Preparation and Characterization of Cobalt (II)-Complexes of 4-Hydroxybenzaldehyde Semicarbazone and Amino Acid Esters Ligands

Zuhoor F. Dawood                    Mushal W. Ibrahim
Department of Chemistry / College of Education
Mosul University

Received 23 / 09 / 2007  Accepted 07 / 04 / 2008

ABSTRACT

Cobalt (II) complexes with mixed ligands including 4-hydroxybenzaldehyde semicarbazone (HBSCH) and esters of amino acids - A {phenol glycine ester (GlyP), phenol alanine ester (AlaP), 2-aminophenol glycine ester (GlyA) and 2-aminophenol alanine ester (AlaA)} have been prepared and characterized by physical chemical techniques. General formulaes \([\text{Co(HBSCH)(A)}_2(\text{NO}_3)]\text{NO}_3\), \([\text{Co(HBSCH)(A)}_2(\text{NO}_3)_2]\), \([\text{Co(HBSCH)}_2(A)(\text{NO}_3)]\text{NO}_3\) and \([\text{Co(HBSCH)}_2(A)(\text{NO}_3)_2]\) have been proposed for the complexes prepared in neutral medium. Whereas, the
formulae [Co(HBSC)(A)₂] and [Co(HBSC)₂(A)] have been proposed for
the complexes prepared in basic medium (where HBSC = deprotonated
HBSCH ligand). The study suggested that all the complexes had
octahedral geometries.

INTRODUCTION

Cobalt is known to be one of the trace elements essential to human
nutrition. It is present in meat and dairy products and in vitamin B₁₂. It is
an important substance that can prevent the disease known as precious
anemia, in which the blood was depleted of a adequate numbers of its
carrying red cells [1].

The chemistry of transition metal complexes of semicarbazones
has been receiving considerable attention because of their biological
activities and providing models for metal ligand bonding sites in several
enzymes [2-4]. In the solid state, these semicarbazones were existed in
the keto form (Figure 1a). In solution, however, they were known to
tautomerize into the enol form (Figure 1b). Complexation usually took
place through the N and O donor atoms [2,5-8], resulting in the formation
of a five-membered chelate ring (Figure 1c and 1d).

Amino acids and their derivatives have been used for different
purposes [9-13]. A good deal of work has been reported on the formation
of amino acid esters chelates involving ligands containing different
donating atoms such as nitrogen, oxygen and sulfur [14-20].

Coordination compounds of mixed ligands were of a considerable
importance in the field of metalloenzymes and biological activities in
addition to other purpose [21-26]. Hence a large number of coordination
compounds containing mixed ligands with transition and non-transition
metal ions have been reported recently [27-30]. Due to the importance of
semicarbazone, amino acid esters and mixed ligands complexes we took a
humble part in the chemistry of their complexes. Recently, some articles
have been published concerning their coordination chemistry with transition and non-transition metal ions [31-36].

In the present work new cobalt (II) complexes with mixed ligands 4-hydroxybenzaldehyde semicarbazone and amino acid esters (Figure 2) has been prepared and characterized physico-chemically.

Figure 2: Structures of the ligands

**EXPERIMENTAL**

1. **Synthetic methods**

4-Hydroxybenzaldehyde semicarbazone (HBSCH) has been prepared according to the standard method [37]. Amino acid esters have been prepared according to the previous method [37].

A general procedure has been adopted for the preparation of the complexes in neutral and basic medium.

1. **In neutral medium**

A solution of 0.5 g (1.72 mmole) of cobalt (II) nitrate in 5 ml distilled water has been added to the solution of 1.72 or 3.44 mmole 4-hydroxybenzaldehyde semicarbazone in 20 ml hot ethanol and 3.44 or 1.72 mmole of amino acid ester in 25 ml hot ethanol (the amounts in grams have been listed in Table 1). The mixtures have been refluxed for two hours followed by evaporation to about half their volumes then cooled. The products were filtered off, washed with diethylether and dried.
II. In basic medium

Complexes of the types \([\text{Co(HBSC})(\text{A})_2]\) and \([\text{Co(HBSC)}_2(\text{A})]\) have been prepared by applying same amounts used in neutral medium, after mixing the metal salts with the ligands solutions and on heating on a water bath, potassium hydroxide solution 1M has been added dropwise until complete precipitation (pH ≈ 8-9). The mixtures have been heated on a water bath for half an hour then allowed to stand then cooled. The products were filtered off, washed with diethylether and dried.

2. Analytical and physical measurements

Cobalt contents have been determined by applying gravimetric method [38]. Relative molecular weights of the ligands and their complexes have been determined cryoscopically [39]. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using \(10^{-2}\) M dimethylformamide solution at room temperature. Infrared spectra has been recorded on FT-IR Bruker type Tensor 27 in the range 400-4000 cm\(^{-1}\) using KBr pellets. Electronic spectra has been recorded by Shimadzu UV-1601 Spectrophotometer for \(10^{-3}\) M or \(10^{-4}\) M solution of the ligands and their complexes in dimethylformamide at 25 °C. Magnetic susceptibilities of the complexes have been measured by Bruker B.M6.

RESULTS AND DISCUSSION

The reaction of cobalt (II) nitrate with 4-hydroxybenzaldehyde semicarbazone and amino acid esters in both neutral and basic medium can be represented by the following reactions:

\[
\begin{align*}
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + \text{HBSCH} + 2\text{A} & \rightarrow [\text{Co(HBSCH)(A)}_2(\text{NO}_3)]\text{NO}_3 + 6\text{H}_2\text{O} \\
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + \text{HBSCH} + 2\text{G}_2 & \rightarrow [\text{Co(HBSCH)}(\text{G}_2)_2(\text{NO}_3)_2] + 6\text{H}_2\text{O} \\
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + 2\text{HBSCH} + \text{A} & \rightarrow [\text{Co(HBSCH)}_2(\text{A})(\text{NO}_3)_2] + 6\text{H}_2\text{O} \\
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + 2\text{HBSCH} + \text{A} - & \rightarrow [\text{Co(HBSCH)}_2(\text{A}^-)(\text{NO}_3)_2] + 6\text{H}_2\text{O} \\
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + \text{HBSCH} + 2\text{A} + 2\text{KOH} & \rightarrow [\text{Co(HBSCH)(A)}_2] + 2\text{KNO}_3 + 8\text{H}_2\text{O} \\
\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} + 2\text{HBSCH} + \text{A} + 2\text{KOH} & \rightarrow [\text{Co(HBSCH)}_2(\text{A})] + 2\text{KNO}_3 + 8\text{H}_2\text{O}
\end{align*}
\]

(where \(\text{A}^- = \text{G}_1\) or \(\text{A}_2\))

The complexes under investigation were colored, solid, soluble in dimethylformamide and dimethylsulphoxide. Cobalt contents and relative molecular weights (Table 2) revealed that the complexes had the general formulae \([\text{Co(HBSCH)(A)}_2(\text{NO}_3)_2]\), \([\text{Co(HBSCH)}(\text{G}_2)_2(\text{NO}_3)_2]\), \([\text{Co(HBSCH)}_2(\text{A})(\text{NO}_3)_2]\) or \([\text{Co(HBSCH)}_2(\text{A}^-)(\text{NO}_3)_2]\) and \([\text{Co(HBSCH)}(\text{A})_2]\) or \([\text{Co(HBSCH)}_2(\text{A})]\) respectively. The values of the molar conductivities (\(\Lambda_M\)) shown in Table (2) approached those expected for 1:1 and non-electrolytes [40] for complexes prepared in neutral medium, and non-electrolytes for complexes prepared in basic medium. The room temperature magnetic moments (\(\mu_{\text{eff.}}\)) of cobalt (II) complexes were in the range of 3.83-3.97 B.M (Table 2) indicating the presence of
three unpaired electron and assigned to high spin monomeric structures having octahedral geometries [32,41].

Infrared spectra of semicarbazone ligand (Table 3) showed a strong band at 1656 cm\(^{-1}\) which was attributed to \(\nu_{\text{C}=\text{O}}\). This value shifted towards a lower frequency (1613-1617 cm\(^{-1}\)) on coordination, in neutral medium, indicating a coordination of the oxygen atom of \(\text{C}=\text{O}\) group to the metal ion [32,42]. Whereas, the infrared spectra of the complexes 9 and 15 showed two bands at 1656 and 1614 cm\(^{-1}\), this splitting may be due to the coordination of only one \(\text{C}=\text{O}\) group to the metal ion [7,42]. In basic medium, this band was disappeared in the infrared spectra of the complexes and a new band was observed at 1107-1138 cm\(^{-1}\) due to bonding enolic \(\text{C}-\text{O}\) thereby establishing coordination of the ligand through the enolic oxygen atom [5,42]. The appearance of strong bands at 1636-1640 cm\(^{-1}\) and 1575-1581 cm\(^{-1}\) which were attributed to \(\nu_{\text{C}=\text{N}} + \nu_{\text{O}=\text{C}=\text{N}}\) and azine chromophore \(\text{C}=\text{N}-\text{N}=\text{C}\), respectively, supported the formation of enolic structure in a basic medium [5,7]. The strong band at 1608 cm\(^{-1}\) attributed to \(\nu_{\text{C}=\text{N}}\) has been shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation [5,32]. The band in the region 3187 cm\(^{-1}\) was attributed to \(\nu_{\text{NH}}\), the broadening of this band was due to the hydrogen bonding phenomenon. By complexation, this phenomenon becomes more complicated due to different factors such as the effect of hydrogen bonding and the presence of other group (\(\text{NH}_2\)) situated at the same position [2,6]. The \(\nu_{\text{NH}}\) band remained unaltered in the spectra of the complexes prepared in neutral medium indicating that \(\text{NH}\) group was uncoordinated. Whereas in a basic medium, it is more difficult to notice the absence of \(\text{NH}\) group due to the presence of hydrogen bonding and other functional groups (OH, \(\text{NH}_2\)), but it is well known that this band has been disappeared [2,5] due to the enolic form. The strong bands appeared at 3440-3447 cm\(^{-1}\) and 1450-1456 cm\(^{-1}\) due to \(\nu_{\text{NH}_2}\) and \(\delta_{\text{NH}_2}\), respectively, remained unchanged on complexation indicated the uncoordination of this group with the metal ion [2,5].

Infrared spectra of amino acid esters (Table 3) showed two bands at 1593-1605 cm\(^{-1}\) and 1354-1403 cm\(^{-1}\) assigned to the symmetric and asymmetric stretching frequency of \(\text{COO}\) group, respectively. On complexation these bands were shifted to 1485-1511 cm\(^{-1}\) and 1308-1338 cm\(^{-1}\), respectively. The difference between these bands (\(\Delta\nu = 170-178\) cm\(^{-1}\)) indicated that \(\text{COO}\) group coordinated to the central metal ion in a monodentate manner [16,42]. The next wide bands 3088-3105 cm\(^{-1}\) and 3376-3424 cm\(^{-1}\) were attributed to \(\nu_{\text{NH}_2}(\text{amino acid})\) and \(\nu_{\text{NH}_2}(\text{Ph})\), respectively. In the spectra of the complexes, prepared in neutral medium, these bands remained unaltered indicating the uncoordination of these groups to the metal ion [14,16,42]. Whereas the spectra of the complexes prepared in
Preparation and Characterization of Cobalt (II)- Complexes ...

basic medium showed that the first band only was shifted to lower frequency indicating the coordination of the nitrogen atom of amino acid group forming 5-membered ring, giving more stable complexes [14,16].

The spectra of all the complexes prepared in neutral medium showed bands at 1374-1421, 1259-1305 and 957-958 cm\(^{-1}\) due to \(\nu_{s\text{NO}_3}\), \(\nu_{as\text{NO}_3}\) and \(\nu_{\text{NO}}\) respectively. The difference between \(\nu_{s\text{NO}_3}\) and \(\nu_{as\text{NO}_3}\) (\(\Delta\nu = 115\ \text{cm}^{-1}\)) supported the bonding of nitrato group as monodentate ligand through the oxygen atom [33,41,42]. Moreover, complexes 1,3,7,11 and 13 showed band at 1385-1386 cm\(^{-1}\) due to ionic bonding of NO\(_3^-\) group [42]. Whereas the spectra of the complexes prepared in basic medium did not show any of these bands indicating the non presence of nitrato group. The spectra of all the complexes showed new bands at 524-539 cm\(^{-1}\) and 607-628 cm\(^{-1}\) due to \(\nu_{\text{Co-N}}\) and \(\nu_{\text{Co-O}}\), respectively. The presence of these bands supported the formation of the complexes under investigation [41,32].

The electronic spectra of the complexes in dimethylformamide solution have been recorded giving d-d spectra and charge transfer spectra (Table 4). Cobalt (II) complexes showed absorption bands at 15013-17594 and 18001-22124 cm\(^{-1}\) due to \(v_2\) and \(v_3\) (attributed to the transitions \(4T_1g(F) \rightarrow 4A_2g(F)\) and \(4T_1g(F) \rightarrow 4T_1g(P)\)) respectively. \(v_1\) \(\{7184-8928\ \text{cm}^{-1}\) attributed to the transition \(4T_1g\ (F) \rightarrow 4T_2g\ (F)\}\) has been not observed due to instrumental limitation, it was calculated by the literature method [43]. The ligand field parameter \(B\) and the ligand field splitting energy (10Dq) have been calculated [43]. The values of \(\beta\) of the complexes were 0.72 clearly indicated the covalent character of the bond concerned. The values of Dq/B which were in the range 1.45-1.50 suggested octahedral geometry for all the complexes [32,43]. The values of the C.F.S.E have been also determined which were in the range 8178-8508 cm\(^{-1}\).

**CONCLUSION**

According to the analytical, physical and spectral data, some observations have been achieved that lead to establish the following points:

1. HBSCH ligand acts either as bidentate chelating ligand connected to cobalt (II) ion through the azomethine nitrogen and carbonyl oxygen or as monodentate ligand connected to cobalt (II) ion through the azomethine nitrogen (complex 9 and 15). HBSC\(^-\) or HBSC\(^-2\) (Figure 2) acts as bidentate chelating ligand joints to cobalt (II) ion through the azomethine nitrogen and enolic oxygen.

2. Amino acid esters act either as monodentate ligand joint to Co(II) ion through the carboxylate oxygen (in the neutral medium), or as bidentate chelating ligand connected to Co(II) ion through the carboxylate oxygen and amino nitrogen (in the basic medium).

3. NO\(_3^-\) connected to Co(II) ion in two manners, as monodentate ligand through the oxygen atom and in an ionic manner.
4. Cobalt (II) ion is probably hexacoordinated, leading to octahedral geometry (Figure 4).

**Figure 4:** Proposed structure of the complexes a1-a4 complexes in neutral medium, b1 and b2 complexes in basic medium, R' = Ph or 2-amino phenyl, R = H or CH₃.
Table 1: Medium, amounts used in the preparation of the complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>Medium</th>
<th>Molar ratio</th>
<th>Wt. of HBSCH</th>
<th>Wt. of ester</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Co(HBSCH)(G₁)₂(NO₃)]NO₃</td>
<td>Neutral</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.52</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>[Co(HBSC)(G₁)]</td>
<td>Basic</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.52</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>[Co(HBSCH)(A₁)₂(NO₃)]NO₃</td>
<td>Neutral</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.57</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>[Co(HBSC)(A₁)₂]</td>
<td>Basic</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.57</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>[Co(HBSCH)(G₂)₂(NO₃)₂]</td>
<td>Neutral</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.57</td>
<td>52</td>
</tr>
<tr>
<td>6</td>
<td>[Co(HBSC)(G₂)₂]</td>
<td>Basic</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.57</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>[Co(HBSCH)(A₂)₂(NO₃)]NO₃</td>
<td>Neutral</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.62</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>[Co(HBSC)(A₂)₂]</td>
<td>Basic</td>
<td>1:1:2</td>
<td>0.31</td>
<td>0.62</td>
<td>59</td>
</tr>
<tr>
<td>9</td>
<td>[Co(HBSCH)₂(G₁)(NO₃)₂]</td>
<td>Neutral</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.26</td>
<td>56</td>
</tr>
<tr>
<td>10</td>
<td>[Co(HBSC)₂(G₁)]</td>
<td>Basic</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.26</td>
<td>52</td>
</tr>
<tr>
<td>11</td>
<td>[Co(HBSCH)₂(A₁)(NO₃)]NO₃</td>
<td>Neutral</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.284</td>
<td>58</td>
</tr>
<tr>
<td>12</td>
<td>[Co(HBSC)₂(A₁)]</td>
<td>Basic</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.284</td>
<td>66</td>
</tr>
<tr>
<td>13</td>
<td>[Co(HBSCH)₂(G₂)(NO₃)₂]</td>
<td>Neutral</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.285</td>
<td>82</td>
</tr>
<tr>
<td>14</td>
<td>[Co(HBSC)₂(G₂)]</td>
<td>Basic</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.285</td>
<td>62</td>
</tr>
<tr>
<td>15</td>
<td>[Co(HBSCH)₂(A₂)(NO₃)₂]</td>
<td>Neutral</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.31</td>
<td>74</td>
</tr>
<tr>
<td>16</td>
<td>[Co(HBSC)₂(A₂)]</td>
<td>Basic</td>
<td>1:2:1</td>
<td>0.615</td>
<td>0.31</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 2: Analytical data and physical properties of the complexes

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Greenish blue</td>
<td>206</td>
<td>77</td>
<td>3.83</td>
<td>9.10 (8.50)</td>
<td>648 (644)</td>
</tr>
<tr>
<td>2</td>
<td>Dark brown</td>
<td>120 d</td>
<td>29</td>
<td>3.81</td>
<td>10.09 (9.80)</td>
<td>585 (582)</td>
</tr>
<tr>
<td>3</td>
<td>Yellow</td>
<td>224</td>
<td>76</td>
<td>3.87</td>
<td>8.73 (7.80)</td>
<td>676 (680)</td>
</tr>
<tr>
<td>4</td>
<td>Dark brown</td>
<td>130</td>
<td>27.5</td>
<td>3.93</td>
<td>9.62 (9.30)</td>
<td>613 (582)</td>
</tr>
<tr>
<td>5</td>
<td>Dark brown</td>
<td>206</td>
<td>22</td>
<td>3.97</td>
<td>8.70 (7.80)</td>
<td>678 (680)</td>
</tr>
<tr>
<td>6</td>
<td>Brown</td>
<td>182 d</td>
<td>16</td>
<td>3.87</td>
<td>9.59 (9.10)</td>
<td>615 (582)</td>
</tr>
<tr>
<td>7</td>
<td>Black</td>
<td>230</td>
<td>50</td>
<td>3.94</td>
<td>8.36 (8.10)</td>
<td>706 (680)</td>
</tr>
<tr>
<td>8</td>
<td>Brown</td>
<td>180 d</td>
<td>17</td>
<td>3.91</td>
<td>9.18 (9.00)</td>
<td>643 (610)</td>
</tr>
<tr>
<td>9</td>
<td>Pale yellow</td>
<td>250</td>
<td>14</td>
<td>3.92</td>
<td>8.94 (8.70)</td>
<td>660 (680)</td>
</tr>
<tr>
<td>10</td>
<td>Pale yellow</td>
<td>260</td>
<td>12</td>
<td>3.92</td>
<td>11.05 (9.30)</td>
<td>534 (532)</td>
</tr>
<tr>
<td>11</td>
<td>Pale yellow</td>
<td>236</td>
<td>52</td>
<td>3.89</td>
<td>8.75 (7.90)</td>
<td>674 (680)</td>
</tr>
<tr>
<td>12</td>
<td>Dark pink</td>
<td>266 d</td>
<td>24.5</td>
<td>3.95</td>
<td>10.77 (9.30)</td>
<td>548 (556)</td>
</tr>
<tr>
<td>13</td>
<td>Black</td>
<td>230</td>
<td>60</td>
<td>3.85</td>
<td>8.59 (7.30)</td>
<td>687 (680)</td>
</tr>
<tr>
<td>14</td>
<td>Brown</td>
<td>182 d</td>
<td>28</td>
<td>3.85</td>
<td>10.52 (9.00)</td>
<td>561 (556)</td>
</tr>
<tr>
<td>15</td>
<td>Dark brown</td>
<td>256</td>
<td>35</td>
<td>3.90</td>
<td>8.56 (8.50)</td>
<td>689 (680)</td>
</tr>
<tr>
<td>16</td>
<td>Brown</td>
<td>174 d</td>
<td>25</td>
<td>3.95</td>
<td>10.48 (8.80)</td>
<td>563 (556)</td>
</tr>
</tbody>
</table>
Table 3: IR spectral data of the ligands and their complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>$\nu_{C=N}$ (semi)</th>
<th>$\nu_{C=O}$ (semi)</th>
<th>$\nu_{C=O}^{\text{u}}$ (ester)</th>
<th>$\nu_{C=O}^{\text{s}}$ (ester)</th>
<th>$\Delta\nu$ (ester)</th>
<th>$\nu_{\text{NH}_2}$ (ester)</th>
<th>$\nu_{\text{NO}_2}$</th>
<th>$\Delta\nu$</th>
<th>$\nu_{\text{NO}_3}$</th>
<th>$\nu_{\text{Co-N}}$</th>
<th>$\nu_{\text{Co-O}}$</th>
<th>Other bands</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HBSCH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1542 s</td>
<td>1616 s</td>
<td>-</td>
<td>1508 s</td>
<td>1338 s</td>
<td>170</td>
<td>3444 m</td>
<td>1374 m</td>
<td>1259 m</td>
<td>115</td>
<td>1385</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1541 s</td>
<td></td>
<td>1125 m</td>
<td>1507 s</td>
<td>1335 s</td>
<td>172</td>
<td>3636 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>1585 s</td>
<td>1615 s</td>
<td>-</td>
<td>1509 s</td>
<td>1335 s</td>
<td>174</td>
<td>3280 m</td>
<td>1374 m</td>
<td>1259 m</td>
<td>115</td>
<td>1385</td>
<td>526 m</td>
</tr>
<tr>
<td>4</td>
<td>1541 s</td>
<td></td>
<td>1115 m</td>
<td>1507 s</td>
<td>1335 s</td>
<td>172</td>
<td>3632 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>1558 s</td>
<td>1617 s</td>
<td>-</td>
<td>1508 s</td>
<td>1335 s</td>
<td>173</td>
<td>3276 m</td>
<td>1420 m</td>
<td>1305 m</td>
<td>115</td>
<td>-</td>
<td>539 m</td>
</tr>
<tr>
<td>6</td>
<td>1550 s</td>
<td></td>
<td>1107 m</td>
<td>1486 s</td>
<td>1308 s</td>
<td>178</td>
<td>3257 m</td>
<td>3322 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>539 m</td>
</tr>
<tr>
<td>7</td>
<td>1586 s</td>
<td>1613 s</td>
<td>-</td>
<td>1508 s</td>
<td>1335 s</td>
<td>173</td>
<td>3276 m</td>
<td>1374 m</td>
<td>1259 m</td>
<td>115</td>
<td>1386</td>
<td>524 m</td>
</tr>
<tr>
<td>8</td>
<td>1590 s</td>
<td></td>
<td>1138 m</td>
<td>1485 s</td>
<td>1315 s</td>
<td>170</td>
<td>3276 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1584 s</td>
<td>1614 s</td>
<td>1656 s</td>
<td>-</td>
<td>1508 s</td>
<td>1335 s</td>
<td>173</td>
<td>3263 m</td>
<td>1420 m</td>
<td>1305 m</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>1585 s</td>
<td></td>
<td>1128 m</td>
<td>1508 s</td>
<td>1335 s</td>
<td>173</td>
<td>3266 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>1585 s</td>
<td>1614 s</td>
<td>-</td>
<td>1511 s</td>
<td>1334 s</td>
<td>177</td>
<td>3244 m</td>
<td>1420 m</td>
<td>1305 m</td>
<td>115</td>
<td>1385</td>
<td>524 m</td>
</tr>
<tr>
<td>12</td>
<td>1542 s</td>
<td></td>
<td>1121 m</td>
<td>1508 s</td>
<td>1335 s</td>
<td>173</td>
<td>3264 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>1585 s</td>
<td>1615 s</td>
<td>-</td>
<td>1485 s</td>
<td>1314 s</td>
<td>171</td>
<td>3276 m</td>
<td>1374 m</td>
<td>1259 m</td>
<td>115</td>
<td>1386</td>
<td>525 m</td>
</tr>
<tr>
<td>14</td>
<td>1585 s</td>
<td></td>
<td>1138 m</td>
<td>1487 s</td>
<td>1315 s</td>
<td>172</td>
<td>3257 m</td>
<td>3222 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>539 m</td>
</tr>
<tr>
<td>15</td>
<td>1586 s</td>
<td>1614 s</td>
<td>1656 s</td>
<td>-</td>
<td>1485 s</td>
<td>1315 s</td>
<td>170</td>
<td>3276 m</td>
<td>1420 m</td>
<td>1305 m</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>1587 s</td>
<td></td>
<td>1138 m</td>
<td>1487 s</td>
<td>1315 s</td>
<td>172</td>
<td>3221 m</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Zuhoor F. Dawood & Mushal W. Ibrahim
Table 4: Electronic spectral data of the complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
<th>$\nu_3/\nu_2$</th>
<th>$\nu_2/\nu_1$</th>
<th>$\nu_3/B$</th>
<th>B</th>
<th>Dq</th>
<th>Dq/B</th>
<th>10Dq</th>
<th>$\beta$</th>
<th>C.F.S.E</th>
<th>C.T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7197</td>
<td>15490</td>
<td>19920</td>
<td>1.286</td>
<td>2.768</td>
<td>2.152</td>
<td>28.10</td>
<td>709</td>
<td>1063.50</td>
<td>1.50</td>
<td>10635</td>
<td>0.72</td>
<td>8508</td>
</tr>
<tr>
<td>2</td>
<td>7366</td>
<td>15856</td>
<td>20390</td>
<td>1.286</td>
<td>2.768</td>
<td>2.152</td>
<td>28.84</td>
<td>707</td>
<td>1060.50</td>
<td>1.50</td>
<td>10605</td>
<td>0.72</td>
<td>8484</td>
</tr>
<tr>
<td>3</td>
<td>7184</td>
<td>15427</td>
<td>19144</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>27.16</td>
<td>705</td>
<td>1057.50</td>
<td>1.50</td>
<td>10575</td>
<td>0.72</td>
<td>8460</td>
</tr>
<tr>
<td>4</td>
<td>7838</td>
<td>16871</td>
<td>21697</td>
<td>1.286</td>
<td>2.768</td>
<td>2.152</td>
<td>30.78</td>
<td>705</td>
<td>1022.25</td>
<td>1.45</td>
<td>10223</td>
<td>0.72</td>
<td>8178</td>
</tr>
<tr>
<td>5</td>
<td>8193</td>
<td>17594</td>
<td>21834</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>30.98</td>
<td>706</td>
<td>1023.70</td>
<td>1.45</td>
<td>10237</td>
<td>0.72</td>
<td>8190</td>
</tr>
<tr>
<td>6</td>
<td>7993</td>
<td>17204</td>
<td>22124</td>
<td>1.286</td>
<td>2.768</td>
<td>2.152</td>
<td>31.25</td>
<td>708</td>
<td>1062.00</td>
<td>1.50</td>
<td>10620</td>
<td>0.72</td>
<td>8496</td>
</tr>
<tr>
<td>7</td>
<td>7689</td>
<td>16512</td>
<td>20492</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>28.94</td>
<td>708</td>
<td>1062.00</td>
<td>1.50</td>
<td>10620</td>
<td>0.72</td>
<td>8496</td>
</tr>
<tr>
<td>8</td>
<td>8193</td>
<td>17594</td>
<td>21834</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>30.84</td>
<td>708</td>
<td>1026.60</td>
<td>1.45</td>
<td>10266</td>
<td>0.72</td>
<td>8248</td>
</tr>
<tr>
<td>9</td>
<td>7457</td>
<td>15013</td>
<td>18001</td>
<td>1.199</td>
<td>2.414</td>
<td>2.013</td>
<td>25.53</td>
<td>705</td>
<td>1022.25</td>
<td>1.45</td>
<td>10223</td>
<td>0.72</td>
<td>8178</td>
</tr>
<tr>
<td>10</td>
<td>7453</td>
<td>16005</td>
<td>19862</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>28.21</td>
<td>704</td>
<td>1056.00</td>
<td>1.50</td>
<td>10560</td>
<td>0.72</td>
<td>8448</td>
</tr>
<tr>
<td>11</td>
<td>7730</td>
<td>16582</td>
<td>19881</td>
<td>1.199</td>
<td>2.572</td>
<td>2.145</td>
<td>28.16</td>
<td>706</td>
<td>1059.00</td>
<td>1.50</td>
<td>10590</td>
<td>0.72</td>
<td>8472</td>
</tr>
<tr>
<td>12</td>
<td>7985</td>
<td>17074</td>
<td>19276</td>
<td>1.129</td>
<td>2.414</td>
<td>2.138</td>
<td>27.23</td>
<td>708</td>
<td>1062.00</td>
<td>1.50</td>
<td>10620</td>
<td>0.72</td>
<td>8496</td>
</tr>
<tr>
<td>13</td>
<td>8928</td>
<td>16759</td>
<td>21552</td>
<td>1.286</td>
<td>2.414</td>
<td>1.877</td>
<td>30.44</td>
<td>708</td>
<td>1062.60</td>
<td>1.45</td>
<td>10626</td>
<td>0.72</td>
<td>8213</td>
</tr>
<tr>
<td>14</td>
<td>7785</td>
<td>16718</td>
<td>20747</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>29.43</td>
<td>705</td>
<td>1022.25</td>
<td>1.45</td>
<td>10223</td>
<td>0.72</td>
<td>8178</td>
</tr>
<tr>
<td>15</td>
<td>8852</td>
<td>16615</td>
<td>21368</td>
<td>1.286</td>
<td>2.414</td>
<td>1.877</td>
<td>30.31</td>
<td>705</td>
<td>1057.50</td>
<td>1.50</td>
<td>10575</td>
<td>0.72</td>
<td>8460</td>
</tr>
<tr>
<td>16</td>
<td>8193</td>
<td>17594</td>
<td>21834</td>
<td>1.241</td>
<td>2.665</td>
<td>2.147</td>
<td>30.80</td>
<td>709</td>
<td>1063.50</td>
<td>1.50</td>
<td>10635</td>
<td>0.72</td>
<td>8508</td>
</tr>
</tbody>
</table>

* calculated
REFERENCES