Figure 5 shows a plot of J/k vs. the bridging Mn–Cl–Mn angle for TMMC-like chains in three salts: TMMC, DMMC [≡(CH3)2NH2MnCl3][8], and T3Mn2Cl7. This shows exactly what is expected from superexchange arguments, the antiferromagnetic coupling getting stronger as the bridging angle deviates further from 90°. The apparent linear relation must be regarded as tenuous, due to the insensitivity of the T3Mn2Cl7 data to changes in J/k; nevertheless the trend must be correct since McElearney's data indicate that J/k is closer to −11. Further studies such as those proposed above on a salt like T3MnZnCl7 would be useful in helping to establish quantitatively the variation of J with bridging angle in these salts.

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Two Independent Heisenberg Linear-Chain Species in Tris(trimethylammonium) *catena*-Tri-μ-chloro-manganate(II) Tetrachloromanganate(II), [(CH3)3NH]3Mn2Cl7

J. N. McELEARNEY

Magnetic susceptibility measurements on a single crystal of [(CH3)3NH]3Mn2Cl7 parallel and perpendicular to the crystal's hexagonal c axis have been made between 1.5 and 30 K. The results show the presence of anisotropy over the entire temperature region. A quantitative fit to the parallel susceptibility has been achieved using a model in which the compound is considered to be composed of two different types of Heisenberg linear chains: one with intrachain exchange of −11 ± 6 K and one with intrachain exchange of −0.20 ± 0.01 K. The model also qualitatively explains the anisotropy observed.

Recently there has been increased interest in compounds which display pseudo-one-dimensional magnetic behavior.[1] Such materials are of interest since many of their properties can be described by relatively simple theories and thus they serve as important testing grounds for various aspects of the theories. In the course of an attempt to obtain a nonhydrated analog of the widely studied linear-chain series[2] [(CH3)3NH]MX3·2H2O (M = transition metal; X = halide) single crystals of [(CH3)3NH]3Mn2Cl7 were obtained. The stoichiometry, growth habit, and optical behavior of this material suggested that it probably was analogous to, if not isomorphous with, the corresponding Cu(II) compound, [(CH3)3NH]3Cu2Cl7. The structure of that material has been reported[3] and is unusual in that it contains two types of copper anions: infinite $(CuCl3)_n{}^{n-}$ chains and isolated $(CuCl4)^{2-}$ tetrahedra. Since they are surrounded by trimethylammonium cations, the infinite $(CuCl3)_n{}^{n-}$ chains are effectively magnetically insulated from each other as well as from the $(CuCl4)^{2-}$ tetrahedra. Since one of the more widely studied one-dimensional materials,[4-7] [(CH3)4N]MnCl3 (TMMC), contains similar infinite $(MnCl3)_n{}^{n-}$ chains, studies of [(CH3)3NH]3Mn2Cl7 are deemed important. Thus, single-crystal magnetic susceptibility measurements from 1.5 to 30 K were undertaken on this material. Upon completion of this work it was learned that similar powder susceptibility measurements, as well as a complete structure determination, had been performed elsewhere.[8] The structural results indicate that, indeed, [(CH3)3NH]3Mn2Cl7 is essentially isostructural

with its copper analogue (although the two materials are not strictly isomorphic). Although the single-crystal susceptibility results presented here are not in contradiction to the powder results, a novel interpretation is given to them.

Experimental Section

Single crystals of [(CH3)3NH]3Mn2Cl7 were obtained by slow evaporation of a methanolic solution of equimolar amounts of (CH3)3N·HCl and MnCl2. The red-orange crystals grow as long thin needles, becoming thick only after long periods of time. The crystal used in the present study was grown over a period of 1 year and weighed 0.1 g. Anal. Calcd for [(CH3)3NH]3Mn2Cl7: C, 20.08; H, 5.62; N, 7.80; Mn, 20.41; Cl, 46.09. Found (commercially): C, 20.06; H, 6.04; N, 7.77; Mn, 20.08; Cl, 45.62. The agreement is excellent.

Isothermal magnetic susceptibilities parallel and perpendicular to the crystallographic c axis were measured using apparatus that has been described elsewhere.[9] The most important point about the method is that it involves a low-frequency mutual-inductance technique applied in near-zero field (less than 5 Oe). The calibration of the system is considered to be accurate within 2–3%. Temperatures were measured with a commericaly calibrated germanium resistance thermometer and generally were stable to within 0.02 K for each data point measured.

Results and Analysis

The results are shown in Figure 1. Three important features are to be noted: (1) the relatively reduced magnitude of the susceptibility, (2) the rounded maximum near 2 K observed in both data sets, (3) the anisotropy between the
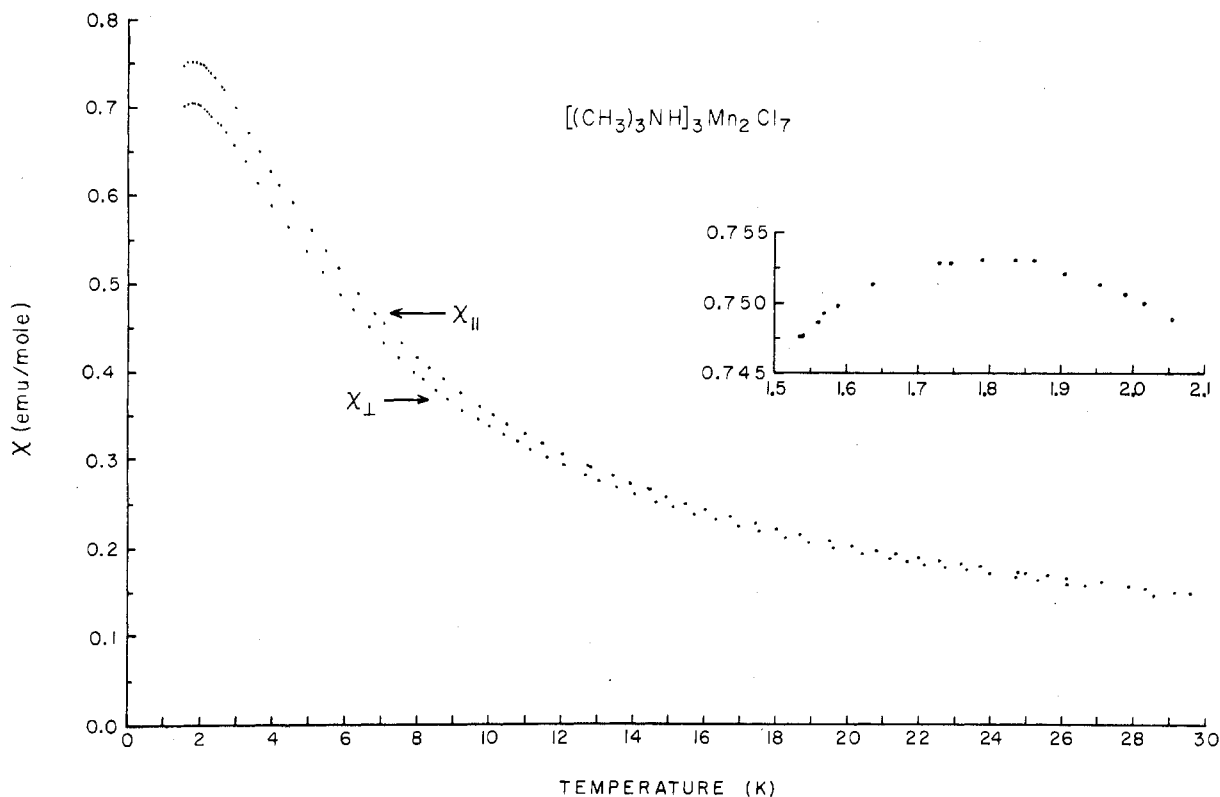
Figure 1. Magnetic susceptibility of $[(CH_3)_3NH]_3Mn_2Cl_7$ measured parallel and perpendicular to the c axis. The parallel susceptibility is greater than the perpendicular susceptibility over the entire region shown. The inset is an expanded view of the behavior of the parallel data near 2 K.

parallel and perpendicular orientations observed over most of the temperature region. The first two features are indications of the presence of antiferromagnetic exchange. The anisotropy, however, is not as easily understood, since Mn(II) generally displays little anisotropy.

As a first step in interpreting the data it is logical to consider the magnetic behavior of $[(CH_3)_3NH]_3Mn_2Cl_7$ to result from the superposition of two independent spin systems: the TMMC-like infinite $(MnCl_3)_n{}^{n-}$ chains and the isolated $(MnCl_4)^{2-}$ tetrahedra. It is also reasonable to assume the susceptibility of the TMMC-like chains to be similar to the results reported[4] for TMMC. In that compound the intrachain exchange interaction was found to be −6.3 K. Furthermore, field-dependent studies[5] indicated the presence of anisotropy in TMMC, with that anisotropy becoming larger as the measuring field was reduced. At a measuring field of 250 Oe, a *minimum* of about 10% anisotropy in the susceptibility was found below 30 K. Most of the anisotropy was a result of field-dependent changes in the susceptibility measured perpendicular to the infinite $(MnCl_3)_n{}^{n-}$ chains. Thus, in analyzing the present near-zero-field data, for the contribution from the TMMC-like infinite chains one should use the classical Heisenberg linear-chain equation found applicable for TMMC[10]

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

where $u = (T/T_0) - \coth(T_0/T)$ and $T_0 = 2J_{LC}S(S+1)/k$. The intrachain exchange is given by J_{LC}, and for Mn(II), S equals $5/2$ and g commonly is found to be 2.00. It is important to note that eq 1 better describes measurements taken parallel to the infinite $(MnCl_3)_n{}^{n-}$ chains in TMMC, rather than measurements perpendicular to them. As a first approximation, the isolated tetrahedra can be assumed to contribute according to the Curie law: $\chi_C = Ng^2\mu_B{}^2S(S+1)/3kT$. Using the sum of eq 1 and the Curie law it is not possible to

describe the data; there must be further exchange contributions which reduce the susceptibility. If it is assumed that the tetrahedra are weakly interacting, then their contribution to the susceptibility can be calculated in the molecular field approximation[9,11] as

$$\chi_{TET} = \frac{\chi_C}{1 - (2zJ_{TET}/Ng^2\mu_B{}^2)\chi_C} \tag{2}$$

Using the sum of eq 1 and 2 a reasonable fit to the parallel data can be obtained from about 2.3 to 30 K, although there are consistent deviations of up to 6%. Furthermore, the fit becomes even worse below 2.3 K and the rounded maximum near 2 K is not reproduced. The parameters resulting from such a fit are $J_{LC}/k = -5.8$ K and $zJ_{TET}/k = -0.58$ K. (For small values of zJ_{TET}/k, this above molecular field analysis is not drastically different from one using the Curie–Weiss law in place of eq 2. Indeed, these numbers are essentially consistent with those found in the powder susceptibility work.[8])

The nonnegligible value of zJ_{TET}/k, combined with the maximum in the susceptibility near 2 K, indicates significant exchange effects among the isolated tetrahedra. A clue to the type of exchange involved is given by the fact that no inflection point in the data was found within 16% of $T(\chi_{max})$. For three-dimensional magnets, an inflection point, corresponding to a long-range ordering transition, is generally found within 5% of $T(\chi_{max})$.[12] Thus the exchange influencing the susceptibility of the tetrahedra must be lower dimensional exchange. Examination of the structure shows that the most likely explanation is that the isolated tetrahedra are, in fact, themselves formed into linear chains with the intrachain exchange achieved through Cl–Cl contacts. The $(MnCl_4)^{2-}$ tetrahedra in $[(CH_3)_3NH]_3Mn_2Cl_7$ are arranged such that one of the Cl atoms of any given tetrahedron is within about 4 Å of each of three Cl atoms of the next closest tetrahedron along the c axis. These Cl–Cl contacts thus result in chains of interacting $(MnCl_4)^{2-}$ tetrahedra parallel to the c axis. It
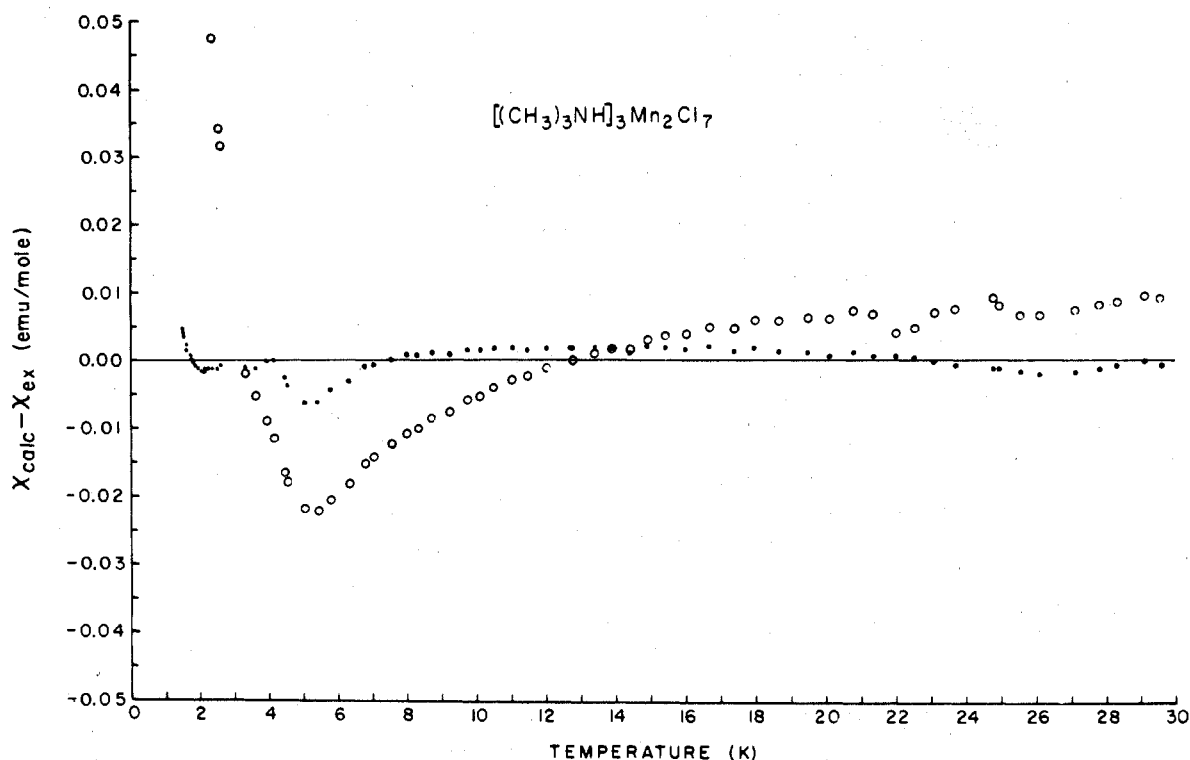
Figure 2. Comparison of the deviations of the fitted susceptibility from that experimentally measured for the two cases described in the text. Open circles are for the molecular field model and dots are for the model using two independent chains. Note that below about 2.3 K the molecular field model deviations are off-scale. The small anomaly near 5 K is an artifact of the measurement technique.

is important to point out that 4 Å is only slightly greater than twice the crystal ionic radius of Cl. Furthermore, it has recently been shown that close Cl–Cl contacts in the compound Cs_2CoCl_4 result in observable exchange in the liquid helium region.[13] Thus it is reasonable to treat the contribution to the susceptibility of $[(CH_3)_3NH]_3Mn_2Cl_7$ from the $(MnCl_4)^{2-}$ tetrahedra in the same manner as the contribution from the infinite $(MnCl_3)_n{}^{n-}$ chains, using, however, a different intrachain exchange constant, J'_{LC}. With this approach an excellent fit to the parallel data from 1.5 to 30 K can be achieved, with differences between the fit and the data being less than 1% over the entire region. The resulting exchange parameters are $J_{LC}/k = -11 \pm 6$ K and $J'_{LC}/k = -0.20 \pm 0.1$ K. The large uncertainty in J_{LC} is a direct result of the fact that such a large exchange constant leads to a small contribution to the total susceptibility and that such a small value is comparable to the measuring system's calibration uncertainty. A plot of the deviations of the experimental points from the fitted curve is shown in Figure 2 along with the deviations which resulted from the molecular field fit. The double-chain model clearly is superior. Although there are consistent deviations for that fit, since they all are less than 1%, they should not be considered as serious.

Discussion

The quality of the fit is so good as to leave little doubt that there are two independent species of linear chains in $[(CH_3)_3NH]_3Mn_2Cl_7$. This conclusion qualitatively explains the unusual amount of anisotropy observed, since one would expect the $(MnCl_4)^{2-}$ tetrahedral chains to exhibit anisotropy similar to that displayed by the infinite $(MnCl_3)_n{}^{n-}$ chains in TMMC. Thus the anisotropy observed at the higher temperatures in $[(CH_3)_3NH]_3Mn_2Cl_7$ is probably due to the anisotropy resulting from the contribution from the TMMC-like chains, while at lower temperatures it is probably due to a similar effect becoming significant for the $(MnCl_4)^{2-}$ tetrahedral chains. (This argument is, in fact, why the parallel data were used in the fitting process.)
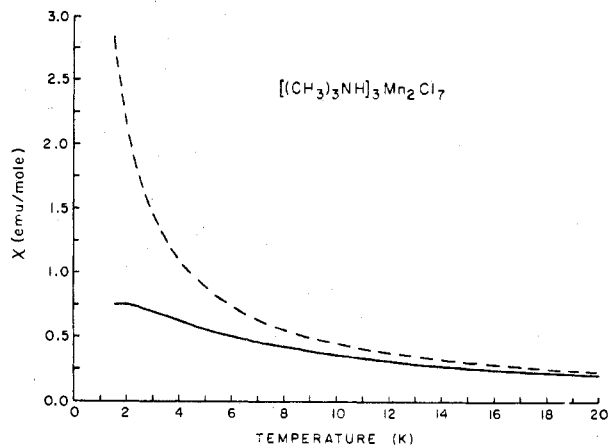

Figure 3. Comparison of the predicted susceptibility for the case with interactions between tetrahedra which create chains (solid curve) and the case with no such interactions (dashed curve).

Although the value determined for J'_{LC} is relatively small, it is interesting to note that it has a significant effect on the susceptibility behavior in the observed region. Figure 3 compares the behavior calculated for the fitted value of J'_{LC} and for the case where $J'_{LC} = 0$, which is equivalent to the tetrahedra contributing to the susceptibility according to the Curie law.

There are some obvious further experimental measurements which should be made on this compound. In particular, EPR line width studies, especially temperature-dependent ones, similar to those done on other Heisenberg linear-chain systems[7,14] should prove quite interesting. Also, low-temperature heat capacity measurements should resolve the heat capacity anomaly associated with the tetrahedral chains since it should be much larger than the contributions from the lattice and the infinite $(MnCl_3)_n{}^{n-}$ chains. In other heat capacity studies on Heisenberg linear-chain systems the linear-chain anomaly has been masked by the lattice.[15-19]

Finally, considering possible interchain interactions, one notes that the closest approach of the two different types of chains is about the same as the closest approach between the $(MnCl_4)^{2-}$ tetrahedral chains. It thus seems likely that interchain interactions between the two different types of chains will be responsible for any long-range transition which occurs in $[(CH_3)_3NH]_3Mn_2Cl_7$. Because of the small intrachain exchange in the tetrahedral chains, it would seem that there is a reasonable possibility that such a transition will occur at a lower temperature than the one observed in TMMC. In any case, lower temperature measurements should provide useful insight into the interchain interactions and may well prove $[(CH_3)_3NH]_3Mn_2Cl_7$ to be a more ideal one-dimensional material than TMMC.

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Physical Properties of Linear-Chain Systems. III. Absorption Spectra of RbFeBr₃, CsFeBr₃, RbFeCl₃, CsFeCl₃, and CsMg₁₋ₓFeₓCl₃

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The polarized, single-crystal absorption spectra of the linear-chain compounds $RbFeBr_3$, $CsFeBr_3$, $RbFeCl_3$, $CsFeCl_3$, and $CsMg_{1-x}Fe_xCl_3$ have been measured between 298 and 4.2 K. The spectra of the pure salts and the dilute samples are similar in terms of absorption positions but the spin-forbidden transitions in the pure salts show anomalous intensity. The intensity of spin-forbidden absorptions in some cases nearly equals that of the spin-allowed $^5T_2(D) \rightarrow {}^5E(D)$ absorption. The spectra are assigned to the octahedral, ligand field states of the high-spin d^6 electronic configuration. The intensity of the spin-forbidden transitions results from a cooperative mechanism which relaxes the spin selection rule without energetically perturbing the electronic states involved. The results of this work add significant features to the empirical characterization of this mechanism and may aid theoretical progress in this area.

Introduction

The unusual physical properties displayed by certain materials of the ABX_3 formulation derive from the unique structure of these compounds. When $A^+ = Cs^+$, Rb^+, or $(CH_3)_4N^+$, B = a divalent, first-row transition metal ion, and $X^- = Cl^-$, Br^-, or I^-, these materials crystallize as a hexagonal array of infinite linear chains of face-sharing $[X_3BX_3]^{4-}$ octahedra separated by the A cations. The interchain separation afforded by the A cations acts as an effective magnetic insulation which constrains exchange interactions to one dimension, that along the chains.[2]

The unique character of these systems is evidenced in their magnetic and spectral properties. Tetramethylammonium trichloromanganate(II), TMMC, orders in three dimensions only at 0.84 K[3] while spin correlation in one dimension is evident at much higher temperatures.[4] Measured absorption spectra reveal a cooperative mechanism which relaxes the $\Delta S = 0$ spin selection rule and results in marked enhancement of absorptions corresponding to formally spin-forbidden transitions.[3,5-7] Such enhancement is observed in materials which possess isotropic exchange coupling but appears to be most pronounced in the ABX_3 linear-chain materials.

In an effort to characterize these unique compounds more fully and to resolve better the effect of unidimensional magnetic exchange on the electronic properties of the system, the absorption spectra of $RbFeBr_3$, $CsFeBr_3$, $RbFeCl_3$, $CsFeCl_3$, and $CsMg_xFe_{1-x}Cl_3$ have been investigated between room temperature and 4.2 K. $CsFeCl_3$[8] and $RbFeCl_3$[8-10] are reported to possess intrachain ferromagnetic coupling and interchain antiferromagnetic coupling with $T_N < 1.3$ K and $T_N = 2.54$ K, respectively. $RbFeBr_3$ is reported to possess intrachain and interchain antiferromagnetic coupling with $T_N = 5.5$ K. The magnetic properties of $CsFeBr_3$ have not been studied in detail but measurements of powder susceptibility between room temperature and 4.2 K correlate well with those of $RbFeBr_3$.[12] Thus, these materials provide a means of comparing the effects of ferromagnetic and antiferromagnetic intrachain exchange coupling on the absorption spectra of isoelectronic, isostructural materials.

This study also serves a second fundamental purpose by providing a better empirical characterization of the triplet structure of iron(II). The electronic structure of this ion in an octahedral field is dominated by spin-forbidden $^5T_2(D) \rightarrow {}^3\Gamma$ transitions with only one quintet–quintet excitation possible.