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Covalent Bonding in *cis*-Bis(2,2′-bipyridyl)dichloroiron(III) Tetrachloroferrate(III)

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A polarized neutron diffraction experiment on the *Pccn* polymorph of deuterated *cis*-[$Fe(bpy)_2Cl_2^+$][$FeCl_4^-$] yielded 207 unique magnetic structure factors that were analyzed in terms of spin populations on all the atoms. On the two different iron(III) atoms the presence of a diffuse population, modeled as 4p-like, was examined, as also were the 3d t_{2g} and e_g orbital populations. Refinement proceeded to $R_w = 0.050$ and $\chi = 1.42$. It was found that in the cation 15% of the spin resides on the ligand atoms, more particularly the chlorine atoms. In the anion 17% of the spin is located on the chlorine atoms, about the same amount at each of the two crystallographically distinct types. In the cation, there is a significant loss of spin between the iron atom and the ligand atoms, corresponding to spin density in antibonding orbitals. In the anion there is strong polarization of the spin density by the presence of the ligand chlorine atoms, effected through 3d–4p mixing, so that the distribution around the iron atom is also aspherical with a loss of spin density between Fe and Cl. In neither ion is a net significant diffuse orbital population found. The small net negative spin on the carbon and deuterium atoms of the bipyridyl ligand is not distributed with any obvious pattern, except that the spin on each deuterium atom is opposite in sign to that of the carbon atom to which it is bonded. The overall picture, on both ions, of a moderate amount of spin (16%) delocalized for metal 3d to ligand orbitals via antibonding interactions is similar to that observed in the $CoCl_4^{2-}$ ion. However, the covalence in this case is distinctly larger, as is expected for Fe(III) compared to Co(II). It is unexpected that the spin does not seem to be much delocalized away from the nitrogen atoms in the bipyridyl molecules.

Introduction

Previous studies of the spin distribution in transition-metal complexes as determined by polarized neutron diffraction (pnd) have essentially concentrated on one of the ends of a spectrum. On the one hand, accurate and fairly extensive data sets have been measured and analyzed for fairly small and symmetrical molecules ($CoCl_4^{2-}$ ion[2], $CoBr_4^{2-}$ ion,[3] CrF_6^{3-} ion,[4] $Ni(NH_3)_4(NO_2)_2$[5]). There, it has been possible to answer quite detailed questions about the distribution of unpaired electrons around the metal atom and its ligand donor atoms. On the other hand, less accurate and extensive data sets have been obtained on larger and lower symmetry molecules ((phthalocyaninato)cobalt(II) and -manganese(II)[6] and aquabis(bipyridyl)bis(μ-hydroxo)(sulfato)dicopper(II)[7]). In those cases it has been possible to obtain with confidence information only about general features of the unpaired spin distribution such as the total amount of spin transferred from the metal to the ligand molecule.

In this study we report the measurement of a data set of good accuracy, but as yet of only moderate extent, on a complex of moderate size, and its interpretation in terms of questions of moderate complexity.

The complex we have chosen to study is the salt composed of the cation $[Fe(bpy)_2Cl_2]^+$, of formal octahedral stereochemistry, and the anion $FeCl_4^-$, of slightly distorted tetrahedral stereochemistry (bpy = 2,2′-bipyridyl). The presence of high-spin d^5 iron(III) in both stereochemistries provides an invaluable internal check on the consistency of interpretation of the data, but at the expense of complexity in that interpretation. The use of the ligand 2,2′-bipyridyl allows us to try to investigate the transfer of spin well beyond the immediate donor atom without meeting all the limitations that were imposed by the large size of the phthalocyanine macrocycle in earlier studies.

The compound $Fe(bpy)Cl_3$ crystallizes in the orthorhombic space group *Pccn* with $Z = 8$. The structure has been determined with good accuracy by X-ray diffraction at 295 K[8a] and by neutron diffraction at 4.2 and at 115 K.[8b] The latter work concentrated on the deuterated material, which is the subject of the present work. The cation, $Fe(bpy)_2Cl_2^+$, has the cis octahedral stereochemistry with C_{2v} (*mm*) symmetry and donor atoms fairly close to the formal octahedral positions, as shown in Figure 1a. The $FeCl_4^-$ anion is a slightly distorted tetrahedron with *c* as an approximate S_4 ($\bar{4}$) axis. This is illustrated in Figure 1b. The asymmetric unit of the cation consists of an iron atom with one bipyridyl ligand and one chlorine atom, along with an iron atom with two chlorine atoms for the anion. *c* is a twofold axis.

The magnetic susceptibility of the compound corresponds closely with that expected for a high-spin iron(III) complex ($S = 2^1/_2$) at ambient temperature, giving $\mu_{eff} = 5.90\ \mu_B$.[9] The effective magnetic moment falls with decreasing temperature, corresponding to $\Theta = -4$ K in the Curie–Weiss law, $\chi_{Fe} = C(T - \Theta)^{-1}$, down to ca. 3 K and then 0.8 K down to ca. 1.8 K. The magnetic susceptibility is isotropic above ca. 50 K but increasingly anisotropic below that temperature, to the extent of ca. 50% at 4.2 K. The magnetization at 4.2 K along each crystal axis direction follows the Brillouin function for $S = 2^1/_2$ for magnetic fields up to ca. 1.0 T.[9b] These features obviously reflect the presence of a small magnetic exchange interaction. In a system of symmetry as low as that of the present compound, it is expected that the magnetic exchange will be of complicated nature. The results at hand do not allow

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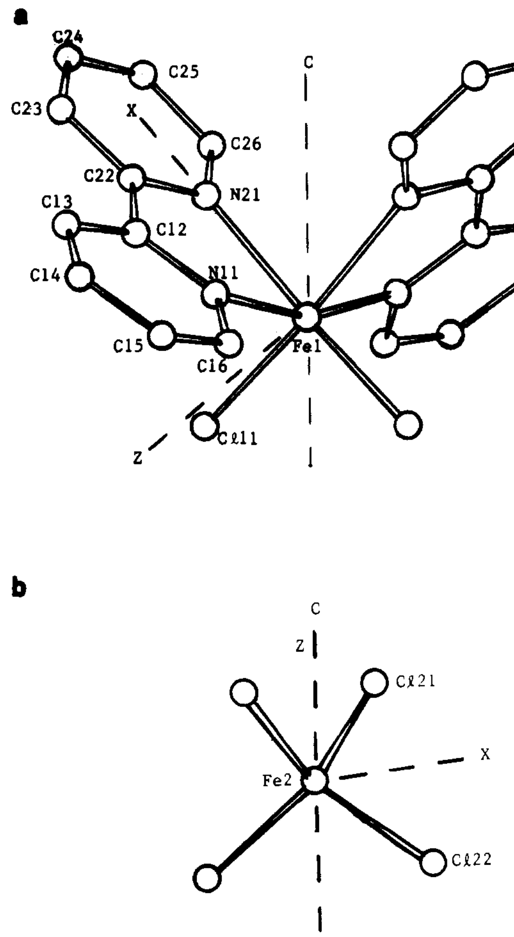

Figure 1. (a) The cation $[Fe(bpy)_2Cl_2]^+$ and (b) the anion $[FeCl_4]^-$ showing the relationship of the *z* and *x* axes to molecular features and to the crystal *c* axis. The *y* axis forms a right-handed coordinate system with *x* and *z*. The hydrogen atoms are omitted for clarity.

any proper description of the interaction but do make it clear that the magnetic ordering takes place at a temperature well below that of the pnd experiment, 4.2 K. At 4.2 K the effective magnetic moment at low magnetic field strength is 4.09 μ_B. Neglecting anisotropy, if the magnetization continues to obey the Brillouin function above 1.0 T, it is expected that the magnetic moment per iron atom $\langle\mu\rangle = \chi_{Fe}H/N\beta$ will be 2.65 μ_B at 4.6 T, the field of the pnd experiment. Such a value should provide sufficient magnetization to allow reasonable accuracy in the determination of flipping ratios in the pnd experiment.

Experimental Section

2,2′-Bipyridyl (bpy) was deuterated as described previously,[8b] to the extent of 90 (2)%. Deuteration serves to reduce the background of incoherently scattered neutrons that is generated by the presence of protons and also reduces the zero-point motion. Large transparent brown single crystals of $Fe(bpy)Cl_3$ were grown by slow evaporation of a solution of stoichiometric amounts of anhydrous $FeCl_3$ and the ligand in nitromethane. The prismatic crystal chosen for the present experiment was 1.8 × 4.5 × 2.2 mm ([100] × [010] × [001]) in dimensions.

The orthorhombic *Pccn* crystal (a = 1.497 (2), b = 1.224 (2), c = 1.321 (2) nm; Z = 4; T = 4.2 K) was mounted with the *c* axis offset by ca. 15° from the magnetic field direction of the D3 normal-beam polarized neutron two-axis diffractometer of the High-Flux reactor at the Institut Laue-Langevin, Grenoble. The offset helps to reduce the contribution of multiple scattering to Bragg peak intensities.[6a]

The flipping ratio for a reflection, $R(hkl)$, is defined by $R(hkl) = I_\uparrow(hkl)/I_\downarrow(hkl)$, where $I_\uparrow$ and $I_\downarrow$ are the respective diffracted intensities with the incident neutron beam polarization parallel and antiparallel to the applied magnetic field. With a knowledge of the nuclear neutron-scattering factors of this centrosymmetric crystal, $F_N(hkl)$, and after correction for beam polarization efficiency and flipping efficiency, the flipping ratio may be used to deduce the magnetic structure factor $F_M(hkl)$.

$$R(hkl) = [F_N^2(hkl) + 2S^2(F_N(hkl))(F_M(hkl)) + S^2F_M^2(hkl)]/[F_N^2(hkl) - 2S^2(F_N(hkl))(F_M(hkl)) + S^2(F_M(hkl))] \quad (1)$$

S is the sine of the angle between the scattering vector and the magnetic field direction. The quantities $F_N(hkl)$ are available from the neutron structure determination at 4.2 K, performed on a crystal from the same batch.[8b] Since we measure a ratio of intensities, the absorption correction cancels and need not be corrected for.

The flipping ratios of 773 reflections were measured 4.2 K and a magnetic field strength of 4.6 T. In general four equivalents ($\pm h,\pm k,l$) were measured to a $(\sin\theta)/\lambda$ maximum of 7.35 nm^{-1} for reflections with $F_N(hkl)$ greater than about 10^{-13} m. The wavelength of the neutron beam was 90.50 (3) pm after reflection from the Heusler alloy polarizing monochromator. The beam polarization was 0.9821 (3), and the flipping efficiency was 1.0000 (3). Also, the flipping ratios for the reflections 440, 460, 330, and 510 were measured at the same field and at a number of temperatures between 2.07 and 41.0 K and at 1.5 T at temperatures between 3.2 and 10.9 K. These measurements were made to aid in understanding the magnetic exchange interactions and to make sure that if magnetic ordering occurred it did so at a temperature well below 4.2 K. Several reflections forbidden by the space group were studied so that a correction for multiple scattering could be established.

The main limitation in the data set obtained lies in the restriction in the range available in l, experimentally imposed because the motorized counterlifting arm could not be raised to give the higher values of ν required to observe the upper layers along c.

The values of $F_M(hkl)$ can be obtained from eq 1 by solving a quadratic equation. The choice between the two roots of the equation is guided by our expectation that the magnetization distribution will be centered on the iron atoms and will be predominantly 3d-like in character. The choice is rarely ambiguous. The phases of $F_M(hkl)$ are determined by the experiment, unlike the case for X-ray and neutron diffraction structure factors.

Experience in the neutron diffraction structure determination of this crystal[8b] led us to expect that extinction should be negligible in our crystal, and so no correction was made. However, this determination indicates that a contribution to Bragg peak intensities from multiple scattering must be considered. It was for that reason that no reflections with $|F_N(hkl)|$ values less than 10 × 10^{-14} m were measured in our experiment except for a few very low-angle reflections. This was because the multiple scattering components in the flipping ratio are not small when $F_N(hkl)$ is small, and the value of $F_M(hkl)$ that would be deduced would be inaccurate.[2a] This compounds the effect of the relatively high total cross section usual in neutron diffraction compared to X-ray diffraction experiments.

A comparison of the reflection data showed that the major source of uncertainty arose from counting statistics. The equivalent reflections were averaged, and a constant value of 2.0 × 10^{-28} m^2 was added to the numerator and denominator of eq 1 as a crude correction for multiple scattering.[2a] There resulted 207 unique values of $F_M(hkl)$ with $\sum\sigma(F_M)/\sum|F_M| = 0.08$. The errors, estimated as in ref 2a, finally assigned to each $F_M(hkl)$ include contributions of 0.3 × 10^{-14} m from uncertainty in $F_N(hkl)$, estimated from the accuracy of the structure determination, and 0.7 × 10^{-14} m for uncertainty in the multiple scattering correction, in addition to the error arising from neutron counting statistics. The agreement between equivalents before averaging was consistent with these sources of error.[2a]

Since the Fe^{3+} ion is known to possess the $^6A_{1g}$ ground term, with $S = 2^1/_2$ and $g = 2$, in the formal octahedral or tetrahedral symmetry, no correction to the values of $F_M(hkl)$ for an orbital scattering effect is required. A measurement of the bulk magnetization of the compound at 4.2 K and 4.6 T is not available, so that if it is not possible to put the data on an absolute scale. It must be scaled with the knowledge that the saturation magnetic moment associated with each iron atom, $\langle\mu\rangle = gS\beta$, is 5.00 μ_B and the assumption that all sources of magnetization in the unit cell have been accounted for in any model developed.

Results

Since our data are limited in the number of observations, we adopt, as in our previous work, the approach of modeling

Table I. Calculated Scattering Curves for Fe(II) with 3d^{5}4p^1 Valence Configuration

κ, nm^{-1}	j_0(3d–3d)	j_2(3d–3d)	j_4(3d–3d)	j_3(3d–4p)	j_0(4p–4p)	j_2(4p–4p)
0	1.0	0.0	0.0	0.0	1.0	0.0
0.6	0.9607	0.0155	0.0002	0.0033	0.4337	0.1859
1	0.8965	0.0399	0.0011	0.0114	0.0947	0.2057
2	0.6673	0.1161	0.0113	0.0304	−0.0204	0.0488
3	0.4374	0.1704	0.0324	0.0267	−0.0001	0.0032
4	0.2618	0.1889	0.0557	0.0133	0.0049	−0.0016
5	0.1442	0.1814	0.0740	0.0011	0.0045	−0.0004
6	0.0712	0.1604	0.0849	−0.0071	0.0028	0.0011
7	0.0285	0.1346	0.0889	−0.0114	0.0013	0.0019
8	0.0051	0.1092	0.0877	−0.0128	0.0003	0.0021
9	−0.0067	0.0864	0.0831	−0.125	−0.0002	0.0018
10	−0.0117	0.0672	0.0763	−0.0112	−0.0003	0.0014

[a] κ is the scattering vector, and j_0(3d–3d) is the function $\langle j_0(\text{3d–3d})(|\kappa|)\rangle$.

it in terms of chemically important parameters, employing least-squares refinement methods rather than the analysis of Fourier maps. The choice of model and its details are described elsewhere.[5c] Since the data also are limited in extent along the *c* axis, we constrain the parameters that we employ so that they do not probe that direction in depth.

As in the case of Ni(NH$_3$)$_4$(NO$_2$)$_2$,[5a,c] we model the spin density in [Fe(bpy)$_2$Cl$_2$][FeCl$_4$] in terms of the sum of atomic orbitals on all the various constituent atoms, plus some representing "overlap" in iron–ligand bonds. In view of the limitations in the information along *c*, we restrict the refinement we perform so as to maintain spherical symmetry on all atoms. In a further refinement we allowed cubic aspherical terms on the iron atoms by using separate occupation parameters for the t$_{2g}$ (3d$_{xy}$, 3d$_{xz}$, 3d$_{yz}$) orbital set and for the e$_g$ (3d$_{x^2-y^2}$, 3d$_{z^2}$) set, as well as for the spherical 4p set to model diffuse iron-centered density. For the cation the *x* axis was defined to be along the Fe(1)–N(21) bond, with *z* lying close to the Fe(1)–Cl(11) bond direction. For the anion the *x* axis bisects the angle Cl(21)–Fe(2)–Cl(22), and the *z* axis is along *c*. These relationships are illustrated in Figure 1.

In the case of the anion, where the symmetry is tetrahedral, we also include C°_{dp}, the parameter that allows for the mixing of the 3d and 4p orbitals in that symmetry. This parameter has been discussed in some detail in connection with the CoCl$_4$$^{2-}$ ion.[2] It corresponds to the spherical harmonic Y_3^{-2} in a multipolar expansion of the magnetization density and describes the transfer of spin across the central metal atom so that positive spin accumulates at alternate corners of a cube, those occupied by the ligand tetrahedron, at the expense of the creation of negative spin at the remaining corners. The parameter was labeled $C^\circ_{321,410}$ or "3d–4p overlap" in the earlier work. It does not make a contribution to the net spin on the metal atom.

On the chlorine atoms of both the cation and the anion we allow a 3s–3p population and on the nitrogen atoms of the cation a 2s–2p population. On the carbon atoms of the bipyridyl ligand we place 2s–2p orbitals and on the hydrogen atoms 1s orbitals. As a crude representation of possible metal–ligand overlap density in the cation, we place hydrogen-like 1s orbitals in the centers of the Fe(1)–Cl(11), Fe(1)–N(11), and Fe(1)–N(21) bonds. The same procedure is not used in the case of the anion because, due to the tetrahedral stereochemistry, it would not be meaningful to distinguish such a "true" overlap population from the redistribution of spin described by the 3d–4p mixing parameter.

The total spin populations on cation and anion have been separately renormalized to five spins. This approximation is consistent with the weak interion magnetic exchange observed. The renormalization factor observed for each ion (1.44 and 1.82, refinement R3) is close to the value calculated from the Brillouin function (1.89 = 5/2.65). The differences of the two numbers from this are explicable by weak antiferromagnetic exchange, different for cation and anion.[9b]

The scattering curves used for the atoms, apart from iron, were taken from ref 10. In the cases of the immediate donor atoms, the chlorines and nitrogens, the scattering curves were allowed to change corresponding to an expansion or contraction of the radial extent of the relevant atomic orbitals. The change was effected by including a refinable parameter, $\kappa_{n\text{sp}}$, such that the scattering curve function was $\langle j_0(\kappa_{n\text{sp}}|\kappa|)\rangle$ rather than $\langle j_0(|\kappa|)\rangle$. κ is the scattering vector and j_0 the spherical Bessel function of order zero.

For the iron atoms we obtained radial wave functions for the 3d and 4d orbitals by using the program ATOMSCF[11] for an iron atom with the configuration (Ar core)3d^{5}4p^1. The basis functions used, typical in such calculations, were 21 STO's including four 3d and two 4p functions. The two most diffuse 3d and the two 4p STO exponents were optimized in the calculation reaching 2.23, 1.42 (3d) and 1.29, 0.69 (4p) au, respectively. The scattering curves corresponding to the functions $\langle j_0(\text{3d–3d})(|\kappa|)\rangle$, $\langle j_2(\text{3d–3d})(|\kappa|)\rangle$, $\langle j_4(\text{3d–3d})(|\kappa|)\rangle$, $\langle j_3(\text{3d–4p})(|\kappa|)\rangle$, $\langle j_0(\text{4p–4p})(|\kappa|)\rangle$, and $\langle j_2(\text{4p–4p})(|\kappa|)\rangle$ were derived by using a local program to implement relationships between the types of orbitals, the scattering vector, and the spherical Bessel functions of order 0, 2, 4, 3, 0, and 2, respectively, and are given in Table I. The relationships required have been set out by Avery and Watson.[12] The iron 3d scattering curves were permitted to vary through parameter $\kappa_{3\text{d}}$ as described above for Cl and N curves.

Modeling the Data

(1) A model based upon spherical symmetry at all atoms, using 3d and 4p orbitals on the iron atoms and allowing the radial parameters $\kappa_{3\text{d}}$, $\kappa_{3\text{sp}}{}^{\text{Cl}}$, and $\kappa_{2\text{sp}}{}^{\text{N}}$ to vary produced on least-squares refinement using our local program ASRED a very reasonable fit to all 207 data, with $R_w = 0.059$ and $\chi = 1.64$. The principal features are in Table II. There, and in the subsequent discussion, the numbers in parentheses after a quantity are the least-squares errors estimated from the refinement process. It can be noted that there appears to be a net negative spin distributed on the C and H atoms of the bipyridyl ligand that cancels positive spin on the nitrogen donor atoms so that the net ligand spin is close to zero.

However, the refinement had the unsatisfactory feature that the coefficients $\kappa_{3\text{sp}}{}^{\text{Cl}}$ and $\kappa_{2\text{sp}}{}^{\text{N}}$ and the populations on the donor atoms of the cation as well as the iron 4p populations had uncertainties as large or larger than their refined values. The parameters $\kappa_{3\text{sp}}{}^{\text{Cl}}$ and $\kappa_{2\text{sp}}{}^{\text{N}}$ had changed from unity by amounts that seemed unlikely to be physically real ($\kappa_{3\text{sp}}{}^{\text{Cl}} = 0.5$ (4), $\kappa_{2\text{sp}}{}^{\text{N}}$

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Table II. Major Features of Refinements of the Pnd Data on *cis*-[Fe(bpy)$_2$Cl$_2$][FeCl$_4$][a]

refinement	NV[b]	χ	cation[c]				anion	
			p[Fe(1)]	p[Cl(11)]	{p[N(11)] + p[N(21)]}	p[bpy]	p[Fe(2)]	{p[Cl(21)] + p[Cl(22)]}
R1	34	1.64	4.79	0.10	0.10	0.00[d]	4.46	0.27
R2	32	1.45	4.18	0.22	0.255	0.185[d]	4.31	0.34
R3	35	1.42	4.24 (20)	0.23 (2)	0.24 (1)	0.145 (60)[d]	4.13 (16)	0.44 (3)

refinement	NV[b]	χ	3d populations				4p populations	
			p[Fe(1)]	κ[Fe(1)]	p[Fe(2)]	κ[Fe(2)]	p[Fe(1)]	p[Fe(2)]
R1	34	1.64	4.41 (11)	0.994 (7)	4.16 (11)	0.996 (10)	0.38 (60)	0.30 (60)
R2	32	1.45	4.30 (10)	1.000 (7)	3.83 (12)	0.989 (9)	−0.07 (80)	0.48 (60)
R3	35	1.42	4.39 (13)	0.999 (7)	4.04 (10)	1.011 (11)	−0.12 (28)	0.09 (36)

[a] p(X) is the spin population on atom or molecule X. [b] NV is the number of variables used in the refinement. [c] Cation population is p[Fe(1)] + 2p[Cl(11)] + 2p[bpy]. Atomic populations include a contribution of $^1/_2\Sigma p$[1s], this being the sum of the populations placed as H(1s) orbitals in each Fe–(donor atom) bond for R2 and R3 divided by 2. [d] Includes p[N(11)] + p[N(21)].

= 0.4 (8)). The correlation coefficients between the population and radial parameters were also high (>0.9). It is obvious that the present data set is not able to support a study of both the radial factors and the populations of the orbitals concerned. Previous experience with more complete data sets have shown that the κ parameters for Cl and N donor atoms in other complexes change relatively little from unity. The radial parts of their valence functions seem to be little changed by their bonding to the metal atom.[2-5] Consequently, for the subsequent refinements of the data for the present compound the donor atom radial parameters were fixed at unity.

(2) A refinement was performed retaining spherical symmetry on all atoms but restricting the donor atom radial parameters $\kappa_{3sp}{}^{\mathrm{Cl}}$ and $\kappa_{2sp}{}^{\mathrm{N}}$ to be unity. In order to provide flexibility in the description of the bonding interaction between the donor atoms and iron atom in the cation, hydrogen 1s orbitals were placed at the center of each such bond. On each iron atom 3d and 4p orbitals were employed, the radial parameter κ_{3d} being varied. There resulted an appreciable improvement in the fit to the 207 data, $R_w = 0.052$ and $\chi = 1.45$. The center bond/Fe(4p) correlation is small (maximum 0.318), reflecting the more diffuse nature of the 4p radial function, the bond "blobs" being relatively localized at the bond centers. The major features of the model are in Table II, refinement R2.

The principal features of this refinement differ substantially from those of refinement R1 only, as might be expected, in the population parameters of the donor atoms of the cation and in the metal 4p orbital populations. The ligand donor atom populations are now fairly well-defined. The iron atom 3d population and radial parameters also are well-defined, being 4.30 (10) spins with $\kappa_{3d} = 1.000$ (7) for Fe(1) in the cation and 3.83 (12) spins with $\kappa_{3d} = 0.989$ (9) for Fe(2) in the anion. However, the iron atom 4p populations in each case are still not defined, being −0.07 (80) spins in the cation and 0.48 (60) spins in the anion. The 1s orbitals placed in the (iron atom)–(donor atom) bond centers in the cation to represent "overlap" have populations that exceed the uncertainties by varying amounts: Fe(1)–Cl(11), −0.11 (1); Fe(1)–N(11), 0.05 (2), Fe(1)–N(21), 0.01 (1). The total spin on the bipyridyl C and H atoms, −0.07 (6) spins, is barely defined within the least-squares errors, but the interesting features of the distribution of this spin outlined in the next refinement are also observed here.

(3) A refinement in which the symmetry at the iron atoms was allowed to reduce to cubic rather than spherical was conducted. The t_{2g} and e_g orbitals on Fe(1) in the cation and the t_2 and e orbitals on Fe(2) in the anion were allowed to vary in populations independently. Also, on the anion, the 3d–4p mixing parameter $C^{\circ}{}_{dp}$ was allowed to vary. Otherwise, the restrictions were as described for refinement R2. There was a small improvement in the fit to the 207 data: $R_w = 0.050$, $\chi = 1.42$. The magnetic moment per iron atom was calculated to be $\langle\mu\rangle = 2.66\ \mu_B$. The principal features of the refinement are in Table II, refinement R3.

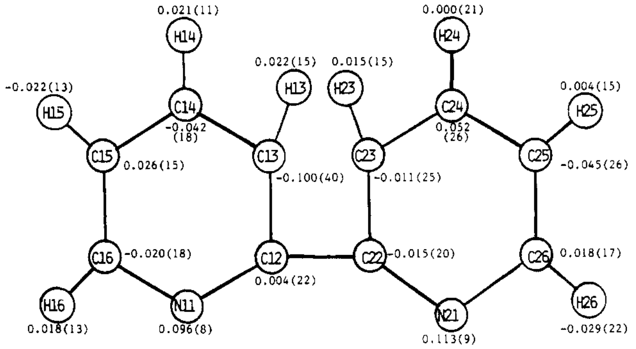

Figure 2. Spin distribution in the bipyridyl ligand.

The changes in overall populations relative to the model described in refinement R2 are quite minor. On Fe(1) the total 3d population is 4.39 (13) spins with $\kappa_{3d} = 0.999$ (7), and on Fe(2) the population is 4.04 (10) spins with $\kappa_{3d} = 1.011$ (11). The 4p populations are changed, particularly on the anion, but remain ill-defined because of their diffuse nature, −0.12 (28) spins on Fe(1) and 0.09 (36) spins on Fe(2), although the lack of definition is not as severe as for refinement R2. The cation "overlap" populations are very similar and with similar confidence levels: Fe(1)–Cl(11), −0.09 (2); Fe(1)–N(11), 0.05 (2); Fe(1)–N(21), 0.02 (2). The bipyridyl ligand C and H atom total population is −0.10 (6) spins.

On Fe(1) in the cation the population of each t_{2g} orbital is obtained as 0.88 (5) and in each e_g orbital as 0.86 (8). Total occupancies of the two orbital types: t_{2g}, 2.66 (10) spins; e_g, 1.73 (12) spins. On Fe(2) in the anion the per-orbital populations are 0.65 (5) for t_2 and 1.04 (9) for e, with respective total populations of 1.95 (9) and 2.09 (12) spins, and the 3d–4p mixing parameter $C^{\circ}{}_{dp}$ is 1.9 (8).

The bipyridyl total spin distribution outside the nitrogen atoms is barely defined outside the error, and this reflects the fact that the populations on the individual C and H atoms are mostly at about the error level. However, in spite of the lack of definition, it is of interest to examine relationships on a statistical basis. The spin distribution for the bipyridyl molecule is illustrated in Figure 2.

Of the parameters varied, the only pairs that show strong correlation are the t_{2g} and e_g orbital populations on the cation, the t_2 and e populations on the anion (coefficients ~0.95), and the 4p populations on the cation and the anion (coefficient 0.88). There is some correlation between the anion 4p population and the $C^{\circ}{}_{dp}$ mixing parameter (coefficient 0.70). The

4p correlations are high because they affect only the few very low-angle reflections substantially. the high t$_2$/e correlation mainly reflects our concentration on medium-angle data (to define spin-transfers best), rather than higher angle data.

Discussion

In [Fe(bpy)$_2$Cl$_2$][FeCl$_4$] both cation and anion are observed to transfer about 16% of the spin to the ligand atoms, presumably through covalent bonding. As expected, because of the higher formal charge on the central atom, this is half as large again as the fraction, 10%, transferred in the CoCl$_4^{2-}$ ion. It is quite markedly less than the fraction transferred in the complex Ni(NH$_3$)$_4$(NO$_2$)$_2$, 27%, in spite of again the higher formal charge on the central metal atom.

The fact that the spin transfer is essentially equal for the cation and the anion is perhaps surprising: chemical experience would suggest that the bipyridyl ligand is much more covalently bound to an iron(III) atom than is a chloride ion, and so we should see more spin on the nitrogen atoms. Taken together with the fact that the cation coordination number is 6 rather than 4 for the anion, one had anticipated appreciably more loss of spin by the iron atom in the cation than in the anion. The spin transfer to each chlorine atom is very similar in the cation (0.27 without the Fe(1)–Cl(11) "overlap" population) and in the anion (0.22).

In the cation the spin populations on the chlorine atoms are substantially higher than those on the nitrogen atoms of the bipyridyl ligands. In addition, the spin transfer to the nitrogen atoms is less by some 25% because of the negative spin on the rest of the bipyridyl molecule. This latter must arise from spin polarization by the positive spin on the nitrogen atoms. The relatively small spin transfer to the nitrogen atoms is rather a surprising result. In the FeCl$_4^-$ anion the difference between the chlorine atom spin populations is not large, although it is significant on the basis of the least-squares errors, being 0.25 (1) for Cl(21) and 0.19 (2) for Cl(22). As the distortion of the FeCl$_4$ tetrahedron is only slight, no obvious difference in spin transfer between the two types of chlorine atom is expected. If the difference is real, it seems more likely that it reflects longer range interaction with other parts of the crystal lattice.

The d-orbital population on the iron atom in the Fe(bpy)$_2$Cl$_2^+$ cation is spherical within our experimental errors; the t$_{2g}$ and e$_g$ populations per orbital are 0.88 (5) and 0.86 (6), respectively, in refinement R3. The values are too highly correlated in our refinement for any meaningful differentiation (coefficient −0.96).

In the anion, the populations of the e and t$_2$ orbitals, 1.04 (9) and 0.65 (9), respectively, are markedly different, but given the large correlation (coefficient −0.94), significance is not to be attached to that difference. The 3d–4p mixing population, C°_{dp}, corresponds to the transfer of ca. 0.1 spins across the iron atom from the vicinity of each tetrahedral vertex occupied by a chlorine atom. Here, the absence of a center of symmetry allows a very considerable polarization of the iron(III) electronic system. As pointed out above, the spin transfer described by C°_{dp} may contain a component that arises from overlap in the Fe(2)–Cl bonds. If this is of the same magnitude as in the Fe(1)–Cl(11) bond, and half of it is assigned as associated with the iron atom and half with the chlorine atoms, then the majority of the apparent 3d–4p mixing is accounted for.

The diffuse orbital populations modeled as 4p (4p$_x$ = 4p$_y$ = 4p$_z$) on the iron atoms of both the cation and the anion are not significant within the least-squares errors. This result conforms with the findings based on our previous more accurate and complete pnd data sets on other compounds, which were that while large amounts of *charge* can accumulate in diffuse orbitals on bonding, little net spin does. In the present case the errors are substantially larger, probably reflecting the lack of low-angle reflections not affected by multiple scattering. There is correlation between these 4p populations on the cation and on the anion, the source of which is again the paucity of low-angle data. In the previous studies mentioned, while the net diffuse orbital populations were small, individual components of them were significant at levels well outside the errors—that is, there was found to be a highly anisotropic diffuse distribution. Our present data set is not sufficiently accurate and complete to allow us to investigate whether there is an anisotropic diffuse orbital population on the iron atoms of [Fe(bpy)$_2$Cl$_2$][FeCl$_4$].

The net spin on the carbon and deuterium atoms of the bipyridyl ligand is scarcely significant, in view of the errors, and this applies also to most of the individual atoms involved. There appears to be no pattern in the populations of the carbon atoms, whether in sign or size. In particular the expected mirror symmetry in the plane perpendicular to the C(12)–C(22) bond (see Figure 2) is not observed. However, one correlation is very obvious. It is that the sign of the spin on a deuterium atom is always opposite to that of the carbon atom to which it is attached. The ratio (deuterium spin/carbon spin) varies between 0 and −1.9, the average being −0.7 (6). The transfer of spin around the ring system of this ligand can take place either through σ-bonding interactions, which may be expected to reverse the sign of spin on adjacent atoms, or through π bonding, which should lead to the same sign of spin throughout. It seems that the results observed arise from a complicated mixture of these two mechanisms. However, it is clear that the σ nature of the C–H interaction is, indeed, confirmed.

Summary

The spin distribution in the cation of [Fe(bpy)$_2$Cl$_2$][FeCl$_4$] can be usefully analyzed at the level of spherical symmetry at all the atoms. About 15% of the spin is lost from the iron atom by transfer to the ligand donor atoms, most to the chlorine atoms. With this data we cannot distinguish the σ- from the π-based component of spin transfer. Evidence for a small net diffuse iron-centered spin population is provided, but the data cannot detect differences between 3d orbitals on an iron atom. The net spin on the bipyridyl ligands, apart from that on the nitrogen atoms, is quite small and is negative. We cannot rationalize its distribution except to observe that spin on the deuterium atoms is negative, and somewhat smaller in magnitude, relative to that on the carbon atoms to which they are attached.

The spin distribution on the anion is nonspherical in nature, corresponding to polarization of the electron distribution made possible by the absence of a center of symmetry. The transfer of spin to the chlorine ligand atoms amounts to 17% and is fairly evenly distributed between the two types.

It is anticipated furthermore that when three-dimensional data that make the set more accurate and complete becomes available, it will be possible to resolve some of the questions unanswered in this study such as whether anisotropic diffuse iron-centered populations are present and perhaps to develop a simple molecular orbital description of the interaction between the iron atoms and their donor atoms.

Registry No. *cis*-[Fe(bpy)$_2$Cl$_2$][FeCl$_4$], 88269-35-6.

Supplementary Material Available: A listing of observed and calculated magnetic structure factors for refinement R3 (5 pages). Ordering information is given on any current masthead page.