

($E_{1/2} = 0.08$) is more negative than the value for $\text{Fe}(\text{TPP})\text{ClO}_4$ ($E_{1/2} = 0.14$) but less negative than that of the usual chloride high-spin derivative ($E_{1/2} = -0.29$), indicating the bonding strength is greater for $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3$ than for $\text{Fe}(\text{TPP})\text{ClO}_4$ but weaker than for the high-spin complexes. This evidence is complemented by the order of pyrrole proton resonances of $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3 > \text{Fe}(\text{TPP})\text{C}(\text{CN})_3 > \text{Fe}(\text{TPP})\text{ClO}_4$. Also, the Soret band and the ~ 500 -nm region band positions follow an order parallel to the NMR and cyclic voltametry results. With toluene as the solvent, the Soret bands for $\text{Fe}(\text{TPP})\text{Cl}$, $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3$, and $\text{Fe}(\text{TPP})\text{ClO}_4$ are located at 402, 408, and 415 nm, respectively. In contrast, the major visible region band is increased in energy from 518 to 512 to 505 nm for $\text{Fe}(\text{TPP})\text{Cl}$, $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3$, and $\text{Fe}(\text{TPP})\text{ClO}_4$, respectively. The other absorption bands are not as well defined. This indicates that the trifluoromethanesulfonate ligand is bound more strongly than the perchlorate ion but weaker than in the high-spin halide compounds. Thus, the order of ligand strengths appears to be halide $\gg \text{SO}_3\text{CF}_3^- > \text{C}(\text{CN})_3^- > \text{ClO}_4^-$. The ESR g_{\perp} values, however, do not follow a clear pattern in that $g_{\perp} = 5.2$ for $\text{Fe}(\text{TPP})\text{C}(\text{CN})_3$, but the g_{\perp} value for $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3$ (4.3) is lower than that for $\text{Fe}(\text{TPP})(p\text{-OCH}_3)\text{ClO}_4$ (4.5).⁸ Variable zero-field-splitting values among the anionic complexes could serve to explain the lack of correspondence.

An unusual solid-state structure is found for the $\text{C}(\text{CN})_3^-$ complex, in which the anion serves as a bridging ligand to make the iron center six-coordinate. Structural and Mössbauer parameters have been interpreted to favor a pure $S = 3/2$ state in the solid.¹⁰ In solution the complex appears to be five-coordinate, as judged by splitting of the meta phenyl proton signal at low temperature. A pure $S = 3/2$ complex is expected to have the pyrrole proton resonance shifted in a far upfield position through a π -type unpaired spin delocalization mechanism.⁴ However, the observed downfield position and anomalous temperature dependence is consistent with $S = 5/2$, $3/2$ spin admixture. The possible appearance of a pure $S = 3/2$ configuration for the $\text{C}(\text{CN})_3^-$ complex may thus be described as a "solid-state effect".

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Registry No. $\text{Fe}(\text{TPP})\text{SO}_3\text{CF}_3$, 70936-35-5; $\text{Fe}(\text{TPP})\text{C}(\text{CN})_3$, 25704-06-7; $\text{Fe}(\text{TPP})\text{CO}_2\text{CF}_3$, 79872-93-8; $\text{Fe}(\text{OEP})\text{SO}_3\text{CF}_3$, 79872-94-9; $\text{Fe}(\text{OEP})\text{C}(\text{CN})_3$, 80105-66-4; $\text{Fe}(\text{ETIO})\text{SO}_3\text{CF}_3$, 79898-45-6.

Supplementary Material Available: Tables of proton and carbon-13 NMR shift values (6 pages). Ordering information is given on any current masthead page.

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Exchange Interactions in the Linear-Chain Compounds Azidobis(pentane-2,4-dionato)manganese(III) and (Thiocyanato)bis(pentane-2,4-dionato)manganese(III)

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Powder magnetic measurements on the linear-chain compounds $\text{Mn}(\text{acac})_2\text{X}$ (Hacac = pentane-2,4-dione; $\text{X} = \text{N}_3^-$, NCS^-) show the presence of antiferromagnetic intrachain interaction. The one-dimensional Heisenberg model leads to $J(\text{N}_3) = 5.3 \text{ cm}^{-1}$ and $J(\text{NCS}) = 1.5 \text{ cm}^{-1}$. Sharp increases in the susceptibilities precede phase transitions at 11.3 and 6.9 K, respectively, and are probably the result of a small canting introduced by the zero-field splitting associated with the Mn(III) ion.

Introduction

Octahedral complexes of high-spin Mn(III) are interesting because they are expected to be susceptible to Jahn-Teller distortions causing them to deviate from idealized O_h symmetry, either by a trigonal distortion or by a tetragonal compression or elongation. This is well illustrated by the recent structural work on the β^1 and γ^2 forms of $\text{Mn}(\text{acac})_3$ (Hacac = pentane-2,4-dione) and $\text{Mn}(\text{trop})_3$ (Htrop = tropolone). The magnetic properties of β - $\text{Mn}(\text{acac})_3$ and $\text{Mn}(\text{trop})_3$ have also been shown to be compatible with the different types of distortion found in these structures.⁴

A new series of high-spin Mn(III) complexes having the general formula $\text{Mn}(\text{acac})_2\text{X}$ ($\text{X} = \text{N}_3^-$, NCS^-) has been prepared and characterized recently.⁵ The crystal structures of both materials^{5,6} showed that, rather than being 5-coor-

dinate, the Mn(III) ion was 6-coordinate, the anionic N_3 or NCS bridge adjacent metal ions forming a chain (Figure 1). In both cases a tetragonally elongated octahedral coordination polyhedron about the Mn(III) ion was present. We have been interested in the magnetic properties of metal β -diketonate compounds^{4,7,8} particularly when the structures indicate the possibility of exchange interaction.^{4,8} In the present case we might anticipate magnetic interaction to be associated with the polymeric one-dimensional chains. Accordingly we report here the low-temperature magnetic properties of $\text{Mn}(\text{acac})_2\text{N}_3$ and $\text{Mn}(\text{acac})_2\text{NCS}$ where we show that there is significant intrachain-exchange interaction present.

Experimental Section

The two compounds were prepared by previously published methods.^{5,6} $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ was dissolved in water, Hacac and KMnO_4 were added, and the solution was stirred for 15 min. KSCN was then added with stirring for a further 30 min. The olive green precipitate

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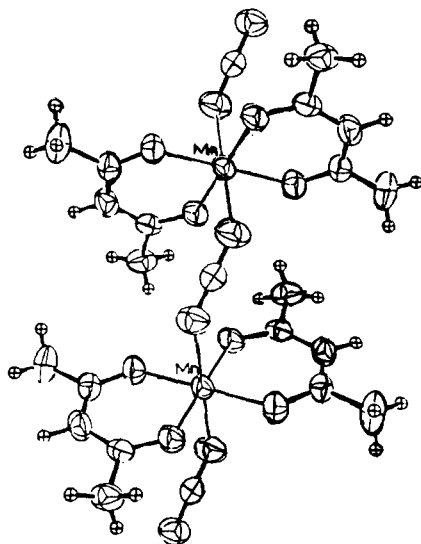


Figure 1. ORTEP drawing of $\text{Mn}(\text{acac})_2\text{N}_3$ showing the infinite chain structure along the c crystallographic axis (from ref 5). The structure of $\text{Mn}(\text{acac})_2\text{NCS}$ is similar with infinite chains generated along the a crystallographic axis.

of $\text{Mn}(\text{acac})_2\text{NCS}$ was filtered, washed with methanol, and dried under vacuum. Light brown $\text{Mn}(\text{acac})_2\text{N}_3$ was made in a similar manner by substituting NaN_3 for KSCN . When both compounds were recrystallized from methanol, significant amounts of a paramagnetic impurity (presumably $\text{Mn}(\text{acac})_3$) were formed and were only evident in the magnetic susceptibility below 10 K. The amount of impurity was also shown to be related to the amount of KSCN and NaN_3 used in the preparation and the age of the sample. Accordingly magnetic measurements were only made on freshly prepared unrecrystallized samples which had been precipitated with a large excess of KSCN or NaN_3 . The infrared spectra and melting points of both compounds were identical with those published by Stults et al.^{5,6} Unfortunately, the crystals we have so far been able to prepare are unsuitable for magnetic measurements.

The magnetic susceptibilities of powdered samples were measured with the SQUID susceptometer described recently.⁴ Some data down to 100 K were measured on a small Gouy balance that had been calibrated with $\text{Hg}_2\text{Co}(\text{CNS})_4$. All the magnetic data were corrected for the diamagnetism of the constituent atoms with the use of Pascal's constants.⁹

Results and Discussion

The average magnetic moments and susceptibilities for $\text{Mn}(\text{acac})_2\text{N}_3$ and $\text{Mn}(\text{acac})_2\text{NCS}$ between 4 and 300 K are plotted in Figures 2 and 3, respectively. The room-temperature values of 4.36 and 4.85 μ_B for $\text{Mn}(\text{acac})_2\text{N}_3$ and $\text{Mn}(\text{acac})_2\text{NCS}$, respectively, agree well with those quoted by Stults et al.;⁵ at lower temperatures the falling magnetic moments with decreasing temperature indicate the presence of significant antiferromagnetic interaction. This is also compatible with the characteristically broad maximum in the susceptibility of the two compounds. However, the situation is obviously more complicated than a simple intrachain antiferromagnetic interaction because in both cases there is a sharp increase in susceptibility superimposed on the broad maximum before the susceptibility drops toward 0. The magnetic data are then analyzed conveniently in two temperature ranges, above and below about 50 and 20 K for the N_3 and NCS derivatives, respectively.

The high-spin $\text{Mn}(\text{III})$ ion is expected to be Heisenberg-like except perhaps at the lowest temperatures where the effects of zero-field splitting may produce anisotropy. Since both compounds form linear chains via the bridging N_3 and NCS groups (Figure 1), the one-dimensional Heisenberg chain is

Table I. Some Magnetic Parameters for $\text{Mn}(\text{acac})_2\text{X}$, $\text{X} = \text{N}_3^-$, NCS^-

	T_{max}/K	T_c/K	$10^3 \chi_{\text{max}}/\text{cm}^3 \text{mol}^{-1}$	J^a/cm^{-1}	J^c/cm^{-1}	zJ'/cm^{-1}
N_3	50	11.3	18.3	5.8(1.1) ^b	5.3	-1.6(0.6)
NCS	13	6.9	67	1.6(1.5)	1.5	-0.06(1.5)

^a Using eq 1. ^b Values in parentheses refer to R where $R = [\sum(\mu_{\text{obsd}} - \mu_{\text{calcd}})^2 / \sum \mu_{\text{obsd}}^2]^{1/2} \times 100\%$. ^c Using eq 2.

then probably the most appropriate exchange coupling model, at least in the high-temperature range. The susceptibility of a linear chain of Heisenberg atoms, scaled to the appropriate value of spin, is given by¹⁰ eq 1 where $u = \coth(T_0/T) - T/T_0$

$$\chi = \frac{Ng^2\beta^2S(S+1)}{3kT} \frac{1+u}{1-u} \quad (1)$$

with $T_0 = -2JS(S+1)/k$ and J is defined as positive for antiferromagnetic coupling, i.e., $\mathcal{H} = \sum_{ij} 2JS_i S_j$.

Quite good fits were obtained with this model in the temperature regions 50–300 and 20–300 K for the N_3 and NCS derivatives, respectively, by assuming $g = 2.00$, which is reasonable for the $\text{Mn}(\text{III})$ ion, and varying J . These fits are shown in Figures 2 and 3. In view of the complications which obviously arise below 50 and 20 K, respectively, an interchain interaction was allowed for by modifying eq 1 via

$$\chi' = \chi / (1 - (2zJ'/Ng^2\beta^2)\chi) \quad (2)$$

where z is the number of nearest-neighbor chains and J' is the exchange integral for the magnetic interaction between nearest-neighbor chains. This made little difference for the NCS derivative but halved the discrepancy factor [$R = [\sum(\mu_{\text{obsd}} - \mu_{\text{calcd}})^2 / \sum \mu_{\text{obsd}}^2]^{1/2}$] in the N_3 derivative although it is difficult to gauge whether this is significant. All the relevant magnetic parameters are collected together in Table I.

In the high-temperature region, the magnetic properties appear to be well described by a Heisenberg linear-chain model with perhaps the possibility of a little interchain interaction. At this stage it is interesting and pertinent to inquire into the relative magnitudes of the two exchange coupling constants for these two similar three-atom-bridged compounds where $J(\text{N}_3) = 5.3$ and $J(\text{NCS}) = 1.5 \text{ cm}^{-1}$. The metal-metal distance in both compounds is too large for direct metal-metal interaction, for example, $\text{Mn}-\text{Mn}(\text{N}_3) = 5.63 \text{ \AA}$, so superexchange via the bridging group must be responsible for the observed interaction. Quite apart from possible changes due to the different electronic configurations of the two bridging anions, the metal to bridging atom bond lengths are different enough to suggest that the exchange interaction would be smaller in the NCS derivative. Although the $\text{Mn}-\text{N}$ bond length in the NCS derivative is shorter than the two equal $\text{Mn}-\text{N}$ distances in the N_3 derivative, the $\text{Mn}-\text{S}$ bond length is long (2.88 \AA), even allowing for the larger covalent radius of sulfur.^{5,6} This distance is to be compared with the short $\text{Mn}-\text{S}$ bond lengths (2.4 \AA) in the tetragonally elongated tris(N,N -diethyldithiocarbamate)manganese(III) or even the long $\text{Mn}-\text{S}$ bond lengths of 2.55 \AA .¹¹ A formal bonding interaction between Mn and S in $\text{Mn}(\text{acac})_2\text{NCS}$ to form a chain must exist but it is obviously much weaker than the equivalent $\text{Mn}-\text{N}$ bonds in $\text{Mn}(\text{acac})_2\text{N}_3$. It is then not unreasonable to expect that any exchange interaction which is to be propagated along the chain direction must then be weaker in the NCS derivative.

The susceptibilities of the two derivatives in the low-temperature region are very interesting (Figure 4). The broad

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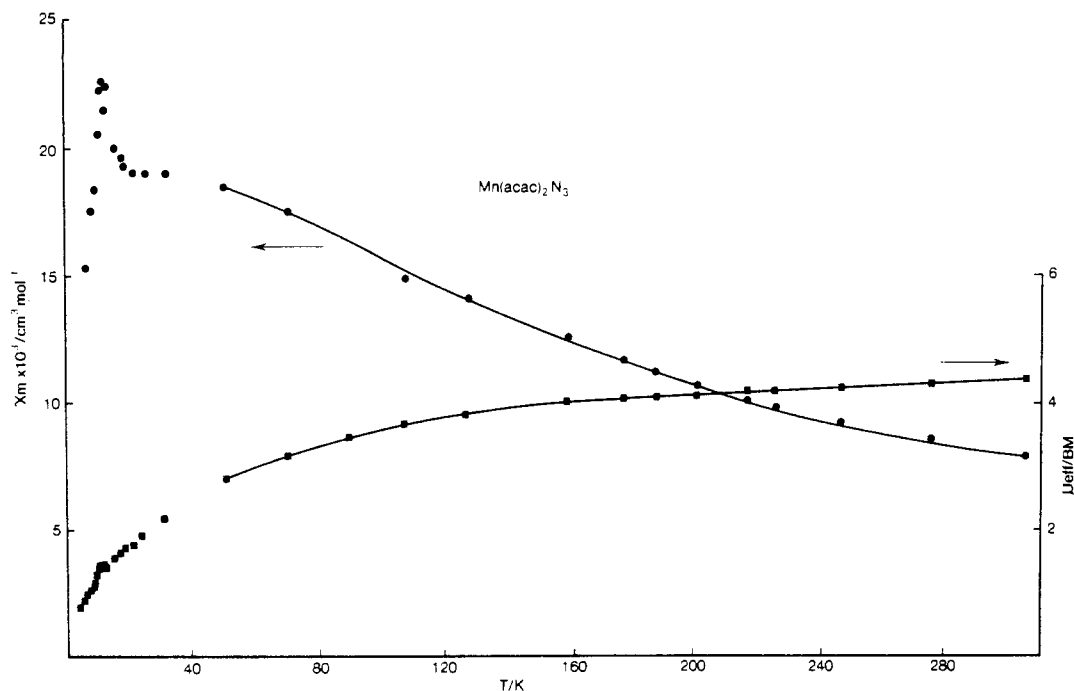


Figure 2. Magnetic moment (■) and magnetic susceptibility (●) for $\text{Mn}(\text{acac})_2\text{N}_3$. The solid lines are calculated with use of the one-dimensional Heisenberg model with the parameters listed in Table I.

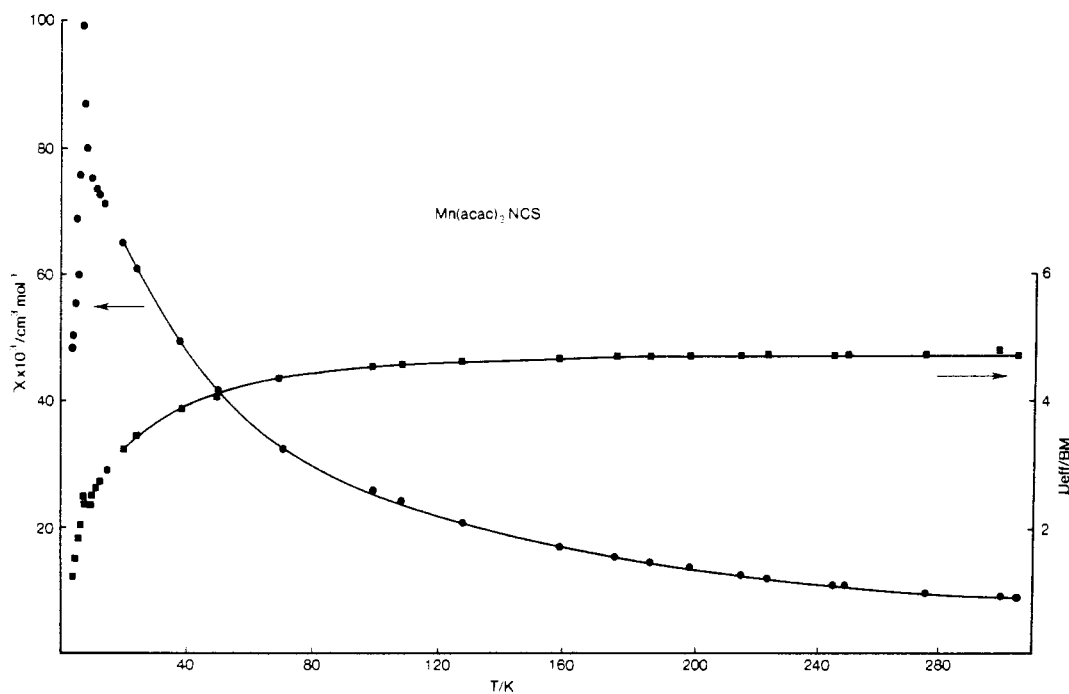


Figure 3. Magnetic moment (■) and magnetic susceptibility (●) for $\text{Mn}(\text{acac})_2\text{NCS}$. The solid lines are calculated with use of the one-dimensional Heisenberg model with the parameters listed in Table I.

maxima are typical of the behavior expected for antiferromagnetic interactions in a Heisenberg linear chain. The temperature at which the susceptibility reaches a broad maximum (T_{max}) and the value of the susceptibility at T_{max} are a little difficult to determine accurately because of the phase transitions and the field dependent behavior of the azide derivative (see below). However, the values of J derived from $kT_{\text{max}}/|J| = 7.1$ and $\chi_{\text{max}}|J|/Ng^2\beta^2 = 0.094$ for a Heisenberg chain of $S = 2$ ions agree well with those derived from eq 1.¹² Also the experimental values of $\chi_{\text{max}}T_{\text{max}}/g^2$ (0.22, 0.23) are quite close to the theoretical value of ~ 0.25 for a Heisenberg

chain.¹² For comparison, the theoretical value for an Ising chain is ~ 0.28 . The susceptibility of the azide derivative is field dependent below about 100 K; in Figures 2 and 4 we have shown the lowest field data (2.23 mT). In applied magnetic fields of 0.3934 T (our highest) the susceptibility is reduced by about 10% although T_c is unaffected. However, the most striking observation in both compounds is the increase in the susceptibility below the χ_{max} and the eventual very sharp transition at 11.3 and 6.9 K for the N_3 and NCS derivatives, respectively. This behavior of the critical temperature being significantly lower than the broad maximum in susceptibility is typical of three-dimensional ordering of a system of linear chains. Below these temperatures the susceptibility falls dramatically although the paramagnetic impurity can domi-

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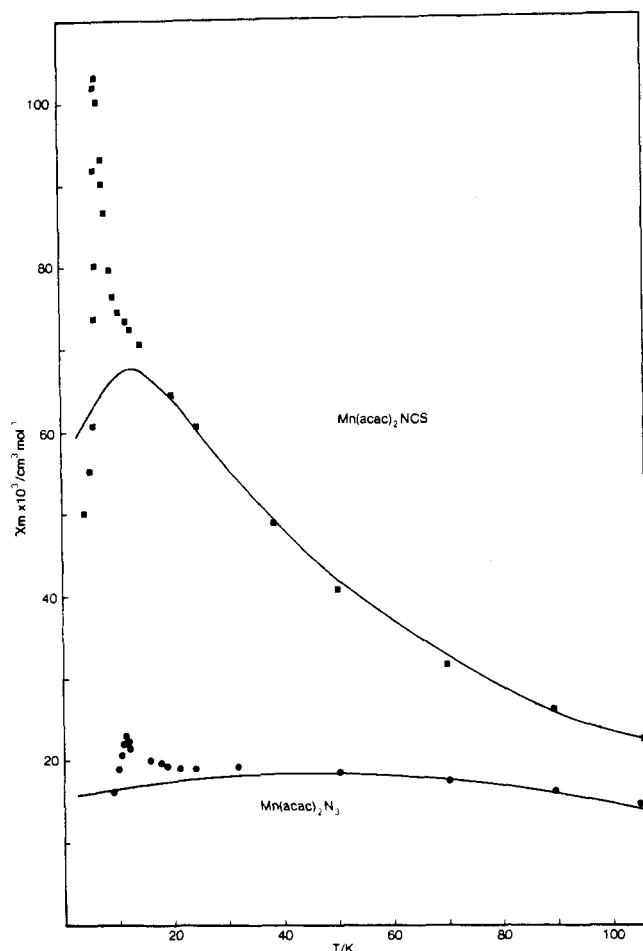


Figure 4. Magnetic susceptibilities of $\text{Mn}(\text{acac})_2\text{N}_3$ (●) and $\text{Mn}(\text{acac})_2\text{NCS}$ (■) showing the sharp transitions at 11.3 and 6.9 K, respectively. The solid lines represent the best high-temperature fit from eq 2 and the parameter values from Table I.

nate the susceptibility below 5 K (see Experimental Section). Consequently it is difficult to determine exactly where the susceptibility will extrapolate to at $T \rightarrow 0$. For a three-dimensional antiferromagnet we expect $\chi_{T=0} = 2/3 \chi_{\text{max}}$ and this is probably the experimental situation.

In the low-temperature region there are probably two important complications which may effect the magnetic susceptibility, apart from the intrachain interactions. These are the effects of zero-field splitting on each Mn(III) ion and possible interchain interactions. Both of these may be important factors in determining the nature and mechanism of the long-range ordering which is reflected in the sharp transitions at 11.3 and 6.9 K.

The zero-field splitting (D) in the Mn(III) ion is usually of the order of a few reciprocal centimeters, but the sign of D and so the actual ground spin level depends critically on the symmetry of the ligand field about the metal ion. This in turn will determine whether magnetic ordering can be sustained: if D is negative then the $M_s = \pm 2$ spin levels are lowest and so magnetic ordering is possible whereas if D is positive the $M_s = 0$ spin level is lowest and so magnetic ordering is impossible. In the two present compounds, the tetragonally elongated octahedral array about each Mn(III) ion guarantees D to be negative⁴ so the observed magnetic ordering is consistent with the structure and the sign of D . However, the zero-field splitting had no effect on the average susceptibility of the $S = 5/2$ linear-chain compound $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$ ¹³ so it has been neglected in the analysis of the high-temperature

Table II. Some Ligand Field Parameters for $\text{Mn}(\text{acac})_2\text{X}$, $\text{X} = \text{N}_3^-$, NCS^-

	obsd bands/cm ⁻¹	Dq/cm^{-1}	Ds/cm^{-1}	Dt/cm^{-1}
N_3^-	~10 600, 16 390, 20 240	16 390	2064	468
NCS^-	~9900, 17 540, 20 830	17 540	1884	473

susceptibility data of our $S = 2$ compounds.

The structures of both compounds suggest that both should only have small interchain interactions although both must be present to sustain the observed phase transitions. The rather larger than expected values of zJ' (Table I), which were derived from the high-temperature susceptibility data, are probably more the result of absorbing all the interactions ignored by the model Hamiltonian than just being due to an interchain interaction. The most likely interaction ignored in this context is the effect of anisotropy which may arise from the presence of single-ion zero-field splitting. Further confirmation that the derived values of zJ' contain interactions other than the interchain coupling come from a consideration of Oguchi's relation¹⁴ which relates the unambiguous values of J and T_c to zJ' via

$$\frac{kT_c}{|J|} = \frac{4S(S+1)/3}{I(\eta)} \quad (3)$$

$\eta = J'/J$, and $I(\eta)$ is a function which is inversely proportional to η . Using the values of J and T_c from Table I, we find that $J'(\text{NCS}) \approx 2.5 J'(\text{N}_3)$, quite the reverse of the derived values of J' listed in Table I. In the absence of zero-field splitting effects, the relatively low value of $T_c(\text{N}_3)$ is then due to a smaller interchain interaction. However, the derived molecular field corrections from the high-temperature magnetic properties are greater in the azide derivative, presumably because the intrachain interaction is larger, the zero-field splitting is different, or because of other deficiencies in the simple model. It is possible to obtain an idea of the magnitude of the zero-field splitting from the optical spectra. We have done this previously with $\text{Mn}(\text{acac})_3$ where we calculated D from the eigenvalues of the matrices describing the d^4 electronic configuration in D_4 symmetry.⁴ The unknowns are the Racah parameters B and C , and the spin-orbit coupling constant ζ ; the ligand field parameters Dq , Ds , and Dt can be obtained from the optical spectra. We find that both $\text{Mn}(\text{acac})_2\text{N}_3$ and $\text{Mn}(\text{acac})_2\text{NCS}$ have poorly resolved spectra with three broad bands at approximately 10600, 16390, 20240 and 9900, 17540, and 20830 cm^{-1} , respectively. These lead to the ligand field parameters listed in Table II. If we assume values of 970, 3124, and 250 cm^{-1} for B , C , and ζ , respectively,⁴ then we calculate $D(\text{N}_3) = -2.6$ and $D(\text{NCS}) = -2.7$ cm^{-1} so differences in D are probably unimportant. On the other hand it is well-known that the Fisher model (eq 1 and 2) is only exact when $S \rightarrow \infty$. Small departures are probably evident in the $S = 5/2$ linear-chain compound $[(\text{CH}_3)_4\text{N}][\text{MnCl}_3]$ ¹⁵ so larger departures would be expected for $S = 2$, and these would be proportional to the size of J , as is observed. We have also noted departures from the simple model in the $S = 2$ linear-chain CsCrCl_3 .¹⁶

The observed sharp transitions are then probably a result of a small canting of the spins which arises from the zero-field splitting; the magnetic ordering is also consistent with the sign of D and the structure of each compound. Further evidence for the canted behavior of the spins comes from the field-dependent behavior of the susceptibility of the azide derivative where the intrachain interaction is more pronounced. As the

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field increases, the measured susceptibility decreases slightly and is probably due to a small net ferromagnetic moment which can arise in a canted system of antiferromagnetically coupled spins.

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Solid-Phase Thermal Cis-Trans Isomerization of Bis(diamine)chromium(III) Complexes Containing *d,l*-2,3-Butanediamine, *d,l*-1,2-Cyclohexanediamine, or *d,l*-2,4-Pentanediamine

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The bis(diamine)chromium(III) complexes *trans*- and *cis*-[CrX₂(aa)₂]X·*n*H₂O, where X is chloride or bromide ion, aa is a diamine selected from *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn), and *n* = 1-3, were prepared, and their thermal cis-trans isomerizations were investigated both nonisothermally (derivatographically) and isothermally in the solid phase. The isomerization of the bn and chxn complexes was *trans*-to-*cis*, whereas that of the ptn complex was *cis*-to-*trans*. The enthalpy changes and activation energies were estimated for dehydration and/or dehydrohalogenation (ΔH_d and E_d) and for isomerization (ΔH_i and E_i). Bond rupture is proposed to be operative in the pathway of the isomerization from the facts that (1) the isomerization does not require the participation of lattice water, (2) the isomerization proceeds exothermically in all cases, and (3) the intermediate *mer*-[CrCl₃(bn)₂] was isolated during the isomerization of *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O. The isomerization of the above complexes is also discussed in connection with that of the other related bis(diamine) complexes.

Introduction

Several studies have been carried out on the cis-trans isomerization of the simple bis(diamine)chromium(III) complexes [CrX₂(aa)₂]X² in the solid phase, where X is chloride or bromide ion and aa is ethylenediamine (en), *d,l*-1,2-propanediamine (pn), or 1,3-propanediamine (tn).³⁻⁶ *Trans*-to-*cis* isomerization was detected in the compounds containing en or pn, which are able to form a five-membered chelate ring with the chromium(III) ion, whereas *cis*-to-*trans* isomerization was recognized in the complexes containing tn, which forms a six-membered chelate ring. The mixed bis(diamine) complexes [CrX₂(aa)(bb)]X,² in which aa and bb are different diamines selected from en, pn, and tn, have recently been found to isomerize from *trans* to *cis* even with the complexes containing tn.⁷ More information is therefore needed to conclude that the diamines in the complexes play an important role in the direction of isomerization (whether it occurs *trans*-to-*cis* or *cis*-to-*trans*). The primary purpose of the present work is to investigate the details of the isomerization of the simple bis(diamine) complexes containing *d,l*-2,3-butanediamine (bn), *d,l*-1,2-cyclohexanediamine (chxn), or *d,l*-2,4-pentanediamine (ptn): the former two can form five-membered chelate rings, and the latter, a six-membered chelate ring.

In the cobalt(III) complexes in the same category, the isomerization was found to take place along with the dehydration of lattice water, and intermolecular aquation-anation was proposed to be a favorable mechanism for the reaction.⁸⁻¹¹ On the other hand, the previous studies pointed out that the chromium(III) complexes isomerize in the anhydrous state and the reaction always proceeds exothermically.³⁻⁶ These facts imply that some different mechanism (e.g., intramolecular bond rupture) may be operative in the reaction of the chromium(III) complexes. Another purpose of the present study is to clarify this implication in regard to the bn, chxn, and ptn chromium(III) complexes and to discuss the isomerization in connection with that of the other related complexes.

Experimental Section

Preparation of Diamines. The diamines bn¹² and ptn¹³ were prepared by the literature methods. chxn was available from Tokyo Kasei Kogyo Co., Ltd.

Preparation of Complexes. *trans*-[CrCl₂(bn)₂]Cl·HCl·2H₂O (I), *trans*-[CrBr₂(bn)₂]Br·HBr·2H₂O (II), *trans*-[CrCl₂(chxn)₂]Cl·HCl·2H₂O (III), and *trans*-[CrCl₂(ptn)₂]Cl·HCl·2H₂O (IV) were derived from *trans*-[CrF₂(aa)₂]ClO₄ (aa: bn, chxn, or ptn), which was prepared by modifying the methods described earlier.^{14,15} One gram of *trans*-[CrF₂(aa)₂]ClO₄ was dissolved in 10 mL of concentrated hydrochloric or hydrobromic acid and allowed to stand for about 12 h in the dark. The crude products thus obtained were collected by

- (1) To whom correspondence should be addressed.
- (2) In this paper, the terms "simple bis(diamine) complexes" and "mixed bis(diamine) complexes" are used to express the dihalogenobis(diamine)chromium(III) complexes containing the same two diamines ([CrX₂(aa)₂]X) and those containing two different diamines ([CrX₂(aa)(bb)]X).
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