A Low Temperature Magnetic Suceptibility Study of the Zero Field Splitting in Seven Coordinate High-Spin Iron(III) Complexes Based on a Pentadentate Macrocyclic Nitrogen Ligand

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Low temperature magnetic susceptibility studies are used to determine the magnitudes of the zero field splittings for powder samples of seven coordinate high spin Iron(III) compounds exhibiting large g factor anisotropy.

Introduction

Zero field splitting can be observed in iron(III) complexes where spin orbit coupling and mixing in of higher lying energy levels leads to partial removal of the ground state degeneracy. The ground term is split into three Kramer's doublets. In such systems where the metal–metal distances are large, slow paramagnetic relaxation can be observed at low temperatures, for negative zero field splitting. This has been observed in a series of seven coordinate high spin iron(III) complexes. These compounds can be written as $[FeBX_2]ClO_4$, where B is the pentadendate macrocycle 2,13-di-methyl-3,6,9,12,18 pentaazabicyclo (12,3,1) - octadeca-1(18),2,12,14,16-pentaene and $X = Cl^-$, Br^-, I^-, NCS^-, and N_3^-. These are prepared by the Schiff base condensation of 2,6 diacetylpyridine and triethylenetetraamine [1]. The total coordination environment of the chloro complex [2] is shown in Fig. 1. The chlorine ligands are normal to the plane, in *trans* axial positions. The symmetry is approximately D_{5h}. The complex crystallizes as monoclinic crystals with $a = 8.91$ Å, $b = 17.96$ Å, $c = 14.37$ Å, $\delta = 92.30°$.

ESR spectra were obtained by Cotton [3] for nitromethane glasses and are characteristic of near axial symmetry. Estimates of D and λ (=E/D) were obtained from the spectra, where D is the axial zero field splitting parameter and λ is a measurement of the degree of axial symmetry. Axial symmetry corresponds to $\lambda = 0$. The ESR values of D and λ are 0.5 and 0.3 for $X = NCS^-$ and 0.3 and 0.13 for $X = Cl^-$, for $X = Br^-$, I^-, $\lambda = 0$ and $D > 1$ cm^{-1}. The numerical sequence of D values, $Cl^- < NCS^- <$

A)

⊖ = Fe
O = N

B)
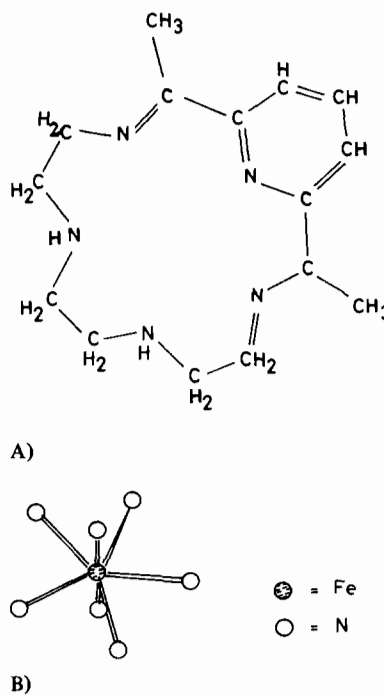
Fig. 1. A) Structure of the macrocyclic ligand, B. B) Prospective drawing of $Fe(N)_5X_2^+$.

Br^-, I^- implies a negative D for the NCS^- complex in accord with the spectrochemical series. This means that for the thiocyanate complex the slowly relaxing $S = 5/2$ Kramer's doublet lies lowest and for the others the rapidly relaxing $S = 1/2$ doublet is lowest. Although not directly calculated, it is obvious from the spectra that $g_{\parallel} = 2$ and $g_{\perp} = 6$.

The Mössbauer spectra of the series were studied by Deeney and Nelson [4]. At room temperature all compounds gave a very broad singlet. The Cl^- remains a singlet to 4.2 K, while the Br^- and I^- formed well resolved doublets with a narrow line width. The NCS^- and N_3^- complexes show progressive hyperfine splitting of doublet spectra at low

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temperatures. These results can be explained on the basis of slow spin-spin relaxation. Spin–spin relaxation is the interaction of two electronic spins, *i.e.* mutual spin flip. If the precession time of the nucleus is shorter than the spin relaxation time, a hyperfine field will be observed. This is because the electronic field perceived by the nucleus induces a magnetic field, giving rise to a Zeeman effect. If the ground Kramer's doublet is significantly separated from the other two only this state will be populated at lowest temperatures and the relaxation process can be observed. When the $S = 5/2$ Kramer's doublet is lowest a hyperfine field or relaxation broadening of the Mössbauer spectra will be observed. If the $S = 1/2$ Kramer's doublet is lowest, the relaxation is rapid and no spectral broadening will be observed. Thus the temperature dependence of the zero field Mössbauer spectra can be used to determine the sign of the zero field splitting. On the basis of the preceding Mössbauer data, D is *positive* for the *halogen complexes* and *negative* for the *pseudohalogen* complexes.

Powder magnetic susceptibility measurements are normally used to determine only the absolute value of the zero field splitting. When single crystals are also available for study, the sign of D can also be determined via measurement of the principle susceptibilities [5]. The theoretical variation in moment with temperature for single crystals aligned parallel and perpendicular to the magnetic field is shown in reference 5. When D is positive, $\mu_\perp > \mu_\parallel$ and $\mu_\perp$ rises to a maximum of ~6 μ_β before decreasing to ~4 μ_β. In D negative systems, $\mu_\parallel > \mu_\perp$ and $\mu_\parallel$ rises to ~8 μ_β before decreasing to 5 μ_β. These results are calculated for $|D| \sim 1$ cm^{-1} and essentially axial symmetry.

Recent studies in this laboratory [6] of $(\phi_4 As)_2$-Fe(N$_3$)$_5$ indicate that 'single crystal like' behavior can sometimes be observed in *polycrystalline* ferric systems with near axial symmetry. The anion of this salt contains a trigonal bipyramidal arrangement of five azides around high spin iron(III). The temperature dependence of the magnetic moment of a powder sample rises to ~7.4 μ_β at 5 K before decreasing to ~6 μ_β at 1.6 K, close to that predicted for a single crystal with $\mu_\parallel > \mu_\perp$ and $D \sim -2$ cm^{-1}. The temperature dependence of the zero field Mössbauer spectra clearly indicate D negative. This foregoing moment behavior was observed using the Faraday method for uncompressed samples whose microcrystallites were free to orient in the applied field. Redetermination of the moment-temperature dependence for similar applied fields (~5 kG) using a vibrating sample magnetometer and compressed samples resulted in the observance of the expected typical polycrystalline or powder ferric behavior, *i.e.* a steady decrease in moment to a limiting value of $\sqrt{19}$, *i.e.* no maxima.

We have measured the temperature dependence of the magnetic susceptibility for the macrocyclic iodide (D > 0) and thiocyanate (D < 0) complexes to see if 'single crystal like' magnetic behavior and orientation effects are readily observed for ostensibly polycrystalline samples of other ferric systems exhibiting large axial g factor anisotropy. The g values for these systems are close to $g_\parallel = 2$ and $g_\perp = 6$. Our results are now presented in this note.

Experimental

All complexes were prepared by the literature methods [1].

Preparation of Hydroxy-(2,13-dimethyl-3,6,9,12,18-pentaazabicyclo (12,3,1) - octadeca - 1(18),2,12,14-pentaene)iron(III) Perchlorate, Fe$_2$B$_2$O(ClO$_4$)$_2$·H$_2$O

Finely ground 2,6-diacetylpyridine (0.005 mol) was added to a filtered solution of 0.005 mol ferrous chloride hydrate in 150 ml water. To this pale yellow slurry, 0.02 mol triethylenetetraamine was added dropwise, immediately followed by four drops concentrated hydrochloric acid. This deep purple mixture was filtered into 0.1 mol KClO$_4$·H$_2$O. Air flow was initiated and an orange precipitate immediately formed. After 36 hours, the solution was filtered and washed with ethanol. The product was recrystallized from 1:1 v:v ethanol/water solution by heating to 45 °C and cooling. The white precipitate of KClO$_4$ was filtered off and the mother liquor was evaporated to dryness to yield an orange solid.

Preparation of FeBX$_2$·ClO$_4$ where X = I$^-$, NCS$^-$

The iodide and thiocyanate complexes were prepared by cleaving the dimer prepared above. A warm 0.01 molar solution of Fe$_2$B$_2$O·ClO$_4$ in water was filtered into a warm solution of 0.01 molar NaX in water. The product precipitated immediately as needle like crystals. The solid was filtered, washed with water and dried in vacuo.

Physical Measurements [10]

Variable temperature magnetic susceptibility measurements were made at Northeastern University on a Faraday balance composed of a Cahn RG electrobalance, a Varian Model 4000 electromagnet with 4-in. constant-force pole caps and a Janis Super Vari-Temp cryostat over the range 1.5–300 K for ten fields between 1.6 and 5.1 kG. Temperature measurement and control were typically of the order ±0.01 K or better and were achieved using a Leeds-Northrup K-5 potentiometer and a Lake Shore Cryotronics Model DT-500C set point controller, respectively, in conjunction with a calibrated silicon temperature sensor diode, a 10-μA constant current source and an uncalibrated gallium arsenide control

diode. Temperatures below 4.2 K were measured via the vapor pressure of helium using Wallace–Tiernan Models FA-160 and 61-050 absolute pressure gauges while pumping was precisely controlled with an L.J. Engineering Model 329 vacuum regulator valve. Temperatures below 78 K, to as low as 50 K, were also achieved using liquid nitrogen by pumping (Welch 1397) to well below the tripe point of nitrogen. Both the vapor pressure of nitrogen and a calibrated silicon diode were used to monitor the temperature. An F.W. Bell Model 610 gaussmeter with a transverse Hall probe was used for measurement of magnetic fields. The balance was calibrated with $HgCo(NCS)_4$ [11].

Mössbauer spectra were obtained on a conventional constant-acceleration spectrometer operated in the time mode using a γ-ray source of 100-mCi ^{57}Co in a rhodium metal matrix. Temperature control was achieved using an uncalibrated silicon diode coupled to a Lake Shore Cryotronics Model DT-500C set point controller. Temperature measurements were made with a Leeds–Northrup K-4 potentiometer or a 6-place Dana Model 5330 digital voltmeter using a calibrated silicon diode driven by a 10-μA constant current source. The temperature stability was continuously monitored by following the error signal of a silicon diode (~50 mV/K) after precise compensation via the K-4 potentiometer and was typically of the order ±0.005 K. Temperatures less than 4.2 K were obtained through controlled pumping on the Janis cryostat diffuser assembly. Least-squares Lorentzian fits to Mössbauer spectra were accomplished using the program of Stone [12].

Results

The magnetic susceptibility, reciprocal susceptibility, and magnetic moment for the two complexes are shown in Fig. 2 and 3, and Table I. Table II lists the effective moment, paramagnetic Curie temperature, θ, and Curie constant as determined from a least squares fit of χ_M^{-1} *vs.* T. The susceptibility is unremarkable and clearly shows both systems to be simple paramagnets, exhibiting 'normal' powder behavior consistent with high spin iron(III). The small, negative theta values indicate that no significant interionic exchange is occurring, as expected from the large metal separation. Below 7 K there is a rapid drop in moment for both complexes, to 4.31 μ_β for the iodide and 3.67 μ_β for the thiocyanate. No maximum was observed in either complex, eliminating the possibility of elucidating the sign of the D value from powder data. Obviously, many factors influence the observance of 'single crystal like' behavior in powder samples aside from large axial g factor anisotropy. These are primarily physical factors, that is sample texturing, packing, and grain
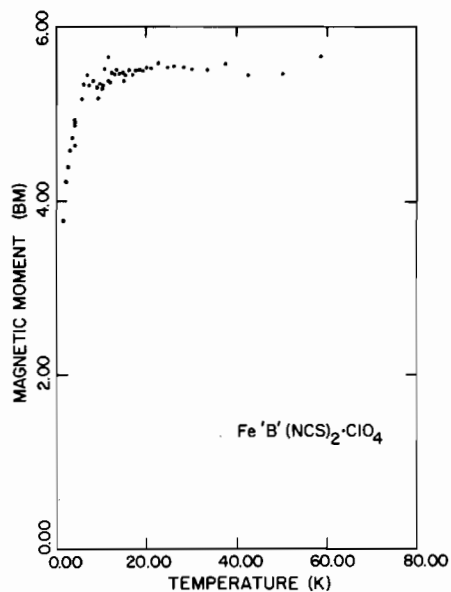

Fig. 2. Magnetic moment *versus* temperature for Fe'B'-$(NCS)_2 \cdot ClO_4$.
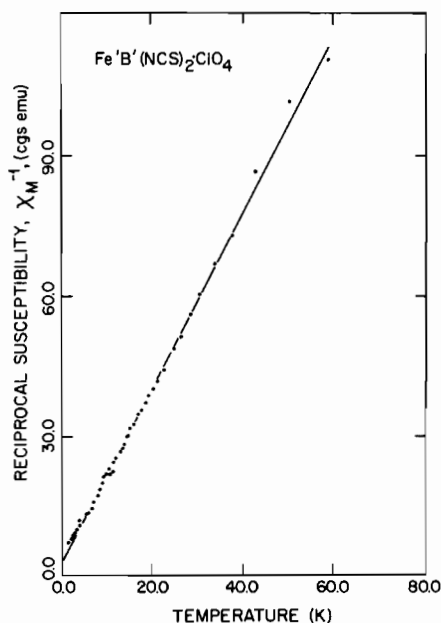

Fig. 3. Reciprocal susceptibility *versus* temperature for Fe'B'$(NCS)_2 \cdot ClO_4$.

size. Even though the hoped for 'single crystal like' behavior was not observed, the *absolute magnitude* of the zero field splitting parameter can be determined from the susceptibility behavior.

The magnitude of the splitting was determined using the theoretical expression derived by Kotani [7]. This equation is derived form the Zeeman splitting of the energy levels using the spin Hamiltonian

TABLE I. Sample Magnetic Moments for $FeBX_2ClO_4$.

Temperature (K)	Moment for Fe'B'(NCS)$_2$ClO$_4$ $\mu\beta$	Moment for Fe'B'I$_2$ClO$_4$ $\mu\beta$
1.70	3.77	4.30
2.2	4.22	4.68
2.7	4.44	4.69
3.2	4.58	5.20
4.2	4.89	5.37
6.5	5.32	5.96
7.6	5.32	5.88
8.9	5.35	6.03
10.5	5.32	6.17
11.8	5.64	6.13
12.8	5.44	6.26
13.8	5.49	6.04
14.8	5.46	5.75
15.4	5.42	6.19
16.2	5.48	6.36
18.8	5.51	6.31
20.6	5.53	6.52
22.8	5.57	6.41
24.2	5.53	6.35
25.9	5.55	6.35
27.9	5.52	6.33
30.7	5.50	6.22
33.2	5.50	6.30
35.7		5.92
27.7	5.56	
44.4		6.22
50.5	5.46	6.15

$$H = DS_z^2 - 2\beta SH \tag{1}$$

This Hamiltonian assumes no mixing in of higher lying energy states.

The magnetic moment is found from $\delta E/\delta H$, yielding the following equations
for $H_{\parallel z}$:

$$\mu_{eff}^2 = \frac{3}{1 + e^{-2x} + e^{-6x}} \left[1 + 9e^{-2x} + 25e^{-6x}\right] \tag{2}$$

for $H_{\perp z}$:

$$\mu_{eff}^2 = \frac{3}{1 + e^{-2x} + e^{-6x}} \left[9 + \frac{8}{x} - \frac{11}{x} - \frac{15}{2x} e^{-6x}\right] \tag{3}$$

Taking a weighted average for random orientation (powder samples)

$$\mu_{eff}^2 = \frac{1}{1 + e^{-2x} + e^{-6x}} \left[19 + \frac{16}{x} + \left(9 - \frac{11}{x}\right) e^{-2x} - \left(25 - \frac{15}{x}\right) e^{-6x}\right] \tag{4}$$

where $X = D/kT$.

These equations predict a high temperature moment of 5.92 μ_β. As $T \to 0$, the *average (powder) moment* falls to 4.36 μ_β, for $H_{\parallel z}$, $\mu = \sqrt{3}\mu_\beta$ and for $H_{\perp z}$, $\mu = 3\sqrt{3}\mu_\beta$. Least squares fits of the present susceptibility data using equation (4) are shown in Figs. 2 and 5. Best fits were obtained for D = 7.98 cm^{-1} for the NCS$^-$ and 10.3 cm^{-1} for the iodide.

These values are considerably different from the D values determined from the ESR data. Cotton did not obtain fits of his ESR data to determine D, but only estimated the magnitude from the spectra. However, for ferric hemin and related compounds,
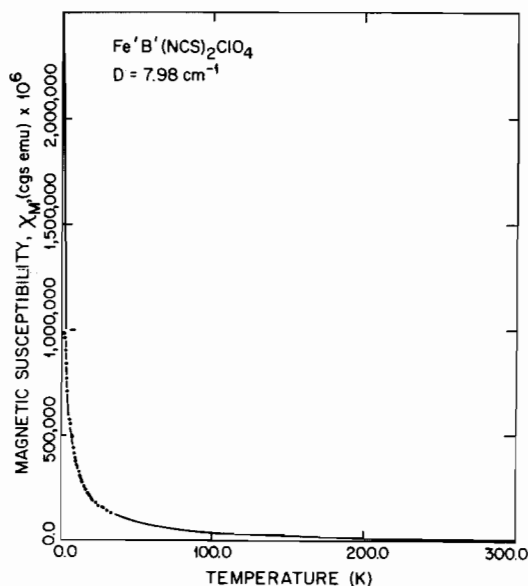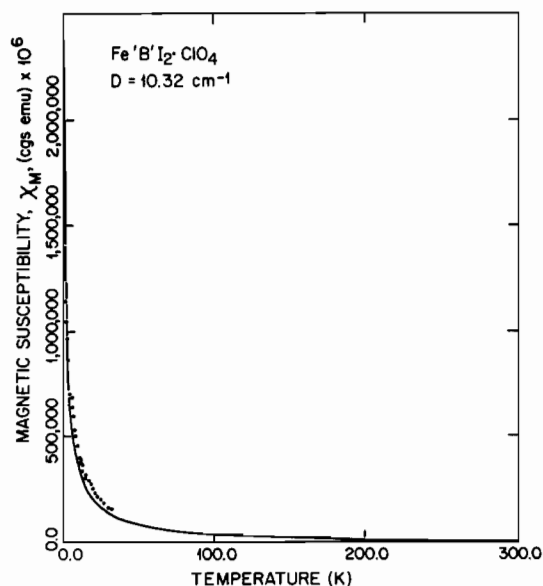

Fig. 4. Magnetic susceptibility *versus* temperature for Fe'B'-(NCS)$_2$·ClO$_4$. The solid line represents the best fit for the zero field splitting parameter as determined from equation 4.

TABLE II. Magnetic Parameters for $FeBX_2ClO_4$.

Compound	Temp. range (K)	μ_{eff} ($\mu\beta$)	θ (K)	C (emu/mol)	Moment at lowest temp.
FeB(NCS)$_2$ClO$_4$	50–1.6	5.69	−0.237	3.718	3.670
FeBI$_2$ClO$_4$	50–1.6	6.31	−0.843	4.905	4.315

Fig. 5. Magnetic susceptibility *versus* temperature for Fe'B'-I$_2$·ClO$_4$. The solid line represents the best fit for the zero field splitting parameter as determined from equation 4.
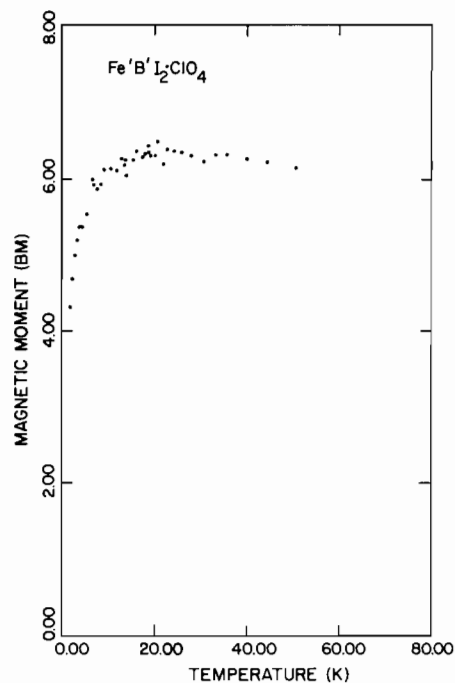

Fig. 6. Magnetic moment *versus* temperature for Fe'B'I$_2$·ClO$_4$.

the values determined by Maricondi and Straub [8] from thermo-magnetic measurements using Kotani's theory range from 4.9 to 12.0 cm^{-1}. These values are in better agreement with our data. *The temperature moment variation of the latter systems is very similar to that observed here* for seven coordinate ferric systems. Later, more refined theoretical treatments of susceptibility data for (tetraphenylporphyrinato)iron(III) chloride [9] did not significantly change the absolute D values. It should be expected that the D values are in a range consistent with the hemins due to the similar coordination environment. We are led to the conclusion that the D values quoted in the ESR study [3] of the present seven coordinate systems are seriously underestimated.

Acknowledgments

References

1 J. D. Curry and D. H. Bush, *J. Am. Chem. Soc., 86*, 592 (1964).
2 E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc., 89*, 720 (1967).
3 S. A. Cotton, *Chem. Phys. Lett., 41*, 606 (1976).
4 F. A. Deeney and S. M. Nelson, *J. Phys. Chem. Solids, 34*, 277 (1973).
5 M. Gerloch, J. Lewis and R. C. Slade, *J. Chem. Soc. A*, 1422 (1969).
6 W. M. Reiff, H. Wong, M. Tuiroc and G. Eisman, *J. de Physique Colloque, C2, 40*, C2–234 (1979).
7 M. Kotani, *Prog. Theor. Phys. Suppl., 17*, 4 (1961).
8 C. Maricondi, W. Swift and D. K. Straub, *J. Am. Chem. Soc., 91*, 5205 (1969).
9 D. V. Behere and S. Mitra, *Inorg. Chem., 18*, 1723 (1969).
10 C. Cheng and W. M. Reiff, *Inorg. Chem., 16*, 2097 (1977).
11 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
12 G. M. Bancrof, A. G. Maddock, W. K. Ong, R. H. Prince and A. J. Stone, *J. Chem. Soc., A*, 1966 (1967).