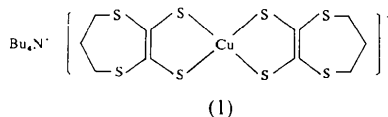


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$[M(\text{ddd}t)_2]^{n-}$  (Schultz, Wang, Soderholm, Shifter & Williams, 1987) and  $[M(\text{dmit})_2]^{n-}$  (Fan, Li, Ou & You, 1992), have been studied extensively. The title complex (1) is an analogue of  $\text{Bu}_4\text{N}[\text{M}(\text{ddd}t)_2]$  but differs in the external ligand unit. An X-ray analysis was undertaken to investigate the importance of the ligand unit in determining molecular structure and crystal packing.



The dithiolate ligand of complex (1) was prepared as a dipotassium salt following a method described by Kato, Kobayashi & Sasaki (1986), but using nitrogen instead of argon. The salt (1.2 g) was dissolved in methanol and 0.21 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol was added dropwise. Stirring was continued for 1 h. Air was bubbled through the reaction mixture for 15 min. After filtration, 1.5 g of tetrabutylammonium bromide was added to the brown filtrate. The dark-brown precipitate was collected by filtration, washed with methanol and dried in air. The powder product was recrystallized in acetone by slow evaporation. Single crystals were obtained in 2 weeks. Analysis for  $\text{C}_{26}\text{H}_{48}\text{CuNS}_8$ : calculated C 44.95, H 6.96, N 2.02%; found C 44.31, H 6.70, N 1.70%.

The four S atoms surround the Cu atom to yield a square-planar environment. The  $\text{CuS}_4$  core is distorted from  $D_{2h}$  symmetry by a twist angle of  $6.10(1)^\circ$  in contrast with that of  $29^\circ$  in  $\text{Bu}_4\text{N}[\text{Cu}(\text{ddd}t)_2]$ . The ligand, with the exception of the external propene unit, is almost planar. The maximum displacement from the least-squares plane defined by  $\text{S}(1)–\text{C}(2)–\text{S}(3)$  is  $0.076(8) \text{ \AA}$ . It is apparent that this complex has better planarity than  $\text{Bu}_4\text{N}[\text{Cu}(\text{ddd}t)_2]$  (Vance, Welch & Bereman, 1989). The average  $M–\text{S}$  ( $2.181 \text{ \AA}$ ) and  $\text{C}=\text{C}$  ( $1.342 \text{ \AA}$ ) bond distances are close to the corresponding values in  $\text{Bu}_4\text{N}[\text{Cu}(\text{ddd}t)_2]$ . The  $\text{C}–\text{S}$  bond distances in the dithiolene group vary from  $1.743(6)$  to  $1.768(6) \text{ \AA}$  and are intermediate between those of  $\text{C}=\text{S}$  and  $\text{C}–\text{S}$ . The shorter  $\text{C}–\text{S}$  bond length shows partial double-bond character. The  $\text{C}–\text{S}$  distances in the five-membered ring formed through coordination with the Cu atom are shorter than those in the periphery of the ligand. This may indicate slight electron delocalization in the coordination ring. The electron delocalization makes it difficult to assign an oxidation state to the central metal ion.

The external seven-membered rings adopt a chair conformation and the two propene groups have a *trans* orientation.

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## Copper Complex of 6,7-Dihydro-5H-1,4-dithiepine-2,3-dithiolate

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### Abstract

A short  $\text{C}–\text{S}$  bond distance and a planar ligand structure indicate extensive delocalization of electron density in the anion of tetrabutylammonium bis(6,7-dihydro-5H-1,4-dithiepine-2,3-dithiolato)copper(III),  $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Cu}(\text{C}_5\text{H}_6\text{S}_4)_2]$ . The central metal ion, formally  $\text{Cu}^{\text{III}}$ , has an unusual oxidation state. The crystal has a layer-like structure formed by the anions, while the tetrabutylammonium cations intercalate between them.

### Comment

Multi-sulfur 1,2-dithiolene complexes have attracted much attention from chemists because of their structural similarity to BEDT-TTF salts, which are molecular organic superconductors (Williams, Ferraro, Thorn, Carlson, Geiser, Wang, Kini & Whangbo, 1992). Some of these complexes, such as

The crystal has a layer-like structure in which the anions stack along the *a* and *c* axes. The shortest Cu...Cu and S...S intermolecular distances are 8.642 and 4.379 Å, respectively. The complex, with larger external ligand units, has shorter Cu...Cu and S...S intermolecular contacts, compared with those of 10.34 (1) and 4.47 (1) Å, respectively, found in Bu<sub>4</sub>N[Cu(ddd<sub>t</sub>)<sub>2</sub>].

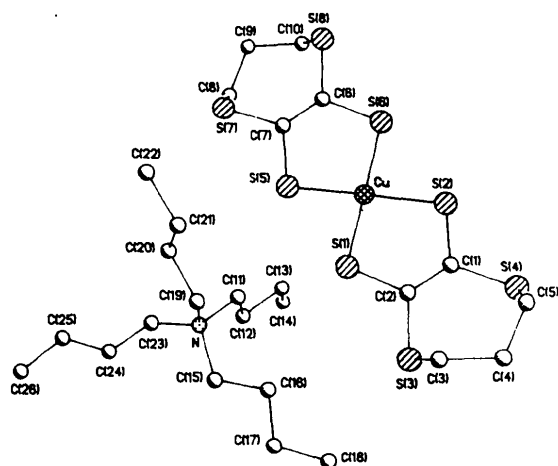


Fig. 1. The structure of compound (1).

## Experimental

### Crystal data

[N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][Cu(C<sub>5</sub>H<sub>6</sub>S<sub>4</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 694.70

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 17.596 (4) Å

*b* = 10.915 (2) Å

*c* = 17.774 (4) Å

β = 91.39 (2)°

*V* = 3412.4 (13) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.352 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 16 reflections

θ = 1.5–25°

μ = 1.129 mm<sup>-1</sup>

*T* = 296 K

Hexagonal sheet

0.50 × 0.40 × 0.35 mm

Dark brown

### Data collection

Siemens R3m/V diffractometer

ω scans

Absorption correction:

by integration from crystal shape

*T<sub>min</sub>* = 0.914, *T<sub>max</sub>* = 0.978

6577 measured reflections

6027 independent reflections

4138 observed reflections

[*F* > 4.0σ(*F*)]

*R<sub>int</sub>* = 0.0303

θ<sub>max</sub> = 25.0°

*h* = -20 → 0

*k* = 0 → 12

*l* = -21 → 21

2 standard reflections

monitored every 100

reflections

intensity variation: 3%

### Refinement

Refinement on *F*<sup>2</sup>

*R* = 0.051

*wR* = 0.0637

*S* = 1.94

4138 reflections

326 parameters

All H atoms calculated using a riding model with fixed

*U<sub>iso</sub>* = 1/[σ<sup>2</sup>(*F*) + 0.0002*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.033

Δρ<sub>max</sub> = 0.46 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.45 e Å<sup>-3</sup>

Extinction correction: *F*<sup>\* = *F*(1 + 0.002*F*<sup>2</sup>/sin2θ)<sup>-1/4</sup></sup>

Extinction coefficient: 0.00016

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Lorentz-polarization corrections were applied in data collection. All non-H atoms were obtained by direct methods and difference Fourier synthesis. The structure was refined on *F*<sup>2</sup> by full-matrix least squares. All calculations were performed with *SHELXS86* (Sheldrick, 1985) on a VMS computer.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Cu	0.2547 (1)	0.0191 (1)	-0.0013 (1)	0.038 (1)
S(1)	0.1614 (1)	0.1516 (1)	-0.0064 (1)	0.046 (1)
S(2)	0.2021 (1)	-0.0909 (1)	-0.0907 (1)	0.050 (1)
S(3)	0.0294 (1)	0.1969 (2)	-0.1089 (1)	0.060 (1)
S(4)	0.0728 (1)	-0.0631 (2)	-0.1972 (1)	0.057 (1)
S(5)	0.3130 (1)	0.1334 (2)	0.0818 (1)	0.060 (1)
S(6)	0.3426 (1)	-0.1212 (1)	0.0103 (1)	0.049 (1)
S(7)	0.4325 (1)	0.0993 (2)	0.1980 (1)	0.078 (1)
S(8)	0.4647 (1)	-0.1787 (2)	0.1213 (1)	0.067 (1)
N	0.2415 (2)	0.5313 (4)	0.0888 (2)	0.036 (1)
C(1)	0.1227 (3)	-0.0038 (5)	-0.1179 (3)	0.040 (2)
C(2)	0.1062 (3)	0.1002 (5)	-0.0828 (3)	0.042 (2)
C(3)	-0.0534 (3)	0.1015 (6)	-0.0937 (3)	0.056 (2)
C(4)	-0.0740 (3)	0.0120 (6)	-0.1551 (3)	0.055 (2)
C(5)	-0.0210 (3)	-0.0961 (6)	-0.1623 (4)	0.054 (2)
C(6)	0.3973 (3)	-0.0712 (6)	0.0883 (3)	0.045 (2)
C(7)	0.3841 (3)	0.0378 (6)	0.1193 (3)	0.048 (2)
C(8)	0.5299 (4)	0.1106 (7)	0.1690 (4)	0.076 (3)
C(9)	0.5753 (4)	-0.0079 (7)	0.1729 (4)	0.071 (3)
C(10)	0.5551 (3)	-0.1017 (6)	0.1113 (4)	0.067 (3)
C(11)	0.2971 (3)	0.4600 (5)	0.0408 (3)	0.043 (2)
C(12)	0.3467 (3)	0.5356 (5)	-0.0100 (3)	0.046 (2)
C(13)	0.3931 (4)	0.4521 (6)	-0.0587 (4)	0.061 (3)
C(14)	0.4500 (4)	0.5248 (7)	-0.1043 (4)	0.084 (3)
C(15)	0.1847 (3)	0.6019 (5)	0.0387 (3)	0.042 (2)
C(16)	0.1423 (3)	0.5294 (5)	-0.0223 (3)	0.045 (2)
C(17)	0.0811 (3)	0.6104 (6)	-0.0586 (3)	0.053 (2)
C(18)	0.0377 (4)	0.5490 (6)	-0.1206 (4)	0.070 (3)
C(19)	0.1974 (3)	0.4415 (5)	0.1367 (3)	0.040 (2)
C(20)	0.2408 (3)	0.3858 (5)	0.2030 (3)	0.040 (2)
C(21)	0.1954 (3)	0.2811 (5)	0.2355 (3)	0.048 (2)
C(22)	0.2374 (4)	0.2256 (6)	0.3040 (4)	0.068 (3)
C(23)	0.2852 (3)	0.6231 (5)	0.1377 (3)	0.040 (2)
C(24)	0.2386 (3)	0.7063 (5)	0.1863 (3)	0.043 (2)
C(25)	0.2876 (3)	0.7755 (6)	0.2418 (3)	0.048 (2)
C(26)	0.2471 (4)	0.8761 (6)	0.2801 (4)	0.071 (3)

Table 2. Selected geometric parameters (Å, °)

Cu—S(1)	2.187 (2)	Cu—S(2)	2.180 (2)
Cu—S(5)	2.172 (2)	Cu—S(6)	2.183 (2)
S(1)—C(2)	1.743 (6)	S(2)—C(1)	1.749 (6)
S(3)—C(2)	1.768 (6)	S(3)—C(3)	1.816 (6)
S(4)—C(1)	1.767 (6)	S(4)—C(5)	1.813 (6)
S(5)—C(7)	1.748 (6)	S(6)—C(6)	1.756 (6)

S(7)—C(7)	1.752 (6)	S(7)—C(8)	1.805 (7)
S(8)—C(6)	1.759 (6)	S(8)—C(10)	1.812 (6)
C(1)—C(2)	1.331 (8)	C(3)—C(4)	1.503 (9)
C(4)—C(5)	1.512 (9)	C(6)—C(7)	1.335 (9)
C(8)—C(9)	1.521 (10)	C(9)—C(10)	1.534 (10)
S(1)—Cu—S(2)	91.7 (1)	S(1)—Cu—S(5)	89.4 (1)
S(2)—Cu—S(5)	175.8 (1)	S(1)—Cu—S(6)	175.5 (1)
S(2)—Cu—S(6)	88.2 (1)	S(5)—Cu—S(6)	91.0 (1)
Cu—S(1)—C(2)	102.9 (2)	Cu—S(2)—C(1)	102.9 (2)
C(2)—S(3)—C(3)	103.3 (3)	C(1)—S(4)—C(5)	103.8 (3)
Cu—S(5)—C(7)	103.8 (2)	Cu—S(6)—C(6)	103.3 (2)
C(7)—S(7)—C(8)	104.2 (3)	C(6)—S(8)—C(10)	104.1 (3)
S(2)—C(1)—S(4)	113.6 (3)	S(2)—C(1)—C(2)	121.1 (4)
S(4)—C(1)—C(2)	125.2 (4)	S(1)—C(2)—S(3)	114.9 (3)
S(1)—C(2)—C(1)	121.0 (4)	S(3)—C(2)—C(1)	124.1 (4)
S(3)—C(3)—C(4)	116.4 (4)	C(3)—C(4)—C(5)	115.5 (5)
S(4)—C(5)—C(4)	116.2 (4)	S(6)—C(6)—S(8)	114.1 (3)
S(6)—C(6)—C(7)	120.4 (4)	S(8)—C(6)—C(7)	125.4 (5)
S(5)—C(7)—S(7)	113.9 (4)	S(5)—C(7)—C(6)	120.3 (4)
S(7)—C(7)—C(6)	125.8 (5)	S(7)—C(8)—C(9)	115.5 (5)
C(8)—C(9)—C(10)	115.0 (6)	S(8)—C(10)—C(9)	115.3 (5)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71418 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1051]

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