Synthesis & Properties of Some Polynuclear Mono(carboxylato)mono(β-diketonato) Complexes of Cobalt(III)

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A number of polynuclear mixed (carboxylato)(β-diketonato) complexes of cobalt(II) have been synthesized by the trans-acylation reactions of cobalt acetate first with higher carboxylic (palmitic, stearic and behenic) acids and then with β-diketones (acetylacetone, benzoylacetone and dibenzoylmethane) in equimolar ratios in refluxing toluene. The structures of the reaction products have been discussed on the basis of their elemental analyses, infrared and electronic spectra, magnetic susceptibility measurements and molecular weight determinations.

In recent years, extensive studies have been carried out on the β-diketonate and carboxylate derivatives of various transition metals. These derivatives show a strong tendency to undergo addition reactions with various oxygen and nitrogen donor ligands to form coordination complexes with interesting structural properties. However, substitution reactions of transition metal acetates have received very little attention. In the present paper, we report the substitution reactions of cobalt(II) acetate. It is found to react with higher carboxylic acids giving mixed (acetato) (higher carboxylato) complexes of cobalt(II). These compounds react further with β-diketones to give mono(carboxylato)mono(β-diketonato) derivatives of cobalt(II). These derivatives represent a new class of mixed ligand complexes, synthesized for the first time by exploiting the substitution reactions of cobalt(II) acetate, and can not be so easily synthesized by any other route. Various physicochemical studies have been carried out in order to characterise these derivatives.

Materials and Methods

All the reactions were carried out under anhydrous conditions using glass apparatus with interchangeable joints. All the carboxylic acids (BDH) and β-diketones (BDH) were used after distillation or drying under reduced pressure. Toluene (BDH) was rigorously dried over sodium. Anhydrous cobalt(II) acetate was prepared by drying Co(OAc)₂·4H₂O under reduced pressure (1.0 mm/130°C).

Infrared spectra were recorded in the range 4000-400 cm⁻¹ on a Beckman ‘Acculab-9’ spectrophotometer using KBr pellets. Visible reflectance spectra were recorded on a Beckman model-26 spectrophotometer, near IR spectra were recorded on Perkin-Elmer 4000A. Cobalt was estimated gravimetrically as its anthranilate complex and acetic acid was titrated with standard sodium hydroxide solution using phenolphthalein as an indicator.

Synthesis of mono(carboxylato)mono(β-diketonato) complexes of cobalt(II)

To a weighed amount of cobalt acetate (~ 4g) suspended in toluene (70 ml), the required amount of carboxylic acid (in 1:1 molar ratio) was added. Contents were refluxed for 5-6 h with slow and continuous azeotropic fractionation of liberated acetic acid with toluene (106°C). After the completion of reaction, the product, which appeared to be soluble in toluene, was isolated by removing excess solvent under reduced pressure (60°C/1.5 mm). The products obtained from the reactions of various carboxylic acids were found to be mono-substituted mixed carboxylates of Co(II). To a weighed amount of the mixed carboxylate (~ 2.0 g) dissolved in toluene (60 ml) was added the required amount of β-diketone (in equimolar ratio) and contents were refluxed with constant fractionation (3-4 h) of the liberated acetic acid as toluene azeotrope when a coloured solution was obtained. A coloured solid was obtained in each case on drying the contents under reduced pressure and recrystallizing from benzene/alcohol mixture (Table I).

Results and Discussion

Trans-acylation reactions of anhydrous cobalt acetate first with higher carboxylic acids and then with β-diketones, carried out in the present study may be represented by Eqs 1 and 2.

\[
\text{Co(OOCCH₃)₂ + RCOOH} \xrightarrow{\text{Toluene}} \text{Co(OOCCH₃)(OOCR) + CH₃COOH} \quad \ldots (1)
\]

\[
\text{Co(OOCCH₃)(OOCR) + Hβdk} \xrightarrow{\text{Toluene}} \text{Co(OOCR)(βdk) + CH₃COOH} \quad \ldots (2)
\]
Table I—Mixed (Carboxylato)-β-Diketonato Complexes of Cobalt(II)

<table>
<thead>
<tr>
<th>Reactants (in 1:1 molar ratio)</th>
<th>Product (colour)</th>
<th>Acetic acid in azeotrope (g)</th>
<th>Co(II)%</th>
<th>C%</th>
<th>H%</th>
<th>Mol. Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hacac</td>
<td>Co(acac)(OOCC₁H₃₂) (Purple red)</td>
<td>0.42</td>
<td>14.16</td>
<td>60.52</td>
<td>9.20</td>
<td>1267</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hbzac</td>
<td>Co(bzac)(OOCC₁H₃₂) (Brick red)</td>
<td>0.47</td>
<td>13.22</td>
<td>65.05</td>
<td>8.32</td>
<td>1395</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hdbzm</td>
<td>Co(dbzm)(OOCC₁H₃₂) (Red)</td>
<td>0.37</td>
<td>11.03</td>
<td>69.01</td>
<td>7.74</td>
<td>1563</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hacac</td>
<td>Co(acac)(OOCC₁H₃₂) (Red)</td>
<td>0.40</td>
<td>13.29</td>
<td>61.96</td>
<td>9.53</td>
<td>1284</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hbzac</td>
<td>Co(bzac)(OOCC₁H₃₂) (Blood red)</td>
<td>0.34</td>
<td>11.60</td>
<td>66.47</td>
<td>8.70</td>
<td>1434</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hdbzm</td>
<td>Co(dbzm)(OOCC₁H₃₂) (Reddish brown)</td>
<td>0.40</td>
<td>10.34</td>
<td>70.20</td>
<td>8.14</td>
<td>1580</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hacac</td>
<td>Co(acac)(OOCC₁H₃₂) (Purple red)</td>
<td>0.34</td>
<td>11.70</td>
<td>66.78</td>
<td>8.80</td>
<td>1503</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hbzac</td>
<td>Co(bzac)(OOCC₁H₃₂) (Blood red)</td>
<td>0.40</td>
<td>11.84</td>
<td>65.16</td>
<td>10.13</td>
<td>1497</td>
</tr>
<tr>
<td>Co(OOCC₂H₅)(OOCC₁H₃₂) + Hdbzm</td>
<td>Co(dbzm)(OOCC₁H₃₂) (Dark red)</td>
<td>0.35</td>
<td>9.56</td>
<td>71.16</td>
<td>8.71</td>
<td>1675</td>
</tr>
</tbody>
</table>

Hacac = acetylacetone; Hbzac = benzoylacetone; Hdbzm = dibenzoylmethane

The reactions are found to be facile and their progress can be followed by the estimation of acetic acid content in the azeotrope collected. Mono- as well as di-substituted products have been obtained in quantitative yields. All the mono(carboxylato)-mono(β-diketonato) complexes isolated during the present investigations are non-volatile coloured solids which are soluble in benzene and toluene and insoluble in alcohols. These derivatives were, therefore, precipitated by adding alcohol (methanol or ethanol) to their benzene solutions. On recrystallization from benzene-alcohol mixture (2:1), adducts with the formula Co(OOCR)(βdk).R'OH (where R' = CH₃ or C₂H₅) crystallized out. The additional molecule of alcohol is lost at ~130°C/1.0 mm pressure leaving the mixed (carboxylato)-β(diketonato) derivatives of cobalt(II) in pure state.

The characteristic ν(C=O) and δOH modes of the free carboxylic acids occurring at ~1710 and ~935 cm⁻¹ respectively were not present around these positions in the spectra of the present complexes. Also, no band was observed in the region 3600-3200 cm⁻¹ indicating complete absence of OH. No bands were found in the region 1626-1695 cm⁻¹ where ketonic carbonyl modes for Pt(II)⁵,⁶ acetylacetonate containing uncoordinated carboxyl groups have been reported previously. A strong band around 1600 cm⁻¹ is assigned to ν(C=O) indicating the chelating nature of the β-diketones and carboxylic acids giving either bidentatically chelated (I) or bridged (II & III) polymeric structures:

Two absorption bands appearing at 1570 and 1530 cm⁻¹ may be assigned to ν(C=C) and ν(C=O) + CH bending, respectively. Many detailed infrared spectral studies have been carried out to distinguish the different modes of coordination in metal acetate complexes. Nakamura⁷ has suggested that OCO angle increases in bridging structure relative to that in bidentate one; consequently, antisymmetric C=O stretching (νas(COO)) frequency is expected to increase in bridging acetates. On the other hand, bidentate chelated structure (I) should result in a decrease in both νas(COO) and ν(C=O) modes relative to ionic acetate group as a result of decrease in bond orders of both the C=O bonds. In the acetate ion, the νas(COO) and ν(C=O) frequencies appear at ~1578 and ~1435 cm⁻¹. In the present complexes, these frequencies, have been observed at ~1570 and ~1450 cm⁻¹, respectively. The decrease in νas(COO) frequency is indicative of the presence of both bridging as well as bidentate...
Table 2—Electronic Spectra* and Magnetic Moments of Mixed (Carboxylato)β-Diketonato Complexes of Cobalt(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v1)</th>
<th>(v2)</th>
<th>(v3)</th>
<th>10Dq</th>
<th>B</th>
<th>β</th>
<th>μ_{eff} (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(acac)(OOC12H31)</td>
<td>8000</td>
<td>16800</td>
<td>19600</td>
<td>8960</td>
<td>858</td>
<td>0.88</td>
<td>4.87</td>
</tr>
<tr>
<td>Co(bzac)(OOC12H31)</td>
<td>8065</td>
<td>16935</td>
<td>19420</td>
<td>9030</td>
<td>842</td>
<td>0.87</td>
<td>4.83</td>
</tr>
<tr>
<td>Co(dbzm)(OOC12H31)</td>
<td>8165</td>
<td>17145</td>
<td>19195</td>
<td>9120</td>
<td>818</td>
<td>0.84</td>
<td>4.91</td>
</tr>
<tr>
<td>Co(acac)(OOC12H3S)</td>
<td>8130</td>
<td>17075</td>
<td>19305</td>
<td>9090</td>
<td>828</td>
<td>0.85</td>
<td>4.96</td>
</tr>
<tr>
<td>Co(bzac)(OOC12H3S)</td>
<td>8333</td>
<td>17500</td>
<td>19010</td>
<td>9295</td>
<td>793</td>
<td>0.82</td>
<td>5.07</td>
</tr>
<tr>
<td>Co(dbzm)(OOC12H3S)</td>
<td>8265</td>
<td>17355</td>
<td>19050</td>
<td>9220</td>
<td>800</td>
<td>0.82</td>
<td>4.93</td>
</tr>
<tr>
<td>Co(acac)(OOC12H43)</td>
<td>8333</td>
<td>17500</td>
<td>19230</td>
<td>9310</td>
<td>810</td>
<td>0.83</td>
<td>4.89</td>
</tr>
<tr>
<td>Co(bzac)(OOC12H43)</td>
<td>8165</td>
<td>17145</td>
<td>19420</td>
<td>9125</td>
<td>835</td>
<td>0.86</td>
<td>4.94</td>
</tr>
<tr>
<td>Co(dbzm)(OOC12H43)</td>
<td>8400</td>
<td>17640</td>
<td>19800</td>
<td>9395</td>
<td>847</td>
<td>0.87</td>
<td>4.82</td>
</tr>
</tbody>
</table>

*Values of transitions. 10Dq and B in cm^{-1}; v_1 = ^4T_{1g} \rightarrow ^4T_{2g}, v_2 = ^4T_{1g} \rightarrow ^4A_{2g}, v_3 = ^4T_{1g} \rightarrow ^4T_{1g}(P)

Carboxylate groups in the above derivatives^{10,11}. Some other bands below 700 cm^{-1} may be ascribed to νCo−O vibrations.

Electronic spectra of all the derivatives were recorded in the range 4000-28000 cm^{-1} in nujol or in benzene solution, and no marked difference could be noticed between the two. The spectra are typical of divalent cobalt in an octahedral environment^{12} which exhibits two transitions, ^4T_{1g} \rightarrow ^4T_{2g}, ^4T_{1g} \rightarrow ^4T_{1g}(P)$, at 8000-9000 cm^{-1} ($v_1$) and 19000-20000 cm^{-1} ($v_3$) respectively. The positions of the bands, the proposed assignments, the ligand field parameters ($Dq$), the interelectron repulsion parameters ($B$) and the covalency factors ($β$) are listed in Table 2. The parameters 10Dq and B have been calculated by the method of Underhill and Billing^{13}. The band due to the transition $^4T_{1g} \rightarrow ^4A_{2g}(v_2)$ was not observed in the spectra but could be calculated^{12}, and calculated values are listed in Table 2. The values of $B$ fall in the range 790-860 cm^{-1}, which is much lower than the value observed for free Co^{2+} ion (971 cm^{-1}) showing appreciable covalent character of the metal-ligand bonds in all these derivatives.

Cobalt(II) derivatives should show magnetic moment values between $[4S(S+1)]^{1/2} (μ_{eff} = 3.90$ B.M.) and $[4S(S+1) + L(L+1)]^{1/2} (μ_{eff} = 5.2$ B.M.) when Co^{2+} is present in high-spin state ($S = 3/2$) in an octahedral geometry. The experimental values reported for cobalt(II) in an octahedral geometry lie in the range 4.7-5.2 B.M.$^{14,15}$. Magnetic moments of all the present derivatives have been measured at room temperature (Table 2). All the complexes show magnetic moments in the range 4.8-5.1 B.M. which are typical of high-spin cobalt(II) in an octahedral environment.

Molecular weights of all the complexes have been determined ebullioscopically in refluxing benzene and the results show that all are trimeric in nature. Both the magnetic and spectral studies indicate that in all the complexes, the cobalt atom is situated in an octahedral environment. Although more direct experimental evidence is required before a final view of structure could be arrived at, the linear type of structure suggested for bis(acetylacetonato) complex of nickel(II)$^{16}$ appears to be most plausible for all the above trimeric species, as in these complexes also there are four oxygen atoms per cobalt atom. At room temperature, the possibility of these derivatives being tetrameric species, similar to linear tetrameric structure suggested for bis(acetylacetonato) complex of cobalt(II)$^{17,18}$, can not be neglected. In refluxing benzene, the tetrameric species may be dissociated to give simple trimers. The presence of bridging as well as bidentate carboxylate ions, as shown by infrared spectra, is also justified in both the trimeric (IV) and tetrameric (V) structure.

![Diagram](image)
Acknowledgement

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