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LETTERS TO THE EDITOR

Bidentate Complex of Triisopropyl Tetrathiophosphate with Copper(I) Bromide

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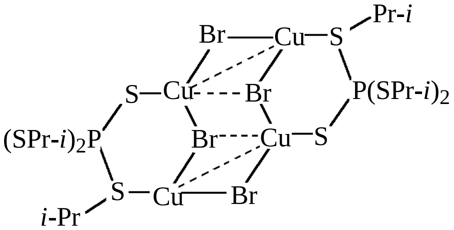
Thioesters of trivalent phosphorus acids attract considerable interest in the field of studying of their coordinating ability in the complexes with transition metals. We have shown that coordinational properties of thiophosphate ligands besides the steric factors and the effect of solvent are also determined by the character of substituents on phosphorus and sulfur atoms of the ambident P–S system. That leads to formation of complexes with different types of coordination depending on the number of atoms taking part in the coordinational bonds with metals [1]. In some cases disproportion of thiophosphite complexes in the coordinational sphere of metal is observed [2, 3].

We have found that copper complex of diisopropyl dithiophosphorochloridite $(i\text{-PrS})_2PCl \cdot CuBr$ **I** of the composition 1 : 1 [2] in which, according to IR and ^{31}P NMR spectra the monodentate type of coordination by the phosphorus atom takes place, in the course of prolonged handling in CH_2Cl_2–$CHCl_3$ solution undergoes the unusual transformation to give the complex $(i\text{-PRS})_3P{=}S \cdot [CuBr]_2$ **II** of the 1 : 2 composition. Formation of the complex **II** is judged about by the disappearance of signal with δ_P at 135 ppm and the appearance of signal at δ_P 87 ppm. According to X-ray data this new complex **II** has the step-like structure consisting of the skeletone of the heavy atoms with two annelated 6-member heterorings. Formation of the secondary Cu–Cu bonds (2.769 Å) is accompanied by the loosening of the Cu–Br bonds (2.827 Å). Bidentate coordination of metal in this complex is carried out simultaneously by two different atoms of sulfur. One of them is thiolic, while the another one is thionic.



Triisopropyl tetrathiophosphate di(bromocopper) (II). From 0.05 g of complex **I** obtained as a viscous liquid [2] and left for a long time in CH_2Cl_2–$CHCl_3$ solution in a flask with the lapped stopper with the purpose of obtaining of crystals for X-ray analysis 0.02 g of complex **II** was isolated. δ_P 87 ppm. Found, %: P 5.38. $C_9H_{21}Br_2Cu_2PS_4$. Calculated, %: P 6.0. X-ray studies were carried out on a 4-curcle Enraf-Nonius CAD-4 K-diffractometer at 20°C.

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