Cobalt(II), nickel(II) and copper(II) complexes with 1-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane

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A series of complexes having the formula $[M(HL)_{2}(H_{2}O)_{2}]X_{2}$, where $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}; X = \text{Cl}^{-}, \text{Br}^{-}$ and $HL = 1$-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane has been synthesized by allowing the ligand and the metal salts to react in the 2:1 molar ratio in an ethanolic medium. Besides this, another series of complexes of the type $ML_{2}$, has been synthesized by allowing the ligand and metal acetates to react in the molar ratio 2:1 in an aqueous medium made alkaline with $\text{NH}_{4}\text{OH}$. The complex $CuL_{2}$, when allowed to react with $CuX_{2}$ salts, gives another series of binuclear complexes having the formula, $Cu_{2}L_{2}X_{2}[X = Cl^{-}, Br^{-}, ClO_{4}^{-}, NO_{3}^{-}]$. The characterization of the complexes has been done on the basis of elemental analysis, magnetic moment, conductance and spectral studies.

Metal complexes of monoximes and their derivatives have been extensively studied in recent years due to their capabilities to form organometallic and encapsulation compounds. This prompted us to prepare metal complexes with the ligands of type (I) obtained by the condensation of 2-aminopyridine and 1,2-diphenyl-1-hydroxyiminoethane-2-one. This promising ligand acts in a bidentate manner to form two series of complexes having the formulae $[M(HL)_{2}(H_{2}O)_{2}]X_{2}$ and $ML_{2}$ when it is allowed to react with metal salts in the molar ratio 2:1 in ethanolic and aqueous (basic) media respectively. The complex $CuL_{2}$ further reacts in an ethanolic medium with $CuX_{2}$ to give yet another series of binuclear complexes of the type $Cu_{2}L_{2}X_{2}$.

Materials and Methods

All the chemicals used were BDH or E. Merck reagents except 1,2-diphenylethane-1,2-dione which was an Aldrich reagent. 1,2-Diphenyl-1-hydroxyiminoethane-2-one was prepared according to the literature method (m.p. 180°C; lit. 140°C). Bromide salts of cobalt(II), nickel(II) and copper(II) were prepared by dissolving the respective metal carbonates in the minimum volume of hydrobromic acid followed by crystallization.

The ligand 1-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane was synthesized by the method reported earlier (m.p. 176°C).

A similar procedure was used for the preparation of all the complexes. The preparation of one typical complex is described below for each of the series of complexes.

**Bis-[1-hydroxyimino-1,2-diphenyl(2’-iminopyridyl)ethane](diaquo)nicket(II) chloride,** $[Ni(HL)_{2}(H_{2}O)_{2}]Cl_{2}$

The Ni(II) chloride solution (0.01 mol) in absolute ethyl alcohol was mixed with a warm ethanolic solution of the ligand (0.02 mol) and the mixture was shaken vigorously. The colour of the solution changed immediately to blue. The solution, on standing, gave a blue crystalline product which was filtered, washed with ethanol and solvent ether, and dried in vacuo.

**Bis-[1-hydroxyiminato-1,2-diphenyl(2’-iminopyridyl)ethane]copper(II), CuL_{2}**

An ethanolic solution of the ligand (0.02 mol) was treated with a few ml of sodium acetate solution and an aqueous solution of cupric acetate monohydrate (0.01 mol) was added to it with vigorous shaking. A green crystalline product was obtained which was filtered, washed with ether and dried in vacuo.

**Dichloro-bis-[1-hydroxyiminato-1,2-diphenyl(2’-iminopyridyl)ethane]dicopper(II), Cu_{2}L_{2}Cl_{2}**

An ethanolic solution of the ligand (0.02 mol) was treated with a few ml of sodium acetate solution and an aqueous solution of cupric acetate monohydrate (0.01 mol) was added to it with vigorous shaking. A green crystalline product was obtained which was filtered, washed with ether and dried in vacuo.
pyridyl)ethane}copper(II) (0.01 mol) was dissolved in ethanol and to it an ethanolic solution of cupric chloride (0.01 mol) was added with constant stirring. A greyish-green crystalline solid was obtained which was filtered, washed with ether and dried in vacuo.

Elemental analyses were done using standard procedure. The infrared spectra of the complexes were recorded on a Beckmann IR-20 spectrophotometer. Magnetic moments were measured by the Gouy method using Hg[Co(CNS)₄] as the calibrant. Conductivity measurements were made on a Systronic Conductometer Model 303 using dimethyl sulphoxide as a solvent. Analytical, spectral, conductance and magnetic moment data are recorded in Table I.

Results and Discussion

The infrared spectrum of the ligand shows a strong band at 3310 cm⁻¹ and a medium one at 3320 cm⁻¹ which have been assigned to the symmetric and asymmetric stretching vibrations of the –NH group. It also exhibits a sharp band at 1660 cm⁻¹ which has been assigned to the νC = N mode of the oxime group. Two bands at 1610 and 1545 cm⁻¹ have been ascribed to the ring breathing mode of the pyridine nucleus. The ligand shows a characteristic group of bands for the phenyl ring vibrations.

In the lower energy region, the ligand shows bands at 1005, 790 and 770 cm⁻¹. The band at 1005 cm⁻¹ has been assigned to the νN – O vibrations of the oxime group and the remaining bands to the C – H deformation mode of the ligand¹⁻⁵.

The complexes of the type [M(HL)₂(H₂O)₂]X₂ show a broad band centred at 3300 cm⁻¹ assignable to νO – H mode of the N – O – H group, the broadening may be due to coupling with νO – H of coordinated water molecules. The presence of this band in these complexes indicates existence of the ligand in its neutral form. Significantly, this band is absent in the spectra of the complexes of the type ML₂ or Cu₂L₂X₂, where deprotonation has taken place during coordination of the ligand with the metal ions.

A band present at 1660 cm⁻¹ in the ligand is consid-

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Colour</th>
<th>Found (Calc.), %</th>
<th>λmax (electronic) cm⁻¹</th>
<th>μeff. (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(HL)₂(H₂O)₂]Cl₂</td>
<td>Light blue</td>
<td>8.02 (11.80)</td>
<td>25100 4.80</td>
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<tr>
<td>[Co(HL)₂(H₂O)₂]Br₂</td>
<td>Pink</td>
<td>7.22 (10.52)</td>
<td>25400 4.81</td>
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<tr>
<td>CoL₂</td>
<td>Red</td>
<td>8.95 (12.74)</td>
<td>22000 2.00</td>
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<tr>
<td>[Ni(HL)₂(H₂O)₂]Cl₂</td>
<td>Blue</td>
<td>8.10 (11.68)</td>
<td>23800 15000 3.25</td>
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<tr>
<td>[Ni(HL)₂(H₂O)₂]Br₂</td>
<td>Bluish violet</td>
<td>7.21 (10.44)</td>
<td>26000 14900 3.18</td>
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<tr>
<td>NiL₂</td>
<td>Yellow</td>
<td>8.95 (12.74)</td>
<td>19000 Diamag.</td>
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<tr>
<td>[Cu(HL)₂(H₂O)₂]Cl₂</td>
<td>Deep red</td>
<td>8.35 (11.70)</td>
<td>14850 1.89</td>
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<tr>
<td>[Cu(HL)₂(H₂O)₂]Br₂</td>
<td>Greyish red</td>
<td>7.59 (10.60)</td>
<td>14800 1.85</td>
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<tr>
<td>CuL₂</td>
<td>Green</td>
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<td>14500 1.75</td>
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<tr>
<td>Cu₂L₂Cl₂</td>
<td>Green</td>
<td>15.91 (17.20)</td>
<td>12100, 17200 1.76</td>
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<tr>
<td>Cu₂L₂Br₂</td>
<td>Brownish green</td>
<td>14.32 (9.47)</td>
<td>12600, 17500 1.81</td>
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<tr>
<td>Cu₂L₂(NO₃)₂</td>
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<td>14.92 (13.16)</td>
<td>12500, 17300 1.85</td>
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<tr>
<td>Cu₂L₂(ClO₄)₂</td>
<td>Green</td>
<td>13.71 (9.07)</td>
<td>12600, 17400 1.90</td>
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</table>

Table I—Colour, analytical data, electronic spectra and magnetic moment values of metal complexes of 1-hydroxyimino-1,2-diphenyl(2'-iminopyridyl)ethane (HL)
erably lowered (1635-1600 cm\(^{-1}\)) in the spectra of all the three series of complexes, namely, \([\text{M(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\), \(\text{ML}_2\) and \(\text{CuL}_2\text{X}_2\) indicating involvement of the exocyclic \(C = N\) group in complex formation. The lowering is more in the complexes \(\text{CuL}_2\text{X}_2\) in comparison to that in \([\text{M(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\).

The characteristic pyridine ring vibrations do not show any appreciable perturbation thus clearly indicating non-participation of the pyridine nitrogen in coordination. The \(v\text{N} - \text{O}\) band of the ligand at 1005 cm\(^{-1}\) is almost unperturbed in the complexes (1000-995 cm\(^{-1}\)) the slight lowering is due to involvement of adjacent \(C = N\) group in coordination in the spectra of the complexes of the type \([\text{M(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\). But the band appears at a higher frequency (1025 cm\(^{-1}\)) in the complex \(\text{ML}_2\) indicating formation of new links between the copper(II) inner complexes (\(\text{CuL}_2\)) and copper(II) salts (\(\text{CuX}_2\)) through oxygen atom of the \(N - O\) group. A new band, however, appears in all the bis (aquo) complexes around 865 cm\(^{-1}\) which is characteristic vibration of the coordinated water molecules.

On the basis of above discussion, complexes \([\text{M(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\), \(\text{ML}_2\) and \(\text{CuL}_2\text{X}_2\) may be assigned the structures II, III and IV, respectively. These structures are supported by magnetic moment, electronic spectral and conductivity data as discussed in the following paragraphs.

During the course of the present investigation, it has been found (Table I) that the copper(II) complexes of the type, \([\text{Cu(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\) have magnetic moment values in the range 1.85-1.95 B.M., which is usually observed for octahedral copper(II) complexes. Visible spectra of the complexes show a broad band spanning the region 15,000-14,500 cm\(^{-1}\). This band may arise due to \(^2E_g \rightarrow ^2T_{2g}\) transition in an octahedral field.

The binuclear complexes of copper(II) of the type \(\text{CuL}_2\text{X}_2\) show two broad ligand field bands in the regions 12,800-12,000 and 18,000-17,000 cm\(^{-1}\) and have magnetic moments in the region 1.7-1.9 B.M. Both the electronic spectral bands seem to be due to the same \(d-d\) transition differing in energy due to presence of different ligand fields. The high energy band may be due to chromophore, \(\text{CuN}_4\), in \(D_{4h}\) symmetry while the low energy band may be due to the chromophore, \(\text{CuX}_2\) and a lower symmetry such as \(C_2\) (ref. 10). Alternatively, the two bands might also be due to difference in coordination numbers of copper(II) ions and possibility of complexes having a polymeric structure (V) cannot be ruled out.

A single broad band in the electronic spectrum of the complex \(\text{CuL}_2\), centred at 14,500 cm\(^{-1}\), has been attributed to the ligand field band due to the chromophore \(\text{CuN}_4\) (ref. 1).

The nickel(II) complexes of the type \([\text{Ni(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\) have magnetic moment values in the region 3.15-3.35 B.M. at room temperature. These values are typical of a nickel(II) ion in an octahedral environment. The two typical bands occurring at 26,000 and 15,000 cm\(^{-1}\) are due to the transitions \(^3A_2g \rightarrow ^3T_{1g}(P)\) and \(^3A_2g \rightarrow ^3T_{1g}(F)\) respectively in an octahedral field (10). The nickel(II) complex \(\text{NiL}_2\) is diamagnetic and its spectrum consists of a broad band centred at 19,000 cm\(^{-1}\). This suggests a planar environment around nickel(II) with the chromophore \(\text{NiN}_4\) (ref. 10). The cobalt(II) complexes of the type \([\text{Co(HL)}_2\text{(H}_2\text{O)}_2]\text{X}_2\) possess magnetic moment values in the range 4.75-4.85 B.M. at 25°C, which are typical of cobalt(II) ion in an octahedral environment. A broad band centred at 25,000 cm\(^{-1}\) is observed in the electronic spectra of the complexes and it supports octahedral stereochemistry (10). Broadness is most presumably due to superimposition of two to three bands. Cobalt(II) complex \(\text{CoL}_2\) has magnetic moment of 2.0 B.M. with a broad electronic spectral band centred at 22,000 cm\(^{-1}\) indicating planar environment of the ligand atoms around cobalt(II) ion.

All the metal complexes are insoluble in water but
soluble in DMSO and DMF on warming. The molar conductance values of the complexes in DMSO (10^{-3} \text{ M}) lie in the range 115-130 ohm^{-1} \text{ cm}^2 \text{ mol}^{-1} and are typical of 1:2 electrolytes except for the complexes of the type ML₂ which are non-electrolytes with negligible conductance values.

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**References**