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# Coordination diversity of *N*-phosphoryl-*N'*-phenylthiourea (LH) towards Co<sup>II</sup>, Ni<sup>II</sup> and Pd<sup>II</sup> cations: Crystal structure of ML<sub>2</sub>-*N,S* and ML<sub>2</sub>-*O,S* chelates

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## Abstract

Thiourea, PhNHC(S)NHP(O)(OPr<sup>*i*</sup>)<sub>2</sub> (LH) chelates of Co<sup>II</sup>, Ni<sup>II</sup>, and Pd<sup>II</sup> ions have been obtained and investigated by single-crystal X-ray diffraction, UV, IR, NMR spectroscopy, and EI mass-spectrometry. The unusual 1,3-*N,S*-coordination via sulfur and NP(O) nitrogen atoms has been found in the *trans*-square-planar NiL<sub>2</sub> and PdL<sub>2</sub> complexes, whereas the 1,5-*O,S*-coordination is realized in the tetrahedral CoL<sub>2</sub> complex. DFT calculations have revealed significant stabilization of the 1,3-*N,S*-structures due to stronger crystal field and the NH–O=P hydrogen bonds.

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## 1. Introduction

$\beta$ -Dicarbonyl compounds (*N*-acylureas **1**, acetylacetonates, etc.) and their phosphorus containing analogs (*N*-acylamidophosphinates **2**, imidodiphosphinates **3**) (Fig. 1) were found to be very attractive ligands for variety of metal ions [1–4].

$\beta$ -Bifunctional ligands **1–3** contain three potential donor centers: X, Y and internal nitrogen atoms. Nucleophilic ability of the latter donor is significantly reduced by the two neighboring electron-withdrawing groups. That is why the alkylation of *N*-thioacylamido(thio)phosphates-

RC(S)NHP(Y)(OR')<sub>2</sub> (Y = O,S) always proceeds on the thiocarbonyl sulfur atom [1a,5].

There is a fair amount of the data concerning the structures of complexes of divalent transition metal ions of Ib, IIb, VIIIb groups with *N*-thioacylamidothiophosphinates (**2**) (X, Y = S) [1–5,7–10]. The 1,5-bidentate coordination of deprotonated ligands through sulfur atoms takes place in all these cases.

The substituents (or other factors) are hardly capable of changing a coordination mode in the complexes of *dithio*-derivatives of **2** with divalent cations of VIIIb group. Due to the strong  $\pi$ -interactions, the formation of metal–sulfur bonds is most energetically favorable in all these cases.

Replacement of one sulfur atom in conjugated [RC(X)NP(Y)R'<sub>2</sub>]<sup>(-)</sup> moiety to oxygen (X = S, Y = O or X = O, Y = S) leads to appearance of the ambivalent coordination modes and possible competition between the three donor centers in the binding anion species. As a result, the

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