

# Crystal structure and Mössbauer spectroscopy studies of the ferrimagnetic complex bimetallic salt hexaamminechromium(III) hexachloroferrate(III), $[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$

William E. Hatfield\* and Jeffrey H. Helms†

Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290, USA

Phirtu Singh

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650, USA

William M. Reiff\* and Laszlo Takács†

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115, USA

Jürgen Ensling

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg Universität, Mainz, Federal Republic of Germany

## Summary

The crystal and molecular structures of the ferrimagnetic bimetallic complex salt hexaamminechromium(III) hexachloroferrate(III),  $[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$ , have been determined from single-crystal, three-dimensional x-ray diffraction counter data. The compound crystallizes as orange coloured crystals in the space group  $C2/c$  of the monoclinic system with  $Z = 4$  and has cell dimensions  $a = 11.325(1) \text{ \AA}$ ,  $b = 11.387(1) \text{ \AA}$ ,  $c = 11.233(1) \text{ \AA}$ , and  $\beta = 90.83(1)^\circ$ . The structure was refined by using segmented block diagonal least-squares techniques to discrepancy indices  $R$  and  $R_w$  of 0.0233 and 0.0285, respectively. The metal ions occupy sites with symmetry  $\bar{1}$  and are nearly octahedrally coordinated. In the  $[\text{FeCl}_6]^{3-}$  anion there are three independent Fe—Cl distances with a mean of 2.393 (2)  $\text{ \AA}$ , and the maximum angular deviation from octahedral geometry is  $1.2^\circ$ . In the  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  cation, the mean of the three independent Cr—N distances is 2.079 (7)  $\text{ \AA}$ , and the maximum angular deviation from octahedral geometry is  $0.7^\circ$ . The structural data provide an explanation for the observed quadrupole splitting of  $0.214 \text{ mm s}^{-1}$  as seen in the Mössbauer spectrum at 292.6 K and reveal superexchange pathways *via* close amine proton-chloride anion contacts with lead to 3D-ferrimagnetic ordering near 2.8 K.

## Introduction

As a continuing part of our studies of the magnetic properties of complex bimetallic salts, we have observed ferrimagnetic ordering near 2.8 K in the compound hexaamminechromium(III) hexachloroferrate(III),  $[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$ <sup>(1)</sup>. Furthermore, Mössbauer spectra revealed a temperature dependent quadrupole splitting ( $\Delta E_Q$ ) which ranged from  $0.214 \text{ mm s}^{-1}$  at 292.6 K to  $0.321 \text{ mm s}^{-1}$  at 3.0 K. A quadrupole  $\Delta E_Q$  splitting of this magnitude was not expected in view of the structure<sup>(2)</sup> and Mössbauer spectra<sup>(3)</sup> of the analogous compound  $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$  ( $\Delta E_Q = 0$ ). Repeated attempts to

obtain single crystals suitable for crystallographic and molecular structure determinations by x-ray diffraction have finally been successful. The results are described herein along with additional applied field Mössbauer spectroscopy studies that shed further light on the magnetic structure.

## Experimental

### Sample preparation

$[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$  was prepared by the procedure that was described earlier<sup>(4)</sup>. A sample of the compound was submitted to Galbraith Laboratories for elemental analyses: ( $\text{H}_{18}\text{Cl}_6\text{CrFeN}_6$  calcd.: H, 4.3; Cl, 50.3; N, 19.9. Found: H, 4.2; Cl, 50.1; N, 19.6%).

At a later time, the sample used for the magnetic susceptibility determination was submitted to Galbraith Laboratories for water analysis by the Karl Fischer method, and only a trace (0.05%) was found. The sample used for the Mössbauer measurements was also analyzed for water at the DuPont Company, and, in agreement with the earlier analysis, only a trace (0.03%) was found. Much of this is moisture adsorbed on the surface of the powdered samples, although there is the possibility that a trace of aquapentaamminechromium(III) hexachloroferrate(III) was present. However, the quantity of  $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{FeCl}_6]$  present, if any, would be far too small to affect the results of the magnetic susceptibility measurements or the Mössbauer spectroscopy studies.

### Applied field Mössbauer spectra

Mössbauer spectra in large longitudinal fields were determined using a new superconducting magnet-cryostat system which has been described in detail recently<sup>(5)</sup>. Moderate transverse field spectra were determined using a closed cycle carbon sorption pump Helium-3 Cryostat<sup>(6)</sup> incorporated with a Walker-Magnion 12" Electromagnet.

### X-ray data collection

Orange crystals of the compound were multifaceted, equidimensional, and mostly twinned. A small single

\* Authors to whom all correspondence should be directed.

† Present address: Department of Physics, University of Maryland, Baltimore County, Maryland, USA.

**Table 1.** Crystal data for [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>].

formula: CrFeN <sub>6</sub> Cl <sub>6</sub> H <sub>18</sub>	$a = 11.325(1) \text{ \AA}$
mol wt.: 422.8	$b = 11.387(1) \text{ \AA}$
size: (0.25 × 0.25 × 0.25) mm	$c = 11.233(1) \text{ \AA}$
space group: C2/c (No. 15)	$\beta = 90.83(1)^\circ$
Z = 4	$V = 1448.4(2) \text{ \AA}^3$
$D_x = 1.94 \text{ g cm}^{-3}$	$\mu(\text{MoK}\alpha) = 28.3 \text{ cm}^{-1}$

crystal was mounted on a glass fiber and used for data collection at room temperature. Cell dimensions and intensity data were measured on a Nicolet P3/F 4-circle automatic diffractometer. Intensities were measured by the  $\theta/2\theta$  scan method with variable scan speeds of 3.91 to 29.3° min<sup>-1</sup> by using graphite-monochromatized MoK<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Stationary background counts were measured at the beginning and end of a scan, each for one-half of the total scan time. Three reflections were measured at intervals of 47 measurements to check on crystal orientation and stability. The intensities of 1683 independent reflections were measured between 3° and 55° in  $2\theta$  yielding 1354 reflections with  $I \geq 3\sigma(I)$ . Lorentz and polarization corrections as well as empirical absorption corrections were applied to the observed intensity data. No correction for secondary extinction was necessary. Crystallographic data are given in Table 1, and experimental details are given in Table S1 in supplementary material.

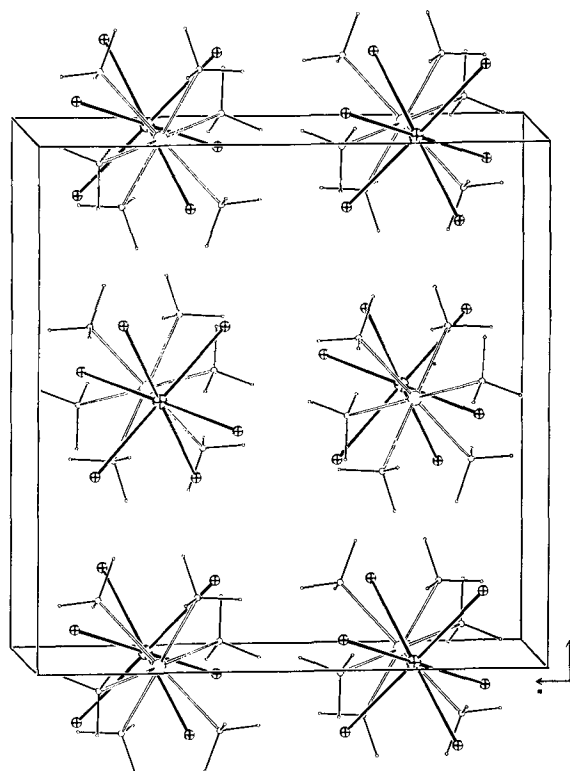
#### Structure solution and refinement

An examination of the systematic extinctions in the intensity data revealed the space group to be either *Cc* or *C2/c*. The latter space group was assumed and later confirmed by successful refinement of the structure. The structure was solved by Patterson and difference Fourier methods, and refined using segmented block-diagonal least-squares techniques. The hydrogen atoms were placed in calculated positions at 0.96 Å from the attached nitrogen atoms and were assigned an isotropic *U* of 0.06. The conventional discrepancy indices *R* and *R<sub>w</sub>* were 0.0233 and 0.0285 respectively with a GOF of 1.412. The data to parameter ratio is 20 to 1. The largest shift/ $\sigma$  in the last cycle of refinement was 0.01 and the largest peak in the final difference Fourier was 0.33 e<sup>-</sup>/Å<sup>3</sup>. All calculations were performed using the SHELXTL system of computer programs as implemented by the Nicolet Instrument Company for the Data General Micro-Eclipse computer.

#### Results and discussion

##### Crystal and molecular structure of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>]

An ORTEP<sup>(1)</sup> drawing of the crystal structure of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] is shown in Figure 1. The structure is quite similar to that of the analogous [Co(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] compound<sup>(3)</sup>. The latter, however, crystallizes in the cubic space group *Pa3* with  $a = 11.2506 \text{ \AA}$ , whereas the present compound crystallizes in a monoclinic cell, Table 1, having almost equal cell dimensions *a*, *b*, and *c* with values very close to the cubic cell dimension given above for the cobalt analog. The metal atoms occupy a lower site symmetry,  $\bar{1}$ , in the present structure than in the cobalt compound where they occupy sites of  $\bar{3}$  symmetry. The relative positions of the metal atoms in



**Figure 1.** An ORTEP<sup>(1)</sup> drawing of the crystal structure of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] viewed approximately along the *b*-axis. One unit cell is outlined with Fe—Cl bonds shown in darker print.

both structures are identical in terms of the fractions of cell edges. The Fe and Co coordinates given for the cobalt analog<sup>(2)</sup> can be converted to the Fe and Cr coordinates in the chromium analog given in Table 2 by adding (1/4, 3/4, 0) to their *x*, *y*, and *z* coordinates, respectively.

The three independent Fe—Cl distances, Table 3, are different statistically, but they are still very similar. Their mean, 2.393(2) Å, is the same as that found by Beattie and Moore for the cobalt analog<sup>(2)</sup>. The coordination environment of the iron atom is octahedral with a maximum deviation of 1.2° from an ideal octahedral symmetry. The coordination around chromium is also nearly octahedral, as expected, with a maximum angular deviation of 0.7° from the ideal values for an octahedron. The three independent Cr—N distances are quite similar with a mean of 2.079(7) Å, Table 3, which is considerably longer than the Co—N distance of 1.965 Å<sup>(2)</sup>.

**Table 2.** Fractional atomic coordinates ( $\times 10^4$ ) and temperature factors Å<sup>2</sup> ( $\times 10^3$ ) for non-hydrogen atoms.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sup>a</sup></i>
Fe	7500	2500	0	21(1)
Cl(1)	8809(1)	1604(1)	-1376(1)	26(1)
Cl(2)	6712(1)	3779(1)	-1538(1)	30(1)
Cl(3)	6044(1)	1082(1)	-514(1)	33(1)
Cr	2500	2500	0	17(1)
N(1)	1348(2)	3273(2)	-1217(2)	24(1)
N(2)	1810(2)	3561(2)	1333(2)	27(1)
N(3)	1243(2)	1227(2)	385(2)	29(1)

<sup>a</sup>Equivalent isotropic *U* defined as 1/3 of the trace of the orthogonalized *U<sub>ij</sub>* tensor.

**Table 3.** Bond distances (Å) and angles (°)<sup>a</sup>.

Fe—Cl(1)	2.386(1)	Cr—N(1)	2.072(2)
Fe—Cl(2)	2.420(1)	Cr—N(2)	2.085(2)
Fe—Cl(3)	2.373(1)	Cr—N(3)	2.081(1)
Cl(1)—Fe—Cl(2)	91.22(3)	Cl(1)—Fe—Cl(3)	89.29(3)
Cl(2)—Fe—Cl(3)	89.29(3)	Cl(1)—Fe—Cl(1a)	180
Cl(2)—Fe—Cl(1a)	88.78(3)	Cl(3)—Fe—Cl(1a)	90.71(3)
Cl(1)—Fe—Cl(2a)	88.78(3)	Cl(2)—Fe—Cl(2a)	180
Cl(3)—Fe—Cl(2a)	90.71(3)	Cl(1a)—Fe—Cl(2a)	91.22(3)
Cl(1)—Fe—Cl(3a)	90.71(3)	Cl(2)—Fe—Cl(3a)	90.71(3)
Cl(3)—Fe—Cl(3a)	180	Cl(1a)—Fe—Cl(3a)	89.29(3)
Cl(2a)—Fe—Cl(3a)	89.29(3)	N(1)—Cr—N(2)	89.3(1)
N(1)—Cr—N(3)	90.4(1)	N(2)—Cr—N(3)	89.4(1)
N(1)—Cr—N(1a)	180	N(2)—Cr—N(1a)	90.7(1)
N(3)—Cr—N(1a)	89.6(1)	N(1)—Cr—N(2a)	90.7(1)
N(2)—Cr—N(2a)	180	N(3)—Cr—N(2a)	90.6(1)
N(1a)—Cr—N(2a)	89.3(1)	N(1)—Cr—N(3a)	89.6(1)
N(2)—Cr—N(3a)	90.6(1)	N(3)—Cr—N(3a)	180
N(1a)—Cr—N(3a)	90.4(1)	N(2a)—Cr—N(3a)	89.4(1)

<sup>a</sup>Cl(1a), Cl(2a), and Cl(3a) refer to the symmetry position (1.5 - x, 0.5 - y, -z); N(1a), N(2a), and N(3a) refer to the symmetry position (0.5 - x, 0.5 - y, -z).

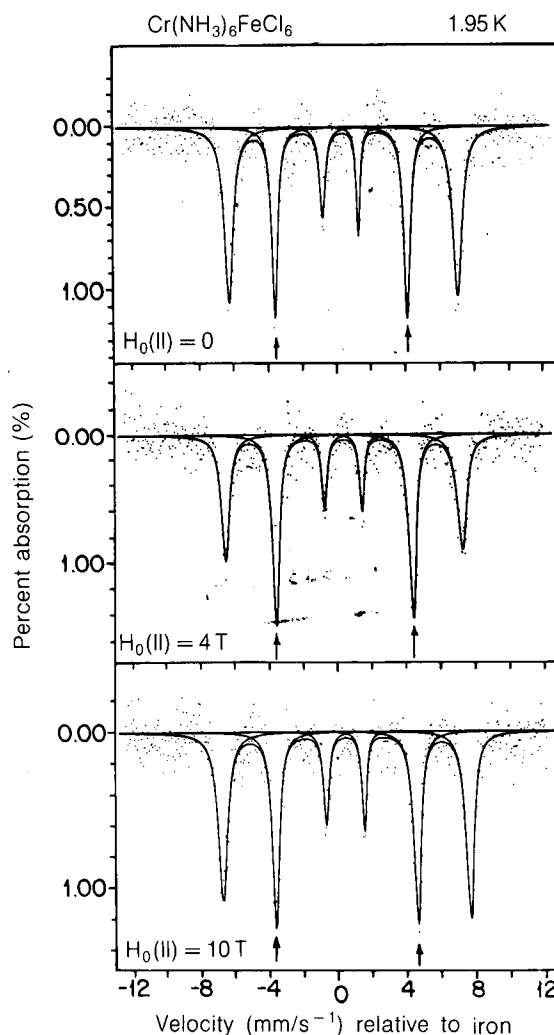
### Mössbauer spectroscopy

Mössbauer spectroscopy data for  $[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$  were collected both in and out of the presence of longitudinal  $H_0 \parallel E_y$  (Helium-4 measurements) and transverse (Helium-3) applied magnetic fields. As shown in Figure 2, the intensities<sup>(8)</sup> of the  $\Delta M_I = 0$  transitions (see arrows in the figures) initially begin to increase relative to the  $\Delta M_I = \pm 1$  transitions in the presence of the longitudinally applied magnetic field. This indicates the occurrence of an antiferromagnetic to spin flop transition within an antiferromagnetically coupled  $[\text{FeCl}_6]^{3-}$  sublattice. However, at higher fields (10 Tesla), the intensity of these transitions begins to decrease. This overall behaviour is characteristic of an antiferromagnetic to spin-flop followed by a spin-flop to paramagnetic phase transition for a complex antiferromagnetically coupled multi-sublattice system. The transverse field Helium-3 range spectra shown in Figure 3 also suggest spin-flop behaviour ( $H_{\text{sf}} \sim 1.0$  T) since the intensity of the  $\Delta M_I = 0$  transitions have clearly decreased relative to the  $\Delta M_I = \pm 1$  transitions on reaching 12.4 kOe at 0.52 K. This more complex magnetic structure, which was anticipated in our earlier work on this system, has now been confirmed<sup>(1)</sup>. The complete details of the magnetic structure must await further study.

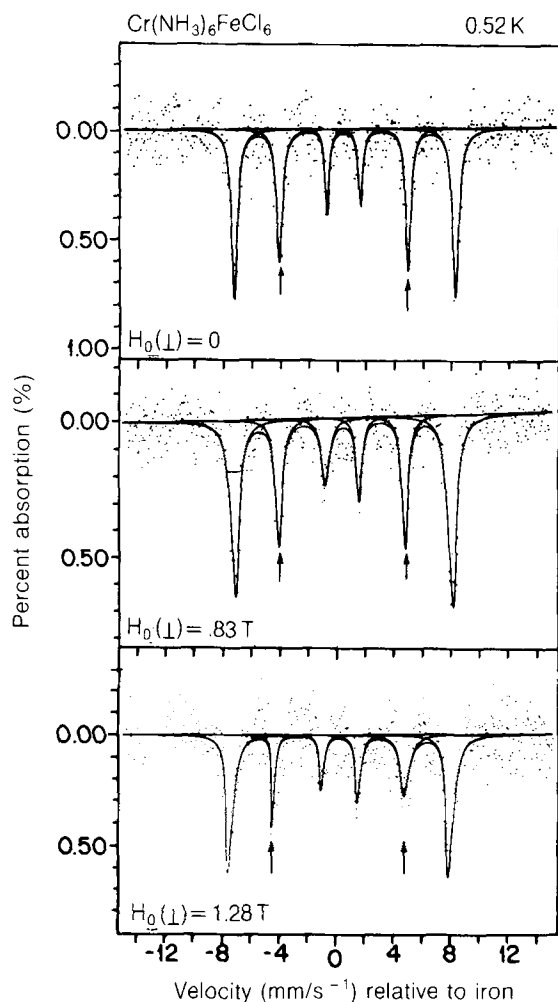
The observed quadrupole splitting of  $[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$  ranging from  $0.214 \text{ mm s}^{-1}$  at room temperature to  $0.321 \text{ mm s}^{-1}$  at 3.0 K was not expected due to the similarities between this system and that of the cobalt analog where no quadrupole splitting was observed at room temperature. A Mössbauer spectrum in a longitudinal applied magnetic field of 5 Tesla was determined for the paramagnetic phase in order to ascertain the sign of the principal component of the electric field gradient tensor, EFG, and the value of the asymmetry parameter,  $\eta$ . Analysis of the spectrum shown in Figure 4 using the procedure developed by Spiering<sup>(9)</sup> yields a positive electric field gradient and  $\eta = 0.6 \pm 0.2$ .

A computational approach was also investigated where the lattice and coordinated ligand contributions to the EFG as well as the quadrupole splitting were calculated explicitly. Calculations for the lattice contributions to the

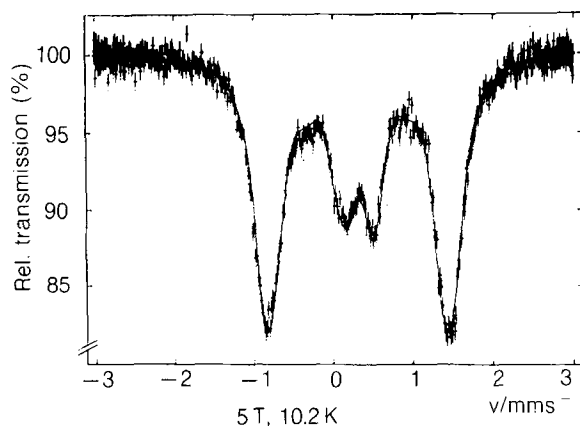
EFG tensor and quadrupole splitting for the chromium salt resulted in a quadrupole splitting of  $-0.522 \text{ mm s}^{-1}$  and asymmetry parameter,  $\eta = 0.120$ . An *ab initio* approach was used to estimate the coordinated ligand



**Figure 2.** Mössbauer spectra at 1.95 K in longitudinally applied magnetic fields.



**Figure 3.** Mössbauer spectra at 0.52 K in transversely applied magnetic fields.



**Figure 4.** Mössbauer spectrum of the paramagnetic phase of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] at 10.2 K in an applied field of 5 Tesla.

**Table 4.** Electric field gradient vectors in the principal axes system (Debye-Å) and unrestricted Hartree-Fock electronic energies (atomic units) for [Co(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] and [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>].

Cation	$V_{zz}$	$V_{xx}$	$V_{yy}$	$E(UHF)$
Co(NH <sub>3</sub> ) <sub>6</sub>	-0.017605	0.008805	0.008801	-4014.27
Cr(NH <sub>3</sub> ) <sub>6</sub>	0.358044	-0.264969	-0.093075	-4009.72

contributions to the EFG using Gaussian 86<sup>(10)</sup> and the Gaussian basis set MINI-4<sup>(11)</sup>. SCF minimization was performed using the direct minimization SCF program with the initial guess formed by diagonalization of the core Hamiltonian for both the cobalt and chromium salts. The data resulting from the MINI-4 SCF is given in Table 4.

Experimentally, the cobalt system does not exhibit quadrupole splitting due to the octahedral coordination around iron(III) and the cubic space group. The parameters from the SCF approach are  $V_{zz} = -0.017605$  and  $\eta = 0$  producing a calculated quadrupole splitting of  $-0.03559 \text{ mm s}^{-1}$  using the expression

$$\Delta E_Q = eQv_{zz}[3M_1^2 - I(I+1)](1 + \eta^{2/3})^{1/2}/4I(2I-1)$$

A calculation for the chromium system results in an asymmetry parameter,  $\eta$ , equal to  $+0.480092$ ,  $V_{zz} = 0.358044$ , and a calculated quadrupole splitting resulting from coordination effects of  $0.751 \text{ mm s}^{-1}$ . It is interesting to note that the sum of the contributions to the quadrupole splitting resulting from the lattice and valence shell covalence anisotropy calculations produces a resultant  $\Delta E_Q = 0.229 \text{ mm s}^{-1}$ , a value very close to that found experimentally. Using the cobalt salt result, it can be assumed that the error in the valence EFG calculation is approximately  $-0.03 \text{ mm s}^{-1}$ . The corrected  $\Delta E_Q$  is then,  $0.2 \text{ mm s}^{-1}$ , even closer to the experimental number. Furthermore, the sums of the magnitudes of the asymmetry parameters from these calculations reproduces the experimental value derived from the analysis of the applied field spectrum. It can be assumed therefore, that the quadrupole splitting is not unusually large, as was first thought, although the temperature dependence is novel. Instead, the combination of the lower symmetry of the site occupied by the ferrate ion and the crystal symmetry, are sufficient to severely modulate the EFG tensor.

#### Superexchange pathways and ferrimagnetic ordering

The ambient temperature magnetic moment of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] is 4.86 B. M., a value that is slightly lower than the theoretically predicted value of 5.0 B. M.<sup>(1)</sup>. Presumably, antiferromagnetic interactions between the [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [FeCl<sub>6</sub>]<sup>3-</sup> ions have reduced the effective magnetic moment even at temperatures as high as room temperature. The observed low-temperature limiting value of the magnetic moment at 1.85 K is 2.75 B. M., a value which agrees well with a spin-only value of 2.83 B. M. mole<sup>-1</sup> expected for an  $S = 1$  system which arises from the complete antiparallel arrangement of the  $S = 3/2$  chromium(III) sublattice and the  $S = 5/2$  iron(III) sublattice of a classical collinear Néel ferrimagnet. Upon analysis of the temperature dependence of the magnetic susceptibility data above the ferrimagnetic ordering temperature, the intersublattice coupling constant  $J_{\text{Cr-Fe}}$  has been determined to be  $-0.21 \text{ cm}^{-1(1)}$ .

Bimetallic complex salts which exhibit ferrimagnetic ordering are rare. The structure of [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>] and the cobalt analog may be crudely characterized as being of the rock salt type with the structure formed by stacking layers along the  $b$ -axis. Extensive hydrogen bonding exists in these systems between amine protons of the cation and chloride ligands of the ferrate anion. In [Cr(NH<sub>3</sub>)<sub>6</sub>][FeCl<sub>6</sub>], nitrogen-hydrogen-chloride superexchange pathways range from 2.3 to 2.65 Å with

angles lying in the range of 130° to 175°, and these can be expected to produce complex cation-anion magnetic interactions. A full understanding of these interactions and the overall magnetic structure will require single crystal susceptibility and more particularly neutron diffraction studies.

#### Acknowledgements

This research was conducted in part by using the Pittsburgh Supercomputing Center, which receives major funding from the National Science Foundation. We are grateful to the staff at PSC for their help and support. The research was supported by the National Science Foundation through Grants DMR 83 13710 (WMR) and CHE 88 07498 (WEH). The x-ray diffractometer at North Carolina State University was upgraded through a grant (CHE 87 07022) from the National Science Foundation.

#### Supplementary material available

Tables S1-S3 listing crystallographic data, collection and refinement parameters, anisotropic temperature factors, hydrogen coordinates and temperature factors, and Table S4 listing observed and calculated structure factors have been deposited with the Editor, from whom copies are available on request.

#### References

- (1) J. H. Helms, W. E. Hatfield, M. J. Kwiecien and W. M. Reiff, *J. Chem. Phys.*, **84**, 3993 (1986).
- (2) J. K. Beattie and C. J. Moore, *Inorg. Chem.*, **21**, 1292 (1982).
- (3) J. H. Zhang, W. M. Reiff, J. H. Helms, W. E. Hatfield, N. Dixon and L. Fritz, *Inorg. Chem.*, **25**, 2936 (1986).
- (4) W. E. Hatfield, R. C. Fay, C. E. Pfluger and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).
- (5) L. Takacs and W. M. Reiff, *Hyperfine Interactions*, **42**, 1177 (1988).
- (6) W. M. Reiff, *Hyperfine Interactions*, **40**, 195 (1988).
- (7) C. K. Johnson, ORTEP-II: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- (8) The intensity of the  $\Delta M_1 = 0$  magnetic dipole transitions for the  $|I = 1/2 \rangle \rightarrow |I = 3/2 \rangle$  manifold is proportional to the angular factor  $\sin^2 \theta$  where  $\theta$  is the angle between the  $\gamma$  radiation probability (and  $H_0$  for the longitudinal case) and the easy axis of magnetization. The corresponding factor for the  $\Delta M_1 = \pm 1$  transitions is  $1 + \cos^2 \theta$ . (See Greenwood, N. N. Gibb, T. C. *Mössbauer Spectroscopy*, Chapman and Hall: London; p. 67.)
- (9) H. Spiering, *Hyperfine Interactions*, **5**, 265 (1978).
- (10) M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuger and J. A. Pople, *Gaussian 86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA 1984.
- (11) H. Tatewaki, Y. Sakai and S. Huzinaga, *J. Comp. Chem.*, **2**, 278 (1981).

(Received 13 May 1991)

TMC 2535