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Three new flexidentate 5-substituted salicylaldimino Schiff base ligands (L1-OH−L3-OH) based on 1-(2-aminocetyl)piperazine (X = H, L1-OH; X = NO2, L2-OH; and X = Br, L3-OH) and their nickel(II) complexes (1a, 1b, 2, and 3) have been reported. The piperazinyl arm of these ligands can in principle have both boat and chair conformations that allow the ligands to bind the Ni(II) center in an ambidentate manner, forming square-planar and/or octahedral complexes. The nature of substitution in the salicylaldehyde aromatic ring and the type of associated anion in the complexes have profound influences on the coordination geometry of the isolated products. With the parent ligand L1-OH, the product obtained is either a planar red compound [Ni(L1-O)]+, isolated as tetraphenylborate salt (1a), or an octahedral green compound [Ni(L1-NH)(H2O)3]2+, isolated with sulfate anion (1b); both have been crystallographically characterized. In aqueous solution, both these planar (S = 0) and octahedral (S = 1) forms are in equilibrium that has been followed in the temperature range 298−338 K by 1H NMR technique using the protocol of Evans’s method. The large exothermicity of the equilibrium process [Ni(L1-O)]+ + 3H2O + H+ ⇋ [Ni(L1-NH)(H2O)3]2+ (ΔH° = −46 ± 0.2 kJ mol⁻¹ and ΔS° = −133 ± 5 J K⁻¹ mol⁻¹) reflects formation of three new Ni−OH₂ bonds in going from planar to the octahedral species. With the 5-nitro derivative ligand L2-OH, the sole product is an octahedral compound 2, isolated as a sulfate salt while with the bromo derivative ligand L3-OH, the exclusive product is a planar molecule 3 with associated tetraphenylborate anion. Both 2 and 3 have been structurally characterized by X-ray diffraction analysis.

Introduction

The possibility of the existence of an equilibrium in solution between the octahedral and planar forms of nickel(II) complexes was reported for the first time with some sterically constrained ligands, viz. stilbenediamine (stien) by Lifschitz et al.1,2 The proposed equilibrium [Ni(stein)X₂] ⇋ [Ni(stien)²⁺] + 2X⁻ (X⁻ = various anions) was latter established by magnetic, spectroscopic, and X-ray structure analyses.3,4 Over the years, several other such equilibria have been reported using macrocyclic5−12 and open chain analyses.3,4

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polyamines and Schiff base ligands.\textsuperscript{13–16} These reported equilibria are generally of two types (Scheme 1). The most common one involves axial attachment of ligand \( X \) (\( X = \) anions or solvent molecules, predominantly water) to square-planar species \( \text{NiL} \), largely of macrocyclic ligands \( L \) (Scheme 1A) to generate the octahedral counterpart \( \text{NiLX}_2 \).\textsuperscript{5–14} The second type of equilibrium (Scheme 1B), on the other hand, involves flexidentate ligands \( L' \) which form bis complexes of composition \( \text{Ni}(L')_2 \). At lower temperatures, these ligands bind nickel(II) in tridentate fashion to render octahedral geometry which reduces to a planar one at elevated temperatures due to steric constraints of the associated ligands.\textsuperscript{15,16} Most of these equilibrium studies were followed by spectroscopic techniques, and only in a few cases were the species involved characterized in the solid state by X-ray diffraction analysis.\textsuperscript{4,12}

Recently, reports have been made on pH-dependent reversible translocation of Ni(II) ion from octahedral to the square-planar site in ditopic ligand systems.\textsuperscript{17} Such a translocation phenomenon can be used effectively as a light emission switch by tagging the ditopic ligand systems with fluorescent probes.\textsuperscript{18,19} Herein, we report the nickel(II) complexes of three new flexidentate Schiff base ligands (L\textsuperscript{1-}OH–L\textsuperscript{3-}OH; Chart 1).\textsuperscript{20} The piperazinyl arm of these ligands can, in principle, have both boat and chair conformations that force these molecules to display ambidentate ligation behavior, leading to both octahedral and square-planar geometry for the Ni(II) complexes. The structures of these complexes in the solid state have been examined by X-ray diffraction analysis. The

\begin{align*}
\text{Complexes.} \quad & \text{[Ni(L\textsuperscript{1-}O)](BPh}_4\text{) (1a). To a stirred solution of L\textsuperscript{1-}OH (0.23 g, 1 mmol) in methanol (20 mL) was added a solution of Ni(ClO}_4\text{)\textsubscript{2}·6H}_2\text{O (0.36 g, 1 mmol) taken also in methanol. The resultant orange solution was refluxed for 2 h. Solid NaBPh}_4\text{(0.50 g) was then added to the solution while it was hot and filtered immediately. The filtrate was kept in the air for ca. 12 h to obtain an orange microcrystalline solid. It was collected by filtration, washed with Et}_2\text{O (5 × 2 mL), and dried in a vacuum. The compound was recrystallized from CH}_3\text{Cl}_2/n\text{-hexane mixture. Diffraction quality crystals were obtained by diffusing n-hexane into a dichloromethane solution of the compound. Yield: 0.34 g (55%). Anal. Calcd for C}_37\text{H}_38\text{BNiN}_3\text{O: C, 72.76; H, 6.23; N, 6.88.}}
\end{align*}

\begin{align*}
\text{Chart 1}
\end{align*}

\[\begin{array}{c}
\text{X} \quad \text{L-OH} \\
\text{H} \\
\text{NO}_2 \quad \text{L\textsuperscript{2-}OH} \\
\text{Br} \quad \text{L\textsuperscript{3-}OH}
\end{array}\]

square-planar–octahedral equilibrium in solution is followed in detail by \( ^1\text{H} \) NMR and electronic spectroscopies.

\section*{Experimental Section}

Materials. 1-(2-Aminoethyl)piperazine, 5-bromosalicylaldehyde, and 5-nitrosalicylaldehyde were obtained from Aldrich. Salicylaldehyde (Aldrich) was distilled before use. Solvents were reagent grade, dried from appropriate reagents,\textsuperscript{21} and distilled under nitrogen prior to their use. Spectroscopic grade D\textsubscript{2}O was also obtained from Aldrich. All other chemicals were commercially available and used as received.

Syntheses. Ligands. The Schiff base ligands (L\textsuperscript{1-}OH–L\textsuperscript{3-}OH) were prepared following a general procedure. Synthesis of 1-(2-salicylaldiminoethyl)piperazine (L\textsuperscript{1-}OH) is described below as a prototype.

To a stirred solution of salicylaldehyde (2.44 g, 20 mmol) in absolute ethanol (20 mL) was added dropwise an equimolar amount (2.58 g) of 1-(2-aminoethyl)piperazine, and the resulting mixture was refluxed for 1 h to obtain an orange solution. The solvent was then removed by rotary evaporation to obtain a red oil which on standing for days in a vacuum produced a yellow hygroscopic solid. Several attempts to recrystallize the compound were unsuccessful.

Both ligands L\textsuperscript{2-}OH and L\textsuperscript{3-}OH are also extremely hygroscopic yellow solids, which eluded our repeated attempts at recrystallization. The ligands were then used for metalation without further purification.

\begin{align*}
\text{Complexes.} \quad & \text{[Ni(L\textsuperscript{1-}O)](BPh}_4\text{) (1a). To a stirred solution of L\textsuperscript{1-}OH (0.23 g, 1 mmol) in methanol (20 mL) was added a solution of Ni(ClO}_4\text{)\textsubscript{2}·6H}_2\text{O (0.36 g, 1 mmol) taken also in methanol. The resultant orange solution was refluxed for 2 h. Solid NaBPh}_4\text{(0.50 g) was then added to the solution while it was hot and filtered immediately. The filtrate was kept in the air for ca. 12 h to obtain an orange microcrystalline solid. It was collected by filtration, washed with Et}_2\text{O (5 × 2 mL), and dried in a vacuum. The compound was recrystallized from CH}_3\text{Cl}_2/n\text{-hexane mixture. Diffraction quality crystals were obtained by diffusing n-hexane into a dichloromethane solution of the compound. Yield: 0.34 g (55%). Anal. Calcd for C}_37\text{H}_38\text{BNiN}_3\text{O: C, 72.76; H, 6.23; N, 6.88.}}
\end{align*}

\begin{align*}
\text{Found: C, 73.03; H, 6.29; N, 6.70. IR (KBr disk, cm}^{-1}): \nu(N–H), 3263s; \nu(C=NH), 1618s; \nu(C=O/phenolate), 1530s; \nu(phenyl ring), 738s, 706s.}
\end{align*}

\[\text{[Ni(L\textsuperscript{1-}N\textsubscript{2})(H}_2\text{O})\textsubscript{3}]SO}_4\cdot6\text{H}_2\text{O (1b). An aqueous solution (25 mL) of NiSO}_4\cdot6\text{H}_2\text{O (0.26 g, 1 mmol) was added dropwise to a solution of the ligand L\textsuperscript{1-}OH (0.23 g, 1 mmol) taken in methanol (10 mL). The resultant green solution was stirred for 30 min and}
\end{align*}

\begin{align*}
\text{Mukhopadhyay et al.}
\end{align*}
filtered. The filtrate was concentrated under reduced pressure to drive off methanol and filtered again. The filtrate was layered with acetone and kept at 4 °C for several days to obtain a moss-green crystalline compound along with some X-ray diffraction quality crystals. The product was collected by filtration and dried in a vacuum. The compound was recrystallized from an acetone-petroleum ether (60:40) mixture. X-ray diffraction quality crystals were obtained by diffusing C25H20BrNiN3O: C, 64.50; H, 5.37; N, 6.10. Found: C, 64.10; H, 6.72; N, 7.63. IR (KBr, disk, cm−1): ν(C=O)/ν(N), 1656s; ν(υ2, ν1 ν(N)), 1648s; ν(υ2, ν1 ν(N)), 1623s; ν(C=O/phenolate), 1527s; ν(BPh3), 735s, and 707s.

Physical Measurements. Room-temperature magnetic moments, UV–vis spectra, and IR spectra (as KBr disk) were obtained as described elsewhere. 1H NMR measurements were performed with a Bruker Model Avance DPX 300 apparatus. Elemental analyses (for C, H, and N) were performed in this laboratory (at IACS) using a Perkin-Elmer 2400 analyzer.

X-ray Crystallography. Selected crystallographic data are given in Table 1, and complete data are given in the supplementary CIF file (see Supporting Information). Intensity data for 1a were collected at room temperature on a Bruker 1K SMART CCD diffractometer using θ–2θ technique, while for 1b, 2, and 3 data were collected on a Nonius Kappa CCD diffractometer, with both diffractometers using Mo Kα X-radiation (λ = 0.71073 Å). No crystal decay was observed during the data collections. The analyzed crystals of 1b, 2, and 3 were covered with a thin layer of light oil and cooled at 110 K in order to minimize structural disorder and thermal motion effect and to increase the precision of the results. Intensity data for all the complexes were measured within the θ range of 2.42–27.90°. The structures were solved by direct and Patterson methods and refined by a full matrix least-squares procedure based on F2 using the SHELXS-97 (1a), SIR-92 (1b and 2), and SHELXD-96 (3), and SHELXL-97 software. 24–26

Variable Temperature Magnetic Susceptibility Measurements. The octahedral–square-planar equilibrium of 1a–1b in solution was monitored by susceptibility (χM) measurement at variable temperatures following Evans’s method. 27 The working solution in D2O containing 2% tert-butyl alcohol as a reference compound was prepared by dissolving 0.0427 g of 1b per milliliter of the solvent. The solution was taken in a NMR tube. The same combination of solvent (2% tert-butyl alcohol in D2O) was also used as external standard and taken in a capillary tube of 2 mm outer diameter. The latter was placed inside the NMR tube, and the combination was used for χM measurements in the temperature range of 2.42–27.90°.

Table 1. Relevant Crystal Data for [Ni(L1–O)(BPh3)] (1a), [Ni(L1–NH)(H2O)][SO4]•6H2O (1b), [Ni(L2–NH)(H2O)][SO4]•2H2O (2), and [Ni(L3–O)](BPh4) (3)

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<th>1b</th>
<th>2</th>
<th>3</th>
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<td>C32H24BN5O5</td>
<td>C32H24BN5O5</td>
<td>C32H24BN5O5</td>
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<td>550.23</td>
<td>550.23</td>
<td>689.13</td>
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<td>0.10 ± 0.15 × 0.25</td>
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<td>P1</td>
<td>P1</td>
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<td>2</td>
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ligand L2 -OH, however, the only product obtained is the
in the solid state only in the presence of sulfate anion by

and bromo derivatives. The conformational flexibility of the
ethyl)piperazine and salicylaldehyde or its 5-substituted nitro
prepared by Schiff base condensation between 1-(2-amino-

green crystalline compound

2

the bromo derivative ligand L3 -OH, the exclusive product
the solid state only in the presence of sulfate anion. With

1b

°

SO 4 2

solutions are yellow to orange in color. We have been
to be green at room temperature in the presence of Cl
much dependent on the counteranion. The solution appears

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Results and Discussion

Synthesis. Three new ligands (L1 -OH–L3 -OH) have been
prepared by Schiff base condensation between 1-(2-amino-
ethyl)piperazine and salicylaldehyde or its 5-substituted nitro
and bromo derivatives. The conformational flexibility of the
piperazine ring (from boat to chair form and vice versa)
makes one of these ligands (L1 -OH) capable of coordinating

Figure 1. Molecular structure of complex 1a showing the atom numbering scheme.

ligand is tridentate with piperazine moiety in chair conformation,
making only a single ring nitrogen atom available for
coordination to the nickel center, while the other in the
protonated form stays away from coordination. The remain-
ing coordination sites in 1b are taken up by three water
molecules. The overall composition of 1b is [Ni(L1 -NH)-(H2O)3](SO4)-6H2O, in which L1 -NH stands for the N-
protonated form of the ligand L1 -OH.20 Compounds 2 and 3
have geometry and coordination environments closely similar
to those of 1b and 1a, respectively.

IR spectra of the complexes have a couple of prominent
bands appearing at ca. 1640 and 1535 cm\(^{-1}\) regions,
assignable to \(\nu(C=\text{N})\) and \(\nu(C-O/\text{phenolate})\) stretching
modes, respectively. In the high-frequency region, a broad
medium intensity band in the 3500–3400 cm\(^{-1}\) range due
to \(\nu(O-H)\) vibration indicates the presence of coordinated
water molecules in 1b and 2. Compounds 1a and 3, on the
other hand, show a strong sharp band due to \(\nu(N-H)\)
stretching at ca. 3270 cm\(^{-1}\). In addition, the octahedral
complexes 1b and 2 display two strong bands at 1100 and 620
\(^{-1}\) confirming the presence of ionic sulfate.29 Likewise,
1a and 3 show two strong bands at ca. 710 and 610 \(^{-1}\) due to phenyl ring vibrations, associated with
tetraphenylborate anion.

Description of Crystal Structures. Figures 1 and 2 show
the perspective views of the square-planar complexes of 1a
and 3, respectively. Their selected bond distances and angles
are given in Table 2. Complex 1a crystallizes in the triclinic
space group \(P\bar{1}\) with two molecules per unit cell, while 3
has the hexagonal space group \(P6_3\) with six molecules in
the unit cell. The observed crystal structures confirm the boat
conformation of the associated piperazine ring in the ligands.
The latter binds to Ni(II) in tetradeinate fashion, providing
an \(\text{N}_2\text{O}\) donor set. In both molecules, the \(\text{Ni}-\text{N}\) bond
distances are slightly different, with the piperazine associated
\(\text{Ni}-\text{N}(3)\) bond being the longest: 1.931(2) Å in 1a and
1.915(6) Å in 3. The trans angles O(1)–Ni–N(2) and Ni(1)–
N(3) in 1a are 172.88(7° and 163.79(7°, respectively.
Corresponding angles in 3 are almost identical (Table 2).
The two halves of the molecule (Ni, O(1), and N(1)) and


tridentate ligands generates cationic nickel(II) complexes that.

The overall electroneutrality of the coordinated

O(3), toward the apical oxygen atom

O(3) from a coordinated water molecule,

and two water molecules present in

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(Figure 2). Molecular structure of complex 3 showing the atom numbering

Figure 2. ORTEP drawing and crystallographic numbering scheme for

flexidentate Schiff Base Ligand Complexes

(Ni, N(2), and N(3)) are twisted by 7.9° in 1a. The corresponding angle for 3 is 6.8°.

The molecular structures and atom numbering schemes

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes

require sulfate anion for their crystallization. There are six

and two water molecules present in 1b and 2, respectively,

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes

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Table 4. Hydrogen Bonding Parameters for Compounds 1b and 2

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<tr>
<th>A</th>
<th>H</th>
<th>B</th>
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<th>A−H</th>
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</table>

*O2–O4 represent water molecules coordinated to the Ni cation. O5–O9 are part of the SO4 anion, and O9–O14 represent other free water molecules incorporated into the crystal lattice. *O9 and O10 represent free water molecules incorporated into the crystal lattice.

to their crystallization. Details of the hydrogen bonding parameters are listed in Table 4, while Figure S1 (in the Supporting Information) provides a complete view of the atoms participating in hydrogen bonding in 1b. In the octahedral complexes, the Ni–O and Ni–N distances are in the ranges 2.0232(15)–2.0915(14) and 1.9997(16)–2.2321(16) Å, respectively, which are as expected for high-spin Ni(II) complexes reported so far.30,31 When these distances are compared with the corresponding bond lengths of the square-planar complexes, an interesting correlation emerges between the structural features of 1a and 1b. The bond lengths in 1b are systematically larger compared to the corresponding distances in 1a. This is, however, not unexpected considering in the high-spin complex 1b the presence of a singly populated d^2_3,2 orbital, which is antibonding in nature. This, in consequence, results in an expansion of the basal core, leading to longer bond distances in 1b compared to the square-planar analogue 1a.

Electronic Spectra. Electronic spectral data for the complexes are summarized in Table 5. In acetonirole, 1a displays a medium intensity band at 451 nm (λ_{max}, for the corresponding band in 3 is 466 nm) in the form of a shoulder due to the spin-allowed 1^1A_{1g} → 1^1A_{2g} transition, typical of square-planar d^8 species.33 The second ligand-field band, 1^1A_{1g} → 1^1B_{1g}, expected to appear at higher energy is probably obscured by the tail of a near-UV absorption present in 1a and 3.

The green octahedral complexes 1b and 2, isolated as their sulfate salts, are only soluble in water. In the visible region, aqueous solutions of these complexes display three weak band maxima (ε, 5–18 mol^{-1} cm^2) at 944 (938 for 2), 746 (746), and 617 nm (610 nm) (Figure 5i) corresponding to the spin-allowed transitions 3^1T_{2g} → 3^1T_{1g}, 3^1T_{2g} → 3^1T_{1g}, and 3^1A_{2g} → 3^1T_{1g}(P), respectively, as expected for Ni(II) in a distorted octahedral environment.33

When the temperature of an aqueous solution of 1b is slowly increased, its color gradually changes from green to light orange with a concomitant change in spectral intensity. In the visible region, all the d−d bands show a decrease in spectral intensities with the rise in temperature as shown in Figure 5. The appearance of isobestic points at 568 nm is a clear indication of the existence of an equilibrium in solution between the octahedral species 1b and its square-planar counterpart 1a formed at higher temperatures (vide supra) and is represented by eq 2.

Electronic absorption spectra of 1b (concentration 4.7 × 10^{-3} M) in aqueous solution as a function of temperature: (i) 298, (ii) 308, (iii) 318, (iv) 328, and (v) 338 K.

Equilibrium Studies. Since one component of this equilibrium is a paramagnetic species while the other is a

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diamagnetic one, this offers an opportunity to follow the above equilibrium by magnetic measurements in solution using $^1$H NMR technique as proposed by Evans. With an aqueous solution of 1b, the magnetic moments have been measured in the temperature range 298–338 K following this methodology as summarized in the Experimental Section. A gradual decrease in the magnetic moment value, as displayed in Table 6, with the rise in temperature is a clear indication of the transformation of 1b into the diamagnetic species 1a. The percentage of diamagnetic species present in solution has been calculated using

$$\% \text{ diamagnetic species} = 100\left[1 - \mu^2/(3.32)^2\right]$$

(3)

where $\mu$ is the magnetic moment of the solution at any particular temperature and 3.32 $\mu_B$ is the magnetic moment of pure 1b in the solid state.

The equilibrium constant $K_{eq}$ for eq 2 is defined as $K_{eq} = [\text{octahedral}]/[\text{planar}]$. Since eq 2 is pH dependent, $K_{eq}$ here is a composite parameter that includes the contribution due to temperature dependence of pH. The percentage of the planar species increases from 8.3 at 298 K to 42.9 at 338 K with $K_{eq} = 11.04$ and 1.33 at the above two temperatures, respectively. A plot of log $K_{eq}$ versus $1/T$ is linear (Figure 6), giving $\Delta H^o = -46 \pm 0.2$ kJ mol$^{-1}$ from the least-squares slope (correlation coefficient 0.999 58). The values of $\Delta S^o$ obtained at each temperature from the equation $\Delta G^o = \Delta H^o - T\Delta S^o$ give an average value of $-133 \pm 5$ J K$^{-1}$ mol$^{-1}$. However, the sizes of these thermodynamic parameters appear questionable considering the composite nature of the equilibrium constants.

### Concluding Remarks

Structural and equilibrium studies of nickel(II) complexes of flexidentate salicylaldimino Schiff base ligands (L$^1$-OH–L$^3$-OH) have been reported here. The piperazinyl arm of these ligands can in principle have either a boat or a chair conformation, leading to square-planar or octahedral geometry, respectively, of the reported complexes. Both remote substitution in the ligand aromatic ring and the nature of the associated anions have profound influences on the coordination geometry of the complexes. With the ligand L$^1$-OH, both square-planar (1a) and the octahedral (1b) complexes have been isolated and crystallographically characterized. In solution, these compounds are in equilibrium (eq 2), which is unique in the sense that both solvation and the change of ligand denticity are simultaneously in operation here. All the other equilibria involving square-planar and octahedral nickel(II) complexes reported so far are either due to solvation or due to change in ligand denticity. Also, unlike the previous examples, the ligand denticity here increases as we go up the temperature scale when the octahedral species (1b) is gradually converted to the square-planar one (1a). Also, this is one of the rare examples where both forms involved in equilibrium have been isolated in the solid state and characterized crystallographically.

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**Supporting Information Available:** Figure S1; X-ray crystallographic files in CIF format for compounds 1a, 1b, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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