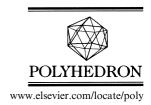


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A "sodium trap" based on benzo-15-crown-5 with an exocyclic N-(thiophosphoryl)thiourea moiety

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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), $\mathbf{BaL^V}$ have been synthesized and investigated. Compounds $\mathbf{NaL^{I,II}}$ 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(Me₂CO)L^{III}] have been investigated by X-ray crystallography. © 2006 Elsevier Ltd. All rights reserved.

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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 $[M(crown)]^+A^-$ 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⁺, Ba²⁺.

It is known [6] that N-(thio)phosphorylthioureas in aqueous alcohol medium are weak acids: HLIII pK 8.1 (96% aq. EtOH) [7], 8.28 (96% aq. *i*PrOH) [8]; **HL**^{IV} pK 6.93 (96% aq. *i*PrOH) [8]; $\mathbf{H_2L^V}$ $pK_1 = 9.2$, $pK_2 = 10.2$ (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(CCl₃C(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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