

## Salen 型双肟镍(II)簇合物的合成与晶体结构

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## Synthesis and Crystal Structure of Nickel(II) Cluster with Salen-Type Bisoxime Ligand

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**Abstract:** A nickel(II) cluster,  $\{[\text{Ni}(\text{L})\text{H}_2\text{O}]_2(\text{OAc})_2\text{Ni}\} \cdot 2\text{EtOH}$ , has been synthesized by the means of the complexation of nickel(II) acetate tetrahydrate with a new Salen-type bisoxime ligand ( $\text{H}_2\text{L}$ , 4,4'-dimethoxy-2,2'-[ethylenedioxybis(nitrilo-methylidene)]diphenol). The crystal structure shows that the hexacoordinated terminal nickel(II) ions lie in the  $\text{N}_2\text{O}_2$  coordination sphere of Salen-type bisoxime ligands, quadruple  $\mu$ -phenoxo oxygen atoms from two  $[\text{NiL}]$  chelates coordinated to the central nickel(II) ion, and the two acetate anions coordinated to three nickel(II) ions through Ni-O-C-O-Ni bridges. Thus, all the three nickel atoms of the cluster have distorted octahedral geometries. CCDC: 736762.

**Key words:** nickel(II) cluster; salen-type bisoxime ligand; synthesis; crystal structure

Salen-nickel(II) complexes have recently attracted much attention because they are used extensively in the design and construction of new magnetic materials and models for the nickel(II) centers of enzymes. Although the studies of Salen-nickel(II) complexes have made some advance<sup>[1]</sup>, to tune or improve the functions, chemical modifications of the ligand, e.g., introduction of some functional groups or substitution of some parts with appropriate ones, are effective and inevitable. In particular, replacement of some atoms of the ligand with other elements often changes its properties drastically<sup>[2]</sup>. If an O-alkyl oxime moiety ( $-\text{CH}=\text{N}-\text{O}-(\text{CH}_2)_n-\text{O}-\text{N}=\text{CH}-$ ) is used instead of the imine moiety, the larger electronegativity of oxygen atoms is expected to affect

strongly the electronic properties of  $\text{N}_2\text{O}_2$  coordination sphere, which can lead to different and novel properties and structures of the resulting complexes. For example, several works have been devoted to synthesize and characterize mononuclear, homo- or heterodinuclear transition metal complexes bearing a Salen-type bisoxime ligand or its derivatives<sup>[3-7]</sup>.

Herein, in continuation of our previous studies on synthesis and structural characterization of copper(II) and cobalt(II) complexes<sup>[8]</sup>, we report the synthesis and structure of a new Ni(II) cluster containing the Salen-type bisoxime ligand ( $\text{H}_2\text{L}$ , 4,4'-dimethoxy-2,2'-[ethylenedioxybis(nitrilomethylidene)]diphenol):  $\{[\text{Ni}(\text{L})\text{H}_2\text{O}]_2(\text{OAc})_2\text{Ni}\} \cdot 2\text{EtOH}$ . And it gave the trinuclear cluster, in

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which all the nickel atoms have an octahedral geometry.

## 1 Experimental

### 1.1 Materials and instruments

2-Hydroxy-5-methoxybenzaldehyde from Alfa Aesar was used without further purification. 1,2-dibromoethane was redistilled before using. 1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier<sup>[3]</sup>. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

Elemental analyses 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 Variuo EL V3.00 automatic elemental analyzer. The <sup>1</sup>H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using CDCl<sub>3</sub> as solvent. IR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with sample prepared as KBr (500~4 000 cm<sup>-1</sup>) and CsI (100~500 cm<sup>-1</sup>) pellets. The single crystal structure was determined on a Bruker Smart APEX CCD area detector. Melting points were obtained by use of an X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

### 1.2 Preparation of nickel(II) cluster

#### 1.2.1 Synthesis of H<sub>2</sub>L

H<sub>2</sub>L (4,4'-dimethoxy-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol) was synthesized by modification of the reported method<sup>[4]</sup>. To an ethanol solution of 2-hydroxy-5-methoxybenzaldehyde (307.6 mg, 2.00 mmol) was added an ethanol solution of 1,2-bis(aminooxy)ethane (92.2 mg, 1.00 mmol). The mixture solution was stirred at 55 °C for 4 h. After cooling to room temperature, the precipitate was filtered, and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum,

and obtained white microcrystal. Yield, 54.6%. m.p. 120~121 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.59 (s, 2H), 3.77 (s, 6H), 4.48 (s, 4H), 6.67 (d, *J*=2.4 Hz, 2H), 6.89 (d, *J*=3.2 Hz, 2H), 8.19 (s, 2H), 9.35 (s, 2H). Anal. Calcd. for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>(%): C 59.99; H 5.59; N 7.77. Found(%): C 59.82; H 5.64; N 7.89.

#### 1.2.2 Synthesis of cluster {[Ni(L)H<sub>2</sub>O]<sub>2</sub>(OAc)<sub>2</sub>Ni}·2EtOH

A solution of nickel(II) acetate tetrahydrate (26.2 mg, 0.1 mmol) in ethanol (15 mL) was added dropwise to a solution of H<sub>2</sub>L (37.8 mg, 0.1 mmol) in chloroform (15 mL) at room temperature. The color of the mixing solution turned a bright green immediately, and then continued to stirring for 4 h at room temperature. The mixture solution was filtered and the filtrate was allowed to stand at room temperature for about four week, the solvent was partially evaporated and obtained several prismatic green single crystals suitable for X-ray crystallographic analysis. Anal. Calcd. for C<sub>44</sub>H<sub>58</sub>N<sub>4</sub>Ni<sub>3</sub>O<sub>20</sub> ([{Ni(L)H<sub>2</sub>O]<sub>2</sub>(OAc)<sub>2</sub>Ni}·2EtOH)(%): C 46.40; H 5.13; N 4.92; Ni 15.46. Found(%): C 46.35; H 5.17; N 4.98; Ni 15.41.

### 1.3 Crystal structure determination

The X-ray diffraction measurement for the cluster was performed on Bruker Smart Apex CCD diffractometer with graphite monochromatized Mo *K*α radiation (λ=0.071 073 nm) at 273(2) K. Empirical absorption correction was applied to the data using SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares method on *F*<sup>2</sup> using the SHELXTL program<sup>[9]</sup>. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection and refinements for the cluster are summarized in Table 1.

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**Table 1** Crystal data and structure refinement for cluster {[Ni(L)H<sub>2</sub>O]<sub>2</sub>(OAc)<sub>2</sub>Ni}·2EtOH

Empirical formula	C <sub>44</sub> H <sub>58</sub> N <sub>4</sub> Ni <sub>3</sub> O <sub>20</sub>	Absorption correction	Multi-scan
Formula weight	1 139.07	<i>F</i> (000)	594
<i>T</i> / K	273(2)	Crystal size / mm	0.13×0.10×0.08
Wavelength / nm	0.071073	θ range for data collection / (°)	2.35~19.41
Crystal system	Triclinic	Index ranges	-11 ≤ <i>h</i> ≤ 11, -10 ≤ <i>k</i> ≤ 14, -12 ≤ <i>l</i> ≤ 14

Continued Table 1

Space group	$P\bar{1}$	Completeness to $\theta=25.01^\circ$ / %	98.9
$a$ / nm	0.975 50(10)	Reflections collected	6 284
$b$ / nm	1.194 30(12)	Independent reflections ( $R_{int}$ )	4 230 (0.0495)
$c$ / nm	1.224 60(15)	Reflections observed [ $I>2\sigma(I)$ ]	2 394
$\alpha$ / ( $^\circ$ )	67.378(2)	Refinement method	Full-matrix least-squares on $F^2$
$\beta$ / ( $^\circ$ )	67.425(2)	Data / restraints / parameters	4 230 / 0 / 329
$\gamma$ / ( $^\circ$ )	85.834(3)	Goodness-of-fit on $F^2$	1.006
$V$ / nm <sup>3</sup>	1.211 3(2)	Final R indices [ $I>2\sigma(I)$ ]	$R_1=0.064$ 6, $wR_2=0.143$ 6
$Z$	1	R indices (all data)	$R_1=0.135$ 5, $wR_2=0.147$ 2
$D_c$ / (Mg $\cdot$ m <sup>-3</sup> )	1.562	$(\Delta\rho)_{max}$ / (e $\cdot$ nm <sup>-3</sup> )	503
$\mu$ (Mo $K\alpha$ ) / mm <sup>-1</sup>	1.237	$(\Delta\rho)_{min}$ / (e $\cdot$ nm <sup>-3</sup> )	-471

## 2 Results and discussion

### 2.1 Crystal structure of $\{[\text{Ni}(\text{L})\text{H}_2\text{O}]_2(\text{OAc})_2\text{Ni}\} \cdot 2\text{EtOH}$

The crystal structure of the cluster reveals formation of a trinuclear structure, which consists of one nickel(II) atom, one  $\text{L}^{2-}$  unit, two acetate anions, two coordinated water molecules and two crystallizing ethanol molecule. Selected bond distances and bond angles are listed in Table 2. The crystal structure is shown in Fig.1.

The cluster is to be a linear array of three Ni(II) atoms coupled by both doubly  $\mu$ -phenoxo oxygens of  $\text{L}^{2-}$  and two acetate anions in the *syn-syn* bridging mode. The coordination geometry around the terminal Ni(II)

centers may be regarded as distorted octahedral geometry with hexa-coordination. The equatorial plane of each of the two equivalent terminal Ni(II) atoms (Ni1 and Ni1<sup>i</sup>) are formed by the two oxime nitrogen atoms (N1, N2) and two  $\mu$ -phenoxo oxygen atoms (O3, O5) coming from the  $\text{L}^{2-}$  moiety. The apical positions are occupied by one oxygen atom (O9) of water molecule and one oxygen atom (O7) from the bridging acetate group. The dihedral angle between the two coordination planes, N1-Ni1-O3 and N2-Ni1-O5, is  $5.66^\circ$ . The bond distances of Ni1-N of oxime, Ni1-O of  $\mu$ -phenoxo oxygen are in the range observed for similar systems<sup>[10,11]</sup>.

However, the coordination geometry of the central Ni2 atom deviates slightly from an ideal octahedron. The central Ni2 atom has an  $\text{O}_2\text{O}_2$  donor set from four  $\mu$ -

Table 2 Selected bond distances (nm) and bond angles ( $^\circ$ ) for the cluster

Ni1-O5	0.199 6(4)	Ni1-O7	0.204 5(4)	Ni2-O3	0.208 4(4)
Ni1-O3	0.200 3(4)	Ni1-O9	0.215 6(4)	Ni2-O3 <sup>i</sup>	0.208 4(4)
Ni1-N1	0.203 8(5)	Ni2-O8	0.205 1(4)	Ni2-O5	0.208 8(4)
Ni1-N2	0.204 1(5)	Ni2-O8 <sup>i</sup>	0.205 1(4)	Ni2-O5 <sup>i</sup>	0.208 8(4)
O5-Ni1-O3	82.88(16)	O3-Ni2-O3 <sup>i</sup>	180.00(1)	O7-Ni1-O9	176.14(17)
O3-Ni1-N2	170.24(19)	O8-Ni2-O5 <sup>i</sup>	89.70(16)	N1-Ni1-O9	85.4(2)
O3-Ni1-O9	93.10(17)	O3-Ni2-O5 <sup>i</sup>	78.78(15)	O8-Ni2-O8	180.0(3)
O5-Ni1-N2	88.44(18)	O8-Ni2-O5 <sup>i</sup>	90.30(16)	O8-Ni2-O3 <sup>i</sup>	91.23(16)
O5-Ni1-N1	171.0(2)	O3-Ni2-O5 <sup>i</sup>	101.22(15)	O8-Ni2-O3	88.77(16)
N2-Ni1-O7	95.04(19)	O3-Ni1-O7	89.59(17)	O8-Ni2-O5	90.30(16)
N2-Ni1-O9	82.72(19)	O3-Ni1-N1	88.60(19)	O3-Ni2-O5	101.22(15)
N1-Ni1-N2	99.8(2)	O5-Ni1-O7	91.03(17)	O8-Ni2-O5	89.70(16)
O8-Ni2-O3	88.77(16)	O5-Ni1-O9	92.04(17)	O3-Ni2-O5	78.78(15)
O8-Ni2-O3	91.23(16)	N1-Ni1-O7	91.88(19)	O5-Ni2-O5 <sup>i</sup>	180.00(1)

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>  $-x+2, -y+1, -z$ .

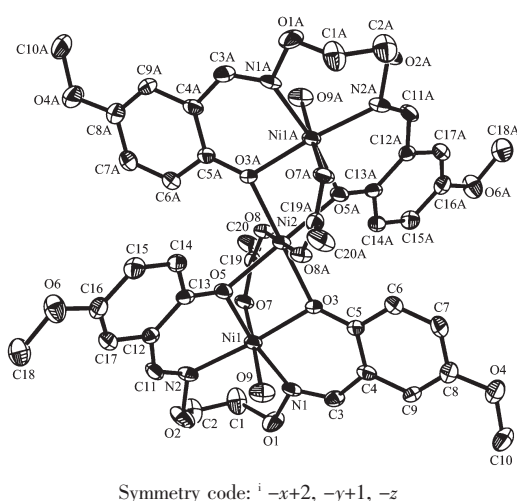
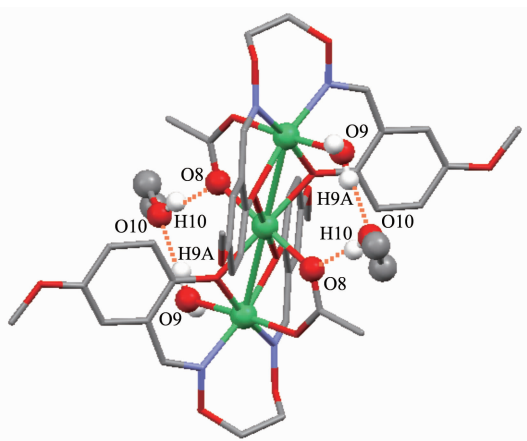


Fig.1 Structure of the cluster with the atom numbering, Thermal ellipsoids are plotted at 30% probability level, Hydrogen atoms and solvent molecules are omitted for clarity, Each of the nickel atoms sit in an octahedral geometry

phenoxo oxygen atoms ( $O3$ ,  $O5$ ,  $O3^i$  and  $O5^i$ ) of the two  $L^{2-}$  moieties. Meanwhile, each of acetate anions bridges the terminal Ni1 and central Ni2 atoms in a *syn-syn* fashion. Hence the central Ni2 atom finally has an  $O_2O_2O_2$  donor set. Thus, the trinuclear structure is stabilized by the two  $\mu$ -acetato ligands bridging, which neutralize the whole charge of cluster. Similar trinuclear structures supported by two acetato ligands are also found in salicylidene imine complexes containing zinc(II)<sup>[12]</sup>, cadmium(II)<sup>[13]</sup> and copper(II)<sup>[3]</sup>.

In the crystal structure of the cluster, there exist four strong intermolecular hydrogen bonds,  $O10-H10 \cdots O8$  and  $O9-H9A \cdots O10$  (Fig.2). Two are formed



Hydrogen atoms are omitted for clarity

Fig.2 Intermolecular hydrogen bonds of the cluster

between the hydroxyl ( $H10-O10$ ) of each crystallizing ethanol molecule and the oxygen atoms ( $O8$ ) of the bridging acetate group and the two others are formed between the oxygen atoms ( $O10$ ) of each crystallizing ethanol molecule and the hydroxyl ( $H9A-O9$ ) of the coordinated water molecule.

## 2.2 IR spectral analysis

The IR spectra of the free ligands and their corresponding nickel(II) cluster exhibit various bands in the  $500 \sim 4\,000\text{ cm}^{-1}$  region. The O-H stretching frequency of Salen-type ligands is expected in the  $3\,300 \sim 3\,800\text{ cm}^{-1}$  region, however, this frequency is generally displaced to the  $3\,200 \sim 3\,450\text{ cm}^{-1}$  region due to the internal hydrogen bond  $OH \cdots N=C$ <sup>[14]</sup>. For the nickel(II) cluster, the disappearance of this band is expected due to the substitution of hydrogen for the nickel(II) on the cluster formation<sup>[15]</sup>. A very broad absorption band at  $3\,435\text{ cm}^{-1}$  in cluster is assigned to -OH groups of uncoordinated ethanol molecule as well as stretching vibration for water as is substantiated by crystal structure.

The free ligand of  $H_2L$  exhibits characteristic  $C=N$  stretching bands at  $1\,610\text{ cm}^{-1}$ , while the  $C=N$  of the nickel(II) cluster was observed in the  $1\,576\text{ cm}^{-1}$ . The  $C=N$  stretching frequencies are shifted to lower frequencies by *ca.*  $34\text{ cm}^{-1}$  upon complexation, indicating a decrease in the  $C=N$  bond order due to the coordinated bond of the nickel(II) with the oxime nitrogen lone pair<sup>[14]</sup>. In the  $1\,454 \sim 1\,578\text{ cm}^{-1}$  region, the observed bands were attributed to aromatic  $C=C$  vibrations. Upon coordination these bands shift to lower frequencies for the nickel(II) clusters of ligands<sup>[16]</sup>. The Ar-O stretching frequency occurs at  $1\,263\text{ cm}^{-1}$  for  $H_2L$ , and at  $1\,225\text{ cm}^{-1}$  for cluster. The Ar-O stretching frequency is shifted to a lower frequency, indicating that the Ni-O bond was formed between the nickel(II) ion and oxygen of phenolic group<sup>[16,17]</sup>.

The far-infrared spectrum of cluster was also obtained in the region  $500 \sim 100\text{ cm}^{-1}$  in order to identify frequencies due to the Ni-O and Ni-N bonds. The band at  $440\text{ cm}^{-1}$  in cluster is assigned to  $\nu(\text{Ni-O})$ , while band at  $484\text{ cm}^{-1}$  is assigned to  $\nu(\text{Ni-N})$ . These bands are observed as new peaks for the clusters and are not

present in the spectra of the free ligands. As pointed out by Percy and Thornton<sup>[18]</sup>, the metal-oxygen and metal-nitrogen frequency assignments are at times very difficult.

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