product **2b** (oil) showed IR (film) 5.74 (C═O) μ; NMR (CCl_4) δ 2.13–1.77 (m, 4 H, CHs and allylic CH_2), 1.70 (br s, 3 H, vinyl CH_3), 1.63 (br s, 3 H, vinyl CH_3), 1.25–0.85 (m, 16 H, CH_3 and C_2H_5); mass spectrum parent (70 eV) *m/e* 274.

(9) Similar shift reagent studies on **2a** gave rise to a clear increasingly downfield-shifted one-proton quartet (*J* = 7 Hz) indicating that, had the rearrangement product from **1b** been **2b′**, it could have been detected.

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(11) Both **2** (X = Y = H; Z = CH_3) and **5** (X = Y = H; Z = CH_3) have previously been characterized and are readily available via photolysis of 6,7-dimethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone.[5] To date, compound **5** (X = Y = Z = CH_3) has not been detected in the rearrangement of **1a**.

(12) Irradiation of the duroquinone–butadiene Diels–Alder adduct, mp 55.0–55.5 °C, in benzene afforded cyclobutanone **1** (X = Y = CH_3; Z = H) in essentially quantiative yield: mp 75.5–76.5 °C; IR (CCl_4) 5.64, 5.82 (C═O) μ; NMR ($CDCl_3$) δ 5.94 (m, 2 H, vinyls), 2.65 (q, *J* = 7.5 Hz, 1 H, acidic CH), 2.30 (m, 1 H, allylic CH), 2.13 (m, 2H, allylic CH_2), 1.22 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 1.11 (d, *J* = 7.5 Hz, 3 H, C-4 CH_3), 1.06 (s, 3 H, CH_3); mass spectrum parent (70 eV) *m/e* 218. The rearrangement product **2** (X = Y = CH_3; Z = H), mp 71.5–72.5 °C, showed IR (CCl_4) 5.74 (C═O) μ; NMR ($CDCl_3$) δ 5.81 (m, 2 H, vinyls), 2.39 (d, *J* = 6 Hz, 1 H, allylic CH), 2.20 (q, *J* = 7.5 Hz, 1 H, exchangeable CH), 2.09 (m, 2 H, CH_2), 1.20 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 0.89 (d, *J* = 7.5 Hz, 3 H, *endo*-CH_3), 0.80 (s, 3 H, CH_3); mass spectrum parent (70 eV) *m/e* 218. Catalytic hydrogenation of **1** (X = Y = CH_3; Z = H) afforded compound **6**: mp 46.5–48.5 °C; IR (CCl_4) 5.65 and 5.83 (C═O) μ; NMR ($CDCl_3$) δ 2.86 (q, *J* = 7.5 Hz, 1 H, exchangeable CH), 1.90 (m, 3 H), 1.60 (m, 4 H), 1.16 (s, 6 H, CH_3s), 1.13 (d, *J* = 7.5 Hz, 3 H, C-4 CH_3), 1.05 (s, 3 H, CH_3); mass spectrum parent (70 eV) *m/e* 220.

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A New Series of Antiferromagnets

Sir:

We report here the preparation, characterization, and magnetic behavior of a series of compounds of iron(III), $A_2FeX_5{\cdot}H_2O$, where A is an alkali ion and X is chloride or bromide. Although the materials contain discrete octahedra, they exhibit certain features of lower dimensional magnets at low temperatures, and they all undergo long-range magnetic ordering at easily accessible temperatures. The variation of the critical temperature, T_c, as the constituent ions A and X are changed exhibits the influence of the size and polarizability of the A and X ions, respectively.

The crystals are easily grown by slow evaporation from acidic solution of the appropriate alkali halide and ferric halide. They have been characterized by elemental analysis and crystallographic procedures (precession camera) that lead to the unit cell information presented in Table I.[1] Complete crystal structures of $(NH_4)_2[InCl_5{\cdot}H_2O]$,[2] $(NH_4)_2[FeCl_5{\cdot}H_2O]$,[3] and $K_2[InCl_5{\cdot}H_2O]$[4] have been reported in which discrete octahedral $[MCl_5(H_2O)]^{2-}$ ions are observed. The water molecules are not oriented randomly, but occupy particular corners of the octahedra that lie on the symmetry planes in the cell. All these orthorhombic materials as well as those reported here appear to be isostructural. The indium compounds are well known as hosts for EPR studies of metal ions, including iron.[5] The compound $Cs_2FeCl_5{\cdot}H_2O$ appears to be isostructural with $Cs_2RuCl_5{\cdot}H_2O$.[6]

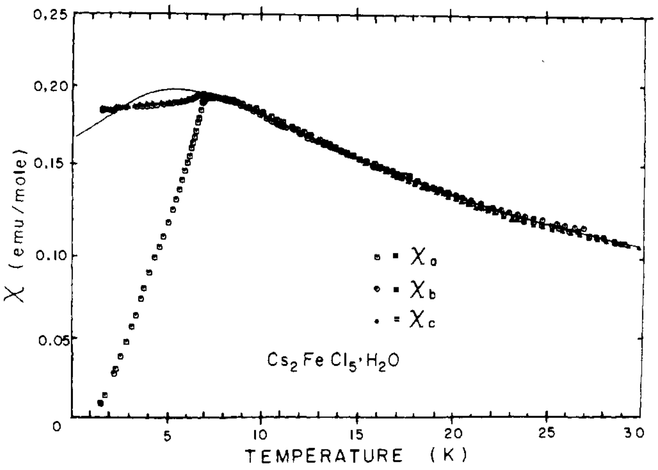

Figure 1. Magnetic susceptibility of $Cs_2FeCl_5{\cdot}H_2O$ along the three crystal axes. Fitted curve is described in the text.

The three orthogonal, isothermal susceptibilities of $Cs_2FeCl_5{\cdot}H_2O$ are illustrated in Figure 1; the data are representative of all those in the series. The results appear to indicate a normal three-dimensional antiferromagnetic ordering, T_c = 6.43 ± 0.05 K, with the *a* axis the preferred axis of spin alignment. Little or no anisotropy is apparent in the data above T_c, suggesting that this could be a Heisenberg model system.[7,8] It is apparent, however, that the magnitude of the susceptibilities throughout the paramagnetic region is too small to be fit in a straightforward fashion; though the data illustrated can in fact be fit by the Curie–Weiss law above 10–12 K, with a reasonable *g* value of 2.08 for $S = {}^5/_2$, the derived Weiss constant θ is −14.6 K (antiferromagnetic). This is too large a value to accept as a valid limiting asymptote from the data presented, for the highest temperature accessible to us is 30 K, or only about $2|\theta|$.[9] The zero-field splitting for iron in the $(NH_4)_2[Fe,InCl_5(H_2O)]$ EPR study at 77 K is $D = -1894$ G ∼0.25 K, a value too small to influence the susceptibilities in this temperature region. The situation is even worse with $Rb_2FeCl_5{\cdot}H_2O$, where the Curie–Weiss law fit requires $g = 2.4$ and $\theta = -60$ K. The transition temperatures are relatively high for hydrated transition metal halide double salts and provide evidence for extensive exchange interactions.

The crystal structure of the $A_2MX_5{\cdot}H_2O$ compounds suggests that hydrogen bonding may occur between adjacent molecules along the *a* axis in $Cs_2FeCl_5{\cdot}H_2O$, forming a chain in this direction. If it is assumed that the magnetic behavior follows this structural pattern, then a good fit to the data can be obtained. In fact, the curve drawn through the data (Figure 1) is a fit to the equation of Fisher for one-dimensional classical

Table I. Crystallographic and Magnetic Properties of $A_2FeX_5{\cdot}H_2O$

A,X	Cs,Cl	Rb,Cl	Cs,Br	Rb,Br
Space group	*Cmcm*	*Pnma*	*Pnma*	*Pnma*
a, Å	7.4	13.8	14.7	14.2
b, Å	17.4	9.8	10.7	10.4
c, Å	8.0	7.1	7.6	7.4
$\rho_{calcd}(Z = 4)$	3.3	2.9	4.1	3.9
ρ_{obsd}	3.24	2.86	4.02	3.80
$T_c(C_p)$, K	6.57 ± 0.05	10.03 ± 0.05	14.06 ± 0.10[a]	22.90 ± 0.05
$T_c(\chi)$, K	6.43 ± 0.05	10.20 ± 0.08	14.21 ± 0.07	22.91 ± 0.05
J/k, K	−0.65	−1.39	−1.6	−2.5
zJ′/k, K	−0.46	−1.86	−2.3	−2.5

[a] A second λ anomaly was also observed at 12.92 K.

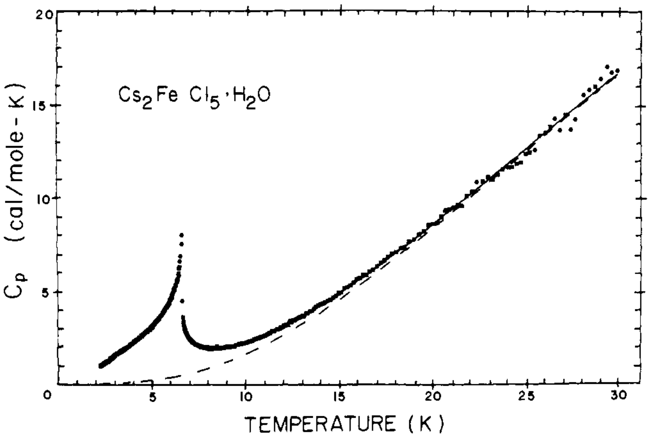

Figure 2. The specific heat of $Cs_2FeCl_5 \cdot H_2O$. The smooth curve represents the fit of the magnetic and lattice contributions; the dashed curve represents the lattice contribution alone.

spin systems as normalized for a spin of $5/2$,[10] with $g = 2.0$. The fitted exchange parameter is -0.65 ± 0.05 K, and a molecular field correction to account for interchain interactions takes the value $zJ'/k = -0.46 \mp 0.05$ K. Several equally good fits can be obtained by varying J/k in one direction and then compensating by a change in the value of zJ'/k. These values combine to yield an average value of $2J/k + zJ'/k \simeq -1.76$ K, which may be compared to the value -1.97 K obtained in the following fashion. The relationship $\chi_\perp(0) = Ng^2\mu_B{}^2/4|zJ|$ is obtained from both molecular field and spin-wave theories,[8,11] where $\chi_\perp(0)$ is the perpendicular susceptibility in the ordered state, extrapolated to 0 K. For $Cs_2FeCl_5 \cdot H_2O$, our data along the *b* and *c* axes suggest $\chi_\perp(0) = 0.19$ emu/mol, which leads to the value of zJ/k given above. Zero-point spin deviations[8] should decrease the experimental value of $\chi_\perp(0)$ by some 5% for $S = 5/2$, causing the exchange constant evaluated in this way to be too large. As with $MnCl_2 \cdot 2H_2O$,[12] intrachain and interchain exchange are of comparable magnitude, causing the usual broad maximum anticipated in the susceptibilities of a chain magnet to be obscured.

On the other hand, a sharp λ peak at 6.57 ± 0.05 K is observed (Figure 2) in the specific heat of $Cs_2FeCl_5 \cdot H_2O$, but none of the usual features expected[7,8] for linear chain magnets are apparent. The measured critical temperatures agree within experimental error. The lattice heat capacity has been evaluated tentatively by an empirical procedure.[1] The magnetic contribution to the heat capacity was evaluated by difference, and allowed an estimate of the magnetic entropy. A value of $\Delta S = R \ln (2S + 1) = 3.56$ cal/mol·K is calculated for iron(III) systems, and $\Delta S = 3.65$ cal/mol·K was determined in the case of $Cs_2FeCl_5 \cdot H_2O$. One is forced to conclude that the assignment of one-dimensional character from the susceptibility results is more extreme than the true situation.

The parameters describing the other members of the series are included in Table I. The high transition temperatures cause considerable difficulty in an analysis in terms of magnetic model systems, and the other exchange parameters provided must be considered only as suggestive at this time. With the possible exception of the ferromagnetic $A_2CuX_4 \cdot 2H_2O$ series,[8] this set of iron compounds (along with the ammonium and potassium analogues[13]) appears to be the largest series of isostructural ordered magnets currently known. A careful analysis of the heat capacity results is in progress, and the degree of anisotropy present can be best derived from the magnetic phase diagram. It is of interest to note that, for a given alkali ion, T_c for a bromide compound is always higher than that of the chloride analogue. While that is behavior characteristic of many such isomorphous pairs of hydrated halides,[14] what is novel in these results is the discovery of the T_c dependence upon the alkali ion, A. Since superexchange interactions are known to have approximately an r^{-12} dependence between metal ion centers,[15] a complete crystal structure analysis of each member of this series is required before a rationale can be provided for this result.

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Photoelectrosynthesis of Ethane from Acetate Ion at an n-Type TiO_2 Electrode. The Photo-Kolbe Reaction

Sir:

Most of the recent interest in semiconductor electrodes has been concerned with their application to photovoltaic cells and to the photoelectrolysis of water to hydrogen and oxygen.[1] Although some studies of the electrochemical behavior of organic substances at semiconductor electrodes have been reported,[2,3] little attention has been paid to photoassisted synthesis at semiconductor electrodes (photoelectrosynthesis). We thought it of interest to extend these studies to a classical electrochemical synthetic reaction, the oxidation of carboxylates (the Kolbe reaction),[4] and report here the photoassisted oxidation of acetate ion to ethane in acetonitrile (ACN) solutions at n-type TiO_2 electrodes in both the single-crystal and chemically vapor deposited polycrystalline[5] form. This reaction is of interest because it should provide a means of using solar