New Co(II) Complexes with Some Quadridentate Schiff Bases Derived from 2-Hydroxy-1-naphthaldehyde & \( \sigma \)-Hydroxyacetophenone

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A series of new Co(II) complexes of quadridentate Schiff bases derived from 2-hydroxy-1-naphthaldehyde and ethylenediamine, trimethylenediamine, tetramethylenediamine, and from \( \sigma \)-hydroxyacetophenone and ethylenediamine, have been synthesized and characterized on the basis of elemental analysis, infrared and electronic spectra and magnetic susceptibility measurements. The complexes have the general formula \([\text{Co}(BBBB)]\) (where \(BBBB = \text{quadridentate Schiff base} \)) except the complex with \(NN'\)-trimethylenediamine(2-hydroxynaphthylidenemine) which has the formula \([\text{Co}(\text{H}2\text{O})_2(BBBB)]\). This complex has a pseudooctahedral structure. The complexes with \(NN'\)-ethylenediamine(2-hydroxynaphthylidenemine) and \(NN'\)-ethylenediamine(ortho-hydroxyacetophenonemine) are square-planar, and the complexes with \(NN'\)-tetramethylenediamine(2-hydroxynaphthylidenemine) and \(NN'\)-hexamethylenediamine(2-hydroxynaphthylidenemine) have pseudotetrahedral structures. The infrared spectral data indicate coordination of the ligands through the nitrogens of \(C = N\) groups.

In the recent years considerable interest has been shown in the transition metal complexes of quadridentate Schiff bases of type \((I)^1-4\). As the number of the carbon atoms in the methylene bridge increases from \(n = 2\) to \(n = 3\) or 4, the stereochemistry of the metal (II) complexes [where \(M = \text{Co(II) and Cu(II)}\)] changes from square-planar to pseudotetrahedral\(^5-7\). In this note we report the synthesis of some new Co(II) complexes of Schiff bases of the type \((II)\) in order to investigate the dependence of stereochemistry on the number of methylene bridges. It will also be of interest to see the effect of more planar nature of naphthalene ring as compared to benzene ring on the stereochemistry of the complexes. The synthesis and characterization of Co(II) complex of \(NN'\)-ethylenediamine(orthohydroxyacetophenonemine) are also reported.

Cobalt(II) acetate tetrahydrate and ethylenediamine were Sarabhai Merck reagents while trimethylenediamine, tetramethylenediamine and 2-hydroxy-1-naphthaldehyde were Fluka reagents. Hexamethylenediamine and \(\sigma\)-hydroxyacetophenone respectively were Aldrich and Eastman Kodak products.

**General method of synthesis of the complexes** — All the manipulations were carried out under nitrogen atmosphere. The Schiff base \((0\,0003\,\text{mole})\) was dissolved in 30 ml of hot 95% ethanol and \(N_2\) bubbled through it. Cobalt(II) acetate tetrahydrate \((0\,75\,\text{g}, 0\,0003\,\text{mole})\) was dissolved in 5 ml of hot 95% ethanol and \(N_2\) bubbled through it. These two solutions were mixed and refluxed on a water-bath for 2 hr. The separated precipitates were suction filtered, washed with acetone and dried *in vacuo*; yield was 75-80% in all except for \([\text{Co}(\text{hap-en})]\), which was 40%. The analytical data of the complexes are given in Table 1. The complexes are stable under dry conditions and do not undergo oxidation even on heating at 100°.

The syntheses of the complexes were carried out under nitrogen atmosphere in order to prevent any possible oxidation to Co(III) state. The magnetic moments of the Co(II) complexes (determined by Gouy method using Hg[Co(NCS)] as standard) are quite diagnostic of their structures. Magnetic moments in the ranges 4-7-5-3, 4-3-4-74 and 2-1-2-9 BM are expected for spin-free octahedral, tetrahedral and square-planar Co(II) complexes respectively\(^8\).

For an octahedral spin-paired case, the complexes have much lower orbital contribution and the magnetic moment usually lie in the range 1-7-2-0 BM. The complexes \([\text{Co}(\text{hydrox-en})]\) and \([\text{Co}(\text{hap-en})]\) exhibit moments of 2-19 and 2-48 BM respectively (Table 1) indicating the presence of a square-planar structure. The analogous complex \([\text{Co}(\text{salam})]\) which has a magnetic moment of 2-25 BM is also square-planar\(^9\). The complexes \([\text{Co}(\text{hydrox-bn})]\) and \([\text{Co}(\text{hydrox-ln})]\) have magnetic moment of 4-30 BM indicating a tetrahedral structure. The complex \([\text{Co}(\text{H}_2\text{O})_2(\text{hydrox-tn})]\) is six-coordinate and exhibits a magnetic moment of 5-15 BM indicating an octahedral structure. The corresponding

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complex with the ligand derived from salicylaldehyde, [Co(H₂O)₂(saltnj] has a magnetic moment of 5.52 BM and is also octahedral. The complexes [Co(hydrox-hn)] exhibit an electronic spectral (reflectance spectra of Co(II) in the visible region with maxima at 19000 and 21000 cm⁻¹ are assigned to the split components of the transition. Using the method of Cotton and Goodgame various crystal field parameters for tetrahedral Co(II) complexes have been calculated. The energies of υ₁ and υ₂ were obtained by averaging the values for double peaks. The electronic parameters for [Co(hydrox-hn)] are as follows: υ₁ = 5162 cm⁻¹, υ₂ = 893 cm⁻¹, υ₃ = 20000 cm⁻¹, B' = 893 cm⁻¹, s = 0.92. The spin-orbit coupling constant was calculated using the relation: F₂ = 15·56 λ/Δ. λ for the complex [Co(hydrox-hn)] is 136. The reduction of B' and λ from the free ion value of 967 and 180 cm⁻¹ respectively is indicative of considerable covalence in the metal ligand bond. The spectral bands for the complex [Co(hydrox-hn)] are not well resolved and we could only locate two bands of comparable intensity at 23260 and 24390 cm⁻¹. These bands are assigned to the split components of the υ₂ transition in a pseudotetrahedral symmetry. The magnetic moment of the complex, as discussed earlier, supports a tetrahedral structure. The six-coordinated complex [Co(H₂O)₂(hydrox-tn)] exhibits bands at 8000, 10200, 15200 and 18600 cm⁻¹. The first two bands are assigned to the low symmetry components of the transition 4T₁g→4T₂g in an octahedral field. The bands at 15200 and 18600 cm⁻¹ are assigned to the transitions 4T₁g→4A₁g and 4T₁g→4T₂g respectively.

The infrared bands (recorded in KBr on a Perkin-Elmer model 21 spectrophotometer) of the free ligands around 1615-1620 cm⁻¹ are assigned to νC=N. These are lowered by 5-30 cm⁻¹ in the spectra of Co(II) complexes indicating coordination through azomethine nitrogen of the quadridentate ligands. The intramolecularly hydrogen bonded νOH occurs around 2800 cm⁻¹ in the ligands and it disappears in all the complexes indicating coordination through OH group of the ligands. The complex [Co(H₂O)₆(hydrox-hn)] exhibits a broad band at 2990 cm⁻¹ and this may be assigned to the νOH stretch of the coordinated water. Thus, Co(II) complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and e-hydroxyacetophenone maintain the same trend of structures as the corresponding complexes derived from salicylaldehyde.

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References


### Table 1 - The Analytical and Magnetic Susceptibility Data of Cobalt(II) Schiff Base Complexes

<table>
<thead>
<tr>
<th>Complex (stoichiometry)</th>
<th>Found (calcd.), %</th>
<th>Temp. (°K)</th>
<th>10g(BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(hydrox-en)]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co₂⁺H₂O₂(saltnj]</td>
<td>65·1</td>
<td>6·6</td>
<td>302·5</td>
</tr>
<tr>
<td>(Co₂⁺H₂O₂(saltnj]</td>
<td>(67-76)</td>
<td>(6-59)</td>
<td></td>
</tr>
<tr>
<td>[Co(H₂O)₂(hydrox-tn)]</td>
<td>61·1</td>
<td>5·3</td>
<td>302·0</td>
</tr>
<tr>
<td>(Co₂⁺H₂O₂(saltnj]</td>
<td>(63-16)</td>
<td>(5-05)</td>
<td></td>
</tr>
<tr>
<td>[Co(hydrox-hn)]</td>
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<td>5·2</td>
<td>306·0</td>
</tr>
<tr>
<td>(Co₂⁺H₂O₂(saltnj]</td>
<td>(68-87)</td>
<td>(6-18)</td>
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</tr>
<tr>
<td>[Co(hydrox-hn)]</td>
<td>69·5</td>
<td>5·3</td>
<td>305·0</td>
</tr>
<tr>
<td>(Co₂⁺H₂O₂(saltnj]</td>
<td>(69-85)</td>
<td>(5-41)</td>
<td></td>
</tr>
<tr>
<td>[Co(hap-en)]</td>
<td>59·4</td>
<td>4·6</td>
<td>302·0</td>
</tr>
<tr>
<td>(Co₂⁺H₂O₂(saltnj]</td>
<td>(61-19)</td>
<td>(5-10)</td>
<td></td>
</tr>
</tbody>
</table>

*Abbreviations: en = ethylenediamine, tn = trimethylenediamine, bm = hexamethylenediamine, hydrox = 2-hydroxy-1-naphthaldehyde and hap = orthohydroxyacetophenone.