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A New Type of Coordination in Copper(I) Complexes with Trivalent Phosphorus Compounds Containing Phosphorus−Sulfur Bonds

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A series of copper(I) complexes with trialkyl trithiophosphite ligands have been prepared and crystallographically characterized to investigate possible binding modes of potentially tetradentate ligands: $(EtS)_3P\cdot CuHal$ with Hal = Cl, Br, and I; $(i\text{-}PrS)_3P\cdot CuBr\cdot CH_3CN$. Complexes of copper(I) monohalides with triethyl trithiophosphite appeared to be isostructural, exhibiting a bidentate coordination mode via the phosphorus atom of one thiophosphite molecule and the sulfur atom of another, with formation of polymeric chains along the x-axis. In the complex of copper monobromide with triisopropyl trithiophosphite and acetonitrile monodentate coordination via the phosphorus atom is observed. Crystal data [space group, a, b, c, α, β, γ, Z (only undefined cell parameters are listed)]: $(EtS)_3P\cdot CuCl$, monoclinic $P2_1/c$, 7.377(2) Å, 14.522(4) Å, 12.275(4) Å, 100.28(2)°, 4; $(i\text{-}PrS)_3P\cdot CuBr\cdot CH_3CN$, triclinic $P\bar{1}$, 8.612(5) Å, 9.401(5) Å, 13.254(5) Å, 81.49(4)°, 86.66(4)°, 63.24(5)°, 2.

Introduction

The coordination chemistry of phosphorus−sulfur-containing compounds, in contrast to phosphines, whose coordination behavior in complexes with metals has been extensively studied,[1−4] is unpredictable and, thus, much more interesting. The diversity of the possible ligation sites of phosphorus−sulfur-containing compounds and, in particular, of thiophosphites, makes these molecules versatile ligand systems. Despite this fact very little has been done to explore their coordination chemistry.

Trithiophosphites possessing four donor atoms are potentially tetradentate ligands and may form a variety of complexes with different coordination modes, binding metal centers either through the phosphorus atom, sulfur atoms, or both. However, in the few known complexes of trithiophosphites, metals were found to be coordinated only by the phosphorus atom.[5] Realization of such coordination is quite understandable, as the coordinating ability of thioethers is known to be poorer compared with phosphines.[6] One binding mode, with a metal−phosphorus donor−acceptor bond, is also observed in complexes with phosphites[1,2] and amidophosphites.[7]

The only examples of ambidentate binding modes are known for those phosphorus−sulfur-containing molecules in which the phosphite and thioether moieties are separated by the $(CH_2)_n$-groups, $R_2P(CH_2)_nSR'$,[8−10] or for ortho-disubstituted benzenes, o-$Ph_2PC_6H_4SR$.[8,11] These compounds form chelate complexes. Side-on coordination of metal atoms is observed in molybdenum and iron complexes with molecules containing thiophosphoryl bonds, in which the formation of three-membered cycles comprised of metal, phosphorus, and sulfur atoms has been shown by X-ray studies.[12,13]

In this paper we wish to report on the synthesis and structure of novel complexes of trithiophosphites with copper(I) monohalides, exhibiting a new type of coordination, and the factors determining the coordination modes.

Experimental Section

Syntheses. General Information. ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer at 162 MHz, using $CHCl_3$ or CH_3CN as solvents, which were purified and dried by conventional procedures before use.

(Triethyl trithiophosphite)chlorocopper(I), $(EtS)_3P\cdot CuCl$ (1a). The salt CuCl (2.3 g, 23 mmol) was added with stirring to $(EtS)_3P$ (5 g, 23 mmol). After refluxing of the reaction mixture in $CHCl_3$ for 1 h and cooling to room temperature, the unreacted salt was filtered off. Evaporation of the filtrate gave complex **1a**, which was recrystallized from $CHCl_3$: yield 4.5 g (61%); mp 79−81 °C; ^{31}P NMR (CH_3CN), $\delta(^{31}P)$ 104 ppm. Anal. Calcd for $C_6H_{15}ClCuPS_3$: C, 22.9; H, 4.83; P, 9.89. Found: C, 22.3; H, 4.86; P, 10.04.

(Triethyl trithiophosphite)bromocopper(I), $(EtS)_3P\cdot CuBr$ (1b). Complex **1b** was prepared analogously to complex **1a** from 3 g, 14 mmol, of $(EtS)_3P$ and 2 g, 14 mmol, of CuBr with refluxing in acetonitrile. Recrystallization from CH_3CN gave complex **1b**: yield 2.3 g (53%); mp 128−130 °C; ^{31}P NMR (CH_3CN) $\delta(^{31}P)$ 99 ppm. Anal. Calcd for $C_6H_{15}BrCuPS_3$: C, 20.11; H, 4.19; P, 8.66. Found: C, 19.83; H, 4.13; P, 8.56.

(Triethyl trithiophosphite)iodocopper(I), $(EtS)_3P\cdot CuI$ (1c). Complex **1c** was prepared analogously to complex **1a** from 4.7 g, 20 mmol,

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Table 1. Crystallographic Data for Complexes **1a**[a] and **2b**

Complex **1a**

chem formula $(EtS)_3P{\cdot}CuCl$
$a = 7.377(2)$ Å
$b = 14.522(4)$ Å
$c = 12.275(4)$ Å
$\beta = 100.28(2)°$
$V = 1294$ Å^3
$Z = 4$
$T = 20$ °C
fw 313.35
space group $P2_1/c$ (No. 14)
$\lambda = 0.710\,73$ Å
$\varrho_{calc} = 1.608$ g·cm^{-3}
$\mu_{calc} = 24.44$ cm^{-1}
$R(F_o) = 0.049$[b]
$R_w(F_o^2) = 0.064$[c]

Complex **2b**

chem formula $(i\text{-}PrS)_3P{\cdot}CuBr{\cdot}CH_3CN$
$a = 8.612(5)$ Å
$b = 9.401(5)$ Å
$c = 13.254(5)$ Å
$\alpha = 81.49(4)°$, $\beta = 86.66(4)°$, $\gamma = 63.24°$
$V = 947.8$ Å^3
$Z = 2$
fw 440.94
space group $P\bar{1}$ (No. 2)
$T = 20$ °C
$\lambda = 0.710\,73$ Å
$\varrho_{calc} = 1.545$ g·cm^{-3}
$\mu_{calc} = 36.32$ cm^{-1}
$R(F_o) = 0.062$[b]
$R_w(F_o^2) = 0.090$[c]

[a] Cell parameters a, b, c, and β for isostructural complexes **1b,c** are as follows. $(EtS)_3P{\cdot}CuBr$: 7.42(1) Å, 14.51(3) Å, 12.30(5) Å, 101.2(2)°. $(EtS)_3P{\cdot}CuI$: 7.487(2) Å, 14.560(4) Å, 12.438(4) Å, 101.25(2)°. [b] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [c] $R_\omega = [\Sigma\omega(\Delta F)^2/\omega F_o^2]^{1/2}$.

of $(EtS)_3P$ and 3.49 g, 20 mmol, of CuI with refluxing in $CHCl_3$. Recrystallization from $CHCl_3$ gave complex **1c**: yield 1.02 g (12%); mp 135–138 °C; ^{31}P NMR (CH_3CN) $\delta(^{31}P)$ 108 ppm. Anal. Calcd for $C_6H_{15}ICuPS_3$: C, 17.83; H, 3.74; P, 7.66. Found: C, 17.20; H, 3.5; P, 7.5.

(Triisopropyl trithiophosphite)bromocopper(I), $(i\text{-}PrS)_3P{\cdot}CuBr$ (2a). To a solution of 1.62 g, 6.3 mmol, of triisopropyl trithiophosphite in 15 mL of n-hexane was added with stirring 1 g, 6.3 mmol, of CuBr in 10 mL of n-hexane. 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 the crystalline complex **2a**: yield 2.3 g (87%); mp 87–89 °C; ^{31}P NMR (CH_3CN) $\delta(^{31}P)$ 96 ppm. Anal. Calcd for $C_9H_{21}BrCuPS_3$: C, 27.03; H, 5.29; P, 7.74. Found: C, 27.8; H, 5.21; P, 8.00.

(Triisopropyl trithiophosphite)(acetonitrile)bromocopper(I), $(i\text{-}PrS)_3P{\cdot}CuBr{\cdot}CH_3CN$ (2b). Complex **2b** was obtained by recrystallization of complex **2a** from acetonitrile, its structure being identified by X-ray analysis. During the X-ray experiment complex **2b** was found to be unstable. After the experiment it was found to be as follows. Anal. Calcd for $C_{11}H_{24}BrCuPNS_3$: C, 29.95; H, 5.48; P, 7.03; N, 3.17. Found: C, 28.19; H, 5.09; P, 6.85; N, 1.75.

X-ray Structure Determination. The X-ray data were measured for crystals **1a** and **2b** on an "Enraf-Nonius" CAD4 automatic diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 20 °C. The space group for complex **1a** was unambiguously determined using systematically absent reflections. Unit cell parameters and their esd's were derived by least-squares fittings of the setting angles of 25 reflections in the range $20° < 2\theta < 30°$. Intensity data were collected using $\omega/2\theta$ scan mode with variable scan speeds with a maximum time per datum of 60 s. The relevant experimental parameters and crystallographic data are given in Table 1. Corrections for Lorentz and polarization effects were applied. An empirical absorption correction was based on ψ-scan data at high χ angle using the EAC SDP program. The stability of the crystals and of the experimental conditions was checked every 1 h using two control reflections, while the orientation was monitored every 200 reflections by centering two standards. No decay correction was needed for crystals of **1a**. Crystals of **2b** appeared to be unstable. The intensities of two control reflections decreased by 51% for an exposure time of 13 h, and this was accounted for by applying appropriate scaling factors.

Table 2. Positional Parameters of Non-Hydrogen Atoms for Complex $(EtS)_3P{\cdot}CuCl$ and Their Isotropic Equivalent Thermal Parameters[a]

atom	x	y	z	B (Å^2)
P	0.5721(2)	0.0951(1)	0.3864(1)	3.41(3)
S(1)	0.5032(2)	0.2084(1)	0.4735(2)	4.27(3)
S(2)	0.6024(2)	0.1391(2)	0.2288(1)	5.44(4)
S(3)	0.3085(2)	0.0321(1)	0.3444(1)	3.26(3)
Cu	0.79471(8)	0.01724(6)	0.49105(6)	3.75(1)
Cl	1.0544(2)	0.1044(1)	0.5752(1)	4.30(3)
C(1)	0.3143(9)	0.2655(5)	0.3839(7)	5.9(2)
C(2)	0.273(1)	0.3550(6)	0.4293(9)	8.8(3)
C(3)	0.8492(9)	0.1412(8)	0.2439(6)	8.5(3)
C(4)	0.916(1)	0.1450(7)	0.1424(7)	7.2(2)
C(5)	0.366(1)	−0.0728(5)	0.2721(6)	5.2(2)
C(6)	0.257(1)	−0.0829(7)	0.1670(9)	10.4(3)

[a] $B_{iso}^{eq} = {}^4/_3\Sigma_{i,j=1}^{3}(\vec{a}_i\vec{a}_j)B(i,j)$.

Table 3. Positional Parameters of Non-Hydrogen Atoms for Complex $(i\text{-}Pr)_3P{\cdot}CuBr{\cdot}CH_3CN$ and Their Isotropic Equivalent Thermal Parameters[a]

atom	x	y	z	B (Å^2)
Br	0.0550(4)	0.6424(4)	0.0623(3)	3.97(9)
Cu	0.1208(5)	0.3541(4)	0.0831(3)	4.0(1)
S(1)	0.132(1)	0.0060(9)	0.2289(6)	4.7(3)
S(2)	0.093(1)	0.2932(9)	0.3699(7)	4.2(2)
S(3)	−0.2320(9)	0.3250(8)	0.2485(7)	4.1(2)
P	0.035(1)	0.2535(9)	0.2280(7)	3.3(2)
N	0.376(3)	0.227(2)	0.055(2)	4.1(7)
C(1)	0.063(3)	−0.075(3)	0.351(2)	4.2(9)
C(2)	0.210(4)	−0.163(4)	0.428(2)	6(1)
C(3)	−0.031(4)	−0.166(4)	0.328(3)	14(1)
C(4)	0.298(4)	0.297(3)	0.345(3)	5(1)
C(5)	0.455(4)	0.129(3)	0.337(3)	6(1)
C(6)	0.336(4)	0.364(4)	0.439(3)	9(1)
C(7)	−0.331(4)	0.534(3)	0.187(2)	4.3(9)
C(8)	−0.521(3)	0.565(3)	0.163(3)	5(1)
C(9)	−0.338(4)	0.660(4)	0.255(3)	7(1)
C(10)	0.525(3)	0.156(3)	0.061(2)	4.2(9)
C(11)	0.708(3)	0.085(3)	0.051(3)	5(1)

[a] $B_{iso}^{eq} = {}^4/_3\Sigma_{i,j=1}^{3}(\vec{a}_i\vec{a}_j)B(i,j)$.

The positions of the copper and bromine atoms were determined by the Patterson method. The other non-hydrogen atoms were found from successive difference Fourier syntheses, and their positions were refined by full-matrix least-squares methods with anisotropic temperature factors to minimize $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 4|F_o|^2/[\sigma^2(I) + (0.07|F_o|)^2]$. The hydrogen atoms were partly revealed from difference Fourier syntheses; the rest were placed in idealized positions, all hydrogen atoms being added to final structure factor calculations with fixed positional and thermal parameters.

Crystals of **1b,c** were found to be isostructural to crystals of **1a** (cell parameters are presented in Table 1), and thus, no data collection and processing have been carried out for them.

All calculations were carried out on a PDP 11/23 computer using SDP programs. Final atomic coordinates and isotropic equivalent thermal parameters for complexes **1a** and **2b** are given in Tables 2 and 3 respectively.

Results and Discussion

The coordination mode of a multidentate ligand depends not only on the nature and oxidation state of the central metal atom and ligating abilities of the donor atoms but also on steric factors and the reaction conditions. Thus, by varying the conditions and the alkyl groups in trialkyl trithiophosphites, we were able to synthesize complexes with different types of coordination.

The reaction of trialkyl trithiophosphites with copper(I) salts easily proceeds to give 1:1 adducts:

$$(RS)_3P + CuX \rightarrow (RS)_3P{\cdot}CuX$$

$$\begin{aligned} &\mathbf{1a},\ R = Et,\ X = Cl\\ &\mathbf{1b},\ R = Et,\ X = Br\\ &\mathbf{1c},\ R = Et,\ X = I\\ &\mathbf{2a},\ R = i\text{-}Pr,\ X = Br \end{aligned}$$

Recrystallization of **2a** from acetonitrile gave complex $(i\text{-}PrS)_3P{\cdot}CuBr{\cdot}CH_3CN$ (**2b**).

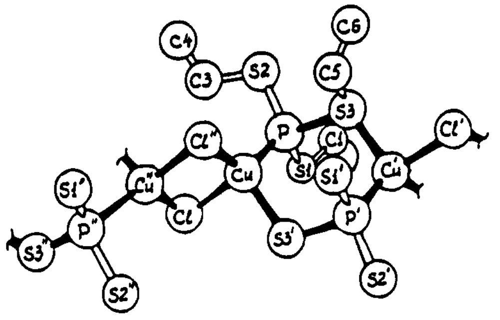
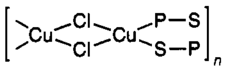


Figure 1. Atom-labeling scheme and geometry of complex **1a**.

The structure of the complexes **1a**−**c** and **2b** was determined by X-ray diffraction studies. A new type of coordination mode was revealed in the copper(I) complexes with triethyl trithiophosphite, **1a**−**c**, in which copper is coordinated by both phosphorus and sulfur atoms (Figure 1).

Crystals of **1a**−**c** appeared to be isostructural and, thus, possess similar geometry, while in the corresponding series of the copper(I) monohalide complexes with disulfides[14,15] different ligand to CuHal ratios and structures of complexes were observed for chloride and iodide. Complexes **1a** form regular polymeric chains



along the *x*-axis with altemating four- and six-membered cycles. Planar four-membered cycles are formed by two copper atoms, bridged by the chlorine atoms, the pairs of Cu and Cl atoms being related by inversion ($1 - x$, $-y$, $1 - z$). The six-membered cycle adopts a centrosymmetrical chair conformation. The copper atoms are bonded to the phosphorus atom of one trithiophosphite fragment, and the sulfur atom of another fragment is related to the first one by the same inversion operation. The coordination of the copper atoms is tetrahedral, with two chlorine atoms, sulfur, and phosphorus comprising its coordination sphere.

The geometry around the copper atom is considerably distorted, the bond angles reflecting the most obvious considerations of ligand size. The bond angles with participation of phosphorus are significantly opened up to 122.8°, and the SCuCl angles are compressed to 98.4° (Table 4). The Cu−Cl bond lengths are significantly different (Table 4), this difference (0.061 Å) corresponding to 60 standard deviations. The Cu−S bond length is equal to the sum of the covalent radii Cu(I)−S taken from Pauling data[16] and is slightly shorter than in copper(I) complexes with disulfides,[14,15] while the Cu−P bond length in complex **1a** appeared to be significantly smaller than in phosphine complexes.[17,18]

The distortions of ligand geometry upon formation of the complex are minimal. The bond angles at phosphorus and sulfur in "free" trithiophosphites are close to 100°.[19,20] In complex **1a** only two of them, $S^1PS^2 = 108.16(9)°$ and $PS^1C^1 = 106.4(2)°$ are significantly increased, while the valence angle PS^3C^5 at sulfur coordinated to copper is undistorted. Additional coordination of this sulfur atom results in elongation of its P−S and S−C bonds by 0.04−0.06 Å comparing to other P−S and S−C bonds. The conformation of triethyl trithiophosphite fragment in complex **1a** is also typical of "free" trithiophosphites, for which gauche and trans orientations of the thioalkyl groups to the phosphorus lone electron pair are observed in gaseous and liquid phases.[19,20]

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **1a**[a]

P−S(1)	2.074(2)	S(2)−C(3)	1.797(6)
P−S(2)	2.086(2)	S(3)−Cu′	2.392(1)
P−S(3)	2.128(2)	S(3)−C(5)	1.849(6)
P−Cu	2.208(1)	Cu−Cl	2.373(1)
S(1)−C(1)	1.815(5)	Cu−Cl″	2.312(1)
S(1)−P−S(2)	108.16(9)	P−S(3)−C(5)	101.1(2)
S(1)−P−S(3)	99.72(7)	Cu′−S(3)−C(5)	107.0(2)
S(1)−P−Cu	109.34(7)	P−Cu−S(3)′	109.21(5)
S(2)−P−S(3)	98.72(7)	P−Cu−Cl	116.04(6)
S(2)−P−Cu	120.31(7)	P−Cu−Cl″	122.79(6)
S(3)−P−Cu	118.26(7)	S(3)′−Cu−Cl	98.39(5)
P−S(1)−C(1)	106.4(2)	S(3)′−Cu−Cl″	108.30(6)
P−S(2)−C(3)	100.6(2)	Cl−Cu−Cl″	99.14(5)
P−S(3)−Cu′	109.82(6)	Cu−Cl−Cu″	80.86(5)

[a] Symmetry operation for atoms marked with primes is $1 - x$, $-y$, $1 - z$ and symmetry operation for atoms marked with double primes is $2 - x$, $-y$, $1 - z$.

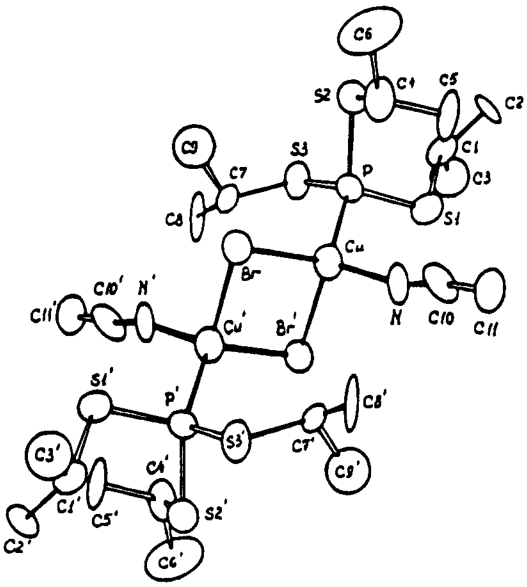


Figure 2. ORTEP view of complex **2b**.

In contrast to complexes **1**, another type of coordination is realized in complex **2b** (Figure 2). The crystal structure of **2b** consists of centrosymmetric dimers with two copper atoms bridged by two bromine atoms, one molecule of triisopropyl trithiophosphite, and one molecule of the solvent also bonding to copper. Thus, the coordination sphere of copper is formed by two bromine, phosphorus, and nitrogen atoms, its geometry being tetrahedral. More detailed consideration of the geometrical parameters is impossible, as they were determined with low accuracy due to poor quality of the crystals.

Synthesis of complex **2a** was carried out in reaction conditions different from those for complexes **1**: triisopropyl trithiophosphite reacted with CuBr in n-hexane. Crystals of **2a**, recrystallized from both n-hexane and $CHCl_3$, appeared to be unsuitable for X-ray analysis, and the structure of this complex was not determined. After the recrystallization from CH_3CN complex

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2a converted into complex **2b**, in which one molecule of acetonitrile was included into the coordination sphere of copper and the usual type of coordination via phosphorus was observed (Figure 2). It is reasonable to suppose that different conditions of reaction and recrystallization resulted in a different type of coordination in complex **2b** in comparison with complexes **1**. However, the recrystallization of complex **1b** from acetonitrile was not accompanied by insertion of the solvent into the copper coordination sphere. So, it may be supposed that the type of coordination may be determined not only by the reaction conditions but also by the size of substituents at the sulfur atoms.

Conclusion

Complexes of copper(I) monohalides with trialkyl trithiophosphites with different types of coordination depending on the reaction conditions and the bulkiness of the alkyl groups at ligand sulfur atoms have been synthesized and studied. In triethyl trithiophosphite complexes, coordination of copper via both phosphorus and sulfur is observed, which is the first example of bidentate coordination for compounds containing the P−S bond. The usual binding mode via the phosphorus atom was observed in the complex of copper(I) monobromide with triisopropyl trithiophosphite and acetonitrile.

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Supporting Information Available: Tables of crystallographic data, atomic positional and thermal parameters, anisotropic thermal factors, bond lengths, and valence angles for crystals **1a** and **2b** (6 pages). Ordering information is given on any current masthead page.

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