Complexation of Some Divalent Metal Ions by Pentaammineglycinatocobalt(III), Pentaammine-\(\beta\)-alaninatocobalt(III), cis-Bis(ethylenediamine) diglycinatocobalt(III) \& \(\alpha\)-cis(trien)diglycinatocobalt(III)

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Potentiometric titrations reveal the formation of mixed metal bi- and tri-nuclear complexes between oxygen-bonded aminoacidatocobalt(III) complexes, \([\text{Co(NH}_3\text{)}_5\text{gly}^2]^+\), \([\text{Co(NH}_3\text{)}_3\beta\text{-ala}^2]^+\), \(\text{cis-Co(en)}_2\text{gly}_2]^+\) and \(\alpha\text{-cis-(trien)gly}_2^+\) and Cu(II), Ni(II) and Co(II). At 27.0 ± 0.1 °C and \(I = 0.1 \text{ mol dm}^{-3}\) the values of the stability constants are: \(\log K_1 = 5.61 \pm 0.05\) (Cu(II)), 3.91 ± 0.01 (Ni(II)), 3.04 ± 0.04 (Co(II)) for pentaammineglycinato complex; \(\log K_1 = 5.26 \pm 0.11\) (Cu(II)), 3.44 ± 0.08 (Ni(II)), 2.61 ± 0.09 (Co(II)) for pentaammine \(\beta\)-alaninato complex; \(\log K_1 = 9.00 \pm 0.10\) (Cu(II)), \(\log K_2 = 13.65 \pm 0.15\) (Cu(II)); \(11.2 \pm 0.20\) (Ni(II)) and 7.1 ± 0.10 (Co(II)) for \(\alpha\)-cis-(ethylenediamine)diglycinato complex; \(\log K_1 = 8.90 \pm 0.10\) (Cu(II)); \(\log K_2 = 13.70 \pm 0.15\) (Cu(II)); 12.10 ± 0.11 (Ni(II)) and 9.80 ± 0.10 (Co(II)) for \(\alpha\)-cis-(trien)(diglycinato) complex, where \(\beta_1 = K_1 K_2\) denotes the overall stability constant of species having Co(II)/M(II) in the ratio of 2:1. Spectral characterization of the Cu(II) species has been attempted.

Formation of various oxo- and hydroxo-bridged binuclear complexes of metal ions has been investigated\(^{1-5}\) but measurement of formation constants of such binuclear species with two different metal ions has been rarely attempted. Recently Cannon and Benjarvongkulchai\(^6\) studied the complex formation of \([\text{Co(en)}_2\text{(OH)}_2]^+\) with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and reported the formation constants of the respective hydroxo-bridged binuclear complexes. Dash and Nanda\(^8\) measured the stabilities of the binuclear complexes, having oxalate bridge, formed between oxalatopentaamminecobalt(III) and different metal ions. Dash and Mohapatra\(^9\) determined the formation constants of binuclear complexes of different metal ions with pyridine-2-carboxylato- and pyridine-3-carboxylato-pentaamminecobalt(III). Dash\(^10\) also reported the stabilities of the binuclear complexes of Al(III) with salicylatopentaaminecobalt(III) ions. A recent study by Dash et al.\(^11\) indicates that half-bonded oxalate and salicylate may function as bridging ligands. Presently we have determined the stabilities of different binuclear complexes formed between Co(III) species, \(\text{Ni}_2\text{CoX}_2^{2+}\) and \(\text{Ni}_2\text{CoX}_2^{3+}\) (X = O-bonded glycinate, \(\beta\)-alaninate) and Cu(II), Ni(II) and Co(II) ions. The possible equilibria in solution are shown in Eqs (1) and (2)

\[
\text{M}^{m+} + n[\text{Co(NH}_3\text{)}_5\text{gly}^2]^+ \rightleftharpoons [\text{M(gly)}_2]\text{Co(NH}_3\text{)}_3\text{gly}^2]^{m+n+} + n\text{H}^+ \quad \ldots (1)
\]

\[
\text{M}^{m+} + n[\text{Co(en)}_2\text{gly}_2]^+ \rightleftharpoons [\text{M(gly)}_2]\text{Co(en)}_2\text{gly}_2]^{m+n+} + n\text{H}^+ \quad \ldots (2)
\]

Materials and Methods

\([\text{Co(NH}_3\text{)}_5\text{gly}^2]^+\text{ClO}_4^-\) \& H\(_2\text{O}\) (complex I) and \([\text{Co(NH}_3\text{)}_3\beta\text{-ala}^2]^+\text{ClO}_4^-\) (complex II) were prepared by the published method\(^12\), \(\text{cis-Co(en)}_2\text{gly}_2^+\text{ClO}_4^-\) \& H\(_2\text{O}\) (complex III) and \(\alpha\text{-cis-(trien)gly}_2^+\text{ClO}_4^-\) \& H\(_2\text{O}\) (complex IV) were prepared by dissolving corresponding carbonate compounds in required amount of perchloric acid and warming the solution with glycine (in slightly greater than 1:2 mol proportion) at \(\text{pH} 4-5.0\). The reaction mixture was cooled to \(5^\circ\text{C}\) and absolute ethanol added to it dropwise till a purple solid precipitated out. The crystals were filtered off and recrystallized by dissolving it in minimum volume of water and then adding ethanol alongwith a few drops of HClO\(_4\). Purple crystals were obtained from the solution on refrigeration overnight. Complex(III) has also been synthesised by Buckingham and coworkers\(^13\). The characterization data of complexes I—IV are presented in Table 1.

Solutions of Cu(NO\(_3\))\(_2\), Ni(NO\(_3\))\(_2\) and Co(NO\(_3\))\(_2\) (all reagent grade) were prepared in doubly distilled water and standardised\(^14\). An ELICO digital pH meter (model LI 120) with glass-reference electrode assembly combination (CL 51) was used for potentiometric titration. The pH meter was standardised with NBS buffers before titration. The activity of H\(^+\) was converted into concentration using activity coefficient calculated with Davies' equation\(^15\). The UV-vis-
Table I—Characterization Data of Complexes (I-IV)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (calc), %</th>
<th>(\lambda_{\text{max}, \text{nm}})</th>
<th>((\varepsilon, \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3)_5(glyH)]^+)</td>
<td>10.8</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>((\text{ClO}_4)_2\text{H}_2\text{O})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Co(NH}_3)_5(\beta\text{-alaH})</a>_2)</td>
<td>10.7</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{cis}[\text{Co(en)}_2(glyH)_2]^+)</td>
<td>8.9</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>((\text{ClO}_4)_2\text{H}_2\text{O})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(III)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\alpha\text{-cis-[Co(trien)(glyH)]}^3+)</td>
<td>8.7</td>
<td>505</td>
<td></td>
</tr>
<tr>
<td>((\text{ClO}_4)_2\text{H}_2\text{O})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(IV)</td>
<td></td>
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</tbody>
</table>

Fig. 2—Absorption spectra of \(\alpha\text{-cis-[Co(trien)(glyH)]}^3+\) and its binuclear complex with \([\text{Cu(II)}][\text{Co(III)}]_r = 0.01, [\text{Cu(II)}]_r = 0.003\) mol dm\(^{-3}\), \(pH = 6.22\) and absorbance versus \(\lambda\) nm plots (a) \([\text{Co(III)}]_r + [\text{Cu(II)}]_r\) mixture; (b) sum of absorbances for \([\text{Cu(II)}]_r\) and \([\text{Co(III)}]_r\) taken independently; (c) \([\text{Co(III)}]_r\) only; (d) \([\text{Cu(II)}]_r\) only at \(pH 5.5\); and (e) (a-b)

Results

Spectrophotometric evidence for cobalt(III)-copper(II) complex formation

Spectra of solutions of complexes I and IV and that of 2:1 mixtures of each of the complexes and copper(II) at \(pH 5.5\) show (Figs 1 and 2) that in the presence of Cu(II), the maximum absorption of the complexes I and IV appearing at 500 and 505 nm shifts to 505 to 510 respectively. There is also a significant enhancement of absorbance in the UV region. These spectral shifts indicate specific interaction between Cu(II) and Co(III) complexes. The difference absorption spectrum (\(\Delta A\) versus \(\lambda\) nm plot, Fig. 2) of Cu(II)-\(\alpha\text{-cis-[Co(trien)(gly)]}^3+\) system with \([\text{Cu(II)}]_r/ [\text{Co(III)}]_r = 1/3\), at \(pH 6.22\) also provides good evidence for the formation of a Co(III)-Cu(II) binuclear species, the absorption maximum of which appears around 650 nm, which is quite apart from \(^2E_g \rightarrow ^2T_2g\) transition (830 nm)\(^{16}\) of \([\text{Cu(H}_2\text{O)}_6]^2+\). The absorption maximum at 650 nm may be ascribed to Cu(II) having N\(_4\)O\(_2\) ligand environment.

Potentiometric measurements

From the \(pH\)-titration data the values of the acid dissociation constants of the complexes(I—IV) were obtained by the method of Irving and Rosotti\(^{17}\). The equilibria of interest are given by Eqs (3) and (4).
\[ N_5 \text{CoOC(NH}_3\text{)}_2^{3+} + k_1 \overset{K_1}{\rightleftharpoons} N_5 \text{CoOC(NH}_3\text{)}_2^{2+} + \text{H}^+ \quad \ldots (3) \\
N_5 \text{CoOC(OH}_3\text{)}_2^{3+} + k_2 \overset{K_2}{\rightleftharpoons} \left[ N_5 \text{CoOC(OH}_3\text{)}_2^{2+} - k_2 \right] + \text{H}^+ \quad \ldots (4) \\
\]

where, \( N_5 = 5(\text{NH}_3) \); \( N_4 = 2(\text{en}) \) or trien and \( R = \text{CH}_3 \) or \( \text{CH}_2 \). The values of \( \tilde{n}_A \) [average number of protons bound per cobalt(III) species] were evaluated at various \( \rho \)H values from titration curves for complex + HClO\(_4\) and HClO\(_4\) alone using the formula of Irving-Rossotti\(^{17}\) (Eq. 5).

\[
\tilde{n}_A = \frac{Y \text{T}^o + (V^o - V')N}{V^o} \quad \ldots (5)
\]

In Eq. (5) \( \text{T}^o = [\text{complex}] \); \( N = \text{alkali concentration} \); \( V^o = \text{total initial volume of the mixture} (= 50 \text{ cm}^3) \); \( Y = \text{number of dissociable protons per molecule of the complex exclusive of the protons of the amine ligands attached to Co(III)} \); and \( V, V' \) respectively are the volumes of alkali of strength \( N \) needed to raise the \( \rho \)H of 50 ml of HNO\(_3\) of a given strength and 50 ml of a solution containing HNO\(_3\) of same strength and complex solution of definite strength to the same value. The values of the proton ligand stability constants collected in Table 2 were computed\(^{18}\) from the plots of \( \tilde{n}_A \) versus \( \rho \)H. The stepwise formation constants of the metal complexes were evaluated from the formation curves\(^{17}\) [\( \tilde{n} \) versus \( \rho L \) plots, where \( L \) denotes the concentration of cobalt(III) complexes, \( \tilde{n} = \text{average number of } L \text{ bound per } M^2^+ \text{ ion} \)]. The values of \( \tilde{n} \) and the exponent \( \rho L \) for the uncomplexed cobalt(III) substrate were calculated from the titration curves for cobalt(III) substrates in the presence and absence of \( M^2^+ \) ions using the formula of Irving and Rossotti\(^{18}\) [Eqs (6) and (7)]

\[
\tilde{n} = \frac{(V^o - V')N}{V^o} \quad \ldots (6)
\]

\[
\rho L = \log_{10} \left\{ \sum_{j=0}^{\infty} \beta_j (1/\text{antilog } \beta_j) \right\} + \left( T_l - \tilde{n} T_m \right) \quad \ldots (7)
\]

In Eqs (6 and 7) \( T_m = [M^{n+}]; V^o, V' \) are the volumes of alkali referring to the same \( \rho \)H for titration of \( M^{n+} + \text{complex} + \text{HNO}_3 \) and \( \text{complex} + \text{HNO}_3 \) mixtures respectively, \( 1/\text{antilog } \beta = [H^+] \); and \( \beta \) is the practical overall formation constant. The calculated values of formation constants are given in Table 2.

Plots of \( K(N,CoX-M)\) against \( K(X-M) \) [\( X = \text{gly}^-, \beta-\text{ala}^- \)] (Fig 3), where \( K(N,CoX-M) \) and \( K(X-M) \) denote the respective formation constants, are linear with slopes of 0.69 ± 0.01.

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### Table 2—Proton-ligand Stability Constant of Complexes and Formation Constants of Bi- and Tri-nuclear Species of Co(II), Ni(II) and Cu(II)

<table>
<thead>
<tr>
<th>Ligand used</th>
<th>Constants</th>
<th>( H^+ )</th>
<th>( Co^{2+} )</th>
<th>( Ni^{2+} )</th>
<th>( Cu^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_2\text{gly}]^{2+})</td>
<td>( \log K_1 )</td>
<td>8.55 ± 0.01</td>
<td>3.04 ± 0.04</td>
<td>3.91 ± 0.01</td>
<td>5.61 ± 0.05</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_2\text{β-ala}]^{2+})</td>
<td>( \log K_1 )</td>
<td>9.12 ± 0.02</td>
<td>2.61 ± 0.09</td>
<td>3.44 ± 0.08</td>
<td>5.26 ± 0.11</td>
</tr>
<tr>
<td>(\text{cis}[\text{Co(en)}_2\text{gly}]^{2+})</td>
<td>( \log K_1 )</td>
<td>8.80 ± 0.05</td>
<td>4.00 ± 0.05</td>
<td>6.50 ± 0.10</td>
<td>9.00 ± 0.10</td>
</tr>
<tr>
<td>(\log K_2 )</td>
<td>7.50 ± 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_2 )</td>
<td>16.30 ± 0.15</td>
<td>7.10 ± 0.10</td>
<td>11.2 ± 0.20</td>
<td>13.65 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>(\text{α-cis}[\text{Co(trien)}\text{gly}]^{2+})</td>
<td>( \log K_1 )</td>
<td>8.75 ± 0.03</td>
<td>6.00 ± 0.05</td>
<td>6.80 ± 0.06</td>
<td>8.90 ± 0.10</td>
</tr>
<tr>
<td>(\log K_2 )</td>
<td>7.63 ± 0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\log K_2 )</td>
<td>16.38 ± 0.06</td>
<td>9.80 ± 0.10</td>
<td>12.10 ± 0.11</td>
<td>13.70 ± 0.15</td>
<td></td>
</tr>
</tbody>
</table>

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Temp = 27°C; ionic strength = 0.3 mol dm\(^{-3}\)  
Temp = 34°C; ionic strength = 0.1 mol dm\(^{-3}\)
Discussion

It is worth noting that the 1:1 binuclear complexes of $M^{2+}$ with $[(\text{NH}_3)_2\text{Co(gly)}]^2^+$, $[(\text{NH}_3)_5\text{Co(}\beta\text{-ala})]^2^+$ and 1:2 trinuclear complexes with $[\text{N}_4\text{Co(gly)}_2]^+$ ($\text{N}_4 = \text{en or trien}$) follow Irving-Williams stability order: $\text{Co}^{II} < \text{Ni}^{II} < \text{Cu}^{II}$. The formation constants further reflect that complexing ability of the half-bonded glycine in $[(\text{NH}_3)_2\text{Co(gly)}]^2^+$ is higher than that of $\beta$-alanine in $[(\text{NH}_3)_2\text{Co(}\beta\text{-ala})]^2^+$ as observed in the corresponding mononuclear metal ligand chelate complexes due to ring size effect. This together with the fact that the stability sequence of these binuclear species is opposite to that of $pK$ of the corresponding $\text{Co(III)}$ substrates suggest that the binuclear species have chelate structures involving $M$. The formation constants of $\text{N}_4\text{Co(gly)}^3^+$ species are significantly higher than those of $[(\text{NH}_3)_5\text{Co(gly)}]^4^+$ which cannot be reconciled with the charge factor alone. Potentiometric titration data do not give indication of a 1:1 species, $\text{N}_4\text{Co(gly)}^3^+$, which suggest that the free $\text{NH}_2$ groups of both the half-bounded glycinate residues are coordinated to $M^{2+}$ ions in $\text{N}_4\text{Co(gly)}_2^3^+$.

The overall formation constants ($\log \beta_2$) of the trinuclear species also decrease in the order $\text{Co(II)} < \text{Ni(II)} < \text{Cu(II)}$ with $\beta_2/K_1$ significantly less than $K_1$ in each case, as normally expected for the successive stepwise constants.

References