Mixed Ligand Heterochelate of VO(IV), Mn(II), Co(II), Ni(II), Cu(II) & Zn(II) with 8-Hydroxyquinoline & 2-Aminobenzoic Acid

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Mixed ligand complexes of composition, M(Q)(AB), nH2O, [M=VO(IV), Mn(II), Co(II), Ni(II), Cu(II) & Zn(II); HQ=8-quinolinol; ABH=2-aminobenzoic acid; n=1 or 2] have been prepared and characterized employing analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral measurements.

Heterochelates containing two different uninegative bidentate ligands of which 8-quinolinolate is one such ligand are known1-7. However, heterochelates of bivalent 3d-metal ions containing 8-quinolinolate and 2-aminobenzoate as the ligands have not been reported so far. We report in this note the synthesis and characterization of the title complexes.

All the chemicals used were of BDH or equivalent quality. The complexes were prepared as follows: Aquo(2-aminobenzoate) (8-quinolinolato) oxovanadium(IV) was prepared by mixing a solution of 8-quinolinol (HQ, =5mmol) in 2N acetic acid and sodium salt of 2-aminobenzoic acid (NaABH=5mmol) in water and then adding to it slowly with stirring an aqueous solution of V2O5 (5mmol). Mono or diquo (2-aminobenzoato) (8-quinolinolato) metal(II) [metal(II)=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were obtained by mixing aqueous solution of metal chloride and ethanolic solution of HQ and 2-aminobenzoic acid (ABH) in 1:1 molar ratio and then gradually adding two equivalents of aqueous solution of NaOH.

All the complexes which precipitated almost immediately were suction-filtered, washed with 50% ethanol, ether, dried at room temperature and analysed employing standard methods8.

The analytical data (Table I) show the formation of mixed ligand complexes of the type M(Q)(AB), nH2O. The complexes do not melt or decompose until 250°C. The loss of water at a relatively high temperature (150-150°C) indicates the coordinated nature of water molecule(s). The complexes are insoluble in water and common organic solvents but are soluble in DMF. The low values of the molar conductance (2.83-10.03 mhos cm²/mol) of the solutions (10⁻⁴M) of the complexes in DMF points to their non-ionic nature8.

The room temperature magnetic moments [measured on Cahn-Faraday electrobalance with HgCo(NCS)₄ as calibrant; experimental γ_M corrected for diamagnetism] of the hydrated as well as the anhydrous cobalt(II) and nickel(II) complexes are consistent with a spin-free octahedral geometry9 around these metal ions while μ_eff values of manganese(II) complexes correspond to five unpaired electrons indicating a spin-free tetrahedral or octahedral geometry (Table I). The magnetic moments of copper(II) complexes (Table I) correspond to one unpaired electron and do not provide specific information about their stereochemistry10. The subnormal magnetic moments of oxovanadium(IV) complexes (Table I) may be due to one or more factors such as spin-orbit coupling, antiferromagnetism and V=O......V interaction11.

The electronic spectra of the complexes were recorded in nujol on a Cary-14 spectrophotometer. Hydrated Co(II) complex exhibits two bands at 9525 and 20000 cm⁻¹ and the anhydrous complex also yields two bands at 8695 and 19050 cm⁻¹. These are assigned to ³T₂g(F)→²T₂g(F) and ³T₂g(F) transitions respectively in each case. The two bands in the hydrated Ni(II) complex (16660 and 25640 cm⁻¹) and the anhydrous complex (16260 and 25000 cm⁻¹) are attributed to ³A_{2g}(F)→²T₂g(F) and ³A_{2g}(F) transitions respectively. The additional band in the anhydrous Ni(II) complex at 9760 cm⁻¹ is assigned to ³M_{3g}(F)→²T₂g(F) transition. These data indicate that nickel(II) and cobalt(II) complexes have an octahedral environment around the metal ion.

The hydrated and anhydrous copper(II) complexes yield one broad band centered at 16000 and 14290 cm⁻¹ respectively indicating distorted octahedral geometry in each case12. The hydrated oxovanadium(IV) complex exhibits two d-d transition bands at 14290 and 17390 cm⁻¹ assignable to d₅→d₇ and d₅→d₇ transitions respectively in an octahedral geometry13. The spectrum of the anhydrous oxovanadium(IV) complex, however, exhibits three bands at 13990, 18180 and 24390 cm⁻¹ assigned to d₅→d₇, d₅→d₇ and d₅→d₇ transitions respectively. This indicates that the metal ion acquires a square pyramidal geometry (C₄₅ symmetry) evidently by the loss of the coordinated water molecule14.

The 1R spectra of the complexes were also recorded in nujol on Perkin-Elmer model 621 spectrophotometer. Since the spectra of the complexes are quite complicated, only those bands which are useful in establishing the bonding sites are discussed. The bands in the region 3600-3340 cm⁻¹ in the hydrated complexes due to ν(OH) disappear in the anhydrous complexes. The ν₅(N-H) and ν₆(N-H) of the aminobenzoato15 at 3436 and 3330 cm⁻¹ respectively undergo shift to lower wave number (Δν=120-140 and 130-200 cm⁻¹) respectively in the hydrated as well as anhydrous complexes indicating coordination through nitrogen atom of amino group. The ν₂₂(COO⁻) and ν₃(COO⁻) of aminobenzoato15 at 1521 and 1398 cm⁻¹ are shifted to higher and lower wavenumbers (Δν₂₂=7-30 cm⁻¹, Δν₃=13-22 cm⁻¹)
Table I—Analytical Data, Magnetic Moments and Various Ligand-field Parameters of Ternary Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (Calc) %</th>
<th>Wt. Joss</th>
<th>μett</th>
<th>10 Dq</th>
<th>B'</th>
<th>β</th>
<th>β°</th>
<th>LESE</th>
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<tbody>
<tr>
<td>VO(Q)(AB)H₂O</td>
<td>Greenish</td>
<td>13.27</td>
<td>7.60</td>
<td>3.91</td>
<td>1.33</td>
<td>17390</td>
<td>—</td>
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<tr>
<td>Mn(Q)(AB)H₂O</td>
<td>Light Brown</td>
<td>14.81</td>
<td>7.63</td>
<td>5.83</td>
<td>6.00</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Co(Q)(AB)H₂O</td>
<td>Reddish Brown</td>
<td>16.02</td>
<td>7.35</td>
<td>5.82</td>
<td>5.16</td>
<td>10750</td>
<td>779</td>
<td>0.81</td>
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<tr>
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<td>16.23</td>
<td>7.57</td>
<td>4.37</td>
<td>3.14</td>
<td>11020</td>
<td>572</td>
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<tr>
<td>Cu(Q)(AB)₂H₂O</td>
<td>Brown</td>
<td>16.00</td>
<td>7.11</td>
<td>8.48</td>
<td>2.03</td>
<td>16000</td>
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<tr>
<td>Zn(Q)(AB)H₂O</td>
<td>Yellow</td>
<td>17.13</td>
<td>7.33</td>
<td>5.28</td>
<td>5.10</td>
<td>18180</td>
<td>7.0</td>
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<td>14.08</td>
<td>7.89</td>
<td>—</td>
<td>1.26</td>
<td>18180</td>
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<tr>
<td>Mn(Q)(AB)</td>
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<td>8.16</td>
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<td>4.95</td>
<td>9910</td>
<td>768</td>
<td>0.79</td>
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<tr>
<td>Ni(Q)(AB)</td>
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<td>8.13</td>
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<td>3.31</td>
<td>9760</td>
<td>798</td>
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<tr>
<td>Cu(Q)(AB)</td>
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<td>8.22</td>
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<td>1.79</td>
<td>14290</td>
<td>—</td>
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</tr>
<tr>
<td>Zn(Q)(AB)</td>
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<td>18.36</td>
<td>8.15</td>
<td>—</td>
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respectively in the spectra of hydrated as well as anhydrous complexes of oxovanadium(IV) and hydrated Cu(II) complex. These modes in all other hydrated and anhydrous complexes undergo shift to higher wavenumbers. These observations suggest monodentate coordination of carboxylato group in the former complexes and its bidentate coordination in the latter. The v(C-O) and 8(C-O) modes of 8-quinolinol, which appear at 1090 and 464 cm⁻¹ respectively, shift to higher frequencies in the binary 3d metal(II) oxinates from which uninegative bidentate behaviour of Q⁻ has been suggested. Positive shifts of 12-25 cm⁻¹ and 25-65 cm⁻¹ respectively in these modes in the present mixed ligand complexes, therefore, suggest similar bonding behaviour of Q⁻. The non-ligand bands observed in the regions 430-285 and 310-240 cm⁻¹ are tentatively assigned to v(M-O) and v(M-N) modes respectively.

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References


