

## Chemistry of Thiocarboxylates: Synthesis and Structures of Neutral Copper(I) Thiocarboxylates with Triphenylphosphine

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Received June 22, 1999

The reactions of  $\text{Na}^+ \text{R}\{\text{O}\}\text{CS}^-$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with mixtures of  $\text{CuCl}$  and  $\text{PPh}_3$  in stoichiometric ratios yielded the compounds  $[\text{Cu}_4(\text{SC}\{\text{O}\}\text{Me})_4(\text{PPh}_3)_4]$  (**1**),  $[\text{Cu}_4(\text{SC}\{\text{O}\}\text{Ph})_4(\text{PPh}_3)_3]$  (**2**),  $[\text{Cu}_2(\text{SC}\{\text{O}\}\text{Me})_2(\text{PPh}_3)_4]$  (**3**),  $[\text{Cu}(\text{SC}\{\text{O}\}\text{Ph})(\text{PPh}_3)_2]$  (**4**), and  $[\text{Cu}_2(\text{SC}\{\text{O}\}\text{Ph})_2(\text{PPh}_3)_3]$  (**5**) quantitatively. Compound **2** was also obtained from mixtures of  $\text{CuCl}$ ,  $\text{PPh}_3$ , and  $\text{NaSC}\{\text{O}\}\text{Ph}$  in the ratio 1:1:1. The analogous thioacetate compound similar to **2** and the thiobenzoate analogue of **1** could not be obtained. Attempts to prepare the unsymmetrical dimer of a thioacetate compound similar to **5** gave a mixture of **1** and **3**. The structures of **1–4** have been determined by single-crystal X-ray diffraction methods. Crystal data for **1**: triclinic space group  $P\bar{1}$ ,  $a = 11.5844(3) \text{ \AA}$ ,  $b = 13.2459(3) \text{ \AA}$ ,  $c = 14.3433(3) \text{ \AA}$ ,  $\alpha = 64.019(1)^\circ$ ,  $\beta = 79.297(1)^\circ$ ,  $\gamma = 69.426(1)^\circ$ ,  $V = 1850.98(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_{\text{calcd}} = 1.439 \text{ g}\cdot\text{cm}^{-3}$ . Crystal data for **2**·0.5 $\text{CH}_2\text{Cl}_2$ · $\text{H}_2\text{O}$ : triclinic space group  $P\bar{1}$ ,  $a = 12.4413(1) \text{ \AA}$ ,  $b = 15.5443(1) \text{ \AA}$ ,  $c = 20.4637(3) \text{ \AA}$ ,  $\alpha = 94.974(1)^\circ$ ,  $\beta = 95.976(1)^\circ$ ,  $\gamma = 100.450(1)^\circ$ ,  $V = 3848.09(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.416 \text{ g}\cdot\text{cm}^{-3}$ . Single-crystal data for **3**: monoclinic space group  $P2_1/n$ ,  $a = 15.2746(2) \text{ \AA}$ ,  $b = 23.2947(2) \text{ \AA}$ ,  $c = 19.0518(3) \text{ \AA}$ ,  $\beta = 96.713(1)^\circ$ ,  $V = 6732.5(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.309 \text{ g}\cdot\text{cm}^{-3}$ . Crystal data for **4**: triclinic space group  $P\bar{1}$ ,  $a = 10.2524(3) \text{ \AA}$ ,  $b = 12.9826(4) \text{ \AA}$ ,  $c = 14.5340(4) \text{ \AA}$ ,  $\alpha = 87.723(1)^\circ$ ,  $\beta = 75.322(1)^\circ$ ,  $\gamma = 75.978(1)^\circ$ ,  $V = 1815.14(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.327 \text{ g}\cdot\text{cm}^{-3}$ . Compound **1**,  $[(\mu_3\text{-SC}\{\text{O}\}\text{Me-S})_2(\mu\text{-SC}\{\text{O}\}\text{Me-S})_2(\text{CuPPh}_3)_4]$ , is a tetramer with a distorted stepladder structure in which two copper atoms are trigonally coordinated and the other two are tetrahedrally coordinated. Two bonding modes, namely,  $\mu_3\text{-S}$  and  $\mu_2\text{-S}$ , were observed for the  $\text{Me}\{\text{O}\}\text{CS}^-$  anion. The structure of **2** may be described as a highly distorted cubanoid structure and formulated as  $[(\mu_3\text{-SC}\{\text{O}\}\text{Ph-S}_3)(\mu_3\text{-SC}\{\text{O}\}\text{Ph-S}_2, \text{O})_3(\text{Cu})(\text{CuPPh}_3)_3]$ . In **2**, three copper atoms have tetrahedral coordination geometry and one copper atom is trigonally coordinated. Unprecedented bonding modes, namely,  $\mu_3\text{-S}$ , have been observed for the  $\text{R}\{\text{O}\}\text{CS}^-$  anions, in **1** and **2** and  $\mu_3\text{-S}_2, \text{O}$  in **2**. Compound **3**,  $[(\mu\text{-SC}\{\text{O}\}\text{Me-S})(\mu\text{-SC}\{\text{O}\}\text{Me-S}, \text{O})\{\text{Cu}(\text{PPh}_3)_2\}_2]$  is a dimer with  $\mu_2\text{-S}$  and  $\mu_2\text{-S}, \text{O}$  bonding modes of  $\text{Me}\{\text{O}\}\text{CS}^-$  ligands. Monomeric structure was found in **4** in which the copper atom has trigonal planar geometry with a very weak intramolecular interaction with O. Variable temperature  $^{31}\text{P}$  NMR studies in solution show the presence of various species in equilibria.

### Introduction

Neutral monodentate tertiary phosphine and arsine complexes of the copper(I) halides  $[(\text{PR}_3)_n\text{CuX}]$  ( $n = 1\text{--}4$ ) have been the subject of extensive investigations.<sup>1</sup> For the different values of  $n$ , monomer, dimer, and tetramer compounds have been isolated.<sup>2</sup> Of these,  $[\text{PR}_3\text{CuX}]$  display a wide diversity of structural types involving varying degrees of association. For example,  $[\text{Cu}_4\text{Cl}_4(\text{PPh}_3)_4]$  adopts a cubanoid structure,<sup>3</sup> while  $[\text{Cu}_4\text{Br}_4(\text{PPh}_3)_4]$  forms both cubanoid<sup>4</sup> and stepladder structures,<sup>5</sup> and  $[\text{Cu}_4\text{I}_4(\text{PPh}_3)_4]$  was found to have a step-like structure only.<sup>6</sup> For this given composition,  $[\text{C}_3\text{P}\text{CuCl}]$  exists as a dimer.<sup>7</sup> In the corresponding thiolate chemistry a tetramer structure is known for the monophosphine adducts of copper(I) thiolates.<sup>8</sup> A trimer having a composition  $[(\text{PPh}_3)_4\text{Cu}_3(\text{SPh})_3]$  was reported

by Dance et al.<sup>9</sup> There appears to be no extensive parallel chemistry developed with other similar sulfur-containing ligands.

Monothiocarbamates and other structurally similar ligands exhibit diversified bonding modes.<sup>10–12</sup> An analogous thiocarboxylate ligand with a similar functionality is expected to exhibit similar bonding modes. However, only a few have been observed so far. For the past several years we have been interested in the chemistry of the thiocarboxylates.<sup>13–20</sup> For

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group 12 metals, thiobenzoate ion acts like a hindered thiolate ligand.<sup>14</sup> The most common bonding mode is bidentate through S and O.<sup>21</sup> In other words, the S and O donor atoms of R{O}CS<sup>-</sup> can be bidentate<sup>22,23</sup> as well as a chelating<sup>19</sup> ligand. However, the  $\mu_2$  bridging mode of the sulfur atom which is ubiquitous in the thiolate chemistry<sup>24,25</sup> has not been observed in the thiocarboxylates except for the dimer [(PPh<sub>3</sub>)<sub>2</sub>Cu( $\mu$ -SC{O}Ph)<sub>2</sub>Cu(PPh<sub>3</sub>)].<sup>26</sup>

In this paper we present the synthesis and structural characterization of several neutral triphenylphosphine copper thiocarboxylates exhibiting hitherto unknown bonding modes, namely,  $\mu_3$ -S<sub>2</sub>O and  $\mu_3$ -S in metal thiocarboxylate compounds. We have also presented the variable temperature (VT) <sup>31</sup>P NMR of these compounds in solution.

## Experimental Section

All materials were obtained commercially and used as received. The solvents were dried by allowing them to stand over 3 Å molecular sieves overnight. The preparations were carried out under a nitrogen atmosphere. The yields are reported with respect to the metal salts. The compounds are fairly stable; however, they were stored under nitrogen at 5 °C to avoid any decomposition. The <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H, and <sup>31</sup>P NMR spectra were recorded on a Bruker ACF300 FT-NMR instrument using TMS as internal reference at 25 °C in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>. The IR spectra (KBr pellet) were recorded using a Bio-Rad FTIR spectrophotometer. The elemental analyses were performed in the microanalytical lab in the Department of Chemistry, National University of Singapore. The purity of the bulk of the materials was checked by comparing the X-ray powder patterns obtained from a D5005 Siemens X-ray diffractometer at 25 °C with those of the simulated X-ray powder diagrams from the single-crystal studies.

[( $\mu_3$ -SC{O}Me-S<sub>3</sub>)<sub>2</sub>( $\mu$ -SC{O}Me-S)<sub>2</sub>(CuPPh<sub>3</sub>)<sub>4</sub>] (**1**). To deprotonated thioacetic acid prepared in situ by reacting 0.5 mL of CH<sub>3</sub>{O}-CSH (7.0 mmol) with 0.28 g of NaOH (7.0 mmol) in 10 mL of water was added a suspension of CuCl (0.69 g, 7.0 mmol) in 20 mL of CH<sub>2</sub>-Cl<sub>2</sub> containing triphenylphosphine (1.84 g, 7.0 mmol). The reddish CH<sub>2</sub>-Cl<sub>2</sub> layer was separated and layered with Et<sub>2</sub>O. Orange color crystals were filtered off, washed with Et<sub>2</sub>O, and dried under vacuum. Yield: 2.34 g (83.4%). Anal. Calcd for C<sub>80</sub>H<sub>72</sub>Cu<sub>4</sub>O<sub>4</sub>P<sub>4</sub>S<sub>4</sub> (mol wt 1603.66): C, 59.91; H, 4.53; S, 7.99; P, 7.73; Cu, 15.85. Found: C, 60.54; H, 4.25; S, 7.04; P, 7.62; Cu, 14.70. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ , ppm 2.03 (12H, CH<sub>3</sub>), 7.24–7.47 (60H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ , ppm. For the thioacetate ligand: 35.5 (CH<sub>3</sub>COS), 205.9 (CH<sub>3</sub>COS). For the PPh<sub>3</sub>: 128.4 (C<sub>3</sub>, <sup>3</sup>J(P–C) = 9.1 Hz), 129.6 (C<sub>4</sub>), 132.7 (C<sub>1</sub>, <sup>1</sup>J(P–C) = 31.6 Hz), 133.8 (C<sub>2</sub>, <sup>2</sup>J(P–C) = 14.8 Hz). <sup>31</sup>P NMR:  $\delta$ , ppm –2.10 (s). IR data (cm<sup>-1</sup>): 3052.9 (w), 2921.7 (w), 2852.2 (w), 1648.0 (s), 1482.0 (m), 1435.7 (s), 1347.0 (w), 1119.3 (s), 1096.1 (s), 999.6 (w), 949.4 (m), 744.9 (s), 694.7 (s), 621.4 (m), 521.0 (s), 505.6 (s).

A similar attempt to prepare the analogous thiobenzoate complex gave **2** (see below).

[( $\mu_3$ -SC{O}Ph-S<sub>3</sub>)<sub>2</sub>( $\mu$ -SC{O}Ph-S<sub>2</sub>O)<sub>3</sub>(Cu)(CuPPh<sub>3</sub>)<sub>3</sub>] (**2**). This compound was synthesized similarly to **1** except that NaSC{O}Ph was used instead of NaSC{O}Me. The yield of reddish yellow crystals was 85%. Anal. Calcd for the desolvated **2**, C<sub>82</sub>H<sub>65</sub>Cu<sub>4</sub>O<sub>4</sub>P<sub>3</sub>S<sub>4</sub> (mol wt 1589.79): C, 61.95; H, 4.12. Found: C, 61.81; H, 4.40. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ , ppm. For thiobenzoic acid ligand: 127.2 (C<sub>2/6</sub> or C<sub>3/5</sub>), 128.8 (C<sub>2/6</sub> or C<sub>3/5</sub>), 129.4 (C<sub>4</sub>), 141.1(C<sub>1</sub>), 201.6(PhCOS). For the

PPh<sub>3</sub>: 128.3 (C<sub>3</sub>, <sup>3</sup>J(P–C) = 9.1 Hz), 130.9 (C<sub>4</sub>), 132.9 (C<sub>1</sub>, <sup>1</sup>J(P–C) = 30.3 Hz), 133.8 (C<sub>2</sub>, <sup>2</sup>J(P–C) = 14.7 Hz). <sup>31</sup>P NMR:  $\delta$ , ppm –1.66 (s). IR data (cm<sup>-1</sup>): 3052.9 (m), 2921.7 (w), 2852.2 (w), 1640.3 (m), 1582.4 (m), 1547.7 (s), 1532.2 (m), 1482.1 (m), 1435.7 (s), 1308.4 (w), 1200.3 (s), 1169.4 (s), 1096.1 (m), 999.6 (w), 922.4 (s), 867.7 (m), 775.8 (m), 744.9 (s), 690.9 (s), 648.4 (w), 521.0 (s).

The same compound was also obtained when the synthesis was carried out using the starting materials according to the stoichiometric ratio of the products. A similar synthetic attempt to prepare the corresponding thioacetate analogue yielded **1**.

[( $\mu$ -SC{O}Me-S)( $\mu$ -SC{O}Me-S,O){Cu(PPh<sub>3</sub>)<sub>2</sub>}] (**3**). Compound **3** was obtained as yellow crystals, when the reaction was carried out similarly to that described for **1** but the ratio of NaSC{O}Me, CuCl, and PPh<sub>3</sub> was 1:1:2. Yield: 84%. Anal. Calcd for C<sub>76</sub>H<sub>66</sub>Cu<sub>2</sub>O<sub>2</sub>P<sub>4</sub>S<sub>2</sub> (mol wt 1326.37): C, 68.82; H, 5.02; P, 9.34; Cu, 9.58. Found: C, 69.14; H, 4.73; P, 9.19; Cu, 9.37. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ , ppm 2.03 (6H, CH<sub>3</sub>), 7.2–7.4 (60H, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P). <sup>13</sup>C NMR:  $\delta$ , ppm 36.1 (CH<sub>3</sub>-COS), 208.9 (CH<sub>3</sub>COS). For PPh<sub>3</sub>: 128.4 (C<sub>3</sub>, <sup>3</sup>J(P–C) = 8.8 Hz), 129.5 (C<sub>4</sub>), 133.2 (C<sub>1</sub>, <sup>1</sup>J(P–C) = 26.4 Hz), 133.7 (C<sub>2</sub>, <sup>2</sup>J(P–C) = 15.1 Hz). <sup>31</sup>P NMR:  $\delta$ , ppm –2.025 (s). IR data (cm<sup>-1</sup>): 3050.2 (m), 2919 (m), 2851.5 (m), 1618.7 (s), 1541.5 (s), 1481.7 (m), 1434.6 (s), 1093.9 (s), 1026.4 (w), 951.1 (w), 743.2 (s), 694.9 (s), 515.1 (s).

[Cu(SC{O}Ph)(PPh<sub>3</sub>)<sub>2</sub>] (**4**). Greenish yellow crystals of **4** were obtained when the synthesis was carried out similarly to that described for **2** with the starting materials PPh<sub>3</sub>, CuCl, and NaSC{O}Ph in the ratio 1:1:2. Yield: 73%. Anal. Calcd for C<sub>43</sub>H<sub>35</sub>P<sub>2</sub>CuSO (mol wt 725.25): C, 71.2; H, 4.86; S, 4.42; P, 8.54; Cu, 8.76. Found: C, 71.02; H, 5.16; S, 4.43; P, 8.59; Cu, 8.61. <sup>13</sup>C NMR data (CDCl<sub>3</sub>):  $\delta$ , ppm. For thiobenzoic acid ligand: 127.2 (C<sub>2/6</sub> or C<sub>3/5</sub>), 128.4 (C<sub>2/6</sub> or C<sub>3/5</sub>), 129.5 (C<sub>4</sub>), 142.5(C<sub>1</sub>), 205.3 (C<sub>6</sub>H<sub>5</sub>COS). For the PPh<sub>3</sub>: 128.4 (C<sub>3</sub>, <sup>3</sup>J(P–C) = 9.3 Hz), 130.4 (C<sub>4</sub>), 133.2 (C<sub>1</sub>, <sup>1</sup>J(P–C) = 27.1 Hz), 133.8 (C<sub>2</sub>, <sup>2</sup>J(P–C) = 15.1 Hz). <sup>31</sup>P NMR:  $\delta$ , ppm, –1.83. IR data (cm<sup>-1</sup>): 3052.1 (m), 2920.9 (w), 2851.5 (w), 1612.9 (w), 1585.9 (w), 1572.4 (w), 1518.3 (m), 1479.8 (s), 1433.5 (s), 1306.1 (w), 1207.7 (s), 1165.3 (m), 1092.0 (s), 1070.8 (w), 1026.4 (w), 997.4 (w), 947.3 (m), 912.6 (w), 773.6 (w), 744.7 (s), 692.6 (s), 648.2 (w), 519.0 (w), 501.6 (w).

[Cu<sub>2</sub>( $\mu$ -SC{O}Ph)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**5**). When the ratio of starting materials NaSC{O}Ph, CuCl, and PPh<sub>3</sub> was 1:1:1.5, the preparation similar to that described for **4** yielded **5** as red crystals. Yield: 73%. Anal. Calcd for C<sub>68</sub>H<sub>55</sub>Cu<sub>2</sub>O<sub>2</sub>P<sub>3</sub>S<sub>2</sub> (mol wt 1188.23): C, 68.73; H, 4.67; Cu, 10.69. Found: C, 68.00; H, 4.20; Cu, 10.17. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ , ppm. For thiobenzoic acid ligand: 127.2 (C<sub>2/6</sub> or C<sub>3/5</sub>), 128.4 (C<sub>2/6</sub> or C<sub>3/5</sub>), 129.4 (C<sub>4</sub>), 141.1 (C<sub>1</sub>), 203(PhCOS). For the PPh<sub>3</sub>: 128.3 (C<sub>3</sub>, <sup>3</sup>J(P–C) = 9.8 Hz), 130.7 (C<sub>4</sub>), 132.9 (C<sub>1</sub>, <sup>1</sup>J(P–C) = 29.4 Hz), 133.8 (C<sub>2</sub>, <sup>2</sup>J(P–C) = 15.3 Hz). <sup>31</sup>P NMR:  $\delta$ , ppm –1.22 (s). IR data (cm<sup>-1</sup>): 3050.2 (w), 2921.7 (w), 2855.4 (w), 1609 (s), 1591.7 (s), 1568.5 (s), 1481.7 (s), 1434.3 (s), 1306.1 (m), 1210.2 (s), 1167.2 (s), 1095.8(s), 1090.6 (m), 1026.4 (s), 1000.3 (m), 940 (s), 914.5 (s), 849.5 (m), 779.7 (m), 748.4 (m), 690.2 (s), 520 (s), 506.3 (m).

Attempts to prepare the corresponding thioacetate analogue by a similar synthetic route resulted in the formation of a mixture of reddish block-like crystals of **1** and yellow platy crystals of **3**.

**X-ray Crystallography.** The diffraction experiments were carried out on a Bruker SMART CCD diffractometer with a Mo K $\alpha$  sealed tube at 23 °C. The software SMART<sup>27</sup> was used for collecting frames of data, indexing reflection, and determination of lattice parameters, SAINT<sup>27</sup> for integration of the intensity of reflections and scaling, SADABS<sup>28</sup> for absorption correction, and SHELXL<sup>29</sup> for space group and structure determination and least-squares refinements on F<sup>2</sup>. One of the phenyl rings of the thiocarboxylate ligand (C31–C36), one phenyl ring (C11–C16) attached to the P3 atom and the solvents were found to be disordered in **2**. Two orientations of the phenyl rings were modeled for the thiocarboxylate ring and the PPh<sub>3</sub> phenyl ring

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**Table 1.** Crystallographic Data for Compounds [Cu<sub>4</sub>(SC{O}Me)<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>] (**1**), [Cu<sub>4</sub>(SC{O}Ph)<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**2**), [Cu<sub>2</sub>(SC{O}Me)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (**3**), and [Cu(SC{O}Ph)(PPh<sub>3</sub>)<sub>2</sub>] (**4**)

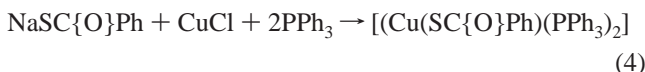
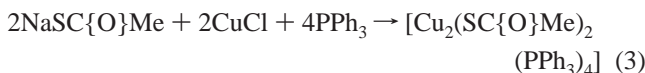
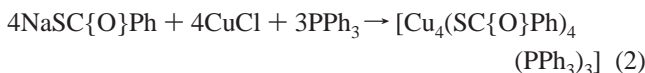
	1	2	3	4
chem formula	C <sub>80</sub> H <sub>72</sub> Cu <sub>4</sub> O <sub>4</sub> P <sub>4</sub> S <sub>4</sub>	C <sub>82.5</sub> H <sub>67</sub> ClCu <sub>4</sub> O <sub>5</sub> P <sub>3</sub> S <sub>4</sub>	C <sub>76</sub> H <sub>66</sub> Cu <sub>2</sub> O <sub>2</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>43</sub> H <sub>35</sub> CuOP <sub>2</sub> S
fw	1603.66	1649.12	1326.37	725.25
T, °C	23	23	23	23
λ, Å	0.71073	0.71073	0.71073	0.71073
space group	P $\bar{1}$	P $\bar{1}$	P2(1)/n	P $\bar{1}$
a, Å	11.5844(3)	12.4413(1)	15.2746(2)	10.2524(3)
b, Å	13.2459(3)	15.5443(1)	23.2987(2)	12.9826(4)
c, Å	14.3433(3)	20.4637(3)	19.0518(3)	14.5340(4)
α, deg	64.019(1)	94.974(1)	90	87.723(1)
β, deg	79.297(1)	95.976(1)	96.713(1)	75.322(1)
γ, deg	69.426(1)	100.450(1)	90	75.978(1)
V, Å <sup>3</sup>	1850.98(7)	3848.09(7)	6732.5(2)	1815.14(9)
Z	1	2	4	2
ρ <sub>calcd.</sub> , g/cm <sup>3</sup>	1.439	1.416	1.309	1.327
abs coeff, mm <sup>-1</sup>	1.382	1.346	0.834	0.780
R1 (F <sub>o</sub> ≥ 4σ(F <sub>o</sub> )) <sup>a</sup>	0.0493	0.0580	0.0618	0.0499
wR2(F <sub>o</sub> ≥ 4σ(F <sub>o</sub> )) <sup>a</sup>	0.0982	0.1163	0.0996	0.0958

$$^a R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|; wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}.$$

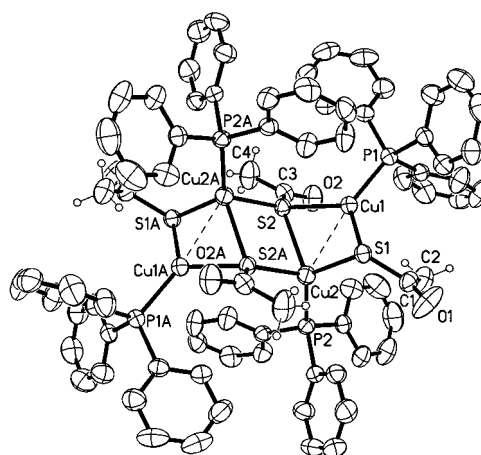
(occupancies, 0.55/0.45; common isotropic thermal parameters for each disordered ring). These disordered phenyl rings were treated as regular hexagons. In the solvent region, one-half molecule of CH<sub>2</sub>Cl<sub>2</sub> (common isotropic thermal parameters for non-hydrogen atoms) and a H<sub>2</sub>O (disordered over three sites with occupancies 0.5, 0.25, 0.25) were found. In **3**, a phenyl ring (C1D–C6D) attached to phosphorus atom P2 was disordered. Two orientations were modeled with 0.5:0.5 occupancy. These two disordered rings were treated as regular hexagons, and their common isotropic thermal parameters were refined for each ring. The relevant crystallographic data and refinement details are shown in Table 1.

## Results and Discussion

**Synthesis.** The compounds **1–5** were prepared by the addition of the corresponding thiocarboxylates to a CH<sub>2</sub>Cl<sub>2</sub> solution containing PPh<sub>3</sub> and a suspension of the CuCl. For a 1:1:1 stoichiometric ratio of CuCl:NaSC{O}R:PPh<sub>3</sub>, the thioacetate anion gave the tetramer **1**, [(μ<sub>3</sub>-SC{O}Me-*S*)<sub>2</sub>(μ-SC{O}Me-*S*)<sub>2</sub>(CuPPh<sub>3</sub>)<sub>4</sub>], and the thiobenzoate ligand yielded the product **2**, [(μ<sub>3</sub>-SC{O}Ph-*S*)<sub>2</sub>(μ-SC{O}Ph-*S*)<sub>2</sub>(Cu)(CuPPh<sub>3</sub>)<sub>3</sub>], with a different stoichiometric ratio. Compound **2** could also be prepared by reacting CuCl, NaSC{O}Ph, and PPh<sub>3</sub> in the ratio 4:4:3. The corresponding reaction of NaSC{O}Me with CuCl and PPh<sub>3</sub> in the ratio 4:4:3 yielded **1** and not the thioacetate analogue of **2**. When the stoichiometric ratio CuCl:NaSC{O}R:PPh<sub>3</sub> is 1:1:2, the products obtained by thioacetate and thiobenzoate ligands have the same ratio of the reactants, but different molecular formula and structures. Thioacetate and thiobenzoate ligands gave a dimer, **3**, [(μ-SC{O}Me-*S*)(μ-SC{O}Me-*S,O*)-{Cu(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>], and a monomer, [Cu(SC{O}Ph)(PPh<sub>3</sub>)<sub>2</sub>], **4**, respectively. The reactions are summarized in eqs 1–4.

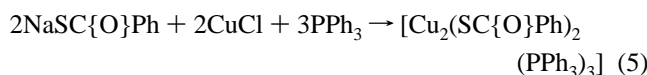


When R = Ph, the 1:1:1.5 ratio of the reactants gave the expected unsymmetric dimer, [Cu<sub>2</sub>(μ-SC{O}Ph)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] (**5**),



**Figure 1.** Perspective view of **1** with 50% probability thermal ellipsoids. The hydrogen atoms on the phenyl rings are omitted for clarity.

which was obtained by a different route by Speier, Fulop, and Arguy.<sup>26</sup> It is interesting to note that, under the same experimental conditions and reactant ratio, R = Me gave a mixture of **1** and **3**.



Attempts to prepare the complex [Cu<sub>4</sub>(SC{O}Ph)<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>] by slow evaporation of the reaction mixture in toluene or benzene as solvent yielded a mixture of **2** and the known unsymmetrical dimer **5**.

## Structural Description

**Structure of Compound 1.** The results of X-ray diffraction studies reveal that the unit cell contains one tetramer with a crystallographic center of symmetry. A view of **1** is shown in Figure 1, and selected bond distances and angles are given in Table 2. In **1**, the Cu and the S atoms are alternatively bonded to form an eight-membered ring in which two sulfur atoms are further bridging two copper atoms to form a highly distorted stepladder arrangement or a highly distorted chair-like conformation. The copper atoms are bonded to a phosphine ligand in such a way that two Cu atoms have approximate CuPS<sub>2</sub> trigonal planar geometry and the other two have CuPS<sub>3</sub> tetrahedral

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compound 1

Bond Lengths			
Cu(1)–P(1)	2.2372(9)	Cu(2)–P(2)	2.2331(9)
Cu(1)–S(1)	2.2792(9)	Cu(2)–S(1)	2.3329(9)
Cu(1)–S(2)	2.3123(9)	Cu(2)–S(2)	2.5876(9)
Cu(2)–S(2) <sup>a</sup>	2.3790(9)	C(1)–S(1)	1.786(4)
C(3)–S(2)	1.777(4)	C(1)–O(1)	1.199(4)
C(3)–O(2)	1.205(4)	C(1)–C(2)	1.503(5)
C(3)–C(4)	1.497(5)	Cu(1)–Cu(2)	2.7477(6)

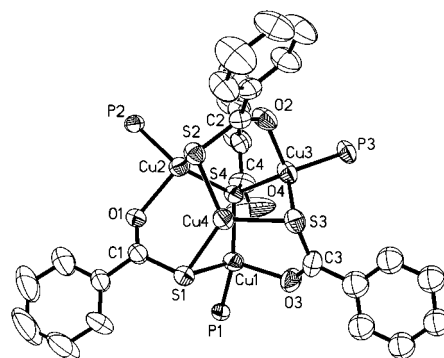
  

Bond Angles			
P(1)–Cu(1)–S(1)	127.22(4)	P(2)–Cu(2)–S(1)	125.05(3)
P(1)–Cu(1)–S(2)	122.05(3)	P(2)–Cu(2)–S(2)	118.51(3)
P(2)–Cu(2)–S(2) <sup>a</sup>	118.48(3)	Cu(1)–S(1)–Cu(2)	73.12(3)
Cu(1)–S(2)–Cu(2)	67.95(2)	Cu(1)–S(2)–Cu(2) <sup>a</sup>	126.87(4)
Cu(2)–S(2)–Cu(2) <sup>a</sup>	98.90(3)	S(1)–Cu(1)–S(2)	109.74(3)
S(1)–Cu(2)–S(2)	99.36(3)	S(2)–Cu(2)–S(2) <sup>a</sup>	81.10(3)
S(1)–Cu(2)–S(2) <sup>a</sup>	104.72(3)	S(2) <sup>a</sup> –Cu(2)–Cu(1)	111.06(3)
S(2)–Cu(2)–Cu(1)	51.26(2)	S(1)–C(1)–C(2)	119.5(3)
S(2)–C(3)–C(4)	116.5(3)	S(1)–C(1)–O(1)	119.5(3)
S(2)–C(3)–O(2)	121.3(3)	O(1)–C(1)–C(2)	121.0(4)
O(2)–C(3)–C(4)	122.2(3)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: 1 – x, 1 – y, 1 – z.

coordination geometry. There are two types of bridging sulfur atoms present, namely,  $\mu_2$ - and  $\mu_3$ -S. The structure is similar to the tetramer, [( $\mu_3$ -SPh)<sub>2</sub>( $\mu$ -SPh)<sub>2</sub>(CuPPh<sub>3</sub>)<sub>4</sub>](2toluene) reported by Dance, Scudder, and Fitzpatrick.<sup>8</sup> The Cu–S distances at the trigonal Cu center (2.2792(9) and 2.3123(9) Å) are shorter than corresponding distances at the tetrahedral Cu center (2.3329(9), 2.379(9), and 2.5876(9) Å). These Cu–S distances are longer than the Cu–S distance, 2.151(3) Å, observed in the [Cu(SC{O}Me)<sub>2</sub>]<sup>–</sup> anion<sup>30</sup> with terminal thioacetate ligands. The Cu(1)–S distances observed here are comparable to the corresponding Cu–S distances observed in the copper thiolate tetramer.<sup>8</sup> However, the triply bridging sulfur atom S(2) in **1** is not symmetrically bonded to the copper atoms in the central plane. The lengthening of Cu(2)–S(2) bond may be attributed to the steric crowd of the CH<sub>3</sub> group along this bond. The central Cu<sub>2</sub>S<sub>2</sub> plane is reclined at an angle of 126.28(3)° with the Cu(1)Cu(2)S(2) plane. The Cu–P distances are normal and warrant no further discussion. The atoms Cu(1), P(1), S(1), S(2) lie on a plane (rms deviation, 0.056). The closest Cu...O distance is between Cu(1) and O(2), 3.238 Å, which rules out any possibility of weak interaction between these two atoms.

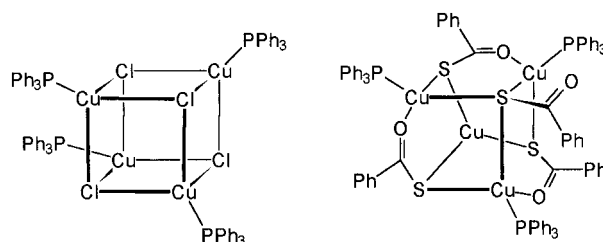
**Structure of Compound 2.** A perspective view of **2** is shown in Figure 2, and selected bond distances and angles are given in Table 3. This neutral cluster consists of four Cu(I) atoms, of which three form the triangular base of a tetrahedron. Each one of these three copper atoms is bonded to a PPh<sub>3</sub> ligand and bridged by two Ph{O}CS<sup>–</sup> ions through S and O atoms in such a way that all the sulfur atoms are above the Cu<sub>3</sub> plane. These sulfur atoms are further bonded to the fourth Cu atom at the apex of Cu<sub>4</sub> tetrahedron and provide a trigonal planar coordination geometry to Cu(4). The sulfur atom of the fourth thiobenzoate ligand is bonded to Cu(1), Cu(2), and Cu(3) from the bottom of the Cu<sub>4</sub> tetrahedron, through a  $\mu_3$  bridging. The copper atoms Cu(1), Cu(2), and Cu(3), therefore, have a CuPOS<sub>2</sub> skeleton and tetrahedral coordination geometry. Compound **2** may also be viewed as derived from a cubanoid structure. In a cubane-like compound, [(Ph<sub>3</sub>PCu)<sub>4</sub>( $\mu_3$ -Cl)<sub>4</sub>], all the chloride ions are involved in  $\mu_3$  bridging.<sup>3</sup> On the other hand, each sulfur atom of the three Ph{O}CS<sup>–</sup> anions is bonded to two Cu(I)

**Figure 2.** View of the compound **2**. The atoms are drawn with 50% probability thermal ellipsoids. The phenyl rings attached to the phosphorus atoms and the hydrogen atoms are omitted for clarity.**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for Compound 2

Bond Lengths			
Cu(1)–P(1)	2.247(1)	Cu(2)–P(2)	2.254(2)
Cu(3)–P(3)	2.231(2)	Cu(1)–S(1)	2.511(2)
Cu(2)–S(2)	2.358(2)	Cu(3)–S(3)	2.421(2)
Cu(4)–S(1)	2.247(2)	Cu(4)–S(2)	2.304(2)
Cu(4)–S(3)	2.246(2)	Cu(1)–S(4)	2.289(1)
Cu(2)–S(4)	2.344(2)	Cu(3)–S(4)	2.307(2)
Cu(1)–O(3)	2.174(4)	Cu(2)–O(1)	2.193(4)
Cu(3)–O(2)	2.179(4)	C(1)–S(1)	1.763(6)
C(2)–S(2)	1.758(6)	C(3)–S(3)	1.754(6)
C(4)–S(4)	1.813(6)	C(1)–O(1)	1.238(6)
C(2)–O(2)	1.237(6)	C(3)–O(3)	1.236(6)
C(4)–O(4)	1.202(7)	Cu(1)–Cu(4)	2.8423(9)
Cu(2)–Cu(4)	2.7526(9)	Cu(3)–Cu(4)	2.966(1)

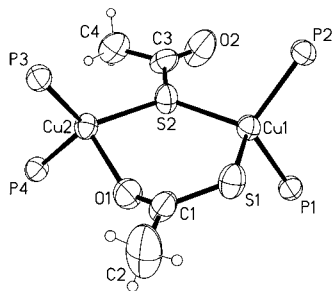
  

Bond Angles			
P(1)–Cu(1)–S(1)	102.02(6)	P(1)–Cu(1)–O(3)	102.5(1)
P(1)–Cu(1)–S(4)	132.56(6)	S(1)–Cu(1)–O(3)	98.8(1)
P(2)–Cu(2)–S(2)	114.34(6)	P(2)–Cu(2)–O(1)	94.1(1)
P(2)–Cu(2)–S(4)	125.10(6)	S(2)–Cu(2)–O(1)	103.2(1)
P(3)–Cu(3)–S(3)	112.83(6)	P(3)–Cu(3)–O(2)	104.1(1)
P(3)–Cu(3)–S(4)	125.70(6)	S(3)–Cu(3)–O(2)	95.8(1)
Cu(1)–S(1)–Cu(4)	73.13(5)	Cu(2)–S(2)–Cu(4)	72.36(4)
Cu(3)–S(3)–Cu(4)	78.85(5)	Cu(1)–S(4)–Cu(2)	105.95(6)
Cu(2)–S(4)–Cu(3)	98.23(5)	Cu(1)–S(4)–Cu(3)	101.19(6)
S(1)–Cu(4)–S(2)	124.17(6)	S(2)–Cu(4)–S(3)	128.44(5)
S(1)–Cu(4)–S(3)	123.99(6)	C(1)–S(1)–Cu(4)	73.13(5)
C(2)–S(2)–Cu(4)	103.34(18)	C(3)–S(3)–Cu(4)	106.4(2)
C(1)–O(1)–Cu(2)	132.6(4)	C(2)–O(2)–Cu(3)	126.4(3)
C(3)–O(3)–Cu(1)	130.2(4)	S(1)–Cu(1)–S(4)	106.71(5)
S(2)–Cu(2)–S(4)	112.24(5)	S(3)–Cu(3)–S(4)	107.21(5)
O(3)–Cu(1)–S(4)	109.4(1)	O(1)–Cu(2)–S(4)	102.2(1)
O(2)–Cu(3)–S(4)	106.8(1)	C(4)–S(4)–Cu(1)	113.9(2)
C(4)–S(4)–Cu(2)	123.0(2)	C(4)–S(4)–Cu(3)	111.5(2)
S(1)–C(1)–O(1)	122.9(4)	S(2)–C(2)–O(2)	123.3(4)
S(3)–C(3)–O(3)	123.8(4)	S(4)–C(4)–O(4)	118.6(5)
Cu(2)–Cu(4)–Cu(3)	75.77(3)	Cu(1)–Cu(4)–Cu(3)	75.34(2)

**Figure 3.** Schematic representation of [(Ph<sub>3</sub>PCu)<sub>4</sub>( $\mu_3$ -Cl)<sub>4</sub>] (left) and **2** (right) showing the relationship between these two structures.

atoms and the oxygen atom of the carbonyl group is bonded to a third Cu(I) atom in **2** as in Figure 3. Only one thiobenzoate anion is involved in the  $\mu_3$ -S bridging. The compound **2** is, therefore, highly distorted from the cubanoid structure. The

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**Figure 4.** Structure of **3** showing 50% probability thermal ellipsoids. The phenyl rings attached to the phosphorus atoms have been omitted.

trigonal planar geometry causes Cu(4) to be closer to the Cu<sub>3</sub> triangle. This resulted in shorter Cu···Cu distances (2.753(1)–2.966(1) Å) between Cu(4) and the rest of the copper atoms and smaller Cu–S–Cu(4) angles (73.15(5)°, 72.36(4)°, and 78.85(5)°). Consequently, the distances between Cu(1), Cu(2), and Cu(3) are longer (3.516(1)–3.700(1) Å) than Cu···Cu(4) distances. The S(4)–C(4) bond distance, 1.813(6) Å, of the μ<sub>3</sub>-S bridged Ph{O}CS<sup>−</sup> ligand is longer than the other S–C distances, 1.754(6)–1.763(6) Å. The oxygen atoms of the thiobenzoate ligands are bonded to the tetrahedral Cu atoms; as a result, the C(1)–O(1), C(2)–O(2), and C(3)–O(3) distances (1.238(6), 1.237(6), and 1.236(7) Å, respectively) are longer than the C(4)–O(4) distance, 1.202(7) Å. The Cu–S distances around the trigonal planar copper(I) center, Cu(4) (2.246(2)–2.304(2) Å), are shorter than the corresponding distances of the tetrahedral copper(I) centers (2.289(1)–2.511(2) Å). A survey of Cambridge Structure Database search<sup>31</sup> shows that the Cu–S distances in similar compounds containing bridging sulfur ligands and trigonal CuS<sub>3</sub> geometry are in the range 2.166–2.371 Å. The nonbonded distance between Cu(4) and S(4) is 2.981(1) Å, which is less than the sum of the van der Waals radii, 3.2 Å.<sup>32</sup>

From the thiobenzoate perspective, there are two types of bonding modes present in **2**. In one mode of bonding, the sulfur atom is bridging two metal atoms while the oxygen atom is bonded to the third. A different μ<sub>3</sub>-S<sub>2</sub>O bonding mode was observed in neutral metal–monothiocarbamate complexes of the type [M(SC{O}NR<sub>2</sub>)<sub>6</sub>] (M = Cu and Ag)<sup>33,34</sup> and [Ni(SC{O}NR<sub>2</sub>)<sub>2</sub>]<sub>6</sub><sup>35</sup> in which S and O of the ligand are chelated to the metal. In the second bonding mode, the thiobenzoate S atom binds to three different metals. This μ<sub>3</sub>-S bridging is not known either in monothioxanthates or in monothiocarbamates. However, such a bonding mode is quite common in metal thiolate chemistry.<sup>8,24,25,36–38</sup>

**Structure of Compound 3.** For the given stoichiometry, the neutral bis(phosphine) adduct of the copper thioacetate compound **3** exists as a dimer, [(μ-SC{O}Me-S)(μ-SC{O}Me-S,O)-{Cu(PPh<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>, in the solid state as shown in Figure 4. In this dimer two different bonding modes were observed for the thioacetate ligands bridging the two copper atoms. One Me{O}CS<sup>−</sup> is bridged through a S atom, and the other thioacetate is bonded through S and O atoms. Two PPh<sub>3</sub> ligands

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for Compound **3**

Bond Lengths			
Cu(1)–P(1)	2.3240(9)	Cu(1)–P(2)	2.3219(9)
Cu(2)–P(3)	2.2814(9)	Cu(2)–P(4)	2.2879(9)
Cu(1)–S(1)	2.365(1)	Cu(1)–S(2)	2.3400(9)
Cu(2)–S(2)	2.3128(9)	Cu(2)–O(1)	2.173(2)
C(3)–S(2)	1.741(3)	C(1)–S(1)	1.728(4)
C(1)–O(1)	1.221(4)	C(3)–O(2)	1.213(4)
C(1)–C(2)	1.513(5)	C(3)–C(4)	1.509(5)
Cu(1)–Cu(2)	4.074(1)		
Bond Angles			
P(1)–Cu(1)–P(2)	109.41(3)	P(3)–Cu(2)–P(4)	116.26(3)
S(1)–Cu(1)–P(1)	100.17(3)	S(2)–Cu(2)–P(3)	120.72(3)
S(1)–Cu(1)–P(2)	115.59(4)	S(2)–Cu(2)–P(4)	116.48(3)
S(1)–Cu(1)–S(2)	104.73(3)	O(1)–Cu(2)–S(2)	88.61(7)
S(2)–Cu(1)–P(2)	107.87(3)	O(1)–Cu(2)–P(3)	105.23(8)
S(2)–Cu(1)–P(1)	119.22(3)	O(1)–Cu(2)–P(4)	101.78(7)
S(1)–C(1)–O(1)	127.2(3)	Cu(1)–S(2)–Cu(2)	122.23(4)
O(2)–C(3)–S(2)	123.3(3)	O(2)–C(3)–C(4)	120.1(3)
S(2)–C(3)–C(4)	116.6(3)	S(1)–C(1)–C(2)	116.9(3)
O(1)–C(1)–C(2)	115.9(3)	C(1)–O(1)–Cu(2)	143.2(2)

are bonded to each copper atom to complete the tetrahedral geometry with different coordination environments around two copper atoms.

Selected bond distances and angles are displayed in Table 4. The Cu–P distances around Cu(1) having a CuP<sub>2</sub>S<sub>2</sub> skeleton are slightly longer than the distances around Cu(2) with the CuOP<sub>2</sub>S kernel. The bridging S(2) atom is unsymmetrically bonded to the copper atoms. It is interesting to note that the bridging Cu(1)–S(2) and Cu(2)–S(2) distances (2.340(1) and 2.313(1) Å respectively) are shorter than the Cu(1)–S(1) distance, 2.365(1) Å, in which the sulfur atom is attached to a Cu atom only. On the other hand, the S(2)–C(3) distance, 1.741(3) Å, is longer than the S(1)–C(1) distance, 1.728(4) Å. In the bidentate CH<sub>3</sub>{O}CS<sup>−</sup> ligand, since both O(1) and S(1) atoms are involved in bonding, one would expect that the electrons are delocalized to give a partial double bond character for S(1). It is, therefore, expected that S(1) would bind weakly to Cu(1) as compared to S(2) and thus account for the observed anomaly. The C–O distances also show the expected trend (Table 4). The six-membered ring is highly distorted. The atoms Cu(1), S(2), Cu(2), and S(1) are on one plane (rms deviation, 0.046 Å), and the S(1), C(1), and O(1) atoms are in another plane (rms deviation, 0.002 Å). The dihedral angle between these two planes is 18.5(1)°. The Cu(2)–O(1) distance, 2.173(2) Å, is comparable to those observed in **2** (see Table 3).

**Structure of Compound 4.** The neutral (bisphosphine) adduct of the copper thiobenzoate compound is a monomer in the solid state as shown in Figure 5. Two PPh<sub>3</sub> ligands and a Ph{O}CS<sup>−</sup> anion are bonded to the copper atom. Table 5 shows that the Cu–P distances are normal. The Cu(1), P(1), P(2), and S(1) atoms are in a plane (rms deviation, 0.044 Å), and the sum of the angles around Cu(1) is 359.4°. The thiobenzoate ligand, therefore, is mainly bonded through the S atom to provide a trigonal planar geometry for Cu(1) in **4**. There is, however, a weak interaction between Cu(1) and O(1) as shown by the bond distance, 2.439(2) Å, which is less than the sum of the van der Waals radii, 2.9 Å.<sup>32</sup> The Cu–S distance, 2.3267(8) Å, is slightly longer than those observed for the trigonal planar copper in **2** (Table 3). The phenyl ring and the plane containing the C(1), C(2), O(1), S(1), and Cu(1) atoms are twisted from each other (dihedral angle, 5.4(2)°), which is quite normal in the chemistry of metal thiobenzoates.<sup>14</sup> The bond mode of sulfur

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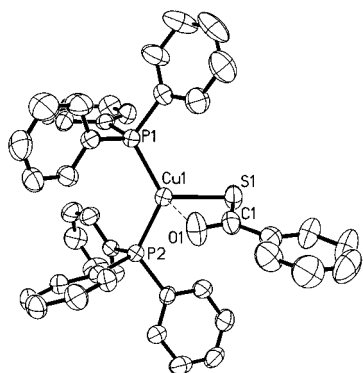
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**Figure 5.** Molecular structure of **4** showing 50% probability thermal ellipsoids. The hydrogen atoms are not shown for clarity.

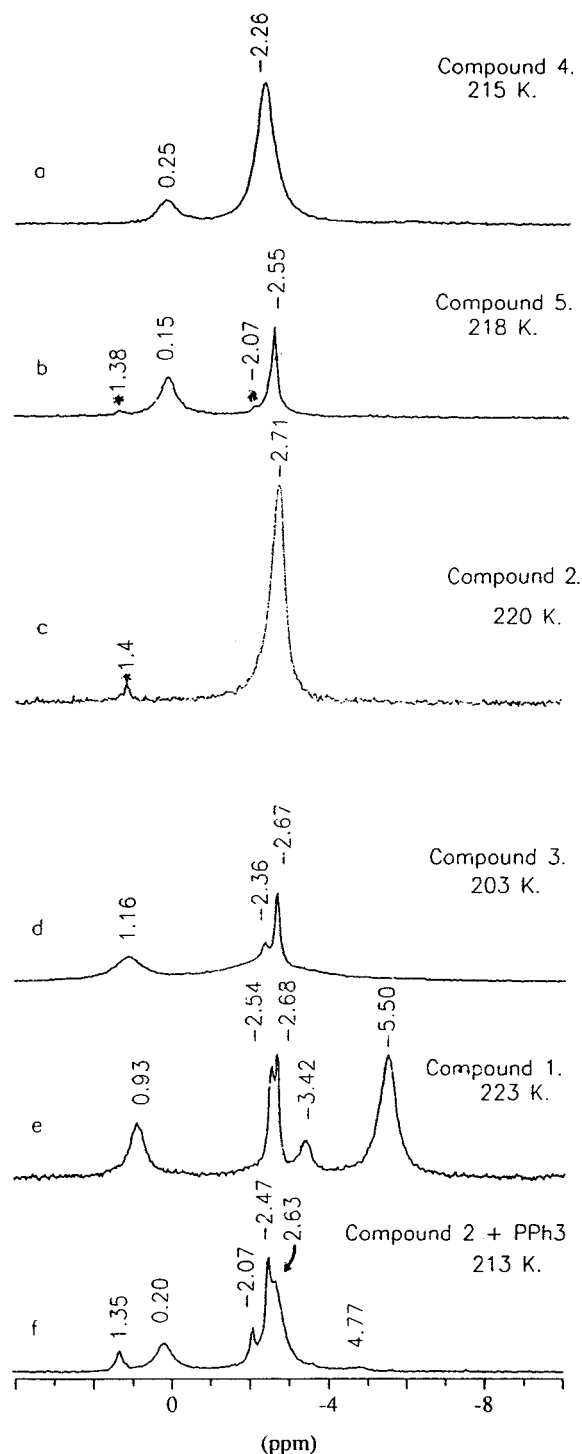
**Table 5.** Selected Bond Lengths (Å) and Bond Angles (deg) for the Compound **4**

Bond Lengths			
Cu(1)–S(1)	2.3267(8)	Cu(1)–O(1)	2.439(2)
Cu(1)–P(1)	2.2567(8)	Cu(2)–P(2)	2.2686(8)
C(1)–O(1)	1.242(3)	C(1)–S(1)	1.708(3)
Bond Angles			
P(1)–Cu(1)–P(2)	126.68(3)	O(1)–Cu(1)–S(1)	65.19(6)
O(1)–Cu(1)–P(1)	113.02(7)	O(1)–Cu(1)–P(2)	95.28(7)
S(1)–Cu(1)–P(1)	118.36(3)	S(1)–Cu(1)–P(2)	114.36(3)
S(1)–C(1)–O(1)	120.3(2)	O(1)–C(1)–C(2)	119.0(3)
S(1)–C(1)–C(2)	120.6(2)		

in **4** is common and observed in many compounds of monothioxanthates and monothiocarbamates.<sup>39,40</sup>

**VT <sup>31</sup>P NMR Studies.** Phosphine adducts of neutral copper halides and copper mono- and dithiocarbamate compounds are known to associate and/or dissociate in solution.<sup>10,41,42</sup> Tanaka et al.<sup>43,44</sup> have studied the nature of species formed by dissolving the adducts of copper(I) monothiocarbamate with phosphine in solution, using molecular weight determination, conductivity measurements, and <sup>1</sup>H NMR spectra and found that these compounds undergo dissociation and/or association in solution to give an equilibrium mixture of those with various copper ligand ratios, depending on the composition of the adducts, nature of the solvents, concentration, temperature, etc. The solution structures of these compounds have not been probed in detail by <sup>31</sup>P NMR spectroscopy, probably due to fast exchange between the phosphine and copper at all the temperatures.<sup>45</sup>

The general features observed in this study are summarized as follows. (1) All the compounds gave broad singlets in <sup>31</sup>P spectra, as a result of rapid exchange of the PPh<sub>3</sub> ligands at room temperature in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> solution. However, when the solutions were cooled, more than one line was observed (see Supporting Information). Figure 6 shows the low-temperature spectra of compounds **1–5** and a 1:1 mixture of **2** and PPh<sub>3</sub>. (2) A narrow range of chemical shifts were observed at room temperature (–1.2 to –2.1 ppm) and at low temperatures



**Figure 6.** Low-temperature <sup>31</sup>P NMR spectra for compounds **1–5** and for a **2**/PPh<sub>3</sub> mixture.

(1.4 to –5.5 ppm). (3) The lines were broad and no couplings were observed at any temperature. (4) Slow exchange limits were not reached for any compound at any temperature studied. The assignments of chemical shifts were only tentative and were based on the assumption that the chemical shifts at low temperatures vary according to the coordination geometry of the copper atom to which the phosphorus atoms are attached, in the following order: linear ( $\delta \geq 1.5$  ppm) > trigonal planar ( $1.5 \geq \delta \geq -1.0$  ppm) > tetrahedral ( $-1.0 \geq \delta \geq -4.0$  ppm) geometry.

The monomer **4** gave a broad single resonance at –1.90 ppm. When the solution had been cooled, the line had broadened

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(Supporting Information), and at 215 K, two signals were observed at 0.25 ( $\Delta\nu_{1/2} \approx 73$  Hz) and  $-2.26$  ppm ( $\Delta\nu_{1/2} \approx 72$  Hz). It is proposed that the parent monomer compound with trigonal planar  $\text{CuPS}_2$  geometry ( $\delta$ , 0.25 ppm) is in equilibrium with the dimer, in which the Cu atoms have tetrahedral geometry ( $\delta$ ,  $-2.26$  ppm). The predominant species in solution is the dimeric compound as seen by the intensity of the signal at  $-2.26$  ppm (Figure 6a). Compound **5** with two different coordination geometries gave similar chemical shifts at 218 K confirming the assignments for **4**. However, the resonance at  $-2.55$  ppm ( $\Delta\nu_{1/2} \approx 22$  Hz) in **5** has sharpened compared to that in **4**. There are some additional minor species present in the solution (as indicated by asterisks in Figure 6b). The cubanoid compound **2** gives a broad singlet at room temperature at  $-1.48$  ppm ( $\Delta\nu_{1/2} \approx 63$  Hz). The singlet is slightly shielded ( $\delta$ ,  $-2.71$  ppm) and sharpened at 220 K as shown in Figure 6c. It appears that the cluster retains its core even in solution. Again the chemical shift is assigned to the phosphorus in the tetrahedral  $\text{CuPS}_3$  core.

Compound **3** gave one broad singlet at room temperature at  $-2.01$  ppm ( $\Delta\nu_{1/2} \approx 85$  Hz). On cooling of the solution at 203 K, the intensity of this singlet diminished and three additional signals were observed at  $-2.67$ ,  $-2.36$ , and  $+1.16$  ppm (Figure 6d). On the basis of our assumption, the chemical shift at 1.15 ppm has been assigned to the phosphorus attached to the copper with trigonal planar geometry, and the other two shifts have been assigned to P atoms of the tetrahedral cores,  $\text{CuPS}_3$  and  $\text{CuP}_2\text{OS}$ . The LT  $^{31}\text{P}$  NMR spectrum for **3** appears to indicate that the dimer is in equilibrium with monomer and the  $\delta$  1.16 ppm may be assigned to the  $\text{CuP}_2\text{S}$  core.

Compound **1** gave a broad singlet at  $\delta$   $-2.11$  ppm at ambient temperatures. Upon lowering of the temperature to 223 K, five signals appeared (0.93,  $-2.54$ ,  $-2.68$ ,  $-3.42$ , and  $-5.50$  ppm, Figure 6e). On the basis of the tetrameric structure of **1**, only two singlets are expected, one for the trigonal  $\text{CuPS}_2$  core and

the other for the tetrahedral  $\text{CuPS}_3$  core. The signal at  $-5.50$  ppm is predominant and close to the chemical shift of the free phosphine. If this is so, it may be assumed that the tetramer loses  $\text{PPh}_3$  partially to give the cubanoid compound similar to **2**. Additional resonance lines found in the region due to the tetrahedral copper core appear to support this. In the absence of slow exchange spectra, the chemical shift assignments are only tentative; nevertheless, the  $^{31}\text{P}$  NMR studies indicate that more than one species present is in equilibrium in solution.

To find out whether **2** forms a 1:1:1 compound analogous to **1**,  $^{31}\text{P}$  NMR spectra were recorded at various temperatures for the **2**/ $\text{PPh}_3$  mixture (Supporting Information). While the room temperature spectrum has a singlet at  $\delta$   $-1.15$  ppm, the  $^{31}\text{P}$  spectrum at 213 K shows several singlets spaced together in two regions as given in Figure 6f. These two regions have been assigned to trigonal and tetrahedral copper cores along with a small amount of what appears to be free  $\text{PPh}_3$  as shown in Figure 6. Although the  $^{31}\text{P}$  NMR spectrum does not look quite similar to Figure 6e, due to different substituents, chemical shifts were observed as expected, in two regions, namely, trigonal and tetrahedral copper centers. In other words,  $[(\mu_3\text{-SC}\{\text{O}\}\text{Ph-S})_2(\mu\text{-SC}\{\text{O}\}\text{Ph-S})_2(\text{CuPPh}_3)_4]$  may be present in solution along with **2**.

**Acknowledgment.** This research work is supported by the National University of Singapore through a research grant (Grant RP970618) to J.J.V. G.X.L. from Raffles Junior College is under Students Research Program.

**Supporting Information Available:** Complete variable temperature  $^{31}\text{P}$  NMR spectra for complexes **1–5**. X-ray crystallographic files in CIF format for the structure determinations of complexes **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC9907314