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Complexes of crown-containing *N*-thioacylamido(thio)phosphates with Zn(II) and Co(II) cations

Damir A. Safin *, Maria G. Babashkina, Felix D. Sokolov, Nail G. Zabirov

Department of Chemistry, Kazan State University, Kremlevskaya St. 18, 420008 Kazan, Russia

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Abstract

Reaction of the potassium salts of *N*-acylamido(thio)phosphates [4′-benzo-15-crown-5]NHC(S)NHP(Y)(O*i*Pr)$_2$ (Y = S, $\mathbf{HL^{I}}$; Y = O, $\mathbf{HL^{II}}$) with Zn(II) and Co(II) cations in aqueous EtOH leads to complexes of formulae Zn(L^{I,II} − *S*,*Y*)$_2$ (Y = S, **1**; Y = O, **2**) and Co(L^{I}-*S*,*S*′)$_2$ (**3**), while interaction of the potassium salt of [4′-benzo-15-crown-5]C(S)NHP(O)(O*i*Pr)$_2$ ($\mathbf{HL^{III}}$) with Zn(II) in the same conditions leads to a complex of composition Zn(HL^{III})(L^{III}-*S*,*O*)$_2$ (**4**).
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Compounds containing two essentially different complexing groups simultaneously – a chelating fragment and a macrocycle – draw the attention of researchers as potential bimetallic catalysts [1], models at studying intracomplex redox processes [2–5] and reagents for the synthesis of supramolecular compounds [6,7].

Presence of the exocyclic functional groups in a molecule of crown-ether, interacting with atoms of a cycle or metal cations, increases complexing selectivity and complexing ability in relation to metal ions, and results in a change of the hydrophilic–hydrophobic balance and surface-active properties [8,9].

Earlier, we had reported about bis-thioureas, containing diaza-18-crown-6 and diaza-15-crown-5 [10], thiourea on the basis of monoaza-18-crown-6 [11] and thiophosphorylated thiobenzamide [12], containing a benzo-15-crown-5 cycle, possessing the ability for complexes with alkaline and transition metal cations.

Combination of crown-ether and thioacylamido(thio)-phosphate fragments C(S)NHP(Y) in one molecule opens greater opportunities for the synthesis of various supramolecular coordination compounds. Herein, we present complexes of Zn(II) and Co(II) cations (**1–4**) with ligands $\mathbf{HL^{I–III}}$ (Scheme 1) [13]. They are of doubtless interest as building blocks for creation in a molecule of combinations from crown-ethers, allowing increasing probability to form complexes with in advanced set structure.

The IR spectrum of **1** in Nujol is similar to the spectrum of **3**. The absorption bands of the P=S group of the anionic forms $\mathbf{L^{I}}$ in complexes **1** and **3** are shifted by approximately 30 cm^{-1} to low frequencies relative to the band of the parent ligand $\mathbf{HL^{I}}$. This confirms their participation in chelate formation. The absorption band of the P=O group of the $\mathbf{L^{II}}$ in complex **2** is also shifted to low frequencies relative to the band of the ligand $\mathbf{HL^{II}}$, but the shift is 80 cm^{-1}. There is only one signal for the NH proton in the IR spectra of complexes **1–3** in the area 3236–3264 cm^{-1}. In the spectrum of **1–3**, there is an intense absorption band at 1508–1524 cm^{-1} corresponding to the conjugated SCN fragment. This fact also confirms about the formation of complexes. Besides a wide intensive band of the POC group at 992–1008 cm^{-1}, in the IR spectra of **1–3** there are a set of absorption bands in the area 1098–1128 cm^{-1}, corresponding to the COC fragment. It confirms the preservation of structure of a ligand in the obtained complexes.

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* Corresponding author. Tel./fax: +7 843 2543734.
E-mail addresses: damir.safin@ksu.ru (D.A. Safin), felix.sokolov@ksu.ru (F.D. Sokolov).

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