



# Synthesis and characterization of $[\text{Me}_2\text{NC}(\text{S})\text{NP}(\text{S})(\text{OiPr})_2]^-$ complexes of Co(II), Ni(II), Zn(II) and Cd(II)

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## ARTICLE INFO

### Article history:

Available online 23 June 2009

### Keywords:

Cobalt  
Nickel  
Zinc  
Cadmium  
N-thiophosphorylthiourea  
Crystal structures

## ABSTRACT

Reaction of the potassium salt of N-thiophosphorylthiourea  $\text{Me}_2\text{NC}(\text{S})\text{NHP}(\text{S})(\text{OiPr})_2$  (**HL**) with Co(II), Ni(II), Zn(II) and Cd(II) cations in aqueous EtOH leads to  $\text{M}(\text{L-S,S}')_2$  (**ML**<sub>2</sub>) chelate complexes. The structures of the resulting compounds were studied by IR, UV-Vis, <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and micro-analysis. The metal center is found in a tetrahedral environment in complexes **CoL**<sub>2</sub>, **ZnL**<sub>2</sub>, **CdL**<sub>2</sub> and square-planar in **NiL**<sub>2</sub> formed by the C=S and P=S sulfur atoms of two deprotonated ligands **L**. According to the NMR and UV-Vis spectroscopy data it was established that the metal cation of **NiL**<sub>2</sub> is in a square-planar environment in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$ , whereas **NiL**<sub>2</sub> shows features of tetrahedral or octahedral complexes in acetone, DMSO and DMF. Molecular structures of complexes were elucidated by single crystal X-ray diffraction analysis.

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## 1. Introduction

There have been a great number of studies of the coordination chemistry of imidodiphosphinates  $\text{R}_2\text{P}(\text{X})\text{NHP}(\text{Y})\text{R}'_2$  (**HZ**) (X, Y = O, S; R, R' = Alk, Ar) with various metal cations [1–17]. In particular, complexation properties of **HZ** towards Co(II) and Ni(II) are of great interest due to the coordination versatility: octahedral, tetrahedral and square-planar. Overwhelming majority of Co(II) and Ni(II) complexes contain symmetric anionic ligands **Z**, containing both identical donor atoms (X = Y) and substituents (R = R') simultaneously [9–16], although some studies on unsymmetrical **HZ** ligands have been reported [17]. However, these investigations have been devoted to either mixed chalcogens or mixed substituents complexes. Co(II) complexes with **HZ** usually show tetrahedral or octahedral geometry, while Ni(II) compounds contain a square-planar or octahedral complex core. The tetrahedral environment in Ni(II) complexes with **HZ** is rare and not understood, although some examples have been reported [12–17].

Thus, it would be very useful to synthesize and investigate Co(II) and Ni(II) complexes with the close unsymmetrical analog of **HZ**—acylamidophosphates and their thioanalogs of the general formula  $\text{RC}(\text{X})\text{NHP}(\text{Y})\text{R}'_2$  (**HQ**) (X, Y = O, S). **HQ** forms a stable chelate complexes with a number of divalent metal ions [18,19]. The presence of the (thio)carbonyl and (thio)phosphoryl groups and the acidic NH proton in molecules of N-(thio)phosphorylated

(thio)ureas and (thio)amides predetermines the possibility of chelating coordination of these ligands through the sulfur and oxygen donor centers with the formation of a stable six-membered chelate ring [20,21].

Herein, we present the square-planar Ni(II) and tetrahedral Co(II), Ni(II), Zn(II) and Cd(II) complexes with N-thiophosphorylated thiourea  $\text{Me}_2\text{NC}(\text{S})\text{NHP}(\text{S})(\text{OiPr})_2$  (**HL**). We have also discussed the square-planar–tetrahedral isomerization for the **NiL**<sub>2</sub> complex.

## 2. Experimental

### 2.1. Physical measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600  $\text{cm}^{-1}$ . NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} spectra were recorded at 299.948 and 121.425 MHz, respectively. Chemical shifts are reported with reference to  $\text{SiMe}_4$  (<sup>1</sup>H) and  $\text{H}_3\text{PO}_4$  (<sup>31</sup>P{<sup>1</sup>H}). Electronic absorption spectrum of solution was recorded in the range 200–900 nm on a Perkin-Elmer Lambda 35 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser.

### 2.2. Synthesis of **HL**

A solution of 0.450 g (10 mmol)  $\text{Me}_2\text{NH}$  in anhydrous  $\text{CH}_2\text{Cl}_2$  (15 mL) was treated with vigorous stirring with a solution of 2.868 g (12 mmol, 10% excess) of  $(i\text{PrO})_2\text{P}(\text{S})\text{NCS}$  in anhydrous

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