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A Supramolecular Ni(II) Complex Based on a Bisoxime Compound: Synthesis and Crystal Structure

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A new Ni(II) complex, {[NiL(THF)]$_2$(μ-OAc)$_2$Ni} (H_2L = 4,4'-dibromo-2,2'-[(ethylene)dioxybis(nitrilomethylidyne)]diphenol), has been synthesized and characterized structurally. The results show that the complex consists of three Ni(II) atoms, two tetradentate $(\mu\text{-L})^{2-}$ units, two coordinated μ-acetate ions which coordinate to three Ni(II) atoms in μNi-O-C-O-Ni mode and two coordinated THF molecules. All the hexa-coordinated Ni(II) atoms of the complex have a distorted octahedral geometry. The crystal packing of the complex shows that a notable feature of this structure resides in the formation of an infinite 2D supramolecular networks through intermolecular C-H···O hydrogen-bonding and C-H···π interactions.

Key Words: Bisoxime ligand, Ni(II) complex, Supramolecular structure.

INTRODUCTION

Although some advance has been made in the studies of Salen-Ni(II) complexes[1-3], it still seems there could be new and specific applications for such a unique group of compounds. To change the structures or improve the functions of the resulted complexes, chemical modifications of the elemental Salen-type ligand are effective and inevitable[4-7]. Herein, a new Ni(II) complex with a Salen-type bisoxime ligand based on O-alkyloxime instead of the imine moiety has been synthesized and structurally characterized by X-ray crystallography.

EXPERIMENTAL

5-Bromo-2-hydroxybenzaldehyde (≥ 98 %) was purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analysis for Ni was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-Ray single crystal structure determination was carried out on a Bruker Smart 1000 CCD area detector. Melting points were measured with a microscopic melting point apparatus made by the Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

General procedure: 4,4'-Dibromo-2,2'-[(ethylene)dioxy-*bis*(nitrilomethylidyne)]diphenol (H_2L) was synthesized according to an analogous method reported earlier[8].

A solution of Ni(II) acetate tetrahydrate (2.5 mg, 0.01 mmol) in ethanol (3 mL) was added dropwise to a solution of H_2L (4.6 mg, 0.01 mmol) in THF (5 mL) at room temperature. The colour of the mixing solution turned to pale-green immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for *ca.* 2 weeks, the solvent was partially evaporated and obtained green single crystals suit for X-ray crystallographic analysis. Anal. calcd. (%) for $C_{44}H_{46}N_4O_{14}Br_4Ni_3$: C, 39.13; H, 3.43; N, 4.15; Ni, 13.04. Found (%): C, 39.15; H, 3.45; N, 4.12; Ni, 12.87.

X-Ray structure determination: The single crystal of the Ni(II) complex, with approximate dimensions of 0.17 mm × 0.16 mm × 0.06 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[9] and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97[10]. Details of the data collection and refinements of the Ni(II) complex are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 876226.

TABLE-1
CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE Ni(II) COMPLEX

Empirical formula	$C_{44}H_{46}N_4O_{14}Br_4Ni_3$
Formula weight	1350.62
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 15.7493(16) Å, b = 15.3900(16) Å, c = 21.738(2) Å, β = 101.027(2)
Volume	5171.6(9) $Å^3$
Z	4
Density (calculated)	1.735 mg/m^3
Absorption coefficient	4.237 mm^{-1}
$F_{(000)}$	2696
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 17$, $-25 \le 1 \le 19$
Reflections collected	13189 [$R_{(int)}$ = 0.0407]
Independent reflections	6375
Data/restraints/parameters	6375/2/577
Goodness of fit indicator	1.044
R [I > 2σ(I)]	R_1 = 0.0342, wR_2 = 0.1109
Largest diff. peak and hole	1.977 and -1.088 e $Å^2$

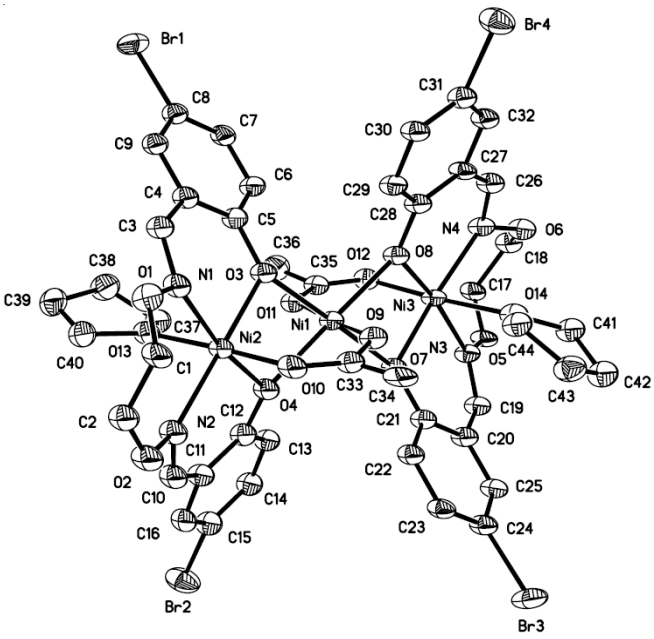

Fig. 1. Molecular structure of the Ni(II) complex with the atomic numbering

RESULTS AND DISCUSSION

X-Ray crystallographic analysis reveals the crystal structure of the Ni(II) complex. The ORTEP representation of the Ni(II) complex is shown in Fig. 1. Selected bond lengths and angles are summarized in Table-2. The Ni(II) complex crystallizes in the monoclinic system, space group Cc, which consists of three Ni(II) atoms, two tetradentate $(\mu\text{-L})^{2-}$ units, two coordinated μ-acetate ions and two coordinated tetrahydrofuran molecules. Three hexa-coordinated Ni(II) atoms of the Ni(II) complex have a distorted octahedron. The two terminal Ni(II) atoms (Ni2 and Ni3) are both located in the *cis*-N_2O_2 coordination cavity of the $(\mu\text{-L})^{2-}$ unit and coordinated to the O10 (or O12) atom from the μ-acetato ions and the O13 (or O14) atom from the THF molecule in the axial positions. The dihedral angle between the coordination plane of O3-Ni2-N1 and that of O4-Ni2-N2 is *ca.* 8.05(3)º, whereas that of O7-Ni3-N3 and O8-Ni3-N4 is about 10.63(2)º indicating the formation of the distortion octahedral geometry around terminal Ni(II) atoms. Meanwhile, the coordination sphere of the central Ni(II) atom (Ni1) is completed by quadruple μ-phenoxo oxygen atoms (O3, O4, O7 and O8) from two $(\mu\text{-L})^{2-}$ moieties and double μ-acetato oxygen atoms (O9 and O11) which adopt a familiar μ-O-C-O fashion. The dihedral angle between the coordinated planes O3-Ni1-O4 and O7-Ni1-O8 is 1.02(2)º, indicating the formation of the slight distortion octahedral geometry around central Ni(II) atoms. Furthermore, the distances of Ni1···Ni2 and Ni1···Ni3 are 3.117(3)Å and 3.112(3) Å, indicating metal-metal bond or the metal surface electron spin exchange is not exist. The angles of Ni1-O3-Ni2 and Ni1-O8-Ni3 are 96.42(3)º and 97.11(3)º, indicating Ni-O-Ni is non-collinar, thus not easy in electronic exchange.

In the crystal structure, the Ni(II) complex molecules are linked into an infinite 2D supramolecular layer structure (Fig. 2) by two pair of intermolecular C18-H18A···O1 and C18-H18B···$\pi_{centroid\ (C11\text{-}C16)}$ hydrogen-bonding interactions and lie in the accepted distance range for this type of contacts (Table-3)[11,12].

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (º) FOR THE Ni(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O11	2.08(3)	Ni2-O10	1.99(3)	Ni3-O8	2.030(2)
Ni1-O9	2.10(3)	Ni2-O4	2.02(2)	Ni3-O12	2.06(3)
Ni1-O7	2.10(2)	Ni2-O3	2.06(2)	Ni3-O7	2.061(2)
Ni1-O3	2.12(2)	Ni2-N1	2.06(3)	Ni3-N4	2.10(3)
Ni1-O8	2.12(2)	Ni2-N2	2.10(3)	Ni3-N3	2.14(2)
Ni1-O4	2.15(2)	Ni2-O13	2.22(3)	Ni3-O14	2.23(3)
Bond	Angles	Bond	Angles	Bond	Angles
O11-Ni1-O9	178.1(9)	O4-Ni2-O3	82.1(8)	O8-Ni3-O7	81.4(8)
O7-Ni1-O3	178.4(1)	O4-Ni2-N1	167.2(9)	O8-Ni3-N4	92.0(9)
O7-Ni1-O8	78.4(8)	O3-Ni2-N1	85.5(9)	O7-Ni3-N4	168.1(1)
O3-Ni1-O8	103.2(8)	O4-Ni2-N2	90.4(9)	O8-Ni3-N3	169.1(9)
O7-Ni1-O4	100.7(8)	O3-Ni2-N2	169.8(1)	O7-Ni3-N3	88.0(8)
O3-Ni1-O4	77.7(8)	N1-Ni2-N2	101.5(1)	N4-Ni3-N3	98.0(1)
O8-Ni1-O4	178.8(1)	O10-Ni2-O13	177.8(9)	O12-Ni3-O14	176.9(8)

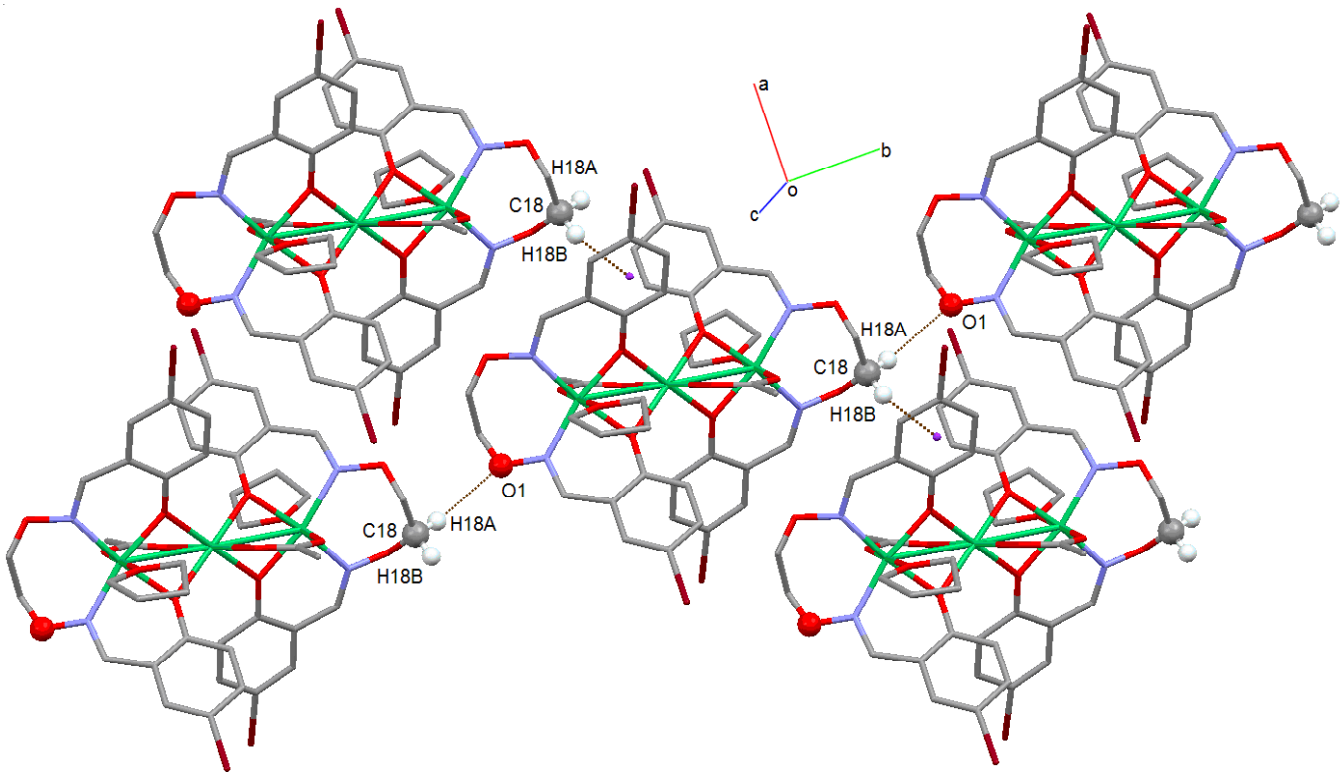

Fig. 2. View of the 2D supramolecular layer within the Ni(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

TABLE-3
DATA FOR HYDROGEN-BONDING
AND C-H···π INTERACTIONS [Å, º]

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
C18-H18A···O1	0.98	2.62	3.399(3)	137
C18-H18B···Cg1[a]	0.97	2.97	3.900(4)	160

[a]Cg1 is the C11-C16 ring centroid.

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