# Bis(tetraethylammonium) bis(2-thioxo-1,3-dithiole-4,5-dithiolato)cuprate(II)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.019 Å
R factor = 0.051
wR factor = 0.118
Data-to-parameter ratio = 11.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title complex, $(C_8H_{20}N)_2[Cu(C_3S_5)_2]$, each Cu atom is tetracoordinated by four dmit S atoms (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate), forming a slightly distorted square-planar arrangement. The average Cu—S bond length is a little larger than the sum of the single-bond covalent radii. The S—Cu—S bond angles for the vicinal S atoms are somewhat larger than the typical right angle and the other two angles are much smaller than 180°. The $[Cu(dmit)_2]^{2-}$ anions and tetraethylammonium counter-cations form a layered arrangement in the crystal structure.

Comment

Over the past two decades, an enormous amount of research has gone into the synthesis and characterization of 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) complexes and related selenium- and oxygen-substituted analogues. As special π-electron conjugated systems, dmit and related ligands have been used in the assembly of highly electrically conducting radical anion salts and charge-transfer complexes. They are used as building blocks for organic, organometallic and coordination-complex electrical conductors and superconductors (Svenstrup & Becher, 1995; Cassoux, 1999; Pullen & Olk, 1999; Robertson & Cronin, 2002).

(I)
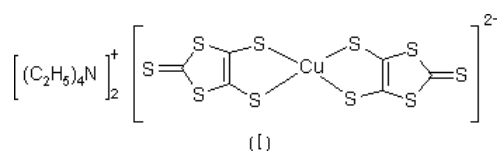
The π-electron delocalization in conjugated systems can also contribute to an ultrafast optical response capability and large third-order nonlinearity effects. Recently, many of these dmit complexes have been reported as possessing good
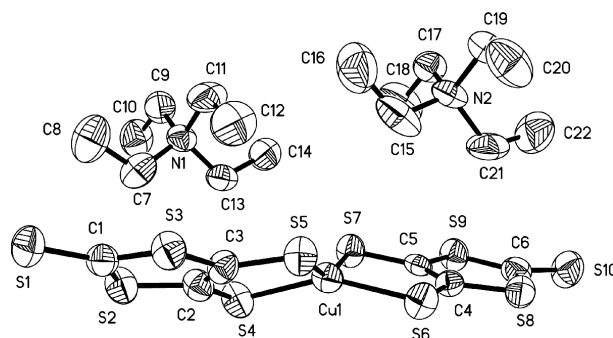
Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

second-order nonlinear (Fang *et al.*, 1994; Zhai *et al.*, 1999) and third-order nonlinear optical properties (Winter *et al.*, 1992; Zuo *et al.*, 1996; Wang *et al.*, 1999; Bai *et al.*, 1999; Dai *et al.*, 2000; Liu *et al.*, 2002). The title complex, (I), is a new salt of the general form $Q_2[M(dmit)_2]$ (M is a transition metal, and here, Q, the counter-cation, is NEt_4). (I) is also a novel nonlinear optical material.

In the structure of (I), (Fig. 1), dmit shows its typical behaviour as a bidentate ligand and the Cu^{2+} ion is coordinated by four S atoms from two dmit molecules in a distorted square-planar geometry. The Cu—S bond lengths (Table 1) range from 2.259 (3) to 2.292 (3) Å, with an average of 2.276 Å. All the Cu—S bond lengths are a little larger than the sum of the single-bond covalent radii and are similar to those found previously in the four-coordinate copper(II) complex $[(C_4H_9)_4N]_2[Cu(C_3S_5)_2]$ (Wang *et al.*, 1985). The S—Cu—S bond angles for the vicinal S atoms cover the range 92.66 (10)–94.14 (10)°, with an average value of 93.3°, and are noticeably larger than the nominal right angle. The other two S—Cu—S angles of 150.94 (12) and 153.19 (11)° are much smaller than 180°. Together, these data indicate a significant distortion from square-planar geometry.

The most striking physical characteristic of (I) is the extended electronically delocalized core, comprising the central Cu^{2+} ion, four S atoms and the adjacent C=C units. It has been shown that when Cu^{2+} takes the place of group 12 metal ions (Zn^{2+}, Cd^{2+} and Hg^{2+}), the electron delocalization is enhanced (Li *et al.*, 2003). This is thought to be due to the unfilled d electron shell of Cu^{2+}, which allows the possibility of low-energy charge-transfer transitions, and is an important contribution to optical nonlinearity. In particular, the $3p$ orbitals of S and $3d$ orbitals of Cu^{2+} can overlap to form a highly delocalized system. This delocalization will greatly enhance the hyperpolarizability and the nonlinear susceptibility, and lead to large third-order nonlinear optical properties.

The third-order nonlinear optical properties of (I) were measured by the Z-scan technique (Sheik-Bahae *et al.*, 1989, 1990) in a several-mM solution of acetone at 1064 nm. This revealed that the nonlinear refractive index n_2 of (I) was superior to that of CS_2.

Experimental

The synthesis of (I) involved a modification of literature methods (Steimeck & Kirmse, 1979; Wang *et al.*, 1998). To degassed dimethylformamide (DMF, 48 ml), CS_2 (24 ml) was added and the mixture was cooled to 273 K. Sodium (1.45 g) was added to the solution and the mixture was vigorously stirred with cooling until the reaction was complete. Several ml of MeOH was slowly added. To this solution, separate solutions of first $CuCl_2 \cdot 2H_2O$ (2.66 g) dissolved in 25–28% NH_3 (40 ml), and then Et_4NBr (6.60 g) in water (30 ml), were added consecutively with stirring at room temperature. The mixture was stirred overnight, and the product was isolated by filtration and washed with water and MeOH, affording black crystals of (I). The high optical-quality single crystals used for X-ray structure analysis were obtained by slow evaporation of an acetone solution.
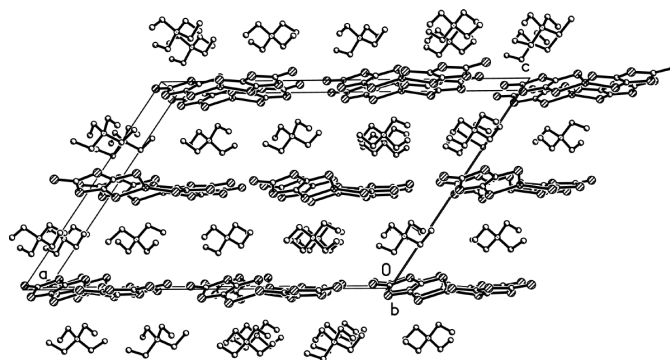
Figure 2
The crystal packing in (I), viewed along the b axis. H atoms have been omitted.

Crystal data

$(C_8H_{20}N)_2[Cu(C_3S_5)_2]$	$D_x = 1.455$ Mg m^{-3}
$M_r = 716.70$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 36
$a = 26.880 (4)$ Å	reflections
$b = 8.0090 (11)$ Å	$\theta = 10.3$–$12.5°$
$c = 18.294 (3)$ Å	$\mu = 1.32$ mm^{-1}
$\beta = 123.836 (8)°$	$T = 293 (2)$ K
$V = 3271.4 (8)$ Å^3	Plate, black
$Z = 4$	$0.43 \times 0.41 \times 0.02$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.060$
ω scans	$\theta_{max} = 27.0°$
Absorption correction: ψ scan	$h = -1 \rightarrow 34$
($XSCANS$; Bruker, 1996)	$k = -1 \rightarrow 10$
$T_{min} = 0.50$, $T_{max} = 0.97$	$l = -23 \rightarrow 19$
4357 measured reflections	3 standard reflections
3797 independent reflections	every 97 reflections
2119 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$wR(F^2) = 0.118$	$\Delta\rho_{min} = -0.38$ e Å^{-3}
$S = 0.95$	Extinction correction: $SHELXL97$
3797 reflections	Extinction coefficient: 0.00184 (14)
325 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	with 232 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2]$	Flack parameter = -0.01 (2)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.658 (10)	C4—S6	1.740 (9)
C1—S3	1.724 (10)	C5—S7	1.713 (10)
C1—S2	1.725 (10)	C5—S9	1.754 (9)
C2—C3	1.353 (12)	C6—S10	1.672 (10)
C2—S4	1.736 (10)	C6—S9	1.711 (10)
C2—S2	1.744 (11)	C6—S8	1.715 (11)
C3—S5	1.730 (10)	S4—Cu1	2.292 (3)
C3—S3	1.761 (10)	S5—Cu1	2.259 (3)
C4—C5	1.360 (12)	S6—Cu1	2.288 (3)
C4—S8	1.738 (9)	S7—Cu1	2.266 (3)
C2—S4—Cu1	98.5 (4)	S5—Cu1—S6	94.14 (10)
C3—S5—Cu1	98.8 (4)	S7—Cu1—S6	92.66 (10)
C4—S6—Cu1	99.6 (3)	S5—Cu1—S4	93.53 (10)
C5—S7—Cu1	99.6 (3)	S7—Cu1—S4	93.00 (10)
S5—Cu1—S7	150.94 (12)	S6—Cu1—S4	153.19 (11)

All H atoms were placed in idealized positions, with C—H = 0.97 Å for methylene groups and C—H = 0.96 Å for methyl groups, and refined as riding with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$(carrier) or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$(methyl carrier).

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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