

# Synthesis, characterization and X-ray study of (Methyl-2-((E)-2-hydroxy-5-((E)-*p*-tildiazenyl)benzylideneamino)ethylamino)cyclopent-1-ene carbodithioato)nickel(II) complex

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**Abstract.** A novel tetradentate ligand with NN'OS coordination spheres was prepared and then the corresponding nickel(II) complex was synthesized. The ligand and the complex were characterized by elemental analyses, IR, and <sup>1</sup>HNMR spectroscopy. The structure of (Methyl-2-((E)-2-hydroxy-5-((E)-*p*-tildiazenyl)benzylideneamino)ethylamino)cyclopent-1-ene carbodithioato)nickel(II) has been determined by X-ray crystallography. The X-ray results confirm that the geometry of the complex is slightly distorted square-planar structure. The nickel(II) ion coordinate to two nitrogen atoms from the imine moiety of the ligand, a sulfur atom from the methyl dithiocarboxylate moiety and a phenolic oxygen atom.

**Keywords:** Schiff base complexes; X-ray crystal structure; Azo compounds; Asymmetry complexes; Nickel(II) complexes.

## 1. Introduction

There is a continuing interest in transition metal complexes of unsymmetrical Schiff bases because of the presence of hard oxygen, nitrogen and soft sulphur donor atoms in the backbones of these ligands. Some of these complexes have been exhibit interesting physical and chemical properties [1] and potentially useful biological activities [2]. Also, these transition metal complexes are used in clinical [3] and analytical fields [4] and as model molecules for biological oxygen carrier systems [5]. Tetradentate Schiff base complexes are well known to form stable complexes, where the coordination takes place through the NN'OS donor set [6]. The number of the Schiff bases derived from condensation of various aldehyds with methyl-2-{N-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) and their transition metal complexes with Ni(II) have been reported in the literature [7]. In this paper, we report a synthetic approach and structural characterization of a Schiff base derived from condensation of azo-containing aldehyde with Hcden complex with Nickel(II).

## 2. Experimental

### 2.1. Synthesis of Methyl-2-{N-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate

Hcden was prepared by published method [8].

### 2.2. Preparation of (E)-2-hydroxi-5-(para-tolildiazenyl)benzaldehyde. (4)

Azo dye 1a was synthesized according to the well-known literature procedure [9]. A mixture of 1.38 g (10 mmol) of 4-methylaniline in 36 ml of hydrochloric acid, and 16 ml of water was heated to 70 °C to complete solution. The clear solution was poured into an ice-water mixture, and was diazotized between 0 °C

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and 5 °C with 0.69 g (10 mmol) of sodium nitrite dissolved in 5 ml of water. The cold diazo solution was added to the solution of 1.07 ml (10 mmol) of salicylaldehyde in 19 ml of water containing 0.4 g (10 mmol) sodiumhydroxide and 4.23 g (40 mmol) of sodium carbonate during the period of 30 min at 0 °C. during the adding process, the diazo solution was vigorously stirred. The product was collected by filtration and washed with 100 ml of NaCl solution (10%) under vacuum. Then, the solid was dried under vacuum at 80 °C overnight. The purity of the compound was controlled by TLC (n-hexane:ethylacetate/60:40).

$C_{14}H_{12}O_2N_2$ , Yield: 75%. m.p 150-152 °C . *Anal.* Calc. for  $C_{14}H_{12}O_2N_2$ : C, 69.99; H, 5.03; N, 11.66. Found: C, 70.03; H, 5.08; N, 11.57%. IR (KBr,  $cm^{-1}$ ): 3182  $\nu$ (O-H), 1656  $\nu$ (C=O), 1619  $\nu$ (C=C), 1573  $\nu$ (-N=N-, *cis* and *trans*), 1479 (Phenol ring), 1278  $\nu$ (C-O), 1171, 1106, 849, 764.  $^1H$  NMR  $\delta$  (500MHz;  $CDCl_3$ ): 2.46 (3H, s), 7.13 (1H, s), 7.35 (2H, d), 7.83 (2H, d), 8.17 (1H, s), 8.19 (1H, s), 10.03 (CHO, s), 11.33 (OH, s).

### 2.3. Synthesis of Schiff base Methyl2-(2-((E)-2-hydroxy-5-((E)-para-tolildiazenyl)benzylidenamino)ethyleamino)cyclopent-1-ene-carbodithioate (6)

Methyl2-(2-((E)-2-hydroxy-5-((E)-*para*-tolildiazenyl)benzylidenamino)ethyleamino)cyclopent-1-ene-carbodithioate was prepared by addition 0.24 g (1 mmol) of the (E)-2-hydroxi-5-(*para*-tolildi azenyl)benzaldehyde in 10 ml methanol to a methanolic solution of 0.22 g (1 mmol) Hcden. The mixture was stirred for about 30 min and allowed to react at room temperature for about 24 h. The red powder was recrystallized from chloroform/methanol (1:1) v/v solution.

$C_{23}H_{26}N_4OS_2$ , Yield: 70%. m.p: 170 °C. *Anal.* Calc. for  $C_{23}H_{26}N_4OS_2$ : C, 62.97; H, 5.97; N, 12.77. Found: C, 62.69; H, 5.81; N, 12.67 %. IR (KBr,  $cm^{-1}$ ): 1630  $\nu$ (C=N), 1584  $\nu$ (N=N), 1486 (Phenol ring), 1270  $\nu$ (C-O), 1107, 844, 601.  $^1H$  NMR  $\delta$  (500 MHz;  $CDCl_3$ ): 2.43 (-CH<sub>3</sub>, s), 2.56 (SCH<sub>3</sub>, s), 2.73 (6H, m), 3.76 (2H, t), 3.87 (2H, t), 7-7.9 (Phenol ring), 8.51 (1H, s, CH=N), 12.40 (1H, br, NH), 13.39 (1H, br ,OH).

### 2.4. Synthesis of (Methyl2-(2-((E)-2-hydroxy-5-((E)-para-tolildiazenyl)benzylidenamino) ethyle-amino)cyclopent-1-ene-carbodithioato)nickel(II) complex, [NiL]

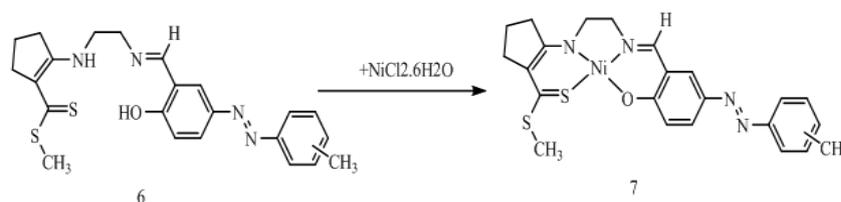
To a solution of the appropriate ligand  $4.56 \times 10^{-2}$  g (0.1 mmol) in 15 ml of choloform /methanol (2:1 v/v), was added a solution of nickel(II) chloride hexahydrate  $2.3 \times 10^{-2}$  g (0.1 mmol) in 15 ml of methanol. The solution was stirred for 15 min and then allowed to stand at room temperature for 24 h. The resulting powder was filtered and recrystallized from chloroform /methanol (1:1 v/v) solution.

$C_{23}H_{24}N_4OS_2Ni$  Yield: 49%. m.p: 274 °C. *Anal.* Calc. for  $C_{23}H_{24}N_4OS_2Ni$ : C, 55.77; H, 4.88; N, 11.31. Found: C, 55.82; H, 4.71; N, 11.25. IR (KBr,  $cm^{-1}$ ): 1619  $\nu$ (C=N), 1467  $\nu$ (Phenol ring), 1283  $\nu$ (C-O), 496-564  $\nu$ (Ni-N), 415-435  $\nu$ (Ni-O).

## 3. Results and discussion

Methyl-2-{N-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate is a convenient starting material for the synthesis of asymmetric ligands containing NNOS coordination spheres. Schiff base condensation of the methyl-dithiocarboxylate ester with (E)-2-hydroxi-5-(*para*-tolildiazenyl)benzaldehyde yields the desired ligand in a facile manner and with high yields.

The complex has a sulfur donor atom that can act as a  $\pi$  acceptor, an oxygen donor atom as a  $\pi$  donor and the coordination around the nickel ion allows for  $\pi$  electronic delocalization, as deposited in Scheme 1. The compounds were characterized by elemental analysis, IR and NMR. The [NiL] complex was characterized further by X-ray crystallography in order to determine that molecular and crystal structure to evaluate the degree of tetrahedral distortion in square planar geometry.



**Scheme 1.** General synthesse of (7a) complex.

### 3.1. Crystal structure of [NiL] complex

Selected bond distances and bond angles for [NiL] complex are collected in Table 1. The ORTEP representation of the structure of this complex with atomic numbering Scheme is presented in Fig. 1. The bond distances and bond angles are within the expected range for nickel(II) complexes with Schiff base ligand. [NiL] crystallize in the spatial group *Pbca*, with eight molecules per unit cell. The nickel(II) ion coordinates to two nitrogen atoms from the imine moiety of the ligand, a sulfur atom the methyl dithiocarboxylate moiety and phenolic oxygen atom. In this complex, the Ni center and its four neighbors (O(1), N(1), N(2) and S(1)) are nearly coplanar. The deviations from the mean coordination plane are at the best 0.002 Å for the donors and equal to 0.005(4) Å for the metal ion. Tetrahedral distortion relative to the square-planar geometry is 4.05(9)°. In this complex, the geometry around the coordination centre is more planar than that in the homologous N<sub>2</sub>OS complex with the dihedral angle of 5.28° and 11.52° (for the two crystallographically independent molecules) [7], homologous N<sub>2</sub>S<sub>2</sub> complex with the dihedral angle of about 20° [10], and analogous N<sub>2</sub>O<sub>2</sub> complex with dihedral angle of about 7° [11].

Table1: Selected bond distance (Å) and bond angles (°) for [NiL<sub>1</sub>] complex.

[NiL <sub>1</sub> ]			
Ni1-N1	1.858(4)	N1-Ni1-S1	173.12(17)
Ni1-N2	1.867(4)	N2-Ni1-O1	173.12(17)
Ni1-O1	1.879(3)	N1-Ni1-O1	176.3(2)
Ni1-S1	2.1524(17)	O1-Ni1-S1	93.16(19)
		S1-Ni1-N2	82.22(14)
		S1-Ni1-N2	97.9(2)
		S1-Ni1-N2	87.0(2)

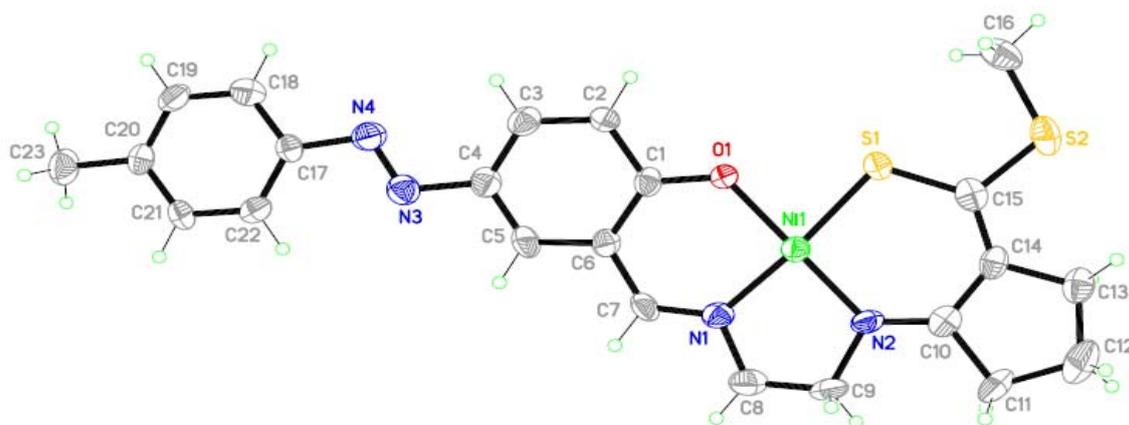


Fig. 1. Graphical representations of 1 (30% probability for the thermal ellipsoids) with the adopted numbering scheme.

### 4. Conclusions

Condensation of Methyl-2-{N-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) with (E)-2-hydroxi-5-(para-tolildiazenyl)benzaldehyde yields an asymmetric tetradentate that is favorable to formation of the complex with Ni(II) ion. Molecular structure of the complex are slightly distorted square-planar structure based on experimental studies.

### 5. References

- [1] Y. P. Tian, C. Y. Duan, C. Y. Zhao, X. Z. You, T. C. W. Mak, Z. Zhang, *Inorg. Chem.* 1997, **36**: 1247-1252.
- [2] S. Karabocek, S. Guner, N.J. Karabocek. *Inorg. Biochem.* 1997, **66**: 57-61.
- [3] A.M. Mahindra, J.M. Fisher, Rabinovitz, *Nature(London)* 1983, **303**: 64-69.

- [4] P. R. Palet, B. T. Thaker, S. Zele, *Indian J. Chem.A* 1999, **38**: 563. *Acta* 2000, **409**: 65-73.
- [5] R.E. Hester, E.M. Nour, *J. Raman SPECTROSC.* 1981, **11**: 49-58.
- [6] T. Sedaghat, S. Menati, *Inorg. Chem. Commun* 2004, **7**: 760-762.
- [7] E. Pereira, L.R. Gomes, J. N. Low, B.D. Castro. *Polyhedron* 2008, **27**: 335-343.
- [8] K. Nag, D.S. Jordar, *Inorg. Chim. Acta* 1975, **14**: 133-141.
- [9] Botros, Azomethine dyes derived from an o-hydroxy aromatic aldehyde and a 2-aminopyridine. *US Patent* 4051119, 1977.
- [10] A. D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, *Coord. Chem. Rev.* 1993, **126**: 1-69.
- [11] Von C. Freiburg, W. Reicht, W. Melchers, B. Engelen, *Acta Crystallogr., Sect. B* 1980, **36**: 1209-1213.