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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Exchange Coupling in the Sulfur-Bridged Quasi-Linear-Chain Compound Bis(dimethyldithiocarbamato)copper(II). Observations on Exchange in Sulfur-Bridged Copper(II) Compounds

WILLIAM E. HATFIELD,* ROBERT R. WELLER, and JAMES W. HALL

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Magnetic susceptibility data have been collected on a powdered sample of the linear-chain compound bis(dimethyldithiocarbamato)copper(II). The data are fitted to a Heisenberg linear-chain model for exchange coupled $S = {}^1/_2$ ions including an interchain correction term. The best fit parameters are $J(\text{intrachain}) = -1.22\ \text{cm}^{-1}$ and $J(\text{interchain}) = 0.47\ \text{cm}^{-1}$ with the EPR average g value of 2.03. Data for $[\text{Cu(dmtc)}_2]_\infty$ and three other sulfur-bridged copper(II) compounds exhibit a correlation between the exchange coupling constant and the geometry of the Cu_2S_2 bridging unit.

Introduction

Exchange coupling propagated by sulfur donor atom bridges continues to attract considerable attention because of the prominence of sulfur-bridged metal ions in biological systems[1] and of the more recent observation that complexes with sulfur donor ligands undergo facile partial oxidations to yield highly conducting synthetic materials.[2] In order to provide additional information on exchange coupling in sulfur-bridged copper(II) compounds, we have measured the magnetic susceptibility of the quasi-linear-chain compound bis(dimethyldithiocarbamato)copper(II),[3] $[\text{Cu(dmtc)}_2]_\infty$, and report the results of our work. In addition, we have collected structural and magnetic data for other sulfur-bridged copper(II) compounds and discuss the relationship between structural features and exchange coupling.

Experimental Section

Bis(*N*,*N*-dimethyldithiocarbamato)copper(II) was prepared by mixing a solution of copper chloride in water with a stoichiometric amount of the sodium salt of the ligand dissolved in water. The precipitate was filtered, washed with water, and dried. Anal. Calcd: C, 23.71; H, 3.98; N, 9.22; Cu, 20.90. Found: C, 23.86; H, 3.74; N, 9.78; Cu, 20.90.

Magnetic susceptibility data were collected with a Princeton Applied Research vibrating-sample magnetometer which was calibrated with ultrapure nickel metal[4] and with $HgCo(NCS)_4$.[5] The two calibrations agreed very well and it is estimated that the limits of error on the measured magnetic susceptibilities are ±1%. The temperatures were measured with a calibrated gallium arsenide diode as has been described elsewhere.[6] The sample was contained in a Lucite sample holder, and the magnetometer output was corrected for the diamagnetism of the sample holder and the underlying diamagnetism of the constituent atoms by using Pascal's constants.[7] A value of 60×10^{-6} emu/mol was assumed for the temperature-independent paramagnetism of the copper(II) ion.[8] All curve fitting was carried out with the use of a SIMPLEX function minimization program.[9-12]

Electron paramagnetic resonance spectra were recorded with use of a Varian E-3 spectrometer at X-band, ~9.5 GHz. The magnetic field was determined from the chart paper which had been calibrated[13] with a Magnion G-502 precision gaussmeter, a Hewlett-Packard 5340A frequency counter, and a DPPH sample. The agreement was better than 1%.

Results

The magnetic susceptibility of a powdered sample of the linear-chain compound bis(dimethyldithiocarbamato)copper(II) is plotted as a function of temperature in Figure 1, where it may be seen that the susceptibility exhibits a maximum value at ~2.5 K. This behavior is indicative of a magnetically condensed substance, and since the compound has a linear-chain structure, the data were analyzed by using the Heisenberg linear-chain theory of Bonner and Fisher.[14] The Hamiltonian in eq 1 was used by Bonner and Fisher to produce

$$\mathcal{H} = -2J\sum_n(\hat{S}_z^i\hat{S}_z^{i+1} + \hat{S}_x^i\hat{S}_x^{i+1} + \hat{S}_y^i\hat{S}_y^{i+1}) \qquad (1)$$

numerical results for the temperature variation of the magnetic susceptibility of exchange-coupled chains of $S = {}^1/_2$ ions. Hall has fit Bonner's numerical data to eq 2 where $x = kT/|J|$.

$$\chi_m \approx \frac{Ng^2\beta^2}{kT}\,\frac{0.25 + 0.14995x + 0.30094x^2}{1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3} \qquad (2)$$

Since, as described in the next section, the chains in $[\text{Cu(dmtc)}_2]_\infty$ are in rather close contact, substantial interchain interactions were anticipated. The problem was treated as one involving Heisenberg interactions along a chain with a correction for interchain interactions being accounted for in the expression

$$\chi_n = \chi_H/(1 - 2zJ'\chi_H/Ng^2\beta^2) \qquad (3)$$

where χ_H is the magnetic susceptibility of an isolated Heisenberg chain of $S = {}^1/_2$ ions, z is the number of near neighbors in adjacent chains, and J' is the interchain exchange parameter. In this case, z was taken to be 4. Expression 3 was fit to the experimental magnetic susceptibility and temperature data by using as the criterion of best fit the minimum value of $\sum_i(\chi_i^{\text{calcd}} - \chi_i^{\text{obsd}})^2/(\chi_i^{\text{obsd}})^2$. The parameters which were obtained by using the g value of 2.03 determined from the EPR spectrum were $J = -1.22\ \text{cm}^{-1}$ and $J' = +0.47\ \text{cm}^{-1}$. Since the ratio of J' to J is relatively large, the applicability of the linear-chain model to $[\text{Cu(dmtc)}_2]_\infty$ is open to some question. The expression for two exchange-coupled $S = {}^1/_2$ ions gives a re-

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Table I. Structural and Magnetic Data in Sufur-Bridged Copper(II) Compounds

compd	J, cm^{-1}	Cu-S$_b$,^{a} Å	Cu-S$_b$,^{b} Å	Cu-S$_b$-Cu, deg	φ/r_0, deg Å^{-1}	ref
$[Cu(dmdtc)_2]_\infty$	−1.22	3.159 (2)	2.302 (2)	94.2	29.8	3, this work
$[Cu(detc)_2]_2$	12	2.851	2.339 (2)	86.9	30.5	15, 19, 20
	6.5 ± 0.5					21
	4, 3.3					18
$[Cu(TCH)Cl_2]_2Cl_2$	−12.4 ± 1	3.310 (6)	2.271 (5)	88.4	26.7	16, 25
$[Cu(KTS)]_\infty$	−8	3.101		89.8	29.0	17, 26
		3.312		86.5		

[a] This is the long, out-of-plane bridging bond distance. [b] This is the short, in-plane bridging bond distance.

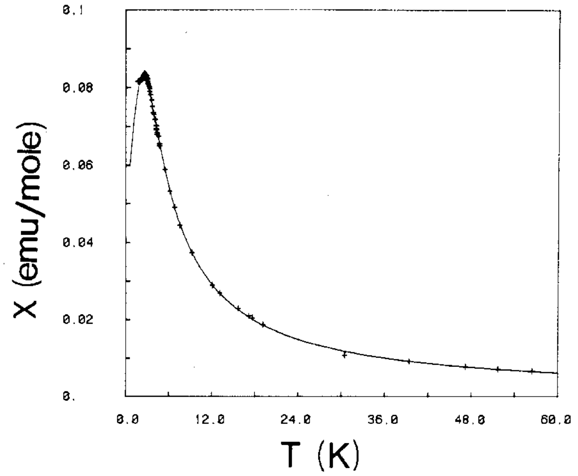

Figure 1. Magnetic susceptibility vs. temperature for the linear-chain compound $[Cu(dmtc)_2]_\infty$. The solid line is the best fit of the Heisenberg linear chain $S = {}^1/_2$ model to the data with the EPR g value of 2.03 and J(intrachain) = −1.22 cm^{-1}. A correction for an interchain interaction gave J(interchain) = 0.47 cm^{-1}.

sonable fit to the data with the EPR $\langle g \rangle$ value of 2.03 and $J = -1.3$ cm^{-1}. However, this latter model is probably not applicable to $[Cu(dmtc)_2]_\infty$, since the high-temperature structure is known to be a uniformly spaced linear chain and since the magnetic susceptibility data appear to be tending toward a nonzero value as the temperature approaches zero. Extensive measurements on single crystals in the low-temperature range will be required before an exact description of the magnetic interactions may be had.

Discussion

First the available structures of sulfur-bridged copper(II) compounds will be described, then the magnetic properties of these compounds will be discussed, and finally a correlation between the magnetic properties and the geometry of the bridged Cu_2S_2 unit will be drawn.

Structures. As determined by Einstein and Field[3] the copper(II) ion in $[Cu(dmtc)_2]_\infty$ is octahedrally coordinated to six sulfur donor atoms with the bond distances Cu–S(1) = 2.302 (2), Cu–S(2) = 2.319 (2), and Cu–S(1′) = 3.159 (2) Å. The short copper–sulfur distances involve sulfur atoms of two dimethyldithiocarbamato ligands in the plane of a tetragonally elongated octahedron, and the long bond distances involve sulfur atoms in adjacent $Cu(dmtc)_2$ units. The Cu–S(1)–Cu′ bridging angle is 94.2°. The chain that is formed by the sharing of sulfur atoms runs along the c axis of the C-centered monoclinic cell. The closest contact between chains is between a sulfur atom on one chain and a hydrogen atom on an adjacent chain at 2.80 Å, but it is unlikely that this contact is important in superexchange pathways. More important in this regard are the sulfur–sulfur contacts of 5.023 Å which occur between the chains at the corners of the cells. These interactions link the chains into two-dimensional networks in the ab plane. There are also short sulfur–sulfur contacts of 5.7 and 5.9 Å between the two chains in the same cell.

The structure of $[Cu(detc)_2]_2$ was reported by Bonamico et al.[15] in 1965. The structure consists of a pair of square-planar $Cu(detc)_2$ units linked into a dimer by coordination of one in-plane sulfur in an out-of-plane site of the adjacent copper ion. Thus, the coordination geometry about copper is tetragonal pyramidal with four short in-plane copper–sulfur bond distances of approximately 2.3 Å and one long out-of-plane bond distance of 2.851 Å. It is this latter bond which leads to bridge formation. The Cu–S$_b$–Cu angle is 86.9°. The sixth coordination site of copper is blocked by a hydrogen atom from an ethyl group of a neighboring dimer. The copper–hydrogen distance was calculated by Bonamico et al. to be 2.859 Å.

In the dimer dichloro(thiocarbanohydrazid-1-ium-N,S)-copper(II) chloride, $[Cu_2(TCH)_2Cl_4]Cl_2$, the copper ion is coordinated by six donor atoms in the often seen "4 + 1 + 1" arrangement.[16] The four short bonds are to two chlorides and to nitrogen and sulfur donors from the cationic, bidentate ligand. The in-plane bonded sulfur atom of one fragment occupies an out-of-plane site of the adjacent copper ion leading to the Cu_2S_2 bridged unit. The out-of-plane copper–sulfur distance is 3.310 (6) Å. Even though this distance is rather long, the interaction, as well as extensive hydrogen bonding between the ammonium groups and the coordinated chlorides, serves to bind the fragments together.

The planar units of (3-ethoxy-2-oxobutyraldehyde)bis(thiosemicarbazonate)copper are stacked to give a di-μ-sulfur-bridged alternating chain.[17] The out-of-plane copper–sulfur distances in the alternating chain are 3.101 (2) and 3.312 (2) Å, with the Cu–S$_b$–Cu bridging angle in the more tightly bound fragment being 89.8°. The corresponding angle in the unit with the longer bridge is 86.5°.

The structural features which are important for the discussion of the magnetic properties are the copper–sulfur bond distances and the Cu–S$_b$–Cu angle at the bridging sulfur atom. These data are collected in Table I. It is important to note that the in-plane bond distances are nearly constant at 2.3 ± 0.04 Å, while the out-of-plane distances vary from 2.85 Å in the tightly bound dimer $[Cu(detc)_2]_2$ to 3.3 Å in $[Cu(TCH)Cl_2]_2Cl_2$ and the alternating chain $[Cu(KTS)]_\infty$.

Magnetic Properties. The magnetic susceptibility data for $[Cu(dmtc)_2]_\infty$ are given in Figure 1, where the antiferromagnetic interaction is clearly indicated by the maximum in magnetic susceptibility at ~2.5 K. The data may be described by a modified Heisenberg chain model with the EPR g value of 2.03 and the parameters J(intrachain) = −1.22 cm^{-1} and J'(interchain) = 0.47 cm^{-1} or by a dimer model with $J = -1.3$ cm^{-1}. These data are adequate for the present work which

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documents the effectiveness of sulfur donor bridges to transmit superexchange interactions, even though the bridging bond distances are very long. If possible, additional measurements on single crystals in the low-temperature range would be very desirable, for such information would permit an exact description of the exchange interactions.

The first extensive work on the magnetic properties of $[Cu(detc)_2]_2$ was the paramagnetic anisotropy measurements of Gregson and Mitra,[18] who deduced values for the exchange coupling parameters, $J_{\parallel}$ and $J_{\perp}$, of 8.0 and 6.6 cm^{-1} respectively. Additional magnetic susceptibility and magnetization measurements made on powdered samples at low temperatures[19,20] yielded an average J value of 12 cm^{-1}, but more recent highly sensitive multifrequency pulse and spin-echo EPR measurements[21] yielded a singlet–triplet splitting of 13 ± 1 cm^{-1}. In view of the extensive EPR data[22,23] on the triplet state in $[Cu(detc)_2]_2$, the report by Carlin and co-workers[24] that there is no exchange coupling in the dimeric molecule can be dismissed. In any event, since there is exchange coupling in the three other known sulfur-bridged copper complexes, all of which have much longer copper–sulfur out-of-plane bond distances, then it is very difficult to see how the copper ions would not be exchange coupled in $[Cu(detc)_2]_2$.

Magnetic susceptibility data obtained[25] on a small powdered sample of $[Cu(TCH)Cl_2]_2Cl_2$ show a maximum in susceptibility at ~25 K, and the data may be fit to the Van Vleck equation for a pair of exchange-coupled copper(II) ions with the EPR g value of 2.13 ± 0.02 and $2J = -24.8 \pm 2.0$ cm^{-1}. This is perhaps a surprisingly large value for the singlet–triplet splitting, especially in view of the very long copper–sulfur out-of-plane bond distance. The results reflect the large radial extensions of the sulfur orbitals involved in the superexchange interaction.

As of yet, adequate magnetic susceptibility data for the alternating linear-chain compound $[Cu(KTS)]_\infty$ are not available, but Blumberg and Peisach have estimated a "singlet–triplet" splitting of 16 cm^{-1} for a singlet ground-state system on the basis of temperature-dependent EPR signal intensities.[26]

Correlation of Magnetic Properties with Structures. Structural and magnetic data for the sulfur-bridged copper(II) compounds are compiled in Table I. There are several conclusions which may be drawn from the data. The first and most important point is that even long out-of-plane bridging bond distances provide pathways for appreciable singlet–triplet splittings resulting from superexchange coupling. Next, the short in-plane copper–sulfur bond distances which are involved in the bridge are relatively constant at 2.3 ± 0.04 Å, but the out-of-bond distances vary from 2.851 Å in $[Cu(detc)_2]_2$ to 3.3 Å in $[Cu(TCH)Cl_2]_2Cl_2$. In addition, there is a fairly wide range of $Cu–S_b–Cu$ angles at the bridging sulfur atom.

It has been established that the singlet–triplet splitting is a linear function of the angle at the bridging oxygen atom in a series of di-μ-hydroxo-bridged copper(II) compounds.[27] Also, Roundhill et al.[28] have noted that the singlet states are similarly stabilized as the bridge angle increases in chloro-bridged copper(II) systems. For this particular group of sulfur-bridged compounds there is an additional variable, which also arises in several parallel planar chloro-bridged copper compounds, and that is the out-of-plane bridging bond distance. Since the extent of exchange coupling is known to decrease as the internuclear separation of exchange-coupled sites increases, we were led to investigate the relationship between the exchange-coupling constants for these sulfur-bridged compounds and the function φ/r_0, where φ is the $Cu–S_b–Cu$ angle and r_0 is the out-of-plane copper–sulfur bond distance. This relationship is shown in Figure 2, where it may be seen that a smooth curve may be drawn through the experimental data. For the purpose of this work the exchange-coupling constant for $[Cu(detc)_2]_2$ determined earlier in our laboratory was used, although there may be some question concerning the magnitude of this number in view of the EPR investigations of Al'tshuler et al.[21] Also, the geometry of the more tightly bound unit of $[Cu(KTS)]_\infty$ was used to obtain φ/r_0 for the compound, since this unit may be expected to dominate exchange coupling in the range of Blumberg and Peisach's measurements.

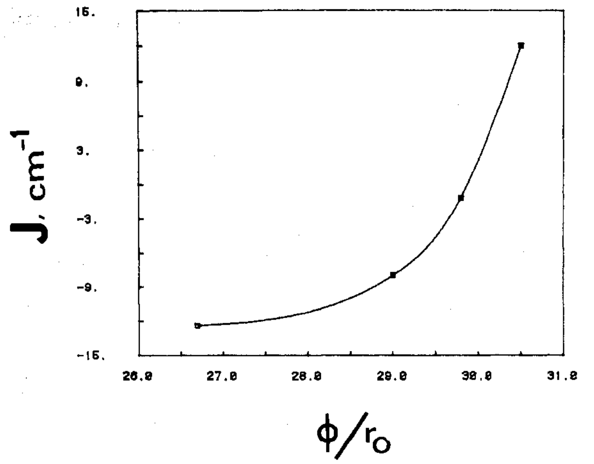

Figure 2. Plot of J vs. φ/r_0, where φ is the $Cu–S_b–Cu$ bridging angle in a series of sulfur-bridged copper compounds and r_0 is the long out-of-plane bond distance.

The observation of the relationship between the exchange parameter and φ/r_0 has stimulated additional research in our laboratory on other systems which exhibit the two variables φ and r_0. A similar relationship exists for a series of di-μ-chloro-bridged parallel planar copper(II) dimers with the ligands dimethylglyoxime,[29,30] *N,N,N′,N′*-tetramethylethylenediamine,[31] *N,N*-dimethylethylenediamine,[32,33] 2-methylpyridine,[34,35] and tetramethylene sulfoxide.[36] In these latter compounds the angles at the chloride bridge range from 86° in $[Cu(\mu\text{-}Me_2en)Cl_2]_2$[33] to 100° in $[Cu(\alpha\text{-pic})_2Cl_2]_2$,[34] the long, out-of-plane bonds range from 2.70 Å in $[Cu(dmg)_2Cl_2]_2$[29] to 3.37 Å in $[Cu(\alpha\text{-pic})_2Cl_2]_2$,[34] and the singlet–triplet splittings range from -16 cm^{-1} in [Cu-

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$(TMSO)_2Cl_2]_2$[36] to +6.3 cm^{-1} in $[Cu(dmg)Cl_2]_2$.[30] The relationship between J and φ/r_0 is essentially linear for the chloride-bridged dimers, but the range of J and φ/r_0 is more limited than that of the sulfur-bridged compounds and curvature is anticipated.

Since the angle at the bridge determines the sign of the exchange-coupling constant, we may expect that the line in Figure 2 will reach a maximum value at some larger value of φ/r_0 and then begin to decrease with an increase in φ/r_0. There are data which support this view. The compounds Cu(dimethyl sulfoxide)$_2Cl_2$,[37,38] $Cu(H_2O)(caffeine)Cl_2$,[39,40] Cu(imidazole)$_2Cl_2$,[40],[42] and Cu[2-(2-(methylamino)ethyl)pyridine]-Cl_2[32,40,42] have single-chloride-bridged chain structures with angles which range from 113° in Cu(MAEP)Cl_2[43] to 144° in $Cu(Me_2SO)_2Cl_2$.[37] Except for Cu(imidazole)$_2Cl_2$, which undergoes long-range ordering below 7.7 K,[40] the exchange-coupling constant decreases (from +1.48 cm^{-1} for Cu(MAEP)Cl_2[32,40] to −6.1 cm^{-1} for $Cu(Me_2SO)_2Cl_2$[38]) as φ/r_0 increases. Should examples of copper complexes with larger angles be found, it is likely that the exchange coupling constants will be negative.

The results of this study have shown that sulfur donor bridges between copper ions in dimers and chains transmit superexchange interaction and that these interactions are large even though long bonds are involved in the bridged units. In addition it appears that the angle at the bridge and the length of the bridge bonds determine the nature of the exchange coupling in a systematic way.

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Registry No. $[Cu(dmtc)_2]_\infty$, 54469-32-8.

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Contribution from the Laboratoire de Cristallochimie,[1]
Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France

Molybdenum–Porphyrin Derivatives: Synthesis and X-ray Crystal Structure of Bis(phenyldiazo)(*meso*-tetra-*p*-tolylporphyrinato)molybdenum(IV) Phenylhydrazine Solvate, $Mo(N_2C_6H_5)_2(TTP)\cdot C_6H_5NHNH_2$

JOCELYNE COLIN, GRAHAM BUTLER, and RAYMOND WEISS*

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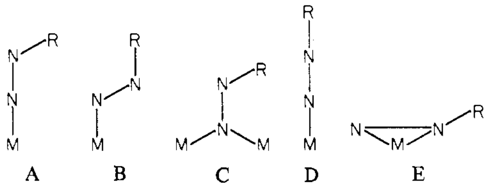
Reaction of phenylhydrazine with the dichloromolydbenum(IV) porphyrin complex $MoCl_2(TTP)$ leads to the corresponding diazomolybdenum complex $Mo(N_2C_6H_5)_2(TTP)$ (TTP is the dianion of the *meso*-tetratolylporphyrin). The molecular structure of this complex has been determined by X-ray diffraction techniques. The molybdenum is hexacoordinated with the diazo ligands in trans position with respect to the porphyrin plane. The complex is located on a crystallographic inversion center and thus presents C_i molecular symmetry. The geometry of the aryldiazo group is intermediate between singly and doubly bent. Some relevant metrical parameters are Mo–N(diazo) = 2.060 (5) Å, N–N = 1.133 (9) Å, N–C = 1.448 (12) Å, M–N–N = 149.1 (9)°, and N–N–C = 128.6 (9)°. $Mo(N_2C_6H_5)_2(TTP)$ crystallizes in space group $C2/c$ with a = 26.734 (20) Å, b = 13.842 (9) Å, c = 17.883 (11) Å, β = 124.71 (9)°, and Z = 4. The structure determination and refinement were based on 2222 reflections with $I > 3\sigma(I)$. Final values of R and R_w are 0.078 and 0.098, respectively.

Introduction

Aryldiazo ligands may represent models for intermediates in chemical reduction of dinitrogen to ammonia or hydrazine.[2] They can adopt various coordination geometries: A–E.



In the bonding modes A–C the aryldiazo ligand (obtained from diazonium salts[3,13] or aromatic hydrazines[4]) behaves as the isoelectronic nitrosyl group. Nitrosyl and aryldiazo ligands have been compared structurally in almost identical coordination environments.[5] The bonding modes D[6] and E[7] were obtained with neutral RN_2 species. Recently, we reported the synthesis and structural study of a nitrosylmolybdenum por-

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