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A “sodium trap” based on benzo-15-crown-5 with an exocyclic *N*-(thiophosphoryl)thiourea moiety

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Abstract

For *N*-(thio)phosphorylthioureas of the common formula $RC(S)NHP(X)(OiPr)_2$ HL^I ($R = N$ -(4'-aminobenzo-15-crown-5), $X = S$), HL^{II} ($R = N$ -(4'-aminobenzo-15-crown-5), $X = O$), HL^{III} ($R = PhNH$, $X = S$), HL^{IV} ($R = PhNH$, $X = O$), and $(N,N'$ -bis-[$C(S)NHP(S)(OiPr)_2$]₂-1,10-diaza-18-crown-6) H_2L^V , salts $LiL^{I,III,IV}$, NaL^{I-IV} , KL^{I-IV} M_2L^V ($M = Li^+$, Na^+ , K^+), $Ba(L^{I,III,IV})_2$, and BaL^V have been synthesized and investigated. Compounds NaL^{III} quantitatively drop out as a deposit in ethanol medium, allowing the separation of Na^+ and K^+ cations. This effect is not displayed for the other compounds. The crystal structures of HL^{III} and the solvate of the composition $[K(Me_2CO)L^{III}]$ have been investigated by X-ray crystallography.

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1. Introduction

Crown-ethers and azamacrocycles modified by exocyclic groups are widely applied as complexing agents, selective to cations of alkaline, earth-alkaline, and d-metals [1,2], lanthanides and actinides [3], and Tl(I) [4]. However, in the literature there is no data about direct (not-extraction) highly effective separation of alkaline metal cations using crown compounds.

On the formation of complexes of alkaline metal salts $[M^+A^-]$ with crown-ethers, as a rule, there is an increase in solubility of the formed adduct $[M(\text{crown})]^+A^-$ in an organic phase [5]. However, a combination of crown-ether and negative charged chelating units in a ligand molecule can lead to interesting cooperative effects.

Herein we present data about the structures and properties of *N*-(thio)phosphorylthioureas of the common formula $RC(S)NHP(X)(OiPr)_2$, (HL^{I-IV}) and *N,N'*-bis-[$C(S)NHP(S)(OiPr)_2$]₂-1,10-diaza-18-crown-6 (H_2L^V) (Scheme 1), and their salts with Li^+ , Na^+ , K^+ , Ba^{2+} .

It is known [6] that *N*-(thio)phosphorylthioureas in aqueous alcohol medium are weak acids: HL^{III} p*K* 8.1 (96% aq. EtOH) [7], 8.28 (96% aq. *i*PrOH) [8]; HL^{IV} p*K* 6.93 (96% aq. *i*PrOH) [8]; H_2L^V p*K*₁ = 9.2, p*K*₂ = 10.2 (96% aq. EtOH) [7]. These compounds are able to form salts with cations of alkaline metals. There is no information on the crystal structures of salts of *N*-(thio)phosphorylthioureas in the literature. However, the structures of some close analogues of these compounds – salts of *N*-(thio)phosphorylamides and thioamides, containing the fragment $C(X)NHP(Y)R'_2$ ($X, Y = O, S$), have already been investigated. Compounds of the formula $[M(CCl_3C(O)NP(O)(OMe)_2)]$ as crystals form dimers ($M = Na^+$) or polymeric chains $M = Rb^+$ [9]. Potassium salts of thioamides

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