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Preparation, Structure, and Properties of an Anionic Tetrameric Copper Complex Containing a Planar, Eight-Membered Ring Core

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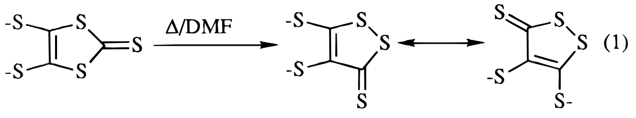
Introduction

Square planar metal complexes (e.g., of Ni(II), Pt(II), and Pd(II)) with bis-coordination by the ligand dmit (dmit = $C_3S_5^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato) have been actively researched as electronically conducting molecular materials over the past 10−15 years.[2] Chemists and physicists alike have studied their novel metallic and superconducting properties. Combined with proper metal ions, the sulfur-rich ligand can form planar anionic units resulting in extended intermolecular interactions to form metallic-like systems.[2,3] Several other ligand systems similar to dmit have been studied but have not afforded comparable electronic properties. One system in particular that has received less attention is that of the ligand dmt (dmt = $C_3S_5^{2-}$ = 3-thione-1,2-dithiole-4,5-dithiolato) (**1**). Dmt can be synthesized directly from dmit via the "Steimecke rearrangement", where the dmit ligand rearranges to the thermodynamically more stable product dmt at increased temperature in dimethylformamide as shown in reaction 1.[2b,c]



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Using a unique and facile three-solvent method, we recently reported the synthesis of the bimetallic copper(II) complex $(Bu_4N)_2\{tto[Cu(dmit)]_2\}$.[4] This anionic complex has a tetrathiooxalate ligand bridging two copper(II) metal centers which are "capped" with the dmit ligand. Altering the cation of this complex may potentially lead to highly electrically conducting complexes. Using the same synthetic methodology, attempts were made to synthesize a new complex with dmt replacing the dmit ligand. We report the synthesis of the anionic cluster complex $(Bu_4N)_2[Cu(dmt)]_4$ (**2**). The tetrameric, dianionic complex is composed of four dmt ligands and four copper ion metal centers with two tetrabutylammonium cations.

Experimental Section

All reactions were carried out in air and at 25 °C. IR spectra were obtained using a KBr pellet on a Bio-Rad FTS-40A FTIR spectrometer. UV−vis spectra were obtained using a Varian Instruments Cary 5E spectrophotometer. Melting points were obtained under vacuum using a Thomas-Hoover capillary melting point apparatus. Cyclic voltammetry results were obtained using an EG & G Princeton Applied Research Model 273 potentiostat. Elemental analysis were completed at Robertson Microlit Laboratories Inc., Madison, NJ.

Table 1. Crystallographic Data for $(Bu_4N)_2[Cu(dmt)]_4$ (**2**)

$C_{44}H_{72}N_2Cu_4S_{20}$	$P2_1/c$ (14)
fw = 1524.40	T = 25 °C
a = 13.228(2) Å	λ = 0.710 73 Å
b = 19.584(3) Å	ρ_{calcd} = 1.509 g cm^{-3}
c = 26.007(4) Å	μ = 19.0 cm^{-1}
β = 95.06(1)°	$R(F_o)^a$ = 5.58%
V = 6711(2) Å^3	$R_w(F_o)^b$ = 5.00%
Z = 4	

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$.

Materials. All solvents, unless otherwise stated, were used as received from Aldrich Chemical Co. $(Bu_4N)_2[Zn(dmt)_2]$ was prepared according to Olk,[5] and the preparation of $(Et_4N)_2$tto was similar to the published procedure of Jeroschewski.[6]

$(Bu_4N)_2[Cu(dmt)]_4$. A 472 mg (0.500 mmol) sample of $(Bu_4N)_2[Zn(dmt)_2]$ was dissolved in ~30 mL of CH_2Cl_2. In a separate vessel, 103 mg (0.250 mmol) of $(Et_4N)_2$tto was dissolved in ~25 mL of H_2O purified by a Millipore Milli-Q water system. The two solutions were combined and stirred. To the stirring mixture was added a solution of 85 mg (0.500 mmol) of $CuCl_2$ dissolved in a minimal amount of methanol. The organic layer was separated from the mixture and filtered to remove insoluble oligomeric $[Cu(tto)]_n$. The aqueous layer was washed with two portions of CH_2Cl_2, isolated, and filtered, and all solutions were combined. An equivalent amount of *i*-PrOH was added, and the mixture was evaporated to less than half-volume and filtered again, this time to remove the less soluble desired product from $[Cu(dmt)_2]^{2-}$. More product was obtained by evaporating the remaining solution to dryness, and the residue was crystallized in 1:1 acetone/*i*-PrOH three subsequent times. Yield: 30 mg (8%). Mp: 261−262 °C dec. Anal. Calcd for $C_{44}H_{72}N_2S_{20}Cu_4$: C, 34.66; H, 4.77; N, 1.84. Found: C, 34.67; H, 4.64; N, 1.83. IR (KBr, cm^{-1}): ν(C−H) 2953, 2867, 733; ν(C−N) 1456; ν(C=C) 1338, 1283; ν(C=S) 1044; ν(C−C) 943; ν(C−S) 835. UV−vis [methylene chloride, nm (log ϵ)]: 269 (4.80), 344 (4.70), 374 (4.77), 508 (4.71).

X-ray Structure Determination. The crystallographic data are located in Table 1. Fractional coordinates and equivalent isotropic thermal parameters for the non-H atoms of **2** are given in Table 2. The crystal chosen for data collection had dimensions 0.42 × 0.25 × 0.13 mm. X-ray intensity data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). Thirty-two reflections with 20.0° ≤ 2θ ≤ 22.0° were used to refine cell parameters. Four reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was <1%).

The structure was solved by the heavy-atom method in SHELXTL Plus, from which the four Cu atoms were obtained. The rest of the non-hydrogen atoms were obtained from a subsequent difference Fourier map. The structure was refined in SHELXTL Plus using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the positions of the hydrogen atoms were calculated in ideal positions and their isotropic thermal parameters were fixed.

Results and Discussion

The anion of complex **2** consists of four dmt ligands and four copper ion metal centers as shown by the thermal ellipsoid diagram in Figure 1. Each dmt ligand is coordinated to two Cu ions. Of the over 30 dmt ligand complexes that have been reported, the ligand has never been seen to coordinate in this fashion.[2] It is intriguing to note that the complex has an overall

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Table 2. Fractional Coordinates and Equivalent Isotropic[a] Thermal Parameters (Å^2) for the Non-H Atoms of Compound **2**

atom	*x*	*y*	*z*	*U*	atom	*x*	*y*	*z*	*U*
Cu1	0.12181(10)	−0.07914(7)	0.15460(5)	0.0605(6)	C12	0.3267(8)	−0.1364(6)	0.1267(4)	0.054(5)
Cu2	0.04880(10)	−0.05878(8)	0.32191(5)	0.0667(6)	N1	0.1258(9)	0.2445(7)	0.0045(4)	0.085(5)
Cu3	0.31438(11)	0.09133(8)	0.35298(5)	0.0732(7)	C13	0.0750(12)	0.2845(9)	−0.0402(6)	0.114(9)
Cu4	0.36513(11)	0.08063(7)	0.18416(5)	0.0664(6)	C14	0.0172(14)	0.3448(12)	−0.0262(6)	0.167(12)
S1	0.0491(2)	−0.0817(2)	0.23324(11)	0.0670(13)	C15	−0.032(2)	0.3783(12)	−0.0749(12)	0.27(2)
S2	−0.0336(2)	−0.0558(2)	0.10900(11)	0.0744(14)	C16	−0.071(2)	0.4433(13)	−0.0592(7)	0.32(2)
S3	−0.2267(2)	−0.0148(2)	0.14553(11)	0.0654(13)	C17	0.0517(11)	0.2140(7)	0.0380(5)	0.091(7)
S4	−0.2608(2)	−0.0080(2)	0.22149(11)	0.0589(12)	C18	−0.0240(12)	0.1646(8)	0.0116(6)	0.122(9)
S5	−0.1208(2)	−0.0288(2)	0.31270(12)	0.0717(14)	C19	−0.0944(13)	0.1378(9)	0.0475(7)	0.149(11)
S6	0.1827(2)	0.0114(2)	0.35597(12)	0.0807(15)	C20	−0.1724(14)	0.0872(10)	0.0195(7)	0.22(2)
S7	0.0856(3)	−0.1407(2)	0.38596(12)	0.0746(14)	C21	0.1856(11)	0.1903(8)	−0.0201(5)	0.097(7)
S8	0.2523(3)	−0.1504(2)	0.46585(13)	0.096(2)	C22	0.2441(11)	0.1411(8)	0.0158(5)	0.106(8)
S9	0.3728(3)	−0.0837(2)	0.47910(13)	0.104(2)	C23	0.3028(12)	0.0940(9)	−0.0153(6)	0.129(9)
S10	0.4079(3)	0.0394(2)	0.42188(13)	0.095(2)	C24	0.3617(12)	0.0430(8)	0.0140(6)	0.144(10)
S11	0.3674(2)	0.1141(2)	0.27089(11)	0.0687(14)	C25	0.1944(11)	0.2901(7)	0.0399(5)	0.091(7)
S12	0.2934(3)	0.2086(2)	0.36679(14)	0.106(2)	C26	0.2793(12)	0.3250(9)	0.0154(6)	0.131(9)
S13	0.2278(3)	0.3109(2)	0.2887(2)	0.111(2)	C27	0.338(2)	0.3740(14)	0.0526(9)	0.22(2)
S14	0.2416(3)	0.3044(2)	0.2106(2)	0.105(2)	C28	0.301(2)	0.4190(14)	0.0736(10)	0.35(3)
S15	0.3243(3)	0.1904(2)	0.15631(13)	0.090(2)	N2	0.2944(9)	0.7287(6)	0.2855(4)	0.079(5)
S16	0.2609(2)	−0.0076(2)	0.15044(13)	0.0698(13)	C29	0.358(3)	0.7987(10)	0.2764(8)	0.23(2)
S17	0.5083(2)	0.0265(2)	0.15729(12)	0.0714(14)	C30	0.338(2)	0.848(2)	0.2943(10)	0.30(3)
S18	0.5381(2)	−0.1152(2)	0.12803(14)	0.083(2)	C31	0.407(2)	0.9164(9)	0.2877(7)	0.20(2)
S19	0.4274(3)	−0.1886(2)	0.11510(14)	0.084(2)	C32	0.503(2)	0.9167(14)	0.2949(10)	0.37(3)
S20	0.2094(2)	−0.1722(2)	0.12409(12)	0.0667(13)	C33	0.3378(13)	0.6784(10)	0.2521(9)	0.172(13)
C1	−0.0717(8)	−0.0494(5)	0.2121(4)	0.046(4)	C34	0.334(2)	0.6687(14)	0.2042(7)	0.22(2)
C2	−0.1032(8)	−0.0418(5)	0.1598(4)	0.054(5)	C35	0.3570(14)	0.6170(9)	0.1701(8)	0.134(10)
C3	−0.1404(8)	−0.0304(5)	0.2472(4)	0.051(4)	C36	0.346(2)	0.6202(10)	0.1209(7)	0.218(15)
C4	0.2375(9)	−0.0434(6)	0.4042(4)	0.054(5)	C37	0.182(2)	0.7294(10)	0.2750(8)	0.175(13)
C5	0.1906(9)	−0.1052(6)	0.4159(4)	0.060(5)	C38	0.114(2)	0.6787(13)	0.2726(10)	0.28(2)
C6	0.3298(9)	−0.0268(6)	0.4314(4)	0.065(5)	C39	0.005(2)	0.6852(15)	0.2740(15)	0.46(4)
C7	0.3146(8)	0.1951(6)	0.2626(5)	0.057(5)	C40	−0.044(2)	0.6306(13)	0.2594(13)	0.53(4)
C8	0.2838(9)	0.2332(6)	0.3037(5)	0.072(6)	C41	0.322(2)	0.7102(10)	0.3396(8)	0.26(2)
C9	0.2973(8)	0.2241(6)	0.2138(5)	0.070(6)	C42	0.379(2)	0.7160(10)	0.3762(8)	0.178(13)
C10	0.3514(8)	−0.0681(6)	0.1382(3)	0.047(4)	C43	0.407(2)	0.6872(12)	0.4250(7)	0.213(14)
C11	0.4568(8)	−0.0507(5)	0.1409(4)	0.054(5)	C44	0.450(2)	0.6985(13)	0.4654(7)	0.36(3)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{\mathrm{eq}} = {}^{1}/_{3}\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the *i*th and *j*th direct-space unit cell vectors.

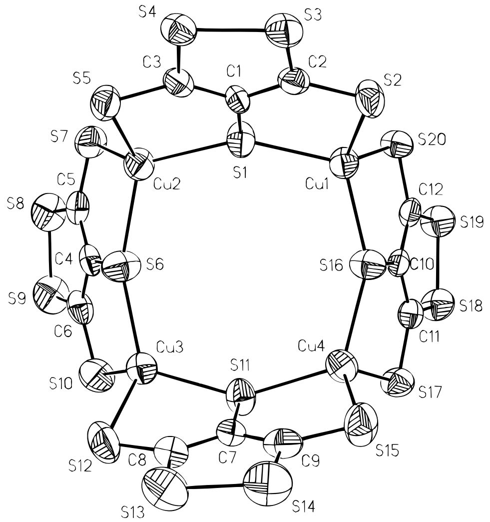

Figure 1. Thermal ellipsoid drawing and atomic labeling scheme of the dianion of **2** with 40% probability ellipsoids.

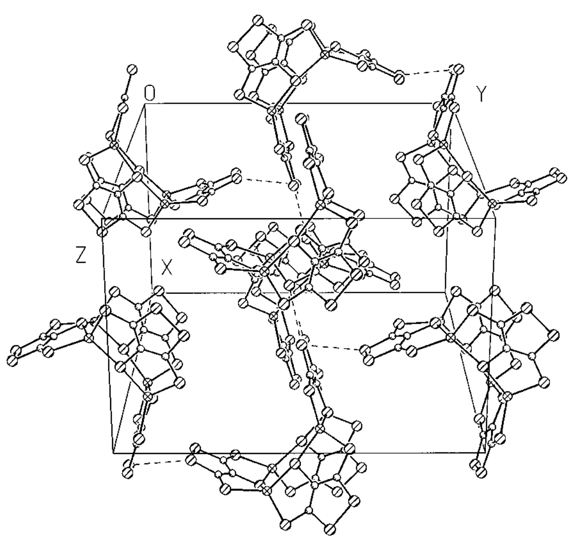

Figure 2. Packing diagram with unit cell labels of **2** showing columnar arrays of dianions with nonbonding S···S interactions (dashed lines). Tetrabutylammonium cations have been omitted for clarity.

charge of −2, whereas one would expect a simple reaction between four Cu^{2+} and four dmt^{2-} ligands to yield a neutral complex. The tto^{2-} ligand thus plays an active role in the tetramerization as a reducing agent. The major products after the addition of methanolic $CuCl_2$ in the synthesis of **2** are $(Bu_4N)_2[Cu(dmt)_2]$ and the insoluble oligomeric $[Cu(tto)]_n$.[7,8] Without tto^{2-} present, only metal exchange occurs between $[Zn(dmt)_2]^{2-}$ and Cu^{2+} to form $[Cu(dmt)_2]^{2-}$.

As seen in the unit cell in Figure 2, the crystal packing is characterized by a columnar array of anions. The tetrabutylammonium counterions are intercalated throughout the lattice. There are S···S interactions between neighboring anions resulting from contacts of the thiole groups of the dmt ligand. The distances are labeled in Figure 2 and are less than the sum of

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Table 3. Bond Lengths (Å) and Angles (deg) for the Dianion of $(Bu_4N)_2[Cu(dmt)]_4$ (**2**)

1	2	3	1−2	1−2−3
S1	Cu1	S2	2.336(3)	92.10(11)
S1	Cu1	S16		116.28(12)
S2	Cu1	S16	2.327(3)	121.72(13)
S2	Cu1	S20		115.01(12)
S16	Cu1	S20	2.323(3)	92.08(12)
S20	Cu1	S1	2.336(3)	122.38(13)
S1	Cu2	S5	2.350(3)	91.85(11)
S1	Cu2	S6		114.52(12)
S5	Cu2	S6	2.311(3)	125.61(13)
S5	Cu2	S7		112.85(13)
S6	Cu2	S7	2.352(3)	91.73(12)
S7	Cu2	S1	2.333(3)	123.45(13)
S6	Cu3	S10	2.348(4)	91.65(13)
S6	Cu3	S11		116.02(12)
S10	Cu3	S11	2.321(4)	127.12(14)
S10	Cu3	S12		111.93(14)
S11	Cu3	S12	2.348(3)	90.14(13)
S12	Cu3	S6	2.345(4)	123.32(15)
S11	Cu4	S15	2.346(3)	91.41(12)
S11	Cu4	S16		121.69(13)
S15	Cu4	S16	2.316(4)	117.11(13)
S15	Cu4	S17		120.08(14)
S16	Cu4	S17	2.332(3)	91.12(12)
S17	Cu4	S11	2.330(3)	118.25(12)
C1	S1	Cu1	1.761(10)	98.7(4)
C1	S1	Cu2		99.1(4)
Cu1	S1	Cu2		153.05(14)
C2	S2	Cu1	1.697(11)	98.7(4)
S4	S3	C2	2.069(4)	95.6(4)
C2	S3		1.726(10)	
C3	S4	S3	1.728(11)	94.7(4)
C3	S5	Cu2	1.702(11)	99.2(4)
C4	S6	Cu2	1.758(11)	99.3(4)
C4	S6	Cu3		99.8(4)
Cu2	S6	Cu3		155.9(2)
C5	S7	Cu2	1.681(12)	99.1(4)
S9	S8	C5	2.066(5)	96.2(4)
C5	S8		1.718(11)	
C6	S9	S8	1.726(11)	95.0(4)
C6	S10	Cu3	1.689(12)	99.1(4)
C7	S11	Cu3	1.740(12)	97.9(4)
C7	S11	Cu4		99.5(4)
Cu3	S11	Cu4		147.3(2)
C8	S12	Cu3	1.703(13)	97.4(4)
S14	S13	C8	2.057(6)	95.5(5)
C8	S13		1.722(12)	
C9	S14	S13	1.735(12)	94.8(5)
C9	S15	Cu4	1.702(14)	98.4(4)
C10	S16	Cu1	1.734(11)	99.1(4)
C10	S16	Cu4		100.4(4)
Cu1	S16	Cu4		150.9(2)
C11	S17	Cu4	1.697(11)	99.3(4)
S19	S18	C11	2.058(5)	95.6(4)
C11	S18		1.711(11)	
C12	S19	S18	1.726(12)	96.1(4)
C12	S20	Cu1	1.699(11)	98.3(4)
C2	C1	C3	1.396(15)	117.0(9)
C2	C1	S1		121.8(8)
C3	C1	S1	1.39(2)	121.2(8)
S2	C2	S3		116.8(6)
S2	C2	C1		127.3(8)
S3	C2	C1		115.9(8)
S4	C3	S5		115.8(6)
S4	C3	C1		116.5(8)
S5	C3	C1		127.6(8)
C5	C4	C6	1.41(2)	118.3(10)
C5	C4	S6		121.2(8)
C6	C4	S6	1.39(2)	120.5(9)
S7	C5	S8		117.1(7)
S7	C5	C4		128.2(8)
S8	C5	C4		114.7(8)
S9	C6	S10		115.7(6)
S9	C6	C4		115.6(9)
S10	C6	C4		128.6(9)
C8	C7	C9	1.39(2)	116.5(11)
C8	C7	S11		122.3(9)
C9	C7	S11	1.39(2)	121.2(10)
S12	C8	S13		117.5(7)
S12	C8	C7		125.9(9)
S13	C8	C7		116.5(9)
S14	C9	S15		115.5(8)
S14	C9	C7		116.7(10)
S15	C9	C7		127.8(9)
C11	C10	C12	1.432(15)	116.4(10)
C11	C10	S16		120.9(8)
C12	C10	S16	1.40(2)	122.7(8)
S17	C11	S18		117.6(6)
S17	C11	C10		126.3(8)
S18	C11	C10		116.1(8)
S19	C12	S20		117.7(7)
S19	C12	C10		115.7(8)
S20	C12	C10		126.6(9)

the van der Waals radii 3.70 Å.[9] The structure of the anion consists of a central eight-membered ring core, with four Cu and four S atoms. Each of the four sulfurs are bonded to two Cu atoms and one carbon atom. The Cu−S distances in the core are on average 2.341(3) Å (see Table 3) with S−Cu−S bond angles ranging from 114.52(12) to 121.69(13)°. The Cu−S−Cu angles range from 147.3(2) to 155.9(2)°, making the core a distorted octagon compared to a perfect octagon of 135° bond angles. All other Cu−S distances are on average 2.327(3) Å. The Cu−S bond distances are all slightly longer than commonly seen in Cu(II) bis(dithiolene) complexes.[2] The coordination about the Cu metal centers is distorted tetrahedral.

In the four dmt ligands, the peripheral S−S bonds are all approximately 2.063(5) Å as expected. The distances of the eight-membered ring sulfur atoms and bonded carbon atoms have average values of 1.748(11) Å, similar to other dmt complexes. The C−S distances of the related groups such as C3−S5, C5−S7, and C9−S15 are shorter than expected with average lengths of 1.696(12) Å. Last, the ethylene C−C bond lengths are observed to be slightly longer than usually seen at 1.40(2) Å.[2,10]

On the basis of the structural data, the dmt ligands are likely completely delocalized. Unlike $[Cu(dmt)_2]^{2-}$, the dianionic cluster lacks electron density localized on the central ethylene and peripheral thione groups. This greater electronic delocalization may be a driving force for the formation of the cluster complex. Considering the octagonal structure of the core of the molecule, interesting interactions with various cations may be possible.

The redox behavior of the anionic tetrameric complex has been investigated by cyclic voltammetry (CV) in 0.1 M TBAP/CH_2Cl_2, at a Pt button working electrode. The CV data exhibit two anodic processes ($E_{p,a}$ = 0.15 and 1.05 V vs Ag/Ag^+), correlated with two cathodic processes ($E_{p,c}$ = −0.45 and −0.75 V). These data suggest that higher oxidation states of **2** may be obtained.

The absorption properties of the complex were studied by UV−vis spectroscopy. The complex is red in methylene chloride solution as a result of an absorption band at 508 nm. This band, along with one found at 269 nm, may be attributed to excitations within the dmt ligand.[11] Absorptions at 344 and

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374 nm can be assigned to Cu−L charge transfer bands as similarily seen for $Cu(mnt)_2^{2-}$ complexes.[12] All the absorption bands have molar absorptivities greater than 5.0×10^4 L mol^{-1} cm^{-1}.

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Supporting Information Available: An expanded description of the X-ray experimental work and full tables of crystallographic data, hydrogen coordinates, bond lengths and angles, and non-hydrogen anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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