



Synthesis, Crystal and Supramolecular Structure of Nickel(II) Complex with Asymmetrical Salamo-type Ligand

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A Salamo-type ligand 5-methoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidene)]diphenol (H_2L) and its corresponding Ni(II) complex have been synthesized. The Ni(II) complex has been characterized by single crystal X-ray crystallography. The crystal structure shows that two water molecules coordinated to the hexa-coordinated terminal Ni(II) ($Ni1$ and $Ni1^{#1}$) atoms which lie in the N_2O_2 coordination sphere of the Salamo-type ligand, quadruple μ -phenoxo oxygen atoms from two L^{2-} units coordinated to the central Ni(II) atom and two acetate anions coordinated to three Ni(II) atoms through Ni-O-C-O-Ni bridges. Thus, all the three Ni(II) atoms have distorted octahedral geometries.

Key Words: : Asymmetrical Salamo-type ligand, Ni(II) complex, Synthesis, Crystal structure.

INTRODUCTION

Salen-type ligands and its analogues are most versatile chelate ligands in inorganic and organometallic chemistry owing to their various functions. Photochemical¹⁻⁴ and redox⁵⁻⁸ properties arising from hybridization between the organic and metal complex moieties are successfully applied to guest sensing or detection. Particularly, the asymmetrical Salen-type ligands can generate the supported metal complexes in a more flexible fashion, often resulting in more desirable catalytic properties⁹⁻¹². Although most of the metal complexes containing Salen-type ligands are stable in solution and in the solid state, C=N bonds often suffer exchange reaction^{13,14} as well as hydrolysis¹⁵. Hence, designing and synthesizing the new Salamo-type ligand on the basis of O-alkyl oxime instead of the imine moiety are necessary. Rate constants of oxime formation are smaller than those of imine formation and the equilibrium constants are larger by several orders¹⁶. Thus, the oxime-type ligands should be stable enough to resist the metathesis of the C=N bonds. Recent studies have demonstrated that asymmetrical Salamo-type ligands, in terms of two distinct substituents on the two aromatic rings^{17a,b}, hold important advantages¹⁸. Moreover, the desymmetrization of the core would introduce more structural variations that allows a deliberate optimization of both steric and electronic properties of the ligands.

Herein, we reported the synthesis and crystal structure of a trinuclear Ni(II) complex with a new asymmetrical Salamo-

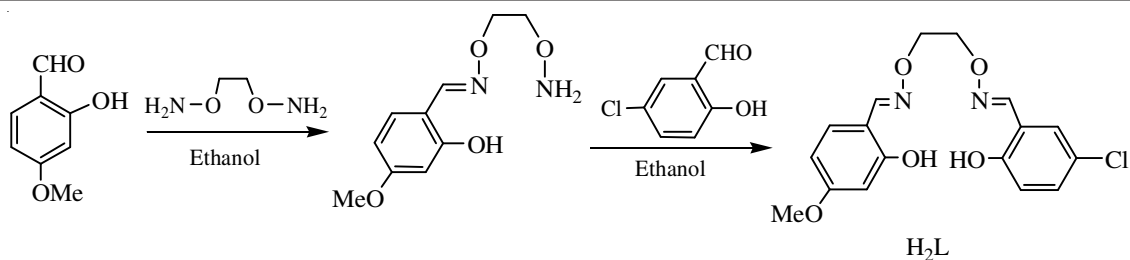
type ligand 5-methoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidene)]diphenol (H_2L).

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde ($\geq 99\%$) and 2-hydroxy-5-chlorobenzaldehyde ($\geq 99\%$) were purchased from Alfa Aesar and used without further purification. 1,2-Bis(aminoxy)ethane was synthesized according to an analogous method reported earlier¹⁹⁻²². The others are the same as reported earlier^{17g}.

Synthesis of ligand H_2L : The major 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^{17,18}. Yield 87%. m.p. 383-385 K. Anal. Calcd. for $C_{17}H_{17}N_2O_5Cl$ (%): C, 55.97; H, 4.70; N, 7.68. Found: C, 55.81; H, 4.86; N, 7.53.

Synthesis of Ni(II) complex: A solution of $Ni(OAc)_2 \cdot 4H_2O$ (3.72 mg, 0.015 mmol) in methanol (2 mL) was added dropwise to a solution of H_2L (3.65 mg, 0.010 mmol) in acetonitrile (2 mL) at room temperature. The mixing solution turned to green immediately. After continuing stirring for 2 h at room temperature, the mixture was filtered off and the filtrate was allowed to stand at room temperature for more than 3 weeks. Then the solvent partially evaporated and green prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Anal. calcd. for $C_{38}H_{44}N_4O_{18}Cl_2Ni_3$ (%): C, 41.80; H, 4.06; N, 5.13; Ni, 16.13. Found: C, 42.02; H, 4.19; N, 4.97; Ni, 15.96.

Scheme-I: Synthetic route to the asymmetrical Salamo-type ligand H₂L

X-Ray structure determination: The X-Ray structure determination is the same as literature early¹⁷. Details of the data collection and refinements of the Ni(II) complex are given in Table-1.

TABLE-1 CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE Ni(II) COMPLEX	
Empirical formula	C ₃₈ H ₄₄ N ₄ O ₁₈ Cl ₂ Ni ₃
Formula weight	1091.80
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/c
Cell dimensions, (Å, deg)	a = 10.8900(9), b = 16.8501(15), c = 15.1809(13), β = 125.940(2)
Volume (Å ³)	2255.4(3)
Z	2
Density (calculated) (mg/m ³)	1.608
Absorption coefficient (mm ⁻¹)	1.436
F ₍₀₀₀₎	1124
Crystal size	0.32 × 0.17 × 0.14
Index ranges	-12 ≤ h ≤ 7, -20 ≤ k ≤ 20, -15 ≤ l ≤ 18
Reflections collected	11226/3961 [R(int) = 0.0986]
Independent reflections	1114
Data/restraints/parameters	3961/0/297
Goodness of fit indicator	1.080
R [I > 2σ(I)]	R ₁ = 0.0659, wR ₂ = 0.1351
Largest diff. peak and hole (e Å ⁻³)	1.602 and -1.040

RESULTS AND DISCUSSION

Crystal structure of Ni(II) complex: X-ray crystallographic analysis reveals formation of a trinuclear structure, which consists of three Ni(II) atoms, two L²⁻ units, two acetate anions, two coordinated and one non-coordinated water molecules. ORTEP-style drawing of the Ni(II) complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table-2.

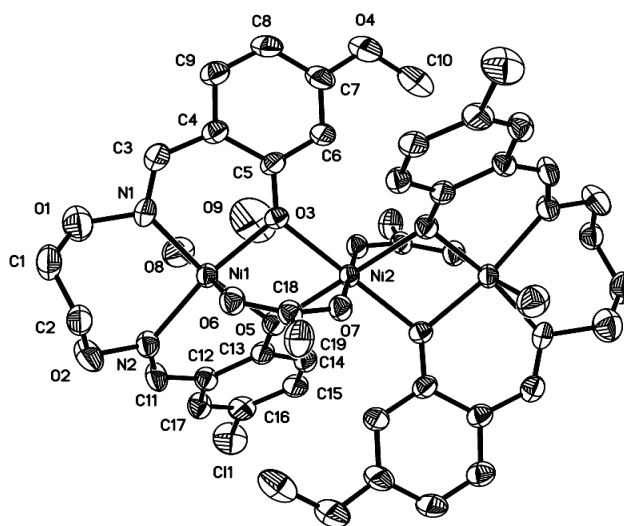


Fig. 1. ORTEP-style drawing of the Ni(II) complex

TABLE-2 SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Ni(II) COMPLEX					
Bond	Lengths	Bond	Lengths	Bond	Lengths
Ni1-O3	2.014(7)	Ni1-N2	2.089(9)	Ni2-O5	2.071(6)
Ni1-O5	2.037(7)	Ni1-O8	2.195(8)	Ni2-O5 ^{#1}	2.071(6)
Ni1-N1	2.059(9)	Ni2-O7 ^{#1}	2.056(8)	Ni2-O3	2.101(7)
Ni1-O6	2.067(7)	Ni2-O7	2.056(8)	Ni2-O3 ^{#1}	2.101(7)
Bond	Angles	Bond	Angles	Bond	Angles
O3-Ni1-O5	82.5(3)	N2-Ni1-O8	85.7(4)	O5 ^{#1} -Ni2-O3 ^{#1}	79.6(2)
O3-Ni1-N1	88.6(3)	O7 ^{#1} -Ni2-O7	180.0(1)	O3-Ni2-O3 ^{#1}	180.0(1)
O5-Ni1-N1	169.1(3)	O7 ^{#1} -Ni2-O5	92.7(3)	C3-N1-Ni1	123.7(8)
O3-Ni1-O6	90.2(3)	O7-Ni2-O5	87.3(3)	O1-N1-Ni1	116.8(7)
O5-Ni1-O6	92.3(3)	O7 ^{#1} -Ni2-O5 ^{#1}	87.3(3)	C11-N2-Ni1	121.6(9)
N1-Ni1-O6	94.1(3)	O7-Ni2-O5 ^{#1}	92.7(3)	O2-N2-Ni1	125.3(6)
O3-Ni1-N2	168.6(3)	O5-Ni2-O5 ^{#1}	180.0(1)	C5-O3-Ni1	129.3(6)
O5-Ni1-N2	86.3(3)	O7 ^{#1} -Ni2-O3	88.9(3)	C5-O3-Ni2	132.6(7)
N1-Ni1-N2	102.3(4)	O7-Ni2-O3	91.1(3)	Ni1-O3-Ni2	96.0(3)
O6-Ni1-N2	92.2(3)	O5-Ni2-O3	79.6(2)	C13-O5-Ni1	122.7(6)
O3-Ni1-O8	92.3(3)	O5 ^{#1} -Ni2-O3	100.4(2)	C13-O5-Ni2	132.5(7)
O5-Ni1-O8	89.3(3)	O7 ^{#1} -Ni2-O3 ^{#1}	91.1(3)	Ni1-O5-Ni2	96.3(3)
N1-Ni1-O8	84.7(3)	O7-Ni2-O3 ^{#1}	88.9(3)	C18-O6-Ni1	127.2(8)
O6-Ni1-O8	177.2(3)	O5-Ni2-O3 ^{#1}	100.4(2)	C18-O7-Ni2	130.6(7)

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-H8C...O9	0.85	1.57	2.42(2)	179	x, y, z
O8-H8D...O4	0.85	2.21	3.06(1)	178	1-x, 1/2+y, 1/2-z
O9-H9C...O7	0.85	1.95	2.80(2)	175	1-x, 1-y, 1-z
O9-H9D...C11	0.85	2.52	3.37(1)	175	x, 3/2-y, -1/2+z
C1-H1A...O9	0.97	2.48	3.31(2)	143	1+x, 3/2-y, 1/2+z
C2-H2A...O6	0.97	2.24	3.15(2)	155	x, y, z
C6-H6...O5	0.93	2.54	3.26(2)	135	1-x, 1-y, 1-z
C1-H1B... $\pi_{\text{centroid(C4-C9)}}$	0.97	2.93	3.87(2)	163	2-x, 1-y, 1-z

The Ni(II) complex is to be a linear trinuclear array of three Ni(II) atoms coupled by both doubly μ -phenoxo oxygen atoms of the L^{2-} units and two acetate anions in the *syn-syn* bridging mode. The coordination geometry around the two terminal Ni(II) (Ni1 or Ni1^{#1}) atoms may be regarded as distorted octahedral geometries with hexa-coordination, in which one oxygen (O8) atom from the coordinated water molecule occupied the apical positions around the terminal Ni(II) (Ni1 or Ni1^{#1}) atom which lies in the N_2O_2 coordination sphere of the L^{2-} units, quadruple μ -phenoxo oxygen (O3, O5, O3^{#1} and O5^{#1}) atoms from two L^{2-} units are located on the equatorial plane of the central Ni(II) (Ni2) atom and two acetate anions coordinated to three Ni(II) atoms through Ni-O-C-O-Ni bridges. Thus, all the three Ni(II) atoms have distorted octahedral geometries. Meanwhile, the terminal Ni(II) (Ni1 or Ni1^{#1}) atom is 0.081(3) Å out of the N_2O_2 equatorial plane designed by atoms (N1-O3-O5-N2), but the central Ni(II) (Ni2) atom lies in the corresponding O_2O_2 equatorial plane.

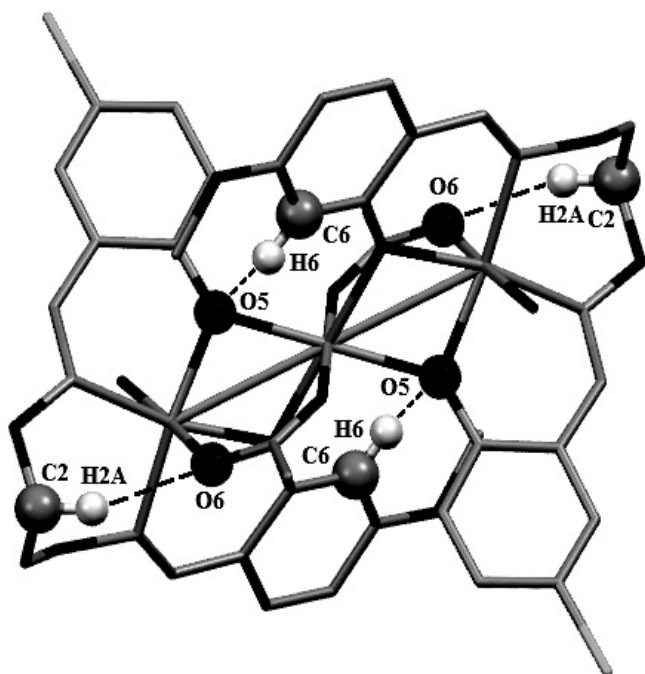


Fig. 2. View of the intramolecular hydrogen-bonding interactions of the Ni(II) complex.

Intermolecular interactions of the Ni(II) complex: The extended hydrogen bonding network is formed by O-H...O, O-H...Cl, C-H...O and C-H... π intramolecular, intermolecular

hydrogen bonds between the Ni(II) complex and crystallizing water molecules, respectively. It also could be pointed out that the hydrogen-bonding interactions play a critical role in formation, stability and crystallization of the Ni(II) complex. Hydrogen bond data are summarized in Table-3.

The Ni(II) complex has two pairs of weak intramolecular C2-H2A...O6 and C6-H6...O5 hydrogen-bonding interactions (Fig. 2). Furthermore, the Ni(II) complex is stabilized by three pairs of strong intermolecular O8-H8C...O9, O8-H8D...O4 and O9-H9C...O7 hydrogen-bonding interactions into an infinite 1D chain (Fig. 3). Synchronously, this linkage is further stabilized by two pairs of intermolecular C1-H1B... $\pi_{\text{centroid(C4-C9)}}$ hydrogen bonding interactions between the methylene (-C1H1B) unit of the O-alkyl chain and the benzene ring (C4-C9) of the coordinated L^{2-} unit, with the addition of two weak O9-H9D...C11 and C1-H1A...O9 hydrogen bonding interactions,

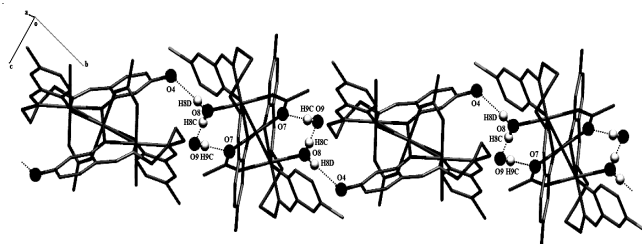


Fig. 3. View of the 1D chain motif of the Ni(II) complex units (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

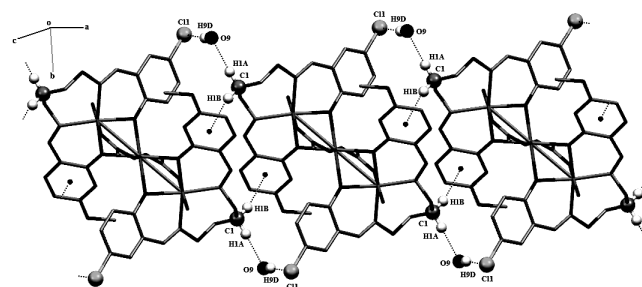


Fig. 4. View of the 1D chain motif of the Ni(II) complex units along the a axis (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

to form the other 1D infinite chain along the a axis, as illustrated in Fig. 4. Thus, each Ni(II) complex molecule links eight other molecules by four crystallizing water molecules to form an infinite 3D network supramolecular structure (Fig. 5) through intermolecular hydrogen bond interactions.

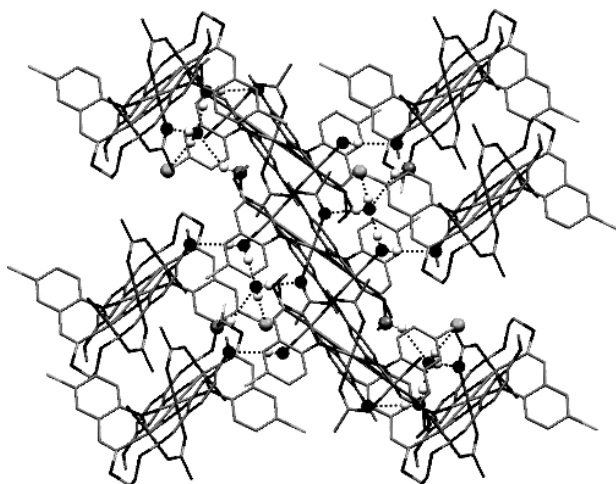


Fig. 5. View of the 3D supramolecular network motif of Ni(II) complex (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

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