Coordination Mode of the Nickel(II) Cation with N-Diisopropoxyphosphinyl-pbromothiobenzamide

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Abstract. Reaction of the potassium salt of *N*-diisopropoxyphosphinyl-*p*-bromothiobenzamide *p*-BrC₆H₄C(S)NHP(O)(O*i*Pr)₂ (HL) with Ni(NO₃)₂ in aqueous EtOH leads to complex of formula [Ni(HL-*O*)₂(L-*O*,*S*)₂] (1). The structure of **1** was investigated by single crystal X-ray diffraction analysis, IR, ¹H and ³¹P{¹H} NMR spectroscopy, MALDI and microanalysis. The nickel(II) ion in **1** has a tetragonal-bipyramidal environment, $(O^{ax})_2(O^{eq})_2(S^{eq})_2$, with

two neutral ligand molecules coordinated in axial positions through the oxygen atoms of the P=O groups. The equatorial plane of bipyramide is formed by two anionic ligands involving 1,5-O,Scoordination mode. The chelating ligands are bound in *trans* configuration.

Keywords: Nickel; Amidophosphate; Chelates; Crystal structure

Complexes of Ni^{II} with (thio)(seleno)phosphorus ligands $[R^1R^2P(X)Y]^-$, $[R^1R^2P(X)NP(Y)R^3R^4]^-$ and $[R^1R^2C(X)NP(Y)R^3R^4]^-$ (X, Y = O, S, Se) are of incessant interest because of their diversity in composition of obtained complexes, versatility of the coordination modes around the central ion and different magnetic properties of Ni^{II} containing compounds [1-6]. Overwhelming majority of these complexes contain the ligands containing two donor chalcogen atoms simultaneously (X = Y) [4-6]. Complexes of the (thio)(seleno)phosphorus ligands, containing different donor atoms are considerably less understood, especially with "hard" oxygen and "soft" sulfur or selenium atoms [1-3].

Recently, interesting features, concerning the complexation properties of N-phosphorylthioureas of common formula $RC(S)NHP(O)(OiPr)_2$ (R = p-MeOC₆H₄NH, p-BrC₆H₄NH, tBuNH, c-HexNH) (HZ) towards Ni^{II}, were found [1, 2]. It was established that thioureas HZ form 1,3-N,S-chelates with Ni^{II} cation, containing square-planar NiN2S2 complex core [1]. In the case of $\mathbf{R} = i\mathbf{Pr}$, complex of Ni(Z-N,S)₂·2HZ was obtained [2]. According to the X-ray crystal structure analysis, the neutral ligands in this complex have not interacted directly with the metal ion and being in the second sphere interacted via hydrogen bonds between the P(O)NH protons of free ligands and the P=O oxygen atoms of coordinated ligand. Application of the same synthetic procedure using thioureas $RC(S)NHP(O)(OiPr)_2$ with $R = Et_2N$, morpholine-N-yl did not result in isolation of single products. According to the IR and ¹H NMR spectra a complicated mixture of complex species were formed and it was difficult to analyze [1].

Thus, versatile coordination properties of ligands **HZ** towards Ni^{II} inspired us to continue earlier investigations. In this article *N*-diisopropoxyphosphinyl-p-bromotniobenzamide *p*-BrC₆H₄C(S)NHP(O)(O*i*Pr)₂ (**HL**) was used as a ligand. It was interesting to investigate the influence of the substituent at the thiocarbonyl fragment on the complexation properties of **HL** and **HZ**.

Results and Discussion

The ligand HL was prepared by reaction of *p*-bromothiobenzamide p-BrC₆H₄C(S)NH₂ with diisopropyl chlorophosphate (*i*PrO)₂P(O)Cl.

Complex of **HL** with the Ni^{II} (1) was prepared by the following procedure: ligand was converted into potassium salt **KL**, and followed by reaction with Ni(NO₃)₂ in aqueous EtOH in the presence of KOH (Scheme 1).

The compound obtained is crystalline solid that is soluble in most polar solvents. Reaction of the salt **KL** with Ni(NO₃)₂ in aqueous EtOH leads only to the formation of complex Ni(HL-O)₂(L-O,S)₂ (1). It was previously described that the reaction of the nonsubstituted *N*-phosphorylated thiobenzamide C₆H₅C(S)NHP(O)(OiPr)₂ (**HQ**) with Zn^{II} leads to complex Zn(Q-O,S)₂ (2), while in the case of the Cd^{II} two different complexes were formed: Cd₂(Q-O,S)₄ (3) and Cd(HQ-O)₂(Q-O,S)₂ (4) [7]. For Co^{II} three types of complexes were isolated in the reaction with the potassium salt of **HQ**: Co^{II}(Q-O,S)₂ (5), Co^{II}(HQ-O)₂(Q-O,S)₂ (6), Co^{III}(Q-O,S)₃ (7) [8].

The molecular structures of HL and complex 1 were investigated by IR, 1 H, 31 P{ 1 H} NMR spectroscopy, MALDI and elemental analysis. Crystal structure of 1 was established by single crystal X-ray diffraction analysis.



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Scheme 1 Preparation of complex 1 (R = p-BrC₆H₄)

IR spectrum of HL has shown bands of all characteristic groups. The P=O group is observed as an intense band at 1256 cm⁻¹. The band at 1504 cm⁻¹ corresponds to the S=C-N fragment. The NH group shows an absorption band at 3080 cm⁻¹.

The IR spectrum of complex 1 contains two bands for different phosphorus groups. Along with the above band corresponding to L form at 1148 cm⁻¹, a strong P=O band is observed at 1248 cm⁻¹ because of the bound neutral HL molecules. Its frequency decreased when compared to that of the band of the free ligand by 8 cm⁻¹. The absorption band of NH group at 3136 cm⁻¹ also supports the presence of HL molecules in complex 1. The conjugated SCN group exhibits an intensive band at 1543 cm⁻¹ indicating the presence of the anionic forms L⁻, whereas the S=C-N fragment of the neutral ligand HL is practically at the same area and shows at 1500 cm⁻¹.

The IR spectra of HL and complex 1 contain a very intensive band at 1008-1012 cm⁻¹ corresponding to POC group.

 ${}^{31}P{^{1}H}$ NMR spectrum of HL contains a narrow singlet signal at -5.9 ppm, which is in the region characteristic for neutral *N*-phosphorylated thioamides and thioureas [9].

The signals in the ${}^{31}P{}^{1}H$ NMR spectrum of complex 1 are absent because of strong contact or pseudocontact interactions between the paramagnetic central ion and the phosphorus atoms [4]. These pseudocontact interactions are practically absent for the protons where the dipole-dipole interactions dominate.

The ¹H NMR spectrum of complex **1** contains a double set of equal intensity signals for $(iPrO)_2P(O)$ and C_6H_4 protons. For clarity concerning OCH proton signals of complex **1**, the spectrum of **1** and **HL** was run at 2:1 molar ratio. The increase in intensities of the high-field OCH group signal and the signal for the *o*- C_6H_4 and *m*- C_6H_4 at 7.96 and 8.85 ppm, respectively, concerning the neutral **HL** form, together with the COSY spectrum of **1**, confirms the assignment made. ¹H NMR spectrum of **1** shows also signal at 11.36 ppm, corresponding to the NH group of the phosphorylamide fragment. This indicates the presence of **HL** molecules in complex **1**.

The signals in the proton spectrum of 1 are broaden because of the paramagnetic ion presence and possible partial dissociation in the solution [10]:

 $Ni(HL)_2L_2 \rightleftharpoons Ni(HL)L_2 + HL \rightleftharpoons NiL_2 + 2HL$

The MALDI mass spectrum of **HL** contains the $[M + H]^+$ molecular ion peak with the highest intensity. There are peaks with the medium intensities for the molecular ions $[M + Na]^+$ and $[M + K]^+$. The spectrum contains also $[2M + Na]^+$ structure dimeric ion peak; however, its intensity is very low.

The molecular ion peaks of $1 [M + H]^+$, $[M + Na]^+$ and $[M + K]^+$ are unstable under the same measurement conditions. Its MALDI spectrum contains all ions characteristic for $[NiL_2]$ complex core i.e. $[NiL_2 + H]^+$, $[NiL_2 + Na]^+$ and $[NiL_2 + K]^+$.

The MALDI data of 1 show propensity to dimer formation. The intensity of the $[Ni_2L_3]^+$ peak in the spectrum of complex 1 is close to 9 %. The peaks corresponding to the dimer species were also observed in the ES (electrospray) mass spectra of complexes 2–4 [7].

According to the X-ray data, the molecule of complex 1 in the crystal is located in a special position at the symmetry centre. The coordination of the Ni^{II} atom is tetragonal bipyramidal (D_{2h}) (Fig. 1).



Figure 1 Thermal ellipsoid representation of complex 1 (hydrogen atoms are omitted for clarity). Ellipsoids are drawn at the 50% probability level.

The equatorial positions of the bipyramid are occupied by two *N*-phosphoryl-*p*-bromothiobenzamide anions L^- , bonded through sulfur and oxygen atoms of thiocarbonyl and phosphoryl groups, respectively. The six-membered Ni-O-P-*N*-C-S cycle has a half-chair conformation; the O-P-*N*-C-S backbone is flat. The ligands are in *trans* configuration. Neutral ligand molecules are coordinated in the axial positions through the oxygen atoms of the phosphoryl groups. The lengths of the Ni-O bonds in the chelate rings are 2.027(3) Å and the bonds with the axial oxygen atoms are 2.111(2) Å. The phenylene ring of the anionic ligand L^- is slightly rotated relative to the plane of the SCN moiety (torsion angles are N(1)-C(1A)-C(2A)-C(7A) 16.6(3)° and S(1)-C(1A)-C(2A)-C(3A) 16.8(2)°, while in the neutral ligand the aromatic ring is considerably rotated relative to the plane of

the S=C-N group (torsion angles N(2)-C(1B)-C(2B)-C(7B) $35.6(2)^{\circ}$ and S(2)-C(1B)-C(2B)-C(3B) $33.7(2)^{\circ}$.

The character of the intramolecular hydrogen bond in complex 1 differs from the compounds 4 and 6. There are two intramolecular NH···O bonds between the oxygen atom of the P=O group of the anionic ligand L⁻ and the hydrogen atom of the NH fragment of the neutral ligand HL in the crystal of complex 1, while in isostructural complexes 4 and 6 the intramolecular NH···S bonds are formed by the sulfur atom of the P=S group of the anionic ligand L⁻. The hydrogen bond parameters in the molecule are as follows: N(2)-H(2)···O(11) (-x+1, -y+1, -z+1), d(N-H) 0.79 Å, $d(H \cdots O) 2.04$ Å, $d(N \cdots O) 2.808(2)$ Å, $\angle (N-H \cdots O) 162^{\circ}$.

In summary, a novel Ni^{II} complex has been successfully synthesized. Complex obtained is the first example of Ni^{II} with the asymmetric RC(S)NHP(O)(O*i*Pr)₂ ligand. The distinction in kind of the hydrogen bond formation in a crystal of complex **1**, can be consequence of the influence of the substituent steric size (*p*-BrC₆H₄ *vs*. Ph) on the packing of molecules in a crystal.

Experimental Section

Physical measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400-3600 cm⁻¹. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ¹H and ³¹P{¹H} spectra were recorded at 299.948 and 75.429 MHz, respectively. Chemical shifts are reported with reference to SiMe₄ (¹H) and H₃PO₄ (³¹P{¹H}). MALDI mass spectra of **HL** and **1** were obtained using a Bruker Reflex IV spectrometer, and elemental analyses were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster, Germany. Elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyser.

Data collection and refinement for Ni(HL₂)L₂ (1)

Crystals of 1 were obtained by slow evaporation of the solvent from dichloromethane/*n*-hexane solutions of complex. $C_{52}H_{74}Br_4N_4Ni$ - $O_{12}P_4S_4$, $M_r = 1577.67$ g mol⁻¹, yellow blocks, orthorhombic, space group *Pbca a* = 12.738(3) Å, *b* = 22.288(5) Å, *c* = 23.475(6) Å, *V* = 6665(3) Å³, $\rho = 1.572$ g cm⁻³, μ (Mo- K_{α}) = 2.968 mm⁻¹. The X-ray intensity data were measured at 100(2) K on a KM4CCD diffractometer and graphite-monochromatied Mo- K_{α} radiation generated by middle-focus X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated and scaled using the KUMA data reduction package. The unit cell parameters were refined. The structure was solved by direct method using SHELIXX-97 [11] program. Hydrogen atoms were placed in the calculated positions and were refined using riding model except H2 witch was located on difference map. The numbering of the atoms is shown in Fig. 1 (ORTEP) [12].

Synthesis of p-BrC₆H₄C(S)NHP(O)(OiPr)₂ (HL)

A suspension of *p*-bromothiobenzamide (0.65 g, 3 mmol) in anhydrous dimethyl sulfoxide (50 mL) and benzene (100 mL) was mixed with potassium hydroxide (3.36 g, 60 mmol) for 2 h and then cooled till 2 °C. A benzene (40 mL) solution of diisopropyl chlorophosphate (0.6 g, 3 mmol) was added dropwise under vigorous stir-

ring to the resulting potassium salt. The mixture was stirred at 2-4 °C for a further 3 h and left overnight at room temperature. To the obtained suspension deionized water (100 mL) was added. Water phase was separated and treated with HCl (0.1 N solution) till reaching pH 4–5. The resulting product was extracted with benzene and dried with anhydrous MgSO₄. The solvent was then removed in vacuo. An orange precipitate was isolated from dichloromethane by *n*-hexane. Yield: 0.72 g (63 %). M.p. 134 °C. C₁₃H₁₉BrNO₃PS (380.24): calcd. C 41.06, H 5.04, N 3.68; found: C 41.13, H 4.97, N 3.76 %.

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Synthesis of Ni(HL)₂L₂ (1)

A suspension of **HL** (1.91 g, 5 mmol) in aqueous ethanol (20 mL) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 mL) solution of Ni(NO₃)₂· 6H₂O (0.81 g, 2.8 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with dichloromethane, washed with water and dried with anhydrous MgSO₄. The solvent was then removed in vacuo. The residue was recrystallised from a dichloromethane/*n*-hexane mixture. Complex **1** was obtained as orange crystals. Yield: 1.42 g (72 %). M.p. 159 °C. $C_{52}H_{74}Br_4N_4NiO_{12}P_4S_4$ (1577.63): calcd. C 39.48, H 4.79, N 3.53; found: C 39.62, H 4.70, N 3.65 %.

¹H NMR (CDCl₃): $\delta = 0.76$ (br. s, 12 H, CH₃, HL), 0.76 (br. s, 12 H, CH₃, HL), 0.94 (br. s, 12 H, CH₃, L⁻), 1.79 (br. s, 12 H, CH₃, L⁻), 1.87 (br. s, 12 H, CH₃, L), 3.73 (br. s, 4 H, OCH, HL), 5.04 (br. s, 4 H, OCH, L⁻), 7.31 (br. s, 4 H, *m*-H, C₆H₄, HL), 9.06 (br. s, 4 H, *m*-H, C₆H₄, HL), 8.85 (br. s, 4 H, *o*-H, C₆H₄, HL), 9.06 (br. s, 4 H, *o*-H, C₆H₄, L⁻), 11.36 (br. s, 2 H, NH). ³¹P{¹H} NMR (CDCl₃): the signal is absent because of extremely broadening. IR: $v^- = 1012$ (POC), 1148 (P=O, L⁻), 1248 (P=O, HL), 1500 (S=C-N, HL), 1543 (SCN, L⁻), 3136 (NH) cm⁻¹. MS (MALDI): *mlz* (%) = 819 (27) [NiL₂ + H]⁺, 841 (63) [NiL₂ + Na]⁺, 857 (100) [NiL₂ + K]⁺, 1257 (9) [Ni₂L₃]⁺.

CCDC 661321 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via **http://www.ccdc.cam.ac.uk/conts/retrieving.html**, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail deposit@ccdc.cam.ac.uk.

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