48175-68-4; BMe_3Bz, 99922-38-0; $BMe_3Bz(ClO_4)_2$, 99922-39-1; C, 18444-42-3; CMe_2, 100017-84-3; CMe_3, 99922-40-4; CMe_4, 57427-08-4; D, 72984-97-5; *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2{\cdot}2H_2O$, 100017-83-2; *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2$, 100017-81-0; $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$, 59461-42-6; $[Ni(C_{14}H_{32}N_4)]I_2$, 100017-82-1; $[Ni(C_{14}H_{32}N_4)](ClO_4)_2$, 41296-56-4; 1-benzyl-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane, 99922-43-7; 1-benzyl-4-methyl-1,4,8,11-tetraazacyclotetradecane, 99922-42-6; 5-benzyl-8-methyl-1,5,8,12-tetraazadodecane, 99922-41-5; *N*-benzyl-*N'*-methylethylenediamine, 56904-09-7; acrylonitrile, 107-13-1; trifluoromethanesulfonate, 37181-39-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and structure factors for *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2{\cdot}2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$ (20 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514, and University of California at Davis, Davis, California 95616

Magnetic Properties and Structural Characterizations of Dichloro(2,5-dithiahexane)copper(II) and Dichloro(4,7-dithiadecane)copper(II): Observation of Heisenberg Alternating-Chain Magnetism

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Received April 8, 1985

The syntheses, crystal and molecular structure determinations, and magnetic properties of the compounds dichloro(2,5-dithiahexane)copper(II), $[Cu(C_4H_{10}S_2)Cl_2]$, and dichloro(4,7-dithiadecane)copper(II), $[Cu(C_8H_{14}S_2)Cl_2]$, are reported. $[Cu(C_4H_{10}S_2)Cl_2]$ crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions $a = 6.875$ (2) Å, $b = 8.963$ (2) Å, $c = 14.513$ (4) Å, and $\beta = 90.48$ (2)° at 293 K. $[Cu(C_8H_{14}S_2)Cl_2]$ crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 9.592$ (2) Å, $b = 17.193$ (4) Å, $c = 7.813$ (2) Å, and $\beta = 101.03$ (2)° at 140 K. The structures were solved by direct methods to final $R_w = 0.038$ based on 1075 independent data with $I > 3\sigma(I)$ for $[Cu(C_4H_{10}S_2)Cl_2]$ and $R_w = 0.035$ based on 1604 independent data with $I > 3\sigma(I)$ for $[Cu(C_8H_{14}S_2)Cl_2]$. The structures of both compounds consist of parallel-planar dimers of $[Cu(RSC_2H_4SR)Cl_2]$ units, which are arranged in alternatingly bridged chains by long copper(II)-sulfur contacts of greater than 5 Å. The centrosymmetric chloro-bridged dimers are formed by axial coordination to a given copper(II) ion by a chloride ligand in the plane of the adjacent copper(II) ion. The axial bond distances are 3.075 (1) Å for $[Cu(C_4H_{10}S_2)Cl_2]$ and 2.663 (1) Å for $[Cu(C_8H_{14}S_2)Cl_2]$, and the Cu-Cl$\cdots$Cu' angles are 94.3 (1) and 93.8 (1)°, respectively. Magnetic susceptibility data reveal antiferromagnetic interactions that may be described by Heisenberg alternating-chain theory with exchange coupling constants and alternation parameters (J, α) being -10 cm^{-1}, 0.87 and -20.6 cm^{-1}, 0.35 for $[Cu(C_4H_{10}S_2)Cl_2]$ and $[Cu(C_8H_{14}S_2)Cl_2]$, respectively.

Introduction

We have previously reported that *catena*-dichloro(3,6-dithiaoctane)copper(II), Cu(4,6-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.[1] This was an unexpected result in view of the known structure of bis(μ-chloro)bis[chloro(5,8-dithiadodecane)copper(II)],[2] which has been described as being a bis(μ-chloro)-bridged dimer. With an aim toward increasing the number of alternatingly bridged, alternatingly spaced copper(II) chain compounds, we have prepared and characterized two additional compounds with dithiaalkane bidentate ligands, those being Cu(2,5-DTH)Cl_2 (where DTH is 2,5-dithiahexane) and Cu(4,7-DTD)Cl_2 (where DTD is 4,7-dithiadecane). The syntheses, crystal and molecular structures, and results of magnetic studies are discussed in this article.

Table I. Crystal Data

	$[Cu(2,5\text{-}DTH)Cl_2]_2$	$[Cu(4,7\text{-}DTD)Cl_2]_2$
formula	$Cu_2Cl_4S_4C_8H_{20}$	$Cu_2Cl_4S_4C_{16}H_{36}$
fw	513.40	625.61
a, Å	6.875 (2)	9.592 (3)
b, Å	8.963 (2)	17.193 (4)
c, Å	14.513 (4)	7.813 (2)
β, deg	90.48 (2)	101.03 (2)
μ(Mo K$\bar{\alpha}$), cm^{-1}	34.5	24.2
Z	2	2
D_{obsd}(298 K), g cm^{-3}	1.89	1.60
D_{calcd}, g cm^{-3}	1.91 (298 K)	1.64 (140 K)

Experimental Section

Syntheses. All materials were reagent grade. The ligand 2,5-dithiahexane was obtained from Aldrich Chemical Co., Milwaukee, WI.

The ligand 4,7-dithiadecane was prepared by adding 38.27 g (0.50 mol) of $CH_3CH_2CH_2SH$ to 1 L of absolute methanol. Freshly cut sodium (12 g, 0.52 mol) was added with stirring. $ClCH_2CH_2Cl$ (24.74 g, 0.25 mol) was added dropwise to the reaction mixture over 30 min. After the mixture was stirred overnight, the methanol was removed by use of a rotary evaporator. The residue was treated with water and extracted with ether. The combined ether extracts were dried over anhydrous Na_2SO_4 and reduced in volume by use of a rotary evaporator. Distillation yielded 14.97 g (0.0837 mol, 34% yield) of a clear oil, bp 70-72 °C (0.15 torr). ^{1}H NMR ($CDCl_3$, ppm): 1.28 (t, 3, CCH_3), 1.82 (m, 2, CCH_2C), 2.52 (m, 4, $-CH_2SCH_2-$).

[Cu(2,5-DTH)Cl_2]. A solution of 2,5-DTH (0.122 g, 1.00 mmol) in 1.00 mL of anhydrous methanol was added to a solution of $CuCl_2$ (0.134 g, 1.00 mmol) in 10.0 mL of anhydrous methanol. The mixture turned dark olive green immediately, and small dark crystals formed after a few moments. The reaction flask was capped and stored overnight at -5 °C. The product was collected by filtration and air-dried; yield 64.8% (0.166 g) of dark green microcrystals. UV-vis (Nujol mull, nm): 825 (w), 465, 395, 290.

[Cu(4,7-DTD)Cl_2]. Dark green needles of this compound were obtained by following a procedure identical with that above; yield 58.6% (0.184 g). UV-vis (Nujol mull, nm): 815 (2), 452, 385, 290, 210 (sh).

Spectra. Visible spectra were recorded on a Varian Instruments Cary 17 spectrophotometer, NMR spectra were recorded on a Varian Instruments EM360 spectrometer, and EPR spectra were recorded on a Varian Instruments E109 spectrometer.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were collected with the use of a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) operating at an applied field strength of 10 kOe. Temperatures at the sample were measured with a calibrated GaAs diode by observing the voltage on a Fluke 8502A 6.5 place digital multimeter; further details of the apparatus and measure-

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(1) Olmstead, M. M.; Musker, W. K.; ter Haar, L. W.; Hatfield, W. E. *J. Am. Chem. Soc.* **1982**, *104*, 6627.

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Table II. Atomic Coordinates for $[Cu(2,5\text{-}DTH)Cl_2]_2$ ($\times 10^4$)

atom	x	y	z
Cu	4788 (1)	2811 (1)	4885 (1)
Cl(1)	2362 (1)	1854 (1)	5707 (1)
Cl(2)	6224 (1)	4174 (1)	6009 (1)
S(1)	3198 (1)	2162 (1)	3540 (1)
S(2)	7769 (1)	2353 (1)	4177 (1)
C(1)	2822 (6)	184 (4)	3572 (3)
C(2)	5138 (5)	2327 (4)	2713 (3)
C(3)	7040 (5)	1641 (4)	3062 (2)
C(4)	8594 (5)	4192 (4)	3871 (3)

Table III. Atomic Coordinates for $[Cu(4,7\text{-}DTD)Cl_2]_2$ ($\times 10^4$)

atom	x	y	z
Cu	3125 (1)	83 (1)	70 (1)
Cl(1)	1918 (1)	891 (1)	−1959 (1)
Cl(2)	4343 (1)	−571 (1)	−1738 (1)
S(1)	2333 (1)	762 (1)	2260 (1)
S(2)	2788 (1)	−1086 (1)	1503 (1)
C(1)	6104 (5)	−2381 (3)	4275 (6)
C(2)	4594 (5)	−2201 (3)	3328 (6)
C(3)	4560 (4)	−1387 (3)	2556 (6)
C(4)	2074 (5)	−764 (3)	3356 (6)
C(5)	2600 (5)	41 (3)	3976 (6)
C(6)	408 (5)	821 (3)	1696 (6)
C(7)	−262 (5)	1243 (3)	3031 (7)
C(8)	−11 (7)	2117 (4)	3051 (8)

ment techniques have been given elsewhere.[3] The magnetometer was calibrated with $HgCo(NCS)_4$.[4,5] Finely ground polycrystalline samples of approximately 150 mg were packed in precision-ground Lucite sample holders. Diamagnetic corrections were made with use of Pascal's constants and tabulated data.[6-8]

X-ray Data Collection and Reduction

Data were collected with a Syntex $P2_1$ diffractometer using Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite monochromator.

$[Cu(2,5\text{-}DTH)Cl_2]$. A dark green needle obtained from a cooled methanol solution was cut to dimensions 0.20 × 0.30 × 0.42 mm, and data were collected at room temperature since several other crystals had shattered when they were cooled to 140 K. The space group $P2_1/n$ (alternate setting of $P2_1/c$, No. 14) was confirmed by axial photographs and the following conditions: $0k0$, $k = 2n$; $h0l$, $h + l = 2n$. Data were collected in the quadrant (h, k, $\pm l$) to $2\theta_{max} = 45°$ with use of an ω-scan technique. A total of 1116 independent data were obtained, of which 1075 had $I > 3\sigma(I)$; only these latter data were used in the subsequent calculations. Data were corrected for Lorentz–polarization effects and absorption. Cell dimensions and additional crystal data are listed in Table I.

$[Cu(4,7\text{-}DTD)Cl_2]$. A similar procedure was used for data collection on a dark green needle of dimensions 0.09 × 0.22 × 0.38 mm. The crystal was successfully cooled to 140 K. The space group, $P2_1/c$ (No. 14), was determined from axial photographs and the following conditions: $0k0$, $k = 2n$; $h0l$, $l = 2n$. A total of 1764 unique data were collected, of which 1604 were considered observed and used in the subsequent calculations.

Solution and Refinement of the Structures

Both structures were solved by direct methods. Computer programs used were Long's sign determination program, SHELXTL (July 1981, version 3), and a local absorption correction program. Scattering factor tables and corrections for anomalous dispersion were from ref 9.

$[Cu(2,5\text{-}DTH)Cl_2]$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms riding on the bonded carbon atom: $R = 0.037$; $R_w = 0.038$; mean shift/esd = 0.005 in the final cycle of refinement (82 least-squares parameters). Final atomic coordinates are given in Table II.

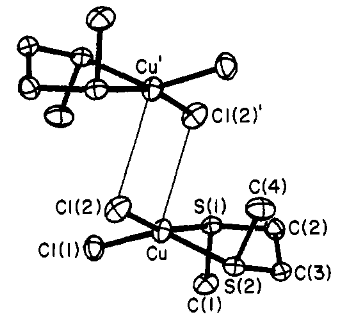

Figure 1. View of the structure of dichloro(2,5-dithiahexane)copper(II) that shows the bis(μ-chloro)-bridged dimeric unit.

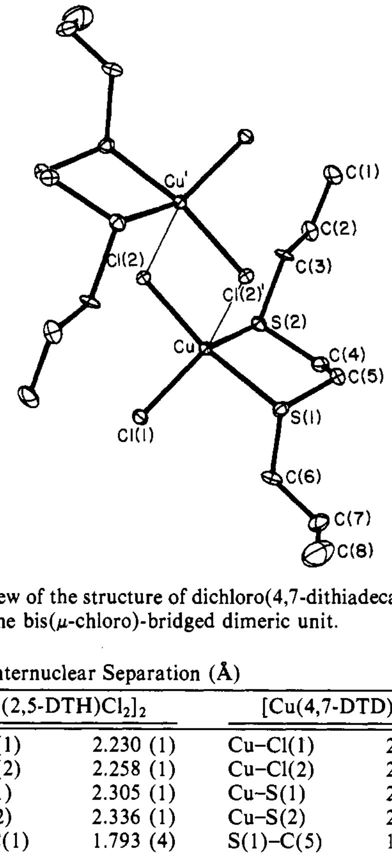

Figure 2. View of the structure of dichloro(4,7-dithiadecane)copper(II) that shows the bis(μ-chloro)-bridged dimeric unit.

Table IV. Internuclear Separation (Å)

$[Cu(2,5\text{-}DTH)Cl_2]_2$		$[Cu(4,7\text{-}DTD)Cl_2]_2$	
Cu–Cl(1)	2.230 (1)	Cu–Cl(1)	2.255 (1)
Cu–Cl(2)	2.258 (1)	Cu–Cl(2)	2.292 (1)
Cu–S(1)	2.305 (1)	Cu–S(1)	2.317 (1)
Cu–S(2)	2.336 (1)	Cu–S(2)	2.353 (1)
S(1)–C(1)	1.793 (4)	S(1)–C(5)	1.808 (5)
S(1)–C(2)	1.807 (4)	S(1)–C(6)	1.818 (4)
S(2)–C(3)	1.807 (4)	S(2)–C(3)	1.816 (4)
S(2)–C(4)	1.801 (4)	S(2)–C(4)	1.803 (5)
C(2)–C(3)	1.528 (5)	C(1)–C(2)	1.527 (6)
		C(2)–C(3)	1.523 (6)
		C(4)–C(5)	1.522 (7)
		C(6)–C(7)	1.511 (7)
		C(7)–C(8)	1.520 (8)
Cu–Cl(2)′[a]	3.075 (1)	Cu–Cl(2)′[b]	2.663 (1)
Cu···Cu′	3.948 (1)	Cu···Cu′	3.630 (1)

[a] Primed atoms are at $1 - x$, $1 - y$, $1 - z$. [b] Primed atoms are at $1 - x$, $-y$, $-z$.

$[Cu(4,7\text{-}DTD)Cl_2]$. Refinement was carried out as above, with $R = 0.029$, $R_w = 0.035$, mean shift/esd = 0.007, and 118 least-squares parameters. Final atomic coordinates are given in Table III.

The following listings are available as supplementary material for both structures: anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom coordinates, and observed and calculated structure factors.

Description of the Structures

Both structures consist of centrosymmetric chloro-bridged dimer units, essentially identical with the structure of [Cu(5,8-DTD-

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(3) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297.

(4) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 4190.

(5) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

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(7) Konig, E. "Magnetic Properties of Transition Metal Compounds"; Springer-Verlag: West Berlin, 1966.

(8) Weller, R. R.; Hatfield, W. E. *J. Chem. Educ.* **1979**, *56*, 652.

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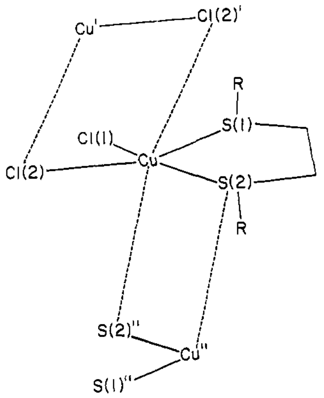

Figure 3. Key to atom-labeling scheme used in Table VI.

D)Cl$_2$]^2 (5,8-DTDD = 5,8-dithiadodecane). These dimeric units are packed in the solid state to form alternating chains with long copper–sulfur contacts. Drawings of the dimeric units in [Cu(2,5-DTH)Cl$_2$] and [Cu(4,7-DTD)Cl$_2$] are shown in Figures 1 and 2, respectively, and internuclear separations and angles are given in Tables IV and V. The copper atom is five-coordinate, and the two structures resemble each other in general shape. As can be judged from the angles given in Table V, the geometry about copper cannot be described as either idealized square pyramidal or trigonal bipyramidal. However, since the distance to the bridging chlorine atom is long (3.075 (1) Å for the 2,5-DTH compound and 2.663 (1) Å for the 4,7-DTD derivative), it is convenient to consider the geometry to be derived from a tetrahedrally distorted CuS$_2$Cl$_2$ square plane with a long axial contact to the bridging chlorine atom.

In [Cu(3,6-DTO)Cl$_2$]$_\infty$[1] (3,6-DTO = 3,6-dithiaoctane), crystal packing differs from the above three structures. Adjacent dimeric units are bridged by centrosymmetric Cu$_2$S$_2$ bridges with a Cu···S(2)″ distance of 3.361 (2) Å. This pattern is shown in Figure 3. The Cu···Cl(2)′ distance in this same complex is relatively long, 3.234 (1) Å. Our interest in the structures of the 2,5-DTH and 4,7-DTD derivatives initially stemmed from the observation of the alternating-chain structure of [Cu(3,6-DTO)Cl$_2$]$_\infty$. We were surprised to find that [Cu(2,5-DTH)Cl$_2$], in particular, did not have the same alternating-chain structure, since it has a less bulky alkyl substituent.

The dimeric, chloro-bridged units in the three compounds [Cu(2,5-DTH)Cl$_2$], [Cu(4,7-DTD)Cl$_2$], and [Cu(5,8-DTDD)Cl$_2$] pack in the solid state to form alternating chains with long copper–sulfur contacts, and typical Cu$_2$S$_2$ bridging units are not formed. Instead, as shown in the stereoview in Figure 4, adjacent CuS$_2$Cl$_2$ planes are positioned such that a given copper atom is nearly equidistant from both sulfur atoms in the coordination plane of the neighboring CuS$_2$Cl$_2$ moiety. From Table VI we see that the Cu···S(1)″ and Cu···S(2)″ distances are 5.193 (2) and 5.140 (2) Å in [Cu(2,5-DTH)Cl$_2$] and that the corresponding distances are 5.833 (2) and 5.404 Å in [Cu(4,7-DTD)Cl$_2$]. It will be shown below that these contacts are important in determining the magnetic properties of the compounds.

Table V. Interatomic Angles (deg)

[Cu(2,5-DTH)Cl$_2$]$_2$		[Cu(4,7-DTD)Cl$_2$]$_2$	
Cl(1)–Cu–Cl(2)	98.4 (1)	Cl(1)–Cu–Cl(2)	97.1 (1)
Cl(1)–Cu–S(1)	90.3 (1)	Cl(1)–Cu–S(1)	90.7 (1)
Cl(2)–Cu–S(1)	161.8 (1)	Cl(2)–Cu–S(1)	168.6 (1)
Cl(1)–Cu–S(2)	146.1 (1)	Cl(1)–Cu–S(2)	139.7 (1)
Cl(2)–Cu–S(2)	91.9 (1)	Cl(2)–Cu–S(2)	90.4 (1)
S(1)–Cu–S(2)	89.7 (1)	S(1)–Cu–S(2)	89.1 (1)
Cl(2)′–Cu–Cl(2)	85.7 (1)	Cl(2)′–Cu–Cl(2)	86.1 (1)
Cl(2)′–Cu–Cl(1)	113.4 (1)	Cl(2)′–Cu–Cl(1)	116.6 (1)
Cl(2)′–Cu–S(1)	76.1 (1)	Cl(2)′–Cu–S(1)	82.9 (1)
Cl(2)′–Cu–S(2)	99.5 (1)	Cl(2)′–Cu–S(2)	103.4 (1)
Cu–S(1)–C(1)	107.2 (1)	Cu–S(1)–C(5)	100.5 (2)
Cu–S(1)–C(2)	101.2 (1)	Cu–S(1)–C(6)	108.1 (2)
Cu–S(2)–C(3)	102.6 (1)	Cu–S(2)–C(3)	104.9 (1)
Cu–S(2)–C(4)	103.1 (1)	Cu–S(2)–C(4)	103.2 (2)
Cu–Cl(2)–Cu′	94.3 (1)	Cu–Cl(2)–Cu′	93.8 (1)
C(1)–S(1)–C(2)	101.9 (2)	C(5)–S(1)–C(6)	102.2 (2)
C(3)–S(2)–C(4)	100.8 (2)	C(3)–S(2)–C(4)	100.9 (2)
S(1)–C(2)–C(3)	112.4 (3)	S(1)–C(5)–C(4)	113.4 (3)
S(2)–C(3)–C(2)	112.6 (3)	S(1)–C(6)–C(7)	113.9 (3)
		S(2)–C(4)–C(5)	112.4 (4)
		S(2)–C(3)–C(2)	112.9 (3)
		C(1)–C(2)–C(3)	108.9 (4)
		C(6)–C(7)–C(8)	113.2 (5)

Corresponding inter- and intradimeric unit distances and angles for the four structures [Cu(RSCH$_2$CH$_2$SR)Cl$_2$]$_x$ with R = CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$, and CH$_2$CH$_2$CH$_2$CH$_3$ are collected in Table VI. Certain trends are evident, although they do not parallel the increasing size of the R group. There is very little variation in the corresponding Cu–Cl and Cu–S bond distances throughout the series, in spite of the wide fluctuations in the contact distances exemplified by Cu···Cl(2)′ and Cu···S(2)″. On the average, Cu–Cl(2) and Cu–S(2) bonds are longer than Cu–Cl(1) and Cu–S(1) bonds. The longer set of bonds belong to the donor groups involved in bridging. There is very little change in the Cu′···Cl(2)–Cu bridging angle (ϕ); thus, the Cu···Cu′ distance parallels the Cu···Cl(2)′ distance. However, it is known that subtle changes in bridge angles can result in large changes in magnetic parameters,[10] and as described below, there are significant dif-

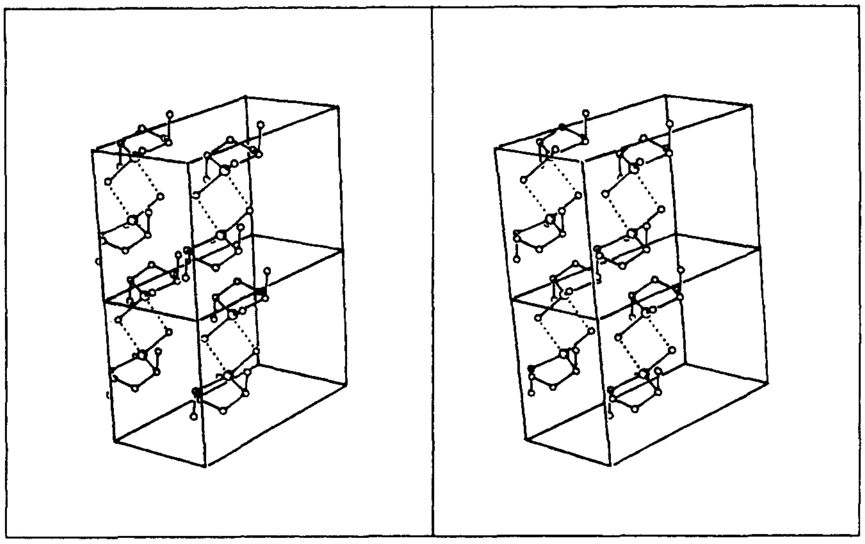

Figure 4. Stereoview of the two closest chains of dimers, stacked along *b*, in [Cu(2,5-DTH)Cl$_2$]. The *b* axis is nearly parallel with the plane of the page.

Table VI. Comparison of Inter- and Intradimer Distances and Angles in $[Cu(RSCH_2CH_2SR)Cl_2]_x$[a]

	R = CH_3[b] (2,5-DTH)	R = CH_2CH_3[c] (3,6-DTO)	R = $CH_2CH_2CH_3$[b] (4,7-DTD)	R = $CH_2CH_2CH_2CH_3$[d] (5,8-DTDD)
Cu-Cl(1)	2.230 (1)	2.230 (1)	2.255 (1)	2.242 (2)
Cu-Cl(2)	2.258 (1)	2.264 (1)	2.292 (1)	2.266 (2)
Cu···Cl(2)′	3.075 (1)	3.234 (1)	2.663 (1)	2.825 (2)
Cu···Cu′	3.948 (1)	4.046 (1)	3.630 (1)	3.749 (1)
Cu′···Cl(2)-Cu	94.3 (1)	93.1 (1)	93.8 (1)	94.22 (5)
Cu-S(1)	2.305 (1)	2.311 (1)	2.317 (1)	2.308 (2)
Cu-S(2)	2.336 (1)	2.327 (1)	2.353 (1)	2.369 (2)
Cu···S(1)″	5.193 (2)	5.560 (3)	5.833 (2)	5.536 (2)
Cu···S(2)″	5.140 (2)	3.361 (2)	5.404 (2)	5.694 (2)
Cu···Cu″	5.060 (1)	4.679 (1)	5.983 (1)	5.926 (1)
Cu″···Cu···Cu′	168.6 (1)	127.6 (1)	172.3 (1)	170.9 (1)
$\sum\Delta^2(CuS_2Cl_2$ plane), Å^2	1.12 (1)	0.79 (1)	1.07 (1)	1.30 (1)
ϕ/r	30.67	28.79	35.22	33.35

[a] Refer to Figure 3 for key to atom labels. Distances are in angstroms and angles are in degrees. [b] This work. [c] Reference 1. [d] Reference 2 (atoms renumbered for correspondence).

ferences in the magnetic properties of these compounds.

The observed trend in the Cu···Cl(2)′ and Cu···S(1)″, Cu···S(2)″ distances can be interpreted in terms of competition for axial electron density from copper. In $[Cu(3,6\text{-}DTO)Cl_2]_\infty$, there is little doubt that the incipient Cu···S(2)″ bond has weakened the bridging Cu···Cl(2)′ contact. In the 4,7-DTD and 5,8-DTDD derivatives, contacts between Cu and S(1)″, S(2)″, and Cu″ are long, allowing the Cu···Cl(2)′ distances to shorten. The 2,5-DTH derivative is intermediate between these two extremes, perhaps reflecting the less bulky alkyl substituent.

Of the four compounds, the 3,6-DTO derivative has the best CuS_2Cl_2 plane and more nearly approximates octahedral geometry. Although the other three compounds were described above as being five-coordinate, there are two sulfur atoms from an adjacent dimer at slightly more than 5 Å from copper. The magnetic properties of the 2,5-DTH and 4,7-DTD compounds show that there is significant overlap of the magnetic orbitals of copper with the orbitals of these atoms, and these long nonbonded contacts give rise to alternating-chain magnetism.

Additional interchain Cu···Cu, Cu···Cu, and S···S distances are given in Table VII. Two of these distances are especially important for the discussion of the magnetic properties of the compounds. The S(2)···S(1) distance of 3.857 Å is the shortest interchain contact in $[Cu(2,5\text{-}DTH)Cl_2]$. This S···S distance is shorter than those within a given dimer (S(1)···S(1) = 7.058 Å; S(1)···S(2) = 5.969 Å; S(2)···S(2) = 6.547 Å) and also shorter than the S···S distances between dimers in a given alternating chain (S(1)···S(1) = 6.241 Å; S(1)···S(2) = 5.276 Å; S(2)···S(2) = 6.175 Å). There is also a relatively short Cu···S(2) interchain distance of 4.943 Å, which, when taken in pairs, appears to link dimers in a spin-ladder arrangement. The significance of these interchain distances is considered in the Discussion.

The situation is quite different for the 4,7-DTD compound. The shortest S···S distance between chains is 6.102 Å. Within the dimer there is a S(1)···S(2) distance of 6.009 Å, and in the propagation of the chain, S(1)···S(2) = 5.249 Å while S(1)···S(1) = 5.774 Å. As may be seen in Table VII, in $[Cu(4,7\text{-}DTD)Cl_2]$ there is only one chain that brings the coppers into a proximity of less than 9 Å, and there are three such distances. In the 2,5-DTH compound, there are nine Cu···Cu distances less than 9 Å, as a result of the smaller size of the R group.

Magnetic Properties

Magnetic susceptibilities of powdered samples of $[Cu(2,5\text{-}DTH)Cl_2]$ and $[Cu(4,7\text{-}DTD)Cl_2]$ are plotted in Figures 5 and 6, respectively. The maxima in susceptibilities near 17 K for $[Cu(2,5\text{-}DTH)Cl_2]$ and 45 K for $[Cu(4,7\text{-}DTD)Cl_2]$ are indicative of antiferromagnetic exchange interactions. In addition, there is an indication of a phase transition in the magnetic susceptibility data for $[Cu(2,5\text{-}DTH)Cl_2]$ near 26 K. The magnitudes of the exchange energies as signaled by the temperatures of the maxima were unexpected in view of the existing data for other chloro-bridged copper(II) dimeric compounds.[10]

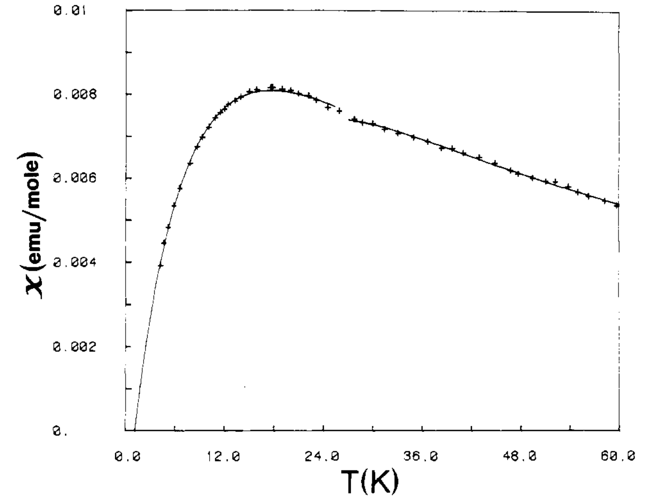

Figure 5. Magnetic susceptibility data for dichloro(2,5-dithiahexane)copper(II). The solid line below 26 K was generated by Heisenberg alternating-exchange theory using the equation and parameters given in the text. The solid line above 26 K was generated by the Van Vleck equation for an exchange-coupled pair of $S = {}^1/_2$ spins.

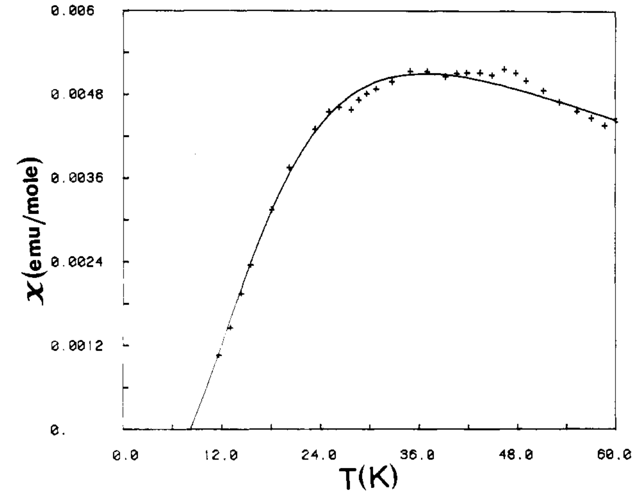

Figure 6. Magnetic susceptibility data for dichloro(4,7-dithiadecane)copper(II). The solid line was generated by Heisenberg alternating-exchange theory using the equation and parameters given in the text.

Heisenberg-Dirac-Van Vleck exchange theory has been assumed with use of the Hamiltonian $\mathcal{H} = -2J\hat{S}_1\cdot\hat{S}_2$. It was not

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Table VII. Interchain Distances Involving Cu···Cu, Cu···S, Cu···Cl, and S···S (Å)

[Cu(2,5-DTH)Cl_2] (Chain Propagated along *b*)			
(1) Chain at 1 + *x*, *y*, *z*			
Second Atom at 1 + *x*, *y*, *z*			
Cu···Cu	6.875	Cl(2)···Cu	6.244
S(2)···S(1)	3.857	Cu···S(1)	6.146
S(2)···Cu	4.943		
Second Atom at 2 − *x*, 1 − *y*, 1 − *z*			
Cu···Cu	8.174	S(2)···S(2)	6.124
Second Atom at 2 − *x*, −*y*, 1 − *z*			
Cu···Cu	8.765	S(2)···S(2)	5.725
(2) Chain at $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$			
Second Atom at $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$			
Cu···Cu	8.023	S(1)···Cu	5.781
Second Atom at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$			
Cu···Cu	8.806	S(1)···S(1)	5.483
(3) Chain at $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$			
Second Atom at $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$			
Cu···Cu	8.075	Cl(1)···Cu	6.338
(4) Chain at −1 + *x*, *y*, *z*			
Second Atom at −1 + *x*, *y*, *z*			
Cu···Cu	6.875	S(1)···Cu	6.146
Cu···Cl(1)	5.401		
Second Atom at −*x*, 1 − *y*, 1 − *z*			
Cu···Cu	7.674		
Second Atom at −*x*, − *y*, 1 − *z*			
Cu···Cu	8.300		
[Cu(4,7-DTD)Cl_2] (Chain Propagated along *a*)			
Chain at *x*, *y*, 1 + *z*			
Second Atom at *x*, *y*, 1 + *z*			
Cu···Cu	7.813	S(1)···Cu	6.115
Second Atom at 1 − *x*, −*y*, 1 − *z*			
Cu···Cu	7.860	S(1)···S(2)	6.102
Second Atom at *x*, −*y*, −1 − *z*			
Cu···Cu	8.979		

possible to fit the complete data for either compound with use of the Van Vleck equation[11] for a pair of exchange-coupled $S = \frac{1}{2}$ ions, although the data for [Cu(2,5-DTH)Cl_2] above 26 K may be fit by the equation

$$\chi_m = [Ng^2\beta^2/3k(T - \Theta)][1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1}$$

with the magnetic parameters $J = -10.0$ cm^{-1}, $g = 2.26$, and $\Theta = -16.8$ K. A nonlinear Simplex fitting program was used for the data analysis,[12] with the criterion of best fit being the minimum value of the function

$$F = \sum_i \frac{(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2}{\chi_i^{\text{obsd}}}$$

Although the fit is excellent, the values of the parameters signal the inapplicability of the $S = \frac{1}{2}$ pair model and indicate the presence of additional exchange pathways and a higher magnetic dimensionality.

The magnetic susceptibility data for [Cu(2,5-DTH)Cl_2] below 26 K may be fit by Heisenberg alternating-chain theory. The Hamiltonian for Heisenberg alternating exchange is

$$\mathcal{H} = -2J \sum_{i=1}^{(N/2)-1} [\hat{\mathbf{S}}_{2i}\cdot\hat{\mathbf{S}}_{2i-1} + \alpha\hat{\mathbf{S}}_{2i}\cdot\hat{\mathbf{S}}_{2i+1}]$$

where J is the exchange integral for a spin and one of its nearest neighbors, and αJ is the exchange integral for that spin and its other nearest neighbor. At the extremes, when $\alpha = 0$, the model reduces to the dimer case, and when $\alpha = 1$, the model reduces to the uniform linear-chain model. This problem has been studied in detail from a theoretical point of view,[13-18] but only recently have examples with transition-metal ions been identified.[1,19,20]

The temperature dependence of the magnetic susceptibility of Heisenberg alternating chains with $-J$ and $+\alpha$ may be described by the equation[13]

$$\chi_M(\alpha) = \frac{Ng^2\beta^2}{kT}\,\frac{A(\alpha) + [B(\alpha)]x + [C(\alpha)]x^2}{1 + [D(\alpha)]x + [E(\alpha)]x^2 + [F(\alpha)]x^3}$$

where $x = |J|/kT$, α is the alternation parameter, and the coefficients A–F are power series in terms of α. The best fit of the equation to the data for [Cu(4,7-DTD)Cl_2] yielded $J = -20.6$ cm^{-1} and $\alpha = 0.35$ with the g value held constant at the EPR experimentally determined value of 2.08. The best fit of the equation to the data below 26 K for [Cu(2,5-DTH)Cl_2] yielded $J = -10$ cm^{-1} and $\alpha = 0.87$ with the EPR g value of 2.03 being held constant. Fits of the Heisenberg alternating-chain equation to the data above 26 K for [Cu(2,5-DTH)Cl_2] were ambiguous in that equally good fits resulted from a range of values for the parameters.

Discussion

In the absence of data from the magnetic experiments, a description of the structures of the compounds [Cu(2,5-DTH)Cl_2], [Cu(4,7-DTD)Cl_2], and [Cu(5,8-DTDD)Cl_2] as bis(μ-chloro)-bridged dimers would have been justified in terms of available information on other such compounds. However, it is clear that there is significant overlap of the magnetic orbitals on copper with sulfur atoms that are centered more than 5 Å away, and the magnetic data are accurately fit by Heisenberg alternating-chain theory. The magnetic interactions that lead to the alternating chain occur between nonbonded copper–sulfur contacts.

The exchange coupling constants are considerably larger than would have been expected for ϕ/r values of 30.7 for [Cu(2,5-DTH)Cl_2] and 35.2 for [Cu(4,7-DTD)Cl_2]. Other bis(μ-chloro)-bridged copper(II) dimers with similar ϕ/r values exhibit J values in the range −2 to −3 cm^{-1}.[10,13] If the J value of −20.6 in [Cu(4,7-DTD)Cl_2] describes the exchange interaction between the sulfur-bridged copper ions, then the α value of 0.35 indicates that the exchange for the chloro-bridged pair is −7 cm^{-1}, a value that is still large in comparison to other exchange coupling constants that have been reported for bis(μ-chloro)-bridged copper.[10] On the basis of the copper–copper internuclear separations, the larger $|J|$ value may be associated with the bis(μ-chloro)-bridged exchange-coupled pair, but there is no way to verify this.

The large α value of 0.87 for [Cu(2,5-DTH)Cl_2] suggests that the dimers have reoriented at 26 K and that the superexchange along the chain is enhanced. Since [Cu(2,5-DTH)Cl_2] crystals shatter upon cooling, it is possible that phase transitions occur, and the structure of the compound at lower temperatures may be different from the structure at room temperature.

The much larger exchange coupling constants in [Cu(2,5-DTH)Cl_2] and [Cu(4,7-DTD)Cl_2] than in [Cu(3,6-DTO)Cl_2]$_\infty$ may also reflect another structural difference. The exchange-coupled Cu_2Cl_2 and Cu_2S_2 planes in [Cu(3,6-DTO)Cl_2]$_\infty$ are nearly mu-

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tually perpendicular.[1] In [Cu(2,5-DTH)Cl_2] and [Cu(4,7-DTD)Cl_2], the Cu_2Cl_2 plane essentially bisects the angle formed by the two Cu_2S_2 planes. It has been observed that the relative orientation of the exchange-coupled entities in chains influences the magnitude of the exchange coupling constant,[20] and this work shows that this feature is particularly important in determining the magnitude of J in these alternating-chain compounds.

As noted above, there are two short interchain contacts which could lead to superexchange pathways and magnetic interactions. The S(2)···S(1) interchain distance of 3.857 Å would provide the superexchange pathway Cu–S···S–Cu, but this may reasonably be expected to be less important than the shorter Cu–S···Cu pathway. There is also a short S(2)···Cu interchain distance of 4.943 Å, and these contacts, when taken in pairs, appear to link dimers into spin ladders. However, exchange by a single interchain Cu···S–Cu pathway should be less important than exchange through two Cu···S–Cu pathways, and in view of the alternating-chain magnetism, the latter must predominate.

Exchange coupling may be transmitted through long nonbonded contacts involving sulfur atoms. The sulfur–sulfur contact between molecular units in [$(C_2H_5)_4N$][Ni(DDDT)$_2$] (DDDT is 5,6-dihydro-1,4-dithiin-2,3-dithiolate) is 3.98 Å, yet these are exchange-coupled into two-dimensional layers with $J = -8.5$ cm^{-1}, and even though the nickel–nickel interlayer separation is 8.152 Å, [$(C_2H_5)_4N$][Ni(DDDT)$_2$] undergoes long-range order near 15 K.[21] EPR evidence and molecular orbital calculations show that there is substantial delocalization of electron density onto the ligand in [$(C_2H_5)_4N$][Ni(DDDT)$_2$], and this permits the intermolecular exchange interaction.

The structure and properties of the mixed-valence compound $Cu^I_2Cu^{II}$(2,5-DTH)$_6$(ClO_4)$_4$ are germane to this discussion.[22,23] Copper ions in [Cu(2,5-DTH)$_2$]$^{q+}$ (q = 1 or 2) complexes have tetrahedral coordination, and there is no distinction between copper(I) and copper(II). That is, the copper(I) and copper(II) ions are randomly distributed in the cations in the solid state. The mechanism responsible for making all copper ions equivalent, even though they are separated by 8 Å, is probably mediated by long nonbonded sulfur–sulfur interactions that facilitate rapid electron transfer.

Long, nonbonded sulfur–copper contacts of 3.98 Å in [Cu(4-METZ)(DMF)Cl_2]$_2$ gave rise to ladderlike magnetism, and a relatively large mean-field J' of -1.0 cm^{-1} has been found for [Cu(C_4H_5NS)$_2Cl_2$·CH_3OH]$_2$.[24] These intermolecular interactions may be understood in terms of superexchange pathways involving long nonbonded contacts between dimeric units. The large radial extensions of the sulfur orbitals permit these unexpectedly large interdimer exchange interactions.

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Registry No. [Cu(2,5-DTH)Cl_2]$_2$, 99727-67-0; [Cu(4,7-DTD)Cl_2]$_2$, 99727-68-1; 4,7-DTD, 22037-97-4; $CH_3CH_2CH_2SH$, 107-03-9; $ClCH_2CH_2Cl$, 107-06-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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The $XeN(SO_2F)_2^+$ and $F[XeN(SO_2F)_2]_2^+$ Cations: Syntheses, Raman and Multinuclear Magnetic Resonance Studies of the AsF_6^- and $Sb_3F_{16}^-$ Compounds, and X-ray Structure of $XeN(SO_2F)_2^+Sb_3F_{16}^-$

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Like its XeF_2 precursor, the Xe–N-bonded $FXeN(SO_2F)_2$ molecule exhibits fluoride ion donor properties that, in the present work, have resulted in the syntheses of adducts having the stoichiometries $FXeN(SO_2F)_2·AsF_5$, $FXeN(SO_2F)_2·3SbF_5$, and $2FXeN(SO_2F)_2·AsF_5$. All compounds have been enriched to 30% with ^{15}N and studied by ^{15}N, ^{19}F, and ^{129}Xe NMR spectroscopy and Raman spectroscopy. The spectroscopic studies have shown the above stoichiometries to be consistent with the predominantly ionic formulations $XeN(SO_2F)_2^+AsF_6^-$, $XeN(SO_2F)_2^+Sb_3F_{16}^-$, and $F[XeN(SO_2F)_2]_2^+AsF_6^-$. In general, the cations are thermally less stable than their fluorine analogues, XeF^+ and $Xe_2F_3^+$. The crystal structure of $XeN(SO_2F)_2^+Sb_3F_{16}^-$ has been obtained at −64 °C from three-dimensional X-ray data. [Bis(fluorosulfuryl)amido]xenon(II) hexadecafluorotriantimonate(V) crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules in a unit cell of dimensions a = 10.320 (2) Å, b = 10.642 (2) Å, c = 18.167 (3) Å, and β = 108.94 (1)°. The structure was solved by the heavy-atom method and refined by least-squares and Fourier methods to a final R factor of 0.061 for 2376 observed ($F > 0$) reflections. The structure analysis has established the existence of discrete $XeN(SO_2F)_2^+Sb_3F_{16}^-$ molecules and shows that the $XeN(SO_2F)_2^+$ cation is Xe–N bonded and that the Xe–N bond (2.02 (1) Å) is significantly shorter than in $FXeN(SO_2F)_2$ (2.200 (3) Å). The $Sb_3F_{16}^-$ anion is cis-fluorine bridged and weakly covalently bonded by means of a fluorine bridge to the $XeN(SO_2F)_2^+$ cation (Xe- - -F = 2.457 (8) Å).

Introduction

Compounds containing xenon–fluorine and xenon–oxygen bonds have been known since the inception of noble-gas chemistry.[1] They include such compounds as XeF_2,[2] XeF_4,[3] XeF_6,[4] $XeOF_4$,[4] XeO_2F_2,[5] $FXeOSO_2F$,[6,7] $FXeOTeF_5$,[8] and $F_3XeOIOF_4$.[9] The first xenon–nitrogen compound to be reported, $FXeN(SO_2F)_2$,

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