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Synthesis and Crystal Structure of Some Phosphite, Thiophosphite, and Amidophosphite Copper(I) Halide Complexes

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ABSTRACT: *Some Cu(I) halides complexes based on P(III) acid esters,{[$(RE)_3$PCuBr] (where E = O, N, S); R = n-Pr, i-Pr, Et_2N} were obtained and characterized using IR, ^{31}P NMR spectroscopy, and single crystal X-ray diffraction. The comparative structural characteristics of complexes with various donor atoms (E = O, N, S) are analyzed.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:483–489, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20459

INTRODUCTION

The diversity in structural chemistry of copper(I) is well illustrated in complexes of copper(I) halides especially with the monodentate tertiary phosphines [1]. The tetrameric "cubane" structure was found to be the most common for such complexes, although an open "chair" (or "step') structure was also observed in several cases. The polymeric chain and monomeric structure was observed for some acyclic and cyclic diphophine ligands [2–5]. As for the Cu(I) halide complexes with the esters of P(III) acids, there are relatively few structural data in the literature [6–15], although the complexation of the esters of P(III) acids, especially phosphites and amidophosphites, with Cu(I) halides has been widely investigated. Phosphorus ligands $P(ER_n)_3$ ($n = 1$ or 2) containing several donor atoms such as E = O, N, S are potentially polydentate ligands, which may form a variety of complexes with different coordination modes. Owing to unusual donor properties of the ambident system P-E, such ligands are of great interest in organometallic chemistry and catalysis [6–9,15].

However, to date, the X-ray data have been reported for Cu(I) halide complexes mainly with bulky and chiral P—N, P—O— ligands, e.g., for the 6-membered cyclic P–N ligand [6] or bulky chiral P—O— ligands [7,8,10–12,15], which have the cubane-like structure. It is shown that the bulky ligands are essential but insufficient for the formation of tetramers [7,8,10–12]. The conditions of realization of the bond between transition metal atoms and ligand are also essential. If in [11] the structure of Cu(I)Cl and Cu(I)Br complexes with triphenyl phosphite was found to be a cubane tetrameric one, the authors [13,14] have observed the dimeric structure for Cu(I)Cl and Cu(I)I complexes with the same ligand. In several cases, cubane-like structure was observed in the

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equilibrium with a dimeric or tetrameric–dimeric forms in solution, as for the Cu(I) chloride complex with phosphite $P(odag)_3$(odag = 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside) [8] or for the Cu(I) halides with the caged phosphites 4-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane and its 4-nitro-derivative [12]. The structure of Cu(I) chloride complex with triisopropylphosphite ligand is shown to be a centrosymmetric dimer [9]. The search of phosphite and amidophosphite complexes with Cu(I) halides in the Cambridge Crystallographic Database [5] yielded only compounds with monodentate coordination of metal by phosphorus atom; no compounds with bidentate coordination of copper(I) by phosphorus and oxygen or nitrogen are being found. In total, considerations cited above are limited to the structures for Cu(I) complexes with P(III) esters with such characteristics as the steric hindrance, in which the monodentate type of coordination of Cu(I) via P atom is realized, whereas the binding ability of such ligands for copper(I) halides depending on a second donor atom (O, N, S) is not considered. Earlier we have reported our studies on the coordination properties of thioesters of P(III) acids. The series of complexes of trialkyltrithiophosphites with Cu(I) halides were synthesized, and the structure of most of these complexes in solid state has been studied [16,18–21]. It was found that the thiophosphite ligands have significantly different coordination properties as compared with phosphite or amidophosphite ligands. The major difference refers to the participation in coordination of the second donor center–the sulfur atom. Thiophosphites form the Cu(I) complexes of various structures: dimeric, tetrameric cubane-like, and step-like structure as well as polymeric and cluster structure [16–24] and exhibit the variety of coordination modes: “classical” monodentate coordination via phosphorus, bidentate coordination with participation of both donor atoms phosphorus and sulfur, both types of coordination in one complex and tridentate coordination via phosphorus and two sulfur atoms.

RESULTS AND DISCUSSION

In a course of our studies of new complexes based on the esters of P(III) acids, we have synthesized several complexes with Cu(I) halides, namely tripropyl-**1**, tri-isopropyl-**2**, tris(diethylamido)-**3**, tris(isopropylthio)-**4** phosphites, with Cu(I)Br, and complex of tris(diethylamido)phosphite with Cu(I)Cl **5**. Complexes **2–5** were investigated by single crystal X-ray diffraction, and their structures being reported here to compare the structural characteristics for P—O—, P—N—, P—S— ligands.

The ligands, excluding the commercial triisopropylphosphite and triamidophosphite, were synthesized by reacting PCl_3 with the equimolecular amount of alcohol (propanol) or thiol (isopropyl mercaptan) [25]. All ligands are colorless liquids and extremely soluble in hydrocarbons and other nonpolar and polar solvents. The single peaks in the ^{31}P NMR spectra at $\delta + 138$, 137, 118, 104 ppm are in the expected ranges for appropriate esters of P(III) acids.

These esters have been treated with Cu(I) halides to give the complexes CuXLn **1–5**. Complexes **2–5** are white crystalline compounds. There is the similar 1:1 stoichiometry (ligand : metal) for complexes **1, 2, 4, 5**, the different 2:1 stoichiometry being only observed for the compound **3**. The complexation results in the significant high-frequency shifts of the PO_3, PN_3, or PS_3 stretching vibrations in the IR spectra of complexes **1–5** as compared with the spectra of respective free ligands. The ^{31}P NMR spectra of all complexes show a single peak at $\delta + 114.9$ (**1**), 114.6 (**2**), 105.2 (**3**), 91.1(**4**), and 103.9(**5**), respectively, the high-field shifts ($\Delta\delta p$ ~15–30 ppm) of the phosphorus signal are being observed for complexes in comparison with free P(III) esters. The crystal and molecular structures of complexes **2–5** were determined by single crystal X-ray diffraction (Figs. 1–3). Crystals of complexes suitable for X-ray analysis were grown from benzene (complexes **2, 3, 5)** and chloroform (complex **4**). Unfortunately, our attempts to obtain single crystals of complex **1** with tris(*n*-propyl)phosphite ligand suitable for X-ray diffraction study failed.

According to the X-ray data, in the Cu(I)Br complexes the monodentate type of coordination via the P atom is realized regardless of the P—O—, P—N—, and P—S— ligands (Figs. 1–3). However, different types of self-assembly are observed: tetrahedral monomeric structure $CuBrL_3$, $L = (i\text{-PrO})_3P$ **2** and $CuBrL_2$, $L = (Et_2\ N)_3P$ **3**; tetrameric $[CuXL]_4$, $L = (i\text{-PrS})_3P$; X = Br **4**; $L = (Et_2\ N)_3\ P$, X = Cl **5**.

A complex of the Cu(I)Br with tris(isopropyl)phosphite **2** has the monomeric structure, two molecules in asymmetric part of unit cell in this structure are being revealed (Fig. 1). It should be mentioned that in the case of Cu(I)Cl complex with the same ligand, authors [9] have observed the centrosymmetric dimeric structure.

The monomeric structure is also revealed for the complex of Cu(I)bromide with tris(diethylamido)phosphite, **3**; however, as mentioned above, this complex has the ligand:metal stoichiometry, 2:1, and the copper(I) atom has the planar-trigonal configuration (Fig. 2), unlike the complexes **2** and **4** with a tetrahedral copper atom.

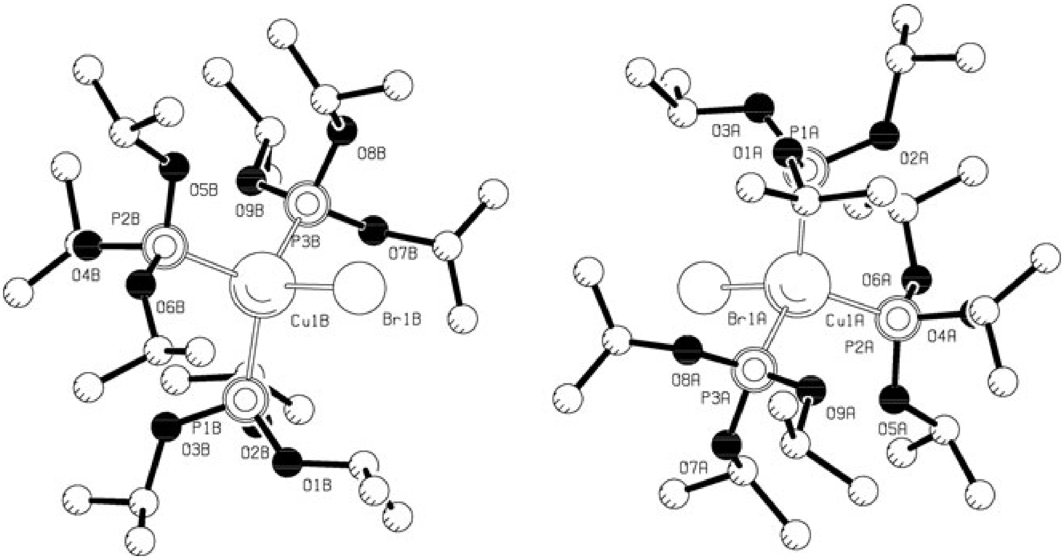

FIGURE 1 Molecular structure of complex (*i*-PrO)$_3$P•CuBr **2**.

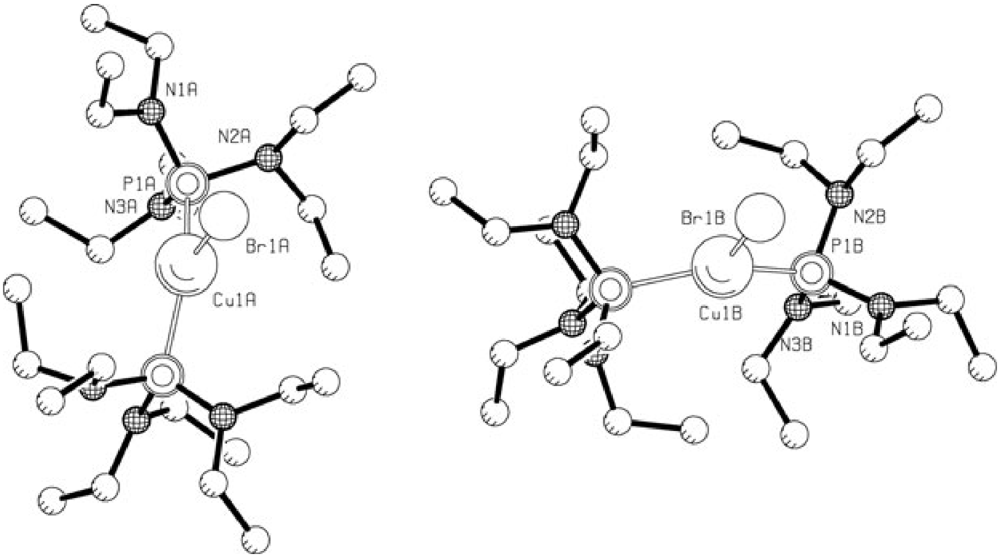

FIGURE 2 Molecular structure of complex {[(Et$_2$N)$_3$P]$_2$•CuBr} **3**.

Meanwhile, complex **5** of Cu(I) chloride with the same P—N— ligand, tris(diethylamido)-phosphite, has the 1:1 stoichiometry and the cubane-like structure with tetrahedral configuration of copper atom. The tetrameric core consisting of copper and chlorine atoms as well as the monodentate (via P) coordination mode was determined. More detailed consideration of the geometrical parameters of complex **5** is impossible because of the low accuracy due to poor quality of the crystals and their instability, which did not allow us to localize all of the terminal carbon atoms. It is reasonable to suppose that differences, which are observed in the structure of Cu(I) complex described in [9] and complex **2** discussed here, as well as **3** and **5** ones, may be due to the volume of halogen and also the conditions of crystal growth.

For the Cu(I) complexes with trialkyltrithiophosphite ligands, the cyclic chain polymeric structure and the bidentate type of copper coordination (via P and S) are found to be the most common ones [16–22]. However, for the complex **4** of Cu(I)Br with tris(iso-propylthio)phosphite, steric factors exclude the participation of sulfur in coordination bond with copper; thus, monodentate type of Cu coordination via P-atom and the tetrameric cubane structure were

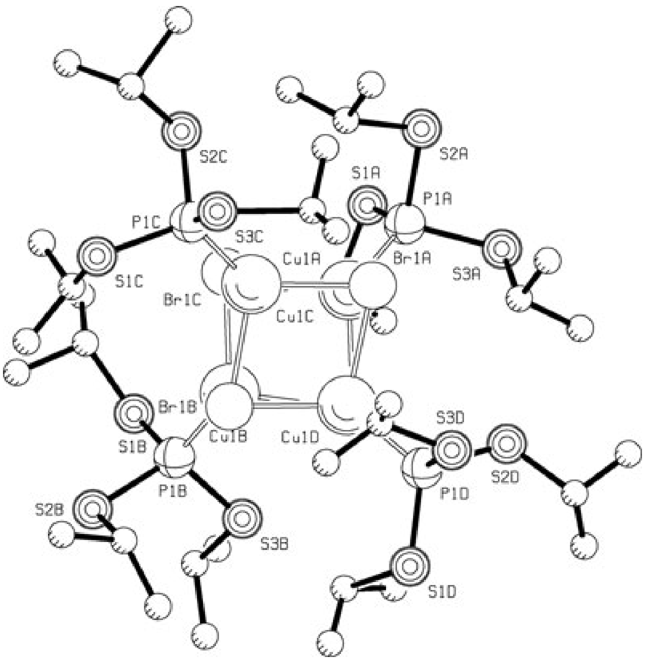

FIGURE 3 Molecular structure of complex [(*i*-PrS)$_3$P•CuBr]$_4$ **4**.

found (Fig. 3). Each copper(I) atom is in a distorted tetrahedral coordination environment being linked to one ligand molecule and to three bridging bromine atoms, because such tetrameric cubane Cu_4Br_4 core is much distorted and strained. The distorted "cubane-like" structure is also observed for the complex of Cu(I)I [23], whereas for the complex of Cu(I)Cl a unique cluster structure and tridentate type of coordination via P and two S atoms were realized with the same ligand [23]. It should be noted that "cubane-like" structure was often observed for the complexes with bulky phosphite and amidophosphite ligands [6–8,10–12,15].

In all studied crystals the Cu$\cdots$P distances range from ~2.212 (8) Å in tetrameric complex **4** to 2.238 (1) Cu–P(2)–2.245 (2) Cu–P(1) Å in dimer [9] and 2.267(3) Å as well as 2.2484 (8) Å in monomeric complexes **2** and **3**, respectively (Table 1).

These results have shown that Cu(I) displays a wide structural diversity in studied complexes of Cu(I) halides with the P(III) acid esters with a different stoichiometry, configuration, and structure in such complexes regardless of the nature of second donor atom at phosphorus. Structure of Cu(I) halide complexes with phosphites, amidophosphites, and thiophosphites are generally determined by the volume and nature of ligand, the binding ability of such ligands, the conditions of crystal growth, the solvent used and the volume of halogen atom as well.

EXPERIMENTAL

All manipulations involving P(III) acid esters were carried out under argon using dry solvents. The IR spectra were recorded as Nujol mulls on a Specord UR-20 and M-80 spectrometers in the range 400–4000 cm^{-1}. The ^{31}P NMR spectra: Bruker MSL-400, (162 MHz); CXP-100 (36.47 MHz), standard: external 85% H_3PO_4); solvents: C_6H_6 or $CHCl_3$. The melting points were determined on a Boetius apparatus and are uncorrected. All commercial reagents were used without further purification. The P-ligands, triisopropyl phosphite, and tri(diethylamido)- phosphite were purchased from Alfa Aesar (a Johnson Matthey Company: UK, Heysham, Lancashire LA3 2XY).

The P-ligands, tri-*n*-propyl-, and tri(isopropylthio)phosphites were obtained according to the method described in [25].

Tri-n-propyl Phosphite

A solution of PCl_3 (6.86 g, 0.05 mol) in dry ether (40 mL) was added dropwise to a stirred solution containing 9 g (0.15 mol) of dry *n*-propanol and 15.1 g (0.15 mol) dry triethylamine in dry ether (80 mL) for 2 h at −10°C. The reaction mixture was then heated with the vigorous stirring for 2 h at 35°C to form the precipitate of ammonium hydrochloride. The latter was filtered off and washed with two portions of the ether (2 × 20 mL). After concentration filtrate, the residue was distillated to give ~7 g (60%) of tri-*n*-propyl phosphite, bp 90–95°C (15 mm/Hg); δp 138. Anal. Calcd for $C_9H_{21}O_3P$ [208]: C, 51.92; H, 10.09; P, 14.9. Found: C, 51.31; H, 10.2; P, 15.10.

Triisopropylthiophosphite

PCl_3 (9.2 g, 0.07 mol) was added dropwise to the solution of isopropyl mercaptan (15 g, 0.2 mol) in dry ether (100 mL) at 0°C for 1.5 h. After complete addition, the ether was removed; the residue was distillated to give 13.3 g (55%) of triisopropylthiophosphite, bp 90–100°C (10 mm/Hg); δp104. Anal. Calcd for $C_9H_{21}S_3P$ [256]: C, 42.2; H, 8.2; P, 12.2; S, 37,5. Found: C, 41.8; H, 8.3; P, 12.35; S, 36.85.

*[Tri(n-propyl)phosphite]copper(I) Bromide (**1**) and [Tri(iso-propyl)phosphite]copper(I) Bromide (**2**)*

CuBr (2.8 g, 0.02 mol) was added by portions at the stirring to 4 g (0.02 mol) of corresponding phosphite. The temperature increasing of the reaction mixture from 18 to 40°C was observed. Then C_6H_6(7 mL) was added to the reaction mixture with its following

TABLE 1 Selected Bond Distances (Å), and Bond Angles (°) for Complexes **2–4**

Complex **2**

Bond	*d (Å)*	*Bond*	*d (Å)*
Cu(1A)–Br(1A)	2.4748(14)	P(2A)–Cu(1A)	2.269(3)
Cu(1B)–Br(1B)	2.4670(15)	P(1B)–Cu(1B)	2.265(3)
P(1A)–Cu(1A)	2.278(3)	P(3B)–Cu(1B)	2.258(3)
Bond angles	ω (°)	Bond angles	ω (°)
P(3A)–Cu(1A)–P(2A)	114.51(10)	P(3B)–Cu(1B)–P(2B)	114.64(10)
P(3A)–Cu(1A)–P(1A)	116.46(10)	P(3B)–Cu(1B)–P(1B)	117.08(11)
P(2A)–Cu(1A)–P(1A)	112.38(10)	P(2B)–Cu(1B)–P(1B)	110.72(11)
P(3A)–Cu(1A)–Br(1A)	101.41(8)	P(3B)–Cu(1B)–Br(1B)	101.65(8)
P(2A)–Cu(1A)–Br(1A)	101.14(8)	P(2B)–Cu(1B)–Br(1B)	103.09(8)
P(1A)–Cu(1A)–Br(1A)	108.93(8)	P(1B)–Cu(1B)–Br(1B)	108.00(8)

Complex **3**

Bond	*d (Å)*	*Bond*	*d (Å)*
Cu(1A)–P(1A)[a]	2.2513(9)	Cu(1B)–P(1B)[b]	2.2456(8)
Cu(1A)–P(1A)	2.2513(9)	Cu(1B)–P(1B)	2.2456(8)
Cu(1A)–Br(1A)	2.4115(8)	Cu(1B)–Br(1B)	2.4151(8)
Bond angles	ω (°)	Bond angles	ω (°)
P(1A)[a]–Cu(1A)–P(1A)	142.20(5)	P(1B)[b]–Cu(1B)–P(1B)	142.67(5)
P(1A)[a]–Cu(1A)–Br(1A)	108.90(3)	P(1B)[b]–Cu(1B)–Br(1B)	108.67(2)
P(1A)–Cu(1A)–Br(1A)	108.90(3)	P(1B)–Cu(1B)–Br(1B)	108.67(2)

Complex **4**

Bond	*d (Å)*	*Bond*	*d (Å)*
Br(1D)–Cu(1A)	2.492(4)	Br(1A)–Cu(1D)	2.554(4)
Br(1D)–Cu(1D)	2.515(5)	Br(1B)–Cu(1D)	2.458(4)
Br(1D)–Cu(1B)	2.590(4)	Br(1B)–Cu(1B)	2.523(4)
Br(1C)–Cu(1B)	2.502(4)	Br(1B)–Cu(1C)	2.559(4)
Br(1C)–Cu(1C)	2.527(4)	Cu(1A)–P(1A)	2.203(8)
Br(1C)–Cu(1A)	2.551(4)	Cu(1B)–P(1B)	2.222(7)
Br(1A)–Cu(1C)	2.483(4)	Cu(1C)–P(1C)	2.211(8)
Br(1A)–Cu(1A)	2.499(4)	Cu(1D)–P(1D)	2.213(8)
Bond angles	ω (°)	Bond angles	ω (°)
Cu(1A)–Br(1D)–Cu(1D)	77.42(13)	Cu(1C)–Br(1C)–Cu(1A)	75.41(12)
Cu(1A)–Br(1D)–Cu(1B)	78.87(12)	Cu(1C)–Br(1A)–Cu(1A)	77.12(13)
Cu(1D)–Br(1D)–Cu(1B)	75.86(12)	Cu(1C)–Br(1A)–Cu(1D)	78.41(12)
Cu(1B)–Br(1C)–Cu(1C)	81.36(13)	Cu(1A)–Br(1A)–Cu(1D)	76.59(13)
Cu(1B)–Br(1C)–Cu(1A)	79.46(12)	Cu(1D)–Br(1B)–Cu(1B)	78.11(13)
Cu(1B)–Br(1B)–Cu(1C)	80.34(13)	Cu(1D)–Br(1B)–Cu(1C)	78.75(12)
P(1A)–Cu(1A)–Br(1D)	118.7(3)	Br(1D)–Cu(1A)–Br(1A)	102.32(15)
P(1A)–Cu(1A)–Br(1A)	116.4(2)	P(1A)–Cu(1A)–Br(1C)	114.3(3)
Br(1C)–Cu(1B)–Br(1B)	98.62(14)	Br(1D)–Cu(1A)–Br(1C)	99.98(13)
P(1B)–Cu(1B)–Br(1D)	107.7(2)	Br(1A)–Cu(1A)–Br(1C)	102.62(15)
Br(1C)–Cu(1B)–Br(1D)	98.68(13)	P(1B)–Cu(1B)–Br(1C)	123.1(3)
Br(1B)–Cu(1B)–Br(1D)	100.53(13)	P(1B)–Cu(1B)–Br(1B)	123.6(3)
P(1C)–Cu(1C)–Br(1A)	123.7(2)	P(1C)–Cu(1C)–Br(1B)	115.7(3)
P(1C)–Cu(1C)–Br(1C)	113.2(3)	Br(1A)–Cu(1C)–Br(1B)	99.52(15)
Br(1A)–Cu(1C)–Br(1C)	103.75(15)	Br(1C)–Cu(1C)–Br(1B)	97.00(13)
P(1D)–Cu(1D)–Br(1D)	111.4(3)	P(1D)–Cu(1D)–Br(1B)	126.2(3)
Br(1B)–Cu(1D)–Br(1D)	104.46(14)	Br(1B)–Cu(1D)–Br(1A)	100.33(15)

[a] Symmetry code, $-x+3/2$, y,$-z+1/2$

[b] Symmetry code, $-x+3/2$, y, $-z+3/2$

TABLE 2 Crystal Data, Data Collection, and Refinement Details for Complexes 2–4

	2	**3**	**4**
Empirical formula	$(i\text{-PrO})_3P\bullet CuBr$	$[(Et_2N)_3P]_2\bullet CuBr$	$[(i\text{-PrS})_3P\bullet CuBr]_4$
Formula weight	768.13	638.17	1599.43
Space group	$P2_1/a$ (two independent molecules)	$P2/n$ (two independent molecules)	$P2_12_12_1$
a (Å)	19.975(3)	19.246(3)	13.872(2)
b (Å)	20.906(4)	9.2150(10)	19.649(3)
c (Å)	20.838(4)	19.479(3)	25.402(2)
α (°)	90	90	90
β (°)	104.35(3)	101.42(2)	90
γ (°)	90	90	90
V (Å^3)	8430(3)	3386.2(8)	6923.8(2)
Z	8	4	4
D_{calc} (mg m^{-3})	1.21	1.25	1.53
F(000)	3248	1360	3232
Crystal color	Colorless	Colorless	Colorless
Crystal form	Prismatic	Prismatic	Prismatic
Crystal size (mm)	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.1
Radiation (Å)		0.71073	
Temperature (K)	293	293	293
Scan mode	$\omega/2\theta$	$\omega/2\theta$	ω
Recording range θ_{max} (°)	2.31–22.77	2.45–26.29	2.17–24.98
Absorption correction μ (cm^{-1})	16.18	19.41	39.98
Scan speed (deg · min^{-1})		Variable, 1–16.4	
Number of recorded reflections	10,313	7,063	8,608
Number of independent reflections	9,617	6,857	7,905
Number of independent reflections with $F^2 \geq 2\sigma(F^2)$	4485	3,916	2,884
R (%)	0.0552	0.0361	0.0812
R_w (%)	0.1310	0.0755	0.1814
S	0.988	0.974	0.903

heating for 2–2.5 h at 40–45°C. The mixture was cooled to room temperature and then concentrated under reduced pressure to give complexes. Complex **1** (370 mg, 57%) was obtained as a colorless viscous liquid. ^{31}P NMR, δ: 114.9; $\Delta\delta$ 23. IR (ν/cm^{-1}): 560 (CO), 745–840 (PO). Anal. Calcd for $C_9H_{21}CuBrO_3P$ (351.76): C 30.72, H 6.02, Cu 18.18, Br 22.72; P 8.81. Found: C 31.67; H 6.03; Cu 17.79; Br 22.01, P 8.37. Complex **2** was crystallized to give colorless crystals of (350 mg, 51.5%); mp 155–158°C. ^{31}P NMR, δ: 114.6; $\Delta\delta$ 26. IR (ν/cm^{-1}): 545 (CO), 750–770 (PO). Anal. Calcd for $C_9H_{21}CuBrO_3P$ (351.76): C 30.72, H 6.02, Cu 18.18, P 8.81. Found: C 30.66; H 6.01; Cu 18.14; P 8.85.

*[Tri(diethylamido)phosphite]copper(I) Bromide (**3**)*

CuBr (0.59 g, 0.004 mol) was added to a stirred solution of tri(diethylamido) phosphite (1 g, 0.004 mol) in 5 mL of C_6H_6. The reaction mixture was stirred for 1.5–2 h without heating and then was allowed to stay for crystallization during 2 weeks. After that, the solvent was removed to give the complex **3** (87 mg, 67%) of the 2:1 ratio; mp 116–118°C. ^{31}P NMR, δ: 105.2; $\Delta\delta$ 12.0. IR (ν/cm^{-1}): 930 (PN). Anal. Calcd for $C_{24}H_{60}BrCu\ N_6P_2$ (638.22): C 45.16, H 9.47, P 9.71. Found: C 45.40; H 9.82; P 10.0.

*[Triisopropylthio phosphite]copper(I) Bromide (**4**)*

CuBr (1.5 g, 0.01 mol) was added to a stirred solution of triisopropylthio phosphite (3.5 g, 0.01 mol) in 10 mL $CHCl_3$. The temperature of the reaction mixture increased from 14 to 22°C. After refluxing for 1 h and following cooling to room temperature, unreacted salt was filtered off from the reaction mixture. The filtrate was evaporated, and the residue was recrystallized from $CHCl_3$, to give complex **4** (3.3 g, 66%); mp 88–92°C. ^{31}P NMR, δ: 91.1; $\Delta\delta$ 14.1. IR (ν/cm^{-1}): 630 (CS), 500 (PS). Anal. Calcd for $C_9H_{21}BrCuS_3P$ (399.94): C 27.03, H 5.29, P 7.75. Found: C 27.58; H 5.21; P 8.0.

*[Tri(diethylamido)phosphite]copper(I) Chloride (**5**)*

In a similar manner to that described above, from CuCl (0.4 g, 0.004 mol) and tri(diethylamido) phosphite (1 g, 0.004 mol), the complex **5** (0.8 g, 57%)

was obtained, m.p. .97–100°C. ^{31}P NMR, δ: 103.9; $\Delta\delta$ 15.4. IR (ν/cm^{-1}): 928 (PN). Anal. Calcd for $C_{12}H_{30}ClCuN_3P$ (346.36): C 41.61, H 8.73, P 8.95. Found: C 41.04; H 8.69; P 8.87.

X-Ray Crystallographic Study

The X-ray diffraction data for the crystals of **2–4** were collected on a CAD4 Enraf-Nonius automatic diffractometer using graphite monochromated Mo K$_\alpha$ (0.71073 Å) radiation. The crystal data, data collection, and the refinement are given in Table 2. The stability of crystals and experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. An empirical absorption correction based on ψ-scans was applied. The structure was solved by the direct method using the SIR [26] program and refined by the full matrix least-squares using SHELX-97 [27] program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. All calculations were performed on PC using WinGX [28] program. Cell parameters, data collection, and data reduction were performed on an Alpha Station 200 computer using MolEN [29] program. All figures were made using the program PLATON [30].

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 647543, 647544, and 647545. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-(1223)-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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