Spin Density and Bonding in the $CoCl_4^{2-}$ Ion in Cs_3CoCl_5. Part 2.[†] Valence Electron Distribution in the $CoCl_4^{2-}$ Ion

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We present an interpretation of the polarised neutron diffraction data for Cs_3CoCl_5 in terms of a simple molecular-orbital description of the $CoCl_4^{2-}$ ion, with direct modelling of the spin-density features. A direct observation of the overlap spin density in each Co–Cl bond has been obtained, and a probable overlap population of −0.13 ± 0.01 spins has been deduced.

We have found that the cobalt atom 3*d* orbital populations are essentially t_2 2.71 ± 0.15, *e* 0.0 ± 0.1 spins, no statistically significant differentiation of the t_2 orbital populations on account of departure from cubic symmetry being observed. There is a further significant centrosymmetric spin population (0.50 ± 0.10) on the cobalt atom, but in a diffuse orbital (maximising at *ca.* 100 pm from the nucleus) whose angular variation cannot be specified. The spin population of each chlorine atom is, as expected, mainly in the p_σ orbital (0.062 ± 0.006 spins) with a total p_π contribution less by a factor approaching three. Fairly minor changes in Co^{2+} 3*d* and Cl^0 3*p* free-ion orbital wavefunctions are deduced for the atoms in the complex ion.

In general, it is found that our data are sufficiently numerous and accurate that we are able to test the validity of simple ligand-field and molecular-orbital models. A ligand-field treatment of the $CoCl_4^{2-}$ ion describes the data well, but not completely, even if we allow for the occurrence of the diffuse cobalt-centred spin distribution. In terms of a simple molecular-orbital model a mixing parameter A_σ 0.15 ± 0.05 is deduced. The model is further qualitatively successful in accounting for the overlap spin population provided the ' diffuse ' orbital is considered to contribute significantly to the metal–ligand overlap integrals. However, it is not possible to quantify this aspect nor to exclude spin-polarisation effects as a major contribution to the observed apparent overlap population of −0.13 spins. The total cobalt spin population is greater than 3.0 (3.18 ± 0.06) which is evidence for spin-polarisation effects. In terms of usual fractional spin-transfer coefficients, *f*, we have f_σ 6.2, f_π 1.1, and f_s 0.3% for spin transferred to the bonded chlorine atoms.

CHEMISTRY is largely based upon the interactions of electrons which occupy the highest-lying orbitals of atoms and molecules. However, until recently, the redistribution of these electrons could only be inferred from indirect evidence. The study of the physical properties of atoms and molecules nearly always relates back to the energy of the systems involved; rarely can direct conclusions about spatial distributions be drawn, except on very general lines required by symmetry arguments. For example, it is very difficult to proceed from, say, spectroscopic experiments which reflect energy, to spatial properties, except by means of crude approximations to the Hamiltonian for the system.

There are many molecular properties of chemical interest which are determined by the behaviour of electrons in regions which do not contribute strongly to the total energy of a system. These regions are basically those far from the atomic nuclei, and occupied by the valence electrons. Since the methods of theoretical chemistry for molecules rely on the optimisation of the total energy, they often deal better with the behaviour of the electrons in the regions where they contribute more strongly to the energy *viz.* closer to the atomic nuclei. The usual bias of both quantum mechanics and energy-based experiments towards regions near nuclei reduces their relevance to chemical bonding.

Recently, improvements in the precision of *X*-ray diffraction data and their interpretation have allowed the direct observation of the three-dimensional distribution of electrons in small molecules containing elements from the first row of the periodic table.[1] Such diffraction experiments are more sensitive towards diffuse, bonding, regions of the wavefunction. It is, for example, possible to assess charges on atoms, occupation of non-bonding ' lone pairs ' of electrons, and changes of the 2*s* and 2*p* orbital wavefunction exponents from free-atom values, all with worthwhile accuracy.

For heavier elements, the experimental difficulties increase, the valence electrons being only a small fraction of the total. Descriptions of valence-electron distributions which give any ' new ' information in heavier element compounds can, however, be obtained from very accurate *X*-ray diffraction data (see ref. 2 and refs. therein).

The technique of polarised neutron diffraction, in favourable circumstances, allows direct observation of the three-dimensional spin-density distribution within a molecule. The advantage in the case of the transition metals is that the partially occupied orbitals are essentially those of the valence shells. The polarised neutron data may then be analysed primarily in terms of fractional valence-shell orbital occupations. Apart from polarisation effects, the polarised neutron diffraction experiment does not contain contributions from doubly occupied orbitals, core or valence, and therefore does not directly give information about paired electrons in bonding interactions. The information obtained usually concerns electrons in antibonding orbitals. However, because bonding and antibonding interactions are intimately connected in any simple theory of chemical bonding, it may be possible to deduce from their properties and behaviour much about the bonding in general.

In this paper we discuss the polarised neutron diffrac-

[†] Part 1 is ref. 3.

tion data described in Part 1 of this series [3] in terms of the bonding in the $CoCl_4^{2-}$ ion. Given the observation of many of the Fourier components of the spin density, there are two likely different strategies for understanding them. One may perform an *a priori* modelling of the observed spin density using multipole functions located upon the nuclei of the appropriate atoms.[4,5] Subsequently one may hope to analyse those multipoles in terms significant to chemistry, if it proves possible to move from spin density back to the wavefunction in the general case. Alternatively, one may take a simple molecular wavefunction, about which the spin density gives unambiguous information. Consistent with previous relevant experiments and theory, one may examine what chemically reasonable changes in the wavefunction are necessary to accommodate the new data. We adopt the latter approach here, in which the natural evolution of overlap terms, not atom-centred, may be an improvement on the multipole analysis. Conversely, a reluctance to employ, for example, 4*f* or 5*g* functions centred on the cobalt atom (which may be generated by, for example, *pd* overlap) and 3*d* or 4*f* functions on the chlorine atoms may be a limitation on this model-dependent method of analysis. In the next two sections we discuss previous descriptions of the wavefunction and bonding of the $CoCl_4^{2-}$ ion, and the model they lead us to attempt to fit to the data.

THE WAVEFUNCTION OF THE $CoCl_4^{2-}$ ION

The Free Ion.—In a restricted Hartree–Fock formulation, where spin polarisation and configurational interaction are not considered, the spin density in the free $CoCl_4^{2-}$ ion in ideal tetrahedral geometry may be ascribed to the electron density in the highest, half-filled t_2 molecular orbitals. These orbitals on qualitative grounds are expected to be σ-antibonding and π-bonding in nature, and in the simplest model may be defined by equation (1) where $|3d>_{\mathrm{Co}}$ is the

$$\psi_{t_2} = C_{\mathrm{M}}|3d>_{\mathrm{Co}} + C_\sigma|3p_\sigma>_{\mathrm{Cl}} + C_\pi|3p_\pi>_{\mathrm{Cl}} \quad (1)$$

appropriate symmetry-adapted combination of the free-ion cobalt $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, $|3p_\sigma>_{\mathrm{Cl}}$ and $|3p_\pi>_{\mathrm{Cl}}$ are the symmetry-adapted combinations of chlorine $3p_\sigma$ and $3p_\pi$ orbitals respectively, and C_{M}, C_σ, and C_π are the three appropriate mixing coefficients (C_{M} and $C_\pi > 0$, $C_\sigma < 0$).

A restricted Hartree–Fock *ab initio* quantum-mechanical calculation has been performed for a tetrahedral $CoCl_4^{2-}$ unit.[6] In this calculation, in addition to the chlorine 3*p* and cobalt 3*d* orbitals, diffuse 4*s* and 4*p* functions on the cobalt atom were introduced. Some allowance for changes in the radial distribution functions was made *via* a single parameter in the six Gaussian functions representing each atomic orbital. Although the 4*s* and 4*p* components did not appear in the half-filled highest t_2 orbital ($10t_2$) in significant amount, the configuration of the cobalt atom calculated on the basis of a Mulliken population analysis was $3d^{6.97}4s^{0.29}4p^{0.51}$. The degree of covalence deduced in the antibonding $10t_2$ orbital was *ca.* 4%. Simple electrostatic calculations indicate that changes of up to 10% in the 3*d*-orbital exponents may occur on incorporating a metal ion into a ligand charge arrangement. For the cobalt atom in $CoCl_4^{2-}$, functions as diffuse as 4*s*, 4*p*, and 4*d* orbitals may be important.[7] It therefore seems important to allow the modelling of the spin distribution on the metal atom to be quite flexible as far as radial extent is concerned.

Spin polarisation, an electron correlation effect, may also be important and is a complex phenomenon. Qualitatively, one may state that an unpaired up-spin electron in an orbital, by exchange interaction, tends to polarise suitable filled orbitals so that the up-spin electron density increases in the vicinity of the up-spin electron, and conversely for the down-spin. In our case this means that while delocalisation puts spin of the same sign as that on the cobalt atom onto the ligand chlorine atoms, spin polarisation tends to put spin of opposite sign there. In unrestricted Hartree–Fock calculations on both the free Ni^{2+} ion and Ni^{2+} in an octahedral electrostatic field,[8] it seems that there is substantial polarisation of the other *d* electrons by the two unpaired electrons in the e_g orbitals. The polarisation of the core electrons is also complex, but is smaller in size than the polarisation of the t_{2g} set. The spin polarisation of the t_{2g} orbitals in the Ni^{2+} ion is large enough to have been observed directly.[9] The results follow the reasonable pattern that the t_{2g} electron distribution is radially polarised, so that like spins in the e_g and t_{2g} orbitals are closer together in real space. However, we should note that this is an indirect effect, obtained *via* the core orbitals, as there is no overlap of the t_{2g} and e_g orbital sets. Again, unrestricted *X*-α scattered wave calculations suggest that the MX_6^{n-} ions, besides showing substantial delocalisation of electrons, also have substantial spin polarisation in most orbitals.[10] A recent unrestricted double-zeta Hartree–Fock *ab initio* calculation on the $CoCl_4^{2-}$ ion also shows significant spatial and energetic difference between ' up ' and ' down ' spin orbitals.[11]

The mixing of the higher states into the $^4A_2$ ground term of the $CoCl_4^{2-}$ ion is not insignificant, as is obvious from the fact that the e.s.r. *g* value (2.40) departs from the spin-only value of 2.00. Hillier *et al.*[6] found a substantial effect in connection with the transition energies and oscillator strengths in the optical spectrum. We have performed a crystal-field calculation of the ground state employing the $(l,m_l;s,m_s)$ coupling scheme and the entire d^3 manifold. A spin–orbit coupling constant of 500 cm⁻¹ and a *d*-orbital splitting scheme which reproduces the $^4A_2 \longrightarrow {}^4T_2$ transition of 3 000 cm⁻¹ were introduced as parameters. The resulting ground state contains a large number of components, none of which is dominant. The $^4A_2$ ground state shows a spin occupation of the *d* orbitals $d_{xy}^{0.987}d_{xz}^{0.987}d_{yz}^{0.987}d_{z^2}^{0.02}d_{x^2-y^2}^{0.02}$ which is not very different from the simplistic strong ligand-field configuration $d_{xy}^{1.0}d_{xz}^{1.0}d_{yz}^{1.0}d_{z^2}^{0.0}d_{x^2-y^2}^{0.0}$.

THE $CoCl_4^{2-}$ ION IN Cs_3CoCl_5

In the crystal of Cs_3CoCl_5 the ground-state wavefunction of the $CoCl_4^{2-}$ ion is changed by the lower site symmetry ($\bar{4}2m$; D_{2d}). The $CoCl_4^{2-}$ ion is slightly distorted from tetrahedral symmetry and there is a substantial electrostatic field of tetragonal symmetry. The e.s.r. and magnetic susceptibility experiments [12,13] indicate a zero-field splitting of −8.6 cm⁻¹ in the $^4A_2$ ground term, giving two doublets, $M_S = \pm\frac{3}{2}$ and $M_S = \pm\frac{1}{2}$, with the former the ground state. That is, $D = -4.3$ cm⁻¹. This fairly large negative splitting ensures that at all magnetic fields and crystal orientations, at a temperature of 4.2 K the ground state remains essentially $|M_S| = \frac{3}{2}$.

Crystal-field calculations as before, but with a small change in the d-orbital energy scheme so as to reproduce the 260 cm^{-1} splitting of the $^4T_2$ term,[12] give a ground-state splitting of -5.3 cm^{-1} and a value of $g_{\|}$ of 2.36. These figures are to be compared with the experimental values of -8.6 cm^{-1} and 2.40. The calculated ground state contains a large number of components and the d-orbital spin populations, now no longer cubic in symmetry, correspond to $d_{xy}^{0.971}d_{xz}^{0.995}d_{yz}^{0.995}d_{z^2}^{0.012}d_{x^2-y^2}^{0.028}$.

Optical Zeeman effect experiments on Cs_3CoCl_5 [14] show that such a simple description of the ground state and of the magnetic-field dependence of its splitting is not correct in detail. The splittings at fields up to 5 T do not quite maintain circular symmetry around the c axis and the g factors differ a little from the e.s.r. values. Much of this difference can be accommodated by a more complex ground state and spin Hamiltonian.[15] Such uncertainty in the ground state probably contributes to the systematic error of ± 0.1 spins we are led to assign to the d-orbital populations we deduce.

FORMULATION OF A SPIN-DENSITY MODEL FOR THE $CoCl_4^{2-}$ ION

The simple model already presented as equation (1) has been fitted to the ligand-field spectrum of Cs_3CoCl_5.[16] After constraining the ratio C_σ/C_π, the 11 observed spectral energies are sufficient to define C_M for the t_2 orbitals and also for the e orbitals. The ratio of observations to parameters, 2.75 : 1, precludes a more sophisticated model, or even a reasonable test of the assumptions built into the one proposed.

In a more sophisticated model, besides the σ and π delocalisation onto the chlorine atoms, guided by theory, we should seek to model some or all of the following features; radial change in the cobalt $3d$ orbitals, cobalt $3d$, $4s$, $4p$, and $4d$ and chlorine $3p$ individual orbital populations, as well as the effects of spin polarisation. In this connection we may note that spin polarisation removes the simple relationship between the overlap and the metal and ligand orbital populations inherent in equation (1). Since we have available 164 observations of structure factors (F_M) we can test such a more sophisticated model.

Quantum mechanical models generally involve an orthonormal basis set of multipolar atom-centred functions. We represent these for the $CoCl_4^{2-}$ ion by an expression of the form (2) and we note that, due to the crystal symmetry

$$\psi = C_M\langle M| + C_{Cl}\langle Cl| \qquad (2)$$

and the symmetry properties of $\psi^*\psi$, for the l-odd hkl reflections in Cs_3CoCl_5, equation $f(3)$ holds where the bars over the quantities indicate Fourier transformation. On

$$F_M \propto C_M C_{Cl}\langle \overline{M}|Cl\rangle + C^2{}_{Cl}\langle \overline{Cl}|\overline{Cl}\rangle \qquad (3)$$

the other hand, for the l-even reflections equation (4) holds. Intensity in the l-odd reflections can only arise from spin

$$F_M \propto C^2{}_M\langle \overline{M|M}\rangle + C_M C_{Cl}\langle \overline{M|Cl}\rangle + C^2{}_{Cl}\langle \overline{Cl|Cl}\rangle \qquad (4)$$

density distributed non-centrosymmetrically about the cobalt centre. In a simple ionic crystal-field model, involving only d-electron density on the cobalt atom, l-odd reflections are forbidden (which is contrary to our observations).

We represent the Fourier transform of the spin density as an 'angular' expansion over the cobalt and chlorine atom orbitals [equation (5)],[17] with spin occupation numbers

$$\langle \overline{M|M}\rangle = \sum_{nlm} a_{nlm} \sum_{L} i^L(2L+1)C^L(l,m;l,m)\langle j'_L(|s|)\rangle_{nl} \qquad (5)$$

a_{nlm} where n,l,m are the usual orbital quantum numbers, the $C_L(l,m;l,m)$ are Condon–Shortley coefficients,[18] and $\langle j'_L(|s|)\rangle_{nl}$ is a form factor at [(sin θ)/λ], $|s|$. This expression is equivalent to a multipole expansion of the same order, L.[5] The coefficients in this series depend on the angle between the scattering vector and the axis of orbital quantisation. A least-squares refinement of the spin populations, a_{nlm}, is accomplished by use of the computer program ASRED.[2]

To ensure sufficient flexibility in the radial function we presume that the radial expansion of the form factor in equation (6) is possible where $N_{nl}{}^L$ is a normalising constant

$$\langle j'_L(|s|)\rangle_{nl} = N_{nl}{}^L \sum_{1}^{p} C_{pnl}{}^L \langle j_L(r_{pnl}|s|)\rangle_{nl} \qquad (6)$$

and $C_{pnl}{}^L$ and r_{pnl} are coefficients to be optimised in the least-squares refinement process. The $\langle j_L(|s|)\rangle_{nl}$ are theoretical form factors given in the literature.[19] In our case we will use the Co^{2+} functions for all cobalt centred terms (including the diffuse ones) and Cl^0 functions for the chlorine centred and overlap regions. In general, this series contains too many terms for use with our set of observations, even for $L = 0$, 2, or 4 and a small value for p, so we shall limit the number of components as necessary; we also wish to retain a simple relation between coefficients of the wavefunction and the spin density. For the cobalt spin density we shall use two terms ($p = 2$) in equation (6) and for the chlorine atom one term. The coefficient r_{pnl} allows the refinement of a radial 'scale' for these components. Variation of the coefficients $C_{pnl}{}^0$ allows the refinement of the relative amounts of $3d$ and diffuse components. Variation of $C_{pnl}{}^2$ changes the angular behaviour of the diffuse component from spherical to d type. We will assume $C_{232}{}^4 = C_{232}{}^2$, which is equivalent to imposing cubic symmetry on the diffuse component, as $C_{232}{}^4$ is not well determined by the data.

We must also consider the region of overlap, $\langle \overline{Co|Cl}\rangle$. As we shall see later in the paper, this also can be approximated by equations (5) and (6) with $p = 1$, $L = 0$, $n = 3$, and using a Cl^0-like form factor $\langle j_L(|s|)\rangle$.

Thus we have, from equation (5), five $3d$ populations for the cobalt atom, *e.g.* 'd_{z^2}' $\equiv a_{320}$, of which two are constrained equal by the tetragonal symmetry, three chlorine $3p$ populations *e.g.* $p_z \equiv a_{310}$, and one overlap population, $p_{ov.} \equiv a_{300}$. The radial extent of the spin density in the three regions of equations (3) and (4) is described by two radial parameters for the cobalt atom ['$3d$'(r_{3d}) and 'diffuse' ($r_{diff.}$)], one for the chlorine atom ['$3p$'(r_{3p})], and one for the size of the overlap region ($r_{ov.}$). In addition there are parameters $C_{232}{}^L$ which can describe the relative amount of the diffuse component and some angular differences between the diffuse and the $3d$ components. Together with a positional parameter for the overlap region, these 15 parameters should give sufficient flexibility to our model so that the spin distributions possible on theoretical grounds can be modelled. We note that, based upon chemical knowledge, we can invoke a sum rule constraint to make the total spin population three per ion, and this reduces the number of parameters by one.

FITTING THE SPIN-DENSITY MODEL TO THE DATA

Experimental Considerations.—The experimental magnetic structure factors, $F_M^{\text{obs.}}(hkl)$, upon which our analysis is based consist of two data sets,[3] which we label according to the crystal axis parallel to the aligning magnetic field, which is also the axis of rotation of the crystal, as *a* and *c*. The structure factors are affected by any extinction present in the crystal and by an unknown amount of neutron beam depolarisation, $D(hkl)$. A correction must be made for both of these effects. We shall assume an average beam depolarisation for each data set, *viz.* $\bar{D}_a$ and $\bar{D}_c$. Fortunately, extinction effects in the crystal which we used are not severe. For only three reflections is a correction of more than 10% called for by the method now described. We apply an extinction correction [20] using the experimental value of $g = 3.3(1) \times 10^2$ for the crystal.[21] If we define $I_{\text{obs.}} = yI_{\text{calc.}}$ in the nuclear scattering experiment Bragg intensity, then a corrected value for F_M is given in first approximation by $F_M = F_M^{\text{obs.}} \cdot [2/(1+y^2)\bar{D}]$. Since this equation uses a theory of extinction which is simple but of limited accuracy we shall inflate the errors assigned to the $F_M^{\text{obs.}}$ values by one fifth of the extinction correction. This conservative procedure produces a large effect on the mean errors and decreases the goodness-of-fit values achieved in refinement by some 50%.

We have no independent estimate of the parameters $\bar{D}_a$ and $\bar{D}_c$, and therefore we shall treat them as refinable variables. Their size is determined by the concordance of the two data sets ($\bar{D}_a - \bar{D}_c$) and by the concordance of the extrapolated values of $F_M(000)$ and the experimental magnetisations in the *a* and *c* crystal axis directions.[12,13] The values obtained by the refinement may well reflect other errors in the modelling and should not be taken to mean that beam depolarisation is significant, only that the two data sets and bulk magnetisation may not be quite compatible.

We must also correct for the orbital component of the magnetisation which contributes to F_M and which does not arise from spin-density magnetisation. This orbital contribution arises from the mixing of orbitally degenerate higher states into the orbitally non-degenerate $^4A_2$ ground term by spin–orbit coupling. As we have already mentioned, a large number of such states derived from different configurations are mixed into the ground term. The dipole approximation correction [22] provides an estimate of the spherical component contribution in terms of an experimental electron-spin resonance *g* value and a theoretical form factor $<j_2>_{3d}$ for a free Co^{2+} ion.[19] We shall assume that correction to the spherical component is sufficient, since the many different configurations mixed into the ground term are likely to produce only a small average asphericity. We shall further assume that the change in $<j_2>$ on going from a free Co^{2+} ion to $CoCl_4^{2-}$ is small enough to be neglected. We should note that because of crystal symmetry, while there is a spherical orbital correction to the *l*-even data, there is *none* to the *l*-odd data. We can now compare the $F_M^{\text{obs.}}$ values with the spin-only Fourier components of the magnetisations through equations (7) and (8).

Results of the Fitting.—If we refine the fit of the model of equations (5), (6), (7), and (8), which contain 16 freely variable parameters (NV), to all 164 observed magnetic structure factors (NO) from both sets of data and the two observed magnetisations (14.5 B.M.* for H//*c*; 2.56 B.M.

$$F_{\text{spin},c} = F_{\text{M},c}^{\text{obs.}}[2/(1+y^2)\bar{D}_c - \frac{(g_{\parallel} - 2)}{g_{\parallel}} <j_2>_{3d}] \quad (7)$$

$$F_{\text{spin},a} = F_{\text{M},a}^{\text{obs.}}[2/(1+y^2)\bar{D}_a - \frac{(g_{\perp} - 2)}{g_{\perp}} <j_2>_{3d}] \quad (8)$$

for H//*a*) we obtain χ^2 1.43 with a weighted *R* factor $R'(F)$ 0.028. The values obtained for the various variables are listed in the Table as refinement 1 (R1).

The effect of systematic errors in limiting the accuracy of the analysis of the results can be gauged by fitting the same model to various parts of the data. These refinements, R2 to R5, are respectively based upon: only *l*-even reflections (R2); only *l*-odd reflections (R3); the *c*-data set (R4); and the *a*-data set (R5). In refinement R3 the metal-centred parameters are *not* refined as they do not contribute to the *l*-odd data. In refinements R4 and R5 *only* the metal-centred parameters are refined, the overlap and chlorine-based parameters being fixed at the values given by R3. Similarly, in R2 a few of the less sensitive parameters are constrained at the R3 values. We note that because of the crystal symmetry the chlorine and overlap parameters enter into the *l*-odd data but the cobalt parameters do not. Since the values of the F_M for the *l*-odd data are the more precisely measured, the chlorine and overlap parameters are most accurately determined in R3. In refinements of the *l*-even data (R2) the chlorine and overlap populations, being small, are less well determined and may be affected by systematic errors in the modelling of the spin density around the cobalt atom and the orbital contribution correction. It is therefore pleasing that the *l*-even data also reproduce the features of the chlorine and overlap density. These features are the large value of the ‘ overlap ’ population, and the concentration of spin density in the p_x orbital. The cobalt parameters of R1 have least-squares errors which show a significant difference in the ‘ d_{xy} ’, ‘ d_{xz} ’, and ‘ d_{yz} ’ populations, but this result is misleading. The refinements of the separate data sets, R4 and R5, show that the systematic errors are larger than the differences and that the real errors in the ‘ *d* ’ populations are the order of 0.1 spins. Within this approximation our results show that the populations ‘ $d_{x^2-y^2}$ ’ and ‘ d_{z^2} ’ are equal and zero (±0.1) spins, and the populations ‘ d_{xy} ’, ‘ d_{xz} ’, and ‘ d_{yz} ’ are equal to one-third of the total *d* population, that is 1.06 ± 0.02 spins each. The error in the total *d* population is much less than in the individual ‘ *d* ’ populations as it is well determined by the spherical component of the form factor. The increase in ‘ *d* ’ population above unity is statistically significant and is only physically possible if our ‘ *d* ’ populations are the sum of *more than three* molecular orbitals which include 3*d*-like contributions and much more diffuse distributions. This is the only evidence we have that spin-polarisation effects are significant. There might seem to be substantial correlation in the refinement between the amount of the centrosymmetric cobalt-centred diffuse component (C_{232}^0) and the ‘ overlap ’ population ($p_{\text{ov.}}$) since the refined value of $r_{\text{diff.}}$ places the diffuse and overlap ’ populations at the same distance from the cobalt

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

nucleus. In the l-even data we can only distinguish the two through their differing angular properties, making their correlation *in this part of the data* very high. However, the l-odd data contain *only* the effects of the non-centrosymmetric ' overlap ' density (p_{ov}). and *no* contribution from $C_{232}{}^0$. This breaking of the correlation between $p_{\text{ov.}}$ and $C_{232}{}^0$ is yet another result of the favourable crystal symmetry that also allows the separation of covalence effects. From the Table and equations (5) and (6) we can therefore say with some confidence that there is a substantial amount of the spin (0.50 ± 0.10 spins) on the cobalt atom in a centrosymmetric diffuse orbital, together with -0.5 ± 0.05 spins in the non-centrosymmetric ' overlap ' regions. The residue of the three spins leaves 0.90 ± 0.05 spins in each $3d$-like ' t_2 ' orbital. Apart from its centrosymmetry, the angular nature of the diffuse orbital, specified by the coefficient $C_{232}{}^2$, is not well determined as the data contain too few low-angle reflections.

Modelling of the magnetic structure factors with estimated standard deviations in parentheses

Refinement		R1	R2	R3	R4	R5
Data type		all	all, l-even	all, l-odd	c, l-even	a, l-even
Cobalt total ' d ' spin [a] populations	(' d_{xy} ')	0.953(25)	0.899(46)		1.18(13)	1.15(12)
	(' d_{yz} ')	1.114(36)	1.029(58)		0.87(16)	1.03(4)
	(' d_{xz} ')	1.114(36)	1.029(58)		0.87(16)	1.03(4)
	(' $d_{x^2-y^2}$')	−0.067(52)	−0.103(76)		0.06(9)	0.17(6)
	(' d_{z^2} ')	0.097(33)	0.039(64)		0.33(12)	−0.13(13)
Cobalt radial parameters [b]	r_{3d}	0.966(8)	0.971(8)		0.927(19)	0.960(16)
	$r_{\text{diff.}}$	2.52(5)	3.16(52)		2.56(36)	2.55(17)
Diffuse orbital parameters	$C_{232}{}^0$	0.157(37)	0.029(101)		0.208(48)	0.126(52)
	$C_{232}{}^2$ $(= C_{232}{}^4)$	0.076(66)	0.028(69)		0.23(8)	−0.02(11)
Chlorine spin populations	p_x (p_σ)	0.062(6)	0.053(13)	0.054(6)	As in R3	As in R3
	p_y (p_π)	0.004(6)	0.008(13)	0.001(6)	As in R3	As in R3
	p_z (p_π)	0.018(3)	0.030(13)	0.011(3)	As in R3	As in R3
Chlorine radial parameters [b]	r_{3p}	0.991(38)	As in R3	1.028(31)	As in R3	As in R3
Overlap population	$p_{\text{ov.}}$	−0.137(10)	−0.066(52)	−0.126(20)	As in R3	As in R3
Overlap position [c]	$x_{\text{ov.}}$	85(2) pm	As in R3	78(4) pm	As in R3	As in R3
Overlap radial parameter [b]	$r_{\text{ov.}}$	0.85(10)	As in R3	0.85(10)	As in R3	As in R3
Experimental depolarisation ratios	$\bar{D}_a$	0.91(1)	0.89(1)			0.88(1)
	$\bar{D}_c$	0.95(1)	0.94(1)		0.97(1)	
No. of observations	NO	166	144	22	67	77
No. of variables	NV	16	13	7	8	8
χ^2 [d]		1.43	1.58	1.06	1.54	1.06
$R'(F)$ [d]		0.028	0.027	0.103	0.023	0.027
$R(F)$ [d]		0.029	0.029	0.276	0.024	0.038

[a] The cobalt total populations include $3d$ and ' diffuse ' components, *e.g.* the $3d_{xy}$ population is ' d_{xy} ' $(1 - C_{232}{}^0)$. The ' diffuse' orbital population is $C_{232}{}^0 \sum_{i=1}^{5}$ ' d_i '. [b] Form factor curves used in the calculations are given for Co^{2+} and Cl^0 in ref. 19. [c] $x_{\text{ov.}}$ is defined as the distance from the cobalt nucleus measured along a Co–Cl vector. The Co–Cl distance at 4.2 K is 226.3(1) pm.[21] [d] $\chi^2 = [\Sigma(F_{\text{obs.}} - F_{\text{calc.}})^2/\sigma_{\text{obs.}}{}^2]/(\text{NO} - \text{NV})$; $R'(F) = [\Sigma(F_{\text{obs.}} - F_{\text{calc.}})^2/\sigma^2{}_{\text{obs.}}]^{\frac{1}{2}}/(\Sigma F_{\text{obs.}}{}^2/\sigma^2{}_{\text{obs.}})^{\frac{1}{2}}$; $R(F) = [\Sigma|F_{\text{obs.}} - F_{\text{calc.}}|]/[\Sigma|F_{\text{obs.}}|]$; $\sigma_{\text{obs.}}$ is the estimated standard deviation in F_{obs}.

We note that the *negative* overlap density, while it reduces the positive spin density due to cobalt and chlorine centred orbitals also renders the total spin density slightly negative in some regions.

We have made many further refinements of the data, introducing further variables and providing more constraints. We now comment on the results of certain of them which were carried out to see if more chemical information could be extracted from the data, as evidenced by a reduction in χ^2.

(*i*) *Is there spin density in regions apart from the* $CoCl_4{}^{2-}$ *ion?* The difference-Fourier maps show peaks in other regions of the unit cell which could either be real or the effect of the incompleteness of our data set. Refinement of models which placed up to three independent spherical spin distributions at the peaks of the difference-Fourier maps and also at Cs^+ and Cl^- ions produced no reduction in χ^2, with less than 3% of the spin outside the $CoCl_4{}^{2-}$ ionic region.

(*ii*) *Is the spin on the chlorine atom well represented by* 3p-*like functions?* Refinement of r_{3p} did not change its value significantly from unity, as calculated for a free Cl atom. We also find that the local Cartesian axes of quantisation are not rotated (within ±2°), and the magnetic density associated with the chlorine atom is centred 5 ± 8 pm towards the cobalt atom. Simple calculations show that the $3s$ spin population is $(5 \pm 8)\%$ of the $3p_\sigma$ population.

(*iii*) *Is the σ-overlap region well represented by a contracted chlorine* 3s-*like orbital?* Theoretical calculations using simple molecular-orbital models and $3d(Co^{2+})$ functions suggest that there should be a σ-overlap spin density significantly smaller than the spin population on the chlorine atom, with a centroid *ca.* 60 pm from the cobalt nucleus, and whose density is elongated in the Co–Cl bond direction. Our ' overlap ' spin density is considerably larger in magnitude than the chlorine spin density, and this suggests that it may have a different physical origin. Moreover, it is centred 85 pm from the cobalt nucleus, and this implies a very large expansion of the $3d$ orbitals, an effect which we do *not* observe. The overlap integral of the chlorine $p\sigma$ orbitals with a ' diffuse ' cobalt orbital would be larger in magnitude than for the $3d$ orbitals, and would lead to an overlap density in the Co–Cl bond further from the cobalt nucleus and whose shape might be more nearly spherical. Given the resolution of our data [$(\sin\theta)/\lambda \leqslant 7.0$ nm^{-1}], the σ-overlap region is sufficiently well represented by a contracted chlorine $3s$-like orbital.

(*iv*) *Is there evidence for a π-overlap region?* Calculation indicates that cobalt ($3d$)–chlorine ($3p$) π overlap would be small and would take the form of an annulus about the Co–Cl bond vector, centred *ca.* 100 pm from the cobalt nucleus. A model refinement showed that the π-bonding overlap in the $CoCl_4^{2-}$ ion is not detectable by our experiment.

(*v*) *Is the spin on the cobalt atom well represented by* ' 3d' *and* ' *diffuse* ' *components?* The introduction of extra terms of equation (6) ($p > 2$) into the refinement produced no significant reduction of χ^2. From this fact we deduce (*a*) that the ' 3*d* ' orbitals are well represented by the theoretical 3*d* function of the Co^{2+} ion but slightly contracted in real space ($r_{3d} = 0.966$), and (*b*) that the amount of ' diffuse ' function is sufficiently small that, apart from $<r^2>$, the details of its radial distribution are not well defined by the data. The lowering of the ' experimental depolarisation ratios ' ($\bar{D}_a$ and $\bar{D}_c$) from unity could alternatively be due to a rather uniform, small positive, very diffuse spin-density component.

(*vi*) *What is the ground state of the* $CoCl_4^{2-}$ *ion?* Provided that proper correction has been made for the orbital magnetisation and, under the experimental conditions, the ground state, $|M_S| = \frac{3}{2}$, is the same for the *a*-data as for the *c*-data sets, the results of the refinements R4 and R5 should be the same within appropriate statistical error. In fact they differ by a small but statistically significant amount. The difference between the data sets corresponds to at most a change in magnetic structure factors of *ca.* 1%. The difference between the two sets is a component of quadrupole symmetry in the magnetisation in each of the *a* and *c* directions. This is also evident from a comparison of refinements R4 and R5, since the $d_{x^2-y^2}$ and d_{z^2} spin populations change in opposite directions.

Unless there is a systematic error in the data the difference between the analyses of the data sets must reflect an inadequate treatment of the wavefunctions of the occupied states. The necessity for the consideration of a more complex and magnetic-field-dependent ground state has been pointed out above in connection with the optical Zeeman effect spectra.[14,15] In our analysis we have assigned errors to those populations such that the effects of the disagreement between the two data sets are fully covered, whether they arise from the use of too simple a ground state or from systematic error.

(*vii*) *How different are our deductions from those of an* ab initio *calculation?* The *ab initio* molecular-orbital calculation [11] on the $CoCl_4^{2-}$ ion shows σ bonding with a negative spin density in the overlap region and a spin population in the $p_\sigma(p_x)$ orbital of the chlorine atom and our results conform with this. We can say that in crude features of chemical interest the data on the $CoCl_4^{2-}$ ion in Cs_3CoCl_5 agree with free-ion based molecular-orbital deductions.

DISCUSSION AND CONCLUSIONS

We summarise the results of the fitting of the model as follows.

(1) The spin density in the $CoCl_4^{2-}$ ion can be partitioned into three regions: (i) cobalt ' 3*d* '; (ii) a diffuse component centred on the cobalt atom; and (iii) chlorine ' 3*p* '.

(2) The cobalt atom has a 3*d* population which is indistinguishable from cubic symmetry ($d_{xy} = d_{xz} = d_{yz}$; $d_{x^2-y^2} = d_{z^2}$), *viz.* $t_2^{2.71}e^{0.0}$, in which the 3*d* orbitals are slightly contracted in real space relative to theoretical calculations on the free Co^{2+} ion,[19] as evidenced by a form factor which varies in the same manner as for that ion but with $r' = 0.966r$.

(3) Each chlorine atom has a 3*p* population of 0.084 spins in orbitals possibly slightly contracted relative to theoretical calculations on the Cl atom ($r' = 0.99r$).[19] The spin is more concentrated in the $p_x(p_\sigma)$ orbital, the occupation number being 0.062 spins.

(4) The diffuse density around the cobalt atom is comprised of two parts. (*a*) A negative region, non-centrosymmetric about the cobalt atom. We model this as four spherically symmetrical regions each centred 85 pm from the cobalt nucleus along each Co–Cl bond, each with a population of —0.137 spins. These regions are slightly *smaller* in radius than a theoretical chlorine 3*s*-like orbital. We shall call these the overlap regions. (*b*) A centrosymmetric positive region totalling 0.50 spins centred on cobalt and maximising at *ca.* 100 pm from the cobalt nucleus and of angular distribution not well defined by the present data.

The correlation between these two parts is *small* since the crystal symmetry allows us to determine (*a*) from the *l*-odd data, to which (*b*) does not contribute at all. Conversely, in the *l*-even data only the sum of (*a*) and (*b*) is well determined.

To understand these results it is necessary to turn to a quantum-mechanical description of the system. Historically, the simple, ionic crystal-field model has had a great deal of success. Our results again show just how good a first-order approximation it is. In the $CoCl_4^{2-}$ ion crystal-field theory predicts a simple $t_2^3e^0$ configuration of the 3*d* orbitals, and we find $t_2^{2.71}e^0$ with only 0.29 spins (10% of the total) in other orbitals.

Early ligand-field models using metal 3*d* and ligand 3*p* orbitals [equation (1)] predict a reduction in the t_2 population, a small negative overlap population, since the spin is assigned to an antibonding molecular orbital, with the residue, positive, in the chlorine 3*p* orbitals. If we analyse the radial portion of our results we find the configuration $t_2^{2.71}$(diffuse region)$^{-0.05}$ on the cobalt atom and $3p^{0.34}$ on the chlorine atoms, with the 3*d* and 3*p* radial functions hardly changed from those of the theoretical free Co^{2+} ion and Cl atom. These are just the results we might expect to find on the basis of this type of model. This ' overlap ' diffuse region includes all the population outside the metal 3*d* and chlorine 3*p* orbitals, which we have shown lies *ca.* 100 pm from the cobalt nucleus. We compare this result with that of Bird *et al.*[16] using a similar simple ligand-field model to analyse the ligand-field spectrum of Cs_3CoCl_5. They find the populations $t_2^{2.58}$(overlap)$^{-0.10}3p^{0.53}$, which compare well with our deductions.

However, when considered in detail, our results differ significantly from those expected from a simple ligand-field model. The small changes in magnetic structure factors resulting from angular rearrangements of the spin around the cobalt atom highlight the inadequacy of the simple model. At this point we should note that spectroscopic measurements, because of the limited data available and their relative insensitivity to diffuse regions and to angular changes in charge density, do not give such obvious differences.[23] Around the cobalt atom the two diffuse components [see (4) above] have relatively large spin populations and this implies the need to include diffuse functions in basis sets for fitting experimental results or performing *ab initio* calculations. Conventionally, this has been done by the inclusion of 4*s*, 4*p*, and even 4*d* cobalt functions.[6] Our diffuse region spin populations imply a ' diffuse ' orbital charge of from 0.55 to 1.05, depending on how much the two diffuse spin components overlap.

The simple molecular-orbital set of equation (1) for the bonding in the $CoCl_4^{2-}$ ion may be written as in equation (9) where $t_2^i(Co)$ is a linear combination of

$$\psi_{t_2}{}^i = N_{t_2}[t_2{}^i(\mathrm{Co}) + \sum_{j=1}^{4} \pm A_\sigma p_\sigma{}^j + \sum_{k=1}^{8} \pm b_k A_\pi p_\pi{}^k] \quad (9)$$

cobalt-based atomic orbitals. Most obviously it is of 3*d* origin, but may include more diffuse components; $i = xy$, xz, or yz, N_{t_2} is a normalising coefficient, j and k range over the four chlorine atom p_σ and p_π orbitals respectively, and the signs before the mixing coefficients A_σ and A_π are chosen for antibonding or bonding overlap phase respectively, and $b_k = 0$ or ± 1, as appropriate. If the π bonding is neglected equation (9) simplifies to (10) and using the numbering system of Ballhausen and

$$\psi_{t_2,\sigma}{}^i = N_{t_2,\sigma}(t_2{}^i + \sum_{j=1}^{4} \pm A_\sigma p_\sigma{}^j) \quad (10)$$

Liehr,[24] one of the antibonding half-filled orbitals is, for example, given by equation (11).

$$\psi_{xy,\sigma} = N_{t_2}[\text{‘}\, d_{xy}\text{’} - A_\sigma(p_\sigma{}^1 - p_\sigma{}^2 + p_\sigma{}^3 - p_\sigma{}^4)] \quad (11)$$

Then, the spin density in a chlorine ligand p_σ orbital and the ' overlap ' population may be used to try to obtain the mixing coefficient parameter for σ bonding, A_σ. We have the relationships $3A_\sigma{}^2/(1 - 2A_\sigma S_\sigma + 4A_\sigma{}^2) = 0.062 \pm 0.006$ and $6S_\sigma A_\sigma = 0.137 \pm 0.010$ where S_σ is the σ cobalt–chlorine overlap integral. They yield $A_\sigma = 0.15 \pm 0.05$ and $S_\sigma = 0.15 \pm 0.05$.

The small changes in the cobalt 3*d* and the chlorine 3*p* radial wavefunctions from the theoretical free Co^{2+} ion and Cl atom radial dependences have been estimated in the least-squares process. If we use them to evaluate S_σ by standard techniques we obtain $S_\sigma(3d\text{–}3p) = 0.047$, and the overlap population is predicted to be centred some 60 pm from the cobalt nucleus. These calculations do not fit in at all well with the deductions of the experiment, which give S_σ 0.15 and overlap centred *ca.* 85 pm from the cobalt nucleus.

There are at least two ways of accounting for this discrepancy, but our experiment does not distinguish between them. The interpretation more attractive in chemical terms is that the ' overlap ' region indeed arises from ' true ' overlap, but that it is larger in magnitude and displaced away from the cobalt nucleus. This is because it arises not only from interaction of the chlorine 3*p* orbitals with the cobalt 3*d* orbitals, but also with cobalt-based ' diffuse ' orbitals. The ratio of ' diffuse ' to 3*d* contributions to the overlap integral S_σ would need to be *ca.* 2 : 1, and this would seem to be a not unreasonable figure. The ' d_{xy} ' orbital of equation (11) would include not only a major 3*d* component but also a substantial ' diffuse ' orbital contribution of t_2 symmetry.

The alternative explanation of the discrepancy is that a much smaller ' true ' cobalt (3*d*)–chlorine (3*p*) overlap spin density causes spin polarisation of polarisable ' diffuse ' orbitals. In principle this could produce a negative region in the total spin density, which would be evidence of spin polarisation. However, our results show no significant, large, negative region. Spin polarisation will also increase the cobalt spin population above three. We observe 3.18 ± 0.06 spins (all in t_2 orbitals). This is evidence that spin polarisation has a significant effect on the total spin density. Unfortunately, it is not practicable to quantify arguments on spin polarisation at a simple level The results of an extensive unrestricted *ab initio* calculation [11] on the $CoCl_4^{2-}$ ion may serve to do this and to distinguish the spin polarisation from the ' diffuse ' orbital-overlap mechanism. It may be noted, however, that if spin polarisation is the important factor the net charge population to be assigned to the ' diffuse ' orbital is increased. If only the 3*d*–3*p* overlap integral calculated above is employed, we deduce that there is a ' true ' overlap spin population of *ca.* —0.041 in each cobalt–chlorine bond, and this leads to a ' diffuse ' orbital charge population of from 0.4 to 0.9, a very substantial figure. The uncertainty in this charge is due to our lack of information about the angular nature of the centrosymmetric ' diffuse ' component.

To summarise, the overlap spin-density component in the diffuse region is strongly correlated with possible spin-polarisation effects, and within the accuracy of the experiment it is not possible to be clear about its origin without aid from theoretical chemistry. However, overlap arising from the cobalt-based ' diffuse ' orbital can, in principle at any rate, provide a satisfactory account of the bonding and simultaneously require only a moderate ' diffuse ' orbital population.

The angular distribution of spin closer to the cobalt nucleus, the 3*d* region, shows no significant difference from a simple $t_2{}^{3n}e^0$ configuration. Our uncertainty of 0.1 spins in each of the 3*d* orbital populations is too large for us to draw conclusions about the non-cubic ground-term effects deduced from our crystal-field calculations or about the possible small *e*-orbital populations induced by spin polarisation and which have been claimed to have been observed in other similar experiments. However slight inconsistencies between the *a* data and *c* data suggest that the ground state (' $M_S = |\frac{3}{2}|$ ') which we are observing may not be exactly identical in the two different experimental magnetic fields.

The angular distribution of spin around the chlorine atom in 3*p* orbitals conforms with the expectations of a simple molecular-orbital model, *viz.* $p_x{}^a p_y{}^b p_z{}^b$ with $a > b$ (local frame, x along Co–Cl bond). Our finding that most of the chlorine-based spin resides in the p_σ orbital shows that the model is qualitatively successful.

If we use equation (9) to evaluate the π-bonding mixing coefficient A_π from the observed chlorine atom p_π orbital spin population, *ca.* 0.011 spins in each, we obtain $A_\pi = 0.06 \pm 0.03$. Such a population corresponds to a very small π-overlap population so that S_π is much less than S_σ. In our experiment we find a negligible π-overlap population, 0.002 ± 0.10 spins. Consequently, it is even less profitable to try to distinguish between π overlap and spin-polarisation effects than it was for the σ overlap case. Further resolution of the π-bonding interaction in the $CoCl_4^{2-}$ ion must await the results of further polarised neutron diffraction experiments and of the unrestricted *ab initio* calculation.[11] These should give guidance as to what extent spin polarisation places spin in the chlorine-atom orbitals.

Our observation that the 3*d* orbitals of the cobalt(II) atom are slightly contracted radially but that there is a ' diffuse ' orbital which could also have *d*-type angular variation is of relevance to the interpretation of the optical spectrum of this and other ions. In the analysis of the spectrum of the $CoCl_4^{2-}$ ion it was concluded, as is usually found, that there is a nephelauxetic effect.[25] The parameters of interelectronic repulsion between the *d* electrons, specifically the Racah parameters B and C, as well as the spin–orbit coupling parameter are reduced in magnitude from the free-ion values, presumably on account of expanded radial functions. If the molecular-orbital basis set is restricted to the cobalt 3*d* and chlorine 3*p* functions then our findings are in conflict with the spectral results. The slightly contracted 3*d* functions would raise the interelectronic repulsion and spin–orbit coupling parameters thus requiring too large a ' delocalised ' chlorine population to fit the data. However, if the metal ' *d* ' orbitals are a more complex mixture of significant basis functions, then our ' diffuse ' orbital immediately provides the mechanism for an expansion of the cobalt radial function and a reduction of the apparent covalency parameters. Unfortunately, because we cannot yet define well the angular variation of the ' diffuse ' orbital, we cannot cast light on the proposal that there may be differential expansion of the t_2 and e type ' *d* ' orbitals of the metal ion, such as has been thought to give differing nephelauxetic ratios for them.[25]

A remarkable feature of our results is that the spin density in the crystal is, within experimental error, of high symmetry, being locally cubic around the Co atom and cylindrically symmetrical in the Co–Cl bond. Although the $CoCl_4^{2-}$ ion is only slightly distorted from a regular tetrahedron,[21] there is strong anisotropy in the magnetic and e.s.r. properties and the optical spectrum shows splittings due to low-symmetry ligand-field components, which splittings are of magnitude perhaps one tenth of the primary tetrahedral ligand field.[12–15] It had been expected that the spin-density distribution would reflect these lower symmetry effects. The result that it does not serves to show that the total energy of an ion and details of its bonding electron distribution are not necessarily well connected.

To compare our deductions with experimental results from other studies on covalence in transition-metal complex ions it is convenient to use the parameters f_σ, f_π, f_s, and f_d, which provide a measure of the fraction of spin delocalised from the metal *d* orbitals into, in our case, respectively the chlorine $3p_\sigma$, $3p_\pi$, and 3*s* orbitals and into the cobalt ' diffuse ' orbital. So transformed, our results are f_σ 6.2 ± 0.6, f_π 1.1 ± 0.6, f_s 0.3 ± 0.5, and f_d 18 to 35%, the variation depending on the model used.

In a recent review Tofield[26] has pointed out the theoretical assumptions required in deriving these parameters from resonance experiments. The techniques n.q.r., n.m.r., and e.s.r. can be used to estimate various combinations of the *f*'s which, together with powder neutron diffraction data, can be used for comparison with our results. The n.q.r. experiments on, for example, $TiCl_4$ and $CsMnCl_3$ (octahedral Mn^{2+}) can be reconciled with the n.m.r. and e.s.r. data if some 10 to 20% population of ' outer ', diffuse, orbitals on the metal atom is assumed. The other studies have mainly involved the oxides and fluorides of the ions Ni^{2+}, Mn^{2+}, Fe^{3+}, and Cr^{3+}. Electronegativity arguments predict that the Co^{II}–Cl bond should be more covalent than the bonding in any of those compounds, except perhaps the Fe^{III}–O systems. This we observe. For example, for Mn^{II}–F bonding f_σ 1.2, f_π 0.8, and f_s 0.5%, while for the Fe^{III}–O bond f_σ 7, f_π 1.2, and f_s 1%. Our qualitative agreement with these results, *viz.* $f_\sigma \gg f_\pi$, $f_s \sim 0$, is pleasing. In a sense, then, we can say that our experiment, being virtually free of theoretical assumptions, provides evidence that such intercomparison of various resonance and diffraction experiments is valid. This is equivalent to saying that our experiment is a test of the underlying ligand-field model, and that that model is not seriously in error, although there are, of course, some deviations from its predictions.

For the theoretician, our results are a challenge. To advance beyond a simple 3*d*(Co)–3*p*(Cl) molecular-orbital theory of the $CoCl_4^{2-}$ ion in Cs_3CoCl_5 one needs, as a minimum, (i) to introduce more diffuse orbitals into the basis set, and (ii) to introduce spin polarisation *via* an unrestricted Hartree–Fock calculation or by configurational interaction. For the chemist, however, the fact that our data on the electronic structure of the $CoCl_4^{2-}$ ion seem to conform with simple existing concepts of chemical bonding should be a pleasing result.

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