water.[27-29] One mechanism for inner-sphere nitrate penetration in electrolytes could involve one monodentate oxygen bond of nitrate by replacement of one inner-sphere water.[18] Then, subsequent bidentate bonding could occur on crystallization by displacement of three inner-sphere waters by two nitrates.

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Registry No. $La(ClO_4)_3$, 14017-46-0; $LaCl_3$, 10099-58-8; $La(NO_3)_3$, 10099-59-9; $Pr(ClO_4)_3$, 13498-07-2; $PrCl_3$, 10361-79-2; $Pr(NO_3)_3$, 10361-80-5; $Nd(ClO_4)_3$, 13498-06-1; $NdCl_3$, 10024-93-8; $Nd(NO_3)_3$, 10045-95-1; $Sm(ClO_4)_3$, 13569-60-3; $SmCl_3$, 10361-82-7; $Sm(NO_3)_3$, 10361-83-8; $EuCl_3$, 10025-76-0; $Eu(NO_3)_3$, 10138-01-9; $Gd(ClO_4)_3$, 14017-52-8; $GdCl_3$, 10138-52-0; $Gd(NO_3)_3$, 10168-81-7; $Tb(ClO_4)_3$, 14014-09-6; $TbCl_3$, 10042-88-3; $Tb(NO_3)_3$, 10043-27-3; $Dy(ClO_4)_3$, 14017-53-9; $DyCl_3$, 10025-74-8; $Dy(NO_3)_3$, 10143-38-1; $Ho(ClO_4)_3$, 14017-54-0; $HoCl_3$, 10138-62-2; $Ho(NO_3)_3$, 10168-82-8; $Er(ClO_4)_3$, 14017-55-1; $ErCl_3$, 10138-41-7; $Er(NO_3)_3$, 10168-80-6; $Tm(ClO_4)_3$, 14014-10-9; $TmCl_3$, 13537-18-3; $Tm(NO_3)_3$, 14985-19-4; $Yb(ClO_4)_3$, 13498-08-3; $YbCl_3$, 10361-91-8; $Yb(NO_3)_3$, 13768-67-7; $Lu(ClO_4)_3$, 14646-29-8; $LuCl_3$, 10099-66-8; $Lu(NO_3)_3$, 10099-67-9; YCl_3, 10361-92-9; $Y(NO_3)_3$, 10361-93-0.

Supplementary Material Available: Listings of computer values of integral work of desolvation, enthalpy changes and entropy changes from 0.1 *m* to crystal hydrate formation at 298 K and the BASIC program for eq 2 (5 pages). Ordering information is given on any current masthead page.

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Ferrimagnetism in $MnFeF_5\cdot2H_2O$

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The magnetic susceptibility of $MnFeF_5\cdot2H_2O$ was measured at temperatures from 5 to 300 K for applied fields of up to 1 kOe with a SQUID susceptometer. A ferrimagnetic phase transition was observed at 38 ± 0.25 K. At temperatures between 200 and 300 K the susceptibility followed a Curie-Weiss law $\chi = C/(T - \Theta)$ with $\Theta = -164$ K and an effective magnetic moment of 7.4 ± 0.1 μ_B. The Mössbauer resonance spectrum gave a quadrupole-split doublet with an isomer shift of 0.483 mm/s relative to α-iron, indicating that all of the iron was Fe^{3+}.

Introduction

Fluoride complexes of the transition metals have been studied extensively in recent years. A large number of compounds $M^{II}M^{III}F_5\cdot7H_2O$ are known, where M^{II} is the divalent ion of Mn, Fe, Co, Ni, or Zn and M^{III} is the trivalent ion of Cr, V, Mn, Fe, or Al. The related dihydrates have been formed from the heptahydrates by thermal decomposition[1-5] and by precipitation from solution.[6]

Mössbauer-effect measurements of the mixed-valence iron fluoride dihydrate ($Fe_2F_5\cdot2H_2O$) reported by Imbert et al.[7] and by Balcerek et al.[5] along with magnetic susceptibility measurements by Jones and Dawson[8,9] and Walton et al.[10] showed ferrimagnetic ordering below 48.5 K. Susceptibility measurements of the dihydrate $CoFeF_5\cdot2H_2O$ by Jones and Dawson[11] showed it also to be ferrimagnetic at temperatures below 27 K. We have investigated the low-temperature magnetic susceptibility of the related dihydrate $MnFeF_5\cdot2H_2O$ to determine if it too undergoes similar magnetic ordering. Mössbauer resonance spectra verified the valence state of the iron ions.

Experimental Section

$MnFeF_5\cdot2H_2O$ was prepared by mixing HF solutions of Mn(II) and Fe(III). The crystalline product precipitated at 80 °C was the dihydrate;[6] other samples were prepared by crystallization at room temperature and dehydration at 140 °C under vacuum. The identity of the samples was verified by X-ray diffraction patterns,[4] which were completely identified for $MnFeF_5\cdot2H_2O$ up to $2\theta = 52°$ and agreed well with the literature for both position and intensity of the lines. No extraneous lines were found; thus the compound was well identified.

The magnetic susceptibility measurements were made with an SHE Model VTS-805 superconducting quantum interference device (SQUID) susceptometer. The polycrystalline powder samples were placed in a fused-quartz container for the magnetic measurements. The measurements were made over the temperature range of 5-300 K at applied fields of up to 1 kOe.

Mössbauer resonance studies were performed at room temperature on a spectrometer operated in the constant-acceleration mode and employing transmission geometry. The samples were sealed in paraffin and mounted on aluminum foil.[5] The source consisted of ^{57}Co diffused into a rhodium matrix. Calibration spectra were made by using an NBS standard absorber of sodium nitroprusside.

Results and Discussion

The temperature dependence of the reciprocal molar susceptibility of $MnFeF_5\cdot2H_2O$ is shown in Figure 1 for temperatures between 5 and 300 K at an applied magnetic field of 100 Oe. Measurements at an applied field of 1 kOe gave identical results within experimental uncertainties. The curve displays the characteristic shape of a ferrimagnet and indicates a transition near 38 K. In the molecular field approximation for temperature above the phase transition, the reciprocal susceptibility of a ferrimagnet may be described by[12]

$$\frac{1}{\chi} = \frac{(T - T_c)(T - T_c')}{C(T - \Theta')} \tag{1}$$

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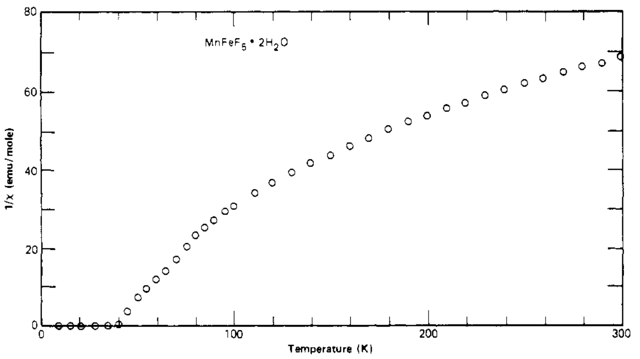

Figure 1. Reciprocal susceptibility of $MnFeF_5 \cdot 2H_2O$ as a function of absolute temperature for temperatures above the Néel point.

Table I. Summary of Magnetic Data

sample	T,[a] K	Θ,[b] K	μ_{eff}, μ_B exptl	μ_{eff}, μ_B calcd[c]	T_c,[d] K
$Fe_2F_5 \cdot 2H_2O$[e]	94–300	−138	7.5 ± 0.1	7.68	48.4 ± 0.25
$CoFeF_5 \cdot 2H_2O$[f]	80–296	−56	6.8 ± 0.1	7.08	27.0 ± 0.25
$MnFeF_5 \cdot 2H_2O$	200–300	−164	7.4 ± 0.1	8.37	38.0 ± 0.1

[a] Temperature region of Curie–Weiss fit. [b] Constant from Curie–Weiss law $\chi = C/(T - \Theta)$. [c] Effective moment calculated for spin-only values. [d] Ordering temperatures. [e] Jones, E. R., Jr.; Dawson, R. *J. Chem. Phys.* **1978**, *69*, 3289. [f] Jones, E. R., Jr.; Dawson, R. *J. Chem. Phys.* **1979**, *71*, 202.

where T_c, T_c', and Θ' are functions of the molecular field. Equation 1 describes a hyperbola for which the susceptibility approaches the Curie–Weiss behavior at high temperatures and diverges at the ferrimagnetic Néel temperature T_c. At the high-temperature limit, eq 1 reduces to the Curie–Weiss form

$$1/\chi = (T - \Theta)/C \qquad (2)$$

where the effective Curie–Weiss temperature Θ is related to the constants in eq 1 by

$$\Theta = T_c + T_c'\Theta' \qquad (3)$$

Attempts to fit the data of Figure 1 with eq 1 over the entire temperature range using the Statistical Analysis Systems[13] (SAS) routines for nonlinear curves were not satisfactory. A fit to the data above 150 K required unreasonably large values for T_c but gave values for C that yielded a magnetic moment of 8.4 ± 0.4 μ_B. However, attempts to fit only the data below 150 K were not successful.

For temperatures above 200 K, a fit of the Curie–Weiss law (eq 2) to the data gave an effective magnetic moment of 7.4 ± 0.1 μ_B and $\Theta = -164 \pm 5$ K. This value of the magnetic moment is smaller than the value obtained from eq 1, as might be expected since the reciprocal susceptibility has not yet reached the high-temperature asymptote. Both values of the effective moment may be compared to the spin-only value of 8.37 μ_B predicted for two independent paramagnetic ions of Mn(II) and Fe(III), which give a resulting moment of

$$\mu = (\mu_a^2 + \mu_b^2)^{1/2} \qquad (4)$$

where μ_a and μ_b are the magnetic moments of the individual ions. The magnetic data are summarized in Table I, where the effective moment was taken from the fit to Curie–Weiss law.

Precise determination of the transition temperature T_c was obtained from the magnetization curve, Figure 2. In the region immediately below the transition temperature a small argument expansion of the Brillouin function yields

$$[\sigma(T)/\sigma(0)]^2 = A[1 - T/T_c] \qquad (5)$$

where σ is the specific magnetization, T_c is the Néel temperature, and A is a constant. When the magnetic data were presented as $[\sigma(T)/\sigma(0)]^2$ vs. T, a straight line resulted as seen in Figure 3. From the intercept of this line the transition temperature was

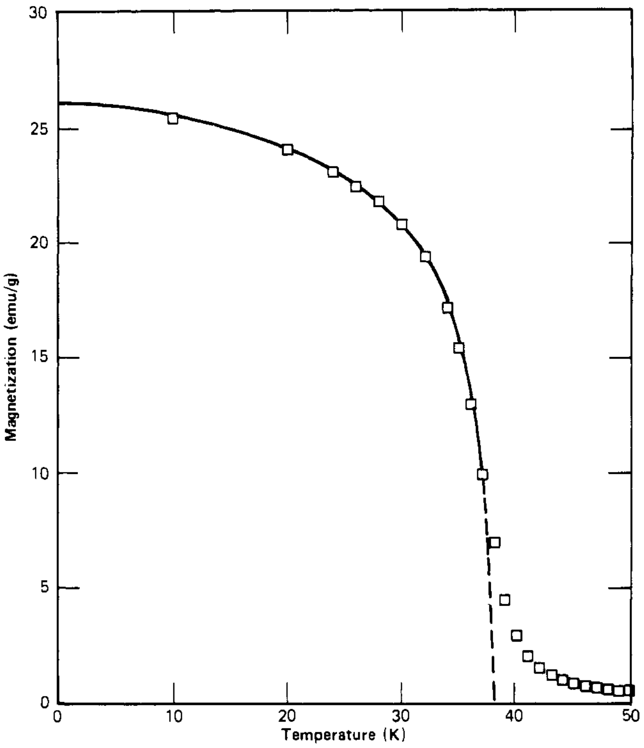

Figure 2. Specific magnetization vs. temperature for $MnFeF_5 \cdot 2H_2O$.

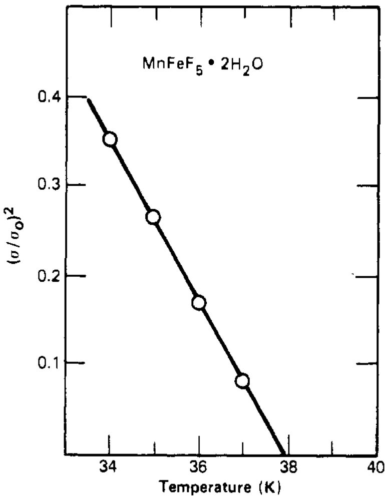

Figure 3. Determination of the Néel temperature in $MnFeF_5 \cdot 2H_2O$ from the intercept of $(\sigma/\sigma_0)^2$ vs. absolute temperature.

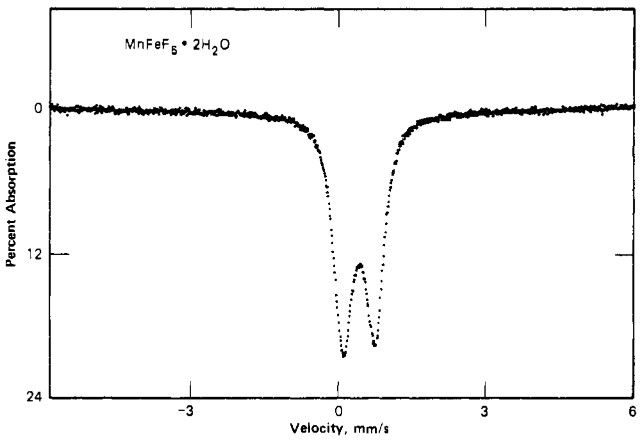

Figure 4. Mössbauer spectrum of $MnFeF_5 \cdot 2H_2O$ at 295 K.

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Table II. Summary of Mössbauer Data

sample		δ,[a] mm/s	Δ, mm/s	temp, K	ref
$Fe_2F_5 \cdot 2H_2O$	Fe(II)	1.34	2.44	295	*b*
	Fe(III)	0.44	0.65		
$Fe_2F_5 \cdot 2H_2O$	Fe(II)	1.215	3.284	297	*c*
	Fe(III)	0.393	0.590		
$CoFeF_5 \cdot 2H_2O$		0.399	0.589	297	*c*
$MnFeF_5 \cdot 2H_2O$		0.483	0.56	295	

[a] Isomer shifts are with respect to α-iron. [b] Walton, E. G.; Brown, D. B.; Wong, H.; Reiff, W. M. *Inorg. Chem.* **1977**, *16*, 2425. [c] Balcerek, T. W.; Cathey, L.; Karraker, D. G. *J. Inorg. Nucl. Chem.* **1978**, *40*, 773.

determined to be 38.0 ± 0.25 K.

The field dependence of the magnetization was measured for several temperatures between 37 and 52 K for fields from 100 to 800 Oe. At temperatures above 40 K the magnetization isotherms showed a linear paramagnetic behavior.

Because there were difficulties in the fit of eq 1 to the data and because the measured effective moment obtained from eq 3 was somewhat lower than expected, Mössbauer-effect studies of $MnFeF_5 \cdot 2H_2O$ were undertaken to determine the valence states of the iron ions. The Mössbauer spectrum obtained at room temperature (295 K) displayed a pair of closely spaced absorption lines, as shown in Figure 4. These lines are interpreted as a quadrupole doublet with a splitting Δ = 0.568 mm/s. The position of the center of the doublet, which corresponds to an isomer shift of 0.483 mm/s relative to α-iron, confirms that there is only one type of iron ion present, viz., Fe(III). The Mössbauer parameters of $MnFeF_5 \cdot 2H_2O$ are compared with those of $Fe_2F_5 \cdot 2H_2O$ in Table II.

Extrapolation of the magnetization data gave a saturation moment of 1.13 μ_B/formula unit. This value is quite close to the value $\mu_{sat} = 1.2\ \mu_B$ reported for $Fe_2F_5 \cdot 2H_2O$.[10] In our experiment, however, the interpretation is not so straightforward because the magnetic moments of the iron and the manganese are expected to be nearly identical. The simple model of negative exchange between M(II) and M(III) that accounted for ferrimagnetism in $Fe_2F_5 \cdot 2H_2O$ would predict antiferromagnetism in $MnFeF_5 \cdot 2H_2O$. Thus there must be a more complicated arrangement of magnetic sublattices, which results in the average saturation moment observed.

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Magnetic Susceptibility and Mössbauer Study of $Mg_4FeH_6Br_{3.5}Cl_{0.5}(C_4H_8O)_8$

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Room-temperature Mössbauer spectroscopic measurements and magnetic susceptibility measurements between 298 and 80 K indicate that the iron(II) in $Mg_4FeH_6Br_{3.5}Cl_{0.5}(C_4H_8O)_8$ is consistent with a $^1A_1$ ground term. The isomer shift is +0.02 mm/s with no evidence of a quadrupole split. Residual paramagnetism of uncertain origin was observed.

Introduction

In 1977 Gibbins reported the formation of $Mg_4FeH_6Br_{3.5}Cl_{0.5}(C_4H_8O)_8$, abbreviated as YCS in this paper, by reacting $FeCl_3$ with excess hydrogen and phenylmagnesium bromide followed by vapor phase extraction with tetrahydrofuran.[2] The product was a yellow crystalline solid that was air and water sensitive. More recently Bau et al. analyzed the compound by single-crystal X-ray and neutron diffraction methods and discovered that the iron was six-coordinate with respect to the hydrogen, forming a hexahydridoferrate(II) unit, $[FeH_6]^{4-}$.[3,4]

This study was a natural extension of the work done by some of us with some group 8[29] transition-metal ternary hydrides, in particular the ruthenium ternary metal hydrides of the form M_2RuH_6, where M = Ca, Sr, Eu, Yb.[5-7] Like the iron, the ruthenium in each of the four compounds is six-coordinate with respect to the hydride ions and possesses a +2 oxidation state. The magnetic and Mössbauer[8] results confirmed the oxidation state and structural assignments. Ruthenium(II) is always found in a low-spin configuration, presumably due to the large ligand field splitting of the two degenerate subsets of d orbitals. In the case of octahedrally coordinated Fe(II), four categories have been observed: (a) high-spin complexes with a spin quintet ground state, $^5T_2$; (b) intermediate-spin complexes with a spin triplet ground state, $^3T_1$; (c) spin crossover systems in which an equilibrium exists between $^5T_2$ and $^1A_1$; (d) a low-spin category with a singlet spin ground state, $^1A_1$.[9] The specific category adopted by the iron is governed by the nature of the coordinating ligands. For example, low-spin iron(II) is found for those complexes in which the ligands are CN^-, CNO^-, NO_2^-, bipyridyl, diarsine, or some of their mixed derivatives.[10-15] Magnetic susceptibility and Mössbauer measurements are used to identify the spin configuration of the ground state.

Traditionally, the position of the hydride ion in the spectrochemical series suggests that it exerts a strong ligand field. Bancroft and his co-workers[16] have shown in their study of the Mössbauer spectra of a large number of iron(II) low-spin com-

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