

**Figure 1.** Maximum quantum yields<sup>13</sup> for bicyclopentanol + ketone formation vs. triplet reactivities of substituted valerophenones.

operative, an enhancement in the triplet state reactivity of ketone **1a** would not result in a corresponding increase in quantum efficiency. This follows from eq 1 and eq 2 where the corresponding efficiencies for hydrogen abstraction ( $k_r/k_r + k_{-i}$ ) and ( $k_r/k_r + k_d$ ), would approximate unity. Alternatively, if mechanism 3 is correct or mechanism 1 with  $k_r \approx k_{-i}$ , the quantum yield for reaction of ketone **1a** would be directly related to its triplet state reactivity. From eq 3 mechanism 3 can be further distinguished from mechanism 1 with  $k_r \approx k_i$ . Under conditions where  $\alpha k_r < k_d$ , eq 3 predicts that the quantum yields for reaction of the substituted phenyl cyclobutyl ketones **1b–d** will be directly proportional to the triplet  $k_r$  values of the correspondingly substituted valerophenones. This does not hold for eq 1 and mechanism 1 with  $k_r \approx k_{-i}$ . Furthermore, under these conditions mechanism 3 predicts that the triplet lifetimes of ketones **1a–d** each being dominated by  $k_d$  will be comparable.

The quantum efficiencies for reaction of the phenyl substituted ketones **1b–d** were determined to be 0.001, 0.050, and 0.089, respectively.<sup>13</sup> In addition the triplet lifetimes of ketones **1c–d** were determined from linear Stern–Volmer plots and were found to be in good agreement with the triplet lifetime of ketone **1a**.<sup>13,3e</sup> A plot of the quantum yields vs. the triplet reactivity values of the correspondingly substituted valerophenones<sup>12</sup> is shown in Figure 1. The linear plot clearly demonstrates the direct relationship of quantum efficiency to triplet state reactivity in the cyclic ketone system (**1**) and

(13) All quantitative measurements were performed on degassed samples (three freeze–thaw cycles to  $5 \times 10^{-4}$  mm) mounted on a rotating merry-go-round apparatus with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450 W). A filter solution consisting of 0.002 M potassium chromate and 1% potassium carbonate was used to isolate the 3130-Å mercury line.<sup>14</sup> Benzophenone-benzhydryl actinometry<sup>15</sup> was used for quantum yield determinations, and photoconversions were carried to 15% or less. Maximum<sup>16</sup> quantum yields were determined on solutions consisting of 0.05 M ketone with added *tert*-butyl alcohol (0.05 M) in benzene (washed with sulfuric acid, dried, and distilled with phosphorus pentoxide). Quenching studies were performed using naphthalene.

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verifies mechanism 3. From the slope of the curve,  $3.3 \times 10^{-10}$  sec, and eq 2, the fraction of reactive conformer A can be approximated. Correcting the slope downward for the larger  $k_r$  value ( $4 \times 10^9$ ) expected<sup>5,17</sup> for conformer A relative to valerophenone decreases the slope to  $1.2 \times 10^{-11}$ . Using  $1.3 \times 10^6$  as the value<sup>13</sup> for  $k_d$ , the relative concentration of reactive conformer A is found to be  $1.6 \times 10^{-5}$ , and a pseudo-rate constant equal to  $6.2 \times 10^4$  can be calculated for ketone **1a**. The calculated value is in excellent agreement with that measured for cyclobutylphenyl ketone **1a**.<sup>13</sup> From Figure 1 pseudo-rate constants for the substituted phenyl cyclobutyl ketones (**1b–c**) are obtained which also show close agreement to the measured values.<sup>13</sup>

Figure 1 predicts nonphotoreactivity for *p*-methoxyphenyl cyclobutyl ketone (**1f**), and this in fact is observed. Ketone **1f** is found to undergo no detectable reaction after 4 days of irradiation.

We are investigating the solvolytic reactivity of the aryl bicyclo[1.1.1]pentanols produced in the above reactions and are exploring their synthetic utility as precursors to other highly strained ring systems.

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Edward C. Alexander,\* Joseph A. Uliana

Department of Chemistry, University of California, San Diego  
La Jolla, California 92037

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### Crystallographic Evidence for Copper–Copper Bonding at 2.8 Å. The Crystal and Molecular Structure of Tetrakis(tetraphenylphosphonium) Hexakis(1,2-dithiosquarato)octacuprate(I)

Sir:

Recently there has been much interest in metal cluster compounds and the bonding therein. In many cases it is difficult to unequivocally state that bonding interactions are present even when crystallographic structure determinations have been performed, due to the wide variance in both the bonded and nonbonded metal–metal distances. Additionally, theoretical criteria for invoking metal–metal bonding in clusters are generally vague.

In the case of copper(I) clusters, Cu–Cu distances as short as 2.38 Å in the (4-methyl-2-cupriobenzyl)dimethylamine tetramer<sup>1</sup> and as long as 3.45 Å in the “step” conformation of  $[\text{Ph}_3\text{PCuBr}]_2$ <sup>2</sup> have been observed. This latter distance is certainly nonbonded, but there are numerous other copper(I) cluster compounds with Cu–Cu distances which are intermediate between these two extremes.<sup>3–10</sup>

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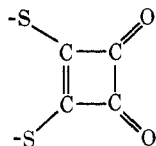


Figure 1. The 1,2-dithiosquarate dianion.

In the cubic octanuclear copper(I) cluster  $\text{Cu}_8(i\text{-MNT})_6^3$  ( $i\text{-MNT} = 1,1\text{-dicyano-2,2-ethylenedithiolate}$ ,  $\text{S}_2\text{CC}(\text{CN})_2^{2-}$ ) the authors postulated that each copper was bound to the three adjacent copper atoms with a bond order of  $2/3$  in order to satisfy the "closed shell" condition. However, a molecular orbital calculation based on atomic functions of the eight copper and 12 sulfur atoms and idealized  $O_h$  symmetry indicated the Cu-Cu interaction was on the whole slightly repulsive rather than attractive.<sup>11</sup>

We recently synthesized and structurally characterized a second cubic copper(I) cluster complex with the 1,1-dicarboethoxy-2,2-ethylenedithiolate ( $\text{DED}^{2-}$ ) ligand,<sup>10</sup> which possesses a  $\text{Cu}_8\text{S}_{12}$  core very similar to that in the  $\text{Cu}_8(i\text{-MNT})_6$  cluster. We now report the synthesis and structural characterization of a cubic octanuclear cluster complex of copper(I) with the 1,2-dithiosquarate ( $\text{DTS}^{2-}$ ) dianion (Figure 1), which also possesses this same cubic arrangement of copper atoms despite radically different ligand geometry. Our results lead us to conclude that (a) the  $\text{Cu}_8\text{S}_{12}$  structural unit appears to be a characteristic feature of Cu(I) complexes with dianionic sulfur chelates and (b) the stability of the copper cube must result at least in part from copper-copper bonding interactions.

The 1,2-dithiosquarate ligand was prepared as reported in the literature.<sup>12</sup> The tetraphenylphosphonium ( $\text{Ph}_4\text{P}^+$ ) salt of the copper(I) cluster was prepared by treating either  $(\text{Ph}_4\text{P})_2\text{ZnDTS}_2$  or  $(\text{Ph}_4\text{P})_2\text{DTS}$  with  $\text{Cu}(\text{NCCH}_3)_4\text{ClO}_4$ <sup>13</sup> in acetonitrile. The dark red crude product was recrystallized from hot acetonitrile. Carbon-hydrogen analysis indicated a stoichiometry of  $(\text{Ph}_4\text{P})_2\text{Cu}_4\text{DTS}_3$  (Anal. Calcd: C, 52.78; H, 2.95. Found: C, 52.71; H, 2.87.) A single-crystal X-ray structure determination was undertaken to determine whether the compound had the cubic structure observed for the 1,1-dithiolate copper(I) species<sup>3,10</sup> or the tetrahedral cluster structure which was originally postulated for them.<sup>14</sup>

Crystal and refinement data for  $(\text{Ph}_4\text{P})_4\text{Cu}_8\text{DTS}_6$  are shown in Table I. Intensity data were collected from a well-formed crystal on a Picker-Nuclear FACS-I automatic diffractometer using a  $\theta$ - $2\theta$  scan technique and graphite monochromatized Mo  $\text{K}\alpha$  radiation

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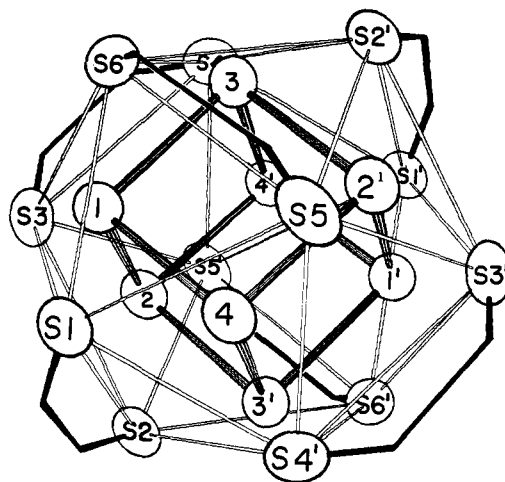


Figure 2. Structure and labeling of the  $\text{Cu}_8\text{S}_{12}$  core of the  $\text{Cu}_8\text{DTS}_6^{4-}$  cluster. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces. The 1,2-dithiosquarate ligands are represented by the angular solid lines connecting pairs of sulfur atoms. Primed atoms are related to unprimed atoms by the crystallographic center of inversion at the center of the cube.

Table I. Crystal and Refinement Data for  $(\text{Ph}_4\text{P})_4\text{Cu}_8\text{DTS}_6$

Cell dimensions <sup>a</sup>	$a = 29.952(13) \text{ \AA}$ $b = 14.547(6) \text{ \AA}$ $c = 28.003(13) \text{ \AA}$ $\beta = 106.87(3)^\circ$
Space group, $Z$	$C2/c, Z = 4$
$D_{\text{calcd}}$	1.55 g/cm <sup>3</sup>
$\mu$	18.03 cm <sup>-1</sup>
Crystal dimensions	0.23 × 0.32 × 0.48 mm
$2\theta_{\text{max}}$	40°
Unique reflections	5348
Reflections used ( $F^2 > 3\sigma(F^2)$ )	4069
Parameters <sup>b</sup>	367
$R_1^c$	0.064
$R_2^d$	0.089

<sup>a</sup> Determined by least-squares refinement on the setting angles of 12 reflections between  $2\theta$  of 25° and 30° ( $\lambda$  0.7107 Å). <sup>b</sup> The phenyl rings of the cations are being refined as groups, all other atoms refined with anisotropic thermal parameters. <sup>c</sup>  $R_1 = \sum|\Delta|F|/\sum|F_o|$ . <sup>d</sup>  $R_2 = [\sum w(\Delta|F|)^2/\sum wF_o^2]^{1/2}$ .

( $\lambda$  0.7107 Å,  $2\theta_m = 12.20^\circ$ ). The structure was solved by conventional Patterson and Fourier techniques and has been refined by full-matrix least squares to a conventional  $R$  value of 0.064. Refinement will continue after absorption corrections have been applied to the data.

A clearly recognizable pattern in the Patterson map indicated that the structure contained a cube of copper atoms. The full structure shows that the 1,2-dithiosquarate ligands bridge the six faces of the cube in a manner entirely similar to the bonding observed for the two 1,1-dithiolate copper clusters. A cube of copper atoms is located inside a slightly distorted icosahedron defined by the 12 sulfur atoms of the ligands. Each copper is coordinated by three sulfur atoms from different ligands and each sulfur atom coordinates two copper atoms on an edge of the cube. As in the other two clusters the  $\text{Cu}_8\text{S}_{12}$  core of the cluster has symmetry very close to  $T_h$ , even though a center of inversion is the only crystallographically required symmetry. Figure 2 shows the core of the  $\text{Cu}_8\text{DTS}_6$  cluster. The icosahedron

hedron of sulfur atoms has been emphasized, and the ligands are indicated schematically.

The most striking feature of this structure, when the  $\text{Cu}_8\text{DTS}_6$  cluster is compared to the  $\text{Cu}_8(i\text{-MNT})_6$  and  $\text{Cu}_8\text{DED}_6$  clusters, is that while the ligand geometry and steric requirements have changed drastically, the average copper-copper distance has not changed significantly. Table II shows pertinent molecular parameters for the

**Table II.** Selected Molecular Parameters of the  $\text{Cu}_8\text{S}_{12}$  Core of  $\text{Cu}_8\text{DTS}_6$ ,  $\text{Cu}_8(i\text{-MNT})_6$ , and  $\text{Cu}_8\text{DED}_6$  (Distances in Å, angles in degrees)

Parameter	$\text{Cu}_8\text{DTS}_6$	$\text{Cu}_8(i\text{-MNT})_6^a$	$\text{Cu}_8\text{DED}_6^b$
Cu-Cu	(min)	2.787 (2) <sup>c</sup>	2.782 (3)
	(max)	2.906 (2)	2.870 (3)
	(av)	2.844 (20)	2.829 (14)
Cu-S	(min)	2.229 (4)	2.239 (4)
	(max)	2.268 (3)	2.261 (4)
	(av)	2.247 (3)	2.250 (4)
S-S	(av)	3.920 (10)	3.080 (5)
	(bite)		3.043 (12)
	S-S	(min)	3.713 (5)
S-S (other)	(max)	3.866 (5)	3.917 (5)
	(av)	3.814 (12)	3.870 (7)
			3.88 (1)
Cu-Cu-Cu	(min)	88.7 (1)	87.4 (1)
	(max)	91.2 (1)	92.2 (1)
	(av)	90.0 (2)	90.0 (5)
S-Cu-S	(min)	111.4 (2)	116.7 (2)
	(max)	118.7 (2)	120.5 (2)
	(av)	116.2 (6)	118.6 (4)
Cu-S-Cu	(min)	76.5 (1)	76.4 <sup>d</sup>
	(max)	80.9 (1)	79.4 <sup>d</sup>
	(av)	78.6 (8)	77.9 (5)
$\text{S}_8$ plane to cube center	1 2 <sup>e</sup>	2.90 2.90	2.72 2.69
	3 4	2.91 2.94	2.73 2.72
	(av)	[2.91 (1)]	[2.72 (1)]
Cu to cube center	1 2	2.45 2.46	2.47 2.39
	3 4	2.49 2.44	2.43 2.50
	(av)	[2.46 (1)]	[2.45 (2)]

<sup>a</sup> Parameters taken from ref 4 after further refinement from those reported in ref 3. <sup>b</sup> Parameters from ref 10. <sup>c</sup> Estimated standard deviations of the least significant digit(s) as calculated by least squares appear after the (max) and (min) entries. The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation of the mean. <sup>d</sup> Esd's were not available for this parameter. <sup>e</sup> The numbering of the plane and Cu distances for a given column correspond. No correspondence is implied between columns.

$\text{Cu}_8\text{S}_{12}$  cores of the three clusters thus far studied. Note that the  $\text{S}\cdots\text{S}$  "bite" distance of the DTS ligand is 0.9 Å greater than it is for the 1,1-dithiolate ligands and that the nonbite edges of the  $\text{S}_{12}$  icosahedron in the  $\text{Cu}_8\text{DTS}_6$  cluster have actually shortened by a small amount.

The fact that the copper cube has varied insignificantly compared to the change in the ligand geometry is even clearer if we look at the distances from the center of the cube to the planes of the sulfur atoms which coordinate to each copper (e.g., S1, S3, and S6 in Figure 2). In the  $\text{Cu}_8\text{DTS}_6$  cluster these planes are 0.2 Å further from the center of the cube than they are for the other two clusters. The copper atoms of the  $\text{Cu}_8\text{DTS}_6$  cluster, however, are an average of only 0.01 Å further from the center than they are in the  $\text{Cu}_8(i\text{-MNT})_6$  cluster and only 0.04 Å further from the center than they are in the  $\text{Cu}_8\text{DED}_6$  cluster. The fact that the copper atoms could move further away from the center of the cube without seriously changing any of the molecular parameters other than the copper-copper distance

suggests strongly that there is an attractive interaction (bonding) between the copper atoms of the cube.<sup>15</sup>

The fact that the molecular orbital calculation yields no net attractive force between the copper atoms probably reflects inadequacies inherent in the assumed model, such as the assumption of idealized  $O_h$  symmetry and the inclusion of only the basic  $\text{Cu}_8\text{S}_{12}$  core in the calculation.<sup>11</sup>

**Acknowledgment.** We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research.

(15) One referee suggested that the Cu-Cu distance might be dictated by the nonbonded  $\text{S}\cdots\text{S}$  interligand contacts. We feel that this hypothesis cannot explain the slight but significant ( $5\sigma$ ) shortening of the average  $\text{S}\cdots\text{S}$  distance in  $\text{Cu}_8\text{DTS}_6$  or the apparent constancy and stability of the cubic structure.

(16) Fellow of the Alfred P. Sloan Foundation and author to whom correspondence should be addressed.

F. J. Hollander, D. Coucouvanis\*<sup>16</sup>

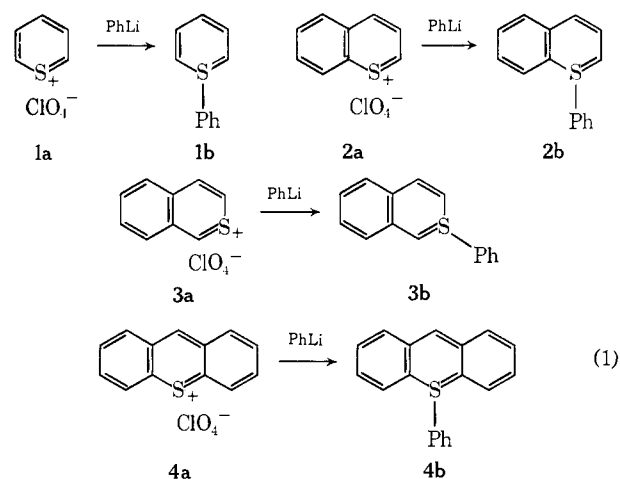
Chemistry Department, University of Iowa  
Iowa City, Iowa 52242

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### Thiabenzenes. I. A Reinvestigation of "Stable Thiabenzenes"<sup>1</sup>

Sir:

The red-brown amorphous solids isolated from the reaction of phenyllithium with thiopyrylium salts, **1a-4a**, were assigned structures **1b-4b** (eq 1) on the basis of



their chemical and physical properties.<sup>2,3</sup> From a reinvestigation of these substances, we conclude that they are, in fact, oligomeric materials of undetermined structure, rather than the stable representatives of an interesting class of aromatic compounds, as previously claimed.<sup>2,3</sup>

Deprotonation of appropriately substituted sulfonium salts as a method for preparing thiabenzenes had been utilized by Price and Follweiler<sup>4</sup> in the synthesis of 1,2-diphenyl-2-thianaphthalene and by Hortmann and Harris in their synthesis of 1-methyl-3,5-diphenylthiabenzenes (**5**).<sup>5,6</sup> However, it was recently noted by Hori,

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