Diffraction experiments and the theory of simple transition-metal complexes

B. N. Figgis[a]; P. A. Reynolds[a]

[a] School of Chemistry, University of Western Australia, Nedlands, W.A., Australia

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Diffraction experiments and the theory of simple transition-metal complexes

by B. N. FIGGIS and P. A. REYNOLDS

School of Chemistry, University of Western Australia,
Nedlands, W.A., 6009, Australia

Polarized neutron and X-ray diffraction experimental results on simple Cr(III), Ni(II) and Co(II) complexes are compared with theoretical calculations. A simple ionic (crystal-field) model is a useful first approximation for the description of the spin and charge densities. For the more covalently bound cases the effects of electron–electron correlation in the metal–ligand bonding are as important as the spin and charge transferred via simple covalence. Thus simple M.O. models do not offer much improvement, nor do *ab initio* calculations which do not include configurational interaction (viz. restricted Hartree–Fock). Unconstrained calculations which partly incorporate electron–electron correlation are in qualitative, but not quantitative, agreement with the experiments. The polarized neutron diffraction experiments provide such sensitive tests of theory because they spatially separate the small effects in the bonding region from the metal atom 3d region, whereas these are inextricably mixed in the energetic properties measured by spectroscopic techniques.

1. Introduction

Diffraction experiments measure properties involving the spatial nature of the wavefunctions describing atoms or molecules, whereas spectroscopy reflects the energies they specify. The two are, of course entirely complementary, but diffraction information is conceptually easier to compare directly with the wavefunctions, since they themselves are formulated in spatial terms through the choice of basis sets. In recent years both polarized neutron diffraction (p.n.d.) and X-ray diffraction techniques have become sufficiently accurate to provide useful information about bonding involving transition-metal atoms. In this article we restrict ourselves to a set of our experiments relevant to the quantum theory of simple transition-metal complexes, neglecting the wider aspects involving larger molecules of more general chemical interest (e.g. Coppens *et al.* 1982, 1983, Figgis *et al.* 1980 c, 1984).

Bragg reflection intensities observed by X-ray diffraction from a crystal give Fourier components of the total one-electron charge density

$$\rho_c(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r}) \tag{1}$$

P.n.d. similarly gives the Fourier components of the total magnetization density. In the cases discussed here the orbital contribution to the magnetization is either zero or small enough to be easily corrected, and we obtain the Fourier components of the electronic spin density

$$\rho_s(\vec{r}) = \rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r}) \tag{2}$$

$\rho_\uparrow$ is the density of 'up' spin and $\rho_\downarrow$ of 'down' spin. The two functions ρ_s and ρ_c are fundamental, and are easily calculated from the wavefunction for the system. We note that ρ_s, and thus p.n.d., is much more sensitive to bonding effects since the large number

of core electrons contribute little to it, whereas the converse is true for ρ_c from X-ray diffraction.

Both ρ_c and ρ_s can be derived directly from the experimental data by Fourier transformation of the set of Bragg reflection structure factors. However, the experimental resolution is limited by the maximum momentum transfer, or wavevector, employed. In addition, both ρ_c and ρ_s are smeared by thermal motion within the crystal, corresponding to the temperature of the experiment. Comparison of a thermally smeared ρ_c or ρ_s derived from experiment with a theoretical, static ρ_c or ρ_s can only be qualitative. Quantitative comparison of theory and experiment can be made only by making assumptions about the thermal motion. We assume atom-centred distributions

$$\rho(\text{dynamic}) = \sum_{\text{atomic}} \rho_i T_i \tag{3}$$

Here T_i is the thermal motion factor for atom i. We then model

$$\rho_i = \sum_{abc} C_{abc} R^a(|\tilde{r}|) A_c^b(\theta, \phi) \tag{4}$$

where $R^a(|\tilde{r}|)$ is a radial function (usually chosen as an atomic radial function, e.g. 3d) and $A_c^b(\theta, \phi)$ is an angular function. The angular functions can be linear combinations of spherical harmonics, as suggested by the angular dependences of atomic orbitals. The coefficients, C_{abc}, can be extracted from the data by least-squares refinement techniques by comparing the Fourier transforms of models of $\rho(\text{dynamic})$ with the observed Bragg structure factors, although the algebra is tedious and the computation long.

We can then reconstruct an experimental static density to compare with theory by omitting T_i in (3) and (4). Other workers (e.g. Holladay *et al.* 1983) have tended to use angular functions, A, which are simply the spherical harmonics ('multipole analysis'). However, we have found our 'valence orbital' parameterization to require fewer functions for a given quality of fit to the data (Figgis *et al.* 1985 a). With the use of a sufficient number of functions the two approaches become identical. The reliability of such reconstructed densities has been tested by comparing a *theoretical* spin density for $CoCl_4^{2-}$ with a *model* density reconstructed (viz equations 3 and 4) from *theoretical* structure factors, themselves derived from the theoretical spin density (Chandler *et al.* 1982). The agreement is good.

At the present stage of analysis we compare the C_{abc} parameters, which have been loosely called orbital populations, or the atomic charges, with theoretical Mulliken populations. This approach neglects the different treatment of overlap densities in the theory and the analysis of the experimental data. These overlap densities are significant, and in many cases their explicit introduction in equation (4) has greatly improved the fit to the experimental data.

We shall compare our results, partly for didactic reasons, with three increasingly sophisticated levels of theory; (*a*) crystal-field theory (the 1950s); (*b*) simple empirical ligand-field or Wolfsberg–Helmholtz LCAO models (1960s); and (*c*) recent *ab initio* treatments at various levels.

2. Crystal-field model

In this model the effective charges set up an electric field gradient at the central metal ion. This causes it to polarize, as far as it can, so as to place electron density away from the metal–ligand axes. The charge transfers to and from the ligand atoms are

taken to be zero. The energetic consequences of the polarization were evaluated in detail and compared with theory thirty years ago. For such a simple model it gives remarkably good agreement with experiment. Indeed, in an updated and theoretically reformulated version, as the angular-overlap model (Gerloch and Slade 1973, Gerloch 1984) it is still of great utility for complex and unsymmetrical molecules. The spatial consequences of crystal-field theory are well known (Figgis 1966). For example, in the Cr^{3+} ion with the 3d configuration we obtain $t_{2g}^3 e_g^0$. In addition, the e_g and t_{2g} orbitals are predicted to change in radial extent (Craig and Magnusson 1958). In general, the more bonding an orbital (e.g. e_g) the more it is predicted to contract, while non-bonding orbitals expand even more. Some pertinent experimental results are listed and compared with the theory in table 1.

As with spectroscopy, the spatial aspects of the model stand up in first approximation to a test against diffraction results. The experimental 3d configurations vary from the predictions by up to an electron, but even in the worst case ($Cr(CN)_6^{3-}$, X-ray) the observed $t_{2g}^{2.5(2)} e_g^{1.2(2)}$ is still some what similar to $t_{2g}^3 e_g^0$. Charge and spin transfers are less than 0·5 electron per ligand. However, we do find large diffuse charge and spin populations which we label as '4s'. As Craig and Magnusson predicted, in strongly bonded cases (e.g. $Ni(NH_3)_4(NO_2)_2$, spin) the 3d radius is contracted while in the non-bonded case ($Cr(CN)_6^{3-}$, spin) it is expanded.

It is, however, clear that while the crystal-field model gives a rough explanation of the data, our experimental accuracy, particularly in the spin-density distributions, is sufficient that a more realistic theoretical account must be sought.

3. Empirical M.O. theories

Such theories, in the case of octahedral symmetry say, write a metal–ligand σ-bonding wavefunction as a linear combination of the metal 3d orbitals and a set of ligand orbitals

$$\Psi_i = \frac{1}{N}\{|3d_\sigma\rangle + \lambda_\sigma|\chi\rangle\} \tag{5}$$

There is a corresponding orthogonal antibonding, σ^*, orbital, and equivalent π bonding and antibonding molecular orbitals. A total of four parameters arise, two covalence parameters λ_σ and λ_π and two overlap integrals,

$$S_\sigma = \langle 3d_\sigma|\chi\rangle$$

and an equivalently defined S_π. These parameters are best regarded as empirical and used to fit the experimental data. While the information in table 1 is merely a summary of the full results obtained (e.g. we have in fact extracted both σ and π spin and charge transfers and overlap densities) and there are only 1·5 observations per data set per parameter, maximum, the λs and Ss which are derived appear reasonable. σ effects dominate π and we find covalence orders in accord with expectations, e.g. Cr–CN > Cr–F. The orders obtained sometimes differ radically from spectroscopic deductions, and this is qualitatively predicted within the framework of the Wolfsberg–Helmholtz approximation (Wolfsberg and Helmholtz 1952). For example, in Ni(II)(thiourea)$_4$Cl$_2$ (Figgis and Reynolds 1985 c) the charge donated by the chlorine atom is found to be about three times that donated by the thiourea molecule. In the analysis of the spectroscopic data, however, thiourea molecules are seen to affect the energy levels more than do the chlorine atoms. Because the chlorine atom has much less tightly bound, more easily polarizable valence electrons than has sulphur, charge

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Table 1.   Some experimental charge and spin populations and transfers for a range of simple transition metal molecules and ions compared with crystal-field theory

		X-ray results				P.n.d. results				
		$Cr(CN)_6^{3-}$ (a)	$Ni(NH_3)_4(NO_2)_2$ (b)	$FeCl_4^-$ (c)	$Ni(tu)_4Cl_2$ (d)	$Cr(CN)_6^{3-}$ (e)	$Ni(NH_3)_4(NO_2)_2$ (f)	$CoCl_4^{2-}$ (g)	$FeCl_4^-$ (h)	CrF_6^{3-} (i)
Metal 3d configuration	t_{2g} expt	2·5(2)	5·0(1)	3·9(1)	5·0(2)	2·30(3)	−0·03(8)	2·86(3)	2·5(j)	2·66(5)
	t_{2g} theory	3	6	3	6	3	0	3	3	3
	e_g expt	1·1(2)	2·6(1)	1·7(1)	2·5(2)	0·12(4)	1·71(8)	−0·22(3)	1·7(j)	−0·06(5)
	e_g theory	0	2	2	2	0	2	0	2	0
Metal 3d radius		0·93(3)	1·01(1)	1·062(4)	1·01(1)	1·082(4)	0·92(1)	0·961(5)	1·01(1)	1·001(7)
Ligand/charge spin transfer (per ligand, to metal)	axial or entire (k)	0·27(7)	0·38(8)	0·37	0·5(2)	0·04(8)	−0·11(1)	−0·078(6)	−0·22	0·00(1)
	equatorial	—	0·11(6)	—	0·2(2)	—	−0·08(1)	—	—	—
Metal '4s'		1·4(4)	1·5(2)	1·6(3)	1·0(7)	0·83(7)	0·1(1)	0·06(5)	0·1(4)	0·4(1)

(a) Average of three experiments; Figgis and Reynolds (1985 a, b), Iwata (1977).
(b) Figgis et al. (1983 a).
(c) Figgis et al. (1985 b).
(d) Figgis and Reynolds (1985 c).
(e) Figgis et al. (1985 a).
(f) Figgis et al. (1983 b), Chandler et al. (1983).
(g) Figgis et al. (1980 a), Chandler et al. (1982).
(h) Figgis et al. (1984).
(i) Figgis et al. (1980 b).
(j) Divided on the assumption that the population/orbital is the same for t_{2g} as for e_g. The total is 4·13(16).
(k) If it is not sensible to classify ligands into axial and equatorial groups, the overall average is quoted here.

transfer from it is greater. However, the energy levels of the complex are more sensitive to overlap than to charge transfer, so that the former is more important for the spectroscopy, and seems to be greater for sulphur than for the chloride ion.

Although this empirical parametrization procedure produces more satisfactory explanations of results than does the crystal-field model, it still has severe limitations. The covalance parameters evaluated from spin densities on the one hand and from charge densities on the other for the molecule $Ni(II)(NH_3)_4(NO_2)_2$ do not agree well; the 'spin' covalence is significantly less than the 'charge' covalence (Figgis *et al.* 1983 b). The spin densities also show significant negative regions (i.e. where the spin is of opposite sign to the majority spin). The empirical M.O. models put spin in a single or possibly degenerate molecular spin-orbital (Ψ_i), and thus the spin density,

$$\rho_s = \langle \Psi_i | \Psi_i \rangle$$

is positive everywhere, in the model. In addition, spin appears in places where it is expected to be zero (e.g. the 3d (e_g) orbitals of the $[Cr(III)(CN)_6^{3-}]$ ion). For these reasons we must regard such simple treatments as unsatisfactory, even for parametrization of our results.

4. *Ab initio* theory

Many all-electron calculations on relevant systems of the restricted Hartree–Fock (RHF), unrestricted Hartree–Fock and Xα (both 'muffin-tin' and discrete variation (DV)) types have been made. Calculations including configurational interaction (CI) from RHF initial wavefunctions are available for some small molecules but not yet for transition metal systems. A selection of recent UHF calculations and experimental results is given in table 2. In table 3 RHF and DV–Xα results for the $[Cr(CN)_6^{3-}]$ ion are listed.

It is clear from table 3 that the RHF calculations give a system that is much too ionic. In addition, RHF calculations necessarily give the spin density positive everywhere, in contradiction to the experimental observations. These latter seem to show that electron correlation effects, as demonstrated by the presence of negative spin, are as important as covalent spin transfer. This confirms the conclusion already developing from fits to spectroscopic data, that RHF calculations are a rather poor description of the bonding for transition-metal systems. The UHF calculations (table 2) are an improvement, and give spin populations in qualitative agreement with observations (Chandler *et al.* 1982), but are still too ionic—particularly in the more covalent cases such as $Ni(NH_3)_4(NO_2)_2$. The DV–Xα calculations appear to give a more covalent description, although this conclusion is based solely on the case of the $[Cr(CN)_6^{3-}]$ ion.

It is obvious that future good quality calculations must allow for spin polarization in order to reproduce the negative spin regions in transition-metal complexes. However, extensive CI calculations with HF initial wavefunctions of good quality (i.e. large basis sets) will be very long and difficult. In addition, the experiments show small but highly significant deviations from the ideal stereochemistries assumed. For example, in the $[Cr(CN)_6^{3-}]$ ion we have three experimental t_{2g} spin populations of 0·71(2), 0·80(1) and 0·73(1) spins when the problem is unrestrained except for the crystallographically imposed symmetry. This observation is presumably a manifestation of the effect of the rest of the crystal on the transition-metal complex ion. The modelling of such results will present a considerable challenge to the theoretical treatments.

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Table 2. Experiment and some U.H.F. theoretical results for spin and charge distributions.

		$CoCl_4^{2-}$ spin		CrF_6^{3-} spin		$Ni(NH_3)_4(NO_2)_2$ spin		$Ni(NH_3)_4(NO_2)_2$ charge	
		Expt (a)	Theory (a)	Expt (b)	Theory (c)	Expt (d)	Theory (c)	Expt (e)	Theory (c)
Metal	$3d(t_{2g})$	2·86(3)	2·95	2·66(5)	2·93	1·71(8)	1·91	5·0(1)	5·95
	$3d(e_g)$	−0·22(3)	0·03	−0·06(5)	0·04	−0·03(8)	0·01	2·6(1)	2·26
	'4s'	0·06(5)	−0·14	0·39(11)	0·01	0·10(7)	−0·02	1·6(3)	0·45
Ligand (per ligand)	axial σ or entire	0·059(8)	0·018	0·021(12)	0·016	−0·110(20)		0·27(6)	0·19
	π	0·019(8)	0·021	−0·020(5)	−0·012	0·000(13)	−0·021	0·11(6)	
	equatorial	—	—	—		−0·082(8)	−0·011	0·11(6)	0·003

(a) Chandler *et al.* (1982).
(b) Figgis *et al.* (1980 b).
(c) Chandler and Phillips.
(d) Figgis *et al.* (1983 b).
(e) Figgis *et al.* (1983 a).

Table 3. *Ab initio* theoretical and experimental spin and charge distribution results for $Cr(CN)_6^{3-}$.

	Spin			Charge		
	Expt (a)	DV–Xα (b)	RHF (c)	Expt (d)	DV–Xα (b)	RHF (e)
Cr 3d(t_{2g})	2·30(3)	2·62	2·94	2·5(2)	2·88	2·97
3d(e_g)	0·12(4)	0·30	0·0	1·1(2)	1·28	0·81
'4s'	0·83(7)	0·12	0·0	1·4(4)	0·62	0·63
C $\{$ σ	−0·044(8)	−0·07	0·0	−0·26(6)	−0·17	−0·45
$\{$ π	−0·044(8)	−0·03	0·0			
N $\{$ σ	−0·034(7)	0·00	0·0	−0·47(5)	−0·53	−0·34
$\{$ π	−0·087(4)	0·09	0·01			

(a) Figgis *et al.* (1985 a).
(b) Sano *et al.* (1981).
(c) Vanquickenbourne *et al.* (1984).
(d) Figgis and Reynolds (1985 a).
(e) Sano *et al.* (1982).

Future lines of work following from these experiments then include

(a) limited CI calculations;
(b) modelling of the actual local site symmetry electronic properties, and
(c) DV–Xα calculations to investigate to what extent they are an improvement on UHF treatments;
(d) the use of more extended basis sets to model the diffuse metal-centred spin and charge densities observed.

When calculations begin to reproduce the experimental covalence parameters for spin and charge transfer within a factor of two, comparison of theory and experiment will need to be more direct—comparison of Mulliken and least-squares model populations will not suffice. We shall then have to compare thermally smeared theoretical densities with the experimental ones, or the equivalent reciprocal space Fourier transforms. Such comparisons will involve much computation, but a start has been made at the UHF level with the $CoCl_4^{2-}$ ion (Chandler *et al.* 1982), and provides the least-biased estimates of the defects in the theoretical calculations.

5. Conclusion

The experimental results, particularly from the p.n.d. data, do not agree at all well with current bonding treatments for transition-metal complexes. In particular the effects of electron–electron correlation, manifest in spin polarization and negative spin regions, may be at least as important as the effects of covalence. This observation precludes the modelling of the data by simple empirical M.O. models, and renders suspect the associated parameters extracted from spectroscopic studies. This conclusion illustrates the usefulness of diffraction *vis-à-vis* spectroscopy for the study of bonding in transition-metal systems—our spatial resolution can separate the covalent and correlation effects from the energetically dominant metal atom region. The observation of diffuse metal-centred spin and charge populations emphasizes the need for the more flexible basis sets required for C.I. calculations.

Current theories involving electron–electron correlation (UHF, DV–Xα) reproduce our experimental results qualitatively but are too ionic in nature. The reasons for this are not well enough understood for computationally-feasible modifications to theory to be made readily, although this is an area of active investigation.

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