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LETTERS TO THE EDITOR

New Polynuclear Complex of Copper(I) with *N*-Diethylthiophosphoryl-*N*'-isopropylthiourea

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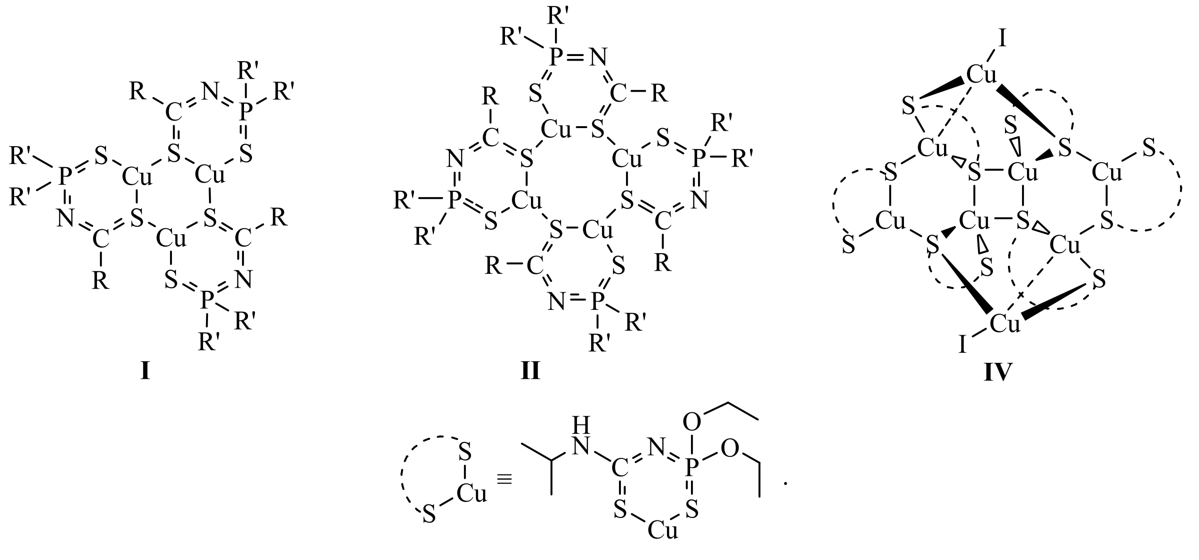
Complexes of Cu(I) with the sulfur-containing ligands can form cyclic polynuclear chelates [MnL_n] (n = 3, 4, 6, 8, etc.) [1–3]. According to X-ray diffraction data, the cyclic associates formed by bridging bonds with the sulfur atoms of the ligand. In the case of phosphorylated thioamides and thiourea derivatives of the general formula $\mathrm{R^1C(S)NHP(S)R^2_2}$ (HL) there is the tridentate coordination. The bridging binding between the cycles M–S–C–N–P–S always included the sulfur atoms of thiocarbonyl groups to form polynuclear chelates [$\mathrm{M_3L_3}$] (**I**) [2] and [$\mathrm{M_4L_4}$] (**II**) [1]. More complex polynuclear compounds [3] with $n > 4$ are the fragments [$\mathrm{M_3L_3}$] and [$\mathrm{M_4L_4}$] linked through the bridging bonding with the sulfur atoms of thiophosphoryl groups. In this case, compounds HL behave as tetradentate ligands (Scheme 1).

Polynuclear complexes of copper(I) were obtained by reacting a suspension of copper(I) iodide with a solution of potassium salt of the ligand (KL) in 96% aqueous ethanol. Earlier by an example of thiobenzamide $\mathrm{PhC(S)NHP(S)(O}i\mathrm{Pr)_2}$ ($\mathrm{HL^1}$), we have shown that at excess of the salt $\mathrm{KL^1}$ leads to the mixture of polynuclear chelate [$\mathrm{M_4L^1_4}$] and alongside adduct **III** [$\mathrm{KCuL^1_2}$] providing polymer chains in the crystal [1].

In the reaction of the potassium salt of *N*-diethylthiophosphoryl-*N*'-isopropylthiourea ($\mathrm{HL^2}$) 10-fold excess of CuI was used in order to avoid the

Scheme 1.



I **II** **IV**

formation of byproducts like complex **III**. It was found that an excess of copper iodide also affects the structure of the formed complexes to give polycyclic chelates $[Cu_6L^2_6]\cdot 2CuI$ (**IV**). Polynuclear chelates of this type are not described in the literature.

The structure of **IV** was identified by XRD. The complex consists of two cyclic moieties $[Cu_3L^2_3]$ linked by the bridging bonds involving the sulfur atoms of thiocarbonyl groups, the copper cations of CuL^2 fragment, and copper iodide. Complex **IV** is not stable in solutions and decomposes slowly to give copper(I) iodide. We assume that such compounds can be intermediate in the formation of polynuclear structures with $n > 4$.

Bis-μ^2-*S*^{1},*S*$^{1'}$-[tris{[*N*-(diethylthiophosphoryl)-*N*'-isopropylthiocarbamido-μ-*S*^{1},*S*^{2}]copper(I)}-μ^2-*S*^{2},*S*$^{5'}$-copper(I)] diiodide (IV). Yield 1.3 g (72% with respect to KL^2), mp 129°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.22 d (6H, CH_3, *i*Pr, ^3J 5.9), 1.34 m (6H, CH_3, Et, ^3J 6.9), 4.04–4.15 m (5H, OCH_2 + NCH), 4.83 d. septet (4H, OCH, $^3J_{PH}$ 10.6, ^3J 6.2), 6.24 br.s (1H, NH). $^{31}P–\{H\}$ NMR spectrum ($CDCl_3$): δ_P 50.8 ppm. Found, %: C 24.30; H 4.52. $C_{48}H_{108}Cu_8I_2N_{12}O_{12}P_6S_{12}$ (*M* 2378.24). Calculated, %: C 24.24; H 4.58.

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