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

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Schiff base azamacrocyclic nickel(II) complex [NiL]·SCN·SO₄·H₂O (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) Å, b = 8.9998(13) Å, c = 19.513(2) Å, α = 84.1430(10)°, β = 87.005(2)°, γ = 67.3480(10)°, V = 1171.6(3) Å³, Z = 2, M_r = 511.32, D_c = 1.449 Mg/cm³, μ = 1.043 mm⁻¹, F₍₀₀₀₎ = 542, T = 298(2) 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 [NiL]·SCN·SO₄·H₂O (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. [NiL]·2ClO₄ 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 [NiL]·2ClO₄ (1 mmol) was dissolved in acetonitrile (10 mL) and KSCN (4 mmol) and NiSO₄ (1 mmol) in H₂O (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 × 0.40 mm × 0.39 mm) was selected for crystallographic data collection at 298(2) K and structure determined with graphite monochromatic MoK_α radiation (λ = 0.71073 Å). A total of

6103 reflections were collected in the range of 2.01° ≤ θ ≤ 25.01°, of which 4062 reflections were unique with R_{int} = 0.0187 and R = 0.0375 and wR = 0.0882, where w = 1/[s²(F_o²) + (0.0452P)² + 0.5793P], P = (F_o² + 2F_c²)/3. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.408 and -0.224 e/Å³ (CCDC No. 925321), respectively.

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES
(× 10⁴) AND THERMAL PARAMETERS (× 10³ Å²)

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 [NiL]²⁺ cation and one SCN⁻ anion, one SO₄²⁻ anion and one crystallized H₂O

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)

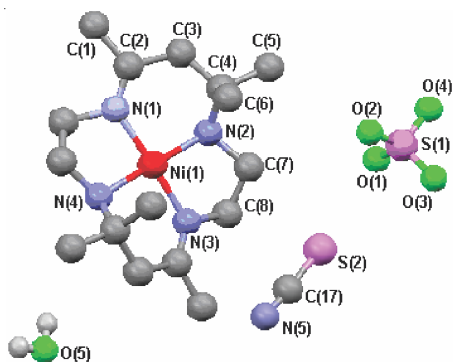


Fig. 1. Molecular structure of the complex $[\text{NiL}] \cdot \text{SCN} \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$

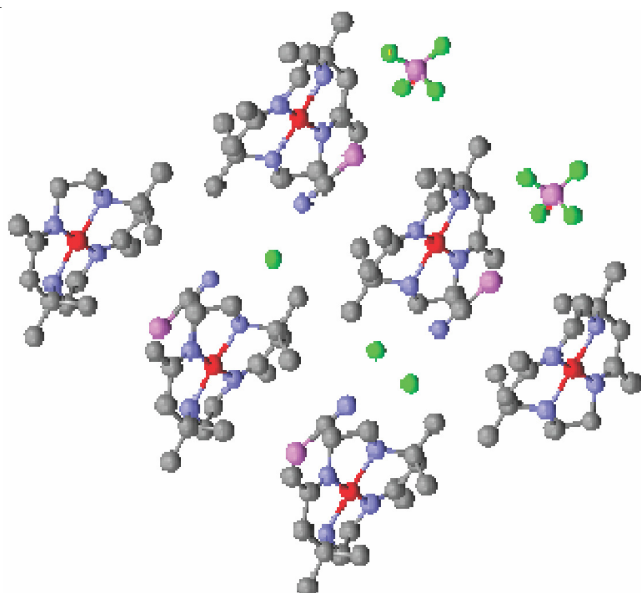


Fig. 2. Molecular packing arrangement in the unit cell

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 $[\text{NiL}]^{2+}$ cation with anions of SCN^- and SO_4^{2-} .

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REFERENCES

1. J.C. Timmons and T.J. Hubin, *Coord. Chem. Rev.*, **254**, 1661 (2010).
2. N.F. Curtis, K. Flood, C.E. Rickard, W.T. Robinson and J.M. Waters, *Polyhedron*, **28**, 739 (2009).
3. J.H. Bi, *Acta Crystallogr. E*, **E65**, m668 (2009).
4. R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
5. J.H. Bi, *Asian J. Chem.*, **23**, 5171 (2011).
6. E. Tamanini, E.J. Stephen, M.M. Rigby, M. Motevalli, M.H. Todd and M. Watkinson, *Chem-Eur. J.*, **15**, 3720 (2009).
7. T. Biver, F. Secco and M. Venturini, *Coord. Chem. Rev.*, **252**, 1163 (2008).
8. O. Das, E. Zangrando and T.K. Paine, *Inorg. Chem.*, **50**, 8012 (2011).
9. D.J. Szalda and E. Fujita, *Acta Cryst.*, **C48**, 1767 (1992).