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## Crystal and Molecular Structure of

### Di- $\mu$ -chloro-bis[chloro(5,8-dithiadodecane)copper(II)], [Cu(BuSCH<sub>2</sub>CH<sub>2</sub>SBu)Cl<sub>2</sub>]<sub>2</sub>

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The crystal and molecular structure of the title compound has been determined from single-crystal three-dimensional X-ray data collected by counter methods. The compound crystallizes as dark green needles in space group  $P\bar{1}$ :  $Z = 1$ ;  $a = 9.646$  (3),  $b = 11.823$  (4),  $c = 7.934$  (2) Å;  $\alpha = 109.61$  (2),  $\beta = 79.23$  (2),  $\gamma = 113.55$  (2)°;  $d_{\text{calcd}} = 1.451$ ,  $d_{\text{obsd}} = 1.45$  (1) g/cm<sup>3</sup>. Least-squares refinement of 2460 reflections having  $I \geq 2\sigma(I)$  gave a conventional  $R$  factor of 0.063. The complex crystallizes as discrete centrosymmetric dichloro-bridged dimers with five-coordinate Cu(II) ions bound by a bidentate thioether ligand and three Cl<sup>-</sup> ions. An ideal square-pyramidal model is marginally superior to the trigonal-bipyramidal alternative for describing the CuS<sub>2</sub>Cl<sub>3</sub> coordination geometry. Cu-S bond lengths (2.308 (2), 2.369 (2) Å) and Cu-Cl bond lengths (2.266 (2), 2.242 (2) Å) within the puckered *cis*-CuS<sub>2</sub>Cl<sub>2</sub> fragment are typical for equatorial bonding of these types. The copper atom is displaced 0.26 Å from this S<sub>2</sub>Cl<sub>2</sub> plane toward an apically bonded chloride ion (Cu-Cl = 2.825 (2) Å). Structural parameters for the planar Cu<sub>2</sub>Cl<sub>2</sub> bridging unit include Cu-Cl bond distances of 2.825 (2) and 2.266 (2) Å, Cu-Cl-Cu' bond angles of 94.22 (5)°, and a Cu...Cu separation of 3.749 (2) Å.

## Introduction

As part of a continuing project dealing with Cu(II) complexes of sulfur-containing ligands,<sup>2-5</sup> we recently described the electronic spectra of several Cu(II) thioether complexes,<sup>6</sup> including the title compound. To establish a reliable structural basis for distinguishing between S → Cu(II) ligand to metal charge transfer (LMCT) and Cl → Cu(II) LMCT absorptions exhibited by the title compound, a crystallographic study was required. We report here the crystal and molecular structure of [Cu(BuSCH<sub>2</sub>CH<sub>2</sub>SBu)Cl<sub>2</sub>]<sub>2</sub>.

These structural results have permitted electronic-spectral comparisons to be made with the structurally similar [Cu-(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)Cl<sub>2</sub>]<sub>2</sub> complex.<sup>7</sup> Further, since the title compound provides an additional example of a dichloro-bridged Cu(II) dimer, the present structural data is expected to facilitate studies concerned with structural-magnetic correlations for such dimers. We are aware of six prior structural characterizations of Cu(II)-S(thioether) bonding,<sup>2,8-12</sup> all in the recent chemical literature.

## Experimental Section

**1. Preparation of [Cu(C<sub>10</sub>H<sub>22</sub>S<sub>2</sub>)Cl<sub>2</sub>]<sub>2</sub>.** The preparation of the bis(thioether) ligand and its Cu(II) complex has been reported elsewhere.<sup>6</sup> Diffraction-quality crystals were prepared by evaporating methanolic solutions of the complex slowly.

**2. Collection of Diffraction Data.** A crystal approximately 0.1 × 0.2 × 0.4 mm was mounted along the long dimension in a sealed capillary which contained mother liquor well removed from the crystal. Preliminary Weissenberg photographs indicated that the crystal was triclinic.

Unit cell constants (Table I) were determined from a least-squares fit of 14 moderately intense reflections accurately centered on a computer-controlled Syntex P2<sub>1</sub> diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  0.71069 Å). A density of 1.451 g/cm<sup>3</sup> was calculated for one [Cu(C<sub>10</sub>H<sub>22</sub>S<sub>2</sub>)Cl<sub>2</sub>]<sub>2</sub> dimer per unit cell; this is in excellent agreement with the value of 1.45 (1) g/cm<sup>3</sup>

Table I

Crystal Data	
space group $P\bar{1}$	mol wt = 681.7
$Z = 1$	$d_{\text{obsd}} = 1.45$ (1) g/cm <sup>3</sup>
$a = 9.646$ (3) Å	$d_{\text{calc}} = 1.451$ g/cm <sup>3</sup>
$b = 11.823$ (4) Å	$V = 780.0$ Å <sup>3</sup>
$c = 7.934$ (2) Å	$\mu = 20.2$ cm <sup>-1</sup>
$\alpha = 109.61$ (2)°	$T = 25 \pm 1$ °C
$\beta = 79.23$ (2)°	$\lambda = 0.71069$ Å
$\gamma = 113.55$ (2)°	

### Reduced Triclinic Cell (Conventional Orientation)

$a' = 9.646$ Å	$\alpha = 109.61$ °
$b' = 11.822$ Å	$\beta = 100.77$ °
$c' = 7.934$ Å	$\gamma = 105.91$ °

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} a' \\ b' \\ c' \end{pmatrix}$$

measured by the density gradient technique.<sup>13</sup>

Intensity data were collected at  $25 \pm 1$  °C using a  $\theta$ - $2\theta$  scan to a maximum of  $2\theta = 55$ °. Each scan covered a range from 0.7° below the calculated  $K\alpha_1$  position to 0.9° above the calculated  $K\alpha_2$  position. All data were collected using a scan rate of 2.55° min<sup>-1</sup>; stationary background counts were taken before and after each scan. The total time for background counting was equal to the scan time and was equally distributed before and after the peak.

The intensities of three standard reflections were recorded every 47 reflections throughout the data collection period; they showed random variations of  $\pm 3\%$  but no significant trend. A total of 2557 reflections out of a possible 3746 had  $I \geq 2\sigma(I)$ . Intensities were determined from the relationship  $I = (P - LB - RB) \times SR$  where  $P$  is the peak count,  $LB$  is the low-angle background count,  $RB$  is the high-angle background count, and  $SR$  is the scan rate. They were corrected for decay by applying average decay factors derived from the three standard reflections; 97 peaks were rejected on the basis of profile scans. The remaining 2460 reflections with  $I > 2\sigma(I)$  were

Table II. Fractional Atomic Coordinates<sup>a</sup> and Thermal Parameters<sup>b</sup>

atom	x	y	z	$U_{11}$ or $B$ ( $\text{\AA}^2$ )	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	1861 (1)	-176 (1)	-86 (1)	50.8 (4)	56.7 (5)	24.5 (3)	28.3 (5)	-5.7 (3)	12 (2)
Cl(1)	1187 (1)	1019 (1)	-1262 (2)	50.4 (4)	63.2 (5)	38.9 (6)	25.5 (5)	-4.7 (3)	23.1 (4)
Cl(2)	2595 (2)	-1389 (1)	-2658 (2)	66.2 (4)	76 (1)	26.8 (6)	40.8 (5)	-3.0 (3)	10.2 (4)
S(1)	2977 (1)	1633 (1)	2341 (2)	41.8 (4)	58.9 (5)	32.1 (6)	20.4 (5)	-3.3 (3)	8.6 (4)
S(2)	1915 (1)	-1501 (1)	1454 (2)	48.9 (4)	60.5 (5)	35.8 (6)	26.0 (5)	0.3 (3)	21.6 (4)
C(1)	4233 (14)	-4139 (9)	2668 (15)	162 (7)	101 (6)	151 (8)	41 (6)	-47 (6)	63 (4)
C(2) <sup>c</sup>	3517 (15)	-3409 (12)	1774 (17)	6.8 (3)					
C(2B) <sup>c</sup>	4546 (33)	-3361 (25)	1519 (38)	7.5 (6)					
C(3)	4270 (8)	-2088 (7)	2191 (9)	108 (3)	122 (6)	61 (4)	82 (4)	0 (3)	33 (2)
C(4)	3823 (6)	-1534 (6)	1063 (8)	69 (8)	95 (4)	39 (3)	58 (3)	2 (2)	16 (2)
C(5)	1946 (6)	-452 (5)	3719 (6)	60 (2)	81 (4)	27 (2)	39 (2)	4 (2)	22 (2)
C(6)	3089 (6)	861 (6)	3935 (7)	65 (2)	95 (5)	30 (3)	52 (3)	-13 (2)	6 (2)
C(7)	1492 (6)	2261 (5)	3387 (7)	51 (2)	54 (3)	38 (3)	26 (2)	-5 (2)	6 (2)
C(8)	1891 (7)	3296 (6)	5156 (8)	72 (3)	58 (4)	42 (3)	34 (3)	-9 (2)	4 (2)
C(9)	819 (8)	4018 (6)	5769 (10)	80 (4)	64 (4)	63 (4)	40 (3)	-4 (3)	-1 (3)
C(10)	1176 (12)	5025 (8)	7588 (12)	132 (6)	81 (6)	71 (5)	52 (5)	-13 (5)	-22 (4)

atom	x	y	z	$B$ , $\text{\AA}^2$	atom	x	y	z	$B$ , $\text{\AA}^2$
H(C2-1)	236	-370	211	6.7	H(C5-2)	203	-82	436	3.2
H(C2-2)	357	-386	35	6.7	H(C6-1)	382	94	385	3.5
H(C2B-1)	404	-392	31	7.5	H(C6-2)	298	144	515	3.5
H(C2B-2)	565	-321	97	7.5	H(C7-1)	143	257	260	3.0
H(C3-1)	541	-239	203	5.8	H(C7-2)	54	164	332	3.0
H(C3-2)	404	-159	342	5.8	H(C8-1)	299	389	492	4.0
H(C4-1)	385	-194	7	3.7	H(C8-2)	187	288	602	4.0
H(C4-2)	433	-57	138	3.7	H(C9-1)	86	450	450	4.9
H(C5-1)	93	-43	385	3.2	H(C9-2)	-36	348	583	4.9

<sup>a</sup> Nonhydrogen coordinates are  $\times 10^4$ ; hydrogen coordinates are  $\times 10^3$ . <sup>b</sup> Anisotropic thermal parameters are  $\times 10^3$ ; the form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^* + U_{22}k^2b^* + U_{33}l^2c^* + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ . <sup>c</sup> The atom multiplier of C(2) is 0.67 and that of C(2B) is 0.33.

corrected for Lorentz and polarization effects and were used in the structure solution and refinement. The polarization correction for the parallel-parallel mode of the  $P2_1$  diffractometer was chosen assuming the monochromator crystal to be 50% perfect and 50% mosaic. Standard deviations were calculated as  $\sigma(F_o^2) = (Lp)^{-1}(\sigma^2(I) + (0.03I)^2)^{1/2}$  where  $\sigma(I) = (P + LB + RB)^{1/2} \times SR$ . Absorption corrections were not applied. Absorption factors ranged from 1.20 to 1.34 using a linear absorption coefficient of  $20.2 \text{ cm}^{-1}$  for Mo  $K\alpha$  radiation; thus, the maximum effect of absorption is expected to be approximately  $\pm 3\%$  of  $F$ .

**3. Solution and Refinement of the Structure.**<sup>14</sup> The structure was solved by the heavy-atom method and refined using full-matrix least-squares techniques. Approximate coordinates for the Cu and both Cl atoms were obtained readily from a normal sharpened Patterson map. Two successive difference Fourier maps revealed the positions of all remaining nonhydrogen atoms.

Refinement was initiated using neutral-atom scattering factors.<sup>15</sup> Isotropic refinement, based on  $F^2$  with weights set according to  $w = 1/\sigma^2(F_o^2)$ , reduced  $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$  to 0.17. At this point, anisotropic refinement was initiated, and both real and imaginary parts of the anomalous dispersion corrections<sup>15</sup> were applied to Cu, Cl, and S. Refinement proceeded smoothly except for atom C(2) which consistently showed unusually large temperature factors. Examination of electron density maps revealed a small ( $1.3 \text{ e}/\text{\AA}^3$ ) peak near C(2) which also gave plausible distances to C(1) and C(3). Therefore, we assumed that this site was disordered. Atom multipliers proportional to the electron density at the two sites (C(2) and C(2B)) were assigned and were not refined. Because of the small values of the electron density at these sites, atoms C(2) and C(2B) were refined isotropically. Similar difficulties with alkyl groups have been encountered previously.<sup>16,17</sup> Coordinates for all methylene H atoms were calculated, and these H atoms were added as a fixed-atom contribution to the structure factor with isotropic temperature factors equal to those of the carbon atom to which they are bonded. No attempt was made to locate or calculate the positions of methyl group H atoms.

For the final cycles, refinement was based on  $F$  with weights chosen by an analysis of variance to make  $|\Delta F|/\sigma$  independent of  $|F_o|$ . This led to the following assignments for  $\sigma(F_o)$ :

$$\sigma(F_o) = -0.0378|F| + 2.820 \quad |F| < 22.7$$

$$\sigma(F_o) = 0.0048|F| + 1.861 \quad 22.7 \leq |F| \leq 49.1$$

$$\sigma(F_o) = 0.0594|F| - 0.835 \quad |F| > 49.1$$

Table III. Bond Distances ( $\text{\AA}$ ) and Angles (deg)

Distances			
Cu...Cu'	3.749 (2)	C(2B)-C(3)	1.53 (3)
Cl(1)...Cl(1')	3.489 (3)	C(3)-C(4)	1.476 (12)
Cu-Cl(1)	2.266 (2)	C(4)-S(2)	1.823 (7)
Cu-Cl(1')	2.825 (2)	C(5)-S(2)	1.807 (5)
Cu-Cl(2)	2.242 (2)	C(5)-C(6)	1.476 (7)
Cu-S(1)	2.369 (2)	C(6)-S(1)	1.830 (7)
Cu-S(2)	2.308 (2)	C(7)-S(1)	1.812 (6)
C(1)-C(2)	1.67 (2)	C(7)-C(8)	1.512 (7)
C(1)-C(2B)	1.42 (4)	C(8)-C(9)	1.508 (11)
C(2)-C(3)	1.383 (13)	C(9)-C(10)	1.524 (10)

Angles			
Cu-Cl(1)-Cu'	94.22 (5)	Cu-S(2)-C(4)	106.6 (2)
Cl(1)-Cu-Cl(1')	85.78 (5)	Cu-S(2)-C(5)	99.8 (2)
Cl(2)-Cu-Cl(1)	98.06 (6)	C(1)-C(2)-C(3)	114 (1)
Cl(2)-Cu-Cl(1')	119.73 (5)	C(1)-C(2B)-C(3)	121 (2)
Cl(1)-Cu-S(1)	92.02 (6)	C(2)-C(3)-C(4)	111.3 (9)
Cl(1)-Cu-S(2)	165.02 (5)	C(2B)-C(3)-C(4)	125 (1)
Cl(1')-Cu-S(1)	100.87 (5)	C(3)-C(4)-S(2)	117.8 (4)
Cl(1')-Cu-S(2)	79.34 (5)	C(4)-S(2)-C(5)	102.2 (3)
Cl(2)-Cu-S(1)	138.65 (5)	S(2)-C(5)-C(6)	113.5 (4)
Cl(2)-Cu-S(2)	90.89 (6)	C(5)-C(6)-S(1)	113.8 (4)
S(1)-Cu-S(2)	89.10 (6)	C(6)-S(1)-C(7)	102.5 (3)
Cu-S(1)-C(7)	105.2 (2)	S(1)-C(7)-C(8)	113.7 (4)
Cu-S(1)-C(6)	101.6 (2)	C(7)-C(8)-C(9)	112.3 (6)
		C(8)-C(9)-C(10)	112.5 (8)

Several cycles of refinement led to convergence with  $R_F = 0.063$  and  $R_wF = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.075$ . For the final cycle, all parameter changes were less than  $0.5\sigma$ , where  $\sigma$  is the esd obtained from the inverse matrix. A final difference map showed a general background of approximately  $\pm 0.4 \text{ e}/\text{\AA}^3$  and revealed no significant features. Final atomic parameters, together with their estimated standard deviations, are given in Table II while important interatomic distances and angles are presented in Table III. Views of the structure and of its packing are given in Figures 1 and 2, respectively. A list of observed and calculated structure factors is available.<sup>18</sup>

### Description of the Structure and Discussion

The complex crystallizes as discrete centrosymmetric dichloro-bridged dimers with five-coordinate Cu(II) ions bound

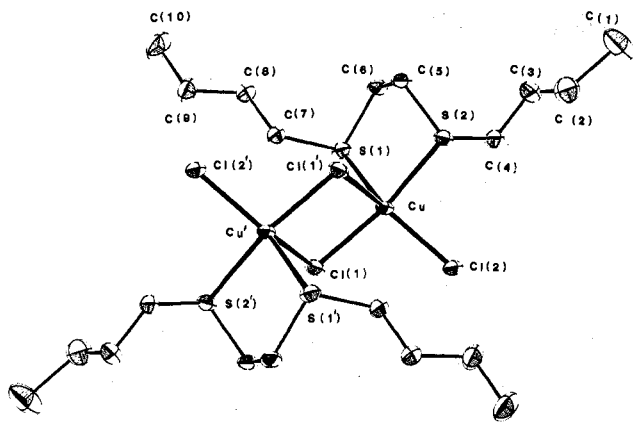


Figure 1. Structure of the title complex showing the atom numbering scheme. Hydrogen atoms and atom C(2B) have been omitted for clarity; 50% probability contours are shown for the thermal ellipsoids.

by a bidentate thioether ligand and three  $\text{Cl}^-$  ions. The coordination geometry may be described approximately as either square pyramidal, with  $\text{Cl}(1')$  apically bound to a pseudoplanar  $\text{Cl}(1)\text{--Cl}(2)\text{--S}(1)\text{--S}(2)\text{--Cu}$  fragment, or trigonal bipyramidal, with  $\text{Cl}(1)$  and  $\text{S}(2)$  axially bound to a trigonal planar  $\text{Cl}(2)\text{--Cl}(1')\text{--S}(1)\text{--Cu}$  fragment.

Observed structural parameters do not facilitate a clear choice between these alternatives. Seven of the ten bond angles within the  $\text{CuS}_2\text{Cl}_3$  unit are identical for both ideal geometries (Table IV). However, the three unique angles of the trigonal-bipyramidal model are in better agreement with the observed angles than are those of the square-pyramidal model. Square-pyramidal models with Cu raised slightly from the  $\text{Cl}(1)\text{--Cl}(2)\text{--S}(1)\text{--S}(2)$  basal plane toward the apical ligand improve the overall angular agreement somewhat, but the agreement is still not as good as with the trigonal-bipyramidal model.

On the other hand, the observed bond distances (Table III) are in better agreement with a square-pyramidal model involving apical  $\text{Cu}\text{--Cl}(1')$  bonding. Although a choice between these alternatives is arbitrary, we feel that accommodation of the long  $\text{Cu}\text{--Cl}(1')$  bond by the square-pyramidal model outweighs the somewhat larger angular deviations from ideality shown by this model. Thus, we adopt the view that the puckered  $\text{Cu}\text{--S}(1)\text{--S}(2)\text{--Cl}(1)\text{--Cl}(2)$  unit (Table V, plane I) constitutes the distorted base of a square pyramid and exhibits (vide infra)  $\text{Cu}$ –ligand bond lengths appropriate for equatorial bonding. Within this *cis*- $\text{CuS}_2\text{Cl}_2$  unit, bond angles involving the Cu atom and any two *cis* ligands exhibit only modest departures from the ideal value ( $90^\circ$ ) and fall in the range  $89.10(6)\text{--}98.06(6)^\circ$ . However, the respective bond angles of  $138.65(5)$  and  $165.02(5)^\circ$  for the *trans*  $\text{Cl}(2)\text{--Cu}\text{--S}(1)$  and  $\text{Cl}(1)\text{--Cu}\text{--S}(2)$  groups fall well short of the ideal value

Table IV. Angular Deviations (deg) in the  $\text{CuS}_2\text{Cl}_3$  Unit from Ideal Five-Coordination Geometries

bond angle	square pyramidal <sup>a</sup>		trigonal bipyramid <sup>b</sup>	
	ideal value	$\Delta^c$	ideal value	$\Delta^c$
$\text{Cl}(2)\text{--Cu}\text{--S}(1)$	180	-41.35	120	18.65
$\text{Cl}(2)\text{--Cu}\text{--Cl}(1')$	90	29.73	120	-0.27
$\text{S}(1)\text{--Cu}\text{--Cl}(1')$	90	10.87	120	-19.13
$\text{Cl}(1)\text{--Cu}\text{--S}(2)$	180	-14.98	180	-14.98
$\text{Cl}(2)\text{--Cu}\text{--Cl}(1)$	90	8.06	90	8.06
$\text{Cl}(2)\text{--Cu}\text{--S}(2)$	90	0.89	90	0.89
$\text{Cl}(1)\text{--Cu}\text{--S}(1)$	90	2.02	90	2.02
$\text{Cl}(1)\text{--Cu}\text{--Cl}(1')$	90	-4.22	90	-4.22
$\text{S}(1)\text{--Cu}\text{--S}(2)$	90	-0.90	90	-0.90
$\text{Cl}(1')\text{--Cu}\text{--S}(2)$	90	-10.66	90	-10.66

<sup>a</sup>  $\text{Cl}(1')$  apical. <sup>b</sup>  $\text{Cl}(1)$  and  $\text{S}(2)$  axial. <sup>c</sup>  $\Delta$  = observed angle - ideal angle.

Table V

Least-Squares Planes							
plane	atoms defining plane		equation of plane <sup>a</sup>				
I	$\text{Cl}(1), \text{Cl}(2), \text{S}(1), \text{S}(2)$		$-0.9649X_0 - 0.0642Y_0 + 0.2546Z_0 = -1.801$				
II	$\text{S}(1), \text{Cl}(2), \text{Cl}(1')$		$0.1900X_0 - 0.8680Y_0 + 0.4587Z_0 = 1.183$				
Deviations of Atoms from the Planes (Å)							
plane I			plane II				
$\text{Cl}(1)$	0.53	$\text{S}(2)$	0.57	$\text{Cl}(2)$	0.0	Cu	-0.12
$\text{Cl}(2)$	-0.68	Cu	0.26	$\text{S}(1)$	0.0	$\text{Cl}(1)$	-2.37
$\text{S}(1)$	-0.41	$\text{Cl}(1')$	3.07	$\text{Cl}(1')$	0.0	$\text{S}(2)$	2.17

<sup>a</sup> Equations have the form  $AX_0 + BY_0 + CZ_0 = D$  where  $X_0, Y_0,$  and  $Z_0$  are Cartesian axes lying along  $b \times c^*$ ,  $b$ , and  $c^*$ , respectively.

of  $180^\circ$ . The Cu atom is displaced  $0.26 \text{ \AA}$  from the best plane defined by the  $\text{S}(1)\text{--S}(2)\text{--Cl}(1)\text{--Cl}(2)$  fragment in the direction of the apical  $\text{Cl}(1')$  ion. This structural role of  $\text{Cl}(1')$  as an apical ligand is supported by the observed  $\text{Cl}(1')\text{--Cu}\text{--S}(2)$ ,  $\text{Cl}(1')\text{--Cu}\text{--Cl}(1)$ ,  $\text{Cl}(1')\text{--Cu}\text{--S}(1)$ , and  $\text{Cl}(1')\text{--Cu}\text{--Cl}(2)$  bond angles which fall in the range  $79.34(5)\text{--}119.73(5)^\circ$ .

Deviations from ideal square-pyramidal bond angles in the title complex are significantly larger than those reported for the structurally analogous square-pyramidal  $\text{CuN}_2\text{Cl}_3$  unit present in  $[(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{CuCl}_2]_2$ .<sup>7</sup> The basal  $\text{Cu}\text{--Cl}$  distances in the title complex are typical ( $2.266(2), 2.242(2) \text{ \AA}$ ) and closely resemble values reported for the  $\text{CuN}_2\text{Cl}_3$  analogue ( $2.264(3), 2.259(2) \text{ \AA}$ ). Therefore, the marked preference  $\text{Cu}(\text{II})$  exhibits for ligation by amine relative to thioether donors is not, within experimental error, reflected by a structural *trans* effect. However, the apical  $\text{Cu}\text{--Cl}(1')$  bond ( $2.825(2) \text{ \AA}$ ) in the title complex is significantly shorter

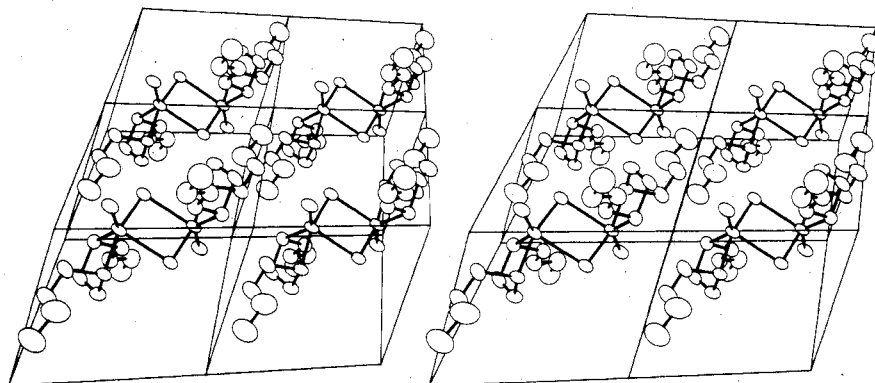


Figure 2. The contents of the unit cell viewed approximately along  $c^*$ . Hydrogen atoms and atom C(2B) have been omitted for clarity.

than the corresponding distance (3.147 (4) Å) in the amine analogue and may reflect this preference.

Observed Cu-S bond distances for the title complex (2.308 (2), 2.369 (2) Å) fall within the range of 2.30–2.45 Å reported by other workers for equatorial ligation of this type.<sup>8–11</sup> In the square-pyramidal model with both S(1) and S(2) equatorial, the nonequivalence of these distances would be associated with the distorted nature of the CuS<sub>2</sub>Cl<sub>3</sub> unit. With a trigonal-bipyramidal model having S(2) axial and S(1) equatorial, this nonequivalence could result from minimization of electron-pair repulsion which is expected<sup>19</sup> to lead to a contraction of the axial bond relative to the equatorial bond for d<sup>9</sup> complexes. Thus, the "axial" Cu-S(2) bond is shorter than the corresponding "equatorial" bond, in analogy with a trigonal-bipyramidal CuCl<sub>5</sub><sup>2-</sup> complex<sup>20</sup> which revealed axial Cu-Cl bonds (2.296 (1) Å) approximately 0.1 Å shorter than the equatorial bonds (2.391 (1) Å). However, the trigonal-bipyramidal model would then be inconsistent with the observation that the Cu-Cl(1) bond (axial) is ~0.02 Å longer than the Cu-Cl(2) bond (equatorial).

With use of either model, the bridged Cu-Cu'-Cl(1)-Cl(1)' fragment contains two equatorial Cu-Cl spans (2.266 (2) Å) and two apical Cu-Cl spans (2.825 (2) Å). Both Cu-Cl-Cu' bridging angles (94.22 (5)°) are required crystallographically to be equal. These structural features yield a Cu...Cu' separation of 3.749 (2) Å. Comparable parameters reported for the [(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)CuCl<sub>2</sub>]<sub>2</sub> complex include Cu-Cl spans of 2.264 (3) and 3.147 (4) Å, Cu-Cl-Cu bridging angles of 96.8 (1)°, and a Cu...Cu' separation of 4.089 (4) Å.<sup>7</sup>

Structural features of the ligand include uneventful C-C and C-S bond distances which, except in the vicinity of the disorder (C(2), vide supra), fall within the ranges reported by other workers for thioether ligands.<sup>8–11</sup>

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**Registry No.** [Cu(BuSCH<sub>2</sub>CH<sub>2</sub>SBu)Cl<sub>2</sub>]<sub>2</sub>, 61128-82-3.

**Supplementary Material Available:** Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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## Neutral Complexes of Gallium(II) Containing Gallium-Gallium Bonds

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The complexes formed between the "gallium dihalides" (Ga<sub>2</sub>X<sub>4</sub>) and 1,4-dioxane (diox), Ga<sub>2</sub>X<sub>4</sub>·2(diox) (X = Cl, Br, I), have been reinvestigated. Ga<sub>2</sub>Cl<sub>4</sub>·2C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> forms triclinic crystals, space group *P* $\bar{1}$ , with *a* = 8.829 (5) Å, *b* = 9.101 (5) Å, *c* = 10.82 (1) Å,  $\alpha$  = 107.27°,  $\beta$  = 97.73 (2)°,  $\gamma$  = 72.34 (2)°, *Z* = 2, *D*<sub>calc</sub> = 1.943 g cm<sup>-3</sup>, and *D*<sub>meas</sub> = 1.95 g cm<sup>-3</sup>. The structure has been solved from 3034 diffractometer-measured intensities with Mo K $\alpha$  radiation ( $\lambda$  0.7107 Å) and refined by full-matrix least squares to *R* = 0.085. The crystal structure shows that the complex is a discrete molecule containing a gallium-gallium bond of length 2.406 (1) Å with dioxane acting as a monodentate ligand. Spectroscopic and other evidence is presented which shows that the bromide and iodide complexes have a similar structure.

### Introduction

The "gallium dihalides" form many complexes with both monodentate and bidentate ligands. With monodentate ligands, these have the stoichiometry Ga<sub>2</sub>X<sub>4</sub>·4L, e.g., L = anisole and dimethyl sulfide, while with bidentate ligands they have stoichiometry Ga<sub>2</sub>X<sub>4</sub>·2L, e.g., L = 1,4-dioxane and morpholine.<sup>1–3</sup> It has been proposed<sup>1</sup> that the complexes have

ionic formulations, e.g., Ga(C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>)<sub>4</sub><sup>+</sup>GaX<sub>4</sub><sup>-</sup> and Ga-(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub><sup>+</sup>GaX<sub>4</sub><sup>-</sup> in which the metal is four-coordinate.

Evidence for such species comes mainly from electrical conductivity measurements of the complexes in nitrobenzene solution.<sup>1</sup> For the ion Ga(diox)<sub>2</sub><sup>+</sup>, evidence also comes from a crystal structure determination of the complex Ga(diox)<sub>2</sub>Cl which may also be isolated from the reaction between Ga<sub>2</sub>Cl<sub>4</sub>