵. All other known structures have lower symmetry. There is quite a large group of compounds which deviate from regular D_{3h} symmetry only in regard to the angles between the equatorial bonds. For example in TiBr₃ · 2NMe₃¹⁶ the Br—Ti—Br angles are 121.25°, 121.25° and 117.5° while in [Co(NCMe)₅] ClO₄¹⁷ the equatorial angles are 115.9°, 115.9° and 128.3° (*Figure 4*).

With the more distorted structures the designation as square pyramid or trigonal bipyramid becomes almost a matter of personal taste, so far are they from the limiting regular configurations.

ELECTRONIC STRUCTURES OF FIVE-COORDINATE COMPLEXES

The electronic configurations of five-coordinate complexes fall into two classes, high-spin and low-spin, but only the configurations d^5 , d^6 , d^7 and d^8 can give both types of compounds. This can be understood by looking at an

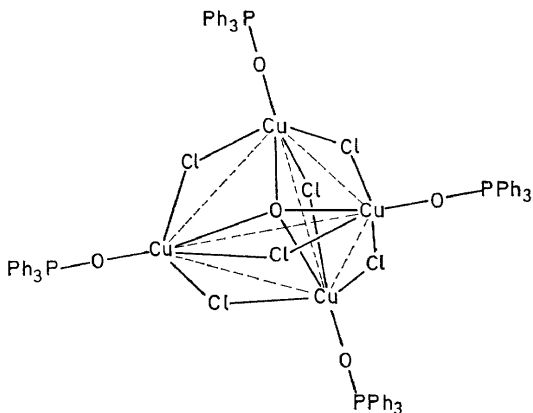
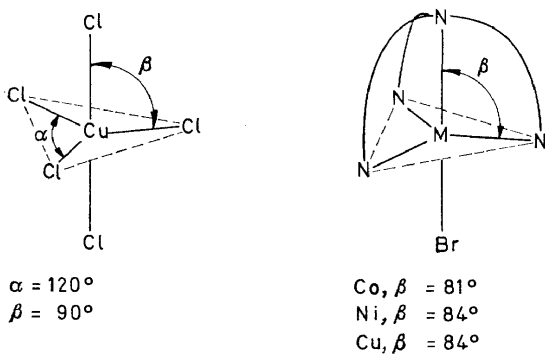


Figure 3. Structural data for $[\text{Cr}(\text{NH}_3)_6][\text{CuCl}_5]^{11}$, $[\text{MBr}(\text{Me}_6\text{tren})]\text{Br}^{13}$ and $\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4^{14}$

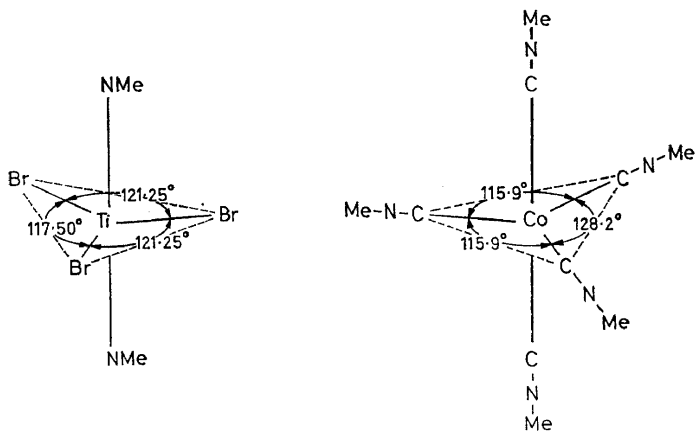


Figure 4. Structural data for $\text{TiBr}_3(\text{NMe}_3)_2^{16}$ and $[\text{Co}(\text{CNMe})_5]\text{ClO}_4^{17}$

orbital splitting diagram for C_{4v} and D_{3h} fields (Figure 5). The highest orbital is well separated in energy from the others, the $d_{x^2 - y^2}$ and the d_{z^2} orbital, respectively. When the energy separation between the highest orbital and

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the next lowest is larger than the spin-pairing energy, the total spin quantum number S is $3/2$, 1 , $1/2$ and 0 for the d^5 to d^8 configurations. Ligands with P, As, and C as donor atoms generally give low-spin complexes, whereas O and N ligands give high-spin complexes, usually. S, Se, Cl, Br and I may give both types of complexes.

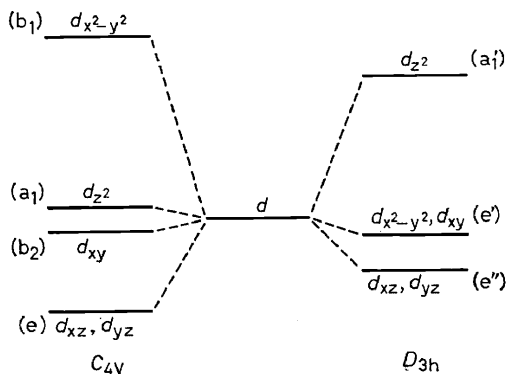


Figure 5. Energies of 3d orbitals in C_{4v} and D_{3h} fields

FIVE-COORDINATE COMPLEXES WITH HIGH-SPIN

For convenience we shall consider inner complexes later on. The type of compounds in this section can be considered as adducts of metal salts with neutral ligands or halide ions; +2 and +3 oxidation states are usually found.

Adducts with monodentate ligands

Data on this type of compounds are summarized in *Table 3*. The series of Ti, V, and Cr tribromide and trichloride (bis) adducts with trimethylamine and thioethers were largely prepared by Fowles and his coworkers, working under rigorously anhydrous conditions. The adduct of $TiBr_3(NMe_3)_2$ ¹⁶ was found to have a distorted trigonal bipyramidal structure, point group C_{2v} ,

Table 3. Five-coordinate adducts of Ti, V and Cr halides

Ti	$TiX_3(NMe_3)_2$ ^{18, 19} , $TiX_4(NMe_3)$ ^{18, 20} , $TiX_4(SR_2)$ ²³
V	$VX_3(NP_3)_2$ ^{21, 22} , $VX_3(SR_2)_2$ ^{19, 22} , $VX_3(PR_3)_2$ ²¹ , $VX_3(OPR_3)_2$ ²¹ , $VX_4(NHMe_2)$ ²⁴ , $VX_4(NMe_3)$ ²⁴ , $VOCl_2(OPPh_3)_2$ ²⁵ , $M_2^IVOC_4$ ($M = pyH^{+26}$, $quinH^+$, $iso-quinH^+$)
Cr	$CrX_3(NMe_3)_2$ ²⁷

and the other analogues with vanadium and chromium were found to be isomorphous. The lowest complex here reported $CrCl_3 \cdot NMe_3$ is the unique authentic compound of chromium(III) which is not octahedral. It is possible that sulphide adducts of vanadium are octahedral dimers in the solid state¹⁹.

Adducts of the titanium and vanadium trihalides with trialkyl phosphines and trialkyl phosphine oxides are also known. Titanium and vanadium tetrahalides give mono-adducts with di- and trimethylamine and with thioethers that are monomeric in benzene. Five-coordinate complexes of

oxovanadium(IV) are also known, such as $\text{VOCl}_2(\text{OPPh}_3)_2$, $\text{M}_2\text{I}[\text{VOCl}_4]$ where M is pyridinium, quinolinium and isoquinolinium.

Examples of high-spin compounds of the type $[\text{MX}_5]^{n-}$ in which five halides are coordinated around one metal ion, are scarce. The only certain examples occur in $[\text{Cr}(\text{NH}_3)_6][\text{CuCl}_5]^{11}$ in which the ion $[\text{CuCl}_5]^{3-}$ has full D_{3h} symmetry and in $[\text{NH}_2\text{Me}_2][\text{CuCl}_3]$ which consists of dimeric Cu_2Cl_6 units (mean Cu—Cl distance 2.3 Å) joined in infinite chains by means of bridging chlorine atoms at a distance of 2.73 Å. Other probable five-coordinate complexes are the penta-chloro and penta-fluoro manganate ions: $(\text{Et}_4\text{N})_2[\text{MnCl}_5]^{29}$ and $(\text{K}, \text{Rb}, \text{Cs})_2[\text{MnF}_5]^{30}$ which have magnetic moments corresponding to four unpaired electrons.

A set of five donor oxygen atoms is found in the compound $[\text{Co}(\text{OAsMePh}_2)_4\text{ClO}_4](\text{ClO}_4)$ which is formed from the bivalent metal perchlorates and the arsine oxide (Figure 6). The derivatives of the bivalent 3d metals have the square pyramidal structure with a perchlorate oxygen atom apical⁵. The compounds are high-spin and the cobalt(II) moment of 5.5 B.M. is unusually high.

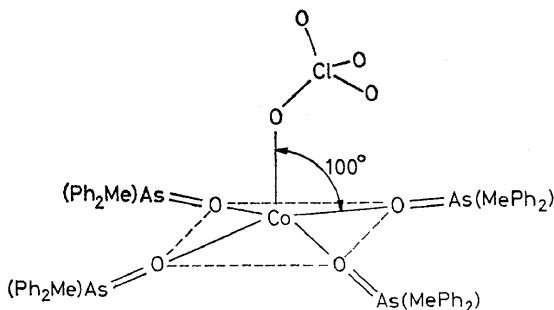


Figure 6. Structural data for the ion $[\text{Co}(\text{ClO}_4)(\text{OAsMePh}_2)_4]^+$ (ref. 5)

The spectra of these Co(II) and Ni(II) square pyramidal compounds³² are given in Figures 7 and 8 together with the energy levels calculated for a crystal field of C_{4v} symmetry⁴. The spectrum of the cobalt compound shows four bands between 5000 and 25 000 cm^{-1} at *c.* 7000, 12 000–17 000 and 23 000 cm^{-1} which are assigned to transitions from $^4A_2(\text{F})$ to $^4E(\text{F})$, $^4B_1(\text{F})$, $^4E(\text{P})$ and $^4A_2(\text{P})$. For the nickel complex (Figure 8) the bands at *c.* 12 000, 19 000 and 23 000 cm^{-1} are assigned as transitions from $^3B_1(\text{F})$ to $^3E(\text{F})$, $^3A_2(\text{P})$ and $^3E(\text{P})$. The very broad shoulder around 9000 cm^{-1} is associated with the excited states $^3A_2(\text{F})$ and $^3B_2(\text{F})$.

Adducts with tridentate ligands

These complexes have the general formula MX_2L where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ and L is a polyamine, Schiff-base or pyridine derivative containing N, O or S donor atoms. They are generally made in scrupulously dry solvents of low solvating power, such as high boiling alcohols, are soluble in organic solvents, and do not tend to dissociate.

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Ligands of the type shown in *Figure 9* (dien) have been used by Ciampolini³³ and by Gray³⁴ to give many five-coordinate complexes. All the complexes with R = Me are five-coordinate in the solid state and in solution³³. The compounds MBr₂ (Me₅ dien) are all isomorphous. The NiCl₂ (Et₄ dien) is a square-planar complex which should be written as [NiCl (Et₄ dien)]Cl.

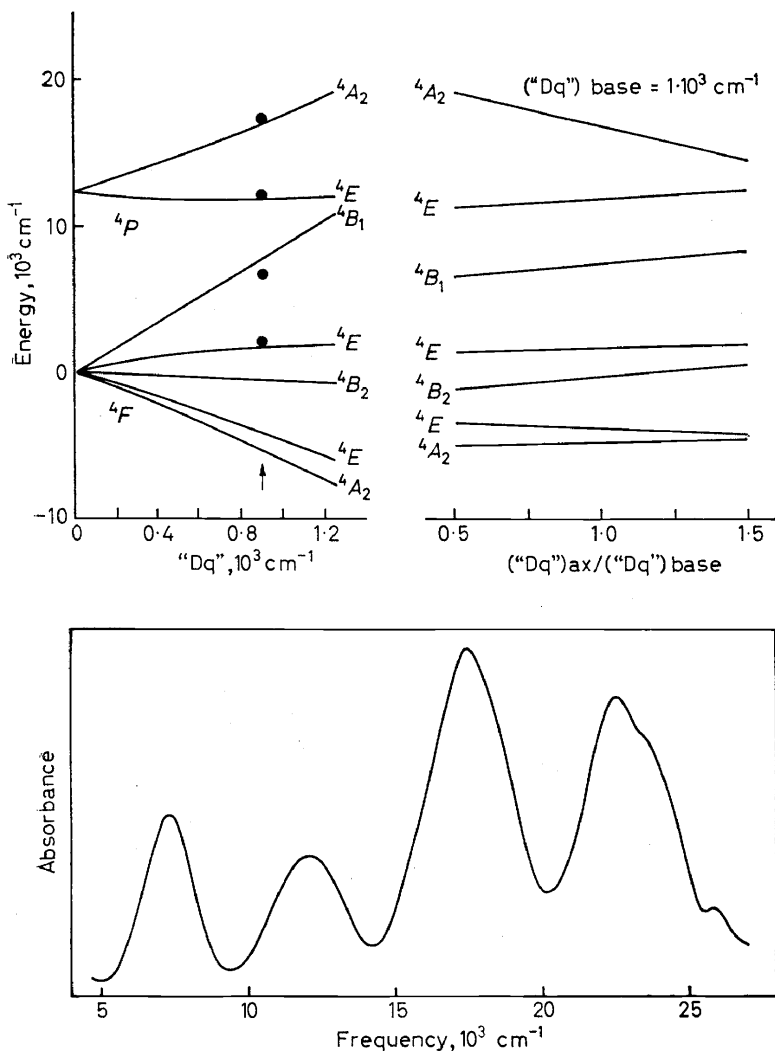


Figure 7. Energy levels diagram for Co²⁺ in square pyramidal fields⁴. Black circles indicate the frequencies of the band maxima in the reflectance spectrum of [Co(ClO₄)(OAsPh₂Me)₄](ClO₄)³²

In organic solvents such as acetone it is partially undissociated as a 5-coordinate species. The complete structures of two of these have been determined:

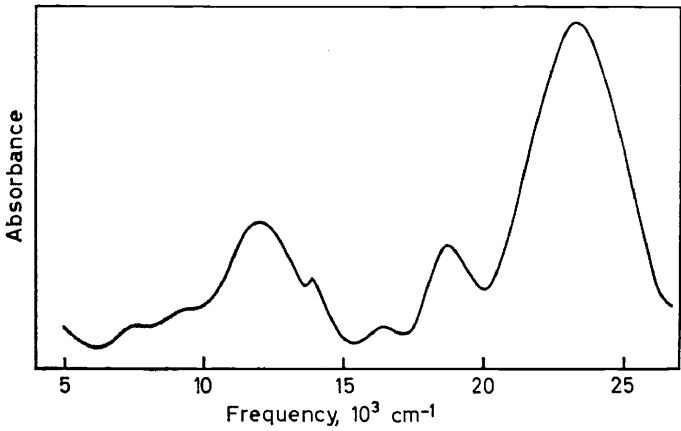
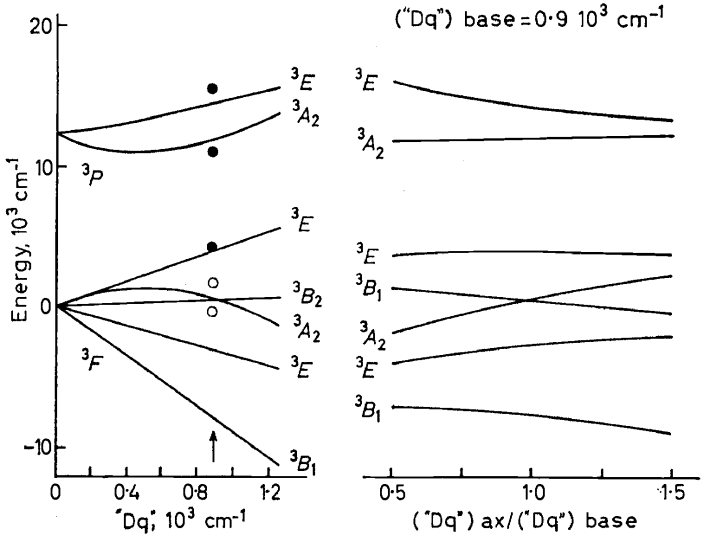


Figure 8. Energy levels diagram for Ni^{2+} in square pyramidal fields⁴. Black circles indicate the frequencies of the band maxima in the reflectance spectrum of $[\text{Ni}(\text{ClO}_4)(\text{OAsPh}_2\text{Me})_4](\text{ClO}_4)$ ³²

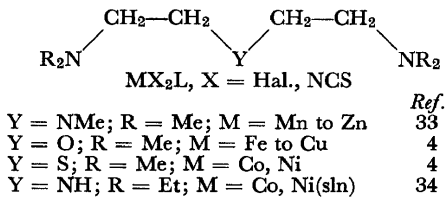


Figure 9. Some tridentate ligands

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$\text{CoCl}_2(\text{Me}_5 \text{ dien})^{35}$ and $\text{CoCl}_2(\text{Et}_4 \text{ dien})^{36}$ (Figure 10). Both have intermediate structures, but the first is more distorted on account of the steric hindrance produced by the central *N*-methyl group.

Schiff bases of the general formula shown in Figure 11 are formed from *N,N*-disubstituted ethylenediamine and *o*-substituted benzaldehyde. According to the nature of *Y* donor atom, the set of donor atoms may be NNN, ONN, and SNN. When NR_2 is a diethylamino group the ligands are suitably disposed for the formation of five-coordinate adducts. The nickel halide adducts, however, give a mixture of five-coordinate and tetrahedral species in non-dissociating solvents. Cobalt(II) salts, on the other hand, form five-coordinate adducts only when $\text{Y} = \text{NH}^{37}$; the ligands with O^{38} and S^{39} as the third donor atom give tetrahedral complexes with this metal.

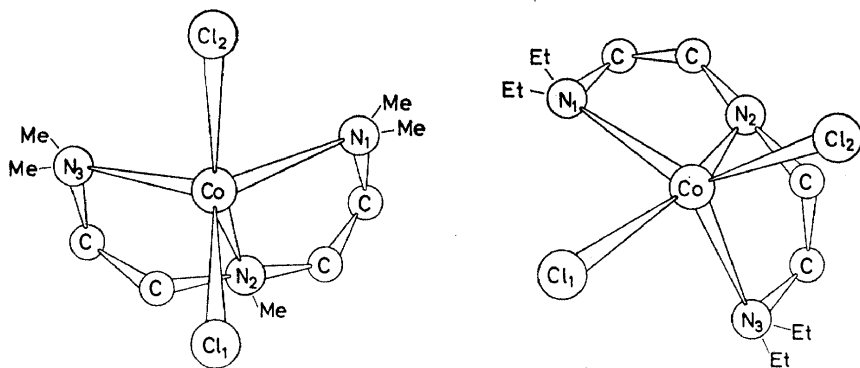


Figure 10. Structures of the compounds $\text{CoCl}_2(\text{Me}_5 \text{ dien})^{35}$ and $\text{CoCl}_2(\text{Et}_4 \text{ dien})^{36}$

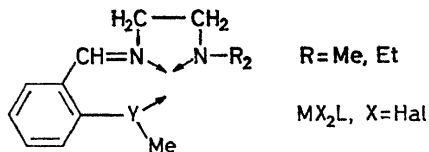


Figure 11. Some tridentate Schiff bases

Some pyridine derivatives such as those shown in Figure 12 contain a set of three nitrogen atoms which are potential donor atoms. The complexes these ligands give differ from those of dien derivatives because in solution they maintain their five-coordinate structure. This may be equated with the possibility of π back-bonding to the pyridine nitrogen atoms, and with the formation of a more stable 5-membered chelate ring. The metals which give five-coordinate complexes with these ligands are also shown in Figure 12.

The complexes of Mn, Co, and Zn with paphy are mutually isomorphous³². $\text{CoCl}_2 \cdot \text{paphy}$ complex has an intermediate structure⁴² (Figure 13). $\text{ZnCl}_2 \cdot \text{terpyridyl}$ has a distorted trigonal bipyramidal structure⁴³ and the Co, Ni, and Cu complexes are isostructural with it³² (Figure 13). The complexes $[\text{CuX}(\text{dipy})_2]\text{X}$ and $[\text{CuX}(\text{phen})_2]\text{X}$ ($\text{X} = \text{halogen}$) are well

known⁴⁴ and x-ray analyses give the distances in $[\text{CuI}(\text{dipy})_2]\text{I}$ as $\text{Cu}-\text{N}$ 2.02 Å, and $\text{Cu}-\text{I}$ 2.71 Å⁴⁵ (Figure 13). The trigonal bipyramid is fairly distorted.

Adducts with tetradentate ligands

These compounds are adducts of the simple salts only in terms of the empirical formula, since the structural formula is $[\text{MLX}]\text{X}$. The structure determination on the copper(II) complex with tris (2-aminoethyl) amine

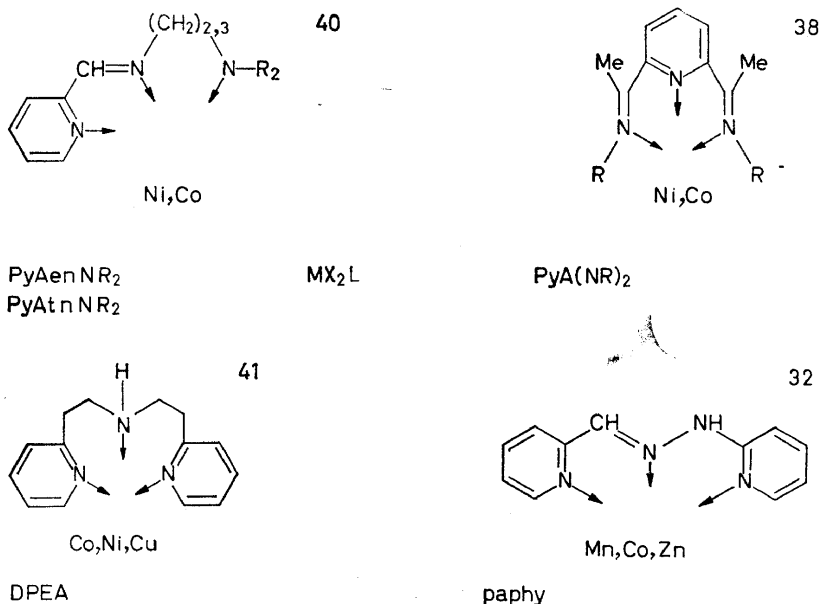


Figure 12. Five-coordinate complexes with N,N,N-tridentate ligands

(tren) $[\text{Cu}((\text{H}_2\text{N}-\text{CH}_2\text{CH}_2)_3\text{N})\text{NCS}]\text{NCS}$, ($[\text{Cu}(\text{tren})\text{NCS}]\text{NCS}$) revealed a trigonal bipyramidal structure⁴⁶ (Figure 14). The equatorial angles and bond lengths were unexpectedly found to be unequal, giving the structure a slight distortion. $\text{Co}(\text{NCS})_2$ and CoI_2 also give five-coordinate adducts with tris-(2-aminoethyl)amine⁴⁷. With nickel(II) however tren gives octahedral adducts⁴⁸ which persist in solution⁴⁹, and a similar situation is not unlikely with $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$ ⁵⁰.

The hexamethyl derivative of tren, $(\text{Me}_6 \text{tren})$, forms only five-coordinate species with the divalent 3d metal halides¹². Each set of halide complexes forms an isomorphous group. The structure of $[\text{CoBr}(\text{Me}_6\text{tren})]\text{Br}$ is shown in Figure 15; it is a trigonal bipyramid with C_{3v} symmetry¹³. The metal atom is situated 0.32 Å below the equatorial plane so that apical angle is 81°. In non-coordinating solvents the compounds of this series behave as 1:1 electrolytes, so maintain their five-coordinate structure¹². Presumably the greater steric hindrance provided by the equatorial methyl groups does not permit the close approach of the sixth ligand that can occur with tren itself.

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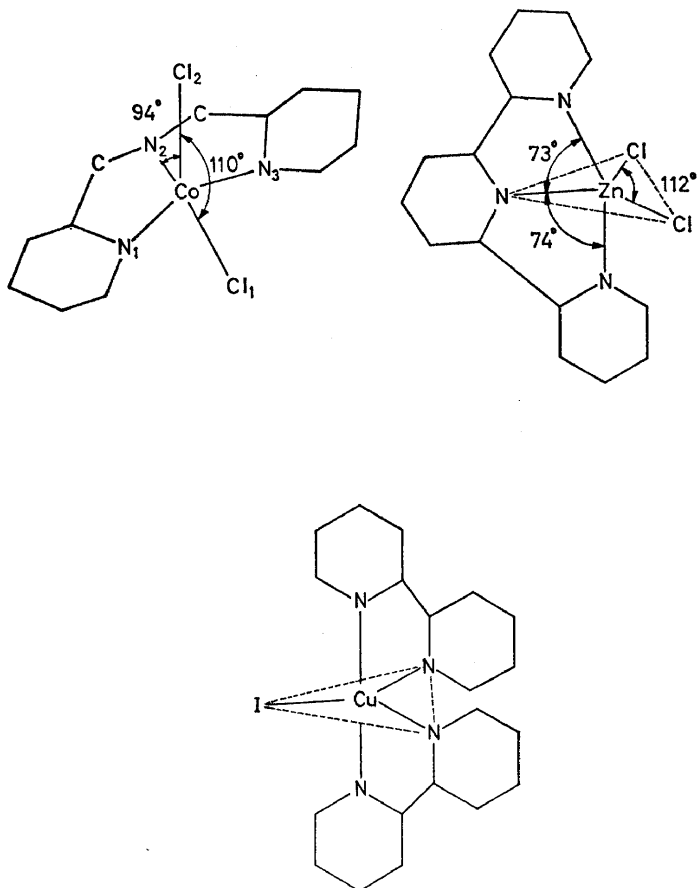
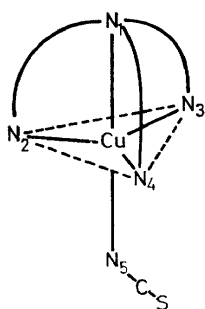


Figure 13. Structures of the compounds $\text{CoCl}_2(\text{paphy})$ ⁴², $\text{ZnCl}_2(\text{terpy})$ ⁴³, and $[\text{CuI}(\text{dipy})_2]\text{I}$ ⁴⁵



$$\text{Cu}-\text{NCS} = 1.95 \text{ \AA}$$

$$\text{Cu}-\text{N}_{(\text{av})} = 2.06 \text{ \AA}$$

$$\text{N}_1-\text{Cu}-\text{N}_5 = 177^\circ$$

$$\text{N}_2-\text{Cu}-\text{N}_3 = \text{N}_3-\text{Cu}-\text{N}_4 = 113-114^\circ$$

$$\text{N}_2-\text{Cu}-\text{N}_4 = 130^\circ$$

Figure 14. Structure of $[\text{Cu}(\text{NCS})\text{tren}](\text{SCN})$ ⁴⁶

Tris(2-methylthioethyl)amine, $[(\text{MeSCH}_2\text{CH}_2)_3\text{N}]$, (set NS_3) forms a complex with cupric bromide which is a 1:1 electrolyte in organic solvents⁴. This compound probably has a bipyramidal structure.

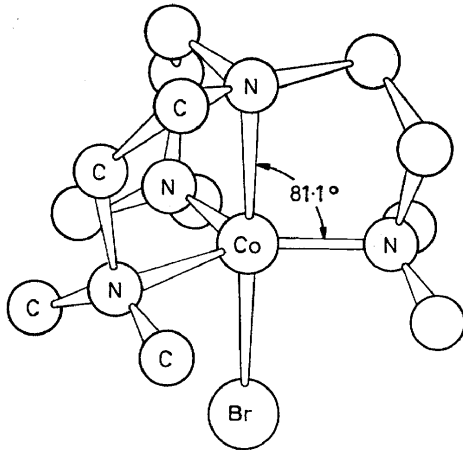


Figure 15. Structure of $[\text{CoBr}(\text{Me}_6\text{tren})]\text{Br}^{13}$

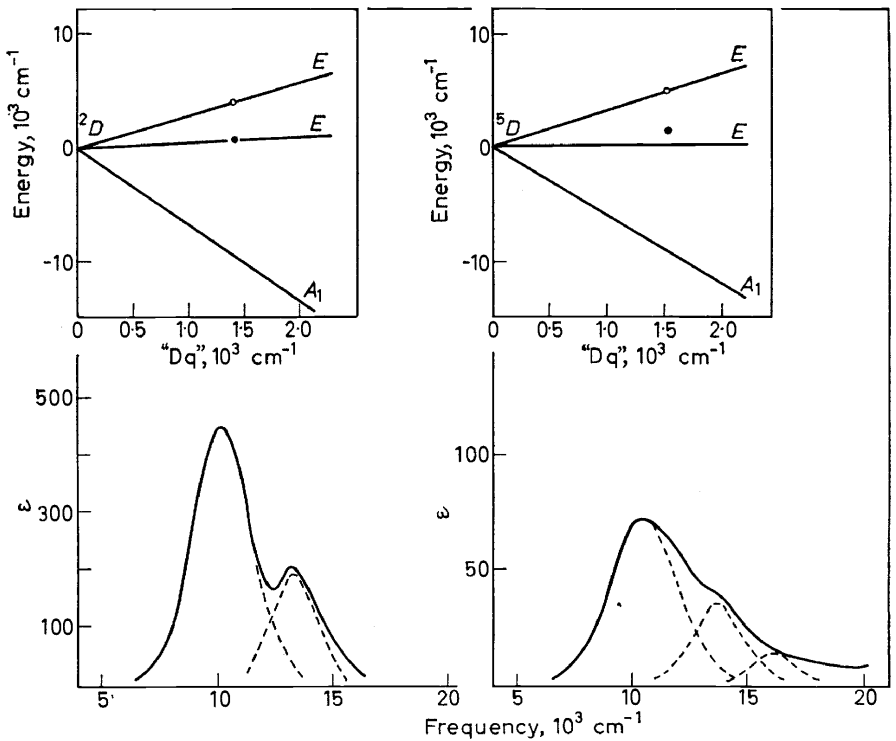


Figure 16. Energy levels diagram^{12b} for Cu^{2+} and Cr^{2+} in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of $[\text{CuBr}(\text{Me}_6\text{tren})]\text{Br}^{12a}$ and $[\text{CrBr}(\text{Me}_6\text{tren})]\text{Br}^{12b}$.

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Using the methods of crystal field theory, Ciampolini has calculated the splitting of the terms of maximum multiplicity in fields of D_{3h} and C_{3v} symmetry^{4, 12b, 51} for the configurations d^4 , d^6 , d^7 , d^8 , and d^9 .^{51a} In the spectra of the complexes $[MX(\text{Me}_6\text{tren})]X$ ($M = \text{Cr(II)}, \text{Fe(II)}, \text{Cu(II)}$) which have true C_{3v} symmetry, two bands attributable to $d-d$ transitions are observed. These are assigned to the two transitions between the three levels ($A_1 + 2E$) derived from the lowest D term^{51b}. The spectra and energy level diagrams are given in *Figures 16 and 17*.

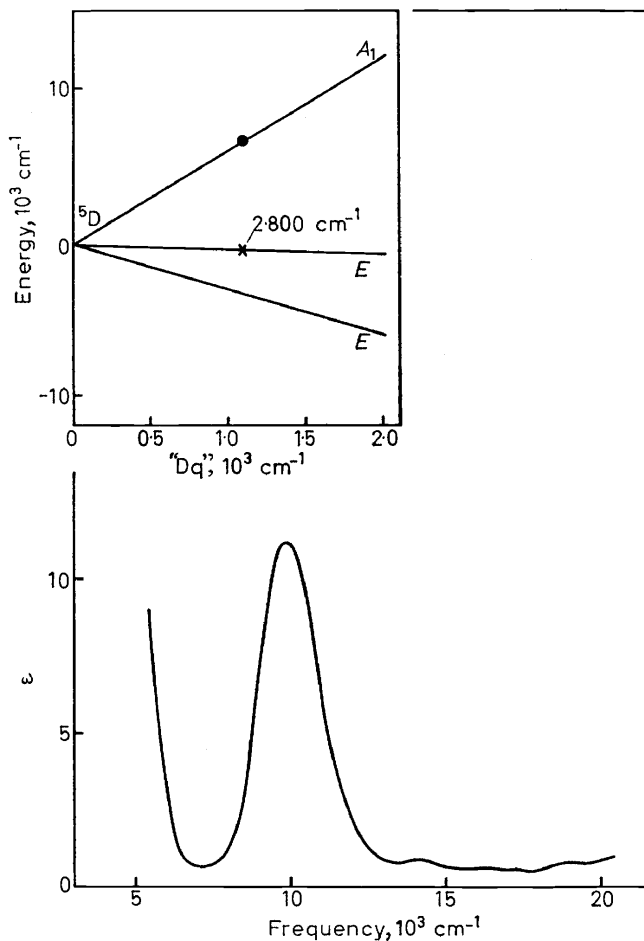


Figure 17. Energy levels diagram^{12b} for Fe^{2+} in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectrum of $[\text{FeBr}(\text{Me}_6\text{tren})]\text{Br}$

The spectra of the Co(II) and Ni(II) analogues are shown in *Figures 18 and 19* respectively. They are much richer in bands and crystal field splitting diagrams show that many transitions are expected. The frequencies of the absorption bands fit fairly well to the appropriate energy level schemes.

High-spin inner complexes

Schiff bases formed from salicylaldehyde and mono-, di-, and triamines may be 2, 3, 4, and 5-dentate and give five-coordinate inner complexes with the bivalent $3d$ metals.

The bidentate *N*-methylsalicylaldimine forms a five-coordinate zinc complex in which the phenolic oxygen atom acts as a bridge between two

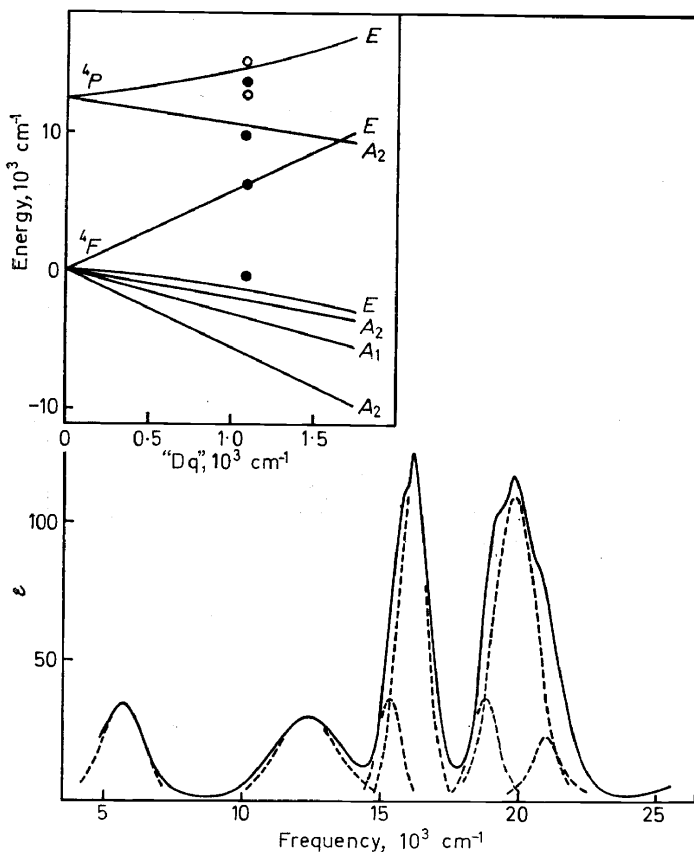


Figure 18. Energy levels diagram^{12a} for Co^{2+} in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of $[\text{CoBr}(\text{Me}_6\text{tren})]\text{Br}$

metal atoms⁵² (Figure 20). The dimeric molecule can be described as being made up of two distorted bipyramids sharing an edge, though $\text{M}-\text{O}$ bonds which hold the dimer together are longer than the $\text{M}-\text{O}$ bonds in the chelate rings. The analogous complexes of Mn and Co are isomorphous with the zinc complex, and so presumably are isostructural.

The α and β forms of bis(*N*-methylsalicylaldiminato)nickel(II), which are both planar and low-spin, dissolve in the crystal lattice of the zinc complex and assume the molecular structure of the host complex⁵³: the nickel becomes five-coordinate and paramagnetic ($\mu_{\text{eff}} = 3.1$ B.M.) with the characteristic

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spectrum of high-spin five-coordinate nickel(II) complexes. The copper complex also displays the same structural mimicry⁵³.

The copper complex, besides having the two crystalline forms α and β in which it is planar, has a third, γ form, in which the copper becomes five-coordinate by means of dimerization through bridging oxygen atoms⁵⁴ (Figure 21).

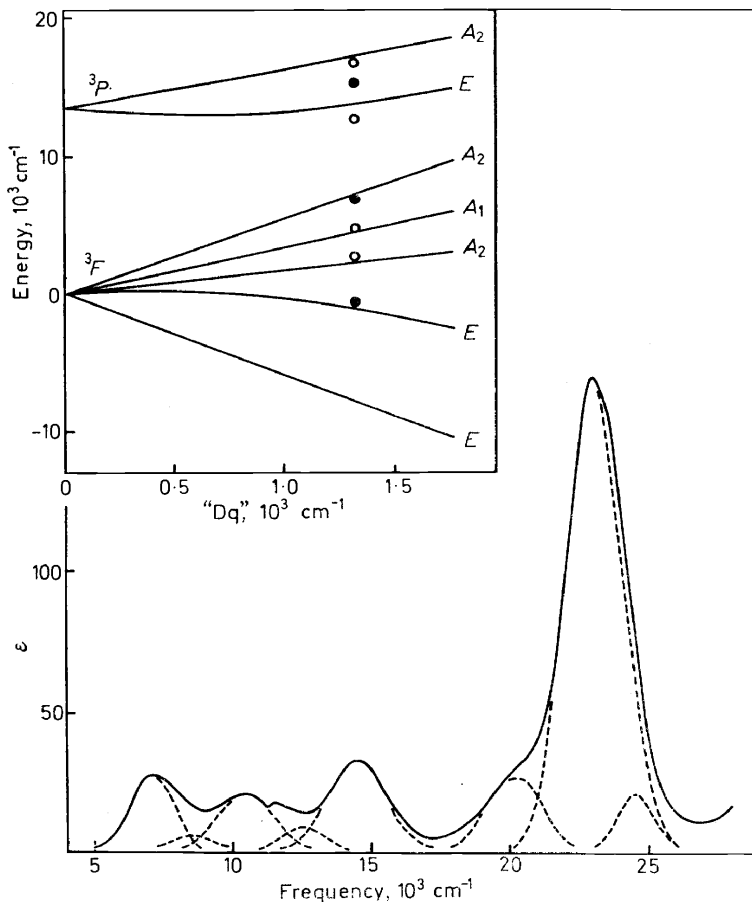
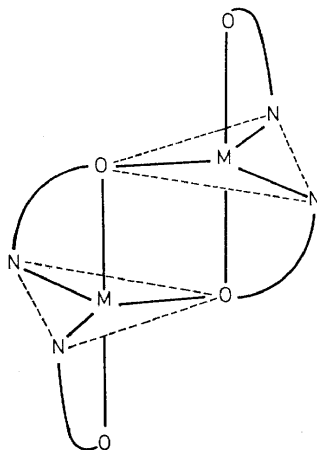


Figure 19. Energy levels diagram^{12a} for Ni²⁺ in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of [NiBr(Me₆tren)]Br

The Schiff bases derived from salicylaldehyde and 2,6-dimethylaniline and 2,4,6-tribromoaniline give cobalt(II) complexes which accept only one molecule of pyridine because of the steric hindrance of the substituted aniline moiety⁵⁵. These high-spin five-coordinate species persist in solution.

The diethylaminoethylsalicylaldehydes ([X—Sal—en—N(R)R']) are potentially tridentate, but the diethylamino group is rather bulky so that once one molecule is attached to the central metal, there is sometimes room only for two other coordinating centres⁵⁶. The two donor atoms may be:



M = Mn, Co, Zn, Ni, Cu

Figure 20. Structure of $[\text{Zn}(\text{H-Sal-N-Me})_2]^{52}$

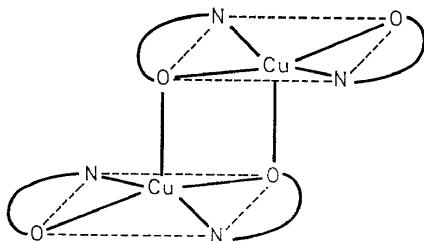


Figure 21. Structures of $[\text{Cu}(\text{H-Sal-N-Me})_2]^{54}$

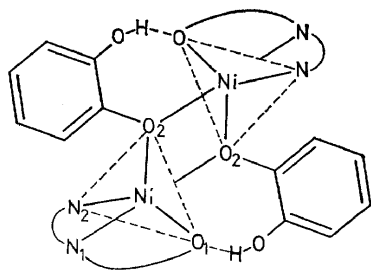
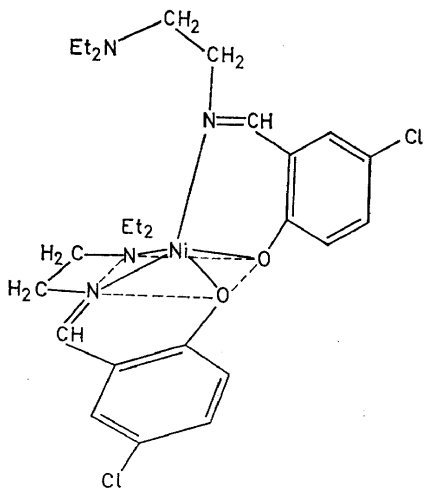


Figure 22. Structure of $\text{Ni}[5\text{Cl-Sal-cn-N}(\text{Et})_2]_2^{57}$ and $[\text{Ni}(\text{H-Sal-cn-N-Et}_2)(\text{catec})_2]^{59}$

FIVE-COORDINATION IN 3d METAL COMPLEXES

(a) Oxygen and nitrogen from a second molecule of the Schiff base. For example, the complex $[5\text{-Cl-Sal-enN}(\text{Et})_2]_2\text{Ni}$ has been shown to have a distorted square pyramidal structure⁵⁷ (Figure 22). The bonded diethylamino group is 0.2 Å farther from the nickel than the other donor groups, because of the steric interactions of the two ethyl groups. The other diethylamino group is not bonded to nickel at all. The nickel atom is 0.36 Å above the mean basal plane giving an apical angle of 101°. An isomorphous cobalt complex can be obtained⁵⁸.

(b) Oxygen atoms from pyrocatechol. The isomorphous complexes $[\text{X-Sal-en-N}(\text{Et})_2](\text{C}_5\text{H}_6\text{O}_2)\text{Ni}$ and Co are dimeric and consist of two distorted bipyramids sharing one edge⁵⁹. One oxygen atom from each catechol moiety is bridging, the other in the form of a hydroxyl group is hydrogen bonded to the salicylaldehyde oxygen atom (Figure 22).

The tetradentate Schiff bases formed from two molecules of salicylaldehyde with one of ethylenediamine or C-methylated ethylenediamine form five-coordinate complexes with copper. The former is dimeric with bridging oxygen atoms⁶⁰ and the latter is a monoquo adduct, in which the water molecule lies in the axial position of a square pyramid⁶¹. The copper is 0.2 Å above the basal plane, giving an apical angle of 96°.

When two salicylaldehyde groups are linked by the ends of a dipropylentriamine molecule, $[\text{HN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]$, or *N*-methyl derivative, $[\text{MeN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]$, pentadentate ligands result (Figure 23). Five-coordinate complexes are formed with all the metals from Mn to Zn⁶². The methyl salicylaldehyde derivatives are all isomorphous. The nickel complex

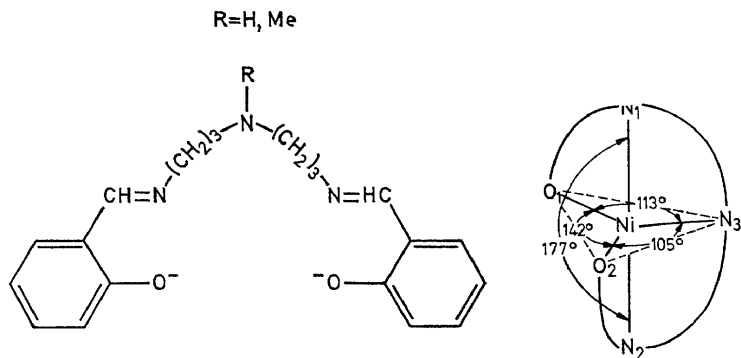


Figure 23. The anion $(\text{Sal})_2\text{-R-DPT}$ and the structure of $[\text{Ni}(\text{H-sal-MeDPT})]^{63}$

has a distorted bipyramidal structure in that the equatorial angles are not 120°. In particular the O—Ni—O angle is 142°, a value that one finds in a number of compounds with this stereochemistry. The n.m.r. spectra in solution, showing two peaks for each ring position, are in agreement with the existence of two nonequivalent aromatic fragments as shown by the structural data (Figure 24)⁶⁴. The nickel complex forms octahedral adducts with bases like pyridine, but the cobalt complex does not⁶², even though it can function as an oxygen carrier.

Vanadyl complexes

Oxovanadium(IV) cation may form five-coordinate complexes with β -diketones, particularly acetylacetonate and their imino derivatives as well as with Schiff bases⁶⁵. Recently five-coordinate oxovanadium(IV) complexes with Schiff bases of salicylaldehyde and *N*-substituted ethylenediamine have

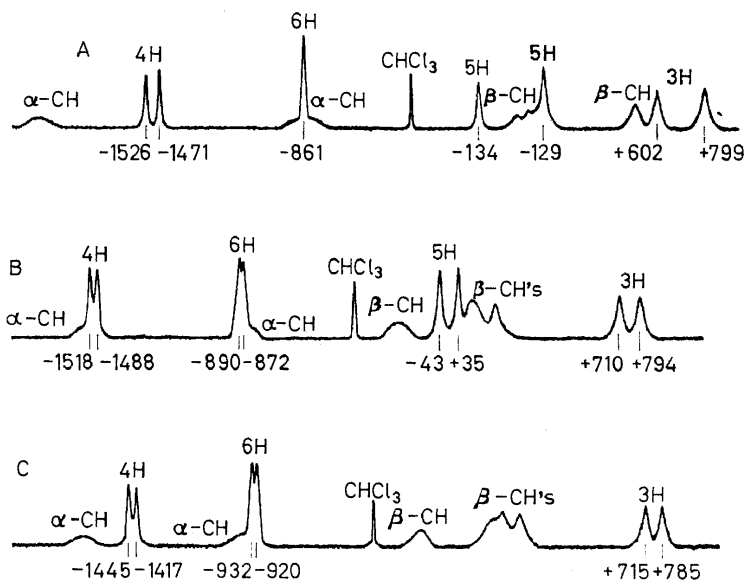


Figure 24. P.m.r. traces for ring protons of (A) $[\text{Ni}(\text{H-Sal-DPT})]$, (B) $[\text{Ni}(\text{H-Sal-MeDPT})]$, and (C) $[\text{Ni}(\text{5Cl-Sal-MeDPT})]$ in CDCl_3 ⁶⁴

been described⁶⁶. The spectrum of the complex deriving from *N*-phenylethylenediamine is reported in Figure 25. According to treatment of Selbin and Morpurgo^{67, 68}, the three low intensity bands between 10 000 and 20 000 cm^{-1} are assigned as $d-d$ transitions from the ground state d_{xy} level to the excited state levels (d_{xz} , d_{yz} , $d_{x^2-y^2}$ and d_{z^2}). This scheme is known as a clustered level scheme since the first three levels are clustered together with the next level, in a closely-knit group. Bands above 20 000 cm^{-1} are assigned as charge transfer from the bonding (mainly an oxygen orbital) to the half-filled vanadium d_{xy} orbital.

Complexes with sulphur chelates

The sulphur containing ligands which form five-coordinate complexes are all bidentate and are dialkyldithiocarbamates⁶⁹, diethyldithiophosphate (DTP)⁷⁰, ethylxantate (EX)^{70a} and dithiolates^{71, 72} (Figure 26). Five-coordination is attained by means of dimerization of the ML_2 components or the addition of a monodentate ligand. The magnetic moment of the complexes so far isolated is not known. Cr, Mn, Fe, Cu, and Zn form isomorphous dimeric, five-coordinate complexes with diethyldithiocarbamate⁶⁹. The dipropylthiocarbamate of copper is also square pyramidal with apical angle 100°. ⁷³

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Five-coordinate adducts are formed by ferric dialkyldithiocarbamates with halide ions, $[\text{FeX}(\text{S}_2\text{CNR}_2)]^{74}$ and by cobalt(II) dimethyldithiocarbamates with nitric oxide, $[\text{Co}(\text{S}_2\text{CNMe}_2)_2\text{NO}]^{75}$. The configuration of this complex (Figure 27) is square pyramidal with the cobalt 0.54 Å above

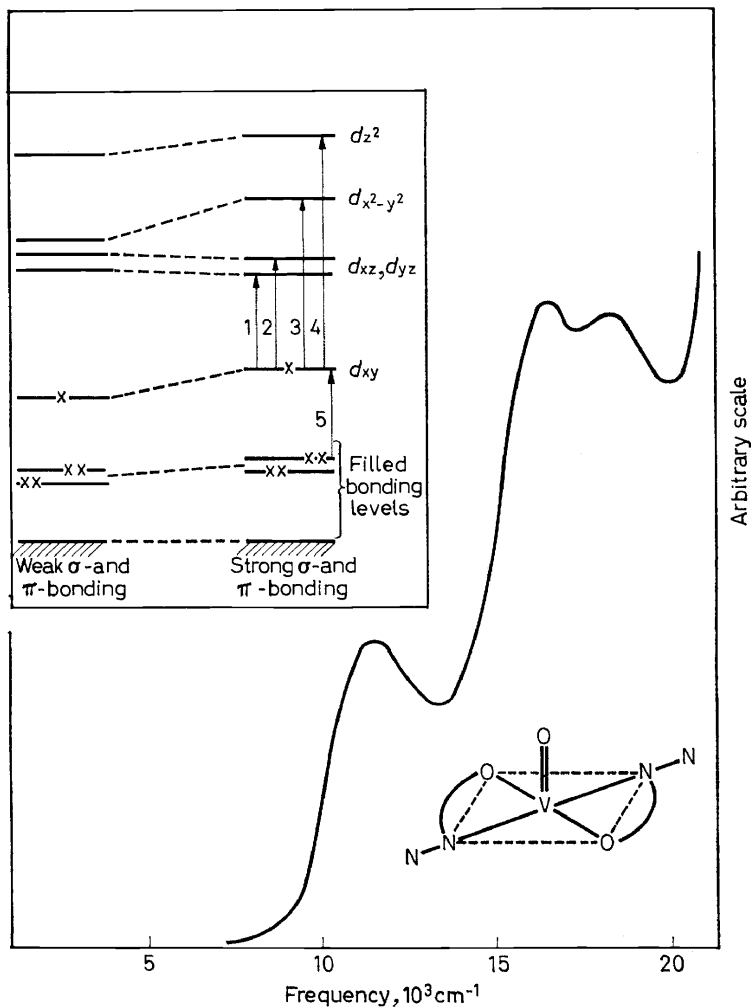


Figure 25. Energy levels diagram for oxovanadium(IV) complexes⁶⁷. Spectrum of $[\text{VO}(\text{H-Sal-en-N}(\text{H})\text{Ph})_2]$ ⁶⁶

the basal plane. The NO group is inclined at 139° to the pyramid axis and is bound to the cobalt by an unsymmetrical π bond⁹. The nickel(II) diethyldithiophosphate and ethylxanthate complexes form five-coordinate adducts with pyridine and quinoline and other organic bases, in solution⁷⁰.

The cobalt(II) dithiolate with $\text{R} = \text{CF}_3$ is dimeric in carbon tetrachloride and in the solid state. The structure is square pyramidal and is shown in

LUIGI SACCONI

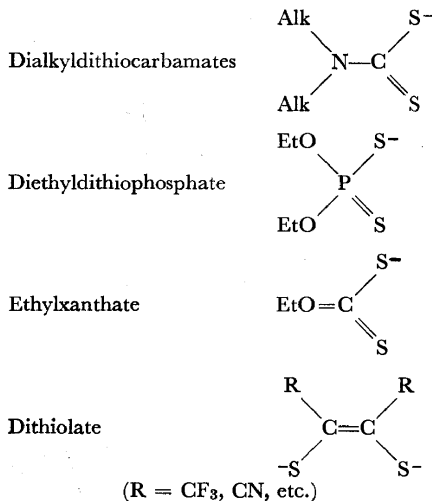


Figure 26. Some sulphur chelating anions

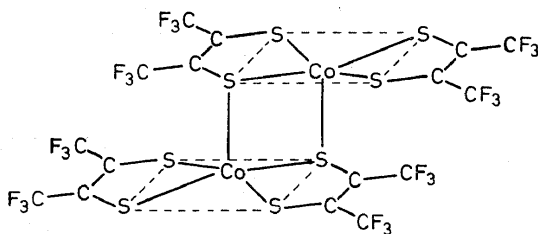
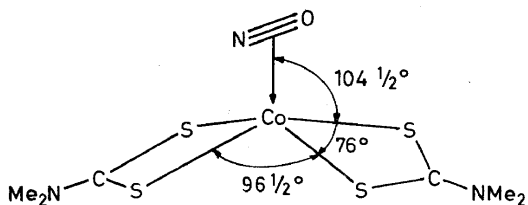


Figure 27. Structures of [Co(NO)(S₂CNMe₂)₂] and Co(dithiolate)₂⁷²

Figure 27. The apical angle is 100°. ⁷² With the dinitrilo dithiolate (R = CN) the cobalt becomes five-coordinate only by the addition of pyridine, NPh₃, PPh₃.⁷¹ These dithiolate complexes are the first examples of diamagnetic cobalt(III) though it is well known that metal oxidation states in dithiolate complexes are somewhat difficult to define. The electronic configuration may more consistently be regarded as d⁸, corresponding to cobalt(I).

FIVE-COORDINATE COMPLEXES WITH LOW-SPIN

Low-spin complexes are only possible with d^5 , d^6 , d^7 , and d^8 configurations. The ligands which give low-spin complexes of this type usually have donor atoms of low electronegativity such as P, As, or C capable of forming π bonds.

Complexes with unidentate ligands

The types of complexes found in this category are summarized in the *Table 4*. Diphenylphosphine appears to have the optimum size for the formation of five-coordinate complexes with nickel and cobalt halides.

Table 4. Five-coordinate complexes of nickel and cobalt with unidentate ligands

$\text{MX}_3(\text{PR}_3)_2^{76}$; X = Cl, Br; R = Alkyl, etc. M = Co, $\mu_{\text{eff}} = 3$ B.M.; M = Ni; $\mu_{\text{eff}} = 2$ B.M. non-polar, probably trigonal bipyramidal complexes $\text{M}^{\text{II}}\text{X}_2(\text{PPh}_2)_3^{71, 78, 80}$; X = Br, I; M = Co, Ni $[\text{Co}^{\text{I}}(\text{CNCH}_3)_5]^{+17}$; $[\text{Co}^{\text{II}}(\text{CNPh})_5]^{2+ 79}$; $[\text{Co}^{\text{II}}\text{X}_2(\text{CO})(\text{PEt}_3)_2]^{80}$; $[\text{Co}^{\text{III}}\text{X}_2(\text{NO})(\text{PEt}_3)_2]^{80}$; $[\text{Co}^{\text{I}}(\text{CO})_3(\text{PEt}_3)_2]^{+ 81}$; $[\text{Co}^{\text{I}}(\text{CO})_3(\text{PPh}_3)\text{X}]^{82}$

$\text{Co}(\text{PPh}_2)_3\text{Br}_2$ and $\text{Ni}(\text{PPh}_2)_3\text{I}_2$ have been shown by x-ray methods to be distorted bipyramids with phosphorus atoms in the apical positions (*Figure 28*)⁸³. These complexes have normal low-spin magnetic moments except the compound $\text{Ni}(\text{PPh}_2)_3\text{I}_2$.^{77, 78} This compound has a moment well below the value required for two unpaired electrons which has been attributed to a thermal population effect involving the singlet ground state and a low-lying triplet excited state. Cobalt(I) and cobalt(II) give isocyanide complexes $[\text{Co}(\text{CNCH}_3)_5]^{+17}$ and $[\text{Co}(\text{CNPh})_5]^{2+ 79}$.

The ion $[\text{Ni}(\text{CN})_5]^{3-}$ which has long been known to exist in solution⁸⁴ has recently been isolated by Raymond and Basolo⁸⁵ in the form of the compounds $[\text{Cr}(\text{NH}_3)_6]$ $[\text{Ni}(\text{CN})_5] \cdot n\text{H}_2\text{O}$ and $[\text{Cr}(\text{en})_3]$ $[\text{Ni}(\text{CN})_5] \cdot n\text{H}_2\text{O}$ and a potassium salt has also been obtained by low temperature crystallization. The unit cell of $[\text{Cr}(\text{en})_3]$ $[\text{Ni}(\text{CN})_5] \cdot 1.5 \text{H}_2\text{O}$ contains two $[\text{Ni}(\text{CN})_5]^{3-}$ units: one is a tetragonal pyramid and the other is a distorted trigonal bipyramid (*Figure 28*).⁸⁶ This bipyramid is flattened because the apical bonds are shorter than the equatorial bonds, and in the equatorial plane the angles are 141° , $(109.5^\circ$ and $109.5^\circ)$ similar to those noted before. In the square pyramid the mean apical angle is 100° and the apical bond is longer than the others.

Complexes with bidentate ligands

The greatest number of low-spin 3d five-coordinate complexes are formed by polyfunctional ligands. The following bidentate ligands have been known to give five-coordinate complexes. Some of these are shown in *Figure 29*. The DAS complexes described by Nyholm were the first low-spin five-coordinate complexes of nickel(II) to be discovered⁸⁸.

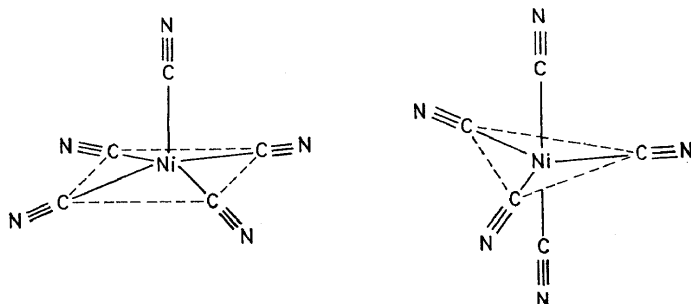
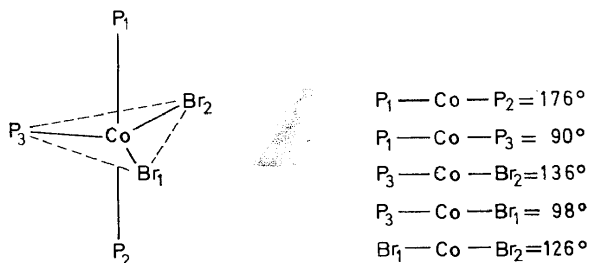


Figure 28. Structures of $CoBr_2(PHPh_2)_3$ ⁸³ and $[Cr(en)_3][Ni(CN)_5] \cdot 1.5 H_2O$ ⁸⁶

		Set of donors	Ref.
$Ph_2P-CH_2-CH_2-PPh_2$	DPPE	PP	87
	DAS	AsAs	88
	AP	PAs	89
	PS	PS	89

Figure 29. Some bidentate ligands

Complexes with tridentate ligands

The following tridentate ligands can give five-coordinate complexes (Figure 30). They form low-spin monomeric complexes with nickel halides

FIVE-COORDINATION IN 3d METAL COMPLEXES

		<i>Set of Donors</i>	<i>Ref.</i>
$\text{PhP} \begin{cases} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsMe}_2 \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsMe}_2 \end{cases}$	DAP	PAs ₂	89
$\text{MeAs} \begin{cases} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsMe}_2 \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsMe}_2 \end{cases}$	TAS	As ₃	90
$\text{S} \begin{cases} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{PPh}_2 \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{PPh}_2 \end{cases}$	PSP	SP ₂	91
$\text{S} \begin{cases} \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsPh}_2 \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{AsPh}_2 \end{cases}$	AsSAs	SAs ₂	38
$\text{PhP} \begin{cases} o\text{-C}_6\text{H}_4\text{-SMe} \\ o\text{-C}_6\text{H}_4\text{-SMe} \end{cases}$	DSP	PS ₂	89

Figure 30. Some tridentate ligands

of the general formula NiLX_2 . These complexes are generally more stable than those involving only bidentate or monodentate ligands. They are non-electrolytes though in some instances a slight dissociation occurs with the production of some square-planar species, as for example $[\text{Ni}(\text{PSP})\text{I}_2]$. The structure of $[\text{Ni}(\text{TAS})\text{Br}_2]$ was one of the first five-coordinate structures described by x-ray analysis⁹².

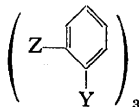
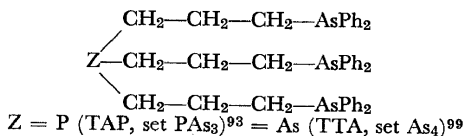
Complexes with quadridentate ligands

Five-coordinate complexes containing quadridentate ligands are the most stable and numerous. They are of the type $[\text{MLX}]\text{Y}$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4, \text{NCS}$ and $\text{Y} = \text{Br}, \text{I}, \text{ClO}_4, \text{BPh}_4$, etc. The ligands so far used are given in the *Table 5*.

All these ligands give five-coordinate complexes with nickel(II). QP⁹⁶ and PTAs⁹³ with cobalt(II) and QP⁹⁸ with iron(II). These complexes are intensely coloured, 1:1 electrolytes in organic media and stable five-coordinate. The geometry of the ligands should give the complexes a configuration which is not far from trigonal. Indeed a recent x-ray study has shown the trigonal bipyramid to be regular in the compound $[\text{NiTAP}(\text{CN})](\text{ClO}_4)$ ¹⁰¹ (*Figure 31*). Tris(*o*-methylthiophenyl)arsine (TSA, set AsS₃) does not react with the nickel halides⁸⁹.

The spectra of $[\text{M}(\text{QP})\text{X}]^+$ with $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ have been studied recently by Norgett, Thornley and Venanzi¹⁰². They have derived crystal field energy level diagrams for D_{3h} symmetry and on the basis of a crystal field model the bands in the region 5000–26 000 cm^{-1} were assigned as $d-d$ transitions. Their high intensities ($\epsilon_{\text{max}} 500-5000$) are probably due to mixing of odd configurations of higher energy.

Table 5. Some tetradentate ligands



Z = P; Y = PPh₂ (QP, set P₄)^{94, 96, 98}; = SMe (TSP, set PS₃)⁹⁹; = SeMe (TSeP, set PSe₃)¹⁰⁰; = AsPh₂ (PTAs, set PAs₃)
 Z = Sb; Y = AsPh₂ (SbTAs, set SbAs₃)⁹⁷;
 Z = As; Y = AsPh₂ (QAs, set As₄)^{94, 96}
 (MXL)⁺; M = Ni^{II} (all of the ligands);
 = Co^{II} (with QP and PTAs); = Fe^{II} (with QP)

probable stereochemistry

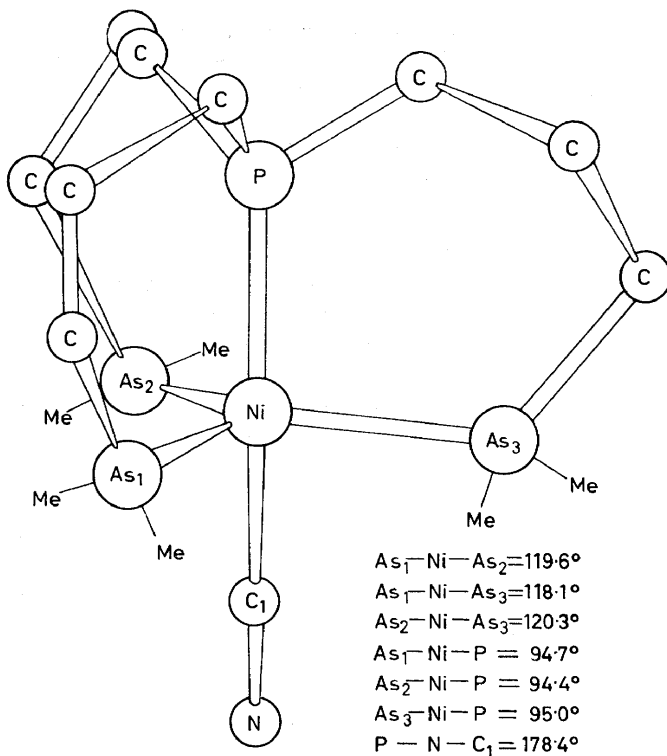


Figure 31. Structure of [Ni(CN)(TAP)](ClO₄)¹⁰¹

FIVE-COORDINATION IN 3d METAL COMPLEXES

The spectrum of $[\text{Fe}(\text{QP})\text{NO}_3]^+$ is given in *Figure 32* with the pertinent energy level diagram. The assignments made are: $(e'')^4 (e')^2 \rightarrow (e'')^3 (e')^3$ at 9000 cm^{-1} ; $\rightarrow (e'')^4 (e')^1 (a_1')$ at *c.* $18\ 000 \text{ cm}^{-1}$; $\rightarrow (e'')^3 (e')^2 (a_1')$ at $25\ 000 \text{ cm}^{-1}$ (shoulder).

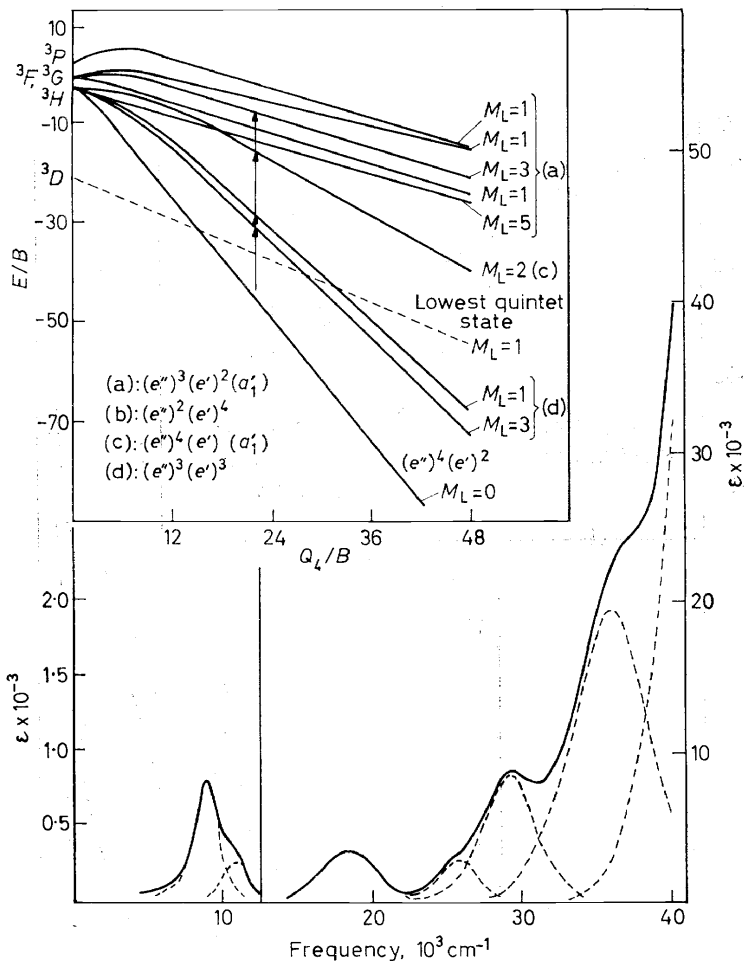


Figure 32. Energy levels diagram for Fe^{2+} in trigonal bipyramidal fields and absorption spectrum of $[\text{Fe}(\text{NO}_3)\text{QP}]^{+102}$

$[\text{Co}(\text{QP})\text{NO}_3]^+$ shows at least four bands at *c.* $10\ 000$, $15\ 000$, $20\ 000$ and $24\ 000 \text{ cm}^{-1}$ (*Figure 33*). The strong-field model leads to the following assignments: the first band is due to the $(e'')^4 (e')^3 \rightarrow (e'')^3 (e')^4$; the set of bands between $15\ 000$ and $20\ 000 \text{ cm}^{-1}$ being associated with the transition $(e'')^4 (e')^3 \rightarrow (e'')^4 (e')^2 (a_1')$. The other one electron transition is probably the shoulder at $24\ 000 \text{ cm}^{-1}$.

The spectrum of $[\text{Ni}(\text{QP})\text{Cl}]^+$ shown in *Figure 34* has two bands which have been assigned to $(e'')^4 (e')^4 \rightarrow (e'')^4 (e')^3 (a_1')$ at $17\ 000 \text{ cm}^{-1}$ and

$\rightarrow (e'')^3 (e')^4 (a_1')^2$. The second band is expected to be weaker on the basis of selection rules. It appears that the $d-d$ transitions move to lower frequency following the spectrochemical series: $P > As > S > Se > N$.

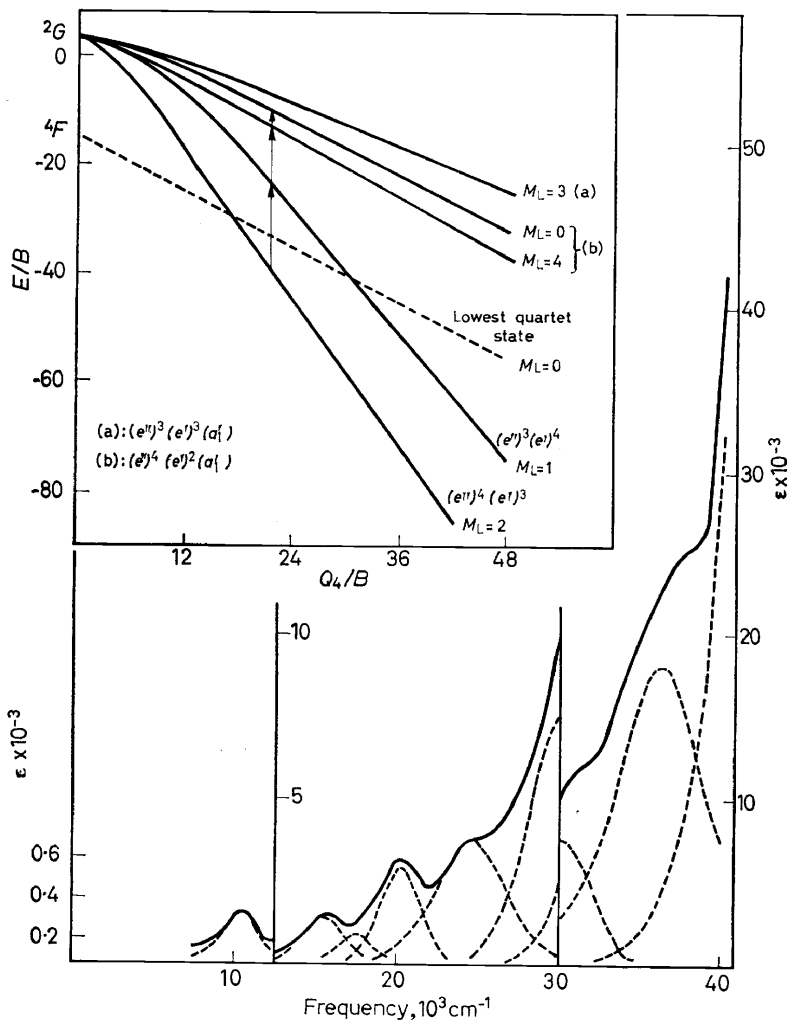


Figure 33. Energy levels diagram for Co^{2+} in trigonal bipyramidal fields and absorption spectrum of $[\text{Co}(\text{NO}_3)_2\text{QP}]^{+102}$

Complexes with hybrid ligands

We have seen that the ligands which produce high-spin complexes usually donate through nitrogen and/or oxygen atoms whereas ligands which give low-spin complexes usually contain P, As, and C, that is π bonding donor atoms of low electronegativity. It seemed then interesting to investigate the complexing capacities of ligands containing both types of donor atoms. So

FIVE-COORDINATION IN 3d METAL COMPLEXES

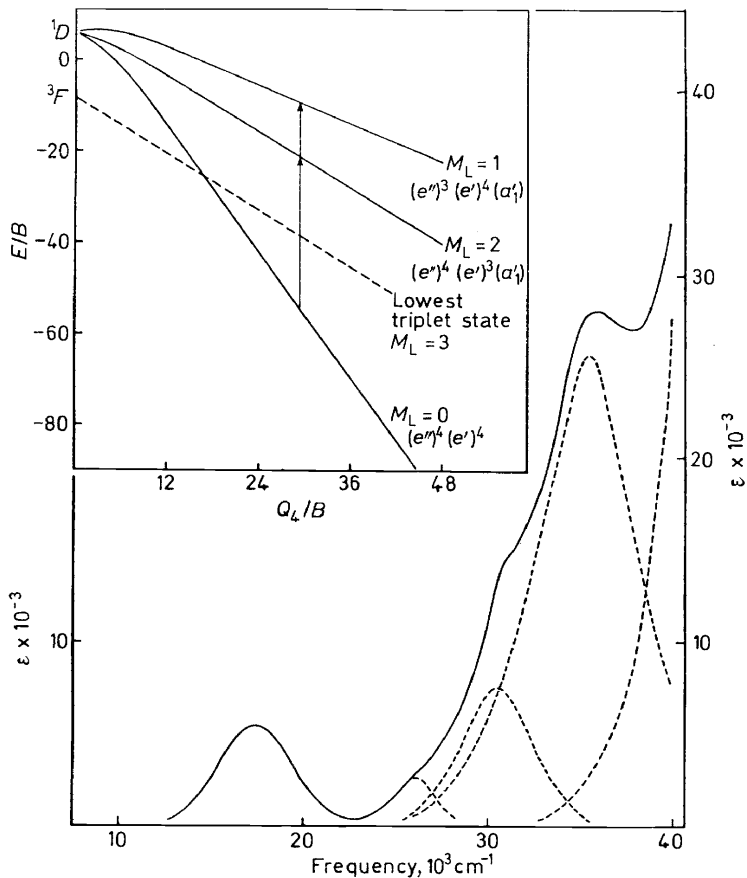


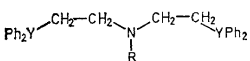
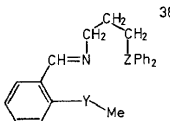
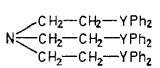

Figure 34. Energy levels diagram for Ni^{2+} in trigonal bipyramidal fields and absorption spectrum of $[\text{Ni}(\text{Cl})\text{QP}]^+$ (ref. 102) far a lot of complexes formed by this kind of ligands which can be named "hybrid ligands" have been reported in Table 6.

The first type of ligands reported in Table 6 contain N and P or As with sets NP_2 or NAS_2 . The complexes with nickel iodide are low-spin and monomeric.

The hybrid ligands of the second type are Schiff bases containing two donor atoms of high-spin type and only one of low-spin character³⁸. The five-coordinate complexes they form with nickel bromide are all high-spin³⁸. Those with nickel iodide are low-spin only when the set of donor atoms contains NNP and SNP. This seems to confirm that the electronegativity of the donor atoms plays an important role in determining the electronic ground state adopted by the metal.

The third type of ligands is tetradentate with a central nitrogen atom and three phosphorus or arsenic atoms in peripheric positions. The complexes they form with nickel are low-spin and show spectra diagnostic of trigonal bipyramidal structure. The cobalt bromide complexes are high-spin³⁸. This seems to indicate that the change from a P_4 to a NP_3 set of donors can influence the spin multiplicity of the ground state only for cobalt. The

Table 6. Some 'hybrid ligands

	38 Y = P, As; NiI ₂ L low-spin sets: NP ₂ , NAs ₂
	38 Z = P, As Y = O, S, NH NiX ₂ L X = Br high-spin X = I high- and low-spin
sets: ONP, NNP, SNP, ONAs NNAs, SNAs	
	103 Y = P, TPN, set NP ₃ Y = As, TAN, set NAs ₃
	X = Hal. M = Co ^{II} : high- and low-spin M = Ni ^{II} : low-spin

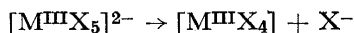
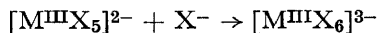
absorption maxima of trigonal bipyramidal low-spin complexes with C_{3v} symmetry are shown in Table 7. Substitution in QP of the apical P by N gives a greater lowering of the frequencies than substitution of the three equatorial P, for example, by three S. This is presumably due to the apical position of the substituted atom (in QP) which causes the highest perturbation on the ground state 1A_1 corresponding to two electrons in the d_{z^2} in C_{3v} symmetry.

Table 7

Complex	Set	$^1A_1(D) \rightarrow ^1E(D)$ and $^1A_1(D) \rightarrow ^1E(D)$ Bands (C_{3v}) for low-spin five-coordinate Ni(II) complexes (cm^{-1})		Ref.
[Ni(QP)Cl] ⁺	PP ₃	17 500	26 600	102
[Ni(TSP)Cl] ⁺	PS ₃	15 400	20 950	99
[Ni(TSeP)Cl] ⁺	PSe ₃	15 150	20 300	100
[Ni(TPN)Cl] ⁺	NP ₃	13 900	19 000	103
[Ni(TPN)Br] ⁺	NP ₃	13 600	18 600	103
[Ni(TAN)Br] ⁺	NAs ₃	13 000	17 800	103
[Ni(QAS)Br] ⁺	AsAs ₃	15 800	21 800	102

THERMODYNAMICS OF FIVE-COORDINATE COMPLEXES

An explanation for the scarcity of simple five-coordinate complexes has been proposed by Nyholm and Tobe¹⁰⁴. In the particular case of bivalent and trivalent metals they showed, using an electrostatic model, that the two processes of the type



are exothermic and the disproportionation also occurs with a decrease in energy in the system.

The stoichiometric formula of a compound is no indication of a possible five-coordinate structure. For example CoCl_2dien is in reality octahedral $\text{Co}(\text{Cl})_2\text{dien}_2$ and tetrahedral CoCl_4 .³³ The tridentate PNP ligands form five-coordinate species with nickel halides $\text{Ni}(\text{PNP})\text{X}_2$ which on warming dissociate into components of the type $[\text{Ni}(\text{PNP})\text{X}]_2[\text{NiX}_4]$ in which all nickel atoms are planar or tetrahedral four-coordinate.³⁸ Whereas the compounds $\text{CoX}_2(\text{Et}_4\text{dien})$ are five-coordinate, the nickel analogues are planar with the formula $[\text{NiX}(\text{Et}_4\text{dien})]\text{X}$.³⁴

The thermodynamics of the equilibria between five-coordinate complexes and four- or six-coordinate species have been studied in a few different systems.

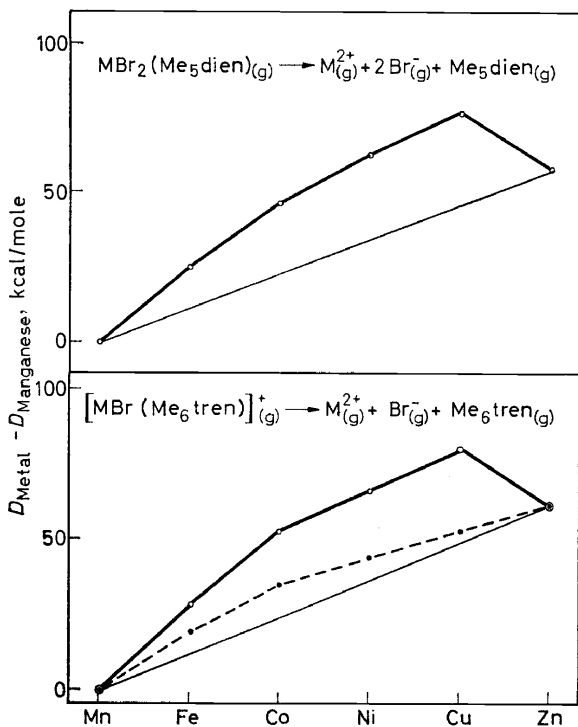
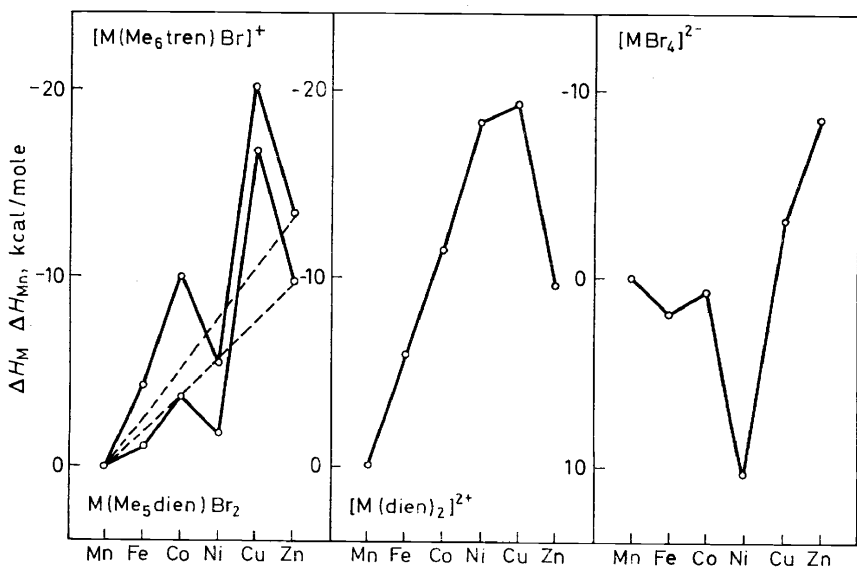
The diethylthiophosphate and ethylxantate complexes of nickel(II) form five- and six-coordinate donor acceptor adducts. The formation of $\text{Ni}(\text{DPT})\text{py}$ is accompanied by $\Delta H = -7.0$ kcal/mole and $\Delta S = -17$ e.u. changes^{70b}. Graddon has studied the formation of adducts of $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{etacac})_2$ with amines and heterocyclic bases spectrophotometrically¹⁰⁵. He correlates the formation constants with the steric requirements of the base. Turco found that the complex $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ dissolves in polar solvents to give an equilibrium mixture of tetrahedral and dimeric five-coordinate species¹⁰⁶. He also studied equilibria of the type $\text{Co}(\text{PR}_3)_2(\text{NCS})_2 + \text{PR}_3 \rightleftharpoons \text{Co}(\text{PR}_3)_3(\text{NCS})_2$ and found that the stability of the five-coordinate species followed the order $\text{PEt}_2\text{Ph} > \text{PEt}_3 > \text{PPr}_3 > \text{PEtPh}_2 > \text{PEt}_2\text{C}_6\text{H}_{11}$. Yamada has shown that tetrahedral complexes of cobalt with sterically hindered Schiff bases of the type give mono-pyridine adducts⁵⁵. On the other hand the five-coordinate complexes $(\text{X}-\text{Sal}-\text{DPT})\text{Ni}$ and $(\text{X}-\text{Sal}-\text{MeDPT})\text{Ni}$ also give mono adducts with pyridine⁶². The equilibria between five- and six-coordinate species were studied in benzene through the nuclear magnetic resonance⁶⁴ and optical spectroscopy⁶². The ΔH values vary from 5.5 to 8.8 kcal/mole that is, about half the values of ΔH for the formation of bis adducts. Surprisingly the cobalt complexes can behave as oxygen carriers but do not form pyridine adducts⁶².

Five-coordinate \rightleftharpoons six-coordinate equilibria are also well known with vanadyl compounds¹⁰⁷. Vanadyl complexes with $\text{Sal}-\text{en}(\text{R})\text{R}'$ form six-coordinate adducts with pyridine, giving equilibria between five-coordinate and six-coordinate species.

Carlin has measured the enthalpy of formation of adducts of vanadyl acetylacetonate with a number of nitrogen and oxygen donors in nitrobenzene¹⁰⁸. The values found are in general correlated to the electron donating power and steric properties of the ligands.

There are a few compounds of cobalt and nickel which may change from five-coordinate to four-coordinate when one atom of a mono or polydentate ligand becomes detached. Examples are furnished by the compounds NiX_2MOB , NiX_2MAB , NiX_2PSP , $\text{MX}_2(\text{daes})$, and $\text{NiX}_2(\text{MSB})$.

Calorimetric measurements on the two series of compounds $[\text{M}(\text{Me}_5\text{dien})\text{Br}_2]$ and $[\text{M}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) give the values of ΔH of formation for both the gaseous compounds (Figure 35), and for aqueous solutions¹⁰⁹ (Figure 36). The enthalpy of the reaction $\text{MBr}_{2(\text{aq})} + \text{Ligand}_{(\text{aq})} \rightarrow \text{M Ligand Br}_{2(\text{s})}$ increases to a maximum with Cu such that the order of stability is $\text{Mn} < \text{Fe} \approx \text{Ni} < \text{Co} < \text{Zn} < \text{Cu}$ for five-coordinate complexes. This order should be compared to the well known


 Figure 35. Relative bond dissociation enthalpies for two series of five-coordinate complexes¹⁰⁹

 Figure 36. Relative enthalpy changes for the formation of three series of complexes in aqueous solution¹⁰⁹

sequence for octahedral compounds¹¹⁰ Mn < Fe < Co < Ni < Cu > Zn and for tetra-halo-complexes Ni < Fe < Co < Mn < Cu < Zn.¹¹¹ This can be attributed at least in part to CFSE differences. Maximum CFSE stabilization of exa-aquo ions occurs with Ni, but in the five-coordinate series it is expected to occur with Cu.¹⁰⁹ These results may explain why the non-methylated ligand tren gives five-coordinate species with Cu(II) and Co(II) in aqueous solution whereas with Ni(II) an octahedral complex is formed.

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