MAGNETISM, BONDING AND STRUCTURE OF COORDINATION COMPOUNDS

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INTRODUCTION

It is not only timely, for the reasons discussed below, to provide a survey of the use of magnetic susceptibility measurements for the study of complex compounds, but also fitting that the subject should be discussed in a country whose scientists have made so many outstanding contributions to quantum mechanics in general and spectroscopy and magnetism in particular. I pay a special tribute to Professor M. Kotani of the University of Tokyo whose important paper published in 1949 added much to the classic book by Professor J. H. van Vleck on magnetic and electric susceptibilities. It is also noteworthy that 1967 marks the centenary of the death of Michael Faraday who discovered many effects relating magnetism and structure, quite apart from his work on electro-magnetism.

A decade ago there was widespread optimism concerning the increasing value of magnetic susceptibility measurements for the study of chemical structure. In more recent years, as the effects of structural distortions, electron delocalization, ion–ion interactions etc. on magnetic moments have been shown to be more serious than was initially believed to be the case, considerable reservations concerning the usefulness of magnetic measurements have been expressed. Here we propose to try to outline the value and limitations of magnetic measurements for the chemist and will conclude that even though for some purposes, e.g. in connection with stereochemistry, magnetism is less useful than once thought, it still provides a very valuable technique for studying many other aspects of structure.

We survey the subject under three main headings:

1. A brief outline of theoretical principles with special reference to the magnetic behaviour of $d^8$ metal complexes—a configuration chosen because of the versatility of oxidation states, coordination numbers, stereochemistries and bond types displayed by many different elements.
2. A discussion of the various kinds of structural information about metal complexes which can be inferred from magnetic measurements. Special attention is drawn to the reliability and the limitations in each case.
3. An indication of the areas where magnetic studies are developing and where more work is needed to enable magnetic measurements to be reliably interpreted.

We are concerned mainly with magnetic susceptibility measurements, supplemented, where useful, by spectroscopic, electron spin resonance and nuclear magnetic resonance studies. The term "structure" is widely inter-
interpreted to cover the following properties of a complex of a metal atom or ion \( M \): (a) oxidation state; (b) coordination number (both nearest neighbours and more distant “outer sphere” atoms where the latter affect the electric field); (c) stereochemistry, and (d) nature of the bonding to the central atom \( M \) and its electronic configuration. Some ambiguity arises in connection with oxidation state, unless the reference atoms are carefully defined or where the ligands are not “innocent”, as will be discussed. We define the oxidation state of an atom \( M \) in a complex as the formal charge left on \( M \) if each of the attached ligands is removed in its “closed shell” configuration, e.g. \( \text{Cl} \) as \( \text{Cl}^- \), \( \text{H}_2\text{O} \) uncharged etc. Clearly it is necessary to decide whether \( \text{H} \) is removed as \( \text{H}^+ \) or \( \text{H}^- \), \( \text{NO} \) as \( \text{NO}^+ \) or \( \text{NO}^- \), etc. but real problems arise with ligands like \( \alpha, \alpha' \)-dipyridyl which can be present as the \( [\text{dipyridyl}]^{-1} \) ion in certain complexes of so-called “zerovalent” metals, e.g. \( \text{[Be(dipyridyl)]}_2 \). Wherever spin pairing occurs between two \( M \) atoms, e.g. in \( (\text{CO})_5\text{Mn—Mn(CO)}_5 \), homolytic fission of the \( \text{Mn—Mn} \) bond will be effected, leading here to an oxidation state of 0.

As discussed in more detail elsewhere, no less than eight different kinds of magnetic susceptibility are recognized based upon the variation of the gram susceptibility \( \chi_8 \) with temperature or field strength applied during the measurement (Table 1). The simplest of these, diamagnetism is of interest almost solely in that it indicates the absence of unpaired electrons and because it must be corrected for when calculating the effective magnetic susceptibility.

### Table 1. Types of magnetic behaviour

<table>
<thead>
<tr>
<th>Type</th>
<th>((\chi_8)) Magnitude at 300°K</th>
<th>Temperature dependence of (\chi_8)</th>
<th>Field strength dependence of (\chi_8)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. DIAMAGNETISM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Atomic (Ne) (or ionic (K(^+)) )</td>
<td>(~- 1 \times 10^{-6})</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>(b) Ring current ((C_6H_6)) ((\propto \text{Number and } r^2 \text{ of all electrons}))</td>
<td>(~+1 \text{ to } +10^2)</td>
<td>Complicated. Big decrease at Curie temperature</td>
<td>Complicated but decreases as (H) increases</td>
</tr>
<tr>
<td><strong>II. COOPERATIVE MAGNETISM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Ferromagnetism (Fe)</td>
<td>(~+1 \times 10^{-6}) to (+10 \times 10^{-6})</td>
<td>Maximum at Neel temperature</td>
<td>Small</td>
</tr>
<tr>
<td>(b) Antiferromagnetism (K(\text{NiF}_3))</td>
<td>(~+1 \times 10^{-6}) to (+10 \times 10^{-6})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Ferrimagnetism (Fe(\text{S}_4\text{O}_4))</td>
<td>(~+10 \times 10^{-6})</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>III. PARAMAGNETISM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Nuclear (H in hydrides)</td>
<td>(~+1 \times 10^{-9})</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>(b) Pauli free electron (metallic K)</td>
<td>(~1 \times 10^{-8})</td>
<td>Slight</td>
<td>Nil</td>
</tr>
<tr>
<td>(c) Van Vleck (or T.I.P.)</td>
<td>(~+1 \times 10^{-8})</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>(d) Normal atomic (H), ionic (Ti(^{3+})) or molecular (NO) paramagnetism</td>
<td>(~+1 \times 10^{-6}) to (+20 \times 10^{-6})</td>
<td>(\propto \frac{1}{T}) or (\propto \frac{1}{T+\theta})</td>
<td></td>
</tr>
</tbody>
</table>
STRUCTURE OF COORDINATION COMPOUNDS

moment $\mu_{\text{eff}}$ of an atom. Difficulties can arise in a few cases in making the latter correction if the diamagnetism of a host lattice—or indeed a ligand with an extensive $\pi$ system—is seriously altered by the inclusion of a paramagnetic species in the lattice or by attaching the ligand to a metal atom. An example of the first of these is provided by the apparent magnetic moment of auric chloride when intercalated in a graphite lattice. When one corrects the paramagnetism of the occluded auric chloride by adding the (presumed) susceptibility of free graphite one calculates magnetic moments ($\mu_{\text{eff}}$) for the Au(iir) atom in the range 1 to 2 B.M. However, when one determines in the same way the susceptibility of intercalated aluminium trichloride ($^{1S}$) or ferric chloride ($^{8S}$) similarly high apparent magnetic moments for the metal atom are calculated. In these cases an increase in $\mu_{\text{eff}}$ from zero and 5.92 B.M. respectively are clearly most improbable and the explanation is presumably that the presence of the intercalated salt has destroyed all or part of the high “ring” diamagnetism of the graphite.

The so-called ring diamagnetism observed in benzene and its derivatives, still has to be convincingly established in coordination compounds. Indeed, the possibility of its existence brings up the whole question of metal—ligand double bonding which is still much debated, at least in those cases where donation of $t_{2g}$ electrons by the metal is presumed to occur.

There can be no doubt that it occurs between binegative ligands (e.g. $\text{O}^{2-}$, $\text{NR}_{2}^{-}$ etc.) and metals with vacant $d$ orbitals but this involves $\pi$ donation by the ligand (see Table 2). The evidence for metal-to-ligand $\pi$ donation for transition metal carboxyls, cyanides, and similar first row ligands at least in low oxidation states is sound. However, the case for $\pi$ bonding to tertiary phosphine, tertiary arsine and similar second and later row ligands has been questioned, especially when the oxidation state of the metal is greater than one (cf. Table 2).

<table>
<thead>
<tr>
<th>Nature of Cr—O bond</th>
<th>Cr—O bond length</th>
<th>Cr—O Stretching Frequency (cm$^{-1}$)</th>
<th>Bond order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr—O—Cr in $\text{Cr}_2\text{O}_7^{2-}$</td>
<td>1.91</td>
<td>770</td>
<td>1.00</td>
</tr>
<tr>
<td>Cr—O in $\text{CrO}_4^{2-}$</td>
<td>1.67</td>
<td>885</td>
<td>1.5</td>
</tr>
<tr>
<td>Cr—O (terminal) in $\text{Cr}_2\text{O}_7^{2-}$</td>
<td>1.63</td>
<td>945</td>
<td>1.67</td>
</tr>
<tr>
<td>Cr—O in $\text{CrO}_2\text{Cl}_2$</td>
<td>1.57</td>
<td>995</td>
<td>2.00</td>
</tr>
</tbody>
</table>

We now consider briefly magnetic behaviour due to cooperative phenomena. Theories of ferro- and anti-ferromagnetism still leave much to be desired even though great advances have been made during the past decade. As we shall confine our attention to compounds in which cooperative phenomena between neighbouring paramagnetic atoms is negligible but we note that when susceptibility—field strength dependence is observed, the interpretation of experimental results is made much more difficult.
The effect of ferromagnetic impurities may, in suitable cases, e.g. K₄FeO₄, be allowed for by determining the susceptibility over a range of field strengths (H), then extrapolating to $H = \infty$. Although ferromagnetism is usually observed in domains in crystals, Ginsberg, Martin and Sherwood have recently reported field strength dependence of $\chi$ for a discrete molecule containing only three paramagnetic atoms, viz. the trimeric compound bis-(acetylacetonato)-nickel(ii). For field strengths above about 2500 oersteds the effective magnetic moment steadily increases from a room temperature value of 3.23 B.M. to 4.1 B.M. at 4.3°K. It is proposed that at 4.3°K all six $e_g$ spins are coupled parallel for the trimer which has an $S = 3$ state. There is a small decrease in $\mu_{\text{eff}}$ below 4.3°K and it is proposed that this is due to the combined effects of a small zero field splitting of the $S = 3$ state and very weak residual lattice antiferromagnetism. Unfortunately ferromagnetism is easier to find at low temperatures than it is to explain and results at very low temperatures need to be interpreted with caution. (cf. Lewis). Antiferromagnetism is detected by a determination of susceptibility over a range of temperature, a characteristic maximum of $\chi$ being observed at the Néel temperature ($T_N$). Values of $T_N$ are usually about 100°K but values as high as 275°K are observed with complex fluorides of the type KMIIF₃ which have a perovskite structure. It is due to anti-parallel alignment of spins on paramagnetic atoms below the Néel temperature ($T_N$), normal paramagnetism being observed above $T_N$. Ferrimagnetism arises from interpenetrating lattices with unequal numbers of paramagnetic atoms with antiparallel spins. It is effectively normal paramagnetism superimposed on antiferromagnetism.

**TYPES OF MAGNETISM**

**Paramagnetism with special reference to $d^8$ complexes**

(a) *Nuclear Paramagnetism* is normally studied by resonance techniques because of its small size. In addition to the use of n.m.r for the determination of chemical shifts for the (largely empirical) assignment of structure based upon the comparison of similar compounds, the use of spin-spin coupling constants for structural studies is increasing in importance. In particular, studies of the P₃₁—Pt¹⁹⁵ coupling constants to provide information about the nature of the phosphorus–platinum bond and the likelihood of double bonding. Pidcock, Richards and Venanzi, for example, have suggested that the trend of P₃₁—Pt¹⁹⁵ coupling constants in a series of Pt¹¹ complexes with halogeno ligands trans to the P₃₁ atom can be explained more readily by polarization effects rather than by double bonding from the platinum to the phosphorus. However, many more results on compounds containing a variety of phosphorus ligands with platinum in various oxidation states and stereochemical arrangements would seem to be necessary before definitive conclusions can be drawn.

(b) *Pauli Free Electron Paramagnetism* will not be discussed here as it is not significant in metal complexes.

(c) *Van Vleck or Temperature Independent Paramagnetism* is of importance in the study of metal complexes from two points of view. First, because it may need to be corrected for when calculating $\mu_{\text{eff}}$ values, and secondly because it
can be used in complexes to obtain an estimate of the ligand field parameter $10Dq$ for $d^n$ systems or the first excited state for $d^0$ systems.

We consider first the $d^6$ system, e.g. diamagnetic $d^6$ complexes with a $(t_2g)^6$ electron configuration ($1A_1g$ ground term). The second order Zeeman effect may be regarded as causing a "polarization" of the diamagnetic ($S=0$, $L=0$) ground term leading to a "mixing-in" of the first excited $t_2g^5 e_g$ electron configuration for which $S = 0$ but where $L$ has a finite value. Figgis has summarized the values of $\chi_{T.I.P.}$ for the three main cases of interest:

(i) For the $1A_1g$ term of $d^6 (t_2g)^6$: $8N \beta^2/10Dq$
   (For $A_2g$ terms the value of the T.I.P. is the same; examples include octahedral $d^3$, e.g. Cr$^{III}$, compounds.)
(ii) For $E_g$ terms the value is $4N \beta^2/10Dq$
(iii) For the $6A_1g$ term of $d^5$ and the $1A_1g$ terms of $d^9$ and $d^{10}$, $\chi_{T.I.P.}$ is zero.

For $d^0$ systems, however, T.I.P. can arise by (formal) promotion of an electron from the ligand to the vacant $e_g$ orbital of the metal. In complex ions such as $[\text{MnO}_4]^{-}$ using a molecular orbital model it can be shown that only a small amount of mixing of the metal $d$ orbital and the ligand $\pi$ orbitals will account for the observed intensity of the transition. The transition is taken to be $1T_2 \leftrightarrow 1A_1$; this is supported by n.m.r. studies on $d^0$ tetrahedral oxyanion systems in which $Q_{17}$ enrichment has been carried out; the large paramagnetic shifts are inversely proportional to this lowest energy transition.

Magnetic susceptibility studies on the tetrahedral $d^1$ systems $[\text{MnO}_4]^{2-}$, $[\text{TeO}_4]^{2-}$ and $[\text{ReO}_4]^{2-}$ have been studied in some detail; in the case of the $[\text{MnO}_4]^{2-}$ ion the total $\chi_{T.I.P.}$ is $\pm 125 \times 10^{-6}$ c.g.s. units. Of this, $+ 67 \times 10^{-6}$ c.g.s. units is attributed to ligand$\rightarrow$metal $(d^9$ type) T.I.P. and 58 units to $2e \rightarrow 2t_2g (d^1)$ promotion.

An example of T.I.P. in a $d^1$ system where a substantial moment (1-4 B.M.) is observed at room temperature is provided by the spin-paired $d^4$ octahedral compound $K_2\text{OsCl}_6$. This has a $3T_1g$ ground state; the two unpaired electrons in the $t_2g$ set can be regarded, effectively, as behaving as $p$ electrons leading to $L = 1$ and $S = 1$.

The effect of spin-orbit coupling is to "mix-in" some of the first excited (paramagnetic) state, the per cent of which is proportional to $\lambda/\Delta$ since $\chi_m$ is independent of $T$ and $\mu_{eff} = 2.84 \sqrt{\chi_m \times T}$ then $\mu_{eff}$ should be proportional to $\sqrt{T}$ at low temperatures. This has been confirmed for $K_2\text{OsCl}_6$ by Johannesen and Lindberg.

The size of the T.I.P. contribution to the susceptibility of compounds with a small value of $\Delta$ can be quite considerable. Thus whereas it is about 60 c.g.s units for Cu$^{2+}$ complexes it is as large as 400-600 c.g.s. units for tetrahedral Co$^{2+}$.

(d) Normal paramagnetism arises from the presence in an atom of one or more unpaired electrons.

In the free atom the observed magnetic moment depends upon the way in which the individual spin ($S$) and orbital angular momenta ($L$) combine to give a total angular momentum ($J$) and the energy separation between possible $J$ values relative to the value of $kT$. In a complex of the metal ion the
properties of the electric field due to the ligand must be considered. These factors are summarized in Table 3.

Table 3. Factors affecting \( \mu_{\text{eff}} \) of isolated atoms (or ions) and complexed atoms (or ions) in compounds

<table>
<thead>
<tr>
<th>Free atom or ion</th>
<th>Atom or ion in electrical field due to ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Number ((n)) of unpaired electrons and orbital(s) occupied by them.</td>
<td>IV Symmetry of electric field</td>
</tr>
<tr>
<td>II Value of formal charge ([\text{can affect } n \text{ and } l \text{ in (I)}])</td>
<td>(a) Basic field (\text{Td, Oh etc.})</td>
</tr>
<tr>
<td>III Value of effective nuclear charge ((Z_{\text{eff}})) and spin orbit coupling constant ((\lambda)) depending thereon.</td>
<td>(b) Distortions thereof†</td>
</tr>
<tr>
<td>Atom or ion in electrical field due to ligands</td>
<td>V (\text{Strength of electric field (determines } \lambda)</td>
</tr>
<tr>
<td>IV Symmetry of electric field</td>
<td>(a) Basic field (\text{Td, Oh etc.})</td>
</tr>
<tr>
<td>(a) Ligand→metal (\sigma) bonding ((\text{increases } \lambda) and decreases (Z_{\text{eff}}))</td>
<td>(b) Ligand→metal (\pi)-bonding ((\text{decreases } \lambda))</td>
</tr>
<tr>
<td>(b) Ligand→metal (\pi)-bonding ((\text{decreases } \lambda))</td>
<td>(c) Metal→ligand (\pi)-bonding ((\text{increases } \lambda) increases (Z_{\text{eff}}))</td>
</tr>
<tr>
<td>VI Extent of metal–ligand covalency</td>
<td>VII Electron delocalization Metal→ligand or Ligand→metal (see below).</td>
</tr>
<tr>
<td>(a) Ligand→metal (\sigma) bonding ((\text{increases } \lambda) and decreases (Z_{\text{eff}}))</td>
<td>†These include (i) use of different ligands ([\text{MCl}<em>{2}\text{Br}</em>{4}]^{-})</td>
</tr>
<tr>
<td>(b) Ligand→metal (\pi)-bonding ((\text{decreases } \lambda))</td>
<td>(ii) (\text{cis-trans isomerism})</td>
</tr>
<tr>
<td>(c) Metal→ligand (\pi)-bonding ((\text{increases } \lambda) increases (Z_{\text{eff}}))</td>
<td>(iii) longer range effects</td>
</tr>
</tbody>
</table>

When using the above equation for \( \mu_{\text{eff}} \) it is assumed that: (i) the diamagnetic contributions arising from the central paramagnetic atom itself, the attached (diamagnetic) ligands, and/or any charge neutralising ions in a crystal, have been allowed for; (ii) a correction has been made for any temperature independent paramagnetism; (iii) the paramagnetic ion or atom is “magnetically dilute”, i.e. that interactions of the ferro- or anti-ferromagnetic type have been shown to be negligible by susceptibility–temperature or susceptibility–field strength dependence measurements.

The \( \text{Ni}^{2+} \) ion is used for consideration because of the large amount of work done thereon in metal complexes\(^{19}\), and the variety of coordination numbers and stereochemical arrangements which it displays. Furthermore, some data are available for the corresponding isoelectronic \(d^8\) ions \(\text{Fe}^\circ\), \(\text{Co}^{1+}\), and the congeners \(\text{Pd}^{2}\) and \(\text{Pt}^{2+}\). For the \( \text{Ni}^{2+} \) (free ion) the relevant spectroscopic data are\(^{20}\): \(3\text{F}\) ground state \(J = 4, 0 \text{ cm}^{-1}; J = 3, 1332.3 \text{ cm}^{-1}; J = 2, 2216 \text{ cm}^{-1}\). This leads to a spin-orbit coupling constant \((\lambda)\) for the \(d^8\) set of \( -315 \text{ cm}^{-1}\). The corresponding values of \(\lambda\) for \(\text{Fe}^\circ\) (\(d^8\)) and \(\text{Co}^{1+}\) (\(d^8\)) are \( -227 \text{ cm}^{-1}\) and \( -126 \text{ cm}^{-1}\) respectively. The weighted separation between \(3\text{F}\) and \(3\text{P}\) is \(15,748 \text{ cm}^{-1}\). The value of \(B\) (used by Jorgensen\(^{21}\) to calculate the nephelauxetic ratio† \(B^4 = B^1/B^3\)) is then \(1050 \text{ cm}^{-1}\). For the \(\text{Pd}^{2+}\) ion, \(\lambda\) is estimated as \(453 \text{ cm}^{-1}\) (for the first \((J_4 \rightarrow J_3)\) separation). As expected, the \(B\) value \((913 \text{ cm}^{-1})\) is less for \(\text{Pd}^{2+}\) than for \(\text{Ni}^{2+}\) owing to the larger size. The value for \(\text{Pt}^{2+}\) is unknown.

It is convenient to discuss the value of \( \mu_{\text{eff}} \) as the degree of complexity of the free ion or the factors affecting it in the complex increase.

(a) \(\text{Free Ion}\). Five possibilities need to be considered:

†A measure of inter-electron repulsion in the non-bonding electron set.
(i) **Large energy separation** (cf. $kT$) between lowest and next $J$ value. This is the so-called "rare-earth" case for which $\mu_{\text{eff}} = g\sqrt{J(J+1)}$. $J$ having values $(L+S)$ to $(L-S)$, the smallest value of $J$ lying lowest if the electron shell is less than half-full (e.g. $d^2$, $\text{V}^3+$, $\text{3F}^2$) and conversely if the shell is more than half-full. $g$ has the value $1 + [J(J+1) + S(S+1) - L(L+1)]/[2J(J+1)]$. This formula holds good only if $\hbar v(J_0 - J_1) \geq 1500 - 2000$ cm$^{-1}$ as obtains for the tervalent rare earth ions except Eu$^{3+}$ and Sm$^{3+}$ (For Ni$^{2+}$, $3\text{P}^4$ $\mu_{\text{eff}}$ using this expression is 5-56 B.M.).

(ii) **Intermediate energy separation** (cf. $kT$) between successive $J$ values. This is the situation in Eu$^{3+}$, Sm$^{3+}$, NO, etc. The moment is calculated by summing susceptibilities over the range of $J$ values.

(iii) **Small energy separations** (cf. $kT$) between successive $J$ values. This situation obtains for the first row transition metal ions, especially in low oxidation states. In this instance $L$ and $S$ orient independently with $H$, and the calculated magnetic moment is $\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)}$. For Ni$^{2+}$, $\mu_{\text{eff}}$ is 4-24 B.M.

(iv) **Spin only moments** for the special case of $L = 0$, the spin-only formula, $\mu_{\text{eff}} = \sqrt{4S(S+1)}$ or $\mu_{\text{eff}} = \sqrt{n(n+2)}$, obtains. It is important for $d^5$ spin-free atoms where $L = 0$ (e.g. Fe$^{3+}$ and Mn$^{2+}$) and for many ions for which the symmetry of the field [(e.g. Cr$^{3+}$ (Oh), Ni$^{2+}$ (Oh)], or marked distortion, destroys orbital degeneracy (e.g. grossly distorted tetrahedral Ni$^{2+}$ [e.g. NiBr$_2$ (Ph$_3$P)$_2$)]. It holds also where there are unpaired electrons in a non-magnetic (orbital) doublet e.g. octahedral Cr$^{3+}$($d^4$) or Cu$^{2+}$($d^9$).

(v) **$J$–$J$ Coupling.** Finally, for very large values of the $J_0$–$J_1$ separation $J$–$J$ coupling may arise. Few cases have been worked out in detail but fortunately it is negligible for the first row transition elements and usually so for the second row although it can be noticeable for high oxidation states of the second row, e.g. for the $d^2$ ion Mo$^{IV}$. It is really significant for the third row transition metals (e.g. W$^{4+}$) and may contribute as much as 20 per cent to the final paramagnetism.$^6$, $^{15}$

(b) **Complexes.** The effect of the symmetry of an electrostatic field due to ligands has been extensively discussed and the subject will only be summarized here.

It is usual to start using a crystal field model. The surprising feature of this approach is not that it was qualitatively successful with metal complexes but that the model worked at all. It is now obvious that covalency is much more important than was originally believed to be the case. Fortunately in octahedral metal complexes the symmetry of the ligand field is the same whether the ligand are point charges ion-dipoles or covalently bound to the metal. However, in the last case the close proximity of the electron pair of the $\sigma$ bond explains, even with a simple model, why the value of $A$ or 10 $Dq$ increases so much with $\sigma$-type covalency.

According to Jorgensen$^{22}$ “it is a fallacy to present the electrostatic model of the ligand field even as a good pedagogic starting point for further discussion. There is no sense in which the covalent bonding is a weak second
order correction to the electrostatic model and the mathematics of the physically unreasonable electrostatic model is by no means particularly simple". Thus, a priori calculations of $10Dq$ for the $[\text{Cr(H}_2\text{O)}_6]^{3+}$ ion originally gave a value of $-5500$ cm$^{-1}$ as compared with the experimental figure of $+17500$ cm$^{-1}$. In this calculation the exchange integral had been ignored. On incorporating this, $10Dq$ was estimated at $+48000$ cm$^{-1}$; still three times too big but at least with the right sign! It is clear that covalency and its effect upon the charge on the metal and the size of the $d$ orbits is very important.

More recently Shuliman and Sugano have obtained a much better agreement between theory and experiment for crystalline NiF$_2$ but even here they had to postulate a considerable amount of $\pi$ bonding and interaction between $\sigma$ and $\pi$ electrons, i.e. marked covalency effects$^{23}$.

Nevertheless, if we assume that a cubic field of negative charges splits the degeneracy of the five $d$ orbitals in the usually accepted manner with a large $\Delta$, which in an octahedral complex is a measure of the $t_{2g} - e_{g}^{*}$ separation, then orbital magnetism is expected to arise in a perfect octahedral (O$_h$) or tetrahedral (T$_d$) field, other effects being absent, as shown below. For an octahedron this means when the $t_{2g}$ set is empty ($d^0$), half full ($t_{2g}^3$) or full ($t_{2g}^6$).

<table>
<thead>
<tr>
<th>Symmetry of electric field of negative charges</th>
<th>Orbital magnetism expected for</th>
<th>Spin-only magnetism expected for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral (Perfect O$_h$)</td>
<td>Spin-free $d^1, d^3, d^5, d^7$</td>
<td>Spin-free $d^3, d^5, d^7$</td>
</tr>
<tr>
<td></td>
<td>Spin-paired $d^4, d^6$</td>
<td></td>
</tr>
<tr>
<td>Tetrahedron (Perfect T$_d$)</td>
<td>Spin-free $d^2, d^4, d^6, d^8$</td>
<td>Spin-free $d^1, d^2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spin-paired $d^3$</td>
</tr>
</tbody>
</table>

However, any distortion of the octahedral field which splits the degeneracy of the $t_{2g}$ set will have the effect of decreasing or destroying orbital magnetism and the magnetic moment will tend towards the spin only moment. Figgis$^{15}$ has studied the effect of distortion from a regular ligand field upon the magnetic moment of a complex ion. He summarises his results in terms of a parameter $v = \Delta/\lambda$ and has shown that, as $v$, increases, so the magnetic moment approaches more closely the spin-only value for the number of unpaired electrons involved.

(c) The strength of the ligand field decides whether spin-pairing will occur, or with paramagnetic complexes, how much mixing of excited states takes place. Thus the free ion moment (4.24 B.M.) of the Ni$^{2+}$ ion based on the $\sqrt{4S(S + 1) + L(L + 1)}$ expression is reduced to the spin only 2.83 B.M. if the value of $10Dq$ is infinitely large. In an octahedral field of negative charges, $\mu_{\text{eff}}$ is given by the expression 2.83 $(1 + (4\lambda/\Delta))^{1/2}$; since $\mu_{\text{eff}}$ for the $[\text{Ni(H}_2\text{O)}_6]^{2+}$ ion is about 3.1 B.M., it is easy to show that this corresponds to a "mixing-in" of about 10 per cent of the first excited state ($t_{2g}^5 e_{g}^{*}$) with the ground state ($t_{2g}^6 e_{g}^2$) via spin-orbit coupling. But it must be stressed that this is not the only factor influencing the increase in moment over the spin-only value.
Both $\sigma$ and $\pi$ covalency affect the value of $\mu_{\text{eff}}$. As referred to above, $\sigma$ bonding produced a stronger effective ligand field by bringing electron pairs closer to the metal ion; the effect of this is to increase $\Delta$. However, by reducing the effective nuclear charge on the metal atom the apparent value of $\lambda$ is decreased. Values of for [Ni(H$_2$O)$_6$]$^{2+}$ and [Ni(NH$_3$)$_6$]$^{2+}$ are respectively $-245$ cm$^{-1}$ and $-200$ cm$^{-1}$. Comparison with the Ni$^{2+}$ ($-315$ cm$^{-1}$), Co$^{3+}$ ($-227$ cm$^{-1}$) and Fe$^{+}$ ($-126$ cm$^{-1}$) ions indicates an apparent decrease in effective charge on the "Ni$^{2+}$" ion to just above and just less than $+1.0$. This will reduce the value of $\lambda$ and, in turn, the $4\lambda'/\Delta$ term. As discussed below a reduction in $Z_{\text{eff}}$ can also lead to a change in electron configuration, e.g. Cr$^0 = d^5s^1$, Fe$^{1+} = d^6$.

The effect of $\pi$ bonding from ligand to metal will further reduce the charge on the metal atom and, as discussed below, in the case of the [MnO$_4$]$^{2-}$ anion the metal atom behaves effectively as if it had a charge of zero. When the $\pi$ bonding is from metal to ligand, as with CO and CN$^-$ the value of $\Delta$ is increased. A possible example of the effect of this occurs in complexes of the type (Ph$_2$AsMe)$_3$Cl$_2$Rh—X where X is a halogen, —HgCl, —HgBr, —HgI etc. It has been shown$^{24}$ that the —HgCl, —HgBr and —HgI groups have higher values of $\Delta$ than the halogen atoms. This is difficult to understand in terms of accepted electronegativity values or size and it seems more likely that overlap between a $t_2g$ orbital of the rhodium atom and a $p$ orbital of the mercury atom takes place.

### (e) The orbital reduction factor "$k$"

This factor, which measures the decrease in $l$ of an unpaired $d$ electron, was first introduced by Stevens$^{25}$ to explain the hyperfine splitting of the e.s.r. spectrum for the $d^5$ compound K$_2$IrCl$_6$. (A simple spectrum is expected if the Ir$^{3+}$ . . . Cl binding were purely ionic.) Owens$^{26}$ correlated "$k$" with the "time spent by" the unpaired electron on the chlorine ligands.

Clearly the tendency was to associate the reduction in $l$ with a delocalization effect which, for octahedral complexes, implies some "$\pi$" bonding. However, Stevens did not specifically describe the effect in this way nor did he imply that $\pi$ bonding was the only way in which $l$ could be reduced. However, any reduction does imply some valency mechanism whereby there is a mixing of a metal and ligand orbital. (It is of interest to note that Ballhausen$^{15}$ has pointed out that electron delocalization on to the metal need not involve a reduction in $l$.)

To handle the subject mathematically it is convenient to introduce the operators $(kL + 2S) \hat{B}$.H. for magnetic moments and kL.S for spin orbit coupling. Obviously if $k<1$, the effect of introducing $k$ into $\mu_{\text{eff}}$ calculations is to cause the moment to approach the spin only value, i.e. $|kL + 2S| \to 2S$. Curves of $\mu_{\text{eff}}$ for various configurations $^2T_2$, $^3T_1$, $^4T_1$, $^5T_2$ have been calculated by Figgis et al.$^{27}$ using various values of $k$.

For (orbitally) non-degenerate terms, $k$ is introduced by the spin-orbit coupling term, i.e.

$$\mu_{\text{eff}} = \mu_{\text{spin only}} \left(1 - \frac{ak^2\lambda}{\Delta}\right);$$

it also affects T.I.P., e.g., for F terms one must multiply $2.01/\Delta$ by $k^2$ and in the case of D terms $1.05/\Delta$ by $k^2$. 

9
It is now generally recognised that the most effective way of reducing $l$ for a $d$ electron in a system is to introduce $p$ orbital character from the metal atom. For the octahedral case this cannot occur simply by mixing $p$ orbitals of the metal because $p \rightarrow t_{1u}$ and $d \rightarrow t_{2g}$. However the formation of an M.O. by using $p$ character of the ligand can achieve this. But if the centre of symmetry is removed, e.g., in a tetrahedral complex, then additionally mixing of $d$ and $p$ orbitals of the metal can take place readily.

We can then understand why $k$ is so much smaller in tetrahedral systems. Indeed it may be as small as $\sim 0.5$ in some cases [e.g. $[NiX_4]^{2-}$ complex anions]. The importance of $k$ in reducing $l$ in tetrahedral systems cannot be overemphasised. Thus, the low moment of $NiX_2.2Ph_3P$ appears to be due primarily to $k$ and not to distortion causing splitting of $d$ orbitals as often assumed.

Although the reduction in $k$ is smaller in octahedra, the values observed for $k$ in many octahedral complexes still pose a difficult problem. Thus, for the $(d^1) [Ti(H_2O)6]^{3+}$ ion $k \approx 0.6$. There are no vacant $p$ orbitals in $H_2O$ and presumably anti-bonding orbitals of the oxygen are involved unless

more experimental data, especially in conjunction with e.s.r. studies, are urgently needed to throw light on this problem. The way in which the delocalization factor $k$ affects $\mu_{\text{eff}}$ with, and without, distortion of the ligand

Table 4. Factors influencing $\mu_{\text{eff}}$ of $Ni(II), ^3F_a$ and its complexes

<table>
<thead>
<tr>
<th>Free Ion</th>
<th>$S = 1, L = 3$</th>
<th>(J_\text{4} \rightarrow J_\text{3} = 0)</th>
<th>(J_\text{4} \rightarrow J_\text{3} = 1361 \text{ cm}^{-1})</th>
<th>(J_\text{4} \rightarrow J_\text{3} = \infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g = 1.25$</td>
<td>4.47 B.M.</td>
<td>5.56 B.M.</td>
<td>5.59 B.M.</td>
<td></td>
</tr>
</tbody>
</table>

\[\text{Add cubic charges} \quad \text{regular field of charges}\]

<table>
<thead>
<tr>
<th>Strong field (\rightarrow D_{4h})</th>
<th>Add Calc. S.O. coupling ((-315 \text{ cm}^{-1}))</th>
<th>Spin-only moment (2.83 \text{ B.M.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 B.M. e.g. square tetragonal etc.</td>
<td>Add $\sigma$ covalency reducing $\lambda$</td>
<td>Add $\sigma$ covalency reducing $\lambda$</td>
</tr>
<tr>
<td>Weak (J_\text{4})</td>
<td>Distortions</td>
<td>Add effect of S.O. coupling (\lambda = -315 \text{ cm}^{-1})</td>
</tr>
<tr>
<td>Weak (O_h)</td>
<td>Add $\text{&quot;k&quot; (electron delocalization)}$</td>
<td>Add $\text{&quot;k&quot; (electron delocalization)}$</td>
</tr>
</tbody>
</table>
field has been summarized by Figgis.\textsuperscript{15} As with distortion, the overall effect is to cause the magnetic moment to approach the spin-only value for the number of unpaired electrons involved.

In Table 4 the factors affecting the magnetism of Ni\textsuperscript{2+} complexes are summarized.

APPLICATIONS OF PARAMAGNETIC SUSCEPTIBILITY MEASUREMENTS TO STRUCTURE AND BONDING IN COORDINATION COMPOUNDS

1. Determination of (formal) non-bonding\textsuperscript{†} configuration of metal atom

(a) Distinction between spin-free (e.g. FeF\textsubscript{6}\textsuperscript{3−}) and spin-paired (e.g. Fe(CN)\textsubscript{6}\textsuperscript{3−}) complexes. When spin-paired and spin free complexes were first investigated the energy difference between the two configurations was usually sufficiently large enough to ensure that one or the other only of the two electronic arrangements was observed. Recently, however, several cases of temperature dependent equilibria have been observed and studied. Free energy and enthalpy values, for the equilibria, have been determined in several instances. Now that the factors governing the size of \( \Delta \) are better understood, complexes for which \( \Delta \) and the \( d \) electron repulsion parameters are nearly equal can be designed and prepared.

Examples of these equilibria include the following: (i) \( d^8 \) (diamagnetic) \( \Leftrightarrow d^8 \) (2 unpaired electrons). This is probably the most extensively studied system involving a transition from (usually) red planar (or tetragonal) Ni(II) complexes to tetrahedral (or, in suitable solvents) octahedral compounds. (ii) \( d^7 \) (1 unpaired electron) \( \Leftrightarrow d^7 \) (3 unpaired electrons) systems are illustrated by the five-coordinate Co(II) complexes of Schiff's bases. Earnshaw, Hewlett, King and Larkworthy\textsuperscript{28} have reported recently a particularly interesting series of compounds involving the five coordinate monohydrate of the 2-ethoxy Schiff's base derivative. (iii) \( d^5 \) (3 unpaired electrons) = \( d^5 \) (5 unpaired electrons). Five coordinate complexes of Fe(III) with dithiocarbamates have been investigated by a number of workers\textsuperscript{29}.

(b) The orbital (s) occupied by unpaired electron(s). This is dependent upon formal charge and the strength of the ligand field. Change in \( Z_{\text{eff}} \) due to changes in formal charge can affect orbitals occupied by unpaired electrons, e.g. K\textsuperscript{+} (4s) cf. Ti\textsuperscript{3+} (3d\textsuperscript{1}). A special case of note is the actinide series \( 4f^n \) cf. \( 5d^n \), a "Fourth" Transition series.

Many other cases of the effect of \( Z_{\text{eff}} \) warrant further investigation. Thus, it has been proposed that the unexpectedly high \( \mu_{\text{eff}} \) of the magnetically (dilute) \([\text{FeCl}_4]\)\textsuperscript{2−} ion may be due to mixing of the \( 3d^5 \) 4s\textsuperscript{1} configuration with the \( 3d^6 \). The Fe\textsuperscript{2+} ion in \([\text{FeCl}_4]\)\textsuperscript{2−} is in a D state and for \( \Delta = \infty \), a moment of 4.90 B.M. is expected. Mixing due to spin-orbit coupling changes \( \mu_{\text{eff}} \) according to the expression 4.90 \([1 + 2\lambda/\Delta]\) where \( \lambda = -102 \) cm\textsuperscript{-1} and \( \Delta = 4000 \) cm\textsuperscript{-1} giving a value of 5.1 B.M. However \( \lambda \) is reduced by complex formation and this, together with distortion, are expected to reduce

\textsuperscript{†} The term "non-bonding" is formal because these electrons often contribute to metal→ligand \( \pi \) bonding.
\( \mu_{\text{eff}} \) below 5.1 B.M. It is proposed that the \( \sigma \) bond covalency of the formal \( \text{Fe}^{2+} \) ion with the four \( \text{Cl}^- \) ions reduces the charge on the metal atom to a point where a significant contribution from the \( 3d^54s^1 \) configuration (\( \mu_{\text{eff}} = 6.92 \) B.M.) to the \( 3d^6 \) configuration is feasible (see Figure 1). Only about 5 per cent of the former is necessary to account for the observed \( \mu_{\text{eff}} \) of 5.4–5.5 B.M.

Other examples where a marked change in \( \mu_{\text{eff}} \) is expected to occur as the result of a marked change in \( Z \) include: \( \text{Ni}^0 \) (\( 3d^84s^2 \)) \( \rightarrow \text{Cu}^{1+}(3d^{10}) \); \( V^0 \) (\( 3d^34s^2 \)) \( \rightarrow \text{Cr}^{1+}(d^5) \) and \( \text{Mn}^{2+}(d^5) \).

(c) Spin pairing owing to covalent bonding. Thus paramagnetic \( \text{V(CO)}_6 \), \( (d^5t) \) becomes diamagnetic in dimeric Diarsine(\( \text{CO}_3 \))V—V(\( \text{CO}_3 \))Diarsine (\( d^4 \)).

(d) Spin-spin interaction via ferro- or antiferromagnetic interaction. It has been suggested that the increase in \( \mu_{\text{eff}} \) of trimeric[bisacetylacetonate \( \text{Ni(II)} \)]\(_3 \) is due to the former and the decrease in \( \mu_{\text{eff}} \) of \( \text{KNiF}_3 \) (from \( \sim 3.2 \) B.M. to 1.9 B.M. at 300°C) via the \( \text{F}^- \) ions is attributed to the latter.

2. Determination of formal oxidation state

This is probably the best known use of magnetic susceptibility measurements for the study of coordination compounds and depends on being able to infer the number of unpaired electrons from the magnetic moment. Due allowance must be made for the diamagnetism of the attached ligands, but this rarely causes problems. Difficulties can arise, however, owing to the following:

(a) Large orbital contribution. Thus certain spin-paired \( \text{Co(II)} \) complexes (with one unpaired electron) can have \( \mu_{\text{eff}} \) as large as 2.9 B.M. Similarly, the \( \mu_{\text{eff}} \) of octahedral spin-free \( \text{Co(II)} \) complexes (with three unpaired electrons) is close to that for four unpaired electrons (4.90 B.M.). In these cases temperature-susceptibility studies may be necessary.
STRUCTURE OF COORDINATION COMPOUNDS

(b) Large spin-orbit coupling effects. This is illustrated by comparing the \( \mu_{\text{eff}} \) values for spin-paired complexes of Fe(IV), Ru(IV) and Os(IV). The first two of these fortuitously have moments at 300\(^\circ\)K fairly close to the spin-only value for two unpaired electrons (2.83 B.M.). However, at room temperature the \( \mu_{\text{eff}} \) of \( \text{K}_2\text{OsCl}_6 \) is only 1.4 B.M. The theory of this has been established by Kotani\(^1\) and little difficulty arises in the interpretation if one determines the moment over a range of temperature.

(c) Electron delocalization and the use of “non-innocent” ligands. As discussed above, the reduction of the effective “\( l \)” values of the unpaired electron(s), e.g. in \( \text{NiCl}_4^{2-} \) complexes, can cause some difficulty, but much greater problems are posed by the use of what Jorgensen\(^3\) has called “non-innocent” ligands. In effect these can behave as anions. Thus, as mentioned earlier, the compound [Be(2:2'-bipyridyl)\(_2 \)]\(^0\) is paramagnetic; if it were a derivative of Be\(^0\) with two donor bipyridyl chelate ligands diamagnetism is expected. But if the ligand can accommodate one or more unpaired electrons in suitable molecular orbitals, then a paramagnetic Be(II) complex can be formed, e.g., [Be\(^{2+}\) (bipyridyl)\(_2 \)]. Much attention is being paid to ligands such as NC—C===C—CN at present which are of this type\(^3\)\(^2\). Many more experimental data involving e.s.r. spectra and x-ray results to indicate the extent to which the unpaired electron(s) are on the ligand(s) are needed before one can be sure of the formal oxidation state in these cases.

(d) Metal-to-metal interaction. Simple M—M covalent binding can lead to electron pairing and the extent to which this occurs will depend upon the ligands employed. Thus \( \text{V(CO)}_6 \) is paramagnetic with one unpaired electron (\( d^5 \)); but [Diarsine \( \text{CO}_4\text{V—V(CO)}_4 \) Diarsine]\(^0\) is diamagnetic\(^3\)\(^8\), although the oxidation state of the vanadium atom is the same in each case. Clearly a determination of the molecular weight is essential in cases such as this to interpret the results. Anti-ferromagnetic (as in \( \text{KNiF}_3 \)) or ferromagnetic interaction (as in \( \text{Fe}_8\text{O}_4 \)) can be resolved as a rule by temperature-susceptibility or field-strength susceptibility measurements; the possibility of their occurrence in magnetically concentrated compounds must always be borne in mind.

3. Determination of coordination number

Although the reasons for its widespread application are still the subject of discussion\(^3\)\(^4\), the so-called “noble-gas” rule of “eighteen electron” rule assists greatly in explaining the structure of metal carbonyls. Thus for metal carbonyls only in the case of \( \text{V(CO)}_6 \) (which is paramagnetic with \( \mu_{\text{eff}} = 1.73 \) B.M.) is paramagnetism, and deviation from the “noble gas rule” observed. It would seem that the major factor of importance is the need to ensure that the energy separation between \( (n - 1)d, ns \) and \( np \) orbitals (or the bonding molecular orbitals derived from these) is relatively small. Calculations by Craig and Doggett\(^3\)\(^4\) certainly lend support to the idea that the charge on the central metal atom is fairly close to zero (as expected from the Pauling electroneutrality principle). If the separation between atomic orbitals is substantial and/or if the heat of atomization of the metal is large compared to the number of CO groups attached, then an alternative way in
which the metal atom can form stable carbonyls is by metal cluster formation. Thus the “instability” of the noble-gas configuration carbonyl Os(CO)$_5$ as compared with Os$_3$(CO)$_{12}$ may be due simply to the high heat of atomization ($\Delta H_{At}$) of osmium (186 kcal/mole). The formation of a cluster of three metal atoms effectively diminishes $\Delta H_{At}$.

As an extension of the noble-gas rule we have the nine-orbital rule which says that non-bonding orbitals may be occupied by single-unpaired electrons provided that most of the ligands are CO or like CO. Used with discretion and in general, treating complexes of metals at the beginning and the end of the transition series with special caution, the magnetic moment can be a good guide to coordination number, especially if used with molecular weight and conductivity data. Examples of unusual coordination number include:

- Eight coordination $K_3$Mo(CN)$_8$ ($d^1$) and [Re(Diarsine)$_2$Cl$_4$]ClO$_4$ ($d^2$, diamagnetic)
- Seven coordination $K_4$V(CN)$_7$ ($d^2$, two unpaired electrons)
  $K_4$Mo(CN)$_7$ ($d^3$, one unpaired electron)
  [Re(Diarsine)$_2$(CO)Br$_3$]$^0$, ($d^4$, diamagnetic).
- Five coordination $[Ni(CN)_5]^3-$ ($d^8$, diamagnetic)
  CoBr$_2$.Triarsine ($d^7$, one unpaired electron)
  FeBr$_2$.Triphosphine ($d^6$, two unpaired electrons)
  FeCl$_5$(dialkylthiocarbamate)$_2$ ($d^5$, three unpaired electrons). No example of a five-coordinate $d^4$ complex in which there are four unpaired electrons has yet been clearly established.

Substitution of CO groups by other ligands usually leads to a greater positive charge on the metal, a greater $d$-$s$-$p$ orbital separation and hence often, a decreased coordination number, e.g. for $d^8$ complexes Fe$^0$ is five-coordinate in Fe(CO)$_5$, but Pt$^{II}$ is four coordinate in Pt(CO)$_2$I$_2$.

4. Determination of stereochemistry

Two main methods are available for determining the stereochemical arrangement of ligands about a transition metal atom by paramagnetic measurements. One depends on a determination of the number of unpaired electrons; the second upon the size of the orbital contribution to the magnetic moment. But much of the early confidence in the use of the number of unpaired electrons as a criterion of stereochemistry has long since evaporated. Taking as an example the $d^8$ complexes of Ni(n), it was originally assumed that if spin free (2 u.e.), a nickel(n) complex would be either six-coordinate and octahedral or, less likely, four-coordinate and tetrahedral; if, however, it were diamagnetic it was assumed that the complex would be four coordinate and square. However, it has become clear during the last decade that a determination of the number of unpaired electrons provides, at best, a means of putting a complex into one of two classes. Thus complexes of nickel(n) which contain two unpaired electrons may be six-coordinate (octahedral), e.g. $[Ni(NH_3)_6]^{2+}$, five coordinate (square bipyramidal) e.g. $(Ph_2MeAsO)_4[NiClO_4]$ ClO$_4$, or four-coordinate (tetrahedral, e.g. $[NiCl_4]^{2-}$.
STRUCTURE OF COORDINATION COMPOUNDS

Diamagnetic complexes may be four-coordinate square planar (e.g. NiBr₂. 2Et₃P)¹⁸, five-coordinate (square pyramidal³⁵, e.g. [Ni(CN)₅]³⁻ or trigonal bipyramidal³⁵, e.g. also [Ni(CN)₅]³⁻ and six-coordinate (e.g. tetragonal, e.g. [Ni(Diarsine)₂]²⁻)⁰.¹⁹.

The second and perhaps classical case where the number of unpaired electrons is strongly indicative of the stereochemistry is with Co(n). The presence of three unpaired electrons (μₐₑᵗᵗ ≈ 4·85–5·2 B.M.) almost invariably indicates an octahedral configuration, whilst one unpaired electron (μₐₑᵗᵗ = 2·2–2·9 B.M.) is associated with a square pyramidal or square planar structure. Nevertheless, the regular octahedral structure of the [Co(NO₂)₆]⁴⁻ anion is unexpected in view of the low magnetic moment (≈ 1·9 B.M.).

It seems likely that the occurrence of low magnetic moment and (probably) octahedral coordination in this instance is connected with the fact that in both compounds there is the possibility of π bonding from the metal to the ligand.

Table 5. Stereochemistry of Ni(n) and the number of unpaired electrons

<table>
<thead>
<tr>
<th></th>
<th>Paramagnetic (two unpaired electrons)</th>
<th></th>
<th>Diagonal (no unpaired electrons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Six-coordinate</td>
<td>Regular [Ni(NH₃)₆]²⁺</td>
<td></td>
<td>Tetragonal [Ni(Diars.)₂]₀</td>
</tr>
<tr>
<td>Five-coordinate</td>
<td>(a) Square [Ni(Ph₃MeAsO)₄ClO₄]⁺</td>
<td>(b) Trigonal [Ni Trid.* Hal₅]⁰</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyramid</td>
<td>Bipyramid</td>
<td></td>
</tr>
<tr>
<td>Four-coordinate</td>
<td>Tetrahedral [NiCl₄]²⁻</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The second method of using magnetic susceptibility measurements to determine stereochemistry depends upon the determination of the size of the orbital contribution to the moment. The case of high spin Co(n) complexes has been extensively discussed¹⁵. Since the Co(n) ion in a tetrahedral environment is orbitally non-degenerate, the moment expected is the spin only value of 3·88 B.M. (assuming no mixing of excited states via spin orbit coupling). The latter does, in fact, increase the moment to about 4·5 B.M. In the octahedral case, however, the asymmetry of the t₂g sub-shell ensures that a large orbital magnetism is to be expected μₐₑᵗᵗ ≈ 5·10 B.M.).
Although widely used, this criterion for distinguishing between tetrahedral and octahedral Co(II) complexes must be used with caution in the following circumstances: (a) if the magnetic moment is on the “borderline” (μ_tet is between 4.5 and 4.7 B.M.); (b) if there is gross distortion of the octahedron leading to splitting of the t_{2g} levels; (c) if the value of Δ in the tetrahedral complex is small, leading to a large value of the orbital contribution via the spin orbit coupling term (Δ/Δ).

To determine stereochemistry of Co(II) complexes with confidence, it is now clear that magnetism must be used in conjunction with other physical data, especially electronic absorption spectra. Indeed a high extinction coefficient (ε ~ 100–1000) and a low Δ (~3500) are associated with tetrahedral structures whilst octahedral arrangements have lower extinction coefficients (ε = 1–10) and higher Δ values (Δ ≈ 10 000 cm⁻¹).

5. Determination of the nature of the bond between metal and ligand

Although Pauling did not in fact propose that magnetic measurements distinguished between purely “ionic” and “covalent” bonding it was frequently assumed 20 years ago that magnetic measurements did indeed enable one to do this. Thus [FeF₆]³⁻ was regarded as “ionic” and [Fe(CN)₆]³⁻ as “covalent”. It is now recognized that spin-pairing is simply an indication of the strength of the ligand field and except where spin-free/spin-paired temperature dependent equilibria are observed, a measurement of the paramagnetism can only distinguish a strong field from a weak one. Nevertheless if one takes into account spectroscopic data as well it is possible from an estimate of the reduction in the spin-orbit coupling constant λ to get some idea of the electron transfer from ligand to metal. Also, in ideal cases, a measure of the electron delocalization factor k allows one to infer the extent of π bonding from metal to ligand. But the theory of these effects still leaves much to be desired.

But the early optimism of the 1930s has had to be modified as it has been obvious that several different stereochemical arrangements frequently occur with the same number of unpaired electrons. Also, it is clear that many of the “spin-only” magnetic moments arose by pure chance because many measurements at 300°C fortuitously happened to fall in the spin-only range. Also, it was fortunate that in many of the complexes studies in the 1930s and 1940s the distortion gave rise to a near spin-only moment. It is also of interest to note that had Van Vleck’s classic work on crystal field theory been carried out 4 years earlier, i.e. before Pauling obtained such success with an over-simplified valence bond/orbital model, chemists would have “discovered” and used crystal and ligand field theory 15 to 20 years earlier than they did. But we have now passed from the stage where chemists simply measure the magnetism of complex compounds to obtain structure to one where we are investigating the magnetism as such of complex compounds. To do this effectively we need to know many fine details of structure in advance from x-ray studies and have to make use of much complementary data from spectroscopic methods of investigation.

But there are many unsolved problems calling for investigation in this
Area and better models of the systems being studied are badly needed. Indeed, magnetism is a field par excellence which illustrates the well known—but often overlooked maxim—that one must not assume that if a model explains the available facts then the model is correct. As has been pointed out the susceptibility of, say, the [NiCl₄]²⁻ ion is affected by eight or more parameters. Given this number of variables, even though some of these are fairly well known, it is possible to “fit” almost any experimental curve of susceptibility against temperature.

Areas of current development and problems arising

Except for the important accidental discoveries, science progresses by two main methods: first, the experimental testing of current (and sometimes too readily accepted) theories and secondly by the enunciation of new theories which lead to more experimental work. For a better understanding of the magnetic susceptibility of chemical compounds today advances in the theory and further experimental data are badly needed. It has been pointed out that a good deal of useful structural information can be obtained from a knowledge of the number of unpaired electrons and the size of the orbital contribution to the magnetic moment of these electrons. Even room temperature measurements can provide much valuable information on oxidation states, coordination numbers and stereochemistry if used in conjunction with other data such as spectra of molecular weights etc.

It is suggested that studies on the following are needed to enable the subject to advance:

1. Experimental determination of susceptibilities over a greater temperature range—particularly below 80°K and down to liquid helium temperatures. Surprisingly few data are available from near absolute zero to 300°K.
2. Investigations on cooperative phenomena. In particular many so-called “dilution” experiments (e.g. of the [CuCl₄]²⁻ ion in a diamagnetic [ZnCl₄]₂⁻ matrix) are suspect unless it can be clearly established that domain formation by the [CuCl₄]²⁻ units has been eliminated.
3. More detailed information is needed concerning the effect on the ligand field of “non-nearest neighbour” atoms in condensed phases. In a complex such as K₃TiF₆, for example, it is essential to know the strength and symmetry of the electric field at the titanium atom arising from atoms or complex ions other than the six nearest F⁻ ions in the [TiF₆]³⁻ unit.
4. Studies of magnetic anisotropy are clearly going to yield big rewards in the understanding of magnetism—particularly if taken in conjunction with accurate crystal structure work and the determination by e.s.r. of “g” values in various directions. The late Professor Rundle showed, for example, ten years ago that the [Cu₂Cl₆]³⁻ anion gives rise to ferromagnetism in a crystalline salt. Clearly it is almost impossible to interpret a powder susceptibility on a substance such as this and single crystal studies are essential.
5. Purposeful preparative work has an important part to play in these investigations. It is no good in many cases simply measuring susceptibilities of compounds which happen to be available. The understanding of stereochemical and valency problems of complex compounds has been greatly advanced by the design, preparation and use of new ligands.
which form complexes suitable for the study of the effect being investigated.

6. Covalency effects present a major challenge because it is more difficult to separate effects due to covalency to the metal, bonding from the metal, electron delocalization onto the ligand and orbital polarization (d—p mixing) on the metal itself. To assist in this there will need to be many studies using related techniques, e.g. n.m.r., n.q.r., visible u.v. and i.r. spectroscopy and newer techniques such as Mossbauer spectroscopy. It is a sobering thought to realise that even in well studied compounds such as the dimeric cupric acetate dihydrate we do not really know the type of Cu—Cu interaction. Our knowledge of the meaning of a k factor in \([\text{Ti(H}_2\text{O)}_6]^3^+\), for example, in terms of modern valency theory, presents a major challenge.

To sum up, although there are severe limitations to the use of magnetism for stereochemical assignments, it is still a valuable tool for many other structural assignments.

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