NOTE

Synthesis and Structural Characterization of a Schiff Base Azamacrocyclic Nickel(II) Complex

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Schiff base azamacrocyclic nickel(II) complex $[\text{NiL}]\cdot\text{SCN}\cdot\text{SO}_4\cdot\text{H}_2\text{O}$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene) was synthesized and characterized by IR spectra and single-crystal X-ray diffraction analysis. The crystal belongs to triclinic, space group P-1 with unit cell parameters: $a = 7.2678(11)\text{Å}$, $b = 8.9998(13)\text{Å}$, $c = 19.513(2)\text{Å}$, $\alpha = 84.1430(10)^\circ$, $\beta = 87.005(2)^\circ$, $\gamma = 67.3480(10)^\circ$, $V = 1171.6(3)\text{Å}^3$, $Z = 2$, $M_r = 511.32$, $D_c = 1.449\text{ Mg/cm}^3$, $\mu = 1.043\text{ mm}^{-1}$, $F_{(000)} = 542$, $T = 298(2)\text{ K}$, $R = 0.0375$, $wR = 0.0882$ for 6103 reflections with $I > 2(I)$. In the molecular structure unit, the center nickel(II) ion is four-coordinated in a slightly distorted plane square geometry.

Key Words: Nickel(II) complex, Schiff base azamacrocyclic, Crystal structure.

In recent years, Schiff base azamacrocyclic metal complexes have become one of the active research hotspot in the chemical research field¹⁻³. They not only have attractive topology structure but also have potential application prospects in stability, catalytic activity, biological activity, magnetic and selective recognition^{1,4-8}.

Herein, we described the synthesis and the structural characterization of a Schiff base azamacrocyclic nickel(II) complex $[\text{NiL}]\cdot\text{SCN}\cdot\text{SO}_4\cdot\text{H}_2\text{O}$ (L = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-diene).

All the solvents and chemicals were of analytical grade and used without further purification. $[\text{NiL}]\cdot 2\text{ClO}_4$ was prepared according to the literature⁹. IR spectrum was recorded on an Nexus-870 spectrometer. The X-ray structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis: The $[\text{NiL}]\cdot 2\text{ClO}_4$ (1 mmol) was dissolved in acetonitrile (10 mL) and KSCN (4 mmol) and NiSO_4 (1 mmol) in H_2O (20 mL) were added and the mixture was stirred for 3 h. After being filtered, the solution was stand at room temperature for one week. The dark green four square cylinder crystals were collected, Yield 33 %. IR spectrum (KBr, ν_{max} , cm^{-1}): 3447, 3188, 2056, 1653, 1464, 1398, 1099, 621.

Structure determination: A single crystal (0.49 mm $\times$ 0.40 mm $\times$ 0.39 mm) was selected for crystallographic data collection at 298(2) K and structure determined with graphite monochromatic MoK_α radiation ($\lambda = 0.71073\text{ Å}$). A total of

6103 reflections were collected in the range of $2.01^\circ \leq \theta \leq 25.01^\circ$, of which 4062 reflections were unique with $R_{\text{int}} = 0.0187$ and $R = 0.0375$ and $wR = 0.0882$, where $w = 1/[s^2(F_o^2) + (0.0452P)^2 + 0.5793P]$, $P = (F_o^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.408 and -0.224 e/Å^3 (CCDC No. 925321), respectively.

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES
($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3\text{ Å}^2$)

Atom	X	Y	Z	U (eq)
Ni(1)	8077(1)	7341(1)	7482(1)	33(1)
N(1)	8810(3)	8445(3)	8118(1)	37(1)
N(2)	8265(3)	5584(3)	8155(1)	36(1)
N(3)	7600(3)	6153(3)	6817(1)	37(1)
N(4)	7731(3)	9145(3)	6817(1)	36(1)
N(5)	1503(5)	7714(5)	5780(2)	90(1)
S(1)	3359(1)	2341(1)	8739(1)	49(1)
S(2)	2712(2)	5531(1)	6939(1)	74(1)
O(1)	5226(5)	1857(5)	8446(2)	126(1)

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond lengths and bond angles are given in Table-2, respectively. The molecular structure of the complex is shown in Fig.1, which contains $[\text{NiL}]^{2+}$ cation and one SCN^- anion, one SO_4^{2-} anion and one crystallized H_2O

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	Length	Angle	(°)	Angle	(°)
Ni(1)-N(1)	1.880(2)	N(1)-Ni(1)-N(2)	92.60(10)	O(1)-S(1)-O(2)	110.6(13)
Ni(1)-N(2)	1.916(2)	N(1)-Ni(1)-N(3)	174.53(10)	O(1)-S(1)-O(3)	115.2(9)
Ni(1)-N(3)	1.888(2)	N(1)-Ni(1)-N(4)	87.93(10)	C(2)-N(1)-Ni(1)	130.8(2)
Ni(1)-N(4)	1.917(2)	N(3)-Ni(1)-N(2)	88.02(10)	C(4)-N(2)-Ni(1)	114.08(17)
S(1)-O(1)	1.369(3)	N(3)-Ni(1)-N(4)	91.75(10)	C(7)-N(2)-Ni(1)	107.86(18)
S(2)-C(17)	1.620(5)	N(2)-Ni(1)-N(4)	176.80(10)	C(10)-N(3)-Ni(1)	129.9(2)

Fig. 1. Molecular structure of the complex [NiL]-SCN-SO₄-H₂O

Fig. 2. Molecular packing arrangement in the unit cell

molecule. The molecular pack arrangement in the unit cell is shown in the Fig. 2, the center nickel(II) cation is four-coordinated in a slightly distorted plane square geometry. There is a positive negative charge interaction of [NiL]²⁺ cation with anions of SCN⁻ and SO₄²⁻.

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