

Magnetism and the Metal–Ligand Bond in Coordination Complexes

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We review the position that has been reached in the interpretation of paramagnetic susceptibilities of transition metal complexes. We summarize also the very recent determinations of magnetisation densities of crystals using polarized neutron scattering techniques, and the level of valence theory that is necessary to describe experimental spin densities in open shell molecules.

Introduction

Experimentally and theoretically we have come a long way since Pauling's series of papers [1] introduced the 'magnetic criterion for bond type'. That early criterion has come to be recognized, inevitably perhaps after nearly 50 years, as too simplistic and occasionally wrong. But it remains the case that the way in which Pauling exploited contemporary physics dominates the tone of present magnetochemical studies [2]. Faced with an increasingly technical magnetochemical literature, the mainstream inorganic chemist could be forgiven if he came to the view that the subject had become irrelevant if not actually passé. So it is worth showing here that the subject has in fact evolved so that the complexities of real molecular systems, while often lacking the apparently simplifying feature of high symmetry, present opportunities for the determination of chemical parameters having day-to-day currency.

The chemical possibilities of ligand field theory broadly lie in the phenomenological spectrochemical and nephelauxetic series which, of course, owe nothing to group theory. The angular overlap model (AOM) [3–7] is a ligand field approach which brings to studies of complexes the notion of the functional group. Other, more symmetry-based, models confine their attention – through quantities [8] such as Dq , Ds , Dt , $D\sigma$, $D\tau$, Cp and even more comprehensive variables [9] – to the complex (chromophore) as a whole and therefore are at a disadvantage when one wants to discuss individual metal–ligand interactions within the molecule.

Any analysis of electronic spectra, e.s.r. or magnetic susceptibilities, based on the localized AOM, must proceed with an effectively complete, self-consistent treatment of the technical aspects of angular momentum and ligand field theories [10]. Undue simplification and approximation characterized many early studies although they were often required, given the lengthy nature of more complete calculations, especially in the context of molecular paramagnetism [2]. Reasonably complete calculations are now computationally feasible and we can discern, for example, how modelling based upon unduly truncated basis function sets can be in gross error; and also that no generalizations are yet to hand which provide confident predictions as to when a simple, approximate, model would be adequate. Thus we accept as normal the inclusion of all terms of the same spin-multiplicity as the ground term and frequently the basis spanned by the complete d^n configuration is used to ensure meaningful results. Idealization of molecular symmetries (for example, describing a *trans* MA_4B_2 complex as having D_{4h} or D_4 symmetry) may yield plausible interpretations of electronic d–d spectra but is frequently found to be totally inadequate for a description of paramagnetic susceptibilities and g-values. In short, we have come to recognize that the precise molecular geometry, detailed by diffraction methods, is an essential prerequisite to a critical analysis of all ligand field properties. While gross features of coordination number or geometry may have been obtained in the past from simple spectra and average susceptibility data, the current emphasis is to move from a structure determination to a description of intramolecular bonding which includes a semi-quantitative determination of the electron distribution. Real molecules frequently have little symmetry: traditional ligand field approaches, relying upon the special results in high symmetry environments, have limited use. The AOM works best when there is a minimum of special, symmetry-based, correlations between modelling parameters: it is a ligand-field rather than a molecular-orbital model, the basis for both ligand field and

AOM themes having been re-examined in some detail recently [6, 7].

We refer, then, to an effective potential acting upon a pure d orbital basis (for the transition series), the potential being divided spatially into discrete, independent cells. The cellular potentials can always be made diagonal and characterized by *local* ' σ ' and ' π ' labels. The AOM presumes that the axes of such diagonal perturbations coincide, more or less, with features of the local pseudo-symmetry in a given metal–ligand interaction. We note the unfortunate early introduction of the AOM as a quasi-variation of the Wolfsberg–Helmholz MO approach: however, the well-known objections to the W–H approximation do not carry over; we might better refer to the AOM as a 'localized potential model' [6].

The application of the AOM to the interpretation of d – d spectra often gives rise, in low-symmetry complexes, to rather a large number of parameters which may not be defined adequately by the few observed electronic transitions: in principle, only four AOM variables may be determined from spectral transitions within a basis formed from the five d orbitals. But we recognize that the same AOM parameters also determine eigenvectors so that this number is increased from 4 to 15 and it is here that magnetochemistry emerges strongly, for it provides, *inter alia*, a means by which the character of the wavefunctions may be determined. The relative utility of optical spectroscopy, paramagnetic anisotropy and its temperature variation, and e.s.r. spectroscopy in determining unique AOM parameter values for each metal–ligand interaction in a molecule is a matter for individual, rather than general, judgement but it is clear that together these experiments now permit chemically meaningful analyses of transition metal complexes of any symmetry and coordination number, using bases from any d^n configuration. Three coherent sets of studies illustrate this proposition.

Complexes with N-donor Ligands

The complete susceptibility tensors for the complexes $Mpy_4(NCS)_2$; $M = Co(II)$ and $Fe(II)$ have been analysed [11] within complete maximum-spin bases perturbed by interelectron repulsion, ligand-field, and spin-orbit effects:

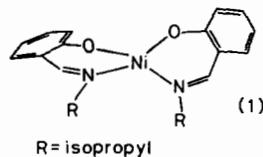
$$\mathcal{H}' = \sum_{i < j} \frac{e^2}{r_{ij}} + V_{AOM} + \zeta \sum_i l_i \cdot s_i \quad (1)$$

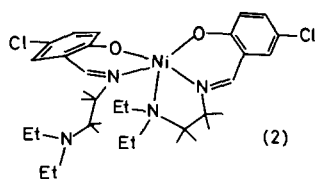
In addition to the Racah B parameter and spin-orbit ζ , values for the AOM parameters $e_\sigma(py)$, $e_\sigma(NCS)$; $e_n(NCS)$; $e_{\pi//}(py)$ and $e_{\pi\perp}(py)$ were determined. It was found that the calculated orientations of the molecular magnetic susceptibilities is such that no principal magnetic direction lies close to any bond

vector or bisector thereof: thus, in this approximately tetragonally distorted MA_4B_2 octahedron, the B–M–B vector does not describe a principal magnetic direction. This result, typical of its kind, illustrates the dangers of idealizing molecular symmetry so far as magnetism is concerned. The results of real chemical interest, however, are as follows. The σ bonding parameters, though not determined with good precision, are each approximately 4000 cm^{-1} ; the ligand field parameter $10Dq$, equivalent to $3e_\sigma - 4e_\pi$ for octahedral chromophores, is therefore about $12,000 \text{ cm}^{-1}$ which is unexceptionable. A zero value found for $e_{\pi//}(py)$ is transparently what one expects for M–py π bonding in the plane of the heterocycle, and the value of 50 – 130 cm^{-1} for $e_{\pi\perp}(py)$ describes a small π donor role of these ligands with respect to the metal atom. Support for these interpretations, especially for positive and negative values referring to ligand donor and acceptor properties, comes empirically from a number of studies [12–20] and also from recent theoretical analyses [6, 7] of the AOM.

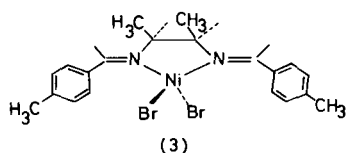
Two trigonally distorted, tetrahedral ions $M(\text{quinoline})Br_3$, $M = Co(II)$ and $Ni(II)$, crystallize in the triclinic system, a circumstance which provides much independent data on principal molecular susceptibilities and their relation to crystallographic properties. The full interpretational analysis [15] was based also upon 4 K transmission spectra in the near IR, visible and UV regions; and on polarized absorption and e.s.r. single-crystal spectra of the cobalt complex. All these data are reproduced by a single set of modelling parameters, the most significant finding being the demonstration of π acidity for the quinoline ligand ($e_{\pi\perp} \sim -500 \text{ cm}^{-1}$). Current analyses [21] of some exchange-coupled binuclear cobalt(II) benzoates demonstrate similar π acidity for the (terminal) quinoline ligands and a recent AOM analysis [17] of the crystal transmission spectrum of a biquinoline complex – $Ni(\text{biquinoline})Br_2$ – gives $e_{\pi\perp}$ as *ca.* -1000 cm^{-1} . It is reassuring, obviously, that the AOM results, though arrived at only after thorough, technical procedures, are intuitively obvious and immediately transparent: they furnish the inorganic chemist with some quantitative appreciation of ligand functionality.

Salicylaldiminato complexes [(1) and (2)] have provided comparisons of bonding in four- and five-coordinate species and, particularly, variations in π bonding. Again single-crystal susceptibility data have been allied with diffuse reflectance and solution optical spectra to provide consensus parameters [12,





13]. e_{σ} values for the donor atoms in the sal ligands are all $\sim 4000 \text{ cm}^{-1}$; $e_{\pi}(imine) = 0$; $e_{\pi_1}(imine) \sim 900 \text{ cm}^{-1}$ —an indication of significant π basicity; $e_{\sigma}(amine) \sim 2500 \text{ cm}^{-1}$, a low value consistent with the long nickel–amine bond length of *ca.* 2.2 Å compared with 1.96 Å for the nickel–imine bonds. The noteworthy differences in the values of $e_{\pi_1}(O)$ are held to reflect the enhanced π basicity of the phenolic oxygen group in the presence of the *para* chloro-substituent. In a rather similar way, the spectrum of complex (3), reproduced [17] only for

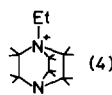


$e_{\pi_1}(imine) \sim -250 \text{ cm}^{-1}$ —in contrast with the value of $+900 \text{ cm}^{-1}$ found for the sal species—provides evidence of the sensitivity of the imine ligand towards, here, the *ortho* substituent phenolic oxygen.

Concurrent with the determination of AOM parameters in these and following systems has been the

determination of Racah B parameters. Nephelauxetic effects represent the chemical content of ligand field theory as much as the spectrochemical or AOM series: they are not 'localizable', however, referring to the complex as a whole. Perusal of the data summarized in Table I, shows that sensible trends emerge throughout, an obvious example being the increased nephelauxetic effect along the series Cl, Br, I. Note, however, that B values are significantly lower in the salicylidimino and diimine complexes than in those involving simple amine and chlorine or bromine ligands. The B values identify the *gross* π bonding while the AOM parameters describe the algebraic or *net* π bonding.

The amine groups just cited refer to a study [14] of some, almost perfectly, trigonally distorted tetrahedral complexes $ML_N^+X_3$; $M = \text{Co(II)}, \text{Ni(II)}$; $X = \text{Cl, Br}$; $L_N^+ = \text{dabco}$, a positively charged, bicyclic tertiary amine (4). We emphasise the marked increase



in e_{σ} values for the tertiary amines on replacing Co(II) by Ni(II). It is expected that such sterically undemanding tertiary amine ligands will act as strong bases, of course: further we might anticipate large AOM parameters due to the larger effective nuclear charge in the d^8 system. However, in the nickel com-

TABLE I. Angular Overlap and Racah B Parameters (cm^{-1}) for Phosphine, Halogen and Nitrogen Ligators in some Complexes of Nickel(II) and Cobalt(II).

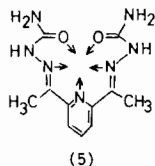
Complex	$e_{\sigma}(P)$	$e_{\pi}(P)$	$e_{\sigma}(\text{Hal})$	$e_{\pi}(\text{Hal})$	$e_{\sigma}(N)$	$e_{\pi_1}(N)$	B	Reference	Note
Ni(PPh ₃)Br ₃ ⁻	5000	-1500	3000	700			620		
Ni(PPh ₃)I ₃ ⁻	6000	-1500	2000	600			490		
Ni(PPh ₃) ₂ Cl ₂	(4500)	(-2500)	(4500)	(2000)			(550)		
Ni(PPh ₃) ₂ Br ₂	(4000)	(-1500)	(4000)	(1500)			(550)		
Co(PPh ₃) ₂ Cl ₂	(4000)	(-1000)	(3500)	(2000)			(575)		
Co(PPh ₃) ₂ Br ₂	(3500)	(-1000)	(3500)	(1500)			(575)		
Ni(POP)Cl ₂	5000	-1500	3600	1500			550		(i)
Co(PPhEt ₂) ₂ (mes) ₂	(6000+)	-3400					(280)		(ii)
NiL _N ⁺ Cl ₃			3250	1000	6100	0	760		(iii)
NiL _N ⁺ Br ₃			3000	850	5900	0	720		(iii)
CoL _N ⁺ Cl ₃			3500	1100	4250	0	740		(iii)
CoL _N ⁺ Br ₃			3500	1000	4000	0	700		(iii)
Ni(quin)Br ₃ ⁻			3600	500	3600	-600	720		
Co(quin)Br ₃ ⁻			3000	450	3500	-500	670		
Ni(biquin)Br ₂			3500	850	4200	-1000	790		
Ni(sal) ₂					(4000)	+900	(660)		(iv)
Ni(diimine)Br ₂			3500	800	5200	(-250)	630		(v)

(i) POP = oxydiethylenbis(diphenylphosphine). (ii) mes = mesityl. (iii) L_N⁺ = 'dabco', N-ethyl-1,4-diazabicyclo[2,2,2]-octonium⁺ (formula 4). (iv) sal = N-isopropyl salicylidimino (formula 1). (v) diimine = *cis-endo*-N,N'-di(4-methyl-benzylidene)-meso-2,3-butanediimine.

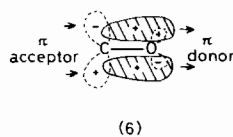
plex, those for the halogens show no such marked change: instead, in view of the larger effective nuclear charge, the $e(\text{halogen})$ parameters appear to describe relatively weaker metal-ligand interactions. The situation is clarified, though, when it is recognized that the extra electron in the d^8 system resides (as it turns out) in the $d_{xy}/d_{x^2-y^2}$ orbital pair which cannot interact with the amine along the z direction. The resulting decrease in the acceptor function of these metal orbitals weakens interaction with the halogens. An overall trend in the molecules towards atomic neutrality then requires the amine to donate electrons more strongly to the metal. In support of this view, we note the Ni–N bond lengths as being some 0.2 Å shorter than those of Co–N, while relatively little change is observed for the metal–halogen bonds. Thus we may rationalize changes in AOM e parameters in terms of bond length variations but at the same time quantitatively explain those bond length changes in terms of the electronic configuration of the central metal.

Seven-coordinate Species

An exactly similar rationalization of bond length variation has been proposed in studies [19, 20] of the magnetism and spectroscopy of some seven-coordinate complexes $\text{ML}(\text{H}_2\text{O})\text{X}$; $\text{M} = \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$; $\text{X} = \text{H}_2\text{O}, \text{Cl}$; L is the, essentially planar, pentadentate ligand dapsc (5). Parameters for

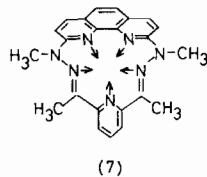


all ligands throughout the metal series are unsurprising excepting those for the keto groups. In the $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$ systems studied, the keto groups are characterized by low e_σ values (*ca.* 2500 cm^{-1}) and high, positive $e_{\pi\perp}$ values (*ca.* 2000 cm^{-1}). The weak σ basicity of the keto groups, which is not associated with unduly long $\text{M}-\text{O}$ bond lengths, undoubtedly does represent a true situation: these ligands are neutral groups (compare the phenolic oxygen ligands in the Schiff base complexes above) and the corresponding conjugate acid is strong. Much more surprising is that the shift in the d orbital energy caused by keto π donation is nearly as large as that caused by σ donation. This has been interpreted as manifesting the π donor role of a ketone as being associated in part with the π acceptor role of a carbonyl, as illustrated schematically in (6). On passing to the d^8 , $\text{Ni}(\text{II})$ analogue, the π donor role of the keto groups disappears, in line with the observation of increased $\text{M}-\text{O}$ bond lengths. As for the amine com-

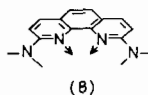


plexes, this increase in metal–keto bond length is argued to result from a decreased metal σ acceptor role of the filled orbital essentially directed towards the oxygen ligands. Addition of a further electron in the d^9 , $\text{Cu}(\text{II})$ system also lengthens the $\text{Cu}-\text{N}$ bonds and so a self-consistent view of the detailed bonding in the coordination shells of these complexes has emerged.

Compare here the pentagonal bipyramidal, seven-coordinate complexes, involving a macrocyclic ligand (7), geometrically and chemically similar to the dapsc



system just discussed. In the macrocycle, the semi-carbazone groups have been replaced by a phenanthroline moiety, so that the, nearly planar, pentadentate macrocycle offers five donor nitrogen atoms arranged in a fairly regular pentagon. However, the magnetic anisotropy data cannot be reproduced at all within an idealized five-fold symmetry, and a detailed AOM analysis [22] reveals that the ligand field is dominated by the phenanthroline moiety which acts as a strong σ donor and a strong π donor. This surprising result contrasts with the more usual behaviour of 'free' phenanthroline as a π acceptor. It appears in the present macrocyclic complex that the dominant ligating moiety is the phenanthroline, modified by electron-rich sp^2 nitrogen substituents as in (8). New avenues of current synthetic chemical



research [23] have been suggested in part by this result, which emphasizes again that contemporary magneto-chemical and ligand-field techniques are genuinely vital areas of enquiry in inorganic chemistry.

Phosphine Ligands

We turn finally to a series of analyses of the antibonding factors in phosphine-containing complexes. Table I lists AOM parameters determined [24, 16–18], from both optical spectroscopy and single-crystal paramagnetism for several four-coordinate

complexes of nickel(II) and cobalt(II). In the trigonally distorted tetrahedral complexes $\text{Ni}(\text{PPh}_3)\text{X}_3$; $\text{X} = \text{Br}, \text{I}$, the phosphine interactions are characterized by large σ basicity and large π acidity in a manner entirely consistent with the Dewar–Chatt model of synergic ‘back-bonding’. Further, the smaller donor properties of three iodines relative to three bromines results in a larger e_σ value for the phosphine in the former case together with a decrease in the Ni–P bond length by 0.04 Å. The bis-phosphine complexes, including that involving a bisphosphine chelate, similarly demonstrate the phosphine π -acceptor function but differ from the monophosphine systems in respect of the halogen π donor functions. It appears that the presence of two phosphines in the coordination shell requires a greatly enhanced degree of π donation from the halogens, generally in response to the electroneutrality principle. Throughout this whole series of phosphine complexes, the nephelauxetic reduction in the Racah B parameters is large, again consistent with the proposed extensive π bond network throughout these molecules. Elsewhere [25], we have examined the evidence for metal–phosphine π bonding that is available from metal–ligand bond lengths. The magnetic evidence for π bonding seems entirely self-consistent; more importantly, it may provide a much more sensitive probe of M–P π bond orders than an analysis of bond lengths.

A Consensus

A systematic application of the AOM in conjunction with single-crystal magnetic, e.s.r. and spectroscopic measurements has proved most rewarding and should bring to an end the era of magnetochemistry being simply a technique for counting unpaired electrons or of being too technical for worthwhile chemical application. Although the theoretical problems are more formidable, there is no reason why analyses [26–28] of exchange-coupled systems should not be tailored to chemistry in an analogous way: we may hope to see more studies stepping beyond the phenomenological spin-hamiltonians of models like the Heisenberg–Dirac–Van Vleck scheme. After all, the fundamental nature of exchange phenomena are sufficiently well understood that chemists should now be more interested in applications. The very parametric nature of the AOM, and ligand field theory in general, means that results of studies like those reviewed above are necessarily only semi-quantitative. There is no need to worry that a connection between them and molecular orbital mixing coefficients is not apparent, for there is no good reason why M.O. theory should be regarded as intrinsically more ‘true’ than ligand field theory. In ligand field models, the unknowns of ‘configuration interaction’, of the relative contributions of π and π^* ligand functions,

and so on, are all quite legitimately sequestered into the parameters. That many approximate or semi-empirical molecular orbital models either neglect or idealize various contributions to the bonding picture is no defence for their intrinsic ‘reality’! More successful M.O. calculations may provide an understanding of the occupied bonding orbitals, that is of ground states. Ligand field models parameterize excited states and the connections between AOM parameters, say, and ground state features are complex. Further the ligand field approach both as theory and in practice is rarely accurate to better than 10%: it is doubtful, however, if any other technique, theoretical or experimental, has a much better track record within transition metal chemistry.

Direct Determination of Molecular Spin Densities in Paramagnets

The background to our next discussion lies in diffraction experiments providing a direct link between observations (Fourier coefficients–diffraction intensities) and molecular electronic densities: spectroscopy is more directly concerned with energy levels and therefore only indirectly with spatial relationships of electrons in bonds.

The X-ray diffraction method leads, by one route or another [29], to electron densities in crystals. Valence electrons contribute only slightly to the elastic scattering processes and so there are some practical problems in assuring significant results from crystals of transition metal complexes. An increasing number of experimental results, however, demonstrate asymmetric electron densities around metal ions which have an interpretation in simple crystal field terms [30]; have, though perhaps less convincingly, illustrated covalence and features of wave function contraction or expansion *vis à vis* that in the free metal ions [31]; and have (relatedly) often pointed to the lack of significant electron density between metal ions in binuclear complexes which were thought to possess metal–metal bonds [32]. In this latter respect, such studies have therefore raised the question of the significance of the relation between formal bond order and overlap density between adjacent orbitals whose charge centroids are small ($3d$) compared with the metal–metal bond radius or large and diffuse (for example, the metal $4s$ orbital).

A very selective method of studying electron (spin) densities in singly occupied molecular orbitals is *via* the scattering of (magnetically) polarized neutrons. We have described [33, 34] the salient features of the method elsewhere and so give only a very brief summary here. The magnetic structure factors, coming from a polarized neutron diffraction experiment, can be interpreted either by a non-

spherical orbital model approach [35] or *via* a least-squares analysis based on local multipole expansions to parameterize the spin-density distributions [36]; moreover, the total spin-density in a molecule can be reconstructed from the multiple density fragments in a way that affords direct comparison with an 'at rest' theoretical calculation of spin density and its results from this approach [34] that we now describe.

K_2NaCrF_6 forms highly symmetric crystals with the chromium ions in a ligand field of exact O_h symmetry. We showed, quite early [35], how the approximate t_{2g}^3 configuration 'fitted' the magnetic structure factors to a significantly better extent than a spherically symmetric spin distribution and began also to describe the early evidence for metal-to-ligand spin transfer. The complete results, illustrated in Fig. 1, describe three main features:

(i) the essentially non-bonding character of the metal $3d$ spin density: the radial and angular parts of the wave-function are not greatly different from those

of the free ion, in contrast with the $3d$ function in the antibonding levels of CoCl_4^{2-} (*vide infra*).

(ii) the accumulation of positive spin density in the fluorine $2p\pi$ orbitals, and

(iii) negative spin density concentrated along the Cr–F bond axes, either side of the fluorine nuclei. Quantitative analysis provided the following orbital spin populations,

$$\text{Metal } \{3d, t_{2g}^{2.76(1)}; 4s^{0.31(10)}\} \text{ Ligand } \{2p\sigma^{-0.05}; 2p\pi^{0.03}\},$$

which can be identified with electronic populations in the approximation of negligible orbital contribution to the magnetization density. Spin-polarized, Hartree–Fock calculations give the spin transfer coefficients as -0.022 e and $+0.026$ e for $f\sigma$ and $f\pi$ [37] while corresponding figures derived from an X- α calculation [38] are -0.048 e and $+0.010$ e: the X- α calculation clearly has the σ – π net transfer

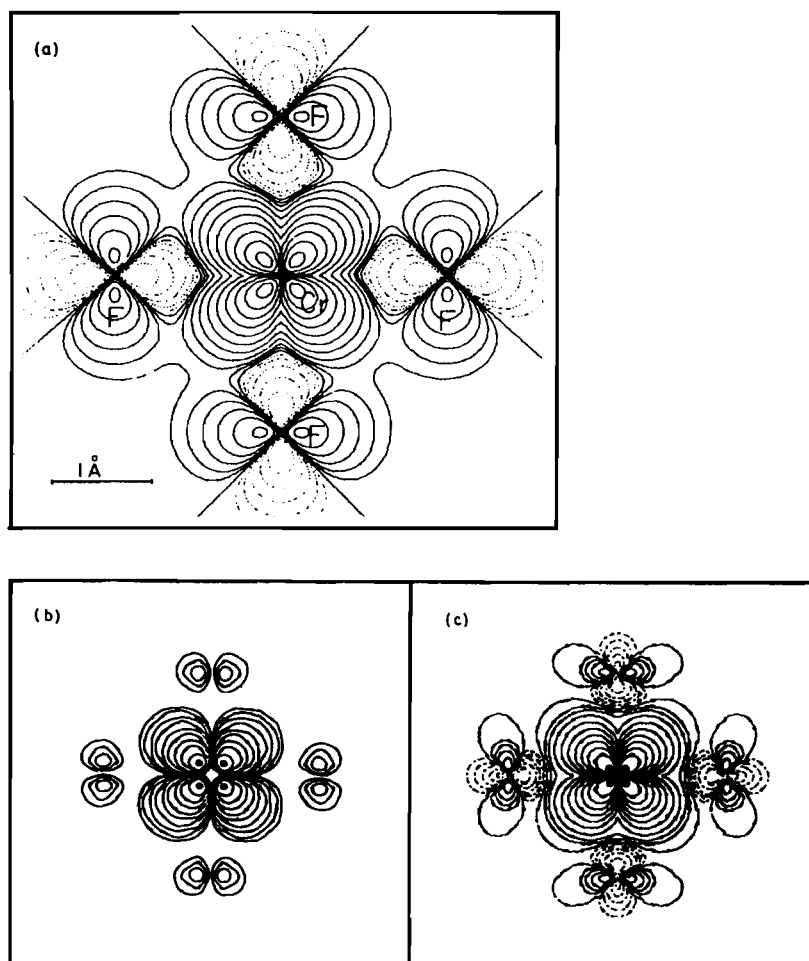


Fig. 1. (a) Experimental spin density in CrF_6^{3-} . (b) Calculated at restricted Hartree–Fock level. (c) Calculated at unrestricted Hartree–Fock level.

quantitatively right if, simplistically, underestimating the absolute extent of π bonding. We have recently completed a rather full, unrestricted Hartree-Fock calculation and the theoretical spin density in the complex, shown alongside the experimental data in Fig. 1, is in generally very good agreement with experiment.

Our second example concerns the spin density in CoCl_4^{2-} ions occurring in crystals of Cs_3CoCl_5 which have been the object of studies by a battery of spectroscopic and diffraction techniques. The observed and calculated spin densities are shown in Figs. 2 and 3. The (correlation) negative spin density

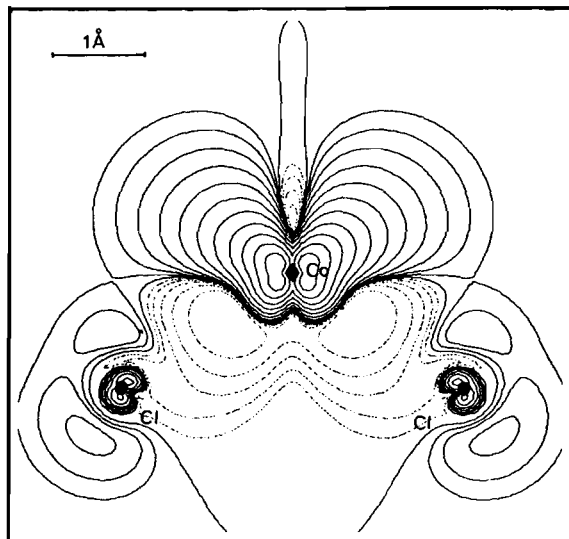


Fig. 2. Experimental spin density in the Cl-Co-Cl plane in CoCl_4^{2-} .

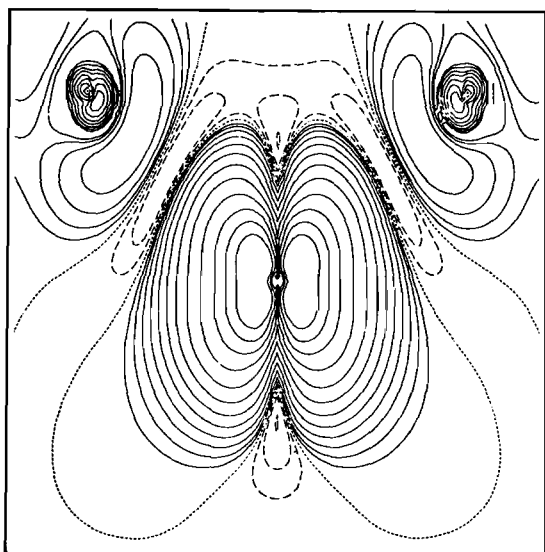


Fig. 3. Calculated spin density in the Cl-Co-Cl plane in CoCl_4^{2-} .

separating the spin densities around the cobalt and chlorine atoms is striking. The theoretical density, calculated (as yet) using a contracted Gaussian basis set, reflects the experimental trend but underestimates the correlation density and, relatedly, makes the metal orbital less antibonding. Orbital populations are t_2^2 (the e population in this d^7 complex is found to be statistically insignificant) with chlorine $p_x^{-0.01(2)}$ and the (σ) p_y and p_z population being 0.03(2) and 0.06(1) electrons.

Finally, we have analysed the spin distribution in some phthalocyanato complexes, the observed data for the cobalt(II) species being shown in Fig. 4.

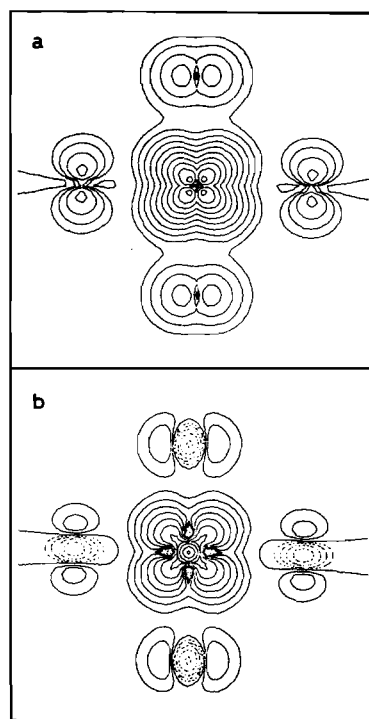


Fig. 4. Experimental spin density (a) in the molecular plane of phthalocyanato cobalt(II), and (b) 0.2 Å above the mean molecular plane.

Orbital spin populations emerge as $d_{z^2}^{0.8(1)}$, $d_{x^2-y^2}^{-0.1(1)}$, $d_{xy}^{0.3(1)}$ and d_{yz} , $d_{xz}^{0.0(1)}$ with p_x and p_y (nitrogens) being 0.10(4) and $-0.12(4)$, respectively, and $p_z^{0.01(2)}$. Corresponding values are found for the manganese(II) complex. The σ framework, negative spin density is obviously the common feature surrounding all of these results as, indeed, is the general σ to π redistribution of spin, the quantitative extent of which is clearly determined by the ligand π activity.

A comparison has been made of spin and electron populations in manganese phthalocyanine derived from polarized neutron scattering, X-ray diffraction data and an angular overlap calculation. The spin populations, given in Table II, derived from the ligand field analysis were based on diagonalization of the

TABLE II. Orbital Spin Populations in Phthalocyanato-Manganese(II) and -Cobalt(II) [40] [41].

Orbital on metal	MnPc (neutron)	MnPc (X-ray)	MnPc (AOM)	CoPc (neutron)
e_g	2.0(2)	1.3(3)	2.00	3.7(2)
b_{2g}	1.3(2)	1.5(2)	1.80	1.6(2)
a_{1g}	0.8(2)	0.9(2)	0.97	1.2(2)
b_{1g}	0.1(1)	0.1(2)	0.21	0.2(2)
$a_{1g}(4s)$	1.6(2)	2.0(3)		1.9(2)

complete d^5 basis under the Hamiltonian (1). In this semi-quantitative study, exploration of parameter space was incomplete, the aim of the analysis being restricted to the quantitative reproduction of the relative magnitudes of observed e.s.r. g-values. With Condon-Shortley parameters set near the free-ion value (1440 and 96 cm^{-1} for F_2 and F_4), a very large value for $e_\sigma(N)$ of ca. 12,000 cm^{-1} had to be taken in order to reproduce the intermediate-spin ground term. Elsewhere [18], we have demonstrated a very large Nephelauxetic effect in some planar, low-spin cobalt(II) systems, which allows a more modest σ bond interaction to yield the required cross-over of low- and high-spin states. Further, in complexes with planar geometries it now appears common that $4s-3d_{z^2}$ interaction lowers the energy of the $3d_{z^2}$ orbital by up to 6000 cm^{-1} , a circumstance which clearly must be taken into account in any AOM analysis. While some doubt must therefore attach to the AOM analysis for manganese phthalocyanine, the general order of agreement between spin populations calculated from the ligand field model and those determined by the polarized neutron diffraction experiment may be taken as some support for the newer, less worked technique.

The Way Ahead

These early analyses by the polarized neutron diffraction of relatively complex molecular crystals were carried out as much to test the efficacy of the procedures, especially with respect to the statistical problems associated with the limiting neutron flux, as to determine spin density distributions. The results are undoubtedly sufficiently encouraging for further studies to be undertaken. However, as the experiment presses against the statistical limit, it is important to make the fullest use of results from other techniques. The initial expression of the data in terms of a multipole expansion and subsequent construction of an 'at rest' spin-density map has been especially successful and provides a point of contact for theoretical calculations of molecular spin distributions. The

further steps leading to an orbital spin-population analysis are more difficult, however, and might well be better carried out using, as data, the detailed metal atom d electron configuration determined by a thorough ligand field (AOM) analysis based on the fullest possible range of the more traditional techniques. The parametric nature of ligand field theory should not prevent the establishment of a reasonably true d electron configuration. In turn, the degrees of freedom remaining to the polarized neutron experiment could be concentrated upon those questions not reliably accessible to ligand field techniques: namely, the extent of metal orbital contraction or expansion on bond formation, and an increased confidence in the description of delocalization of spin onto ligands, together with the effects of spin correlation. Altogether traditional magnetochemistry and ligand field theory are somewhat complementary to the polarized neutron diffraction technique so that each may serve the other in deepening our understanding of magnetism and the metal-ligand bond.

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