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Powder and Crystal Electron Resonance Studies of Iron(III) in $(NH_4)_2[InCl_5H_2O]$

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Received November 8, 1973

AIC30819K

The molecular ion $[FeCl_5H_2O]^{2-}$ in the host $(NH_4)_2[InCl_5H_2O]$ has been studied by electron resonance at 300 and 77°K. oriented single-crystal rotation patterns were used to extend epr powder techniques to d^5 systems. Large g shifts and quadratic zero-field splitting parameters (D, E) were observed along with rather small quartic splitting parameters (a, F, K). The large rhombic parameter E was used to infer π-bonding interactions by the water ligand.

Introduction

Ammonium aquopentachloroindate, $(NH_4)_2[InCl_5H_2O]$, is an excellent host lattice for paramagnetic resonance studies of the ferric ion because both the indium salt[1] and the analogous iron salt[2] are readily obtainable from aqueous solution as isomorphous compounds with known structures containing discrete molecular ions. This host has been previously used for epr studies of vanadyl, molybdenyl, and chromium(III) complexes,[3,4] and the indium compound itself was studied by nuclear quadrupole resonance.[5] These studies demonstrated that the guest complexes, while being geometrically oriented by the environment, are only loosely coupled to the lattice. These features offer the opportunity to study iron(III) in a chemically anisotropic environment and to compare the spin-Hamiltonian parameters with those of the analogous chromium(III) complex.[4] This host, also, allows us to extend the powder epr techniques previously developed for d^3 chromium complexes[6] to d^5 systems.

The existence of a single-orbital state of maximum multiplicity (^{6}S) for the d^5 electronic system has been the source of some difficulty in explaining the origin of the spin-Hamiltonian parameters.[7] Sharma, Das, and Orbach[8] have investigated the origin of the quadratic zero-field splitting parameter, D, for S-state ions utilizing both ionic and covalent models. Gabriel, Johnston, and Powell[9] studied the quartic zero-field parameter, a, using a crystal field model. The contribution of such factors as ligand spin-orbit effects[10] and charge-transfer state admixture[11] to the g shifts of d^5 systems have been considered but not quantitatively examined. The most significant factor in the poor understanding of the origins of the zero-field parameters D and a for d^5 systems is the fact that lattice compressions or lattice distortions have been dominant in nearly all of the iron(III) systems studied to date.[7,12-14] A real understanding of the origins of the spin-Hamiltonian parameters for d^5 systems will develop only through extensive studies of molecular iron(III) complexes.

Powder epr spectra of iron-doped $(NH_4)_2[InCl_5H_2O]$ crystals similar to the samples studied in this work have been observed previously, but the spectra were not properly assigned nor interpreted.[6,15] Rotation patterns of approximately aligned single crystals were used to develop an understanding of the epr powder spectra from which we have extracted accurate spectra for the three principal axes of the rhombic spin Hamiltonian. The interpretations focus attention on the chemical information contained in the data and on the qualitative aspects of the spin-Hamiltonian parameters which relate to the origin of these parameters.

Experimental Section

All epr spectra were obtained on a Varian E12 system spectrometer with a rotating magnet using the 9.5-GHz frequency for some preliminary spectra and the 35-GHz frequency for the remainder of the work. Resonance line positions were measured to within 1 G (limited by line widths and signal intensities) with a Spectromagnetic Industries Model 5200 nmr gauss meter. Optical spectra were obtained on a Cary Model 14 spectrometer.

The compounds $(NH_4)_2[FeCl_5H_2O]$ and $(NH_4)_2[InCl_5H_2O]$ form isomorphous, orthorhombic crystals of known structure[1,2] when grown from acidic, aqueous solutions of the stoichiometric mixtures of NH_4Cl and the metal trichloride. The unit cells contain four chemically identical molecular ions which appear magnetically as two geometric sites related by an approximately 90° rotation about the b axis. Figure 1 contains an a–c projection of a portion of the unit cell which illustrates the two geometric sites. Magnetically dilute single crystals of the iron complex were obtained in the indium host compound as approximately 0.5 and 5% samples. These samples gave identical epr spectra except that the more concentrated sample gave more intense and slightly broader lines. Powder samples were obtained by grinding portions of the single crystals. Single-crystal epr data for a rotation about the b axis with the magnetic field in the a–c plane gave two displaced Z to X rotation patterns as illustrated in Figure 1. A second rotation about the bisector of the a and c axes varied the orientation of the magnetic field from the dashed-line direction in Figure 1 to the b axis. This rotation gave, simultaneously, an X to Y pattern for site A and a Z to Y pattern for site B. The composite angular dependence of the resonance lines is shown in Figure 2. The mountings for both rotations were obtained within about 2° of the desired orientation, but the powder spectrum still gives a much more accurate representation of the line positions along the principal axes.

Accurate single-crystal rotation patterns are tedious to obtain because of the large amount of data required to determine the spin-Hamiltonian parameters and because of the difficulty of obtaining precise mountings of the crystals. Powder samples are much easier to use because the extreme resonant fields represented by lines in the powder spectra correspond accurately to single-crystal spectra with the magnetic field along each of the three principal axes of the spin Hamiltonian. The d^5 powder spectrum, shown in Figure 2., is quite similar to those previously obtained for d^3 systems[6] except that two

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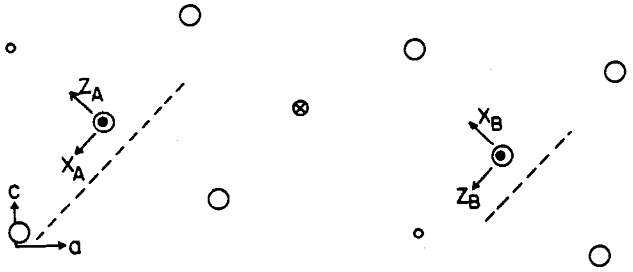

Figure 1. An *a-c* projection of two sites in the unit cell of $(NH_4)_2[InCl_5H_2O]$ illustrating the orientation of the spin-Hamiltonian principal axes of the guest $[FeCl_5H_2O]^{2-}$: ●, In, Fe; ○, Cl; ∘, OH_2; ⊗, NH_4^+.

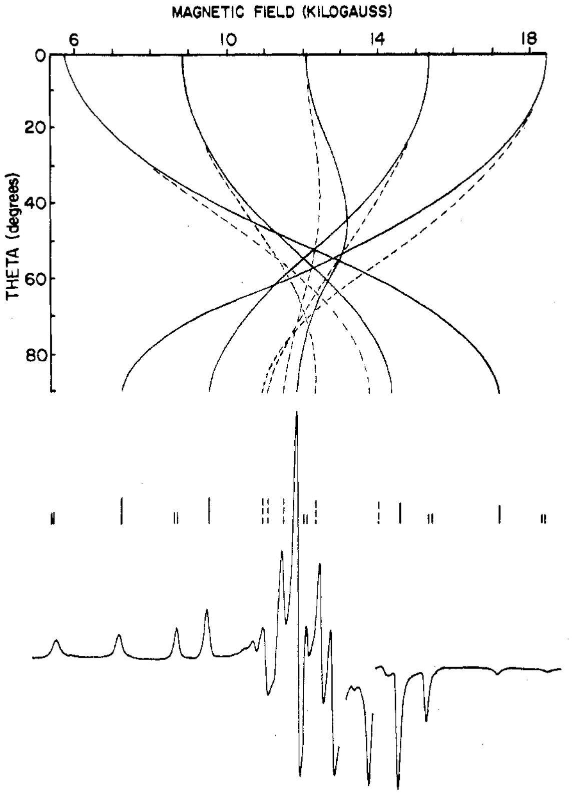

Figure 2. Angular-dependent single-crystal resonant fields aligned with the powder epr spectrum of $[FeCl_5H_2O]^{2-}$ in $(NH_4)_2[InCl_5H_2O]$. The solid curves represent a *Z-Y* rotation, and the dashed curves correspond to a *Z-X* rotation. Responses in the powder spectrum correspond to angular extremes of the resonant fields as indicated. The two extra lines on the high-field side of the center section of the powder spectrum result from the nonprincipal axis extrema of the central resonance.

more transitions are observed for each of the three principal axes. The assignment of the powder lines is illustrated in Figure 2 by alignment of the single-crystal angular-dependent data with the powder spectrum. The weak derivative shaped lines of the interior perpendicular spectrum (*X* axis) were difficult to recognize primarily because they were virtually submerged under the intense center section by the large rhombic distortion. The powder assignments were completed by comparison with single-crystal data in this case, but in less severely distorted systems this comparison should be unnecessary. The resonance line positions for a room-temperature powder spectrum are given in Table I. A similar powder spectrum was obtained at liquid nitrogen temperature. The fitting of these powder spectra to the spin Hamiltonian is quite simple but deserves specific comment.

Table I. Resonant Magnetic Fields (in Gauss) for the $\Delta M_s = 1$ Transitions in a Powder Spectrum of $(NH_4)_2[FeCl_5H_2O]$:In, (ν = 34.476 GHz, T = 25°)

Parallel	Perpendicular	
Z	*X*	*Y*
5,880	11,090	7,421
8,961	11,267	9,704
12,206	11,669	12,004
15,492	12,449	14,520
18,685	14,011	17,430

Table II. Coefficients in the Spin Hamiltonian with the Magnetic Field along the Principal Axes of a Rhombic Crystalline Field[a]

	H along		
	Z	*X*	*Y*
G	$g_z\beta H$	$g_x\beta H$	$g_y\beta H$
α	$\frac{a}{6}+\frac{F}{9}$	$\frac{a}{6}+\frac{3F}{72}+\frac{5}{2}K$	$\frac{a}{6}+\frac{3F}{72}-\frac{5}{2}K$
β	K	$-\left(\frac{K}{2}+\frac{F}{72}\right)$	$-\left(\frac{K}{2}-\frac{F}{72}\right)$
γ	$-\frac{a}{6}$	$\frac{a}{6}+\frac{7F}{72}-\frac{7K}{2}$	$\frac{a}{6}+\frac{7F}{72}+\frac{7K}{2}$
δ	D	$\frac{-D-3E}{2}$	$\frac{-D+3E}{2}$
ϵ	E	$\frac{D-E}{2}$	$\frac{-D-E}{2}$

[a] It is assumed that the *g* tensor and the second- and fourth-rank zero-field splitting tensors have coincident principal axis systems.

In the case of a d^5 ion with tetragonal and rhombic distortions from cubic symmetry, the *g* tensor and the quadratic and the quartic zero-field splitting tensors are expected to have nearly coincident principal axis systems. This allows the spin Hamiltonian to be written in a representation such that Zeeman interaction is diagonal for each of the three principal axes of the crystalline field and such that the matrix of the spin Hamiltonian has the same form for each of the principal axis directions

$$H = GS_z + \alpha O_F + \beta O_2 + \gamma O_4 + \delta O_D + \epsilon O_E$$

The quartic spin operators consist of a diagonal term

$$O_F = (1/20)\{35S_z^4 + [25 - 30S(S+1)]S_z^2 - 6S(S+1) + 3S^2(S+1)^2\}$$

a second off-diagonal term

$$O_2 = (1/4)[(S_+^2 + S_-^2)(7S_z^2 - S^2 - S - 5) + (7S_z^2 - S^2 - S - 5)(S_+^2 + S_-^2)]$$

and a fourth off-diagonal term

$$O_4 = (1/8)(S_+^4 + S_-^4)$$

while the quadratic spin operators are

$$O_D = S_z^2 - (1/3)S(S+1) \qquad O_E = (1/2)(S_+^2 + S_-^2)$$

Different combinations of the usual spin-Hamiltonian parameters occur for the three orientations of the magnetic field along principal axes, and these are given in Table II. The matrix of the spin Hamiltonian thus has diagonal elements from S_z, O_D, and O_F, second off-diagonal elements from O_2 and O_E, and fourth off-diagonal elements from O_4. The 6 × 6 matrix of a $^5/_2$ spin system is thus block diagonal as two 3 × 3 matrices which can be solved with cubic equations. The fitting of the spin Hamiltonian can be handled with a programable desk calculator such as the Hewlett-Packard Model 9810A which was used in this work. The spin-Hamiltonian parameters for both room temperature and liquid nitrogen temperature powder spectra are given in Table III.

Room-temperature optical spectra of the dilute single crystals used in this work were obtained on a Cary Model 14 spectrophotometer. These spectra were quite similar to the reflectance spectra reported by Balt and Verwey[16] for the pure iron compound with the exception that the charge-transfer band extends down to 20,000 cm^{-1} and the crystal field bands are at slightly different posi-

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Table III. Spin-Hamiltonian Parameters[a] for $(NH_4)_2[FeCl_5H_2O]$ Diluted in the Analogous Indium Host Compound

	Room-temp spectrum		77°K spectrum[b]
	G	10^{-4} cm^{-1}	G
D	−1618.1 ± 0.5	−1519.1	−1894
E	301.9 ± 0.3	283.1	302
a	22.3 ± 1	21.5	17
F	0.57 ± 0.1	0.54	0.6
K	0.65 ± 0.01	0.61	0.55
$g_{\parallel}$	2.0109 ± 0.0004		
$g_{\perp}$	2.0091 ± 0.0004		

[a] Only the relative signs of the parameters are determined from the spectra. [b] Temperature fluctuations with resultant frequency variations in the low-temperature spectrum precluded accurate determination of the g factors and limited the accuracy of the determination of the remaining parameters to the number of significant figures shown.

Table IV. Optical Absorption Band Positions of Pure and Dilute $(NH_4)_2[FeCl_5H_2O]$ (10^3 cm^{-1})

Pure[a]	14.2	12.0	9.2
Dilute[b]	12.90	12.13	9.35

[a] Reference 15. [b] Present work; samples of approximately 0.5 and 5% gave the same results.

tions as can be seen from the comparison with Table IV. A different assignment of the crystal field bands is discussed elsewhere.[17]

Discussion

Before any inquiry into the meaning of the spin-Hamiltonian parameters can be attempted, we must consider whether these parameters are dominated by the lattice or if they are predominantly intramolecular properties of the molecular ion $[FeCl_5H_2O]^{2-}$. Two observations relative to the temperature dependence favor the latter interpretation. First, a detailed quadrupole resonance study[5] of the host compound $(NH_4)_2[InCl_5H_2O]$ revealed a strong temperature dependence of the asymmetry parameter at the indium site, which measures differences between electric gradients along the X and Y directions. The analogous epr parameter, E, is temperature independent over the same range suggesting that the quadratic zero-field splitting tensor is decoupled from the lattice. Second, the axial part of the quadratic tensor, D, is moderately temperature dependent gaining 17% in magnitude when the temperature is decreased from 300 to 77°K. Considering the fact that the lattice contains two substitutional sites for the iron complex which differ geometrically by an approximately 90° rotation of the Z axis, it is difficult to conceive of a temperature-dependent lattice effect which could cause a response along the Z axis of both sites and still leave the XY plane of both sites unaffected. An intramolecular effect along the Z axis within each complex would account for the observations. Thus, the quadratic zero-field splitting is primarily an internal property of the molecular complex whose geometry is partially determined by interactions with the lattice. We may also infer that the spin-Hamiltonian parameters g and a are molecular properties because of the similarity of the values to those observed for $[FeCl_6]^{3-}$.[17] Now, we may examine the various spin-Hamiltonian parameters in a molecular context.

The g factors ($g_{\parallel} = 2.0109$, $g_{\perp} = 2.0091$) obtained for this complex are among the largest yet observed for six-coordinate iron complexes with deviations from the free-electron g factor ($g_e = 2.0023$) which are comparable to those for chromium(III) complexes. Since the parallel g shift ($g_e - g_{\parallel}$) arises from excited state admixture into the ground state *via* the z component of the angular momentum operator[7] which corresponds to a rotation about the z axis, we expect $g_{\parallel}$ to be controlled by the bonding to the equatorial chlorine ligands in sixfold coordination. The g factor for the complex $[FeCl_6]^{3-}$ has essentially the same value as $g_{\parallel}$ for $[FeCl_5H_2O]^{2-}$.[17] The value of $g_{\perp}$ includes contributions due to the axial Fe-OH$_2$ bond which should cause $g_{\perp}$ to deviate from $g_{\parallel}$ toward the g value of $[Fe(H_2O)_6]^{3+}$ ($g \simeq 2.003$)[7] and this is the case. The magnitude and anisotropy of the g tensor for $[FeCl_5H_2O]^{2-}$ are in accord with the usual second-order spin-orbit mixing origin for the g shifts with a large contribution from charge-transfer state mixing and ligand spin-orbit effects.[4,17] Further consideration of the g factors would lead us into a detailed molecular orbital analysis of the complex which we shall not pursue here.

The large, temperature-independent rhombic zero-field parameter E (302 G, $E/D \simeq 0.17$) of $[FeCl_5H_2O]^{2-}$ is reminiscent of the similar rhombic terms in the aquochromium(III) complexes $[CrCl_5H_2O]^{2-}$ ($E = 50$ G, $E/D = 0.085$)[4] and $[Cr(NH_3)_5H_2O]^{3+}$ ($E = 125$ G, $E/D = 0.136$).[18] In each of these cases the rhombic term has been shown to be intramolecular in origin. These observations can be explained by assuming π bonding of the water to one of the xz or yz metal d orbitals. The water molecule must be locked into a specific orientation (not rotating about the metal-oxygen bond) to account for the data. Similar rhombic contributions to the g tensor would be unobservably small, but we have observed a small temperature-independent rhombic component K of the quartic zero-field splitting (see Table III).

The chemical or bonding anisotropy introduced by the presence of a water molecule in $[FeCl_5H_2O]^{2-}$ gives rise to an axial quadratic zero-field parameter D (~1700 G) which is of similar magnitude to the values found for strongly compressed and distorted environments such as Al_2O_3 ($D \approx 1700$ G),[13] tetragonal $BaTiO_3$ ($D \approx 1000$ G),[12] and $CaCO_3$ ($D \approx 1000$ G).[14] Thus the effects of strong lattice distortions and bond anisotropy on D may be difficult to separate in some cases. Another interesting comparison can be made with $[CrCl_5H_2O]^{2-}$ for which $D = 640$ G in the same $(NH_4)_2[InCl_5H_2O]$ host.[4] The unpaired spin density in the σ orbitals of the iron system which makes extra contributions to the anisotropy of the spin-orbit interaction probably accounts for the larger D of the iron complex.

The quartic parameter of the cubic symmetry, a, for iron(III) systems appears to be sensitive to lattice compressions as indicated by the widely ranging values of a observed in different hosts involving the same anions. In oxide hosts containing Fe^{3+}, a varies from about 20 G in tetragonal $BaTiO_3$ to about 200 G in Al_2O_3 with an extreme value near 400 G in TiO_2.[7,12,13] In fluorides a varies from 50 G in molecular $[FeF_6]^{3-}$ to about 200 G in AlF_3.[7,19] The only molecular complexes of iron(III) for which the cubic parameters have been determined are $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$ ($a \approx 130$ G),[7] $[FeCl_6]^{3-}$ ($a \approx 15$ G),[17] and the present example $[FeCl_5H_2O]^{2-}$ ($a \approx 20$ G). Comparisons of these data suggest that the cubic parameter may be characteristic of the ligands in molecular situations but tend to increase when the lattice compresses the ligands onto the ferric ion.

All determinations of the sign of the cubic parameter a for d^5 systems in both fourfold and sixfold coordination have

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yielded positive values.[7] Initially, the small magnitudes of *a* for the chloro complexes led us to consider the possibility of negative contributions, but molecular orbital analyses of these systems[17] indicate that *D* is negative for $[FeCl_5H_2O]^{2-}$. The signs of *a* and *D* are opposite according to our experiments; thus no evidence of negative contributions to *a* has been found. The magnitude of *a* does appear to depend strongly on the ligand, and further studies of the quartic parameters in molecular complexes are needed to clarify their origins.

Registry No. $(NH_4)_2[FeCl_5H_2O]$, 16774-56-4; $(NH_4)_2[InCl_5\text{-}H_2O]$, 17949-59-6; Fe^{3+}, 20074-52-6.

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Electron Resonance of Some Tetraamminechromium(III) Complexes

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Received January 28, 1974

AIC40061K

Powder electron paramagnetic resonance (epr) spectra of *trans*-$[Cl_2(NH_3)_4Cr]^+$ and *trans*-$[Cl(H_2O)(NH_3)_4Cr]^{2+}$ have been examined in a variety of host lattices. Even though the preparations of the chromium complexes yield mixtures of species and multiple spectra, a comparison of the data for different hosts allows an unequivocal assignment of the spectra. The spin-Hamiltonian parameters are shown to be molecular properties and are compared with the parameters of the pentaamminechromium analogs.

Introduction

In a series of electron resonance (epr) studies of chromium(III) complexes we have been examining the effects of lattice perturbations and chemical substitution on the *g* shifts and the zero-field splittings.[1-4] Previous studies[3] of the chloro- and aquopentaamminechromium(III) complexes give an excellent basis for comparison with the trans disubstituted chloro- and aquotetraamminechromium(III) complexes. The disubstituted complexes are much less stable in solution precluding slow crystal growth; thus, epr studies of powder samples are necessary. The use of powder samples is convenient because this allows rapid evaluation of the effects of temperature and host lattice variations. In this study we have attempted to determine the intramolecular spin-Hamiltonian parameters for *trans*-$[Cl_2(NH_3)_4Cr]^+$, *trans*-$[Cl(H_2O)(NH_3)_4Cr]^{2+}$, and *trans*-$[(H_2O)_2(NH_3)_4Cr]^{3+}$. Preparations of the latter complex did not yield interpretable spectra.

The theory of the spin-Hamiltonian parameters for trans disubstituted chromium(III) complexes is essentially the same as that for the monosubstituted complexes.[1] The *g* factors are determined by the orbital angular momentum admixture of excited states into the ground state. This means that for these tetragonal complexes g_z is determined by σ–π mixing due to an effective rotation about the *z* axis and is thus a property of the bonding of the equatorial ligands alone. Similarly, $g_{x,y}$ is determined by an admixture involving ligands of both axial and equatorial types. Thus, in a mixed ligand tetragonal complex the value of $g_{x,y}$ is expected to lie in the range between the values of the *g* factors characteristic of the axial and equatorial ligands. These qualitative expectations were borne out with monosubstituted complexes,[3] and similar results are found for the disubstituted complexes.

The axial zero-field splitting parameter, *D*, measures the difference between the spin–orbit mixing about the *z* axis and that about an axis in the *xy* plane. Thus, if inductive effects are small, a disubstituted complex should have an axial splitting, *D*, of about twice the magnitude of the corresponding monosubstituted complex. The rhombic zero-field splitting parameter, *E*, measures differences in the spin–orbit mixing about the *x* and *y* directions. Thus, *E* should vanish for a tetragonal complex. The observed values of *E* reflect either lattice distortions of the complex or the effect of a low symmetry axial ligand such as water. No attempt will be made to examine the spin-Hamiltonian parameters with a detailed molecular orbital fitting as has been done in previous work.[1,3] Rather we content ourselves with a qualitative interpretation of the magnitudes and differences of the spin-Hamiltonian parameters.

Experimental Section

Each of the guest and host compounds used in this study was first prepared and identified separately before magnetically dilute powder samples were made. Acid cleavage of the ion[5] $[(NH_3)_5Cr\text{-}OHCr(NH_3)_4Cl]^{4+}$ provided entry into the series of trans disubstituted tetraamminechromium(III) complexes.[6] The *trans*-dichlorotetraamminechromium(III) chloride (*trans*-$[Cl_2(NH_3)_4Cr]Cl$) and *trans*-chloroaquotetraamminechromium(III) chloride (*trans*-$[Cl(H_2O)(NH_3)_4Cr]Cl_2$) were obtained directly upon cleavage of the binuclear complex and aquation of the latter salt yielded[7] *trans*-$[(H_2O)_2(NH_3)_4Cr](ClO_4)_3$. Chloropentaamminechromium(III) chloride and the cobalt compounds *trans*-$[Cl_2(NH_3)_4Co]Cl$, *trans*-$[Cl(H_2O)(NH_3)_4Co]Cl_2$, and *trans*-$[(H_2O)_2(NH_3)_4Co]Cl_3$ were obtained by standard methods[8] as was the *trans*-$[Cl_2(NH_3)_4Rh]Cl$.[9] The $[Cl(NH_3)_5Co]Cl_2$ was recrystallized from commercially available material.

Magnetically dilute samples of chromium(III) complexes were obtained as approximately 1% impurities in the cobalt or rhodium

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