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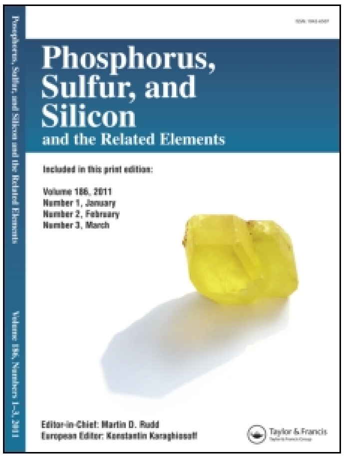

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Self-Assembly of the Complexes of Bipodal Thiophosphorylated Thioureas

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SELF-ASSEMBLY OF THE COMPLEXES OF BIPODAL THIOPHOSPHORYLATED THIOUREAS

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N-Thiophosphorylated thioureas, of general formula $[(i\text{-}PrO)_2P(S)NHC(S)]_2Z$ *(*$Z = \alpha,\omega$*-diamino(oxy)alkyl or 1,10-diaza-18-crown-6), in the form of potassium salts, react with a number of soft ions (*Cd^{2+}*,* Zn^{2+}*,* Co^{2+}*,* Ni^{2+}*,* Pd^{2+}*) to form novel dimeric complexes. The cadmium (*$Z = HN(CH_2)_2NH$*), palladium (*$Z = HN(CH_2)_2O(CH_2)_2NH$*), and cobalt (*$Z = 1,10$*-diaza-18-crown-6) complexes were analyzed by x-ray crystallography. In the former complex, crown cavities remain free. This fact will allow us to obtain "guest–host" complexes with alkali metal cations.*

Keywords: Bridging ligands; chelates; crown compounds; macrocycles; self-assembly; N-thiophosphorylthioureas

As analog of β-diketones, ligands **1** and **2** belong to class of the N—H acids and, depending on the nature of the X and Y atoms (X, Y = O, S, Se, NH), fairly readily form complexes with various soft and hard metals (Figure 1). Methods of synthesis of these ligands were described in detail in reviews.[1–3]

Such methods allow one to vary the substituents R, R^1, R^2, and R^3 attached to the carbon, phosphorus, and nitrogen atoms over a wide range, thus changing properties and the stability of complexes, and giving broad structural diversity to the obtained ligands and complexes.

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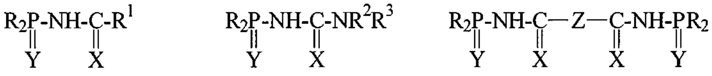


$R_2P(=Y)\text{-NH-}C(=X)\text{-}R^1$ (1)

$R_2P(=Y)\text{-NH-}C(=X)\text{-}NR^2R^3$ (2)

$R_2P(=Y)\text{-NH-}C(=X)\text{—}Z\text{—}C(=X)\text{-NH-}P(=Y)R_2$ (3)

FIGURE 1

Bipodal ligands (**3**) having two amidophosphate units, which are spatially separated by bridging chain Z or by crown, should be especially distinguished. Because of the presence of two chelating centers in the bisurea molecules, complexes with composition 1:1 and 2:2, as well as oligomeric and polymeric ones, can form.

RESULTS AND DISCUSSION

Complexes in a broad range of bipodal bisthioureas have been synthesized by the reaction of bisthiophosphorylthioureas $[(i\text{-PrO})_2P(S)NHC(S)]_2Z$; $Z = HN(CH_2)_2NH$ (**4**), $HN(CH_2)_7NH$ (**5**), $HN(CH_2)_2O(CH_2)_2NH$ (**6**), $HN(CH_2)_2[O(CH_2)_2]_2NH$ (**7**), diaza-18-crown-6 (**8**) with a number of soft ions[4] (Figure 2).

The molecular structure of the complexes was established by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy and confirmed by elemental analysis. Most prepared compounds are amorphous solid substances. That fact complicates elucidation of their structure. Fortunately, we had obtained crystals of some complexes and their crystal structures have been analyzed by x-ray single crystal diffraction. These are the cadmium complex of **4**, palladium complex of **6**, and cobalt complex of **8**. X-ray investigations indicate that these complexes are dimeric in crystal form. General formula of dimeric complexes is shown in Figure 3. The metal-containing macrocycles are formed together with two spirocycles. Metals are four-coordinated and stay in the expected configuration: tetrahedral for cadmium and cobalt and square-planar for palladium.

An 18-member macrocycle, formed by two cadmiums with two molecules of **4**, seems to be too small and lacks both sufficient and effective donor groups to bind into complexes with alkali metal cations; also, as well as it cannot be employed in hydrophobic binding, for example with solvent molecule. The much greater on size macrocycle is formed in

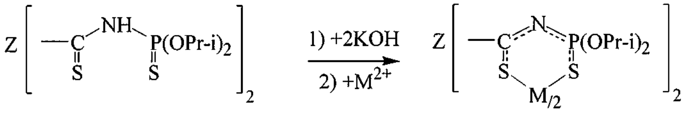
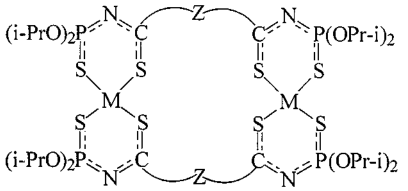


FIGURE 2 $M = Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}$.



1) M=Cd; Z=HNCH$_2$CH$_2$NH
2) M=Pd; Z=NH(CH$_2$)$_2$O(CH$_2$)$_2$NH
3) M=Co; Z=DiAza-18-Crown-6

FIGURE 3 General formula of the dimeric complexes of bipodal thiophosphorylated thioureas.

binuclear palladium(II) complex containing oxapentane bridging chain. All complexes of palladium known at present have a trans square planar structure. In our case, the chelate cores have an unusual cis configuration of the distorted square plane.

Figure 4 illustrates crystal structure of **8**, with cobalt(II). The complex has two 18-member rings separated by tetrahedral chelate units. Such structures are referred as ditopic cryptands. Diaza-18-crown-6 units in this complexe are somewhat distorted but quite able to accommodate alkali metal cations in the host–guest fashion. The new cavity formed with cobalt ions is large and is able to bind not only metal cations but also organic molecules.

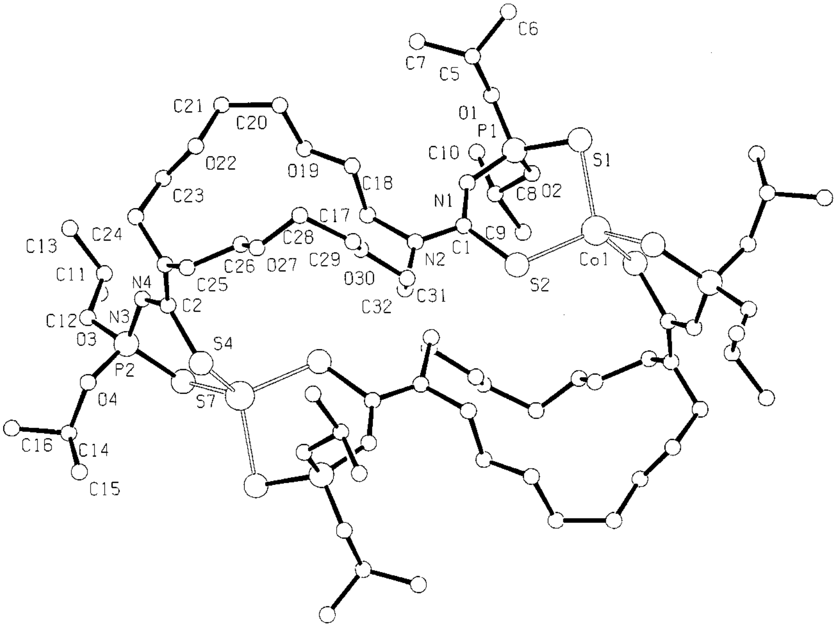


FIGURE 4 Crystal structure of **8**, with cobalt(II).

Similar complexes with Cu(II) also have been prepared and investigated by electron paramagnetic resonance (EPR) in solutions, and they were shown to have very distorted tetrahedral arrangement.[5]

In addition to cyclic complexes of cobalt and copper with 2:2 composition, the oligomeric complexes of mercury, cobalt, nickel, palladium ions, and the mixed complex with palladium and mercury were prepared.

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