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 exceptional. 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 structure (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 conclusion. 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–non-bonded electron pair interactions, the trigonal bipyramidal configuration is favoured. 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 expected. 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 configurations. 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 $d^4$, $d^5$ and low-spin $d^8$. If the ligand is polydentate, the steric...
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 complexes

<table>
<thead>
<tr>
<th>d</th>
<th>S</th>
<th>Square Pyr.</th>
<th>Trig. Bipy.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>β = 90°</td>
<td>β = 105°</td>
</tr>
<tr>
<td>d⁵</td>
<td>3/2</td>
<td>0.894</td>
<td>0.628</td>
</tr>
<tr>
<td>d⁶</td>
<td>1</td>
<td>1.192</td>
<td>0.812</td>
</tr>
<tr>
<td>d⁷</td>
<td>1/2</td>
<td>1.131</td>
<td>0.920</td>
</tr>
<tr>
<td>d⁸</td>
<td>0</td>
<td>1.192</td>
<td>0.888</td>
</tr>
</tbody>
</table>

#### Low-Spin

#### High-Spin

| d, d⁶ | 0.298  | 0.184  | 0.168 |
| d², d⁷ | 0.596  | 0.368  | 0.337 |
| d³, d⁸ | 0.635  | 0.476  | 0.397 |
| d⁴, d⁹ | 0.596  | 0.444  | 0.456 |

### Table 2. Apical angles of square pyramidal structures

<table>
<thead>
<tr>
<th>Complex</th>
<th>β</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(C104)(OAsMePh2)4]ClO4</td>
<td>100°</td>
<td>5</td>
</tr>
<tr>
<td>[Cr(en)]2[Ni(CN)6].1.5 H2O</td>
<td>100°</td>
<td>6</td>
</tr>
<tr>
<td>α-Chlorohaeminiron(iii)</td>
<td>102°</td>
<td>7</td>
</tr>
<tr>
<td>Methoxyiron(m)mesoporphyrin</td>
<td>103°</td>
<td>8</td>
</tr>
<tr>
<td>Co(S2CNMe2)2(NO)</td>
<td>103°</td>
<td>9</td>
</tr>
<tr>
<td>VO(acac)2</td>
<td>106°</td>
<td>10</td>
</tr>
</tbody>
</table>

regular trigonal bipyramidal structure occurs in the complex [Cr (NH3)6] [CuCl3]11 (Figure 3). However, the complexes [MBr (Me₆ tren)] Br12 [Me₆ tren = tris (2-dimethylaminoethyl)amine; M = Mn to Zn] retain the three-fold symmetry axis, with the angle β ≈ 82° ranging from 81° to 84°,13 and C₃ symmetry is also retained in the cluster compounds Cu₄ OCl₆ (OPPh₃)₄14 (Figure 3) and Cu₄ OCl₆ (py)₄15. All other known structures have lower symmetry. There is quite a large group of compounds which deviate from regular D₃h 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] ClO₄ 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 d⁵, d⁶, d⁷ and d⁸ can give both types of compounds. This can be understood by looking at an
Figure 3. Structural data for [Cr(NH₃)₆][CuCl₅]₁₁, [MBr(Me₆tren)]Br, and Cu₄OCl₆(OPPh₃)₄. The orbital splitting diagram for C₄ᵥ and D₃h fields (Figure 5). The highest orbital is well separated in energy from the others, the dₓ² - y² and the dₕ orbital, respectively. When the energy separation between the highest orbital and
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.

![Diagram of 3d orbitals]

_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$_3$)$_2$ was found to have a distorted trigonal bipyramidal structure, point group $C_{2v}$.

<p>| | |</p>
<table>
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<tbody>
<tr>
<td>Ti</td>
<td>TiX$_3$(NMe$_3$)$<em>2$$</em>{18, 19}$, TiX$_4$(NMe$<em>3$)$</em>{18, 20}$, TiX$_4$(SR)$<em>2$$</em>{23}$</td>
</tr>
<tr>
<td>V</td>
<td>VX$_3$(NP$_3$)$<em>2$$</em>{21, 22}$, VX$_3$(SR)$<em>2$$</em>{19, 22}$, VX$_3$(PR)$<em>3$$</em>{21}$, VX$_3$(OPR)$<em>3$$</em>{21}$, VX$_4$(NHMe$_2$)$<em>2$$</em>{24}$, VX$_4$(NMe$_3$)$<em>2$$</em>{24}$, VOCl$_2$(OPPh$_3$)$<em>2$$</em>{25}$, M$_2$VOCl$_4$ (M = pyH$^+$, quinH$^+$, iso-quinH$^+$)</td>
</tr>
<tr>
<td>Cr</td>
<td>CrX$_3$(NMe$_3$)$<em>2$$</em>{27}$</td>
</tr>
</tbody>
</table>

and the other analogues with vanadium and chromium were found to be isomorphous. The lowest complex here reported CrCl$_3$·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 state.

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 \( \text{VOCl}_2 (\text{OPPh}_3)_2 \), \( M_2^1 [\text{VOCl}_4] \) where \( M \) is pyridinium, quinolinium and isoquinolinium.

Examples of high-spin compounds of the type \([MX_5]^{n-}\) in which five halides are coordinated around one metal ion, are scarce. The only certain examples occur in \([\text{Cr(NH}_3)_6][\text{CuCl}_5]\) in which the ion \([\text{CuCl}_5]^{3-}\) has full \( D_{3h} \) symmetry and in \([\text{NH}_2\text{Me}_2][\text{CuCl}_5]\) which consists of dimeric \( 	ext{Cu}_2\text{Cl}_6 \) units (mean \( \text{Cu—Cl} \) 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: \((\text{Et}_4\text{N})_2[\text{MnCl}_5]\) and \((\text{K}, \text{Rb}, \text{Cs})_2[\text{MnF}_5]\) which have magnetic moments corresponding to four unpaired electrons.

A set of five donor oxygen atoms is found in the compound \([\text{Co(OAsMePh}_2)_4\text{ClO}_4]\) (dO4) 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 apical. The compounds are high-spin and the cobalt(II) moment of 5.5 B.M. is unusually high.

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

**Adducts with tridentate ligands**

These complexes have the general formula \( MX_2L \) where \( X = \text{Cl, Br, I, NCS and} \) \( L \) 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.
Ligands of the type shown in Figure 9 (dien) have been used by Ciampolini and by Gray to give many five-coordinate complexes. All the complexes with \( R = \text{Me} \) are five-coordinate in the solid state and in solution. The compounds \( \text{MBr}_2 (\text{Me}_5 \text{dien}) \) are all isomorphous. The \( \text{NiCl}_2 (\text{Et}_4 \text{dien}) \) is a square-planar complex which should be written as \([\text{NiCl} (\text{Et}_4 \text{dien})]\text{Cl} \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Energy levels diagram for \( \text{Co}^{2+} \) in square pyramidal fields. Black circles indicate the frequencies of the band maxima in the reflectance spectrum of \([\text{Co(ClO}_4](\text{OAsPh}_2\text{Me})_4]\text{(ClO}_4) \).}
\end{figure}

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:

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Figure 8. Energy levels diagram for Ni$^{2+}$ in square pyramidal fields. Black circles indicate the frequencies of the band maxima in the reflectance spectrum of [Ni(ClO$_4$)$_2$(OAsPh$_2$Me)$_4$](ClO$_4$)$_2$. $^{3E}$ base = 0.9 $10^3$ cm$^{-1}$.

Figure 9. Some tridentate ligands

\[
\begin{align*}
&\text{MX}_2L, \text{X} = \text{Hal., NCS} \\
&\text{Y} = \text{NMMe} ; R = \text{Me} ; M = \text{Mn to Zn} \\
&Y = \text{O} ; R = \text{Me} ; M = \text{Fe to Cu} \\
&Y = \text{S} ; R = \text{Me} ; M = \text{Co, Ni} \\
&Y = \text{NH} ; R = \text{Et} ; M = \text{Co, Ni(sln)} \\
\end{align*}
\]

Ref. 33

Ref. 4

Ref. 34

Figure 9. Some tridentate ligands
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CoCl₂(Me₅ dien)³⁵ and CoCl₂(Et₄ 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 NR₂ 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 Y = NH³⁷; the ligands with O³⁸ and S³⁹ as the third donor atom give tetrahedral complexes with this metal.

![Figure 10. Structures of the compounds CoCl₂(Me₅dien)³⁵ and CoCl₂(Et₄dien) ³⁶](image.png)

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. CoCl₂·paphy complex has an intermediate structure⁴² (Figure 13). ZnCl₂·terpyridyl has a distorted trigonal bipyramidal structure⁴³ and the Co, Ni, and Cu complexes are isostructural with it³² (Figure 13). The complexes [CuX(dipy)₂]X and [CuX(phen)₂]X (X = halogen) are well
known\textsuperscript{44} and x-ray analyses give the distances in $[\text{CuI(dipy)}_2]\text{I}$ as Cu—N 2.02 Å, and Cu—I 2.71 Å\textsuperscript{45} (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 (tren) $[\text{Cu}((\text{H}_2\text{N—CH}_2\text{CH}_2)_3\text{N})\text{NCS}]\text{NCS}$, $([\text{Cu(tren)NCS}]\text{NCS})$ revealed a trigonal bipyramidal structure\textsuperscript{46} (Figure 14). The equatorial angles and bond lengths were unexpectedly found to be unequal, giving the structure a slight distortion. Co(NCS)\textsubscript{2} and CoI\textsubscript{2} also give five-coordinate adducts with tris-(2-aminoethyl)amine\textsuperscript{47}. With nickel(II) however tren gives octahedral adducts\textsuperscript{48} which persist in solution\textsuperscript{49}, and a similar situation is not unlikely with Mn(II) and Fe(II)\textsuperscript{50}.

The hexamethyl derivative of tren, (Me\textsubscript{6} tren), forms only five-coordinate species with the divalent 3d metal halides\textsuperscript{12}. Each set of halide complexes forms an isomorphous group. The structure of [CoBr(Me\textsubscript{6}tren)]Br is shown in Figure 15; it is a trigonal bipyramid with $C_{3v}$ symmetry\textsuperscript{13}. 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 structure\textsuperscript{12}. 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 12. Five-coordinate complexes with N,N,N-tridentate ligands*
Tris(2-methylthioethyl)amine, [(MeSCH$_2$CH$_2$)$_3$N], (set NS$_3$) forms a complex with cupric bromide which is a 1:1 electrolyte in organic solvents$^4$. This compound probably has a bipyramidal structure.
Figure 15. Structure of [CoBr(Me₅tren)]Br

Figure 16. Energy levels diagram for Cu²⁺ and Cr³⁺ in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of [CuBr(Me₅tren)]Br and [CrBr(Me₅tren)]Br.
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\(^4,^{12b, \text{p}1} \) for the configurations \( d^4, d^6, d^7, d^8, \) and \( d^9 \).\(^{51a} \) In the spectra of the complexes \([MX(Me_6tren)]X (M = \text{Cr}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Cu}^{\text{II}})\) 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.

\[ \text{Figure 17. Energy levels diagram}^{12b} \text{ for Fe}^{\text{III}} \text{ in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectrum of [FeBr(Me_6tren)]Br.} \]

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 metal atoms\textsuperscript{53} (Figure 20). The dimeric molecule can be described as being made up of two distorted bipyramids sharing an edge, though M—O bonds which hold the dimer together are longer than the M—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 complex\textsuperscript{53}: 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 mimicry.

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 atoms (Figure 21).

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 moiety. These high-spin five-coordinate species persist in solution.

The diethylaminoethylsalicyldimines ([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 centres. The two donor atoms may be:

![Energy levels diagram for Ni²⁺ in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of [NiBr(Me₆tren)]Br.](image)

*Figure 19. Energy levels diagram for Ni²⁺ in trigonal bipyramidal fields. Black circles indicate the frequencies of the band maxima in the spectra of [NiBr(Me₆tren)]Br.*
Figure 20. Structure of \([\text{Zn}(\text{H-Sal-N-Me})_2]\)\(^{58}\)

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

Figure 22. Structure of \([\text{Ni}(5\text{Cl-Sal-en-N(Et)_2})_2]\)\(^{57}\) and \([\text{Ni}(\text{H-Sal-en-N-Et}_2)_{(\text{catec})_2}]^{59}\)
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(a) Oxygen and nitrogen from a second molecule of the Schiff base. For example, the complex \([\text{5-Cl-Sal-enN(Et)}_2\text{Ni}]\) has been shown to have a distorted square pyramidal structure (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 obtained.

(b) Oxygen atoms from pyrocatechol. The isomorphous complexes \([\text{X-Sal-en-N(Et)}_2\text{Ni}]\) and \([\text{X-Sal-en-N(Et)}_2\text{Co}]\) are dimeric and consist of two distorted bipyramids sharing one edge. 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 atoms and the latter is a monoaquo adduct, in which the water molecule lies in the axial position of a square pyramid. 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 dipropylene-triamine molecule, \([\text{HN(CH}_2\text{CH}_2\text{CH}_2\text{NH}_2}_2\text{Ni}]\) or \([\text{N-methyl derivative, MeN(CH}_2\text{CH}_2\text{CH}_2\text{NH}_2}_2\text{Ni}]\), pentadentate ligands result. Five-coordinate complexes are formed with all the metals from Mn to Zn. The methyl salicylaldehyde derivatives are all isomorphous. The nickel complex 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 unequivocal aromatic fragments as shown by the structural data (Figure 24). The nickel complex forms octahedral adducts with bases like pyridine, but the cobalt complex does not, even though it can function as an oxygen carrier.
Vanadyl complexes

Oxovanadium(IV) cation may form five-coordinate complexes with $\beta$-diketones, particularly acetylacetone and their imino derivatives as well as with Schiff bases. Recently five-coordinate oxovanadium(IV) complexes with Schiff bases of salicylaldehyde and N-substituted ethylenediamine have been described. The spectrum of the complex deriving from N-phenyl-ethylenediamine is reported in Figure 25. According to treatment of Selbin and Morpurgo, 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 dialkylthiocarbamates, diethylthiophosphate (DTP), ethylxantate (EX) and dithiolates (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 diethylthiocarbamate. The dipropyliothiocarbamate of copper is also square pyramidal with apical angle 100°.
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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) dimethylthiocarbamates with nitric oxide, \([\text{Co}(\text{S}_2\text{CNMe}_2)_2\text{NO}])^{78}\). The configuration of this complex (Figure 27) is square pyramidal with the cobalt 0.54 Å above the basal plane. The NO group is inclined at 139° to the pyramid axis and is bound to the cobalt by an unsymmetrical \(\pi\) bond\(^9\). The nickel(II) diethyl-dithiophosphate and ethylxanthate complexes form five-coordinate adducts with pyridine and quinoline and other organic bases, in solution\(^70\).

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

Figure 25. Energy levels diagram for oxovanadium(IV) complexes\(^87\). Spectrum of \([\text{VO}(\text{H—Sai—en—N(H)Ph})_2])^{66}\)
Figure 26. Some sulphur chelating anions

![Diagram of sulphur chelating anions]

Figure 27. Structures of [Co(NO)(S_2CNMe_2)_2] and Co(dithiolate)_2

![Diagram of Co(dithiolate)_2 structures]

Figure 27. The apical angle is 100°. With the dinitrilo dithiolate (R = CN) the cobalt becomes five-coordinate only by the addition of pyridine, NPh_3, PPh_3. 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 d^8, corresponding to cobalt(II).
Five-coordinate complexes with low-spin

Low-spin complexes are only possible with d⁵, d⁶, d⁷, and d⁸ 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

| MX₃(PR₃)₂₇₆; X = Cl, Br; R = Alkyl, etc. | M = Co, μₑffective = 3 B.M.; M = Ni; μₑffective = 2 B.M. |
| non-polar, probably trigonal bipyramidal complexes | |
| M = Co, Ni | |
| [Co(CNCH₃)₅]²⁺ | |
| [Co(CNPh)₅]²⁺ | |
| [Co(CO)₃(NO)(PEt₃)₂]²⁺ | |
| [Co(CO)₃(PPh₃)X]³⁺ | |
| Co(PPh₂)₃Br₂ and Ni(PPh₂)₃I₂ have been shown by x-ray methods to be distorted bipyramids with phosphorus atoms in the apical positions (Figure 28). These complexes have normal low-spin magnetic moments except the compound Ni(PPh₂)₃I₂. 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 [Co(CNCH₃)₅]⁺ and [Co(CNPh)₅]²⁺. The ion [Ni(CN)₅]³⁻ which has long been known to exist in solution has recently been isolated by Raymond and Basolo in the form of the compounds [Cr(NH₃)₆][Ni(CN)₅]·nH₂O and [Cr(en)₃][Ni(CN)₅]·nH₂O and a potassium salt has also been obtained by low temperature crystallization. The unit cell of [Cr(en)₃][Ni(CN)₅]·nH₂O contains two [Ni(CN)₅]³⁻ units: one is a tetragonal pyramid and the other is a distorted trigonal bipyramid (Figure 28). 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° and 109.5°) 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 discovered.
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

<table>
<thead>
<tr>
<th>Set of Donors</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–AsMe$_2$</td>
<td>DAP</td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–AsMe$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_3$–CH$_2$–CH$_2$–AsMe$_2$</td>
<td>MeAs</td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–PPh$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–PPh$_2$</td>
<td>S</td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–PPh$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–AsPh$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$–CH$_2$–CH$_2$–AsPh$_2$</td>
<td></td>
</tr>
<tr>
<td>o-C$_6$H$_4$–SMe</td>
<td></td>
</tr>
<tr>
<td>o-C$_6$H$_4$–SMe</td>
<td>PhP</td>
</tr>
</tbody>
</table>

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 [Ni(PSP)$_2$]. The structure of [Ni(TAS)Br$_2$] was one of the first five-coordinate structures described by x-ray analysis$^{92}$.

**Complexes with quadridentate ligands**

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

All these ligands give five-coordinate complexes with nickel($\eta$). QP$^{96}$ and PTA$_8$ with cobalt($\eta$) and QP$^{98}$ with iron($\eta$). 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 [NiTAP(CN)](ClO$_4$)$_2$ (Figure 31). Tris(o-methylthiophenyl)arsine (TSA, set AsS$_3$) does not react with the nickel halides$^{89}$.

The spectra of [M(QP)X]$^+$ with M = Fe, Co, Ni have been studied recently by Norgett, Thornley and Venanzi$^{102}$. 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 ($\varepsilon_{\text{max}}$ 500–5000) are probably due to mixing of odd configurations of higher energy.
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Table 5. Some tetradentate ligands

<table>
<thead>
<tr>
<th>Ligand Structure</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$—CH$_2$—CH$_2$—AsPh$_2$</td>
<td></td>
</tr>
<tr>
<td>Z—CH$_2$—CH$_2$—CH$_2$—AsPh$_2$</td>
<td></td>
</tr>
<tr>
<td>CH$_2$—CH$_2$—CH$_2$—AsPh$_2$</td>
<td></td>
</tr>
<tr>
<td>Z = P (TAP, set PAs$_3$)$_9$ = As (TTA, set As$_4$)$_9$</td>
<td></td>
</tr>
</tbody>
</table>

Z = P; Y = PPh$_3$ (QP, set P$_4$)$_{94,96,98}$; = SMe (TSP, set PS$_3$)$_{99}$; = SeMe (TSeP, set PSe$_3$)$_{100}$; = AsPh$_3$ (PTAs, set PAs$_3$) $Z =$ Sb; $Y =$ AsPh$_2$ (SbTAs, set SbAs$_3$)$_{97}$; $Z =$ As; $Y =$ AsPh$_2$ (QAs, set As$_4$)$_{94,96}$ (MXL)$^+$; $M =$ Ni$^{II}$ (all of the ligands); $= $ Co$^{II}$ (with QP and PTAs); $= $ Fe$^{II}$ (with QP)

probable stereochemistry

![Structure of [Ni(CN)(TAP)][ClO$_4$] $^{101}$](image)

Figure 31. Structure of [Ni(CN)(TAP)][ClO$_4$] $^{101}$
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$^{-1}$; $(e'')^4 (e')^1 (a_1')$ at c. 18 000 cm$^{-1}$; $(e'')^3 (e')^2 (a_1')$ at 25 000 cm$^{-1}$ (shoulder).

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

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

The spectrum of $[\text{Ni(QP)Cl}]^+$ 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 cm$^{-1}$ and
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$\rightarrow (e'^{\prime})^{2} (e'^{\prime})^{4} (a''_{1})^{2}$. 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$^{3+}$ in trigonal bipyramidal fields and absorption spectrum of [Co(NO$_{3}$)QP]$^{+}$](image)

**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 $\pi$ bonding donor atoms of low electronegativity. It seemed then interesting to investigate the complexing capacities of ligands containing both types of donor atoms. So
Figure 34. Energy levels diagram for Ni$^{2+}$ in trigonal bipyramidal fields and absorption spectrum of [Ni(Cl)$_2$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 character$^{38}$. The five-coordinate complexes they form with nickel bromide are all high-spin$^{38}$. 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-spin$^{38}$. 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
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Table 6 Some 'hybrid ligands

![Chemical structure]

\[ \begin{align*}
\text{Y} &= \text{P, As;} \\
\text{NiI}_2\text{L} \text{ low-spin sets: NP}_2, \text{NAS}_2 \\
\text{Z} &= \text{P, As;} \\
\text{Y} &= \text{O, S, NH;} \\
\text{NiX}_2\text{L} \\
\text{X} &= \text{Br high-spin;} \\
\text{X} &= \text{I high- and low-spin}
\end{align*} \]

sets: \text{ONP, NNP, SNP, ONAs NNAs, SNAs}

103 absorption maxima of trigonal bipyramidal low-spin complexes with \( C_{3v} \) symmetry are shown in Table 7. Substitution in QP of the apical \( \text{P} \) by \( \text{N} \) gives a greater lowering of the frequencies than substitution of the three equatorial \( \text{P} \), for example, by three \( \text{S} \). This is presumably due to the apical position of the substituted atom (in QP) which causes the highest perturbation on the ground state \( ^1\text{A}_1 \) corresponding to two electrons in the \( d_{z^2} \) in \( C_{3v} \) symmetry.

Table 7

<table>
<thead>
<tr>
<th>Complex</th>
<th>Set</th>
<th>( \Delta \text{cm}^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(QP)}\text{Cl}]^+)</td>
<td>\text{PP}_3</td>
<td>17 500 26 600</td>
<td>102</td>
</tr>
<tr>
<td>([\text{Ni(TSP)}\text{Cl}]^+)</td>
<td>\text{PS}_3</td>
<td>15 400 20 950</td>
<td>99</td>
</tr>
<tr>
<td>([\text{Ni(TSeP)}\text{Cl}]^+)</td>
<td>\text{PSe}_3</td>
<td>15 150 20 300</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Ni(TPN)}\text{Cl}]^+)</td>
<td>\text{NP}_3</td>
<td>13 900 19 000</td>
<td>103</td>
</tr>
<tr>
<td>([\text{Ni(TPN)}\text{Br}]^+)</td>
<td>\text{NP}_3</td>
<td>13 600 18 600</td>
<td>103</td>
</tr>
<tr>
<td>([\text{Ni(TAN)}\text{Br}]^+)</td>
<td>\text{NAS}_3</td>
<td>13 000 17 800</td>
<td>103</td>
</tr>
<tr>
<td>([\text{Ni(QAS)}\text{Br}]^+)</td>
<td>\text{AsAS}_3</td>
<td>15 800 21 800</td>
<td>102</td>
</tr>
</tbody>
</table>

THERMODYNAMICS OF FIVE-COORDINATE COMPLEXES

An explanation for the scarcity of simple five-coordinate complexes has been proposed by Nyholm and Tobe\(^{104}\). In the particular case of bivalent and trivalent metals they showed, using an electrostatic model, that the two processes of the type

\[ [\text{M}^{III}\text{X}_5]^{2-} + \text{X}^- \rightarrow [\text{M}^{III}\text{X}_6]^{3-} \]

\[ [\text{M}^{III}\text{X}_6]^{2-} \rightarrow [\text{M}^{III}\text{X}_4] + \text{X}^- \]

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$_2$dien is in reality octahedral Codien$_2$ and tetrahedral CoCl$_4$. The tridentate PNP ligands form five-coordinate species with nickel halides Ni(PNP)X$_2$ which on warming dissociate into components of the type [Ni(PNP)X]$_2$[NiX$_4$] in which all nickel atoms are planar or tetrahedral four-coordinate. Whereas the compounds CoX$_2$(Et$_4$dien) are five-coordinate, the nickel analogues are planar with the formula [NiX(Et$_4$dien)]X.

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

Five-coordinate ⇄ six-coordinate equilibria are also well known with vanadyl compounds. Vanadyl complexes with Sal—en(R)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 acetylacetone with a number of nitrogen and oxygen donors in nitrobenzene. 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$_2$MOB, NiX$_2$MAB, NiX$_2$PSP, MX$_2$(daes), and NiX$_2$(MSB).

Calorimetric measurements on the two series of compounds [M(Me$_5$dien)Br$_2$] and [M(Me$_6$tren)Br]Br (M = Mn, Fe, Co, Ni, Cu, Zn) give the values of $\Delta H$ of formation for both the gaseous compounds (Figure 35), and for aqueous solutions (Figure 36). The enthalpy of the reaction MBr$_2$(aq) + Ligand(aq) ⇄ M Ligand Br$_2$(aq) increases to a maximum with Cu such that the order of stability is Mn ≈ Fe < Ni < Co < Zn < 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 complexes.

Figure 36. Relative enthalpy changes for the formation of three series of complexes in aqueous solution.
sequence for octahedral compounds\textsuperscript{10} Mn < Fe < Co < Ni < Cu > Zn and for tetra-halo-complexes Ni < Fe < Co < Mn < Cu < Zn.\textsuperscript{11} 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.\textsuperscript{10} These results may explain why the non-methylated ligand tren gives five-coordinate species with Cu\textsuperscript{II} and Co\textsuperscript{II} in aqueous solution whereas with Ni\textsuperscript{II} an octahedral complex is formed.

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