



Crystal structure and dynamic behavior of $[\text{Ni}\{\text{PhNHC}(\text{S})\text{NP}(\text{S})(\text{OPr}^i)_2\text{-S,S}\}_2]$ complex in dichloromethane solution

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Abstract

The crystal structure of the complex $[\text{Ni}\{\text{PhNHC}(\text{S})\text{NP}(\text{S})(\text{OPr}^i)_2\text{-S,S}\}_2]$ has been determined and its behavior in dichloromethane solution investigated by NMR ^{31}P spectroscopy. The X-ray structural analysis shows the nickel atom at the symmetry center in a distorted square-planar arrangement with *trans*-disposition of the ligands. The six-membered cycle $\text{NiS}(1)\text{PNCS}(2)$ has the form of the asymmetric boat. In dichloromethane solutions of the compound four signals have been detected by $^{31}\text{P}\{-^1\text{H}\}$ NMR method. These signals are related to three diamagnetic square-planar isomers with different dispositions and conformations of two ligands in anti-orientation: *trans*-chair-boat (**A**), *cis*-boat-boat (**B**), and *trans*-boat-boat (**C**). These isomers are in slow exchange equilibria. It was shown that all these forms are in rather fast chemical exchange with minor (unobserved) paramagnetic pseudo-tetrahedral isomers (**A_T**, **B_T**, and **C_T**). The thermodynamic constants of equilibria between **A**, **B**, and **C** as well as rate constants and activation parameters for conversion of three square-planar to respective pseudo-tetrahedral forms were calculated from the $^{31}\text{P}\{-^1\text{H}\}$ NMR data. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

There is continuing interest in Ni(II) complexes with thio-phosphorus ligands containing a NiS_4 core [1,2], partly due to the unusual metal coordination and varying stereochemistry of the chelate cycles. Nickel(II) complexes type I {of dithiophosphoric acids $[(\text{RO})_2\text{PS}_2]_2\text{Ni}$ (R = Me [3], Et [4]) [2] and dithiophosphinic acids $(\text{R}_2\text{PS}_2)_2\text{Ni}$ (R = Me [5], Et [6], Ph [7])} and type II {of bis(thiophosphinoyl)amines $[\text{Ni}\{\text{N}(\text{PR}_2\text{S})_2\text{-S,S}\}_2]$ (R = Me **1** [8], Prⁱ **2** [9], Ph **3** [2,10]) and $[\text{Ni}\{\text{Me}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\text{-S,S}\}_2]$ **4** [2]} have been investigated with X-ray diffractometry. Nickel atom has the slightly

distorted square-planar configuration in all complexes of type I as well as in complexes with dithioacetylacetone [11] and with 1,1-diethyl-3-thiobenzoyl-thiourea [12]. In complexes of type II, the NiS_4 core has tetrahedral configuration in the compounds **1–3** but is square-planar one in the compounds **4** and **3** · 2THF [13]. As pointed out by the authors [2,13] the reasons for this difference are not clear. The complex **3** has been found to show square-planar – tetrahedral isomerization also [13,14]. It is possible that this equilibrium is affected by temperature, solvent, and the structure of ligands [13,15]. The solution of these problems is mainly restricted by the limited set of relevant complexes. Except the compounds mentioned, only complexes $[\text{Ni}\{\text{N}(\text{PPh}_2\text{Se})_2\text{-Se,Se}\}_2]$ [16] and $[\text{Ni}\{\text{CH}(\text{PPh}_2\text{S})_2\text{-S,S}\}_2]$ [17] have been described (see Scheme 1).

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