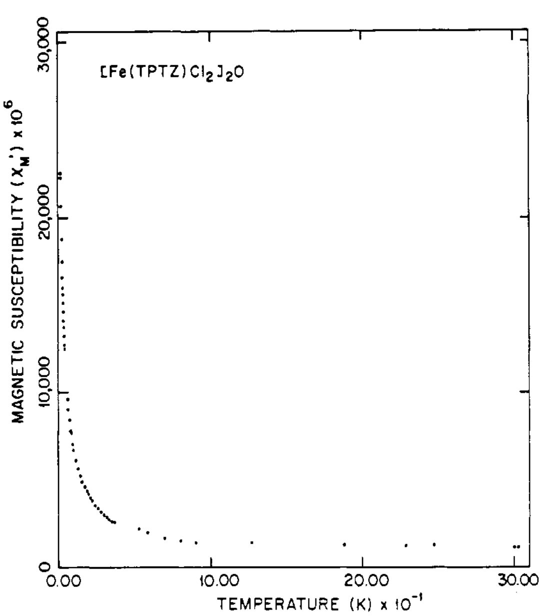

Figure 11. Temperature dependence of the molar magnetic susceptibility of $[Fe(TPTZ)Cl_2]_2O$.

magnetic exchange (where $2J$ = the singlet to triplet separation for $S_{\text{TOTAL}} = 0$ and $S_{\text{TOTAL}} = 1$) is at least ~-100 cm^{-1}.[3,7,15] The susceptibility is low and independent of the temperature until below ~50 K at which it begins to rise (Figure 11). This is attributed to monomeric paramagnetic impurity: in the present case, undoubtedly, the high-spin ferrous precursor $Fe(TPTZ)Cl_2$.

Certain features of the zero- and high-field Mössbauer spectra of $[Fe(TPTZ)Cl_2]O$ are particularly noteworthy and offer additional support of its formulation as an antiferromagnetically coupled, oxo-bridged ferric dimer. First of all, there is the unusally large and temperature-independent quadrupole splitting (~1.9 mm/s). The electric field gradient tensor is usually small of 0 for the ^6A ground term of high-spin Fe(III) since there is no direct valence-shell-electron contribution for the spherically symmetric, d^5 ferric core. Thus, the quadrupole splittings of *simple* ferric monomers are typically in the range 0 to ~1 mm/s, e.g., the last entry of Table I. The large splitting observed for $[Fe(TPTZ)Cl_2]_2O$ and other oxo-bridged ferric dimer systems is attributed to partial metal–oxygen double-bond character for the bridging bonds. This introduces a large negative principal component (V_{zz}) to the electric field gradient tensor and thus a negative quadrupole coupling constant for the case of ^{57}Fe. The latter are correlated with *stronger*, chemical bonding along a unique molecular axis as opposed to in-plane bonding. We have measured Mössbauer spectra of $[Fe(TPTZ)Cl_2]_2O$ at 4.2 K in longitudinal applied fields of up to 60 kG. These spectra show that (1) V_{zz} is, in fact, *negative* and axial and (2) $H_{\text{effective}} = H_{\text{applied}}$. As mentioned before, the absence of an internal hyperfine field is correlated with a nonmagnetic ground state. For the present dimer complex, this corresponds to the isolated, total spin (S_T) equal 0 ground state resulting from strong antiferromagnetic exchange coupling between equivalent, oxo-bridged ferric centers.

Conclusions

The spectroscopic and magnetic data presented herein indicate that thermolysis of the low-spin $[Fe(TPTZ)_2]Cl_2$ leads to a five-coordinate iron(II) monomer that undergoes slow oxidation to a binuclear species. This unusual solid-state oxidation was not expected and to our knowledge has no precedent for simple five-coordinate systems. We have found that analogous ferrous terpyridine complexes are stable toward such oxidation. By way of contrast, Martell has prepared some five-coordinate Schiff base iron(II) complexes which form oxo-bridged complexes in solution but are inert to oxidation in the solid state.[16] This aspect of the problem is the subject of future research.

Acknowledgment. We wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR-80 16441.

Registry No. $Fe(TPTZ)_2Cl_2$, 78529-70-1; $Fe(TPTZ)Cl_2$, 78529-69-8; $[Fe(TPTZ)Cl_2]_2O$, 78529-68-7; $Fe(TPTZ)Cl_3$, 78529-67-6; $Zn(TPTZ)Cl_2$, 78529-66-5.

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Contribution from the Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

Magnetic Susceptibility Study of Bis(diethyldithiocarbamato)manganese(II). A Sulfur-Bridged Linear-Chain Antiferromagnet

GLENN A. EISMAN and WILLIAM MICHAEL REIFF*

The magnetic susceptibility of bis(diethyldithiocarbamato)manganese(II) has been determined from 300 to 2 K for fields varying from 0 to 14 kG. The magnetic moment decreases from ~5.4 to 0.4 μ_B, and the susceptibility exhibits a broad maximum at ~65 K. These results are correlated with an intrachain antiferromagnetic exchange, $J/k = -7.5$ K.

Introduction

In continuing with the study of polymeric transition-metal chains, it was thought that the compound bis(diethyldithiocarbamato)manganese(II), hereafter $Mn(dtc)_2$, could exhibit interesting low-temperature magnetic behavior because of preliminary magnetic work[1] to 84 K that indicated the possibility of antiferromagnetic interactions. The dithiocarbamate ligand, pictured in Figure 1 (top), is an ideal ligand for systematic transition-metal magnetism studies. It not only allows

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(1) M. Ciampolini and C. Mengozzi, *J. Chem. Soc., Dalton Trans.*, 2051 (1975).

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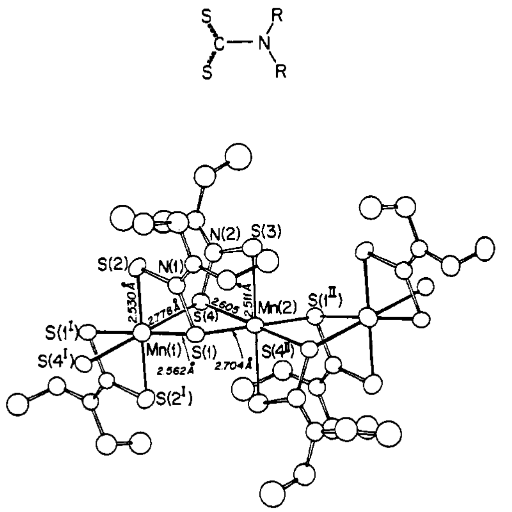

Figure 1. Schematic of the dialkyl-substituted dithiocarbamato ligand (top) and the polymeric chain structure of $[Mn(dtc)_2]^1$ (bottom).

a study of the effects of sulfur bridging on the magnetic properties of linear systems but also allows for dilution studies. This can be achieved by changing the R substituents from small alkyl groups to larger bulkier ring systems. In addition, by changing R from an electron-withdrawing group to an electron-donating substituent, the metal–dithiocarbamate bond strength should be affected. This change may be reflected in the magnetic properties.

The *basic structure* of transition-metal dithiocarbamate complexes can be modified by variation of the substituents R and R′. An example of this effect can be seen in the Fe(II) analogues of the $(dtc)_2$ compounds. If R and R′ are ethyl, the resulting structure is an antiferromagnetically coupled *dimer*.[2,3] When R and R′ are methyl groups, a polymeric structure has been postulated.[4]

The complex $Mn(dtc)_2$ has been shown to have a linear polymeric structure[1] with one sulfur atom of each dtc ligand shared by two adjacent manganese ions. This structure is shown in Figure 1 (bottom). The crystal belongs to the triclinic space P_1 with $a = 11.039$ (5) Å, $b = 10.055$ (5) Å, $c = 7.529$ (3) Å, $\alpha = 70.9$ (1)°, $\beta = 82.7$ (1)°, $\gamma = 82.2$ (1)°, and $Z = 2$. The shortest intrachain Mn–Mn distance is 3.76 Å, and the two Mn–S–Mn bond angles are 88.7 (1) and 91.2 (1)°. Interchain metal–metal separations were not reported. The observed moment at room temperature (5.65 μ_B) is slightly lower than the expected[5] (5.92 μ_B) for a Mn(II) ion having a ^6A ground term in MS_6 coordination. The decrease in the moment to 5.15 μ_B at 84 K is evidence of a significant antiferromagnetic exchange and stimulated the present study to lower temperatures.

Experimental Section

The title compound undergoes rapid oxidation and anerobic conditions are required for its preparation. A deoxygenated aqueous solution of $MnCl_2 \cdot 2H_2O$ (0.01 mol) was added to sodium diethyldithiocarbamate (0.02 mol) dissolved in 20 mL of deoxygenated distilled water. The resulting material (a bright yellow precipitate) was washed several times with deoxygenated water and dried under vacuum. Since a color change accompanies the oxidation, yellow to brown to black, it is easy to observe any Mn(III) formation. This oxidation occurs more rapidly when the product is moist. The dried product had the same color as observed previously.[1]

Table I. Sample Magnetic Moment Data

T, K	μ_{eff}, μ_B	T, K	μ_{eff}, μ_B
300.0	5.38	70.6	3.35
255.7	5.21	50.2	2.79
225.3	5.07	42.2	2.55
190.1	4.89	36.0	2.33
160.0	4.60	26.6	1.95
135.2	4.35	15.0	1.41
115.0	4.06	8.5	0.95
105.9	3.77	4.2	0.52
77.4	3.45	2.0	0.39

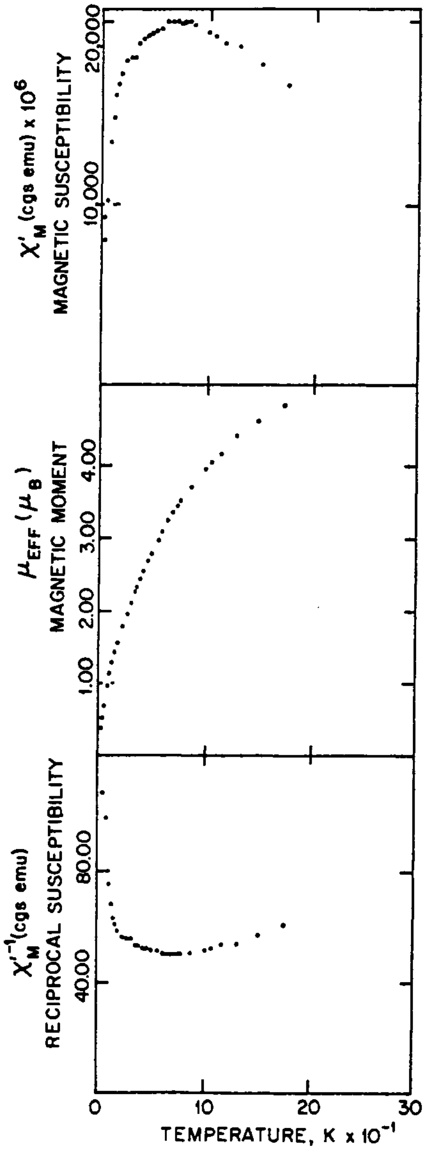

Figure 2. (a) χ_m' vs. T. (b) μ vs. T. (c) $\chi_m'^{-1}$ vs. T.

Magnetic susceptibility measurements and isothermal magnetization field sweeps were determined with the use of a Princeton Applied Research Co. FM-1 vibrating sample magnetometer in conjunction with a Walker 9-in. electromagnet (applied fields varying from 0 to 14 kG), a Walker field sweep unit, a F.W. Bell model 610 Hall probe gaussmeter and a Janis Super-Vari-Temp cryostat. The sample was suspended in a static atmosphere (10 torr) of dry helium gas that had been previously deoxygenated by passing it over hot copper metal filings. Temperature measurement and control were achieved with a combination of calibrated gallium arsenide and uncalibrated silicon diodes. These were driven by a Lakeshore Cryotronics Co. Model CCS-10B 10-μA constant-current source and a Lakeshore Model DTC-500 set point controller, respectively. Temperatures below 4.2 K were determined with the use of a calibrated diode and helium

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vapor-pressure measurements while the rate of helium pumping was controlled via an LJ Engineering Co. Model 329 vacuum regulator valve.

Results and Discussion

The results of the magnetic studies are presented in Figure 2 and Table I. The metal–metal intrachain separation in the present Mn^{II} complex of 3.76 Å is large enough to exclude significant direct metal–metal interactions as the origin of this antiferromagnetic exchange.[6] The latter is most likely transmitted through a superexchange pathway involving the bridging sulfur atoms of the chelating dithiocarbamate ligands. From the articulation and orientation (Figure 1, bottom) of these chelates, it appears that the individual chains in the structure are effectively isolated leading to 1D magnetic behavior. The broad maximum in the molar susceptibility data centered ca. 65 K is characteristic of such interactions.

The sign and magnitude of J, the intrachain exchange parameter, is an important parameter when characterizing a system as it describes the energy separation of the spin states. As usual, if $J < 0$, the interaction is antiferromagnetic. The theoretical treatment of a Heisenberg chain with $S = {}^5/_2$ was carried out by Wagner and Freidberg.[7] In the latter work, the following relationship was derived for the molar susceptibility

$$\chi_{\mathrm{m}} = \frac{Ng^2\beta^2S(S+1)}{3kT}\,\frac{1+U(k)}{1-U(k)}$$

where

$$U(k) = \coth\,(k - 1/k)$$

and

$$k = 2J(S(S+1)/kT)$$

For an $S = {}^5/_2$ ion and with the assumption of $J < 0$

$$\frac{|J|\chi_{\max}}{Ng^2\beta^2} = 0.1004$$

where $\chi_{\max}$ is the molar susceptibility at the maximum of the curve. When this equation is applied to $Mn(dtc)_2$, $J/k = -7.5$ K. The maximum in the susceptibility data was found to be 0.019929 emu/mol at 65 K. The broadness of the susceptibility vs. temperature curve makes it difficult to accurately assign a maximum which in turn leads to uncertainty in J. The uncertainty in $T_{\max}$ is ~±10.0 K. In the above analysis, using the Heisenberg model, the g value is taken as the spin-only value of 2.0, and D, the-zero field splitting parameter, is assumed to be 0.

Due to the paucity of studies of sulfur-bridged manganese(II) compounds in the literature, extensive comparison cannot be made to other systems. However, the magnitude of J/k for the present dithiocarbamato complex is not unreasonable for Mn(II) chains. $[N(CH_3)_4]MnCl_3$ (TMMC), a linear-chain antiferromagnet with chlorine bridges, was shown[8] to have an intrachain exchange parameter value of −6.7 K. This compound, as expected, also exhibited a broad maximum in the molar susceptibility vs. temperature plot at 55 K. The broad maximum observed was concluded to be the result of short-range intrachain interactions. This conclusion was based on the fact that at 0.3 K the molar susceptibility rose discontinuously, indicating long-range three-dimensional order. This result is also supported by a heat capacity study[9] in which a sharp spike was observed in the magnetic heat capacity vs. temperature data. The λ anomaly is a result of the effects of cooperative (long-range) magnetic ordering on the spin entropy of the system and was observed at ~0.2 K.

The differences in the magnitudes of J for the TMMC and $Mn(dtc)_2$ complexes may be related to the metal–metal ion separations, the specific nature of the bridging ligand, and/or the bridging angles. The reported[10] bridge angles of $[(CH_3)_4N]MnCl_3$ are 84.09 and 95.91°. These can be compared to 88.7 and 91.2° observed in the dithiocarbamate complex. Although the metal ion separation was not explicitly reported for the TMMC complex, the metal–metal separations of the two compounds can be compared. The Mn–Cl distance of 2.560 (2) Å in the $RMnCl_3$ compound is similar to the Mn–S distance (2.562 Å) of $Mn(dtc)_2$. Also similar are the bridging angles previously noted. It follows from the above data that the metal–metal separations of the two complexes can be assumed to be nearly identical. It is, therefore, not surprising that the magnitudes of the exchange interactions are similar.

Conclusions

The magnetic susceptibility vs. temperature data presented in this work suggest significant intrachain antiferromagnetic interactions. The considerable similarity of the magnetic data of the present compound to that of $[N(CH_3)_4]MnCl_3$ indicates the intrachain exchange is small (if not absent) even at 1.5 K. A heat capacity study may be useful in further characterizing the nature of the magnetic interactions below 1.5 K. The effect of the sulfur bridging found in $Mn(dtc)_2$ on the exchange will remain unclear until further *polymeric* bis(dithiocarbamato) transition-metal complexes are characterized by magnetic, thermal, and X-ray techniques. With this in mind, the study of bis(dimethyldithiocarbamato)iron(II) is under way. The structure of this compound has not been determined as yet, but it has been suggested[4] that the complex consists of polymeric chains. If the compound polymerizes similarly to the Mn analogue then a magnetic susceptibility study should allow for interesting comparison of the two systems.

Acknowledgment. We are pleased to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR-8016441.

Registry No. $Mn(dtc)_2$, 57683-09-7.

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