EPR Spectroscopy

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Superhyperfine Interaction in $[MnF_6]^{3-}$

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The modification of the EPR response by the superhyperfine interaction is the primary source of information from which metal-ligand bonding characteristics of paramagnetic centers are determined. The plethora of techniques developed to elucidate this quantity have found particular application in the field of biochemistry, and enzymes containing copper(II), iron(III), and manganese(II) centers are regularly probed by pulsed EPR techniques. Owing to the importance of monomeric manganese(III) centers to biocoordination chemistry in metalloenzymes such as superoxide dismutases,[1] and to processes such as catalytic epoxidation[2] and aziridination,[3] the spectroscopic properties of this center have been thoroughly investigated. Nevertheless, there are no reports of superhyperfine interaction in monomeric manganese(III) complexes. Herein, we show that the manganese(III)–fluorine superhyperfine interaction can be observed by using a conventional spectrometer equipped with a parallel-mode X-band cavity. Data from two systems are presented from which principal values of the superhyperfine tensor in the hexafluoromanganate(III) anion are determined. The geometry inferred from the superhyperfine coupling constants does not correlate simply with the Mn−F bond lengths. Apart from this being the first observation of superhyperfine interactions in manganese(III) complexes, this paper provides a textbook example of how the electronic structure of the central ion is reflected in the superhyperfine interaction with the surroundings.

The salt $[Rh(NH_3)_6][GaF_6]_{(1-x)}[MnF_6]_x$ was synthesized according to reference [4], based on the method for the synthesis of $[Rh(NH_3)_6][MnF_6]$ reported by Wieghardt and Siebert.[5] At temperatures below 140 K, the high-frequency high-field EPR spectra of salts with $0.05 \leq x \leq 1$, as well as temperature-dependent inelastic neutron scattering (INS) spectra of the fully deuterated concentrated salt, could be interpreted in terms of the spin Hamiltonian for an $S=2$ spin system [Eq. (1)] with $g_x=g_y=1.993$, $g_z=1.980$, and $D=-3.968\ \text{cm}^{-1}$.

$$\hat{H} = \mu_B(g_x B_x \hat{S}_x + g_y B_y \hat{S}_y + g_z B_z \hat{S}_z) + D\hat{S}_z^2 \tag{1}$$

The sign of the D parameter and the fact that $g_z < g_x, g_y$ are both consistent with an axially elongated[6] structure of the anion. Hence, the $S=2$ ground state is split, and the $M_S=\pm 2$ components are left as the lowest energetic states, separated by approximately $12\ \text{cm}^{-1}$ from the $M_S=\pm 1$ components, which in turn are $4\ \text{cm}^{-1}$ lower than the $M_S=0$ component.

The X-band parallel-mode spectrum of the $[MnF_6]^{3-}$ anion as a 0.1% dopant in $[Rh(NH_3)_6][GaF_6]$ (Figure 1) shows a complicated pattern arising from the combination of Zeeman, hyperfine, and superhyperfine splittings. The spectrum in Figure 1 could be confidently interpreted only after having recorded a spectrum of the $[Mn(salen)F_2]^-$ anion (Figure 2), which exhibits eight lines with approximate relative intensities of 1:3:4:4:4:4:3:1. These eight lines are consistent with six lines resulting from the hyperfine interaction involving the Mn nucleus ($I^{Mn}={}^5\!/_2$), split further by the presence of two fluoride ligands ($I^F={}^1\!/_2$). Note that the splitting due to the superhyperfine interaction is almost as large as that due to the hyperfine interaction. The spectrum can be satisfactorily reproduced by the effective spin Hamiltonian for a non-Kramers doublet [Eq. (2)] which is valid for the lowest energy $M_S=\pm 2$ electronic components.[7]

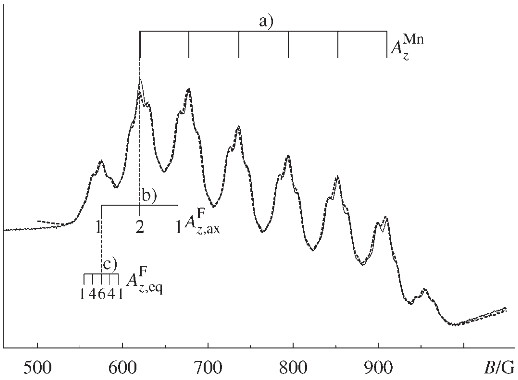

Figure 1. EPR spectrum of finely ground $[Rh(NH_3)_6][GaF_6]_{(1-x)}[MnF_6]_x$ with $x=0.001$. The experimental spectrum (solid line) was obtained at $T=1.5$ K with $B_1 \parallel B$ and $\nu=9.31771$ GHz. The dotted line represents the best fit from Equations (2) and (3) with the parameters given just after Equation (3). a) Illustration of the splitting of the six Mn hyperfine lines. b) Each of these is split into three lines by strong interaction with the two axial fluoride ligands; see also Figure 2. c) Each of these lines is finally split by interaction with the four equatorial fluoride ligands into five lines.

$$\hat{H} = \Delta\hat{S}_x + \mu_B g'_z B_z \hat{S}_z + A'_z \hat{S}_z \hat{I}_z^{Mn} + A'_{z,ax} \sum_{i=1,2} \hat{S}_z \hat{I}_z^{F,i} \tag{2}$$

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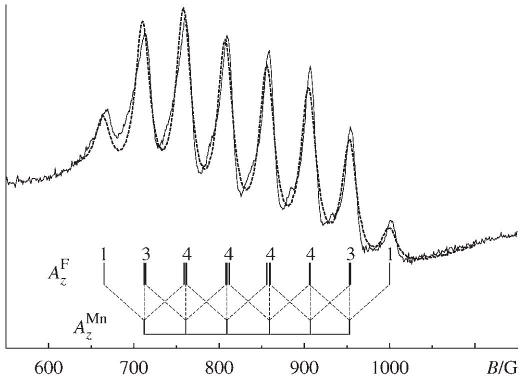

Figure 2. EPR spectrum of $[\mathrm{Mn(salen)F_2}]^-$ in frozen *N*-methyl form amide (NMF) glass. The experimental spectrum (solid line) was recorded at 5 K with $B_1 \parallel B$ and $\nu = 9.44157$ GHz. The dotted line represents the best fit from Equation (2) and the parameters given in the text. The same spectrum was obtained from [Mn(salen)Br] and an excess of $\mathrm{(NEt_4)F}$ dissolved in NMF.

In Equation (2) Δ is the zero-field splitting of the two levels and g'_z, A', and $A'_{\parallel,\mathrm{ax}}$ designate the g factor, the hyperfine coupling constant, and the superhyperfine coupling constant, respectively, for this non-Kramers doublet. Here, and in the following, the subscript z refers to the component parallel to the long Mn−F bond; primed parameters refer to an effective $S = 1/2$ spin Hamiltonian and are four times as large as the unprimed parameters, which refer to an $S = 2$ spin Hamiltonian.

Fitting a theoretical spectrum based on Equation (2) to the experimental spectrum resulted in the parameters $\Delta = 0.0712(11)\ \mathrm{cm^{-1}}$, $A'_z = 0.0180(3)\ \mathrm{cm^{-1}}$, and $A'_{z,\mathrm{ax}} = 0.0169(13)\ \mathrm{cm^{-1}}$. The fact that the superhyperfine interaction with the fluorine nuclei is almost as large as the hyperfine interaction with the manganese nucleus results in the intensity pattern indicated in Figure 2. The fit, superimposed on the experimental spectrum in Figure 2, gives a good reproduction of the experimental data considering that the frozen glass may contain other species in lower concentrations. Furthermore, terms describing unresolved superhyperfine interactions with the salen nitrogen atoms have not been included.

Returning now to the spectrum in Figure 1, we see that the major difference from that in Figure 2 is an additional splitting of the lines producing a pattern with relative intensities of 1:4:6:4:1. The spectrum can be accurately reproduced by Equation (2) augmented with the term (3), which accounts for the interaction between the electronic spin and the equatorial fluoride ligands.

$$A'_{z,\mathrm{eq}} \sum_{i=3}^{6} \hat{S}_z \hat{I}_z^{\mathrm{F},i} \qquad (3)$$

The experimental data did not warrant the use of different superhyperfine coupling constants for the equatorial fluoride ligands; consequently, they were all set equal.

From a fitting of the experimental spectrum the following parameters were obtained: $\Delta = 0.1308(1)\ \mathrm{cm^{-1}}$, $A'_z = 0.02151(3)\ \mathrm{cm^{-1}}$, $A'_{z,\mathrm{ax}} = 0.01622(10)\ \mathrm{cm^{-1}}$, and $A'_{z,\mathrm{eq}} = 0.00395(7)\ \mathrm{cm^{-1}}$. The g' factor was fixed to 7.92, obtained as $4g_z$ [see Eq. (1) and the text just after Equation (2)]. Comparison of the experimental and calculated spectra in Figure 1 shows that they are virtually identical, in contrast to the spectra in Figure 2. The better agreement in this case is ascribed to the fact that only one spin system is present here, and that the operator Equations (2) and (3) account for all spins that are present.

The axial component of the manganese hyperfine coupling constant $A_z = A'_z/4 = 0.00538\ \mathrm{cm^{-1}}$ is consistent with that recently reported for the tetragonally elongated hexaaqua ion ($0.0053\ \mathrm{cm^{-1}}$).[8] On the other hand, the superhyperfine coupling constants have magnitudes opposing what could be inferred directly from the coordination geometry, from which we would have expected that $A_{z,\mathrm{ax}} < A_{z,\mathrm{eq}}$ since $d(\mathrm{Mn{-}F_{ax}}) > d(\mathrm{Mn{-}F_{eq}})$. The parameter $A_{z,\mathrm{ax}} = A'_{z,\mathrm{ax}}/4 = 0.00406\ \mathrm{cm^{-1}}$ describing the interaction with the more distant axial fluoride ligands is more than four times as large as that for the interaction to the equatorial fluoride ligands [Eq. (4); $A_{z,\mathrm{eq}} = A'_{z,\mathrm{eq}}/4 = 0.00099\ \mathrm{cm^{-1}}$].

$$\left(\frac{A_{z,\mathrm{ax}}}{A_{z,\mathrm{eq}}}\right)_{\mathrm{exp}} \approx 4.1 \qquad (4)$$

The ratio can be interpreted in terms of the covalency model outlined in reference [9]; see also reference [10]. Writing the $M_S = 2$ component of the ground state function as $|d^+_{yz} d^+_{zx} d^+_{xy} d^+_{z^2}|$, and using the notation of reference [9], we obtain Equations (5) and (6) for the superhyperfine coupling constants of the axial and equatorial ligands.

$$A_{z,\mathrm{ax}} = A_{\parallel,\mathrm{ax}} = A_\mathrm{s} + 2A_{\sigma\mathrm{p}} - 2A_\mathrm{t} + 2A_\mathrm{d} \qquad (5)$$

$$A_{z,\mathrm{eq}} = A_{\perp,\mathrm{eq}} = \frac{1}{4}A_\mathrm{s} - \frac{1}{4}A_{\sigma\mathrm{p}} + A_\mathrm{t} - A_\mathrm{d} \qquad (6)$$

Here, as in reference [9], the subscripts $\parallel$ and $\perp$ refer to parallel and perpendicular to the individual bonds, respectively. The three parameters A_s, $A_{\sigma\mathrm{p}}$, and A_t are the contributions from the fluorine 2s, $2\mathrm{p}_\sigma$, and $2\mathrm{p}_\pi$ orbitals, respectively. The model parameters A_s, $A_{\sigma\mathrm{p}}$, and A_t all have the same sign, determined by the product of the electronic g factor and the g_N factor of the ligand nucleus.[9] In the present case this is positive. The contact term A_s provides an isotropic contribution to the superhyperfine interaction. The contribution from the remaining terms is anisotropic.

The term A_d is the contribution from the direct dipole–dipole interaction between the electron spin and the fluorine nucleus. Its magnitude can be estimated by using the classical expression for the interaction energy between two magnetic dipoles separated by the distance R [Eq. (7)].

$$A_\mathrm{d} = \frac{\mu_0\, g\, \mu_\mathrm{B}\, g_\mathrm{N}\, \mu_\mathrm{N}}{4\pi R^3} \qquad (7)$$

Using the bond lengths for hexaaqua ion in the axially distorted phase, $R_\mathrm{ax} = 2.06$ Å and $R_\mathrm{eq} = 1.86$ Å, as an estimate for the bond lengths in the hexafluoro anion, we obtain values of 0.00028 and $0.00039\ \mathrm{cm^{-1}}$ for the axial and equatorial ligands, respectively. Hence, by using Equations (5) and (6) the contribution from the direct dipole–dipole interaction to $A_{z,\mathrm{ax}}$ and $A_{z,\mathrm{eq}}$, being small and almost equal, cannot explain the observed values and observed ratio of Equation (4). Therefore, on the basis of the magnitude of the experimentally determined $A_{z,\mathrm{ax}}$ and $A_{z,\mathrm{eq}}$ values, we conclude that the main contributions to the observed superhyperfine coupling constants come from A_s, $A_{\sigma p}$, and A_t, and not from the direct dipole–dipole interaction.

Experimentally, we have extracted but two superhyperfine parameters from the experimental spectra. Therefore, we cannot independently deduce the values of A_s, $A_{\sigma p}$, and A_t. By comparison with values obtained for other di- and trivalent hexafluoro complexes we see that $A_s > A_{\sigma p} > A_t > A_d$. The difference $A_{\sigma p}-A_t$ was in all cases found to be small and comparable to A_d. From accurate Q-band EPR measurements[11] on $[\mathrm{FeF_5}]^{2-}$ as an impurity in $(\mathrm{NH_4})_2\mathrm{SbF_5}$ it was concluded that $A_s \gg A_{\sigma p}, A_t, (A_{\sigma p}-A_t)$. As $A_{\sigma p}$ and A_t appear with opposite signs in both Equations (5) and (6), the superhyperfine coupling constants may be approximated by the first term in these expressions, which results in a theoretical ratio given by Equation (8).

$$\left(\frac{A_{z,\mathrm{ax}}}{A_{z,\mathrm{eq}}}\right)_{\mathrm{theory}} = 4 \tag{8}$$

The factor of four in Equation (8) reflects the geometry of the linear combination of ligand orbitals transforming as and contributing to the molecular orbital predominantly being d_{z^2}. In this linear combination, axial and equatorial ligand orbitals occur with relative weights of +2 and −1, respectively, and the superhyperfine parameters depend on the squared amplitudes.

The almost exact agreement with the experimentally found ratio of Equation (4) is probably fortuitous, as the superhyperfine interaction reported for $[\mathrm{CuF_6}]^{4-}$ is clearly anisotropic.[12] Nevertheless, the experiment yields an unambiguous determination of the electronic and molecular structure of the complex. If the $[\mathrm{MnF_6}]^{3-}$ anion were tetragonally compressed, the HOMO would be predominately $\mathrm{d}_{x^2-y^2}$, in which case the contribution from the A_s term to $A_{z,\mathrm{ax}}$ would be zero.

In summary, we have presented the first EPR spectrum of a manganese(III) complex in which the superhyperfine interaction is clearly resolved. We have shown that this is an important quantity, as the nature of the Jahn–Teller distortion and the concomitant electronic structure can then be deduced from a single EPR spectrum obtained at one temperature.

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[4] Preparation of $[\mathrm{Rh(NH_3)_6}][\mathrm{GaF_6}]_{1-x}[\mathrm{MnF_6}]_x$: Three 20-mL 7% aqueous HF solutions A, B, and C were prepared by adding $\mathrm{GaCl_3}$ (322 mg, 1.83 mmol), $\mathrm{MnCO_3}$ (9.21 mg, 0.08 mmol) followed by 0.02 M $\mathrm{KMnO_4}$ (1 mL, 0.02 mmol), and $[\mathrm{Rh(NH_3)_6}]\mathrm{Cl_3}$ (405 mg, 1.30 mmol), respectively. Solutions A and B were mixed and solution C was added dropwise with immediate precipitation of the product. After cooling in ice, the supernatant was decanted and the microcrystalline light violet product washed with HF (7%), ethanol and diethyl ether. These amounts correspond to Mn/Ga ≈ 5%.

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