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THE CHEMICAL BOND IN TRANSITION METAL COMPLEXES: DIFFRACTION STUDIES IN RETROSPECT AND PROSPECT

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Summary

Diffraction methods present the most direct approach to studying the electron distribution, and hence various theories of the chemical bond, in transition metal complexes. Results that have emerged from X-ray diffraction, the combination of X-ray and neutron diffraction, and finally, polarised neutron scattering by paramagnetic crystals are summarised.

Introduction

Developments in the theory of the chemical bond in inorganic and organic molecules have gone hand in hand with the evolution of experimental studies: the latter, particularly in the past decade, have largely focussed on the predictive value of theory in its provision of molecular eigen-values and their correlation with experimentally observed ionisation energies derived from photoelectron spectroscopy. Quite apart from the implicit difficulties of such correlations, such as are related to the limitations of Koopman's "Theorem", one is removed from what, for most chemists, is the central question in bonding theories: how are the valence electrons of atoms redistributed on bond formation and what, if any, is the predictive value of relatively simple valence theories? Diffraction methods represent, in principle, the most direct method of measuring electron densities: the history of the various approaches is well documented and it is sufficient for our present purpose to emphasise only that diffraction methods have assumed increasing importance because of the enhanced accuracy of experimental and interpretive methods; and that a quite new technique, polarised neutron scattering, can provide uniquely critical information on valence electron distribution in paramagnetic complexes. These two general lines are summarised in this paper.

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* Dedicated to Joseph Chatt on the occasion of his 65th birthday.

(i) Accurate X-ray studies of the chemical bond

Since the observation of aspherical features in difference density maps of hexaminecobalt(III) and hexacyanocobalt(III) by Iwata and Saito [1], which showed eight electron density peaks arranged at the corners of a cube at about 0.45 Å from the cobalt centre, several workers [2—7] have detected similar features in X-ray data of transition metal complexes suggestive of crystal field distortions of the electron density around the central metal ion. In retrospect the detection of this asphericity in the density is hardly surprising in accurate three-dimensional X-ray data as the form factors for 3*d* electrons persists at quite high Bragg angles allowing the angular variations of *d* electrons to be assessed, even if the resolution of the radial function itself is minimal due to thermal smearing and other macroscopic effects.

For the most part bonding electron densities are presented from a diffraction experiment as the difference or deformation function

$$\rho_{\mathrm{def}}(r) = \rho(r) - \sum_{\text{all atoms}} \rho_{i\,\text{spherical atom}}(r - r_i)$$

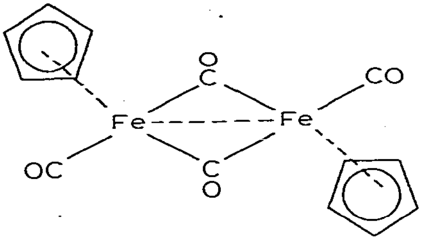
$\rho(r)$ is the electron density in the unit cell, formed by Fourier transformation of as complete a set of structure factor amplitudes as possible; ρ_i is the calculated electron density for the i^{th} non bonded atom modified by a smearing function associated with the atom's vibrational parameters. Given the possibility of measuring diffraction intensities with high precision and making adequate correction for systematic errors due to absorption and extinction, the problem reduces itself to one of delineating the origin(s) of non-sphericity in the electron density due to bonding effects and anisotropic thermal motions. In crystals such as diamond, the problem is minimal since the vibrational amplitudes are very small; low temperature diffraction studies are helpful in a more general way but do not in themselves provide a clear cut solution to the problem; the analytical methods available are to derive nuclear positional and vibrational parameters from neutron diffraction (X—N method) or vibrational parameters from high Bragg angle data where valence electron contributions are small and asphericity effects can be essentially traced to non-isotropic thermal motions (X—X method).

Rees and Coppens [8] have examined benzenechromium tricarbonyl by combining low temperature (78 K) X-ray and neutron diffraction data and showed that the position of the electron deformation peaks from the chromium centre was consistent with theoretical ab-initio calculations on related complexes. Attempts at a more quantitative measure of charge distribution has been made by Rees and Mitschler [9] in an X—N study of chromium hexacarbonyl which gave 25% of the *d*-electrons associated with the chromium atom in the orbitals belonging to the representation e_g of the O_h symmetry group, and 75% belonging to the representation t_{2g}. The σ or π electron transfer was found to be 0.3 ± 0.1 electrons per carbonyl ligand. Recently Maslen et al. [10] have shown that electron population (X—N) analyses of a series of Tutton salts (isomorphous ammonium hexaquo transition metal sulphate complexes) are in broad agreement with those expected from electronegativity considerations, interpreted in terms of Pauling's electroneutrality principle. The transition metal charges are close to zero with small ionic charges residing in the ligands.

A final point can be made: the definition of valence electron densities in transition metal complexes, by X-ray diffraction methods, is obviously difficult in a statistical sense for bonding effects are small compared with the total electron density in the crystals. It is for this reason that the selective technique of polarised neutron scattering is being pioneered (vide infra).

(ii) Studies of the metal—metal bond in bridged binuclear complexes

Simple pragmatic valence "rules" have their basis in the stability of the rare gas electronic configuration. Thus the binuclear complex I is deemed to have a direct metal—metal bond so as to provide an 18-electron configuration for the iron atoms. Mitschler, Rees and Lehmann [11] have used the X—N method to show that there is no significant electron density in the region of the iron—iron bond: electron density is concentrated into the metal μ-carbonyl region, a feature which reminds one of the simple, symmetry-based description of binuclear complexes and the way in which a polycentric orbital model can be interpreted in two-centre bond orders. One additional feature of this accurate analysis is the unequivocal demonstration of distortions in the carbon—carbon bonds of the π-cyclopentadenyl ligands. The "allyl-ene" formulation put forward nearly 15 years ago is substantiated as it is in π-cyclopentadienyl-π-allylnickel (parenthetically one also notes the distortion to C_{3v} symmetry of the arene ligand in benzenechromium tricarbonyl, a feature related to the orientation of the carbon—carbon bonds with respect to the carbonyl ligands).



(I)

An absence of electron density between the metal—metal atoms is also indicated in μ-octatetraenylbis(cyclopentadienylchromium) [12]; the electron density maps in μ-acetylene(cyclopentadienylnickel) [13] are held to "support a straight metal—metal bond" but actually show a double maximum along the metal—metal direction; the analysis is a simple X-ray diffraction study, unsupported by a neutron diffraction analysis and beset by refinement problems associated with ligand disorder.

Most significantly, from the standpoint of simple valence theory, are the results, reported by Coppens and Stevens [14], on dichromium tetraacetate dihydrate. Since the original analysis of molybdenum(II) acetate, Cotton et al. [15] have developed extended studies of so-called multiple metal—metal bonds: chromium(II) acetate is paradigmatic of a possible quadrupole metal—metal bond having the simple molecular orbital configuration $\sigma^2\pi^4\delta^2$ and a Cr—Cr bond length of 2.36 Å. The deformation electron density shows no significant value in the σ-bond region (where $3d$-metal overlap should be maximal) but apparently some features in the π- and δ-regions where simple overlap considerations would argue for smaller densities.

What does all this amount to? Perhaps nothing more than to support obvious assumptions of the simplest of valence theories viz. that second nearest neighbour interactions, as measured by the overlap criterion, are small compared with nearest neighbour (metal—ligand) interactions in bridged bi- or polynuclear systems. The metal $3d$ wave function has a maximum at only 0.7—0.8 Å from the nucleus; that the nd—nd metal—metal overlaps are small vis à vis the $(n + 1)s$ — $(n + 1)s$ or the $(n + 1)p$ — $(n + 1)p$ M—M and the M—L overlap integrals is a basis for the suggestive, if not totally persuasive, analogy between main group and transition metal clusters. In other words, the short-hand convention of two centre—two electron bonds in bridged complexes, predicated for accountancy reasons, may be misleading.

In principle, also important concepts such as the Electroneutrality Rule and the radial wave function of the bonded ion vis à vis the free ion SCF function are examinable and deformation densities can provide molecular multipole moments for comparison with other experimental data; in practice, the state of the experimental and theoretical art is presently such that these studies need considerable further resolution.

Transition metal bonding studies by polarised neutron diffraction

(i) Preamble

Polarised neutron diffraction analysis is capable of probing a specific part of the total electron density and thus of decreasing the relative effect of errors arising from macroscopic effects and thermal anisotropy. Bragg intensities, arising from the scattering of polarised neutrons by an ordered electronic spin system in a single crystal, contain a component dependent on the magnetisation density distribution in the crystal. Thus if under suitable conditions the spins of unpaired electrons in a crystal can be aligned to generate a significant magnetic moment, and if all the magnetisation contributions from the remaining electrons and nuclei are negligible, the electron spin magnetisation distribution arising from these specific unpaired electrons can be assessed by a polarised neutron diffraction experiment. In this way direct studies can then be sustained of covalency in transition metal complexes, and of the ground state wave functions of magnetic ions. While some of the most impressive demonstrations of the power of polarised neutron diffraction in the determination of spin density distribution relate to the metals iron, nickel and cobalt, these will not be considered here. Reviews on early studies of these are by Rimmer [16], Jacobson [17] and Tofield [18].

The early choice of magnetically concentrated materials was mainly dictated by experimental constraints. In magnetically ordered systems the neutron scattering is concentrated in discrete directions in reciprocal space and observed as magnetic Bragg reflections. More dilute paramagnetic systems (with larger ligands) tend to order, if at all, at very low temperatures; contributions to the background from nuclear incoherent and thermal diffuse scattering or nuclear Bragg reflections tend to obscure the resolution of the magnetic scattering.

Where complexes remain paramagnetic to very low temperature, however, the application of a high external magnetic field may make the material quasi-ferromagnetic and thus amenable to study by polarised neutron scattering.

(ii) Experimental conditions

The wavelength of the incident beam is selected by a magnetic monochromator crystal ($Co_{0.92}\,Fe_{0.08}$; Heusler Alloy, Cu_2MnAl and Fe_3Si). The polarisation may be reversed with an efficiency of 99% by a radio frequency field at right angles to the neutron polarisation and matched in frequency to the Larmor precessional frequency of neutron spin in a uniform magnetic field. The beam emerging from the flipper acts as the incident beam to the sample crystal, the polarisation of the incident beam being parallel or antiparallel to the specimen axis, which is also the direction of its magnetisation field. The so-called flipping ratio R, which is the ratio of the spin up intensity I_+ to the spin down intensity I_-, is given for centrosymetric structures by the relation:

$$R = \frac{I_+}{I_-} = \frac{1 + 2P\gamma \sin^2\theta + \gamma^2 \sin^2\theta}{1 - 2P_\eta\gamma \sin^2\theta + \gamma^2 \sin^2\theta} \qquad (1)$$

where θ is the angle between the scattering vector S and the vertical axis, and P the polarisation of the incident beam. The quantity γ is the ratio of the magnetic to nuclear scattering amplitude;

$$\gamma = \frac{F_{\mathrm{mag}}(S)}{F_{\mathrm{nuc}}(S)} \qquad (2)$$

For the simple case of ideal beam polarisation and perfect polarisation reversal, and if the sample is magnetised perpendicular to the plane of scattering eq. 1 reduces to:

$$R = \left(\frac{1+\gamma}{1-\gamma}\right)^2 \qquad (3)$$

The above relation clearly illustrates the advantage of using polarised neutrons to determine weak magnetic reflections: for unpolarised neutrons one observes a scattered intensity proportional to $F^2_{\mathrm{nuc}}(1 + \gamma^2)$ while with a polarised beam the intensity is proportional to $F^2_{\mathrm{nuc}}(1 + 2\gamma)$. However flipping ratios different from unity will only be observed if neither $|F_{\mathrm{mag}}|$ or $|F_{\mathrm{nuc}}|$ is different from zero or in phase quadrature. This means that this technique cannot be used if magnetic reflections are separated from nuclear ones, as in antiferromagnetic structures where the magnetic cell dimensions are multiples of the "chemical cell". Furthermore for acentric structures it can be shown that the flipping ratio does not define γ. For details of the theory of polarised neutron scattering see Marshall and Lovesy [19]. It should be noted that eq. 1 involves measuring the intensity of the two spin states at or near the peak of the reflection, then corrected for background by a similar measurement of background after the crystal is offset by a few degrees, with no absorption correction needed as only the ratio is measured. Solving eq. 1 for γ will give two solutions only one of which is meaningful.

To determine F_{mag} the nuclear scattering amplitude at that value of S has to be measured independently. This is achieved by a conventional determination of the nuclear positional and thermal parameters via an unpolarised neutron diffraction experiment.

(iii) Interpretion of magnetic structure factors

The one electron magnetisation density distribution at a point r in the cell is given by the relation

$$m(r) = \frac{1}{V} \sum_{S} F_{\mathrm{mag}}(S) e^{iSr} \tag{4}$$

the sum being over all the scattering vectors S; V is the volume of the unit cell. In practice only a limited number of $|F_{\mathrm{mag}}|$ are accessible in a polarised neutron experiment so the determination of $m(r)$ is possible only at a finite resolution. In the case where the orbital angular momentum is quenched in the crystal field or is zero due to Hund's rule, the magnetisation density will represent the electron spin distribution of the unpaired electrons in the system. The separation of orbital and spin components has been discussed by Moon [20], and Marshall and Lovesy [19].

Hubbard and Marshall [21] have interpreted polarised neutron data on transition metal complexes in terms of a molecular orbital approach, where molecular bonding and antibonding orbitals are constructed from ionic metal ion wavefunctions and admixture parameters describing σ- and π-type covalency with ligand orbitals. Following the nomenclature of Tofield [18], one can construct for example in a simple octahedral complex of a metal ion such as $(\mathrm{MnF_6})^{4-}$ molecular orbitals out of linear combinations of the metal $3d$ and ligand $2s$ and $2p$ orbitals. The filled bonding orbitals are:

$$\begin{aligned}
\psi_S^{\mathrm{B}} &= N_S^{\mathrm{B}}(\chi_{2s} + \gamma_S d_\sigma + \gamma_{p_\sigma} \chi_{2p_\sigma}) \\
\psi_\sigma^{\mathrm{B}} &= N_\sigma^{\mathrm{B}}(\chi_{2p_\sigma} + \gamma_\sigma d_\sigma + \gamma_{\sigma s} \chi_{2s}) \\
\psi_\pi^{\mathrm{B}} &= N_\pi^{\mathrm{B}}(\chi_{2p_\pi} + \gamma_\pi d_\pi)
\end{aligned} \tag{5}$$

and the unpaired antibonding orbitals, which are sensitive to magnetic scattering, are

$$\begin{aligned}
\psi_\sigma^{\mathrm{A}} &= N_\sigma^{\mathrm{A}}(d_\sigma - \lambda_\sigma \chi_{2p\sigma} - \lambda_s \chi_{2s}) \\
\psi_\pi^{\mathrm{A}} &= N_\pi^{\mathrm{A}}(d_\pi - \lambda_\pi \chi_{2p_\pi})
\end{aligned} \tag{6}$$

where the N's are normalisation constants and the χ's are appropriate linear combinations of ligand $2s$, $2p_\sigma$ and $2p_\pi$. γ_s and γ_σ are the admixture parameters describing the σ covalency between d_σ and the ligand $2s$ and $2p_\sigma$ orbitals respectively, and γ_π measures the π covalency between d_π and $2p_\pi$ orbitals. λ_σ, λ_s and λ_π are related to the γ's by orthogonality between the bonding and antibonding orbitals and, to first order, are given by the relations

$$\begin{aligned}
\lambda_\sigma &= \gamma_\sigma + 2\langle d_\sigma | p_{2p_\sigma} \rangle \\
\lambda_s &= \gamma_s + 2\langle d_\sigma | s_{2s} \rangle \\
\lambda_\pi &= \gamma_\pi + 2\langle d_\pi | p_{2p_\pi} \rangle
\end{aligned} \tag{7}$$

Experiments such as magnetic neutron scattering and spin resonance which measure λ are therefore sensitive to a combination of the covalency admixture parameters γ and the overlap integral $\langle d|\chi\rangle$.

Bonding also takes place between the ligand valence orbitals and the 4*s* and 4*p* metal complexes; but to first order, these interaction are not detected by magnetic neutron diffraction.

The spin density is constructed then from these molecular orbitals: the magnetic form factor, which corresponds to the spin density of the free ion, will be modified by the presence of both the ligand and the overlap densities. The metal ion contribution is reduced by a factor dependent on the ligand admixture parameters and is given by Tofield [18,22] for antiferromagnetic octahedral complexes. The measurement of this moment reduction has been the basis of numerous powder diffraction studies of magnetically ordered salts and oxides. Tofield [18,22] has summarised the results obtained for the admixture parameters in a number of octahedral complexes (and also some results on tetrahedral complexes) and has compared them with parameters obtained by ESR, or those deduced from the quadrupole coupling constant determined in nuclear quadrupole resonance spectroscopy or from the quadrupole interactions observed in magnetic resonance.

Only a few single crystal polarised neutron studies of transition metal complexes have been carried out at sufficient accuracy to observe covalency parameters. Lingard and Marshall [23] have analyzed the polarised neutron data of $MnCO_3$ (Forsyth and Brown [24]) for covalency effects. Their analysis showed significant spin transfer of the Mn^{2+} moment to the ligand with positive spin density on the oxygens and negative spin density on the carbon. However, the accuracy of the low angle diffraction data was insufficient to warrant detailed interpretation of covalency. It should be noted that the ligand form factor is normally sharply peaked at low $\sin\theta$, which corresponds the "diffuse" nature of covalency and contributes 10—15% to the form factor: accuracy of low angle diffraction data is of vital importance to a quantitative assessment of covalency.

The most complete single crystal study reported to date has been the measurement of magnetic structure factors of K_2NaCrF_6 by Wedgwood [25]. The $(CrF_6)^{3-}$ ions are effectively magnetically isolated by the intervening Na^+ and K^+ ions. The polarised beam measurements were made at 4.2 K with an external field of 1.76 T giving the aligned moment per chromium ion of 1.08 μB. Extinction was corrected for experimentally giving sufficient accuracy of the low angle measurements to investigate covalency effects in the spin density. Fourier sections of the spin distribution at 0.4 Å resolution clearly illustrates the t_{2g} nature of the spin distribution, and shows spin density transferred to the fluorine atoms. Wedgwood [25] separated the spin density into spherical and aspherical contributions by the double Fourier transform method of Moss and Brown [26], and evaluated a single covalency admixture parameter by finding a value of the parameter that best fitted the data to the spherical and aspherical contributions. However, the optimum admixture parameter for the spherical contribution was significantly smaller than the same parameter determined for the aspherical part. This inconsistency is evidence of the inadequacy of the single parameter model and is indicative of the problems arising from series termination errors in Fourier analysis. Series termination effects arise from the decrease of magnetic structure factors with increasing sin θ/λ, as magnetic structures are not measured to sin $\theta/\lambda > 1.0 - 1.2$ Å^{-1}. For this reason it is not advisable to use Fourier methods to study bonding effects where series termination errors can give rise to effects as large as those of covalency. The more lengthy procedure of calculating the magnetic scattering amplitudes directly from a model would avoid these effects of series termination. The covalency admixture parameters can be determined by refinement of these parameters by least squares to calculate structure factors in best agreement with experimental F_{mag} values.

Figgis et al. [27] have recently analysed Wedgwood's magnetic data by a least squares refinement of the ground state spin populations of the one-centre atomic orbital expansions using the formulae for the scattering by non-spherical d- and p-electron distributions of Weiss and Freeman [28], together with the relevant orbital scattering factors calculated from Hartree—Fock wavefunctions of Clementi and Roetti [29]. They confirmed the t_{2g} ground state configuration quantitatively and obtained a transfer of 0.11(3) electrons to the fluorine atom.

An alternative approach in studying covalency effects from polarised neutron data using localised atomic deformation functions will be outlined below, details of which shall be discussed in a forthcoming paper by Mason et al. [30]. The model considered is the deformation method of Stewart [31] which has been applied to several X-ray diffraction studies of covalency in first row molecular crystals, e.g. Price, Varghese and Maslen [32]. In this approach the spin density at a point $\boldsymbol{r} = \boldsymbol{r}(r, \theta, \phi)$ can be considered as arising from a superposition of one-centre multipole deformation density functions up to the hexadecapole level of the form (in polar coordinates)

$$m(r) = \sum_{\text{centres}} \sum_{lm} M_l^m N_l^m Z_l^m(\theta, \phi) R(r) \qquad \begin{array}{c} l = 0, 1 \ldots 4 \\ -l \leqslant m \leqslant l \end{array}$$

where the sum is over all the centres considered and Z_l^m are multipole functions (Tesseral Harmonics) given by,

$$\begin{aligned} Z_l^m(\theta, \phi) &= Y_l^{|m|}(\cos\theta)\cos|m|\phi \qquad && m \geqslant 0 \\ &= Y_l^{|m|}(\cos\theta)\sin|m|\phi \qquad && m < 0 \end{aligned} \tag{9}$$

Y_l^m are Associated Legendre functions and N_l^m is the normalisation factor for the density fragment associated with a population parameter M_l^m which can be determined by a least squares fit to the experimental data. $R(r)$ is the radial function chosen for the fragment.

For centres representing first row transition metal ions, if the magnetisation density arises from purely d-orbital electron distributions, the only non-vanishing multipoles populations are the scalar M_0^0, the quadrupoles M_2^2 and M_2^0, and the hexadecapoles M_4^4, M_4^2 and M_4^0. Crystal symmetry can reduce the number of non-vanishing multipoles. In the case of cubic sites only M_0^0 and the linear combination $M_4^4 + M_4^0$ are non-vanishing. Stewart [31] has listed the non-vanishing multipoles under the 32 point groups. It is possible to obtain d-orbital population parameters from multipole populations by comparing the form of the structure factor with the Fourier transform of d-orbital products given by Weiss and Freeman [28]. The multipole method has been applied to the Wedgwood data [25] using 91 observed reflections and counter weights in a least squares refinement.

A purely ionic model with the three unpaired spins of the Cr^{2+} ion in a t_{2g} configuration and no spin transfer to the ligands fitted the data rather well giving a residual R-factor $(\Sigma|\Delta F|/\Sigma|F|)$ of 12.5% and a goodness of fit (χ) of 1.73 based on all 91 observed reflections. Allowing for spin transfer to the fluorine ligands and a possible e_g component on the chromium atom, a fit of R = 10.6% and $\chi = 1.48$ was observed, with d-orbital populations of 0.04(2) electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals and 0.91(3) electrons in the d_{xy}, d_{yz} and d_{xy} orbitals (the x, y, and z directions along the cell edges a, b and c) and a spin of 0.03(1) electrons on the fluorine. A contraction of about 3% was detected in the radial (Hartree Fock) function of the Cr^{3+} ion. The calculated magnetic moment based on this model for the system was 1.10(4) μB, the difference from the observed moment being a measure of the efficiency of projection of the spin density into one centred multipole functions and can be attributed to negative spin density in the overlap regions not sampled by the model.

As noted in an earlier population analysis of X-ray data [32], net populations are very sensitive to changes in the radial functions on each centre. This is particularly true of more covalently bonded systems where the division of bonding overlap charge between adjacent centres is somewhat arbitrary. A preliminary analysis of the Cs_3CoCl_5 polarised neutron data of Figgis et al. [27] changes markedly by using flexible radial functions on the cobalt centre. A multipole analysis confirms the t_2 nature of the spin density about the cobalt centre with a radial expansion of about 9%, and a spin transfer to the chlorines of 0.08(3) electrons. The fit gave a residual R of 5.6% and χ of 1.35. A more extensive analysis of the $CoCl_4^{2-}$ ion is presently being undertaken by Figgis et al. [33], using additional magnetic data.

Although only a limited number of polarised neutron diffraction studies of bonding in transition metal complexes have been conducted it has become quite evident that it can provide a powerful tool in the study of transition metal ligand bonds. Since "bonding" in polarised neutron data is studied in an indirect manner as unpaired spin normally attributed to "antibonding" molecular orbitals, polarised neutron data can serve as a complimentary experiment to accurate X-ray data which is sensitive to "bonding" orbitals.

Prospects

After more than twenty years of "super refinement" in crystal structure analysis, one is finally beginning to realise an integration of experimental and analytic methods which promise significant advances in the determination of accurate electron densities in simple molecules and complex ions. X-ray and neutron studies of electron density in polyhedral molecules, of the relative importance of "direct" and "indirect" bonding in polynuclear complexes, could advance theories of bonding and would link up with long-standing questions relating to spin exchange in magnetic clusters. Together with the prospect of time resolved diffraction studies opportunities will be presented for the evolution of a new structural chemistry which would hardly have been anticipated a decade ago.

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