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Contribution from the Department of Chemistry
and Biochemistry, University of Windsor,
Windsor, Ontario N9B 3P4, Canada

EPR Study of Manganese(II) in Single Crystals of the Spin-Crossover Complex $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$. Evidence for Domains in Transition

Peter E. Doan[†] and Bruce R. McGarvey[*,‡]

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The temperature-dependent spin-crossover transition $^5T \leftrightarrow {}^1A$ in the compounds $[Fe(2\text{-pic})_3]X_2\cdot S$ (2-pic = 2-(aminomethyl)pyridine), with X = Cl or Br and S = C_2H_5OH or CH_3OH, was first reported by Renovitch and Baker.[1] The gradual nature of the transitions in these compounds sets them apart from most of the other Fe(II) systems studied to date.[2-4] Comparisons between the gradual spin crossover in these systems and the abrupt transitions observed in most other Fe(II) spin-crossover systems provide an excellent testing ground for proposed theoretical models.[5,6]

In an earlier paper, Rao et al.[7] used EPR of Mn(II)-doped powder samples of $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ to probe the interactions between molecules during the spin-crossover. Changes in the zero-field-splitting (ZFS) parameters D and E and the resonance line widths as a function of temperature were compared to those found in Mn(II)-doped samples of the Zn analogue. The ZFS parameters in both Zn and Fe systems increased gradually as the temperature was lowered with no unusual changes in the spin-crossover interval of the Fe compound. The resonance line widths in the Fe(II) samples did, however, increase dramatically in the temperature region of the spin-crossover transition. It is clear that some effect related to the crossover transition affects the line widths of the Mn(II) spectrum. Rao et al.[7] proposed that the broadening was due to the increasing spin lifetime of the high-spin Fe(II) as the temperature decreased, creating an effective dipolar broadening. Later ^1H NMR evidence[8] placed this explanation in doubt; the spin lifetimes were observed to stay short on the NMR time scale throughout the spin crossover.

Single-crystal EPR studies yield much more detailed information about the solid-state than power studies. Recent papers from this laboratory[9,10] reporting EPR studies of Mn(II) in single crystals of two other Fe(II) spin-crossover systems have shown the advantage of studying these transitions by using single-crystal EPR. With this in mind, we undertook to grow single crystals of $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ doped with small amounts of Mn(II).

Experimental Section

Sample Preparation. The ligand 2-(aminomethyl)pyridine was obtained from Aldrich Chemical Co. and used without further purification. Ethanol was dried by refluxing over Mg turnings, distilled under inert atmosphere, and degassed by repeated freeze–thaw cycles. All manipulations were carried out in a glovebag under nitrogen. $FeCl_2\cdot 2H_2O$ was prepared by using standard literature techniques.[11]

Powder samples of Mn(II)-doped $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ were made by following the techniques used by Rao et al.[7] using 2% (by mole) $MnCl_2\cdot 4H_2O$ and 98% $FeCl_2\cdot 2H_2O$. The fine yellowish powder gave an EPR spectrum identical with that reported earlier. Large single crystals were obtained by dissolving approximately 2 g of the doped powder into 200 mL of boiling ethanol. The resulting reddish brown solution was filtered while warm into a 350-mL three-neck flask containing ca. 50 mL of warm ethanol (55 °C). This solution was stoppered and allowed to cool slowly overnight. The solvent was evaporated by slowly blowing nitrogen over the surface of the liquid for a period of 3 weeks. Crystals were collected by pouring off the remaining ca. 30 mL of liquid and washing the crystals with small amounts of cold (0 °C) ethanol and hexane. The resulting yellowish brown crystals were dried under reduced pressure and then stored in a stoppered flask under nitrogen. This procedure commonly yielded a number of good sized (3 × 2 × 2 mm) parallelpiped-shaped crystals. The crystals tend to lose solvent over time, breaking into sheets of powder. Storage over strong drying agents, such as P_2O_5, or storage under an active vacuum will destroy the crystals in a short time.

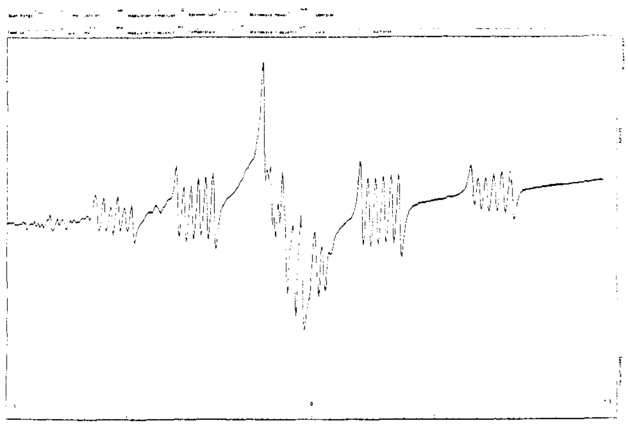

Figure 1. Room-temperature EPR spectrum of Mn(II) in single crystals of $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$. Magnetic field is in the *ac* plane in the direction of maximum ZFS splitting.

EPR Spectra. The crystals were mounted on quartz capillaries with various cyanoacrylate adhesives[12] and sealed under vacuum in a 4.2-mm-o.d. quartz tube. EPR spectra were obtained on an X-band Varian E-12 spectrometer equipped with an E-231 rotating cavity and rotating magnet base. Variable-temperature spectra were obtained with a Varian nitrogen-flow temperature-control system. Spectra at 77 K were obtained by using a quartz finger Dewar. The magnetic field was calibrated by using an NMR magnetometer. The klystron frequency was calibrated with diphenylpicrylhydrazyl and the NMR magnetometer.

Results

Room-Temperature Spin Hamiltonian. X-ray structure determinations[6,13-16] for $[Fe(2\text{-pic})_3]X_2\cdot C_2H_5OH$ show the system to be monoclinic $P2_1/c$ with four molecules in the unit cell. Symmetry requires that we detect two resonances in most orientations except when the magnetic field is in the *ac* plane. In Figure 1 is given the spectrum when the magnetic field is in the

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[†] Present address: Department of Chemistry, Bowdoin College, Brunswick, ME 04011.

[‡] To whom requests for reprints should be addressed.

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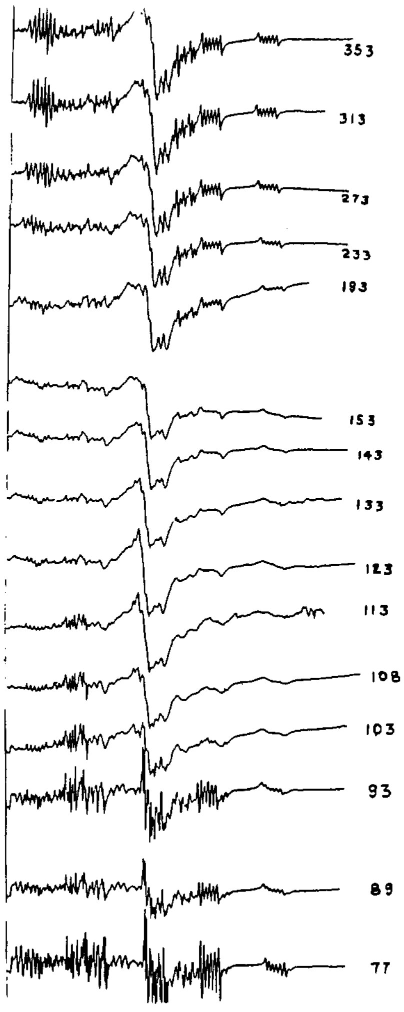

Figure 2. EPR spectra at different temperatures when the magnetic field is parallel to the principal *z* axis of one magnetic site at room temperature.

ac plane at the orientation of maximum fine structure splitting, approximately parallel to the long growth axis. This is the expected EPR spectrum for a $S = {}^5/_2$, $I = {}^5/_2$ system with the zero-field splitting comparable in magnitude to the Zeeman interaction. In most orientations, the two 60-line resonances from the two magnetically inequivalent sites overlap so much that it is difficult to separate them from proper analyses. We had to limit our analysis to the two high-field fine structure components, $({}^1/_2 \leftrightarrow {}^3/_2)$ and $({}^3/_2 \leftrightarrow {}^5/_2)$, in those orientations where these lines for one site were well separated from those of the other magnetic site.

We have fitted the results to the spin Hamiltonian

$$\hat{H} = \beta H\cdot g\cdot\hat{S} + D[\hat{S}_z^2 - {}^1\!/_3 S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2) + \hat{S}\cdot A\cdot\hat{I} \qquad (1)$$

The fourth-order terms have been left out because the limited accuracy of our fitting did not require their inclusion. The orientation of the crystal in which maximum fine structure was found for one of the magnetic sites and the orientation dependence of the two high-field lines was followed for about ±20° from this orientation. This orientation was taken to be the *z* principal axis for one of the magnetic sites. In addition, measurements were made in the *ac* plane, where the two magnetic sites give the same spectrum. The spectrum at each orientation was simulated by using the above spin Hamiltonian and a program optimized for the $S = {}^5/_2$, $I = {}^5/_2$ system.[17] In this simulation, isotropic *g* ($g = 2.00$) and *A* values were assumed. The best fits for the parameters were $D = |0.0634 \pm 0.0010|$ cm^{-1}, $E = |0.0150 \pm 0.0010|$ cm^{-1}, and $A = |0.0073 \pm 0.0005|$ cm^{-1}. These values agree, within experimental error, with the values determined from the earlier powder studies. The *z* principal axis is 17 ± 5° from the *b* axis of the crystal.

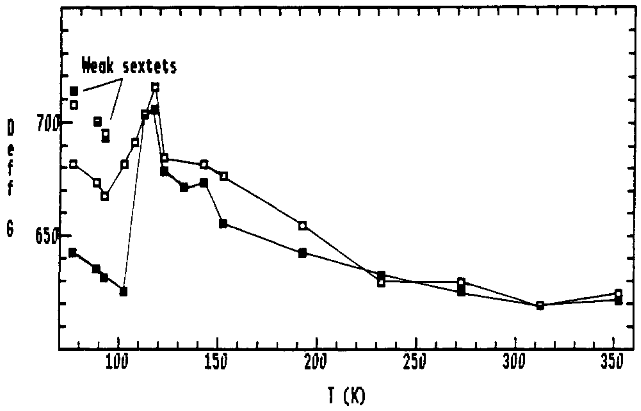

Figure 3. D_{eff} (defined in text) in gauss as a function of temperature: open squares, highest field sextet; solid squares, second highest field sextet.

Variable-Temperature Measurements. Our variable-temperature system does not allow the rotation of the magnet, so we measured the temperature effects for specific orientations of the crystal. In Figure 2 are shown the spectra at various temperatures for a crystal oriented, at room temperature, with the magnetic field close to the principal *z* axis of one of the two magnetic sites in the crystal. Mössbauer results[7,18] show that the spin crossover occurs mainly between 100 K (10% high spin) and 150 K (90% high spin) with $T_c = 121$ K. The broadening of the EPR resonances in the spin-crossover region that was observed for the powder is also seen in the single crystal but is more selective in that the broadening increases with magnetic field. The high-field sextet broadens the most and almost disappears in the spin-crossover region while hyperfine structure in the lowest sextet, in the region of 0–1000 G, remains visible at all temperatures. This observation effectively rules out the earlier explanation of the broadening because any magnetic dipolar broadening mechanism would broaden all lines in the spectrum in equal fashion. It should be noted that below the transition temperature, the high-field sextet $({}^3/_2 \leftrightarrow {}^5/_2)$ has become a superposition of two sextets and the next highest sextet $({}^1/_2 \leftrightarrow {}^3/_2)$ has become the superposition of at least three sextets with different intensities. The intensity of the less intense sextets relative to the most intense sextet decreases as the temperature decreases. We shall return to this in the Discussion.

In Figure 3 is plotted D_{eff} vs temperature for the two highest sextets. For the $({}^3/_2 \leftrightarrow {}^5/_2)$ sextet, D_{eff} is determined by taking the magnetic field difference between the center of the sextet and the field position of DPPH and dividing by 4. D_{eff} for the $({}^1/_2 \leftrightarrow {}^3/_2)$ sextet is obtained by dividing the field difference by 2. If the magnetic field is really along the principal *z* axis, D_{eff} should be close to *D* in value. At the three lowest temperatures, D_{eff} is also plotted for the low-intensity second sextet for both the $({}^3/_2 \leftrightarrow {}^5/_2)$ and $({}^1/_2 \leftrightarrow {}^3/_2)$ transitions. For those temperatures in which the individual hyperfine components could not be observed, the center was taken to be the point halfway between the positive and negative peaks of the derivative curve. The maximum D_{eff} occurs near T_c. Above the transition temperature, D_{eff} increases with decreasing temperature, similar to the situation found for *D* in the powder measurements. The large decrease in D_{eff} for the main sextets below the spin-crossover transition differs from the powder measurements. Furthermore, D_{eff} is considerably different for the two major high-field sextets unlike the situation above the transition. This difference in D_{eff} for these two sextets is most likely due to a change in the orientation of the *z* principal axis relative to the magnetic field. Such a rotation of the *z* principal axis relative to the magnetic field would also account

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[17] This program is modeled after the program DIP, available from the Illinois NIH regional facility.

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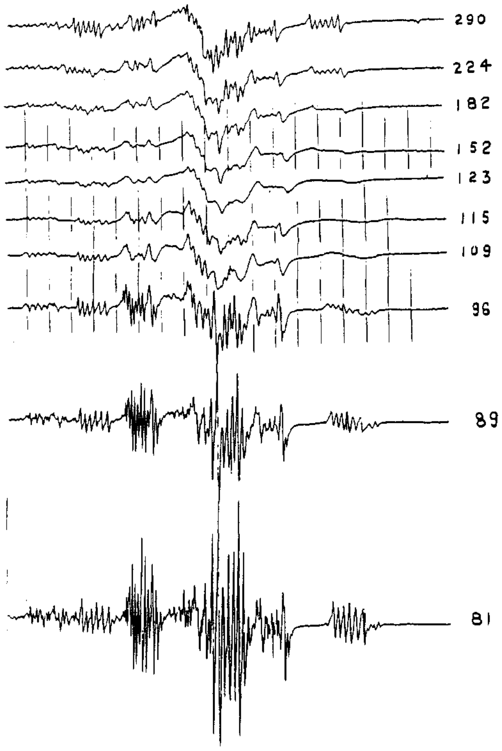

Figure 4. EPR spectra at different temperatures for an orientation of the crystal in which the magnetic field is rotated approximately 10–20° from the *z* principal axis of one of the two magnetic sites.

for the reduction of D_{eff} relative to the value of D found from the powder measurements.

The temperature study was repeated for several orientations slightly off from the *z* principal axis where the sensitivity of the two sextets to the magnetic field orientation was much greater than that found when the magnetic field is aligned with the *z* principal axis. The results of one run are shown in Figure 4. In this run, the separation of the upper sextet into at least two sextets is quite striking as is the relative change in intensity of the two. In particular, note the nearly equal intensity of the two sextets at 96 K in the high-field fine structure line and compare this with the spectrum taken at 81 K.

We have also mounted a crystal in a finger Dewar with the magnetic field aligned nearly parallel with one of the *z* principal axes at room temperature. Liquid N_2 was then added to cool the crystal rapidly to 77 K. After cooling, the sextets were considerably downfield from their room-temperature positions. It took a rotatio of nearly 30° to obtain a maximum zero-field splitting of a magnitude comparable to what the powder measurements of D would predict. This rotation study showed the supper sextet to be split into two resonances of nearly equal intensity.

Discussion

While there is some magnetic broadening of all lines as the temperature is lowered, it is clear that the earlier explanation[7] of the broadening in the spin-crossover transition region cannot be correct. Instead, we must consider some mechanism involving variation of the ZFS parameters (D, E, and the direction of the principal axes associated with them) over various sites from Mn(II). If the sites for the paramagnetic and diamagnetic iron atoms are randomly distributed, we could expect a random distribution of ZFS parameters for the manganese atoms throughout the crystal lattice. This should introduce a broadening of the sort seen in our studies here and the random distribution of environments would give a Gaussian line shape. However, attempts to simulate the broadening of the sextet suggest that the line shape is closer to Lorentzian than Gaussian. Further, the appearance of two or three distinct sextets below the transition whose relative intensities vary with temperature suggest a specific set of ZFS parameters rather than a random distribution. In some temperature runs at certain orientations, we have seen multiple sextets in the high-field sextet at temperatures above the transition temperature T_c as well as below.

The large change in the orientation of the principal *z* axis observed in the low-temperature phase does not mean the iron or manganese complexes have experienced such large rotations. Crystallographic studies,[15] in fact, show a change of 1–2° in the orientation of the ligand planes between the high-spin and low-spin structures. The iron(II), and therefore the Mn(II), ion lies in a site with no point group symmetry, and there is no symmetry requirement for the orientation of the principal axes of the ZFS matrix. The high-spin lattice is a "good" host for the Mn(II) defect as the Fe–N bond lengths should be similar to the Mn–N bond lengths. The Mn(II) complexes should sit in a relatively "relaxed" state, with little added strain energy. The contraction in the unit cell in the low-spin state associated with the shorter Fe–N bond lengths for the low-spin complex should exert forces on the ligands around the Mn(II) ion, causing distortions that show up as a change in the orientation of the principal axes for the ZFS interaction.

The most likely explanation of everything we have observed is one that assumes the transition involves at least three or more domains. For example there could be three domains of the following types: (1) all high spin; (2) half high spin and half low spin; (3) all low spin. Each of these phases would have a particular set of ZFS parameters for the impurity Mn(II), and there would be a gradual change in the quantity of each phase as the temperature changes through the crossover region. It is interesting to note that Meissner et al.[19] have found the transition in $[\mathrm{Fe(2\text{-}pic)_3}]\mathrm{Cl_2{\cdot}C_2H_5OH}$ to be a double transition with two T_c's. There could, of course, be more than three phases, but we see no other way to explain our results but to assume that the Mn(II) ion finds itself in a limited number of distinct lattices during the course of the spin-crossover transition.

Conclusions

The use of Mn(II) EPR as a probe to study the spin crossover in single crystals of $[\mathrm{Fe(II)(2\text{-}pic)_3}]\mathrm{Cl_2{\cdot}C_2H_5OH}$ has provided new information on the nature of the transition. We have interpretated the results as showing that the Mn(II) complex exists in several distinct lattices (domains) in which the ZFS parameters differ both in magnitude and in the orientation of the principal axis relative to the unit cell axes. The intensity of the resonance associated with each domain varies with the temperature. These results along with earlier EPR studies[9,10] from this laboratory demonstrate the unique structural information that can be obtained about the spin-crossover transformation from single-crystal EPR that are not obtainable from the techniques conventionally used to study these systems.

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Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Synthesis of Rhodium-Containing Heterobimetallic Hydride Complexes

Charles P. Casey* and Gregory T. Whiteker

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There has been a great deal of recent interest in the synthesis of heterobimetallic dihydrides[1] in the hope that these compounds

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