center as follows: Mn^+ contributes 24 electrons, three carbonyl ligands donate 6 electrons, two metal–hydrogen–boron bonds contribute 4 electrons, and the halogen contributes the final 2 electrons for a total of 36.

Similar bonding schemes will undoubtedly be found in other metal–borane cluster systems. The presence of multidentate M–H–B bonding to several metal centers may have important implications vis-à-vis our future understanding of the mechanisms of metal cluster growth processes.

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Registry No. $(\mu\text{-Br})(CO)_6(B_3H_8)Mn_2$, 74432-08-9; $(\mu\text{-Cl})(CO)_6(B_3H_8)Mn_2$, 74432-07-8; $(CO)_3MnB_3H_8$, 53801-96-0; $Mn_2(CO)_8Br_2$, 18535-44-9.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Metal–Mercaptide Chemistry. Synthesis and Structural Characterization of the $[Cu(SC_6H_5)_3]^{2-}$ Anion. A Rational Synthesis and the Structure of the $[Cu_4(SC_6H_5)_6]^{2-}$ Cluster

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The reaction of the $[Cu(S_2C_4O_2)_2]^{2-}$ complex anion with KSC_6H_5 in acetonitrile results in the formation of the orange-red, monomeric $[Cu(SC_6H_5)_3]^{2-}$ dianion (I). This complex readily dissociates in solution to form the white monoanion $[Cu(SC_6H_5)_2]^-$. The reaction of I with Cu(I) ions in acetonitrile in a 1:1 molar ratio affords the $[Cu_4(SC_6H_5)_6]^{2-}$ cluster (II). The same cluster also is obtained by a metathesis reaction in which the SC_6H_5 ligand displaces the dithiosquarate ligands in the $Cu_8(S_2C_4O_2)_6{}^{4-}$ cubane. Bis(tetraphenylphosphonium) tris(thiophenolato)cuprate(I) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The cell dimensions are a = 22.300 (7) Å, b = 13.717 (5) Å, c = 17.686 (6) Å, and β = 94.59 (1)°. Bis(tetraphenylphosphonium) hexakis(thiophenolato)tetracuprate(I) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The cell dimensions are a = 26.93 (5) Å, b = 14.121 (7) Å, c = 23.57 (5) Å, and β = 119.41 (2)°. Intensity data for both I and II were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. In both I and II the copper, sulfur, and phosphorus atoms were refined with anisotropic thermal parameters while the remaining nonhydrogen atoms were refined with isotropic thermal parameters. Refinement by full-matrix least squares of 319 parameters on 1806 data for I and 349 parameters on 1744 data for II gave final R values of 0.064 for I and 0.099 for II. The coordination of the Cu(I) ion in I is trigonal and nearly planar with two "small" S–Cu–S angles of 112.95 (19) and 111.65 (18)° and a larger S–Cu–S angle of 135.37 (20)°. The Cu–S bond length opposite to the large S–Cu–S angle, at 2.335 (4) Å, is significantly larger than the other two at 2.274 (4) and 2.276 (4) Å. The mean value of the C–S bond lengths is 1.749 (14) Å. The overall description of the Cu_4S_6 core in II can be considered as a tetrahedron of copper atoms inscribed in a distorted octahedron of sulfur atoms. Each sulfur atom is coordinated to two copper atoms across an edge of the Cu_4 tetrahedron, and each copper is trigonally coordinated by three sulfur atoms of three different ligands. Average values of selected structural parameters in II and the standard deviations of the mean are as follows: Cu–Cu, 2.76 (2) Å; S–S, 3.94 (20) Å; Cu–S, 2.29 (3) Å; Cu–S–Cu, 73.8 (10)°; S–Cu–S, 120 (10)°. An analysis of the data and a comparison to the structures of the $Cu_8L_6{}^{4-}$ cubanes lead to the suggestion that the Cu_4S_6 core which is obtained with monodentate thiolate ligands cannot be obtained with 1,1-dithiolate ligands because of the short intraligand S–S distance of ~3.00 Å. In the Cu_4S_6 core structure the $\overline{\text{S–S}}$ distance is 3.94 (20) Å.

Introduction

An interesting aspect in the studies of copper–sulfur coordination chemistry is the apparent tendency of Cu(I) ions to form various clusters with sulfur ligands. A remarkable variety in composition and structures is observed in these clusters where the molecular architecture is based on the existence of cores such as Cu_4S_8,[1] Cu_5S_7,[2] Cu_5S_6,[3] Cu_4S_6,[4,5] and Cu_8S_{12}.[6]

The Cu_8S_{12} core is a common feature in what appears to be a general class of clusters obtained by the reaction of cuprous ions and bidentate sulfur chelates. An outstanding feature in the structures of the $[Cu_8(i\text{-MNT})_6]^{4-}$,[6b] $[Cu_8(DED)_6]^{4-}$,[6a] and $[Cu_8(DTS)_6]^{4-}$ [6a] clusters is the similarity of the three, nearly perfect Cu_8 cubes. An analysis of the structural features of these clusters has led us to suggest[6a] that the constancy of the Cu–Cu distances in the three Cu_8 cubes at ~2.82 Å indicates weak, attractive Cu–Cu interactions.

Mehrotra and Hoffmann[7] have analyzed the bonding relationships in d^{10}–d^{10} systems for Cu(I) cluster compounds.[7] They found the expected closed-shell repulsions only when the d orbitals of the metal were considered. When an admixture of the metal d orbitals with higher s and p functions were allowed, the metal–metal interactions were found to be slightly attractive in nature. These attractive interactions were found to persist even after the stereochemical requirements of the bridging ligands had been taken into account.

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(2) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 103 (1976).
(3) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976).
(4) (a) D. Coucouvanis, C. N. Murphy, and S. K. Kanodia, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 1976; (b) I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, **19**, L41 (1976).
(5) E. H. Griffith, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 432 (1976).
(6) (a) F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **99**, 6268 (1977). (b) L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, **90**, 7357 (1968). Abbreviations used in text: i-MNT = 1,1-dicyano-2,2-ethylenedithiolate, $[(CN)_2C{=}CS_2]^{2-}$; DED = 1,1-dicarboethoxy-2,2-ethylenedithiolate, $[(COOC_2H_5)_2C{=}CS_2]^{2-}$; DTS = dithiosquarate dianion, $[S_2C_4O_2]^{2-}$.
(7) P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, **17**, 2187 (1978).

0020-1669/80/1319-2993$01.00/0

A different point of view has been presented by Avdeef and Fackler which suggested[8] that the copper–copper interactions in the Cu_8S_{12} clusters are "slightly repulsive". The basis for this argument was the result of a Mulliken–Wolfsberg–Helmholtz theoretical treatment.

The stereochemical importance of the bridging chelate ligands in the formation of the $[Cu_8L_6]^{4-}$ cubanes and the structural constraints imposed by the connectivity of the sulfur donors have not been evaluated. The structural features of a cluster with the same Cu/S ratio but with monodentate sulfur ligands would be beneficial to ascertain the importance of the chelating ligands.

In this paper we report results of our studies on the synthesis and structural characterization of the hitherto unknown tris(thiophenolato)cuprate(I) dianion, $[Cu(SPh)_3]^{2-}$, and its co-oligomerization with Cu(I) ions to form the hexakis(μ-(thiophenolato))-tetracuprate(I) dianion,[4a] $[Cu_4(SPh)_6]^{2-}$.

Experimental Section

The chemicals in this research were used as purchased. Analyses were performed by the analytical services laboratory of the Chemistry Department of the University of Iowa. All syntheses were carried out under a nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox.

Bis(tetraphenylphosphonium) Tris(thiophenolato)cuprate(I), $[(C_6H_5)_4P]Cu(C_6H_5S)_3$. To a solution of $(Ph_4P)_2Cu(DTS)_2$[9] (2.6 g, 2.5 mmol) in 15 mL of acetonitrile was added 1.9 g (12.5 mmol) of potassium thiophenolate, and the mixture was boiled for 10 min. A red-orange precipitate of the crude product was obtained following filtration of the hot solution and addition of ether to the filtrate. Large red crystals of the pure product can be obtained by the careful addition of ether to a solution of the crude product in acetonitrile, previously saturated with KSPh. The initial white precipitate of KSPh was removed by filtration, and the desired product was obtained by further addition of ether. The yield was 60%.

Anal. Calcd for $[(C_6H_5)_4P]_2Cu(SC_6H_5)_3$: C, 74.1; H, 5.2; Cu, 5.9. Found: C, 74.5; H, 5.1; Cu, 5.6.

Tetraphenylphosphonium Bis(thiophenolato)cuprate(I), $[(C_6H_5)_4P]Cu(SC_6H_5)_2$. This complex precipitates as white, hexagonal crystals by the addition of pentane, dropwise, to a concentrated solution of $(Ph_4P)_2Cu(SPh)_3$ in acetone.

Anal. Calcd for $[(C_6H_5)_4P]Cu(SC_6H_5)_2$: C, 69.6; H, 4.9; P, 5.0; S, 10.3; Cu, 10.2. Found: C, 69.5; H, 5.0; P, 5.1; S, 10.4; Cu, 10.1.

Bis(tetraphenylphosphonium) Hexakis(thiophenolato)tetracuprate(I), $[(C_6H_5)_4P]_2Cu_4(SC_6H_5)_6$. (A) To a boiling solution of 0.36 g (1 mmol) of $Cu(CH_3CN)_4ClO_4 \cdot 2H_2O$[10] in 10 mL of acetonitrile was added 1.07 g (1 mmol) of $(Ph_4P)_2Cu(SPh)_3$, and the solution boiled for an additional 5 min. Addition of ether until the first cloudiness appeared and cooling afforded yellow crystals.

Anal. Calcd for $[(C_6H_5)_4P]_2Cu_4(SC_6H_5)_6$: C, 63.55; H, 4.41; S, 12.10; P, 3.91; Cu, 16.0. Found: C, 63.37; H, 4.71; S, 11.93; P, 3.94; Cu, 15.8 (mp 107 °C dec).

(B) Solid KSPh (2 g, 13.5 mmol) was added to a solution of $Cu(CH_3CN)_4ClO_4 \cdot 2H_2O$ (2.9 g, 8 mmol) in 70 mL of CH_3CN. A yellow color developed, and a white precipitate formed. The mixture was allowed to react at room temperature for 20 min and then filtered. To the filtrate was added 1.5 g (4 mmol) of solid Ph_4PCl. Addition of ether to the yellow solution gave yellow crystals. The crude product was recrystallized from an acetonitrile–diethyl ether mixture. The powder pattern of the product was identical with the one of the product obtained by procedure A.

(C) To a solution of 0.5 g (0.18 mmol) of the $(Ph_4P)_4Cu_8(DTS)_6$ cluster, in 4 mL of CH_3CN, was added solid KSPh (0.32 g, 2.1 mmol) with frequent agitation, and the mixture was boiled for 15 min. A white precipitate formed, $K_2(DTS)$, and was filtered off. Addition of a few drops of diethyl ether to the filtrate and cooling of the solution resulted in the formation of yellow crystals. The melting point and powder pattern of these crystals were identical with those of the product obtained by procedures A and B.

Table I. Crystal Intensity Measurement and Structure Determination Data

	$[(C_6H_5)_4P]_2$-$Cu(SC_6H_5)_3$	$[(C_6H_5)_4P]_2$-$Cu_4(SC_6H_5)_6$
mol wt	1070	1588
a	22.300 (7)	26.93 (5)
b	13.717 (5)	14.121 (7)
c	17.686 (6)	23.57 (5)
β	94.59 (1)	119.41 (2)
d(obsd), g cm^{-3}	1.32 ± 0.03^a	1.37 ± 0.03^a
d(calcd), g cm^{-3}	1.32	1.35
Z	4	4
space group	$P2_1/c^b$	$P2_1/c^b$
λ	Mo Kα (0.7107 Å)^c	Mo Kα (0.7107 Å)^c
μ, cm^{-1}	6.35	13.51
cryst dimens, mm	0.20 × 0.15 × 0.30	0.30 × 0.15 × 0.50
reflctns measd	4602	6371
takeoff angle, deg	3.0	3.5
2θ range, deg	$0 < 2\theta < 35$	$0 < 2\theta < 30$
scan width,^{d} deg	1.3	1.8
unique reflctns	2173	3062
atoms in asymmetric unit	72 (+55 H)	96 (+70 H)
final R_1^e	0.064	0.099
final R_2^f	0.088	0.122
reflctns used in refinement	1806	1744
no. of parameters	319	349

[a] Determined by flotation in a hexachlorobutadiene-pentane mixture. [b] Systematic absences $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$. [c] A graphite single-crystal monochromator was used. [d] A 2θ step scan data collection procedure was used. [e] $R_1 = \Sigma|\Delta|F||/\Sigma|F_o|$. [f] $R_2 = (\Sigma w(\Delta|F|)^2/\Sigma w F_o^2)^{1/2}$.

X-ray Diffraction Measurements. Collection and Reduction of Data. Details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I.

Intensity data for both compounds were obtained on a Picker-Nuclear four-circle diffractomer equipped with a scintillation counter and pulse-height analyzer and automated by a DEC PDP 8-I computer and disk with FACS-I DOS software. Graphite-monochromatized Mo Kα radiation ($2\theta_m = 12.50°$) was used for data collection and cell dimension measurements (K$\bar{\alpha}$, λ 0.7107 Å). Intensity data were collected by using a θ–2θ step scan technique. The scan width was centered on the predicted position of the Mo Kα_1 peak and expanded at the high-2θ end to allow for α_1–α_2 separation at higher angles. Stationary-crystal, stationary-counter background measurements were made for 10 s at each end of the scan range. Three reflections well separated in reciprocal space were measured after every 100 data measurements to monitor crystal and instrumental stability.

The raw data were reduced to net intensities, estimated standard deviations were calculated on the basis of counting statistics, Lorentz–polarization corrections and decay corrections (where applicable) were applied, and equivalent reflections were averaged. The estimated standard deviation of the structure factor was taken as the larger of that derived from counting statistics and that derived from scatter of multiple measurements.

The least-squares program used minimizes $\sum w(\Delta|F|)^2$. The weighting function used throughout the refinement of both structures gives zero weight to those reflections with $F^2 \leq 3\sigma(F^2)$ and $w = 1/\sigma^2(F)$ to all others. The ignorance factor p in the expression for $\sigma^2(F^2)$ was 0.04 in both cases.[11]

The scattering factors of the neutral nonhydrogen atoms were taken from the tables of Doyle and Turner,[12] and real and imaginary dispersion corrections[13] were applied to all of them. The spherical hydrogen scattering factor tables of Stewart, Davidson, and Simpson[14] were used. Absorption corrections for both structures were applied by using the analytical program ABSORB[15] which uses the analytical

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(8) A. Avdeef and J. P. Fackler, Jr., *Inorg. Chem.*, **17**, 2182 (1978).

(9) D. Coucouvanis, D. G. Holah, and F. J. Hollander, *Inorg. Chem.*, **14**, 2657 (1975).

(10) P. Hemmerich and C. Sigwart, *Experientia*, **19**, 488 (1963).

(11) $\sigma(F^2) = [\sigma_0^2(F^2) + (pF^2)^2]^{1/2}$.

(12) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **A24**, 390 (1968).

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

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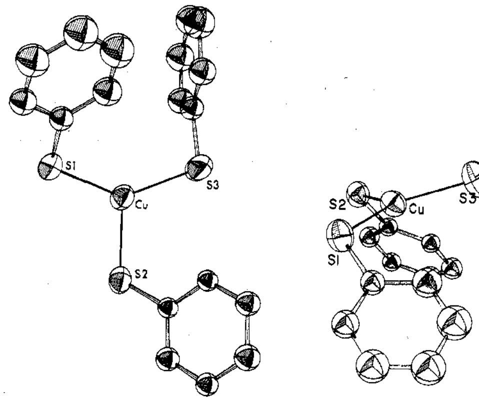

Figure 1. Two views and numbering scheme for the $[Cu(SC_6H_5)_3]^{2-}$ dianion. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

method of de Meulenaer and Tompa.[16]

$[(C_6H_5)_4P]_2Cu(SC_6H_5)_3$. Crystals suitable for X-ray diffraction work were obtained by crystallization from acetonitrile–ether mixtures. A fresh crystal was mounted on a glass fiber in air, coated with Krylon, and used for cell dimension measurements and data collection. The cell dimensions (Table I) were obtained by least-squares refinement on the 2θ values of 18 carefully centered reflections with 2θ between 24 and 30°. A total of 4602 data were collected in the hemisphere of reciprocal space $\pm h,+k,\pm l$ with a scan width of 1.3° in 2θ. At $2\theta > 35°$ few intensities were "observed", and data collection was terminated.

$[(C_6H_5)_4P]_2Cu_4(SC_6H_5)_6$. Single crystals of this compound were obtained from acetonitrile–ether mixtures but were only of marginal crystallographic quality and showed a tendency to decompose slowly in the X-ray beam at room temperature. One of these crystals was mounted on a glass fiber, coated with Krylon, and used for cell dimension measurements and data collection. The cell dimensions were obtained as described previously. A total of 6371 data were collected in the hemisphere of reciprocal space $\pm h,+k,\pm l$ with a scan width of 1.8° in 2θ. At $2\theta > 30$ few intensities were "observed", and data collection was halted.

Determination of the Structures. (A) $[(C_6H_5)_4P]_2Cu(SC_6H_5)_3$. A three-dimensional Patterson synthesis was solved in the centric space $P2_1/c$ to yield the positions of the copper, three sulfur atoms, and the two phosphorus atoms. The other nonhydrogen atoms were located on subsequent Fourier syntheses following least-squares refinements. The refinement of all atoms with isotropic temperature factors gave a conventional R value of 0.11. Further refinement of the structure with anisotropic temperature factors for the noncarbon heavy atoms gave a conventional R value of 0.082. At this stage a difference Fourier map was computed, and all hydrogen atoms were located. The hydrogen atoms were included in the final least-squares calculations but were not refined. The final R value was 0.064; the weighted R (Table I) was 0.088. During the last cycle of refinement all parameter shifts were less than 20% of their esd. The final parameters of the structure with their estimated standard deviations as calculated from the inverse least-squares matrix are given in Table II.

(B) $[(C_6H_5)_4P]_2Cu_4(SC_6H_5)_6$. A procedure similar to the one described previously was followed for the location of all nonhydrogen atoms. Due to the limited data and the large number of atoms in the asymmetric unit (Table I), the refinement of the structure proceeded with considerable difficulty. The low resolution of the data (1.4 Å) is considered to be the source of most of the problems. Refinement with anisotropic thermal parameters for all noncarbon atoms, and isotropic thermal parameters for the carbon atoms converged at an R value of 0.099. However many of the C–C distances in the cations were unreasonable, and thermal parameters for the same atoms were large.

The criterion for rejection of data as "unobserved" was reduced in hope that the increased number of data would improve the refinement. This hope was not validated. The decision was made to collect data on a crystal of the same anion with a different counterion. At this stage a preliminary report appeared in the literature[4b] concerning the synthesis and structural characterization of two "salts" of the $[Cu_4(\mu\text{-SPh})_6]^{2-}$ cluster. The apparent superiority of the data for one of these crystals prompted us to terminate our crystallographic studies concerning the $[Cu_4(\mu\text{-SPh})_6]^{2-}$ anion.

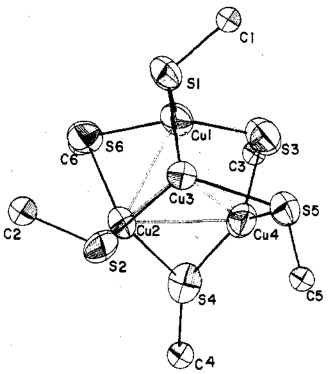

Figure 2. Cu_4S_6 "core" of the $[Cu_4(SC_6H_5)_6]^{2-}$ cluster. Of the phenyl rings, only the carbon atoms attached to the sulfur atoms have been included in the figure. The thermal ellipsoids represent the 50% probability surfaces.

Crystallographic Results. The final atomic positional and thermal parameters for I with standard deviations derived from the inverse matrix of the least-squares refinement are compiled in Table II. Intramolecular distances and angles for I are given in Table III.

A summary of the intramolecular distances and angles in II is given in Table V. The atom labeling schemes are shown in Figures 1 and 2. Tables of the observed values of F, their esd's and the $|F_o| - |F_c|$ values have been deposited for I. The final atomic positional and thermal parameters for the hydrogen atoms in I also will be deposited.

With the assumption that a reexamination of the structure of II will require a better quality data set (most probably at low temperature), we will not deposit structure factor tables for II. However, a complete list of the atomic coordinates is available as supplementary material.

Discussion

Synthesis. Addition of potassium thiophenolate, KSPh, to acetonitrile, CH_3CN, solutions of the $(Ph_4P)_2Cu(DTS)_2$ complex[9] results in the reduction of Cu(II) to Cu(I). In the presence of excess mercaptide, the $[Cu(SPh)_3]^{2-}$ complex anion forms and can be isolated as red $(Ph_4P)_2[Cu(SPh)_3]$ crystals (I). This complex can be recrystallized only from CH_3CN previously saturated with KSPh, and attempts to crystallize this compound from neat CH_3CN result in the isolation of the white, crystalline $(Ph_4P)Cu(SPh)_2$ complex. These observations suggest that the $[Cu(SPh)_3]^{2-}$ anion, in CH_3CN solution, very likely undergoes the equilibrium $[Cu(SPh)_3]^{2-} \rightleftarrows [Cu(SPh)_2]^- + (SPh)^-$. The same type of equilibrium has been reported for the $Cu(SPPh_3)_3^+$ cation which dissociates to $[Cu(SPPh_3)_2]^+$ and $SPPh_3$.[17]

Molecular weight studies on the $(Ph_4P)Cu(SPh)_2$ complex in 1,2-dichloroethane, $C_2H_4Cl_2$, at various concentrations, by vapor-phase osmometry, show the observed molarities nearly twice as large as the calculated values based on the undissociated $(Ph_4P)Cu(SPh)_2$ "salt". In addition, conductivity studies in $C_2H_4Cl_2$ as a function of concentration show equivalent conductance values, very similar to those obtained for $(Ph_4P)Cl$ under the same conditions. The colligative properties of the $(Ph_4P)Cu(SPh)_2$ complex, therefore, suggest that the compound is ionized in solution to $(Ph_4P)^+$ cations and $[Cu(SPh)_2]^-$ anions. The pentafluorothiophenolate analogue of this complex has been reported previously.[18]

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(15) L. K. Templeton and D. H. Templeton, Abstract E10, American Crystallographers Association Summer Meetings, Storrs, Conn., June 1973.

(16) J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(17) J. A. Tiethof, A. T. Hetey, and D. W. Meek, *Inorg. Chem.*, **13**, 2505 (1974).

Table II. Positional and Thermal Parameters for the Noncarbon Atoms,[a] the Carbon Atoms,[b] and the Hydrogen Atoms[b] in $[(C_6H_5)_4P]_2[Cu(SC_6H_5)_3]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	−0.25119 (8)	0.0323 (1)	0.2185 (1)	3.8 (1)	3.4 (1)	4.6 (1)	−0.12 (8)	0.13 (8)	−0.34 (8)
S(1)	−0.2381 (2)	0.1943 (3)	0.2417 (2)	5.1 (3)	3.0 (2)	5.1 (3)	−0.3 (2)	−0.4 (2)	−0.1 (2)
S(2)	−0.3160 (2)	0.0008 (3)	0.1110 (2)	4.4 (3)	3.1 (2)	4.2 (2)	−0.5 (2)	0.4 (2)	0.1 (2)
S(3)	−0.7818 (2)	0.3921 (3)	0.2233 (2)	5.4 (3)	3.6 (2)	7.1 (3)	−0.1 (2)	−1.8 (2)	−0.3 (2)
P(1)	−0.0766 (2)	0.0237 (3)	0.1417 (2)	2.7 (2)	3.0 (2)	3.1 (2)	0.1 (2)	−0.5 (2)	−0.2 (2)
P(2)	−0.5803 (2)	0.0291 (2)	0.3485 (2)	3.7 (3)	2.0 (2)	2.8 (2)	0.2 (2)	−0.2 (2)	0.3 (2)

atom	x	y	z	B	atom	x	y	z	B
C(49)	−0.8498 (6)	0.4044 (9)	0.1655 (8)	3.8 (3)	C(16)	−0.6745 (6)	0.163 (1)	0.5425 (7)	4.1 (3)
C(50)	−0.1513 (7)	−0.074 (1)	0.4098 (8)	4.8 (4)	C(17)	−0.6548 (6)	0.223 (1)	0.4871 (7)	3.8 (3)
C(51)	−0.0939 (8)	−0.065 (1)	0.4536 (8)	6.5 (4)	C(18)	−0.6256 (6)	0.182 (1)	0.4274 (7)	3.5 (3)
C(52)	−0.0409 (7)	−0.083 (1)	0.4200 (9)	5.1 (4)	C(19)	−0.6234 (6)	0.0492 (9)	0.2582 (7)	2.8 (3)
C(53)	−0.0417 (7)	−0.103 (1)	0.3449 (9)	5.2 (4)	C(20)	−0.6705 (6)	0.1143 (9)	0.2516 (7)	3.4 (3)
C(54)	−0.0977 (7)	−0.1093 (9)	0.3004 (7)	4.6 (4)	C(21)	−0.7019 (6)	0.1259 (9)	0.1801 (8)	4.4 (4)
C(55)	−0.2375 (6)	0.217 (1)	0.3385 (7)	3.1 (3)	C(22)	−0.6870 (6)	0.074 (1)	0.1199 (7)	3.7 (3)
C(56)	−0.2517 (6)	0.3083 (9)	0.3672 (7)	3.6 (3)	C(23)	−0.6411 (7)	0.008 (1)	0.1239 (8)	4.9 (4)
C(57)	−0.2529 (6)	0.324 (1)	0.4435 (9)	4.9 (4)	C(24)	−0.6095 (7)	−0.005 (1)	0.1954 (8)	4.6 (4)
C(58)	−0.2403 (7)	0.254 (1)	0.4970 (8)	5.8 (4)	C(25)	−0.1189 (5)	0.5638 (9)	0.4343 (6)	2.1 (3)
C(59)	−0.2252 (7)	0.164 (1)	0.4685 (9)	6.4 (4)	C(26)	−0.1297 (6)	0.5031 (9)	0.4940 (7)	2.9 (3)
C(60)	−0.2240 (6)	0.146 (1)	0.3924 (9)	4.6 (4)	C(27)	−0.1632 (6)	0.5331 (9)	0.5529 (7)	3.2 (3)
C(61)	−0.3760 (6)	−0.0681 (9)	0.1392 (7)	3.0 (3)	C(28)	−0.1872 (6)	0.625 (1)	0.5516 (7)	3.1 (3)
C(62)	−0.3746 (6)	−0.1151 (8)	0.2100 (7)	2.8 (3)	C(29)	−0.1777 (6)	0.6852 (9)	0.4920 (7)	3.7 (3)
C(63)	−0.4239 (6)	−0.1652 (9)	0.2334 (7)	3.6 (3)	C(30)	−0.1452 (6)	0.6564 (9)	0.4339 (7)	3.4 (3)
C(64)	−0.4767 (6)	−0.1684 (9)	0.1856 (8)	3.9 (3)	C(31)	−0.0498 (6)	0.4007 (8)	0.3733 (6)	1.9 (3)
C(65)	−0.4794 (6)	−0.1245 (9)	0.1176 (7)	2.8 (3)	C(32)	0.0101 (6)	0.3783 (9)	0.3766 (6)	3.1 (3)
C(66)	−0.4305 (6)	−0.0744 (9)	0.0940 (7)	3.5 (3)	C(33)	0.0296 (6)	0.284 (1)	0.3855 (7)	3.4 (3)
C(1)	−0.5061 (5)	0.0823 (8)	0.3490 (7)	1.7 (3)	C(34)	−0.0116 (6)	0.2102 (9)	0.3920 (7)	3.4 (3)
C(2)	−0.4725 (6)	0.0701 (9)	0.2885 (7)	3.6 (3)	C(35)	−0.0713 (7)	0.231 (1)	0.3893 (7)	4.0 (3)
C(3)	−0.4139 (6)	0.1064 (9)	0.2904 (7)	3.3 (3)	C(36)	−0.0925 (6)	0.325 (1)	0.3802 (7)	3.6 (3)
C(4)	−0.3916 (6)	0.1546 (9)	0.3531 (8)	3.4 (3)	C(37)	0.1208 (6)	0.035 (1)	0.2307 (7)	2.9 (3)
C(5)	−0.4237 (6)	0.1681 (9)	0.4135 (7)	3.1 (3)	C(38)	0.1498 (7)	−0.046 (1)	0.2642 (9)	5.8 (4)
C(6)	−0.4821 (6)	0.1310 (8)	0.4126 (7)	2.7 (3)	C(39)	0.1888 (7)	−0.033 (1)	0.3314 (9)	6.5 (4)
C(7)	−0.5710 (6)	−0.0985 (9)	0.3633 (6)	2.6 (3)	C(40)	0.1984 (7)	0.057 (1)	0.3602 (8)	5.0 (4)
C(8)	−0.5163 (6)	−0.1395 (9)	0.3875 (6)	3.0 (3)	C(41)	0.1731 (7)	0.138 (1)	0.3262 (9)	5.8 (4)
C(9)	−0.5107 (6)	−0.2393 (9)	0.4026 (7)	3.4 (3)	C(42)	0.1342 (6)	0.125 (1)	0.2606 (8)	5.0 (4)
C(10)	−0.5620 (7)	−0.295 (1)	0.3925 (7)	3.8 (3)	C(43)	−0.0119 (5)	0.6008 (8)	0.3542 (7)	2.4 (3)
C(11)	−0.6159 (6)	−0.258 (1)	0.3706 (7)	4.1 (3)	C(44)	0.0235 (7)	0.5921 (9)	0.2922 (7)	3.7 (3)
C(12)	−0.6221 (6)	−0.160 (1)	0.3528 (7)	3.7 (3)	C(45)	0.0782 (6)	0.640 (1)	0.2907 (8)	4.4 (4)
C(13)	−0.6185 (5)	0.0801 (9)	0.4252 (7)	2.3 (3)	C(46)	0.0952 (6)	0.6981 (9)	0.3509 (8)	3.6 (3)
C(14)	−0.6415 (6)	0.0231 (9)	0.4806 (7)	3.0 (3)	C(47)	0.0621 (6)	0.713 (1)	0.4102 (7)	4.2 (3)
C(15)	−0.6691 (6)	0.064 (1)	0.5390 (7)	3.3 (3)	C(48)	0.0075 (6)	0.6621 (9)	0.4129 (7)	3.1 (3)

atom	x	y	z	B	atom	x	y	z	B
H(50)	−0.1208	−0.1079	0.4398	4.9	H(17)	−0.660	0.2912	0.4895	3.3
H(51)	−0.0586	−0.0823	0.4845	4.9	H(18)	−0.6108	0.2219	0.3891	3.3
H(52)	−0.0010	−0.1014	0.4366	4.9	H(20)	−0.6806	0.1503	0.2946	3.9
H(53)	−0.0016	−0.1257	0.3439	4.9	H(21)	−0.7343	0.1712	0.1745	3.9
H(54)	−0.0627	−0.1412	0.2855	4.9	H(22)	−0.7089	0.0830	0.0721	3.9
H(56)	−0.2608	0.3592	0.3317	4.7	H(23)	−0.6313	−0.0272	0.0804	3.9
H(57)	−0.263	0.3869	0.4617	4.7	H(24)	−0.5776	−0.0511	0.2004	3.9
H(58)	−0.2414	0.2668	0.5496	4.7	H(26)	−0.1131	0.4394	0.4946	3.0
H(59)	−0.2156	0.1132	0.5041	4.7	H(27)	−0.1697	0.4908	0.5940	3.0
H(60)	−0.2138	0.0829	0.3748	4.7	H(28)	−0.2101	0.6462	0.5916	3.0
H(62)	−0.3384	−0.1120	0.2422	3.2	H(29)	−0.1947	0.7489	0.4912	3.0
H(63)	−0.4219	−0.1965	0.2814	3.2	H(30)	−0.1394	0.6992	0.3929	3.0
H(64)	−0.5108	−0.2023	0.2009	3.2	H(32)	0.0385	0.4291	0.3722	3.2
H(65)	−0.5157	−0.1281	0.086	3.2	H(33)	0.0712	0.2689	0.3874	3.2
H(66)	−0.4329	−0.0432	0.0458	3.2	H(34)	0.0017	0.1448	0.3983	3.2
H(2)	−0.4892	0.0364	0.2449	2.9	H(35)	−0.0994	0.1797	0.3938	3.2
H(3)	−0.3902	0.0979	0.2485	2.9	H(36)	−0.1343	0.3386	0.3785	3.2
H(4)	−0.3520	0.1798	0.3546	2.9	H(38)	0.1424	−0.1088	0.2428	5.1
H(5)	−0.4066	0.2023	0.4568	2.9	H(39)	0.2081	−0.0868	0.356	5.1
H(6)	−0.5053	0.1394	0.4549	2.9	H(40)	0.2243	0.0647	0.405	5.1
H(8)	−0.4817	−0.0991	0.3939	3.4	H(41)	0.1817	0.2006	0.3471	5.1
H(9)	−0.4729	−0.2673	0.4191	3.4	H(42)	0.1156	0.1803	0.2362	5.1
H(10)	−0.5591	−0.3634	0.4026	3.4	H(44)	0.0103	0.5515	0.2507	3.5
H(11)	−0.6503	−0.2989	0.3654	3.4	H(45)	0.1023	0.6317	0.2493	3.5
H(12)	−0.660	−0.133	0.3354	3.4	H(46)	0.1324	0.7316	0.3503	3.5
H(14)	−0.6373	−0.0456	0.4784	3.3	H(47)	0.0759	0.7550	0.4504	3.5
H(15)	−0.6838	0.0243	0.5772	3.3	H(48)	−0.0163	0.6698	0.4546	3.5
H(16)	−0.6936	0.1910	0.5835	3.3					

[a] The thermal parameters are in units of Å^2. The temperature factor has the form $T = -\Sigma(^1/_4 B_{ij} H_{ij} H_i H_i a^*_i a^*_j)$, where H is the Miller index, a^* is the reciprocal cell length, and i and j are cycled 1–3. [b] The temperature factor has the form $T = -B((\sin\theta)/\lambda)^2$. B in Å^2.

Table III. Distances and Angles in the $[Cu(SC_6H_5)_3]^{2-}$ Anion

	Distances (Å)		
Cu–S(1)	2.274 (4)	S(1)–C(55)	1.740 (13)
Cu–S(2)	2.335 (4)	S(2)–C(61)	1.742 (14)
Cu–S(3)	2.276 (4)	S(3)–C(49)	1.766 (14)
	Angles (Deg)		
S(1)–Cu–S(2)	112.95 (19)	S(2)–C(61)–C(62)	122.8 (7)
S(1)–Cu–S(3)	135.37 (20)	S(2)–C(61)–C(66)	121.3 (7)
S(2)–Cu–S(3)	111.65 (18)	S(3)–C(49)–C(50)	120.2 (8)
Cu–S(1)–C(55)	110.2 (5)	S(3)–C(49)–C(54)	117.1 (8)
Cu–S(2)–C(61)	107.8 (4)	C(56)–C(55)–C(60)	115.3 (1.3)
Cu–S(3)–C(49)	114.4 (4)	C(62)–C(61)–C(66)	115.8 (1.2)
S(1)–C(55)–C(56)	122.4 (7)	C(50)–C(49)–C(54)	122.7 (1.4)
S(1)–C(55)–C(60)	122.2 (7)		

The similarity of the coordination geometry of copper in the $[Cu(SPh)_3]^{2-}$ anion to that observed for the copper atoms in the cubane clusters with the Cu_8S_{12} core prompted us to explore the feasibility of reaction 1. Such a reaction could give

$$[Cu(SPh)_3]^{2-} + Cu^I \rightarrow [Cu_2(SPh)_3]^- \qquad (1)$$

the simplest repeating $[Cu_2(SPh)_3]^-$ unit which upon oligomerization might result in the formation of the $[Cu_4(SPh)_6]^{2-}$ or $[Cu_8(SPh)_{12}]^{4-}$ cluster.

Reaction 1 proceeds smoothly in boiling CH_3CN under N_2, and the crystalline $[Cu_2(SPh)_3(Ph_4P)]_n$ compound (II) can be isolated in excellent yields. The simple metathesis reactions known[19] to occur between the $[M(DTS)_2]^{2-}$ complexes and KSPh, with the generation of the $[M(SPh)_4]^{2-}$ complexes, suggested that such a reaction between $[Cu_8(DTS)_6]^{4-}$ and KSPh might result in ligand exchange with formation of the hitherto unknown $[Cu_8(SPh)_{12}]^{4-}$ cluster.

Reaction 2 proceeds readily and affords a product with

$$(Ph_4P)_4[Cu_8(DTS)_6] + 12KSPh \xrightarrow[\Delta]{CH_3CN} [Cu_2(SPh)_3(Ph_4P)]_n + 6K_2DTS \quad (2)$$

identical analysis and X-ray powder pattern to those obtained for the product from the previous reaction (eq 1). For determination of the degree of oligomerization in $[Cu_2(SPh)_3(Ph_4P)]_n$, the single-crystal X-ray structure determination of this compound was undertaken.

Structures. (A) $(Ph_4P)_2[Cu(SPh)_3]$. In the structure of I, discrete $[Cu(SPh)_3]^{2-}$ anions are surrounded by the large $(Ph_4P)^+$ counterions. The three-coordinate copper atom in the monomeric anion is located at a distance of only 0.05 Å from the S_1–S_2–S_3 plane. Pronounced deviations from exact trigonal symmetry are evident in the Cu–S bond lengths and the S–Cu–S angles. Two of the Cu–S bonds are nearly equal and appreciably shorter than the third bond (Figure 1, Table III). The S–Cu–S angle between the two shorter bonds (135.4 (2)°) is larger than the other two angles of 112.9 (2) and 109.0 (3)°. The pronounced tendency of I to decrease its coordination number by dissociation of a mercaptide ligand and formation of $[Cu(SPh)_2]^-$ has been noted. It is tempting to describe the observed structure of II as a "frozen out" stage of the transition-state geometry in a process where the trigonal $Cu(SPh)_3^{2-}$ complex dissociates a mercaptide ion to form the linear $[Cu(SPh)_2]^-$ anion. Such a distortion is not evident in the structures of the $[Cu(SPMe_3)_3]^+$ cation[20,21] or the tris(ethylenethiourea)copper(I) complex,[22] $[Cu(entu)_3]^+$, both being monomeric, three-coordinate Cu(I)–sulfur complexes which are planar and possess nearly exact trigonal symmetry. In the structure of the tris(tetramethylthiourea)copper(I) cation,[22] $[Cu(tmtu)_3]^+$, distortions from trigonal symmetry are evident in the range of the Cu–S bond lengths (2.257–2.238 Å) and the three different S–Cu–S angles (109.1, 121.1, and 129.7°). These distortions are attributed to steric interactions between adjacent tetramethylthiourea ligands.

Table IV. Nonbonded Contacts (Å) Shorter Than 3.0 Å

Cu–H(62)	2.83	H(18)–C(62)	2.84
Cu–H(60)	2.91	H(18)–C(63)	2.82
Cu–H(27)	2.98	H(24)–C(64)	2.80
S(1)–H(60)	2.82	H(18)–C(64)	2.87
S(2)–H(62)	2.87	H(4)–C(55)	2.64
S(2)–H(66)	2.83	H(36)–C(55)	2.88
S(2)–H(11)	2.89	H(36)–C(56)	2.64
S(3)–H(62)	2.70	H(4)–C(56)	2.84
		H(35)–C(60)	2.82
		H(4)–C(60)	2.92

Table V. Selected Structural Data of $[Cu_4(\mu\text{-}SPh)_6]^{2-}$

	$(Ph_4P)^+$ salt[a]	$(Me_4N)^+$ salt ethanol solvate[b]
	Cu–Cu	
n[c]	6	6
mean,[d] Å	2.76 (2)	2.76 (4)
range, Å	2.692 (5)–2.772 (5)	
	S–S	
n	12	12
mean, Å	3.94 (20)	3.94 (6)
range, Å	3.55 (1)–4.24 (1)	
	Cu–S	
n	12	12
mean, Å	2.29 (3)	2.29 (1)
range, Å	2.242 (10)–2.338 (10)	
	Cu–S–Cu	
n	6	6
mean, deg	73.8 (10)	74.3 (12)
range, deg	72.5 (4)–75.1 (4)	74.3 (12)
	S–Cu–S	
n	12	
mean, deg	120 (10)	
range, deg	101.2 (7)–138.1 (7)	

[a] This work. [b] Reference 4b. [c] n = number of values in the calculation of σ; σ is calculated as indicated in ref 23. [d] Estimated standard deviations are in parentheses.

The obvious nonequivalence of the three Cu–S bonds and angles in I must arise from crystal packing effects which tend to freeze out only one form of the various, possible dynamic distortion coordinates. A number of short, nonbonding interactions (Table IV) show that packing effects indeed are important in affecting the structure of I in the solid state. In particular, two of the SC_6H_5 phenyl rings (C(55)–C(60)) and (C(61)–C(66)) show strong interactions with the hydrogens of the $(Ph_4P)^+$ cation phenyl rings and particularly with H(4), H(18), and H(36).

The mean value[23] of the two "short" Cu–S bond lengths in I (2.275 (4) Å) is within 3σ from values observed in the $[Cu(SPMe_3)_3]^+$ complex (2.259 (5) Å), in the $[Cu(tumtu)_3]^+$ complex (2.25 (1) Å), and in the $[Cu(entu)_3]^+$ complex (2.27 (1) Å). Similar values for the mean Cu–S bond lengths, for trigonally coordinated Cu(I) ions, also are found in $[Cu_5(\mu\text{-}SPh)_7]^{2-}$ (2.27 (2) Å),[2] in $[Cu_5(\mu\text{-}S\text{-}t\text{-}Bu)_6]^-$ (2.27 (2) Å),[3] and in $[Cu_4(\mu\text{-}SPh)_6]^{2-}$ (2.29 (1) Å).[4]

The structures of the $(Ph_4P)^+$ cations are unexceptional and will not be discussed any further.

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(23) $\sigma = (\sum_i (d_{av} - d_i)^2/n(n-1))^{1/2}$.

Table VI. CuS_3 Units in the $[Cu_4(SPh)_6]^{4-}$ Complex[a]

i	*j*	Cu(*i*)–S(*j*),[b] Å	*i*	*j*	*k*	S(*i*)–Cu(*j*)–S(*k*),[c] deg	Δ,[d] Å
1	1	2.338	1	1	3	120.8	
1	3	2.242	1	1	6	101.2	
1	6	2.253	3	1	6	137.8	0.04 (2)
2	2	2.274	4	2	6	127.7	
2	4	2.301	4	2	2	115.8	
2	6	2.310	6	2	2	116.1	0.06 (2)
3	1	2.276	1	3	2	121.7	
3	2	2.279	1	3	5	117.1	
3	5	2.306	2	3	5	120.5	0.08 (2)
4	3	2.316	3	4	4	117.8	
4	4	2.271	4	4	5	103.8	
4	5	2.262	5	4	4	138.1	0.06 (2)

[a] The numbering scheme is identical with that shown in Figure 2. [b] Estimated standard deviation 0.010 Å. [c] Estimated standard deviation 0.7°. [d] Distance of Cu(*j*) from the Cu(*j*)S_3 plane and away from center of the Cu_4S_6 core.

(B) $(Ph_4P)_2[Cu_4(SPh)_6]$. In the structure of $[Cu_4(SPh)_6]^{2-}$ anion the six $(SPh)^-$ ligands in a distorted-octahedral arrangement bridge the edges of a tetrahedron defined by the four copper atoms (Figure 2). The coordination about each copper is distorted trigonal and nearly planar. The structure of the Cu_4S_6 core in II is very similar to that of the $(Cu_4I_6)^{2-}$ anion[24] and to that of the Cu_4S_6 core reported recently for the $[Cu_4(thiourea)_6]^{4+}$ cation.[5] The Cu–Cu distances in II range from 2.692 (5) to 2.772 (5) Å with a mean Cu–Cu distance of 2.76 (2) Å. This value is in excellent agreement with corresponding values reported[4b] for the $(Me_4N)^+$ salt of II (Table V). Satisfactory agreement between the two structures also is evident in the Cu–S bond lengths, the Cu–S–Cu angles, and the S–S interligand distances (Table V). The coordination about each copper is distorted trigonal and nearly planar. The distances of the copper atoms from the respective S(3) planes (Table VI) on the average are 0.08 Å and away from the center of the Cu_4 tetrahedron. The dihedral angles between the S(3) planes range from 69.1 to 71.8°, and the Cu–Cu–Cu angles range from 58.3 (5) to 61.6 (5)°.

Bonding Interactions in the $(Cu_2S_3)_n$ Cores. An examination of the structure of II reveals the reason for the apparent nonexistence of $(Cu_4L_3)^{2-}$ cluster complexes with L = 1,1-dithiolate ligands. The S–S intraligand distance for the 1,1-dithiolate ligands (~3.00 Å) is far too short to span the edge of the S_6 octahedron in the Cu_4S_6 core which in II is 3.94 Å. It appears that, in the absence of chelate constraints, the Cu_4S_6 core is preferred over the Cu_8S_{12} "cubane", although for both types of structure the coordination geometry about the copper atoms is trigonal planar.

In an idealized Cu_4S_6 structure with trigonal-planar coordination for the copper atoms and a Cu–S bond length of 2.29 Å, a Cu–Cu distance of 2.64 Å is calculated. The distortion of $[Cu_4(RS)_6]^{2-}$ from ideality consists of a slight expansion of the Cu_4 tetrahedron (and Cu–Cu distances of 2.76 (2) Å). This expansion clearly indicates that repulsions very likely occur between the copper atoms at 2.64 Å. It is important to note, however, that the $[Cu_8(SPh)_{12}]^{4-}$ cluster with Cu–Cu distances greater than 3 Å does not form either. If one assumes similar Cu–S bond length constraints and S–S distances of 3.94 Å, a Cu–Cu distance of 3.40 Å and a Cu–S–Cu angle of 95.8° are calculated for the hypothetical $[Cu_8(PhS)_{12}]^{4-}$ cluster of T_h symmetry. A similar cluster of cuboctahedral symmetry requires a Cu–Cu distance of 3.80 Å and a Cu–S–Cu angle of 109.5°.

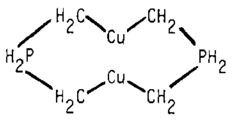

Figure 3.

Values for the M–S–M angle in mercaptide complexes vary from 74 (1)° in the present structure to 113 (1)° in the structure of the $[Co_4(SPh)_{10}]^{2-}$ complex.[25] On this basis one could argue that the size of the M–S–M angle, very likely, is not a significant factor in determining the stereochemistry of the copper framework in the $(Cu_2S_3)_{2n}$ cores. In such cores and with trigonal-planar copper coordination being maintained, the Cu–Cu distances assume an optimum distance of ca. 2.8 Å for $n = 1$. In the absence of chelate constraints the formation of $[Cu_4(SPh)_6]^{2-}$ rather than $[Cu_8(SPh)_{12}]^{4-}$ supports the conclusion that the Cu–Cu interactions in $(Cu_2S_3)_{2n}$ cores are weakly attractive in nature. A similar conclusion was reached[6a] by an analysis of the structural details of the $(Cu_8L_6)^{4-}$ cubanes in which the Cu–Cu distances, observed at 2.8 ± 0.1 Å, represent the optimum conditions where the attractive interactions prevail with repulsion arising at closer distances.

It is very interesting that, in their study of bonding relationships in d^{10}–d^{10} systems, Mehrotra and Hoffmann[7] have reached similar conclusions by invoking the admixture of s and p functions. Thus in the hypothetical $(CH_3Cu)_4$ cluster, the Cu–Cu interactions are "clearly attractive", and an energy minimum is set by the balance of the Cu–Cu attractive interactions with the "angularly dependent bonding requirements" of the bridging ligand. Even more interesting is the report that, for a hypothetical dimeric copper(I) ylide complex (Figure 3), the computed Cu–Cu distance optimizes at 2.7 Å. The dimethyl analogue of this ylide complex has been reported,[26] and its structure shows a Cu–Cu distance of 2.84 Å.

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Registry No. $[Ph_4P]_2Cu(SPh)_3$, 74231-14-4; $[Ph_4P]Cu(SPh)_2$, 74231-16-6; $[Ph_4P]_2Cu_4(SPh)_6$, 74231-18-8; $(Ph_4P)_2Cu(DTS)_2$, 56498-50-1; $Cu(CH_3CN)_4ClO_4$, 14057-91-1; $(Ph_4P)_4Cu_8(DTS)_6$, 64600-75-5.

Supplementary Material Available: Tables of positional and thermal parameters and a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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