Metal Complexes of N-hydroxyethylnaphthalideneimine Schiff Base

R. K. MEHTA and V. C. SINGHI
Department of Chemistry, University of Jodhpur, Jodhpur (India)

(Z. Naturforsch. 27 b, received September 14, 1971, revised October 2, 1971)

The Schiff base, N-hydroxyethylnaphthalideneimine forms solid complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II) and UO$_2$ (II). The structures of these compounds have been discussed on the basis of their elemental analysis, magnetic moment values and electronic spectral data. These studies have conclusively proved that UO$_2$ (II) and Mn(II) complexes are octahedral in shape whereas the Cu(II) complex molecule displays a square planar or tetragonally distorted octahedral configuration. Co(II), Ni(II), Zn(II) and Cd(II) complexes are tetrahedral in structures while the Pd(II) compound is square planar.

Although N-aryl and N-alkyl salicyldieneimines Schiff bases and their metal complexes have been intensively studied, those of the ligands in which the amino groups are attached to hydroxyalkyl groups have received little attention. It is, therefore, considered interesting to study, the metal complexes of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and ethanolamine. The present paper describes the results of the investigation on the complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II) and UO$_2$ (II) with N-hydroxyethylnaphthalideneimine Schiff base and these are represented by the Structures I and II.

Experimental

Materials: N-hydroxyethylnaphthalideneimine was prepared by boiling a mixture of equimolecular proportions of 2-hydroxy-1-naphthaldehyde and ethanolamine in dry benzene over a waterbath under reflux for two
hours. Afterwards, excess of benzene was distilled off and the solid residue was extracted into methanol. The clear solution was filtered, concentrated and cooled when yellow crystals of Schiff base were obtained. These were filtered out and recrystallised from methanol, m.p. 145 °C. Found: C 72.41, H 6.02, N 6.49, \([C_{10}H_4(OH)CH = N(CH_2)_2OH]\) requires C 72.55, H 6.05, and N 6.51%.

The complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), and UO_2(II) with N-hydroxyethylphenaldehydeimine were prepared by the method of YAMADA et al. 4.

All these compounds are found to be insoluble in water but partially soluble in alcohol, pyridine and other organic solvents.

**Measurements:** The combustion analysis was conducted by using Hosli's electrical micro combustion furnace. Gallenkamp Semi-micro ebulliometer was employed for molecular weight determinations using ethanol as the solvent. The magnetic measurements were made on Gouy apparatus. Diamagnetic corrections were applied and finally the molar susceptibility and magnetic moment were evaluated at 303 °K. The electronic absorption spectra of the complexes in solution were determined with a VEB Carl Zeiss Jena, VSU-2P spectrophotometer at room temperature.

Colour, molecular weight and elemental analyses data of these compounds are given in Table 1 and the magnetic data in Table 2.

### Results and Discussion

**Manganese(II) Complex:** It corresponds to the composition \([\text{MnL}_2]\) where \(LH = [C_{10}H_6(OH)CH = N(CH_2)_2OH]\) and its magnetic moment is found to be 5.83 B.M. at room temperature (30 °C). The magnetic moments of both octahedral or tetrahedral Mn(II) compounds should be nearly 5.92 B.M. since a \(^6\text{S}\) ground state persists in all symmetries of Mn(II) complexes \(^5\). The little lower value of the magnetic moment of this compound may be due to spin exchange in its solid state or to the presence of little Mn(II) species which may be caused due to aerial oxidation as reported earlier \(^1\) for such complexes.

In order to decide whether hexacoordination is due to intermolecular association or to intramolecular combination of \(-\text{OH}\) group with the central Mn(II), the knowledge pertaining to its molecular weight is quite helpful. The molecular weight of the Mn(II) complex under investigation is found to be 475 which excludes the probability of intermolecular association and it is most likely that the intramolecular M—OH bond may be present in the compound. This situation is best represented by an octahedral structure for the Mn(II) complex which seems to have been favoured by steric condition.

Thus based on elemental analysis, molecular weight and magnetic results an octahedral structure is assigned to this complex in which the third coordination position of the Mn(II) is occupied by the \(-\text{OH}\) group and the Schiff base functions as a tridentate ligand (Fig. 1).

**Cobalt(II) Complex:** The data summarized in Table 1, give the composition \([\text{CoL}_2]\) for this compound in which \(LH = [C_{10}H_6(OH)CH = N(CH_2)_2OH]\) and thus indicate 1:2 metal-ligand stoichiometry in it. The magnetic moment of this compound at room temperature (30 °C) is found to be 4.61 B.M. The electronic absorption spectra of this complex in dioxane and pyridine consist of only one absorption band with its peak at 13,700 cm\(^{-1}\). The band may be assigned to the transition \(^4\text{T}_1 \leftrightarrow ^4\text{A}_2\) which may be due to the tetrahedral configuration of the complex. Thus based on molecular weight spectral and magnetic data a high-spin tetrahedral structure (I) is assigned to the Co(II) complex under study, in which the Schiff base functions as a bidentate ligand.

**Ni(II) Complex:** The greenish yellow Ni(II) complex displaying a metal-ligand ratio of 1:2, can be represented by the formula \([\text{NiL}_2]\), where \(LH = [C_{10}H_6(OH)CH = N(CH_2)_2OH]\). The magnetic moment of this compound at room temperature (30 °C) is found to be 3.82 B.M. In a four covalent, paramagnetic, high-spin, tetrahedral Ni(II) complex the ground term is \(^3\text{T}_1\) and the moments lie...
between 3.2 and 4.0 B.M. at room temperature. Based on this the Ni(II) compound under study should display tetrahedral configuration (I) in which the ligand acts as a bidentate one.

Copper(II) Complex: The molecular weight and the elemental analyses (Table 1) of the olive-green copper(II) compound suggest 1:2 metal-ligand stoichiometry. Its composition may therefore be given by $[\text{CuL}_2]$ where $\text{LH} = [\text{C}_{10}\text{H}_6(\text{OH})\text{CH}_2\text{N}(\text{CH}_2)_2\text{OH}]$. The molecular weight results clearly indicate its existence as a monomer in the solid state. The copper(II) complex under study exhibits a magnetic moment of 1.87 B.M. at room temperature (30°C). The magnetic-moment of planar-complexes are generally lower (1.8 — 1.9 B.M.) than those of octahedral complexes ($\mu_{\text{eff}} = 1.9 — 2.0$ B.M.). As planar stereochemistry may be considered as the limiting case of a tetragonally distorted octahedral stereochemistry, the separation of the interaction terms (i.e. between ground term $2B_{1g}$ and the components of $2T_{2g}$ term) is large in square-planar complexes than in octahedral complexes which possibly explains the lower magnetic moments of square-planar complexes than in octahedral complexes due to spin-orbit coupling and are temperature dependent. The electronic absorption spectra in methanol of the Copper(II) compound consists of a broad band at about 16750 cm$^{-1}$ and second band at 24210 cm$^{-1}$.

The appearance of an absorption band at 16750 cm$^{-1}$ and the magnetic moment value of 1.87 B.M. support a square planar or tetragonally distorted octahedral configuration of the complex. The band exhibit bathochromic shift in pyridine which may be attributed to the association of two pyridine molecules to the Cu(II) ion thus forming an octahedral complex. The Schiff base appears to exhibit bidentate function in this case.

Zinc(II), Cadmium(II), Uranyl(II) and Palladium(II) Complexes

These compounds were found diamagnetic, as expected and possess 1:2 metal-ligand stoichiometry as supported by their elemental analysis and molecular weight data. Thus their composition may be expressed by $[\text{CuL}_2]$ where $\text{LH} = [\text{C}_{10}\text{H}_6(\text{OH})\text{CH}_2\text{N}(\text{CH}_2)_2\text{OH}]$, where M stands for Zn(II), Cd(II), UO$_2$(II) and Pd(II). Consequently Zn(II) and Cd(II) com-
pounds possess tetrahedral configuration in which the Schiff base functions as a bidentate ligand. UO$_2$(II) complex, probably possesses an octahedral structure as is usually displayed by UO$_2$(II) $^9$. In this complex the Schiff base acts as a bidentate ligand. Pd(II) greatly favours a square planar configuration. YAMADA et al. $^{10}$ have suggested square planar structure for a number of N-alkylsalicylideneiminato Pd(II) complexes. A similar structure is suggested for the Pd(II) complex under investigation, in which the Schiff base functions as a bidentate ligand. The solution spectra of Pd(II)

Table 2. Magnetic data of the complexes of N-hydroxyethylnaphthalimine Schiff base at 303 °K.

<table>
<thead>
<tr>
<th>Formulae</th>
<th>Mass Susceptibility $Zs \times 10^6$</th>
<th>Molar Susceptibility $Zm \times 10^6$</th>
<th>Magnetic Moments $\mu_{\text{eff}}$ in B.M.</th>
<th>No. of unpaired electrons</th>
<th>Possible bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Mn})}$</td>
<td>28.2767</td>
<td>13658.34</td>
<td>5.83</td>
<td>5</td>
<td>sp$^3$d$^2$</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Co})}$</td>
<td>17.3498</td>
<td>8447.60</td>
<td>4.61</td>
<td>3</td>
<td>sp$^3$</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Ni})}$</td>
<td>11.7577</td>
<td>5722.54</td>
<td>3.82</td>
<td>2</td>
<td>sp$^3$</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Cu})}$</td>
<td>2.4057</td>
<td>1182 42</td>
<td>1.87</td>
<td>1</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Zn})}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Cd})}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{Pd})}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>$[{\text{C}_{10}\text{H}_6\text{O}(\text{CH} = \text{N}(\text{CH}_2\text{OH})_2\text{UO}_2)}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>diamagnetic</td>
</tr>
</tbody>
</table>

The configurations reported in this communication are in agreement with those of N-hydroxyethylsalicylideneiminato complexes $^5$ with which it is structurally similar.

The authors are thankful to University Grants Commission New Delhi (India) for the award of a fellowship to one of them (V.C.S.).