

Synthesis and Coordination of Tripodal-Containing Copper(I) Complexes

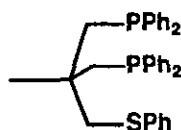
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Reaction of copper(I) chloride with 2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane P_2S produced a dimeric species $[(P_2S)CuCl]_2$ (**2**). Treatment of **2** with silver nitrate in acetonitrile gave a hexameric crystalline metal complex $\{[(P_2S)Cu(CH_3CN)]_6^+6NO_3^-\}$ (**4**), which had a "cyclodextrin-type" structure. A linear polymeric copper complex $[(P_2S)Cu(NO_3)]_n$ was obtained by recrystallization of **4** in chloroform. These complexes were characterized by single crystal analyses, and their coordination behaviors in solution are discussed.

INTRODUCTION

Research involving the coordination chemistry of copper(I) metal is important in relation to biological and structural studies.^{1,2} Many coordination geometries of various donors toward copper(I) complexes have been reported, but little is known about the coordination behavior of such metal with mixed multidentates.² It is known that the triphos ligand reacts with $CuCl$ to give a monomeric species $(Triphos)CuCl$; whereas bisphosphines give oligomeric or polymeric species.³

Part of our research interest in tripodal ligands is to synthesize such terdentates with mixed donor atoms which allow us to study selective coordination toward transition metals.⁴⁻⁷ We recently described the synthesis of 2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane **1**, (P_2S) along with its group VI carbonyl complexes.⁴ Because of the softness of copper(I), sulfur and phosphorus donors are expected to be better ligands for stabilization of such an oxidation state than that of copper(II).² The work reported here involves the ligating properties of P_2S toward copper(I).

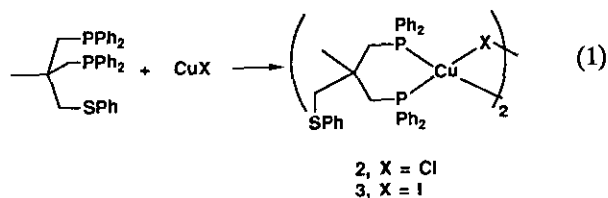


1 (P_2S)

RESULTS AND DISCUSSION

Synthesis and Structural Analyses

The reaction of P_2S with a stoichiometric amount of $CuCl$ in refluxing acetone under a nitrogen atmosphere gave the copper(I) complex **2** as the exclusive product (Eq. 1), and it was obtained as a colorless crystalline solid upon recrystallization from acetone and hexane. The ^{31}P nmr of this complex consisted of a sharp singlet at -26.7 ppm with coordination chemical shift -1.1 ppm (Table 1), indicating that two phosphorus donors coordinate to the metal center. Beside the absorptions of aromatic protons in the 1H nmr spectrum of **2**, a singlet at 2.92 ppm (methylene adjacent to sulfur), two doublets of doublets at 2.67 and 2.33 ppm (methylene adjacent to phosphorus) and another singlet at 0.78 ppm (methyl group), these spectral data gave no conclusive information about the coordination sphere around metal center, i.e. the coordination situation of sulfur donor. A complete structural analysis of complex **2** was determined by X-ray diffraction.



The crystal structure drawing of **2** is shown in Fig. 1 and some pertinent bond distances and bond angles are listed in Table 2. In this dimeric species, chlorides bridge



Table 1. The Physical Property of Copper(I) Complexes

Compd	mp	¹ H NMR	³¹ P NMR ^a	Conductivity ^b	Analysis
2	173-174 (dec)	7.84-7.13 (<i>m</i> , 25 H), 2.92 (<i>s</i> , 2 H), 2.67 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 12 Hz, 2 H), 2.33 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 2 Hz, 2 H), 0.78 (<i>s</i> , 3 H)	-26.66 (-1.1)	6.0	C ₃₅ H ₃₄ P ₂ SClCu Calcd: C, 64.91; H, 5.29 Found: C, 64.77; H, 5.12
3	174-177 (dec)	7.87-7.16 (<i>m</i> , 25 H), 2.94 (<i>s</i> , 2 H), 2.65 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 11 Hz, 2 H), 2.41 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 2 Hz, 2 H), 0.76 (<i>s</i> , 3 H)	-30.02 (-4.4)	5.0	C ₃₅ H ₃₄ P ₂ SiCu Calcd: C, 56.88; H, 4.64 Found: C, 56.32; H, 4.75
7	c	7.74-7.26 (<i>m</i> , 25 H), 3.03 (<i>s</i> , 2 H), 2.79 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 13 Hz, 2 H), 2.43 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 2 Hz, 2 H), 0.62 (<i>s</i> , 3 H) [in CD ₃ CN]	-21.35 (4.2)	129.8 (in CH ₃ CN)	c
6	c	7.76-7.24 (<i>m</i> , 25 H), 2.96 (<i>s</i> , 2 H), 2.75 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 13 Hz, 2 H), 2.37 (<i>dd</i> , J _{H-C-H} = 15 Hz, J _{P-C-H} = 2 Hz, 2 H), 0.74 (<i>s</i> , 3 H)	-20.91 (4.7)	0.5	c

^a Coordination chemical shifts ($\Delta\delta$) are given in parentheses. $\Delta\delta = \delta(\text{complex}) - \delta(\text{free ligand})$.

^b Conductivity ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) measured in acetone, except as noted.

^c Not available.

the two copper atoms to provide a planar four-membered ring [Cl-Cu-Cl'-Cu'], and the inversion center is seated on the center of this plane. Each copper atom is essentially in tetrahedral geometry by bonding with two phosphorus atoms and two chlorides. The distance between two copper center is 3.32 Å, clearly beyond the range of bonding interaction. As the angle of Cl-Cu-Cl' [92.59(19)°] is decreased from a reported angle for Cu₂Cl₂(PPh₃)₃ [97.3°],⁸ this is probably due to the relief of steric interaction between the larger diphenylphosphino group and chloride ligand. The bond distances of Cu-P are similar to those reported, whereas the Cu-Cl distances [2.388(5) & 2.373(6) Å] are somewhat shorter than those in Cu₂Cl₂(PPh₃)₃ [2.42

Table 2. Selected Bond Distances(Å) and Bond Angles(deg)

	2	4 [X=N]	5 [X=O]
Cu-P1	2.246(6)	2.254(4)	2.253(4)
Cu-P2	2.263(6)	2.234(5)	2.244(3)
Cu-S		2.437(5)	2.327(4)
Cu-Cl	2.388(5)		
Cu-Cl(a)	2.373(6)		
Cu-X		1.94(2)	2.121(8)
P1-C1	1.82(2)	1.84(1)	1.85(1)
C1-C2	1.50(3)	1.54(2)	1.54(1)
C2-C3	1.53(3)	1.53(2)	1.55(2)
C3-P2	1.82(2)	1.83(1)	1.84(1)
P1-Cu-P2	103.7(2)	103.5(2)	103.0(1)
Cl-Cu-Cl(a)	92.6(2)		
S-Cu-X		94.7(7)	94.6(2)
P1-Cu-Cl	116.8(2)		
P1-Cu-S		100.8(2)	119.7(1)
P1-Cu-Cl(a)	111.8(2)		
P1-Cu-X		119.2(6)	108.7(3)
P2-Cu-Cl	117.4(2)		
P2-Cu-S		110.0(2)	118.4(1)
P2-Cu-Cl(a)	115.0(2)		
P2-Cu-X		125.3(7)	112.2(2)

Table 3. The Torsional Angles (deg) Along the Six-membered Chelate Ring Cu-P1-C1-C2-C3-P2

	2	4	5
Cu-P1-C1-C2	41.3	52.3	51.3
P1-C1-C2-C3	-71.8	-70.1	-72.2
C1-C2-C3-P2	71.0	68.7	71.3
C2-C3-P2-Cu	-41.7	-48.9	-48.8
C3-P2-Cu-P1	14.8	29.3	27.2
P2-Cu-P1-C1	-13.6	-30.8	-28.8

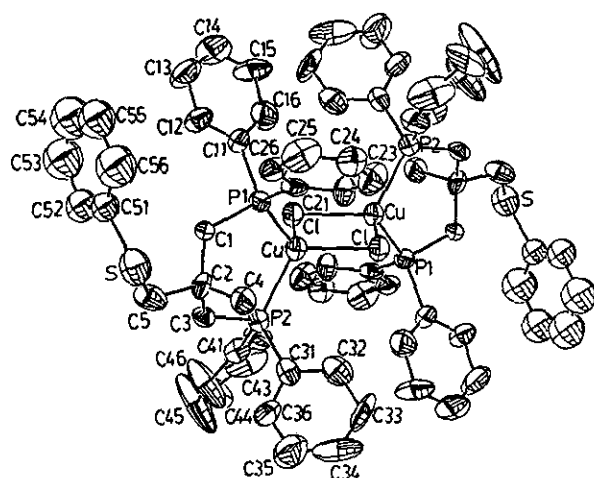


Fig. 1. ORTEP plot of dimeric complex 2.

& 2.45 Å].⁸ The torsional angles around the six-membered chelate ring Cu-P1-C1-C2-C3-P2 (Table 3) having the typical +g, -g alternation indicate that the conformation adopts chair forms. In the dimeric complex **2**, the dangling sulfur donors are situated at an equatorial orientation of the chair form, which places that donor away from the metal center.

Under similar conditions, P₂S reacted with CuI also to give a dimeric product [(P₂S)CuI]₂, **3** (Eq. 1) as identified by its spectral data, conductivity and elemental analysis (Table 1).

On account of the geometrical arrangement of tripod-like P₂S, the formation is favorable for the copper(I) complex in tetrahedral stereochemistry with coordination of all three donors, e.g. (triphos)CuCl. Attempts to prepare a complex of such type by treatment of **2** with silver nitrate in acetonitrile have been unsuccessful. Instead a polymeric compound **4** was formed upon crystallization (Scheme I). The infrared spectrum of **4** in KBr shows absorptions at

2273 cm⁻¹ for ν_{CN} and 1335 cm⁻¹ for uncoordinated NO₃⁻ (see below). The elemental analysis indicates the formula to be {(C₃₅H₃₄P₂S)(CH₃CN)Cu(NO₃)₃}. The detail structural analysis of **4** was done on an X-ray diffractometer.

The sulfur donor in P₂S coordinate to the metal center in an "intermolecular" fashion which resulted in the formation of the oligomer (Fig. 2). Thus, the tetrahedral sphere of copper(I) is surrounded by two phosphorus donors of a P₂S, a sulfur donor from another molecule of P₂S, and a nitrogen donor from acetonitrile. The conformation of the chelate ring adopts a chair form (Table 3), which allows the acetonitrile group to position equatorially and the sulfur group axially. Homogeneous cyclic linked six copper-complex units (Fig. 3) form a "cyclodextrin-type" structural feature for **4**, the first such instance in copper metal complexes. The axial group of sulfur, similar to the glucoside linkage of α-glucose in cyclodextrin, allows the formation of such a cyclic oligomer. A nitrate ligand is seated in the cavity of the cyclic ring. All bond distances

Scheme I

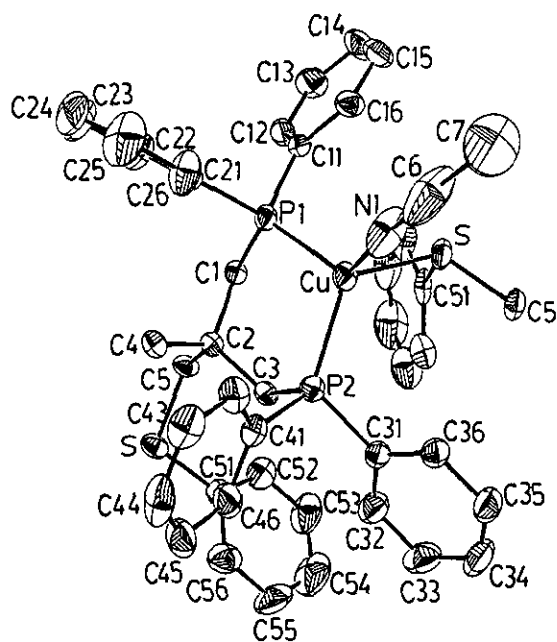
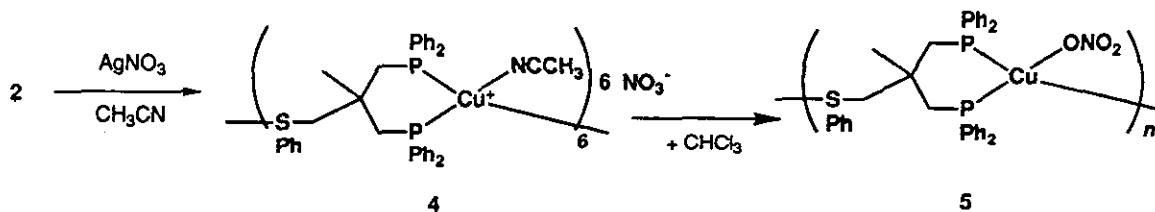


Fig. 2. The Crystal structure of **4** (only one unit of the hexamer presented).

are in normal ranges (Table 2), except Cu-S [2.437(5) Å]. The greater distance between copper and sulfur is believed to be the consequence of steric repulsion of the phenyl groups on both phosphorus and sulfur donors and of the 1,3-diaxial interaction of the sulfur group and axial hydrogens at C1 and C3. In order to relieve the interaction of the phenyl group and acetonitrile, the angles of P1-Cu-N [119.2(6)°] and P2-Cu-N [125.3(7)°] exceed 109°, also causing the decrease of S-Cu-N [94.7(7)°].

Recrystallization of oligomeric complex **4** in chloroform produced another crystalline species **5**, which had the molecular formula {(C₃₅H₃₄P₂S)Cu(NO₃)₃}_n according to its elemental analysis. The difference 92 cm⁻¹ of the wavenumbers of the symmetric and asymmetric stretching vibration of nitrogen-oxygen (1383 and 1291 cm⁻¹ respectively) demonstrated the unidentate coordination of nitrate to metal.^{3,9} Nevertheless, a single-crystal X-ray analysis (Fig. 4) confirms a linear polymeric structural feature for **5**. The sulfur donor is responsible for the occurrence of such a linked structure. The copper center in **5** is surrounded similarly to those of **4**, except that a nitrate ligand replaces the acetonitrile molecule. A distorted

chair conformation of the Cu-P1-C1-C2-C3-P2 ring is confirmed by the characteristic +g, -g alternations (Table 3), and the sulfur group occupies an equatorial position, unlike axial in 4, which leads consequently to the formation of linear polymeric species. The deviation of bond angles P1-Cu-S [119.7(1)°], P2-Cu-S [118.4(1)°] and S-Cu-O [94.6(2)°] from 109° is possibly due to a similar reason as in 4.

Coordination Behavior in Solution

To investigate further the bonding stability of the copper(I)-sulfur bond in the polymer chain, the solution chemistry of two polymeric complexes 4 and 5 was studied in both chloroform and acetonitrile. A determination of molar mass in chloroform by the vapor-pressure method proved 5 to be a monomeric species rather than a polymeric one (see experimental section). Also, the conductivity measurement of 5 in chloroform indicates it to be a non-electrolyte. The infrared spectrum of 5 in chloroform shows absorption at 1452 and 1293 cm^{-1} for symmetric and asymmetric stretching wavenumbers for N-O. The difference ($\Delta = 159 \text{ cm}^{-1}$) of these absorptions indicates a bidentate mode for the nitrate ligand around the metal ion.^{3,9} Obviously, polymer 5 decomposed upon dissolving in solution to form [(P₂S)CuNO₃] (6) (Scheme II).

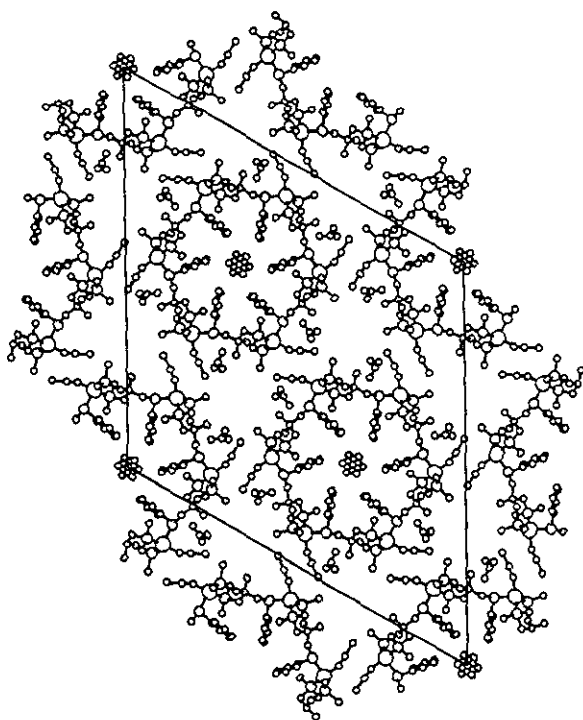
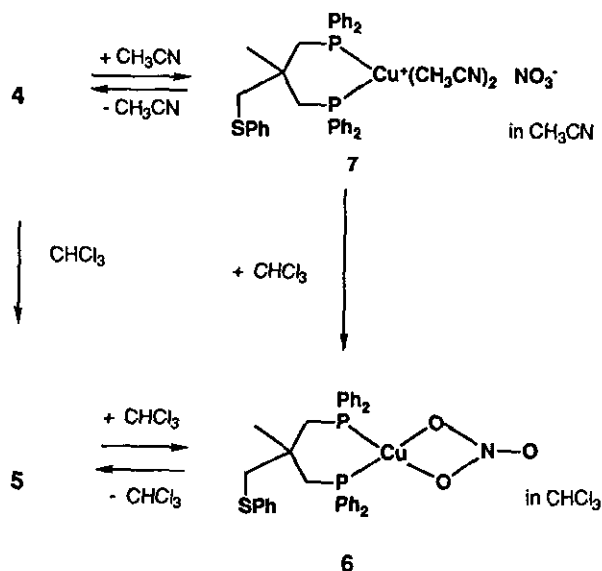


Fig. 3. Unit-cell content of 4 ("cyclodextrin-type" copper complex).

Scheme II The Coordination Behavior of Copper(I) in Solutions



The destruction of the "cyclodextrin-type" species 4 into monomeric species also occurred in acetonitrile solution. The determination of the molar mass in acetonitrile solvent proved it to be monomer, whereas the conductivity measurement showed that it formed a 1:1 electrolyte in that solvent. The infrared absorption at 1339 cm^{-1} for N-O stretching in acetonitrile indicated nitrate to be a free

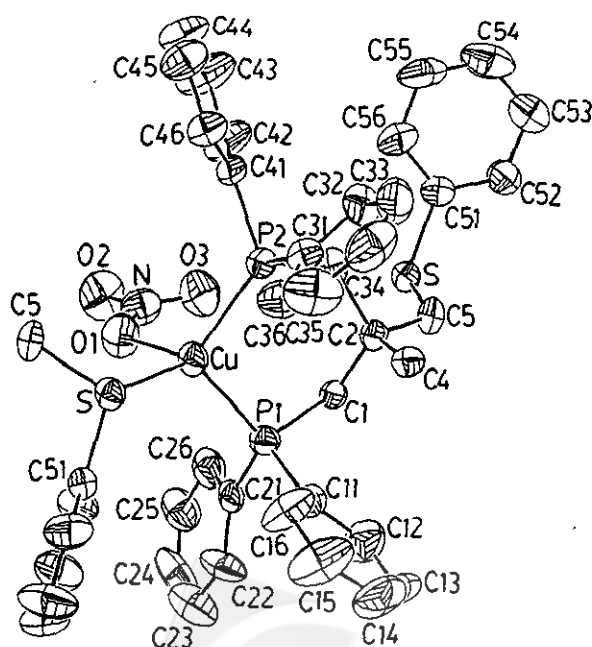


Fig. 4. Projection of the structure of [(P₂S)Cu(NO₃)]_n (one unit presented for clear view).

ligand without coordination to the metal ion. All this information is consistent with the structure $\{[(P_2S)Cu(CH_3CN)_2]^+NO_3^-\}$ (7) in acetonitrile. On replacement of acetonitrile by chloroform, species 7 converted into 6 (Scheme II) immediately as demonstrated by spectral analysis.

Unlike (Triphos)CuCl with all phosphorus donors bound to the metal center, P_2S acts as only a bidentate in solution or a tri-ligating ligand in solid state, presumably due to the weak donating ability of sulfur atom. The chelating effect forcing the thio-ether to form stable copper complexes is well documented.¹⁰ However, the geometrical arrangement in the tripodal system requires the formation of a three-boat conformation in a tridentate mode (Fig. 5). The interaction between sulfur and copper(I) does not apparently overcome the barrier of such unfavorable conformations; thus the sulfur donor behaves a free ligand in solution. As mentioned above, the formation of a "cyclodextrin-type" oligomer is related to the axial position of the sulfur group, but the reason for such an orientation compared with the equatorial one in 5 is unclear.

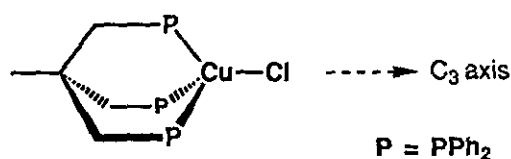


Fig. 5. Boat conformations of Tridentate (Triphos)CuCl

EXPERIMENTAL SECTION

1H NMR spectra were recorded on either a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. Proton-decoupled ^{31}P NMR spectra were determined on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer at 81.01 MHz and 121.49 MHz respectively. Chemical shifts are given in parts per million relative to 85% H_3PO_4 for ^{31}P NMR spectra in $CDCl_3$, unless otherwise noted.

IR and UV/VIS spectra were obtained on a Perkin-Elmer 983G and a Perkin-Elmer Lambda 3B instrument respectively. Elemental analyses were carried out on a Perkin-Elmer 240C instrument. Molar mass was determined by the method of vapor pressure osmometry on a JNAUER 1100 Vapor Pressure Osmometer. Conductivity was measured on a SUNTEX SC-17A conductivity meter.

All of the reactions, manipulations and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Air sensitive liquids were transferred by Teflon flexneedles using nitrogen pressure or by syringe. Acetonitrile, acetone, dichloromethane and chloroform were dried and distilled under nitrogen. 2,2-Bis(diphenylphosphinomethyl)-1-phenylthiopropene (P_2S)⁴ and $CuCl$ ¹¹ were prepared according to the literature methods.

Di- μ -chloro-bis[P,P' -{2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropene}]-dicopper(I) (2)

The reaction of P_2S (164 mg, 0.30 mmol) with $CuCl$

Table 4. Crystallographic Data

Compound	2	4	5
Formula	$CuP_2SC_{35}H_{34}ClCH_3COCH_3$	$CuSP_2C_{37}H_{37}N_2O_3$	$CuP_2SNO_3C_{35}H_{34}(CHCl_3)_2$
Fw	699.68	723.26	910.94
a/Å	14.367(6)	40.536(12)	26.639(9)
b/Å	18.724(7)	40.536(12)	14.917(14)
c/Å	15.213(5)	11.613(2)	22.891(6)
α /deg		90	
β /deg	116.73(3)	90	113.67(3)
γ /deg		120	
V/Å ³	3655(2)	16526(6)	8331(9)
Space group	P 2 ₁ /c	R3	C 2/c
Z	4	18	8
Crystal size/mm ³	0.10x0.30x0.80	0.50x0.50x0.50	0.40x0.40x0.30
T/°C	25	25	25
λ /Å	0.7093	0.7093	0.7093
ρ (calcd)/mgm ⁻³	1.271	1.308	1.453
μ /mm ⁻¹	0.83	0.77	0.68
transm coeff	-	0.857-0.998	0.890-0.998
R(F_o)	0.078	0.073	0.090
R _w (F_o)	0.072	0.093	0.072
S	2.70	1.81	4.31

Table 5. Non-Hydrogen Atomic Coordinates for **2** with Esd's in Parentheses

	x	y	z	B _{iso} , Å ²
Cu	0.58615(19)	0.99518(13)	0.11644(18)	3.38(13)
Cl	0.4353(4)	1.0670(3)	0.0273(4)	3.6(3)
P1	0.5811(4)	0.9210(3)	0.2302(4)	2.9(3)
P2	0.7405(4)	1.0523(3)	0.1974(4)	3.4(3)
S	0.8448(5)	0.9231(4)	0.5736(5)	6.1(4)
C1	0.7093(13)	0.9146(9)	0.3355(13)	2.9(10)
C2	0.7775(14)	0.9786(10)	0.3768(14)	4.0(12)
C3	0.8246(13)	1.0075(10)	0.3117(13)	3.2(11)
C4	0.7136(15)	1.0392(11)	0.3984(15)	4.6(13)
C5	0.8741(15)	0.9562(12)	0.4751(15)	5.0(14)
C11	0.5486(14)	0.8256(10)	0.1987(14)	3.6(13)
C12	0.5919(16)	0.7720(10)	0.2641(15)	4.3(14)
C13	0.5615(18)	0.7017(11)	0.2373(19)	6.9(19)
C14	0.4879(18)	0.6860(12)	0.1437(16)	6.3(17)
C15	0.4440(18)	0.7391(12)	0.0786(17)	6.5(17)
C16	0.4774(15)	0.8085(12)	0.1070(15)	5.1(14)
C21	0.4934(14)	0.9459(10)	0.2836(13)	3.3(11)
C22	0.4125(14)	0.9922(11)	0.2318(14)	4.3(13)
C23	0.3441(17)	1.0097(12)	0.2668(16)	5.7(15)
C24	0.3546(15)	0.9819(11)	0.3537(16)	4.9(14)
C25	0.4305(18)	0.9358(12)	0.4076(16)	5.8(16)
C26	0.5008(15)	0.9192(11)	0.3715(15)	4.4(13)
C31	0.7410(14)	1.1429(11)	0.2364(15)	4.3(13)
C32	0.6517(15)	1.1832(12)	0.1862(17)	5.6(16)
C33	0.6504(17)	1.2572(12)	0.2141(20)	7.5(20)
C34	0.7361(21)	1.2835(13)	0.2885(18)	8.5(20)
C35	0.8205(19)	1.2465(15)	0.3431(20)	9.6(20)
C36	0.8219(17)	1.1779(11)	0.3092(18)	6.3(15)
C41	0.8304(15)	1.0594(11)	0.1416(14)	3.9(13)
C42	0.7877(15)	1.0538(11)	0.0422(17)	5.4(15)
C43	0.8516(21)	1.0629(14)	-0.0076(19)	8.6(23)
C44	0.9532(16)	1.0743(15)	0.0459(20)	8.4(21)
C45	0.9880(17)	1.0804(22)	0.1382(19)	13.9(30)
C46	0.9314(16)	1.0724(18)	0.1851(18)	10.3(24)
C51	0.8322(15)	0.8255(11)	0.5510(15)	4.7(5)
C52	0.8838(17)	0.7933(12)	0.5113(17)	6.2(6)
C53	0.8627(20)	0.7219(15)	0.5039(21)	9.5(9)
C54	0.7926(21)	0.6910(15)	0.5256(21)	9.8(9)
C55	0.7392(18)	0.7262(14)	0.5623(19)	7.9(8)
C56	0.7567(20)	0.7988(15)	0.5806(21)	9.5(9)
O	0.9546(22)	0.3534(16)	0.1130(21)	14.2(10)
C61	0.92708	0.32781	0.14860	19.74
C62	0.93173	0.39001	0.21848	19.74
C63	0.83378	0.28020	0.09345	19.74

(29.9 mg, 0.30 mmol) in boiling acetone gave the desired complex **2** (621.7 mg, 96 %) as a white solid. Recrystallization from acetone and hexane produced a white crystalline solid which was suitable for X-ray structure analysis. The physical and spectral data are listed in Table 1.

Hexa{P,P'-[2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane](acetonitrile)copper(I) nitrate} (4)

To a flask containing AgNO₃ (499.6 mg, 2.94 mmol)

Table 6. Non-Hydrogen Atomic Coordinates for **4** with Esd's in Parentheses

	x	y	z	B _{iso} , Å ²
Cu	0.19068(5)	0.42499(5)	0.12740(17)	3.50(10)
P1	0.15362(11)	0.42083(11)	0.2778(3)	3.05(21)
P2	0.18354(12)	0.46337(12)	0.0045(3)	3.27(21)
S	0.25360(11)	0.45871(13)	0.2157(4)	4.16(24)
N1	0.1945(6)	0.3808(4)	0.0845(20)	9.7(14)
C1	0.1512(4)	0.4648(4)	0.2868(12)	2.9(8)
C2	0.1404(4)	0.4787(4)	0.1771(12)	2.7(7)
C3	0.1719(4)	0.4950(4)	0.0858(13)	3.1(8)
C4	0.1022(4)	0.4488(4)	0.1296(13)	3.5(9)
C5	0.2899(4)	0.4704(5)	0.1073(13)	3.7(9)
C6	0.2079(9)	0.3617(7)	0.088(3)	13.5(25)
C7	0.2276(12)	0.3375(9)	0.093(4)	18.2(39)
C11	0.1739(4)	0.4198(4)	0.4169(13)	3.3(8)
C12	0.1735(5)	0.4394(5)	0.5144(13)	4.2(11)
C13	0.1913(6)	0.4382(6)	0.6136(14)	5.7(13)
C14	0.2104(6)	0.4184(6)	0.6185(15)	6.3(14)
C15	0.2107(6)	0.3984(6)	0.5249(16)	5.6(13)
C16	0.1929(5)	0.3989(5)	0.4243(14)	4.5(11)
C21	0.1048(4)	0.3815(4)	0.2884(14)	3.8(9)
C22	0.0793(5)	0.3810(5)	0.3684(17)	6.0(11)
C23	0.0422(6)	0.3507(6)	0.3765(22)	7.9(14)
C24	0.0317(6)	0.3210(6)	0.3026(25)	9.1(16)
C25	0.0565(7)	0.3210(6)	0.221(3)	9.5(18)
C26	0.0931(5)	0.3514(5)	0.2133(19)	6.3(12)
C31	0.2242(4)	0.4965(5)	-0.0821(13)	3.8(9)
C32	0.2341(5)	0.5344(5)	-0.1058(16)	5.4(11)
C33	0.2651(6)	0.5573(6)	-0.1765(18)	6.7(13)
C34	0.2861(5)	0.5424(7)	-0.2238(17)	6.9(13)
C35	0.2771(5)	0.5056(6)	-0.1999(15)	5.9(12)
C36	0.2463(5)	0.4830(5)	-0.1299(13)	4.4(11)
C41	0.1462(4)	0.4419(4)	-0.1038(13)	3.6(8)
C42	0.1253(5)	0.4031(5)	-0.1148(15)	4.7(10)
C43	0.0972(6)	0.3855(6)	-0.1950(16)	6.3(12)
C44	0.0904(5)	0.4078(7)	-0.2691(16)	7.3(13)
C45	0.1109(5)	0.4473(6)	-0.2612(16)	6.3(13)
C46	0.1386(5)	0.4642(5)	-0.1779(15)	5.0(11)
C51	0.2622(4)	0.5038(5)	0.2666(15)	4.8(10)
C52	0.2704(5)	0.5344(6)	0.1965(17)	5.7(12)
C53	0.2745(6)	0.5669(6)	0.2427(23)	8.1(17)
C54	0.2707(8)	0.5701(7)	0.358(3)	10.3(21)
C55	0.2613(6)	0.5407(7)	0.4286(22)	9.1(17)
C56	0.2573(5)	0.5064(6)	0.3861(17)	6.5(13)
N2	0	0	0	19.1
O1	0.0192	0.0298	0.0496	23.8
N3	0.2746	0.2073	0.1708	9.8
O2	0.2942	0.2145	0.0959	14.1
O3	0.2426	0.1890	0.1740	13.8
O4	0.2851	0.2304	0.235	14.6

was added a solution of complex **2** (1913 mg, 1.47 mmol) in dry acetonitrile (15 mL) at room temperature. The resulting mixture became translucent immediately, and was kept stirred for 8 h. The reaction mixture was filtered and the filtrate was concentrated. The residue was recrystallized from acetonitrile to give the title hexamer as a pale-yellow

Table 7. Non-Hydrogen Atomic Coordinates for **5** with Esd's in Parentheses

	x	y	z	B _{iso} , Å ²
Cu	0.75629(6)	0.27623(9)	0.21899(7)	3.04(7)
P1	0.81276(13)	0.38997(21)	0.22157(15)	2.93(17)
P2	0.73946(13)	0.30039(19)	0.30621(14)	2.57(16)
S3	0.77717(13)	0.13110(20)	0.19884(14)	2.90(16)
O1	0.6843(3)	0.2859(6)	0.1338(4)	4.8(5)
N	0.6531(4)	0.3536(7)	0.1260(4)	4.6(6)
O2	0.6115(3)	0.3613(6)	0.0766(4)	6.2(6)
O3	0.6652(4)	0.4125(6)	0.1672(4)	5.7(6)
C1	0.7961(4)	0.4883(7)	0.2595(5)	2.6(6)
C2	0.7934(4)	0.4773(7)	0.3248(5)	2.8(6)
C3	0.7438(4)	0.4216(7)	0.3232(5)	2.8(7)
C4	0.8468(4)	0.4406(7)	0.3750(5)	3.1(7)
C5	0.7126(4)	0.0732(7)	0.1522(5)	2.9(6)
C11	0.8861(5)	0.3767(8)	0.2648(5)	3.7(7)
C12	0.9222(5)	0.4484(9)	0.2795(6)	5.8(10)
C13	0.9784(5)	0.4361(9)	0.3122(6)	6.1(10)
C14	0.9984(5)	0.3529(11)	0.3322(7)	7.3(10)
C15	0.9638(5)	0.2804(10)	0.3141(7)	7.5(10)
C16	0.9071(5)	0.2934(9)	0.2832(7)	5.9(9)
C21	0.8071(5)	0.4343(7)	0.1452(5)	3.3(7)
C22	0.8489(6)	0.4249(9)	0.1247(6)	5.5(9)
C23	0.8421(6)	0.4529(10)	0.0634(6)	7.0(11)
C24	0.7951(7)	0.4940(9)	0.0261(6)	7.1(11)
C25	0.7523(6)	0.5023(9)	0.0427(6)	5.5(9)
C26	0.7578(5)	0.4735(8)	0.1034(6)	4.8(9)
C31	0.7860(4)	0.2497(7)	0.3815(5)	3.1(7)
C32	0.7852(5)	0.2763(8)	0.4396(5)	4.0(7)
C33	0.8212(6)	0.2383(9)	0.4942(6)	5.5(9)
C34	0.8573(5)	0.1706(10)	0.4926(6)	6.5(9)
C35	0.8556(5)	0.1422(10)	0.4368(6)	6.1(9)
C36	0.8212(5)	0.1840(8)	0.3795(6)	4.6(8)
C41	0.6734(4)	0.2723(7)	0.3081(5)	2.9(6)
C42	0.6280(5)	0.3277(8)	0.2811(6)	5.2(8)
C43	0.5788(5)	0.3050(9)	0.2833(7)	7.1(10)
C44	0.5730(5)	0.2257(10)	0.3105(6)	6.2(10)
C45	0.6163(5)	0.1691(9)	0.3344(6)	5.2(8)
C46	0.6650(5)	0.1927(7)	0.3321(6)	3.9(7)
C51	0.8091(4)	0.1371(8)	0.1439(5)	3.2(7)
C52	0.7933(5)	0.1993(8)	0.0959(6)	4.3(8)
C53	0.8184(6)	0.2055(10)	0.0548(6)	6.1(9)
C54	0.8605(6)	0.1494(10)	0.0618(7)	6.9(11)
C55	0.8765(6)	0.0864(10)	0.1091(7)	7.5(11)
C56	0.8508(5)	0.0808(9)	0.1513(6)	5.4(9)
C10	-0.0393(7)	0.9950(11)	0.3861(7)	8.6(5)
C11	0.00264(20)	1.0731(3)	0.43976(22)	10.00(15)
C12	0.00558(22)	0.9036(4)	0.38675(24)	11.00(16)
C13	-0.0593(3)	1.0370(5)	0.3110(3)	15.70(23)
C20	-0.0351(7)	0.3041(13)	0.9514(8)	11.1(6)
C14	-0.0661(3)	0.3266(5)	0.8616(3)	5.84(19)
C15	-0.0453(5)	0.4093(8)	0.9875(6)	14.1(4)
C16	0.0382(5)	0.3380(8)	0.9624(5)	13.8(4)
C14'	-0.0460(5)	0.3520(9)	0.8834(6)	14.5(4)
C15'	-0.0725(4)	0.3601(7)	0.9856(5)	10.4(3)
C16'	0.0298(5)	0.2987(8)	1.0005(5)	12.6(4)

crystalline solid (1560 mg, 74 %): mp 139-142°C (dec); IR (KBr) 2273 (ν_{CN}), 1335 ($\nu_{\text{N-O}}$) cm^{-1} . Anal. Calcd for $\text{C}_{37}\text{H}_{37}\text{N}_2\text{O}_3\text{P}_2\text{SCu}$: C, 62.13; H, 5.21; N, 3.92. Found: C, 61.63; H, 5.39; N, 3.86.

Poly[(η^1 -nitrate){*P,P'*-2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropene}copper(I)] (5)

Dissolving **4** in chloroform and recrystallization from chloroform/hexane yielded polymer **5** as a pale yellow crystalline solid: mp 114-117°C (dec); IR (KBr) 1383, 1291 cm^{-1} ($\nu_{\text{N-O}}$); Anal. Calcd for $\text{C}_{35}\text{H}_{34}\text{NO}_3\text{P}_2\text{SCu}$: C, 62.35; H, 5.08; N, 2.08. Found: C, 62.40; H, 4.89; N, 2.06.

Crystallography

Crystals of **2,4** and **5** were obtained by recrystallization from cosolvents (vide supra). Cell parameters were determined on a CAD-4 diffractometer at 298 K and refined by a least-squares procedure. The structure was solved by the heavy-atom method. Atomic scattering factors were taken from International Tables for X-ray Crystallography.¹² The computing program was the NRC SDP VAX package.¹³ The crystal data are summarized in Table 4, and the non-hydrogen atomic coordinates are given in Table 5-7.

Determination of Molar Mass

The molar mass was determined by measuring the vapor pressure of **6** in chloroform and **7** in acetonitrile, compared to the standard complex **2** (non-electrolyte) and [(P₂S)Mn(CO)₃]BF₄ (1:1 electrolyte)¹⁴ respectively. Thus the molar mass determined for **6** and **7** are 817 and 836 gmol^{-1} , relevant to the theoretical values 756.3 and 674 gmol^{-1} respectively.

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Key Words

Tripodal phosphine; Copper(I).

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