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Studies on cobalt(II) complexes with *N*-thioacylamido(thio)phosphates: X-ray crystal structure of the $\text{Co}[\text{PhC}(\text{S})\text{NP}(\text{S})(\text{OPri})_2]_2$

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Abstract

Reaction of the potassium salts of *N*-thioacylamidophosphates $\text{RC}(\text{S})\text{NHP}(\text{O})(\text{OPri})_2$ ($\text{R} = \text{Ph}, \text{PhNH}, p\text{-MeOPhNH}, p\text{-BrPhNH}, i\text{PrNH}, t\text{BuNH}, \text{Et}_2\text{N}, c\text{-C}_5\text{H}_{10}\text{N}, c\text{-OC}_4\text{H}_8\text{N}, c\text{-C}_5\text{H}_{11}\text{NH}$) with $\text{Co}(\text{II})$ cation in aqueous EtOH leads to the complexes of $\text{Co}(\text{L-O,S})_2$ type structure. Complexes $\text{Co}(\text{B})\text{L}_2$ were obtained by the reaction of chelate complexes CoL_2 ($\text{R} = \text{Ph}, \text{PhNH}$) with 2,2'-bipyridine and 1,10-phenanthroline. Structures of the compounds obtained were investigated by EIMS, IR, UV–Vis spectroscopy and microanalysis. Complex $\text{Co}[\text{PhC}(\text{S})\text{NP}(\text{S})(\text{OPri})_2]_2$ was investigated by single crystal X-ray diffraction.

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1. Introduction

N-(Thio)acylamido(thio)phosphates $\text{RC}(\text{X})\text{NHP}(\text{Y})\text{R}'_2$ ($\text{X}, \text{Y} = \text{O}$ or S ; $\text{R} = \text{Alk}, \text{Ar}, \text{ArNH}, \text{AlkNH}, \text{Alk}_2\text{N}$; $\text{R}' = \text{OAlk}, \text{OAr}, \text{Ar}$) are important because of the variety of ways of interaction with d^8 - and d^{10} -metal cations [1]. These compounds and their complexes can be used as extractants, analytical reagents [2] and structural fragments for construction of metal-containing macrocycles [3] and polycrown-compounds [4].

Dithioderivatives of these compounds, *N*-thioacylamidothiophosphates $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ (**1**) [5–8] or their diphosphorus analogues $\text{R}_2\text{P}(\text{X})\text{NHP}(\text{X})\text{R}'_2$ ($\text{X} = \text{S}, \text{Se}$) [9,10] and their complexes with divalent d-metal cations

have been extensively investigated. Formation of chelate complexes of the ML_2 structure is characteristic for them. Ligands are coordinated bidentately in these compounds, through the atoms of sulfur of the thiocarbonic and thio(seleno)phosphoric groups. Cobalt(II) chelates with oxygen-containing ligands $\text{RC}(\text{O})\text{NHP}(\text{O})\text{R}'_2$ (**2**) show the expressed propensity to oligomerization in the solid phase and to the formation of complexes with the solvent molecules. Dimeric structures of complexes have been studied, e.g. complexes $\text{Co}_2[\text{L}]_4\text{D}_2$, where $[\text{L}] = [\text{CCl}_3\text{C}(\text{O})\text{NP}(\text{O})(\text{OMe})_2]^-$ or $[\text{CCl}_3\text{C}(\text{O})\text{NP}(\text{O})(\text{NHBz})_2]^-$; $\text{D} = i\text{PrOH}$ [11,12]. An attempt to synthesise the heteroligand $\text{Co}(\text{II})$ complexes by reaction of $\text{Co}(\text{PPh}_3)_2\text{Cl}_2$ or $\text{Co}(\text{PPh}_3)_2\text{NO}_2$ with $\text{Ph}_2\text{P}(\text{Se})\text{NHP}(\text{Se})\text{Ph}_2$ was unsuccessful [13]. Only the $[\text{Co}(\text{Ph}_2\text{P}(\text{Se})\text{NHP}(\text{Se})\text{Ph}_2)_2]$ complex was obtained.

The structure of the $\text{Co}(\text{II})$ cation coordination compounds with $\text{RC}(\text{S})\text{NHP}(\text{O})\text{R}'_2$ (**3**) (HL) ligands, containing donor atoms of sulfur and oxygen simultaneously is practically not studied. On the one hand, prevalence of

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