



NOTE

**A Penta- and Hexa-Coordinated Trinuclear Nickel(II) Complex
[(NiL)₂(OAc)₂Ni]·2(*n*-PrOH)·CHCl₃: Synthesis and Crystal Structure**

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A tri-nuclear Ni(II) complex, [(NiL)₂(OAc)₂Ni]·2(*n*-PrOH)·CHCl₃, has been synthesized by the reaction of Ni(II) acetate tetrahydrate with a salen-type bisoxime chelating ligand (H₂L). The X-ray crystal structure of the complex reveals that there are two acetate ions coordinate to three Ni(II) atoms through Ni-O-C-O-Ni bridges and quadruple μ-phenoxo oxygen atoms from two [NiL] chelates also coordinate to Ni(II) atoms. Interestingly, the Ni(II) complex possessing different conformational metal centers: penta- and hexa-coordinated geometry.

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

Oxime-type compounds have long been used as chelating ligands in the synthesis of transition metal complexes due to their ease of preparation and structural variety. Those derived from salicylaldehyde and various amines have been used to synthesize many complexes of nickel(II) and copper(II)¹⁻³. In recent years, there has been enhanced interest in the synthesis and characterization of such complexes due to their interesting properties⁴ and they have been increasingly used in supramolecular chemistry⁵, medicine⁶, antivirus⁷ and other applications. Herein, a new salen-type bisoxime chelating ligand H₂L and its trinuclear Ni(II) complex, [(NiL)₂(OAc)₂Ni]·2(*n*-PrOH)·CHCl₃ have been synthesized and structurally characterized by X-ray crystallography.

4-Methoxy-2-hydroxy benzaldehyde (≥98 %) was purchased from Alfa Aesar was used without further purification. 1,2-Bis(aminoxy)ethane was synthesized according to an analogous method reported earlier². 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 H₂L was synthesized with a slightly modified method reported literature⁸. Reaction of 1,2-bis(aminoxy)ethane (133.7 mg, 1.45 mmol) with 2 equivalents of 4-methoxy salicylaldehyde (456 mg, 3 mmol) in ethanol (10 mL) at 55 °C for 6 h. After cooling to room temperature, the resulting solid was filtered and washed with

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

Empirical formula	C ₄₇ H ₅₉ N ₉ O ₁₈ Cl ₃ Ni ₃
Formula weight	1250.46
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Cell dimensions	a = 11.2569(11) Å, b = 11.3205(12) Å, c = 12.9672(14) Å, α = 115.7000(10)°, β = 96.1240(10)°, γ = 108.880(2)°
Volume	1348.5(2) Å ³
Z	1
Density (calculated)	1.540 mg/m ³
Absorption coefficient	1.260 mm ⁻¹
F ₍₀₀₀₎	648
Index ranges	-11 ≤ h ≤ 13, -13 ≤ k ≤ 9, -14 ≤ l ≤ 15
Reflections collected	7005
Independent reflections	4679 [R _{int} = 0.0146]
Data/restraints/parameters	4679/0/400
Goodness of fit indicator	1.083
Final R indices [I > 3σ(I)]	R ₁ = 0.0407, wR ₂ = 0.1100
R indices (all data)	R ₁ = 0.0566, wR ₂ = 0.1287
Largest diff. peak and hole	0.836 and -0.714 e. Å ⁻³

ethanol and ethanol/hexane (1:4), respectively. The product was dried *in vacuo* and obtained 456.3 mg of colourless microcrystal. Yield: 78.9 %. m.p. 97-98 °C. ¹H NMR (400 MHz, CDCl₃), δ 3.79 (s, 6H), 4.41 (s, 4H), 6.46 (d, J = 2.8 Hz,

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

Atom	Distance	Atom	Distance	Atom	Distance
Ni1-O7 [#]	2.035(2)	Ni1-O3	2.109(2)	Ni2-O8	2.011(3)
Ni1-O7	2.035(2)	Ni1-O3 [#]	2.109(2)	Ni2-N2	2.025(3)
Ni1-O5 [#]	2.078(2)	Ni2-O3	1.993(2)	Ni2-N1	2.037(3)
Ni1-O5	2.078(2)	Ni2-O5	2.002(2)	—	—
Atom	Angle	Atom	Angle	Atom	Angle
O7 [#] -Ni1-O7	180.00(1)	O7 [#] -Ni1-O3	90.84(1)	O5 [#] -Ni1-O3 [#]	77.55(9)
O7 [#] -Ni1-O5 [#]	89.62(1)	O7-Ni1-O3	89.16(1)	O5-Ni1-O3 [#]	102.45(9)
O7-Ni1-O5 [#]	90.38(1)	O5 [#] -Ni1-O3	102.45(9)	O3-Ni1-O3 [#]	180.00(1)
O7 [#] -Ni1-O5	90.38(1)	O5-Ni1-O3	77.55(9)	O3-Ni2-O5	82.07(9)
O7-Ni1-O5	89.62(1)	O7 [#] -Ni1-O3 [#]	89.16(1)	O3-Ni2-O8	94.53(1)
O5 [#] -Ni1-O5	180.00(1)	O7-Ni1-O3 [#]	90.84(1)	O5-Ni2-O8	92.99(1)
O3-Ni2-N2	162.79(1)	O5-Ni2-N1	168.98(1)	N2-Ni2-N1	97.20(1)
O5-Ni2-N2	89.30(1)	O8-Ni2-N1	94.51(1)	O3-Ni2-N1	89.29(1)
O8-Ni2-N2	100.79(1)	Ni2-O3-Ni1	96.06(9)	Ni2-O5-Ni1	96.80(1)

Symmetry transformations used to generate equivalent atoms: [#]-x, -y + 1, -z + 1.

2H), 6.47 (s, 2H), 7.04 (d, $J = 2.8$ Hz 2H), 8.17 (s, 2H), 9.94 (s, 2H). Anal. calcd. (%) for C₁₈H₂₀N₂O₆ (H₂L): C, 59.99; H, 5.59; N, 7.77. Found (%): C, 59.96; H, 5.85; N, 7.65.

The Ni(II) complex was synthesized as follow procedure: A solution of Ni(II) acetate tetrahydrate (4.1 mg, 0.015 mmol) in *n*-propanol (3 mL) was added dropwise to a solution of H₂L (6.0 mg, 0.016 mmol) in chloroform (3 mL) at room temperature. Vapour phase diffusion of *n*-hexane into the solution afforded green block-like crystals of the complex. Anal. calcd. (%) for C₄₇H₅₉N₄O₁₈Cl₃Ni₃ (%): C, 45.14; H, 4.76; N, 4.48; Ni, 14.08. Found (%): C, 46.18; H, 4.85; N, 4.49; Ni, 14.05.

X-Ray structure determination: The single crystal of the Ni(II) complex with approximate dimensions of 0.49 mm × 0.35 mm × 0.27 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_α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by using the program SHELXS-97⁹ and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97¹⁰. 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 No.: 909427.

The X-ray crystallography indicates that the Ni(II) complex contains three Ni(II) atoms, two tetradentate (μ -L)²⁻ units, two coordinated μ -acetate ions, one crystallizing chloroform molecule and two crystallizing *n*-propanol molecules. The molecular structure of the Ni(II) complex is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The central Ni(II) (Ni1) atom is hexa-coordinated, the coordination sphere is completed by μ -phenoxo oxygen (O3, O5, O3[#] and O5[#]) atoms from two [Ni(L)] chelates and both of oxygen (O7 and O7[#]) atoms from the bridging acetate ions which adopt a familiar μ -O-C-O fashion and constitute a slightly distorted octahedral geometry. It is noteworthy that the terminal Ni(II) (Ni2 and Ni2[#]) atoms are both penta-coordinated and located in the N₂O₂ moieties of the ligand. The oxygen (O8 and O8[#]) atoms from the bridging acetate ions are also coordinated to Ni2 and Ni2[#], respectively. Consequently, the coordination geometry around Ni2 and Ni2[#] approaches to a distorted square pyramid. The trinuclear structure is stabilized by the two

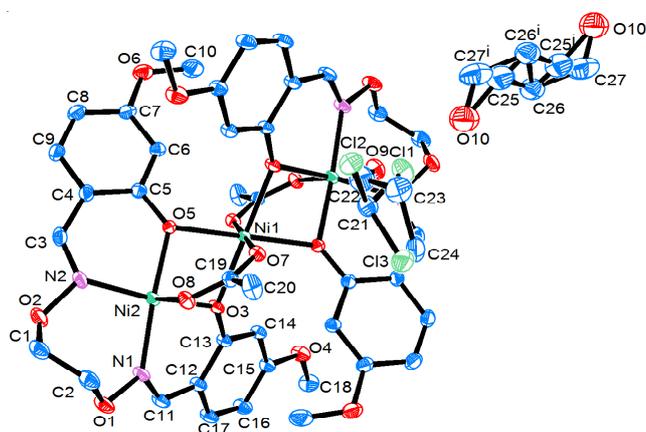


Fig. 1. Molecular structure of the nickel(II) complex

μ -acetato ligands bridging Ni1-Ni2 and Ni1-Ni2[#], which neutralize the whole charge of the Ni(II) complex.

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