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Synthesis, physicochemical properties and crystal structure of isothiocianato [2-(diphenylphosphino)benzaldehyde selenosemicarbazonato(1⁻)] nickel(II)

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Abstract

The syntheses of a new ligand 2-(diphenylphosphino)benzaldehyde selenosemicarbazone (HL) and the corresponding complex with Ni(II) of the formula [Ni(L)(NCS)] are reported. The complex was characterized by single crystal X-ray analysis. The compound complex is diamagnetic and has a markedly deformed square-planar structure with PNSe set of donor atoms of the ligand, the Schiff base monoanion, and the N atom of the coordinated NCS group. The phosphorus atom deviates even by 0.494(3) Å from the mean plane defined by the other coordination atoms (NSeN) and the metal atom. © 2003 Published by Elsevier B.V.

Keywords: Nickel(II) complex; 2-(Diphenylphosphino)benzaldehyde selenosemicarbazone; Crystal structure; IR spectra; Deformed coordination geometry

1. Introduction

The coordination chemistry of thiosemicarbazides and their derivatives began in the 30s of the last century with the works of Jensen and co-workers [1,2]. Because of their good complexation properties, wide spectrum of biological activity, and the application as analytical reagents, these compounds and their metal complexes have become subject of intensive study of a large number of authors [3–8]. Hence it is not surprising that there appeared a lot of papers, among them hundreds of works dealing with the elucidation of crystal and molecular structures of these compounds. In contrast to them, the number of works devoted to selenosemicarbazide and selenosemicarbazones and their metal complexes is much smaller, and only crystalline structures of two complexes with this class of ligands have been reported [9,10].

In our previous works [11,12] we described the crystal and molecular structures of Ni(II) and Cu(I) complexes with the tridentate PNS ligand, 2-(diphenylphosphino)benzaldehyde thiosemicarbazone. In this work we present the crystal and molecular structure of the square-planar Ni(II) complex with the monoanion 2-(diphenylphosphino)benzaldehyde selenosemicarbazone (HL) (Fig. 1) of the formula [Ni(L)(NCS)], as the first example of a complex synthesized with selenosemicarbazone derivatives as ligands and involving phosphorus as one of the ligator atoms.

Synthesis of the ligand HL. A mixture of 0.58 g (2 mmol) of 2-(diphenylphosphino)benzaldehyde and 0.28 g (2 mmol) of selenosemicarbazide, both prepared

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Fig. 1. Structural formula of 2-(diphenylphosphino)benzaldehyde selenosemicarbazone (HL).

according to the previously described procedures [13,14], was dissolved at heating in a mixture of EtOH (10 cm³) and glacial acetic acid (3 cm³); the heating being continued at stirring for 10 min. The yellow needle-like crystals of the ligand, that appeared still in the warm solution, were separated after 5 h by filtration and washed with EtOH and Et₂O. Yield: 0.61 g (74%). Anal. Calcd. for C₂₀H₁₈N₃PSe (M = 410.30 g mol⁻¹): C, 58.54; H, 4.42; N, 10.24%. Found: C, 58.35; H, 4.50; N, 10.43%.

Synthesis of the complex [Ni(L)(NCS)]. A mixture of 0.17 g (0.6 mmol) of Ni(NO₃)₂ · 6H₂O and 0.20 g (0.5 mmol) of HL was poured over with MeOH (10 cm³) and heated. To the red solution, 0.10 g (1 mmol) of KNCS was added and heated for 2–3 min. Along with KNO₃, red thin needle-like crystals appeared already in the warm solution. In the mother liquor, in the course of 10 h, the latter completely transformed into brown monocrystals of title complex. The crystals were filtered, the precipitated KNO₃ removed by washing with water, and the complex was dried on the filter by washing with MeOH and Et₂O. Yield: 0.20 g (78%). Anal. Calcd. for C₂₁H₁₇N₄Ni PS Se (M = 526.06 g mol⁻¹): C, 47.94; H, 3.26; N, 10.65%. Found: C, 48.02; H, 3.41; N, 10.51%.

The X-ray experimental data were collected on an Enraf-Nonius CAD4 diffractometer [15] by using graphite-monochromated Mo K α (0.71073 Å) radiation at 293(2) K. A total of 6421 reflections (in 1.64–29.97° θ range) were collected by using $\omega/2\theta$ scans. The data were corrected for Lorentz and polarization effects [16]. A gaussian-type absorption correction [17,18] based on the crystal morphology was applied ($T_{min} = 0.543$, $T_{max} = 0.673$; single-crystal dimensions were 0.29 × 0.18 × 0.18 mm). Crystallographic data: formula C₂₁H₁₇ N₄NiPSSe, $F_w = 526.06$, triclinic, space group = $P\overline{1}$, a = 9.430(2) Å, b = 9.688(2) Å, c = 12.894(2) Å, $\alpha = 77.67(2)^\circ$, $\beta = 77.29(2)^\circ$, $\gamma = 74.55(2)^\circ$, V = 1092.4(4) Å³, Z = 2, $D_c = 1.599$ g cm⁻³, $\mu = 2.737$ mm⁻¹.

The structure was solved by the heavy atom method [19a] and difference Fourier methods and refined on F^2 by full-matrix least-square method [19b] to $R_1 = 0.0404$ and $wR_2 = 0.0842$ for 262 refined parameters and 3335 reflections with $I > 2\sigma(I)$. Almost all H atoms were

found in difference Fourier maps but they were placed at calculated positions using a riding model and isotropic displacement parameters were set equal to 1.2 times the equivalent isotropic displacement parameter of the parent atoms. Details of the crystal structure analysis, full tables of atomic positions, bond lengths, angles, anisotropic thermal parameters for nonhydrogen atoms, hydrogen coordinates and their respective isotropic displacement parameters, torsion angles and hydrogen bonds are available from the corresponding author on request.

Elemental (C, H, N) analysis of air-dried compounds was carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade. Molar conductivity of freshly-prepared 1×10^{-3} M solution in DMF was measured on a Jenway 4010 conductivity meter. FT-IR spectra (KBr disc) were run on a Perkin–Elmer FT-IR 31725X.

2. Results and discussion

The ligand HL was obtained in a good yield by the reaction of mildly acidic (AcOH) warm EtOH solutions of the stoichiometric amounts of 2-(diphenylphosphino)benzaldehyde and selenosemicarbazide. The realization of the condensation reaction, apart from the elemental analysis, was also confirmed by the absence of the v(C=O) band in the spectrum of the ligand, which in the spectrum of the aldehyde precursor is observed as a very strong doublet at 1696 and 1677 cm^{-1} [13] and by the appearance of a strong $v(C=N) + \delta$ (NH₂) band at 1577 cm⁻¹ [20]. The absence of the v(Se–H) band at 2300 cm^{-1} [21] speaks in favor of a non-enolized form of the ligand in its crystalline state. The obtained ligand is soluble in DMF and DMSO and sparingly soluble in MeOH and EtOH. Brown monocrystals of title [Ni(L)(NCS)] complex were obtained by the reaction of Ni(NCS)₂ with the ligand in a warm MeOH. The isolated complex is diamagnetic, suggesting its squareplanar structure, which was confirmed by X-ray analysis (vide infra). This analysis showed that square-planar surroundings of the nickel atom are formed by the tridentate PNSe coordination of the ligand monoanion and the coordinated monodentate isothiocyanato group (Fig. 2). This mode of ligand coordination was also confirmed by the IR spectra. First of all, in the ligand spectrum, in the region of the $v(NH_2/NH)$ vibrations, there are three bands of medium intensity at 3431, 3288 and 3138 cm⁻¹ which can be ascribed to the $v_{as/s}(NH_2)$ and v(NH) vibrations, respectively. In contrast to this, the spectrum of the complex has in the same range only two bands, at 3280 and 3177 cm⁻¹, corresponding to the $v_{a/s}(NH_2)$ vibrations, which, due to intermolecular hydrogen bonds (Fig. 2), are shifted to lower energies.



Fig. 2. ORTEP [7] drawing of complex dimer with atom numbering scheme. The thermal ellipsoids correspond to 50% probability. Symmetry code: (i) -x + 1, -y, -z + 1. Selected bond lengths (Å) and angles (°): Ni–N4 1.827(3), Ni–N1 1.898(2), Ni–P 2.1791(9), Ni–Se 2.2692(6), Se–C1 1.862(3), P–C4 1.796(3), P–C16 1.814(3), P–C10 1.823(4), S–C9 1.600(4), N1–C2 1.299(4), N1–N2 1.404(3), N2–C1 1.303(4), N3–C1 1.338(4), N4–C9 1.150(4), C2–C3 1.449(4), C3–C4 1.404(4), N4–Ni–N1 174.99(13), N4–Ni–P 90.11(10), N1–Ni–P 93.80(8), N4–Ni–Se 87.32(9), N1–Ni–Se 89.44(8), P–Ni–Se 168.67(3), N4–C9–S 177.5(4).

The v(C=N) band of a medium intensity in the spectrum of the complex, due to the effect of nitrogen coordination, is shifted to higher energies [20,22,23] and is observed at 1629 cm⁻¹. As a consequence of the coordination of the selenium atom the v(C-Se) band is shifted to lower energies [24,25], from 760 to 713 cm⁻¹. In contrast to the v(C=N) and v(C-Se) bands, the position of the v(C-P) band after the phosphorus coordination remains practically unchanged (~1434 cm⁻¹) [20]. Especially strong intensity shows the v(CN) band of the coordinated isothiocyanato group, observed at 2109 cm⁻¹ [26]. The isothiocyanato group remains coordinated in DMF solutions too, which is evident from the very low value of the molar conductivity ($\lambda_M = 7.2$ S cm²mol⁻¹).

In the crystal structure of [Ni(L)(NCS)] Ni is found in a square-planar environment of the P, N1 and Se atoms of the monoanion of the selenosemicarbazone ligand and of the isothiocyanato group nitrogen (Fig. 2). The chelate Schiff base forms with Ni two fused rings, one of which [(2-diphenylphosphino)benzaldehyde] is sixmembered and the other (selenosemicarbazide) fivemembered. The square-planar structure is markedly distorted. Namely, the phosphorus atom deviates from the mean plane defined by the NiN4SeN1 atoms even by 0.494(3) A. It should be noticed that the NiN4SeN1 atoms that define the plane are approximately co-planar, with the mean deviation from the plane of 0.026 A. This structural deformation can be explained by the participation of the phosphorus atom in the formation of the six-membered chelate ring. Namely, the N1, C2, C3, C4 atoms forming this ring are sp^2 -hybridized and consequently they favor a planar form of the ring. Thus, the Ni-N1-C2-C3 and N1-C2-C3-C4 torsion angles are $2.2(6)^{\circ}$ and $11.1(6)^{\circ}$, respectively. Planar form of the six-membered ring would also make possible position of the phosphorus atom in an approximately same plane with the other coordination atoms (N1, Se, N4) so that

the square-planar geometry would be of a regular form. However, since the phosphorus atom in the molecule forms four bonds, the preferred angle between these bonds would be about 109°, which is in contrast to the planar form of the ring, requiring the angle Ni–P–C4 to be about 125° [27]. A consequence of this is that the phosphorus atom is protruding out from the ring plane, attaining thus an Ni–P–C4 angle of 112.63(11)°, and distorting drastically the square-planar surroundings around Ni [the N1–Ni–P–C4 torsion angle is 29.63(2)°]. The mutual positions of the atoms in coordination are visible from Fig. 3.

Similar deformation of the square-planar surroundings of Ni(II) has also been found in the structure of its complex with the analogous thiosemicarbazone ligand [11]. In these two structures the Ni-P and Ni-N1 bonds are practically identical. In contrast to these bonds, the Ni-Se bond in our complex [2.2692(6) A] is somewhat longer than the same in the square-planar Ni(II) complex with the dianionic salicylaldehyde selenosemicarbazone [9] where the Ni–Se bond distance is 2.241(2) Å. The molecules are bound into dimers (Fig. 2), forming two N3-H···N2 intermolecular hydrogen bonds: N3- $H = 0.86 \text{ Å}, N3 \cdots N2^{i} = 3.005(4) \text{ Å}, H \cdots N2^{i} = 2.17 \text{ Å},$ $N3-H \cdot \cdot \cdot N2^{i} = 163.8(2)^{\circ}$; symmetry code: (i) -x + 1, -y, -z+1. The N3H₂ group forms also another intermolecular hydrogen bond with sulfur atom of the NCS N3–H = 0.86 Å, N3···Sⁱⁱ = 3.375(4) group: A. $H \cdot \cdot \cdot S^{ii} = 2.54$ Å, $N3 - H \cdot \cdot \cdot S^{ii} = 162.6(2)^{\circ}$; symmetry code: (ii) -x, -y+1, -z+1. Apart from those already



Fig. 3. View of complex fragment showing the coordination geometry and chelate rings conformation. Displacement ellipsoids are shown at the 20% probability level and H atoms are omitted for clarity.

mentioned, there are no other significant hydrogen bonds or intermolecular interactions.

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- [27] Planar six-membered chelate rings of the composition $M-A_1-A_2-A_3-A_4-A_5$ (where the A_n atoms are most often N,O,C sp²-hybridized; A_1 and A_5 are coordinated to M) have different bond distances ($M-A_1$ and $M-A_5$ are significantly longer than the bonds between A_n atoms). As a consequence the six-membered chelate rings in their planar form deviate significantly from regular hexagones. Thus some of bond angles inside of the ring deviate significantly from 120° and so A_1-M-A_5 angle is about 95° in average, while the $M-A_1-A_2$ and $M-A_5-A_4$ angles are most often about 125°.