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Dipolar Magnetic Anisotropy and Anomalous Susceptibility Behavior in [(CH$_3$)$_3$NH]$_3$Mn$_2$Br$_7$, a Heisenberg Linear-Chain Antiferromagnet

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Magnetic susceptibility measurements between 1.5 and 30 K are reported for a single crystal of [(CH$_3$)$_3$NH]$_3$Mn$_2$Br$_7$. The results are quite similar to those previously reported for the chloride analogue which was shown to be composed of two different types of Heisenberg linear chains. At the lowest temperatures the present compound, however, exhibits different behavior and appears to lose its one-dimensional character and order antiferromagnetically. A model which includes the effect of dipolar intrachain interactions has been successfully used to describe the anisotropy observed in the paramagnetic state with the resulting intrachain exchange parameters of $J_1/k = -4.5 \pm 0.8$ K and $J_2/k = -0.206 \pm 0.007$ K.

Compounds which display lower dimensional characteristics in their magnetic behavior have attracted much interest of late,[1] primarily because of the availability of model solutions applicable to such systems. In particular, Mn(II) compounds are of special interest since that ion usually exhibits low anisotropy thus leading to magnetic behavior which is Heisenberg-like in nature. To a large extent, recent work has involved three relatively different Mn(II) linear chain compounds: CsMnCl$_3$·2H$_2$O,[2-8] [(CH$_3$)$_3$NH]MnCl$_3$·2H$_2$O,[9-11] and [(CH$_3$)$_4$N]MnCl$_3$ (TMMC).[12-21] These materials, as well as some of their analogues, consist of infinite chains of mono-, di-, and trihalide-bridged Mn(II) ions, respectively. More recent work[22,23] has resulted in the discovery of a compound, [(CH$_3$)$_3$NH]$_3$Mn$_2$Cl$_7$ (TTMMC), which has been characterized as containing two different types of magnetically independent linear chains of Mn(II) ions. The structure analysis[23] of this material shows it consists of infinite chains of trihalide-bridged Mn(II) ions (very similar to those found in TMMC) separated by [(CH$_3$)$_3$NH]$^+$ cations and (MnCl$_4$)$^{2-}$ anions. A view of its structure down the chain axis is shown in Figure 1. The magnetic results[22] clearly imply that the (MnCl$_4$)$^{2-}$ ions interact in linear chains, consistent with the structure which shows close Cl–Cl contacts between the otherwise isolated tetrahedra. The separation of the Mn(II) ions in the chains formed by the tetrahedra is twice the separation of the halide-bridged ions.

The magnitude of the exchange associated with the chains of tetrahedra is roughly 50 times smaller than that found for the TMMC-like chains. Thus, since the contribution to the susceptibility from the TMMC-like chains is quite small, the primary source of the magnetic behavior in the temperature region above 1 K is the magnetic exchange in the chains of

tetrahedra, and therefore TTMMC offers an excellent opportunity for studying magnetic effects in a Heisenberg linear-chain system over a temperature region which is large compared to the exchange involved. In particular, TTMMC may provide the first opportunity to study the magnetic heat capacity of a high-spin Heisenberg linear-chain system without having to make large corrections for lattice contributions. However, such measurements would be considerably easier if the intrachain exchange in the chains of tetrahedra were somewhat larger. It is with this idea in mind that the present study, in which the bromide analogue of TTMMC was prepared, was undertaken, since bromide isomorphs of chloride compounds often exhibit greater magnetic exchange.[9] As it turns out, the intrachain exchange in [(CH$_3$)$_3$NH]$_3$Mn$_2$Br$_7$ (TTMMB) is not significantly different from that of TTMMC, but the magnetic behavior at lowest temperatures is.

Experimental Section

Single crystals of TTMMB were obtained in a manner similar to that used to obtain the TTMMC crystals: an absolute methanolic solution of (CH$_3$)$_3$N·HBr and MnBr$_2$ was slowly evaporated in a sealed container over a period of 2 years. The needles obtained tend to grow long and thin and become thick only over an extended period of time. They are orange-red and very similar in habit to those of TTMMC, being six-sided in general, although the side faces are not always equally developed. Use of a polarizing microscope showed the needle axis to be a uniaxial axis, as was the case for TTMMC. Thus, although it is possible that TTMMB and TTMMC may not be strictly isomorphic, their gross physical features indicate a degree of similarity sufficient to allow interpretation of the present results in terms of the TTMMC structure. Anal. Calcd for [(CH$_3$)$_3$NH]$_3$Mn$_2$Br$_7$: C, 12.72; H, 3.56; N, 4.94; Mn, 12.93; Br, 65.84. Found (by Galbraith Laboratories, Inc.): C, 12.54; H, 3.89; N, 4.86; Mn, 12.78; Br 65.74. The agreement is quite satisfactory.
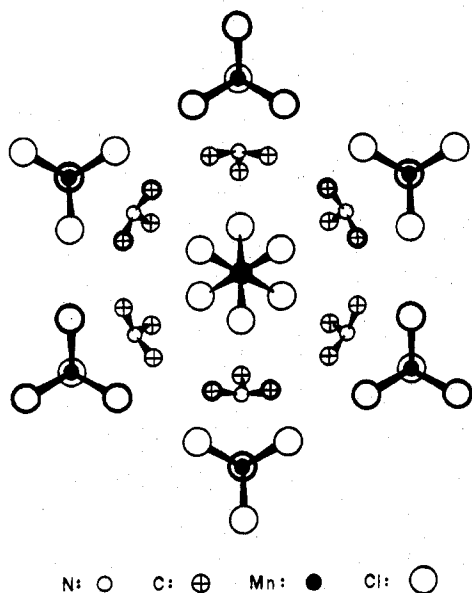
Figure 1. A view of the structure of TTMMC looking down the $-c$ axis (the axis along which the chains run). Not all of the $[(CH_3)_3NH]^+$ ions shown are in the same plane, just as not all of the $(MnCl_4)^{2-}$ ions shown are in the same plane. The atoms which are roughly in the same plane as the central Mn atom have been given darker boundaries.

As a sufficiently thick enough needle was not avialable for study, a single long specimen with a prominent flat face weighing 0.096 g was broken into three parts after being examined with a polarizing microscope to ensure it was perfect and then used for the measurements. The three parts of the sample were always kept carefully aligned relative to each other using the flat faces and the crystal edges so that measurements on them would be equivalent to measurements on a single crystal. Details of the low-frequency near-zero-field mutual-inductance technique used to measure magnetic susceptibilities as a function of temperature parallel and perpendicular to the needle axis of the crystal have been given elsewhere.[24] The absolute accuracy

of the measurements is considered to be about 1–2%.

Results and Analysis

The results, shown in Figure 2, are quite similar to those of the chloride analogue, as expected. The magnitude of the susceptibility is significantly reduced from that of a normal paramagnet and implies the presence of extensive antiferromagnetic exchange; between the two sets of measurements there is considerable anisotropy which increases with decreasing temperature, with the susceptibility measured parallel to the needle axis being greater than that measured perpendicular to it, just as in the case of TMMC and TTMMC, and a maximum, typically expected for a material containing antiferromagnetic exchange, appears in each data set near 2 K. However, there appears to be a significant difference in the detailed behavior of TTMMB and TTMMC at the lowest temperatures; the susceptibility maxima for TTMMB are much sharper than those observed for TTMMC. In addition, an inflection point in the TTMMB $\chi_{\parallel}$ data at $T_N = 1.70 \pm 0.01$ K is clearly evident, as can be seen from the insert in Figure 2. Such an inflection point is evidence that an antiferromagetic–paramagnetic transition occurs at that temperature.[25] In a lower dimensional magnetic material the transition is generally well below the temperature of the susceptibility maximum. Since T_N in TTMMB is within 5% of that temperature (1.79 ± 0.02 K), the results seem to suggest that the paramagnetic state *immediately* above T_N is one in which there is *no* lower dimensional behavior. This is in contrast to the behavior observed for TTMMC (shown in Figure 3), in which any magnetic transition in that material must occur at a temperature at least 16% lower than that of the susceptibility maximum. Another unusual feature which appears in both of the TTMMB sets of measurements is the presence of a kink in the data near 2.1 K. The closeness of this temperature to the ordering temperature of $MnBr_2 \cdot 4H_2O$ might seem suspicious, but the presence of any hydrate is unlikely since water was carefully excluded during the growth of the crystals. Actually, it is only below this temperature that the behavior of the TTMMB data is significantly different
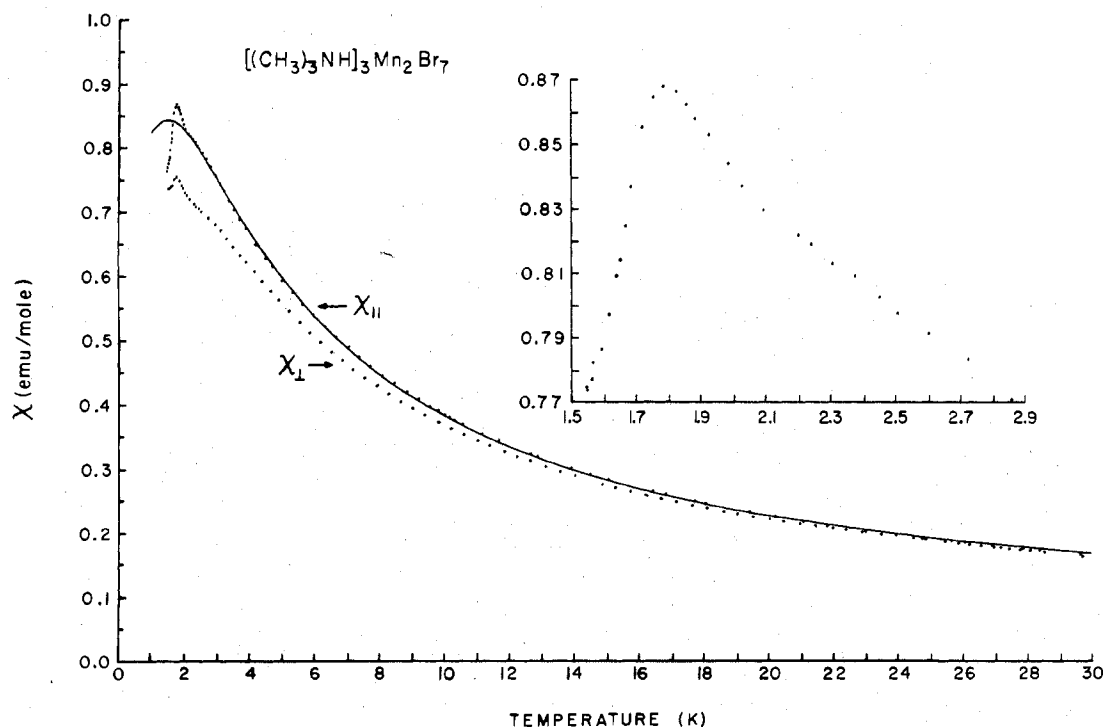

Figure 2. The magnetic susceptibility of TTMMB measured parallel and perpendicular to the needle axis. The parallel susceptibility is greater than the perpendicular susceptibility over the entire region shown. The inset is an expanded view of the behavior of the parallel data near 2 K and the solid curve is the result of fitting the parallel data with the two-independent-chain model discussed in the text.
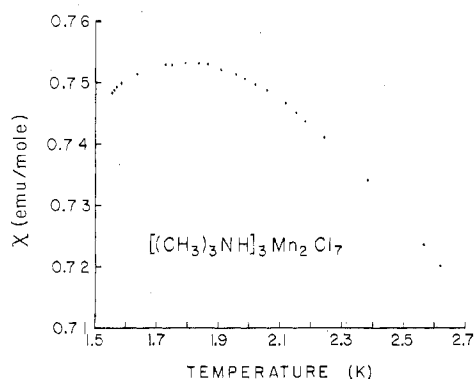
Figure 3. An expanded view of the susceptibility behavior measured parallel to the c axis in the vicinity of 2 K for TTMMC.

from that of the TTMMC data.

Thus, initially, an analysis using the model found applicable to TTMMC is suggested. In that case, the total susceptibility, $\chi_{TOT} = \chi_1 + \chi_2$, is considered to result from the susceptibility due to the halide-bridged chains, χ_1, and that arising from the linear chains of isolated tetrahedra, χ_2. For both susceptibility contributions the classical Heisenberg linear-chain equation previously used for spin 5/2 linear chains[2,12,22] must be used:

$$\chi_i = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \frac{1+u_i}{1-u_i} \tag{1}$$

where $u_i = \coth(1/t) - t$, with $t = T/T_{0i}$ and $T_{0i} = 2J_i S(S+1)/k$.

When this model is applied to the parallel susceptibility, the values $J_1/k = -4.3 \pm 0.9$ K and $J_2/k = -0.185 \pm 0.005$ K result. These are to be compared to $J_1/k = -11 \pm 6$ K and $J_2/k = -0.20 \pm 0.01$ K, respectively, for TTMMC. (The uncertainty in the value of J_2 for TTMMC was originally misprinted to be ten times larger.) A more careful analysis of the effect of the equipment calibration on the parameter values has enabled a tighter estimate of the uncertainties reported here. The fitted curve is included in Figure 2. The fit is clearly quite good, matching all the parallel data between 2.5 and 28 K within 1%, but the isotropic model used does not account for the anisotropy. Indeed, except for the reasoning given in the TTMMC study, the perpendicular data set might well have been used for the fit with slightly different parameter values resulting. Thus, an attempt has been made to modify the model so as to be able to predict the anisotropy also.

Previous studies[2,5,13] of spin 5/2 linear-chain systems have also shown anomalously large anisotropy, although not as large in magnitude as that reported here. There are two obvious possible sources of such anisotropy: either dipolar interactions or single-ion zero-field splitting can give rise to axial anisotropy in linear-chain systems. Dipolar interactions have been shown to give a fairly good qualitative representation of the behavior of TMMC[13] while the susceptibility of CsMnCl$_3$·2H$_2$O has been described both by zero-field splitting effects[2] as well as dipolar effects.[5] Since dipolar interactions must be present in any case, it is best to consider their effects first, before including zero-field effects which are usually small for Mn(II).

The approach used here will be essentially that used in the two studies of CsMnCl$_3$·2H$_2$O.[2,5] That is, a perturbation term involving the anisotropy source is added to the Hamiltonian of the system. Because there are several typographical errors in one of those studies[5] and because that work does not give explicit expressions for the individual susceptibilities, but only their difference, a somewhat detailed presentation of the theoretical calculations involved will be given here.

In general, the energy of interaction of two magnetic moments, $\vec{m}_i$ and $\vec{m}_j$, is given by

$$\mathcal{H}_{ij}^d = \frac{\vec{m}_i \cdot \vec{m}_j}{r_{ij}^3} - \frac{3(\vec{m}_i \cdot \vec{r}_{ij})(\vec{m}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \tag{2}$$

where $\vec{r}_{ij}$ is the vector from the ith to the jth site. By using $\vec{m}_i = g\mu_B \vec{S}_i$, where S_i is the spin of ion i, with eq 2, the total dipolar interaction energy of ion i can be written

$$\mathcal{H}_i^d = g^2\mu_B^2 \sum_j \left[\frac{\vec{S}_i \cdot \vec{S}_j}{r_{ij}^3} - \frac{3(\vec{S}_i \cdot \vec{r}_{ij})(\vec{S}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] \tag{3}$$

If eq 3 is applied to a linear chain of $N+1$ spins in which the spins are separated by the distance c along the z axis and if, for a first approximation, only nearest neighbor interactions are included, then eq 3 can be used to obtain the dipolar Hamiltonian for the entire chain:

$$\mathcal{H}_{dip} = \frac{g^2\mu_B^2}{c^3} \sum_{j=1}^{N} [\vec{S}_j \cdot \vec{S}_{j-1} - 3S_j^z S_{j-1}^z] \tag{4}$$

Thus, the total spin Hamiltonian for a linear chain of $N+1$ spins with dipolar interactions included becomes, to a first approximation

$$\mathcal{H}_{TOT} = \mathcal{H}_{ex}' + \mathcal{H}_{dip}' + \mathcal{H}_{Zeeman} \tag{5}$$

where

$$\mathcal{H}_{ex}' = -2J(1+\alpha) \sum_{j=1}^{N} \vec{S}_j \cdot \vec{S}_{j-1} \tag{6}$$

$$\mathcal{H}_{dip}' = 6J\alpha \sum_{j=1}^{N} S_j^z S_{j-1}^z \tag{7}$$

$$\mathcal{H}_{Zeeman} = -g\mu_B \sum_{j=0}^{N} \vec{S}_j \cdot \vec{H} \tag{8}$$

and

$$\alpha = \frac{1}{2J} \frac{g^2\mu_B^2}{c^3} \tag{9}$$

In the classical limit the equations become

$$\mathcal{H}_{ex}' = -2J(1+\alpha)S(S+1) \sum_{j=1}^{N} \vec{s}_j \cdot \vec{s}_{j-1} \tag{10}$$

$$\mathcal{H}_{dip}' = 6J\alpha S(S+1) \sum_{j=1}^{N} s_j^z s_{j-1}^z \tag{11}$$

and

$$\mathcal{H}_{Zeeman} = -g\mu_B [S(S+1)]^{1/2} \sum_{j=0}^{N} \vec{s}_j \cdot \vec{H} \tag{12}$$

In general, the total spin Hamiltonian and the partition function

$$Z_N = \int \exp(-\mathcal{H}_{TOT}/kT) \frac{d\Omega_0}{4\pi} \frac{d\Omega_1}{4\pi} \cdots \frac{d\Omega_N}{4\pi} \tag{13}$$

(where $d\Omega_i$ refers to the solid angle element associated with $\vec{s}_i$) can be used to calculate the susceptibility from the definition

$$\chi = kT(\partial^2 Z_N/\partial H^2) \tag{14}$$

For the case $\alpha = 0$, the calculation gives

$$\chi = \frac{g^2\mu_B^2 S(S+1)}{kT} \sum_{i=0}^{N} \sum_{j=0}^{N} \langle s_i^z s_j^z \rangle \tag{15}$$

where the zero-field pair correlation function is given by

$$\langle s_i{}^z s_j{}^z \rangle = \frac{1}{Z_N} \int s_i{}^z s_j{}^z$$

$$\exp(-\mathcal{H}_{ex}{}'/kT) \frac{d\Omega_0}{4\pi} \frac{d\Omega_1}{4\pi} \ldots \frac{d\Omega_N}{4\pi} \qquad (16)$$

Fisher[26] has given the results of the calculation indicated in eq 16 as

$$\langle s_i{}^z s_j{}^z \rangle = u^{|j-i|}/3 \qquad (17)$$

where u is defined as in eq 1. When eq 17 is used with eq 15, eq 1 results.

For the case $\alpha \neq 0$, the susceptibility may be easily calculated using eq 10-14 if the dipolar interaction energy of eq 11 is considered to be small compared to kT. The outline of the calculation is as follows. First eq 10-12 are inserted in eq 13 and then the differentiation indicated in eq 14 is performed. To obtain the zero-field result, H is set equal to 0 and the term $\exp(-\mathcal{H}_{dip}{}'/kT)$ is expanded and approximated as $1 - (\mathcal{H}_{dip}{}'/kT)$. The result is

$$\chi = \chi_0 + \frac{g^2\mu_B{}^2 S(S+1)}{kT}\left[\frac{6|J|S(S+1)\alpha}{kT} W\right] \qquad (18)$$

where χ_0 is given by eq 1 with $T_{0i} = 2J(1+\alpha)S(S+1)/k$. The parallel susceptibility, $\chi_\parallel$, is obtained by using $H\parallel z$, then

$$W = \sum_{i=0}^{N}\sum_{j=0}^{N}\sum_{k=0}^{N} (\langle s_i{}^z s_j{}^z s_k{}^z s_{k-1}{}^z\rangle - \langle s_i{}^z s_j{}^z\rangle\langle s_k{}^z s_{k-1}{}^z\rangle) \qquad (19)$$

where the pair correlation terms are given by eq 16 and the fourth-order spin-correlation term is given by

$$\langle s_i{}^z s_j{}^z s_k{}^z s_{k-1}{}^z\rangle = \frac{1}{Z_N}\int s_i{}^z s_j{}^z s_k{}^z s_{k-1}{}^z$$

$$\exp(-\mathcal{H}_{ex}{}'/kT) \frac{d\Omega_0}{4\pi} \frac{d\Omega_1}{4\pi} \ldots \frac{d\Omega_N}{4\pi} \qquad (20)$$

The same calculation with the terms $s_k{}^z$ and $s_{k-1}{}^z$ in eq 19 replaced by $s_k{}^x$ and $s_{k-1}{}^x$, respectively, can be performed to obtain the susceptibility perpendicular to the chain direction, $\chi_\perp$.

In order to evaluate the expressions for the parallel and perpendicular susceptibilities, expressions for the fourth-order spin-correlation terms must be obtained and summed according to eq 19. Nagata and Tazuke have outlined[4] the derivation of the correlation functions and also given the procedure to be used in summing them; in addition a general formula for the correlation functions has been given by Tomita and Mashiyama.[27] For the sake of completeness, and since there is a typographical error in Nagata and Tazuke's result, explicit expressions for the required terms will be given here. In these results $v = 1 - 3ut$, where u is the same as u_i in eq 1, $t = T/T_0$, and where, as in eq 18, $T_0 = 2J(1+\alpha)S(S+1)/k$. Because of the multiple summations in eq 19, several cases must be considered: (1) for $i \leq m$, $j \geq m+1$

$$\langle s_i{}^z s_m{}^z s_{m+1}{}^z s_j{}^z\rangle = \frac{1}{5}u^{j-i-1}(1 - \frac{4}{3}ut) \qquad (21)$$

and

$$\langle s_i{}^z s_m{}^x s_{m+1}{}^x s_j{}^z\rangle = \frac{1}{15}u^{j-i-1}v \qquad (22)$$

(2) for $j \leq m$, $i \geq m+1$ the results are as above with i and j interchanged.

(3) for $i \leq j \leq m$

$$\langle s_i{}^z s_j{}^z s_m{}^z s_{m+1}{}^z\rangle = \frac{1}{9}u^{j-i+1}(1 + \frac{4}{5}v^{m-j}) \qquad (23)$$

and

$$\langle s_i{}^z s_j{}^z s_m{}^x s_{m+1}{}^x\rangle = \frac{1}{9}u^{j-i+1}(1 - \frac{2}{5}v^{m-j}) \qquad (24)$$

(4) for $m+1 \leq i \leq j$

$$\langle s_m{}^z s_{m+1}{}^z s_i{}^z s_j{}^z\rangle = \frac{1}{9}u^{j-i+1}(1 + \frac{4}{5}v^{i-m-1}) \qquad (25)$$

and

$$\langle s_m{}^x s_{m+1}{}^x s_i{}^z s_j{}^z\rangle = \frac{1}{9}u^{j-i+1}(1 - \frac{2}{5}v^{i-m-1}) \qquad (26)$$

Eq 19 may be evaluated for finite values of N by first summing the correlation functions over the i and j indices. The result, a function of k and N, may then be summed over the k index. If N is allowed to become very large, then relatively simple equations for the parallel and perpendicular susceptibilities of an infinite linear chain with dipolar interactions result.

For measuring fields parallel to the chain, W in eq 18 is

$$W_\parallel = \frac{2}{5}(1 - \frac{4}{3}ut)\frac{1}{(1-u)^2} - \frac{2}{9}\frac{u^2}{(1-u)^2} + \frac{8}{135t}\frac{1+u}{1-u} \qquad (27)$$

and for perpendicular fields

$$W_\perp = \frac{2}{15}(1 - 3ut)\frac{1}{(1-u)^2} - \frac{2}{9}\frac{u^2}{(1-u)^2} - \frac{4}{135t}\frac{1+u}{1-u} \qquad (28)$$

These results may be combined to give the differences in parallel and perpendicular susceptibilities reported by Nagata et al.[5]

$$\chi_\parallel - \chi_\perp = \alpha\frac{|J|}{kT^2}\frac{N\mu_B{}^2}{k}g^2[S(S+1)]^2 X \qquad (29)$$

where

$$X = \frac{4}{5}\left[\frac{2-ut}{(1+u)^2} + \frac{2}{3t}\frac{1+u}{1-u}\right] \qquad (30)$$

It is important to note that eq 27 and 28 can be used to predict the susceptibility for a powder. In that case $W_{powder} = (W_\parallel + 2W_\perp)/3$ must be used in eq 18. The result is

$$W_{powder} = \frac{2}{3}(1 - 2ut)\frac{1}{(1-u)^2} - \frac{2}{3}\frac{u^2}{(1-u)^2} \qquad (31)$$

Interestingly, these results indicate that when dipolar effects are included there is a term which must be added to the result calculated classically for powder susceptibilities of linear chains. This is in contrast to the case when single-ion zero-field splitting effects are assumed to be the cause of anisotropy, since the added effects then cancel for a powder measurement.[2] The lack of cancellation in the present case may just be a result of the approximate techniques used in the calculations. Indeed, at low temperatures (where $t \rightarrow 0$ and $u \rightarrow -1$) W_{powder} approaches zero.

In order to apply the above results to a linear-chain magnet, a value for the distance between interacting dipoles, c, is required. As the structural details of TTMMB have not yet been investigated, it is necessary to estimate this value. Since the physical and magnetic properties of TTMMB are so similar to those of TTMMC, it is quite reasonable to assume TTMMB's structure to be essentially the same as that of TTMMC. Then, as an aid in estimating the distances between the Mn(II) ions in the TMMC-like chains, it is useful to consider data which are available for several other compounds which contain similar type chains. These data, given in Table I, lead to an estimate of 3.35 Å for that distance in TTMMB. The Mn(II)–Mn(II) separation for the magnetic chain formed by the (MnBr₄)²⁻ tetrahedra would then be twice this value.

By using the above estimates with the two independent chain model, modified according to eq 18, 27, and 28 to include dipole effects, it is possible to fit the data, including the
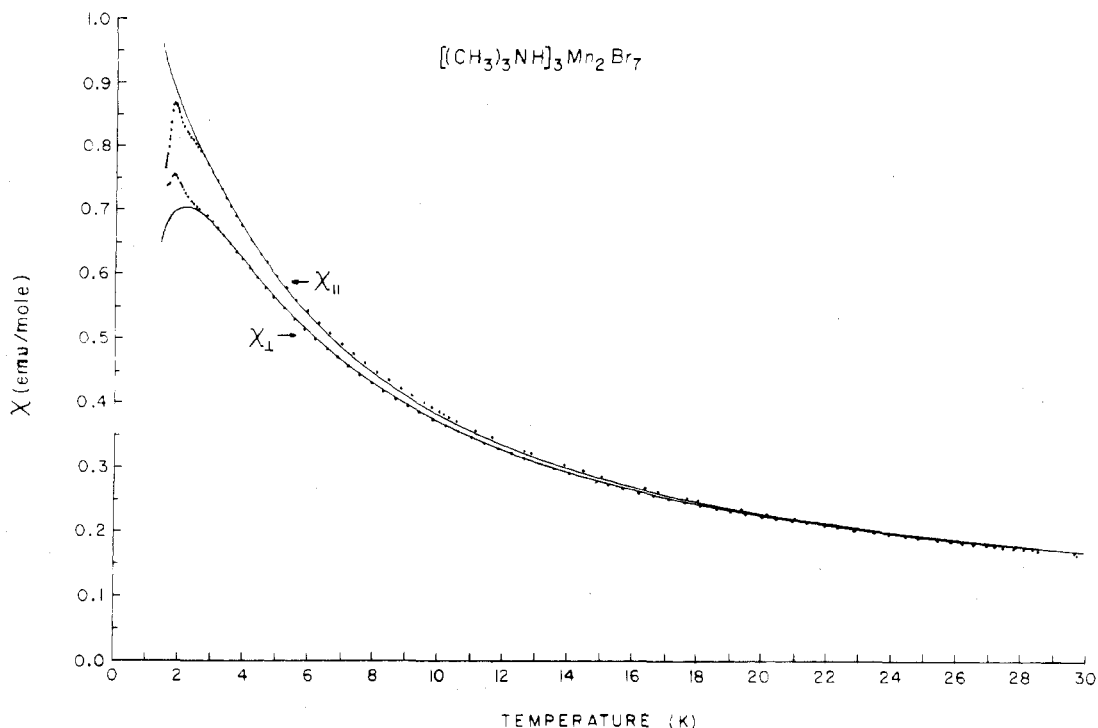
Figure 4. The same data as shown in Figure 2, but with the solid curves representing the fitted results when dipolar anisotropy is included in the model.

Table I. Metal–Metal Intrachain Distances (in Å) in Several Compounds Containing TMMC-like Chains

		M	
	X	Mn	Cd
For [(CH$_3$)$_4$N]MX$_3$	Cl	3.247[a]	3.331[b]
	Br	3.38[c]	
For [(CH$_3$)$_3$NH]$_3$M$_2$X$_7$	Cl	3.207[d]	
	Br		3.434[e]

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anisotropy. The parameter values which result from such a fit are $J_1/k = -4.5 \pm 0.8$ K and $J_2/k = -0.206 \pm 0.007$ K. The results of this fit are shown in Figure 4; the fitted curves match *both* sets of data points within 1.5% from 2.5 to 28 K! It is important to note four points. First, the fit suggests that the perturbation technique used in the calculations gives results which are valid for values of kT/J above 12. The calculation is clearly invalid below a value of kT/J of 5, since it has been shown[13] that at very low temperatures $\chi_\perp$ should be about half of $\chi_\parallel$ for a spin 5/2 Heisenberg chain with dipolar anisotropy. Second, the intrachain exchange values obtained when dipolar interactions are included are close to those obtained from the fit in which such interactions are ignored. Presumably the J_2 value thus obtained using the more complete theory is more trustworthy than the earlier value. Third, the fitted results are not very sensitive to the Mn(II)–Mn(II) distances used and equally good fits may be obtained using other reasonable estimates. In fact, the best fit is obtained when c is assumed to be 3.5 Å for the TMMC-like chains (and 7.0 Å for the chains of (MnBr$_4$)$^{2-}$ tetrahedra), but the quality of the data is not high enough to presume that this value is any more trustworthy than the one used, especially considering that the dipolar interaction is not truly just nearest neighbor in nature, as assumed. With extremely high quality data and further refinements to the approximate theory used here it might prove

possible to actually fit the parameter c. Fourth, the result of including zero-field splitting in addition to the dipolar effects was studied and only an insignificant improvement was found using values of D/k near 0.05 K. Although one of the Mn–Cl bonds in the (MnCl$_4$)$^{2-}$ tetrahedron in the TTMMC structure is 0.03 Å longer than the others, giving rise to a distortion from T_d symmetry, the present results suggest the ions in TTMMB are not distorted enough to give rise to any significant zero-field splitting.

In summary, the results indicate that TTMMB is quite similar in its properties to TTMMC. Indeed, the fit of the unusual amount of anisotropy observed in TTMMB with a chain-like model including dipolar interactions virtually proves the presence of two different types of magnetic chains in it. What is still perplexing is the apparent change from lower dimensional behavior to three-dimensional behavior at a temperature some 25% above the long-range transition temperature. Although the crystals used in the studies showed no obvious signs of having undergone a structural phase transition (such as having shattered), the kink in the data near 2 K could still imply the presence of structural changes which allow a strong enough interaction between the isolated chains such that the dimensional nature of the magnetic interactions is raised. Structural transitions have been observed in TMMC and its analogues,[28] but usually at much higher temperatures. A crystallographic transition at such low temperatures would be quite unusual, however. Furthermore, it is not clear how a compound with a structure presumably similar to that of TTMMC can very easily become three-dimensional in magnetic character. Any exchange pathways which could contribute to interchain exchange are not very short and would be expected to be quite weak. Dipolar interactions conceivably could be the driving force behind interchain interactions in TTMMB, but evidence for them should have been observed in TTMMC also. Further experiments, perhaps including heat capacity measurements and low-temperature structural investigations, are called for.

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Reactions of Coordinated Molecules. 8. Geometrical Isomerization of Tris(acetyl(phenylacetyl)tetracarbonylmanganato)aluminum: an Unsymmetrical Metallo-β-diketonate Complex

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The intramolecular geometrical isomerization of the cis and trans isomers of the unsymmetrical tris-chelate metallo-β-diketonate complex [*cis*-(OC)$_4$Mn(CH$_3$CO)(C$_6$H$_5$CH$_2$CO)]$_3$Al was followed as a function of time by ^{1}H NMR in CCl$_4$ solution at 16, 29, and 36 °C. The first-order rate constant for this isomerism at 298 K is $(0.76 \pm 0.04) \times 10^{-3}$ s^{-1}, and the values of the activation parameters are $\Delta H^\ddagger = 30.2 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = 28.8 \pm 2.6$ eu. The equilibrium constant, defined by [cis]/[trans], was determined at 9, 15, 36, and 45 °C. The calculated ground-state thermodynamic parameters are $\Delta H^\circ = -1.8 \pm 0.6$ kcal/mol, $\Delta S^\circ = -9.0 \pm 2.1$ eu, and $\Delta G^\circ_{298} = 0.89 \pm 0.03$ kcal/mol.

The geometrical isomerization of tris-chelate complexes containing unsymmetrical, β-diketonate ligands has been investigated extensively in recent years.[1,2] Although the elucidation of the mechanism of this isomerization is an exceedingly difficult and usually futile task, the observation of discrete geometrical isomers does confirm the essentially octahedral coordination of the chelating ligands.

In a previous paper of this series the preparation and molecular structure of the first metallocetylacetonate complex, [*cis*-(OC)$_4$Mn(CH$_3$CO)$_2$]$_3$Al, was reported.[3] This complex is a close structural analogue to tris(acetylacetonate)aluminum, Al(acac)$_3$, where the methine group of each acac ligand is replaced formally by the organometallic group, Mn(CO)$_4$. Several other tris-chelate complexes of aluminum and gallium containing a variety of metallo-β-diketonate ligands have been prepared.[4] Also, the preparation and molecular structure of the first metallo-β-diketone molecule were reported recently.[5]

In this paper we wish to substantiate the solution-phase structural similarity of the tris-chelate complexes which contain β-diketonate ligands to those complexes which contain metallo-β-diketonate ligands, since such a comparison of a closely analogous metallo-β-diketonate complex has been reported in the solid state.[3] This solution-phase structural similarity was established by demonstrating the geometrical isomerization of a tris-chelate complex having unsymmetrical metallo-β-diketonate ligands. By use of ^{1}H NMR spectroscopy, the cis–trans isomerization of tris(acetyl(phenylacetyl)tetra-

carbonylmanganato)aluminum, Al(abtm)$_3$ (**1**), was followed
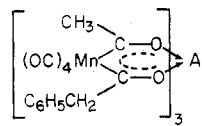
1, Al(abtm)$_3$

as a function of time in carbon tetrachloride solution at three temperatures. The values of the rate of isomerization and the activation parameters are consistent with an intramolecular rearrangement which may occur by a mechanism similar to that proposed for the geometrical isomerization of tris(1-phenyl-5-methylhexane-2,4-dionato)aluminum, Al(pmhd)$_3$,[6] although this comparison is highly tenuous. However, the interconversion of the optical isomers of complex **1** was not studied and such a comparison may be fortuitous. The trans to cis equilibrium constant was recorded at four temperatures and indicated a slightly negative ΔH° for the isomerization.

Experimental Section

Complex **1**, Al(abtm)$_3$, was prepared by a literature method[4] and was recrystallized from a hexane/methylene chloride (1:1) solution at −20 °C affording crystals of the trans isomer only. All kinetic and equilibrium data were recorded on a Joel MH-100 ^{1}H NMR spectrometer equipped with a Model JES-VI-3B variable-temperature unit using the resonances of the methyl substituent of the metallo-β-diketonate ligand as a probe to the isomerization and equilibrium.