

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

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A new nickel(II) complex,  $[(\text{NiL}\{\text{MeOH}\})_2(\text{OAc})_2\text{Ni}]\cdot 2\text{MeOH}$ , has been synthesized *via* the complexation of nickel(II) acetate tetrahydrate with a new Salen-type bisoxime ligand ( $\text{H}_2\text{L}$ ). X-Ray crystal structure determination of the nickel(II) complex shows that the hexa-coordinated terminal nickel(II) atoms 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) atom and the two acetate anions coordinated to three nickel(II) atoms through Ni-O-C-O-Ni bridges. Thus, all the three nickel(II) atoms of the Ni(II) complex have distorted octahedral geometries.

**Keywords:** Nickel(II) complex, Salen-type bisoxime ligand, Synthesis, Crystal structure.

### INTRODUCTION

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<sup>1</sup>. To change the structures or improve the functions of the resulted complexes, chemical modifications of the elemental Salen-type ligand are effective and inevitable<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<sup>3-5</sup>. Herein, a new Ni(II) complex containing the Salen-type bisoxime ligand ( $\text{H}_2\text{L}$ ),  $[(\text{NiL}\{\text{MeOH}\})_2(\text{OAc})_2\text{Ni}]\cdot 2\text{MeOH}$ , has been synthesized and structurally characterized by X-ray crystallography.

### EXPERIMENTAL

4-Methoxy-2-hydroxybenzaldehyde and 1,3-dibromoethane ( $\geq 98\%$ ) were purchased from Alfa Aesar and used without further purification. 1,3-Bis(aminoxy)propane was synthesized according to an analogous method reported earlier<sup>5</sup>. 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.

**General procedure:** The ligand  $\text{H}_2\text{L}$  was synthesized according to an analogous method reported earlier<sup>6</sup>. To an ethanolic solution (12 mL) of 4-methoxy-2-hydroxybenzaldehyde (76.21 mg, 0.50 mmol) was added an ethanolic solution (10 mL) of 1,3-bis(aminoxy)propane (25.96 mg, 0.25 mmol). The mixture solution was stirred at 55 °C for 6 h, after cooling to room temperature and the reaction mixture was filtered, washed successively with ethanol and ethanol/hexane (1:3), respectively. The product was dried under vacuum and obtained colourless crystalline solid. Yield: 68.5%. m.p. 103–104 °C. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.12 (t,  $J = 6.6$  Hz, 2H), 3.81 (s, 6H), 4.26 (t,  $J = 6.20$  Hz, 4H), 6.46 (d,  $J = 2.4$  Hz 2H), 6.50 (d,  $J = 2.4$  Hz 2H), 6.98 (s, 2H), 8.09 (s, 2H), 10.00 (s, 2H). Anal. calcd. (%) for  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_6$ : C 60.95, H 5.91, N 7.47. Found (%): C 61.32, H 5.95, N 7.33.

The nickel(II) complex was synthesized as follow procedure: A solution of Ni(II) acetate tetrahydrate (8.1 mg, 0.03 mmol) in methanol (4 mL) was added dropwise to a solution of  $\text{H}_2\text{L}$  (12.1 mg, 0.03 mmol) in acetone (4 mL) at room temperature. The colour 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 4 weeks. The solvent was partially evaporated and obtained several block-like green single crystals suitable for X-ray crystallographic analysis. Anal. calcd. (%) for  $\text{C}_{46}\text{H}_{62}\text{N}_4\text{O}_{20}\text{Ni}_3$  ( $[(\text{NiL}\{\text{MeOH}\})_2(\text{OAc})_2\text{Ni}]\cdot 2\text{MeOH}$ ): C, 47.34; H, 5.36; N, 4.80; Ni, 15.08. Found (%): C, 46.88; H, 5.65; N, 4.69; Ni, 15.05.

**X-Ray structure determination:** The single crystal of the Ni(II) complex with approximate dimensions of 0.50 mm × 0.45 mm × 0.43 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 298(2) K. The structure was solved by using the program SHELXS-97<sup>7</sup> and Fourier difference techniques and refined by full-matrix least-squares method on F<sup>2</sup> using SHELXL-97<sup>8</sup>. Details of the data collection and refinements of Ni(II) complex are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC No.: 757698.

Empirical formula	C <sub>46</sub> H <sub>62</sub> N <sub>4</sub> O <sub>20</sub> Ni <sub>3</sub>
Formula weight	1167.13
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 13.2925(13) Å, b = 12.8150(12) Å, c = 15.4313(17) Å, $\beta = 103.0840(10)^\circ$
Volume	2560.4(4) Å <sup>3</sup>
Z	2
Density (calculated)	1.514 mg/m <sup>3</sup>
Absorption coefficient	1.172 mm <sup>-1</sup>
F <sub>(000)</sub>	1220
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -18 ≤ l ≤ 9
Reflections collected	12614 [R <sub>(int)</sub> = 0.0266]
Independent reflections	4514
Data/restraints/parameters	4514 / 0 / 350
Goodness of fit indicator	1.098
R [I > 2σ(I)]	R <sub>1</sub> = 0.0334, wR <sub>2</sub> = 0.0761
R indices (all data)	R <sub>1</sub> = 0.0536, wR <sub>2</sub> = 0.0905
Largest diff. peak and hole	0.310 and -0.449 e Å <sup>-3</sup>

## RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of the nickel(II) complex. Selected bond distances

and angles are given in Table-2. The crystal structure of the nickel(II) complex indicating the numbering of the atoms is shown in Fig. 1. The complex crystallizes in the P2(1)/n space group with a linear trinuclear array of three Ni(II) atoms coupled by both doubly  $\mu$ -phenoxo oxygens of L<sup>2-</sup> and simultaneously 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 hexacoordination. The equatorial plane of each of the two equivalent terminal Ni(II) (Ni2 and Ni2<sup>#</sup>) atoms are formed by the two O-alkyl oxime nitrogen (N1, N2) atoms and two  $\mu$ -phenoxo oxygen (O3, O5) atoms coming from the L<sup>2-</sup> moiety. The apical positions are occupied by one oxygen (O9) atom of the coordinated methanol molecule and the other oxygen (O8) atom from the bridging acetate group. The central Ni(II) (Ni1) atom has an O<sub>2</sub>O<sub>2</sub> donor set from four  $\mu$ -phenoxo oxygen (O3, O5, O3<sup>#</sup> and O5<sup>#</sup>) atoms of the two L<sup>2-</sup> moieties. Meanwhile, each of the two acetate anions bridges the terminal Ni(II) (Ni2) and central Ni(II) (Ni1) atoms in a *syn-syn* fashion. Hence the central Ni(II) (Ni1) atom finally has an O<sub>2</sub>O<sub>2</sub>O<sub>2</sub> donor set (four equatorial oxygen atoms coming from four deprotonated  $\mu$ -phenoxo oxygens of the two L<sup>2-</sup> moieties and two axial oxygen atoms from the bridging acetates). Consequently, the coordination geometry of the central Ni(II) (Ni2) atom deviates slightly from an ideal octahedron. The trinuclear structure is probably stabilized by the two  $\mu$ -acetato ligands bridging, which neutralize the whole charge of the Ni(II) complex. Similar trinuclear structures supported by two acetato ligands are also found in salicylideneimine complexes containing Zn(II)<sup>9</sup>, Cd(II)<sup>10</sup> and Cu(II)<sup>3</sup>.

The complex [(NiL{MeOH})<sub>2</sub>(OAc)<sub>2</sub>Ni]·2MeOH contains uncoordinated methanol molecule and there is a hydrogen bond interaction between the crystallizing methanol molecules and [(NiL{MeOH})<sub>2</sub>(OAc)<sub>2</sub>Ni] moieties as shown in Fig. 2. Each of the hydroxyl groups in two crystallizing methanol molecules bonded to the hydroxyl proton (H9) of the coordinated methanol molecule and the oxygen (O7) atom of the bridging acetate group, respectively. Consequently, two pairs of hydrogen bonds, O10-H10...O7 and O9-H9...O10, are also formed (Table-3)<sup>11,12</sup>.

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O5	2.049(2)	Ni1-O7 <sup>#</sup>	2.094(2)	Ni2-O5	2.038(2)
Ni1-O5 <sup>#</sup>	2.049(2)	Ni1-O7	2.094(2)	Ni2-N1	2.082(3)
Ni1-O3	2.084(2)	Ni2-O8	2.020(2)	Ni2-N2	2.083(3)
Ni1-O3 <sup>#</sup>	2.084(2)	Ni2-O3	2.031(2)	Ni2-O9	2.107(2)
Bond	Angles	Bond	Angles	Bond	Angles
O5-Ni1-O5 <sup>#</sup>	180.0	O3-Ni1-O7 <sup>#</sup>	89.92(7)	O8-Ni2-O5	91.01(8)
O5-Ni1-O3	78.14(7)	O3 <sup>#</sup> -Ni1-O7 <sup>#</sup>	90.08(7)	O3-Ni2-O5	79.63(7)
O5 <sup>#</sup> -Ni1-O3	101.86(7)	O5-Ni1-O7	88.37(7)	O8-Ni2-N1	89.70(9)
O5-Ni1-O3 <sup>#</sup>	101.86(7)	O5 <sup>#</sup> -Ni1-O7	91.63(7)	O3-Ni2-N1	86.58(9)
O5 <sup>#</sup> -Ni1-O3 <sup>#</sup>	78.14(7)	O3-Ni1-O7	90.08(7)	O5-Ni2-N1	166.21(9)
O3-Ni1-O3 <sup>#</sup>	180.0	O3 <sup>#</sup> -Ni1-O7	89.92(7)	O8-Ni2-N2	92.08(1)
O5-Ni1-O7 <sup>#</sup>	91.63(7)	O7 <sup>#</sup> -Ni1-O7	180.00	O3-Ni2-N2	164.65(9)
O5 <sup>#</sup> -Ni1-O7 <sup>#</sup>	88.37(7)	O8-Ni2-O3	93.28(8)	O5-Ni2-N2	85.90(9)
N1-Ni2-N2	107.83(1)	O3-Ni2-O9	87.95(8)	N1-Ni2-O9	87.13(1)
O8-Ni2-O9	176.53(8)	O5-Ni2-O9	92.41(8)	N2-Ni2-O9	87.54(1)
Ni2-O3-Ni1	97.24(8)	Ni2-O5-Ni1	98.13(8)	-	-

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

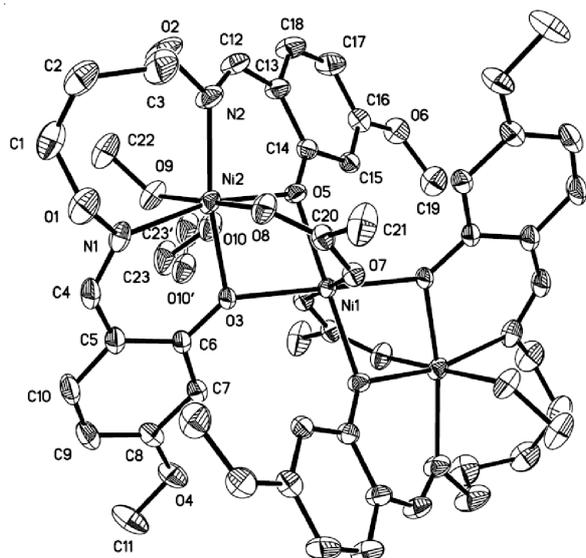


Fig. 1. Molecular structure of the nickel(II) complex with the atomic numbering

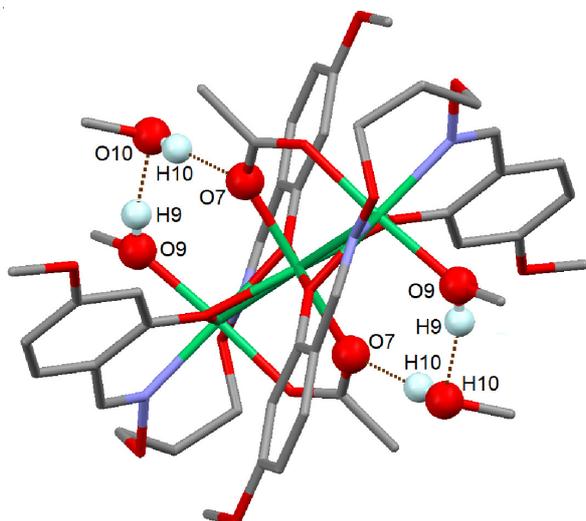


Fig. 2. Intermolecular hydrogen bonds of the nickel(II) complex

TABLE-3  
DATA FOR HYDROGEN-BONDING INTERACTIONS [Å, °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O9-H9...O10	0.82	1.83	2.641(5)	169
O10-H10...O7	0.82	1.95	2.762(6)	174

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#### REFERENCES

1. R. Ziessel, *Coord. Chem. Rev.*, **216**, 195 (2001).
2. L. Gomes, E. Pereira and B. de Castro, *J. Chem. Soc., Dalton Trans.*, 1373 (2000).
3. W.K. Dong, C.E. Zhu, H.L. Wu, Y.-J. Ding and T.-Z. Yu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **37**, 61 (2007).
4. W.K. Dong, J.Y. Shi, L. Xu, J.K. Zhong, J.G. Duan and Y.P. Zhang, *Appl. Organometal. Chem.*, **22**, 89 (2008).
5. W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012).
6. W.K. Dong, L. Li, Y.X. Sun, J.F. Tong and J.C. Wu, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **42**, 716 (2012).
7. G.M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Göttingen, Germany (1996).
8. G.M. Sheldrick, *Acta Cryst.*, **A64**, 112 (2008).
9. J. Reglinski, S. Morris and D.E. Stevenson, *Polyhedron*, **21**, 2175 (2002).
10. K. Ueno and A.E. Martell, *J. Phys. Chem.*, **60**, 1270 (1956).
11. W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012).
12. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch.*, **66b**, 1049 (2011).