



Complexes of *N*-thiophosphorylthiourea (EtO)₂P(O)CH₂C₆H₄-4-[NHC(S)NHP(S)(OiPr)₂] with Zn(II), Cd(II), Co(II) and Cu(PPh₃)(I)

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ABSTRACT

Reaction of *O,O'*-diisopropylthiophosphoric acid isothiocyanate (iPrO)₂P(S)NCS with diethyl 4-aminobenzylphosphonate (EtO)₂P(O)CH₂C₆H₄-4-NH₂ leads to the new *N*-thiophosphorylated thiourea (EtO)₂P(O)CH₂C₆H₄-4-[NHC(S)NHP(S)(OiPr)₂] (**HL**). Reaction of the potassium salt of **HL** with Zn(II), Cd(II) and Co(II) in aqueous EtOH leads to complexes of formula M(L-*S,S'*)₂ (**ML**₂). Heteroligand copper(I) complex of **HL** and triphenylphosphine was prepared by the reaction of the potassium salt **KL** and Cu(PPh₃)₃I. Copper in complex **Cu(PPh₃)L** is bound by one PPh₃ and one SCNPS fragment of the chelating ligand. Compounds obtained were investigated by IR, UV-Vis, ¹H and ³¹P{¹H} NMR spectroscopy, and microanalysis. The structures of **HL** and **Cu(PPh₃)L** were investigated by single crystal X-ray diffraction analysis.

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1. Introduction

Imidodiphosphinates R₂P(X)NHP(X)R'₂ (X = S, Se) [1–5] and their complexes with divalent d-metal cations have been extensively investigated. Formation of chelate complexes of the ML₂ structure is characteristic for them. Ligands are coordinated bidentately in these compounds, through the atoms of X of the thio(seleno)carbonic and thio(seleno)phosphoric groups. Cobalt(II) chelates with oxygen-containing ligands RC(O)NHP(O)R'₂ show the expressed propensity to oligomerization in the solid phase and to the formation of complexes with the solvent molecules [6–8].

Heteroligand copper(I) complexes of triphenylphosphine and XCNPY or XPNPX (X, Y = O, S, Se) backbone ligands [8–11] have been earlier reported. It was established that PPh₃ was used as an additional donor ligand to prepare the non-cluster complex of Cu(I), where the copper atom is bound only to one molecule of chelating SPNPS ligand [10]. In this case, the filling of coordination sites of copper(I) is necessary to prevent cluster formation.

Published data reveal that structure and properties of triphenylphosphine containing complexes of XCNPY or XPNPX are strongly dependent on the nature of chelating ligand. To the best of our knowledge, there are no data explaining reasons of one or two PPh₃ molecules binding with Cu(I) metal centre. For this purpose we conceived to use thiophosphorylated thiourea, containing sterically demanding substituent capable to the hydrogen bonds formation.

Amidophosphates RC(S)NHP(X)R₂ have long attracted attention of researchers due to their ability to form stable chelates with IB, IIB, and VIII B group transition metal cations. These compounds and their complexes exhibit antiviral activity [12]. They can be used as stationary phases for GLC [13], as well as components of ion-selective electrodes [14–17], extractants [18], and masking reagents in analytical chemistry [19].

These investigations are caused by the further utilizing of obtained Zn(II), Cd(II), Co(II) and Cu(I) compounds with dithiocontaining ligand as single source molecular precursors for the preparation of metal sulfide thin films and nanocrystals by chemical vapor deposition [20,21].

We report here the structure of the thiourea (EtO)₂P(O)CH₂C₆H₄-4-[NHC(S)NHP(S)(OiPr)₂] (**HL**) and complex Cu(PPh₃-P)((EtO)₂-P(O)CH₂C₆H₄-4-[NHC(S)NP(S)(OiPr)₂]-*S,S'*) (**Cu(PPh₃)L**) determined by X-ray single crystal diffraction.

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