

Syntheses, Characterization and Structural Studies of Copper Complexes of the 1,2-Dithiolene Ligand, 5,6-Dihydro-1,4-dithiin-2,3-dithiolate

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Abstract

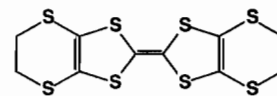
The synthesis and characterization of the Cu(II) and Cu(III) complexes of the ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT²⁻) are reported. Cu(DDDT)₂²⁻ was isolated as the tetraethylammonium salt from the reaction of CuCl₂·2H₂O with K₂DDDT in thoroughly degassed 1/1 ethanol/water under an Ar atmosphere. Cu(DDDT)₂²⁻ was isolated as both the tetrabutylammonium and trimethylammonium salts from similar reactions in the presence of air. Single crystal structural studies have been carried out on the two formally Cu(III) complexes. Crystals of the tetrabutylammonium salt of Cu(DDDT)₂²⁻ belong to the monoclinic space group *P*2₁/*c* with *a* = 17.937(2), *b* = 8.806(1), *c* = 21.962(3) Å, β = 109.8(1)°, *R* = 7.6% for 2984 reflections, and ρ(calc.) = 1.36, ρ(obs.) = 1.34 g/cm³ for *Z* = 4. Crystals of the trimethylammonium salt of Cu(DDDT)₂²⁻ belong to the orthorhombic space group *Pn*nm with *a* = 9.211(2), *b* = 10.114(3), *c* = 10.956(4) Å, *R* = 6.3% for 443 reflections, and ρ(calc.) = 1.58, ρ(obs.) = 1.58 g/cm³ for *Z* = 2. While the CuS₄ core exhibits the *D*_{2h} symmetry expected for the trimethylammonium salt, that of the tetrabutylammonium salt is distorted with a twist angle of 29° between the two CuS₂ planes. A solution and frozen glass ESR study of Cu(DDDT)₂²⁻ yielded *g* value assignments of *g*_{||} = 2.101(1), *g*_⊥ = 2.042(1) and ⟨*g*⟩₀ = 2.069(1) as well as the hyperfine splitting values (in cm⁻¹ × 10⁻⁴) of *A*_{||} = 142.3(5), *A*_⊥ = 33.4(5) and ⟨*A*⟩₀ = 68.6(5). The electrochemical behavior of Cu(DDDT)₂²⁻ indicates that material is plating out on the electrode surface at potentials more positive than *E*_{1/2} for the 0 ↔ -1 couple.

Introduction

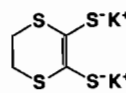
Over the past sixteen years the organic chemistry of sulfur has been highly influenced by the unique

physical properties of tetrathiafulvalene (TTF) [1–4]. Synthesis of the charge transfer salt TTF-TCNQ, resulted in the first report of an 'organic metal' [4]. The discovery of superconductivity in the Bechgaard salts [5–7] based on selenium, (TMTSF)₂X where X = PF₆⁻, ClO₄⁻, AsF₆⁻, was the impetus for the massive research effort that has led to the synthesis of the sulfur based superconductor (BEDT-TTF)₂ReO₄ (*T*_c ~ 1.4 K at 4 kbar) [8]. Substitution of various anions for rhenate has resulted in two superconducting salts at ambient pressure, β-(BEDT-TTF)₂I₃ [9] and (BEDT-TTF)₂IBr₂ [10], where *T*_c ~ 1.5 and 2.7 K, respectively. These compounds led to the proposal by Wudl [11] that the TTF framework possesses the prerequisite properties necessary to yield organic metals. At the same time, there has been a great deal of interest in inorganic complex based conducting species such as the partially oxidized tetracyanoplatinates [12]. We have designed a synthetic program to combine the properties of the 'TTF type' organosulfur molecules and inorganic systems.

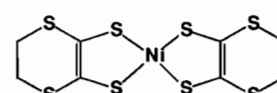
We have reported the synthesis of 1,2-dithiolene 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT²⁻) isolated as the potassium salt [13]. The study of the coordination chemistry of the ligand has resulted in the synthesis of square planar complexes of the general formula M(DDDT)₂²⁻ where M = Ni, Pd, Pt, Co [13–15], precipitated as tetraalkylammonium salts. A crystallographic analysis [13] showed the Ni(DDDT)₂²⁻ anion in [(C₂H₅)₄N][Ni(DDDT)₂] to have structural features quite similar to BEDT-TTF [8]. Magnetization measurements of this Ni complex



BEDT-TTF



K₂DDDT



Ni(DDDT)₂²⁻

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showed long-range antiferromagnetic interactions due to the layered structure that allows for some close sulfur–sulfur contacts [13]. These observations have led us to continue to study complexes of this ligand.

The requirements for the metallic state, both structural and electronic, have been addressed in several reviews [16–19]. A structural investigation of DDDT^{2-} complexes has resulted in crystallographic determinations for $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Co}(\text{DDDT})_2]_2$ [15], $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Pt}(\text{DDDT})_2]$ [20] and three different salts of $\text{Ni}(\text{DDDT})_2^{2-}$, tetraethylammonium [13], tetrabutylammonium [21] and tetramethylammonium [22]. In addition, a polymorph of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ni}(\text{DDDT})_2]$ has been reported as well as the structure of a neutral Au species [23]. These structures showed various motifs of crystal packing such as sheets, layers, columns, stacks and anion pairs, with the closest S–S contacts occurring in the Co structure which is dimeric [15]. A similar study of complexes with dmit^{2-} (2-thioxo-1,3-dithiole-4,5-dithiolate) has yielded highly conductive partially oxidized complexes of nickel with tetraalkylammonium cations as counterions [24, 25]. More recently, the reaction of TTF with $\text{Ni}(\text{dmit})_2$ has produced a complex that is superconducting under pressure [26, 27]. Thus, the role of the counterion has been established.

In a continuation of this work, the Cu(II) and Cu(III) complexes of DDDT^{2-} have been synthesized. We report here the syntheses and physical properties of these complexes as well as the structures of the tetrabutylammonium and trimethylammonium salts of $\text{Cu}(\text{DDDT})_2^{2-}$.

Experimental

Reagents

2,5,7,9-Tetrathiabicyclo[4.3.0]non-1(6)-en-8-on (TTBEO) was prepared by literature methods [28] and characterized by NMR and MP. Tetrabutylammonium perchlorate and cupric chloride were purchased from Fisher Scientific and were used without further purification. Tetrabutylammonium iodide, tetramethylammonium bromide, and tetraethylammonium bromide were purchased from Aldrich Chemicals and dried *in vacuo* prior to use. Argon was purchased from Air Products, Inc. All solvents were dried by standard techniques and freshly distilled prior to use. Water and ethanol were thoroughly degassed by successive freeze–thaw cycles when oxygen-free solvents were required. K_2DDDT was prepared as described earlier [13].

Procedures

Analytical analyses were performed by Atlantic Microlabs, Atlanta, GA.

Syntheses

$[N(\text{C}_4\text{H}_9)_4][\text{Cu}(\text{C}_4\text{H}_4\text{S}_4)_2]$

A solution of 0.33 g (2×10^{-3} mol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of H_2O was added dropwise to 1 g (3.9×10^{-3} mol) of K_2DDDT in 50 ml of basic 1:1 ethanol/ H_2O . The solution color immediately turned purple and was allowed to stir for 1 h after which 1 equivalent of tetrabutylammonium iodide in 25 ml of ethanol was added, and a dark blue–black precipitate formed. The solid was collected by filtering and recrystallized from acetone/isopropanol, yielding 0.33 g (25%) of pure product as dark purple–black crystalline plates (melting point (m.p.) 169–171 °C). *Anal.* Calc. for $\text{CuC}_{24}\text{H}_{44}\text{NS}_8$: C, 43.24; H, 6.65; N, 2.10; S, 38.47. Found: C, 43.27; H, 6.70; N, 2.08; S, 38.30%. IR(KBr) 1472(s), 1411(m), 1385(s), 1288(s), 1169(m), 1125(m), 1035(m), 970(w), 918(s), 879(m), 735(m), 411(s), 370(s).

$[N(\text{C}_2\text{H}_5)_4][\text{Cu}(\text{C}_4\text{H}_4\text{S}_4)_2]$

The procedure followed was identical to that described above with the following exceptions: degassed solvents were used, the reaction was carried out under Ar, and tetraethylammonium bromide was used to precipitate the product. Due to the extreme ease of oxidation of the product it was not recrystallized. The compound was isolated as a blue–black powder in 25% yield. *Anal.* Calc. for $\text{CuC}_{24}\text{H}_{48}\text{N}_2\text{S}_8$: C, 42.13; H, 7.01; N, 4.09; S, 37.48. Found: C, 42.25; H, 7.11; N, 4.16; S, 37.60%. IR(KBr) 1485(s), 1450(s), 1390(s), 1275(m), 1180(m), 1170(s), 1120(w), 1021(m), 1000(s), 911(m), 871(w), 830(m), 780(s), 405(m), 320(m).

$[N(\text{CH}_3)_3\text{H}][\text{Cu}(\text{C}_4\text{H}_4\text{S}_4)_2]$

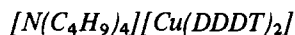
The procedure followed was identical to that of the tetrabutylammonium complex except that 1 equivalent of tetramethylammonium bromide in 25 ml of H_2O was added to precipitate the complex. Apparently the tetramethylammonium salt was contaminated with trimethylamine or trimethylammonium bromide since the complex we isolated had trimethylammonium as the counterion. Yield = 0.16 g, 17% (m.p. 150–152 °C). *Anal.* Calc. for $\text{CuC}_{11}\text{H}_{18}\text{NS}_8$: C, 27.30; H, 3.75; N, 2.89. Found: C, 27.50; H, 3.81; N, 2.80%.

Physical Measurements

All electrochemical measurements were performed by using a BAS CV27 instrument. The electrochemical cell used for cyclic voltammetry employed a platinum working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl reference electrode. Measurements were made on DMF solutions containing 10^{-3} M $\text{Cu}(\text{DDDT})_2^{2-}$ with use of 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Nitrogen was passed for 15 min prior to

taking the measurements. ESR spectra were recorded on a Varian E-3 spectrometer at room temperature and at 100 K. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–300 cm^{-1} . Data were obtained either from KBr pellets or nujol mulls.

Single-crystal X-ray Analysis



Purple rod-shaped crystals, later ground to a sphere, suitable for X-ray analysis, were grown by the slow evaporation of a 5/1 acetone/isopropanol solution. The crystal survey, unit cell dimension determination, and data collection were accomplished on a Syntex P1 diffractometer with the use of copper radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The diffractometer was equipped with a graphite incident-beam monochromator mounted in the perpendicular mode. Final unit cell dimensions were obtained by a least-squares fit of 15 high-angle reflections ($2\theta > 40^\circ$). Systematic absences indicated that the crystal belonged to the monoclinic space group $P2_1/c$ ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). A one Angstrom intensity data set was collected (maximum $\sin \theta/\lambda = 0.5$). One check reflection was monitored every 30 reflections and revealed no unexpected variation in intensity. Details of the crystal survey and data collection parameters are summarized in Table 1.

The diffractometer output and all subsequent crystallographic calculations were processed using subprograms of the CRYM crystallographic computer system [29]. The data processing included corrections for Lorentz and background effects. Polarization due to the monochromator was corrected for by a method suggested by Azaroff [30]. Diffraction data were corrected for absorption by spherical absorption correction [31]. Data processing included the calculation of F^2 and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equation

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$$

where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio.

Finally, the data set was placed on an approximately absolute scale by Wilson statistics [32]. Atomic scattering factors for carbon, nitrogen and sulfur were taken from the International Tables for X-ray Crystallography [33], for copper from Cromer and Mann [34], and for hydrogen from Stewart *et al.* [35]. The scattering factors for sulfur and copper were corrected for the real and imaginary components of anomalous dispersion.

TABLE 1. Single crystal X-ray crystallographic analysis

Crystal parameters		
Formula	CuC ₂₄ H ₄₄ NS ₈ (665.65)	CuC ₁₁ H ₁₈ NS ₈ (484.3)
Crystallization medium	acetone/isopropanol	acetone/isopropanol
Crystal size (mm)	spheres, 0.075	0.07 × 0.09 × 0.27
Cell dimensions	$a = 17.937(2) \text{ \AA}$ $b = 8.806(1) \text{ \AA}$ $c = 21.962(3) \text{ \AA}$ $\alpha = 90.0^\circ$ $\beta = 109.8(1)^\circ$ $\gamma = 90.0^\circ$ $V = 3263.63(47) \text{ \AA}^3$	$a = 9.211(2) \text{ \AA}$ $b = 10.114(3) \text{ \AA}$ $c = 10.956(4) \text{ \AA}$ $\alpha = 90.0^\circ$ $\beta = 90.0^\circ$ $\gamma = 90.0^\circ$ $V = 1020.65(52) \text{ \AA}^3$
Space group	$P2_1/c$	$Pnmm$
Molecules/unit cell	4	2
Density (obs.) (g/cm^3)	1.34	1.58
Density (calc.) (g/cm^3)	1.36	1.58
Linear absorption coefficient (cm^{-1})	56.3	18.7
μ_+ max.		0.548
μ_+ min.		0.131
Refinement parameters		
No. reflections	3354	588
Non-zero reflections ($I > 3.0\sigma(I)$)	2984	443
R index = $\Sigma F_o - F_c /\Sigma F_o $	0.076	0.063
$R_w = \Sigma(w^2 F_o ^2 - F_c ^2)^2/\Sigma w^2 F_o ^4$	0.018	0.008
$GOF = [\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$	3.01	1.84
Scale factor	0.853(3)	0.851(1)
Secondary extinction coefficient	$0.5(1) \times 10^{-6}$	

The positions of the copper and the eight sulfur atoms were determined by using the MULTAN program [36]. The remaining non-hydrogen atoms were located by conventional difference Fourier techniques to give a trial structure. Hydrogen positions were calculated wherever possible. With the exception of the last two carbon atoms of one butyl chain in the counterion, the structure refined routinely. These two atoms were fit by population analysis to two different positions of almost equal populations. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full matrix least-squares contained the scale factor, secondary extinction coefficient, coordinates, and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all less than their corresponding standard deviation for the copper dithiolene and less than 0.25 for the counterion. A final difference Fourier revealed no missing or misplaced electron density.

[N(CH₃)₃H][Cu(DDDT)₂]

Purple rod-shaped crystals suitable for X-ray analysis were grown by slow evaporation of a 5/1

acetone/isopropanol solution. Data collection and reduction were carried out as above with the following changes. Molybdenum radiation ($\lambda = 0.71069 \text{ \AA}$) was used. Final unit cell dimensions were obtained from a least-squares fit of 15 high angle reflections ($2\theta > 20^\circ$). Systematic absences indicated that the crystal belonged to either the orthorhombic space group *Pnn2* or *Pnmm* ($0kl, k+l=2n+1; h0l, h+l=2n+1$). The latter was confirmed as the correct space group by the successful refinement of the structure.

As with the tetrabutylammonium salt, we encountered a disorder problem with the trimethylammonium complex. The counterion occupied two positions, one up and one down, in a 50/50 ratio. After accounting for this the structure refined routinely. No attempt was made to locate the methyl hydrogens.

The refined structures were plotted using the ORTEP program of Johnson [37]. See also 'Supplementary Material'.

Stereoviews of $[N(C_4H_9)_4][Cu(DDDT)_2]$ and $[N(CH_3)_3H][Cu(DDDT)_2]$ with labeling of atoms are shown in Figs. 1 and 2, respectively. Due to the large thermal parameters of some of the carbon atoms in the butyl chain of $[N(C_4H_9)_4][Cu(DDDT)_2]$,

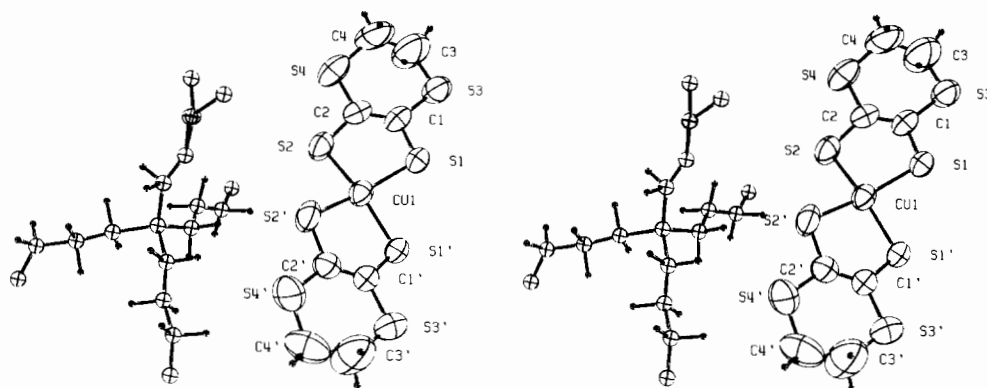


Fig. 1. Stereo ORTEP of $[N(C_4H_9)_4][Cu(DDDT)_2]$.

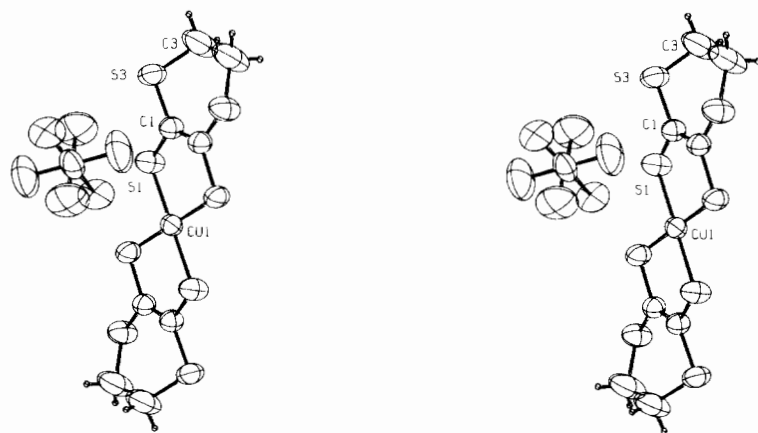


Fig. 2. Stereo ORTEP of $[N(CH_3)_3H][Cu(DDDT)_2]$.

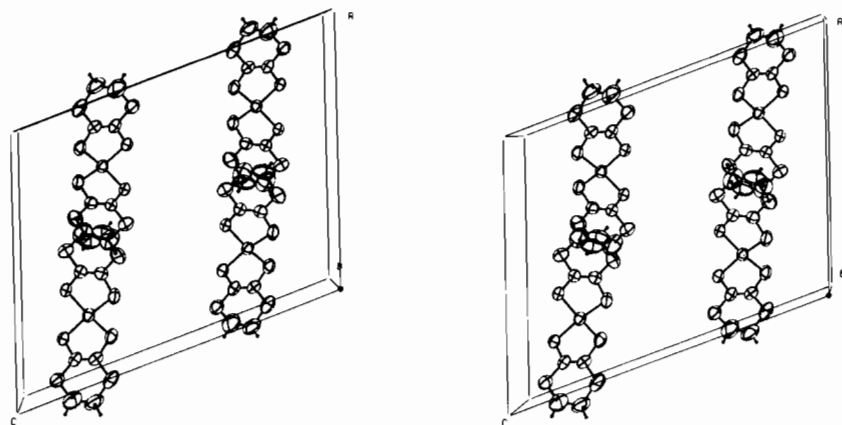


Fig. 3. Stereoview of molecular packing of $[N(C_4H_9)_4][Cu(DDDT)_2]$ with counterions removed.

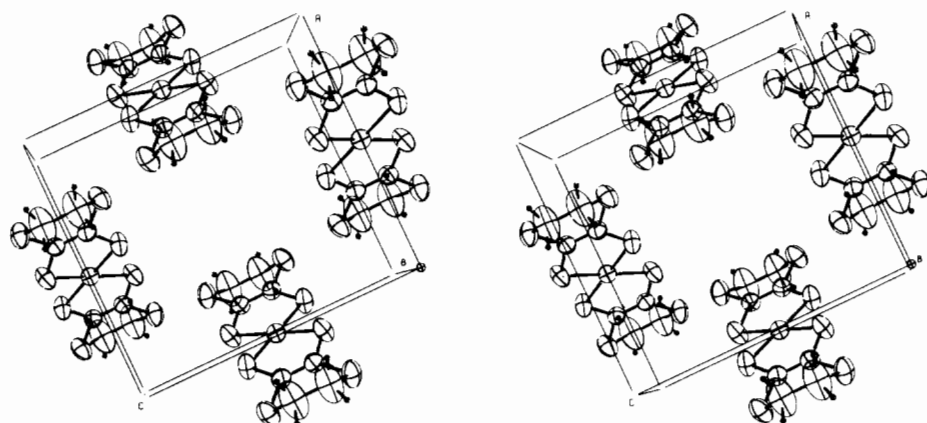


Fig. 4. Stereoview of molecular packing of $[N(CH_3)_3H][Cu(DDDT)_2]$ with counterions removed.

isotropic temperature factors of 12.0 were used in its ORTEP plots. Stereoviews of molecular packing for both structures, with counterions removed for clarity, are shown in Figs. 3 and 4. Lists of intermolecular contacts are given in Table 2. Bond lengths and bond angles for the tetrabutylammonium and trimethylammonium salts are given in Tables 3 and 4. Atomic coordinates for both structures of $Cu(DDDT)_2^-$ are shown in Tables 5 and 6.

Results and Discussion

The synthesis of the formally copper(III) complex of $DDDT^{2-}$ has been achieved. This complex has been isolated as the tetrabutylammonium and trimethylammonium salts. These compounds were made by addition of aqueous solutions of Cu(II) to basic 1/1 (ethanol/ H_2O) solutions of $DDDT^{2-}$. If the ligand solutions were not basic only insoluble metal sulfides were obtained. This is in contrast to other synthetic procedures we have used to prepare other

TABLE 2. Intermolecular contacts for $Cu(DDDT)_2^-$ in A

Tetrabutylammonium counterion		Trimethylammonium counterion	
Cu(A)-Cu(B)	10.91(1)	Cu(A)-Cu(B)	8.75(1)
Cu(A)-Cu(C)	10.34(1)	Cu(A)-Cu(C)	10.10(1)
Cu(A)-Cu(D)	11.50(1)	Cu(B)-Cu(D)	14.29(1)
S3'(A)-S4'(C)	5.11(1)	S3(A)-S3(B)	6.18(1)
S4'(A)-S3'(C)	4.47(1)	S3(A)-S3(E)	7.15(1)

Symmetry operations

A = x, y, z	A = x, y, z
B = $\bar{x}, \bar{y}, \bar{z}$	B = $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$
C = $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	C = x + 1, y, z
D = $x, \frac{1}{2} - y, z + \frac{1}{2}$	D = $x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$
	E = $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

metal complexes of $DDDT^{2-}$. Even with basic ligand solutions the yields for the copper complexes were significantly lower than those for other complexes.

TABLE 3. Bond lengths (Å) and bond angles (°) for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Cu}(\text{DDDT})_2]$

Distances		Angles	
Cu1-S1	2.184(3)	S2-Cu1-S1	92.6(1)
Cu1-S2	2.185(3)	S1'-Cu1-S1	90.3(1)
Cu1-S1'	2.179(3)	S2'-Cu1-S1	160.0(1)
Cu1-S2'	2.176(3)	S1'-Cu1-S2	162.3(1)
S1-C1	1.748(9)	S2'-Cu1-S2	90.9(1)
S2-C2	1.741(9)	S2'-Cu1-S1'	92.3(1)
S3-C1	1.749(9)	C1-S1-Cu1	102.5(3)
S3-C3	1.775(15)	C2-S2-Cu1	102.0(3)
S4-C2	1.764(9)	C3-S3-C1	104.6(5)
S4-C4	1.787(13)	C4-S4-C2	101.8(5)
S1'-C1'	1.695(9)	C1'-S1'-Cu1	102.3(3)
S2'-C2'	1.743(10)	C2'-S2'-Cu1	102.2(3)
S3'-C1'	1.771(10)	C3'-S3'-C1'	107.0(6)
S3'-C3'	1.691(16)	C4'-S4'-C2'	102.5(6)
S4'-C2'	1.746(10)	S3-C1-S1	111.8(5)
S4'-C4'	1.755(15)	C2-C1-S1	120.4(7)
C1-C2	1.342(12)	C2-C1-S3	127.7(7)
C3-C4	1.432(19)	S4-C2-S2	111.9(5)
C1'-C2'	1.342(12)	C1-C2-S2	122.1(7)
C3'-C4'	1.433(22)	C1-C2-S4	125.9(7)
		C4-C3-S3	116.6(11)
		C3-C4-S4	115.4(10)
		S3'-C1'-S1'	113.1(5)
		C2'-C1'-S1'	122.9(7)
		C2'-C1'-S3'	124.0(7)
		S4'-C2'-S2'	112.2(5)
		C1'-C2'-S2'	120.1(7)
		C1'-C2'-S4'	127.7(8)
		C4'-C3'-S3'	121.9(12)
		C3'-C4'-S4'	117.7(11)

TABLE 4. Bond lengths (Å) and bond angles (°) for $[\text{N}(\text{CH}_3)_3\text{H}][\text{Cu}(\text{DDDT})_2]$

Distances		Angles	
Cu1-S1	2.185(3)	C1-S1-Cu1	101.7(3)
S1-C1	1.741(8)	C3-S3-C1	101.1(5)
S3-C1	1.772(8)	S3-C1-S1	114.0(4)
S3-C3	1.744(10)	S1-Cu1-S1	91.8(2)
C1-C1	1.320(13)	C1-S3-C3	122.3(12)
C3-C3	1.346(14)	C1-C1-S3	124.5(7)
N1-CC1	1.530(35)	C1-C1-S1	121.5(7)
N1-CC2	1.463(24)		

The copper(II) complex of DDDT^{2-} was synthesized following the same procedure as above except the reaction was carried out under an argon atmosphere with thoroughly degassed solvents. This complex is rapidly oxidized in solution to the copper(III) species by exposure to O_2 . Because of this, degassed solvents were necessary for the characterization of this complex by ESR spectroscopy.

TABLE 5. Atomic coordinates ($\times 10^4$) for $[\text{N}(\text{CH}_3)_3\text{H}][\text{Cu}(\text{DDDT})_2]$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu1	5000(0)	0(0)	5000(0)
S1	6510(3)	608(3)	6432(2)
S3	9037(3)	2390(3)	6519(2)
C1	7797(8)	1492(8)	5603(7)
C3	10594(10)	2337(15)	5614(9)
N1	5000(0)	5000(0)	5000(0)
CC1	5520(31)	6436(35)	5000(0)
CC2	3899(31)	5369(24)	5901(17)

TABLE 6. Atomic coordinates ($\times 10^4$) for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Cu}(\text{DDDT})_2]$

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu1	7491(1)	9432(1)	2256(1)
S1	7948(1)	9767(3)	1462(1)
S2	8488(2)	10637(3)	2943(1)
S3	9258(2)	11375(4)	1269(1)
S4	9928(2)	12086(4)	2909(1)
S1'	6323(1)	8905(3)	1566(1)
S2'	7224(2)	8332(3)	3045(1)
S3'	4993(2)	7037(4)	1558(1)
S4'	5905(2)	6641(5)	3183(2)
C1	8799(5)	10853(9)	1824(4)
C2	9049(5)	11129(10)	2463(4)
C3	10103(8)	12433(18)	1731(7)
C4	10496(6)	11937(15)	2382(6)
C1'	5921(5)	7829(11)	2016(4)
C2'	6277(5)	7610(11)	2654(4)
C3'	4623(8)	6205(19)	2088(7)
C4'	4882(8)	6625(15)	2758(7)
N	7461(4)	9708(9)	5226(3)
C5	6769(11)	8633(25)	5008(7)
C6	6088(7)	8309(15)	4951(5)
C7	5454(11)	7295(21)	4733(6)
C8	4742(7)	7048(16)	4667(6)
C9	7311(10)	10896(20)	4689(8)
C10	7687(9)	12074(19)	4597(13)
C11	7544(12)	13361(23)	4194(9)
C12	7921(11)	14398(20)	4050(10)
C13	7457(8)	10239(21)	5870(6)
C14	7400(10)	10122(23)	6392(8)
C15	7410(8)	10631(14)	6968(5)
C16	6829(8)	11257(17)	7139(8)
C17	8225(11)	8954(20)	5273(10)
C18	8693(10)	8497(19)	5053(8)
C19 ^a	9441(23)	7147(27)	5104(15)
C20 ^a	10080(20)	7753(51)	5212(19)
C21 ^a	9345(17)	7920(34)	5091(18)
C22 ^a	9702(21)	7366(56)	4692(20)

^aThese carbons have populations of 0.5.

The ESR spectrum of $\text{Cu}(\text{DDDT})_2^{2-}$ was measured in DMF at room temperature and in DMF/ CH_2Cl_2 at 100 K. In the solution spectrum the hyperfine lines

TABLE 7. ESR results for copper dithiolenes

	g_{iso}^a	g_{\parallel}^a	g_{\perp}^a	A_{iso}^b	A_{\parallel}^b	A_{\perp}^b	P/P_0	K	Reference
Cu(DDDT) $_2^{2-}$	2.069	2.1010	2.0416	68.6	142.3	33.4	0.404	0.555	this work
Cu(mnt) $_2^{2-}$	2.044	2.082	2.024	72.9	154.5	37.9	0.457	0.555	39
Cu(dmit) $_2^{2-}$	2.052	2.099	2.0235	67.0	156.0	35.2	0.450	0.527	41

^aStandard deviations of g values are 0.001. ^bHyperfine splitting values in units of $\text{cm}^{-1} \times 10^{-4}$ with standard deviations of 0.5.

due to ^{63}Cu and ^{65}Cu are resolved in the high field (3/2) transition. By analogy to $\text{Cu}(\text{mnt})_2^{2-}$ [38], we have assigned a ground state $^2B_{1g}[\dots(xy)^4]$ to the $S = 1/2$ $\text{Cu}(\text{DDDT})_2^{2-}$ complex. We confirmed this using the equations developed by Maki *et al.* [39] for a d_{xy} ground state which relate g and A values to the bonding parameters P and K through configurational excitation energies C_i . Using this treatment we found the d_{xy} ground state most reasonable for $\text{Cu}(\text{DDDT})_2^{2-}$. This is in agreement with the results obtained by Maki *et al.* for $\text{Cu}(\text{mnt})_2^{2-}$ [39].

By using the reduction of P from its free ion value ($P_0 \sim 3.5 \times 10^{-2} \text{ cm}^{-1}$) [40] as a measure of covalency, the ratio P/P_0 was calculated, which is a measure of the metal spin density. A summary of these results is shown in Table 7. As can be seen from the P/P_0 value of 0.40 for $\text{Cu}(\text{DDDT})_2^{2-}$ it is apparent that there is significant delocalization of electron density in the ground state. This same highly delocalized HOMO has been found for other copper dithiolene complexes.

$\text{Cu}(\text{DDDT})_2^-$ displays a very rich IR spectrum with all of the characteristic absorptions of monoanionic copper dithiolenes present [42]: ν_1 , 'C=C' at 1472 cm^{-1} ; ν_2 , 'C=C' at 1169 cm^{-1} ; ν_3 , 'R-C-S' at

879 cm^{-1} ; and ν_4 and ν_5 , 'M-S' at 411 and 370 cm^{-1} , respectively.

$\text{Cu}(\text{DDDT})_2^-$ has shown some unusual and interesting redox behavior. A great deal of data are available concerning the monoanion to dianion redox couples for copper dithiolenes [42]. However, little if any data can be found concerning the neutral to monoanion couples for these compounds. It is this couple which has proven to be quite interesting in $\text{Cu}(\text{DDDT})_2^-$.

The mono to dianion couple for $\text{Cu}(\text{DDDT})_2^-$ ($E_{1/2} = -0.49 \text{ V}$) shows the classic one electron reversible behavior typical of metal dithiolenes (scans from 0 to -1.0 V). This wave shows no change in behavior with multiple scans. Repeated scans through the monoanion to neutral couple reveals a one electron irreversible process ($E_p = 0.38 \text{ V}$, scans from 0 to $+1.0 \text{ V}$). This alone is rather unusual, since in almost all cases reversible behavior is seen.

If we monitor the cathodic current while changing the switching potential to more and more positive

values we begin to see an unusual phenomenon. As the switching potential enters the range of the monoanion to neutral couple we observe a growth of cathodic current at potentials slightly more positive than the $E_{1/2}$ value for the mono to dianion couple. As this switching potential becomes more and more positive the growth in cathodic current becomes larger and its peak value moves to more negative potentials. As this is occurring the peak current of the monoanion to dianion wave is also increasing and eventually moves to more negative potentials. It is interesting to note that even as these large increases in cathodic current occur there is no change in the anodic current of either the dianion to monoanion wave or the monoanion to neutral wave. A cyclic voltammogram showing the effect of increasing the switching potential to more positive values is shown in Fig. 5, and a summary of some electrochemical results for selected copper dithiolenes is given in Table 8.

At this time we do not have a complete explanation for the redox behavior of $\text{Cu}(\text{DDDT})_2^-$. However, we can qualitatively rationalize some of its behavior. It appears that oxidation to the neutral species causes material to plate out on the electrode surface. This material can be removed by large negative overpotentials. As more material plates out on the electrode (i.e. more positive switching potentials) greater and greater negative overpotentials are required to remove it. Since we do not see any change in the anodic current, the reduced material must be rapidly diffusing away from the electrode surface. The large overpotentials required

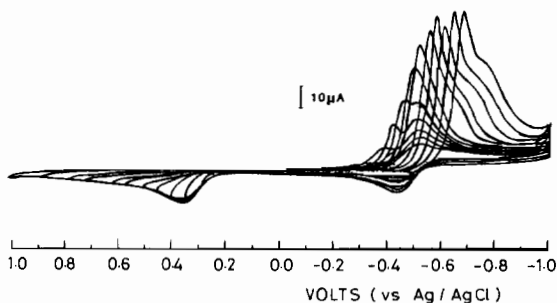
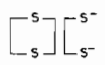
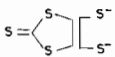
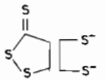
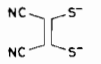


Fig. 5. Repeated scans of $\text{Cu}(\text{DDDT})_2^-$ with switching potential starting at 0.0 V and changing 5 mV more positive after each scan.

TABLE 8. Electrochemical results of copper dithiolenes

Ligand	$E_{1/2}$ (V)		Reference
	$n: -1 \rightleftharpoons -2$	$n: 0 \rightleftharpoons -1$	
	-0.49	+0.38 ^a	this work ^b
	-0.07		43 ^c
	+0.09		43 ^c
	+0.37		42

^a E_p , ^bDMF, vs. Ag/AgCl, 100 mV/s. ^cCH₃CN, vs. SCE, 0 \leftrightarrow -1 not reported.

to reduce the material on the electrode surface may be due to an IR drop caused by an insulating material coating the electrode surface. Further studies of these systems are currently being undertaken.

Over the years there has been a great deal of interest in the structures of metal dithiolenes [44]. Since the mid 1960s many single crystal X-ray diffraction studies have been carried out on these complexes although only one structure of a copper(III) dithiolenes has been reported. The structure of the tetrabutylammonium salt of Cu(mnt)₂⁻ was reported in 1964 by Forrester and coworkers [45]. In this work we are reporting the structures of the tetrabutylammonium and trimethylammonium salts of Cu(DDDT)₂⁻.

The gross geometry of [N(CH₃)₃H][Cu(DDDT)₂] is very similar to that of Cu(mnt)₂⁻. That is, the local CuS₄ symmetry is *D*_{2h}, the C=C chelate bond distance of 1.32(1) Å, and most of the other bond distances and angles are very similar to those of Cu(mnt)₂⁻. However, the Cu-S distance of 2.185(3)

Å is considerably longer than the 2.170(3) Å found in Cu(mnt)₂⁻. This difference is very difficult to explain. Unlike Cu(mnt)₂⁻, which has stacks of anions with close (4.5 Å) Cu-Cu distances, [N(CH₃)₃H][Cu(DDDT)₂] has a stacked structure along the *b* axis with Cu-Cu distances of 10.1 Å with trimethylammonium ions sandwiched in between each anion. This can be seen from Fig. 4 which has the trimethylammonium (in the center of the box) removed for clarity. Columns of alternating cations and anions were also present in the structure of [N(CH₃)₄][Ni(DDDT)₂] which has a small counterion [22]. An interesting perspective of [N(CH₃)₃H][Cu(DDDT)₂] is shown in Fig. 6 and illustrates the planar CuS₄ core.

Due to crystal packing forces the symmetry of the CuS₄ unit in [N(C₄H₉)₄][Cu(DDDT)₂] is distorted from *D*_{2h} symmetry by 29°. This twist angle can be seen in Fig. 7. All of the other bond distances and angles found in [N(C₄H₉)₄][Cu(DDDT)₂] are very close to those found in both Cu(mnt)₂⁻ and [N(CH₃)₃H][Cu(DDDT)₂]. Inspection of the packing diagram of [N(C₄H₉)][Cu(DDDT)₂] (Fig. 3) reveals a layered structure parallel to the *a* axis. This is similar to the layered structure found in Ni(DDDT)₂⁻ [13]. A summary of important bond distances in these complexes is given in Table 9.

Our interests in the crystal structures of these two tetraalkylammonium salts of Cu(DDDT)₂⁻ stems from the importance of crystal packings in determining the electrical conductivity properties of organic metals. It is well established that high conductivities require close intermolecular contacts between molecules in stacks, sheets or three dimensional networks. We were curious to see the effect of varying cation size on the Cu-Cu distances and S-S distances in these two compounds. In a previous paper [13] we observed close (<4 Å) S-S contacts in the tetraethylammonium salt of Ni(DDDT)₂⁻. In this work we chose one ammonium salt larger than tetraethylammonium and one smaller to crystallize Cu(DDDT)₂⁻. As is apparent from Table 2 there are no close Cu-Cu distances in either complex. It was

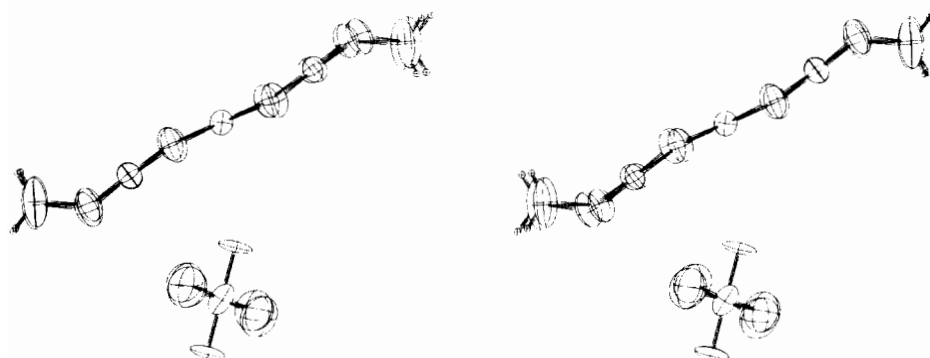


Fig. 6. Edge on stereo ORTEP of [N(CH₃)₃H][Cu(DDDT)₂].

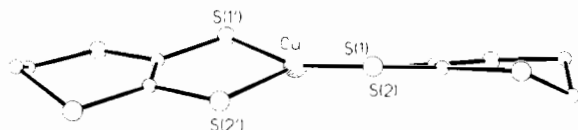


Fig. 7. View of $[N(C_4N_9)_4][Cu(DDDT)_2]$ showing the 29° twist angle of each half of the molecule with respect to the other.

TABLE 9. Selected bond distances of CuL_2^- complexes

L	M-S	S-C	C-C
mnt	2.170(4)	1.72(1)	1.32(2)
DDDT ^a	2.185(3)	1.741(8)	1.32(1)
DDDT ^b	2.184(3)	1.748(9)	1.34(1)
	2.176(3)	1.695(9)	1.34(1)
	2.185(3)	1.74(1)	
	2.179(3)	1.741(9)	

^aTrimethylammonium salt. ^bTetramethylammonium salt.

rather surprising to find that the complex with the much larger tetrabutylammonium counterion has closer S-S intermolecular distances than does the complex with trimethylammonium as the counterion. This occurs despite the fact that the unit cell volume is three times smaller in the trimethylammonium complex. The closest S-S contact in the tetrabutylammonium complex (4.47 Å) is still not as short as those observed in the tetraalkylammonium salts of $Ni(DDDT)_2^-$ [13, 21, 22], the neutral Au species [23] or the Co dimer [15]. From this information it is apparent that smaller counterions do not guarantee closer intermolecular contacts.

Supplementary Material

Listings of anisotropic temperature factors and hydrogen coordinates (4 pages), and a listing of observed and calculated structure factor amplitudes (22 pages) are available from the authors on request.

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