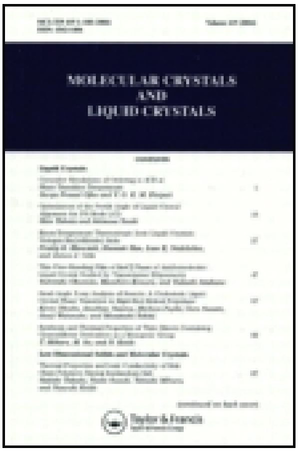

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spectroscopic and Bulk Susceptibility Evidence for Independent Antiferromagnetic Ordering Transitions in the Rock Salt Like Structured Hetero-Bimetallic Complexes [Cr $(NH_3)_6$ [$FeCl_6$ and [Ru(NH_3), [($FeCl_6$): Consequences of Highly Different Magnetic Symmetries

W. M. Reiff [a] & W. E. Hatfield [b]

[a] Department of Chemistry, Northeastern University, Boston, Ma, 02115

[b] Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514

To cite this article: W. M. Reiff & W. E. Hatfield (1995): Spectroscopic and Bulk Susceptibility Evidence for Independent Antiferromagnetic Ordering Transitions in the Rock Salt Like Structured Hetero-Bimetallic Complexes [Cr $(NH_3)_6$ [$FeCl_6$ and [Ru(NH_3), [($FeCl_6$): Consequences of Highly Different Magnetic Symmetries, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 274:1, 33-40

To link to this article: http://dx.doi.org/10.1080/10587259508031863

Mol. Cryst. Liq. Cryst., 1995, Vol. 274, pp. 33–40
Reprints available directly from the publisher
Photocopying permitted by license only

SPECTROSCOPIC AND BULK SUSCEPTIBILITY EVIDENCE FOR INDEPENDENT ANTIFERROMAGNETIC ORDERING TRANSITIONS IN THE ROCK SALT LIKE STRUCTURED HETERO-BIMETALLIC COMPLEXES $[Cr(NH_3)_6][FeCl_6]$ AND $[Ru(NH_3)_6][(FeCl_6)]$: CONSEQUENCES OF HIGHLY DIFFERENT MAGNETIC SYMMETRIES.

W. M. REIFF
Department of Chemistry, Northeastern University,
Boston, Ma 02115

W. E. HATFIELD
Department of Chemistry, University of North
Carolina, Chapel Hill, North Carolina, 27514.

Abstract Entirely separate 3D-A.F. magnetic ordering processes are observed for the ionic components of the rock salt like materials $[Cr(NH_3)_6][FeCl_6]$ and $[Ru(NH_3)_6][FeCl_6]$ through high resolution a.c. susceptibility and Mossbauer spectroscopy measurements.

INTRODUCTION

Previous detailed cooperative magnetic properties studies of $FeCl_6^{3-}$ anions have focused on compounds containing diamagnetic cations such as $[Co(NH_3)_6]^{3+}$ (1) or $[Co(1,3\text{-propane-diamine})_3]^{3+}$ (2) where the S=5/2 hexachloro- ferrate anions of these systems exhibit 3D-A.F. ground states, T_N ~0.9K and 9K respectively and the cations are of course "magnetically silent" owing to their diamagnetism. More recently, we have reported the single crystal x-ray structure and high field Mossbauer spectra of $[Cr(NH_3)_6][FeCl_6]$(3) where the latter clearly suggest an A.F. to spin-flop phase transition for the $FeCl_6^{3-}$ anion lattice between 1 and 2T and a very high field induced spin-flop to paramagnetic phase transition (>4T).

That is, the $FeCl_6^{3-}$ sublattice of $[Cr(NH_3)_6][FeCl_6]$ is clearly antiferromagnetically ordered and apparently independent of the paramagnetic S=3/2 $[Cr(NH_3)_6]^{3+}$ cation sublattice with which it is nevertheless structurally intimately associated.

Results

Herein, this unexpected result is further confirmed for $[Cr(NH_3)_6][FeCl_6]$ and the related S=1/2 $Ru(NH_3)_6^{3+}$ analogue where high resolution ($\Delta T=0.02K$ to $\Delta T=0.05K$) a.c. susceptibility data (H_o=1 Oe, ν=125Hz) (A) exhibit no imaginary component (χ''_m) and (B) do exhibit separate transitions in χ'_m vs T. These are resolved for the cations at 2.1K and 4.6K and anions at 2.4K and 5.2K of (Cr) and (Ru) analogues respectively. Zero field Iron-57 Mossbauer spectra show that the S=5/2 anion lattice orders at the higher temperature in each case, an observation fully consistant with molecular field theory, i.e., $T_c \propto S(S+1)$ (4). In addition, ruthenium-99 Mossbauer spectra also indicate long range order for the $Ru(NH_3)_6^{3+}$ sublattice while d.c. χ_m vs T (vibrating sample magnetometry data at 0.015 and 1T likewise exhibits separate, distinct transitions for the cation and anion of $(Ru(NH_3)_6][FeCl_6]$ in agreement with the a.c. results. The overall behavior and particularly the monotonic decrease of μ and $\chi_m''=0$ indicate that the present complexes can not be simple collinear two sublattice ferrimagnets. The apparent non-interaction of the interpenetrating component sublattices of these systems is likely (at least for the Ru complex) the result of highly different magnetic sublattice symmetries, i.e., Ising (low-spin Ru^{3+}) vs Heisenberg (high-spin Fe^{3+}).

Results

A.C. susceptibility data for the chrome complex compound (0.05K resolution) are given in Figure 1 where separate transitions for the anion and cation lattices at ~ 2.4K and 2.1K are evident. The magnetic moment variation (per mole) corresponding to Figure 1 is seen in Figure 2.

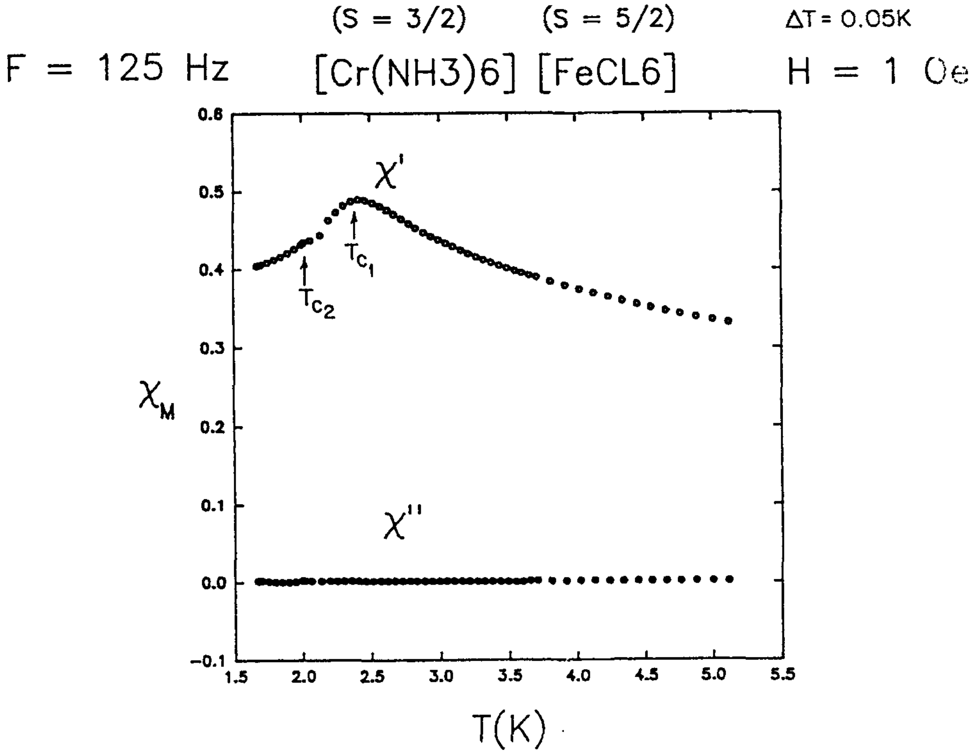

FIGURE 1 Real (χ'_m) and imaginary (χ''_m) components of the a.c. susceptibility of $[Cr(NH_3)_6][FeCl_6]$.

In view of the single ion ground states involved ($^4A_{2g}$-cation and $^6A_{1g}$-anion), it is reasonable to assume spin-only magnetic behavior for the components of the chrome complex . The moment per mole of complex for non-interacting S=3/2 and S=5/2 units is √50 or 7.07 Bohr magnetons while the spin-only moments of the cation and anion are 3.87 B.M. and 5.92 B.M. respectively. Thus, the limiting value of ~ 2.3 B.M./mole at 1.6K in Figure 2 is fully consistent with the postulated (independent) antiferromagnetism of the cation and anion lattices.

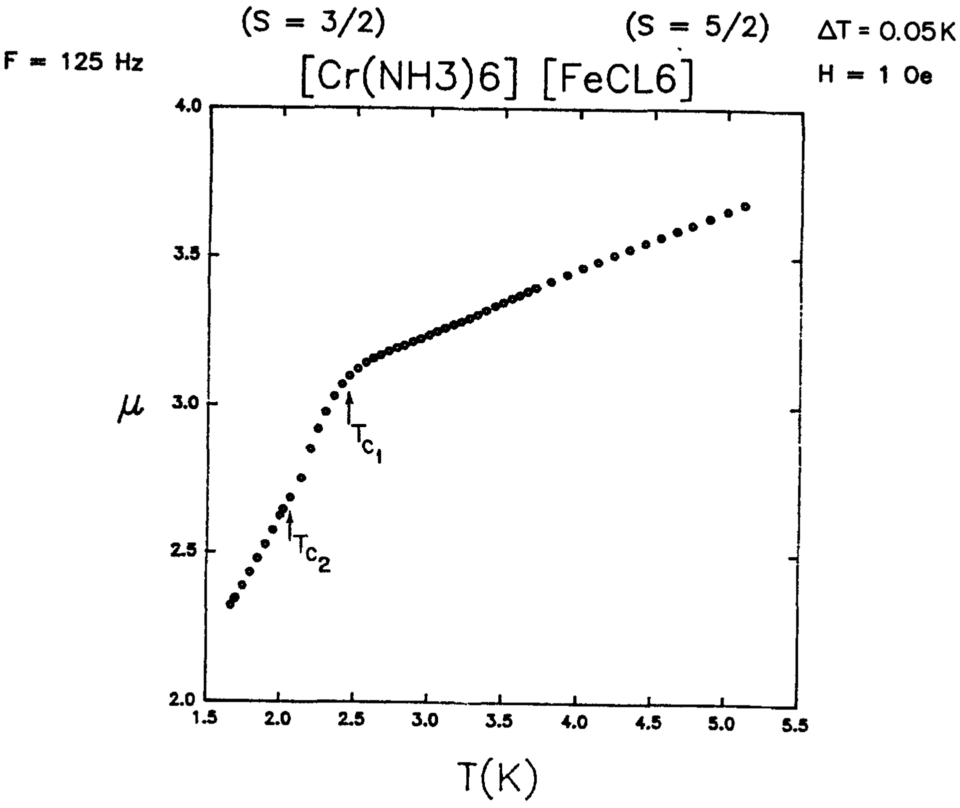

FIGURE 2 Magnetic moment (μ) versus temperature for $[Cr(NH_3)_6][FeCl_6]$

Although considerably lower temperature resolution data Figure 3, vibrating sample magnetometry at 1 Tesla, separate A.F. transitions are evident in the temperature dependence of the reciprocal susceptibility of the ruthenium compound.

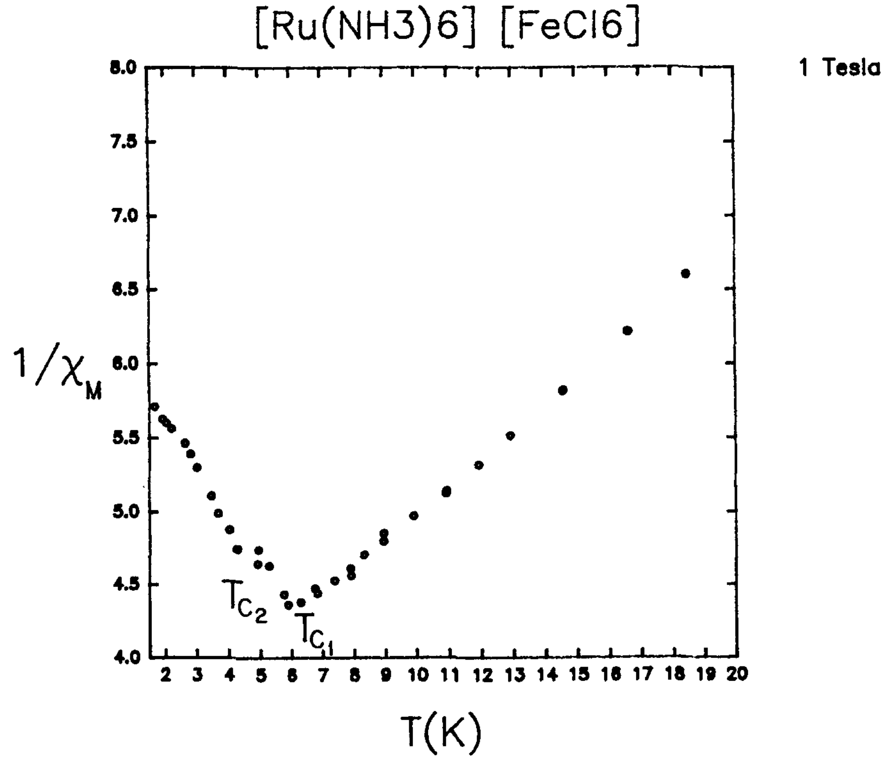

FIGURE 3 χ^{-1}_m versus T for $[Ru(NH_3)_6][FeCl_6]$ (d.c. field vibrating sample magnetometry data).

Its moment variation and limiting value of 1.5 B.M./mole (1.10 B.M./metal) again suggests independent A.F. behavior as the spin only value for non-interacting $S=1/2$ and $S=5/2$ units is 6.16 B.M. while the respective spin-only values are now 1.73 B.M. (cation) and 5.92 (anion). Small orbital contributions for low-spin Ru^{3+} (nominal $^2T_{2g}$ ground state) leading to cation moment values ranging from 2.0 to 2.3 B.M. do not change the conclusions. Previously published(5) zero field iron-57 Mossbauer spectra exhibit the onset of magnetic hyperfine splitting at ~ 2.8K suggesting a T_N of this value for *the iron containing anion lattice* of $[Cr(NH_3)_6][FeCl_6]$ in agreement with a.c. and d.c. χ_m vs T results. Mossbauer spectroscopy data for $[Cr(NH_3)_6][FeCl_6]$ have also been collected both in longitudinal (H_0 parallel to $E\gamma$ at T ~ 1.9K) and transverse (H_o perpendicular to $E\gamma$ at T ~ 0.5K) applied magnetic fields. The intensities of the $\Delta M_I = 0$ transitions initially begin to increase relative to the $\Delta M_I = \pm1$ transitions in the presence of the longitudinally applied magnetic field (spectra not shown). This indicates (6) the occurrence of an antiferromagnetic to spin flop first order phase transition within and antiferromagnetically coupled $[FeCl_6]^{3-}$ anion lattice. However, at higher fields (10 Tesla), the intensities of these transitions are seen to have decreased. The overall field dependence behavior is incontrovertibly characteristic of an antiferromagnetic to spin-flop followed by a spin-flop to paramagnetic phase transition typical of a uniaxial, antiferromagnetically coupled two sublattice system. *In this case the two sublattice system is composed of up and down spin lattices of* $FeCl_6^{3-}$ *units independent of the* $Cr(NH_3)_6^{3+}$ *cation lattice.* The transverse field Helium-3 range spectra shown in Figure 4 also suggest (6) spin-flop behavior (H_{sf} ~ 1.0 T) since the intensity of the $\Delta M_I = 0$ transitions (see arrows in the figure) have clearly decreased relative to the $\Delta M_I = \pm1$ transitions on reaching 12.4 kOe at 0.52K.

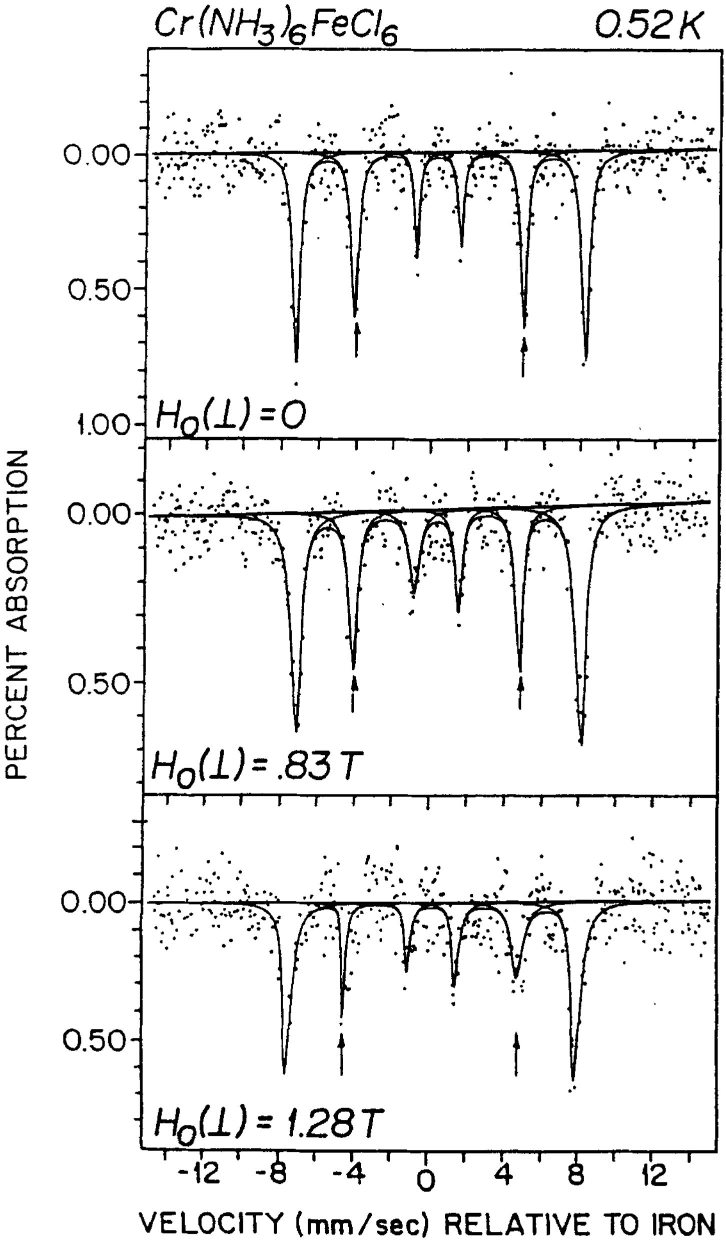

FIGURE 4 Some transverse applied field Mossbauer spectra for $[Cr(NH_3)_6][FeCl_6]$ at 0.52K.

Summary

The behavior reported herein for "rock salt like" structured complexes (7) and likewise exhibited by certain layered ferricenium tetra-halo-ferrates (8) is probably also operative for other chrome III complexes, particularly $[Cr(en)_3][FeCl_6]$, which has recently been reported (9) to order "as a compensated ferrimagnet" at T_N=2.26K with $\chi_m''=0$! The meaning of the latter terminology is not clear to the present investigators. In any event, higher temperature resolution susceptibility data for this system would be valuable and will likely resolve separate cation and anion ordering transitions. More details for the present systems including the Ru-99 Mossbauer spectroscopy results will be reported subsequently elsewhere (10). Research supported by the NSF Division of Materials Research (W.M.R) and NSF Chem Grant #9111408 (W.E.H.).

REFERENCES

1. J.H. Zhang,, W.M. Reiff, J.H. Helms, W.E. Hatfield, N. Dixon, L. Fritz, Inorg. Chem. 25, 2936, (1986)
2. A.N. Scoville, K. Lazar, W.M. Reiff, C. Landee, Inorg. Chem. 22, 3514, (1983)
3. W.E. Hatfield, J.H. Helms, P. Singh, W.M. Reiff, L. Tákacs and J. Ensling; Trans. Met. Chem, 17, 204 (1992).
4. R.L. Carlin, Magnetochemistry, (Springer-Verlag, Berlin, 1986)
5. J.H. Helms, W.E. Hatfield, M.J. Kwiecien, W.M. Reiff, J. Chem. Phys. 84, 3993, (1986)
6. W.M. Reiff, Mol. Cryst. Liq. Cryst., 176, 391, (1989)
7. W.E. Hatfield, R.C. Fay, C.E. Pfluger and T.S. Piper, J. Am. Chem. Soc. 85, 265 (1963)
8. See the article by W.M. Reiff, J.H. Zhang and J.S. Miller in these proceedings
9. M. Carmen Moron, Fernando Palacio, J. Pons, J. Casabo, X. Solans, K.E. Merabet, D. Huang, X. Shi, B.K. Teo, and R.L. Carlin, Inorg. Chem., 33, 746, (1994)
10. W.M. Reiff, W.E. Hatfield and F. Wagner to be submitted.