



Synthesis and crystal structure of a mixed bridged trinuclear Ni(II) complex derived from a tridentate NNO donor Schiff base ligand

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A new trinuclear Ni(II) complex $[\text{Ni}_3\text{L}_2(o\text{-}(\text{NO}_2)\text{C}_6\text{H}_4\text{COO})_2(\mu_1\text{-N}_3)_2(\text{CH}_3\text{OH})_2] \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized using a tridentate NNO donor Schiff base ligand, 1-[(3-dimethylamino-propylimino)-methyl]-naphthalen-2-ol (HL). Complex **1** has been characterized by X-ray crystallography, elemental analysis, IR and UV-Vis spectroscopy. Single crystal X-ray structure shows that complex **1** is a linear trinuclear Ni(II) complex containing μ -phenoxido, μ_1 -azido and *syn-syn* *o*-nitrobenzoato bridges between the terminal and the central Ni(II) ions. Complex **1** is crystallized in the monoclinic sp. gr. *P*21/*c* with the unit cell parameters $a = 12.246(5)$ Å, $b = 14.683(5)$ Å, $c = 17.688(5)$ Å, and $\beta = 104.208(5)^\circ$, $Z = 2$. The terminally coordinated methanol molecule involves in hydrogen bonding through the hydrogen atom H(7) with the oxygen atom O(22) of the solvent water molecule.

Keywords: Synthesis, crystal structure, Schiff base, mixed bridged, Ni(II) complex.

Introduction

Polynuclear nickel(II) complexes of tridentate NNO donor Schiff base ligands have received considerable attention due to their potential applications in the field of structural chemistry, biological systems, catalysis and magnetism¹⁻⁴. These types of NNO donor Schiff base ligands along with various polyatomic anions (N_3^- , NO_2^- , NO_3^- , $\text{N}(\text{CN})_2^-$, RCOO^-) are excellent combination to produce coordination polymers with structural diversity and interesting magnetic properties also^{4,5}. It is difficult to predict the structures of such mixed bridged Ni(II) polynuclear complexes in which Schiff base and more than one polyatomic bridging moieties are present together. In such cases there are too many factors that should be taken into consideration. In contrast to the phenoxido bridged Ni(II) complexes, the metal ions that are connected via mixed bridging ligands are less studied systems⁶. In connection to the synthesis of mixed bridged complexes, both azide and carboxylate ligands deserve special mention due to their wide variety of coordination modes. Among them the most common bridging modes of azide are end-to-end ($\mu_3\text{-N}_3$, EE) and end-on ($\mu_1\text{-N}_3$, EO)⁷. In general, monodentate terminal and bidentate bridging modes of carboxylate ligands are mostly studied but sometimes it may be coordinated to the metal center in tridentate fashion⁸. Fur-

thermore, these bridging ligands (phenoxido, azido and carboxylato) may simultaneously exist in the same species, leading to interesting topologies and magnetic behaviors^{9,10}.

Literature survey reveals that mixed bridged trinuclear Ni(II) complexes containing a tridentate Schiff base ligand along with carboxylate and azide groups are comparatively rare. It should be noted that Ghosh *et al.* previously reported a similar compound of Ni(II) with an NNO donor Schiff base ligand (HL') (2-[(3-dimethylamino-propylimino)-methyl]-phenol) in which the three Ni(II) centers are triply bridged by μ -phenoxido, μ_1 -azido and *syn-syn* acetato bridges⁵. Herein, we report synthesis, crystal structure and spectral studies of a new linear trinuclear Ni(II) complex derived from a tridentate NNO donor Schiff base ligand along with μ_1 -azide and *syn-syn* *o*-nitrobenzoate as two bridging co-ligands.

Experimental

Material:

The N,N-dimethyl-1,3-propanediamine and 2-hydroxy-1-naphthaldehyde were purchased from Lancaster Chemical Co. The chemicals were of reagent grade and used without further purification. *o*-Nitrobenzoate salt of nickel(II) was prepared by the reaction of nickel carbonate and *o*-nitrobenzoic acid in hot aqueous solution.

Physical measurements:

Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr ($4500\text{--}500\text{ cm}^{-1}$) was recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra ($1400\text{--}350\text{ nm}$) of complex **1** in CH_3OH was recorded in a Hitachi U-3501 spectrophotometer.

Synthesis of the Schiff base ligand (HL):

The Schiff base 1-[(3-dimethylaminopropylimino)-methyl]-naphthalen-2-ol was prepared by the condensation of 2-hydroxy-1-naphthaldehyde and N,N-dimethyl-1,3-propanediamine in methanol as reported earlier¹¹.

Synthesis of the complex (1):

$[\text{Ni}(\text{o}(\text{NO}_2)\text{C}_6\text{H}_4\text{COO})_2\cdot 2\text{H}_2\text{O}]$ (2.31 g, 7.5 mmol), dissolved in 10 mL of hot methanol, was added to a methanolic solution (10 mL) of the ligand (HL; 5 mmol) with constant stirring. After about 5 min an aqueous solution (2 mL) of NaN_3 (0.3 g, 5 mmol) was added with slow stirring followed by addition of triethylamine (0.70 mL, 5 mmol) to deprotonate the Schiff base ligand. A light green precipitate appeared immediately. It was then filtered, and the filtrate was left to stand in the air. X-Ray-quality single crystals of complex **1** were obtained on slow evaporation of the filtrate. Yield: 2.15 g; 70%. Anal. Calcd. for $\text{C}_{48}\text{H}_{54}\text{N}_{12}\text{Ni}_3\text{O}_{16}$ (1231.1): C, 46.83; H, 4.42; N, 13.65. Found: C, 46.90; H, 4.51; N, 13.59; IR (KBr pellet, cm^{-1}): 1614 $\nu(\text{C}=\text{N})$, 2072 $\nu_{\text{as}}(\text{N}_3^-)$, 3411 (broad) $\nu(\text{OH})$, 1532 $\nu_{\text{as}}(\text{C}=\text{O})$, 1390 $\nu_{\text{s}}(\text{C}=\text{O})$; $\lambda_{\text{max}}(\text{CH}_3\text{OH})$, 369, 636 and 1003 nm.

Crystallographic data collection and refinement:

Suitable single crystal of complex **1** was mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and Mo-K α ($\lambda = 0.71073\text{ \AA}$) radiation. The structure was solved by Patterson methods using SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined riding on their parent atoms. Hydrogen atoms at O(22) and O(23) of non coordinated solvent water molecules in complex **1** could not be located in the difference Fourier map. The oxygen atoms on O(22) and O(23) in **1** of the solvent water molecules were refined isotropically in the difference Fourier

map. All calculations were carried out using SHELXS 97¹², SHELXL 2013¹³, PLATON 99¹⁴, ORTEP-32¹⁵ and WinGX system-Ver-1.64¹⁶. Data collection and structure refinement parameters and crystallographic data for the complex (**1**) are given in Table 1.

Table 1. Crystallographic characteristics and the X-ray data collection and structure-refinement parameters for $\text{C}_{48}\text{H}_{54}\text{N}_{12}\text{Ni}_3\text{O}_{16}$ (**1**)

Formula	$\text{C}_{48}\text{H}_{54}\text{N}_{12}\text{Ni}_3\text{O}_{16}$
M	1231.10
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
$a, b, c, (\text{\AA})$	12.246(5), 14.683(5), 17.688(5)
β ($^\circ$)	104.208(5)
V (\AA^3)	3083.2(19)
Z	2
D_c (g cm^{-3})	1.326
μ (mm^{-1})	0.976
F (000)	1276
R (int)	0.052
Total, Unique reflections	36263, 6289
$I > 2\sigma(I)$	4656
Residual electron density, $e\text{ \AA}^{-3}$	-0.48, 1.58
R1, wR2	0.0698, 0.2464
Temp. (K)	293

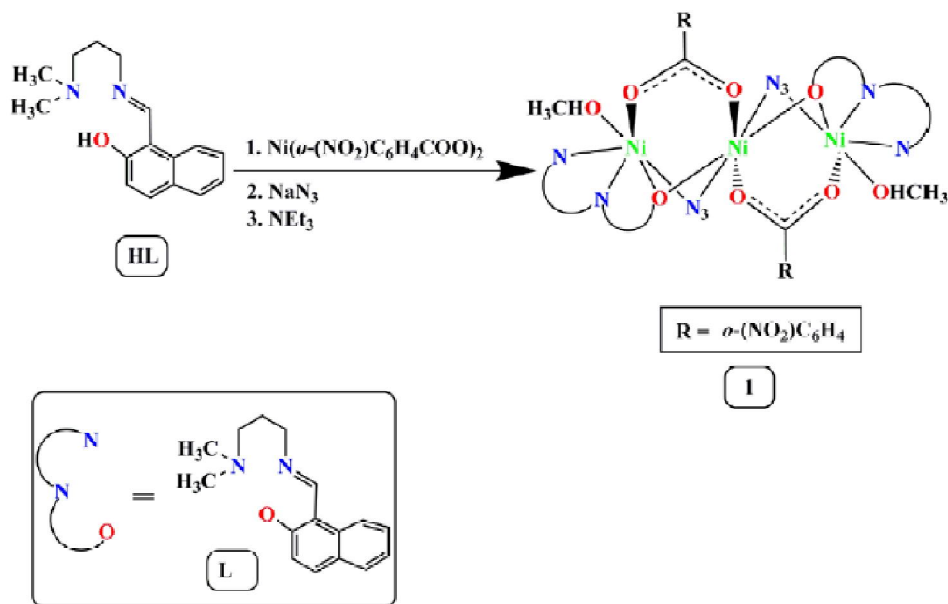
Results and discussion*Formation of the complex:*

The tridentate NNO donor Schiff base ligand HL 1-[(3-dimethylaminopropylimino)-methyl]-naphthalen-2-ol was allowed to react with the methanolic solution of nickel(II) *o*-nitrobenzoate salt in presence of an aqueous solution of NaN_3 in 2:3:2 molar ratio (Scheme 1).

IR and UV-Vis spectroscopy:

In the IR spectra of complex **1** a strong and sharp band due to azomethine $\nu(\text{C}=\text{N})$ appears at 1614 cm^{-1} . Complex **1** exhibits one distinct band at 2072 cm^{-1} , consistent with the presence of azide ligand in the structure. The appearance of a broad band near 3411 cm^{-1} indicates the presence of water molecules in the complex. The IR spectral bands in the $1300\text{--}1650\text{ cm}^{-1}$ region are difficult to be attributed due to the appearance of several absorption bands both from the Schiff base and the carboxylate ligands. Nevertheless, by

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Scheme 1. Synthetic route to complex 1.

comparing the IR spectra of other Ni(II) complexes of the same ligand^{10,11}, the strong bands at 1532 cm^{-1} may be assigned to the anti-symmetric stretching mode of the carboxylate group, whereas the bands at 1390 cm^{-1} to the symmetric stretching modes of the carboxylate ligands in complex 1. Furthermore, the elemental analysis is in good agreement with its solid state structure.

The electronic spectrum of the complex 1 is recorded in CH_3OH solution. The electronic spectrum shows absorption bands at 636, and 1003 nm (for 1). These bands are assigned to the spin allowed d-d transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, respectively. These values are in agreement with the literature values for octahedral Ni(II) compounds¹⁷. Moreover, the band observed at 369 nm for complex 1 is assigned to the L→M charge transfer transition which is characteristic of the transition metal complexes with Schiff base ligands¹⁸.

Crystal structure description:

The crystal structure of 1 consists of discrete centro-symmetric trinuclear unit of formula $[\text{Ni}_3\text{L}_2(o\text{-(NO}_2\text{)C}_6\text{H}_4\text{COO})_2(\mu_1\text{-N}_3)_2(\text{CH}_3\text{OH})_2] \cdot 2\text{H}_2\text{O}$. The structure is shown in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 2. In the structure, the three Ni(II) centers are interlinked through

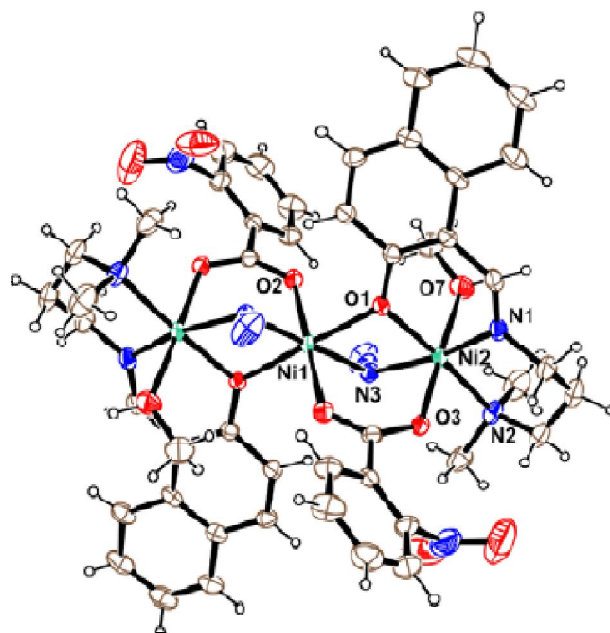


Fig. 1. ORTEP view of the asymmetric unit of 1 with ellipsoids at the 25% probability level.

three different kinds of bridges (μ_1 -azido, μ -phenoxido and *syn-syn* *o*-nitrobenzoato). The central Ni²⁺ ion lies on an inversion centre, resulting in a perfect linear structure. The structure may be assumed to be composed of two terminal mono-

Table 2. Selected bond distances (Å) and bond angles (°) in the metal coordination spheres of complex (**1**)

Atoms	Distance	Atoms	Angle
Ni(1)-O(1)	2.056(4)	O(1)-Ni(1)-O(2)	87.47(13)
Ni(1)-O(2)	2.047(3)	O(1)-Ni(1)-N(3)	79.76(13)
Ni(1)-N(3)	2.102(4)	O(2)-Ni(1)-N(3)	92.53(13)
Ni(2)-O(1)	2.034(3)	O(1)-Ni(2)-O(3)	91.08(12)
Ni(2)-O(3)	2.080(3)	O(1)-Ni(2)-O(7)	89.02(16)
Ni(2)-O(7)	2.147(5)	O(1)-Ni(2)-N(1)	175.08(17)
Ni(2)-N(1)	2.156(5)	O(1)-Ni(2)-N(2)	87.10(17)
Ni(2)-N(2)	2.016(4)	O(1)-Ni(2)-N(3)	80.35(15)
Ni(2)-N(3)	2.098(4)	O(3)-Ni(2)-O(7)	177.31(17)
		O(3)-Ni(2)-N(1)	88.26(15)
		Atoms	Angle
		O(3)-Ni(2)-N(2)	88.36(17)
		O(3)-Ni(2)-N(3)	91.93(15)
		O(7)-Ni(2)-N(1)	91.87(18)
		O(7)-Ni(2)-N(2)	88.95(19)
		O(7)-Ni(2)-N(3)	90.74(18)
		N(1)-Ni(2)-N(2)	97.75(19)
		Ni(1)-O(1)-Ni(2)	98.30(15)
		Ni(1)-N(3)-Ni(2)	94.89(16)

Symmetry codes: 2' = -x, -y, -z.

nuclear units of $[\text{NiL}(\text{N}_3)(\text{CH}_3\text{OH})]$ connected by a central $[\text{Ni}(\text{o}-(\text{NO}_2)\text{C}_6\text{H}_4\text{COO})_2]$ unit through the nitrogen atoms of μ_1 -azide, μ -phenoxido oxygen atoms of the deprotonated Schiff base ligand and the oxygen atoms of *syn-syn* *o*-nitrobenzoate anions. There are two crystallographically independent Ni(II) ions in the molecule with different coordination environments. Each of the two terminal Ni(2) atoms reside in a $[\text{N}_3\text{O}_3]$ octahedral environment where three donor atoms of the tridentate Schiff base ligand, with dimensions Ni(2)-N(1) 2.156(5) Å, Ni(2)-N(2) 2.016(4) Å and Ni(2)-O(1) 2.034(3) Å together with the azide nitrogen atom N(3) at 2.098(4) Å constitute the equatorial plane. Two axial positions are occupied by one oxygen atom of the *syn-syn* *o*-nitrobenzoate ion O(3) [Ni(2)-O(3) = 2.080(3) Å] and another oxygen atom O(7) of coordinated methanol molecule [Ni(2)-O(7) = 2.147(5) Å]. The r.m.s. deviation of the coordinating atoms N(1), N(2), N(3) and O(1) from the mean plane is 0.259(4). Deviation of Ni(2) center from the basal plane is 0.008 Å towards the axially coordinated oxygen atom of the

coordinated methanol molecule. The central Ni(1) is also hexacoordinated but with a centrosymmetric $[\text{N}_2\text{O}_4]$ *trans*-octahedral environment furnished by two oxygen atoms of bridging *o*-nitrobenzoate groups (O(2) and O(2)') (' = -x, -y, -z) and two μ -phenoxido oxygen atoms (O(1) and O(1)') in the basal plane [Ni(1)-O(2) = 2.047(3) Å and Ni(1)-O(1) = 2.056(4) Å] and two μ_1 -azide nitrogen atoms (N(3) and N(3)') in the two axial positions [Ni(1)-N(3) = 2.102(4) Å]. Adjacent Ni(II) atoms are separated by 3.094(14) Å. Two bridging Ni(1)-N(3)-Ni(2) and Ni(1)-O(1)-Ni(2) angles are 94.89(16)° and 98.30(15)° respectively. The hydrogen atom H(7) of the coordinated methanol molecule participates in hydrogen bonding to the oxygen atom O(22) of the solvent water molecule with D...A distance of 2.78(2) Å (Table 3).

Table 3. Hydrogen-bond geometry

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O(7)-H(7)...O(22)	0.86(5)	1.92(5)	2.78(2)	175(4)

From the above crystal structure of complex **1** we found that the bridging bond angles (Ni-O-Ni and Ni-N-Ni) are almost similar in comparison to the previously reported Ni(II) Schiff base complex⁵ with similar type of ligands. In the previously reported Ni(II) complex the Ni-N-Ni angle is 95.51(12)° and Ni-O-Ni angle is 99.50(13)° whether in this present complex **1** the Ni-N-Ni and Ni-O-Ni bridging angles are 94.89(16)° and 98.30(15)° respectively.

Conclusions

In summary, a rare mixed bridged (μ_2 -phenoxido, $\mu_{1,1}$ -azido and *syn-syn* *o*-nitrobenzoato) linear trinuclear Ni(II) complex $[\text{Ni}_3\text{L}_2(\text{o}-(\text{NO}_2)\text{C}_6\text{H}_4\text{COO})_2(\mu_{1,1}\text{-N}_3)_2(\text{CH}_3\text{OH})_2] \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized using a tridentate NNO donor Schiff base ligand 1-[(3-dimethylamino-propylimino)-methyl]-naphthalen-2-ol (HL) along with azide and *o*-nitrobenzoate as anionic coligands. The structure has been determined by single-crystal X-ray diffraction analysis and further characterized by infrared, UV-Vis spectroscopy and elemental analysis. However no significant changes are observed in the bridging bond angles of complex **1** in comparison to the previously reported Ni(II) complex with similar coordination environment.

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Supporting information

Electronic supplementary information CCDC reference number 1909547 (1).

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