Crystal structure and magnetic susceptibility of copper (II) chloride tetramethylsulfoxide [CuCl₂(TMSO)] and copper (II) chloride monodimethylsulfoxide [CuCl₂(DMSO)]: Ferromagnetic spin-$\frac{1}{2}$ Heisenberg linear chains

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The crystal structures of the title compounds [C_4H_8SO (TMSO), C_2H_6SO (DMSO)] have been determined. The TMSO salt is orthorhombic [space group $Pbca$, $a = 13.844(10)$, $b = 6.418(12)$, and $c = 17.480(16)$ Å] while the DMSO salt is monoclinic [space group $P2_1/c$, $a = 7.774(1)$, $b = 13.557(3)$, $c = 6.475(1)$ Å, and $\beta = 103.83(1)$ °]. Each contain linear chains of Cu ions with three bridging ligands (2 Cl, 1 O) between each pair of Cu ions. The bridging Cu-L-Cu angles are $\sim 87°$ for the symmetrical bridges and $\sim 80°$ for the asymmetrical bridges. In each salt, the copper coordination geometry is severely distorted from octahedral with four short Cu-ligand bonds (three chlorine and one oxygen) and two long Cu-ligand bonds (one chlorine and one oxygen). Adjacent chains are well isolated from each other by the sulfoxide groups in one direction, but short sulfur-sulfur contacts occur between adjacent chains in the other direction. The susceptibility of the salts has been measured between 2.0 and 300 K on a PAR vibrating-sample magnetometer and on a Faraday balance. The high-temperature data show positive deviation from Curie behavior, indicative of ferromagnetic coupling. However, considerable magnetic interactions between chains exist and the χT vs T plots show maxima at low temperature. The data have been analyzed with several one-dimensional models. The best fit is obtained with an Heisenberg linear chain with ferromagnetic interaction ($J/k = 39°$K, TMSO; $J/k = 45°$K, DMSO) with a mean-field correction for the antiferromagnetic interchain interactions ($ZJ'/k = -1.6°$K, TMSO; $ZJ'/k = -4.0°$K, DMSO). Thus, the relevant ratio defining the ideality of the system, J/J', is ~ 50 for the TMSO salt and ~ 25 for the DMSO salt.

I. INTRODUCTION

Recent interest in one-dimensional materials has stimulated numerous studies on the role of the ligand in determining magnetic and optical properties. Particular interest in the role of the bridging angles in determining magnetic properties of polymeric compounds and unusual coordinations of some copper-halide compounds lead to a series of studies on the copper-chloride — sulfoxide complexes. The crystal structures of $CuX_2(2DMSO)$, ($X =$ Cl,Br) where DMSO is dimethylsulfoxide, show an unusual five coordination where the fifth coordination site is a long 2.7-Å copper-chlorine interaction. Adjacent copper ions bridge through the 2.7-Å interaction[1] to form infinite chains with antiferromagnetic interactions. A preliminary investigation indicated that $CuCl_2(DMSO)$ consists of infinite chains bridged by two chlorine atoms and one oxygen atom.[2] The above studies created a further interest in determining whether a more bulky group such as TMSO,

tetramethylsulfoxide, might yield a structure in which the infinite chains would be far enough apart so as to give a one-dimensional magnetic material. A preliminary account of the magnetic behavior of $CuCl_2(TMSO)$ has been given.[3] The existence of ferromagnetic *intra*chain interactions in that salt prompted us to undertake a more thorough study of $CuCl_2(DMSO)$. The results, as presented here, represent the first example of ferromagnetic Heisenberg spin-$\frac{1}{2}$ chains with strong exchange coupling and reasonable one dimensionality.

II. PREPARATION, PHYSICAL PROPERTIES, AND CRYSTALLOGRAPHIC DATA

$CuCl_2(TMSO)$ was prepared by dissolving tetramethylene sulfoxide in n propanol at 70 °C and then adding a slight excess of anhydrous copper chloride. Upon cooling the compound crystallizes out of solution as thin orange needles. Lattice constants,

determined by accurate centering of 12 high-angle reflections ($\lambda = 0.71069$ Å) are $a = 13.844(10)$ Å, $b = 6.418(12)$ Å, and $c = 17.480(16)$ Å. Systematic extinctions defined the unique orthorhombic space group $Pbca$. The density, determined by flotation in a mixture of bromomethane and dibromomethane, was $2.06(3)$ g/cm.^{3} The calculated density for $Z = 8$ is 2.04 g/cm^3

The preparation of $CuCl_2(DMSO)$ has been previously reported[4] and crystals are conveniently grown by adding excess $CuCl_2$ to a solution of DMSO in ethanol until all of the green $CuCl_2(2DMSO)$ dissolves. Lattice constants, determined as above, are $a = 7.774(1)$ Å, $b = 13.557(3)$ Å, $c = 6.475(1)$ Å, and $\beta = 103.839(1)°$ for the monoclinic crystal with the uniquely determined space group $P2_1/c$.

Intensity data for the $CuCl_2(DMSO)$ were collected on an automated Picker full circle diffractometer with Mo $K\alpha$ radiation using a 48-sec θ-2θ step scan with 10 sec background. A total of 1503 reflections were measured, of which 1115 had intensity greater than $3\sigma(I)$, where σ is the standard deviation and I is the observed intensity; $\sigma^2(I) = $ (net count) $+ (0.05)^2$(total count)^2. The crystal had dimensions $0.068 \times 0.164 \times 0.344$ mm^3, and the observed intensities were corrected for absorption. The positional parameters were taken from the previous film data structure solution. Least-squares refinement of F_o with weights $\omega = 1/\sigma^2(F_o)$ proceeded to a final weighted residual

$$R_2 \left[= \left(\sum \frac{\omega |F_o - F_c|^2}{\omega F_o^2} \right)^{1/2} \right]$$

of 0.059 with a conventional residual $R_1 (= \sum ||F_o| - F_c|/|F_o|)$ of 0.052 and a goodness-of-fit value of 1.57. (F_o and F_c are the observed and calculated structure factors.)

Intensity data on a crystal of $CuCl_2(TMSO)$ with dimensions $0.21 \times 0.10 \times 0.32$ mm^3 were collected on a Nonius-Weissenberg camera with Ni-filtered Cu $K\alpha$ radiation using a combination of multiple film and timed exposure techniques. The zeroth through the third layer were recorded while rotating about the $\langle 010 \rangle$ direction. In this manner, 918 reflections were recorded, 339 of which were classified as unobserved. The relative intensities were estimated visually against a set of standard intensities and converted to structure factors in the usual manner. All data was scaled to a common factor using a Wilson plot. Spot size corrections were also made.

Examination of a three-dimensional Patterson function indicated that the most likely position for copper was (0.250, 0.250, 0.055). The R factor, based on the structure factors calculated for this position was 0.48. A Fourier synthesis, based on the above atom yielded all other nonhydrogen atoms. Complete block-diagonal least-squares refinement, using appropriate damping factors and anisotropic thermal parameters for all atoms, yielded an R factor of 0.105 (observed reflections only). Three cycles of full-matrix least squares, using the Washington State University Crystallographic Library yielded an R factor of 0.093 (observed reflections only). Unobserved reflections were omitted from the full-matrix refinement if the calculated structure factor was less than $2\sigma(F)$. All reflections were weighed using a modified Hughes scheme.[5] No attempt was made to locate hydrogen atoms. All peaks on the final difference map were less than 0.5 electrons /Å.^{3} All programs were from the Pacific Lutheran University or Washington State University Crystallographic Libraries that include all or part of the following programs: ORFLS,[6] ORFFE,[7] ORTEP,[8] ALFF,[9] and ORABS.[10]

The final positional with standard deviations are listed in Tables I and II. The bond lengths and bond angles with standard deviations are listed in Tables III and IV, respectively. The thermal parameters, as well as a list of observed and calculated structure factors for the two salts have been deposited.[11]

TABLE I. Positional parameters for $CuCl_2(TMSO)$[a,b].

Atom	x	y	z
Cu	2502(1)	2379(6)	570(1)
Cl(1)	1272(2)	4835(6)	544(2)
Cl(2)	3358(3)	4394(6)	1380(2)
S	956(2)	1037(6)	−620(2)
O	2304(7)	991(17)	−366(5)
C(1)	1105(24)	−624(47)	−2025(11)
C(2)	882(12)	−1270(33)	−1209(10)
C(3)	1253(23)	1388(54)	−2118(12)
C(4)	976(14)	2757(31)	−1440(9)

[a]All parameters multiplied by 10^4

[b]Estimated standard deviations in the last figures given are reported in parentheses.

TABLE II. Positional parameters for $CuCl_2(DMSO)$[a,b].

Atom	x	y	z
Cu	3484(1)	2510(1)	1844(1)
Cl(1)	3518(2)	3745(1)	−696(2)
Cl(2)	1582(2)	3371(1)	3258(3)
S	6386(2)	993(1)	1463(2)
O	5621(5)	2046(3)	1059(6)
C(1)	8240(10)	1113(6)	3661(11)
C(2)	7495(10)	844(5)	−623(11)

[a]All parameters multiplied by 10^4.

[b]Estimated standard deviations in the last figures given are in parentheses.

TABLE III. Important bond distances.

	TMSO	DMSO
Cu−Cu	3.209(6)	3.238(1)
Cu−Cl(1)	2.321(5)	2.326(2)
Cu−Cl(2)	2.254(5)	2.352(2)
Cu−Cl(1)′	2.356(5)	2.352(2)
Cu−Cl(2)′	2.663(5)	2.714(2)
Cu−O	1.972(10)	1.959(4)
Cu−O′	2.909(11)	2.901(4)
S−O	1.557(10)	1.543(4)
S−C(1)	1.806(20)	1.769(7)
S−C(4) [S−C(2)]	1.809(18)	1.782(6)
C(1)−C(2)	1.517(28)	···
C(2)−C(3)	1.317(46)	···
C(3)−C(4)	1.524(32)	···
Cu−S	3.106(4)	3.106(2)
S−S′	3.671(7)	3.678(3)

TABLE IV. Important bond angles.

	TMSO	DMSO
Cl(1)−Cu−Cl(1)′	177.5(2)	177.88(7)
Cl(1)′−Cu−Cl(2)	91.8(2)	91.94(6)
Cl(1)−Cu−O′	67.0(2)	66.27(9)
Cl(1)−Cu−Cl(2)	90.5(2)	90.17(6)
Cl(1)−Cu−Cl(2)′	99.8(2)	100.25(5)
Cl(1)′−Cu−Cl(2)′	80.4(2)	79.06(5)
Cl(1)−Cu−O	92.8(3)	94.06(13)
Cl(1)′−Cu−O	84.7(3)	83.93(12)
Cl(1)′−Cu−O′	112.5(2)	114.24(9)
Cl(2)−Cu−Cl(2)′	108.3(2)	107.51(7)
Cl(2)−Cu−O′	77.3(2)	78.16(9)
Cl(2)−Cu−O	162.3(3)	163.24(14)
Cl(2)′−Cu−O′	166.2(2)	165.76(9)
O−Cu−Cl(2)′	88.2(3)	87.70(13)
O−Cu−O′	88.0(4)	88.71(16)
Cu−Cl(1)−Cu′	86.7(1)	87.57(5)
Cu−Cl(2)−Cu′	81.0(2)	80.92(5)
Cu−O−Cu′	79.7(3)	81.04(14)
Cu−O−S	122.9(6)	124.6(2)
O−S−C(1)	101.6(7)	104.7(3)
O−S−C(4) [O−S−C(2)]	102.9(7)	101.8(3)
C(1)−S−C(4) [C(1)−S−C(2)]	92.8(9)	100.2(4)
S−C(1)−C(2)	107.5(16)	···
S−C(4)−C(3)	105.6(16)	···
C(1)−C(2)−C(3)	114.6(20)	···
C(4)−C(3)−C(2)	115.5(21)	···
O−S−S′	121.0(4)	115.8(2)
C(1)−S−S′	89.9(6)	138.4(2)
C(4)−S−S′ [C(2)−S−S′]	134.4(6)	81.7(2)

III. MAGNETIC DATA

Primary measurements were made with a PAR vibrating-sample magnetometer (VSM). A 94-mg sample of $CuCl_2$(TMSO) powder was placed in a gelatin capsule and attached to a plastic screw mount using Duco cement. The sample was then attached to a metal and quartz rod and placed in the VSM. Data initially were collected at 5 kOe from 4.2 to 117 K and the range was subsequently extended to 1.8 K by pumping on the helium. All experimental moments were corrected for background using a bare sample rod. For $CuCl_2$(DMSO), an identical set of measurements were made of a 175-mg sample. A second series of measurements was made on a 9.6-mg sample of $CuCl_2$(TMSO) from 75 to 297 °K using the Faraday technique. Finally, a magnetization study, from 100 to 600 Oe for $CuCl_2$(TMSO) at 7.5 °K (the maximum in χT) confirmed that χ was field independent. All susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants[12] and for temperature-independent paramagnetism (TIP) of copper according to the TIP expression $N\Delta g\beta^2/\lambda = 60 \times 10^{-6}$ cgs units[13] during all least-squares fittings. Magnetization and susceptibility data have been deposited.[11]

IV. STRUCTURAL RESULTS

The structures of both salts consist of $CuCl_2L$ moieties tied together by two chlorine interactions and one oxygen interaction to form infinite chains parallel to the short crystallographic axis. The copper coordination sphere (Cu site symmetry C_1) has an elongated tetragonal distortion giving the typical "4 + 2" coordination geometry. This is shown for $CuCl_2$(TMSO) in Fig. 1. The inplane ligands are three chloride ions [designated Cl(1), Cl(1)′, and Cl(2)] and one oxygen (O) from the sulfoxide molecule. The distances to the out-of-plane ligands [Cl(2)′ and O′] are considerably longer than to the in-plane ligands. The distortions of the coordination sphere from "ideality," while severe, are not unusual for Cu (II) salts and can easily be rationalized in terms of the intersphere interactions.

The structurally significant feature is the linking of the copper-ligand fragments into discrete chains parallel to the short crystallographic axis, as shown in Fig. 2. In each case, the chain is formed by the action of the 2_1 screw axes parallel to the short axis, leading to a structure with three Cu−ligand−Cu bridges between adjacent Cu ions. The most important is the symmetrical Cu−Cl(1)−Cu′ bridge with Cu−Cl distances [for $CuCl_2$(TMSO)] of 2.325 and 2.358 Å and a bridging angle of 86.51°. Two asymmetric bridges also exist: Cu−Cl(2)−Cu′ ($d_{Cu-Cl} = 2.255$ and 2.665 Å, respectively) with a
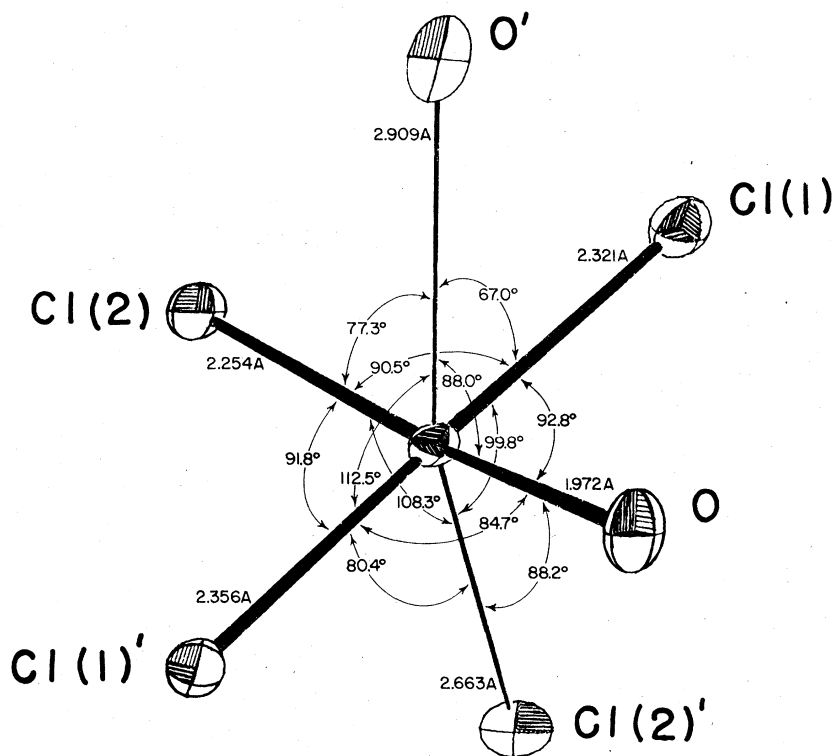
FIG. 1. Coordination geometry of copper ion in $CuCl_2(TMSO)$. Corresponding distances and angles for $CuCl_2(DMSO)$ can be obtained from Tables III and IV.
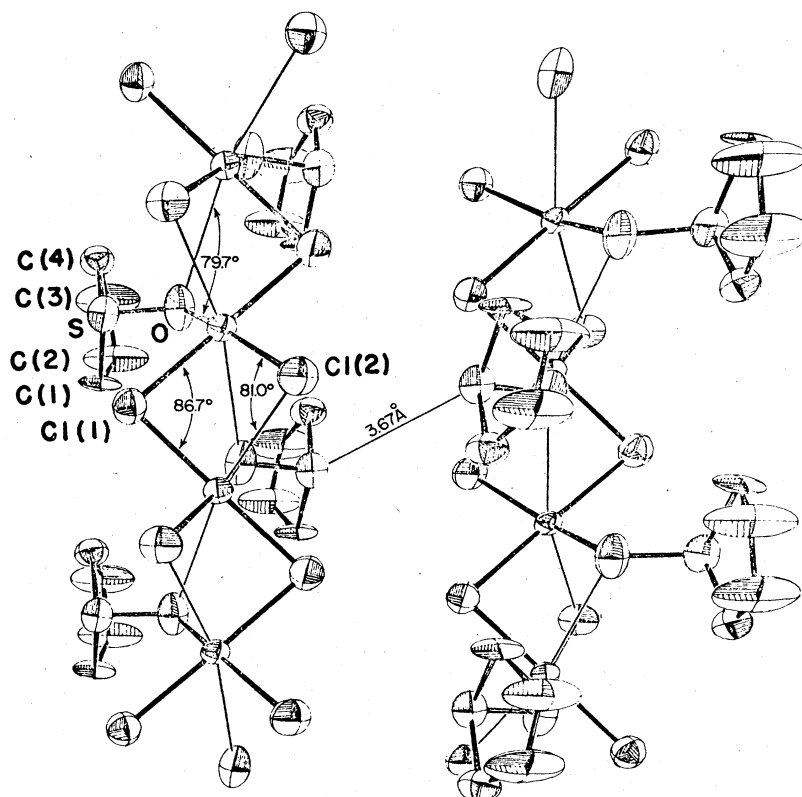

FIG. 2. Packing of chains in $CuCl_2(TMSO)$. The b axis is vertical and the a axis is horizontal.

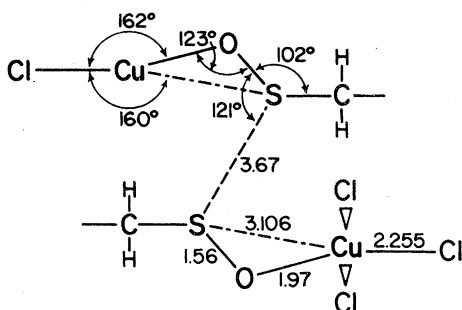FIG. 3. Schematic diagram of interchain interactions in $CuCl_2(TMSO)$.

bridging angle of 80.95° and Cu—O—Cu'
($d_{Cu-O} = 1.974$ and 2.910 Å) with a bridging angle of
79.63°. The data for the $CuCl_2(DMSO)$ are analogous (Tables III and IV) with a significant feature being the lengthening of the Cu—Cu distance and a 1° increase in the Cu—Cl(1)—Cu' bond angle. It is known that superexchange interactions through symmetrical bridges with an angle near 90° give rise to a strong ferromagnetic coupling.[14] The sign of the exchange coupling through asymmetric bridges depends on several structural parameters which, as of yet, have not been precisely defined.[15] It is known, however, that coupling through asymmetric bridges is generally weaker than through symmetric bridges, so a net ferromagnetic interaction is anticipated.

The packing of the TMSO groups in that salt effectively isolates adjacent chains in the c direction from each other but does not prevent close sulfur-sulfur contacts between chains in the a direction (Fig. 2). Thus, indirect exchange pathways of the type Cu—O—S · · · S—O—Cu exist between chains. This interaction is illustrated diagramatically in Fig. 3. If it is assumed that the chloride ions dictate the orientation of the $d_{x^2-y^2}$ orbital (which contains the magnet-
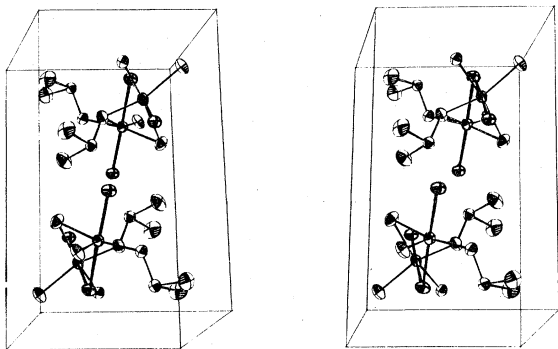

FIG. 4. A stereoscopic illustration of the structure of $CuCl_2(DMSO)$ as viewed down the c axis. The b axis is vertical and the a axis is horizontal.

ic electron), then the remaining lobe of the orbital points towards the S-O bond. Thus, we can confidently state that the wave function for the unpaired electron contains contributions from the sulfur valence orbitals. If it is assumed that the sulfur has sp^3 hybridization of its valence orbitals, the geometry of the TMSO molecule dictates that the lone pair of electrons on each sulfur points towards the centrosymmetrically related sulfur on adjacent chains in the a direction. Thus, a well-defined superexchange pathway exists between chains. Similar features exist in the DMSO salt, as seen in Fig. 4.

V. MAGNETIC RESULTS

A least-square fit of the Faraday data for $CuCl_2(TMSO)$ gave a Curie constant $C = 0.417 \pm 0.010$ and a Weiss constant of 33 ± 2°K. The g value obtained from this data corresponds to $g = 2.11$ for a spin $S = \frac{1}{2}$ system. The corresponding values for the DMSO salt are $C = 0.420 \pm 0.010$ ($g = 2.115 \pm 0.02$) and $\theta = 38 \pm 2$ °K. An EPR measurement of the DMSO compound found a g of 2.095. These positive Weiss constants are indicative of predominant ferromagnetic interactions.

Shown in Fig. 5 is a plot of molar reduced susceptibility, χ/C (C is the Curie constant), times absolute temperature T versus reduced temperature kT/J for the low-temperature data of the two salts. As T decreases, the value of $\chi T/C$ increases, substantiating the inference of ferromagnetic coupling deduced from the Faraday measurements. However, the presence of antiferromagnetic interactions is noted by the maximum in χT at 7.4 and 12.3 °K, respectively, for the TMSO and DMSO compounds. Indeed, the susceptibility reaches a maximum (Fig. 6) at 3.9 and 5.4 °K. No evidence for the onset of cooperative (long-range) effects are seen in the data.

The PAR susceptibility data for $CuCl_2(TMSO)$ were analyzed with several one-dimensional models. For each approach the basic model was modified by the addition of a mean-field correction to account for the interchain interactions. The basic equation has the following form,[16-18]

$$\chi' = \frac{\chi}{1 - (2ZJ'/Ng^2\mu_B^2)\chi} , \tag{1}$$

where Z is the number of nearest-neighbor chains and J' is the exchange integral for the magnetic interaction between nearest-neighbor chains.

Models included Ising for $S = \frac{1}{2}$,[19] anisotropic Ising,[20] Heisenberg in the limit of infinite spin,[21] and the Heisenberg for $S = \frac{1}{2}$, based on a high-temperature Padé expansion technique.[22]

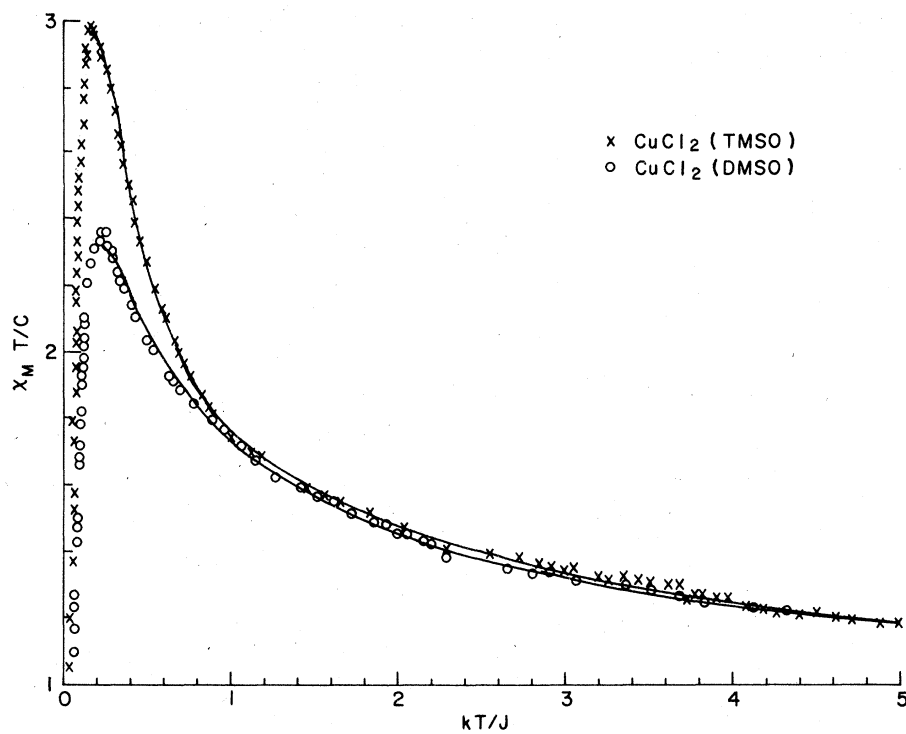The best fit has been obtained using the Padé ex-

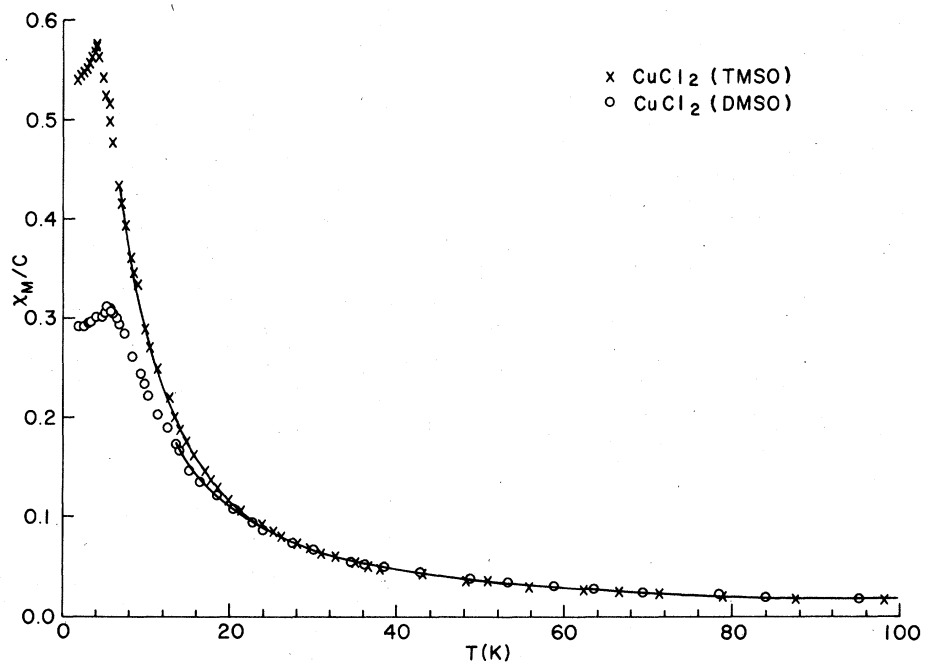FIG. 5. A plot of $\chi T/C$ vs reduced temperature (kT/J) for $CuCl_2(TMSO)$ and $CuCl_2(DMSO)$.

FIG. 6. Reduced susceptibility (χ/C) vs temperature for $CuCl_2(TMSO)$ and $CuCl_2(DMSO)$.

pansion series for the $S = \frac{1}{2}$ Heisenberg model. The accuracy of this expansion decreases

$$\chi(K)/Ng^2\mu_B^2 = [(1 + 5.797\,991\,6K + 16.902\,653K^2 + 29.376\,885K^3 + 29.832\,959K^4$$

$$+ 14.036\,918K^5)/(1 + 2.797\,991\,6K + 7.008\,678\,0K^2 + 8.653\,864\,4K^3 + 4.574\,311\,4K^4)]^{2/3} \quad , \quad (2)$$

$$K = \frac{J}{2kT} \quad ,$$

as $J/2kT$ increases. Also, the mean-field correction does not give reliable fits in the low-temperature region. Using these limitations the susceptibility data of the TMSO salt from 7.1 to 198 °K gave a value of $J/k = 39 \pm 6$ °K and a mean-field correction of $ZJ'/k = -1.60 \pm 0.15$ °K. The two parameters are strongly correlated which accounts for the relatively large imprecision. The imprecision in J also reflects the strong dependence of J upon g. These values were obtained with g set at 2.11. An earlier report[4] of this data reported somewhat different values for the parameters since the previous fitting routines had been based upon a g of 2.24. An analogous analysis for $CuCl_2(DMSO)$ yields $J/k = 45 \pm 6$ °K and $ZJ'/k = -4.0 \pm 0.4$ °K with $g = 2.115$. Figure 6 shows the susceptibility data and the theoretical curve based upon these parameters. As the temperature is lowered, the susceptibility for both compounds increases faster than the predictions of the pure Heisenberg model used. This increase may signify a small amount of Ising-like anisotropy in the exchange Hamiltonian.

Since the analysis of the susceptibilities $S = \frac{1}{2}$ Heisenberg ferromagnets is a new topic, we shall spend some time discussing it here. The predictions of several theoretical calculations are given in Table V. The present analysis was that of Baker et al.,[22] and was based upon a Padé approximant technique. The authors estimated that $\overline{X}$, defined as $\chi_0 kT/Ng^2\mu_B^2$, should diverge as $(T/J)^{-2/3}$ as $T \rightarrow 0$, with an estimated uncertainty of ten percent in the power.

Bonner and Fisher[23] have also calculated the low-temperature behavior of one-dimensional $S = \frac{1}{2}$ Heisenberg ferromagnets, using computer techniques to calculate the properties of finite rings and chains of spins. The predictions of Baker agree with those of Bonner and Fisher down to value of kT/J of 0.1 within the stated uncertainties of Bonner and Fisher. For lower reduced temperature, the disagreement seems to come from the irregularities in the machine calculations. Thus it appears justifiable to use the result of Baker et al. over the entire temperature range, as has been done above.

A high-temperature series expansion has been made for the susceptibility of an $S = \frac{1}{2}$ anisotropic ferromagnetic chain by Obokata et al.[24] However, this expansion only contains seven terms, and cannot be used for low relative temperatures. It differs by

0.4% from the prediction of Baker's series for values of kT/J as high as 1.6. This series does have the advantage of allowing a determination of the amount of Ising-like anisotropy in the Hamiltonian. For comparison purposes, the high-temperature series expansion due to Baker is also given,[25] but it is clear this fails badly for $T < 3J$.

The breakdown of the molecular-field approximation can be seen in Fig. 5 as the theoretical curve which adequately describes the higher-temperature data fails to quantitatively account for the maxima observed in the data. The molecular-field correction to the susceptibility is about one percent at 100 °K, three percent at 50 °K, eight percent at 25 °K, and about thirty percent at 10 °K. The molecular-field approximation is inadequate at these low temperatures: the two-dimensional Heisenberg model would be a more appropriate model for the analysis of this data but such a model has not yet been solved.

VI. DISCUSSION

The structural and magnetic studies reported clearly demonstrate that $CuCl_2(TMSO)$ and $CuCl_2(DMSO)$ contain ferromagnetic linear chains with only relatively weak antiferromagnetic interactions between chains. These are the first example of a ferromagnetic spin-$\frac{1}{2}$ linear chain system with strong exchange coupling within the chain. Above 40 °K, little effect of the interchain interactions is observed upon the susceptibility, consistent with the large ratios obtained for J/J' of 50 and 25, respectively ($Z = 2$). Thus these would appear to be extremely useful systems for studying the spin-correlation function for a one-dimensional ferromagnet. Spin canting is probably an important factor in these salts since adjacent Cu ions are related by a 2_1 screw-axis-symmetry element with substantial tilting of the orientation sphere (and thus the g tenor) from the chain axis. EPR linewidth studies to probe these aspects are underway in this laboratory.

The only previously reported spin-$\frac{1}{2}$ linear chain with ferromagnetic interaction is $(CH_3)_3NHCuCl_3 \cdot 2H_2O$.[26] The value of J/k (0.9 °K) is significantly smaller than in sulfoxide salts although the isolation of the chains is slightly better. It should be noted that $(CH_3)_3NHCuCl_3 \cdot 2H_2O$ contains bridged $CuCl_2(H_2O)_2$ chains with asymmetric $Cu-Cl \cdots Cu$ bridges. These magnetic data corro-

TABLE V. Comparison of the models predictions of the $S = \frac{1}{2}$ Heisenberg ferromagnetic linear chain. $\chi_{reduced}$ is defined as $\chi T / C$, where C is the Curie constant. Note that the values of χ reduced to Baker's Padé-approximant equation had to be divided by a factor of 4 in order to agree with the other models.

kT/J	$\chi_{reduced}$[a] Bonner & Fisher[b]	$\chi_{reduced}$ Baker's Padé Approx. eq.[c]	$\chi_{reduced}$ Baker's 10-term HTSE[d]	$\chi_{reduced}$ Obokatu-Ono- Oguichi Padé[e]
5.0	0.299 43	0.299 43	0.296 76	0.299 43
4.4	0.306 00	0.306 00	0.302 67	0.305 99
3.8	0.314 55	0.314 56	0.310 30	0.314 55
3.2	0.326 15	0.326 15	0.320 55	0.326 14
2.6	0.342 71	0.342 72	0.335 09	0.342 69
2.2	0.358 34	0.358 34	0.348 74	0.358 24
1.8	0.380 14	0.380 15	0.367 18	0.379 71
1.4	0.412 75	0.412 76	0.381 41	0.409 94
1.2	0.436 02	0.436 04	0.336 11	0.427 39
1.00	0.467 2	0.467 24	−.096 2	0.435 29
0.90	0.487 3	0.487 27	−1.124	0.420 00
0.80	0.511 6	0.511 61	−4.75	0.358 32
0.70	0.542 0	0.549 13	−19.59	0.156 26
0.60	0.581(1)	0.580 97	−94.06	−0.522 8
0.50	0.633(5)	0.633 51		
0.40	0.708	0.708 73		
0.30	0.82(7)	0.826 79		
0.25	0.9(18)	0.916 05		
0.2	1.05	1.043 1		
0.175	1.1(4)	1.296		
0.15	1.2(6)	1.240 3		
0.125	1.4(1)	1.387 9		
0.100	1.6(4)	1.596 2		
0.075	0.(75)	1.916 9		
0.050	2.(67)	2.490 6		

[a]Parentheses around the last figure signify an uncertainty of ≥ 3 and parentheses around the last two figures a possible error of $> \pm 10$.
[b]Reference 22.
[c]Reference 21.
[d]Reference 24.
[e]Reference 23.

borate our assumption that exchange is weak in such bridges.

The relationship of the CuCl$_2$-sulfoxide results to the data on CsCuCl$_3$ should be noted. This latter salt contains linear $(CuCl_3^-)_n$ chains with very similar geometry to that reported here. In particular, it contains one symmetric and two asymmetric Cu−Cl−Cu bridges, with bridging angles of 81.12° and 73.80°, respectively.[27] Magnetic and heat-capacity data have been interpreted both in terms of antiferromagnetic[28,29] and ferromagnetic[30] intrachain interactions. It

is clear that with such similar structural parameters, the exchange mechanisms must be same in these two salts and hence the intrachain coupling in CsCuCl$_3$ must be ferromagnetic as proposed by de Jongh.[30]

VII. ACKNOWLEDGMENT

[1] R. D. Willett and Kun Chang, Inorg. Chim. Acta <u>4</u>, 447 (1970); R. D. Willett, F. H. Jardine, and S. A. Roberts, Inorg. Chim. Acta <u>25</u>, 97 (1977).

[2] Roger D. Willett, Duane Swank, Kun Chang, and Stuart Hawkinson, Acta. Crystallogr. A <u>25</u>, S175 (1969).

[3] R. D. Willett, C. P. Landee, and D. D. Swank, J. Appl. Phys. <u>49</u>, 1329 (1978).

[4] J. Selbin, W. E. Bull, and L. H. Holmes, Jr., J. Inorg. Nucl. Chem. <u>16</u>, 219 (1961).

[5] J. P. Steadman and R. D. Willett, Inorg. Chim. Acta <u>4</u>, 367 (1970).

[6] W. R. Busing, K. O. Martin, and H. A. Levy, U.S. AEC Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962 (unpublished).

[7] W. R. Busing, K. O. Martin, and H. A. Levy, U.S. AEC Report No. ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964 (unpublished).

[8] C. K. Johnson, U.S. AEC Report No. ORNL-3794, revised, 1965; overlap correction, 1971 (unpublished).

[9] C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, U.S. AEC Report No. IS-2625, Iowa State University and Institute for Atomic Research, Ames, Ia., 1971 (unpublished).

[10] D. J. Wehe, W. R. Busing, and H. A. Levy, AEC Report No. ORNL-TM-229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962 (unpublished).

[11] See AIP document No. PAPS PRMDO-20-2154-06 for 6 pages of supplementary tables. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N.Y. 10017. The price is $1.50 for each microfiche (98 pages), or $5 for photocopies of up to 30 pages with $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics. This material also appears in *Current Physics Microform,* the monthly microfilm edition of the complete set of journals published by AIP, on the frames immediately following this journal article.

[12] E. Konig, *Magnetic Properties of Coordination and Organometallic Transition Metal Complexes* (Springer-Verlag, Berlin, 1966).

[13] E. Marshall, A. Botterman, S. Vega, and A. Miedema, Physica (Utrecht) <u>41</u>, 473 (1969).

[14] V. H. Crawford, H. W. Richardson, J. R. Wesson, D. J. Hodgson, and W. E. Hatfield, Inorg. Chem. <u>15</u>, 2107 (1976).

[15] V. H. Crawford and W. E. Hatfield, Inorg. Chem. <u>16</u>, 1336 (1977).

[16] T. Watanabe, J. Phys. Soc. Jpn. <u>17</u>, 1856 (1962).

[17] J. N. McElearney, D. B. Losee, S. Merchant, and R. L. Carlin, Phys. Rev. B <u>7</u>, 3314 (1973).

[18] D. B. Losee, J. N. McElearney, G. E. Shankle, R. L. Carlin, P. J. Cresswell, and Ward T. Robinson, Phys. Rev. B <u>8</u>, 2185 (1973).

[19] J. W. Stout and R. C. Chisholm, J. Chem. Phys. <u>36</u>, 979 (1962).

[20] M. E. Fisher, J. Math Phys. <u>4</u>, 124 (1963).

[21] Michael E. Fisher, Am. J. Phys. <u>32</u>, 343 (1964).

[22] George A. Baker, Jr., G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev. <u>135</u>, A1272 (1964).

[23] J. Bonner and M. E. Fisher, Phys. Rev. <u>135</u>, A640 (1964).

[24] T. Obokatu, I. Ono, and T. Oguichi, J. Phys. Soc. Jpn. <u>23</u>, 516 (1967).

[25] H. B. Algra, L. J. de Jongh, W. J. Huiskamp, and R. L. Carlin, Physica (Utrecht) <u>92B</u>, 187 (1977).

[26] H. B. Algra, L. J. de Jongh, H. W. J. Blöte, W. J. Huiskamp, and R. L. Carlin, Physica (Utrecht) <u>78</u>, 314 (1974).

[27] A. W. Schuelter, R. A. Jacobsen, and R. E. Rundle, Inorg. Chem. <u>5</u>, 277 (1966).

[28] N. Achiwa, J. Phys. Soc. Jpn. <u>27</u>, 561 (1969).

[29] F. J. Rioux and B. C. Gerstein, J. Chem. Phys. <u>53</u>, 1789 (1970).

[30] L. J. de Jongh and D. R. Miedema, Adv. Phys. <u>23</u>, 1 (1974).