

Structural variations in Ni(II) complexes of salen type di-Schiff base ligands

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Abstract

Three di-Schiff-base ligands, *N,N'*-bis(salicylidene)-1,3-propanediamine (H₂Salpn), *N,N'*-bis(salicylidene)-1,3-pentanediamine (H₂Salpen) and *N,N'*-bis(salicylidene)-ethylenediamine (H₂Salen) react with Ni(SCN)₂ · 4H₂O in 2:3 molar ratios to form the complexes; mononuclear [Ni(HSalpn)(NCS)(H₂O)] · H₂O (**1a**), trinuclear [{Ni(Salpen)}₂Ni(NCS)₂] (**2b**) and trinuclear [{Ni(Salen)}₂Ni(NCS)₂] (**3**) respectively. All the complexes have been characterized by elemental analyses, IR and UV–VIS spectra, and room temperature magnetic susceptibility measurements. The structures of **1a** and **2b** have been confirmed by X-ray single crystal analysis. In complex **1a**, the Ni(II) atom is coordinated equatorially by the tetradentate, mononegative Schiff-base, HSalpn. Axial coordination of isothiocyanate group and a water molecule completes its octahedral geometry. The hydrogen atom attached to one of the oxygen atoms of the Schiff base is involved in a very strong hydrogen bond with a neighboring unit to form a centrosymmetric dimer. In **2b**, two square planar [Ni(Salpen)] units act as bidentate oxygen donor ligands to a central Ni(II) which is also coordinated by two mutually cis N-bonded thiocyanate ligands to complete its distorted octahedral geometry. Complex **3** possesses a similar structure to that of **2b**. A dehydrated form of **1a** and a hydrated form of **2b** have been obtained and characterized. The importance of electronic and steric factors in the variation of the structures is discussed.

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Keywords: Nickel(II); Schiff base; Thiocyanate; Crystal structures; H-bonding

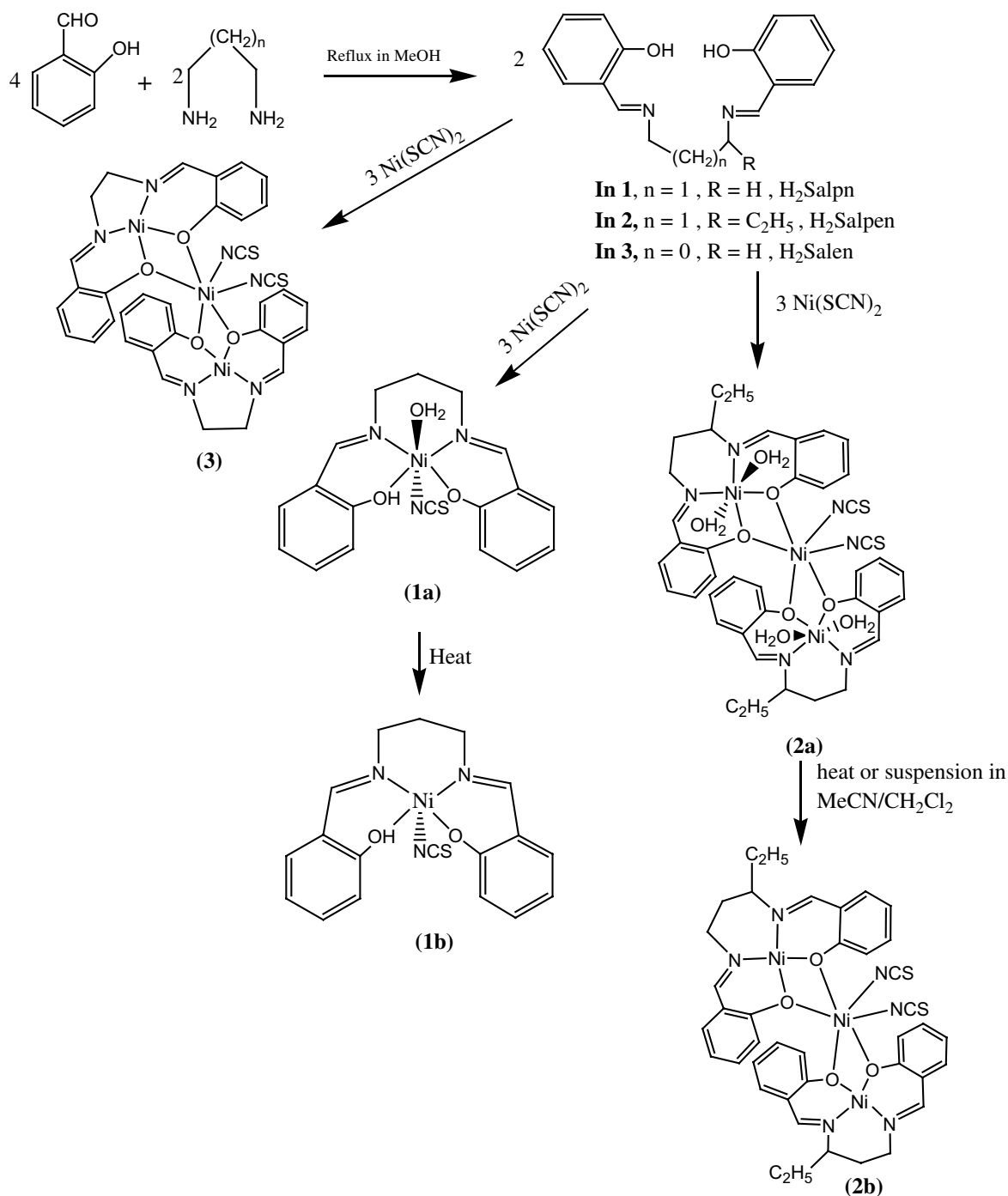
1. Introduction

The salen type di-Schiff base complexes of transition metals are one of the most exhaustively studied topic in coordination chemistry [1]. Their interest stems from the ease with which they can be synthesized, their versatility and wide range of complexing ability. They not only have played an important role in the development of modern coordination chemistry [2], but they can also be found at key points in the development of inorganic biochemistry [3], catalysis [4,5], magnetism, medical imaging [6] etc. Since nickel compounds are present in the active sites of urease and are used extensively in the design and con-

struction of new magnetic materials, the study of nickel compounds is of great interest in various aspects of chemistry [7–9]. In general, the reaction of H₂Salen or related ligands with Ni(II) yields complexes in which the deprotonated, di-negative Schiff base acts as a tetradentate chelating ligand [10–21]. However, in some cases it has been found that the oxygen atoms of the Schiff base can bridge another metal ion to form multinuclear (homo- or heteronuclear) complexes [22–35]. In all the reported homonuclear nickel complexes, the oxygen atoms of two mononuclear units bridge a third Ni(II) to form a trinuclear entity and in all but one case, an additional bridging anionic ligand (e.g. acetate, nitrite etc.) was required to provide the required stability for the polynuclear structure [22–25]. Interestingly, most of the trinuclear complexes reported so far are of Salpn (Scheme 1) and contain the additional anion bridge. The geometry of all three Ni(II)

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Scheme 1.

ions in those complexes is octahedral in a linear structure. To our knowledge, only one trinuclear complex has been reported incorporating Salen as the ligand and that does not have the additional Salen anion bridge [26]. The molecule is bent and the geometry of the three Ni(II) is square planar-octahedral-square planar. On the other hand, a more flexible Schiff base *N,N'*-bis(salicylidene)-1,4-butanediamine shows an interesting conformational isomerism

and different anion bridging behavior in its trinuclear complexes [23]. However, to have a clear idea about the steric and electronic factors that determine the structure and connectivity of such complexes, it is necessary to synthesize some more complexes.

Herein, we report the structural variation in the complexes of three di-Schiff base ligands, H_2Salpn , $H_2Salpen$ and H_2Salen (Scheme 1) with Ni(II) thiocyanate. It is

observed that small differences in the diamine fragment can cause remarkable change in the composition and geometry of the complexes. A probable explanation for such difference in structures has also been provided.

2. Experimental

2.1. Materials

All the chemicals were of reagent grade and used without further purification. The three double-condensed Schiff-base ligands, *N,N'*-bis(salicylidene)-1,3-propanediamine (H_2Salpn), *N,N'*-bis(salicylidine)-1,3-pentanediamine ($H_2Salpen$) and *N,N'*-bis(salicylidine)-ethylenediamine (H_2Salen) have been synthesized in our laboratory by the methods described below.

2.2. Synthesis of the Schiff-base ligands (H_2Salpn , $H_2Salpen$ and H_2Salen)

The three Schiff bases were prepared by standard methods [23,36,37]. Briefly, 10 mmol of salicylaldehyde (1.05 cm³) were mixed with 5 mmol of the required amine, 1,3-propanediamine (0.420 cm³), 1,3-pentanediamine (0.596 cm³) and 1,2-ethanediamine (0.308 cm³) for the ligands H_2Salpn , $H_2Salpen$ and H_2Salen , respectively in methanol (10 cm³). The resulting mixture were refluxed for an hour, filtered when hot and allowed to cool. The desired yellow precipitates were filtered off, washed with methanol and dried in a vacuum desiccator containing anhydrous $CaCl_2$.

2.2.1. Synthesis of $[Ni(HSalpn)(NCS)(H_2O)] \cdot H_2O$ (**1a**)

A solution of $Ni(SCN)_2 \cdot 4H_2O$ (1.84 g, 7.5 mmol) in methanol–water (9:1 v/v) mixture (10 cm³) was added to a solution of H_2Salpn (1.4 g, 5 mmol) in methanol (10 cm³) with constant stirring. The mixture was stirred for 1 h at room temperature and then filtered. The filtrate was left to stand overnight in air, when green X-ray quality single crystals appeared at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed with methanol and dried in vacuum desiccator containing anhydrous $CaCl_2$. Yield: 1.52 g (70%). *Anal.* Calc. for $C_{18}H_{21}NiN_3O_4S$: C, 49.80; H, 4.88; N, 9.68; Ni, 13.52. Found: C, 49.52; H, 4.36; N, 9.57; Ni, 13.14%. $\lambda_{Max/nm}$ (solid, reflectance) 594 and 1042 nm; IR: $\nu(C=N)$, 1634 cm⁻¹, $\nu(SCN)$, 2094 cm⁻¹, $\nu(H_2O)$, 3328 cm⁻¹, $\mu_{eff} = 3.3$ BM.

2.2.2. Synthesis of $[Ni(HSalpen)(NCS)]$ (**1b**)

Complex **1b** was produced as a dirty green compound by heating the complex **1a** at 140 °C for 15 mins. *Anal.* Calc. for: $C_{18}H_{17}NiN_3O_2S$: C, 51.95; H, 4.60; N, 10.10; Ni, 14.10. Found: C, 51.64; H, 4.42; N, 10.17; Ni, 14.01%. $\lambda_{Max/nm}$ (solid, reflectance) 595 and 1148 nm; IR: $\nu(C=N)$, 1611 cm⁻¹, $\nu(SCN)$, 2086 cm⁻¹, $\mu_{eff} = 3.0$ BM.

2.2.3. Synthesis of $[Ni(Salpen)(H_2O)_2]_2Ni(NCS)_2 \cdot 2H_2O$ (**2a**)

A methanol solution of $Ni(SCN)_2 \cdot 4H_2O$ (1.84 g, 7.5 mmol) in methanol–water (9:1 v/v) mixture (10 cm³) was added to a solution of $H_2Salpen$ (1.54 g, 5 mmol) in methanol (10 cm³) with constant stirring. A green precipitate appeared immediately. The mixture was stirred for 1 h at room temperature. The precipitate was filtered, washed with methanol and dried in air. Yield: 1.8 g (70%). *Anal.* Calc. for $C_{40}H_{52}Ni_3N_6O_{10}S_2$: C, 47.24; H, 5.15; N, 8.26; Ni, 17.31. Found: C, 47.02; H, 5.11; N, 8.12; Ni, 17.17%. $\lambda_{Max/nm}$ (solid, reflectance), 595, 908 and 1175 nm; IR: $\nu(C=N)$, 1626 cm⁻¹, $\nu(SCN)$, 2098 cm⁻¹, $\nu(H_2O)$, 3401 cm⁻¹, $\mu_{eff} = 5.1$ BM per trinuclear unit.

2.2.4. Synthesis of $[Ni(Salpen)]_2Ni(NCS)_2$ (**2b**)

The green precipitate of complex **2a** was dissolved in hot MeCN solution. The color of the solution changes from green to yellow during dissolution. On keeping the filtrate overnight in air, red block-shaped crystals of **2b**, suitable for X-ray analysis were obtained. Yield: 1.36 g (60%). *Anal.* Calc. for $C_{40}H_{40}Ni_3N_6O_4S_2$: C, 52.85; H, 4.44; N, 9.25; Ni, 19.37. Found: C, 52.32; H, 4.36; N, 9.12; Ni, 19.48%. $\lambda_{Max/nm}$ (solid, reflectance) 490, 1182 and 1389 nm; IR: $\nu(C=N)$, 1610 cm⁻¹, $\nu(SCN)$, 2090 cm⁻¹, $\mu_{eff} = 3.3$ BM per trinuclear unit.

2.2.5. Synthesis of $[Ni(Salen)]_2Ni(NCS)_2$ (**3**)

A solution of $Ni(SCN)_2 \cdot 4H_2O$ (1.84 g, 7.5 mmol) in methanol–water (9:1 v/v) mixture (10 cm³) was added to a solution of H_2Salen (1.40 g, 5 mmol) in methanol (10 cm³) with constant stirring. An immediate red precipitate appeared. The mixture was stirred for 1 h at room temperature. The solid was collected by filtration, washed with methanol and allowed to dry in air. The complex was only sparingly soluble in hot methanol and in DMF. However, suitable single crystals for X-ray analysis could not be grown. Yield: 1.65 g (80%). *Anal.* Calc. for $C_{34}H_{28}Ni_3N_6O_4S_2$: C, 49.51; H, 3.42; N, 10.19; Ni, 21.35. Found: C, 49.32; H, 3.26; N, 10.12; Ni, 20.37%. $\lambda_{Max/nm}$ (solid, reflectance), 510 800 and 1252 nm; IR: $\nu(C=N)$, 1627 cm⁻¹, $\nu(SCN)$, 2077 cm⁻¹, $\mu_{eff} = 3.2$ BM per trinuclear unit.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. The nickel content in all the complexes was estimated gravimetrically using DMG. IR spectra in KBr (4500–500 cm⁻¹) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1500–350 nm) and in the solid state were recorded in a Hitachi U-3501 spectrophotometer. The thermal analyses (TGA-DTA) were carried out on a Mettler Toledo TGA/DTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 cm³ min⁻¹). The samples were heated in an alumina crucible at a rate of 10 °C min⁻¹.

The effective moments at room temperature were evaluated from magnetic susceptibility measurement with an EG and G PAR 155 vibrating-sample magnetometer.

2.4. Crystallographic studies

Intensity data were measured using the Oxford X-Calibur CCD System using Mo K α radiation. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 3 s. Data analyses were carried out with the CRYSTALIS program [38] to give 5654, 11 524 independent reflections for **1a** and **2b** respectively. The structures were solved using direct methods with the SHELX97 program [39]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In **2b** a sulfur atom of a thiocyanate ligand was disordered over three positions each with occupancy of 0.333. Hydrogen atoms on water molecules and on O(11) were readily located in **1a** from a difference Fourier map. Absorption corrections were carried out using the ABSPACK program [40]. The structures were refined on F² using SHELX97 [39] to give wR 0.0569, 0.1253, wR_2 0.0825, 0.2445 for 3273, 4384 reflections with $I > 2\sigma(I)$. The relatively high R value of **2b** is due to the poor quality of the crystal. Despite our best efforts with a state-of-the-art CCD diffractometer we were unable to get a lower value. The data were collected (and refined) up to a theta angle of 60°; on refinement with a theta max of 50°, the R_1 is 0.0837 and wR_2 is 0.2225. We would like to use as much data as possible and so prefer to report the refinement using all data up to 60°. Details of crystallographic data and refinements of the complexes **1a** and **2b** are summarized in Table 1 while selected bond lengths and bond angles are presented in Tables 2 and 3 respectively. A list of H-bonds in the two complexes is given in Table 4.

Table 1
Crystal data and structure refinement of complexes **1a** and **2b**

	1a	2b
Formula	C ₁₈ H ₂₁ N ₃ NiO ₄ S	C ₄₀ H ₄₀ N ₆ Ni ₃ O ₄ S ₂
M	434.15	908.02
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.724(1)	11.384(2)
b (Å)	12.710(1)	20.800(3)
c (Å)	14.875(1)	18.011(4)
β (°)	104.49(1)	103.74(2)
U (Å ³)	1963.0(2)	4142.7(14)
Z	4	4
D_c (g cm ⁻³)	1.469	1.456
μ (Mo K α) (mm ⁻¹)	1.123	1.497
R_{int}	0.069	0.108
Number of unique data	5654	11524
Number of data with $I > 2\sigma(I)$	3273	4384
R_1, wR_2	0.0569, 0.0939	0.1253, 0.3046

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

Ni1–O31	2.025(2)	Ni1–N19	2.042(2)
Ni1–N23	2.036(2)	Ni1–N1	2.075(3)
Ni1–O11	2.039(2)	Ni–O100	2.132(2)
O11–Ni1–O31	85.47(8)	O100–Ni1–N1	178.40(9)
O11–Ni1–O100	89.46(8)	O100–Ni1–N19	89.95(9)
O11–Ni1–N1	91.96(9)	O100–Ni1–N23	88.01(9)
O11–Ni1–N19	88.44(9)	N1–Ni1–N19	90.83(9)
O11–Ni1–N23	174.23(2)	N1–Ni1–N23	90.52(10)
O31–Ni1–O100	86.10(8)	N19–Ni1–N23	96.73(9)
O31–Ni1–N1	93.27(9)		
O31–Ni1–N19	172.77(9)		
O31–Ni1–N23	89.19(8)		

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

Ni1–O11	2.096(6)	Ni2–O31	1.860(6)
Ni1–O31	2.102(6)	Ni2–N19	1.868(8)
Ni1–O41	2.057(6)	Ni2–N23	1.883(9)
Ni1–O61	2.137(6)	Ni3–O41	1.876(7)
Ni1–N1	2.015(9)	Ni3–O61	1.878(6)
Ni1–N2	2.009(9)	Ni3–N53	1.909(9)
Ni2–O11	1.854(7)	Ni3–N49	1.914(9)
O11–Ni1–O31	70.7(2)	O11–Ni2–O31	81.7(3)
O11–Ni1–O41	156.8(3)	O11–Ni2–N19	92.8(3)
O11–Ni1–O61	93.5(3)	O11–Ni2–N23	172.8(3)
O11–Ni1–N1	101.7(3)	O31–Ni2–N19	172.8(4)
O11–Ni1–N2	94.7(3)	O31–Ni2–N23	91.5(3)
O41–Ni1–O61	70.7(3)	N19–Ni2–N23	94.2(4)
O41–Ni1–N1	95.9(3)		
O41–Ni1–N2	99.0(3)	O41–Ni3–O61	80.6(3)
O61–Ni1–N1	91.9(3)	O41–Ni3–N49	91.6(3)
O61–Ni1–N2	168.7(3)	O41–Ni3–N53	167.9(3)
N1–Ni1–N2	94.1(4)	O61–Ni3–N49	168.4(3)
		O61–Ni3–N53	93.4(3)
		N49–Ni3–N53	95.7(4)

Table 4
Hydrogen bonding distances (Å) and angles (°) for the complex **1a**

Compound	D–H...A	D–H	D...A	A...H	\angle D–H...A
1a	O100–H1...O200	0.90(3)	1.84(3)	2.718(4)	164(3)
	O100–H2...S1 ^j	0.85(3)	2.54(4)	3.379(2)	170(3)
	O200–H4...N1 ^k	0.88(3)	2.44(3)	3.264(4)	156(3)
	O11–H11...O31 ^l	0.90(2)	1.54(2)	2.438(3)	175(2)

Symmetry elements: (j) $x, 1/2 - y, 1/2 + z$; (k) $1 - x, -y, 2 - z$; (l) $1 - x, -y, 2 - z$.

3. Results and discussion

3.1. Synthesis of the complexes

We have synthesized three di-Schiff base ligands, H₂Salen, H₂Salpn, and H₂Salpen (Scheme 1) and allowed them to react separately with Ni(II) thiocyanate in 2:3 molar ratios. Although the ligands are very similar, the

composition and structure of the products are considerably different as shown in Scheme 1. H₂Salpn results a mononuclear complex, [Ni(HSalpn)(NCS)(H₂O)]·H₂O (**1a**) where Ni(II) is chelated by the mono-negative HSalpn. H₂Salpn produces initially a trinuclear complex [$\{Ni(Salpen)(H_2O)_2\}_2Ni(NCS)_2\} \cdot 2H_2O$ (**2a**) in which the geometry around all three Ni(II) atoms is octahedral. **2a** on heating or crystallization from acetonitrile or even in contact with organic solvents e.g. dichloromethane loses the water molecules and transforms into the square planar–octahedral–square planar trinuclear complex, [$\{Ni(Salpen)\}_2Ni(NCS)_2\}$ (**2b**). H₂Salen, on the other hand, yields immediately the ‘square planar–octahedral–square planar’ trinuclear complex [$\{Ni(Salen)\}_2Ni(NCS)_2\}$ (**3**). Complexes, **1a** and **2b** have been characterized by single crystal X-ray analysis. We failed to obtain suitable single crystals for the other complexes and characterized them by elemental analyses, thermal analysis, room temperature magnetic moment measurement, IR and UV–VIS spectra.

3.2. Description of structures of **1a** and **2b**

3.2.1. Complex **1a**

The structure of **1a**, shown in Fig. 1, contains the metal in a six-coordinate, distorted octahedral environment in which O(11), N(19), N(23) and O(31) of the mono-negative Schiff base constitute the equatorial plane. The deviations of the four basal donor atoms from their mean plane are within ± 0.015 Å. The Ni atom deviates from the mean plane by $-0.0567(4)$ Å. The two axial positions are occupied by N(1) of a thiocyanate group and O(100) of a water molecule. The six-membered ring comprising the nickel, imine N atoms and three propylene C atoms adopts a chair conformation. The complex contains another non-coordinated water molecule and there is a strong hydrogen bond between the coordinated and uncoordinated two water molecules as shown in Fig. 1. A weaker H-bond is also formed between one of the hydro-

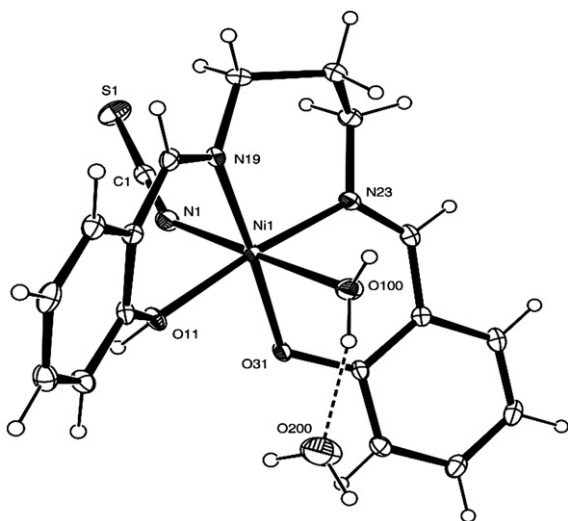


Fig. 1. Ortep-3 view of the complex **1a** with ellipsoids at 50% probability.

gen atoms of this uncoordinated water molecule (H4) and the N(1) atom of the coordinated isothiocyanate (Table 4). One interesting feature of this complex is that one of the oxygen atoms (O11) of the Schiff base is protonated which allows the charge on the complex to be balanced. The presence of H on O(11) is substantiated by the longer Ni(1)–O(11) bond distance of 2.039(3) Å compare to Ni(1)–O(31) bond distance of 2.025(2) Å. However, it should also be noted that the difference in bond distances is not remarkable and the Ni(1)–O(31) bond is rather long compare to that found in octahedral Ni(Salpn) type complex (2.017(2) Å) [13]. This can be explained by the involvement of this hydrogen (H11) in a very strong hydrogen bond with O(31) of another unit to form a centrosymmetric dimer as shown in Fig. 2. The symmetry related dimers are linked by weaker O100–H(2)···S(1) intermolecular hydrogen bonds to form a two dimensional layer structure as shown in Fig. 3. It is interesting to note that the same ligand has previously been reacted with nickel(II) thiocyanate adopting a different procedure [41] to form the complex, [Ni(HSalpn)(NCS)(CH₃OH)] which is analogous to **1a**. The only difference is that the axially coordinated water of **1a** is replaced by a MeOH molecule. The bond angles and distances of the two compounds are very similar. However, the difference (0.040 Å) between two Ni–O (Schiff base) bond distances (2.054 and 2.014 Å) of that complex is slightly higher than that (0.014 Å) in **1a** probably due to the weaker H-bond that is formed involving the hydrogen atom attached to the Schiff base of that compound.

3.2.2. Complex **2b**

The structure of **2b** is a trinuclear compound as shown in Fig. 4 containing three independent nickel atoms. Ni(1) is six-coordinate with a distorted octahedral environment, while Ni(2) and Ni(3) are four-coordinate with a square planar environment. Each of the two

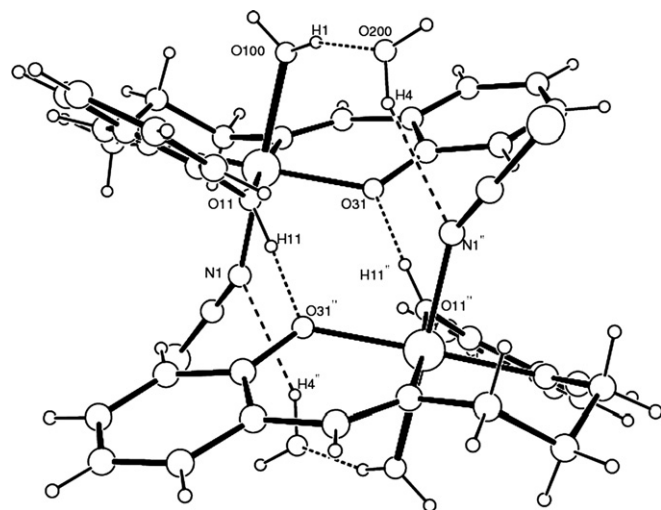


Fig. 2. Ortep-3 view of the dimeric unit *c* of **1a** with ellipsoids at 20% probability.

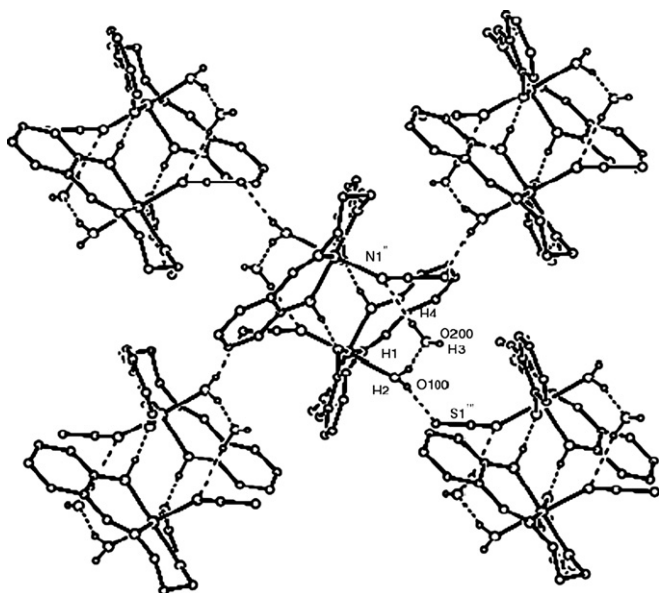


Fig. 3. Extended hydrogen-bonding network in complex **1a**.

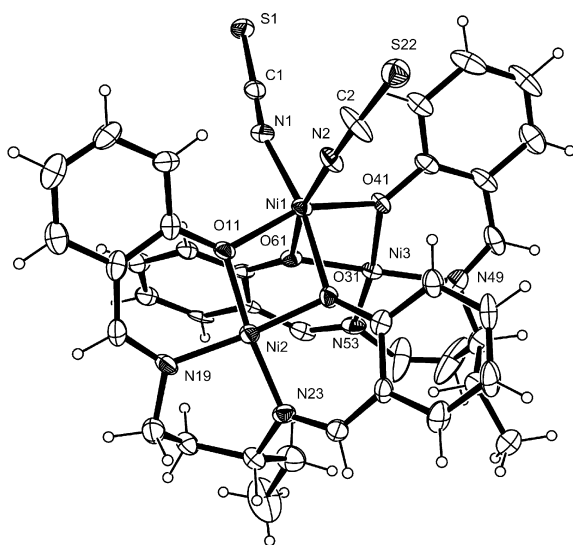


Fig. 4. ORTEP-3 view of the complex **2b** with ellipsoids at 25% probability.

terminal nickel atoms, Ni(2) and Ni(3) are coordinated by the two nitrogen atoms and two oxygen atoms of the deprotonated, chelating Schiff base ligand, H₂Salpen. The average trans angles are 172.8° and 168.2° for Ni(2) and Ni(3), respectively indicate that there is slight tetrahedral distortion from the ideal square planar geometry. The deviations of Ni(2) and Ni(3) from the respective mean planes passing through the coordinating atoms are 0.019(1) and -0.018(1) Å. The six-membered chelate rings containing the diamine fragment and nickel atom adopt boat and half-chair conformations for Ni(2) and Ni(3), respectively.

The four oxygen atoms of the two Ni(Salpen) moieties are also bonded to a third nickel atom Ni(1) forming the phenoxo bridged trinuclear complex. In addition Ni(1) is bonded to two mutually cis isothiocyanate ligands with

Ni(1)–N(1) 2.016(9), Ni(1)–N(2) 2.009(9) Å to complete its distorted octahedral coordination. The small bite of Ni(Salpen) on coordinating to Ni(1) (average angle 70.8°) is the main cause of distortion from the ideal octahedron. The bond lengths, Ni(1)–O(11) 2.096(6), Ni(1)–O(31) 2.102(6) Å with the oxygen atoms bridging to Ni(2) and Ni(1)–O(41) 2.057(6) Å, Ni(1)–O(61) 2.137(6) Å with the oxygen atoms bridging to Ni(3) are significantly longer than Ni(2)–O and Ni(3)–O distances at 1.853(6), 1.859(6), 1.876(6), 1.878(6) Å. This difference is expected as in Ni(II) complexes, the bond distances in square planar geometry are usually less than that in octahedral geometry indicating that the axial coordination weakens the equatorial ligand field strength [12,13,15,41]. The Ni(2)–O and Ni(3)–O bonds are, however, slightly longer than those found in the mono-nuclear square planar Ni(Salpn) complex (1.845 Å) as a result of lower electron density of the oxygen upon bridging. A comparison of the structures of the similar complexes reveals an interesting feature – when trinuclear Ni(II) complexes are formed by both phenoxo- and anion bridges, the resulting complexes are linear in which the four phenoxo groups occupy a square plane (four meridional positions) of the central Ni(II) leaving its *trans* axial positions to be occupied by the bridging anions [22–25]. However in the case of complexes containing phenoxo bridges only (as is **2b**), the four oxygen atoms coordinate in facial manner to the central Ni(II) to result in a bent structure [26]. In **2b**, the Ni(2)–Ni(1)–Ni(3) angle is 87.88(5)° and the two Ni(Salpen) planes are disposed at a dihedral angle of 37.9°, compared to 17.6° for the Ni(Salen) complex [26].

3.3. IR and UV–VIS spectra, thermal analysis and magnetic moment of the complexes

3.3.1. Complexes **1a** and **1b**

The coordination mode of the thiocyanate anion to the transition metal is detected by the intense IR band due to (SCN) which occurs above 2000 cm⁻¹. The CN stretching frequency for N-bonded thiocyanate usually appears below 2100 cm⁻¹ and that of S-bonded thiocyanate appears above 2100 cm⁻¹ [42]. Complex **1a** shows a strong absorption band at 2094 cm⁻¹ corroborating the presence of N-bonded thiocyanate group. It shows a strong and broad band, centering at 3328 cm⁻¹ due to the presence of water molecule. Generally, stretching vibration for water appears above 3400 cm⁻¹. The shift of this band towards lower wave number and its broadness indicate the presence of strong hydrogen bonding as is substantiated by crystal structure. The band due to azomethine (C=N) appears at 1634 cm⁻¹. The magnetic moment ($\mu_{\text{eff}} = 3.3$ BM) and the appearance of two bands in the UV–VIS spectra of the complex corroborate its octahedral geometry. The highest energy d–d transition band is obscured by the CT band at that region.

The simultaneous TGA–DTA curves of complex **1a** reveal that upon heating it starts to lose water molecules at 90 °C and becomes dehydrated at ca. 150 °C in a single step. The observed weight loss (8.6%) corroborates the loss

of two water molecules (calc. 8.29%). Both the coordinated and crystallized water molecules are lost simultaneously as they are linked by strong hydrogen bonds. The dehydrated species (**1b**) is dirty-green in color and reabsorbs the two water molecules on keeping in open atmosphere for several days. It, however, does not absorb any organic solvent (e.g. methanol or acetonitrile) on keeping as suspension in these solvents. The magnetic moment of **1b** ($\mu_{\text{eff}} = 3.0$ BM) shows the presence of two unpaired electrons. Its electronic spectra indicate either penta-coordinated or hexa-coordinated geometry around Ni(II). The IR spectra of **1b** expectedly do not show any band due to water molecule. The (SCN) stretching vibration occurs nearly at the same wave number (2095 cm^{-1}) as in **1a** indicating no change of its coordination behavior on deauration. Therefore, a penta-coordinated geometry around Ni(II) with an N-bonded thiocyanate is suggested for **1b**.

3.3.2. Complexes **2a** and **2b**

The green compound **2a** is unstable and loses its water molecules on drying in a desiccator or in contact with organic solvents such as chloroform, dichloromethane etc. to transform into the red colored compound, **2b**. Therefore, an air dried sample of **2a** has been used for all physico-chemical studies. Complex **2a** shows a single absorption band at 2099 cm^{-1} due to the presence of coordinated isothiocyanate group. A strong and broad band around 3400 cm^{-1} indicates the presence of water molecules in it. The band due to azomethine appears at 1630 cm^{-1} . The magnetic moment ($\mu_{\text{eff}} = 5.1$ BM for trinuclear structure; 3.0 BM per Ni ion) and electronic spectra of the compound are typical of octahedral Ni(II) complexes. Therefore, a phenoxo bridged, trinuclear structure in which the two terminal Ni(II) have axially coordinated water molecules is suggested for it (Scheme 1). Upon heating, it starts to lose water molecules at ca. $40\text{ }^{\circ}\text{C}$ and become anhydrous at ca. $110\text{ }^{\circ}\text{C}$. The observed weight loss (11.0%) corresponds to the presence of six molecules of water per trinuclear unit (calc. 10.6%). The color of the species changes from green to red on dehydration. It does not reabsorb any water molecule on keeping in open atmosphere. The spectral and analytical results of the dehydrated species confirm that it is identical to compound **2b**.

The physico-chemical studies of **2b** corroborate its trinuclear structure as elucidated by X-ray analysis. The electronic spectra clearly show the presence of both octahedral and square planar Ni(II) in the compound. The magnetic moment ($\mu_{\text{eff}} = 3.3$ BM) corresponds to the presence of one paramagnetic octahedral Ni(II) per trinuclear unit. In IR spectra, stretching vibration band due to thiocyanate (SCN) and azomethine (C=N) appears at 2090 cm^{-1} and 1610 cm^{-1} , respectively and there is no band due to water around 3400 cm^{-1} .

3.3.3. Complex **3**

The analytical, spectral and magnetic data of **3** indicate that it has similar composition and structure to that of **2b**.

In IR spectra, no band due to water is found. The (SCN) and (C=N) bands appear at 2077 cm^{-1} and 1627 cm^{-1} , respectively. In the electronic spectra, peaks due to both square planar and octahedral Ni(II) appear and the magnetic moment indicates the presence of one paramagnetic Ni(II) with two unpaired electron per trinuclear unit.

3.4. Variation of structures with chain length and substitution in diamine fragment

The three Schiff bases that have been used here are very similar (Scheme 1). Salen forms a five membered chelate ring with the metal ion by the coordination of two nitrogen atoms. The diamine fragment in Salpn is 1,3-propanediamine and consequently a six membered ring is formed on chelation of the two nitrogen atoms of the Schiff base. Salpen forms a similar six-membered chelate ring but there is an ethyl substitution in one of the ring carbon atoms. On reaction with Ni(II) thiocyanate both Salen and Salpen form phenoxo bridged, square planar–octahedral–square planar trinuclear complexes (**3** and **2b**, respectively). The initial formation of trinuclear species with all three nickel atoms in octahedral environments (**2a**) with Salpen but not with Salen may be explained by their slight difference in ligand field strength. The steric hindrance due to the bulkier trimethylene group between the N atoms causes a weaker ligand field for the Schiff bases derived from 1,3-propanediamine and its derivative. As a result, water molecules can coordinate to Ni(II) axially as is found in **2a**. In fact, for this reason, all the Ni(II) complexes where Salen acts as a chelate are square planar [10–21] but complexes of Salpn type ligands can be square planar [12], penta-[15] or hexa-coordinate [13,41] species. It also explains the existence of several trinuclear Ni(II) complexes which are bridged both by phenoxo and an anionic ligand to form octahedral geometry around all three Ni(II) containing Salpn but not Salen as ligand [22–25].

The composition and structure of **1a**, on the other hand, is very different from the complexes that are usually formed by salen-type Schiff base ligands. The hydrogen atoms present in the –OH group of these types of Schiff bases are acidic in nature. Generally, when metal ion is added, the two oxygen atoms coordinate to the metal center and consequently their acidity is increased so much that these protons are lost readily and a complex with di-negative Schiff base is formed. Complex **1a** is an interesting exception in which the very uncommon mono-negative Schiff base is stabilized making the stoichiometry and structure of **1a** different from other related complexes. An explanation for the formation of this exceptional compound may be as follows:

The weak ligand field of Salpn as discussed above allows axial coordination of a thiocyanate and a water molecule (or methanol [41]). The proton bonded to one of the oxygen atoms is stabilized by the formation of a very strong H-bonded dimer (Fig. 2) The supramolecular two-dimensional H-bond structure involving the water molecules and thiocyanate group (Fig. 3) also tilts the balance

in favor of the mononuclear complex containing the mono-negative Schiff base over the trinuclear one. Salen does not allow the formation of such a complex as axial coordination to Ni(II) is unfavorable. The ethyl group present in the Salpen ligand probably prevents the formation of the H-bonding network and consequently the trinuclear complex is formed. The formation of phenoxo bridged trinuclear or H-bonded mononuclear compounds of Ni(II) is thus a delicate balance of electronic and steric effects of the Schiff base ligand as well as the capability of different donor and acceptor sites to form intermolecular hydrogen bonds to an adjacent coordinated ligand.

4. Conclusion

The present study shows that in Schiff base complexes of Ni(II), the environment at coordination center can be modified by changing the chain length or introducing substitution in carbon atom of the diamine. A minor difference in the subunit structure can bring about drastic change in molecular and crystal structure. The examples nicely illustrate the importance of steric and electronic properties for the fine tuning of composition and structure. Formation of **2a** demonstrates the importance of hydrogen bonding in the formation of unusual compounds.

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Appendix A. Supplementary material

CCDC 633271 and 633272 contain the supplementary crystallographic data for **1a** and **2b**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2007.02.006](https://doi.org/10.1016/j.poly.2007.02.006).

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