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 $\Delta = 0.568$ 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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pounds that the hydride ion occupies a position near or above that of the cyanide ion in the spectrochemical series. It has been recently reported that the magnetic and Mössbauer measurements of Mg_2FeH_6 seemed to indicate that the compound is diamagnetic and the iron adopts a low-spin arrangement.[17]

YCS is the first reported example of a first-row d-block transition-metal hydrido complex in which the coordination sites are occupied entirely by hydrogen. We therefore became interested in the magnetic and Mössbauer parameters as a way of ascertaining the spin configuration of the iron in this interesting compound.

Experimental Section

The method used for the Faraday type magnetic susceptibility measurement of the YCS compound followed the procedure previously described by Thompson, Moyer, and Lindsay.[6] The data were taken over a range of six field strengths from 3000 to 8250 Oe and at 10° temperature intervals from 78 to 295K. The sample of YCS is extremely air sensitive. Therefore, high-vacuum techniques were used to transfer the sample as received in an evacuated ampule to a Pyrex glass tube designed specifically for magnetic susceptibility studies. The tube was approximately 9 cm long. The bottom part of the tube, 5 cm in length, was 2.5 mm in i.d. and 4 mm in o.d. The top half was 5 mm in i.d. and 7 mm in o.d. The sample after transfer to the 2.5 mm i.d. bottom half of the tube was about 13 mm in length and weighted 46.7 mg. Once the transfer was completed, the 2.5 mm i.d. tube was sealed off from the remainder of the tube about 4 cm above the base. When the magnetic susceptibility measurements of the sample were completed, the tube was placed in a glovebox. Under an atmosphere of dry nitrogen the tube was broken in half and the sample was transferred into a Teflon sample holder, covered with a Teflon top, and sealed with epoxy resin for subsequent Mössbauer analysis. The sample mass was determined by difference. The halves of the Faraday tube were then sealed together with a very thin film of Duco Cement (<1 mg). The magnetic correction for the empty tube was determined under the same conditions as the sample. The following values for the diamagnetic corrections in emu were applied: 6 H^-, -31.8×10^{-6}; Fe(II), -13×10^{-6}; 4 Mg(II), -12×10^{-6}; 3.5 Br^-, -126×10^{-6}; 0.5 Cl^-, -13×10^{-6}; 8 THF, -416.4×10^{-6}.[18,19] The total diamagnetic correction was -612.2×10^{-6} emu/mol. The gram molecular mass of the YCS was taken as 1033 g in converting between gram and molar susceptibility.[2]

Mössbauer data of the YCS sample were collected over 512 channels of the multichannel analyzer for 25 h. The source was 80-mCi $^{57}Co/Pd$ purchased from New England Nuclear Corp. The sample was kept at room temperature during the run; the velocity range was 8.5 to −8.5 mm/s. Further details concerning the Mössbauer spectrometer and the Lorentzian curve-fitting program can be found elsewhere.[20]

Results and Discussion

We believe the susceptibility data, taken in conjunction with the Mössbauer data, are generally consistent with iron(II) in the YCS sample being present in a low-spin configuration. However, there are some uncertainties posed by a residual paramagnetism and the apparent presence of a small temperature-dependent ferromagnetic impurity.

The corrected molar magnetic susceptibility, χ_M, of YCS showed a dependence on field strength, H, which was linear in form within experimental error when plotted against $1/H$. This result was interpreted as indicating the presence of a small ferromagnetic impurity. The method of Honda and Owen[21] was used to determine the field-independent molar susceptibility, $\chi_{m\infty}$. $\chi_{m\infty}$ was obtained by fitting the field-dependent data vs. $1/H$ to a straight line with use of the method of least squares. The values of $\chi_{m\infty}$ are plotted as a function of temperature in Figure 1. The standard deviation in $\chi_{m\infty}$ is $\pm 0.2 \times 10^{-3}$ emu/mol and is shown by the single error bar. The possible error in T is ±1 K.

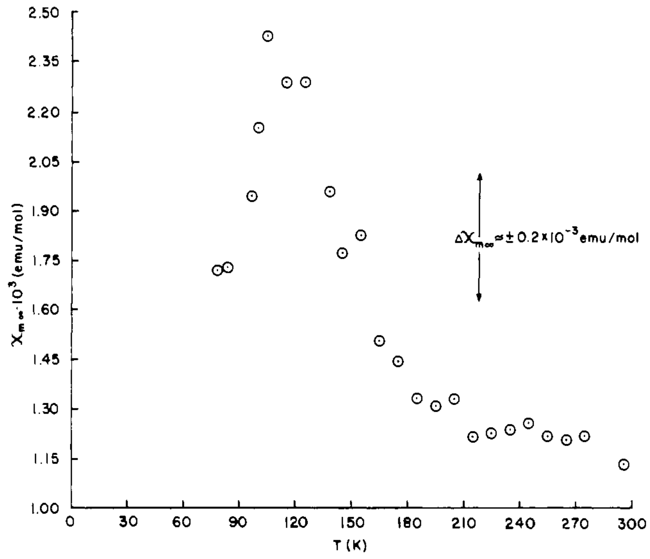

Figure 1. Graph of $\chi_{m\infty} \times 10^{-3}$ (emu/mol) vs. T (K) for $Mg_4FeH_6Br_{3.5}Cl_{0.5}(C_4H_8O)_8$.

The principal feature of the magnetic behavior of the sample is an approximately constant magnetic susceptibility, within the limits of the error bars, from room temperature down to about 180 K. The value is about 1.1×10^{-3} emu/mol in this region. Below 180 K there is a significant increase to a maximum of about 2.4×10^{-3} emu/mol at 125 K followed by a decrease to about 1.7×10^{-3} emu/mol at the lowest available temperature of 78 K.

Ideally in an extremely pure sample containing low-spin iron(II) the only contribution to the magnetic susceptibility should be from the diamagnetism of the ion cores of all the atoms present and from any temperature-independent paramagnetism as described by the Van Vleck theory.[22] The residual paramagnetic susceptibility that was actually observed might be accounted for by one or a combination of the following possibilities: (a) a temperature-dependent residual paramagnetism of unknown origin, (b) impurities, (c) errors in the estimated diamagnetic corrections, and/or (d) slight changes in symmetry. Residual paramagnetism was reported by Baker and Bobonich[23] for $[Fe(phen)_2(CN)_2]\cdot 2H_2O$, a compound with low-spin iron(II), between 297 and 112 K. They reported values of molar susceptibility, corrected for ion core diamagnetism which fluctuated from 235×10^{-6} emu/mol at 297 K to 159×10^{-6} emu/mol at 192 K and to 243×10^{-6} emu/mol at 112 K.

Calculations of the temperature-independent Van Vleck paramagnetism have been made by others[24-26] for transition-metal complexes containing low-spin Co(III). These calculations, which account for the effect of low-lying excited states according to the theory of Van Vleck, indicate that the contribution to the paramagnetic susceptibility could be as high as 200×10^{-6} emu/mol in the Co(III) complexes. There is also evidence that residual paramagnetism can depend on sample preparation and crystallite size.[9,27]

Impurities such as $FeCl_2$, $FeCl_3$, and $FeBr_2$ could also contribute to a paramagnetic background. These compounds are all known paramagnets with sizeable magnetic susceptibilities that follow Curie–Weiss behavior. On the basis of the method of preparation,[2] however, any insoluble impurities of these forms should have been

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removed during the purification process. The analysis for iron confirms these assumptions. As pointed out in the following section, there is about 0.08 mol % iron present in a form which contributes measurably to ferromagnetism.

The estimated diamagnetic correction is a significant fraction of the uncorrected molar susceptibility, with the principal part coming from the THF groups. Errors in these corrections or unaccounted-for changes in these values with temperature would affect the final corrected values of the molar susceptibility of the YCS. The diamagnetic correction was subject to some uncertainty because of the way in which the value for THF was assigned. However, the uncertainty probably does not exceed approximately $\pm 50 \times 10^{-6}$ emu/mol out of a total of 416.4×10^{-6} emu/mol. Bau et al. showed that the room-temperature conformation of the THF rings, characterized as somewhat planar, transformed into the puckered arrangement by the time the temperature had been reduced to 80 K.[4] It is unlikely that this conformational shift would account for more than approximately $\pm 50 \times 10^{-6}$ emu/mol. Thus, the total uncertainty in the diamagnetic correction over the temperature range studied should not have exceeded approximately $\pm 100 \times 10^{-6}$ emu/mol, which is far less than both the magnitude and change with temperature of the susceptibility of YCS.

Slight temperature-dependent shifts in the structural symmetry about the iron site were considered. However, this possibility was ruled out on the basis of the results of the low-temperature neutron diffraction studies of YCS,[4] which did not give any evidence of the O_h symmetry distortion of the $[FeH]_6^{4-}$ units in going from room temperature to 80 K.

The fluctuation in the susceptibility below 180 K with an apparent maximum about 125 K is also difficult to explain. A susceptibility maximum is typical of antiferromagnetism, but none of the constituents or possible impurities are known as antiferromagnetic with Neêl points in that temperature range.

Despite the presence of the residual paramagnetism the possibility of high-spin iron(II) can be ruled out on the basis of the magnitude of the observed susceptibility. If the iron were in the high-spin state, with the effective number of Bohr magnetons being approximately 5 μ_B, the susceptibility would be at least 10 times larger at 295 K and the variation with temperature would be characterized by a fourfold increase at 78 K.

The small ferromagnetic impurity noted above could possibly be contributed by colloidal sized particles of elemental iron and/or ferromagnetic iron oxide, Fe_3O_4. From the measured saturation magnetization of this component of approximately 10 emu/mol, the amount of elemental iron in this sample is estimated to be approximately 0.08 mol %.

The room-temperature Mössbauer spectrum of YCS showed a sharp single line with an isomer shift of +0.02 (1) mm/s. The reference material was metallic α-iron. The χ^2 value for the spectrum fit was 0.94 mm/s, and the line width, Γ, was 0.62 mm/s. No quadrupole splitting was observed, thus indicating the absence of any electric field gradient at the iron nucleus. This nonsplitting singlet is consistent with the O_h symmetry of the $[FeH]_6^{4-}$ units. Both the position of the isomer shift and absence of a quadrupole split are consistent with low-spin iron(II).

The other common oxidation states of iron, high-spin iron(II) and -(III) and low-spin iron(III), were not believed to be present on the basis of the following: (a) the value of the isomer shift, (b) the absence of the quadrupole splitting of the YCS complex, and (c) the well-known Mössbauer isomer shift and quadrupole splitting parameters[28] for these other oxidation states and crystal field orbital occupancies.

These Mössbauer results are entirely consistent with the conclusions drawn from the magnetic susceptibility data. Any impurities or other effects that might give rise to the observed residual paramagnetism may be at such a low concentration that they were not observed in the Mössbauer experiments.

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Syntheses and Variable-Temperature Mössbauer Study of Tin(IV) Cyanide Derivatives

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By reaction of $SnCl_4$ with Me_3SiCN in CCl_4 solution, the compound $SnCl_3CN(Me_3SiCN)$ was obtained. The oxidative-addition reactions of XCN (X = Br, I) to $SnCl_2$ in THF solutions lead to the formation of $SnCl_2XCN(THF)$ (X = Br, I). The three new compounds have bridging cyanide groups as inferred from their IR spectra. By means of a variable-temperature Mössbauer study, a polymeric structure has been proposed for $SnCl_3CN(Me_3SiCN)$ and $SnCl_2BrCN(THF)$, while an oligomeric structure would be possible for $SnCl_2ICN(THF)$. The Goldanskii–Karyagin effect is observed for $SnCl_3CN(Me_3SiCN)$ and might be present, as suggested by computer fitting, in $SnCl_2BrCN(THF)$. During the preparation of this last compound, a solid of approximate composition $SnCl_2BrCN(THF)_{1.5}$ was isolated; its Mössbauer spectra can be explained as a mixture of $SnCl_2BrCN(THF)$ and $SnCl_2BrCN(THF)_2$, suggesting a monomeric structure with the THF ligands in trans position for this last species.

Introduction

Organotin cyanides of the types R_3SnCN and $R_2Sn(CN)_2$ are well-known, but the corresponding inorganic derivatives have received little attention.[2] Organotin cyanides usually have polymeric structures,[3] and the Goldanskii–Karyagin effect has been detected in the Mössbauer spectra of Me_3SnCN.[4] Attempts to prepare $Sn(CN)_4$ from $SnCl_4$ and Me_3SiCN failed, and the formation of mixtures of compounds was observed.[5] Although Me_3SiCN is a useful tool for substitution reactions,[6] it can form

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