Inorg. Chem. **1983**, *22*, 3514–3519

Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115,
and Department of Physics, Clark University, Worcester, Massachusetts 01610

Antiferromagnetic Magnetic Ordering of Complex Ferric Salts: A Mössbauer Spectroscopy and Magnetic Susceptibility Characterization of the Hexachloroferrate Complex $Co(pn)_3FeCl_6$ (pn = 1,2-Propanediamine)

ANN NANCY SCOVILLE, KÁROLY LÁZÁR,[†] WILLIAM MICHAEL REIFF,[*] and CHRISTOPHER LANDEE

Received November 24, 1982

Zero- and high-field Mössbauer spectroscopy, vibrating-sample magnetometry, and Faraday balance measurements have been used to characterize polycrystalline samples of the complex bimetallic salt $[Co(pn)_3][FeCl_6]$. The material orders as a simple, uniaxial three-dimensional antiferromagnet at T(Néel) = ~9 K. The saturation value of its internal hyperfine field is 505 kG. Magnetization measurements for applied fields up to ~14 kG in the range 1.8–4.2 K show an absence of field-induced (spin-flop) behavior. However, high-field Mössbauer spectroscopy measurements at 4.2 K for longitudinal fields of 3 and 6 T are consistent with a field-induced magnetic phase transformation (spin flop) for $H_0 > 14$ kG. Zero-field Mössbauer spectra show that the related system $[Co(NH_3)_6][FeCl_6]$ is a rapidly relaxing paramagnet to as low as 1.6 K.

Introduction

Low-temperature antiferromagnetic ordering has been observed in previous studies of the aquopentachloroferrate salts $M_2(FeCl_5{\cdot}H_2O)$, M = K, NH_4^+, via heat capacity and magnetic susceptibility.[1,2] Mössbauer spectroscopy[3] of these compounds performed in this laboratory also indicates antiferromagnetic transitions, occurring at 15 K in the potassium salt. The hyperfine field at 4.2 K for $K_2(FeCl_5{\cdot}H_2O)$ is 490 kG. The structures of the Rb^+ and Cs^+ isomorphs have been reported,[4] and the iron is octahedrally coordinated by five chloride anions and one water molecule. The packing of the crystal is such that several *Cl–Cl contacts are less than 4.0* Å, i.e. near the van der Waals contact radius. *Hydrogen bonding* has been observed through infrared spectral studies, and it is conjectured that these hydrogen bonds bridge discrete $FeCl_5{\cdot}H_2O^{2-}$ polyhedra, forming infinite chains. *Both phenomena* provide pathways for exchange interactions. Further information on the nature of the exchange and the role of close Cl–Cl contacts is obtained in the present investigation of *hexachloroferrate* salts.

The hexachloroferrates were first prepared and characterized by Hatfield[5] in 1963. The complexes were isolated by using counterions of similar size and equal and opposite charge, such as tris(1,2-propanediamine)cobalt(3+), to stabilize the complex anion in the crystal lattice. Some of these species were found to be members of the isomorphous series $[Co(NH_3)][MCl_6]$, M = Sb, In, Bi, and Ti, by comparison of X-ray powder diffraction patterns. The magnetic susceptibility of the foregoing hexachloroferrates was determined at just three temperatures, 295, 196, and 83 K, and was thought to obey Curie law behavior, i.e., the paramagnetic Curie temperature $\Theta = 0$ K. The magnetic moment was found to be 5.86 μ_B, consistent with a high-spin ferric ion with a $^6A_{1g}$ ground term.

The ESR spectra of $[Co(NH_3)_6][FeCl_6]$ diluted in isomorphous diamagnetic hosts were reported by Stout and Garrett.[6] The g factors were determined to be $g_\parallel = 2.0118$ and $g_\perp = 2.0124$ with a small zero-field splitting. The zero-field splitting should be zero in a symmetric undistorted crystal field; presumably the non-zero value is caused by distortion of the guest by the host molecule. The ESR spectra of the aquopentachloroferrate salts have also been studied.[7]

To our knowledge, no detailed studies of the magnetic susceptibility and Mössbauer spectroscopy behavior of *hexachloroferrates* below 78 K have been reported in the literature save for our preliminary report.[3] Our findings of several new examples of low-temperature antiferromagnetic ordering for tetrachloroferrates (e.g. $[2,2'\text{-bpyH}^+][FeCl_4^-]$, $[2,9\text{-}(CH_3)_2\text{-phenH}^+][FeCl_4^-]$)[8] stimulated us to study the available hexachloroferrates at low temperatures.

Experimental Section

The hexachloroferrate complexes were prepared as described by Hatfield et al.[5] Hexaamminecobalt(III) chloride was obtained from Alfa Inorganics. Tris(1,2-propanediamine)cobalt(III) chloride was prepared with use of the available literature methods.[9] Hereafter, 1,2-propanediamine is denoted as pn.

Tris(1,2-propanediamine)cobalt(III) Chloride. Cobalt(II) carbonate (0.03 mol) was dissolved in 13 mL of concentrated hydrochloric acid to form cobalt(II) chloride. One liter of ethanol was added and the solution refluxed over 30 min. Next, 1,2-propanediamine (0.1 mol) was added dropwise over a 30-min period, followed by the dropwise addition of a saturated solution of chlorine in 200 mL of ethanol. As soon as addition was complete, the hot mixture was filtered. The green product was washed with ethanol and dried in vacuo.

Tris(1,2-propanediamine)cobalt(III) Hexachloroferrate. A filtered solution of 0.1 mol of ferric chloride hexahydrate in 10 mL of hot water was added to 10 mL of a hot 1 M aqueous solution of tris(1,2-propanediamine)cobalt(III) chloride. The resulting orange-brown solution was evaporated to 10 mL and acidified with 3 mL of hydrochloric acid. After the solution stood for several days, orange-yellow crystals formed. These crystals were filtered and recrystallized from water by addition of hydrochloric acid. Anal. Calcd: C, 19.66; H, 5.50; N, 15.28. Found: C, 19.60; H, 5.62; N, 15.07.

Hexaamminecobalt(III) Hexachloroferrate. A filtered solution of ferric chloride hexahydrate (0.005 mol) in 10 mL of hot water was added to a hot solution of 0.0016 mol of hexaamminecobalt(III) chloride in 70 mL of 3.4 N hydrochloric acid. This solution was heated for a few minutes until precipitation of the orange product began. The crystals were filtered, washed with alcohol and ether, and dried in vacuo.

The field and temperature dependence of the magnetic susceptibility and magnetization were determined with use of both the Faraday

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[*] To whom correspondence should be addressed at Northeastern University.

[†] On leave from the Institute of Isotopes, Budapest, Hungary.

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Table I. Mössbauer Parameters[a] for $[Co(pn)_3][FeCl_6]$

temp, K	isomer shift	line widths						H_{1-6}[b]	$\langle H_{3-5}\|H_{2-4}\rangle$[b]	χ^2
		1	2	3	4	5	6			
300	0.407	0.440								664
13.80	0.442	0.504								522
9.94	0.446	0.611								487
9.74	0.436	0.940								583
9.53	0.47	0.813	1.16	0.531	0.538	0.853	1.003	167.5	163.3	487
8.34	0.45	0.865	0.537	0.504	0.467	0.581	0.824	297.9	297.0	495
6.6	0.44	0.584	0.447	0.229	0.365	0.374	0.552	390.4	373.2	476
4.2	0.47	0.408	0.343	0.366	0.449	0.383	0.439	449.6	449.1	413
1.6	0.43	0.336	0.316	0.259	0.246	0.268	0.286	492.9	493.3	433

[a] In mm/s, relative to 6.4 μm thick natural iron foil, unless otherwise indicated. [b] In kG.

method and vibrating-sample magnetometry. Temperature measurement and control were based on calibrated silicon and/or gallium arsenide diodes. Magnetic field measurements were made with a calibrated Hall effect probe. The complete details of temperature calibration and control for the zero-field Mössbauer spectroscopy system are described elsewhere.[10] For the latter, the drive transducer geometry was *horizontal* with the source always at ambient temperature.

High-field Mössbauer spectroscopy measurements were obtained with a Janis "Super-vari-temp" flow cryostat in conjunction with a niobium–titanium solenoid capable of longitudinally applied fields (H_0 parallel to the γ ray) up to 9.1 T in persistent mode. The Mössbauer spectroscopy drive rod–sample holder assembly was incorporated with the foregoing superconducting magnet cryostat in the *vertical* mode with the γ-ray source and absorber at the same temperature. The zero-field line width for the inner lines of a thin (6.4 μm) natural α-iron foil vs. a fresh 106 mCi ^{57}Co (rhodium matrix) source obtained from Amersham Co. averaged 0.22 ± 0.01 mm/s for the preceding drive geometry. The source is located at the center of a "buck-out" opposing magnetic field so that it experiences a fringing field from the main solenoid of <1 kG at the maximum rated field of 9.1 T, thus eliminating source (line width) broadening effects.

Results

Zero-Field Mössbauer Spectroscopy. The temperature dependence of the Mössbauer spectra of $[Co(pn)_3][FeCl_6]$ was studied to 1.6 K. The results are summarized in Table I and Figure 1. The room-temperature isomer shift and line width are in good agreement with Clausen and Good's previously reported spectra[11] and are consistent with six-coordinate, high-spin iron(III). The coordination number of iron(III) is clearly indicated by the isomer shift: for octahedral coordination δ = 0.4–0.6 mm/s, and for tetrahedral coordination δ = 0.2–0.3 mm/s. The line widths are consistent with a single absorption; i.e., no unresolved quadrupole doublet or relaxation broadening is indicated. The absence of quadrupole splitting at the $FeCl_6^{3-}$ sites is considered further in a subsequent discussion of the hyperfine split spectra. Below ~9.8 K the Mössbauer spectra begin to broaden and Zeeman split. We believe that this magnetic hyperfine splitting clearly occurs over too small a temperature interval to be the result of slow paramagnetic relaxation due to negative zero-field splitting, in other words $D < 0$ leading to a slowly relaxing ground $m_s = \pm{}^5/_2$ ground Kramers doublet. Rather, it is the result of magnetic ordering, as discussed subsequently in the magnetic susceptibility section.

Very small quadrupole splittings, if present, can be potentially better observed in the highly resolved, narrow line width hyperfine split spectra at lowest temperatures, where the internal hyperfine field is approaching its saturation value. In the absence of a quadrupole splitting effect the hyperfine field is determined by the eigenvalues

$$E = g\mu_N H M_I \qquad (1)$$

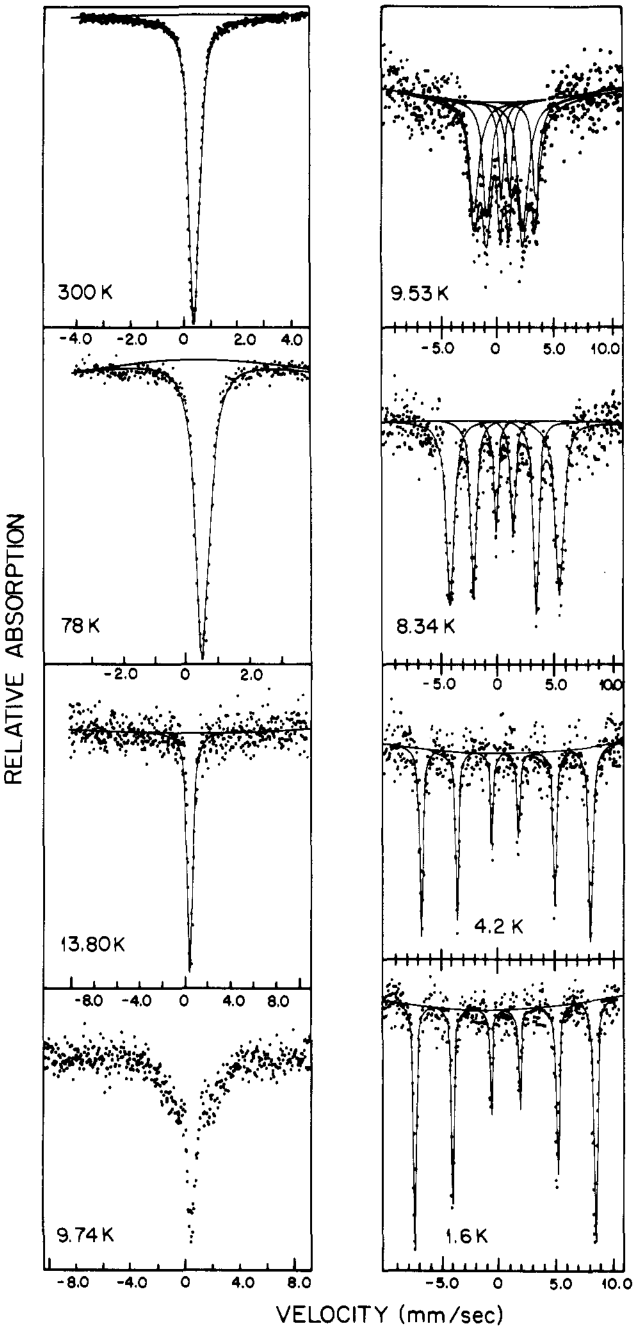

Figure 1. Zero-field Mössbauer spectra for $[Co(pn)_3][FeCl_6]$ at 300, 78, 13.80, 9.74, 9.53, 8.34, 4.2, and 1.6 K.

i.e., only nuclear Zeeman splitting. This gives rise to a six-(symmetrically spaced) transition spectrum for which the internal field (H_n) is simply calculated directly from the separation Δ_{1-6}. The quadrupole interaction (ΔE_Q) is treated as

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(10) Reiff, W. M.; Cheng, C. *Inorg. Chem.* **1977**, *16*, 2097.
(11) Clausen, C. A.; Good, M. L. *Inorg. Chem.* **1970**, *9*, 220.

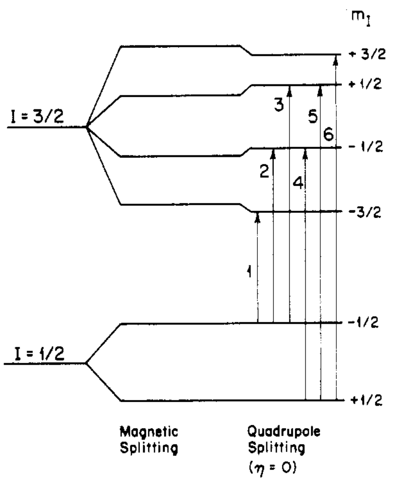

Figure 2. Energy level diagram for iron-57 under the combined effect of an internal hyperfine field (H_n) and an axially symmetric electric quadrupole coupling constant e^2QV_{zz} such that $H_n >> e^2QV_{zz}$. The asymmetry parameter, η, equal to zero corresponds to axial symmetry.

a perturbation to the magnetic interaction for the case $H_n >> \Delta E_Q$. For axially symmetric systems, the resulting eigenvalues are

$$E = -g\mu_N HM_I + (-1)^{|M_I|}\frac{1}{2}\,\frac{e^2qQ}{4}\left(\frac{3\cos^2\theta - 1}{2}\right) \quad (2)$$

where θ is the angle between the principal component of the electric field gradient tensor and the internal hyperfine field and the other variables have their usual significance. This perturbation results in a shift of the inner four transitions of the spectra such that the separation between transitions 1 and 2 and 5 and 6 will be unequal, save for the special case of $\cos^{-1}\theta = 1/3^{1/2}$. Very small quadrupole splittings can then be *detected* by comparing the value of H_n calculated from Δ_{2-4} or Δ_{3-5} to those obtained from Δ_{1-6}. The pairs 2 and 4 and 3 and 5 are due to transitions from the $I = {}^1/_2$ ground state terminating in the *same* m_I sublevel of the $I = {}^3/_2$ excited state as shown in Figure 2. Since there is no quadrupole splitting for the ground state, the foregoing *separations* lead to accurate values of the ground-state Zeeman splitting and hence H_n. The hyperfine fields are calculated from $\langle\Delta_{2-4}$ and $\Delta_{3-5}\rangle/(0.1188$ mm/(s/T)) and $(\Delta_{1-6}/10.63) \times 330$ kG, respectively, where all Δ's are in mm/s. Since values so calculated generally agree quite well, zero quadrupole splitting is indicated and the $FeCl_6^{3-}$ anions lie in sites of essentially octahedral (O_h) symmetry (see Table I).

The magnitude of the internal field is the sum of several contributions

$$H_n = H_F + H_D + H_L \quad (3)$$

where H_F is the Fermi contact term related to unpaired s-electron density at the nucleus, H_D is the dipolar field, and H_L is the orbital moment field. For high-spin iron(III) there is little or no orbital moment, and for spherically symmetric systems there is no dipolar moment. Thus, the hyperfine field for the present case is essentially determined by the Fermi contact interaction. The Fermi term is strongly affected by changes in the degree of iron–ligand covalent bonding. The magnitude of the hyperfine field decreases with increasing covalent bonding, since the spin density at the nucleus is reduced when the iron electrons are delocalized to the ligands. The hyperfine field for anhydrous $FeCl_3$ has been reported between 458 and 478 kG.[12] $FeCl_3$ contains hexacoordinated iron in a highly *covalent continuous macroscopic structure.* In contrast, for $[Co(pn)_3][FeCl_6]$, where the iron is in an isolated ionic environment, the limiting hyperfine field found is 505 kG, determined from a plot of H_n vs. temperature as shown in Figure 3. This is a considerably higher value than for $FeCl_3$ and is due to the difference in iron–chlorine ligation. Considerably less covalency is indicated for the discrete $FeCl_6^{3-}$ clusters as compared to that for the chloro-bridged network structure of ferric chloride. The theoretical value of H_F for high-spin iron(III) with *no covalency reduction* is 550 kG, i.e. 110 kG/unpaired electron.

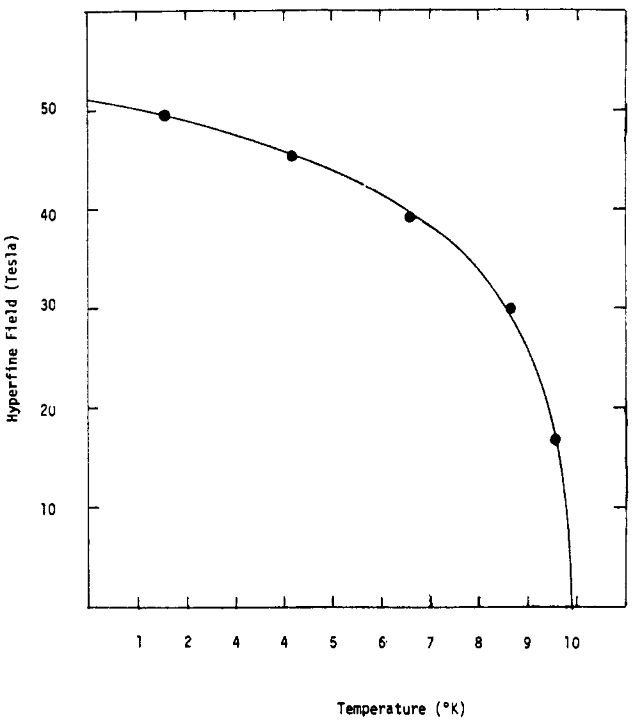

Figure 3. Plot of H_n vs. temperature showing the decrease of H_n to zero at T(Nêel) = 9.9 ± 0.1 K.

In Figure 3, it is seen that $H_n \rightarrow 0$ at ~9.5 K, suggesting a cooperative three-dimensional magnetic ordering transition at this temperature. To confirm that the observed hyperfine splitting does in fact arise from cooperative magnetic ordering as opposed to slow single-ion paramagnetic relaxation, the temperature dependence of the magnetic susceptibility was studied.

Magnetic Susceptibility. The temperature dependence of the magnetic susceptibility was determined by the Faraday method (0–5.1 kG) and vibrating-sample magnetometry (0–14 kG). Additional field dependence of magnetization measurements were also made via the vibrating-sample method. We now summarize the Faraday measurements and then discuss the magnetometry results in greater detail.

Faraday Measurements. The room-temperature moment for $[Co(pn)_3][FeCl_6]$ is 5.73 μ_B, in reasonable agreement with Hatfield's result. The results of a least-squares computer fit of $\chi_M'^{-1}$ vs. T for 56 temperatures and 10 fields show that the material follows a Curie–Weiss law with $\mu_{eff} = 5.90\ \mu_B$, C = 4.36 emu/mol, and a paramagnetic Curie temperature Θ = −15.9 K. Hatfield reports Θ = 0 K. However, his earlier estimate can be expected to reflect some higher degree of uncertainty since the fit was obtained only over three temperatures. The relatively large, negative Θ value found here is indicative of antiferromagnetic exchange. The maximum in the susceptibility at ~9.4 K corresponds very closely to the onset of the hyperfine splitting observed in the Mössbauer spectra (fully resolved splitting between 9.74 and 9.53 K) and clearly confirms cooperative antiferromagnetic ordering as opposed to slow paramagnetic relaxation as the origin of the

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[12] Edwards, P. R.; Johnson, C. E. *J. Chem. Phys.* **1968**, *49*, 211.

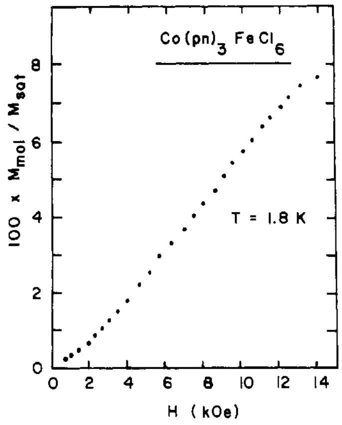

Figure 4. Magnetization vs. applied field (T = 1.8 K).

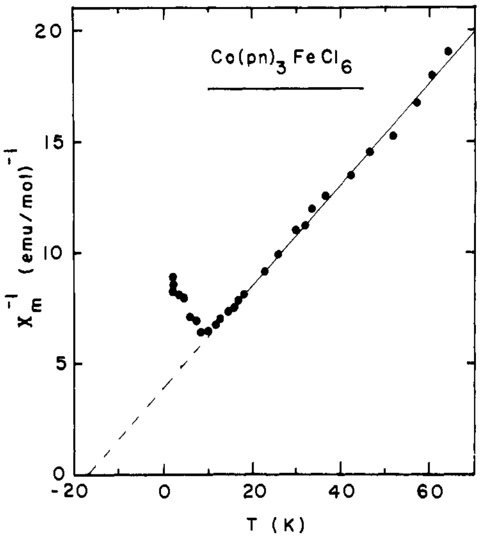

Figure 5. Reciprocal molar susceptibility vs. temperature for H_0 = 1.7 kG.

magnetic hyperfine splitting of Mössbauer spectra. The magnetic moment of $Co(pn)_3FeCl_6$ decreases over the entire temperature range to a value of 1.5 μ_B at 1.6 K. This and the relatively high Néel temperature indicate surprisingly strong antiferromagnetic exchange.

Vibrating-Sample Magnetometer (VSM) Measurements. The magnetization of a powder sample of $[Co(pn)_3][FeCl_6]$ was measured as a function of field at 1.8 and 4.2 K. The sample was cooled to the experiment temperatures from above the ordering temperature while in zero field. The molar magnetization data collected at 1.8 K are plotted as M_{molar}/M_{sat} vs. applied field (H) in Figure 4. M_{sat} is the saturation magnetization $Ng\mu_BS$, which equals 2.78 × 10^4 emu/mol for 1 mol of $S = {}^5/_2$ ions with g = 2.00. The magnetization increases linearly with field for several kilogauss and then increases more rapidly until a field near 9 kG, where an inflection point is found. The data collected at 4.2 K are similar. No hysteresis was observed at either temperature. There is no indication of a field-induced phase transition (spin flop or metamagnetic). The early occurrence of the inflection point found in the M vs. H curve is surprising since the magnetization has only reached 5% of its saturation value at the inflection point, a much lower value than is normally observed.

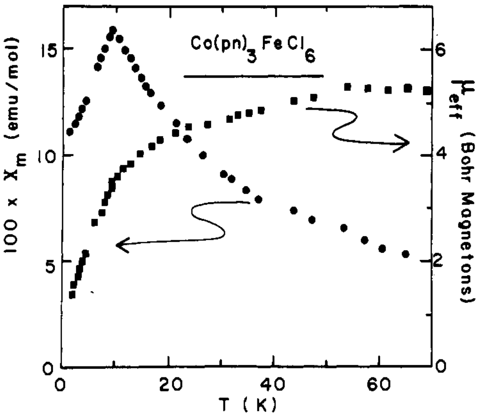

Figure 6. Temperature dependence of the molar susceptibility and magnetic moment, H_0 = 1.7 kG.

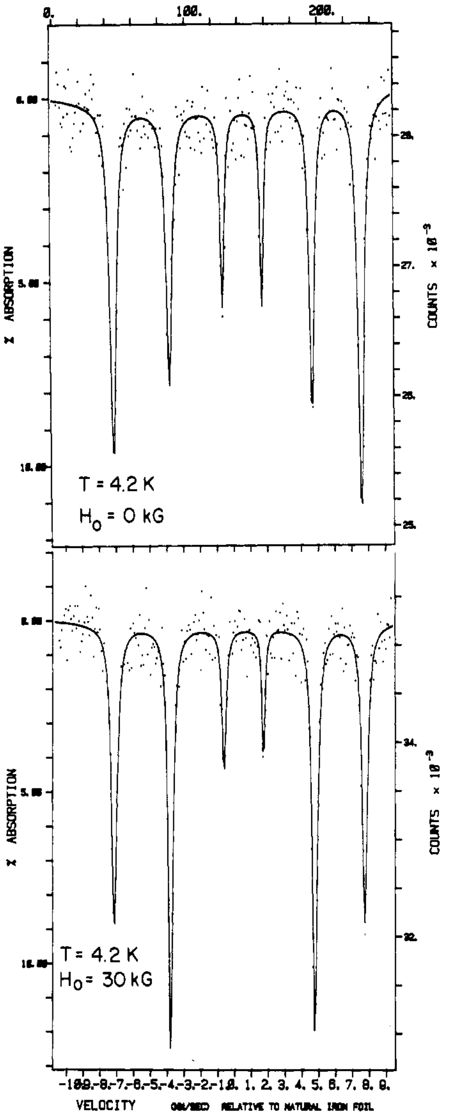

Figure 7. Mössbauer spectrum of $[Co(pn)_3][FeCl_6]$ at 4.2 K in a longitudinal magnetic field of (top) H_0 = 0 and (bottom) H_0 = 30 kG.

The molar susceptibility, χ_m, of the $[Co(pn)_3][FeCl_6]$ compound was determined from moment vs. temperature data collected between 1.8 and 70 K in small applied fields. The data, plotted as $\chi_m'^{-1}$ vs. T and χ_m vs. T are shown in Figures 5 and 6, respectively. The correction for diamagnetism and temperature-independent paramagnetism is always less 0.2% of χ_m and has been neglected. The reciprocal susceptibility data between 14 and 70 K (Figure 5) has been fit to a Curie–Weiss curve with parameters of C = 4.38 emu/mol and Θ = −16.5 K, corresponding to antiferromagnetic interactions. These parameters are in good agreement with those derived from the Faraday balance data. The effective moment, in units

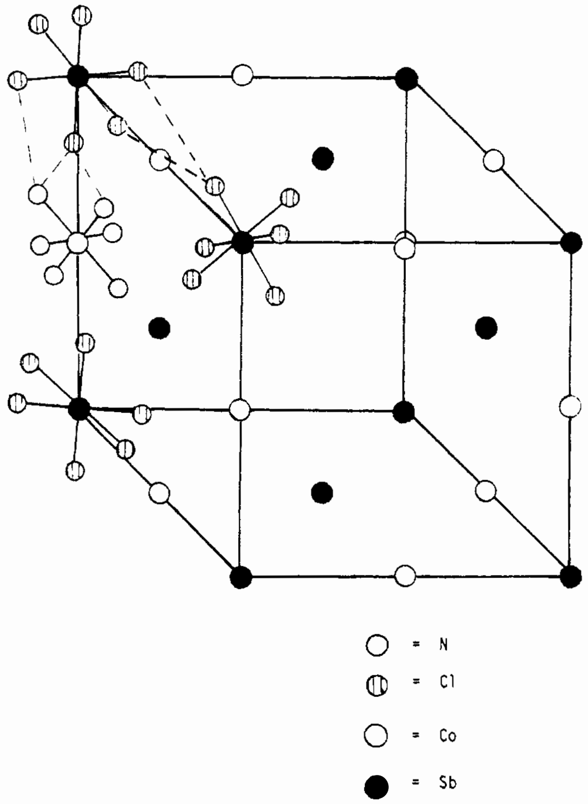

Figure 8. Partial packing diagram schematic based on ref 14.

of Bohr magnetons, is also plotted vs. temperature in Figure 6. As was also seen in the Faraday susceptibility set, the effective moment is reduced below the spin-only value of 5.92 μ_B by antiferromagnetic interactions. The moment is less than 5.3 μ_B at 60 K and drops off rapidly with temperature. The susceptibility peaks at 0.158 emu/mol near 9 K (Figure 6) and decreases rapidly on either side. Extrapolating the low-temperature data to 0 K predicts a value of 0.11 emu/mol, nearly the value of $2[\chi_m(\text{peak})]/3$ expected for a slightly uniaxial 3-D antiferromagnet. There is no local maxima of χ_m at higher temperatures which would indicate the presence of significant lower dimensional interactions. The conclusion that this compound is essentially a three-dimensional system is supported by a single Curie–Weiss law curve which accurately describes the χ_m^{-1} data to within $1.5T\chi_{max}$: the extensive short-range order present in low-dimensional systems causes large deviations from Curie–Weiss behavior at much higher relative temperatures. The susceptibility data is then characteristic of a 3-D antiferromagnetic material whose ordering temperatures are normally several percent less than the temperature for which the susceptibility is maximum. For [Co(pn)$_3$][FeCl$_6$], the Nêel temperature is then 9.0 (3) K, slightly below the value obtained from the Mössbauer spectra.

High-Field Mössbauer Spectra. High-field Mössbauer spectra of polycrystalline [Co(pn)$_3$][FeCl$_6$] were determined over the range of 0–60 kG at 4.2 K. Spectra at 0 and 30 kG are shown in Figure 8. The spectrum at 60 kG is essentially unchanged from that shown for 30 kG in the figure. The angular components of the transition probabilities for a nuclear magnetic dipole (Zeeman splitting) interaction for the case of the $I = {}^1/_2 \rightarrow I = {}^3/_2$ transition of iron-57 are as follows: ${}^9/_4(1 + \cos^2\theta)$ for $\Delta M_I = \pm 1$ transitions 1 and 6, ${}^3/_4(1 + \cos^2\theta)$ for $\Delta M_I = \pm 1$ transitions 3 and 4, and $3 \sin^2\theta$ for $\Delta M_I = 0$ transitions 2 and 5, where θ is the angle between the internal hyperfine field (H_n) and the direction of propagation of the γ ray. The transitions 1–6 are in order of increasing Doppler velocity. Recall that our external field is longitudinal, and thus the γ ray and H_0 are collinear and essentially perpendicular to a best average plane for a typical powder sample. The $\Delta M_I = \pm 2$ transitions are normally forbidden except for the special case of non-axially symmetric ($\eta \neq 0$) quadrupole interaction (ΔE_Q) combined with nuclear Zeeman splitting such that $\Delta E_Q < H_n$. *In zero field* the powder average of the foregoing angular components for an isotropic polycrystalline (thin) absorber is 3:2:1:1:2:3. The computer fit of our zero-field spectrum results in a set of intensities very close to the foregoing values.

For a random, polycrystalline powder form of a uniaxial antiferromagnet, one expects little if any effect from an applied field (H_0) on its Mössbauer spectrum. That is, an approximate 3:2:1:1:2:3 intensity pattern is maintained and the average effective Zeeman splitting (H_{eff}) is unchanged, where $H_{eff} = H_0 + H_n$. This is the case provided H_0 is less than H_{sf}, the so-called spin-flop field at which a first-order phase transformation corresponding to the flopping of the spins to a direction normal to H_0 occurs. Note that for a single-crystal form of a uniaxial (collinear Nêel) antiferromagnet in a longitudinal field such that $H_0 < H_{sf}$ applied along the easy axis, the $\Delta M_I = 0$ transitions have zero intensity; i.e., a 3:0:1:1:0:3 pattern is observed. In addition, the highest and lowest velocity transitions of the spectrum are normally observed to be split into symmetric doublets corresponding to the addition of H_0 to one of the antiferromagnetic sublattices and subtraction of H_0 from the other. For $H_0 \geq H_{sf}$, the foregoing splitting vanishes and the intensity pattern changes to 3:4:1:1:4:3 in accord with the angular components of the selection rules for $\theta = 90°$. The fact that the intensity pattern that we observe for the powder at $H_0 = 30$ kG is close to 3:4:1:1:4:3 strongly suggests that the sample microcrystals are polarized by the applied field and that essentially all of the spins have in fact "flopped" when H_0 has reached 30 kG. The preferential orientation perpendicular to H_0 is expected from the fact that, for a uniaxial antiferromagnet at $T < T_N$, $\chi_\perp > \chi_\parallel$. For comparison, a similar spin-flop transition is observed[13] at $H_0 \approx 27$ kG for FePO$_4$ ($T_N = 25$ K). This value of H_{sf} comes from detailed analysis of the intensity variation of the Mössbauer spectra of a polycrystalline sample in longitudinal fields. As mentioned previously, there is no evidence of spin-flop behavior in the field dependence of the magnetization up to $H_0 \approx 14$ kG. Thus, we conclude that *the* spin-flop field is somewhere between ~14 and 30 kG and that a "sharp" spin-flop transition should be observed in this field range for an appropriately oriented single-crystal sample. This is the subject of further study in our laboratory.

Discussion

It is interesting that antiferromagnetic ordering of [Co(pn)$_3$][FeCl$_6$] occurs at about the same temperature as for the aquopentachloroferrate salt K$_2$FeCl$_5$·H$_2$O. In the latter complex, hydrogen bonding is apparently an important component in the exchange pathway.[1] Antiferromagnetic ordering transitions involving exchange *solely* through very close Cl–Cl contacts are seen in tetrachloroferrates such as AgFeCl$_4$ and TlFeCl$_4$ whose Nêel temperatures are 13.1 and 11.2 K, respectively.

A classic view of the magnetic interaction in all of the foregoing chloroferrates, as well as the present hexachloroferrate, is that it involves delocalization of metal electron *spin density* to the chloride ligands. The driving force for this spin delocalization is reduction of *charge* at the Fe^{3+} centers via back-bonding from Cl$^-$ to Fe^{3+}. That is, a normally diamagnetic "free" chloride anion "approaches" a paramagnetic chlorine atom species nature. This type of behavior has been used to explain the ESR spectra of K$_2$IrCl$_6$.[14] The iridium

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is a paramagnet with $S = {}^1/_2$, and the g value is reduced to 1.79. Also, a complex hyperfine spectrum is observed. The low g value indicates appreciable spin transfer between the iridium and the chlorine atoms. The hyperfine field has been adequately explained in terms of a coupling interaction of iridium electron spin and chlorine nuclear spin. It has been shown that the t_{2g} orbital hole responsible for the ESR is delocalized over the chlorine ligands to the extent that ~70% resides on the central iridium cation. The preceding spin delocalization effects are observed in terms of the *single-ion* (Ir^{4+}) ESR spectrum. In the present work, we are extending their observation to *ordering of delocalized spin density for the* FeCl_6^{3-} *clusters* where nonbonded Cl–Cl contacts are probably at the van der Waals radius. While the single-crystal structure of $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$ has not been determined, those of the related complexes $[\mathrm{Co(NH_3)}][\mathrm{MCl_6}]$, M = Tl, Sb, have been. A partial packing structure[15] of $[\mathrm{Co(NH_3)_6}][\mathrm{SbCl_6}]$ is shown in Figure 8. The complex packs in an NaCl structure containing four anions and four cations per unit cell. The $\mathrm{SbCl_6}^{3-}$ chromophore is in an essentially octahedral environment, with the interanionic Cl–Cl contact distance of 3.79 Å. In addition, *hydrogen bonding* between the cation and anion is clearly indicated by the shorter N–Cl distances, between 3.2 and 3.4 Å. This hydrogen bonding introduces the possibility of complex cation involvement in the magnetic interactions. We hope to study this aspect for $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$ in the near future by cobalt-57 emission Mössbauer spectroscopy studies. If the cation participates in the magnetic interaction, there may well be a transfer of magnetic hyperfine field to the normally diamagnetic cobalt (low-spin d^6 Co(III)) and this can be observed in such emission spectra.

To conclude, we note that our iron-57 Mössbauer spectroscopy study of $[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}]$ shows no evidence of magnetic ordering to 1.6 K. The crystal structure of this material has recently been determined.[16] Using the published unit cell parameters and the appropriate atomic coordinates, we have searched for inter $\mathrm{FeCl_6}^{3-}$ anion Cl–Cl contacts less than 4.2 Å and find none. Subsequently, one of the investigators of ref 16 (J. Beattie) furnished us with the results of a similar search of the data with the same result, i.e., no Cl–Cl contacts <4.2 Å. For the present, we *speculate* that the apparent much weaker zero exchange in $[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}]$ is the result of somewhat larger contact distances and/or weaker hydrogen bonding. A simple varient of $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$, namely $[\mathrm{Co(en)_3}][\mathrm{FeCl_6}]$ (en = ethylenediamine), is also currently under investigation.

Acknowledgment. The authors wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program (Grant No. DMR-80-16441), and the Research Corp. The authors also thank Dr. J. K. Beattie for the results of the Cl–Cl contact search for $[\mathrm{Co(NH_3)_6}][\mathrm{FeCl_6}]$.

Registry No. $[\mathrm{Co(pn)_3}][\mathrm{FeCl_6}]$, 20519-29-3.

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Contribution from the Department of Chemistry, Faculty of Science, Rikkyo University, Nishiikebukuru 3,
Toshima-ku, Tokyo 171, Japan, and Institut für Theoretische Chemie, Universität Düsseldorf, D-4000 Düsseldorf, Germany

Vibrational Fine Structure of the ${}^1\mathrm{B_g} \leftarrow {}^1\mathrm{A_g}(C_{2h})$ Absorption Band of *trans*-$[\mathrm{Co(CN)_2(en)_2}]^+$. Excited-State Conformation

KAZUO HAKAMATA,[†] AKIO URUSHIYAMA,[†] JOACHIM DEGEN,[‡] HANS KUPKA,[‡]
and HANS-HERBERT SCHMIDTKE*[‡]

Received March 3, 1983

The 4.2 K polarized absorption, polarized infrared, and Raman spectra of *trans*-$[\mathrm{Co(CN)_2(en)_2}]\mathrm{ClO_4}$ and its deuterated analogue have been measured. The vibronic spectra due to the first spin-allowed transition, ${}^1\mathrm{B_g} \leftarrow {}^1\mathrm{A_g}$, of small single crystals exhibit distinct vibrational structure from a progression created by a single accepting mode of 236-cm^{-1} frequency. A normal-coordinate analysis identified this mode as being derived from almost equal contributions of Co–N and N–C stretching and NCoN angular vibrations, with a fundamental frequency of 269 cm^{-1} in the ground state. A least-squares fit of the theoretical band profile function to the experimental spectra determined the spectroscopic parameters, which allowed an estimation of the equilibrium geometry changes due to electron excitation.

Introduction

In a previous paper[1] the change in equilibrium geometry of *trans*-$[\mathrm{Co(CN)_2(NH_3)_4}]^+$ in the ligand field excited state, ${}^1\mathrm{A_{2g}}(D_{4h})$, relative to the ground state, ${}^1\mathrm{A_{1g}}$, was determined from the intensity distribution in the vibrational progression of the polarized absorption spectrum. The present study extends this investigation to single crystals of the corresponding chelate complex *trans*-$[\mathrm{Co(CN)_2(en)_2}]^+$, which requires a more elaborate theoretical analysis because of the presence of ring systems.

In general, ligand field spin-allowed absorption spectra of transition-metal complexes can be resolved into vibrational components only on rare occasions; e.g., vibrational structure has been reported for the first spin-allowed transitions in the absorption and the circular dichroism spectra of cobalt(III) complexes with ethylenediamine, tetramethylenediamine, and octaazabicycloeicosane ligands.[2,3]

The spectra of these compounds, however, did not permit resolution of vibronic (false) origins, because of the overlapping of the large number of band components. A relatively simple chelate-containing system, which exhibits sufficiently well-resolved absorption spectra, was found in *trans*-$[\mathrm{Co(CN)_2}$-

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[†] Rikkyo University.

[‡] Universität Düsseldorf.

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