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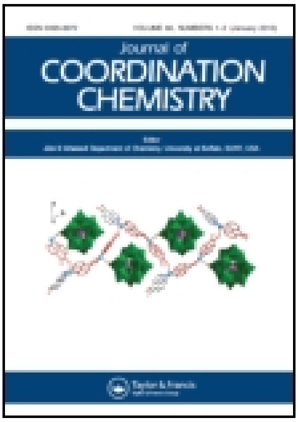

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Sodium-mediated self-assembly of two nickel(II) Schiff base complexes: crystal structure and characterizations

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Accepted author version posted online: 03 Jun 2013.Published online: 04 Jul 2013.

To cite this article: Anamika Das, Shyamapada Shit, Martin Köckerling, Andrei S. Batsanov & Samiran Mitra (2013) Sodium-mediated self-assembly of two nickel(II) Schiff base complexes: crystal structure and characterizations, Journal of Coordination Chemistry, 66:15, 2587-2596, DOI: 10.1080/00958972.2013.810731

To link to this article: http://dx.doi.org/10.1080/00958972.2013.810731

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 15, 2587–2596, http://dx.doi.org/10.1080/00958972.2013.810731

Sodium-mediated self-assembly of two nickel(II) Schiff base complexes: crystal structure and characterizations

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(*Received 16 July 2012; in final form 4 April 2013*)

Sodium-assisted self-assembly of two nickel(II) Schiff base complexes under similar reaction conditions yield hetero-metallic compounds $[\{Ni(salpn)\}_2Na(ClO_4)]$ (**1**) and $[\{Ni(salpr)\}_3Na][Ni(salpr)]_2ClO_4{\cdot}2H_2O$ (**2**) (where salpn = N,N′-bis-(salicylidene)-1,3-diaminopropane and salpr = N,N′-bis-(salicylidene)-1,2-diaminopropane). Both have been characterized by physico-chemical techniques and single-crystal X-ray diffraction. Crystal structure reveals that in the tri-metallic system of **1** sodium is sandwiched between two [Ni(salpn)] units while the hexametallic system of **2** consists of tetrametallic cluster ion $[\{Ni(salpr)\}_3Na]^+$ with encapsulated sodium by three [Ni(salpr)] units. In both complexes, sodium adopts distorted trigonal prismatic geometry leaving nickel(II) in a distorted square-planar environment. Structural characterization also reveals that 2 : 1 (for **1**) and 3 : 1 (for **2**) self-assemblies of metallo-ligand and sodium were achieved with slight variation in ligand backbone.

Keywords: Nickel(II)-sodium; Schiff base; Crystal structure; Characterizations

1. Introduction

Supramolecular chemistry of self-assembled metal-organic systems is an interesting area of research due to their applications as functional materials [1, 2]. Small building units are tuned by covalent, coordinative, and various weak forces [2, 3] leading to such assemblies. In self-assemblies of Schiff base-metal complexes, encoded information in ligands and metal ions are also very important [3]. Among the varieties of Schiff bases [4, 5], the class consisting of salicylaldimine and its alkoxy derivatives at 3 and 3′-positions are significant as salicylaldimines with N_2O_2 donor sets generally form mono-metallated complex while their 3 and 3′-alkoxy substituted derivatives are bicompartmental ligands with an inner tetradentate compartment involving two imine-nitrogens and two phenoxo-oxygens, and an outer compartment with the four oxygens of the phenoxo and alkoxy units [6]. The

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*Corresponding author. Email: smitra@chemistry.jdvu.ac.in metallo-ligand so formed may thus serve as a precursor for self-assembly. For example, 3-methoxysalicylaldimine and 3-ethoxysalicylaldimine bicompartmental Schiff bases incorporating 3d metal ions have been explored as metallo-ligands to form discrete systems [7–11], di- and oligomeric complexes and supramolecular architectures incorporating s, p, d, and f-block elements with applications in magnetic or electric properties, and crystal engineering [6, 7, 12, 13]. However, unlike 3 and 3′-alkoxy derivatives of salicylaldimine, alkali metal incorporated 3d metal-salicylaldimines are less abundant in spite of their applications in small-molecule activation [14], electron storage [15, 16], the carrying of polar organometallics [17, 18], and ferroelectricity [11].

In this article, we explore two nickel(II)–salicylaldimines in self-assembling assisted by sodium and obtained [{Ni(salpn)}$_2$Na(ClO$_4$)] (**1**) and [{Ni(salpr)}$_3$Na][Ni(salpr)]$_2$ClO$_4$·2H$_2$O (**2**) (where salpn and salpr are two different Schiff bases) under similar reaction conditions. Both complexes are characterized by elemental analyses, FT-IR, UV–Vis, and room temperature magnetic susceptibility measurements. Structural characterizations reveal that **1** and **2** differ in molecular organizations. In the tri-metallic system of **1**, sodium is sandwiched between two [Ni(salpn)] units while the hexametallic system of **2** consists of a tetrametallic cluster ion [{Ni(salpr)}$_3$Na]$^+$ with encapsulated sodium by three [Ni(salpr)] units with sodium and nickel(II) having distorted trigonal prismatic and distorted square-planar geometries, respectively.

2. Experimental

2.1. *Materials and physical measurements*

Caution! Perchlorate salts of metals in the presence of organic ligands are potentially explosive. We did not encounter any problem, but they should be prepared in small amounts and handled with caution.

All reagents and solvents were purchased from commercial sources and used as received. Nickel(II) perchlorate hexahydrate, salicylaldehyde, 1,3-diaminopropane, and 1,2-diaminopropane were purchased from Sigma Aldrich Co., Ltd. Sodium perchlorate monohydrate was purchased from E. Merck, India. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out with a PerkinElmer 2400 II elemental analyzer. Nickel(II) content has been estimated quantitatively by standard gravimetric procedures. The FT-IR spectra (4000–400 cm^{-1}) were recorded on a PerkinElmer RX I FT-IR system with solid KBr disk. UV–Vis spectra in solution were recorded at room temperature on a PerkinElmer *Lambda* 40 UV–Vis spectrophotometer using methanol in 1 cm quartz cuvettes. ^{1}H NMR spectra of the complexes were recorded on a Bruker 300 MHz FT-NMR spectrometer using trimethylsilane as internal standard in DMSO-d$_6$. Magnetic susceptibilities were measured with a model 155 PAR vibrating sample magnetometer fitted with a Waker Scientific 175 FBAL magnet using Hg[Co(SCN)$_4$] as the standard. Necessary diamagnetic corrections for the ligand were performed using Pascal's table. Salpn and salpr were prepared as reported [19, 20].

2.2. *Syntheses of 1 and 2*

Synthetic procedure for **1** was as follows: To a methanolic solution (20 mL) of salpn (0.284 g, 1 mM), 10 mL methanolic solution of NiClO$_4$·6H$_2$O (0.366 g, 1 mM) was added. The resulting red mixture was stirred for 30 min followed by addition of NaClO$_4$·H$_2$O (0.141 g, 1 mM) in methanol (10 mL). The resulting mixture stirred for an additional

30 min and filtered. The filtrate was left undisturbed at room temperature for 3 days from which block-shaped light green crystals of **1** were collected by slow evaporation. Yield: 0.347 g (75%). Anal. Calcd for $C_{34}H_{32}ClN_4NaNi_2O_8$ (FW: 800.5) (%): C, 51.02; H, 4.03; N, 7.00; Ni, 14.66. Found: C, 51.00; H, 3.95; N, 7.00; Ni, 14.60. ^{1}H NMR (300 MHz): δ 2.05 (s, $1H_8$), 3.14 (s, $1H_7$), 6.63 (d, $J=7.27$ Hz, $4H_6$), 6.83 (d, $J=4.38$ Hz, $2H_5$), 7.62–7.69 (m, $2H_3$), 7.92 (d, $J=6.63$ Hz, $2H_4$), 8.14 (t, $J=12.80$ Hz, $2H_2$), 8.78 (d, $J=12.59$ Hz, $2H_1$) ppm (scheme 1: Supplementary material). The synthetic procedure for **2** is exactly the same as described for **1** except that salpr (0.284 g, 1 mM) was used instead of salpn. Plate-shaped orange crystals of **2** were collected after 5 days. Yield 0.300 g (65%). Anal. Calcd for $C_{85}H_{84}ClN_{10}NaNi_5O_{16}$ (FW: 1853.5) (%): C, 55.08; H, 4.57; N, 7.56, Ni, 15.83. Found: C, 55.02; H, 4.50; N, 7.55, Ni, 15.80. ^{1}H NMR (300 MHz): δ 1.22 (d, $J=6.15$ Hz, $3H_8$), 3.05 (d, $J=11.76$ Hz, $1H_6$-trans), 3.15 (d, $J=4.65$ Hz, $1H_6'$-cis), 3.54–3.66 (m, $1H_7$), 6.49 (t, $J=7.26$ Hz, 2H [H_4, H_4']), 6.69 (d, $J=8.22$ Hz, 2H [H_1, H_1']), 7.15 (t, $J=7.0$ Hz, 2H [H_3, H_3']), 7.25 (t, $J=6.5$ Hz, 2H [H_2, H_2']), 8.01 (d, $J=4.7$ Hz, 2H [H_5, H_9]) ppm (scheme 2: Supplementary material).

2.3. *Crystal structure determination*

X-ray single-crystal diffraction data for **1** were collected on a Siemens P4-diffractometer and for **2** on a Siemens SMART 1K CCD area-detector diffractometer with fine focus sealed tube graphite-monochromated Mo-Kα radiation ($\lambda=0.71073$ Å). Intensity data for **1** and **2** were collected at 200(2) and 120(2) K using ω scans. No significant intensity variations were observed. For **1**, empirical absorption corrections were applied to the intensity values ($T_{\max}=0.966$, $T_{\min}=0.775$) using SHELXTL program package [21] while for **2** multiscan absorption corrections were applied empirically to the intensity values ($T_{\max}=1.000$, $T_{\min}=0.7913$) using SADABS [22]. Data collections were performed using Siemens XSCANS [23] and Bruker SMART [24] programs for **1** and **2**, respectively. For **2**, data reduction and cell refinement were performed using Bruker SAINT [25] and Bruker SMART [24] programs. The structures were solved by direct methods using SHELXS-97 [26] and refined with full-matrix least-squares based on F^2 using SHELXL-97 [26]. For all non-hydrogen atoms, the anisotropic displacement parameters have been refined successfully. For **1** and **2**, hydrogens were first located in the Fourier difference map then positioned geometrically and allowed to ride on their respective parent. The molecular graphics and crystallographic illustrations were prepared using ORTEP [27] and Bruker SHELXTL [21] programs. Relevant crystallographic data and structure refinement parameters for the complexes are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of 1*

Crystal structure of **1** is shown in figure 1. The molecule lies on a crystallographic twofold axis passing through sodium and chloride. **1** is a sandwich type complex where $NaClO_4$ is sandwiched between two metallo-ligand [Ni(salpn)] units (figure 1(a)) making 2 : 1 oligomeric ensembles with respect to [Ni(salpn)] and sodium. An ORTEP presenting coordination of salpn to nickel(II) and coordination of [Ni(salpn)] to sodium is shown in

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{34}H_{32}ClN_4NaNi_2O_8$	$C_{85}H_{84}ClN_{10}NaNi_5O_{16}$
Formula weight	800.46	1853.61
Crystal size (mm)	0.44 × 0.48 × 0.52	0.03 × 0.30 × 0.37
Crystal system	Monoclinic	Triclinic
Space group	*C2/c* (No. 15)	*P*-1 (No. 2)
a (Å)	22.371(5)	15.138(1)
b (Å)	11.444(3)	15.269(1)
c (Å)	17.001(4)	18.637(2)
α (°)	90	67.81(1)
β (°)	129.49(1)	87.68(1)
γ (°)	90	83.77(1)
V (Å^3)	3359(2)	3965.2(6)
Z	8	2
T (K)	200(2)	120(2)
$\lambda_{\text{Mo-K}\alpha}$ (Å)	0.71073	0.71073
D_c (g cm^{-3})	1.583	1.549
μ (mm^{-1})	1.272	1.281
F (000)	1648	1912
θ range (°)	2.1−25.0	1.2−27.5
hkl ranges	$-1 \leqslant h \leqslant 26$, $-1 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 16$	$-19 \leqslant h \leqslant 19$, $-19 \leqslant k \leqslant 19$, $-24 \leqslant l \leqslant 24$
Total data	3560	42,642
Unique data	2956	18,136
Observed data [$I > 2\sigma(I)$]	1844	10,415
N_{ref}; N_{par}	2956; 227	18,136; 1062
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0554$, $wR2 = 0.1292$	$R1 = 0.0716$, $wR2 = 0.1643$
R indices (all data)	$R1 = 0.1046$, $wR2 = 0.1520$	$R1 = 0.1381$, $wR2 = 0.1887$
Goodness-of-fit on F^2	0.995	1.128
R_{int}	0.047	0.064
$\Delta\rho_{\max}$ (e Å^{-3})	0.47	1.61
$\Delta\rho_{\min}$ (e Å^{-3})	−0.48	−0.95

figure 1(b). In the geometry of **1**, each nickel(II) is coordinated by a N_2O_2 donor set. The four coordination of nickel(II) is considered as distorted square planar as evident from two shorter Ni−O distances defining one side of the square compared to two Ni−N distances (table 2) defining the opposite edge of the square; the deviation of NiO_2N_2 unit from planarity (taking the O1−Ni−O2 unit as planar, the two nitrogen atoms are located 0.39 Å (N1) and 0.37 Å (N2) above and below, respectively). The distortion is also evident from variation in cisoid and transoid angles (table 2). The Ni−O and Ni−N distances in **1** match well with those found in closely related compounds [28, 29] as well as [Ni(salpn)] reported earlier [30]. However, nickel(II) centers in **1** deviate significantly from planarity contrary to [Ni(salpn)] where it is almost coplanar with donor atoms in the square plane. This deviation may be due to the strain imposed by coordination of these units to sodium.

Sodium is surrounded by six oxygens in its coordination sphere, four phenoxo-O [O1, O2, O1A, and O2A] and O3B and O3C from bidentate perchlorate. Three sets of Na–O bond distances are observed. One set of Na–O(phenoxo) distances is slightly longer (2.363 Å) compared to the other set (2.303 Å). The strain imposed by coordinating two [Na(salpn)] units forced perchlorate to a longer distance as evident from the longest Na–O3 distances (2.560 Å). The relative O–Na–O angles and Na–O distances (table 2) suggest that the O_6 coordination polyhedra of sodium can best be described as distorted trigonal prismatic. The metallo-ligand [Na(salpn)] units are connected by sodium via four μ-phenoxo bridges. The Ni···Ni separation is 4.867 Å while Ni–Na distances (3.2333 Å) are equal, indicating slipped sandwich nature of **1**.

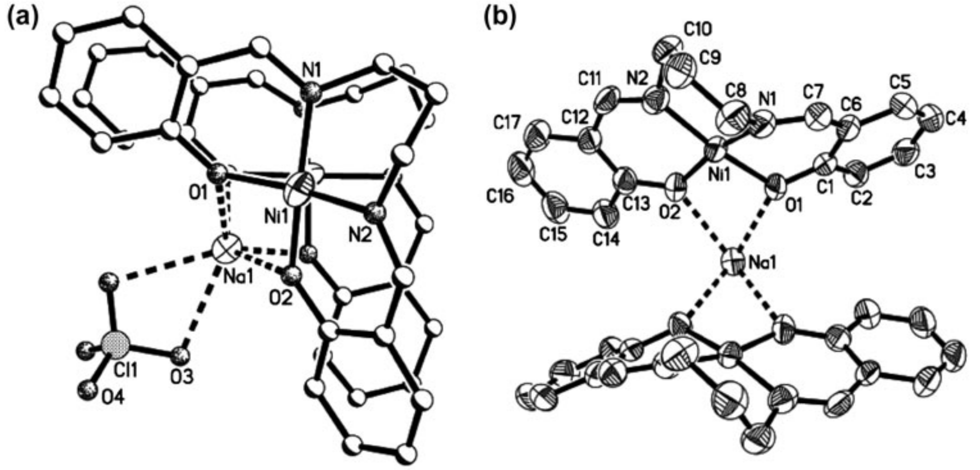

Figure 1. ORTEP view of **1**. 1(a) shows sandwich geometry of sodium and 1(b) shows coordination modes of salpn to nickel(II) and [Ni(salpn)] to sodium. Thermal ellipsoids are drawn with 50% probability level.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ni1–O1	1.862(4)	Na1–O2	2.363(4)
Ni1–O2	1.845(4)	Na1–O1A	2.301(5)
Ni1–N1	1.876(5)	Na1–O2A	2.363(4)
Ni1–N2	1.866(5)	Na1–O3B	2.560(7)
Na1–O1	2.301(5)	Na1–O3C	2.560(7)
O1–Ni1–O2	84.6(2)	O1A–Na1–O2	95.70(2)
O1–Ni1–N1	91.2(2)	O2–Na1–O2A	137.6(2)
O1–Ni1–N2	168.5(2)	O2–Na1–O3B	100.9(2)
O2–Ni1–N1	167.1(2)	O2–Na1–O3C	117.5(3)
O2–Ni1–N2	94.4(2)	O1A–Na1–O2A	64.56(2)
N2–Ni1–N1	92.2(2)	O1A–Na1–O3B	96.2(3)
O1–Na1–O2	64.6(2)	O1A–Na1–O3C	135.7(3)
O1–Na1–O1A	125.6(2)	O2A–Na1–O3B	117.5(3)
O1–Na1–O2A	95.70(2)	O2A–Na1–O3C	100.9(2)
O1–Na1–O3B	135.7(3)	O3B–Na1–O3C	51.5(3)
O1–Na1–O3C	96.2(3)	–	–

Symmetry codes: (A) $-x$, y, $1/2-z$; (B) $1/2-x$, $3/2-y$, $1-z$; (C) $-1/2+x$, $3/2-y$, $-1/2+z$.

3.2. *Crystal structure of 2*

The asymmetric unit of **2** (figure 2) consists of two discrete [Ni(salpr)] units [described as units A (associated with Ni1) and B (associated with Ni2) based on atom labels associated with salpr (figure 2(a) and 2(b))], a tetrametallic cluster cation $[\{Ni(salpr)\}_3Na]^+$ (figure 2 (c)), one perchlorate and two water molecules of crystallization. In the cluster $[\{Ni(salpr)\}_3Na]^+$, sodium ion is encapsulated by three [Ni(salpr)] units (hence described as units C (associated with Ni3), D (associated with Ni4), and E (associated with Ni5) based on same argument described earlier). In contrast to **1**, perchlorate in **2** is not coordinated. All five [Ni(salpr)] units in **2** are crystallographically independent as evident from relevant bonding parameters (table 3). Each A and B unit is associated with one water of crystallization (respectively O1W and O2W, the latter being disordered) probably through a pair of O–H···O hydrogen bonds donated by water and accepted by both phenolic oxygens of the associated salpr.

Encapsulated sodium is six coordinate by six phenolato oxygens (figure 2(c)) of C, D, and E units resulting in a 3 : 1 oligomeric cluster with respect to [Ni(salpr)] and sodium. The coordination polyhedron around sodium can best be described as distorted trigonal prismatic (with the bases O1C, O1D, O1E and O2C, O2D, O2E, respectively) compressed along its threefold axis and twisted around this axis by *ca*. 36°. Two Na–O distances (Na–O1C 2.453(4) and Na–O1E 2.594(4) Å) are much longer than other four (2.352–2.399 Å). However, the Ni–O bond lengths do not correlate with these Na–O distances and, indeed, remain practically the same as in units A and B, as well as with the distances found in **1** and other nickel(II) Schiff base complexes [31], thus indicating the essentially ion-dipole character of the sodium–salpr interaction. The coordination polyhedron of nickel(II) in each [Ni(salpr)] unit is considered as distorted square planar with N_2O_2 donor sets as found in **1** while the distortion associated with nickel(II) is less in **2** than **1**. Within the cluster ion, Ni···Ni separations vary from 4.600 to 6.284 Å while Ni–Na distances vary from 3.211 to 3.357 Å.

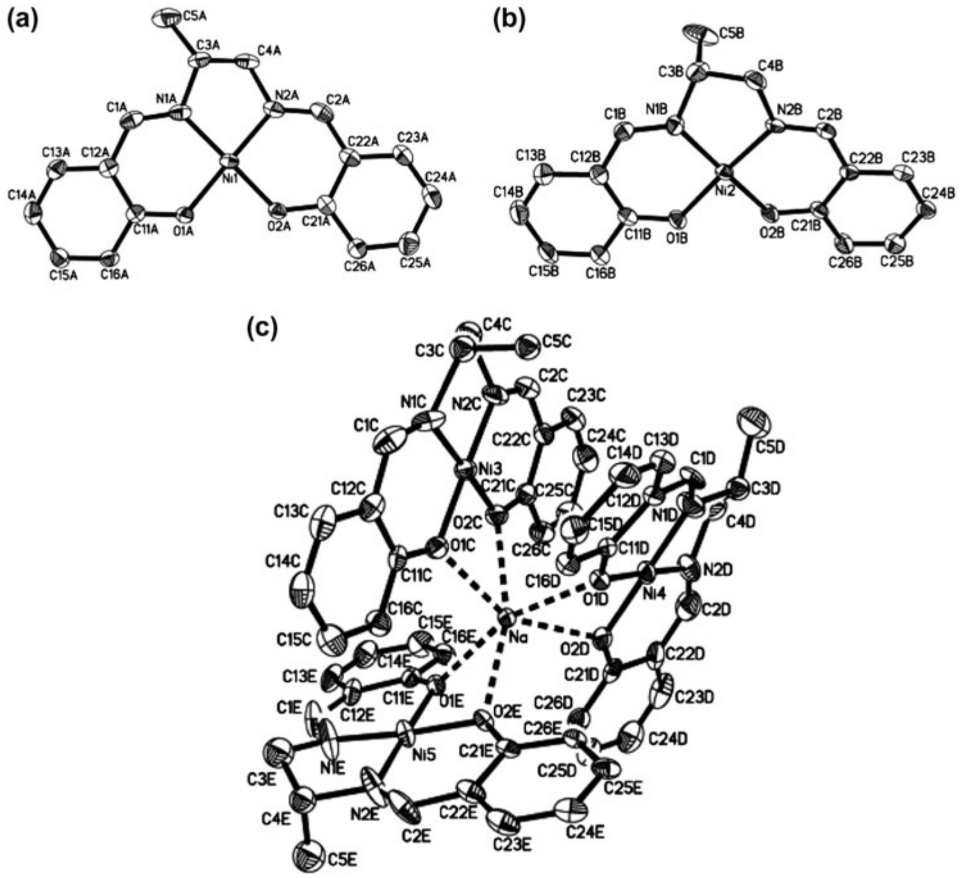

Figure 2. ORTEP view of **2**. 2(a) and 2(b) show two independent [Ni(salpr)] units and 2c shows $[Ni(salpr)_3Na]^+$ unit. Perchlorate and lattice water are omitted for clarity. Thermal ellipsoids are drawn with 50% probability level.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Ni1–N1A	1.837(5)	Ni1–O1A	1.843(3)
Ni1–N2A	1.840(4)	Ni1–O2A	1.842(3)
O1A–Ni1–O2A	84.01(2)	O2A–Ni1–N1A	178.4(2)
O1A–Ni1–N1A	95.1(2)	O2A–Ni1–N2A	94.9(2)
O1A–Ni1–N2A	178.7(2)	N1A–Ni1–N2A	85.9(2)
Ni2–O1B	1.841(3)	Ni2–O2B	1.846(3)
Ni2–N2B	1.853(4)	Ni2–N1B	1.841(5)
O1B–Ni2–N1B	95.5(2)	O1B–Ni2–N2B	175.6(2)
O2B–Ni2–N1B	174.6(2)	N1B–Ni2–N2B	86.0(2)
O2B–Ni2–N2B	94.8(2)	O1B–Ni2–O2B	84.1(2)
Ni3–O1C	1.866(3)	Ni5–O2E	1.845(3)
Ni3–O2C	1.864(4)	Ni5–N1E	1.838(6)
Ni3–N1C	1.847(5)	Ni5–N2E	1.841(6)
Ni3–N2C	1.840(5)	Na–O1D	2.399(4)
Ni4–O1D	1.849(3)	Na–O2E	2.595(4)
Ni4–O2D	1.842(3)	Na–O2D	2.370(4)
Ni4–N1D	1.812(6)	Na–O1C	2.454(4)
Ni4–N2D	1.882(6)	Na–O2C	2.395(4)
Ni5–O1E	1.851(3)	Na–O1E	2.352(4)
O1C–Ni3–O2C	85.4(2)	N1E–Ni5–N2E	86.0(3)
O1C–Ni3–N1C	94.4(2)	O2D–Na–O2E	101.7(1)
O1C–Ni3–N2C	178.2(2)	O1C–Na–O1D	91.7(1)
O2C–Ni3–N1C	177.0(2)	O2C–Na–O2E	108.9(1)
O2C–Ni3–N2C	95.1(2)	O2C–Na–O2D	98.1(1)
N1C–Ni3–N2C	85.2(2)	O1D–Na–O1E	109.2(1)
O1D–Ni4–O2D	84.4(2)	O1C–Na–O1E	105.4(1)
O1D–Ni4–N1D	96.1(2)	O1C–Na–O2C	62.9(1)
O1D–Ni4–N2D	177.9(2)	O1C–Na–O2D	150.3(1)
O2D–Ni4–N1D	179.2(2)	O1C–Na–O2E	106.0(1)
O2D–Ni4–N2D	93.6(2)	O1E–Na–O2E	60.1(1)
N1D–Ni4–N2D	86.0(3)	O1E–Na–O2C	162.5(2)
O1E–Ni5–O2E	84.5(1)	O1E–Na–O2D	97.6(1)
O1E–Ni5–N1E	95.0(2)	O1D–Na–O2D	62.6(1)
O1E–Ni5–N2E	175.3(2)	O1D–Na–O2E	161.1(1)
O2E–Ni5–N1E	178.2(2)	O1D–Na–O2C	85.0(1)
O2E–Ni5–N2E	94.6(2)	–	–

A [Ni(salpr)] would have possessed a local twofold axis, passing through nickel(II) and the midpoint of the C3–C4 bond. But the presence of the methyl substituent such imperfect symmetry is propitious for disorder, which indeed occurs in four out of five independent [Ni(salpr)] units. In each case, the C3–C4 bridge connecting N1 with N2 is disordered between two conformations symmetrical about the molecular mean plane. In units A and D, the methyl at C3 remains in the same (equatorial) position for either conformation. In C and E, this substituent is disordered between axial positions at C3 and C4, that is, the entire salpr is in fact disordered between two orientations, differing by a 180° rotation around the above mentioned pseudo-two-fold axis.

Two complexes were synthesized from similar ligands with a slight change in amine backbone. Indeed, two amines, 1,3-diaminopropane and 1,2-diaminopropane, used are ligand isomers and differ in their bite angles. Since bite angles for 1,3-diaminopropane are more than 1,2-diaminopropane, the metallo-ligand [Ni(salpn] may lead to more steric crowding around sodium compared to [Ni(salpr)], ultimately resulting in 2 : 1 and 3 : 1 molecular compositions with respect to nickel(II)–Schiff base and sodium for **1** and **2**, respectively. Moreover, the 3 : 1 molecular composition in **2** leads to a strong crown effect [3] which forces the perchlorate anion out of the coordination zone of sodium. Such crown effect is absent in **1** and perchlorate anion remains coordinated in bis chelating coordination.

The complexes reported herein may be compared to the nickel(II) complexes reported earlier [32–40] as they possess similarities in the mode of formation with respect to the nickel(II)–Schiff base moieties. Reported complexes were derived from different symmetrical and unsymmetrical tetradentate Schiff base ligands bearing N_2O_2 donor set similar to the complexes reported here. Schiff bases coordinate to nickel(II) via azomethine nitrogen and phenolato oxygen leaving the nickel(II) in square-planar/distorted square-planar geometries similar to our complexes. In the complexes reported by Orabi *et al.* [37], potentially hexadentate Schiff bases are also four coordinate to nickel(II) with N_2O_2 chromophore using their inner coordination sites leaving the nickel(II) in distorted square-planar geometries. In spite of octahedral geometry of nickel(II) and paramagnetic nature of the complexes reported by Parmar *et al.* [38] and Manjunatha *et al.* [36], the coordination mode of the Schiff bases was identical to that of complexes reported herein. All reported square-planar complexes were diamagnetic similar to our complexes.

3.3. *Spectroscopic and magnetic properties*

The FTIR spectra of the complexes were consistent with their crystal structures. The FTIR spectra of **1** and **2** show distinct bands at 1604 and 1607 cm^{-1}, respectively, corresponding to the stretch of azomethine (–C = N–) [29]. A broad band at 3442 cm^{-1}, attributable to the OH stretch present in spectra of **2**, indicated the presence of water molecule. However, such a band does not appear in spectra of **1** and confirms the absence of water in this complex [3]. In spectra of **1**, a broad trifurcated peak corresponding to coordinated perchlorate was found at 1145, 1115, and 1093 cm^{-1} while a single sharp and intense peak appeared at 1092 cm^{-1} in spectra of **2** due to the presence of uncoordinated perchlorate [3].

Electronic spectra of the complexes were recorded using methanol and they appeared very similar to each other. Both complexes show a band at 485 nm corresponding to the d–d transition in square-planar Ni(II). Absence of any absorption at longer wavelengths is consistent with large crystal-field splitting of square-planar nickel(II) compounds [29]. Many high intensity absorptions corresponding to ligand to metal charge transfer were also observed in spectra of the complexes [28, 29].

Room temperature molar magnetic susceptibility measurements show that both the compounds are diamagnetic, confirming the existence of magnetically uncoupled square-planar nickel(II).

4. Conclusions

In this article, we report the synthesis, spectroscopic, and structural characterizations of sodium-mediated self-assembly of two nickel(II)–salicylaldimine Schiff base complexes which indicate oligomeric assembly. Structural characterizations reveal that bite angle due to slight modification in ligand backbone (on amine part) influences the coordination of the nickel(II)–Schiff base complexes around sodium and thereby changes the molecular composition of the complexes which may be utilized in designing polynuclear coordination complexes. Molecular composition 3 : 1 with respect to nickel(II)–Schiff base and sodium in **2** with exclusion of perchlorate from coordination support about the crown effect which is absent in **1**. Antibacterial and antifungal [32–34], DNA-intercalator [35], anti-inflammatory and anthelmintic activities [36] of complexes possessing similarities to our complexes with respect to the nickel(II)–Schiff base moieties also suggest that complexes reported herein may have potential to exhibit these properties.

Supplementary materials

CCDC 291525 and 291526 contain the Supplementary Crystallographic Data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We gratefully acknowledge the Council of Scientific and Industrial Research (CSIR), New Delhi, Government of India for financial support.

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