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THE CHEMICAL INTEREST OF POLARISED NEUTRON STUDIES

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Abstract. - Partial filling of the valence shell orbitals is the origin of most of the interesting features in transition metal chemistry. In molecular coordination complexes these orbitals have substantial metal d-character but a crucial factor in understanding metal-ligand bonding is the delocalization of electron density from ligand to metal or vice versa through covalency. Other techniques give indirect evidence on the spatial distribution of the unpaired spin but polarised neutron diffraction is certainly the most direct means of studying covalency. In addition to reviewing the contribution of polarised neutron diffraction to the study of covalency in coordination complexes the determination of orbital occupancies in lower symmetry complexes and electron delocalization in mixed valency compounds are also considered.

1. Introduction. - Most of the interesting features in the chemistry of transition metals, and especially those which distinguish them from main-group elements, arise from the fact that the valence shell is only partly filled. The electron configuration of most of the free atoms in the first transition series are \( 3d^{n-2}4s^2 \). As we form gaseous ions with increasing positive charge, however, the baricentres of the \( 3d^{n-1}4s^1 \) and \( 3d^{n-1}4s^0 \) configurations fall progressively below \( 3d^{n-2}4s^2 \) until \( 3d^n \) becomes the exclusive ground state configuration for \( M^{2+} \) and upwards. For a given \( M \), the successive ionization potentials \( M^{2+} \rightarrow M^{3+} \rightarrow M^{6+} (3d^n \rightarrow 3d^{n-1} \rightarrow 3d^{n-2}) \) rise on a curve which is neither so steep that it cannot be compensated by gains in electrostatic or covalent bonding energy nor so shallow that it is always energetically advantageous to ionize all the valence shell electrons and so achieve the group oxidation number as in the main group elements. So most transition metals have
a range of oxidation states stabilized by changing chemical environments. Of course this two sentence summary of the basis for the richness of transition metal chemistry still begs practically every question: Why do some ligand environments stabilize high and other low, oxidation states; why do some electron configurations have clear stereochemical preferences etc etc? Chemists have tried to answer such questions with a succession of first empirical and then quantitative models. These they have tested by comparing them with increasingly sophisticated methods for determining electron distributions, of which polarised neutron diffraction is the most recent, and the most sensitive. In this brief survey I shall introduce some of the models, and assess the contribution that polarised neutron diffraction is making to understanding the chemical bonding in transition metal complexes. I shall also mention some of the outstanding problems concerning electronic structure in transition metal chemistry, to which polarised neutron diffraction may contribute solutions.

2. Un peu d'histoire. - Simplest of all the models for valence electron distribution in transition metal complexes is the idea that in a molecule or complex the degeneracy of the five d-orbitals is lifted as the point symmetry around the transition metal centre is lowered from spherical to that of the molecule. In the $O_h$ point group, for example, they transform as $t_{2g} + e_g$. The atomic number and oxidation state of the metal ion then determine the $t_{2g}^n e_g^m$ configuration, provided we know the ordering of the $t_{2g}$ and $e_g$ orbitals. However, the ground state configuration or, more precisely, the ground term is determined by competing one-electron and two-electron contribution to the molecular energy, in the form of the orbital energy and inter-electron repulsion energy. In addition, the simple orbital picture may be complicated by spin-orbit coupling, which is increasingly important in the 4d and 5d elements. Consequently, it become necessary to devise theory of all these energies.

Within a basis set consisting of pure atomic d-orbitals, the earliest model for the orbital energy was that of an electrostatic interaction with the surrounding ions, i.e. the crystal field approach (1). Quantitatively, such a model fails utterly, for instance, to explain the simple observation that the $t_{2g} - e_g$ separation is frequently similar in complexes with neutral and charged ligands. Recourse may be had to purely empirical parametrizations, of course, which simply take account of the symmetry properties of the valence shell wavefunctions, but make no other assumptions about their functional form. Thus it was suggested that the d-orbitals beame 'expanded' when a transition metal ion was placed in the centre of a complex because of screening by the ligand electrons. This is the so-called nephelauxetic effect which is observed in the visible spectrum (2). At the next level of sophistication, this approach could also include a differential expansion of those d-orbitals ($e_g$ in $O_h$) directed towards the ligand centres (3).

Early in the 1950's, however, came the first definitive experimental evidence that wavefunctions centred on the ligands, as well as the metal, must be included in any accurate description of the valence shell in transition metal complexes. Paramagnetic
resonance spectra of IrX$_6^{2-}$ ($X = \text{Cl}, \text{Br}$) in K$_2$PtX$_4$ showed hyperfine splittings due to the interaction of the unpaired spin with the halogen, as well as the Ir, nucleus (4). In fact it was estimated that 26% of the unpaired spin arising from the single hole of the t$_2^5$ ground configuration was situated on the Cl in IrCl$_6^{2-}$. To model this theoretically one must leave behind the assumption that the partly filled valence shell is purely d-like, and move to a molecular orbital formalism, a task which can be approached at several levels of approximation.

3. Models for covalency. - Within the LCAO approximation, in which the valence shell wavefunction is a linear combination of a metal function with an appropriately symmetry adapted set of ligand functions, the simplest model is an extended Hückel one, based on an effective one-electron Hamiltonian. This model, called SCCC (self consistent charge and configuration), was widely applied in the 1960's, especially by Gray and Ballhausen (5) and Cotton (6), but there is no doubt that it grossly overestimates the degree of covalency in metal complexes of the commoner ligands like Cl$^-$, OH$^-$, O$^{2-}$ etc. It survives in a semiempirical form, which bonding parameters determined from experiment (visible and e.p.r. spectra for example) in the form of the 'angular overlap model', widely used to correlate the properties of low symmetry and mixed complexes by applying transferable parameters to individual ligands (7).

Much more elaborate, but also more realistic, models take explicit account of interelectron repulsion by the iterative self-consistent-field method, up to the Hartree-Fock limit. Calculations at this level may be restricted or unrestricted, i.e. they may neglect polarisation due to occupation of orbitals by up and down spins. Finally, with the LCAO approximation, one may choose the analytical atomic basis functions for ab initio calculations in several ways (e.g. double zeta, gaussian) to mimic numerical Hartree-Fock functions calculated for the free atoms (8).

Although it is so widely used that it has become almost a matter of instinct for chemists, the LCAO approximation is only one way of writing a molecular orbital wavefunction. Another, which has more in common with OPW calculations of band structures in continuous lattice solids, is the Hartree-Fock-Slater (HFS) Xα method. In this approach the exchange-correlation term is obtained by averaging the local charge density over spheres centred on each atom. Numerical basis functions for up and down spins are generated as solutions of the atomic HFS equations in which an atom-like potential is constructed by making a spherical average of the molecular potential around the nucleus for the region inside each atomic sphere (9).

4. Results on covalency. - Historically, the first discrete molecular transition metal complex to be subjected to examination by polarised neutron diffraction was CrF$_6^{3-}$ incorporated in the cubic elpasolite salt $\text{K}_2\text{NaCrF}_6$ (10). The crystal field ground state is $^4A_{2g}$ from the t$_2^3g$ configuration. The data were complete out to the (0 0 12) reflection, where $\sin \theta / \lambda = 0.726\lambda^{-1}$ and definite signs of asphericity in the form factor were at once apparent along the symmetry directions [001] and [hhh]. The
simplest approach to such data is just to use the magnetic form factors $f_\omega(k)$ in a
Fourier transformation to give the spin density

$$\rho(r) = \frac{1}{\sqrt{V}} \sum f_\omega(k) e^{ikr}$$

where $m$ is the magnetization. Series termination errors are well known to limit the
quantitative significance of such transformations. One way of reducing these errors
is of course to average the density over a suitably chosen volume element, and a
section through the spin density derived in this way is shown in Fig.1. Taken as

![Fig. 1. Fourier transform of polarised neutron data on $\text{K}_2\text{NaCrF}_6$ (10) in a plane through the Cr and F sites (contours are 0.01$\mu_\text{B}$/$\text{F}^3$).](image-url)

a section through the Cr and F sites the $t_{2g}$ character of the spin density is imme-
diately apparent when we compare the theoretical spin density of Fig.2, as also is
the spin transfer to the fluoride ions. Somewhat similar results, with lower pre-
cision were obtained about the same time by Lynn et al. (11) on the low-spin 5d$^5(t_2^5)
complex $\text{IrCl}_6^{2-}$ in $\text{K}_2\text{IrCl}_6$ where a direct comparison may be made with the extent of
spin transfer to the Cl atoms detected in the early e.p.r. experiments of Griffiths
et al (12). Using a simple molecular orbital wavefunction for $t_{2g}$, and neglecting
overlap, the p.n.d. experiment gave the fraction of spin delocalized on to the six
Cl atoms as 25%, compared with 26% from the e.p.r. experiment.

Another approach to the analysis of experimental $f(k)$ data is to least squares fit to obtain the non-spherical d and p electron distributions by expressing the
magnetic form factors of each atom in the complex by

$$f(k) = \int m(r)e^{ikr}dr^3/\int m(r)dr^3$$

where $m(r)$ is the magnetization density of that atom. If the unpaired electrons in
question occupy a single unfilled shell the form factor is given by a sum of inte-
grals of spherical Bessel functions multiplied by coefficients which depend on the
nature of the orbital (s,p,d) carrying the unpaired spin. Figgis, Mason and their co-
workers (13,14) have used this method to refine orbital configurations for $\text{CrF}_6^{3-}$
based on Weddwood's original data and the tetrahedral 3d complexes $\text{CoX}_4^{2-}$ ($X = \text{Cl,Br}$)
in the tetragonal crystals $\text{Cs}_3\text{CoX}_5$ using data obtained on D3 at the I.L.L. For $\text{CrF}_6^{3-}$
they found $t_{2g}^2$ with 0.11(3) electrons on each F, and in $\text{CoCl}_4^{2-}$, $L_2^{2.71(15)} e_0.0(7)$
with 0.06(1) electrons on Cl mainly in the $p\sigma$ orbitals. These values should be
compared with the simple ligand field estimates of $t_2^3 \cdot 0$ and $t_2^3 \cdot 0$ respectively.

Alternatively the spin density has been expanded as a multipole series in a manner analogous to that used to model molecular charge density distributions (15). If the total spin density is reconstructed from the multipole density fragments one has a clearer picture of the distribution that the simple Fourier transformation procedure would give. Figure 2 shows such a spin density for CrF$_6^-$ (16), compared with one derived from an ab initio Hartree-Fock calculation using 'double-zeta' wave functions.

![Diagram](image)

**Fig. 2.** Spin density in CrF$_6^-$ estimated by (a) a multipole analysis (16) of the polarised neutron diffraction data (10) and (b) an unrestricted Hartree-Fock calculation.

**Table 1.** Comparison of ligand field spectroscopy and polarised neutron diffraction estimates of covalency in CoX$_4^{2-}$ (X = Cl, Br)

<table>
<thead>
<tr>
<th></th>
<th>CoCl$_4^{2-}$</th>
<th>CoBr$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital</td>
<td></td>
<td></td>
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<tr>
<td>populations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_e$</td>
<td>0.83(1)</td>
<td>0.953(2)</td>
</tr>
<tr>
<td>ligand</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_\pi$</td>
<td>0.91(4)</td>
<td>-0.11(3)</td>
</tr>
<tr>
<td>$n_\sigma$</td>
<td>0.10(5)</td>
<td>0.009(7)</td>
</tr>
<tr>
<td>$X$</td>
<td>0.07(5)</td>
<td>0.030(12)</td>
</tr>
<tr>
<td>number of</td>
<td>10</td>
<td>177</td>
</tr>
<tr>
<td>observations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>parameters</td>
<td></td>
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</tbody>
</table>
It has also been pointed out (17) that, for the analysis of chemical bonding in terms of molecular orbitals, the multipole expansion has the convenient feature that the coefficients \( C_{k}^{nlm} \) in the expansion represent the sum over molecular orbitals of the product of the coefficients of the atomic orbitals \( q_{nlm}^{k} \) and \( q_{n'l'm'}^{k} \) making up the molecular orbital in question. Given the atomic form factors, the coefficients can be refined by least-squares methods from the experimental p.n.d. data. It is of some interest to compare the results of such an analysis of \( \text{CoX}_{4}^{2-} \) with the only alternative experimental least squares fit to the population parameters previously available (18). This was based on the most detailed study ever carried out of the ligand field transitions in the optical absorption spectrum. The populations derived by the two methods are listed in Table 1. The optical experiment yields orbital, rather than spin populations and in addition the p.n.d. permits an estimate of the Co 4p population. Most notable of all is the greatly improved precision of the p.n.d. estimates, based on the very much larger ratio of independent observables to parameters. The latter permits a more elaborate parametrization than would have been permissible in treating the optical data. In particular, account could be taken of the differences in population among the \( t_{2g} \) and \( e(T_{d}) \) orbitals brought about by the reduction in symmetry of the \( \text{CoX}_{4}^{2-} \) to \( D_{2d} \) by the lattice. Thus four \( 3d(\text{Co}) \), two \( 4p(\text{Co}) \), two \( sp(\text{X}) \) and two \( p(\text{X}) \) populations were refined, in addition to \( 3d-4p \) overlap and three radial parameters, compared with only two \( 3d(\text{Co}) \), one \( sp(\text{X}) \) and one \( p(\text{X}) \) in the case of the optical data. Clearly p.n.d. experiments of this type will provide extremely sensitive tests of the various molecular orbital models outlined in the previous section.

5. Some chemical bonding problems

The octahedral and tetrahedral complexes with monoatomic ligands, which we have just been discussing, have acted as useful test cases to demonstrate the efficiency of p.n.d. to define accurate ground state wavefunctions for molecules containing partly filled d-shells. Most of the transition metal containing molecules whose bonding is of interest to chemists, however, are rather more complicated than these simple examples. What are the prospects that p.n.d. will be able to answer questions about spin distributions in larger molecules?

One of the qualitative models which has become part of the everyday descriptive vocabulary for complexes with polyatomic and unsaturated ligands is that of \( \pi \)-back-bonding (20). The principle is illustrated in Fig.3. A ligand such as \( \text{CN}^{-} \) has

![Fig. 3. Overlap between metal d-orbitals and ligand orbitals of cyanide. Diagonally hatched orbitals (metal eg and ligand) form σ-bonds. Vertically hatched orbitals on ligand are π-bonding (filled) and unhatched are π-antibonding (empty). Both the latter overlap with unhatched metal t2g orbitals. (after ref.20)
molecular orbitals formed from overlap of 2p C and N orbitals, which have \( \pi \)-symmetry with respect to the M-C-N axis, in addition to orbitals of \( \sigma \)-symmetry. In an octahedral \( M(CN)_6 \) complex symmetry adapted linear combinations of the former overlap with \( t_{2g} \) and of the latter with \( e \) orbitals on the metal. However, in addition to the filled \( \pi \)-orbitals, whose influence on metal-ligand bonding is analogous to that of the 2p orbitals of \( F^- \) in \( CrF_6^{3-} \), there also exist empty \( \pi \)-antibonding orbitals on \( CN^- \), which can also overlap with the \( t_{2g} \) metal orbitals. If the latter are occupied formation of an \( Md-CN \pi^* \) molecular orbital causes a net shift of charge from metal to ligand, which is counterbalanced by donation from the \( CN^- \sigma \)-lone pairs to the metal \( e \) orbitals. If such an effect is significant, it would be expected to show up as unpaired spin in the C and N 2p\( \pi \) orbitals. This would be quite unambiguous in a 'low-spin' complex, i.e. one which has no electrons in \( e \) orbitals. A particularly suitable example is \( Fe(CN)_6^{3-} \), with a \( {5\over 2} \)\( e^0 \) ground state configuration, and for this reason we have embarked on a p.n.d. study of the magnetization density distribution in this molecule. A preliminary note of the results is included in these Proceedings (21) but it is worth drawing attention to two aspects which are typically complicating features of many p.n.d. experiments on coordination complexes. The first is the need to choose carefully among available salts of the complex. \( K_3Fe(CN)_6 \), which at first sight might appear the simplest ferricyanide, has many drawbacks from a crystallographic point of view since it exhibits disorder and structural phase transitions between room temperature and 4K. Another salt, \( Cs_2LiFe(CN)_6 \), which has the cubic elpasolite structure at room temperature, and hence resembles \( K_2NaCrF_6 \), likewise undergoes a phase transition to a monoclinic structure at 155K. Finally we chose \( Cs_2KFe(CN)_6 \) as it is already monoclinic at room temperature. The Fourier map (Figure 4) shows no sign of spin delocalization on to C or N up the level of 5\%, a surprising result in view of the \( \pi \)-back bonding model.

The second point concerns spin-orbit coupling. As chemists we want to associate the measured magnetization density with unpaired spins occupying specific atomic or molecular orbitals. Furthermore it is quite difficult, if not impossible, for theorists to include spin-orbit coupling in calculations, e.g. of the \( X\alpha \) type. This is one reason why the large majority of complexes studied to date have had orbital-singlet ground states (high spin octahedral \( d^3 \), \( d^5 \), \( d^7 \) and tetrahedral \( d^7 \)). Apart from \( Fe(CN)_6^{3-} \), with a \( 2\Gamma_{2g} \) ground term, a further example is phthalocyaninato Mn(II) (23).

Coordination chemists like to believe that the electronic structures of the molecules they study are not modified very much by the lattice they are placed in (or, indeed, on going from the crystal lattice into solution). Alarming evidence that p.n.d. may be sensitive enough to show up such differences comes from the work of Figgis et al (17) on \( CoX_4^{2-} \) in \( Cs_3CoX_5 \) and on trans-Ni(\( NH_3)_3(NO_2)_2 \) (23). Distinct asymmetry in the d-orbital occupancies derived from multipole expansion, and even detectable in the Fourier maps, appears to originate, not from distortions within
the complex molecules themselves, but from the charge distribution of their surroundings. For instance the occupancies of the \( t_2 \) orbitals \( xy, xz, yz \) in \( \text{CoCl}_4^{2-} \) (averaged in Table 1) were refined as 0.06, 1.00 and 1.00 while the Cl atoms are only distorted \( \pm 2^\circ \) from a perfect tetrahedron. In the \( \text{Cs}_3\text{CoCl}_5 \) lattice the \( \text{CoCl}_4^{2-} \) groups form layers separated by layers of \( \text{Cs}^+ \) and \( \text{Cl}^- \), a point which may have to be considered when comparing model spin density maps with calculated ones.

Further areas in chemical bonding theory where p.n.d. has begun to show its potential are in the fields of low symmetry complexes and the interactions between metal ions mediated through bridging ligands. The latter may include not only superexchange between metal ions in clusters but also the delocalization of spin between ions of differing oxidation state in mixed valency compounds. Among lower symmetry systems can be cited the distortion brought about by the Jahn-Teller effect in \( d^4 \) or \( d^9 \) complexes. An example is the tetragonal elongation of octahedral co-ordination found in the \( d^4 \) salt \( \text{Rb}_2\text{CrCl}_4 \), where p.n.d. strikingly confirms the prediction of simple ligand field theory that the occupancy of the \( d \)-orbitals is close to \( (xz)^1(yz)^1(xy)^1(z^2)^1(x^2-y^2)^0 \) (24). Few polynuclear metal cluster compounds have yet been examined by p.n.d., through they provide very simple examples of magnetic exchange. The potentiality of the field is exemplified by what, to a physicist, might seem a rather complicated molecule, \([\text{(H}_2\text{O})(2,2'-\text{bipyridine})\text{Cu(OH)}_2\text{Cu}(2,2'-\text{bipyridine})(\text{OSO}_3^-)]4\text{H}_2\text{O} \) (25). The essential feature of this molecule is the pair of hydroxyl groups forming a bridge between the \( \text{Cu(II)} \) ions, which provide a superexchange pathway leading to a ferromagnetic exchange constant of about \( 24 \text{cm}^{-1} \). Net transfer of some 10% of the spin from the \( \text{Cu(II)} \) to the bridging groups was observed, together with a region of negative spin density 'behind' the oxygen atoms, suggesting that spin polarisation plays an important part in the exchange mechanism, as predicted by recent unconstrained Hartree-Fock and Xa calculations on metal
Mixed valency compounds are formed by nearly 40% of the elements in the Periodic Table, and the relation between their structure and properties has been of great interest to chemists for many years (28). Central to this understanding is the assessment of what we have called 'valence delocalization', (24) the extent to which a single valence bond configuration, e.g. $^{\text{Fe(II)}}_A^{\text{Fe(II)}}_B$ (where A and B are crystallographically distinct sites in the crystal), represents a good approximation to the ground state, or whether it is mixed, to a greater or lesser degree, with the charge transfer configuration $^{\text{Fe(III)}}_A^{\text{Fe(II)}}_B$. In principle p.n.d. should be a sensitive tool for determining intersite spin transfer in mixed valency compounds, especially where one of the oxidation states would have no net spin in the absence of such transfer. A situation of this kind occurs in one of the oldest and most famous mixed valency salts, Prussian Blue, $\text{Fe}_4[\text{Fe(CN)}_6]_3\cdot 14\text{H}_2\text{O}$, where the Fe(II) is low spin. An attempt to measure spin transfer between the high spin Fe(III) $^{6\text{A}}_1$ and Fe(II) $^{1\text{A}}_1$ by p.n.d. on a powder sample (30), gave only an upper limit of a few percent, but better counting statistics, or use of a analogous compound in the form of a single crystal, might help to narrow the estimate.

The future

This brief survey has shown that diffraction experiments using polarised neutrons are already contributing to our information on chemical bonding in a wide variety of transition metal complexes. It will never be a routine tool for chemists, not only because polarised neutron diffractometers are not numerous, but also because of other constraints such as selection of crystals without structural phase transitions between 300 and 4K, and the need to have crystallographic data of excellent quality, properly corrected for extinction. The technique seems likely to make its most effective contribution through careful experiments on small numbers of compounds chosen as paradigms of specific bonding situations rather than by attempting to survey extensive sets of related molecules, a procedure often favoured by chemists. Larger molecules, however, are by no means excluded, provided the crystallographic desideratae can be met. Organometallic molecules, in particular, have scarcely been tackled at all so far. Thus we can confidently anticipate further insights into chemical bonding from this powerful new technique.

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