

qualitatively account for the role of these low-energy, doubly occupied MO's. Later on, we shall propose a quantitative approach of the spin polarization in coupled systems. We can already notice that, in this respect, the situation encountered with the end-on azido bridge is quite peculiar. The quasi-absence of overlap density in π_g pushes away the two paired electrons occupying the same MO toward the extremities of the system. This could be the cornerstone of the large ferromagnetic interaction observed in μ -azido (end-on) copper(II) dinuclear complexes.

Acknowledgment. We are most grateful to L. Salem, J. P. Malrieu, P. de Loth, J. P. Daudey, and our colleagues of the Laboratoire de Spectrochimie des Eléments de Transition for very helpful discussions on the spin polarization.

Registry No. $[\text{Cu}_2(\text{tmen})_2(\text{N}_3)(\text{OH})](\text{ClO}_4)_2$, 86645-78-5; $[\text{Cu}(\text{tmen})(\text{N}_3)_2]_2$, 86667-98-3.

Supplementary Material Available: Listings of structure factor amplitudes and magnetic data (7 pages). Ordering information is given on any current masthead page.

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Planar Bridging Thiolate in $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$

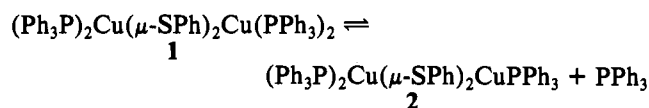
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Pale yellow $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$ has been crystallized from a mixture of CuSPh and Ph_3P in chloroform/propanol. The pseudotetrahedra around the equivalent copper atoms are linked at the common edge formed by the bridging thiolate ligands, such that the four phosphorus atoms and the two copper atoms are virtually coplanar. The molecule contains a crystallographic twofold axis that passes through both benzenethiolate ligands, and accordingly, the stereochemistry at sulfur is strictly planar. This is the first reported instance of planar stereochemistry at sulfur in a thiolate ligand bridging two metal atoms. There is crowded packing of the phenyl rings of the four Ph_3P ligands around the equatorial girdle of the molecule, an effect that restricts any movement of the axial SPh ligands away from planarity at sulfur and also increases the separation between the two copper atoms. Key dimensions: Cu-S, 2.344 (4), 2.415 (4) Å; Cu-P, 2.304 (2), 2.308 (2) Å; S-Cu-S, 79.3 (2)°; P-Cu-P, 118.3 (1)°; Cu-Cu, 3.662 (2) Å. Crystal data: prisms, $\text{C}_{84}\text{H}_{70}\text{Cu}_2\text{P}_4\text{S}_2$, mol wt 1394.6, tetragonal, $a = 14.071$ (1) Å, $c = 17.720$ (2) Å, $P4_2/m$ (disordered structure), $Z = 2$, Mo K α radiation, 1775 observed data, $R = 0.064$, $R_w = 0.077$.

Introduction

Reichle¹ has reported that CuSPh reacts with triphenylphosphine to form $(\text{Ph}_3\text{P})_2\text{CuSPh}$. Osmometric data for this compound in chlorobenzene solution indicate that either it is monomeric or, if dimeric, it is in dissociative equilibrium:



Precedent for the dissociated structure type exists in $(\text{Ph}_3\text{P})_2\text{CuCl}_2\text{CuPPh}_3$ (3).²

As part of our investigation of the coordination chemistry of fundamental thiolate ligands, particularly with copper,³ we have determined the crystal structure of $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$ (1). A second reason for this investigation derived from the considerable crowding of phenyl groups, which appeared to be unavoidable in such a dimeric structure. This compound was therefore expected to be significant in our evaluation of the stereochemical properties of bridging thiolates, where the configurational isomerism due to inversion of pyramidal sulfur and the surface packing of substituents may influence the structures of homoleptic metal thiolate cages.³⁻⁵ This significance was established when the structure of 1 was revealed as the first example of doubly bridging thiolate with planar stereochemistry at sulfur.

Table I. Details of Diffraction Analysis of $(\text{Ph}_3\text{P})_2\text{Cu}(\text{SPh})_2\text{Cu}(\text{PPh}_3)_2$

formula, mass	$\text{C}_{84}\text{H}_{70}\text{Cu}_2\text{P}_4\text{S}_2$, 1394.6
cryst description	capped prisms; {101}, {011}
space group	$P4_2/m$
$a, b/\text{Å}$	14.071 (1)
$c/\text{Å}$	17.720 (2)
$V/\text{Å}^3$	3508.4
Z	2
$d_{\text{obsd}}/\text{g cm}^{-3}$	1.32 (1)
$d_{\text{calc}}/\text{g cm}^{-3}$	1.32
temp/ $^{\circ}\text{C}$	21
radiation, $\lambda/\text{Å}$	Mo K α , 0.710 69
scan mode	$\theta/2\theta$
$2\theta_{\text{max}}/\text{deg}$	50
μ/cm^{-1}	7.98
cryst dimens/mm	$0.17 \times 0.20 \times 0.21$
max and min transmissn coeff	0.890, 0.793
no. of intens measurements	3476
std intens decay	nil
criterion for obsd refln	$I/\sigma(I) > 3$
no. of indep obsd reflns	1775
no. of reflns (m) and variables (n)	1775, 156
in final refinement	
$R = \sum \Delta F / \sum F_o $	0.064
$R_w = [\sum w \Delta F ^2 / \sum w F_o ^2]^{1/2}$	0.077
$[\sum w \Delta F ^2 / (m - n)]^{1/2}$	2.27

Experimental Section

CuSPh was prepared from copper(II) nitrate in ethanol with a small excess of benzenethiol and tertiary amine. The insoluble yellow product was thoroughly washed and vacuum dried.

$(\text{Ph}_3\text{P})_2\text{Cu}_2(\text{SPh})_2$ (1). CuSPh (1.0 g, 5.8 mmol) was added to a solution of triphenylphosphine (3.04 g, 11.6 mmol) in chloroform (30 mL) under nitrogen, and the mixture was stirred and warmed until all solid had dissolved. After filtration the pale yellow solution was diluted with propanol (50 mL) and stored at 0 $^{\circ}\text{C}$. The large,

- (1) Reichle, W. T. *Inorg. Chim. Acta* 1971, 5, 325.
- (2) Lewis, D. F.; Lippard, S. J.; Welcker, P. S. *J. Am. Chem. Soc.* 1970, 92, 3805.
- (3) (a) Dance, I. G. *J. Chem. Soc., Chem. Commun.* 1976, 68. (b) Dance, I. G.; Calabrese, J. C. *Inorg. Chim. Acta* 1976, 19, L41. (c) Dance, I. G. *Aust. J. Chem.* 1978, 31, 2195. (d) Bowmaker, G. A.; Clark, G. R.; Seadon, J. K.; Dance, I. G., to be submitted for publication.
- (4) Dance, I. G. *J. Chem. Soc., Chem. Commun.* 1980, 818.
- (5) Dance, I. G.; Scudder, M. L., to be submitted for publication.

Table II. Atomic Coordinates

atom	x	y	z	atom	x	y	z
Cu	0.402 06 (7)	0.085 70 (7)	0.008 05 (9)	C132	0.213 52 (17)	-0.036 69 (21)	-0.075 04 (15)
P1	0.437 13 (7)	0.245 87 (12)	0.005 42 (7)	C232	0.270 93 (39)	-0.112 81 (41)	-0.094 25 (34)
P2	0.244 78 (10)	0.040 58 (7)	0.003 90 (8)	C332	0.247 41 (52)	-0.171 62 (51)	-0.154 49 (43)
S1	0.500 00 (0)	0.000 00 (0)	0.090 65 (31)	C432	0.166 54 (47)	-0.153 79 (51)	-0.195 11 (41)
C11	0.500 00 (0)	0.000 00 (0)	0.189 38 (26)	C532	0.108 56 (50)	-0.078 92 (55)	-0.177 24 (41)
C21	0.469 84 (67)	0.079 07 (34)	0.229 20 (33)	C632	0.132 19 (38)	-0.020 19 (43)	-0.116 98 (34)
C31	0.469 81 (67)	0.079 13 (37)	0.307 68 (34)	HC21	0.447 44 (115)	0.137 78 (44)	0.200 56 (26)
C41	0.500 00 (0)	0.000 00 (0)	0.345 77 (36)	HC31	0.447 44 (115)	0.137 78 (44)	0.335 77 (26)
S2	0.500 00 (0)	0.000 00 (0)	-0.080 77 (30)	HC41	0.500 00 (0)	0.000 00 (0)	0.403 44 (26)
C12	0.500 00 (0)	0.000 00 (0)	-0.179 51 (25)	HC22	0.359 65 (48)	0.045 26 (149)	-0.190 68 (25)
C22	0.419 46 (36)	0.025 98 (86)	-0.219 33 (32)	HC32	0.359 65 (48)	0.045 26 (149)	-0.325 90 (25)
C32	0.419 39 (39)	0.026 00 (86)	-0.297 80 (33)	HC42	0.500 00 (0)	0.000 00 (0)	-0.393 56 (25)
C42	0.500 00 (0)	0.000 00 (0)	-0.335 89 (35)	HC211	0.561 32 (37)	0.366 22 (58)	-0.083 23 (41)
C111	0.563 42 (12)	0.274 89 (17)	0.009 37 (23)	HC311	0.721 90 (45)	0.419 78 (77)	-0.068 53 (57)
C211	0.601 89 (35)	0.340 53 (42)	-0.040 14 (36)	HC411	0.817 62 (34)	0.359 67 (81)	0.032 64 (61)
C311	0.695 07 (40)	0.371 66 (58)	-0.031 65 (48)	HC511	0.752 63 (41)	0.245 96 (81)	0.119 09 (55)
C411	0.749 13 (40)	0.336 83 (61)	0.026 37 (47)	HC611	0.592 06 (37)	0.192 40 (58)	0.104 39 (41)
C511	0.712 72 (38)	0.271 82 (61)	0.076 11 (47)	HC221	0.364 31 (74)	0.434 74 (33)	-0.025 52 (25)
C611	0.619 53 (34)	0.240 78 (43)	0.067 53 (35)	HC321	0.300 29 (91)	0.510 48 (41)	-0.135 43 (36)
C121	0.398 63 (27)	0.307 73 (16)	-0.079 56 (13)	HC421	0.297 30 (84)	0.427 62 (51)	-0.253 57 (28)
C221	0.363 12 (51)	0.399 33 (33)	-0.075 70 (28)	HC521	0.358 37 (92)	0.268 96 (52)	-0.261 69 (22)
C321	0.325 96 (65)	0.443 34 (42)	-0.139 47 (34)	HC621	0.422 38 (74)	0.193 23 (34)	-0.151 77 (24)
C421	0.324 60 (65)	0.395 32 (41)	-0.206 69 (30)	HC231	0.499 70 (51)	0.410 24 (62)	0.090 81 (55)
C521	0.359 31 (66)	0.304 63 (47)	-0.211 98 (28)	HC331	0.433 82 (74)	0.499 93 (77)	0.193 15 (68)
C621	0.396 45 (51)	0.260 73 (35)	-0.148 16 (25)	HC431	0.282 32 (72)	0.457 08 (78)	0.244 73 (60)
C131	0.386 61 (23)	0.315 10 (18)	0.082 72 (16)	HC531	0.196 76 (63)	0.324 47 (86)	0.193 89 (68)
C231	0.435 23 (44)	0.391 86 (45)	0.112 65 (39)	HC631	0.262 64 (50)	0.234 78 (63)	0.091 54 (55)
C331	0.397 06 (60)	0.443 95 (59)	0.172 04 (50)	HC212	0.082 66 (51)	0.104 86 (44)	0.091 26 (39)
C431	0.310 42 (56)	0.418 83 (61)	0.201 09 (49)	HC312	-0.015 92 (64)	0.243 61 (59)	0.087 30 (53)
C531	0.260 90 (54)	0.343 17 (64)	0.172 46 (50)	HC412	0.004 51 (66)	0.358 24 (49)	-0.011 40 (57)
C631	0.299 19 (42)	0.291 17 (47)	0.113 07 (39)	HC512	0.123 61 (72)	0.334 00 (50)	-0.106 15 (52)
C112	0.160 57 (14)	0.138 59 (14)	-0.005 14 (22)	HC612	0.222 19 (52)	0.195 25 (44)	-0.102 19 (39)
C212	0.091 51 (38)	0.153 51 (38)	0.049 20 (34)	HC222	0.083 88 (42)	-0.082 41 (62)	0.034 17 (27)
C312	0.034 26 (50)	0.234 02 (47)	0.046 95 (45)	HC322	0.030 98 (54)	-0.169 85 (75)	0.142 33 (37)
C412	0.046 56 (53)	0.299 06 (45)	-0.009 72 (44)	HC422	0.120 04 (58)	-0.163 71 (71)	0.257 50 (29)
C512	0.114 40 (55)	0.285 93 (42)	-0.064 15 (45)	HC522	0.262 03 (59)	-0.070 06 (78)	0.264 44 (26)
C612	0.171 58 (40)	0.205 38 (35)	-0.061 81 (34)	HC622	0.314 92 (43)	0.017 38 (62)	0.156 28 (26)
C122	0.203 77 (17)	-0.025 29 (24)	0.086 29 (14)	HC232	0.331 04 (46)	-0.125 75 (54)	-0.063 81 (45)
C222	0.121 90 (36)	-0.079 67 (45)	0.083 10 (28)	HC332	0.290 43 (64)	-0.227 01 (64)	-0.167 63 (56)
C322	0.091 15 (47)	-0.130 44 (57)	0.145 84 (34)	HC432	0.149 22 (62)	-0.196 98 (63)	-0.239 39 (48)
C422	0.142 59 (45)	-0.126 42 (57)	0.211 38 (31)	HC532	0.048 66 (59)	-0.065 61 (71)	-0.207 24 (54)
C522	0.223 84 (50)	-0.073 13 (58)	0.215 97 (29)	HC632	0.089 28 (46)	0.035 64 (55)	-0.103 43 (45)
C622	0.254 49 (37)	-0.022 41 (46)	0.153 18 (26)				

very pale yellow, capped-prismatic crystals that grew were collected, washed with ethanol, and vacuum dried; mp 158 °C. Microanalytical data consistently indicated a composition $\text{CuSPh}(\text{Ph}_3\text{P})_x$, $x = 1.5\text{--}1.8$. Anal. Calcd for $x = 1.5$: C, 70.01; H, 4.90. Found C, 69.71, 69.43; H, 4.96, 4.69.

Crystallography. Investigation of the crystals from the above preparation was made with an Enraf-Nonius CAD4 diffractometer. Unit cell dimensions were determined from accurately centered high-angle reflections. Intensity data were measured with the following parameters: (i) ω scan angle of $(0.80 + 0.35 \tan \theta)^\circ$; (ii) aperture width $(1.00 + 1.00 \tan \theta)^\circ$; (iii) maximum scan time 60 s; (iv) intensity standard measured after 2000 s; (v) orientation control checked every 300 reflections. Absorption corrections were calculated on a $6 \times 6 \times 6$ grid with the program ABSORB.⁶ Numerical details of the diffraction data and the structure refinement are provided in Table I.

Direct methods (MULTAN 80) applied to space group $P4_2$ located the Cu, S, and P atoms at positions that were consistent with special positions of space group $P4_2/m$ (Cu and P on a mirror plane, S on a twofold rotation axis). Systematic absences ($00l$, $l = 2n + 1$) and diffraction symmetry fail to distinguish between $P4_2$ and $P4_2/m$, $Z = 2$. The subsequent Fourier map based on the Cu, S, and P atoms was necessarily of $P4_2/m$ symmetry and indicated two orientations for each phosphine phenyl ring. Only one structural option (and its mirror image) was possible without unrealistically short intramolecular contacts between phenyl rings. This indicated symmetry 2 for the isolated molecule and constrained the S-C bond to lie on the twofold

axis and in the plane of the Cu and S atoms. Least-squares refinement of an ordered structure in space group $P4_2$, with anisotropic thermal parameters for Cu, P, and S and isotropic thermal parameters for the light atoms, gave an R value of 0.097. However, a difference Fourier map again revealed the presence of the mirror-related phosphine phenyl rings. The packing of the structure was then investigated. The crystal may be described as layers of molecules in planes perpendicular to c with $1/2c$ separation between layers. Within a layer, molecules separated by a (or b) must alternate between the mirror-related configurations to avoid impossibly short contacts between adjacent molecules. Within a single layer, the symmetry is thus $P2/n$ for a cell with axes $a' = a + b$, $b' = b - a$. There are two simple space group options associated with an ordering of layers using a larger repeat unit a', b', c' : (i) $c' = c$, space group $P2/n$, layers being related by a pseudo 4_2 operation (the 4_2 operation relates one layer to the next, but a repeat of the operation does not create the third layer); (ii) $c' = 2c$, space group $I4_1$ (the n glide plane relating molecules within a plane does not correctly relate molecules in the adjacent planes). Intermolecular contacts between adjacent layers of molecules do not distinguish between the two possible origins for the second layer relative to the first, and the lack of reflections for the larger unit cell confirms that a disordering of one layer relative to the next has indeed taken place. The data observed (i.e., $h' + k' = 2n$ of cell a', b', c') show the average of electron density at r and $r + 1/2(a' + b')$ (i.e., r and $r + b$),⁷ confirming that $P4_2/m$ is the appropriate space group for refinement using the observed hkl data. The space group $P4_2/m$ involves a disordering of the molecule about the mirror plane, and constrained refinement was then essential to

(6) "ABSORB", absorption correction program for the CAD4 diffractometer, University of Groningen and University of Sydney, 1975.

(7) Rae, A. D. *Acta Crystallogr., Sect. A* 1975, *A31*, 575.

Table III. Intramolecular Bond Distances (Å) and Angles (deg)^a

Dimensions Involving Cu and P Atoms			
Cu-P1	2.308 (2)	Cu-P2	2.304 (2)
Cu-S	2.344 (4)	Cu-S2	2.415 (4)
P1-C111	1.825 (2) ^a	P2-C112	1.825 (3) ^a
P1-C121	1.822 (3) ^a	P2-C122	1.823 (3) ^a
P1-C131	1.825 (3) ^a	P2-C132	1.825 (3) ^a
S-C11	1.750 (3) ^j	S2-C12	1.750 (3) ^j
Cu···Cu'	3.662 (2)		
Cu-S1-Cu'	102.75 (4)	Cu-S2-Cu'	98.63 (4)
P1-Cu-P2	118.29 (5)	S1-Cu-S2	79.3 (2)
P1-Cu-S1	112.91 (6)	P2-Cu-S1	116.30 (7)
P1-Cu-S2	110.64 (7)	P2-Cu-S2	112.94 (7)
Cu-P1-C111	115.2 (1) ^b	Cu-P2-C112	114.7 (1) ^c
Cu-P1-C121	114.8 (1) ^b	Cu-P2-C122	114.7 (1) ^c
Cu-P1-C131	115.0 (1) ^b	Cu-P2-C132	114.8 (1) ^c
C111-P1-C121	102.4 (2)	C112-P2-C122	104.4 (2)
C111-P1-C131	103.4 (2)	C112-P2-C132	103.1 (2)
C121-P1-C131	104.5 (1)	C122-P2-C132	103.6 (1)
Cu-S1-C11	128.6 (1)	Cu-S2-C12	130.7 (1)
S-C11-C21	120.6 (1)	S2-C12-C22	120.6 (1)
P1-C111-C211	120.4 (2) ^d	P2-C112-C212	120.6 (2) ^e
P1-C111-C611	120.4 (2) ^d	P2-C112-C612	120.3 (2) ^e
P1-C121-C221	120.8 (2) ^f	P2-C122-C222	120.8 (2) ^g
P1-C121-C621	120.3 (2) ^f	P2-C122-C622	120.5 (2) ^g
P1-C131-C231	120.8 (2) ^h	P2-C132-C232	120.6 (2) ⁱ
P1-C131-C631	120.5 (2) ^h	P2-C132-C632	120.7 (2) ⁱ
Dimensions of All Phenyl Rings			
C1-C2 = C6-C1	1.384 (4)	C2-C1-C6	118.7 (3)
C2-C3 = C5-C6	1.391 (5)	C1-C2-C3 = C5-C6-C1	120.7 (3)
C3-C4 = C4-C5	1.370 (5)	C2-C3-C4 = C4-C5-C6	119.5 (4)
		C3-C4-C5	121.0 (5)

^a Prime $\equiv 1-x, -y, z$. Dimensions marked with the same superscript were slack constrained to equality during refinement.

obtain a well-behaved and meaningful refinement. A program, RAELS,⁸ was used for this purpose. The disordered molecules lie about a $2/m$ site in $P4_2/m$. The mirror operation clearly relates the disordered molecules, and intramolecular distances imply that the molecules have a twofold axis coincident with the crystallographic twofold axis.

The missing data (i) $h' + k' = 2n + 1$, or (ii) $h' + k' + l' = 2n + 1$ were searched for but not found with use of the diffractometer. These data are the Fourier transform of half of the difference between the electron density at r and $r + 1/2(a' + b')$.⁷ Since the Fourier transform results from contributions from many unit cells, a disorder that confuses sites separated by $1/2(a' + b')$ causes these extra reflections to be observed on a reduced scale and complete disorder causes these reflections to completely disappear.

The Cu and P atoms are not constrained to be exactly on the mirror plane, although almost coincident atoms from different molecules related by the disorder do overlap on the mirror plane. Refinement using both strict⁹ and slack^{10,11} constraints reduced the value of R to 0.064 for the observed reflections and gave chemically sensible bond lengths and angles. Resolution of atoms about the mirror plane was assisted by the use of slack constraints imposing equality of distance and angle between chemically similar atoms (see Table III). The success of this procedure can be assessed by comparing geometrical parameters that were not constrained: C-P-C angles and planarity of



All phenyl rings were made to be identical, as refinable planar objects of $mm2$ symmetry. They were described as rigid bodies for thermal motion (TL model) with their centers of libration on the atom (P or S) to which they were attached.

The use of constraints eliminates correlation problems associated with the refinement of overlapping molecules in a disordered structure by imposing chemical reason where unconstrained refinement would produce unacceptably high standard deviations. The constraints used

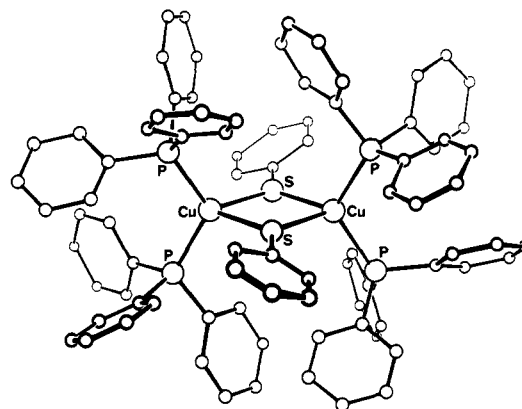


Figure 1. (Ph₃P)₂Cu(μ-SPh)₂Cu(PPh₃)₂ viewed along a direction close to the crystallographic twofold axis that passes through the two bridging benzenethiolate ligands.

imposed self-consistency but not absolute magnitudes.

Of special interest is the thermal motion of the SPh groups, as the planar stereochemistry at sulfur is novel. Initially the SPh groups within a single molecule were made equivalent across the mirror plane. This resulted in a large libration parameter about the twofold axis but effectively zero libration about perpendicular directions. Intramolecular distances suggested the phenyl groups should be made inequivalent, and this was done by using rotations about the twofold axis as dictated by geometry yet preserving the average electron density when disordering across the mirror plane was imposed. The SPh groups were then refined as independent entities with independent rigid-group thermal parameters. Final principal axis libration parameters L_{nn} , $n = 1-3$ (mean square-angular displacement), were 0.0003 (5), 0.0139 (9), and 0.0279 (40) rad² for SPh-1 and 0.0056 (6), 0.0121 (11), and 0.0640 (65) rad² for SPh-2. The largest value in each case describes oscillation about the twofold axis and represents root-mean-square angular displacements of 9.6 and 14.5°, respectively. Librational motion could disguise displacement of an SPh group away from the twofold axis, with subsequent disorder in $P4_2/m$. However, the relatively small librational parameters for L_{11} and L_{22} arising with the assumption of a true twofold axis in the crystal suggest that such displacements have not occurred.

The constrained refinement used 156 independent variables, which, with allowance for slack constraints, represented 138 independent variables for 49 non-hydrogen atoms. Scattering factors were taken from ref 12. The final difference map showed no significant peaks. Thermal parameters have been deposited¹³ as supplementary material.

Atomic coordinates are listed in Table II, with the following atom-labeling scheme: $Crst$ ($r = 1-6$, $s = 1-3$, $t = 1, 2$) for the carbon atoms (r) of the three phenyl rings (s) on the two phosphine ligands (t) on the copper atom of the asymmetric unit; Sn , Cmn ($n = 1, 2$, $m = 1-4$) for the two bridging SPh ligands bisected by the twofold axis.

Results

Molecular Structure. The molecular structure is shown in Figure 1 as a view slightly inclined to the crystallographic twofold axis passing through both SPh bridging ligands. The copper coordination is pseudotetrahedral, and the CuS₂Cu bridging section is strictly planar. The two copper atoms and four phosphorus atoms are coplanar to within 0.04 Å. The planes of the benzenethiolate ligands, normal to the Cu₂P₄ plane, are inclined at 27.9° (ligand 1) and 23.3° (ligand 2) to the Cu-Cu vector. Details of bond lengths and angles are provided in Table III.

We describe first a dominant feature of this molecule, which is the packing of the phenyl groups over its crowded surface. Overall, the molecule is ellipsoidal, with the longest axis in the Cu-Cu direction. The Ph₃P ligands are around the equatorial girdle, and the SPh ligands are directed axially,

(8) Rae, A. D. "RAELS", a comprehensive constrained least-squares program, University of New South Wales, 1976.

(9) Rae, A. D. *Acta Crystallogr., Sect. A* 1975, A31, 560.

(10) Waser, J. *Acta Crystallogr.* 1963, 16, 1091.

(11) Rae, A. D. *Acta Crystallogr., Sect. A* 1978, A34, 578.

(12) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(13) See paragraph at end of paper regarding supplementary material.

Table IV. Shortest Intramolecular Nonbonded Distances (Å)^a

Ph ₃ P- -Ph ₃ P ^b Distances			
C111- -HC232	2.88	C322- -HC511 ^c	2.78
C621- -HC612	2.74	C422- -HC511 ^c	2.77
C112- -HC631	2.61	C411- -C332 ^c	3.25
C212- -HC631	2.77	C411- -C232 ^c	3.39
Distances within Ph ₃ P ^b			
C111- -HC231	2.55	C112- -HC632	2.48
C121- -HC211	2.43	C612- -HC632	2.76
C221- -HC211	2.83	C122- -HC212	2.50
C131- -HC221	2.57	C222- -HC212	2.66
C231- -HC221	2.71	C132- -HC222	2.74
Ph ₃ P- -PhS ^d Distances			
S- -H ^e			
S1- -HC622	2.86	S2- -HC232	2.98
S1- -HC611	3.01	S2- -HC621	3.19
C(SPh)- -H(Ph ₃ P)			
C11- -HC622	2.68 ^e	C21- -HC622	2.68
C11- -HC611	3.36 ^e	C21- -HC611	3.22
C12- -HC621	2.97 ^e	C22- -HC621	2.64
HC(SPh)- -Ph ₃ P			
HC21- -C131	3.36	HC22- -C232	3.07
HC21- -C631	3.38	HC22- -C332	3.50
HC22- -C621	3.17	HC22- -HC621	2.36
HC22- -C132	3.12		

^a Estimated standard deviations: C-C, 0.01 Å; C-H, 0.02 Å; S-H, 0.02 Å. ^b C-H contacts less than 2.9 Å are listed. ^c Atom generated by the molecular twofold axis. ^d H-C < 3.5, H-H < 2.5 Å. ^e The twofold operation generates a second equal contact.

perpendicular to the virtual Cu₂P₄ plane. The contacts between phenyl groups of Ph₃P ligands on different copper atoms are as influential as those between ligands on the same copper atom. As can be seen from Figure 1, each Ph₃P ligand has one phenyl group approximately in the equatorial plane and the other two above and below it, an arrangement that allows tongue-and-groove interaction of Ph₃P ligands around the equatorial girdle. The shortest nonbonding distances between Ph₃P phenyl groups are listed in Table IV, and some are marked on Figure 2. It should be noted that the shortest distances between phenyl groups (i) of Ph₃P ligands on different copper atoms, (ii) of Ph₃P ligands on the same copper atom, and (iii) of the same Ph₃P ligand are all about the same.

Each of the four Ph₃P ligands directs one phenyl ring on each side of the equatorial plane, and each axial SPh group is therefore constrained within an approximately rectangular array of four phenyl rings. Both bridging SPh ligands make a set of contacts (Table IV, Figure 2) with hydrogen and carbon atoms of the surrounding phosphine phenyl rings, these contacts being similarly arrayed but differing slightly in length for the two thiolate ligands. There is a phenyl (P) hydrogen atom ca. 3.0 Å from S and approximately normal to the Cu₂S plane. The first carbon atom (C1_n) of each SPh ligand is 2.68 (n = 1) or 2.97 Å (n = 2) from two phenyl (P) hydrogen atoms. This contact is significant, because it must be decreased by any bending of the Sn-C1_n bond out of the Cu₂S plane. The second (ortho) carbon atom (C2_n) of each SPh ligand has one short contact distance of 2.68 (n = 1) or 2.64 Å (n = 2) from one phenyl (P) hydrogen atom, while the ortho hydrogen atom (HC2_n) has contacts at 3.36 and 3.38 Å (n = 1) or 3.07, 3.12, and 3.17 Å (n = 2) to phenyl (P) carbon atoms. All of these distances, while not particularly short in the structure, would be decreased by bending the PhS ligand out of the Cu₂S plane or by rotation about the S-C bond. The SPh ligand is restricted in all directions by its environment, and no reorientation to reduce contact with the phosphine substituents is possible.

The degree of crowding of the four Ph₃P ligands in the equatorial belt of **1** is comparable with but not greater than

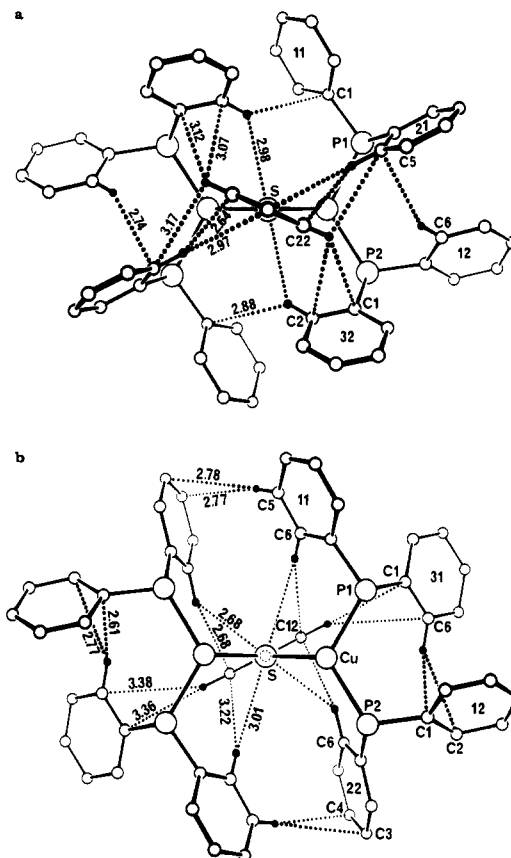


Figure 2. Projection of (Ph₃P)₂Cu(μ-SPh)₂Cu(PPh₃)₂ along the twofold axis showing atom and ring labeling and the shorter contacts between phenyl rings on different ligands. The contacts above (a) and below (b) the Cu₂P₄ equatorial plane are shown separately, omitting the SPh ligand and phenyl rings directed to the other side of the equator.

that in similar molecules. In tetrahedrally coordinated (Ph₃P)₄Pd¹⁴, intramolecular contacts between phosphine ligands range down to H-C = 2.5 Å and C-C = 3.5 Å. There is only one other structure reported for a compound in the class (Ph₃P)₂M(μ-X)₂M(PPh₃)₂ in which a single atom X is the bridging function, viz. (Ph₃P)₂Ag(μ-Br)₂Ag(PPh₃)₂ (**4**),¹⁵ but details have not been published. A related structure is (Ph₃P)₂Cu(μ-Cl)₂CuPPh₃ (**3**),² in which equatorial crowding is relieved by removal of one equatorial Ph₃P ligand.

In [(Ph₃P)₂Hf(μ-Cl)(μ-SPh)₂IrH(PPh₃)₂]⁺,¹⁶ with similar proportions of bridging SPh and terminal Ph₃P ligands, the Ir(μ-SPh)₂Ir section of the bridge adopts a syn-folded configuration in which the bridging thiolate ligands are not restrained from pyramidal stereochemistry at sulfur by the phosphine phenyl rings. The SPh ligands are adjacent and almost parallel to each other.

Stereochemistry at Copper and Sulfur. Important angles in the structure of **1** are P-Cu-P = 118.3, S-Cu-S = 79.3, and Cu-S-Cu = 100.7°. The angles within the bridge rhombus are distinctly different from those in **4** (Br-Ag-Br = 94.6, Ag-Br-Ag = 85.4°) and in **3** (C1-Cu-C1 = 91.6, Cu-C1-Cu = 82.9°). Bridge angles almost identical with those in **4** occur in [(MeS)₂Hg(μ-SMe)₂Hg(SMe)₂]²⁻ ((μ-S)-Hg-(μ-S) = 94.3, Hg-(μ-S)-Hg = 85.7°).¹⁷ Other structures with comparable (d¹⁰) bridge regions are [Cl₂Zn-

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$(\mu\text{-Cl})_2\text{ZnCl}_2]^{2-}$ ($\text{Zn-Cl-Zn} = 87.5^\circ$)¹⁸ and $[\text{o-C}_6\text{H}_4\text{(AsMe}_2\text{)(NMe}_2\text{)]Cu}(\mu\text{-I})_2\text{Cu}[\text{o-C}_6\text{H}_4\text{(AsMe}_2\text{)(NMe}_2\text{)]}$ ($\text{Cu-I-Cu} = 63.5^\circ$).¹⁹ Thus, in **1** the bridging region is substantially elongated (along the M-M axis) in comparison with related compounds, and even more so with reference to the model of two edge-bridged tetrahedra ($\text{X-M-X} = 109.5$, $\text{M-X-M} = 70.5^\circ$).²⁰

The Cu-Cu distance in **1** (3.662 Å) is almost as long as the Ag-Ag distance (3.720 Å) in **4**, and therefore the distances between adjacent Ph_3P ligands on different metal atoms are similar in the two compounds despite the smaller sizes of both metal and bridge atoms in **1**. This implies that repulsions between these phosphine ligands impose a minimum separation between the $[\text{Cu}(\text{PPh}_3)_2]$ halves of the molecule.

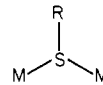
The principles of electronic structure in edge-bridged tetrahedral dimers such as **1**, in relation to details of geometrical structure, have been enunciated by Summerville and Hoffmann²⁰ in terms of the stereochemistry of the linked tetrahedral units. A monometallic reference, such as $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{SPh})_2]^-$, is not known, but its geometry can be predicted²⁰ by assuming that the effects of the π -acceptor ligand Ph_3P outweigh slightly those of the better σ -donor PhS^- . From this, the P-Cu-P angle is predicted to be slightly greater than 109.5° , and the S-Cu-S angle, slightly less. For $\text{Y}_2\text{MX}_2\text{MY}_2$ dimers, Summerville and Hoffmann²⁰ calculate a slight additional elongation relative to the geometry of the single metal complex, and therefore the predicted geometry of **1** would be S-Cu-S = $95\text{--}100^\circ$, Cu-S-Cu = $85\text{--}80^\circ$, and Cu-Cu = $3.0\text{--}3.2$ Å. In fact, the molecule has elongated by an additional $15\text{--}20^\circ$, or $0.65\text{--}0.45$ Å, most of which is ascribed to steric repulsion between Ph_3P ligands across the bridging region.

Crystal Structure. The crystal is disordered by location of both enantiomers of the molecule, which has symmetry $2 (C_2)$, at crystallographic sites with the higher symmetry $2/m$. These sites are separated by 17.7 Å (c) along the twofold axis and by 14.1 Å ($a/2^{1/2}$) within the mirror plane. With complete disorder, there are no short intermolecular contacts along the twofold axis (c) but there are impossibly short contacts between molecules at the same z level. Therefore, the crystal must be ordered *within* layers of constant z (0 or $1/2$) by alternation of enantiomers along both the a and b directions.

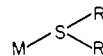
Discussion

In all previous instances of doubly bridging benzenethiolate ligands, two types of geometrical freedom are apparent: one is inclination of the S-C vector on either side of the M-S-M

plane, by $32 \pm 6^\circ$, and the other is rotation about the S-C bond.⁵ Thus, the planar stereochemistry at the sulfur atoms of the doubly bridging benzenethiolate ligands in the present compound **1** is a unique feature. Clearly this nonpyramidal stereochemistry is enforced by the crowding of the phenyl rings on the surface of the molecule. There is no reason emanating from the structure of **1** to expect substantial strain energy due to the planar configuration at sulfur. This is consistent with the various measurements of activation energy for inversion at pyramidal sulfur in



($45\text{--}75$ kJ mol⁻¹)^{21,22} and in



($50\text{--}70$ kJ mol⁻¹)²³⁻²⁵. We are currently investigating other molecules related to **1**, but with lesser crowding by triphenylphosphine ligands, with the expectation that normal pyramidal stereochemistry will occur at the doubly bridging thiolate.

Recently reported²⁶ dimensions of the comparable molecule centrosymmetric $(\mu\text{-OPh})_2\text{Cu}_2(\text{CNC}_6\text{H}_4\text{Me-}p)_4$ (**5**) query the dominance of steric factors in determining the Cu_2S_2 bridge geometry of **1**. The relevant data for **5** are Cu-O-Cu' = 101.9 (2) and O-Cu-O' = 78.1 (2)°, very similar to the corresponding angles in **1** despite the complete absence of equatorial steric crowding in **5**. The implication is that electronic characteristics distinctive of the Cu-EPh-Cu (E = O, S) bridge are influencing bridge geometry: this possibility requires further investigation.

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Registry No. 1, 34013-01-9.

Supplementary Material Available: Listings of F_o and F_c and of atomic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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