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# Nickel(II) complexes with *N*-(thio)phosphorylthioureas AdNHC(S)NHP(X)(OiPr)<sub>2</sub>: Versatile coordination of phosphoryl (X = O) and thiophosphoryl (X = S) derivatives

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## ABSTRACT

The reaction of the potassium salts of *N*-(thio)phosphorylated thioureas of the common formula AdN(H)C(S)N(H)P(X)(OiPr)<sub>2</sub> (X = O, **HL**<sup>I</sup>; X = S, **HL**<sup>II</sup>) with the Ni(II) cation in aqueous EtOH leads to [Ni(L<sup>I</sup>)<sub>2</sub>] chelate complexes. The molecular structures of the thioureas **HL**<sup>III</sup> and the complexes [Ni(L<sup>I</sup>-N,S)<sub>2</sub>] and [Ni(L<sup>II</sup>-S,S')<sub>2</sub>] were elucidated by single crystal X-ray diffraction analysis, IR, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and microanalysis. In the complex [Ni(L<sup>I</sup>)<sub>2</sub>], the metal center is found to be in a square-planar N<sub>2</sub>S<sub>2</sub> environment formed by the C=S sulfur atoms and the P–N nitrogen atoms of two deprotonated L<sup>I</sup> ligands. The ligands are in a *trans* configuration. The Ni(II) atom in complex [Ni(L<sup>II</sup>)<sub>2</sub>], with the deprotonated thiourea L<sup>II</sup>, is coordinated in a square-planar fashion by the C=S and P=S sulfur atoms of two anionic ligands. The ligands are in a *cis* configuration.

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## 1. Introduction

Competitive coordination of polydentate ligands has been of interest over the last four decades [1]. The Hard Soft Acid Base (HSAB) principle has been used to explain the coordination versatility of metal cations with donor centers of polyfunctional ligands [1a]. However, the HSAB principle is not enough if the ligand contains several hard or soft coordination atoms contesting for a place in the coordination environment of a metal cation. The influence of different steric factors, additional intra- and intermolecular bonding (e.g. hydrogen bonds), the electron effects of substituents and many other factors must be taken into account.

We recently published data illustrating the influence of intramolecular hydrogen bonds on the 1,3-*N,S*- and 1,5-*O,S*-coordination of *N*-phosphoryl-*N'*-(*R*)-thioureas RNHC(S)NHP(O)(OiPr)<sub>2</sub> (**HL**) (R = Ph [2]; R = *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-BrC<sub>6</sub>H<sub>4</sub>, *t*-Bu, *c*-Hex [3]) with Ni(II). It was established that intramolecular hydrogen bonds N–H...O=P are a necessary condition for the 1,3-*N,S*-isomer stabilization in square-planar complexes of Ni(II). The destabilization of

Ni(II) complexes and a change of the coordination mode from the 1,3-*N,S*- to the 1,5-*O,S*-isomer chelates takes place when H-bonding in the coordinated anionic ligands L is not possible (R = Et<sub>2</sub>N, morpholine-*N*-yl). Thus, intramolecular hydrogen bonding realized outside the coordination sphere of the metal cation is the reason for the dramatic changes of such important parameters as bite angle and the ligand's field strength.

Herein we present the structure of two new thioureas of the common formula AdNHC(S)NHP(X)(OiPr)<sub>2</sub> and their complexing properties towards the nickel(II) cation. Comparative analysis on the coordination mode of the phosphorylated (X = O) and thiophosphorylated (X = S) derivatives have been performed.

## 2. Experimental

2.1. Synthesis of **HL**<sup>I</sup> and **HL**<sup>II</sup>

A solution of 1.510 g (10 mmol) 1-adamantylamine in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was treated, whilst vigorously stirring, with a solution of 2.676 g (12 mmol) of (iPrO)<sub>2</sub>P(O)NCS or 2.868 g (12 mmol) of (iPrO)<sub>2</sub>P(S)NCS in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred for an additional 30 min to complete the reaction. The solvent was removed in a vacuum, and the product was purified by crystallization from dichloromethane by *n*-hexane.

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