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Electrochemical Synthesis and the Molecular Structure of a Benzeneselenolato Complex of Copper, $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2 \cdot CH_3CN$, Containing Both Three- and Four-Coordinate Copper

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The electrooxidation of a copper anode into a toluene/acetonitrile solution of diphenyl diselenide and triphenylphosphine yields $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2 \cdot CH_3CN$ in excellent yield. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell parameters $a = 12.330$ (1) Å, $b = 12.972$ (7) Å, $c = 20.914$ (3) Å, $\alpha = 98.98$ (3)°, $\beta = 93.15$ (8)°, $\gamma = 115.87$ (7)°, $V = 2944$ (4) Å^3 and $D_{calcd} = 1.383$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 6175 observed reflections ($I \geq 3.0\sigma(I)$) converged at $R = 6.31\%$ ($R_w = 5.35\%$). The central core contains asymmetrically bridged benzeneselenolato ligands bound to the three- and four-coordinate Cu atoms forming a four-membered Cu_2Se_2 ring. The geometry around Cu1 is trigonal whereas it is tetrahedral around Cu2 with an average Cu–Se and Cu–P distance of 2.480 and 2.278 Å respectively. The ^1H and ^{31}P NMR spectra are consistent with the molecular structure and fast exchange of the PPh_3 moieties. Neither ^{77}Se nor ^{63}Cu NMR signals could be observed.

Introduction

The need for improved methods for the synthesis of semiconductor materials has led to the development of organometallic chemical vapor deposition techniques as well as attempts to prepare semiconductor grade material from solutions and by decomposition of thin films. All of these efforts require the preparation of suitable precursor compounds. Approaches have included use of single source precursors such as simple addition compounds and molecules and mixtures of compounds in either the solid or gas phase followed by thermal or photochemical decomposition of solutions or thin films. Among the chalcogenides, In_2Se_3, InSe, and $CuInSe_2$ are noteworthy as photovoltaic and optoelectric materials,[1] but no good procedures have been developed for the preparation of these compounds. Standard techniques for the formation of groups III–V materials have used thermal decomposition of simple adducts and molecular species[2] and have been extended to include use of simple sulfur, selenium, and tellurium species for formation of groups II–VI materials.[3] Other methods such as spraying films of precursor materials on a surface, followed by thermal decomposition, have been developed.[4] None of these techniques has yet yielded a convenient procedure for the formation of copper selenides or copper indium selenides. On the basis of these facts, we have started a series of studies on the preparation of selenides which may serve as precursors for the formation of metal selenides. The first result of this project is the electrochemical synthesis and first structural characterization of a benzeneselenolato complex of copper, $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2 \cdot CH_3CN$, a novel complex which contains both three- and four-coordinate copper, and we believe that benzeneselenolato derivatives of copper may be useful precursors for chalcogenide materials.

Experimental Section

General Data: All solvents were purified and dried by standard techniques.[5] Argon gas was purified by passing it through a series of columns containing Deox catalyst, phosphorus pentoxide, and calcium sulfate. Copper metal (Sargent-Welch, foil 0.002-in. thickness), triphenylphosphine (Aldrich), and diphenyl diselenide (Aldrich) were used as received. All glassware used in the synthetic work was oven dried. The Et_4NClO_4 was prepared from Et_4NCl and $NaClO_4$ and crystallized from deionized water and 95% ethanol at −10 °C. The solutions of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2 \cdot CH_3CN$ are sensitive to oxidation, so standard Schlenk line techniques were employed. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer at room temperature. The chemical shifts (ppm) were referenced to residual protic CD_2Cl_2 peaks ($\delta = 5.32$ ppm). The ^{31}P NMR spectra were obtained on a GN-300 NMR spectrometer operating at 121.47 MHz and are referenced to 85% H_3PO_4. Attempts were made to obtain ^{63}Cu and ^{77}Se NMR spectra on the sample. No signal could be observed for ^{63}Cu or for ^{77}Se. Mass spectra were run with a MS-80 AUTOCONSOLE (Kratos Analytical Instruments) mass spectrometer. A nitrosobenzyl alcohol matrix was used for the positive ion fast atom bombardment mode.

Electrochemical Synthesis. The electrochemical synthesis of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2 \cdot CH_3CN$ was carried out by a slight modification of the literature method.[6] The electrochemical cell consisted of a 100-mL round-bottomed Schlenk flask plugged with a rubber septum from which the platinum cathode and copper anode were suspended with a platinum wire. Current was provided by a Trugon Electronics Model HR60-5B power supply. The system was purged with Ar gas throughout the course of the synthesis.

The electrooxidation of copper was carried out in a mixed solvent of toluene (40 mL) and acetonitrile (10 mL) containing Ph_2Se_2 (2.5 g), PPh_3 (1.5 g), and Et_4NClO_4 (0.200 g) at a constant voltage of 20 V and a constant current of 50 mA. At the end of 2 h of electrolysis, a clear yellow-orange solution resulted which, when left to stand under a gentle flow of argon for a period of 30 h, deposited a yellow crystalline solid. The solid was collected, washed with 10–15 mL of cold acetonitrile and

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(1) Shay, J. L.; Wernick, J. L. In *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications*; Pergamon Press: Elmsford, NY, 1975. Solar Energy Research Institute. *Basic Photovoltaic Principles and Methods*; Van Nostrand-Reinhold: New York, 1984, pp 112–131. Kuriyama, K.; Saitoh, J. *Thin Solid Films* **1984**, *111*, 331.

(2) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248. Chen, C. H.; Larsen, C. A.; Stringfellow, G. B.; Brown, D. W.; Robertson, A. J. *J. Cryst. Growth* **1986**, *77*, 11. Moore, A. H.; Scott, M. D.; Davies, J. I.; Bradley, D. C.; Faktor, M. M.; Chudzynska, H. *J. Cryst. Growth* **1986**, *77*, 19. Reier, F.-W.; Wolfram, P.; Schumann, H. *J. Cryst. Growth* **1986**, *77*, 23.

(3) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200. Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245. Yamamoto, T.; Osakada, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1117. Osakada, K.; Yamamoto, T. *Inorg. Chem.* **1991**, *30*, 2328. Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141. Oikkonen, M.; Tammenmaa, M.; Asplund, M. *Mater. Res. Bull.* **1988**, *23*, 133.

(4) Kim, W.-T.; Yan, C.-S.; Jeong, H.-M.; Kim, C.-D. *J. Appl. Phys.* **1986**, *60*, 2357.

(5) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

(6) Kumar, R.; Tuck, D. G. *Can. J. Chem.* **1989**, *67*, 127.

0020-1669/92/1331-3626$03.00/0

dried in vacuo. Yield was 90% based on 0.241 g of copper dissolved during 2 h of electrolysis. Mp: 138–140 °C. ^1H NMR: 6.5–7.3 (m), PhSe and Ph_3P; 2.4 (s), CH_3CN. $^{31}P\{^1H\}$ (CH_2Cl_2/C_6D_6) –1.1 ppm; neither ^{77}Se nor ^{63}Cu NMR signals could be observed. Mass spectral data, EI mode: $m/e = 262$, $(Ph_3P)^+$; $m/e = 183$, $(Ph_2P)^+$; $m/e = 108$, $(PPh)^+$; $m/e = 77$, (Ph). Mass spectral data, FAB$^+$ mode: $m/e = 807$, $[(Cu_2SePh(Ph_3P)_2]^+$; $m/e = 545$, $[(Cu_2SePhPPh_3)]^+$; $m/e = 325$, $(Ph_3PCu)^+$; $m/e = 263$, $(Ph_3PH)^+$; $m/e = 185$, $(Ph_2P)^+$; $m/e = 77$ $(Ph)^+$. IR (KBr): 3143 (w), 3054 (m), 3000 (w), 2987 (w), 1573 (s), 1480 (s), 1471 (s), 1435 (s), 1330 (w), 1309 (w), 1294 (w), 1264 (w), 1183 (w), 1159 (w), 1095 (m), 1066 (m), 1020 (m), 998 (w), 751 (s), 743 (s), 733 (s), 693 (s), 665 (m), 618 (w), 521 (s), 504 (s), 493 (m), 466 (m).

Structure Determination and Refinement of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$. Crystals of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$ were grown from a dichloromethane/pentane mixed solvent at room temperature. A crystal suitable for X-ray diffraction was glued to a thin glass fiber, mounted on a goniometer head, and placed on a P3/V diffractometer for data collection. Reported cell constants were determined by precise centering of 25 high angle reflections (41.4° ≤ 2θ ≤ 84.6°) extracted from the full data set. Axial lengths were confirmed by photographic methods, and the cell reduction program TRACER II was run to check for higher symmetry lattices.[7] A $\theta/2\theta$ scan was used for the data collection with intensities measured by counter methods. Three standard reflections were measured every 100 reflections collected and were used to calculate a linear decay correction. The data were processed using the diffractometer programs and corrections were made for decay, background, and Lorentz and polarization effects. Twelve moderately intense reflections were used to correct for absorption effects by collection of ψ scans and varying the diffraction vector from 0 to 180° in 10° increments followed by processing with the program XEMP.[8] Complete crystal and experimental parameters are given in Table I. $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$ was found to crystallize in the triclinic crystal system. Examination of the data revealed no systematically absent classes of reflections. On the basis of counting statistics and the successful solution and refinement in the centric space group, the structure was assigned to space group $P\bar{1}$ (No. 2). The structure was solved by Patterson methods, which gave positions for the Cu and Se atoms. The remaining non-hydrogen atoms were located by successive applications of difference Fourier maps followed by least squares refinement. All refinements were carried out using full matrix least squares methods with the Cu, Se, and P atoms allowed to refine anisotropically and all ring carbons refined isotropically. All hydrogen atoms were placed in calculated positions (d(C–H) = 0.96 Å) riding on the respective carbon atoms with a common isotropic thermal parameter which was allowed to refine as a free variable. Five reflections were excluded from the refinement due to secondary extinction. The final difference Fourier showed a maximum residual electron density of 1.15 e/Å^3, 0.70 Å from C63 at $x = 0.4089$, $y = -0.1222$, and $z = 0.4199$. The solution and refinement of the structure were carried out using SHELX-76[9] and SHELXTL.[8] Neutral atom scattering factors were used and were corrected for anomalous dispersion.[10]

Results and Discussion

Electrochemical Synthesis of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$. $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$ was prepared by an electrooxidation of a copper anode in a solution of diphenyl diselenide and triphenylphosphine in acetonitrile/toluene. The new compound was isolated as air-stable yellow crystals, which are soluble in chlorinated and donor solvents. The complex was characterized by infrared spectroscopy, by ^1H and ^{31}P NMR spectroscopy (^{77}Se and ^{63}Cu NMR studies were unsuccessful), by mass spectroscopy and by X-ray crystallography. Precedent for the formation of complexes such as $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$ has been reported. The complex, $Ph_3PCu(\mu\text{-}SPh)_2Cu(PPh_3)_2$, has been proposed to exist in solution in equilibrium with $(Ph_3P)_2Cu(\mu\text{-}SPh)_2Cu(PPh_3)_2$ and has been confirmed by X-ray crystallography for $Ph_3PCu(\mu\text{-}Cl)_2Cu(PPh_3)_2$.[11,12]

Table I. Experimental Parameters for the X-ray Diffraction Study of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$

compd: $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$
formula: $C_{68}H_{58}NP_3Se_2Cu_2$
mol. wt.: 1226.08
cryst color: pale yellow rectangular prisms, ground to spherical, approx 25-mm diameter
cryst syst: triclinic
space group: $P\bar{1}$ (No. 2)
Z: 2 (dimers)
cell constants constrained from 25 high angle reflections: (41.4° ≤ 2θ ≤ 84.6°)
a: 12.330 (1) Å
b: 12.972 (7) Å
c: 20.914 (3) Å
α: 98.98 (3)°
β: 93.15 (8)°
γ: 115.87 (7)°
vol: 2944 (4) Å^3
density (calcd): 1.383 g cm^{-3}
radiation type: Cu K$\bar{\alpha}$; $\lambda = 1.54184$ Å, with a Ni filter
temp: ambient
type of data collecn: $\theta/2\theta$ scan
2θ scan range: 0–110°
scan width: 1.0° below Kα_1 to 1.0° above Kα_2
octants used: +h,±k,±1 (h, 0 to 14; k, –14 to +14; l, –23 to +23)
scan rate: 3–6 deg/min
std. reflcns: 3 measd per 100 reflections, linear decay about 2%
bkgd/scan ratio: 0.5
number of data collcd: 8086
data rejected: 5 reflcns, secondary extinction
no. of unique reflcns: 7425, $R_{int.} = 0.0195$
no. of obsd reflcns with $(F_o) \geq 3.0\sigma(F)$: 6175
linear abs coeff (μ): 38.58 cm^{-1}
$F(000)$: 1520 electrons
abs cor: empirical, ψ scans
transm coeff: 0.277/0.349
merging R before/after correcn: 0.0237/0.0101
no. of params refined: 341
obsd/param ratio: 18.1
$R = \sum(|F_o| - |F_c|)/\sum|F_o|$: 6.31%
$R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$: 5.35%
$w^{-1} = \sigma^2(F_o)$
overall shift/esd: 0.000
max shift/esd: 0.002
residual electron density: 1.15 e/Å^3, 0.70 Å away from C63
coordinates (x, y, z): 0.4089, –0.1222, 0.4199

Structure and Bonding in $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2\cdot CH_3CN$. An ORTEP diagram of the molecule $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2$ is given in Figure 1. Atomic positional parameters and isotropic equivalent thermal parameters for non-hydrogen atoms are given in Table II. Selected bond distances and angles are given in Table III. The structure consists of a benzeneselenolate-bridged dimer containing both three- and four-coordinate copper. The geometry about Cu1 is pseudotrigonal whereas it is pseudotetrahedral about Cu2. The Se atoms are three-coordinate and serve as bridges between the copper atoms. The four-membered Cu_2Se_2 structural unit is nearly planar. Se2 lies 0.073 (8) Å out of the Cu1–Cu2–Se1 plane, Se1 lies 0.0779 (8) Å out of the Cu1–Cu2–Se2 plane, and the maximum deviation for any atom is 0.021 (1) Å if all four atoms are used in the calculations. The four-membered ring is folded only slightly in a "butterfly" fashion about the Cu1–Cu2 axis since the dihedral angle between the relevant planes is only 2.13 (2)°.

The benzeneselenolate groups do not lie in the plane of the four-membered ring. The Se1–C55 and Se2–C61 vectors have angles of 55.4 (8) and 70.4 (8)° with the Cu_2Se_2 plane, respectively.

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(7) Lawton, S. L. TRACER II. Program for Lattice Transformation and Cell Reduction. Northwestern University, 1967.

(8) SHELXTL programs supplied by Seimans Analytical X-ray Instruments, Inc. for data reduction and structure solution.

(9) Sheldrick, G. M. SHELX-76. University Chemical Laboratory, Cambridge, England, 1976.

(10) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (present distributor D. Reidel, Dordrecht, The Netherlands).

(11) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

(12) Lewis, D. F.; Lippard, S. J.; Welcker, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 3805.

Table II. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms in $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2{\cdot}CH_3CN$

atom	*x*	*y*	*z*	U_{eq},[a] Å^2	atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Cu1	0.1871 (1)	0.08788 (9)	0.29527 (5)	0.0434 (5)	C32	–0.2507 (8)	–0.3146 (7)	0.2327 (4)	0.056 (2)
Cu2	0.0421 (1)	–0.11584 (9)	0.20854 (5)	0.0406 (5)	C33	–0.3506 (9)	–0.4248 (8)	0.2329 (4)	0.075 (3)
Se1	0.16849 (8)	0.08967 (7)	0.18040 (4)	0.0446 (4)	C34	–0.465 (1)	–0.4456 (9)	0.2066 (5)	0.096 (4)
Se2	0.08090 (8)	–0.09722 (7)	0.32848 (4)	0.0435 (4)	C35	–0.485 (1)	–0.362 (1)	0.1806 (5)	0.108 (4)
P1	0.3063 (2)	0.2431 (2)	0.3731 (1)	0.0416 (9)	C36	–0.3862 (9)	–0.2548 (8)	0.1798 (4)	0.081 (3)
P2	–0.1350 (2)	–0.0949 (2)	0.2056 (1)	0.0387 (9)	C37	–0.0076 (7)	–0.4089 (6)	0.1686 (4)	0.044 (2)
P3	0.0397 (2)	–0.2714 (2)	0.1389 (1)	0.0388 (9)	C38	0.0050 (7)	–0.4022 (7)	0.2350 (4)	0.058 (2)
C1	0.4672 (7)	0.2846 (6)	0.3788 (4)	0.046 (2)	C39	–0.0322 (8)	–0.5069 (8)	0.2571 (4)	0.076 (3)
C2	0.5010 (8)	0.1970 (8)	0.3866 (4)	0.067 (3)	C40	–0.0754 (8)	–0.6144 (8)	0.2141 (4)	0.076 (3)
C3	0.6244 (9)	0.2220 (8)	0.3882 (4)	0.079 (3)	C41	–0.0860 (8)	–0.6176 (8)	0.1500 (4)	0.074 (3)
C4	0.7107 (9)	0.3322 (8)	0.3823 (4)	0.085 (3)	C42	–0.0538 (8)	–0.5167 (7)	0.1245 (4)	0.064 (3)
C5	0.676 (1)	0.4207 (9)	0.3755 (5)	0.087 (3)	C43	–0.0689 (7)	–0.3168 (6)	0.0641 (4)	0.046 (2)
C6	0.5534 (8)	0.3956 (8)	0.3735 (4)	0.068 (3)	C44	–0.1910 (8)	–0.3761 (7)	0.0695 (4)	0.069 (3)
C7	0.2732 (7)	0.2307 (6)	0.4559 (4)	0.046 (2)	C45	–0.278 (1)	–0.4034 (8)	0.0132 (5)	0.093 (3)
C8	0.1526 (8)	0.1690 (7)	0.4648 (4)	0.057 (2)	C46	–0.238 (1)	–0.3696 (9)	–0.0416 (5)	0.092 (3)
C9	0.1199 (9)	0.1672 (7)	0.5273 (4)	0.071 (3)	C47	–0.120 (1)	–0.3089 (9)	–0.0491 (5)	0.092 (3)
C10	0.2072 (9)	0.2271 (8)	0.5811 (4)	0.074 (3)	C48	–0.0307 (9)	–0.2811 (7)	0.0066 (4)	0.071 (3)
C11	0.3276 (9)	0.2827 (8)	0.5744 (4)	0.076 (3)	C49	0.1839 (7)	–0.2463 (6)	0.1085 (4)	0.043 (2)
C12	0.3637 (8)	0.2876 (7)	0.5115 (4)	0.066 (3)	C50	0.1970 (9)	–0.3334 (9)	0.0669 (4)	0.083 (3)
C13	0.2962 (7)	0.3768 (6)	0.3624 (4)	0.048 (2)	C51	0.310 (1)	–0.3049 (9)	0.0432 (5)	0.096 (4)
C14	0.3121 (8)	0.4626 (8)	0.4168 (4)	0.075 (3)	C52	0.4065 (9)	–0.1947 (8)	0.0619 (4)	0.073 (3)
C15	0.2987 (9)	0.5634 (9)	0.4037 (5)	0.094 (3)	C53	0.3913 (8)	–0.1109 (7)	0.1039 (4)	0.060 (2)
C16	0.2716 (9)	0.5720 (9)	0.3416 (5)	0.088 (3)	C54	0.2785 (7)	–0.1382 (7)	0.1268 (4)	0.051 (2)
C17	0.2551 (9)	0.4857 (8)	0.2898 (5)	0.085 (3)	C55	0.3389 (7)	0.1574 (7)	0.1711 (4)	0.051 (2)
C18	0.2675 (8)	0.3845 (7)	0.3002 (4)	0.064 (3)	C56	0.3697 (9)	0.2107 (8)	0.1164 (4)	0.077 (3)
C19	–0.1757 (7)	–0.0408 (6)	0.1377 (4)	0.042 (2)	C57	0.496 (1)	0.2670 (9)	0.1090 (5)	0.103 (4)
C20	–0.2484 (7)	0.0182 (7)	0.1426 (4)	0.056 (2)	C58	0.579 (1)	0.2652 (9)	0.1533 (5)	0.096 (4)
C21	–0.2779 (8)	0.0535 (7)	0.0876 (4)	0.066 (3)	C59	0.550 (1)	0.2108 (8)	0.2045 (5)	0.091 (3)
C22	–0.2383 (8)	0.0327 (8)	0.0297 (4)	0.073 (3)	C60	0.4260 (9)	0.1542 (8)	0.2155 (4)	0.072 (3)
C23	–0.1649 (8)	–0.0229 (7)	0.0242 (4)	0.071 (3)	C61	0.2280 (7)	–0.1076 (6)	0.3532 (4)	0.049 (2)
C24	–0.1327 (7)	–0.0607 (7)	0.0792 (4)	0.055 (2)	C62	0.2570 (9)	–0.1018 (8)	0.4194 (4)	0.076 (3)
C25	–0.1376 (7)	0.0046 (6)	0.2773 (4)	0.042 (2)	C63	0.367 (1)	–0.1077 (9)	0.4374 (5)	0.095 (4)
C26	–0.0556 (7)	0.1227 (7)	0.2857 (4)	0.056 (2)	C64	0.438 (1)	–0.1174 (8)	0.3938 (5)	0.087 (3)
C27	–0.0484 (8)	0.1996 (7)	0.3418 (4)	0.060 (2)	C65	0.412 (1)	–0.1206 (9)	0.3285 (5)	0.094 (3)
C28	–0.1201 (8)	0.1559 (8)	0.3900 (4)	0.071 (3)	C66	0.2995 (8)	–0.1182 (7)	0.3079 (4)	0.068 (3)
C29	–0.2008 (8)	0.0404 (8)	0.3818 (4)	0.070 (3)	C98	0.036 (1)	0.557 (1)	0.4655 (5)	0.081 (3)
C30	–0.2097 (8)	–0.0349 (7)	0.3251 (4)	0.060 (2)	N99	0.0162 (9)	0.6157 (8)	0.4457 (4)	0.101 (3)
C31	–0.2689 (7)	–0.2309 (6)	0.2063 (4)	0.045 (2)	C99	0.053 (2)	0.463 (2)	0.494 (1)	0.25 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2U(1,1) + b^2U(2,2) + c^2U(3,3) + ab(\cos\gamma)U(1,2) + ac(\cos\beta)U(1,3) + bc(\cos\alpha)U(2,3)]$. All ring carbons and solvate molecule refined isotropically.

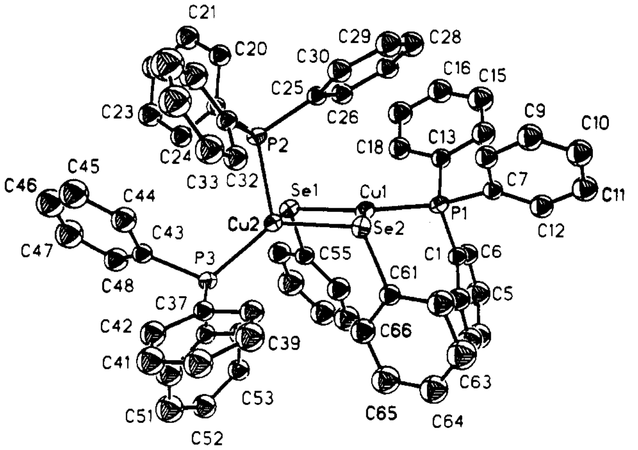

Figure 1. ORTEP diagram of $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2$ molecule with the atoms labeled. Hydrogen atoms have been omitted for the sake of clarity.

Table III. Selected Listing of Interatomic Distances (Å) and Angles (deg) for $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2{\cdot}CH_3CN$

Interatomic Distances			
Cu1···Cu2	2.738 (1)	Cu2–Se2	2.482 (1)
Cu1–Se1	2.406 (1)	Cu2–P2	2.314 (2)
Cu1–Se2	2.416 (1)	Cu2–P3	2.284 (1)
Cu1–P1	2.235 (2)	Se1–C55	1.927 (8)
Cu2–Se1	2.617 (1)	Se2–C61	1.925 (7)
Interatomic Angles			
Cu1–Se1–C55	98.4 (2)	Cu2–P3–C37	117.2 (2)
Cu1–Se2–Cu2	67.95 (3)	Cu2–P3–C43	112.1 (2)
Cu1–Se2–C61	93.7 (2)	Cu2–P3–C49	115.5 (2)
Cu1–P1–C1	115.6 (2)	Se1–Cu1–Se2	117.87 (4)
Cu1–P1–C7	115.5 (2)	Se1–Cu1–P1	124.57 (6)
Cu1–P1–C13	112.9 (2)	Se1–Cu2–Se2	108.20 (4)
Cu2–Se1–C55	125.6 (1)	Se1–Cu2–P2	92.86 (5)
Cu2–Se2–C61	111.3 (2)	Se1–Cu2–P3	115.98 (6)
Cu2–P2–C19	118.3 (2)	Se2–Cu1–P1	117.41 (5)
Cu2–P2–C25	113.5 (2)	Se2–Cu2–P2	97.62 (5)
Cu2–P2–C31	112.6 (2)	Se2–Cu2–P3	120.09 (5)
Cu1–Se1–Cu2	65.91 (3)		

The sums of the angles around Se1, 290°, and Se2, 273°, are in the range expected for selenium compounds. There are, however, substantial distortions in the molecule which appear to result from the steric crowding around the metal centers and lead to the difference in coordination of the two copper centers. The Cu1–Se–C angles of 98.4 (2) and 93.7 (2)° are much smaller than the Cu2–Se–C angles of 125.6 (1) and 111.3 (2)°. To further relieve steric crowding, the C55–C60 plane of Se1 is oriented 60.4 (2)° relative to the Cu_2Se_2 plane. Interestingly, this does not result in any short contacts at Cu1 with only C55 (3.294 Å), C60 (3.313 Å), C61 (3.186 Å), H50(C60) (2.762 Å) being within 3.5 Å with the exception of a long-range interaction with Cu2 at 2.738 (1) Å. This Cu1–Cu2 distance of 2.738 Å is much shorter than the 3.14 Å reported for dichlorotris(triphenylphosphine)-dicopper(I)–benzene[12] or 3.662 Å reported for $(Ph_3P)_2Cu(\mu\text{-}SPh)_2Cu(PPh_3)_2$[11] and is very close to the accepted van der Waals diameter of 2.8 Å for Cu–Cu.[13]

As previously stated, the geometry about Cu2 is pseudotetrahedral. The large P2–Cu2–P3 angle of 117.56 (8)° is a

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(13) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

consequence of the steric repulsions of the adjacent triphenylphosphine groups. This is sufficient to relieve much of the crowding and results in a small number of intermolecular contacts less than 3.2 Å for non-hydrogen atoms (C19···C31, 2.877 Å; C25···C20, 3.127 Å; C31···C25, 2.857 Å; C19···C36, 3.153 Å; C43···C37, 2.861 Å; C44···C37, 3.191 Å; C49···C37, 2.899 Å; C43···C42, 3.126 Å). The geometry around Cu2 can be further described by the angle between the P2–Cu2–P3 and the Se1–Cu2–Se2 planes. For an idealized tetrahedron, this angle is 90°; in the title compound, it is 87.75 (7)°. Apparently, this orientation minimizes nonbonded intermolecular contacts. However, large distortions from tetrahedral geometry are observed in the Cu2 valence angles (Se2–Cu2–P2, 97.62 (5)°; Se1–Cu2–P3, 115.98 (6)°). Further, the bridging selenolates are not symmetric with respect to the Cu atoms. The Cu1–Se distances of 2.416 (1) and 2.406 (1) Å are in close agreement, but there is a significant asymmetry for the Cu2–Se bond lengths (Cu2–Se1, 2.482 (1) Å; Cu2–Se2, 2.617 (1) Å). Cu–Se bond distances in the present study range from 2.406 (1) to 2.617 (1) Å and are longer than the average Cu–Se bond distance of 2.37 Å in $[Ph_4P]_2[Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]$ and 2.325 Å in $[Ph_4P]_4[Cu_2Se_{14}]$.[14] The increased length may result from the steric interactions present in the molecule and the fact that the Se atom is in a bridging site. There are no close contacts of less than 3.4 Å involving any of the ring carbons or Se2 so the asymmetry is probably attributable to subtle packing forces present in the molecule.

The Cu2–P distances of 2.314 (2) and 2.284 (1) Å show a slight increase compared to the Cu1–P1 distance of 2.235 (2) Å, presumably a reflection of four-coordinate versus three-coordinate copper. Another contributing factor may be π bonding involving phosphorus and the remaining orbital on the three-coordinate copper atom. The same trend has been reported for dichlorotris(triphenylphosphine)dicopper(I)–benzene.[12]

The lattice contains an acetonitrile solvent molecule, which does not participate in any interaction with $Ph_3PCu(\mu\text{-}SePh)_2Cu(PPh_3)_2$ but does appear to influence the packing of the dimeric units of the crystal.

NMR studies were carried out in an attempt to provide additional information about the structure of the complex in solution. ^1H spectra showed only one type of Ph_3P and PhSe unit. ^{31}P spectra also showed only a single resonance at −1.1 ppm relative to 85% H_3PO_4. This indicates fast Ph_3P exchange which leads to averaging of the magnetic environment of the ^{31}P nuclei. Efforts to obtain ^{63}Cu and ^{77}Se NMR spectra were unsuccessful. Failure to see these nuclei was attributed to the fast relaxation of the ^{63}Cu in an asymmetric field and the quadrapolar broadening of the ^{77}Se nucleus by the Cu nuclei.

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Supplementary Material Available: A complete listing of interatomic distances and angles and tables of anisotropic thermal parameters, hydrogen atom coordinates and thermal parameters (9 pages); a listing of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

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(14) Cusick, J.; Scudder, M. L.; Craig, D. C.; Dance, I. G. *Polyhedron* **1989**, *8*, 1139. Müller, U.; Ha-Eierdanz, M.-L.; Kräuter, G.; Dehnicke, K. *Z. Naturforsch.* **1990**, *45B*, 1128.