NOTE

Hydrothermal Synthesis and Crystal Structure of a Ni(II) Complex with Diacetyl Dihydrazone Ligand

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A novel nickel(II) complex $\text{NiL}_3 \cdot (\text{ClO}_4)_2$ (L = diacetyl dihydrazone) has been synthesized by hydrothermal method and characterized by IR spectra and single-crystal X-ray method. The crystal is trigonal, space $P\bar{3}c1$ with unit cell parameters: $a = 9.5922(5)$ Å, $b = 9.5922(5)$ Å, $c = 15.1871(14)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1210.16(14)$ Å³, $Z = 2$, $M_r = 600.09$, $D_c = 1.647$ Mg/cm³, $\mu = 1.087$ mm⁻¹, $F_{(000)} = 624$, $T = 293(2)$ K, $R = 0.0474$, $wR = 0.1276$ for 8580 reflections with $I > 2\sigma(I)$.

Key Words: Nickel(II) complex, Diacetyl dihydrazone, Crystal structure.

In recent years, the transition metal coordination chemistry of hydrazone Schiff base ligands has got enormous significance due to its diversity of molecular structures¹⁻⁴ and good biological activity of insecticidal, sterilization and weeding⁴⁻⁷ and excellent anticancer, catalytic, spectral and magnetic properties^{1-3,6}.

Here we report the hydrothermal synthesis and crystal structure of a novel mononuclear nickel(II) complex $\text{NiL}_3 \cdot (\text{ClO}_4)_2$ (L=diacetyl dihydrazone).

$\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was prepared in our laboratory. Diacetyl dihydrazone was prepared by similar procedure in the literature⁸. All reagents were of AR grade and used without further purification. IR spectra were recorded on a Nexus-870 spectrophotometer. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

Synthesis: A mixture of 7 mL acetonitrile solution of diacetyl dihydrazone (3 mmol) and 14 mL H_2O solution of $\text{NiL}_3 \cdot (\text{ClO}_4)_2$ (1 mmol), was carried out in a autoclave and heated to 80 °C for 48 h. After cooling, the well-shaped scarlet four edges column single crystals were obtained. Yield 37 %. IR spectrum (KBr, ν_{max} , cm⁻¹): 3420, 3320 (N-H); 1610 (C=N); 1090, 623 (ClO_4^-).

Crystal structure determination: A scarlet colour single crystal 0.45 mm × 0.35 mm × 0.30 mm was selected for crystallographic data collection at 293(2) K and structure determined with graphite monochromatic MoK_α radiation ($\lambda = 0.71073$ Å). A total of 8580 reflections were collected in

the range of $2.45 \leq \theta \leq 27.48^\circ$, of which 935 reflections were unique with $R_{\text{int}} = 0.0193$ and $R = 0.0474$ and $wR = 0.1276$, where $w = 1/[s^2(F_0^2) + (0.0643P)^2 + 1.0654]$, $P = (F_0^2 + 2F_0^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.324 and -0.496 e/Å³, respectively. The CCDC numbers was 646143.

The atomic coordinates and thermal parameters are listed in Table-1 and the selected bond lengths and bond angles in Table-2, respectively. Fig. 1 shows diagram of the molecular structure of the complex $\text{NiL}_3 \cdot (\text{ClO}_4)_2$. Fig. 2 shows a perspective view of the crystal packing in the unit cell.

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES ($\times 10^4$)
AND THERMAL PARAMETERS ($\times 10^3$ Å²)

Atom	X	Y	Z	U (eq)
Ni	0	0	2500	32(1)
N(1)	2094(3)	800(2)	1770(1)	38(1)
N(2)	2324(3)	1507(3)	960(2)	54(1)
C(1)	3122(3)	431(3)	2072(1)	35(1)
C(2)	4643(3)	807(4)	1617(2)	53(1)

The molecular structure of $\text{NiL}_3 \cdot (\text{ClO}_4)_2$ is shown in Fig. 1. It is easy to see that the center nickel(II) ion is coordinated with six N atoms of the three diacetyl dihydrazone and shows a distorted octahedral geometry. As shown in the molecular packing diagram (Fig. 2), there are positive negative charge interactions between $[\text{NiL}_3]^{2+}$ cation and ClO_4^- .

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

Bond	Length	Angle	(°)	Angle	(°)
Ni-N(1)#1	2.076(2)	C(1)#3-C(1)-C(2)	120.57(15)	N(1)#1- Ni-N(1)	96.11(11)
Ni-N(1)#2	2.076(2)	N(1)#1- Ni-N(1)#2	166.87(11)	N(1)#2- Ni-N(1)	94.16(7)
N(1)-C(1)	1.287(3)	N(1)#2- Ni-N(1)#3	96.11(11)	N(1)#4- Ni-N(1)	166.87(11)
N(1)-N(2)	1.369(3)	N(1)-C(1)-C(2)	124.2(2)	C(1)#3-C(1)-C(2)	120.57(15)
CL-O(1)	1.399(4)	O(2)-CL-O(1)	108.05(16)	O(1)-CL-O(2)#7	109.04(15)

Fig. 1. Molecular structure of the complex $\text{NiL}_3 \cdot (\text{ClO}_4)_2$

Fig. 2. Molecular packing arrangement in the unit cell

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