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Synthesis and Structure of Copper(II) Phosphonodithioite Complexes

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Abstract—A series of new complexes of CuBr with phosphonodithioites were prepared and characterized by NMR and IR spectroscopy. As shown by single crystal X-ray diffraction, diethyl *tert*-butylphosphonodithioite forms with CuBr a tetrameric cubane-like complex with the monodentate coordination of the organophosphorus ligand via the P atom.

Our previous studies [1–7] showed that complexes formed by phosphorothoite with transition metals are more diverse in the structure and coordination mode than complexes formed by other trivalent phosphorus compounds, in particular, phosphines, phosphites, and amides [8–13]. This is due to the specific electronic structure of the ligand molecules containing P–S ambident systems [14]. It can be expected that the replacement of one of the SR groups in a phosphorothoite molecule by an alkyl group will alter the donor properties of the P and S atoms and hence the coordination properties of the ligand. A search in the Cambridge Structural Database [15] revealed no data on the crystal structure of phosphorothoite complexes. Copper(I) phosphorothoite complexes, in which the ligand molecule contains a P–C bond along with two P–S bonds, are of interest from the viewpoint of ligand reactivity in the metal coordination sphere. Our previous studies of copper thiophosphite complexes revealed such phenomena as ligand exchange, disproportionation, ligand transformation, and formation of ligands of a new structure in the metal coordination sphere [2, 5, 16, 17].

Here we report on the complexation of CuBr with a series of diethyl phosphonodithioites containing ethyl, phenyl, and *tert*-butyl substituents at the P atom. Thiophosphonites **Ia**–**Ic** readily react with CuBr. Complexes **IIb** and **IIc** are colorless crystalline substances. According to elemental analysis, the reaction products have 1 : 1 composition. Complexes **IIb** and **IIc** are formed in fairly high yields (80–85%).

Compound **IIb** is soluble in the majority of organic solvents. Complex **IIc** is insoluble in organic solvents, including DMSO and DMF. Complex **IIa** was isolated as an oily precipitate; it rapidly darkens, which suggests its instability and possible decomposition. Products of its secondary transformations were not studied.

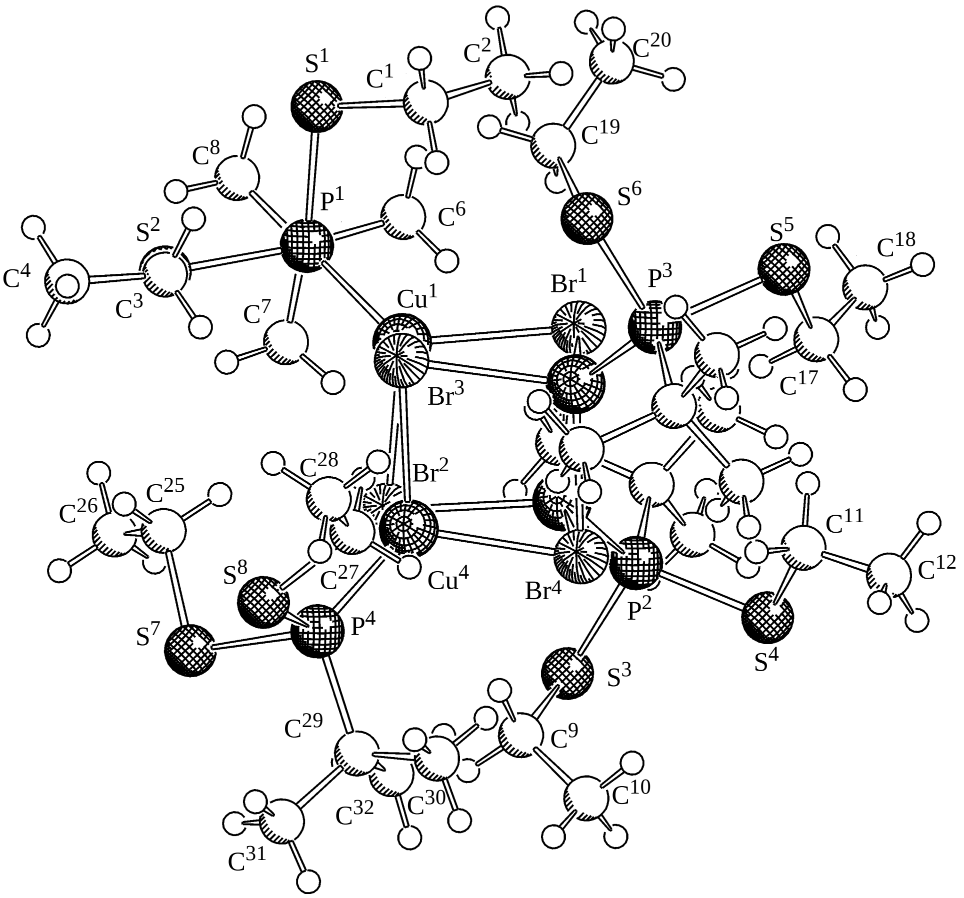
$$\underset{\textbf{Ia–Ic}}{RP(SEt)_2} + CuBr \longrightarrow \underset{\textbf{IIa–IIc}}{RP(SEt)_2 \cdot CuBr},$$

R = Et (**a**), *t*-Bu (**b**), Ph (**c**).

Complexes **IIa**–**IIc** were studied by IR spectroscopy (solid samples). According to the IR data, the P–C stretching frequency does not noticeably change upon complexation and remains about 750 cm^{-1}. At the same time, the P–S bands in the spectra of the complexes become more intense compared to the free ligands and are shifted toward higher frequencies by ~20 cm^{-1}. To compare, in the case of bidentate coordination of triethyl phosphorotrithioite, the shift is toward lower frequencies and is larger in the absolute value (~30–40 cm^{-1}) [2].

In the ^{31}P NMR spectra, the complexation exerts a weaker effect on the phosphorus chemical shift, compared to the complexation with trialkyl phosphorotrithioites [2, 3]. The most significant upfield shift of the P signal upon complexation is observed in **IIb**: from 112 (in **Ib**) to 91 ppm ($\Delta\delta_P$ –21 ppm). We failed to record the ^{31}P NMR spectrum of **IIc** because of its low solubility.

Since Cu(I) phosphonodithioite complexes were unknown previously, it seemed important to elucidate their structure and coordination mode in a crystal. We failed to obtain crystals of **IIa** and **IIc** of X-ray quality. Only in the case of complex **IIb** of CuBr with



Molecular structure of **IIb**.

diethyl *tert*-butylphosphonodithioite **Ib** we were able to prepare satisfactory crystals by recrystallization from hexane. According to the single-crystal X-ray diffraction data, complex **IIb** has a tetrameric cubane-like structure with the monodentate coordination of the organophosphorus ligand (see figure).

Complex **IIb** essentially differs in structure from copper tri-*n*-alkyl phosphorotrithioite complexes, which have a polymeric structure with the bidentate coordination of the ligand. The tetrameric cubane-like structure is among the structures most frequently realized in copper complexes with bulky ligands [12, 13, 15, 18, 19]. In particular, such a structure is realized in crystalline complexes of copper(I) halides with triisopropyl phosphorotrithioite [16].

The copper atom in **IIb** has a tetrahedral configuration and is bonded to three Br atoms and one P atom of the phosphonodithioite ligand. The main geometric parameters are given in the table. The lengths of the four Cu–P coordination bonds in the complex coincide within the experimental error; the mean length is 2.206 Å. The length of the C–P bond in cubane-like complexes varies depending on the ligand and halogen. In the series of triethylphosphine complexes of copper(I) halides, the Cu–P bond length varies from 2.176(2) Å for the chloride to 2.254(3) Å for the iodide [20, 21]. In the complex of CuBr with the same ligand, the Cu–P bond length is 2.199 Å [21], virtually coinciding with the Cu–P bond length in **IIb**. The shortest Cu–P bond was observed in the complex of CuCl with a phosphite containing bulky substituents at the O atoms [18].

It is interesting to study the conformational behavior of the ligands in **IIb**, in view of the possible internal rotation around the P–S and C–C bonds. We showed previously that trithiophosphites in transition metal complexes are characterized by a wide diversity of conformations, untypical of the “free” molecules [6, 7]. If a unit cell contained several independent molecules, the conformational nonuniformity was often observed. In **IIb**, three of the four ligand molecules have the *gauche,gauche* orientation of the EtS bonds relative to the P–Cu bonds, and in the fourth molecule the orientation is *cis,gauche*. The sulfur atoms in two dithiophosphonite molecules are conformationally disordered, and in one of them we failed

Principle geometric parameters of **IIb** (bond lengths *d*, bond angles ω, torsion angles τ)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cu^1–P^1	2.206(1)	Cu^2–P^2	2.205(1)	Cu^3–P^3	2.207(1)
Cu^4–P^4	2.207(1)	P^1–S^1	2.101(1)	P^1–S^2	2.112(2)
P^2–S^3	2.094(2)	P^2–S^4	2.096(2)	P^3–S^5	2.093(2)
P^3–S^6	2.107(2)	P^4–S^7	2.141(2)	P^4–S^8	2.101(2)
P^1–C^5	1.869(5)	P^2–C^{13}	1.864(6)	P^3–C^{21}	1.863(5)
P^4–C^{29}	1.866(5)	S^1–C^1	1.825(5)	S^2–C^3	1.798(5)
S^3–C^9	1.811(6)	S^4–C^{11}	1.854(8)	S^5–C^{17}	1.825(8)
S^6–C^{19}	1.816(6)	S^7–C^{25}	1.817(5)	S^8–C^{27}	1.788(6)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
Cu^{1}P^{1}S^1	116.51(6)	Cu^{1}P^{1}S^2	114.81(7)	Cu^{2}P^{2}S^3	114.85(7)
Cu^{2}P^{2}S^4	116.97(8)	Cu^{3}P^{3}S^5	117.08(7)	Cu^{3}P^{3}S^6	113.25(6)
Cu^{4}P^{4}S^7	112.64(8)	Cu^{4}P^{4}S^8	118.96(7)	P^{1}S^{1}C^1	103.11(17)
P^{1}S^{2}C^3	99.77(16)	P^{2}S^{3}C^9	102.06(17)	P^{2}S^{4}C^{11}	101.2(2)
P^{3}S^{5}C^{17}	99.4(2)	P^{3}S^{6}C^{19}	101.5(2)	P^{4}S^{7}C^{25}	99.88(19)
P^{4}S^{8}C^{27}	102.4(2)				
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
Cu^{1}P^{1}S^{1}C^1	13.5	Cu^{1}P^{1}S^{2}C^3	53.3	Cu^{2}P^{2}S^{3}C^9	–40.1
Cu^{2}P^{2}S^{4}C^{11}	–27.1	Cu^{3}P^{3}S^{5}C^{17}	–30.7	Cu^{3}P^{3}S^{6}C^{19}	–49.1
Cu^{4}P^{4}S^{7}C^{25}	–42.3	Cu^{4}P^{4}S^{8}C^{27}	–30.3	P^{1}S^{1}C^{1}C^2	93.4
P^{1}S^{2}C^{3}C^4	173.2	P^{2}S^{3}C^{9}C^{10}	–82.4	P^{2}S^{4}C^{11}C^{12}	173.7
P^{3}S^{5}C^{17}C^{18}	145.8	P^{3}S^{6}C^{19}C^{20}	–104.2	P^{4}S^{7}C^{25}C^{26}	148.1
P^{4}S^{8}C^{27}C^{28}	178.6				

to describe this disordering adequately. Therefore, peaks of residual electron density are observed in the vicinity of the S^1 and S^2 atoms. The *tert*-butyl groups in all the molecules occupy an “ideal” staggered position.

Thus, we have studied the complexation of CuBr with phosphonodithious acid esters and prepared the corresponding complexes. The structure of the complex of CuBr with diethyl *tert*-butylphosphonodithioite was studied by single-crystal X-ray diffraction. The complex has a cubane-like structure with the monodentate ligand coordination. This structure ensures the longest distance between the bulky ligands forming a coordination bond with the metal atom in the Cu_4Br_4 fragment.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer by the standard procedure. The ^{31}P NMR spectra of solutions of the compounds in acetonitrile and chloroform were recorded on a Bruker CXP-100 spectrometer (working frequency 36.47 MHz, external reference 85% H_3PO_4).

Single-crystal X-ray diffraction analysis of IIb. $C_8H_{19}PS_2 \cdot CuBr$, *M* 353.77, colorless crystals. Crystal size 0.40 × 0.40 × 0.35 mm, triclinic system, space group *P*1, *Z* 8, at 198 K *a* 14.065(1), *b* 14.472(1), *c* 14.742(1) Å; α 96.37(1)°, β 95.18(1)°, γ 105.01(1)°; *V* 2858.2(3) Å^3, ρ_{calc} 1.644 g cm^{-3}, μ 46.90 cm^{-1}, empirical correction for absorption using SORTAV program ($0.256 \le T \le 0.291$), λ 0.71073 Å, 32 439 reflections (±*h*, ±*k*, ±*l*), [(sinθ)/λ] 0.62 Å^{-1}, 14 047 unique reflections (R_{int} 0.037), including 10 626 reflections with $I \ge 2\sigma(I)$, 505 refined parameters, *R* 0.045, *wR*2 0.104, maximal residual electron density 1.48 (–0.79) e Å^{-3}; the positions of the hydrogen atoms were calculated and then refined using the rider model.

The experimental data were obtained with a Nonius-Kappa-CCD diffractometer equipped with a Nonius FR-591 generator with rotating anode. The following programs were used: COLLECT (Nonius B.V., 1998); Denzo-SMN [22]; account of absorption, SORTAV

[23, 24]; structure solution and refinement, SHELXS-97 [25], SHELXL-97 [26]; graphics, SCHAKAL [27].

Thiophosphonites were prepared by published procedures [14, 28]; these were colorless oily liquids with a strong characteristic odor, insoluble in water but soluble in the majority of organic solvents.

All the manipulations during the synthesis and isolation of the starting compounds and reaction products were performed under Ar. The solvents were dried and distilled by standard procedures before use.

A greenish sample of CuBr containing an impurity of SO_4^{2-} was washed with 1% HBr and then with ethanol and dried at 105–110°C with continuous stirring [29].

Diethyl *tert*-butylphosphonodithioite Ib. A flask purged with argon was charged with 19.7 g of sodium ethanethiolate, and ether was added. A solution of 17.9 g of *tert*-butyldichlorophosphine in ether was added dropwise with continuous stirring. The mixture was stirred with heating for 1 h. The NaCl precipitate was filtered off, and the ether was distilled off from the filtrate. The residue was distilled in a vacuum; bp 58–62°C (0.02 mm Hg). ^{31}P NMR spectrum, δ_P, ppm: 112.

Diethyl ethylphosphonodithioite Ia (δ_P 85 ppm) and **diethyl phenylphosphonodithioite** (δ_P 75 ppm) were prepared similarly from ethyldichlorophosphine and phenyldichlorophosphine, respectively.

(Diethyl ethylphosphonodithioite)bromocopper(I) (IIa). A 1.58-g portion of CuBr was added with continuous stirring to 2 g of diethyl phosphonodithioite. A liquid and a viscous precipitate formed. To this mixture, 2 ml of acetonitrile was added, and the mixture was continuously stirred for 1.5 h at 36–40°C. The precipitate dissolved on heating, and the solution became yellow and transparent. An additional 5 ml of the solvent was added, and the solution was left to crystallize. In 2 weeks, compound **IIa** formed on the walls as a viscous colorless precipitate. Yield 1.3 g (40%), mp 108–110°C. IR spectrum, ν, cm^{-1}: 505, 525 (PS). ^{31}P NMR spectrum, δ_P, ppm: 80, $\Delta\delta_P$ 5.0. Compound **IIa** exists as a colorless precipitate only under a layer of acetonitrile; after removing the solvent, it darkens and decomposes. Therefore, we failed to determine its elemental composition.

(Diethyl *tert*-butylphosphonodithioite)bromocopper(I) (IIb). A 1.3-g portion of CuBr was added with stirring to 2 g of diethyl *tert*-butylphosphonodithioite. In the process, the mixture warmed up from 17 to 30°C. Then the mixture was heated for an additional 1.5 h at 30°C and allowed to stand for 2 days; 2.7 g (82%) of complex **IIb** was thus obtained, mp 105– 110°C. IR spectrum, ν, cm^{-1}: 522 (PS). ^{31}P NMR spectrum, δ_P, ppm: 91, $\Delta\delta_P$ 21.0. Found, %: C 27.62; H 5.68; Br 19.31; Cu 19.84; P 9.68; S 20.20. $C_8H_{19}BrCuPS_2$. Calculated, %: C 27.11; H 5.36; Br 22.59; Cu 18.07; P 8.75; S 18.07.

(Diethyl phenylphosphonodithioite)bromocopper(I) (IIc). A 0.5-g portion of CuBr was added with stirring at room temperature to 0.8 g of diethyl phenylphosphonodithioite. Then the mixture was heated for 1 h at 30°C. The precipitate of IIc was filtered off; yield 1.05 g (80%), mp 148–150°C. The product is insoluble in CH_3CN, C_6H_6, $CHCl_3$, CH_2Cl_2, C_6H_{12}, ether, ethyl acetate, DMSO, and DMF. IR spectrum, ν, cm^{-1}: 500 (PS). Found, %: C 32.74; H 4.12; Br 21.48; Cu 17.20; P 8.39. $C_{10}H_{15}BrCuPS_2$. Calculated, %: C 32.08; H 4.01; Br 21.39; Cu 17.1; P 8.29; S 17.1.

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