Chemistry Department
The University of Glasgow
Glasgow G12 8QQ
Scotland

K. J. ELLIS*
A. McAULEY

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*Present address: Biochemistry Department, J.C.S.M.R., Australian National University, Canberra, Australia.

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Electron transfer reaction in amino acid substituted pentamine cobalt(III) ions

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A NUMBER of workers[1–5] have studied reactions involving substitution of aminoacids and their esters in cobalt(III) octahedral complexes. However, little attention was paid to direct substitution of amino acids in pentammino cobalt(III). Investigations in this direction were carried out by Malik and Aslam[6], who synthesised a number of amino acid substituted pentammino cobalt(III) complexes and studied their physico-chemical properties. These investigations have now been extended to some electron transfer reactions, to examine the role of amino acids as electron mediators in such reactions.

EXPERIMENTAL

All solutions were prepared with water distilled from alkaline permanganate solution and redistilled twice. The solution containing chromium(II) was prepared by reducing chromium(III) perchlorate in 0·1 M $HClO_4$ with amalgamated zinc[7]. Chromium(II) acetate was precipitated by adding sodium acetate to remove zinc. The washed precipitate of Chromium(II) acetate was redissolved in 0·1 M $HClO_4$. The whole procedure was carried out in an atmosphere of CO_2, which had been scrubbed with chromium(II) perchlorate to remove all oxidising material. All solutions were de-aerated by bubbling CO_2 before addition to the reaction vessel. The apparatus for storing and dispensing Chromium(II) was similar to that described by Lingane and Pecsok[7]. Solution of chromium(II) perchlorate was prepared by reducing $K_2Cr_2O_7$ in $HClO_4$ with H_2O_2 and removing the $KClO_4$ formed. The solution was boiled for sufficient time to decompose excess of H_2O_2 added.

The amino acid substituted pentammin cobalt(III) complexes were prepared[6] by the following method. Amino acid (0·01 mole) was added to 300 ml of a solution containing 2·49 g (0·01 mole) of $Co^{III}(NH_3)_5ClOCl_2$. The mixture was heated at 60°C in a water thermostat till it turned purple. The resulting solution was concentrated under reduced pressure (below 40 mm Hg) to a volume of 20 ml. After cooling, the solution was held overnight at 0°C in a refrigerator. The purple crystals formed were filtered and washed with 1:1 water–ethanol mixture and finally with absolute alcohol. The product having the composition, $[Co(NH_3)_5OOCRN^+H_3]Cl_3$, was obtained. It was recrystallised from hot water (60°C). The complexes were prepared using DL-alanine, DL-valine, DL-serine, DL-leucine, DL-isoleucine, DL-threonine and L-arginine. The complexes were analysed for cobalt, chlorine and nitrogen using standard methods[8–10] (Table 1). Absorption maxima, recorded on Unicam SP 500, were found to exist between 350 and 360 nm. The absorption maxima of the chromium(III)–amino acid complexes[11] were found to exist between 560 and 570 nm.

The reaction was carried out in a 500 ml flask fitted with four ground glass entries, one to accommodate the delivery tube of the burette, one for introducing reagents and the other two for entry and exit of CO_2. A stop-cock at the bottom of the flask served as drain. The solution for reaction was made up, omitting chromium(II), introduced into the flask, and allowed to stand in a water thermostat for 0·5 hr to attain thermal equilibrium. The reaction was initiated by adding the requisite amount of chromium(II) solution and followed spectrophotometrically at 355 nm using 10 mm silica cells. At this wave length, both chromium(II) and the reaction products show weak absorption. The final O.D. of the mixtures containing excess of the cobalt(III) complex was determined after allowing the reaction mixture to stand overnight at about 20°C. The ionic strength was maintained at 1·0 in all the runs with sodium perchlorate. An inert atmosphere of CO_2 was maintained throughout the experiments.

The following equations[12], were employed to calculate the ratio of the Co(III) complex and Cr(II) at any time "t" during the reaction:

$$\frac{R_t}{Cr_t} = \frac{(O.D.)_t - 1[R_0(\epsilon_p - \epsilon_{Cr}) + Cr_0 \cdot \epsilon_{Cr}}{(O.D.)t - (O.D.)_\infty}$$

where R_t and Cr_t are the concentrations of the cobalt(III) complex and Cr(II) respectively at time "t". R_0 and Cr_0 are the initial concentrations of Co(III) complex and Cr(II) while ϵ_p and ϵ_{Cr} are the extinction coefficients of the products [Co(II) and Cr(III) in equivalent amounts] and Cr(II) respectively. "l" is the cell length (1 cm). When Cr(II) is in excess, the O.D. cannot be determined easily

Table 1. Chemical analysis, molar conductance and absorption spectral data of the amino acid substituted pentammine cobalt(III) chlorides

Ligand	Chemical analysis Co% Found	Co% Calc.	Cl% Found	Cl% Calc.	N% Found	N% Calc.	Molar conductance (Ω^{-1} cm^2)	Wavelength of max. absorption ($\lambda_{max} \pm 1$ nm)
DL-Alanine	17·25	17·36	31·41	31·33	24·91	24·75	295	355,520
DL-Valine	16·15	16·03	29·03	28·93	22·96	22·86	290	360,515
DL-Serine	16·69	16·58	29·98	29·92	23·55	23·65	275	355,515
DL-Threonine	15·80	15·95	28·91	28·79	22·79	22·75	290	360,520
DL-Leucine	15·55	15·45	27·71	27·88	22·07	22·03	275	355,520
DL-Isoleucine	15·31	15·45	27·93	27·88	22·00	22·03	280	355,515
L-Arginine	13·73	13·87	24·42	25·05	29·61	29·68	295	357,520
Chloro-complex							222	357,527

because on keeping the solutions, dissociation of the Cr(III) complex sets in. The following relation was therefore employed to calculate Rt/Cr_t:

$$\frac{Cr_t}{R_t} = \frac{(O.D.)_0 - (O.D.)_t - Cr_0[\epsilon_R - \epsilon_p + \epsilon_{Cr}]}{(O.D.)_0 - (O.D.)_t - R_0[\epsilon_R - \epsilon_p + \epsilon_{Cr}]}$$

where ϵ_R is the extinction coefficient of the Co(III) complex. For a second order reaction:

$$k = \frac{2{\cdot}303}{t(R_0 - Cr_0)} \log \frac{Cr_0 R_t}{Cr_t R_0}$$

or

$$t = \frac{2{\cdot}303}{k(R_0 - Cr_0)} \log \frac{Cr_0}{R_0} + \frac{2{\cdot}303}{k(R_0 - Cr_0)} \log \frac{R_t}{Cr_t}.$$

The specific rates were then obtained from the slopes of plots of log R_t/Cr_t vs time.

RESULTS AND DISCUSSIONS

These electron transfer reactions may be represented as

$$(NH_3)_5CoL^{3+} + Cr^{2+} 5H^+ \rightarrow Co^{2+} + CrL^{3+} + 5NH_4^+.$$

The spectra of the product solutions show absorption maxima between 560 and 570 nm corresponding to CrL^{3+}, which supports the view that the amino acid (L) is transferred from cobalt to chromium. This suggests that the reaction is taking place by an inner sphere mechanism.

Kinetic data for the complexes is summarised in Table 2. Calculations have been based on the plots of log R_t/Cr_t vs time, which were linear to 85–90% completion of the reaction. Runs employing a wide range of condentrations (0·01–0·0005 M) of Cr(II) and the Co(III) complex, show that the reactions follow a second order kinetics. The values of $\Delta H\ddagger$ and $\Delta S\ddagger$ have been calculated from the variations in rate with temperature (2°, 14°, 25° and 37°C). Estimated uncertainties in the activation parameters are ±0·25 kCal/mole in $\Delta H\ddagger$ and ±1 eu in $\Delta S\ddagger$. A number of runs in the range $0{\cdot}01\ M \leq [H^+] \leq 1{\cdot}0\ M$ show that there is no hydrogen ion dependence of the rate of reduction of the cobalt(III) complex by Cr^+ [2].

The similarity of activation parameter values (Table 3) among all the amino acid pentamminocobalt(III) ions studied implies that no change in the reduction mechanism occurs as the chain length of the amino acids varies. Comparison of the activation parameters for the Cr(II) reduction of the acetato and the amino acid complexes shows that the lower rates of reduction for the latter are due to more negative activation entropies. This is consistent with the fact that the complex bears an extra positive charge.

The efficiency of various amino acids as electron mediators can be compared from the kinetic data. The rates show a decrease with the increase in chain length, i.e. alanine to leucine which have one COOH and one NH_2 group only and serine to threonine which have one additional OH group. The decrease in rate is due to steric hinderance to the adjacent attack by Cr(II). The decrease in rate is also reflected in the small difference in ΔS^* values. It thus appears that as long as one α-hydrogen is present, a configuration can be found for which steric repulsions to the approach of the chromous ion to the

Table 2. Kinetic data for the reduction of amino acid pentammine cobalt(III) ions

Ligand	Temp. °C	k_1(M^{-1} $sec^{-1} \times 10^2$) 2	14	25	37
DL-Alanine		1·6	2·9	4·9	8·2
DL-Valine		1·3	2·5	4·2	7·2
DL-Isoleucine		1·15	2·25	3·9	6·7
DL-Leucine		1·9	3·4	5·5	9·0
DL-Serine		2·1	3·7	6·0	9·9
DL-Threonine		0·9	1·8	3·3	6·0
L-Arginine		4·5	7·5	11·5	17·5

$\mu = 1{\cdot}0$; $[H^+] = 0{\cdot}1$ M; Each value is the mean of two runs.

Table 3. Energy data for the reduction of carboxylato pentammine cobalt(III) ions (temp. = 25°C)

Ligand	R* (M^{-1} sec^{-1})	ΔH‡ (kcal/mol)	ΔS‡ (e.u.)	Ref.
DL-Alanine	0·049†	8·0	−37	This work
DL-Valine	0·042†	8·2	−38	This work
DL-Isoleucine	0·039†	8·6	−40	This work
DL-leucine	0·055†	7·6	−37	This work
DL-Serine	0·060†	7·55	−37	This work
DL-Threonine	0·033†	9·2	−43	This work
L-Arginine	0·115†	6·7	−33	This work
$-OOCCH_3$	0·35†	8·2	−33	[16]
$-OOCC(CH_3)_3$	0·007†	11·1	−31	[16]
$-OOCCF_3$	0·017†,‡	9·3	−35	[16]
$-OOCCH_2N^+H_3$	0·064§	7·7	−38	[13]
$-OOCCH_2NH_2(CH_3)^+$	0·044§	8·0	−38	[13]
$-OOCCH_2\overset{+}{N}H(CH_3)_2^+$	0·038§	7·5	−40	[13]
$-OOCCH_2N(CH_3)_3^+$	0·016§	7·7	−41	[13]

*μ = 1·0; †$[H^+]$ = 0·1 M; ‡μ = 0·2; §$[H^+]$ = 0·55.

cobalt(III) complex are not expected to differ significantly from one complex to the next. Similar viewpoint has been put forward by Holwreda[13] and Barrett[14] for the substituted glycinato complexes on the basis of experiments will molecular models.

The low rates of reduction rule out the possibility of direct transfer of the electron. The low values of ΔH‡ are consistent with the formation of bridged activated complex[15] during the reaction, with the amino acid molecule acting as the bridge ligand. The reaction may be represented as:

$$[(NH_3)_5CoL]^{3+} + [Cr(H_2O)_6]^{2+}$$

$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{(NH_3)_5CoL\,Cr(H_2O)_5\} + H_2O.$$

$$[(NH_3)_5CoLCr(H_2O)_5] \xrightarrow{k_2} \text{products.}$$

The rate is given by,

$$-d[Co(III)]/dt = \frac{k_1k_2}{k_{-1}+k_2}[Cr^{2+}][(NH_3)_5CoL^{3+}].$$

Department of Chemistry R. BEMBI
University of Roorkee W. U. MALIK
Roorkee
India

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