# Communications

## Magnetic Ordering in the Linear-Chain Antiferromagnet $K_2[FeF_5(H_2O)]$

*Sir:*

The structural, magnetic, and thermodynamic properties of the $A_2[FeX_5(H_2O)]$ series of compounds, where A = Cs, Rb, K, and $NH_4$ and X = Cl and Br, have recently been of interest.[1-8] In each compound, the iron(III) ion is surrounded by a slightly distorted octahedron, forming $[FeX_5(H_2O)]^{2-}$ groups that interact magnetically in a variety of ways. One of the reasons for studying these compounds is that iron(III) is isoelectronic with manganese(II), whose antiferromagnets are much better known. This is true in part because the syntheses are easier. So much has been learned from the study of the manganese salts that one hopes that further exploration of the iron salts will be equally fruitful. Several of the $A_2$-$[FeX_5(H_2O)]$ compounds are clearly three-dimensional antiferromagnets while several others appear to display lower dimensional interactions. All the compounds exhibit relatively small anisotropy and have spin $S = {}^5/_2$.

We report here a study of $K_2[FeF_5(H_2O)]$, which was expected to exhibit an exchange interaction weaker than that of the other compounds because of the substitution of the halide (Cl or Br) by fluoride. This has proved to be true. The crystal structure[9] gives clear evidence for quasi-one-dimensional superexchange paths, and this compound has indeed been found to be the best example in this series of substances of a linear-chain antiferromagnet. The material indeed appears to provide one of the few examples of a one-dimensional antiferromagnet of iron(III).

This investigation of $K_2[FeF_5(H_2O)]$ is furthermore of interest for other reasons: there are relatively few magnetically ordered compounds of iron(III) known as yet, and there are also relatively few fluoride salts in which magnetic ordering has been found.[10] Both of these small classes of materials are increased by this study. Moreover, it provides a good test
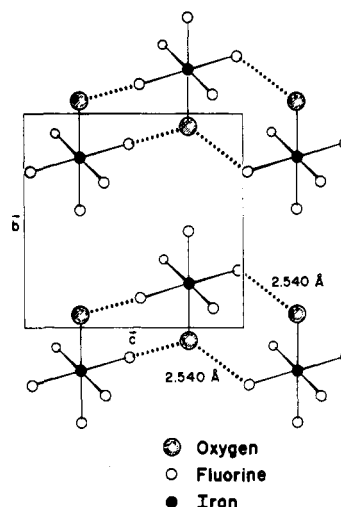


⊙ Oxygen
○ Fluorine
● Iron

**Figure 1.** Hydrogen-bonded chains of metal octahedra in $K_2[FeF_5$-$(H_2O)]$. The dotted lines represent the hydrogen bonds. The unit cell in the *bc* plane is indicated.

for a recently developed theory of lattice-dimensionality crossover in Heisenberg magnets.[11]

**Structural Properties.** The compound was prepared in a fashion similar to that in the earlier report.[9] Single crystals can be grown by slow evaporation of either the mother liquor or aqueous solutions of the compound. However, we observed that crystals obtained from the mother liquor were mostly twinned while good seed crystals could be obtained after 4 months by letting an aqueous solution evaporate slowly. The compound is monoclinic, space group $C2/c$, with $a = 9.71$ Å, $b = 7.79$ Å, $c = 7.95$ Å, $\beta = 96.5°$, and $Z = 4$.[9] The $[FeF_5(H_2O)]^{2-}$ anions are hydrogen bonded in zigzag chains along the $c$ axis, with the $K^+$ lying separately. It is this quasi-one-dimensional structure that suggested the chainlike superexchange path.

The $Fe^{3+}$ ion is in a slightly distorted octahedral coordination with all the $F^-$ ions at distances close to 1.92 Å. The F–Fe–F angles are near 90°. The water molecules complete the octahedral coordination with the oxygen atom in an apical position at 2.07 Å from the $Fe^{3+}$ ion. The arrangement is shown in Figure 1.

**Results.** The magnetic susceptibility of polycrystalline potassium aquopentafluoroferrate(III) has been measured from 4.2 to 280 K. A single crystal was used for measurements below 4.2 K. Measurements along the *b* and *c* axes and in

(1) Carlin, R. L.; Bhatia, S. N.; O'Connor, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 7728–7729.
(2) Paduan Filho, A.; Palacio, F.; Carlin, R. L. *J. Phys., Lett. (Orsay, Fr.)* **1978**, *39*, L279–L281.
(3) O'Connor, C. J.; Deaver, B. S.; Sinn, E. *J. Chem. Phys.* **1979**, *70*, 5161–5167.
(4) Greedan, J. E.; Hewitt, D. C.; Faggiani, R.; Brown, I. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 1927–1929.
(5) Palacio, F.; Paduan Filho, A.; Carlin, R. L. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 296–298.
(6) McElearney, J. N.; Merchant, S. *Inorg. Chem.* **1978**, *17*, 1207–1215.
(7) Carlin, R. L.; O'Connor, C. J. *Chem. Phys. Lett.* **1981**, *78*, 528–530.
(8) Puertolas, J. A.; Navarro, R.; Palacio, F.; Bartolome, J.; Gonzalez, D.; Carlin, R. L. *Phys. Rev. B: Condens. Matter* **1982**, *26*, 395–403.
(9) Edwards, A. J. *J. Chem. Soc., Dalton Trans.* **1972**, 816–818.
(10) Reedijk, J.; ten Hoedt, R. W. M. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 49–57.

(11) Puertolas, J. A.; Navarro, R.; Palacio, F.; Bartolome, J.; Gonzalez, D.; Carlin, R. L. *J. Magn. Magn. Mater.* **1983**, *31–34*, 1243–1245; *Phys. Rev. B: Condens. Matter*, in press.
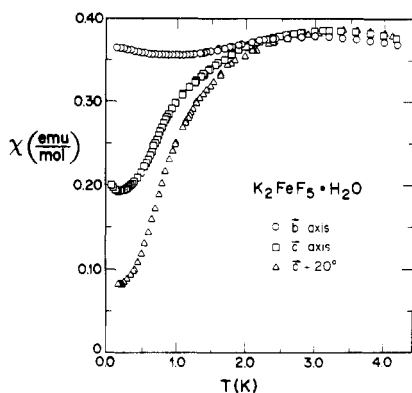
**Figure 2.** Zero-field magnetic susceptibilities of $K_2[FeF_5(H_2O)]$ below 4.2 K. The $b$ axis is the hard one, and the others, $c$ and $c + 20°$, form angles of 50 and 30°, respectively, with the easy axis of the magnetization.

another direction in the $ac$ plane were carried out down to 50 mK in a $^3He$–$^4He$ dilution refrigerator[12] and are shown in Figure 2. The system is quite isotropic down to 3 K. At lower temperatures the susceptibility gradually becomes anisotropic with a minimum found at an angle of 50° from $c$. Zero-field magnetic susceptibility measurements were taken from 1.1 to 4.2 K along the three principal axes and the others used in the low-temperature measurements.

The $b$ axis was found to be the hard axis with the susceptibility remaining fairly constant below 3 K. The three data sets, along each axis, show a maximum at $T_m = 3.4 \pm 0.2$ K with a slightly lower magnitude for the $b$-axis data and an average value of $\chi_m = 0.383$ emu/mol. At $T_c = 0.80 \pm 0.05$ K the slope of the susceptibility has an inflection point in the two directions measured perpendicular to $b$. The system undergoes long-range antiferromagnetic ordering with the preferred direction of spin alignment in the $ac$ plane, pointing at 50° from $c$ toward $-a$.

**Data Analysis.** The $3d^5$ electronic configuration of the $Fe^{3+}$ ion, much like isoelectronic $Mn^{2+}$, gives an isotropic spin $S = 5/2$ magnetic interaction. Compounds similar to the one reported here for which the anisotropy has been measured give values for $\alpha$ between $10^{-2}$ and $10^{-3}$,[5] where $\alpha$ is the ratio of the anisotropy field to the exchange field. We therefore chose an isotropic Heisenberg Hamiltonian for the data analysis. Following the comments presented above concerning the likely superexchange path, and also from the broad maximum observed in the data, we fitted the experimental points to the linear-chain model. Although there is not available an exact result for $S = 5/2$ systems, Fisher[13] has calculated the exact solution for a classical ($S = \infty$) linear chain, normalized for finite spins, which is given by

$$\chi = \chi_C \frac{1 + u(K)}{1 - u(K)}$$

$$u(K) = \coth K - \frac{1}{K} \qquad K = \frac{2JS(S + 1)}{k_B T}$$

The quantity $\chi_C$ is the Curie law susceptibility for spin $S$.

The application of the classical approximation for real systems is known to be reliable for large values of the spin such as in this case, $S = 5/2$.

The experimental results from 280 down to 10 K can be fitted to these theoretical values with an error less than 1% over the whole region with a Landé $g$ factor, typical for the ferric ion, of $1.97 \pm 0.02$ and an exchange constant of $J/k_B$
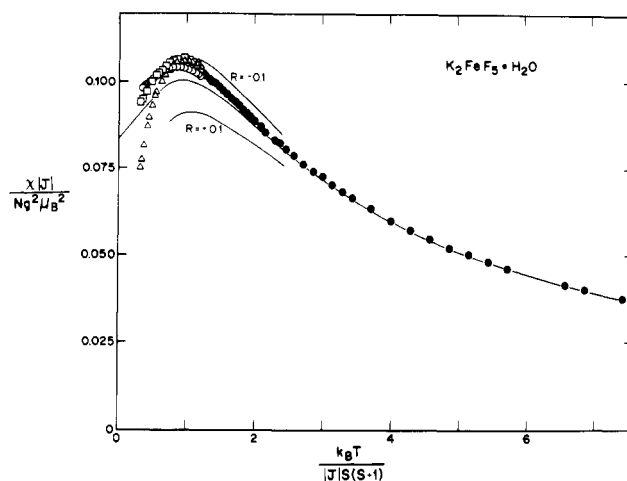


**Figure 3.** Zero-field susceptibilities of $K_2[FeF_5(H_2O)]$ in the paramagnetic region. The solid symbols are data points that have been taken on powders, while the open ones represent the measurements in the three principal directions. The continuous line is the solution for the classical Heisenberg linear chain, as described in the text, and the values of $R$ give the calculated three-dimensional crossover with ferro- and antiferromagnetic interchain constants.

$= -0.40 \pm 0.02$ K. The theoretical curve together with the experimental results in the most significant temperature region are represented in Figure 3.

An alternative approach is to use the high-temperature series expansions for the susceptibility. For an $S = 5/2$ Heisenberg linear chain there are six terms available in the expansion.[14] The theoretical prediction practically coincides in the given temperature range with the classical approach. At temperatures below 10 K the data points increasingly deviate to values higher than the theoretical ones; at low temperatures, interchain interactions become important and long-range magnetic order occurs with the parallel susceptibility dropping to zero.

A consideration of the transition temperature $T_c = 0.80$ K following the Green's function approach[15] of Oguchi yields a value for $R = |J'/J| = 1.4 \times 10^{-2}$, where $J'$ represents the interchain interactions. This value must be taken only as an indication of the order of magnitude of $R$ because of the simplifications of the model.

The one-dimensional magnetic character is not ideal. Weak interactions of the metal ions with their next-nearest neighbors become important below 10 K, and the correlation between magnetic moments on different chains produces a lattice dimensionality crossover from a linear-chain system to an anisotropic simple cubic lattice.

In the case of nonnegligible interchain interaction we must consider the Heisenberg Hamiltonian with two different types of neighbors

$$\mathcal{H} = -2J\sum_{i,j}{}^{(d)}\vec{S}_i \cdot \vec{S}_j - 2J\sum_{i,j}{}^{(3-d)}\vec{S}_i \cdot \vec{S}_j$$

where the first summation runs over nearest neighbors in $d$ lattice directions and the second is along the other $3 - d$ directions. In the present case, $d = 1$. The only high-temperature series expansion calculated for this model has been done in the classical limit $S = \infty$.[16] The series has been analyzed recently for several values of $R = (J'/J)$ and extrapolated to the values at the maximum with use of Padé approximants.[11] The case of a lattice-dimensionality crossover from a linear-chain system to a simple cubic lattice was studied by calculating the height of the reduced susceptibility maxi-

(12) van der Bilt, A.; Joung, K. O.; Carlin, R. L.; de Jongh, L. *J. Phys. Rev. B: Condens. Matter* **1980**, *22*, 1259–1262.
(13) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343–346.

(14) Rushbrooke, G. S.; Wood, P. J. *Mol. Phys.* **1958**, *1*, 257–283.
(15) Oguchi, T. *Phys. Rev.* **1964**, *133*, A1098–A1099.
(16) Lambeth, D. N.; Stanley, H. E. *Phys. Rev. B: Solid State* **1975**, *12*, 5302–5314.

mum $\chi_m|J|/Ng^2\mu_B^2$ and temperature $k_BT_m/|J|S(S+1)$ for different values and signs of $J$ and $J'$. Then the susceptibility was developed as a function of temperature near the maximum for suitable values of the interchain interaction.

From the experimental measurements we get from the average susceptibility in the three main directions

$$\frac{\chi_m|J|}{Ng^2\mu_B^2} = 0.105 \pm 0.001 \qquad \frac{k_BT_m}{|J|S(S+1)} = 1.00 \pm 0.05$$

The fact that the reduced susceptibility is higher than the corresponding one for the pure linear-chain antiferromagnet implies the presence of some ferromagnetic interaction. (Recall that the intrachain interaction was found from the high-temperature analysis to be antiferromagnetic.)

Taking $J < 0$ and $J' > 0$, we obtained the same value of $R$ from both experimental parameters $\chi_m$ and $T_m$. The rounded maximum typical of an antiferromagnet does not define accurately the temperature of the maximum and then allows a range of values for $R$, and we get $R = -0.05 \pm 0.05$. The value of the susceptibility at the maximum is known with more precision, and it yields $R = -0.06 \pm 0.02$. The interchain interaction is small enough for the compound to behave as a good linear chain above the temperature $2T_m$ yet is sufficiently high to allow the observation of the crossover effects in the paramagnetic region and make quantitative comparisons with the theory. The detailed analysis will be presented elsewhere, together with complementary measurements of the heat capacity.

**Registry No.** $K_2[FeF_5(H_2O)]$, 35848-60-3.

---

(17) Present address: Departamento de Termologia, Universidad de Zaragoza.
(18) Departamento de Fisica, ETSIIZ.
(19) Departamento de Termologia.

Department of Chemistry                    **Richard L. Carlin***
University of Illinois at Chicago           **Ramon Burriel**[17]
Chicago, Illinois 60680

Departamento de Fisica, ETSIIZ, e          **J. A. Rojo**[18]
Departamento de Termologia                 **Fernando Palacio**[19]
Universidad de Zaragoza
Zaragoza, Spain

---

# DNA Degradation by Manganese(II)–Bleomycin plus Peroxide

*Sir:*

The DNA-cleaving activity of bleomycin,[1] an antitumor glycopeptide antibiotic, had been shown in vitro to depend on the formation of activated bleomycin, a drug complex containing Fe(III) and oxygen.[2,3] This complex can be formed
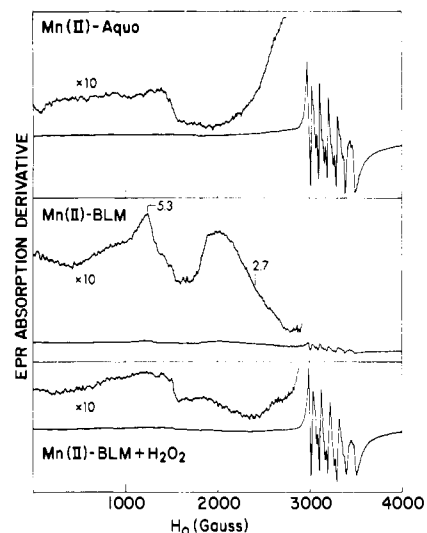
(1) Umezawa, H. In "Anticancer Agents Based on Natural Product Models"; Cassady, J. M., Duros, J. D., Eds.; Academic Press: New York, 1980; pp 147–166. Suzuki, H.; Nagai, K.; Yamaki, H.; Tanaka, N.; Umezawa, H. *J. Antibiot.* **1969**, *22*, 446–448.
(2) Sausville, E. A.; Peisach, J.; Horwitz, S. B. *Biochem. Biophys. Res. Commun.* **1976**, *73*, 814–822. Kuramochi, H.; Takahashi, K.; Takita, T.; Umezawa, H. *J. Antibiot.* **1981**, *34*, 576–582.



**Figure 1.** EPR spectrum of Mn(II)–bleomycin. Samples contain 0.2 mM Mn(II), 10 mM Hepes buffer (pH 8.2), 50% (v/v) ethylene glycol and, where indicated, 0.3 mM bleomycin or bleomycin plus 100 mM $H_2O_2$. Spectra were taken at 77 K on a Varian Model E-12 EPR spectrometer operated at 9.07 GHz, 10-mW power, with 20-G field modulation. Identical spectrometer gain settings were used for all samples; ×10 denotes spectra taken with 10-fold enhanced gain. Values of $g$ are given in the middle panel. An additional broad, $g_{min}$ = 1.3 feature seen with Mn(II)–bleomycin is not shown here.

with Fe(III) and peroxide, Fe(III) plus reductants and $O_2$, or Fe(II) and $O_2$. Other metals gave no detectable DNA degradation in $O_2$-dependent reactions, and many inhibit the iron-requiring reaction.[4] We now report DNA degradation by Mn(II)–bleomycin in the presence of $H_2O_2$. This activity is not due to endogenous iron salts and differs from that of iron–bleomycin in several respects. DNA does not inhibit the Mn(II)–bleomycin reaction, as it does the iron–bleomycin reaction, but optimal activity is only 1–3% of that of the Fe(III)-drug complex with $H_2O_2$. DNA products include free bases and base propenals,[5] as with iron bleomycin, but in different proportions. Aerobic solutions of reducing agents such as 2-mercaptoethanol cannot substitute for peroxide in the reaction with Mn(II) as they do in the reaction with Fe(III). In this respect, Mn(II)–bleomycin parallels the behavior of Mn(II)–cytochrome P-450, which cannot be activated reductively but can be activated with peroxides.[6]

Like many transition-metal ions, Mn(II) forms a complex with bleomycin, as indicated by its EPR spectrum (Figure 1). When bleomycin is added to Mn(II) solutions at pH >7.5, the characteristic resonance of aquo–Mn(II) near $g = 2$ gives way to one with features near $g = 5.3$, 2.7, and 1.3. Subsequent addition of $H_2O_2$ changes the EPR spectrum to resemble that of Mn(II)–aquo near $g = 2$ but with broad differences apparent elsewhere at higher spectrometer gain. This material differs from Mn(II)–aquo and Mn(II)–bleomycin in producing base propenal from DNA.

When Mn(II) was surveyed for activity with bleomycin, a spectrophotometric assay we had used for iron–bleomycin activity[7] was adapted. This assay is based on the reaction of

(3) Burger, R. M.; Peisach, J.; Horwitz, S. B. *J. Biol. Chem.* **1981**, *256*, 11636–11644.
(4) Dabrowiak, J. C. *Adv. Inorg. Chem.* **1982**, *4*, 69–113.
(5) The trivial name base propenal denotes compounds of the form 3-(pyridin-1-yl)-2-propenal and 3-(purin-9-yl)-2-propenal, characterized as bleomycin-induced DNA products by: Giloni, L.; Takeshita, M.; Johnson, F.; Iden, C.; Grollman, A. P. *J. Biol. Chem.* **1981**, *256*, 8608–8615.
(6) Gelb, M. H.; Toscano, W. A., Jr.; Sligar, S. G. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 5758–5762.
(7) Burger, R. M.; Peisach, J.; Blumberg, W. E.; Horwitz, S. B. *J. Biol. Chem.* **1979**, *254*, 10906–10912.