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## CRYSTAL STRUCTURES OF AZIDO OR THIOCYANATO-COORDINATED NICKEL(II) COMPLEXES WITH TRIDENTATE SCHIFF BASES

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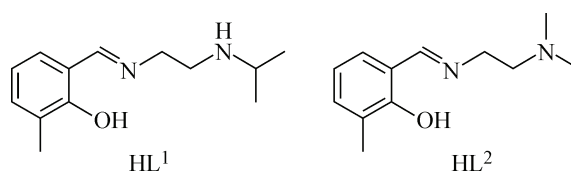
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A new azido-coordinated nickel(II) complex  $[\text{NiL}^1(\text{N}_3)]$  (**1**) and a new thiocyanato-coordinated nickel(II) complex  $[\text{NiL}^2(\text{NCS})]$  (**2**), where  $\text{L}^1$  and  $\text{L}^2$  are the monoanionic forms of Schiff bases 2-[(2-isopropylaminoethylimino)methyl]-6-methylphenol and 2-[(2-dimethylaminoethylimino)methyl]-6-methylphenol respectively, are prepared and structurally characterized by elemental analysis, IR spectra, and single crystal X-ray crystallography. Complex **1** crystallizes in the triclinic space group  $P\bar{1}$  with unit cell dimensions  $a = 8.812(2) \text{ \AA}$ ,  $b = 9.433(3) \text{ \AA}$ ,  $c = 9.488(2) \text{ \AA}$ ,  $\alpha = 81.933(2)^\circ$ ,  $\beta = 69.925(2)^\circ$ ,  $\gamma = 84.591(2)^\circ$ ,  $V = 732.5(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $R_1 = 0.0291$ , and  $wR_2 = 0.0734$ . Complex **2** crystallizes in the monoclinic space group  $P2_1/n$  with unit cell dimensions  $a = 7.4497(4) \text{ \AA}$ ,  $b = 6.1933(3) \text{ \AA}$ ,  $c = 31.5126(18) \text{ \AA}$ ,  $\beta = 92.484(2)^\circ$ ,  $V = 1452.57(13) \text{ \AA}^3$ ,  $Z = 4$ ,  $R_1 = 0.0307$ , and  $wR_2 = 0.0668$ . The Ni atom in each of the complexes is coordinated by three donor atoms of the Schiff base ligand and by one N atom of the azide or thiocyanate ligand, forming a square planar geometry. The azide and thiocyanate anions readily coordinate to the complexes as secondary ligands.

**Keywords:** Schiff base, nickel complex, azide, thiocyanate, crystal structure.

## INTRODUCTION

The Schiff bases derived from salicylaldehyde and its derivatives are a kind of versatile ligands in coordination chemistry [1–3]. Nickel complexes with such Schiff bases have been proved to have diverse properties, such as magnetism [4, 5], catalyst [6, 7] and biological activities [8–10]. As is well known, azide and thiocyanate are two charming ligands for the construction of polymeric structures [11–14]. The search in the Cambridge Crystallographic Database (CSD; version 5.32 with addenda up to February 2012) [15] has revealed that no complexes derived from 2-[(2-isopropylaminoethylimino)methyl]-6-methylphenol ( $\text{HL}^1$ ; Scheme 1) and 2-[(2-dimethylaminoethylimino)methyl]-6-methylphenol ( $\text{HL}^2$ ; Scheme 1) have been reported, and even very few complexes have been reported based on the Schiff bases derived from 3-methylsalicylaldehyde. In this paper, a new azido-coordinated nickel(II) complex  $[\text{NiL}^1(\text{N}_3)]$  (**1**) and a new thiocyanato-coordinated nickel(II) complex  $[\text{NiL}^2(\text{NCS})]$  (**2**) were prepared and characterized.

Scheme 1. The Schiff base  $\text{HL}^1$  and  $\text{HL}^2$

## EXPERIMENTAL

**Materials and measurements.** Starting materials, reagents, and solvents with analytical grade were purchased from commercial suppliers and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on a Jasco FT/IR-4000 spectrometer as KBr pellets in the 4000—200  $\text{cm}^{-1}$  region. Single crystal structural X-ray diffraction was carried out on a Bruker X8 PROTEUM diffractometer.

**Synthesis of HL<sup>1</sup>.** To the methanolic solution (20 ml) of 3-methylsalicylaldehyde (1.0 mmol, 0.14 g) was added a methanolic solution (20 ml) of *N*-isopropylethane-1,2-diamine (1.0 mmol, 0.10 g) with stirring. The mixture was stirred for 30 min at room temperature to give a yellow solution. The solvent was evaporated to give a yellow gummy product of the Schiff base. Characteristic IR data: 1639  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}$ : C, 70.9; H, 9.2; N, 12.7. Found: C, 70.7; H, 9.2; N, 12.8%.

**Synthesis of HL<sup>2</sup>.** HL<sup>2</sup> was synthesized by the similar method as that described for HL<sup>1</sup>, with *N*-isopropylethane-1,2-diamine replaced by *N,N*-dimethylethane-1,2-diamine (1.0 mmol, 0.09 g). Characteristic IR data: 1638  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}$ : C, 69.9; H, 8.8; N, 13.6. Found: C, 69.6; H, 8.9; N, 7.8%.

**Synthesis of the complexes.**  $[\text{NiL}^1(\text{N}_3)]$  (**1**): To the methanolic solution (5 ml) of HL<sup>1</sup> (0.1 mmol, 0.022 g) was added a methanolic solution (5 ml) of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.1 mmol, 0.025 g) and an aqueous solution (1 ml) of sodium azide (0.1 mmol, 0.007 g) with stirring. The mixture was stirred for 30 min at room temperature and filtered. Red block-shaped crystals of **1**, suitable for the X-ray crystal structural determination, formed from the filtrate after a few days. The crystals were isolated by filtra-

Table 1

Crystallographic and experimental data for **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	$\text{C}_{13}\text{H}_{19}\text{N}_5\text{NiO}$	$\text{C}_{13}\text{H}_{17}\text{N}_3\text{NiOS}$
$M_r$	320.0	322.1
$T$ , K	298(2)	298(2)
Crystal shape/color	Block/red	Block/red
Crystal size, mm	0.23×0.22×0.20	0.10×0.07×0.06
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2_1/n$
$a$ , $b$ , $c$ , Å	8.812(2), 9.433(3), 9.488(2)	7.4497(4), 6.1933(3), 31.5126(18)
$\alpha$ , $\beta$ , $\gamma$ , deg.	81.933(2), 69.925(2), 84.591(2)	90, 92.484(2), 90
$V$ , Å <sup>3</sup>	732.5(3)	1452.57(13)
$Z$	2	4
$D_c$ , $\text{g} \cdot \text{cm}^{-3}$	1.451	1.473
$\mu(\text{MoK}\alpha)$ , $\text{mm}^{-1}$	1.327	1.474
$F(000)$	336	672
Independent / Observed reflections ( $I \geq 2\sigma(I)$ )	2666 / 2445	2494 / 2410
Min. and max. transmission	0.750 and 0.777	0.867 and 0.917
Parameters	187	175
Restraints	1	0
Goodness-of-fit on $F^2$	1.057	1.237
$R_1$ , $wR_2$ [ $I \geq 2\sigma(I)$ ] <sup>a</sup>	0.0291, 0.0734	0.0307, 0.0668
$R_1$ , $wR_2$ (all data) <sup>a</sup>	0.0324, 0.0762	0.0323, 0.0675

<sup>a</sup>  $R_1 = F_0 - F_c / F_0$ ,  $wR_2 = [\sum w(F_0^2 - F_c^2) / \sum w(F_0^2)]^{1/2}$ .

Table 2

Selected bond lengths (Å) and angles (deg.) for **1** and **2**

<b>1</b>				<b>2</b>			
Ni1—O1	1.833(2)	O1—Ni1—N1	95.0(1)	Ni1—O1	1.833(2)	O1—Ni1—N1	94.4(1)
Ni1—N2	1.919(2)	O1—Ni1—N3	90.2(1)	Ni1—N2	1.946(2)	O1—Ni1—N3	88.4(1)
Ni1—N1	1.843(2)	N1—Ni1—N3	174.8(1)	Ni1—N1	1.844(2)	N1—Ni1—N3	173.8(1)
Ni1—N3	1.899(2)	O1—Ni1—N2	178.0(1)	Ni1—N3	1.880(2)	O1—Ni1—N2	179.2(1)
		N1—Ni1—N2	86.6(1)			N1—Ni1—N2	86.2(1)
		N3—Ni1—N2	88.1(1)			N3—Ni1—N2	91.0(1)

tion, washed three times with methanol and dried in air. Yield 63 %. Characteristic IR data ( $\text{cm}^{-1}$ ): 3208 (sh), 2050 (vs), 1623 (s). Anal. Calc. for  $\text{C}_{13}\text{H}_{19}\text{N}_5\text{NiO}$ : C, 48.8; H, 6.0; N, 21.9. Found: C, 48.7; H, 5.9; N, 21.7%.

$[\text{NiL}^2(\text{NCS})]$  (**2**): Complex **2** was synthesized by the similar method as that described for **1**, with sodium azide replaced by ammonium thiocyanate (0.1 mmol, 0.008 g), and with  $\text{HL}^1$  replaced by  $\text{HL}^2$  (0.1 mmol, 0.021 g). Red small block-shaped single crystals of **2** formed. Yield 72 %. Characteristic IR data ( $\text{cm}^{-1}$ ): 2107 (vs), 1623 (s). Anal. Calc. for  $\text{C}_{13}\text{H}_{17}\text{N}_3\text{NiOS}$ : C, 48.5; H, 5.3; N, 13.0. Found: C, 48.3; H, 5.4; N, 13.1%.

**X-ray crystallography.** Diffraction intensities for the complexes were collected at 298(2) K using a Bruker X8 PROTEUM diffractometer with  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The collected data were reduced with the SAINT program [16], and multi-scan absorption correction was performed using the SADABS program [17]. The structures were solved by direct methods. The complexes were refined against  $F^2$  by full-matrix least-squares method using the SHELXTL package [18]. All of the non-hydrogen atoms were refined anisotropically. The amino H atom in **1** was located from a difference Fourier map and refined isotropically, with the N—H distance restrained to 0.90(1) Å. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

## RESULTS AND DISCUSSION

**Structure description of the complexes.** Single crystal X-ray diffraction shows that the complexes crystallize as similar azido- or thiocyanato-coordinated mononuclear structures (Fig. 1 for **1**, Fig. 2 for **2**). The Ni atom in each of the complexes is in a square planar coordination environment and is four-coordinated by one phenolate O and two N atoms of the Schiff base ligand and by one N atom of a pseudohalide ligand (azide for **1** and thiocyanate for **2**). A slight distortion of the square planar coordination is revealed by the bond angles.

The perpendicular coordinate bond angles range from 86.6(1)° to 95.0(1)° for **1**, and from 86.2(1)° to 94.4(1)° for **2**. The *trans* bond angles are 174.8(1)° and 178.0(1)° for **1**, and 173.8(1)° and 179.2(1)° for **2**. The deviation of Ni atoms from the best fit square planes are 0.005(2) Å for **1** and 0.050(2) Å for **2**. The Ni—O and Ni—N bond lengths in both com-

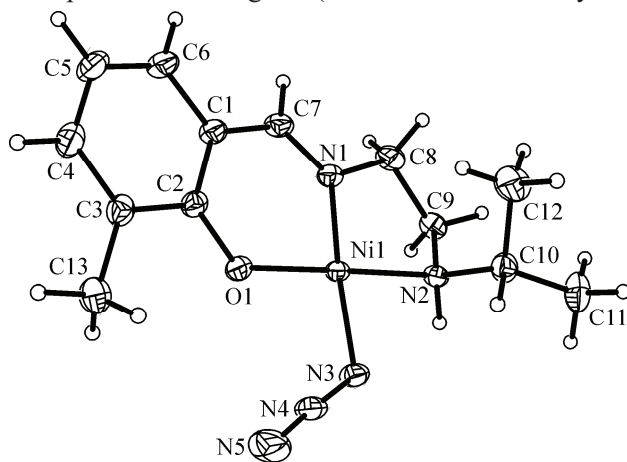


Fig. 1. A perspective view of the molecular structure of **1** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30 % probability level

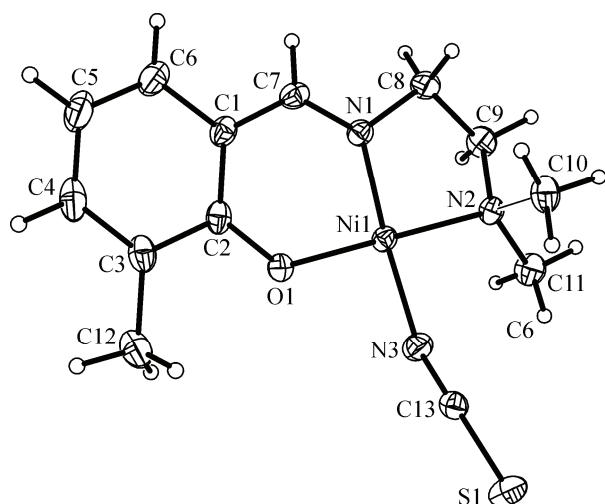


Fig. 2. A perspective view of the molecular structure of **2** with the atom labeling scheme. The thermal ellipsoids are drawn at the 30 % probability level

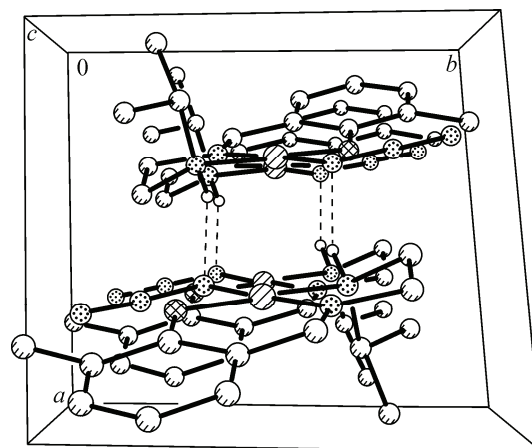


Fig. 3. Packing structure of **1**

plexes are comparable to each other, and are also comparable to those observed in other Schiff base nickel(II) complexes [ 19, 20 ]. The azide and thiocyanate bridging groups are nearly linear and show bent coordination mode with the Ni atoms [for **1**:  $N3-N4-N5/Ni1-N3-N4 = 176.5(2)/122.1(2)^\circ$ ; for **2**:  $N3-C13-S1/Ni1-N3-C13 = 179.1(2)/162.4(2)^\circ$ ].

In the crystal structure of **1**, the adjacent two complex molecules are linked through two intermolecular  $N-H\cdots N$  hydrogen bonds, to form a dimer (Fig. 3). In the crystal structure of **2**, the complex molecules are stacked along the *a* axis with no obvious short contacts (Fig. 4).

**IR spectra.** In the IR spectra of the complexes, the strong absorption bands at  $1623\text{ cm}^{-1}$  can be assigned to the azomethine stretching frequencies of the Schiff base ligands, whereas for the free Schiff base the corresponding band is observed at about  $1638\text{ cm}^{-1}$ . The shift of these bands toward lower frequencies on complexation suggests the coordination to Ni atoms through the imine N atoms. The  $\nu(C-O)$  mode is present as middle bands at about  $1230\text{ cm}^{-1}$  for the complexes. The intense band at  $2050\text{ cm}^{-1}$  for **1** and  $2107\text{ cm}^{-1}$  for **2** are assigned to the stretching vibration of the azide ligand in **1** and the thiocyanate ligand in **2** respectively. The weak bands indicative of the Ni—O and Ni—N bonds are located in the region  $550-350\text{ cm}^{-1}$ .

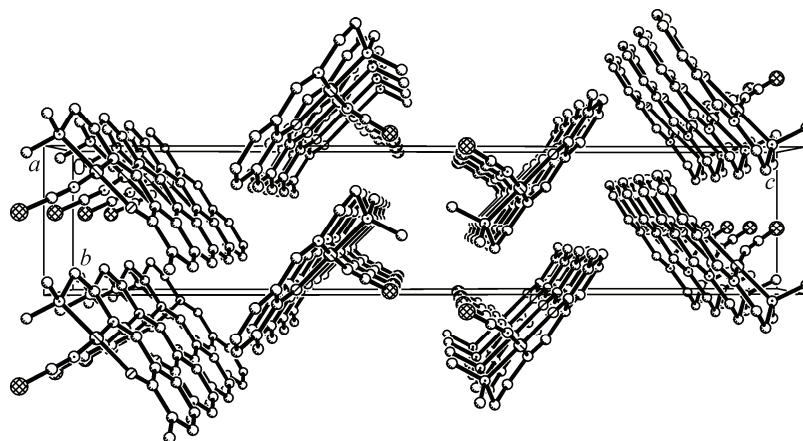


Fig. 4. Packing structure of **2**

**Supplementary data.** CCDC 879634 (**1**) and 879635 (**2**) contain the supplementary crystallographic data for this paper. 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](mailto:deposit@ccdc.cam.ac.uk).

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