Acknowledgment. This work was supported by the NATO Scientific Affairs Division (Research Grant No. 925) and by a grant to the University of Michigan from the National Science Foundation (CHE 76-09572).

Registry No. $DNSOF_2$, 63848-86-2; $HNSOF_2$, 20994-96-1; *cis*-HNSO, 40908-38-1.

References and Notes

(1) (a) Laboratoire de Chimie de Coordination. (b) University of Michigan.
(2) Both HNSO and $HNSOF_2$ have a symmetry plane containing the HNSO group. The cis/trans designation indicates the orientation of hydrogen relative to oxygen. A *trans*-HNSO isomer has also been observed at low temperatures in a matrix.[3] Only the trans isomer of $HNSOF_2$ is known.
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Contribution from the Department of Chemistry,
University of Illinois at Chicago Circle, Chicago, Illinois 60680

Nonisomorphic Antiferromagnetic Behavior of Two Isomorphic Salts: Low-Temperature Heat Capacities and Magnetic Susceptibilities of $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$

J. N. McELEARNEY* and S. MERCHANT

Received August 12, 1977

The heat capacities and principal-axis magnetic susceptibilities at low temperatures are reported for single crystals of the isomorphic compounds $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$. The heat capacity of the diamagnetic isomorph $(NH_4)_2InCl_2 \cdot H_2O$ is also reported. Antiferromagnetic transitions are observed in both iron compounds. There are two in $(NH_4)_2FeCl_5 \cdot H_2O$: one at 6.87 ± 0.01 K and another at 7.25 ± 0.01 K; the single transition observed in $K_2FeCl_5 \cdot H_2O$ occurs at 14.06 ± 0.01 K. Spin canting is observed for $(NH_4)_2FeCl_5 \cdot H_2O$ but not for the potassium analogue. The indium compound has been used in a corresponding-states procedure to determine the magnetic heat capacities of the iron analogues. The results indicate the presence of a significant amount of lower dimensional exchange in $(NH_4)_2FeCl_5 \cdot H_2O$. However, although there is extensive exchange in $K_2FeCl_5 \cdot H_2O$, it is not lower dimensional in nature. The heat capacity and magnetic susceptibility data on $(NH_4)_2FeCl_5 \cdot H_2O$ have been analyzed using lower dimensional models, and an attempt has been made to interpret the differences in the behavior of the iron compounds in terms of the structures, which consist of $[FeCl_5(OH_2)]^{2-}$ and NH_4^+ groups. Hydrogen bonds and Cl–Cl contacts appear to be responsible for the observed exchange.

Introduction

One of the classical and most fruitful methods used to aid in understanding magnetic phenomena is the study of isomorphic materials. Through such studies important insights regarding the interplay of crystal field effects, spin magnitudes, spin dimensionalities, and structural characteristics have been gained. Such has been especially true in recent years regarding the study of lower dimensional compounds.[1] Many of the lower dimensional compounds which have been studied have been double salts of the form AMX_3 or A_2MX_4, where A is an alkali ion or a substituted ammonium group and X is a halide. Some 1:1 hydrated double salts have also been shown to be lower dimensional.[2–7] Usually the 2:1 hydrated salts consist of isolated monomeric species which display interesting, albeit three-dimensional, magnetic characteristics in the 1–4 K region.[8–17] In the case of $Rb_2NiCl_4 \cdot 2H_2O$,[18] however, the presence of hydrogen bonds in the material gave rise to lower dimensional behavior. All of the studies of the magnetic properties of the 2:1 hydrated compounds have involved divalent ions of the first-row transition metals—no such studies on the most stable trivalent species, Fe(III), have been made before. In fact, as a review[19] has recently pointed out, the coordination chemistry of Fe(III) has been neglected until recently.

Thus, since Fe(III) salts, containing high-spin S-state ions, are expected to be good models of Heisenberg systems and since such systems (usually Mn(II) salts) have attracted wide attention in lower dimensional magnetic studies, the first magnetic studies on hydrated double salts of Fe(III) have been made and are reported here. As it turns out, there are many such compounds, all having the general formula $A_2FeX_5 \cdot H_2O$, where A can be K, NH_4, Rb, Cs, or Tl and X can be F, Cl, or Br. In addition, In(III) analogues of the compounds also exist. The attractiveness of this series should be evident since it presents the possibility of studying the effects of relatively small structural variations on magnetic properties. The availability of a diamagnetic isomorph is also quite useful. The studies discussed here involve low-temperature single-crystal magnetic susceptibility and heat capacity measurements of $(NH_4)_2FeCl_5 \cdot H_2O$, $K_2FeCl_5 \cdot H_2O$, and $(NH_4)_2InCl_5 \cdot H_2O$. The ammonium and potassium members of the series were chosen for the initial work since those ions are typically of comparable size and the compounds would therefore be expected to exhibit

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*To whom correspondence should be addressed at 1618 North Central Avenue, Chicago, Ill. 60639.

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Table I. Cell Parameters (Å)

Axis	$(NH_4)_2FeCl_5 \cdot H_2O$	$K_2FeCl_5 \cdot H_2O$
a	13.78	13.75
b	9.85	9.92
c	7.09	6.93

Table II. Interatomic Distances (Å)

Atom pair	$(NH_4)_2FeCl_5 \cdot H_2O$	$K_2FeCl_5 \cdot H_2O$
Fe–Cl(1)	2.35	2.39
Fe–Cl(2)	2.39	2.50
Fe–Cl(3)	2.39	2.39
Fe–Cl(4)	2.43	2.45
Fe–O	2.08	2.05

similar behavior. These compounds are also especially attractive since structural results are available for them. Furthermore, it turns out that these compounds have earlier attracted the attention of spectroscopic investigators. Diffuse-reflectance,[20] infrared,[21,22] and Raman[22-25] spectra have all been reported for these materials. In addition, EPR results for Fe(III) in $(NH_4)_2InCl_5 \cdot H_2O$ have been reported by several investigators.[24,26,27] An NQR study of the indium compound has also been made to investigate the bonding in it.[28] Finally, even the electrical properties of $K_2FeCl_5 \cdot H_2O$ have been investigated.[29]

Structural Characteristics

As indicated above, the structures of both $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$ have been reported[30,31] as have been the structures of the analogous In(III) compounds.[32,33] The compounds are all isomorphic and belong to the orthorhombic space group *Pnma.* The cell dimensions of the iron compounds are given in Table I and it is seen that although the *a* and *b* axes are equivalent within 0.7%, the *c* axes differ by 2%. There are four crystallographically equivalent molecules in a unit cell with the metal atoms octahedrally coordinated by five chlorides and one water molecule. The metal atom of each octahedron as well as the oxygen and three of the chlorides (labeled Cl(1), Cl(2), and Cl(3)) all lie in a mirror plane parallel to the *ac* plane. The four complex $[FeCl_5(OH_2)]^{2-}$ ions in the unit cell are arranged in two antiparallel pairs, with the angles between the Fe–O bonds of the octahedra and the *a* axis being 41° for the ammonium salt and 40° for the potassium salt. In spite of the similarity of the axial dimensions in the two salts, an interesting difference in the bonds about the iron atoms can be seen by examining those values given in Table II. The large 0.1-Å difference for the Fe–Cl(2) distance in the two compounds is quite striking. (An even larger difference of 0.25 Å is found for the In–Cl(2) distance in the corresponding indium isomorphs. However, there the larger distance is found in the ammonium analogue, in contrast to the situation in the iron compounds.) There are two important points to note about the Fe–Cl(2) distances: first, Cl(2) is trans to the more strongly electronegative oxygen of the water molecule; second, the ionic contact distance expected for Fe(III) and the chloride ion is 2.54 Å. Clearly it appears that the ionic–covalent nature of the Fe–Cl(2) bond is different in the two compounds. It must be that stereochemical and packing differences are capable of forcing this difference.

Table III. Interatomic Distances (Å)

Atom pair	$(NH_4)_2FeCl_5 \cdot H_2O$	$K_2FeCl_5 \cdot H_2O$
Cl(2)–Cl(3)	3.82	3.55
Cl(2)–Cl(4)	3.74	3.66
Cl(3)–Cl(4)	3.75	3.76
Cl(1)–Cl(4)	3.94	3.75
Cl(1)–Cl(3)	3.94	3.87

Table IV. Hydrogen-Bond Parameters

	$(NH_4)_2FeCl_5 \cdot H_2O$	$K_2FeCl_5 \cdot H_2O$
Cl(4)–O distance	3.24 Å	3.25 Å
Cl(4)–O–Cl(4) angle	100.5°	101.2°
Cl(4)–O–Fe angle	129.8°	129.2°

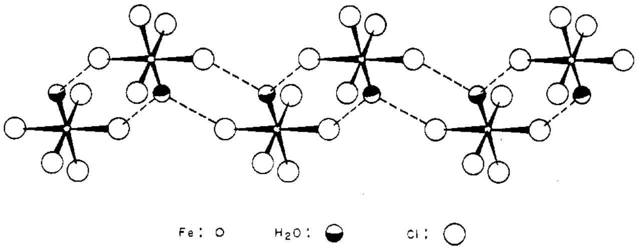

Figure 1. A view of one of the hydrogen-bonded chains of metal octahedra in $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$. The dashed lines represent the hydrogen bonds.

Obviously, such stereochemical and packing differences are also the causes for the differences in the cell parameters of the two salts. However, not so obviously, those small differences, combined with small differences in the fractional cell coordinates of the constituent atoms in each compound, lead to some relatively large differences in the characteristics of each material. In the present case, Cl–Cl distances in the two compounds must be carefully considered, since in any study of magnetic exchange a detailed consideration of exchange pathways is important for a proper understanding of the magnetic effects and since close Cl–Cl contacts have been shown to be important superexchange pathways.[34,35] In Table III all Cl–Cl distances less than 4.0 Å in the two compounds are listed. Considering that the ionic diameter of the chloride ion is about 3.6 Å, one easily sees that there are Cl–Cl approaches within about 0.15, 0.2, and 0.35 Å of this value in the ammonium salt, while the potassium isomorph contains one Cl–Cl approach less than that, one about equal to that, and others within about 0.1 and 0.25 Å of that distance. There are two varieties of contacts which are quite different in the two materials: Cl(2)–Cl(3) and Cl(1)–Cl(4). The main reason for the large difference in the Cl(2)–Cl(3) distances is the longer Fe–Cl(2) bond in the potassium salt. The large difference in the Cl(1)–Cl(4) distances apparently results from combinations of small effects due to packing differences.

Another important magnetic superexchange pathway which normally should also be given detailed consideration is the hydrogen bond. One recent study[18] has shown that such pathways can be of primary importance in influencing the magnetic properties of a material. Unfortunately, none of the structural studies done to date on these compounds (including even the quite recent analysis of $K_2InCl_5 \cdot H_2O$) have resolved the hydrogen positions. However, it is not uncommonly possible to make reasonably good guesses regarding what hydrogen bonds may be present in a material.[36] For example, in the case of water hydrogens, one can expect each hydrogen atom to be about 1 Å away from the oxygen atom and about 2.2 Å away from any chloride ion which it hydrogen bonds. Thus, the total distance between an oxygen and a chloride ion which are hydrogen-bond bridged should be about 3.2 Å. Furthermore, the bonding angles about an oxygen involved in a hydrogen-bond bridge should be roughly tetrahedral. Careful examination of the structures of both $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$ indeed show that a reasonable conjecture about the hydrogen-bonding scheme in these materials can be made on these bases. It turns out that Cl(4) is likely involved in hydrogen bonding, as can be seen upon examination of the relevant distances and angles given in Table IV. The closeness of those parameters for the two salts should be noted. It is important to note that evidence for the presence of hydrogen bonds in these compounds has been supplied by infrared studies.[21] What is most interesting about these conjectured hydrogen bonds is that pairs of them bridge together the discrete $[FeCl_5(OH_2)]^{2-}$ octahedra into infinite chains which parallel the *b* axis in a zigzag manner. A view of one of these hydrogen-bonded chains is shown in Figure 1.

Experimental Section

Orange-red crystals of $(NH_4)_2FeCl_5{\cdot}H_2O$ and $K_2FeCl_5{\cdot}H_2O$ were obtained by slow evaporation of aqueous solutions of reagent grade NH_4Cl or KCl and $FeCl_3{\cdot}6H_2O$ in molar ratios 1.13:1 and 0.58:1, respectively. Stoichiometric amounts of NH_4Cl and $InCl_3{\cdot}4H_2O$ were used to grow $(NH_4)_2InCl_5{\cdot}H_2O$ crystals from aqueous solution. For each compound, crystals must be grown slowly to avoid inclusion of solution; although the crystals used in this study were obtained from neutral solutions, slightly acidified solutions tended to grow better crystals. A polarizing microscope was used to examine the crystals selected for this study to ensure they were free from inclusions. Anal. Calcd for $(NH_4)_2FeCl_5{\cdot}H_2O$: H, 3.40; N, 9.87; Fe, 19.24; Cl, 61.73. Found (commerically): H, 3.51; N, 9.75; Fe, 19.45; Cl, 61.72. Calcd for $K_2FeCl_5{\cdot}H_2O$: H, 0.63; K, 23.28; Fe, 16.84; Cl, 53.58. Found (commercially): H, 0.61; K, 23.75; Fe, 16.96; Cl, 53.83. The agreement is quite satisfactory.

Orientation of the crystals was accomplished using both the reported morphologies for the crystals[37] as well as the interfacial angles calculated using the cell parameters determined in the structural studies. A contact goniometer was used to measure the interfacial angles of the crystals and it was discovered that the crystallographic parameters led to a different labeling of the axes from those used in the morphological studies. The *a* axis of the morphological study must be doubled as well as the *b* and *c* axes switched to obtain correspondence to the x-ray results. This discrepancy has also been noted in one of the EPR studies.[27] Since the crystals are orthorhombic and since the (100) faces of the crystals were well-developed, the orientation of the crystals used to obtain the principal-axis measurements are expected to be highly precise.

Near-zero-field magnetic susceptibility measurements were made from 1.5 to 30 K on single crystals of $(NH_4)_2FeCl_5{\cdot}H_2O$ and $K_2FeCl_5{\cdot}H_2O$ weighing about 0.12 g using apparatus which has been described before.[38] A calibrated germanium thermometer was used to measure temperature.

Heat capacity measurements on $(NH_4)_2FeCl_5{\cdot}H_2O$, $K_2FeCl_5{\cdot}H_2O$, and $(NH_4)_2InCl_5{\cdot}H_2O$ were made on single crystals weighing 2.3, 1.1, and 2.7 g, respectively. The measurements were made using apparatus and a standard heat-pulse technique which have been described elsewhere.[38] Temperatures in these measurements were also determined with a commercially calibrated germanium resistance thermometer. Because of the different features of interest in the different compounds, the temperature region of the measurements varied. For $(NH_4)_2FeCl_5{\cdot}H_2O$ measurements were made from 1.3 to 40 K, while for $K_2FeCl_5{\cdot}H_2O$ measurements from 4.6 to 20 K sufficed. The $(NH_4)_2InCl_5{\cdot}H_2O$ data were taken between 4.4 and 33 K.

Results

The results of all the heat capacity measurements are shown in Figure 2. The difference in the behavior of the three compounds is striking. The indium compound displays the type of behavior more or less expected for a diamagnetic material; however, its heat capacity does not follow any simple T^3 law. Both of the iron compounds exhibit phase transitions: $(NH_4)_2FeCl_5{\cdot}H_2O$ at 6.87 ± 0.01 K *and* at 7.25 ± 0.01 K; $K_2FeCl_5{\cdot}H_2O$ at 14.06 ± 0.01 K. There are two important features to note from these results: first, the presence of two phase transitions in the ammonium compound; second, the difference of nearly a factor of 2 between the transition temperatures of the two compounds. A more detailed view of the low-temperature data showing the two transitions in $(NH_4)_2FeCl_5{\cdot}H_2O$ is given in Figure 3. Multiple phase transitions in magnetic materials at low temperatures have been observed before in other compounds[39,40] and, apparently, usually are related to rearrangements in the magnetic spin systems of these materials. These rearrangements also affect the magnetic susceptibilities of such materials. On the other hand, such a large difference in the transition temperatures of two isomorphic materials is quite unusual. Furthermore, a transition temperature as high as 14.06 K is one of the highest ever reported for a hydrated transition-metal chloride double salt and clearly is indicative of unexpectedly extensive exchange interactions.

The magnetic susceptibilities measured for $(NH_4)_2FeCl_5{\cdot}H_2O$ and $K_2FeCl_5{\cdot}H_2O$ are shown in Figures 4 and 5, respectively. The presence of inflection points in the data indicate magnetic transitions in both compounds.[41] Careful study of the data indicates a magnetic transition occurs at 7.3 ± 0.2 K in $(NH_4)_2FeCl_5{\cdot}H_2O$ and at 14.0 ± 0.2 K in $K_2FeCl_5{\cdot}H_2O$. In addition, there appears to be some sort of plateau between 6.6 and 6.9 K in the ammonium data. These data are completely consistent with the transitions observed in the heat capacity data but also indicate a further drastic difference between the two compounds. The $K_2FeCl_5{\cdot}H_2O$ data clearly indicate that the spins align parallel to the *a* axis in the ordered state, since the susceptibility parallel to that axis approaches zero at 0 K. On the other hand, no easy axis exists in the ammonium compound. In the ordered state of that compound there is little difference between data measured parallel to *a* and those measured parallel to *c*. Neither set of data approaches zero at the lowest temperatures. It is important to note the relative position of the susceptibility maxima in both cases. Considering the *a*-axis data for both compounds, one finds $T(\chi_{\max}) = 11.7 \pm 1.0$ K for $(NH_4)_2FeCl_5{\cdot}H_2O$ and $T(\chi_{\max}) = 16.0 \pm 1.5$ K for $K_2FeCl_5{\cdot}H_2O$. Thus the transitions in $(NH_4)_2FeCl_5{\cdot}H_2O$ occur about 38% below the susceptibility maximum, while for $K_2FeCl_5{\cdot}H_2O$ the transition occurs only 12% below the observed maximum. Finally, it is interesting to note that there appears to be a small but perceptible anisotropy in both compounds in the paramagnetic state even at the higher temperatures. In both cases, χ_a appears to be definitely greater than either χ_b or χ_c which appear, for the most part, to be equal.

Analysis. (a) Susceptibility Results. The position of the susceptibility maximum in each compound being more than about 5% above the transition temperature is an indication that these materials may have lower dimensional characteristics,[41] with $(NH_4)_2FeCl_5{\cdot}H_2O$ being far more lower dimensional than its potassium analogue. Such lower dimensional behavior could well correlate to the hydrogen-bonded chains in this material, and thus it is appropriate to attempt to fit the data with the result predicted for the classical Heisenberg linear chain:[42]

$$\chi_{LC} = \frac{Ng^2\mu_B{}^2S(S+1)}{3kT}\,\frac{1-u}{1+u} \tag{1}$$

where $u = t - \coth(1/t)$, $t = T/T_0$, $T_0 = 2JS(S+1)$, J is the intrachain exchange parameter, and the other parameters have their usual meanings. This result has successfully been used to describe the behavior of spin $^5/_2$ chains in TMMC,[43] $CsMnCl_3{\cdot}2H_2O$,[2] and $[(CH_3)_3NH]_3Mn_2Cl_7$ (TTMMC).[34] In this case, the data are not well-described solely by eq 1, and a molecular field correction[38,44] must be applied to eq 1 to account for the presence of additional exchange:

$$\chi = \frac{\chi_{LC}}{1 - (2zJ'/Ng^2\mu_B{}^2)\chi_{LC}} \tag{2}$$

where J' is the interaction between chains and z is the number of nearest-neighbor chains. Such a procedure has successfully described the spin $^5/_2$ linear chains in $MnCl_2{\cdot}2H_2O$[44] and $[(CH_3)_3NH]MnX_3{\cdot}2H_2O$ (X = Cl or Br).[7] In order to use eq 1 and 2 to fit the data, a value for g must be chosen. Since Fe(III) is a d^5 ion, its g values could normally be assumed to be isotropic and close to the free-electron value, 2.002. However, the EPR studies of Fe(III) in $(NH_4)_2InCl_5{\cdot}H_2O$ have

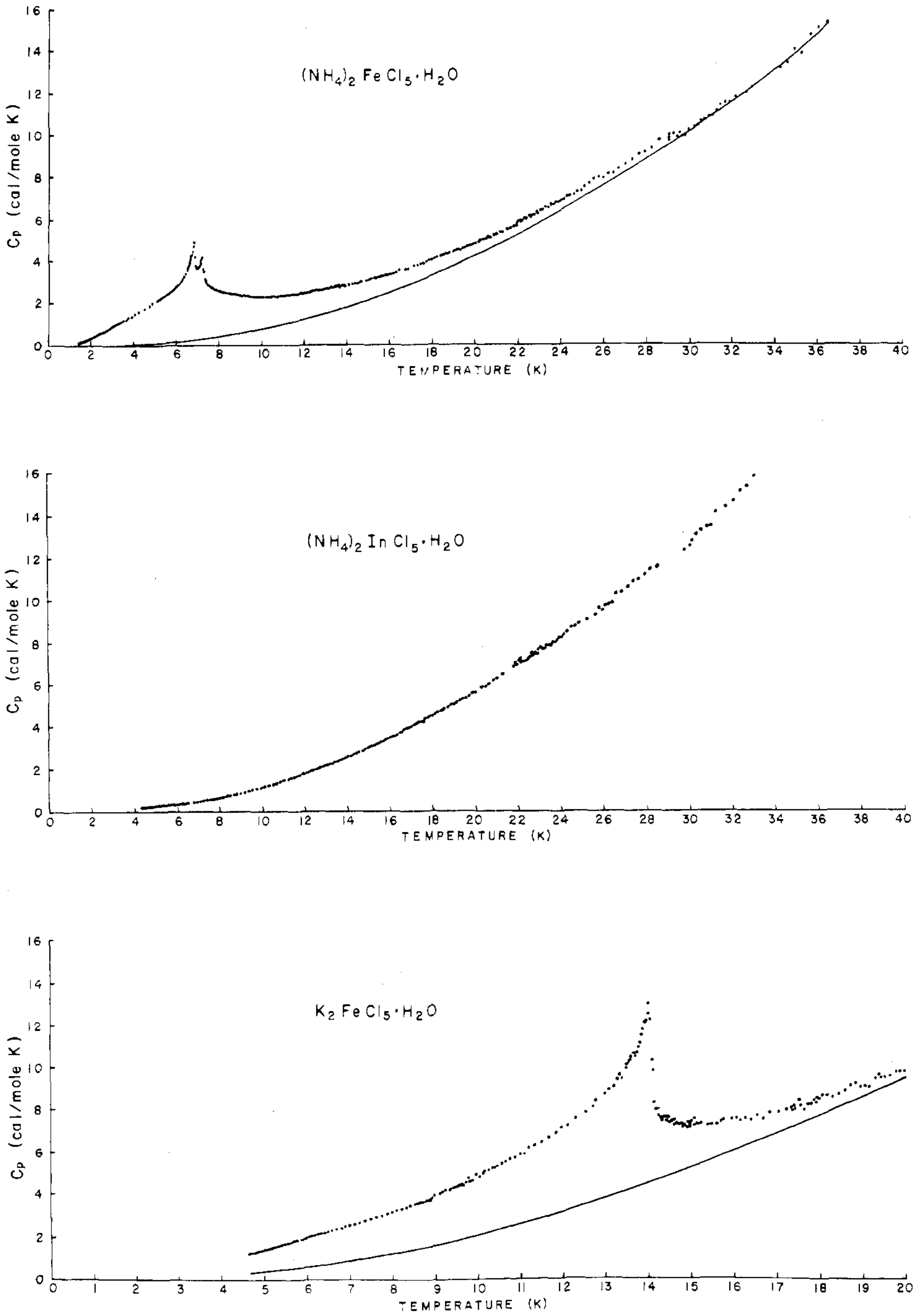

Figure 2. Measured heat capacities of $(NH_4)_2FeCl_5 \cdot H_2O$, $(NH_4)_2InCl_5 \cdot H_2O$, and $K_2FeCl_5 \cdot H_2O$. The solid curve accompanying the data for each iron compound represents the estimated lattice contribution to the total heat capacity.

shown large shifts with resulting *g* values of about 2.010–2.015.[26,27] Thus *g* was arbitrarily chosen to be used as 2.01, since the precision of the data is not high enough to be influenced by the fourth significant figure of *g* (in fact, within experimental uncertainties, $g = 2.00$ gives essentially the same results as $g = 2.01$).

There are some problems in deciding just exactly how much of the data in the paramagnetic regions to fit. One problem in fitting the data is the choice of the low-temperature cutoff of the fit. Since eq 2 introduces a large approximation into the fit, the fit cannot be expected to be good all the way down to the transition temperature. Thus 9 and 15 K were arbitrarily chosen as the low-temperature limits to the susceptibility fits of the ammonium and potassium compounds, respectively. Changing these limits by a degree or so does not essentially influence the final results. Another problem is how to treat the small anisotropy observed in the paramagnetic state. The amount of anisotropy cannot reasonably be expected to be due to *g*-value anisotropy. Thus, since the model to be used in the fit is an isotropic one, the best choice seems to be to include data from all three principal-axis measurements in each fit. The parameters resulting from fitting the data in the manner described are given in Table V, and the curves shown in Figures 4 and 5 correspond to these results. The fit for $(NH_4)_2FeCl_5 \cdot H_2O$ matches the data from 9 to 30 K within about 1%; the data for $K_2FeCl_5 \cdot H_2O$ are matched by the fit

Table V

	J/k, K	zJ'/k, K
$(NH_4)_2FeCl_5 \cdot H_2O$	-1.24 ± 0.08	-2.87 ∓ 0.30
$K_2FeCl_5 \cdot H_2O$	-1.55 ± 0.15	-3.05 ∓ 0.55

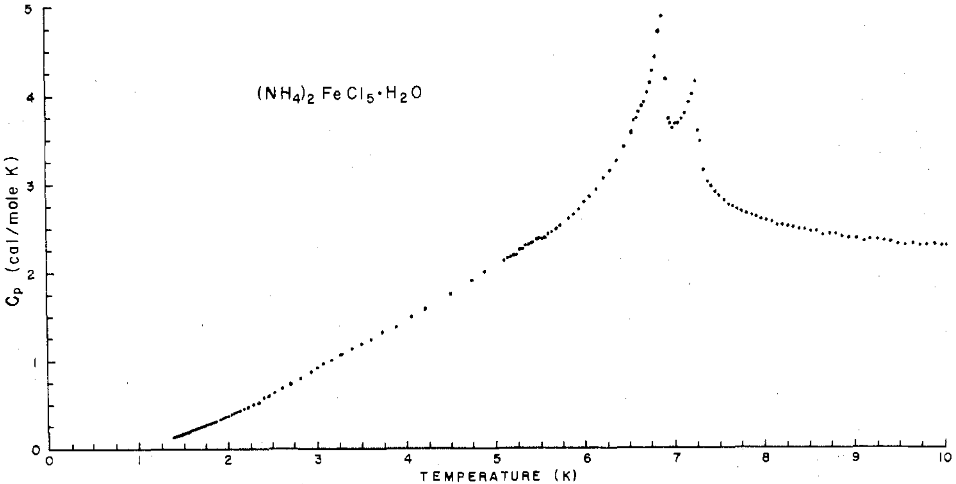

Figure 3. Detailed view of the behavior of the heat capacity of $(NH_4)_2FeCl_5{\cdot}H_2O$ below 10 K.

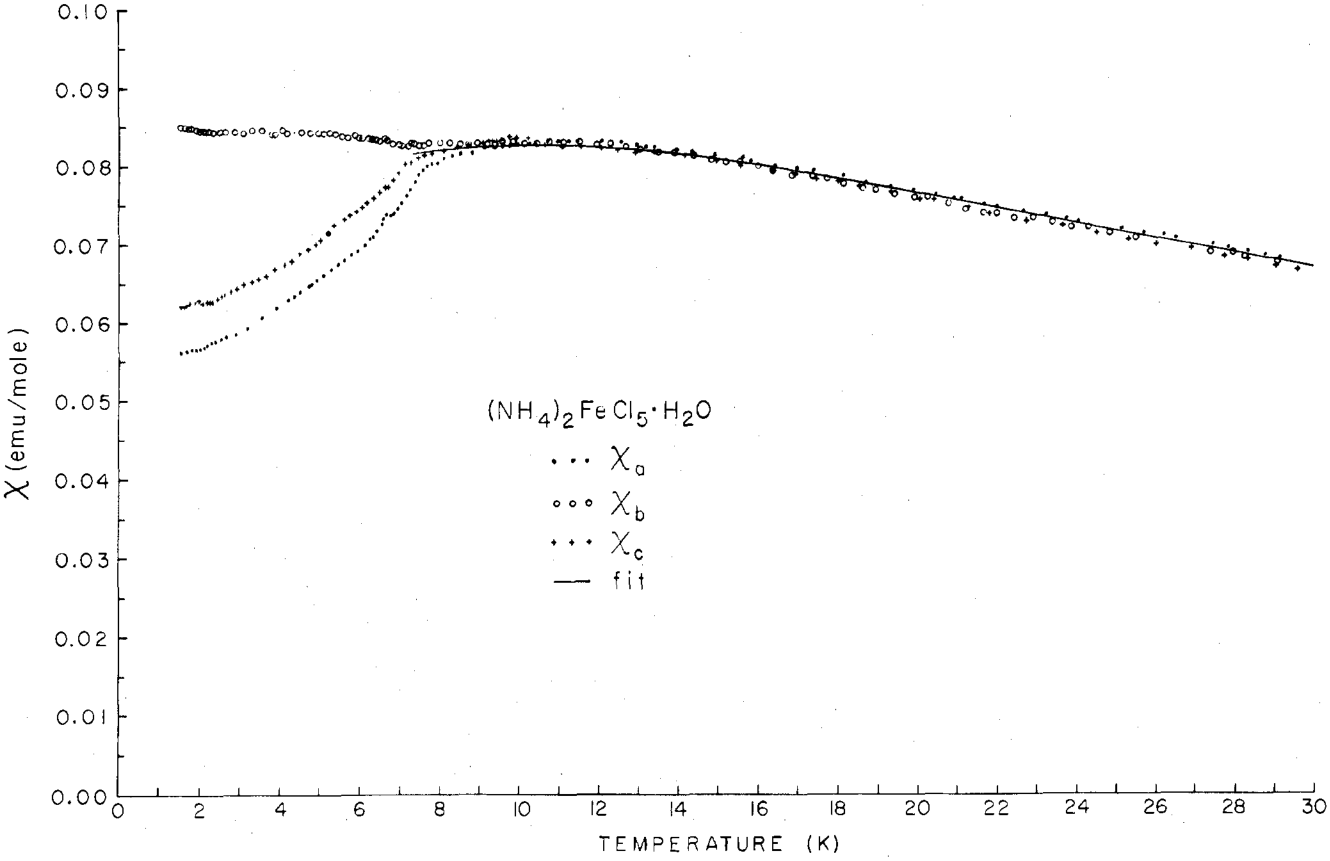

Figure 4. Principal-axis magnetic susceptibilities measured for $(NH_4)_2FeCl_5{\cdot}H_2O$. The solid curve represents the fit to the data discussed in the text.

within 2–3% from 15 to 30 K. Better fits, of course, can be achieved if data from just one principal axis are used in a fit. It seems more appropriate, however, to include all sets of data when fitting the results for each compound and then to use the fact that better fits are attainable on each set individually to obtain some sort of reasonable estimates for the uncertainties in the parameters. This is just how the uncertainties listed in Table V were determined.

(b) Heat Capacity Results. In order to apply any model to the heat capacity results, it is first necessary to separate the magnetic and lattice contributions. Even given the heat capacity of an isomorphic diamagnetic compound, this separation is not easily accomplished. As can be seen from Figure 2, the heat capacity of the indium isomorph relatively quickly becomes greater than the heat capacity of $(NH_4)_2FeCl_5{\cdot}H_2O$, and a simple subtraction of the heat capacity of $(NH_4)_2InCl_5{\cdot}H_2O$ from the iron results would not work. The indium compound's heat capacity is certainly less than that of $K_2FeCl_5{\cdot}H_2O$, but it is so much less that subtraction of it from the data on the potassium compound would lead to a magnetic heat capacity which would be far greater than possible. Of course, these results should not be surprising, in view of the large difference in the atomic weights of iron and indium and the differences between the ammonium and potassium cations. One of the best ways to solve this problem is to use the heat capacity of the diamagnetic compound in a corresponding-states approach.[45] This method has recently been used to a high degree of success in determining the lattice contributions

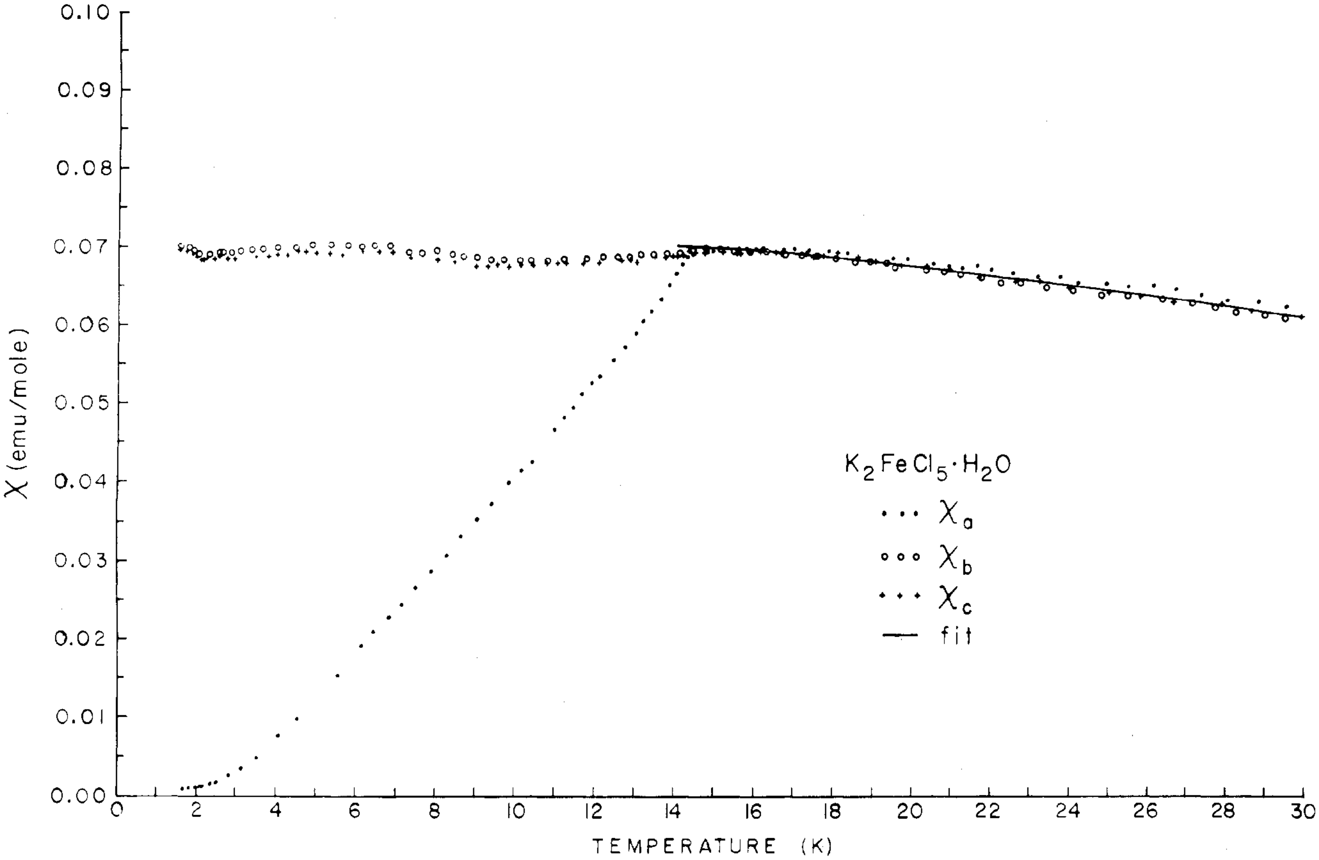

Figure 5. Principal-axis magnetic susceptibilities measured for $K_2FeCl_5 \cdot H_2O$. The solid curve represents the fit to the data discussed in the text.

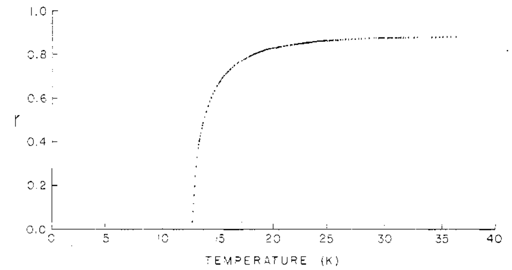

Figure 6. Corresponding-states ratio plot for $(NH_4)_2FeCl_5 \cdot H_2O$ and $(NH_4)_2InCl_5 \cdot H_2O$.

to the heat capacities of several compounds at low temperatures.[5,35] Since the method has been described previously, no details will be given here other than pointing out that the approach involves comparison, as a function of temperature, of the total entropy gain of a magnetic compound (less the expected magnetic contribution to the entropy) to that of an isomorphic diamagnetic compound. The corresponding-states ratio, r, is the ratio of the temperatures at which these two quantities have equal values. If the corresponding-states approach is valid, r must become a constant at high enough temperatures. The previous studies have generally admitted a small temperature dependency to r. The behavior of r as a function of temperature for $(NH_4)_2FeCl_5 \cdot H_2O$, using the indium analogue in the corresponding-states calculation, is shown in Figure 6, and the expected near-constant behavior at the higher temperatures is seen. Somewhat similar results were obtained when the $K_2FeCl_5 \cdot H_2O$ data were used in a similar calculation with $(NH_4)_2InCl_5 \cdot H_2O$ used as the diamagnetic isomorph, although some estimation in the temperature behavior of r was required, since the data for the potassium compound do not go as high in temperature as do the data for the ammonium compound. The uncertainty introduced into the results by this estimation is small, however. Furthermore, some estimation of the entropy gained below the lowest temperature data point in each iron compound was necessary. These estimates were 0.03 cal/(mol K) for the ammonium compound and 0.4 cal/(mol K) in the potassium compound. Although the former estimate has little influence on the results, the estimate for the potassium compound is important. However, it is a very reasonable estimate of the extrapolated low-temperature behavior of the potassium compound and, unlike other estimates, does lead to a correct value for the total magnetic entropy change in that material. The estimated lattice heat capacities determined for the iron compounds through this procedure are shown as solid curves in Figure 2, and Figure 7 shows the resulting magnetic heat capacities when those estimates are subtracted from the data. The difference in the behavior of the magnetic heat capacities of the two compounds is striking!

As a check to the validity of the corresponding-states procedure, the total entropy gain associated with each magnetic heat capacity must be calculated and compared to the theoretically expected value, $R \ln 6$. At 40 K the value calculated for $(NH_4)_2FeCl_5 \cdot H_2O$ is 2% greater than this and the corresponding value for the potassium analogue is within 0.5% of that expected. Ideally, since there is some magnetic entropy above the regions of the measurements, the values should be just a little less than $R \ln 6$. However, considering the fact that above 25 K the magnetic heat capacity of the ammonium compound is less than about 5% of the total measured heat capacity and that similarly for the potassium analogue the magnetic contribution is relatively small at 20 K, the minimal discrepancies between the measured and expected entropy gains are quite within the experimental accuracies and are strong evidence that the magnetic heat capacities have been properly separated from the measured quantities.

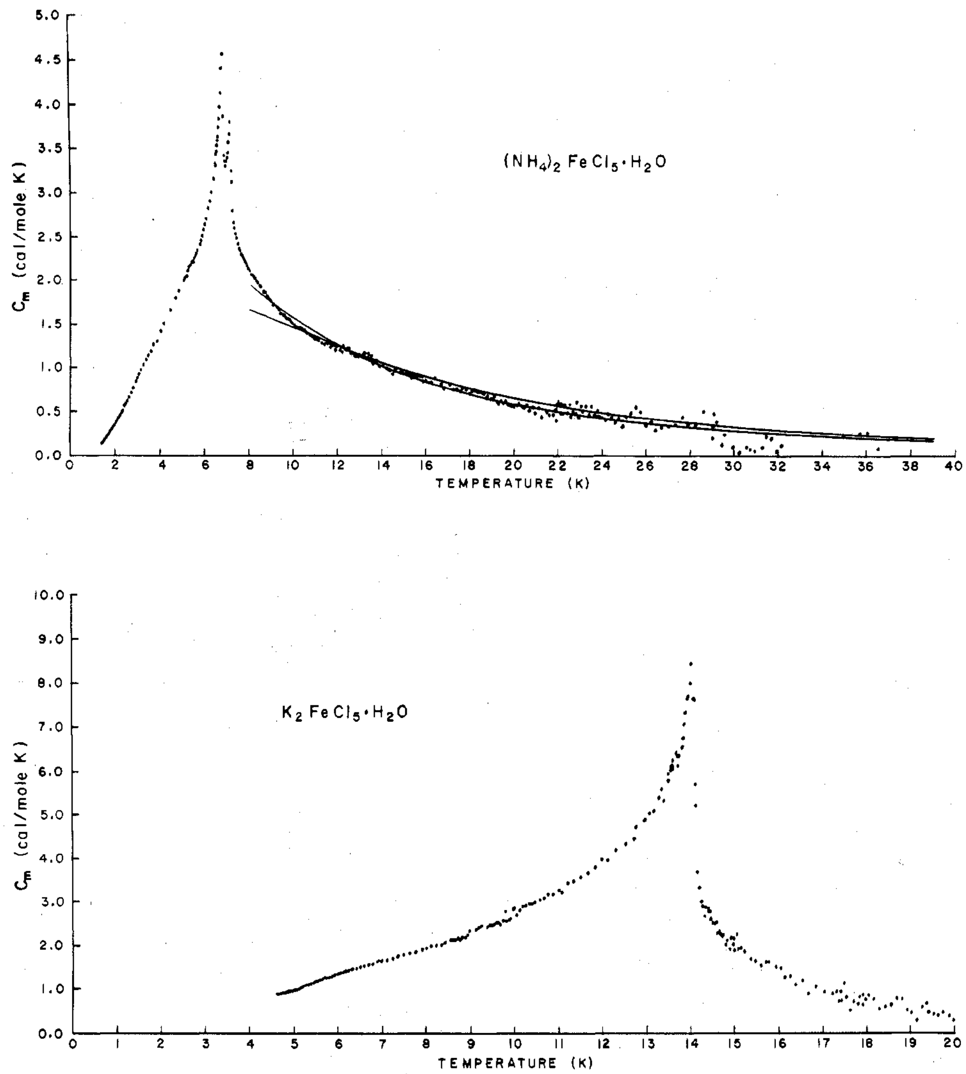

Figure 7. Magnetic heat capacities of $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$. The results of the two different fits of the ammonium data discussed in the text are shown as solid curves accompanying that data. The two curves, which are for values of $J/k = -1.24$ K and $J/k = -1.08$ K, cross near 12 K, with the curve for $J/k = -1.24$ being lower at the lower temperatures.

The entropy gain as a function of temperature generally reveals some information about the dimensionality of a magnetic system. Only about 53% of the total magnetic entropy gain appears below the lowest transition temperature in the ammonium compound (about 5% more appears between that temperature and the other transition); on the other hand, 85% of the total expected magnetic entropy change has already been gained below the transition in the potassium analogue. Since extensive short-range order is usual in the paramagnetic state of a lower dimensional magnet, the heat capacity results indicate that the ammonium compound has a lower dimensional character, while the potassium analogue primarily has a three-dimensional character. These conclusions are consistent with the relative positions of the susceptibility maxima and transition temperatures noted previously. With so little short-range order above the transition in the potassium compound, it is difficult to try to fit any model to the data. On the other hand, an attempt to fit the data in the paramagnetic region for the ammonium compound is worthwhile.

Since the susceptibility results indicated the presence of a significant amount of exchange which was not one-dimensional, a method of analysis must be used which accounts for the non-one-dimensional interactions. One approach which has been successfully used previously[18] is to consider the paramagnetic heat capacity to result from the sum of two terms, $C_{para} = C_{LC}(J) + BT^{-2}$, where $C_{LC}(J)$ represents the heat capacity for a linear chain material with intrachain exchange J and where the term BT^{-2} accounts for the short-range interactions which are not one-dimensional. Numerical estimates for the heat capacity of a spin $^5/_2$ linear chain have recently been reported by two investigators.[46,47] Within the quality of the present data, both results are equivalent and have been used to calculate $C_{LC}(J)$ in a fit of the $(NH_4)_2FeCl_5 \cdot H_2O$ data. Because an approximate approach is involved in the calculation of C_{para}, it is not possible to fit all of the data in the paramagnetic region; some lower limit above the transition temperature must be chosen. Although such a choice is arbitrary, unlike the case of the susceptibility fit, that choice can have large effects upon the fitted parameters. If 8 K is chosen as the lower limit of the fit, then the parameters resulting from the fit are $J/k = -1.08$ K and $B = 33.7$ cal K/mol. If a higher cutoff point is chosen, J/k increases and B decreases. If the intrachain exchange value which resulted from the susceptibility fit, $J/k = -1.24$ K, is used to fit the heat capacity data, then an acceptable fit of the data above 10 K results for $B = 9.4$ cal K/mol. The fits resulting from both of the above values of J/k are shown in Figure 7. The difference between the fits is seen to be small over most of the fitted region and either fit must be considered acceptable in view of the large effect of the lattice contribution in the paramagnetic region. (The difference between the two curves amounts to less than about 8% of the total measured heat capacity at 8 K and less than 4% of the total above 10 K.)

Discussion

Unfortunately, the results presented here are not as unambiguous and useful as might have been hoped. The key to understanding the problem is to note that the susceptibility fits show that the ratio zJ'/J is large for both $(NH_4)_2FeCl_5 \cdot H_2O$ and $K_2FeCl_5 \cdot H_2O$ and thus the numerical results are based much more on the approximate molecular field theory than they are on a lower dimensional analysis. Now, it must be pointed out that the same method of analysis used here for the susceptibility data has been successfully used before to obtain interpretable results. In the case of $Rb_2NiCl_4 \cdot 2H_2O$[18] the ratio zJ'/J was small so that the molecular field approximation was not as important as it is here. On the other hand, in the case of $MnCl_2 \cdot 2H_2O$[44] the ratio zJ'/J was large, but the structure of that compound was simple enough to allow interpretation of the results. In the present case, it is clear that with the many Cl–Cl contacts in either structure it may be questionable to attempt to correlate the parameter J to any specific structural features. Nevertheless, the heat capacity results for $(NH_4)_2FeCl_5 \cdot H_2O$ give evidence for some degree of lower dimensional behavior and some attempt at interpreting the behavior of that material is worthwhile. On the other hand, the heat capacity of the potassium analogue clearly shows a lack of lower dimensional behavior and it would be foolhardy to attempt to relate the parameters fitted from the susceptibility to the structure, although some qualitative understanding of why there is such a difference between the two compounds may be possible.

As it turns out, there are two possible causes for the lower dimensional behavior in $(NH_4)_2FeCl_5 \cdot H_2O$. That behavior might be the result of the hydrogen-bonded chains being the major exchange pathways in that material. Then the presence of higher dimensional exchange effects, as indicated by the significant molecular field correction to the susceptibility fit, must be a result of Cl–Cl near contacts. In that case, Table III shows that at least Cl(2)–Cl(4) and Cl(3)–Cl(4) contacts must be involved. From this point of view, these contacts result in each hydrogen-bonded chain interacting with four others. Of course, there could be other, less important exchange effects from the remaining Cl–Cl contacts. Thus, for this model, the hydrogen-bonded pathways would result in intrachain exchange of about −1.1 or −1.2 K and the interchain exchange would be no more than −0.72 K. Since each iron atom in a hydrogen-bonded chain has four interchain Cl–Cl contacts, each Cl–Cl contact would result in exchange of no more than −0.18 K. This value is not inconsistent with recent results from the study of TTMMC[34] where three Cl–Cl contacts of about 4.0 Å produced an intrachain exchange of about 0.2 K.

On the other hand, the actual situation in $(NH_4)_2FeCl_5 \cdot H_2O$ could be just the reverse: the Cl(2)–Cl(4) and Cl(3)–Cl(4) contacts could be of primary importance and the hydrogen bonds and other Cl–Cl contacts of lesser importance. The effect, then, would be to cause two-dimensional-like exchange, since careful study of the structural features shows that those Cl(2)–Cl(4) and Cl(3)–Cl(4) contacts act to tie the isolated octahedra together into puckered planes which parallel (100). It would then be necessary to interpret the fitted parameters in a manner similar to that done in the case of $Rb_2NiCl_4 \cdot 2H_2O$: the planes would be considered to be composed of cross-linked parallel linear chains, and the fitted J would correspond to the intrachain exchange for one of these chains. Since the Cl(2)–Cl(4) and Cl(3)–Cl(4) paths are essentially equivalent, the interchain exchange for these chains would be expected to be about the same as J. The molecular field parameter, zJ', would then account for these interchain interactions plus all other remaining interactions. Thus zJ' would have to be at least −2.48 K, leaving only about −0.4 K of exchange energy resulting from the hydrogen bonds and other close Cl–Cl contacts. It would seem unlikely that those other contacts, not being drastically different from the Cl(2)–Cl(4) and Cl(3)–Cl(4) contacts, would result in so much less exchange.

In any case, no matter which model is more appropriate to $(NH_4)_2FeCl_5 \cdot H_2O$, it is clear that Cl–Cl near contacts of 3.75 Å or less are important exchange paths in these compounds. Since there are several closer Cl–Cl contacts in $K_2FeCl_5 \cdot H_2O$, it should be obvious that the lower dimensional effects seen in the ammonium compound may well have been destroyed by the presence of enough additional exchange paths. In fact, the situation in the potassium compound is completely unanalyzable without information on the relationship of exchange to Cl–Cl contact distance. For example, the Cl(2)–Cl(3) separation in $K_2FeCl_5 \cdot H_2O$ is less than the ionic diameter of the chloride ion and is 0.2 Å smaller than any Cl–Cl contact in $(NH_4)_2FeCl_5 \cdot H_2O$; these contacts act to tie the isolated octahedra together into chains parallel to the c axis. Whether or not the intrachain exchange for these chains is of comparable or greater magnitude than that for the hydrogen-bonded chains is not determinable. If it is, it would not be hard to believe that the other Cl–Cl contacts are then important enough to lead to the observed three-dimensional behavior.

Ultimately, further experiments on modifications or other analogues of these compounds will be necessary to separate out the effects of the many exchange pathways. The most obvious modification is deuteration. If the hydrogen bonds are important exchange pathways, then deuteration should have an observable effect on the gross behavior. Another possible modification would be to use cations larger than the ammonium or potassium used here. Besides rubidium and cesium, substituted ammonium groups might be useful. Even if such bulky ions successfully separate some of the Cl–Cl contacts, it is unclear from the structure if other Cl–Cl contacts might not then become more important. Perhaps a more interesting way of reducing the Cl–Cl exchange pathways would be to change the chloride ion to a smaller ion such as fluoride. The present results clearly indicate that if a larger ion, such as bromide, is used, the exchange is likely to increase because of the numerous close halide–halide contacts which exist in these compounds.

Besides the difference in the dimensional nature of the exchange in the two iron compounds, the results also indicate that there is another important difference in the character of the exchange. Since, in contrast to the potassium analogue, no easy axis was found in $(NH_4)_2FeCl_5 \cdot H_2O$, it is necessary to conclude that the spins in that material behave as a canted antiferromagnetic spin system. Such behavior is allowed in the space group *Pnma*[48] and is consistent with the structure as described earlier. The susceptibility results clearly show that the spins must lie in the *ac* plane. Since there is little difference in the behavior of χ_a and χ_c at low temperatures, it is necessary to conclude that the spins are canted at roughly 90° to each other. Furthermore, since χ_a is slightly less than χ_c, the a axis is an easier axis than the b axis, and thus the canting angle must be actually somewhat less than 90°, with the spins aligned closer to the a axis than to the c axis. Again, this conclusion is completely consistent with the structural details if one assumes the spins in the ordered state of $(NH_4)_2FeCl_5 \cdot H_2O$ are aligned more or less parallel to the Fe–O bonds.

The interesting question, of course, is why only one of the iron compounds displays spin canting. Single-ion anisotropy,[48] antisymmetric superexchange,[48] and g-value anisotropy[49,50] all have been shown to produce spin canting. Antisymmetric exchange is allowed in the space group *Pnma*, but g-value anisotropy for these compounds should be negligible. Perhaps of more importance, however, EPR studies[24,26] of Fe(III) in $(NH_4)_2InCl_5{\cdot}H_2O$ have shown the zero-field splitting parameter, D, to be on the order of 0.1–0.2 K. While this value is too small to affect the susceptibilities in the temperature range reported here (except, perhaps, for the small amount of anisotropy observed in the paramagnetic region), it certainly could influence the spin Hamiltonian enough so that spin canting would occur. Still, however, one must ask why in the ammonium compound and not in the potassium analogue. A possible answer is that D is different in the two compounds. Such a situation is supported by the difference noted before in the Fe–Cl(2) bond in the two compounds. Since a somewhat similar difference exists in $(NH_4)_2InCl_5{\cdot}H_2O$ and $K_2InCl_5{\cdot}H_2O$, a determination of D for Fe(III) in the latter compound might shed some light on the problem, for then a comparison could be made to the value for D reported for Fe(III) in the former material.

The one other point of interest left unanswered by the present data is why there are two transitions in $(NH_4)_2FeCl_5{\cdot}H_2O$. Since the susceptibility data indicate hardly any change at the lower transition point, it is necessary to assume that the spin configurations associated with each transition are essentially the same. Magnetization and NMR experiments probably will be necessary to provide further understanding of the situation.

Conclusion

Susceptibility and heat capacity measurements on $(NH_4)_2FeCl_5{\cdot}H_2O$ and $K_2FeCl_5{\cdot}H_2O$ have provided evidence for significant antiferromagnetic exchange in both materials due to hydrogen bonds and close Cl–Cl contacts. A comparison of the structural details for the two compounds has led to a qualitative understanding of why the exchange is so much more extensive in the potassium compound. A possible reason for why spin canting is observed in one compound and not in the other has also been proposed. Further studies of these materials, as well as their analogues, will be necessary before any strong conclusions can be reached.

In fact, after the present studies were completed, an investigation involving measurements on the compounds $Cs_2FeCl_5{\cdot}H_2O$, $Rb_2FeCl_5{\cdot}H_2O$, $Cs_2FeBr_5{\cdot}H_2O$, and $Rb_2FeBr_5{\cdot}H_2O$ was made.[51] In agreement with the present results, those measurements all give evidence for the presence of extensive exchange in those materials. Furthermore, *none* of those compounds clearly exhibit the lower dimensional character observed in $(NH_4)_2FeCl_5{\cdot}H_2O$, so the parameters determined from fits to those data sets are no more meaningful than those determined here for $K_2FeCl_5{\cdot}H_2O$ and do not really aid in understanding this series of compounds. That study concluded there is a correlation between the transition temperatures of $A_2FeCl_5{\cdot}H_2O$ (A = NH_4, K, Rb, Cs) and the ionic radii of the cations. Indeed, even though a radius for the ammonium ion inconsistent with the structural results was used to draw that conclusion, it does appear that there is some consistent behavior for the potassium, rubidium, and cesium compounds and that attempts to make compounds with even bulkier complex cations may be fruitful. Because it is clear from the present analysis that the structures of these materials are quite complex in terms of exchange pathways, further detailed study of such pathways will be necessary in order to gain a proper understanding of the magnetic behavior of this series.

Registry No. $(NH_4)_2FeCl_5{\cdot}H_2O$, 16774-56-4; $K_2FeCl_5{\cdot}H_2O$, 15132-22-6; $(NH_4)_2InCl_5{\cdot}H_2O$, 17949-59-6.

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