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Magnetic Properties of Ferrous Chloride Complexes with Two-Dimensional Structures

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The quadrupole and magnetic interactions in compounds of the type $(RNH_3)_2FeCl_4$, where $R = CH_3$, C_2H_5, C_3H_7, and $C_6H_5CH_2$ have been studied. The Mössbauer spectra obtained at room temperature showed a quadrupole doublet with $\Delta E_Q = 2.1-2.3$ mm/sec for all four compounds and an isomer shift I. S. $= 1.2-1.25$ mm/sec referred to stainless steel. The electronic ground state is ${}^5B_{2g}$. The liquid-nitrogen-temperature results showed a magnetic hyperfine splitting for all compounds except the benzyl compound. The internal magnetic field varies from 220 kOe in propyl to 240 kOe in methyl with axis of magnetization in the plane of the sheet. Magnetic-susceptibility measurements for methyl, propyl, and benzyl compounds showed the transition temperatures to be 96, 90, and 72 °K, respectively. They also indicated that significant amounts of short-range order above the transition temperature are absent, and the compounds are antiferromagnetic. Finally, ESR calculations gave a g in the range of 2.01–2.015 and a value of $J = 8 \times 10^{-16}$ erg.

Recently there has been much interest in the properties of two-dimensional magnetic systems. Much of the work has centered on antiferromagnetic divalent transition metal fluorides such as K_2NiF_4,[1] Rb_2MnF_4,[2] Rb_2FeF_4,[3] etc. Recently, however, de Jongh *et al.*[4] have reported on a series of copper (II) chloride complexes of the type $(RNH_3)_2CuCl_4$ which are ferromagnetic. We have synthesized the analogous ferrous complexes and have begun an investigation of their structural and magnetic properties.

The compounds studied have the general formula of $(RNH_3)_2FeCl_4$ where RNH_3^+ is a substituted ammonium ion. We have used $R = CH_3$ (methyl), C_2H_5 (ethyl), C_3H_7 (propyl), and $C_6H_5CH_2$ (benzyl). They are prepared simply by mixing $FeCl_2$ and the substituted ammonium chloride together in alcohol in the absence of oxygen. Crystals of the compounds precipitate as flat yellow plates which turn brown on exposure to air due to oxidation of Fe^{+2} to Fe^{+3}.

Single-crystal structure analyses have not been carried out at this point because of the poor quality of crystals available. However, a powder pattern $(CH_3NH_3)_2FeCl_4$ indicates that it is isomorphous to the corresponding manganese compound.[5] The tetragonal unit cell has approximate lattice constants of $a = 5.1$ and $c = 19.2$ Å. An idealized version of this structure is shown in Fig. 1. The principal features of the structure are the two-dimensional metal-halogen sheets and the dependence of the spacing between the sheets on the length of the substituted ammonium cation. This has been verified in our laboratory by the determination of the structure of $(C_3H_7NH_3)_2MnCl_4$.[6] Here the interlayer spacing is 13 Å compared to 9.6 Å in the methylammonium compound. The other salient feature of the structure of $(C_3H_7NH_3)_2MnCl_4$ is a "puckering" or "washboard" effect introduced into the metal-halogen framework owing to the N-H···Cl hydrogen bonding which causes the metal-chloride octahedra to tip. Each manganese ion has a compressed octahedral coordination geometry with Mn-Cl = 2.48 Å perpendicular to the sheet, and Mn-Cl = 2.63 Å in the plane of the sheet.

Mössbauer spectra have been obtained for the four ferrous compounds at room temperature and at liquid-nitrogen temperature. The spectrometer was based on the design by Kankelheit[7] and Hofmiester *et al.*,[8] modified to ensure that the absorber was in thermal equilibrium with the bath. At room temperature, each compound shows a two-line spectrum typical for ferrous compounds, as shown in Fig. 2, the splitting being due to the interaction of the quadrupole moment with the crystalline electric field gradient. The splitting is approximately 2.1–2.3 mm/sec for all four compounds, as shown in Table I. Spectra of single crystals were obtained, with the two-dimensional sheet oriented perpendicular to the path of the γ rays. The ratio of areas under the peaks is nearly 1:3, indicating that the principal axis of the electric field gradient is parallel to the γ-ray beam,[9] i.e., perpendicular to the sheet. This is consistent with the (nearly)

TABLE I. Room-temperature Mössbauer parameters.

Compound	ΔE (cm/sec)	I. S.[a] (cm/sec)
$(CH_3NH_3)_2FeCl_4$	0.2257 ± 0.009	0.1215 ± 0.002
$(CH_3CH_2NH_3)_2FeCl_4$	0.2241 ± 0.005	0.1205 ± 0.001
$(CH_3CH_2CH_2NH_3)_2FeCl_4$	0.2214 ± 0.004	0.1200 ± 0.001
$(\phi CH_2NH_3)_2FeCl_4$	0.2275	0.1207

[a] Isomer shift with respect to stainless-steel source.

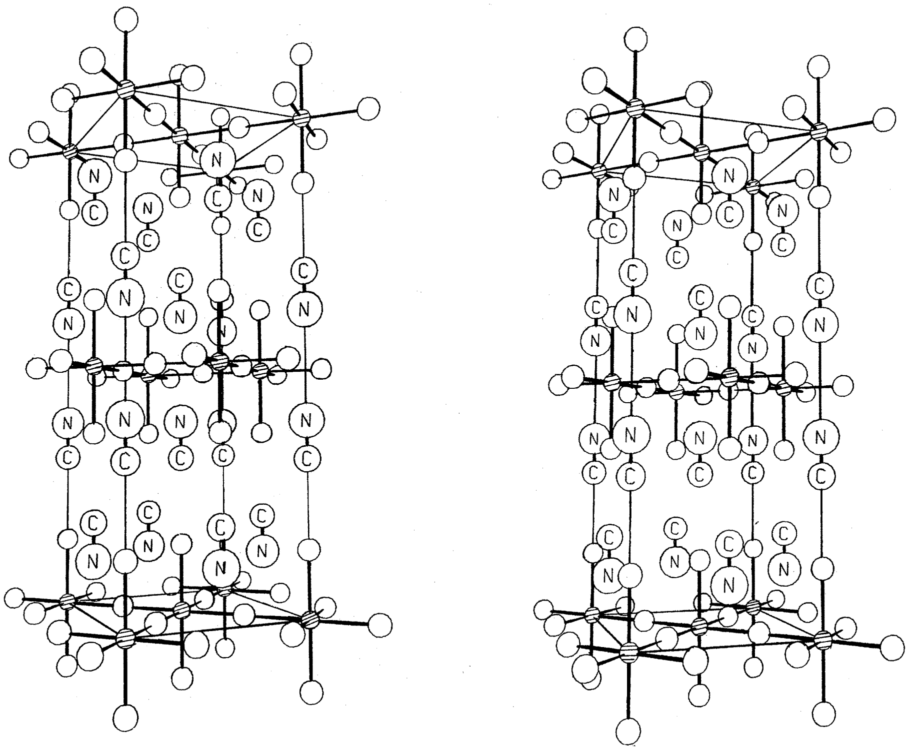

FIG. 1. Proposed structure for $(CH_3NH_3)_2FeCl_4$. The symbols used in the figures are the following: Ⓝ = Nitrogen; Ⓒ = Carbon; ▨ ferrous; ○ = Chloride ion.

tetragonal symmetry of the crystals. The larger of the two peaks is at higher velocity, corresponding to a positive electric field gradient. This is consistent with the $^5B_{2g}$ electronic ground state predicted by crystal-field theory for compressed octahedral geometry.

At liquid-nitrogen temperature, the Mössbauer spectrum of each compound (except the benzyl compound) shows additional splitting due to magnetic hyperfine interaction, as shown in Fig. 3. The spectra were fitted to the theoretical expressions for the energies in a mixed magnetic-field–electric-field-gradient system.[10] The value for the strength of the magnetic field is in the range of 220 kOe (ethyl, propyl) to 240 kOe (methyl). The magnetic field lies in the plane of the sheet. This is analogous to the results found for Rb_2FeF_4.[3]

The magnetic susceptibility of powdered samples of the methyl, propyl, and benzyl compounds were measured using a mutual-inductance technique.[11] The methyl and propyl compounds order above liquid-nitrogen temperature (96 and 90 °K, respectively). The benzyl compound orders at 72 °K.

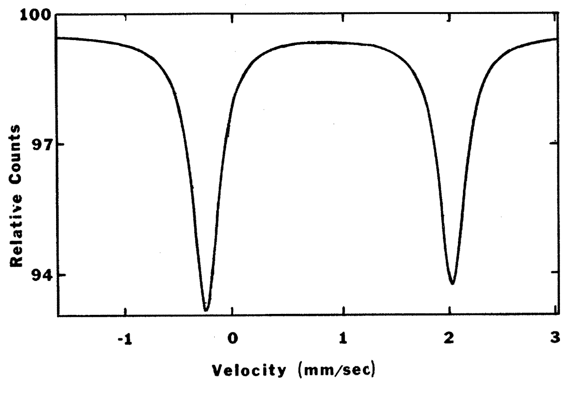

FIG. 2. Mössbauer spectrum of $(C_3H_7NH_3)_2FeCl_4$ at room temperature.

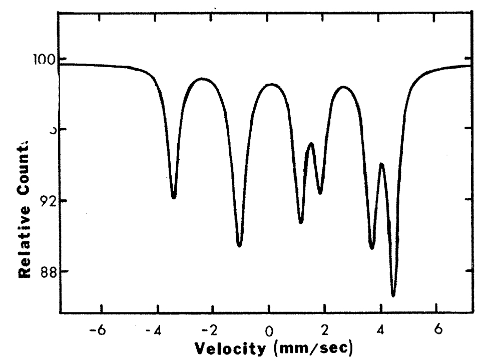

FIG. 3. Mössbauer spectrum of $(C_3H_7NH_3)_2FeCl_4$ at 78 °K.

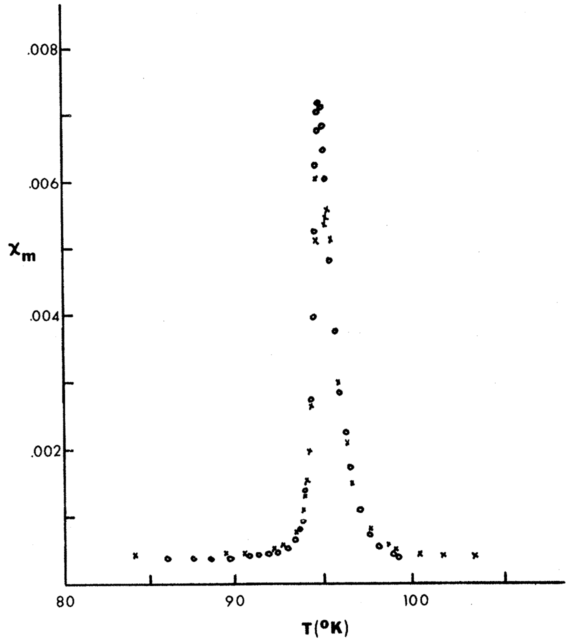

FIG. 4. Magnetic-susceptibility data for $(CH_3NH_3)_2FeCl_4$.

This explains the absence of hyperfine splitting in the Mössbauer spectrum of the benzyl compound. No field dependence was observed below the ordering temperature, indicating that the compounds are antiferromagnetic. The susceptibility curve for $(CH_3NH_3)_2FeCl_4$ exhibits a very sharp maximum at the ordering temperature, as shown in Fig. 4, in contrast to the behavior of Rb_2FeF_4.[3] This would indicate an absence of significant amounts of short-range order above the transition temperature. The maxima for the propyl and benzyl compounds are somewhat broader.

Finally, the ESR spectrum of $(CH_3NH_3)_2FeCl_4$ has been observed at room temperature and liquid-nitrogen temperature. The spectrum consists of a single anisotropic exchange-narrowed line with g in the range of 2.010–2.015. The linewidth is approximately 100 G, yielding a value of $J = 8 \times 10^{-16}$ erg (4 cm^{-1}). The existance of the ESR signal at approximately $g = 2$ in the antiferromagnetic state indicates that the spin-correlation time is shorter than the time constant of the ESR experiment.

More detailed descriptions of each of the above items will be published at a later date.

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