to Ru(II). As expected, irradiation of the coated semiconductor in the presence of added hydroquinone (~0.1 M) to the electrolyte solution resulted in an increase in the observed photocurrents in this case by a factor of 4. Under these conditions, i_{photo} was stable for a period of at least 20 min of photolysis.

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Registry No. TMPD, 27215-51-6; TMBD, 366-29-0; PTZ, 92-84-2; $[Ru(NH_3)_6]Cl_3$, 14282-91-8; TiO_2, 13463-67-7; TEAP, 2567-83-1.

Synthesis, Molecular Structure, and Exchange Coupling in the Alternatingly Bridged and Alternatingly Spaced Linear-Chain Compound *catena*-Dichloro(3,6-dithiaoctane)copper(II)

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Abstract: The crystal and molecular structure of the compound dichloro(3,6-dithiaoctane)copper(II), $Cu(C_2H_5SC_2H_4SC_2H_5)Cl_2$, has been determined from single-crystal, three-dimensional X-ray diffraction counter data. The compound crystallizes as dark green needles in space group $P\bar{1}$ with $Z = 2$ and having unit cell dimensions $a = 7.832$ (4) Å, $b = 7.929$ (5) Å, $c = 9.803$ (6) Å, $\alpha = 69.71$ (4)°, $\beta = 71.36$ (4)°, and $\gamma = 77.84$ (4)°. The observed and calculated densities are 1.71 (298 K) and 1.76 (140 K) g cm^{-3}, respectively. The structure was refined by full-matrix least-squares techniques to a conventional R value of 0.048. Formula units of the compound stack along the a axis to form an alternatingly spaced chain in which the copper(II) ions are six-coordinate. Two chloride ligands and two sulfur atoms from the bidentate thioether constitute the equatorial plane with a sulfur atom and a chloride ion from adjacent monomeric units loosely bound in the two axial positions. Copper–chloride bond distances are 2.264 (1) and 2.230 (1) Å within the equatorial plane, and the copper–chloride interatomic distance to the axial chloride is 3.234 (1) Å. Equatorial copper–sulfur bond distances are 2.311 (1) and 2.327 (1) Å. The copper–copper distance in the Cu_2Cl_2 planar unit is 4.406 (1) Å, and the Cu–Cl–Cu′ bridging bond angle is 93.1 (1)°. The copper–sulfur interatomic distances that propagate the chain are 3.361 (2) Å, the copper–copper separation in the planar Cu_2S_2 portion of the chain is 4.679 (1) Å, and the Cu–S″–Cu″ bridging bond angle is 109.3 (1)°. The magnetic susceptibility of this unique chain exhibits a maximum at 4.2 K that is indicative of an antiferromagnetic intrachain exchange coupling interaction between the alternatingly spaced and alternatingly ligand-bridged copper(II) ions. The best fit of the magnetic susceptibility data by alternating chain theory for $S = {}^1/_2$ ions yields values for the exchange coupling constant and the alternation parameter of -2.73 cm^{-1} and 0.69, respectively, using the EPR g value of 2.084.

Although organic compounds with alternatingly spaced linear-chain structures have been known and studied extensively for many years,[1] exchange-coupled transition-metal compounds with analogous structures and comparable magnetic properties have received much less attention. The most thoroughly studied transition-metal compound which exhibits alternating Heisenberg antiferromagnetic behavior is $Cu(NO_3)_2 \cdot 2.5H_2O$,[2] and it is important to note that the compound has a ladder-like structure at room temperature.[3] Other examples of compounds that are known to have alternating chain structures include the pyrazine-bridged binuclear copper acetate chain, $[Cu_2(OAc)_4pyr]_n$,[4] and the carcinostatic and carcinolytic agent [3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazonato)]copper(II), Cu-KTS.[5,6] On the basis of their magnetic properties the following compounds have been suggested to have alternatingly spaced linear-chain structures at low temperatures: the form of tetrathiafulvalenium bis[*cis*-(1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato)]cuprate(II), which results from a spin Peierls transition at 12 K,[7] *catena*-bis(μ-bromo)bis(N-methylimidazole)copper(II),[8] and *catena*-bis(μ-chloro)bis(4-methylpyridine)copper(II).[9,10] These latter three compounds have uniformly spaced linear-chain structures at room temperature.[11-13]

We have found that *catena*-dichloro(3,6-dithiaoctane)copper(II), $Cu(3,6\text{-}DTO)Cl_2$, has an alternatingly spaced structure at 140 K and exhibits magnetic properties that may be explained by Heisenberg alternating chain exchange theory. The results of our studies are reported in this article.

Experimental Section

Preparation and Characterization of *catena*-Dichloro(3,6-dithiaoctane)copper(II). A solution of $CuCl_2$ in methanol was prepared by dissolving 0.755 g of $CuCl_2$ in 250 mL of methanol (0.0224 M). A solution of the dithioether was prepared by dissolving 2.25 g of 3,6-dithiaoctane (K & K Laboratories, Inc., Hollywood, CA) in 250 mL of

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Table I. Crystal Data and Data Collection Summary for $Cu(C_2H_5SC_2H_4SC_2H_5)Cl_2$

formula wt	284.75
space group	$P\bar{1}$
cell dimens, 140 K	
a, Å	7.832 (4)
b, Å	7.929 (5)
c, Å	9.803 (6)
α, deg	69.71 (4)
β, deg	71.36 (4)
γ, deg	77.84 (4)
V, Å^3	537.7
Z	2
density, g cm^{-3}	1.76 (calcd) (140 K) 1.71 (exptl) (298 K)
cryst dimens, mm	0.25 × 0.30 × 0.45
radiation	Mo Kα (λ = 0.71069 Å)
μ, cm^{-1}	29.0
absorption corr factors	3.2–4.1
2θ max, deg	45
scan type	ω
scan speed, deg min^{-1}	3–60
scan range, deg	1
bkgd counting, deg offst	stationary, 1
unique data measd	1401
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	1380
final no. of parameters	45
R	0.048
R_w	0.048

Table II. Atomic Positional and Isotropic Thermal Parameters for $Cu(C_2H_5SC_2H_4SC_2H_5)Cl_2$

atom	x	y	z	B, Å^2
Cu	0.19628 (7)	−0.05478 (7)	0.10725 (6)	1.02 (3)
Cl(1)	0.1721 (1)	−0.3123 (1)	0.2972 (1)	1.36 (4)
Cl(2)	0.1973 (1)	−0.1595 (1)	−0.0805 (1)	1.35 (4)
S(1)	0.1118 (1)	0.1062 (1)	0.2794 (1)	1.13 (4)
S(2)	0.3576 (1)	0.1797 (1)	−0.0696 (1)	1.05 (4)
C(1)	0.2929 (8)	0.1741 (8)	0.4530 (7)	1.68 (9)
C(2)	0.2974 (6)	0.0438 (7)	0.3675 (6)	1.31 (9)
C(3)	0.1546 (6)	0.3315 (6)	0.1536 (5)	1.18 (8)
C(4)	0.3343 (7)	0.3337 (6)	0.0358 (6)	1.33 (9)
C(5)	0.2222 (7)	0.3034 (7)	−0.1997 (6)	1.31 (9)
C(6)	0.3044 (8)	0.4686 (8)	−0.3169 (7)	2.2 (1)

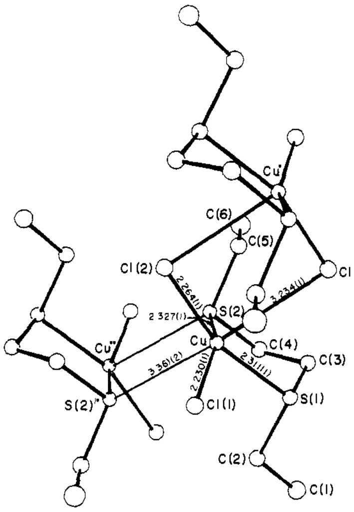

Figure 1. View of a fragment of the alternating chain structure of *catena*-dichloro(3,6-dithiaoctane)copper(II) that illustrates the tetragonal coordination of the copper(II) ion and acute Cu′⋯Cu⋯Cu″ angle.

methanol (0.0559 M). A 100-mL portion of the 3,6-dithiaoctane solution was added to a 100-mL portion of the $CuCl_2$ solution. A dark lime green solution was produced, and dark green needles started forming after an hour. The solution was allowed to evaporate overnight, and the residue was recrystallized from hot methanol, giving 0.75 g of product (77% yield). All materials used in the synthesis were reagent grade. Elemental composition of the product [Cu(3,6-dithiaoctane)Cl_2] was verified by elemental analyses. Anal. Calcd for $C_6H_{14}S_2CuCl_2$: C, 25.31; H, 4.96. Found: C, 25.26; H, 4.88.

The visible spectrum of a Nujol mull was recorded on a Hewlett-Packard 8450A spectrophotometer. The following bands were observed: 800 (sh), 445 (m), 376 (s), and 205 (sh) nm.

X-ray Data Collection. Dark green, irregular-shaped crystals of $Cu(C_2H_5SC_2H_4SC_2H_5)Cl_2$ were isolated from a cooled methanol solution of the compound. A crystal cut to dimensions 0.25 × 0.30 × 0.45 mm was selected for X-ray data collection and mounted on a Syntex $P2_1$ diffractometer with its long axis parallel to ϕ. The temperature of the crystal was maintained at 140 K with a modified LT-1 low-temperature apparatus. With a combination of rotation and axial photographs and an automatic indexing routine, the lattice was assigned as triclinic P. A typical reflection had width at half-height on an ω scan of 0.28°. Final cell dimensions were obtained from a least-squares fit of 24 reflections, including Friedel pairs, in the range $30° < 2\theta < 40°$. Three check reflections were monitored during data collection and fluctuated an average of 1.3%. Crystal data and a summary of the data collection are given in Table I. Intensity data were corrected for Lorentz and polarization effects but not for absorption. Reduction of the data to F_o and $\sigma(F_o)$ were as previously described.[14]

Solution and Refinement of the Structure. The positions of the copper, two chlorine, and two sulfur atoms were determined from a sharpened Patterson map. These five atoms were refined to R of 0.243 by full-matrix least-squares methods, assuming the space group to be $P\bar{1}$. The quantity minimized during refinement was $\sum w(F_o - F_c)^2$, where $w = 1/\sigma^2(F_o)$. The remaining non-hydrogen atoms were located on a Fourier map. Full-matrix least-squares refinement of these 11 atoms using isotropic thermal parameters converged to $R = 0.059$.[15,16] The methyl hydrogen atoms were located on a difference Fourier map, and the methylene hydrogen atoms were given calculated positions. These hydrogen atoms were included in the structure factor calculation in the last two cycles of refinement with $B_{iso} = 1.5$ Å^2. The final R value of 0.048 is computed from 1380 reflections and 45 least-squares parameters. The mean shift/maximum esd in the final cycle of refinement was 0.04. A final difference map was featureless except for a few spurious peaks close to the heavy atoms. Successful refinement of the structure confirms the initial choice of space group as $P\bar{1}$.

Positional and thermal parameters for the non-hydrogen atoms are given in Table II. Tables of hydrogen data and structure factors are available as supplementary material.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of Cu(3,6-DTO)$_2$Cl$_2$ using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM), which was operated from zero field to 10 kOe with procedures that have been described previously.[17] The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li).

The VSM magnetometer was calibrated with $HgCo(NCS)_4$.[18] Powdered samples of the compound and calibrants used in this study were contained in precision-milled Lucite sample holders. Approximately 150 mg of each were used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[19–21]

Electron Paramagnetic Resonance. EPR spectra were obtained with a Varian E-109 spectrometer operating at X band (ca. 9.5 GHz). The magnetic field of the E-109 spectrometer was calibrated by using an NMR gaussmeter (Magnion Model G-502) and a Hewlett-Packard precision frequency counter (Model 5340A). In addition, the klystron frequency was measured directly with the frequency counter. The

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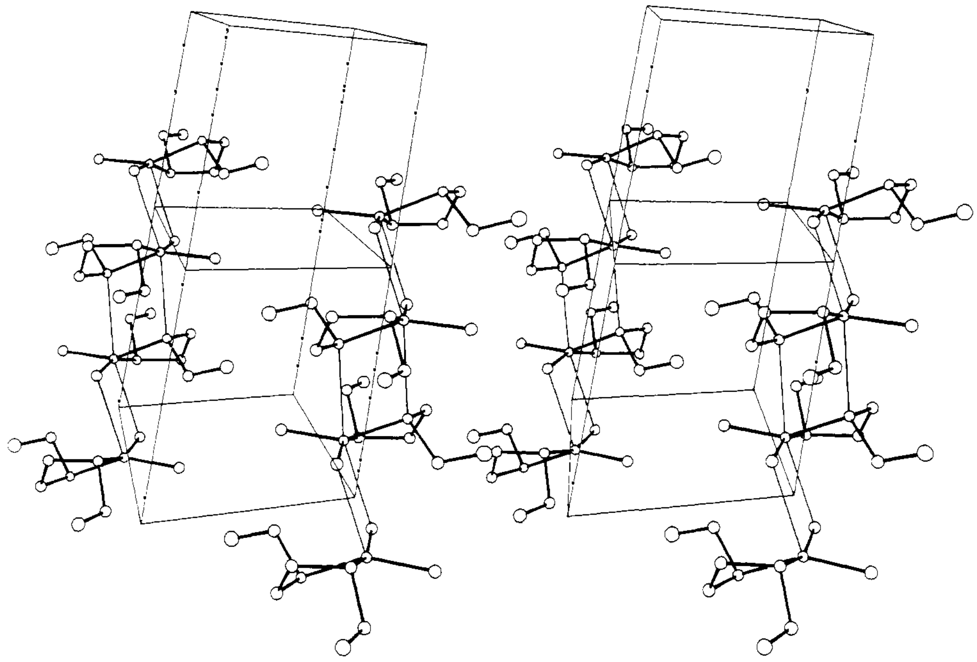

Figure 2. Stereoview of the structure of *catena*-dichloro(3,6-dithiaoctane)copper(II) that shows the alternating chloride and sulfur bridges.

Table III. Bond Distances (Å) and Angles (Deg) for $Cu(C_2H_5SC_2H_4SC_2H_5)Cl_2$

Cu–Cl(1)	2.230 (1)	Cl(1)–Cu–Cl(2)	99.4 (1)
Cu–Cl(2)	2.264 (1)	Cl(1)–Cu–S(1)	89.7 (1)
Cu–S(1)	2.311 (1)	Cl(1)–Cu–S(2)	152.4 (1)
Cu–S(2)	2.327 (1)	Cl(1)–Cu–Cl(2)'	111.6 (1)
C(1)–C(2)	1.528 (8)	Cl(1)–Cu–S(2)"	82.8 (1)
C(2)–S(1)	1.818 (6)	Cl(2)–Cu–S(1)	161.5 (1)
S(1)–C(3)	1.813 (5)	Cl(2)–Cu–S(2)	90.0 (1)
C(3)–C(4)	1.507 (7)	Cl(2)–Cu–Cl(2)'	86.9 (1)
C(4)–S(2)	1.803 (5)	Cl(2)–Cu–S(2)"	93.0 (1)
S(2)–C(5)	1.809 (6)	S(1)–Cu–S(2)	89.4 (1)
C(5)–C(6)	1.513 (8)	S(1)–Cu–Cl(2)'	74.7 (1)
Cu···Cl(2)'	3.234 (1)	S(1)–Cu–S(2)"	104.2 (1)
Cu···S(2)"	3.361 (2)	S(2)–Cu–Cl(2)'	94.8 (1)
Cu···Cu'	4.046 (1)	S(2)–Cu–S(2)"	70.7 (1)
Cu···Cu"	4.679 (1)	Cl(2)'–Cu–S(2)"	165.4 (1)
		C(1)–C(2)–S(1)	111.7 (4)
Cu–S(1)–C(2)	104.0 (2)	C(2)–S(1)–C(3)	102.0 (2)
Cu–S(1)–C(3)	100.4 (2)	S(1)–C(3)–C(4)	112.7 (4)
Cu–S(2)–C(4)	103.1 (2)	C(3)–C(4)–S(2)	112.0 (4)
Cu–S(2)–C(5)	106.6 (2)	C(4)–S(2)–C(5)	102.4 (3)
		S(2)–C(5)–C(6)	112.9 (4)

free-radical DPPH ($g = 2.0036$) was used as a field marker in all cases. Spectra were recorded with finely ground powders enclosed in commercially available quartz sample tubes. Data were collected at room temperature or at liquid nitrogen temperature (77 K), using an insertion Dewar made by Varian.

Results

Description of the Structure. As shown in Figure 1, formula units of the compound are catenated in two directions to neighboring units, forming a chain comprised of alternating sulfur and chlorine bridges. The donor group for copper in one formula unit consists of two chloride ions and a bidentate dithioether ligand. The five atoms CuS_2Cl_2 form a tetrahedrally distorted equatorial unit with the following deviations from the least-squares plane: Cu, −0.09 Å; S(2), +0.45 Å; Cl(1), +0.43 Å; S(1), −0.45 Å; and Cl(2), −0.43 Å. Bond angles for these atoms also reflect this distortion (Table III). The most severe departures from square-planar angles are the Cl(1)–Cu–S(2) angle of 152.4(1)° and the Cl(1)–Cu–Cl(2) angle of 99.4 (1)°. When the interatomic contacts to neighboring formula units are considered, the geometry about copper is distorted tetragonal. By inversion ($-x$, $-y$, $-z$) of the atomic positions, the primed formula unit is obtained, producing a relatively long Cu–Cl(2)' axial contact of 3.234 (1) Å. Translation along a of the inverted group ($1 - x$, $-y$, $-z$) generates the doubly primed unit and the long Cu–S(2)" axial contact of 3.361 (2) Å. This pattern is repeated to form an alternatingly ligand-bridged and alternatingly spaced chain along a. A stereoview of the packing is shown in Figure 2. The copper–copper distance in the Cu_2Cl_2 planar unit is 4.406 (1) Å, and the Cu–Cl(2)'–Cu' bridging angle is 93.1 (1)°. In the Cu_2S_2 planar unit the copper–copper separation is 4.679 (1) Å, and the Cu–S(2)"–Cu" bridging angle is 109.3 (1)°. The copper atoms zigzag down the chain with a fairly acute Cu'–Cu–Cu" angle of 127.6 (1)°. Nonbonded interactions between chains are principally H···H and H···C. The only non-hydrogen interchain separation less than 4 Å is a distance of 3.994 (2) Å between S(1) and S(1)‴ at ($-x$, $-y$, $1 - z$).

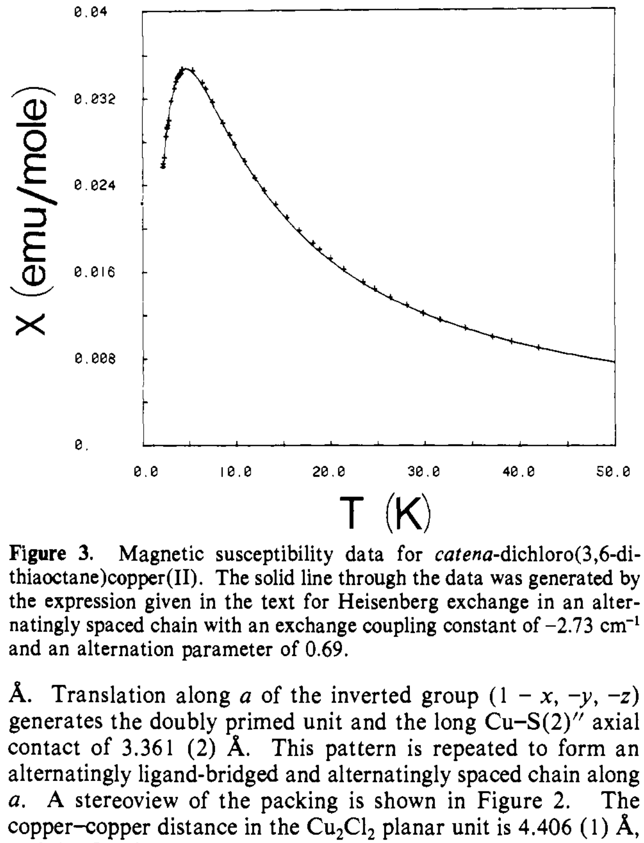

Figure 3. Magnetic susceptibility data for *catena*-dichloro(3,6-dithiaoctane)copper(II). The solid line through the data was generated by the expression given in the text for Heisenberg exchange in an alternatingly spaced chain with an exchange coupling constant of −2.73 cm^{-1} and an alternation parameter of 0.69.

Magnetic Properties. The magnetic susceptibility data displayed in Figure 3 were collected on two different samples, with one data set being collected in the temperature range 4.2–42 K and the second set in the range 2.2–4.2 K. It may be seen that the magnetic susceptibility data exhibit a maximum near 4.2 K that is indicative of an antiferromagnetic interaction. Neither the Van Vleck equation[22] for an exchange-coupled pair of $S = {}^1/_2$ ions (eq 1) nor the Bonner–Fisher results for a uniformly spaced antiferromagnetic Heisenberg linear chain (eq 2)[23-25] where $x = -kT/J$ would explain the temperature dependence of the magnetic susceptibility data with valid parameters.

$$\chi_M = [g^2N\mu_B^2/3k(T-\theta)][1 + {}^1\!/_3 \exp(-2J/kT)]^{-1} \quad (1)$$

$$\chi_M = [Ng^2\mu_B^2/kT][0.25 + 0.14995x + 0.030094x^2] \times [1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3]^{-1} \quad (2)$$

The θ term in eq 1 was included to account for interactions beyond the pairwise cluster limit, and interchain interactions were accounted for in eq 2 by inclusion of a molecular field correction term:

$$\chi^{\mathrm{corr}} = \chi_H/(1 - 2zJ'\chi_H/Ng^2\mu_B^2)$$

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. The function that was minimized in curve fitting using the Simplex[26-28] nonlinear fitting routine was

$$F = \textstyle\sum_i w_i(\chi_i^{\mathrm{obsd}} - \chi_i^{\mathrm{calcd}})^2$$

with the weights being assigned $w_i = (\chi_i^{\mathrm{obsd}})^{-1}$. The best fit of eq 1 to the data yielded $J = -3.55$ cm^{-1} and $\theta = -2.96°$ while the best fit of the linear-chain model yielded $J = -2.86$ cm^{-1} and $zJ' = 2.51$ cm^{-1}. Neither of these fits is acceptable since the correction term in each case is nearly equal to the primary interaction parameter. The EPR-determined g value of 2.084 was held constant during all fitting calculations. However, as discussed in detail in the next section, Heisenberg alternating chain theory, as expected in view of the structure of the compound, provides an accurate description of the temperature dependence of the magnetic susceptibility.

Alternating Heisenberg Chain. The Hamiltonian for the Heisenberg alternating linear chain is

$$\mathcal{H} = -2J\textstyle\sum[S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1}]$$

where the summation runs from $i = 1$ to $n/2$, J is the exchange integral between a spin and one of its nearest neighbors, and αJ is the exchange integral between the same spin and the other nearest neighbor in the chain. The model of immediate interest is for antiferromagnetic exchange ($J < 0$) and for $0 < \alpha < 1$. At the extremes, when $\alpha = 0$, the model reduces to the dimer model with pairwise interactions, and when $\alpha = 1$, the model reduces to the uniform linear-chain model. This problem has been studied in detail by Duffy, and Barr,[29] Friedberg and co-workers,[30,31] Diederix et al.,[2] and more recently by Bonner et al.[32] and Hatfield and co-workers.[10,24,25,33]

The reduced magnetic susceptibilities of short alternating rings of 10 $S = {}^1/_2$ spins for α = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 have been recalculated with by use of the cluster approach,[10] and the results were used to generate the following expression for magnetic susceptibility in terms of the exchange integral and the alternation parameter:

$$\chi_M = (Ng^2\mu_B^2/kT)[A + Bx + Cx^2][1 + Dx + Ex^2 + Fx^3]^{-1}$$

where $x = -J/kT$ and the constants A–F are power series in terms of α.[10] The expression, which is valid for $kT/J > 0.5$ and for negative J values, reproduces the calculated magnetic susceptibilities of the 10-membered rings for the various values of the alternation parameter much better than 1% in moderate magnetic fields. The results for the 10-membered rings are good approximations for infinite systems.[29] The exchange coupling constant and the alternation parameter for the new alternatingly spaced linear-chain compound *catena*-dichloro(3,6-dithiaoctane)copper(II) were obtained by fitting the expression for magnetic susceptibility given above to the experimental data. The best fit obtained from the Simplex nonlinear fitting routine and criteria given above yielded $J = -2.73$ cm^{-1} and $\alpha = 0.69$. In the best fit calculations, the g value was held constant at 2.084, the value determined from EPR measurements.

Table IV. Magnetic Parameters for Alternating Chain Compounds

compd	J, cm^{-1}	α	g
Cu(3,6-DTO)$_2$Cl$_2$	−2.73	0.69	2.084[a]
Cu(*N*-MeImid)$_2$Br$_2$	−7.2	0.40	2.14[b]
Cu(4-Mepy)$_2$Cl$_2$	−9.6	0.67	2.17[c]

[a] This work. [b] References 8 and 10. [c] References 9 and 10.

Discussion

Structure of Cu(3,6-DTO)$_2$Cl$_2$. The crystal structure of Cu($C_2H_5SC_2H_4SC_2H_5$)Cl$_2$ bears comparison to the reported structure of [Cu($C_4H_9SC_2H_4SC_4H_9$)Cl$_2$]$_2$.[34] Superficially, the two complexes differ only in the presence of terminal butyl groups instead of ethyl groups on the dithioether ligand. However, the two complexes differ in the solid state in several important respects. In the butyl analogue the complex is best described as discrete centrosymmetric chloro-bridged dimers with distorted square-pyramidal geometry for copper. This difference is a consequence of the shorter bridging chlorine distance [2.825 (2) Å in the butyl analogue vs. 3.234 (1) Å in the ethyl analogue] and the much longer distance to the nearest dimer neighbor. For example, the analogous Cu–S(2)″ and Cu–S(1)″ distances are 5.694 (4) and 5.536 (4) Å, respectively. It is tempting to ascribe this greater separation between the chloro-bridged dimers to the bulkiness of the alkyl group on sulfur, but the structure of [Cu($CH_3SC_2H_4SCH_3$)Cl$_2$]$_2$ is actually more like that of the butyl analogue than the ethyl.[35] We tentatively conclude that the alternate chlorine and sulfur bridges in Cu($C_2H_5SC_2H_4SC_2H_5$)Cl$_2$ is a fortuitous result of the most favorable crystal packing for this derivative. For the sulfur bridges to form, Cu″ is shifted away from the line of Cu–Cu′ (the two copper atoms bridged by chlorine), resulting in a Cu′–Cu–Cu″ angle of 127.6°. The corresponding angle in the structure with discrete dimers is 170.9°.[34]

Although the axial atoms, Cl(2)′ and S(2)″, are approximately 0.5 Å more distant from copper than commonly seen in typical tetragonal copper(II) complexes,[36] there is little doubt, especially in view of the magnetic superexchange interaction, that they are stereochemically active. Some of the crystallographic evidence for this long-range interaction can be seen in the directional preference of these two atoms with respect to the CuS$_2$Cl$_2$ equatorial plane. For example, the angle between the Cu···Cl(2)′ and Cu···S(2)″ lines and the least-squares plane of CuS$_2$Cl$_2$ is 79.6° and 82.1°, respectively. In addition, the equatorial plane is less distorted than in the butyl analogue with square-pyramidal geometry. This is apparent in $\sum(\mathrm{dev})^2$ for the atoms in the CuS$_2$Cl$_2$

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least-squares plane: A value of 0.79 Å^2 is obtained for the title compound compared to 1.30 Å^2 for the butyl derivative.

Magnetic Studies. There are no structurally and magnetically characterized precedents of alternating chain transition-metal compounds to guide the analysis of the magnetic studies. However, the failure of both the exchange-coupled pair model and Bonner–Fisher[23–25] results for a uniformly spaced Heisenberg chain to account for the magnetic susceptibility data for Cu(3,6-DTO)$_2$Cl$_2$ can be understood in terms of the structural results reported here. As shown in Table IV, the magnetic parameters that result from the analysis of the data with alternatingly spaced Heisenberg chain theory compare favorably with earlier analysis of data for Cu(4-methylpyridine)$_2$Cl$_2$[9,10] and Cu(*N*-methylimidazole)$_2$Br$_2$.[8,10] Although these latter two compounds have uniform chain structures at room temperature, alternating chain theory is required for precise descriptions of low-temperature magnetic data. Evidence for structural phase transitions in both compounds, presumably to alternatingly spaced chain structures, has been presented.[10]

There is now a considerable body of data for stacked, ligand-bridged copper(II) dimers and chains that reveals that the exchange coupling constant is a function of the angle at the ligand bridge and the length of the superexchange pathway.[37] Relatively smooth correlations of J with the quotient ϕ/R_0 exist for chloro- and sulfur-bridged copper complexes. Here ϕ is the angle at the bridging ligand and R_0 is the long, out-of-plane Cu–X interatomic contact which connects the stacked, planar units into dimers or extended chains.

The ϕ/R_0 parameters for the exchange-coupled Cu$_2$Cl$_2$ and Cu$_2$S$_2$ units are 28.8 and 32.5 deg/Å, respectively. On the basis of correlations that are being developed, these values of ϕ/R_0 suggest that antiferromagnetic interactions should occur in both exchange-coupled units. However, the correlation is tentative, and it is not possible to estimate the magnitude of the exchange coupling constants from structural data alone.

There is an additional structural variation in Cu(3,6-DTO)$_2$Cl$_2$ that may be expected to have an effect on the exchange-coupling process. As shown in Figures 1 and 2, the Cu$_2$Cl$_2$ and Cu$_2$S$_2$ units lie in mutually perpendicular planes. Current models for superexchange focus attention on relative orientations of exchange-coupled units, and the influence of the angle between planes on the alternating exchange coupling will be of interest. For example, the Cu$_2$Cl$_2$ exchange-coupled units are coplanar in typical chains such as Cu(py)$_2$Cl$_2$.[38] Additional data on other compounds with this structural feature must be collected so that this effect can be understood.

The out-of-plane Cu···Cl(2)′ and Cu···S(2)″ interatomic separations are relatively long. The longest comparable copper–chloride interatomic separation in an exchange-coupled chain that has been reported is 3.21 Å in Cu(4-Etpy)$_2$Cl$_2$,[39] while the longest distance in a dimeric chloride-bridged molecule is 3.37 Å in [Cu(2-Mepy)$_2$Cl$_2$]$_2$.[40] The longest Cu···S out-of-plane interaction known is in an exchange-coupled copper–sulfur system, 3.310 Å in the dimeric molecule [Cu(H$^+$-TCH)Cl$_2$]$_2$Cl$_2$ (H$^+$-TCH is 1*H*-thiocarbonohydrazidium).[41] It is clear from these data that sulfur and chlorine ligand bridges are very effective in transmitting superexchange interactions even when the interatomic separations are large.

DeJongh and Miedema contend that a search for new magnetic model systems can be justified only if additional experimental work can be expected to mutually stimulate theory and experiment.[42] This present system is an example of such justifiable work. Systematic studies on analogous compounds may be expected to lead to an understanding of factors which affect exchange coupling in alternatingly spaced linear-chain compounds.

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Supplementary Material Available: Tables of hydrogen coordinates and observed and calculated structure factors for Cu(C$_2$H$_5$C$_2$H$_4$SC$_2$H$_5$)Cl$_2$ (10 pages). Ordering information can be found on any current masthead page.

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A Kinetic Study of the Reactions of Carbonyl Ylides Formed by the Addition of Fluorenylidene to Ketones[1]

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Abstract: Fluorenylidene adds to aliphatic ketones to give carbonyl ylide intermediates. With acetone, for example, laser flash photolysis experiments showed that the rate constant for this reaction was 1 × 10^7 M^{-1} s^{-1} in acetonitrile solvent. The resulting carbonyl ylide had an absorption spectrum with $\lambda_{\max}$ = 640 nm and in the absence of quenchers underwent ring closure to the corresponding oxirane. The lifetimes, τ_y, for the ring closure reaction are described by the equation $-\log(\tau_y/\mathrm{s}) = (13.26 \pm 0.11) - (10.96 \pm 0.12)/\theta$ where $\theta = 2.3RT$ kcal mol^{-1}. The spectra of the carbonyl ylides could be quenched with rate constants of ca. 10^7 M^{-1} s^{-1} by electron-deficient olefins or oxygen.

The chemistry of carbonyl ylides has been the subject of extensive research for two decades.[2] The reactions[2,3] and lifetimes[2,6–8] of such ylides depend strongly upon the nature of their substituents. Carbonyl ylides can be formed by thermolysis or

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