Synthesis, spectroscopic and electrochemical studies of novel transition metal complexes with N,N'-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,3-bis-(o-aminophenoxy)propane

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A novel Schiff base obtained by the reaction of 1,3-bis-(o-aminophenoxy)propane and 2-hydroxynaphthalin-1-carbaldehyde, forms complexes with Co(II), Cu(II) and Ni(II). The Schiff base ligand and its metal complexes have been characterized by elemental analysis, microanalytical data, magnetic measurements, UV-visible, 1H NMR, 13C NMR and IR-spectra as well as conductance measurements. Electrochemical data show that NiL and CuL complexes undergo metal based quasi-reversible one-electron redox processes. However, metal complexes also exhibit ligand based irreversible redox waves. The electrochemical results also indicate that the electron transfer rate is higher for NiL complex than the CuL complex. Voltammetric data reveal easier electron donor properties for the NiL complex.

Experimental

All the chemicals, such as the metal salts [Co(OAc)2·4H2O, Cu(OAc)2·H2O and Ni(OAc)2·6H2O] and solvents were purchased from Merck and used without further purification. Conductivities of 10⁻³ M solution of the complexes were measured in DMF at 25°C using a Conductivity Hand-Held Meter LF 330. The electronic spectra of the complexes in UV-Vis region were recorded in DMF solutions using Shimatzu Model 160 UV visible spectrophotometer. The IR spectra of the complexes were recorded on a Michelson FT-IR spectrometer in KBr pellets. ¹H NMR spectra were recorded on a Bruker DRX-400 High Performance Digital FT-NMR spectrometer in DMSO-d₆. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model N0: MK1) at room temperature (23°C) using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal’s constants. The elemental analyses were conducted on Carlo Erba instrument. Voltammetric studies were made using an EcoChemie Autolab potentiostat-12 with electrochemical software GPES 4.9. A three-electrode system was used: a 2 mm sized Pt disc working electrode, an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode was polished with 0.05 µm alumina prior to each experiment. During the experiments, oxygen-free nitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature.

Synthesis of [N,N'-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,3-bis-(o-aminophenoxy)propane] (H₂L)

A solution of 2-hydroxynaphthalin-1-carbaldehyde
(20.00 mmol, 3.44 g) in 50 mL absolute ethanol was added dropwise over 2 h to a stirred solution of 1,3-bis(o-aminophenoxy)propane (10.00 mmol; 2.58 g) dissolved in 50 mL warm absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, ether and subsequently dried over anhydrous CaCl$_2$ in a desiccator. H$_2$L is insoluble in all common organic solvents, viz. acetone, alcohol, benzene, etc. and soluble in polar organic solvents, viz. DMF and DMSO. The yellow imines were purified by recrystallization from dimethyl formamide, m.pt. 210-214°C; yield: 4.81 g (85%). Anal Calc. for C$_{37}$H$_{30}$N$_2$O$_4$: C, 78.44, H, 5.30, N, 4.83. Found: C, 78.51, H, 5.35, N, 4.83.

Spectral characterization of the ligand


Synthesis of Co(II), Cu(II) and Ni(II) complexes

A solution of metal acetate in DMF (20 mmol) was mixed with the Schiff base ligand in DMF (20 mmol, 1.13 g) in a 1:1 molar ratio. The contents were refluxed in 100 mL of DMF on an oil-bath for 2-3 h. The refluxed solution was then poured into ice cold water when a colored solid separation out. The product was isolated by filtration, washed with ether, recrystallized from dimethyl sulfoxide and dimethyl formamide and dried over anhydrous CaCl$_2$ in vacuum at room temperature. The yield was 62-76% in all the complexes with respect to the ligand. They decompose at >284°C and are almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chlorofom. However, they are slightly too fairly soluble in polar organic solvents (dimethyl sulfoxide and dimethyl formamide).

Spectral characterization of Co(II) complex

Anal Calc. for C$_{37}$H$_{32}$N$_2$O$_4$Co: C, 71.27, H, 4.49, N, 4.28. Found: C, 71.99, H, 4.75, N, 4.18, $\Lambda_M = 8.5$ Ω$^{-1}$.cm$^2$.mol$^{-1}$. Yield: 0.77 g, % 62. M. Pt. > 300°C, Color: Dark brown. $\mu_{eff}$ (BM): 5.4. Characteristic IR bands for Co(II) complex (KBr cm$^{-1}$): 3055 (arom., C-H), 2909 (aliph., C-H), 1615 (-C=N), 1252 (phen., C-O), 543 (M-N) and 472 (M-O). Characteristic UV-Vis spectra for Co(II) ($\lambda_{max}$): 276, 332, 438 nm.

Spectral characterization of Cu(II) complex

Anal Calc. for C$_{38}$H$_{32}$N$_2$O$_5$Cu: C, 69.15, H, 4.85, N, 4.25. Found: C, 69.00, H, 4.80, N, 4.10, $\Lambda_M = 6.0$ Ω$^{-1}$.mol$^{-1}$.cm$^2$. Yield: 1.01 g, % 77. M.Pt. 285°C, Color: Brown. $\mu_{eff}$ (BM): 1.6. Characteristic IR bands for Cu(II) complex (KBr cm$^{-1}$): 3037 (arom., C-H), 2879 (aliph., C-H), 1611 (-C=N), 1250 (phen., C-O), 556 (M-N) and 460 (M-O). Characteristic UV-Vis spectra for Cu(II) ($\lambda_{max}$): 272, 319, 407 nm.

Spectral characterization of Ni(II) complex

Anal Calc. for C$_{37}$H$_{28}$N$_2$O$_4$Ni: C, 71.30, H, 4.50, N, 4.49. Found: C, 71.40, H, 4.70, N, 4.49, $\Lambda_M = 10.4$ Ω$^{-1}$.mol$^{-1}$.cm$^2$. Yield: 0.95 g, % 76. M.Pt. 293°C, Color: Green. $\mu_{eff}$ (B.M): 3. Characteristic IR bands for Ni(II) complex (KBr cm$^{-1}$): 3030 (arom., C-H), 2885 (aliph., C-H), 1612 (-C=N), 1248 (phen., C-O), 550 (M-N) and 465 (M-O). Characteristic UV-Vis spectra for Ni(II) ($\lambda_{max}$): 279, 332, 447.

Results and discussion

H$_2$L was synthesized by the condensation of 1,3-bis(0-aminophenoxy)propane$^{14}$ and 2-hydroxynaphthalin-1-carbaldehyde (Scheme 1). Stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductance measured in DMF of 10$^{-4}$ M solutions of these complexes fall in the range 4.6-10.4 ohm$^{-1}$cm$^2$.mol$^{-1}$ that indicates their non-electrolytic behaviour.$^{1-6}$

The reactions of the transition metal acetates with the Schiff base can be represented by:

\[ \text{M(OAc)}_2 \cdot \text{nH}_2\text{O} + \text{H}_2\text{L} \rightarrow \text{[ML]} + 2\text{AcOH} + \text{nH}_2\text{O} \]

The metal/ligand mole ratio was found to be 1:1 according to elemental analysis. The observed magnetic moment of Cu(II) complex was 1.6 BM, suggesting tetrahedral stereo chemistry of complex. The observed magnetic moment of Co(II) complex is 5.4 BM, suggesting tetrahedral stereo chemistry of complex. The observed magnetic moment of Ni(II)
complex is 3.0 BM, suggesting tetrahedral stereochemistry of the complex (Fig. 1). The complexes give fine powders and we could not manage to prepare single crystals to carry out X-rays studies.

The broad band that appeared in the IR spectrum of the Schiff base at 2277 cm⁻¹ is assigned to the stretching vibration of the intramolecular hydrogen bonded –OH in the molecule. Similar bands were observed at the same frequency in the IR spectra of salicylideneanilines. This band disappeared in the IR spectra of the complexes. The band at 1256 cm⁻¹ in the IR-spectrum of ligand is ascribed to the phenolic C-O stretching vibration according to the assignment made by Kovacic in case of salicylideneanilines. This band is found in the region 1250-1252 cm⁻¹ in the IR-spectra of the complexes. These changes suggest that the o-OH group of this Schiff base moiety has taken part in complex formation. The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band 1623 cm⁻¹ is shifted to lower values for complexes 1-6. Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 472-460 cm⁻¹ and 556-543 cm⁻¹ assigned to (M-O) and (M-N) stretching vibrations that are not observed in the spectra of the ligand. The tetrahedral with N 2O 2 coordination sphere where the ether O’s do not bind the metals.

The electronic spectra of all the complexes were recorded in 10⁻³ M DMF at room temperature. The absorption spectra of the Schiff base are characterized by absorption bands in the region 271-469 nm. In the spectra of the Schiff-base ligand, the aromatic bands at 221-300 nm are attributed to a benzene π → π* transition. The other bands are assigned to the imino n → π* transition. The longer wavelength band is assigned to intramolecular charge transfer while the shorter wavelength is due to n → π* transitions within the C=N bands influenced by CT interaction.

The ¹H NMR spectrum of the free ligand shows a singlet in the range 9.51 (d, 2H, -CH=N, J=9.4 Hz) ppm due to imine protons, 7.20-8.39 (m, 20H, aromatic H) ppm due to aromatic protons, and 2.43 (p, 2H, -CH₂, J= 5.8 Hz), δ = 3.37 (t, 4H, -OCH₂, J=9.4 Hz) ppm due to CH₂ and OCH₂, respectively. The ¹³C NMR spectrum of the free ligand shows 178,3 ppm in the range due to imine carbon, 149.3 ppm due to OCH₂ carbon and 149.5 ppm due to C-OH carbon. The complexes are paramagnetic; thus, their ¹H NMR spectra could not be obtained.

**Electrochemistry**

Redox activity of Ni(II) and Cu(II) complexes was studied on a Pt disc electrode in dimethylsulfoxide containing 0.05 M n-Bu₄NClO₄ as the supporting electrolyte. The potentials are referred to Ag/AgCl reference electrode. Table 1 summarizes the electrode potentials for Ni(II) and Cu(II) complexes. NiL complex exhibited a pair of anodic at −1.39 V and cathodic at −1.53 V representing the Ni(II)/Ni(I) couple. The potential difference between forward and backward peaks can provide a rough evaluation of the degree of the reversibility of one electron transfer reaction. The separation in peak potentials (ΔEₚ) is 0.14 V. This behavior shows that the heterogeneous electron transfer rate is relatively slow. This process is consistent with a quasi-reversible one-electron transfer redox reaction. The separation in peak
Complexes exhibit irreversible anodic peaks at $E_{pc} = -0.61$ V and $E_{pa} = -0.83$ V correspondingly to the formation of Cu(II)/Cu(I) couple. No peaks are observed in $–0.56$ V which is attributed to oxidation of the ligand moiety of the NiL complex. NiL complex also exhibited an irreversible anodic peak at $–0.56$ V which is attributed to oxidation of the ligand complex. No peaks are observed in the cathodic branch indicating that the ligand-based oxidation is irreversible. The CuL complex exhibits a reduction peak at $E_{pc} = -0.83$ V with a directly re-oxidation peak at $E_{pa} = -0.61$ V corresponding to the formation of Cu(II)/Cu(I) couple. The separation in peak potentials of the CuL complex indicates that the electron transfer rate is higher for NiL complex than CuL complex. The oxidation/reduction of NiL complex proceeds at less positive potential than that of CuL complex indicating easier electron donor properties for NiL complex.

### Table 1 — Voltammetric data for the metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{pc}$ (V)</th>
<th>$\Delta E_p$ (V)</th>
<th>$\sqrt{Ip/v}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL</td>
<td>-1.39</td>
<td>-1.53</td>
<td>0.14</td>
<td>0.22</td>
</tr>
<tr>
<td>CuL</td>
<td>-0.61</td>
<td>-0.83</td>
<td>0.22</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Supporting electrolyte = 0.05 M n-Bu$_4$NClO$_4$. Scan rate = 100 mVs$^{-1}$

*Late based oxidation of NiL complex.


