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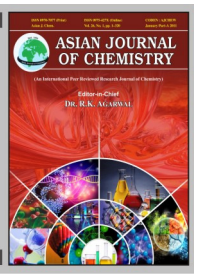

Synthesis and Crystal Structure of Trinuclear Ni(II) Complex with 5-Methoxy-4'-bromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

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A Ni(II) complex with 5-methoxy-4'-bromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_2L) has been synthesized, with the formula {[NiL(*n*-butanol)(μ-OAc)]$_2$Ni}·*n*-butanol. The crystal of the Ni(II) complex belongs to triclinic, space group P-1 with cell dimensions a = 10.897(1) Å, b = 12.439(1) Å, c =12.518(1) Å and Z = 1. In the Ni(II) complex, there are three Ni(II) atoms, two deprotonated L^{2-} moieties which provide N_2O_2 donors, two acetate anions, two coordinated and one non-coordinated *n*-butanol molecules, which result in the formation of a slightly distorted octahedral coordination geometry around each Ni(II) atom, respectively.

Keywords :Asymmetric Salamo-type ligand, Ni(II) complex, Synthesis, Crystal structure.

INTRODUCTION

Transition metal complexes of Salen-type ligands have attracted much interest in the last few decades due to their unique catalytic activity[1,2], photonic devices[3,4], biological activity[5,6] and magnetic properties[7-9], such as epoxidation catalysts, in the presence of a terminal oxidant like iodosylbenzene[10-14], N-salicylideneanilines constitute an important family of photochromic compounds[3,4]. This photochromism has also been observed for the derivative Salen-type compound[15]. Furthermore, Salen-Ni(II) complexes are used extensively in the design and construction of new magnetic materials and models for the Ni(II) centers of enzymes. Hence, structural characteristics of transition metal complexes with Salen-type ligands may be a valuable source of information. Transition metal complexes of Salen-type ligands with oxygen and nitrogen donors are of particular interest[16,17] because of their ability to possess excellent properties[18-20].

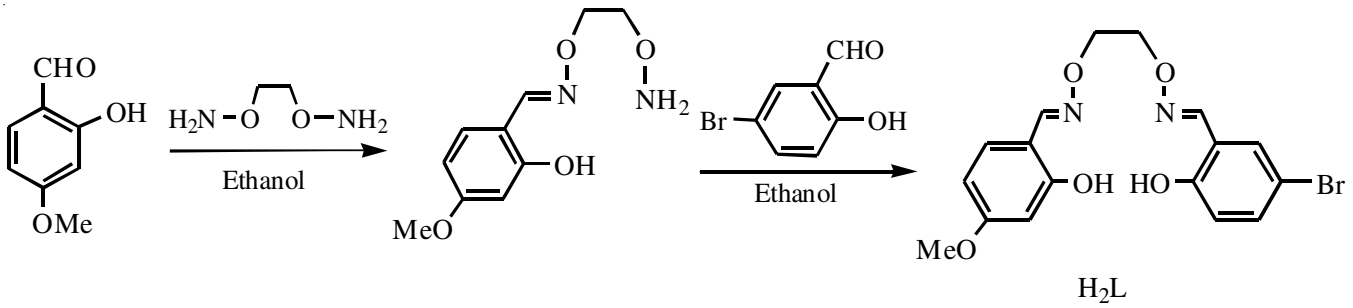
Therefore, we here describe the synthesis and crystal structure of a trinuclear Ni(II) complex containing the asymmetric ligand 5-methoxy-4'-bromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_2L).

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %) and 2-hydroxy-5-bromobenzaldehyde (≥ 99 %) were purchased from Alfa Aesar and used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[21-25]. The other reagents and solvents were analytical grade from Tianjin Chemical Reagent Factory. Elemental analysis for Ni was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. X-ray single crystal structure determination was carried out on a Bruker Smart 1000 CCD diffractometer. 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.

Synthesis of H_2L: The main reaction steps involved in the synthesis of H_2L are given in **Scheme-I**. H_2L was synthesized according to an analogous method reported earlier[24]. Yield 73.8 %. m.p. 385-387 K. Anal. Calcd. for $C_{17}H_{17}N_2O_5Br$ (%): C, 49.89; H, 4.19; N, 6.85. Found: C, 49.75; H, 4.32; N, 6.99.

Synthesis of Ni(II) complex: A solution of $Ni(OAc)_2·4H_2O$ (3.70 mg, 0.015 mmol) in *n*-butanol (2 mL) was added dropwise to a solution of H_2L (4.10 mg, 0.010 mmol) in acetonitrile (2 mL) at room temperature. The color of the mixing solution turned green immediately and then stirring was continued for 0.5 h at room temperature. The mixture was filtered off and the filtrate was allowed to stand at room temperature for about 1 month, the solvent was partially evaporated and obtained green prismatical single crystals suitable for X-ray crystallographic analysis. Anal. calcd. for $C_{54}H_{76}N_4O_{18}Ni_3Br_2$ (%): C, 46.16; H, 5.45; N, 3.99; Ni, 12.53. Found: C, 46.37; H, 5.59; N, 3.82; Ni, 12.38.



Scheme-I: Synthetic route to the asymmetrical Salamo-type ligand H_2L

X-ray structure determination: The crystal data and structure refinement for the Ni(II) complex are given in Table-1. The single crystal of the Ni(II) complex with the approximate dimensions of 0.28 mm × 0.20 mm × 0.14 mm was placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using a graphite monochromated MoKa radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXL-97 and Fourier difference techniques and refined by the full-matrix least-squares method on F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. CCDC: 942408.

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

Empirical formula	$C_{54}H_{76}Br_2N_4Ni_3O_{18}$
Formula weight	1405.14
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 10.8973(11), b = 12.4386(13), c = 12.5175(14), α = 77.601(1), β = 88.596(2), γ = 67.837(1)
Volume ($Å^3$)	1531.7(3)
Z	1
Density (calculated) (mg/m^3)	1.523
Absorption coefficient (mm^{-1})	2.288
$F_{(000)}$	726
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 12$, $-14 \le l \le 14$
Reflections collected	7571/5263 [R(int) = 0.0719]
Independent reflections	1119
Data/restraints/parameters	5263/0/408
Goodness of fit indicator	1.009
R [$I > 2\sigma(I)$]	$R_1 = 0.0307$, $wR_2 = 0.1167$
Largest diff. peak and hole (e $Å^{-3}$)	1.099 and -0.910

RESULTS AND DISCUSSION

Crystal structure of Ni(II) complex: X-ray crystal structure shows that there are three hexa-coordinated Ni(II) atoms with a linear array, two deprotonated L^{2-} moieties, two acetate anions, as well as two coordinated and one non-coordinated *n*-butanol molecules in the Ni(II) complex, which result in the formation of the slightly distorted octahedral coordination geometries around each Ni(II) atom, respectively. The molecular structure is shown in Fig. 1. Selected bond lengths and angles are given in Table-2.

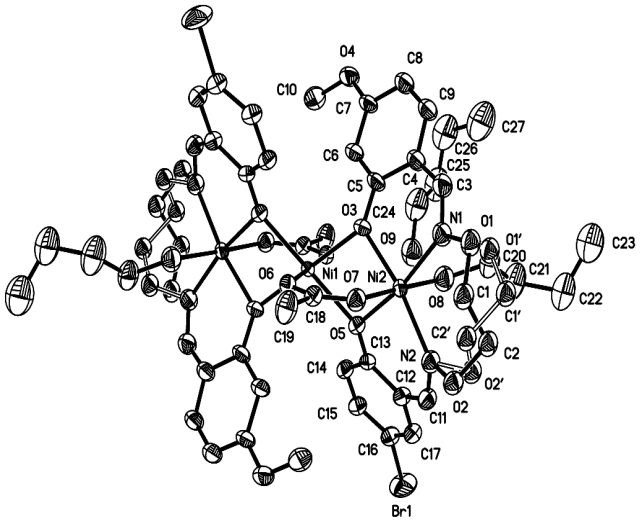


Fig. 1. Molecular structure of Ni(II) complex

In the crystal structure, the Ni(II) complex belongs to triclinic, space group P-1 with cell dimensions a = 10.897(1) Å, b = 12.439 (1) Å, c = 12.518(1) Å and Z = 1. The two terminal Ni(II) (Ni2 and $Ni2^{\#1}$) atoms are coordinated by two nitrogen (N1, N2) atoms and two oxygen (O3 and O5) atoms in the N_2O_2 moieties of the L^{2-} moieties, one oxygen (O7) atom from the bridging acetate anion and one oxygen (O8) atom from the coordinated *n*-butanol molecule in the axial positions. The dihedral angel between the two coordination planes, N1-Ni2-O3 and N2-Ni2-O5 is 3.22(3)º. Meanwhile, Ni(II) (Ni1) atom is located on a centre of inversion and has an O_2O_2 donor set from four μ-phenoxo oxygen (O3, O5, $O3^{\#1}$ and $O5^{\#1}$) atoms from two L^{2-} units and two μ-acetato oxygen (O6 and $O6^{\#1}$) atoms, which adopt a familiar μ-O-C-O fashion and constitute another octahedral geometry. Furthermore, The interatomic distance of Ni2-Ni1 (3.087(4) Å) is significantly longer than all that of the Ni-O and Ni-N bonds in the Ni(II) complex, which is also essentially similar to previously reported octanuclear analogue of $[Zn_8L_4(H_2O)_2X]\cdot 2H_2O\cdot 1.5CHCl_3\cdot 0.5$hexane (X=$H_2O$ or EtOH)[26]. In addition, the trinuclear structure is probably stabilized by the two μ-acetato moieties, which neutralize the whole charge of the Ni(II) complex.

Intermolecular interactions of the Ni(II) complex: In the crystal structure of the Ni(II) complex, there are weak intramolecular C1-H1A···O7 hydrogen bonds (Fig. 2), as well as strong intermolecular O8-H8···O9, O9-H9···O6 and C25-H25A···O9 hydrogen bonds that stabilize the structure of the Ni(II) complex. Hydrogen bond data are given in Table-3.

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O3$^{\#1}$	2.080(11)	Ni1-O6$^{\#1}$	2.124(13)	Ni2-O7	2.047(15)
Ni1-O3	2.080(11)	Ni1-O6	2.124(13)	Ni2-N1	2.066(18)
Ni1-O5$^{\#1}$	2.094(11)	Ni2-O5	2.017(12)	Ni2-N2	2.098(17)
Ni1-O5	2.094(11)	Ni2-O3	2.031(12)	Ni2-O8	2.126(17)
Bond	Angles	Bond	Angles	Bond	Angles
O3$^{\#1}$-Ni1-O3	180.0(1)	O5-Ni2-O3	81.1(5)	C3-N1-Ni2	124.8(16)
O3$^{\#1}$-Ni1-O5$^{\#1}$	78.2(4)	O5-Ni2-O7	91.1(5)	O1'-N1-Ni2	118(3)
O3-Ni1-O5$^{\#1}$	101.8(4)	O3-Ni2-O7	91.4(5)	O1-N1-Ni2	127.1(15)
O3$^{\#1}$-Ni1-O5	101.8(4)	O5-Ni2-N1	168.2(6)	C11-N2-Ni2	122.9(14)
O3-Ni1-O5	78.2(4)	O3-Ni2-N1	87.5(6)	O2-N2-Ni2	128(2)
O5$^{\#1}$-Ni1-O5	180.0(7)	O7-Ni2-N1	92.4(7)	O2'-N2-Ni2	125(5)
O3$^{\#1}$-Ni1-O6$^{\#1}$	88.1(5)	O5-Ni2-N2	87.2(6)	C5-O3-Ni2	127.5(12)
O3-Ni1-O6$^{\#1}$	91.9(5)	O3-Ni2-N2	168.3(6)	C5-O3-Ni1	133.0(12)
O5$^{\#1}$-Ni1-O6$^{\#1}$	88.5(5)	O7-Ni2-N2	88.7(6)	Ni2-O3-Ni1	97.4(4)
O5-Ni1-O6$^{\#1}$	91.5(5)	N1-Ni2-N2	104.2(7)	C13-O5-Ni2	125.5(11)
O3$^{\#1}$-Ni1-O6	91.9(5)	O5-Ni2-O8	89.7(6)	C13-O5-Ni1	133.1(11)
O3-Ni1-O6	88.1(5)	O3-Ni2-O8	90.4(6)	Ni2-O5-Ni1	97.3(5)
O5$^{\#1}$-Ni1-O6	91.5(5)	O7-Ni2-O8	178.1(6)	C18-O6-Ni1	129.1(13)
O5-Ni1-O6	88.5(5)	N1-Ni2-O8	87.2(7)	C18-O7-Ni2	130.2(14)
O6$^{\#1}$-Ni1-O6	180.0(2)	N2-Ni2-O8	89.6(7)	C20-O8-Ni2	118.8(17)

Symmetry transformations used to generate equivalent atoms:$^{\#1}$ -x+1,-y+1,-z+1

TABLE-3
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A	Symmetry code
O8-H8···O9	0.82	1.77	2.59(3)	173	x, y, z
O9-H9···O6	0.82	1.95	2.76(2)	169	1-x, 1-y, 1-z
C25-H25A···O9	0.97	2.30	2.89(6)	118	1-x, 1-y, -z
C1-H1A···O7	0.97	2.35	3.19(5)	143	x, y, z

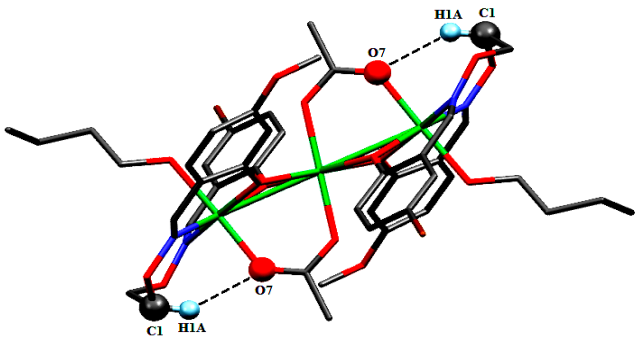


Fig. 2. View of the intramolecular hydrogen-bonding interactions of the complex

Each oxygen (O9) atom of the non-coordinated *n*-butanol molecule is hydrogen-bonded to the -O8H8 group of the coordinated *n*-butanol molecule and the -C25H25A group of the another non-coordinated *n*-butanol molecule, respectively, while its -O9H9 group is hydrogen-bonded to the μ-acetato oxygen (O6) atoms. Thus, each Ni(II) complex links two non-coordinated *n*-butanol molecules by intermolecular O8-H8···O9, O9-H9···O6 and C25-H25A···O9 hydrogen bonds into an infinite 1D chain along the *c*-axis (Fig. 3).

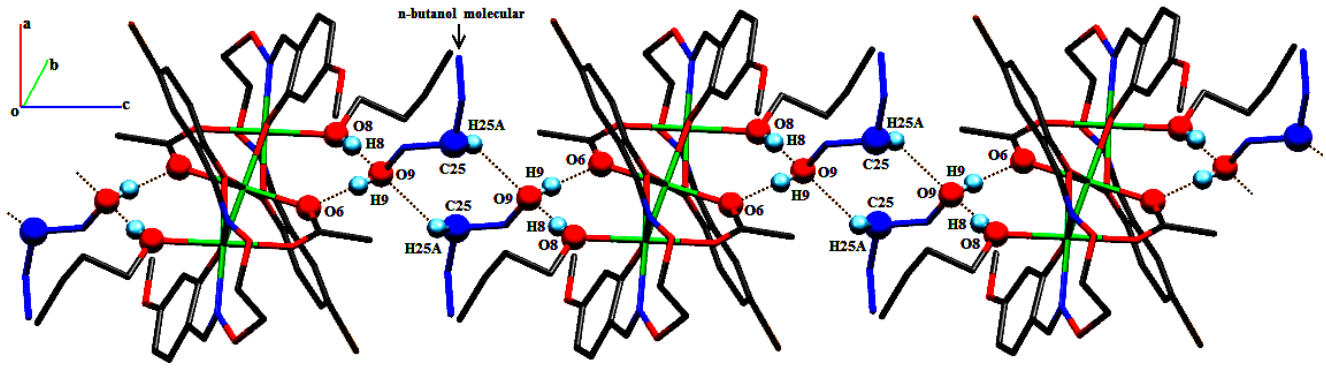


Fig. 3. View of the 1D chain motif of the Ni(II) complex units along the *c* axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

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