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Variation of carboxylate binding mode in self-assembled Ni(II) complexes with tridentate reduced Schiff base ligand: Syntheses, structural analysis

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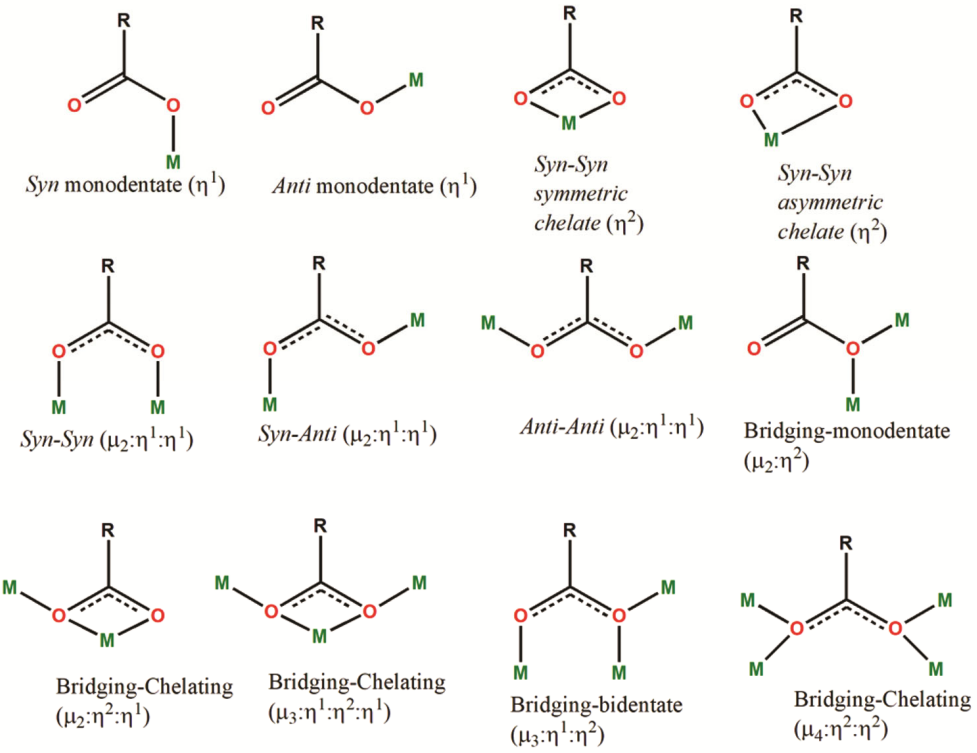
Two new Ni(II) complexes, $[Ni_2L^1_2(C_6H_5CH_2COO)](ClO_4)\cdot 2CH_3CN$ (**1**) and $[Ni_2L^1_2(C_6H_5\ CH_2COO)_2(H_2O)]\cdot 2H_2O$ (**2**) have been synthesized by using $Ni(ClO_4)_2\cdot 6H_2O$, a tridentate NNO donor reduced Schiff base ligand, HL^1 = [(3-dimethylamino-propylamino)-methyl]-phenol and phenylacetic acid as co-ligand. Both complexes have been characterized by single crystal X-ray crystallography, electronic and IR spectroscopy. Structural analysis reveals that Ni(II) ions possess distorted octahedral geometry in both complexes **1**-**2**. Bis-μ_2-phenoxido bridged complex **1** has one *syn-syn* phenylacetate bridging, whereas complex **2** possesses similar type of structure with additional terminal coordination (*syn*-monodentate-η^1 mode) by another phenylacetate molecule.

Keywords: Ni complexes, Reduced Schiff base ligands, Different coordination modes of carboxylate coligand, Structural characterization

In the past few decades, design and synthesis of polynuclear coordination complexes is one of the fastest areas of growing research in inorganic chemistry, due to their versatile structural topologies and application in the field of catalysis, molecular magnetism, medicinal chemistry, bioinorganic chemistry *etc*[1-10]. Several Ni(II) systems are reported to study as model structures of a Ni dependant metalloenzyme *i.e.* Urease[11-13]. The study of model structures and magnetic properties of Ni(II) complexes with monoanionic salicylaldehyde containing tridentate Schiff base ligands is still in that race. Non-symmetric N_2O donor Schiff bases are one of the extensively studied ligands because they can bring fascinating structural diversity in synthesized polynuclear complexes[14-18]. Most studies have focused on self-assembly method, where small building units lead to diversified architectures. However, the prediction of actual structure during self-assembly reaction is little bit of difficult and the outcome always brings structural serendipity[19-23]. The parameters that influence to achieve preferred structures include the different coordination modes of bridging ligands, the steric and electronic factors of auxiliary Schiff base ligands, metal ions and their preferred stereochemistry and reaction conditions also[24-28]. The synthesis of versatile topologies with different dimensionalities by using same metal-ligand systems is a highly challenging and very demanding task. Always, a systematic study is preferred to investigate the role of bridging ligands during design and synthesis of discrete to higher dimensional structures. To get a clear cut idea, concentrations of bridging ligands are varied by keeping other parameters (metal, Schiff base) constant[29-32].

Carboxylato bridged polynuclear complexes draw much attention in this category with their widespread application as model compounds in bioinorganic chemistry and molecular magnetism[33-38]. Carboxylate co-ligand is well known for its ability to introduce diversity in nuclearity of transition metal complexes (e.g discrete, 1D, 2D, 3D). This co-ligand shows different bridging modes (*syn-syn*, *syn-anti*, *anti-anti*) and also terminal binding mode in polynuclear complexes (Scheme 1). Generally, *syn-syn* bridging mode favours binuclear systems, whereas *syn-anti*, *anti-anti* modes are observed in multinuclear, chain and layer structures[39,40].

Herein, I report the synthesis of two new diphenoxo bridged dinuclear Ni(II) complexes, $[Ni_2L^1_2(C_6H_5CH_2COO)](ClO_4)\cdot 2CH_3CN$ (**1**) and $[Ni_2L^1_2(C_6H_5CH_2COO)_2(H_2O)]\cdot 2H_2O$ (**2**) by using an N_2O donor tridentate reduced Schiff bases ligand (HL^1= [(3-dimethylamino-propylamino)-methyl]-phenol. The complexes are characterized by single crystal X-ray crystallography, electronic spectra, IR spectra and elemental analyses.



Scheme 1 — Reported coordination modes of carboxylate anion ($RCOO^-$).

Experimental Section

Starting materials

The reagents and solvents (Salicylaldehyde, N,N-dimethyl-1,3-propanediamine, sodium borohydride, phenylacetic acid, acetonitrile, methanol *etc*.) were obtained from Spectrochem, India. The chemicals were of reagent grade and have been used without further purification.

Caution! Transition metal complexes, formed by their perchlorate salts with organic ligands are generally explosive in nature. Synthesized complexes should be prepared in small amount and should be handled with ultimate care.

Synthesis of the ligand [(3-dimethylamino-propylamino)-methyl]-phenol (HL^1)

Salicylaldehyde (0.52 ml, 5 mmol) and N,N-dimethyl-1,3-propanediamine (0.63 mL, 5 mmol) were mixed and refluxed in methanol (30 mL) for 1 h. After that, the whole solution was cooled to 0°C and solid sodium borohydride (210 mg, 6 mmol) was slowly mixed to mixture solution with constant stirring. After completion of the reaction, concentrated HCl (5 mL) was added with resulting solution. Then, the whole mixture was evaporated to dryness. The reduced Schiff-base ligand (HL^1) was extracted from the solid residue with methanol. This methanolic solution (HL^1) was used for synthesizing the complexes.

Synthesis of $[Ni_2L^1_2(C_6H_5CH_2COO)](ClO_4)\cdot 2CH_3CN$, 1

$Ni(ClO_4)_2\cdot 6H_2O$ (1.82 g, 5 mmol), dissolved in 10 mL of H_2O-CH_3OH mixture, was added to a methanolic solution (10 mL) of the Schiff base (HL^1) (5 mmol) with constant stirring. After 15 minutes, methanolic solution of phenylacetic acid, $C_6H_5CH_2COOH$ (0.68 g, 5 mmol) was added to the stirring solution. Now triethylamine (10 mmol) was slowly mixed with it with continuous stirring. Slow evaporation of the resulting green solution gave a deep green coloured microcrystalline compound. The green solid residue was collected and washed with diethyl ether. Diffractable single crystals of compound **1** were obtained by layer separation of the acetonitrile solution of green solid with diethyl ether.

(Yield: 1.7 g; 80%). Anal. Calcd. For $C_{36}H_{51}N_6Ni_2O_8Cl$: C, 50.95; H, 6.06; N, 9.90. Found: C, 51.05; H, 6.14; N, 9.98. IR (KBr pellet, cm^{-1}): ν(N-H), 3270 cm^{-1}.

Synthesis of $[Ni_2L^1_2(C_6H_5CH_2COO)_2(H_2O)]\cdot 2H_2O$, 2

10 mL methanolic solution of reduced Schiff base ligand (HL^1) was mixed and stirred with dissolved

$Ni(ClO_4)_2·6H_2O$ (1.82 g, 5 mmol) in 10 mL H_2O-CH_3OH mixture. Phenylacetic acid, $C_6H_5CH_2COOH$ (1.36 g, 10 mmol) was dissolved in small amount of methanol and slowly mixed to the stirred solution after *ca.* 15 minutes, followed by addition of triethylamine (2.1 mL, 15 mmol). The whole greenish solution was kept in open air for slow evaporation. Block shaped deep-green X-ray quality single crystals of complex **2** were obtained after few days.

(Yield: 1.6 g; 77%).). Anal. Calcd. For $C_{40}H_{58}N_4Ni_2O_9$: C, 56.11; H, 6.83; N, 6.54. Found: C, 56.19; H, 6.93; N, 6.62. IR (KBr pellet, cm^{-1}): ν(N-H), 3245 cm^{-1}.

Physical Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II elemental analyzer. IR spectra in KBr pellets (4500–500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra (1500–250 nm) were recorded in a Hitachi U-3501 spectro-photometer.

X-ray Crystallographic data collection and refinement

Collected diffractable single crystals of complexes 1 are 2 were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo-Kα (λ = 0.71073 Å) radiation. The crystals were positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The non-hydrogen atoms were refined with independent anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times (1.5 for methyl hydrogens) those of the atom to which they were attached. Absorption corrections were carried out using the SADABS program[41]. All the calculations were carried out using SHELXL 2014/7, PLATON-99, ORTEP-3[42-44]. The hydrogen atoms of non coordinated water molecules could not be located for complex 2. All related crystallographic data of complexes 1 and 2 are summarized in Table 1. CCDC-2285155 (1) and CCDC-2285156 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc. cam.ac.uk/data_request/cif.

Table 1 — Crystallographic parameters for complexes 1 and 2

Complex	**1**	**2**
Chemical formula	$C_{36}H_{51}N_6Ni_2O_4,ClO_4$	$C_{40}H_{54}N_4Ni_2O_9$
Formula weight	848.66	852.25
Crystal system	Monoclinic	Orthorhombic
Space group	*P21/n*	*Pbca*
a(Å)	17.2053(7)	20.208(6)
b (Å)	11.3376(5)	13.471(4)
c (Å)	22.2753(9)	31.481(10)
α (°)	90	90
β (°)	110.248(1)	90
γ (°)	90	90
V (Å³)	4076.7(3)	8570(5)
Z	4	8
ρ_{calc}(g cm^{-3})	1.383	1.321
μ (Mo Kα) (mm^{-1})	1.044	0.934
F(000)	1784	3600
Reflections collected	44979	37615
Independent reflections	7234	7619
Reflections with I > 2σ(I)	5977	5074
R_1[a], wR_2[b]	0.0362, 0.1068	0.0439, 0.1284
GOF [c]	1.029	1.058
Residual electron Density, e/Å^{-3}	–0.44, 0.56	–0.27, 0.54

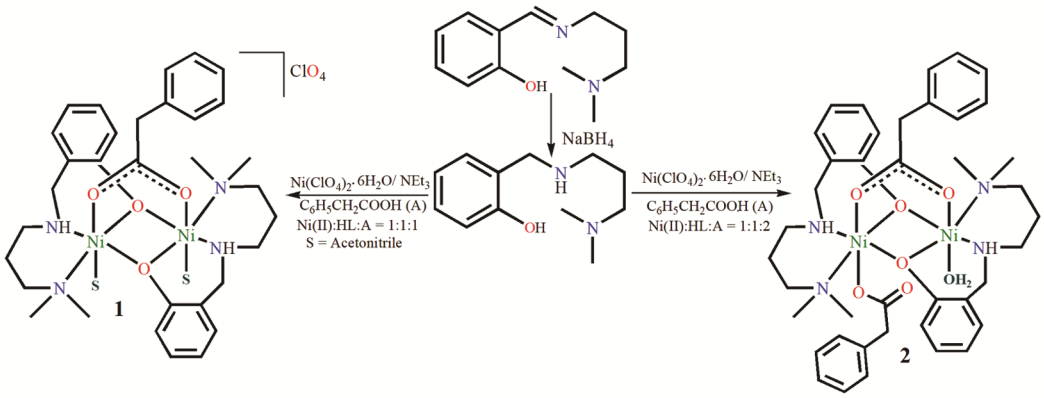
Results and discussion

Synthesis of the complexes

In this present work, tridentate reduced Schiff base ligand, HL^1 was allowed to react with $Ni(ClO_4)_2·6H_2O$ in H_2O-CH_3OH mixture solution, followed by the addition of methanolic solution of phenylacetic acid in 1:1 molar ratios for complex 1. Increasing the amount of phenylacetic acid does not lead to change of complex's nuclearity. Here complex 2 is obtained by reacting $Ni(ClO_4)_2·6H_2O$ and HL^1 in H_2O-CH_3OH mixture, followed by the addition of methanolic solution of $C_6H_5CH_2COOH$ with $Ni(ClO_4)_2·6H_2O$: HL^1: $C_6H_5CH_2COOH$; 1:1:2 molar ratios (Scheme 2). Required amount of triethylamine was added to the reaction mixture for the requirement of deprotonated phenylacetate moiety.

IR and UV–Vis spectra of complexes

In case of complex 1-2, moderately strong and sharp peaks at 3270 cm^{-1}, 3245 cm^{-1}, respectively due to N–H bond stretching vibration show that the imine bonds of Schiff base ligands are reduced. The absence of –C=N– bonds is further confirmed by the non-appearance of typical strong bands in the region of 1620-1650 cm^{-1}, ascribed to imine bond vibration of unreduced Schiff bases in their corresponding complexes. The strong bands (1605 cm^{-1}, 1456 cm^{-1} for 1) and (1618 cm^{-1}, 1440 cm^{-1}) for 2 are likely due to antisymmetric and symmetric stretching modes of vibration of carboxylate groups. The characteristics strong peak at 1115 cm^{-1} is observed for complex 1, attributed to non-coordinated perchlorate group. IR



Scheme 2 — Syntheses of complexes 1 and 2.

data shows a broad band nearly 3450 cm^{-1} for complex 2, may be for O–H stretching mode of water molecules. Electronic spectra of both complexes were recorded in methanolic solution. The spectra show bands at 650 nm, 980 nm for 1 and 644 nm, 968 nm for 2, which can be assigned spin allowed transitions, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{2g}(F) \leftarrow {}^3A_{2g}$, respectively, for octahedral d^8 systems. These values are in agreement with the reported values for octahedral Ni(II) compounds[45-46].

Description of crystal structures

The X-ray crystallographic analysis shows that both complexes 1 and 2 consist of discrete dinuclear diphenoxido bridged units with the formulas $[Ni_2L^1{}_2(C_6H_5CH_2COO)](ClO_4)\cdot 2CH_3CN$ (1), $[Ni_2L^1{}_2(C_6H_5CH_2COO)_2(H_2O)]\cdot 2H_2O$ (2), respectively (Fig. 1-2). In case of complex 1, the dinuclear core has two independent Ni(II) atoms, labelled Ni(1) and Ni(2), bridged by bis-μ_2-phenoxido oxygen atoms, O(10) and O(25) with Ni(1)–Ni(2) distance of 3.114 Å. Two phenoxido bridging angles Ni(1)–O(10)–Ni(2) and Ni(1)–O(25)–Ni(2) are 97.22(8)°, 97.83(8)°, respectively. Each Ni(II) ion presents in distorted octahedral geometry. The coordination environment around each nickel is formed by secondary amine nitrogen atoms [N(18), N(22) for Ni(1) and N(33), N(37) for Ni(2)] of the deprotonated Schiff base ligand, phenoxido oxygen atoms O(10), O(25) of the same ligand, the carboxylate oxygen atoms, O(40) and O(41) of a bridging bidentate phenyl acetate (1κO:2 κO') and by two coordinated acetonitrile molecules [N(1) for Ni(1) and N(2) for Ni(2)] (Fig. S1). All bond lengths are in normal range. The basal plane is formed by four donor atoms N(1), N(18), O(41) and O(25) for Ni(1) with bond distances in the range of 2.044(2)–2.160(3)

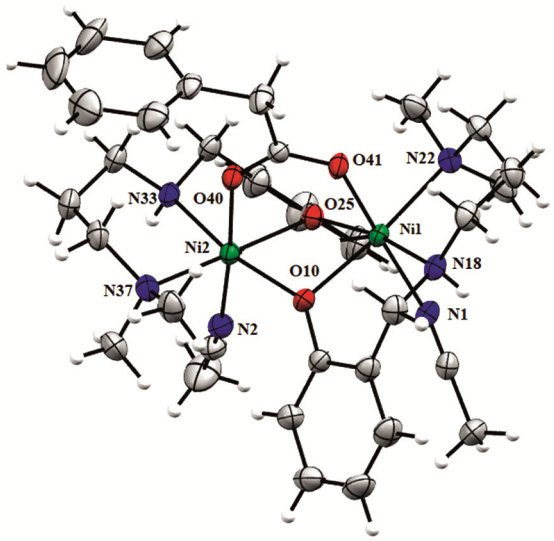


Fig. 1 — The structure of complex **1** with ellipsoids at 30% probability.

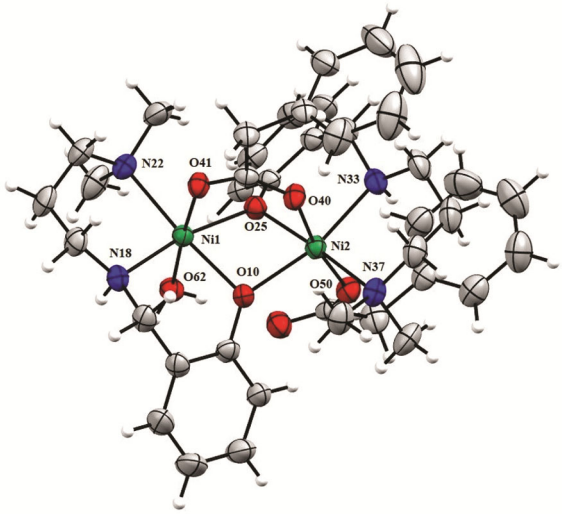


Fig. 2 — The structure of complex **2** with ellipsoids at 30% probability

Å. The deviations of the linked atoms, N(1), N(18), O(41) and O(25) from the least squares mean plane through them are 0.070(2), 0.075(2), −0.072(18) and −0.062(18) Å, respectively. The displacement of Ni(1) from the same plane is 0.106(4) Å towards the axially coordinated N(22) atom. O(10) and N(22) atoms of reduced Schiff base ligands occupy two axial positions with bond lengths; Ni(1)–O(10); 2.0715(18) Å, Ni(1)–N(22); 2.172(2) Å, respectively. Similarly for Ni(2), N(2), N(33), O(40), O(10) atoms construct the basal plane with bond distances in the range of 2.0258(19)–2.131(3) Å. For Ni(2), corresponding axial bonds are Ni(2)–O(25); 2.0693(17) Å, Ni(2)–N(37); 2.168(2) Å. The corresponding deviations of coordinating atoms, N(2), N(33), O(40), O(10) from the least squares mean plane through them are 0.090(3), −0.097(2), 0.096(17) and −0.089(17) Å, respectively and the deviation of Ni(2) atom from the same plane is 0.110(4) Å towards the axially coordinated N(37) atom. The trans bond angles are O(10)–Ni(1)–N(2); 174.36(9)° and O(25)–Ni(2)–N(37) 173.87(8)°.

The complex **2** has similar type of core structure like complex **1**. Only difference is that one terminally coordinated [*syn*-monodentate (η^1)] phenyl acetate anion and water molecule coordinate to Ni(II) instead of two solvent acetonitrile moieties (Fig. S2). Two Ni(II) ions are separated by 3.106 Å with diphenoxido bridging angles Ni(1)–O(10)–Ni(2); 97.23(10)° and Ni(1)–O(25)–Ni(2); 99.04(10)°. Here also, each Ni(II) occupies slightly distorted octahedral geometry. All the coordinating atoms around Ni centers are linked in a like fashion to that of complex **1**. Four donor atoms; O(10), O(25), N(18), N(22) construct the basal plane around Ni(1) centre. The Ni–O and Ni–N bond lengths in the basal plane are in the range of 2.042(2)–2.205(3) Å. The axial bond lengths are Ni(1)–O(41); 2.034(3) Å, Ni(1)–O(62); 2.130(4) Å. In case of Ni(2), the basal plane is formed by four donor atoms; O(10), O(40), N(33), O(50) and corresponding Ni–O, Ni–N bond lengths are in the range of 2.039(3)–2.137(4) Å. The two trans axial sites are occupied by O(25) of tridentate ligand at a distance of 2.042(2) Å and N(37) of the same ligand at a distance of 2.200(3) Å. The deviations of O(10), O(25), N(18), N(22) atoms from the least squares mean plane through them are 0.036(2), −0.034(2), –0.030(4), 0.028(3) Å (for Ni(1)) and N(33), O(10), O(40), O(50) that deviates from the same type plane are 0.139(4), 0.125(2), –0.138(3) and −0.126(3) Å (for Ni(2)). The Ni(1) displaces 0.018(4) Å from the same mean plane towards the axially coordinated O(62) atom and the shifting value Ni(2) atom from the same plane is 0.092(5) Å towards the axially coordinated N(37) atom. The trans bond angles are O(41)–Ni(1)–N(62); 176.56(13)° and O(25)–Ni(2)–N(37); 175.06(10)°. All important bond lengths and bond angles values are summarized in Table S1.

$^{a}R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $^{b}wR_2\ (F_o^2) = [\sum[w(F_o^2 - F_c^2)^2/\sum w\ F_o^4]^{½}$ and $^{c}GOF = [\sum[w(F_o^2 - F_c^2)^2/(N_{obs}- N_{params})]^{½}$

Conclusion

In this work, the reaction of tridentate reduced Schiff base ligand, [(3-dimethylamino-propylamino)-methyl]-phenol with nickel perchlorate and phenylacetic acid in 1:1:1 molar ratios produces a new bis-μ_2-phenoxido bridged and *syn-syn* carboxylato bridged complex 1. The self-assembly approach has been followed for synthesis. For a systematic study, the concentration of phenylacetic acid has been increased, while other parameters (metal and tridentate ligand concentration) are kept constant. Complex 2 has similar diphenoxido and *syn-syn* carboxylato bridging in between two Ni(II) ions like complex 1. But here additional phenylacetate moiety coordinates with one nickel centre *via syn*-η^1 mode through one of its O-donor sites.

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Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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