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Synthesis and Crystal Structure of Nickel(II) Complex with 2-(3,5-Dibromo-2-hydroxyphenyl)-4-methyl-1,2-dihydroquinazoline-3-oxide

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The title complex, [$NiL_2(CH_3OH)$], has been synthesized and characterized structurally and contains one nickel(II) atom, two L-ligands, one methanol molecule (HL = 2-(3,5-dibromo-2-hydroxyphenyl)-4-methyl-1,2-dihydro-quinazoline-3-oxide). The nickel(II) atom have a hexa-coordinated octahedral geometry. The title complex molecule assumes an E configuration with respect to the azomethine C=N bond. There are two fairly strong intramolecular O1-H1···O5 and O2-H5A···O5 hydrogen bonds.

Key Words: Oxime-type compound, Synthesis, Crystal Structure.

INTRODUCTION

The oxime-type compounds are potentially multidentate ligands[1,2], because they can accommodate one, two or more transition metal centers and form metal complexes with interesting properties[3-6]. Recently, a significant increase in the research of coordination supramolecules in which metal ion centers are bridged through organic molecules has been observed because of their enormous variety of intriguing structural topologies and their fascinating properties as well as great potential applications in optoelectronics, magnetism and catalysis[7-14]. Herein, we report on the synthesis and crystal structure of a nickel(II) complex with 2-(3,5-dibromo-2-hydroxyphenyl)-4-methyl-1,2-dihydro-quinazoline-3-oxide (HL).

EXPERIMENTAL

3,5-Dibromosalicylaldehyde was purchased and used without further purification. 1,2-dihydroquinazoline-3-oxide was synthesized according to an analogous method reported earlier[15]. The other reagents and solvents were analytical grade reagents from Tianjing Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited company and the thermometer was uncorrected.

2-(3,5-Dichloro-2-hydroxyphenyl)-4-methyl-1,2-dihydroquinazoline-3-oxide (HL) was synthesized according to an analogous method reported earlier[16]. To an ethanol solution (5 mL) of 3,5-dibromosalicylaldehyde (279.9 mg, 1 mmol) was added an ethanol solution (3 mL) of *o*-aminoacetophenone oxime (150.2 mg, 1 mmol). The reaction mixture was stirred at 323-333 K for 10 h. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/*n*-hexane (1:4). The product was dried under vacuum to yield 316.12 mg of the ligand. Yield, 73.5 %. m.p. 225-227 ºC. Anal. calcd. for $C_{15}H_{12}N_2O_2Br_2$ (%): C, 43.72; H, 2.94; N, 6.80. Found (%): C, 43.94; H, 2.78; N, 6.99.

Complex [$NiL_2(CH_3OH)$]: A solution of Ni(II) acetate tetrahydrate (2.83 mg, 0.005 mmol) in methanol (2 mL) was added to a solution of 2-(3,5-dibromo-2-hydroxyphenyl)-4-methyl-1,2-dihydro-quinazoline-3-oxide (HL) (8.78 mg, 0.01 mmol) in dichloromethane (4 mL). The solution colour turned brown immediately and then the mixed solution was allowed to stand at room temperature for about one week, several brown block-like crystals suitable for X-ray analysis were obtained after one week. Anal. calcd. for [$NiL_2(CH_3OH)$] ($C_{31}H_{26}N_4O_5Br_4Ni$) (%): C, 40.79; H, 2.87; N, 6.14, Ni, 6.43. Found (%): C, 40.92; H, 2.65; N, 6.32; Ni, 6.32.

X-Ray structure determination: The single crystal of the title complex, with approximate dimensions of 0.43 × 0.38 × 0.21 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. Details of the data collection and refinements of the title compound are given in Table-1. The non-

hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 883601.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPLEX

Empirical formula	$C_{31}H_{26}N_4O_5NiBr_4$
Formula weight	912.91
Temperature, K	298(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions, (Å, deg)	a = 11.3734(11), b = 13.1263(14), c = 23.419(3), α = 90.00, β = 92.8100(10), γ = 90.00
Volume, Å^3	3492.0 (6)
Z	4
Density (calculated), mg/m^3	1.736
Absorption coefficient, mm^{-1}	5.176
F(000)	1792.0
Index ranges	-13≤ h ≤ 10, -15 ≤ k ≤15, -27≤1 ≤ 26
Reflections collected	15981/6092 [R(int) = 0.1735]
Independent reflections	3407
Data/restraints/parameters	6092/0/413
Goodness of fit indicator	1.021
R [I > 2σ(I)]	R_1 = 0.0818, wR_2 = 0.2244
Largest diff. peak and hole, e·Å^{-3}	1.388 and -1.325

RESULTS AND DISCUSSION

X-ray crystallographic analysis revealed the crystal structure of the title nickel(II) complex. The structure of the complex is shown in Fig. 1. Selected bond distances and angles are listed in Table-2.

From a 2:1 mixture of ligand HL and nickel (II) acetate, a brown crystalline complex of [$NiL_2(CH_3OH)$] was isolated. X-ray crystallography revealed that the complex contains one nickel(II) atom, two L- ligands, one methanol molecule (Fig. 1). The single crystal structure of the title complex is built up by only the $C_{15}H_{12}Br_2N_2O_2$ molecule. The title complex is a typical complex with normal geometric parameters. The complex molecule adopts an E configuration with respect to the azomethine C=N bond.

The nickel(II) atom has a hexa-coordinated octahedral geometry. In the crystal structure, two fairly strong intramolecular hydrogen bonds O5-H1···O1 and O2-H5A···O5 (Table-3)

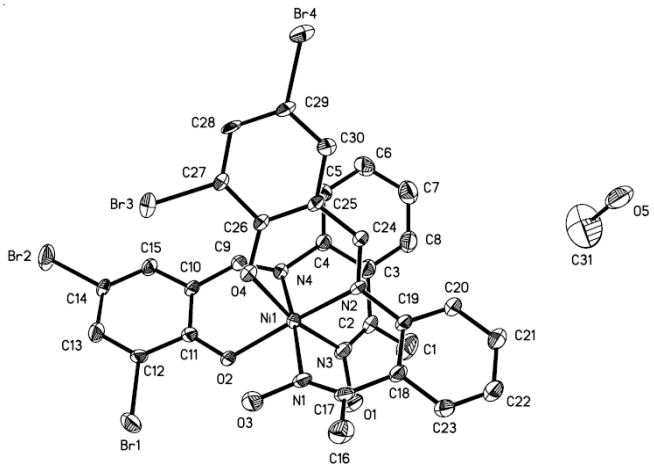

Fig. 1. Molecule structure of the title complex with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

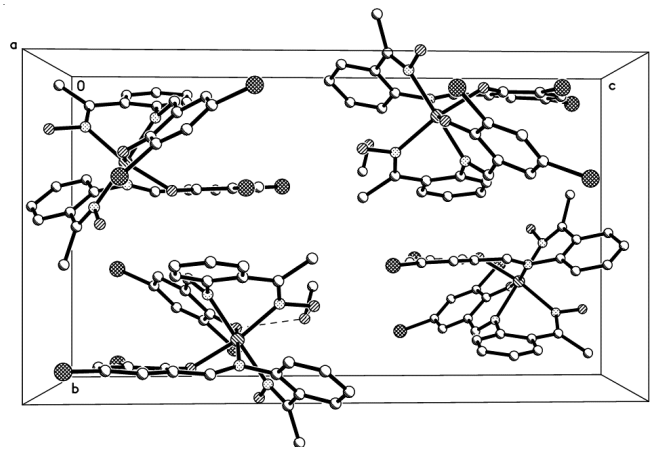

Fig. 2. Packing arrangement of the unit cell of the title complex. H atoms are omitted for clarity

TABLE-3
HYDROGEN BONDS [Å, º] FOR THE TITLE COMPLEX

D–H···A	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)
O5-H1···O1	1.88	0.82	167	2.685(3)
O2-H5A···O5	1.97	0.82	155	1.968(3)

are observed between the hydroxyl groups and methanol molecule, the O1-O5 distance between the hydroxyl group and the methanol O atom is 2.685(3) Å, indicating strong hydrogen bonding interactions. The packing arrangement of the unit cell of the title complex are shown in Fig. 2.

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) FOR THE TITLE COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni(1)-O(2)	2.019(7)	Ni(1)-N(4)	2.02(1)	Ni(1)-O(4)	2.038(8)
Ni(1)-N(2)	2.047(9)	Ni(1)-N(1)	2.08(1)	Ni(1)-N(3)	2.12(1)
Bond	Angles	Bond	Angles	Bond	Angles
O(2)-Ni(1)-N(4)	88.5(3)	O(2)-Ni(1)-O(4)	88.2(3)	N(4)-Ni(1)-O(4)	89.0(3)
O(2)-Ni(1)-N(2)	166.2(4)	N(4)-Ni(1)-N(2)	103.2(4)	O(4)-Ni(1)-N(2)	84.9(3)
O(2)-Ni(1)-N(1)	86.1(4)	N(4)-Ni(1)-N(1)	174.6(4)	O(4)-Ni(1)-N(1)	91.4(4)
N(2)-Ni(1)-N(1)	82.2(4)	O(2)-Ni(1)-N(3)	99.5(4)	N(4)-Ni(1)-N(3)	80.5(4)
O(4)-Ni(1)-N(3)	166.7(4)	N(2)-Ni(1)-N(3)	89.6(4)	N(1)-Ni(1)-N(3)	99.9(4)
C(17)-N(1)-Ni(1)	129.8(9)	O(3)-N(1)-Ni(1)	114.7(7)	C(24)-N(2)-Ni(1)	124.9(7)
C(19)-N(2)-Ni(1)	115.2(7)	C(2)-N(3)-Ni(1)	125.0(9)	O(1)-N(3)-Ni(1)	121.4(8)
C(9)-N(4)-Ni(1)	126.3(8)	C(4)-N(4)-Ni(1)	113.9(7)	C(11)-O(2)- Ni(1)	122.5(7)
C(26)-O(4)-Ni(1)	119.1(7)				

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