Synthesis and characterization of divalent metal complexes with ligand derived from the reaction of 3-aminopyridine and biacetyl

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Abstract: Divalent cobalt, nickel and copper salts reacted in situ with 3-aminopyridine and biacetyl to form complexes of the type: \([\text{M}(\text{Ap}_2\text{biac})_2\text{X}_2]\), where \(\text{Ap}_2\text{biac}\) is the ligand and \(\text{X}=\text{Cl}, \text{Br}, \text{NO}_3\) or \(\text{NCS}\). The complexes were analysed and characterized as distorted octahedral by conductance, molecular weight, magnetic, electronic and IR spectral studies. The electronic spectra were interpreted and tentative assignments made. The infrared spectral studies revealed that two molecules of 3-aminopyridine were joined by molecules of biacetyl through a two carbon atom bridge and that the ligand coordinated through azomethine nitrogen atoms, whereas the pyridine nitrogen does not participate in the coordination. In the far infrared spectra, various metal–ligand vibrations were observed and are discussed.

Keywords: divalent Co, Ni and Cu complexes, Schiff’s base, IR, electronic spectra.

INTRODUCTION

The appearance of several articles covering various aspects of synthetic macrocyclic ligands1,2 and the possibility of their employment as models for intricate biological system has prompted the synthesis and characterization of complexes of multidentate open chain or macrocyclic ligand derived from reactions of various amines or hydrazides with carbonyl compounds.3–6 The present paper describes the synthesis and characterization of the complexes obtained by the reaction of 3-aminopyridine with biacetyl in the presence of metal salts.

EXPERIMENTAL

Materials

3-Aminopyridine was purchased from Koch-Light (U.K.) and biacetyl and other related compounds were obtained from BDH (U.K.).

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Preparation of the complexes

A general procedure was adopted for the preparation of all the complexes. A methanolic solution of biacetyl (0.02 mol) and 3-aminopyridine (0.04 mol) were mixed and boiled under reflux on a water bath for 1 h. To this mixture, the metal salt (0.01 mol) dissolved in a minimum amount of methanol was added and the mixture was refluxed for a further 10 h. The different coloured mixtures were concentrated and kept for a week in a desiccator where upon bright crystals separated. They were filtered and recrystallised from ethanol or H₂O and dried in vacuo, (yield 35%). The cobalt and nickel complexes were soluble in ethanol, warm water and DMF, whereas the copper complexes were soluble in ethanol and DMF. The complexes do not decompose below 250 °C.

Metal bromides and thiocyanates were prepared by the metathesis process by adding KBr or NH₄NCS to an ethanolic solution of the metal chloride with mechanical stirring for 4 h. The precipitate of KCl or NH₄Cl was removed by filtration.

Analytical and physical measurements

The microanalyses of C, H, and N were carried out at the Sophisticated Analytical Instrument Facility, CDRI, Lucknow. The metal contents were determined by standard EDTA methods. The electronic spectra (DMF) were recorded on a Cary 14 spectrophotometer. The magnetic susceptibility measurements were performed at IIT Roorkee. The IR spectra were recorded on an Infrared spectrophotometer in the range 4000–667 cm⁻¹ using the KBr pellet technique. The conductivity was measured on a Toshniwal type CL-01/01 conductivity bridge.

RESULTS AND DISCUSSION

The analytical data of all the complexes corresponded to $[M(C_{28}H_{28}N_{8})X_2]$; where $M$=Co(II), Ni(II) or Cu(II) and $X = \text{Cl}^-$, $\text{Br}^-$, $\text{NO}_3^-$ or $\text{NCS}^-$. All the complexes showed satisfactory elemental analyses (Table I). The molar conductance of these complexes measured in nitrobenzene showed their non-electrolytic nature. The molecular weights of the complexes, determined cryoscopically in nitrobenzene are in agreement with these formulae.

**TABLE I. Analytical data of the divalent Co, Ni and Cu complexes**

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Complexes</th>
<th>Colour</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>X</th>
<th>Mol.Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$[\text{Co}(C_{28}H_{28}N_{8})\text{Cl}_2]$</td>
<td>Dark Brown</td>
<td>9.91 (9.73)</td>
<td>55.70</td>
<td>4.98 (4.62)</td>
<td>18.64 (18.48)</td>
<td>11.79 (11.71)</td>
<td>606</td>
</tr>
<tr>
<td>2.</td>
<td>$[\text{Co}(C_{28}H_{28}N_{8})\text{Br}_2]$</td>
<td>Dark Brown</td>
<td>8.88 (8.48)</td>
<td>48.61 (48.34)</td>
<td>– (4.02)</td>
<td>16.45 (16.11)</td>
<td>23.51 (23.02)</td>
<td>695</td>
</tr>
<tr>
<td>3.</td>
<td>$[\text{Co}(C_{28}H_{28}N_{8})(\text{NO}_3)_2]$</td>
<td>Brown</td>
<td>8.66 (8.95)</td>
<td>4.86 (50.98)</td>
<td>– (4.24)</td>
<td>16.90 (16.99)</td>
<td>18.93 (18.81)</td>
<td>659</td>
</tr>
<tr>
<td>4.</td>
<td>$[\text{Co}(C_{28}H_{28}N_{8})(\text{NCS})_2]$</td>
<td>Reddish</td>
<td>8.94 (9.06)</td>
<td>55.99 (55.29)</td>
<td>– (4.30)</td>
<td>21.76 (21.50)</td>
<td>–</td>
<td>651</td>
</tr>
<tr>
<td>5.</td>
<td>$[\text{Ni}(C_{28}H_{28}N_{8})\text{Cl}_2]$</td>
<td>Blue-Green</td>
<td>9.69 (9.58)</td>
<td>55.48 (55.53)</td>
<td>4.62 (4.30)</td>
<td>18.85 (18.51)</td>
<td>11.70 (11.73)</td>
<td>605</td>
</tr>
<tr>
<td>6.</td>
<td>$[\text{Ni}(C_{28}H_{28}N_{8})\text{Br}_2]$</td>
<td>Brown</td>
<td>8.45 (8.35)</td>
<td>– (4.81)</td>
<td>4.62 (4.03)</td>
<td>16.65 (16.13)</td>
<td>22.90 (23.05)</td>
<td>694</td>
</tr>
</tbody>
</table>
Found (Calcd.) %

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Complexes</th>
<th>Colour</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>X</th>
<th>Mol.Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.</td>
<td>[Ni(C₂₈H₂₈N₈(NO₃)₂]</td>
<td>Light Brown</td>
<td>8.91</td>
<td>51.01</td>
<td>4.73</td>
<td>21.00</td>
<td>19.06</td>
<td>658</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.81)</td>
<td>(51.06)</td>
<td>(4.25)</td>
<td>(21.27)</td>
<td>(18.84)</td>
<td></td>
<td></td>
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<tr>
<td>8.</td>
<td>[Ni(C₂₈H₂₈N₈)(NCS)₂]</td>
<td>Blackish Brown</td>
<td>8.45</td>
<td>56.02</td>
<td>–</td>
<td>21.12</td>
<td>–</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.92)</td>
<td>(55.38)</td>
<td>(4.30)</td>
<td>(21.53)</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>[Cu(C₂₈H₂₈N₈)Cl₂]</td>
<td>Dark Green</td>
<td>10.61</td>
<td>55.09</td>
<td>4.76</td>
<td>18.63</td>
<td>11.98</td>
<td>610.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(10.40)</td>
<td>(55.03)</td>
<td>(4.58)</td>
<td>(18.34)</td>
<td>(11.62)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>[Cu(C₂₈H₂₈N₈)Br₂]</td>
<td>Light Green</td>
<td>8.08</td>
<td>48.43</td>
<td>4.44</td>
<td>15.32</td>
<td>23.25</td>
<td>699.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.07)</td>
<td>(48.03)</td>
<td>(4.00)</td>
<td>(16.01)</td>
<td>(22.87)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>[Cu(C₂₈H₂₈N₈)(NO₃)₂]</td>
<td>Dark Green</td>
<td>9.87</td>
<td>50.81</td>
<td>4.56</td>
<td>20.96</td>
<td>19.11</td>
<td>663.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.57)</td>
<td>(50.64)</td>
<td>(4.22)</td>
<td>(21.10)</td>
<td>(18.68)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.68)</td>
<td>(54.91)</td>
<td>(4.27)</td>
<td>(21.35)</td>
<td>–</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Infrared spectra**

The appearance of various pyridine ring vibrations revealed the non-coordination of the pyridine nitrogen. The in-plane and out-of-plane deformations and ring breathing mode of the pyridine ring did not change their positions. This fact further supports the non-participation of the pyridine nitrogen in the coordination.7,8 The spectra of all the complexes showed sharp bands at ~ 1645–1595 cm⁻¹, due to the presence of (C=N) coordinated to the metal atoms.9,10 Thus, the changes observed in the spectra of the complexes indicate that two amino groups of two molecules of 3-aminopyridine had reacted with a molecule of biacetyl, probably through a template effect of the metal atom, and the azomethine groups of the condensed (AP₂ biac) molecules coordinated to the metal atom. This is supported with the appearance of a group of sharp frequencies characteristic of biacetyl moieties.9

**Magnetic moments and electronic spectra**

The magnetic moments of the divalent cobalt, nickel and copper complexes at room temperature lay in the 4.46–4.64, 2.96–3.12 and 1.77–1.89 μB ranges, respectively, and are close to the predicted values for octahedral geometry around the metal atom.11

The solution spectra of the cobalt(II) complexes exhibited absorptions in the region of ~ 8100–9100 (ν₁), 12550–15750 (ν₂) and 18700–20250 cm⁻¹ (ν₃). The spectra resembled those reported to be distorted octahedral.5

Thus, assuming the effective symmetry to be D₄h, the various bands can be assigned to ⁴T₁g → ⁴T₂g (F) (ν₁) 8100–9100 cm⁻¹; ⁴T₁g → ⁴A₂g (ν₂) 12550–15750 cm⁻¹; ⁴T₁g → ⁴T₁g (P), (ν₃) 18700–20250 cm⁻¹. It appears that the symmetry of
these complexes is not idealized $O_h$ but is $D_{4h}$. The assignment of the first spin-allowed band seems plausible since the first band appears approximately at half the energy of the visible band.\(^{12}\) This is the evidence in view of the $\nu_2/\nu_1$ ratio which lay between 1.72–1.89 and is consistent with the accuracy of the assignment.

The solution spectra of the nickel(II) complexes showed three strong bands at \(~ 10600–12350, 15000–17000\ cm^{-1}\) and \(25000–28000\ cm^{-1}\), with a well discernable shoulder at \(~ 8500–9500\ cm^{-1}\) on the low energy side of the first band. The spectral bands are within the range reported earlier for hexacoordinated octahedral nickel (II) complexes.\(^{14}\) The first two bands result from the splitting of one band, $\nu_1$, and can be assigned to: $3B_{1g} \rightarrow E_a\ g (\nu_1)$ and $3B_{1g} \rightarrow 3B_{2g} (\nu_2)$ assuming the effective symmetry to be $D_{4h}$ (the component of $3T_{2g}$ in $O_h$ symmetry). The other two higher bands can be assigned to: $3B_{1g} \rightarrow 2A_{2g} (F)$, $3F_g a (\nu_3)$ and $3B_{1g} \rightarrow 3A_{2g} (P)$.\(^{12}\) The intense higher energy band at 35000 cm\(^{-1}\) may be due to a $\pi^-\pi^+$ transition of the C=N group. The various bands do not follow any regular pattern and seem to be anion independent. The spectra are consistent with the distorted octahedral nature of the complexes.\(^{13}\) Thus, all the nickel(II) complexes studied herein showed pseudo-octahedral conforming $O_h$ symmetry.

The spectra of copper(II) complexes in solution showed a broad maxima at \(17700–19250\ cm^{-1}\) with a shoulder on the low energy side \(~ 14500–17000\ cm^{-1}\), which indicates that these complexes are distorted octahedral.\(^{14}\) The spectral bands shift towards higher energy in the order: NCS$>$NO\(_3\)$>$Br$>$Cl, \(i.e.,\) in order of weakening interactions of the molecule, the energy level sequence for these complexes may be: $x^2–y^2$ $>$ $z^2$ $>$ $xy$ $>$ $xz$ $>$ $yz$ and the shoulder can be assigned to: \(z^2 \rightarrow x^2–y^2\) ($2B_{1g} \rightarrow 2B_{2g}$) and the broad band contains both the \(xy \rightarrow x^2–y^2\) ($3B_1 \rightarrow 3E_g$) and \(xz, yz \rightarrow x^2–y^2\) ($2B_{1g} \rightarrow 2A_{2g}$) transitions.\(^{15}\) The band separation in the spectra of the complexes is of the order of 2500 cm\(^{-1}\), which is consistent with the proposed geometry of the complexes.\(^{16}\)

\[\text{Where } M = \text{Co(II), Ni(II), Cu(II)} \]

\[X = \text{Cl, Br, NO}_3, \text{NCS}\]

Fig. 1. Proposed structure of complexes.
Far infrared spectra

The far infrared spectra of the chloro-complexes revealed some new bands at ~ 300, ~ 285 and 270 cm\(^{-1}\), which assignable to \(\nu(\text{Co–Cl})\), \(\nu(\text{Ni–Cl})\) and \(\nu(\text{Cu–Cl})\) vibrations,\(^{17}\) respectively. Similar bands in the bromo complexes are observed at 220 and 215 cm\(^{-1}\) for the cobalt and nickel complexes, which can be assigned to \(\nu(\text{Co–Br})\) and \(\nu(\text{Ni–Br})\) vibrational modes, respectively. The presence of a single band and their regions are consistent with the trans-ocatahedral nature of the complexes. The presence of bands at ~ 430–495 cm\(^{-1}\) in all the complexe originates from the \(\nu(\text{M–N})\) (azomethine) vibration and substantiates this coordination. The coordination of nitrate and thiocyanate is further supported by the appearance of new bands at ~ 225–240 cm\(^{-1}\), assignable to \(\nu(\text{M–O})\) of the \(\text{ONO}_2\) group and at 260–285 cm\(^{-1}\) to \(\nu(\text{M–NCS})\) of the NCS groups,\(^{9}\) respectively. Therefore, based on elemental analyses, conductance, magnetic, electronic and IR spectral studies, structure proposed for these complexes is given in Fig. 1.

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