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Crystal and Molecular Structures of Tetranuclear Metal Clusters of Copper(I) Trithioperoxybenzoates

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Abstract

Two new tetrameric orange–red copper(I) cluster compounds, tetrakis[2,4,6-trimethyltrithioperoxybenzoato]tetracopper(I), $Cu_4[2,4,6\text{-}(CH_3)_3C_6H_2CS_2S]_4$ (1) and tetrakis[*o*-methyltrithioperoxybenzoato]tetracopper(I), $Cu_4[o\text{-}CH_3C_6H_4CS_2S]_4$ (2) have been synthesized and their crystal and molecular structures determined by single crystal X-ray diffraction. The anionic ligands used for the syntheses were dithiobenzoates and the starting copper reagent was divalent copper. Thus oxidation of the ligand by the copper preceded cluster formation. The molecules of each cluster consist of four roughly tetrahedrally disposed, possibly weakly bonded, copper atoms each coordinated, and more clearly bonded, to three sulfur atoms.

Introduction

The existence of the trithioperoxy metal linkage M–S–R–S–S, has been established in several compounds and with several different metal centers, M, such as Ni(II), Zn(II), Pd(II), Pt(II), Fe(III), Os(III), and Mo(IV). These compounds are generally formed by oxidative addition of elemental sulfur or anionic polysulfides to transition metal dithioacid complexes to form trithioperoxycarboxylates [1–7]

$$=MS_2C- + \tfrac{1}{8}S_8 \text{ or } S_x^{2-} \longrightarrow =MS_2SC-$$

Single crystal X-ray data have confirmed the disulfide linkage in some of the metal species [3–7], where usually the complexes contain both normal dithiocarboxylate bidentate ligands and the trithioperoxycarboxylate bidentate ligand.

In 1982, sulfur addition to 1,1-dithiolate ligands, L, in $(Cu_8L_6)^{4-}$ cubane clusters was reported, where elemental sulfur addition yielded the 'sulfur-rich' clusters $[Cu_8(LS)_6]^{4-}$ with large organic cations, or $[Cu_4(LS)_3]^{2-}$ with alkali metal cations [8]

$$=C{=}CS_2Cu + \tfrac{1}{8}S_8 \longrightarrow =C{=}S_2SCu$$

Identification of the products was supported by ^{13}C NMR and IR data, but no single crystal X-ray structures were obtained. Although several other copper cluster complexes with sulfur-containing ligands have been characterized (see, for example, the references cited in ref. 8), some by X-ray diffraction, none of these complexes contained the trithioperoxy species.

We have prepared two new tetrameric copper(I) cluster compounds, tetrakis[2,4,6-trimethyltrithioperoxybenzoato]tetracopper(I), $Cu_4[2,4,6\text{-}(CH_3)_3C_6H_2CS_2S]_4$ (1) and tetrakis[*o*-methyltrithioperoxybenzoato]tetracopper(I), $Cu_4[o\text{-}CH_3C_6H_4CS_2S]_4$ (2) and report here their single-crystal X-ray structures. After we had completed this work we discovered that an analogous tetranuclear cluster complex with the α-trithioperoxynaphthoate ligand, $Cu_4(\alpha\text{-}C_{10}H_7CS_2S)_4$, had been prepared by Chinese workers and its X-ray structure reported [9].

Experimental

Preparation of Tetrakis[2,4,6-trimethyltrithioperoxybenzoato]tetracopper(I), $Cu_4[2,4,6\text{-}(CH_3)_3C_6H_2CS_2S]_4$ (1)

Method a

To a stirred solution of 0.0300 g (0.0786 mmol) of $n\text{-}Pr_4N[2,4,6\text{-}(CH_3)_3C_6H_2CS_2]$ (the dithiobenzoate) in 10 ml of DMF was added 0.0185 g (0.0766 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 10 ml of DMF. The solution was stirred for 2 h and allowed to stand. After three days a precipitate began to form and a week later the mixture was suction filtered. The orange–purple precipitate was air-dried overnight and dissolved in a 1:1 CS_2/acetone solution. This orange solution was placed in an NMR tube for slow evaporation and crystal growth. After ten days orange–red crystals were obtained which were suitable for single-crystal X-ray study.

Method b

To a stirred solution of 0.189 g (0.782 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 30 ml of DMF was added 0.300 g (0.786 mmol) of $n\text{-}Pr_4N[2,4,6\text{-}(CH_3)_3C_6H_2CS_2]$ (the dithiobenzoate) dissolved in 30 ml of DMF. The solution was stirred overnight, then gravity filtered. The

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TABLE I. Crystal Data and Data Collection Parameters

Compound	**1**·Acetone	**2**
Formula	$Cu_4S_{12}C_{40}H_{44}\cdot C_3H_6O$	$Cu_4S_{12}C_{32}H_{28}$
Formula weight	1221.8	1051.5
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.742(4)	12.792(2)
b (Å)	15.148(2)	12.810(4)
c (Å)	15.284(2)	13.034(2)
α (°)	111.244(9)	94.94(2)
β (°)	91.90(2)	103.997(12)
γ (°)	102.02(2)	98.76(2)
V (Å^3)	2670(2)	2031(2)
Z	2	2
T (°C)	22	25
Density (g cm^{-3})	1.519	1.719
Radiation	Cu Kα (λ = 1.54184 Å)	Mo Kα (λ = 0.71073 Å)
Crystal size (mm)	0.10 × 0.14 × 0.16	0.12 × 0.24 × 0.28
μ (cm^{-1})	63.5	26.9
Min. relative transmission	0.726	0.753
Data collection range	$2° < \theta < 70°$	$1° < \theta < 25°$
Scan rates (° min^{-1})	1.25–4.0	0.91–4.0
Max. scan time (s)	45	60
Intensity decay (%)	19.3	
Unique data	10133	7129
Observed data	5702	4086
Variables	506	434
R	0.050	0.038
R_w	0.068	0.038
Extinction	$3.1(2) \times 10^{-7}$	
Max. residual density (e Å^{-3})	0.78	0.44
Color	orange	red–orange

purple product was air-dried, then dissolved in a 3:2 CS_2/acetone solution. The resulting orange solution was placed in an NMR tube for slow evaporation and crystal growth. After two weeks orange–red crystals were obtained which were suitable for single-crystal X-ray structure determination.

Preparation of Tetrakis[o-methyltrithioperoxybenzoato]tetracopper(I), $Cu_4[o\text{-}CH_3C_6H_4CS_2S]_4$ *(2) and p-Phenyltrithioperoxybenzoatocopper(I),* $Cu_x[p\text{-}C_6H_5C_6H_4CS_2S]_x$ *(3)*

These two products were obtained using the same procedure as in method b above. Only compound **2** formed crystals suitable for X-ray diffraction study. The value of x in compound **3** is undetermined, but presumably it is 4.

X-ray Structure Determinations

Intensity data were obtained on Enraf-Nonius CAD4 diffractometers equipped with Mo Kα or Cu Kα radiation and graphite monochromators. Cell dimensions and crystal orientation were obtained from the setting angles of 25 reflections having $12° < \theta < 14°$(Mo) or $25° < \theta < 30°$(Cu). Crystal data are given in Table I. Data were collected by ω–2θ scans of variable speed in order to measure all significant intensities with approximately equal relative precision. All data in one hemisphere within the angular limits specified in Table I were measured for each crystal. Data reduction included corrections for background, Lorentz, polarization, decay (for **1**), and absorption effects. The absorption corrections were based on Ψ scans of reflections near $\chi = 90°$. Data having $I > 3\sigma(I)$ were used in the refinements.

The structures were solved by direct methods and refined by full-matrix least-squares based on F with weights $w = \sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs [10]. Non-hydrogen atoms were refined anisotropically, except for those of the acetone molecule. Electron density in the solvent region is very diffuse, and the model used treated all four atoms as carbon in fixed positions, with $B = 25$ Å^2. Most of the tetramer hydrogen atoms were located in difference maps, and all were included as fixed contributions. Solvent H atoms were ignored. Final R values and residual electron densities are given in Table I.

The crystals of **1** are unstable with respect to solvent loss over a period of months. When this compound was crystallized from 3:2 CS_2/acetone, orange hexagonal needles were formed, which were much more stable to loss of solvent. These crystals have hexagonal space group $P6_122$ (or $P6_522$), $a = 15.881(3)$, $c = 37.341(11)$ Å, $Z = 6$. X-ray data were collected from these crystals using Cu Kα radiation. At the present stage of refinement, $R = 0.048$ for 2243 observations. The Cu tetramer lies on a crystallographic twofold axis, and solvent disorder is severe.

Results and Discussion

The reactions between copper(II) nitrate and, separately, the three dithiobenzoates: *p*-phenyl-, *o*-methyl-, and 2,4,6-trimethyldithiobenzoate, all yielded dark crystalline products. With the latter two ligands orange–red crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation from a 1:1 CS_2/acetone solution in an NMR tube. The crystal and molecular structures were determined (details in 'Experimental'). Atomic coordinates are given in Tables II and III and the molecular structures are pictured in Figs. 1 and 2. The molecules are seen to consist of four roughly tetrahedrally disposed copper atoms each coordinated to three sulfur atoms. More significantly, each ligand, having begun as a dithiobenzoate is now a trithiobenzoate, and the oxidation state of the copper has changed from two to one. It seems clear that copper(II) has served to oxidize the sulfur ligands, perhaps producing first free sulfur which then oxidizes the ligand to the trithio species by sulfur insertion or addition. It is not clear whether the ligand is oxidized before or after it has coordinated to the metal, but it is more likely that the dithio ligand complexes to the copper and is then oxidized by the sulfur.

TABLE II. Coordinates for 1

Atom	*x*	*y*	*z*	*B* ($Å^2$)
Cu1	0.7412(1)	0.06186(8)	0.81187(8)	5.59(3)
Cu2	0.8913(1)	−0.01001(7)	0.66571(7)	5.16(3)
Cu3	0.6927(1)	0.00365(7)	0.58296(8)	5.27(3)
Cu4	0.6234(1)	−0.12299(7)	0.68838(8)	5.63(3)
S1	0.9172(2)	0.0986(1)	0.8131(1)	5.17(5)
S2	0.9639(2)	0.0216(1)	0.8867(1)	5.32(5)
S3	0.9473(2)	−0.1297(1)	0.6918(1)	5.58(6)
S4	0.8506(2)	−0.0078(1)	0.5255(1)	4.72(5)
S5	0.9107(2)	0.1344(1)	0.5382(1)	5.14(5)
S6	0.6991(2)	0.1601(1)	0.6118(2)	5.49(5)
S7	0.5408(2)	−0.1048(1)	0.5667(2)	5.37(5)
S8	0.5608(2)	−0.2232(1)	0.4552(2)	5.70(6)
S9	0.6636(2)	−0.2653(1)	0.6100(2)	5.88(6)
S10	0.6312(2)	−0.0553(1)	0.8448(1)	5.49(5)
S11	0.4937(2)	−0.0041(1)	0.8624(1)	5.71(5)
S12	0.6301(2)	0.1596(1)	0.8221(2)	6.05(6)
C1	0.9718(6)	−0.0895(5)	0.8066(5)	4.6(2)
C2	1.0048(6)	−0.1515(5)	0.8556(5)	4.6(2)
C3	1.1144(7)	−0.1425(5)	0.8807(5)	5.6(2)
C4	1.1435(7)	−0.2014(5)	0.9227(6)	6.4(2)
C5	1.0647(7)	−0.2723(5)	0.9386(5)	6.2(2)
C6	0.9567(7)	−0.2788(5)	0.9140(5)	6.0(2)
C7	0.9267(6)	−0.2186(5)	0.8726(5)	5.1(2)
C8	1.2014(7)	−0.0678(7)	0.8644(7)	8.0(3)
C9	1.0978(9)	−0.3405(6)	0.9819(6)	8.9(3)
C10	0.8078(7)	−0.2278(6)	0.8473(6)	7.4(3)
C11	0.8163(6)	0.2002(5)	0.5814(5)	4.6(2)
C12	0.8512(6)	0.3029(4)	0.5903(5)	4.7(2)
C13	0.9014(7)	0.3743(5)	0.6767(5)	5.6(2)
C14	0.9296(8)	0.4714(5)	0.6881(6)	6.9(3)
C15	0.9054(7)	0.4992(5)	0.6138(6)	6.9(3)
C16	0.8525(8)	0.4274(5)	0.5286(6)	7.2(3)
C17	0.8239(7)	0.3275(5)	0.5149(5)	5.9(2)
C18	0.9253(9)	0.3457(6)	0.7595(6)	8.7(3)
C19	0.930(1)	0.6059(6)	0.6252(7)	9.9(3)
C20	0.770(1)	0.2530(6)	0.4222(6)	9.2(3)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C21	0.6201(6)	-0.2908(5)	0.4982(5)	4.8(2)
C22	0.6327(7)	-0.3834(5)	0.4228(5)	5.1(2)
C23	0.5454(7)	-0.4637(5)	0.3864(5)	5.4(2)
C24	0.5630(8)	-0.5505(5)	0.3223(6)	6.4(2)
C25	0.6666(8)	-0.5555(6)	0.2940(6)	6.8(3)
C26	0.7483(7)	-0.4747(6)	0.3288(6)	6.9(3)
C27	0.7355(7)	-0.3875(5)	0.3921(6)	6.0(2)
C28	0.4363(7)	-0.4622(6)	0.4157(6)	6.9(3)
C29	0.6798(9)	-0.6536(7)	0.2265(7)	10.0(4)
C30	0.8295(8)	-0.2987(7)	0.4271(7)	8.3(3)
C31	0.5147(6)	0.1018(5)	0.8458(5)	4.7(2)
C32	0.4181(6)	0.1435(5)	0.8511(5)	4.7(2)
C33	0.4036(6)	0.2141(5)	0.9362(5)	5.3(2)
C34	0.3207(7)	0.2616(6)	0.9369(5)	6.0(2)
C35	0.2539(7)	0.2387(6)	0.8544(6)	6.3(2)
C36	0.2663(7)	0.1649(6)	0.7710(6)	6.8(3)
C37	0.3501(7)	0.1175(5)	0.7682(5)	6.0(2)
C38	0.4766(8)	0.2427(6)	1.0252(6)	7.4(3)
C39	0.1687(8)	0.2983(6)	0.8536(7)	8.5(3)
C40	0.3652(8)	0.0434(6)	0.6754(6)	7.7(3)
C1S	0.6046	0.4651	0.8758	25
C2S	0.5074	0.3969	0.8193	25
C3S	0.6520	0.5506	0.8553	25
C4S	0.6542	0.4478	0.9526	25

The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha]$.

TABLE III. Coordinates for 2

Atom	x	y	z	B (Å^2)
Cu1	0.85980(5)	0.10275(6)	0.72821(6)	4.18(2)
Cu2	0.71521(6)	0.17680(6)	0.83326(6)	4.41(2)
Cu3	0.90413(6)	0.32343(6)	0.84409(6)	3.77(2)
Cu4	0.94140(6)	0.15069(6)	0.95176(6)	3.94(2)
S1	0.6810(1)	0.0930(1)	0.6649(1)	4.47(4)
S2	0.6168(1)	-0.0581(2)	0.6853(1)	5.29(4)
S3	0.6506(1)	0.0408(1)	0.9108(1)	5.11(4)
S4	0.7506(1)	0.3495(1)	0.8968(1)	3.73(4)
S5	0.6740(1)	0.4212(1)	0.7724(1)	4.14(4)
S6	0.8630(1)	0.3807(1)	0.6851(1)	3.91(4)
S7	1.0604(1)	0.3044(1)	0.9586(1)	3.50(3)
S8	1.0450(1)	0.3915(1)	1.0917(1)	3.66(3)
S9	0.8712(1)	0.2023(1)	1.0838(1)	3.60(3)
S10	0.9370(1)	0.0018(1)	0.8484(1)	4.30(4)
S11	1.0952(1)	0.0297(1)	0.8361(1)	4.46(4)
S12	1.0055(1)	0.1676(1)	0.6729(1)	4.00(4)
C1	0.6108(4)	-0.0596(5)	0.8145(5)	4.3(2)
C2	0.5646(5)	-0.1672(5)	0.8365(5)	4.8(2)
C3	0.6368(6)	-0.2360(6)	0.8687(6)	6.6(2)
C4	0.5960(8)	-0.3350(6)	0.8916(6)	8.4(3)
C5	0.4855(7)	-0.3632(6)	0.8844(6)	8.5(3)
C6	0.4153(7)	-0.2933(6)	0.8516(6)	7.6(2)
C7	0.4538(5)	-0.1952(5)	0.8276(5)	5.6(2)
C8	0.3761(6)	-0.1227(7)	0.7913(6)	7.5(2)
C9	0.7492(4)	0.4259(4)	0.6802(4)	3.4(1)

(continued)

TABLE III. *(continued)*

Atom	*x*	*y*	*z*	*B* (Å^2)
C10	0.6987(4)	0.4815(5)	0.5895(4)	4.0(1)
C11	0.7138(5)	0.5921(5)	0.6060(5)	5.3(2)
C12	0.6716(6)	0.6477(6)	0.5241(6)	7.2(2)
C13	0.6101(6)	0.5913(6)	0.4280(6)	6.9(2)
C14	0.5916(5)	0.4834(6)	0.4117(5)	6.1(2)
C15	0.6366(5)	0.4248(5)	0.4923(5)	4.6(2)
C16	0.6184(6)	0.3064(6)	0.4739(6)	6.8(2)
C17	0.9414(4)	0.3215(4)	1.1342(4)	3.3(1)
C18	0.9147(4)	0.3848(4)	1.2233(4)	3.5(1)
C19	0.8708(5)	0.4744(5)	1.2014(5)	4.4(2)
C20	0.8410(5)	0.5352(6)	1.2806(6)	6.3(2)
C21	0.8579(6)	0.5016(6)	1.3801(6)	7.4(2)
C22	0.9008(6)	0.4148(7)	1.4027(5)	7.0(2)
C23	0.9317(5)	0.3516(5)	1.3254(5)	5.1(2)
C24	0.9821(7)	0.2562(7)	1.3548(6)	7.6(2)
C25	1.1045(4)	0.1147(4)	0.7440(4)	3.5(1)
C26	1.2194(4)	0.1384(5)	0.7350(5)	3.8(1)
C27	1.2979(5)	0.1962(6)	0.8220(5)	5.6(2)
C28	1.4051(6)	0.2198(7)	0.8192(7)	7.3(2)
C29	1.4345(5)	0.1837(6)	0.7294(6)	6.5(2)
C30	1.3585(5)	0.1259(6)	0.6427(5)	5.8(2)
C31	1.2481(5)	0.1025(5)	0.6444(5)	4.5(2)
C32	1.1684(6)	0.0378(7)	0.5499(6)	7.9(2)

The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma + acB_{13}\cos\beta + bcB_{23}\cos\alpha]$.

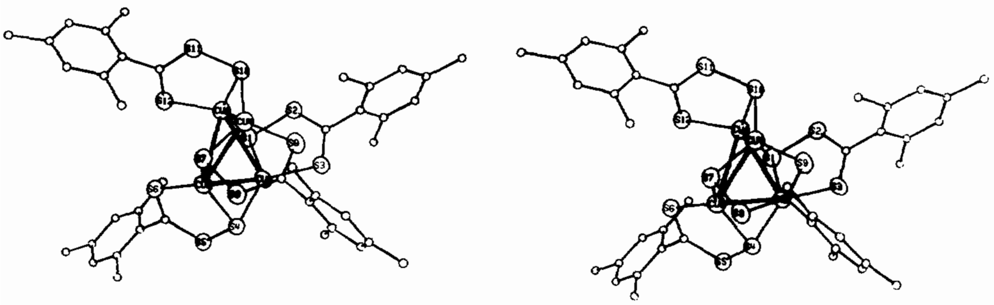


Fig. 1. The molecular structure of **1**, in stereopair. Cu and S are represented by ellipses enclosing 40% probability, while C atoms are drawn as circles of arbitrary radius.

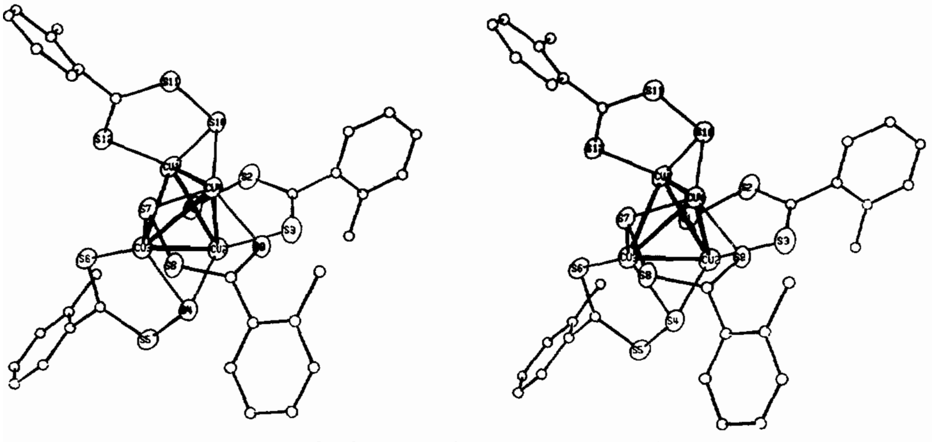
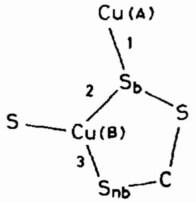


Fig. 2. The molecular structure of **2**, in stereopair, represented as in Fig. 1.

TABLE IV. Distances and Angles Involving Cu and S

Atoms	**1**	**2**
Cu1–Cu2	3.038(2)	2.7807(9)
Cu1–Cu3	3.286(2)	2.993(1)
Cu1–Cu4	2.808(1)	2.825(1)
Cu2–Cu3	2.870(2)	2.7919(9)
Cu2–Cu4	3.575(2)	3.015(1)
Cu3–Cu4	2.947(2)	2.761(1)
Cu1–S1	2.193(2)	2.215(2)
Cu1–S10	2.243(2)	2.256(2)
Cu1–S12	2.222(3)	2.228(1)
Cu2–S1	2.221(2)	2.268(2)
Cu2–S3	2.236(3)	2.237(2)
Cu2–S4	2.202(2)	2.232(2)
Cu3–S4	2.236(2)	2.292(1)
Cu3–S6	2.232(2)	2.228(1)
Cu3–S7	2.204(2)	2.248(1)
Cu4–S7	2.237(3)	2.279(2)
Cu4–S9	2.231(2)	2.222(1)
Cu4–S10	2.224(2)	2.223(2)
S1–S2	2.043(4)	2.049(2)
S4–S5	2.065(3)	2.048(2)
S7–S8	2.048(3)	2.047(2)
S10–S11	2.047(3)	2.049(2)
S1–Cu1–S10	131.5(1)	124.49(6)
S1–Cu1–S12	126.92(9)	133.89(6)
S10–Cu1–S12	99.2(1)	99.72(6)
S1–Cu2–S3	99.07(9)	99.11(6)
S1–Cu2–S4	135.0(1)	131.37(6)
S3–Cu2–S4	125.27(8)	127.00(6)
S4–Cu3–S6	100.04(9)	98.76(5)
S4–Cu3–S7	132.89(8)	123.04(6)
S6–Cu3–S7	122.9(1)	134.58(6)
S7–Cu4–S9	98.68(9)	98.02(5)
S7–Cu4–S10	134.8(1)	123.05(6)
S9–Cu4–S10	124.5(1)	138.37(6)
Cu1–S1–Cu2	86.97(8)	76.65(5)
Cu1–S1–S2	101.3(1)	103.52(9)
Cu2–S1–S2	101.6(1)	100.44(8)
Cu2–S4–Cu3	80.59(8)	76.19(5)
Cu2–S4–S5	105.48(9)	104.33(7)
Cu3–S4–S5	100.4(1)	100.17(7)
Cu3–S7–Cu4	83.14(8)	75.19(5)
Cu3–S7–S8	102.2(1)	98.79(7)
Cu4–S7–S8	101.5(1)	101.33(7)
Cu1–S10–Cu4	77.91(8)	78.22(5)
Cu1–S10–S11	100.8(1)	100.42(7)
Cu4–S10–S11	102.5(1)	98.65(8)

The pertinent bond distances and bond angles are given in Table IV for compounds **1** and **2**. There appear to be two categories of Cu–Cu interactions. Of the six imagined copper tetrahedron edges, four are bridged by sulfurs (S1, S4, S7 and S10) and the average Cu–Cu distance is 2.916 Å (range: 2.808(1)–3.038(2)) for compound **1** and 2.7806 Å (range: 2.761(1)–3.015(2)) for compound **2**. The non-S-bridged edges have Cu–Cu distances of 3.286(2) and 3.575(2) Å for compound **1** and significantly shorter distances of 2.993(2) and 3.015(2) Å for compound **2**. Coordination by sulfur at each copper center is trigonal. The Cu–S distances to non-bridging sulfurs (S_{nb} = S3, S6, S9, S12), from coppers Cu2, Cu3, Cu4, Cu1, respectively, (length 3 shown below) average 2.230 Å (range: 2.222(3)–2.236(3)) for compound **1** and average 2.229 Å (range: 2.222(3)–2.237(3)) for compound **2**.



The average Cu–S distances involving the bridging sulfur (S_b = S1, S4, S7, S10), (lengths 1 and 2 shown above) are 2.206 and 2.234 Å, respectively, for compound **1**, and 2.230 and 2.274 Å, respectively, for compound **2**. Thus the bridging sulfur, S_b, is roughly 0.03 Å closer to copper(A) (than to copper(B)) even though copper(A) is not part of the chelate ring involving S_b.

The S–S bond lengths are in the range 2.043(4)–2.065(3) Å with an average of 2.051 Å for compound **1**, and 2.047(3)–2.049(3) Å with an average of 2.048 Å for compound **2**, typical for such sulfur–sulfur single bonds.

The conformations of the ligands are such that the best planes of the aromatic rings are roughly orthogonal to the trithioperoxybenzoate planes. For trimethyl compound **1**, these dihedral angles range from 78.3(2)–88.1(2)° and average 84.6°. Those of the less sterically demanding methyl compound **2** are less orthogonal and more variable, ranging from 65.7(2)–88.8(2)° and averaging 75.3°.

Comparison of the present structures to that of the trithioperoxynaphthoate analog [9] indicate that the latter is much more similar to **2** than to **1**, reflecting the similar steric requirements of the *o*-methylphenyl and α-naphthoate groups. In that complex, the Cu–Cu bridged distances average 2.789 Å; the Cu–Cu non-bridged distances are 2.991 and 3.064 Å; the Cu–S average distances for various types are 1:2.228 Å, 2:2.270 Å, 3:2.223 Å; and the S–S distances average 2.044 Å.

Supplementary Material

The following supplementary material for compounds **1** and **2** is available from the authors on request: coordinates and isotropic thermal parameters assigned to hydrogen atoms, anisotropic thermal parameters, angles for Cu atoms (**1**), bond distances, bond angles and structure factor amplitudes.

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