Influence of Electrolytic Dissociation upon Rates of Reactions. Part 10.[1] Acid-catalysed Aquations of some Penta-ammine(carboxylato)cobalt(III) Ions in Aqueous Solutions

Derek Smith, Mohamed F. Amira, Pauzi B. Abdullah, and Cecil B. Monk *
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, Dyfed SY23 1NE

Rate coefficients of aquation at constant ionic strength in lithium perchlorate–perchloric acid media of a series of penta-ammine(carboxylato)cobalt(III) complexes $[Co(NH_3)_5L]^{n+}$ have been calculated from u.v. absorbance measurements. With most of these, increases in the observed rate coefficients are not proportional to increases in the acid concentrations. The data have been used to calculate association constants of protonated forms of the complexes and the corresponding rate coefficients of aquation. The obtained association constants are 0.64 (L = acetate; I = 2.0, 40 °C), 0.1 (L = *o*-methoxybenzoate; I = 2.0, 40 °C), 116 (L = oxalate; first association constant, I = 0.5, 60 °C), 0.24 (L = malonate; second association constant, I = 2.0, 40 °C), 0.69 (L = succinate; second association constant, I = 2.0, 40 °C), 0.02 dm^3 mol^{-1} (L = *o*-phthalate; second association constant, I = 2.0 mol dm^{-3}, 40 °C). With the tartrato-complex the observed rate coefficients increased linearly with increasing $[HClO_4]$ and this is also so with the oxalato-complex for $I > 0.5$ mol dm^{-3} but such increases are small when compared with those of the other dicarboxylato-complexes of the present studies. U.v. spectral decreases at constant wavelength with increasing $[HClO_4]$ under virtually static conditions have also been used to estimate the association constants of the protonated complexes. The exceptions, since no spectral decreases were found, are the *o*-methoxybenzoato-complex, the oxalato-form at $[HClO_4] > 0.5$ mol dm^{-3}, and the doubly protonated tartrato-complex. The values obtained are 0.68 (L = acetate; I = 2.0, 30 °C), 125 (L = oxalate; first association constant, I = 0.5, 60 °C), 0.37 (L = malonate; second association constant, I = 2.0, 40 °C), 0.67 (L = succinate; second association constant, I = 2.0, 40 °C), 0.1 dm^3 mol^{-1} (L = *o*-phthalate; second association constant, I = 2.0 mol dm^{-3}, 40 °C). These are in reasonable agreement with the above values derived from the kinetic data and from the latter the rate coefficients of aquation of the protonated species have been estimated. There appear to be broad relationships between the rate coefficients of the protonated forms and the association constants (comparing acetate with *o*-methoxybenzoate and succinate with malonate). This can perhaps account for the oxalate, tartrate, and *o*-phthalate complexes showing little evidence of double protonation. This feature is also discussed in terms of ligand chain lengths and it is also noted that in contrast to the first association constants of the protonated dicarboxylate complexes which are large but have relatively little catalytic effect, the second association constants are small but have strong influences upon the rates of aquation.

In acidic media, rates of aquation of metal complex ions containing anionic ligands of weak acids are usually related to the H^+ ion concentrations of the media. Under conditions of constant ionic strength (I), if only one such ligand is involved, and it is monoprotic, a relationship frequently used is equation (1) where k represents rate coefficients.

$$k(\text{obs.}) = k_0 + k'_{H1}[H^+] \qquad (1)$$

A few results have been obtained [2-4] under conditions of varying ionic strengths, and these have been fitted to expressions such as (2) where B' and C' are empirical parameters, but it has been proposed [5] that a more correct form [*e.g.* for penta-ammine(azido)cobalt(III)] is equation (3) where A' is the

$$k(\text{obs.}) = k_0 + B'[H^+] + C'[H^+]^2 \qquad (2)$$

$$k(\text{obs.}) = k_0 + 10^{4A'/(1+I^{\frac{1}{2}})}k'_{H1}[H^+] \qquad (3)$$

Debye–Hückel activity coefficient factor. This interpretation is based upon the supposition that an activated complex is formed between the complex ion (charge +2) and the H^+ ion.

It has also been proposed [6,7] that these anionic ligands become protonated while in the complex ion and this weakens the metal–ligand bond. Thus, in terms of the reactions (4) and (5) where L represents the replaceable anionic ligand and Cp

$$\text{CpL} + H_2O \longrightarrow \text{activated complex} \xrightarrow{k_0} \text{CpH}_2\text{O} + \text{L} \qquad (4)$$

$$\text{CpLH} + H_2O \longrightarrow \text{activated complex} \xrightarrow{k_{H1}} \text{CpH}_2\text{O} + \text{HL} \qquad (5)$$

represents the inert part of the complex ion, activated complexes are formed by both unprotonated and protonated species. The latter is the more kinetically active, *i.e.* $k_{H1} > k_0$.

The association constant K_{A1} for the equilibrium (6) can be expressed by equation (7) where c_1 and c_2 are the stoicheiometric concentrations of complex ion and H^+ ion respectively and x represents the concentration of CpLH. K_{A1} can be assessed by spectrophotometry where $c_2 \gg c_1$, so a combination of equation (7), using c_2 for $(c_2 - x)$, with equation (8) gives equation (9). Equations (9) and (1) are virtually

$$\text{CpL} + H^+ \rightleftharpoons \text{CpLH} \qquad (6)$$

$$K_{A1} = x/(c_1 - x)(c_2 - x) \qquad (7)$$

$$k(\text{obs.})c_1 = k_0(c_1 - x) + k_{H1}x \qquad (8)$$

$$k(\text{obs.}) = k_0 + K_{A1}c_2(k_{H1} - k_0)/(1 + K_{A1}c_2) \qquad (9)$$

Table 1. Rate coefficients of aquation and association constants of penta-aquo(cyano)chromium(III)

(*a*) $I = 1.0$ mol dm^{-3} [a]

Temp. (θ_c/°C)	35	54	55
Medium	$NaClO_4$–$HClO_4$	$NaClO_4$–$HClO_4$	$LiClO_4$–$HClO_4$
K_{A1}/dm^3 mol^{-1}	0.30	0.43	0.29
10^3k_0/s^{-1}	0.029	0.56	0.96
10^3k_{H1}/s^{-1}	4.02	25.1	34.8

(*b*) $I = 2.0$ mol dm^{-3} [b]

Temp. (θ_c/°C)	25	35	40
Medium	$NaClO_4$–$HClO_4$	$NaClO_4$–$HClO_4$	$NaClO_4$–$HClO_4$
K_{A1}/dm^3 mol^{-1}	0.19	0.25	0.25
10^3k_0/s^{-1} —	0.011	0.04	0.11
10^3k_{H1}/s^{-1}	3.2	7.5	13.0

[a] Data of Birk and Espenson.[9] [b] Data of Wakefield and Schaap.[8]

equivalent when K_{A1} is very small but k'_{H1} of (1) is then equal to $K_{A1}(k_{H1} - k_0)$ of (9).

Studies such as those of Monacelli *et al.*[6] at a low constant ionic strength ($I = 0.1$ mol dm^{-3}) with a series of $[M(NH_3)_5L]^{2+}$ ions (M^{III} = Co, Rh, or Ir; L = monocarboxylate) appear to be well fitted by equation (1) although there are marked catalytic effects and this implies that only one activated complex is formed, *i.e.* between CpL and H^+(aq), or that K_{A1} is very small. Better conditions in which to promote the formation of CpLH are provided by the use of high constant ionic strengths and this has been done by Wakefield and Schaap[8] for studies of the aquation rates of penta-aqua(cyano)chromium(III). They used $HClO_4$–$NaClO_4$ media at $I = 2.0$ mol dm^{-3} and their interpretation of the rates is based on a modification of equation (9), namely equation (10), together with use of linear least-mean-squares

$$1/[k(\text{obs.}) - k_0] = 1/(k_{H1} - k_0) + 1/[K_{A1}c_2(k_{H1} - k_0)] \quad (10)$$

(LLMS) analysis. They adjusted k_0 to the point of minimum standard deviation of a ' plot ' of the left-hand terms against $1/c_2$. Some of the K_{A1}, k_{H1}, and k_0 values thereby obtained are shown in Table 1 together with those we have derived from a similar study by Birk and Espenson.[9] The K_{A1} values are small and the large k_{H1}/k_0 ratios suggest that a small degree of protonation has a profound effect upon the rates of aquation.

Deutsch and Taube[10] in an analogous study of aquation rates of acetatopenta-aquachromium(III) obtained $K_{A1} = 5.3 \pm 0.5$ dm^3 mol^{-1} at $I = 4.0$ mol dm^{-3} and 25 °C, and in addition noted spectral decreases of the complex at a fixed wavelength with increasing values of c_2. These readings were taken at short time intervals so that changes due to aquation were negligible. For 1-cm cells, a combination of equation (11) (A = absorbance, ε = molar absorption coefficient) with equation (7) gives equation (12). The values of K_{A1},

$$\varepsilon(\text{obs.}) = A(\text{obs.})/c_1 = \varepsilon_{CpL}(c_1 - x) + \varepsilon_{CpLH}x \quad (11)$$

$$\varepsilon(\text{obs.}) = \varepsilon_{CpL} + K_{A1}c_2(\varepsilon_{CpLH} - \varepsilon_{CpL})/(1 + K_{A1}c_2) \quad (12)$$

ε_{CpL}, and ε_{CpLH} which gave the best fit to ε(calc.) compared with ε(obs.) were found. This produced $K_{A1} = 3.25 \pm 0.2$ dm^3 mol^{-1} at $I = 4.0$ mol dm^{-3} and 25 °C, which is in acceptable agreement with the above estimate from the kinetic data. What might be termed ' static spectral decreases ' have also been noted with other complexes containing monoprotic ligands, *e.g.* nitro-[2] and azido-penta-amminecobalt(III),[3] penta-ammine(azido)rhodium(III),[3] and penta-ammine(azido)-chromium(III).[7]

When the replaceable ligand is a dicarboxylate, two stages of protonation can be envisaged. The most studied of such complexes is penta-ammine(oxalato)cobalt(III). At $I = 1.0$ mol dm^{-3}, Andrade and Taube[11] found that plots of k(obs.) *versus* c_2 are strongly curved up to c_2 *ca.* 0.4 and then linear up to $c_2 = 1.0$. They interpreted the rate coefficients in terms of equation (13). The values of k_{H1} and k_2 were obtained from

$$k(\text{obs.})c_1 = k_0[Cp(C_2O_4)^+] + k_{H1}[Cp(C_2O_4H)^{2+}] + k_2[Cp(C_2O_4H)^{2+}]c_2 \quad (13)$$

the k(obs.) values at $c_2 = 0.4$ and 1.0 where $[Cp(C_2O_4)^+] \simeq 0$ and $[Cp(C_2O_4H)^{2+}] \simeq c_1$. The k(obs.) values for $c_2 < 0.4$ mol dm^{-3} were then used to calculate $[Cp(C_2O_4)^+]$, k_0, and K_{A1}, and the whole scheme improved by iteration. Static spectral decreases at $I = 1.0$ mol dm^{-3} and 25 °C were also found and K_{A1} was derived from equation (14) [ox = oxalate-

$$K_{A1} = [\varepsilon_{Cp(Ox)} - \varepsilon(\text{obs.})]/c_2[\varepsilon(\text{obs.}) - \varepsilon_{Cp(Hox)}] \quad (14)$$

(2–)] for which $\varepsilon_{Cp(Ox)}$ was taken from ε(obs.) in NaOH solutions and $\varepsilon_{Cp(Hox)}$ from ε(obs.) in 1 mol dm^{-3} $HClO_4$. At 70 °C, the kinetic data yielded $K_{A1} = 59 \pm 9$ dm^3 mol^{-1} while at 25 °C the spectral decreases gave $K_{A1} = 113 \pm 3$ dm^3 mol^{-1}.

Further figures for this complex at $I = 0.3$ have been published by Dash and Nanda.[12] These were examined using equation (15). Linear plots of k(obs.) against c_2 for c_2 =

$$k(\text{obs.}) = [k_0/(c_2K_{A1}) + k_{H1} + k_2c_2]/[1 + 1/(c_2K_{A1})] \quad (15)$$

0.15—0.3 mol dm^{-3} gave k_{H1} (intercept) and k_2 (slope) while plots of $[k(\text{obs.}) - k_{H1} - k_2c_2]$ against c_2 for $c_2 > 0.15$ mol dm^{-3} gave k_0/K_{A1} (intercept) and $1/K_{A1}$ (slope). Dash and Nanda[12] also obtained direct values of K_{A1} from static measurements using equation (16). We assume $\varepsilon_{Cp(Ox)}$ was

$$1/[\varepsilon_{Cp(Ox)} - \varepsilon(\text{obs.})] = 1/[\varepsilon_{Cp(Ox)} - \varepsilon_{Cp(Hox)}] + 1/K_{A1}[\varepsilon_{Cp(Ox)} - \varepsilon_{Cp(Hox)}]c_2 \quad (16)$$

obtained from ε(obs.) in NaOH solution. $\varepsilon_{Cp(Hox)}$ is not needed since K_{A1} is the reciprocal of the slope of the plot of the left-hand term against $1/c_2$. At 66 °C, for example, the kinetic analysis gave $K_{A1} = 54$ while the spectral shifts gave K_{A1} = 79 dm^3 mol^{-1} at 45 °C and 97 dm^3 mol^{-1} at 28 °C.

Dash and Nanda[13] have also reported rates of aquation of malonato-, succinato-, *o*-phthalato-, and *o*-methoxybenzoato-penta-amminecobalt(III) complexes at $I = 0.3$ mol dm^{-3}, c_2 = 0.005—0.3 mol dm^{-3}, and 55—70 °C. The rates all appear to fit equation (1) in terms of equation (17) where k_1

$$k(\text{obs.}) = k_1 + k_2c_2 \quad (17)$$

and k_2 signify rate coefficients for the spontaneous and acid-catalysed aquation respectively of the CpLH forms.

Thus in general, several types of mechanism are postulated and the main objective of the present work has been to seek further evidence by obtaining results at high constant ionic strengths.

Experimental

The starting material for making the complexes was[14] penta-ammine(carbonato)cobalt(III) nitrate. Better yields are

Table 2. Association constants (K_{A1}, K_{A2}/dm^3 mol^{-1}) and absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) from static measurements

(*a*) Acetatopenta-amminecobalt(III)

$I = 2.0$ mol dm^{-3}, 30 °C, $10^4 c_1 = 3.71$ mol dm^{-3}, 255 nm. $K_{A1} = 0.68 \pm 0.02$

c_2/mol dm^{-3}	0.10	0.20	0.30	0.50	0.80	1.00	1.20	1.40	1.60	1.80	2.00
ε(obs.)	2 798	2 660	2 528	2 315	2 065	1 930	1 822	1 728	1 636	1 563	1 493
ε(calc.)	2 799	2 656	2 530	2 316	2 066	1 933	1 819	1 722	1 637	1 562	1 496

(*b*) Penta-ammine(*o*-methoxybenzoato)cobalt(III)

$I = 2.0$ mol dm^{-3}, 30 °C. No spectral decreases found.

(*c*) Penta-ammine(oxalato)cobalt(III)

$I = 0.5$ mol dm^{-3}, 40 °C, $10^4 c_1 = 4.77$ mol dm^{-3}, 300 nm. $K_{A1} = 117 \pm 3$,[a] 122 ± 3[b]

$10^4 c_1$/mol dm^{-3}	11.0	20.0	31.0	40.0	51.0	111.0	199.0	310.0	509
ε(obs.)	1 826	1 692	1 547	1 450	1 352	1 020	766	609	474
ε(calc.)[a]	1 827	1 689	1 550	1 455	1 355	1 007	763	610	478

$10^4 c_1$/mol dm^{-3}	603	704	799	902	1 016	1 452	1 742	2 033	2 541
ε(obs.)	443	413	397	374	357	315	302	285	281
ε(calc.)[a]	443	414	393	374	358	319	302	—	—

$I = 0.5$ mol dm^{-3}, 60 °C. $K_{A1} = 120 \pm 3$,[a] 128 ± 3.[b]
$I = 2.0$ mol dm^{-3}, 30 °C, $c_2 = 0.5$—2.0. No spectral decreases found.

(*d*) Penta-ammine(malonato)cobalt(III)

$I = 2.0$ mol dm^{-3}, 40 °C, $10^3 c_1 = 1.50$ mol dm^{-3}, 264 nm. $K_{A2} = 0.37 \pm 0.15$

c_2/mol dm^{-3}	0.20	0.40	0.60	0.80	1.00	1.40	1.60
ε(obs.)	645	641	638	633	629	627	622
ε(calc.)	645	641	637	633	630	625	623

$I = 2.0$ mol dm^{-3}, 30 °C. $K_{A2} = 0.36 \pm 0.10$

(*e*) Penta-ammine(succinato)cobalt(III)

$I = 2.0$ mol dm^{-3}, 40 °C, $10^3 c_1 = 2.11$ mol dm^{-3}, 260 nm. $K_{A2} = 0.67 \pm 0.03$

c_2/mol dm^{-3}	0.10	0.20	0.40	0.60	0.80	1.00	1.30	1.60	2.00
ε(obs.)	524	510	471	447	427	412	392	373	349
ε(calc.)	525	506	475	449	428	410	389	371	352

$I = 2.0$ mol dm^{-3}, 30 °C. $K_{A2} = 0.56 \pm 0.02$

(*f*) Penta-ammine(tartrato)cobalt(III)

$I = 2.0$ mol dm^{-3}, 30 °C, $10^3 c_1 = 1.63$ mol dm^{-3}, 255 nm.
$c_2 = 0.10$ mol dm^{-3}, ε(obs.) $= 617$; $c_2 = 2.00$ mol dm^{-3}, ε(obs.) $= 612$

Insufficient spectral decreases for calculating K_{A2}.

(*g*) Penta-ammine(*o*-phthalato)cobalt(III)

$I = 2.0$ mol dm^{-3}, 40 °C, $10^4 c_1 = 1.276$ mol dm^{-3}, 252 nm. $K_{A2} = 0.1 \pm 0.05$

c_2/mol dm^{-3}	0.20	0.50	0.75	1.00	1.25	1.50	1.75	2.00
ε(obs.)	7 147	7 085	7 045	7 014	6 959	6 928	6 897	6 865
ε(calc.)[a]	7 147	7 087	7 042	7 001	6 962	6 927	6 895	6 865

[a] Determined using the terms in (19). [b] Determined using the terms in (18).

obtained by allowing the reacting mixture to stand for a few days in a cool fume-cupboard, rather than in bubbling air for 24 h. The carbonato-form was converted to and precipitated as the perchlorate of the aqua-form by perchloric acid. This was washed free of nitrate and samples were digested at about 70 °C with solutions of organic acids. After precipitation of the products with perchloric acid, these were collected on a glass filter crucible and washed free of acid by water, alcohol, and diethyl ether (the latter filtrate monitored with B.D.H. Universal Indicator), then dried at 110 °C. $LiClO_4$ solutions were made from AnalaR $HClO_4$ and Li_2CO_3 and adjusted to a pH of about 6.

Absorption measurements were made with a Pye-Unicam SP8-200 spectrophotometer which held four sets of cells (1 cm) for test and reference solutions. The instrument was also fitted with a cell temperature controller, temperature probe, Westrex model 43 printer and program control module for promoting timed print-outs of the absorbances. The reference cells held water. At the end of a run the test cells were wiped and re-read to check for contamination of the cell surfaces. Any differences were incorporated in the A_∞ readings (obtained as described in the text).

Results and Discussion

Association Constants.—Static spectral decreases at constant wavelengths with increasing values of c were found (Table 2) with the acetato-complex and were used for evaluating K_{A1}. No such decreases were found with the *o*-methoxybenzoato-complex. With the oxalato-complex, marked decreases were found in low acid concentrations, in agreement with Andrade and Taube [11] and with Dash and Nanda.[12] These decreases were used to calculate K_{A1}. No decreases were found for the oxalato-complex at high acid concentrations, where a second stage of protonation might occur, but decreases in these acid regions were found (Table 2) with the

Table 3. Rate coefficients of aquation (k/s^{-1}) and calculated association constants (K_{A1}, K_{A2}/dm^3 mol^{-1})

(*a*) Acetatopenta-amminecobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 248 nm. K_{A1} = 0.65 ± 0.03

c_2/mol dm^{-3}	0.025	0.050	0.10	0.30	0.60	0.80
10^5k(obs.)	0.20	0.37	0.70	1.85	3.25	4.12
10^5k(calc.)	0.17	0.36	0.71	1.92	3.31	4.04

c_2/mol dm^{-3}	1.00	1.20	1.40	1.60	1.80	2.00
10^5k(obs.)	4.69	5.21	5.65	6.01	6.38	6.69
10^5k(calc.)	4.66	5.19	5.64	6.04	6.39	6.70

(*b*) Penta-ammine(*o*-methoxybenzoato)cobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 244 nm. K_{A1} = 0.14 ± 0.02

c_2/mol dm^{-3}	0.05	0.10	0.20	0.40	0.80	1.00
10^5k(obs.)	0.35	0.55	0.85	1.50	2.90	3.60
10^5k(calc.)	0.32	0.51	0.88	1.59	2.90	3.50

c_2/mol dm^{-3}	1.20	1.40	1.60	1.80	2.00
10^5k(obs.)	4.00	4.65	5.17	5.65	6.10
10^5k(calc.)	4.08	4.62	5.15	5.65	6.13

(*c*) Penta-ammine(oxalato)cobalt(III)

I = 0.5 mol dm^{-3}, 60 °C, 263 nm. K_{A1} = 116 ± 2

10^4c_2/mol dm^{-3}	14.9	24.5	34.2	53.6	63.5	73.4	83.2	103.0
10^6k(obs.)	1.93	2.25	2.67	3.15	3.32	3.64	3.81	4.07
10^6k(corr.) [a]	1.92	2.23	2.63	3.09	3.24	3.55	3.71	3.94
10^6k(calc.)	1.87	2.27	2.60	3.13	3.35	3.53	3.70	3.98

10^4c_2/mol dm^{-3}	123.0	212.0	317.0	439.0	659.0	2 460	4 910
10^6k(obs.)	4.42	5.19	5.65	6.07	6.44	9.3	12.3
10^6k(corr.) [a]	4.27	4.93	5.26	5.53	5.64	—	—
10^6k(calc.)	4.21	4.85	5.24	5.49	5.74	—	—

I = 2.0 mol dm^{-3}, 40 °C, 250 nm. No evidence to permit calculation of K_{A2}

c_2/mol dm^{-3}	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00
10^6k(obs.)	1.06	1.30	1.57	1.80	2.14	2.37	2.70	2.98
10^6k(calc.)	1.02	1.30	1.58	1.85	2.13	2.40	2.68	2.96

(*d*) Penta-ammine(malonato)cobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 264 nm. K_{A2} = 0.24 ± 0.03

c_2/mol dm^{-3}	0.050	0.075	0.10	0.20	0.40	0.60
10^5k(obs.)	0.087	0.120	0.160	0.27	0.56	0.72
10^5k(calc.)	0.095	0.127	0.159	0.28	0.51	0.72

c_2/mol dm^{-3}	0.80	1.00	1.25	1.50	1.75	2.00
10^5k(obs.)	0.93	1.03	1.32	1.50	1.62	1.83
10^5k(calc.)	0.92	1.09	1.30	1.48	1.65	1.81

(*e*) Penta-ammine(succinato)cobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 256 nm. K_{A2} = 0.69 ± 0.08

c_2/mol dm^{-3}	0.10	0.20	0.30	0.40	0.60	0.80	1.25	1.50	1.75	2.00
10^5k(obs.)	0.45	0.83	1.05	1.61	2.13	2.52	3.25	3.55	3.84	4.20
10^5k(calc.)	0.43	0.83	1.19	1.51	2.06	2.51	3.28	3.61	3.88	4.12

(*f*) Penta-ammine(tartrato)cobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 255 nm. No evidence to permit calculation of K_{A2}

c_2/mol dm^{-3}	0.20	0.30	0.40	0.60	0.80	1.00	1.40	1.60	1.80	2.00
10^6k(obs.)	1.08	1.61	2.17	3.25	4.38	5.33	7.85	9.30	10.5	11.7
10^6k(calc.) [b]	0.92	1.51	2.10	3.29	4.50	5.70	8.00	9.20	10.4	11.6

(*g*) Penta-ammine(*o*-phthalato)cobalt(III)

I = 2.0 mol dm^{-3}, 40 °C, 250 nm. K_{A2} = 0.02 ± 0.01

c_2/mol dm^{-3}	0.10	0.20	0.30	0.40	0.60	0.80	1.00	1.25	1.40	1.75	2.00
10^6k(obs.)	0.38	0.69	0.99	1.26	1.85	2.35	2.96	3.64	4.01	4.88	5.68
10^6k(calc.)	0.40	0.69	0.98	1.26	1.82	2.38	2.93	3.62	4.02	4.96	5.62

[a] Using a plot of c_2 = 0.246 and 0.491 mol dm^{-3} against k(obs.) to correct for hydrolysis due to second stage protonation.. [b] Determined by LLMS.

Table 4. Summary of association constants (K_{A1}, K_{A2}/dm^3 mol^{-1}) and rate coefficients of aquation of [Co^{III}(NH$_3$)$_5$L]; $I = 2.0$ mol dm^{-3}, at 40 °C

L	k_0/s^{-1}	k_{H1}/s^{-1}	k_{H2}/s^{-1}	K_{A1}	K_{A2}	Slopes [a]
Acetate	3.0×10^{-7}	1.19×10^{-4}	—	0.65,[b] 0.68 [c]	—	7.7×10^{-5}
o-Methoxybenzoate	1.3×10^{-5}	2.73×10^{-4}	—	0.14 [b]	—	3.9×10^{-5}
Oxalate [d]	1.1×10^{-6}	6.3×10^{-6}	—	116 ± 2,[b] 125 ± 5 [c]	—	7.6×10^{-4}
Oxalate	—	1.9×10^{-7}	(4×10^{-5}) [e]	—	(0.03) [e]	1.4×10^{-6}
Malonate	—	2.9×10^{-7}	5.5×10^{-5}	—	0.24,[b] 0.37 [c]	1.33×10^{-5}
Succinate	—	1.0×10^{-7}	7.1×10^{-5}	—	0.69,[b] 0.67 [c]	4.9×10^{-5}
Tartrate	—	5.0×10^{-7}	(4×10^{-5}) [e]	—	(0.15) [e]	6.0×10^{-6}
o-Phthalate	—	1.0×10^{-7}	(4×10^{-5}) [e]	—	0.02,[b] 0.1 [c] (0.08) [e]	3.0×10^{-6}

[a] Slope = $K_{A1}(k_{H1} - k_0)$ for acetate, *o*-methoxybenzoate, and oxalate; slope = $K_{A2}(k_{H2} - k_{H1})$ for the others. [b] From the kinetics. [c] From spectrophotometic shifts. [d] $I = 0.5$ mol dm^{-3}, at 60 °C. [e] Estimated (see text).

succinato-, malonato-, and *o*-phthalato-complexes and from these, K_{A2} values were calculated for comparison with those deduced from k(obs.) data.

The K_{A1} values of the acetato- and oxalato-complexes were obtained by a non-linear least-squares method. This was based on the matrix inversion method of Moore [15] for analysing kinetic data of first-order reactions when only approximate initial and final absorbance readings are known. For the static situation, providing readings approaching those of ε_{CpL} and of ε_{CpLH} can be obtained and thus a rough value of K_{A1}, the terms required are, from equation (12), defined by the terms (18).

$$\begin{aligned}\delta\varepsilon/\delta\varepsilon_{CpLH} &= c_2/(K_{D1} + c_2)\\ \delta\varepsilon/\delta\varepsilon_{CpL} &= K_{D1}/(K_{D1} + c_2)\\ \delta\varepsilon/\delta K_{D1} &= c_2(\varepsilon_{CpL} - \varepsilon_{CpLH})/(K_{D1} \times c_2)^2\\ K_{D1} &= 1/K_{A1};\ \varepsilon = \varepsilon(\text{obs.}) \qquad (18)\end{aligned}$$

This approach is preferable to those of Andrade and Taube [11] and of Dash and Nanda [12] for obtaining K_{A1} since in our experience measurements in NaOH solutions to obtain ε_{CpL} for expressions such as (14) can drift rapidly with time due to base hydrolysis. Also, another form [13] of equation (14) which requires ε_{CpLH} from measurements in excess acid but does not require ε_{CpL} cannot be used if K_{A1} is relatively small since complete conversion to CpLH may not be achieved.

A second but more primitive method is to apply LLMS to equation (12) with the terms (19) and adjust K_{A1} until the

$$Y = \varepsilon(\text{obs.});\ X = c_2/(1 + K_{A1}c_2) \qquad (19)$$

minimum average deviation between ε(obs.) and ε(calc.) is reached. K_{A1} for the oxalato-complex was calculated by both methods and the answers agree to within about 3% (Table 2).

The above non-linear least-squares method was also used to calculate K_{A2} values for the malonato- and succinato-complexes. For these the appropriate terms are $\delta\varepsilon/\delta\varepsilon_{CpLH_2}$; $\delta\varepsilon/\delta\varepsilon_{CpLH}$; $\delta\varepsilon/\delta K_{D2}$; $K_{D2} = 1/K_{A2}$. This was not successful for the *o*-phthalato-complex. A plot of ε(obs.) against c_2 was found to be almost linear so that at $c_{max.} = 2.0$ mol dm^{-3} conversion to CpLH was not approached. The second method was thus used to get an estimate of K_{A2} [replacing K_{A1} in the terms (19) by K_{A2}].

With the kinetic data, plots of k(obs.) against c_2 for the acetato- and *o*-methoxybenzoato-complexes are convex although the curvature is slight for the latter. K_{A1} values were calculated by applying the above matrix inversion procedure to equation (9). The terms required to replace those in (18) are $\delta k/\delta k_1$; $\delta k/\delta k_0$; $\delta k/\delta K_{D1}$; $k = k$(obs.).

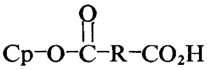
Rate Coefficients.—To obtain k(obs.) values for the oxalato-complex Andrade and Taube [11] took timed samples and cooled these before measuring the absorbances while Dash and Nanda [12] subjected cooled timed samples to cation resin exchange and titrated the separate oxalate with permanganate. For the present work we have used direct timed spectrophotometry and calculated k(obs.) by LLMS analysis with $Y = \ln[A_\infty - A(\text{obs.})]$ and $X = t$, where A_∞ is the absorbance corresponding to complete aquation and t = time. This term was obtained by either following A(obs.) until it became constant or by keeping samples at 80—90 °C until this condition was reached. The matrix inversion method of Moore [15] was also applied to some reactions when A(obs.) had reached about 90% of reaction. Also, since Andrade and Taube [11] reported that the oxalato-aquation reaches an equilibrium which is slightly short of complete conversion to the aqua-form, direct final readings do not correspond to $A_\infty = A$(aq). Hence this term was obtained from solutions of the aqua-complex (oxalate does not absorb at the wavelengths used) and k(obs.) calculated using the above method with absorbances for less than 25% of reaction. In addition, a few of the oxalato-aquations were followed almost to equilibrium and k(obs.) calculated by the treatment described by Moelwyn-Hughes [16] for opposing reactions. This requires A(eq) (the absorbance at equilibrium). An approximate value of A(eq) was found by the above method of Moore [15] for unopposed first-order reactions and this A(eq) adjusted until k(obs.) was constant for a range of timed measurements. Such k(obs.) values agreed within 1—3% with those obtained by the limited use of the method described above. Values of k(obs.) are in Table 3.

Table 4 contains the association constants and rate coefficient of aquation obtained from the present work, together with some related factors and estimated values.

Considering firstly the two complexes containing monocarboxylate ligands, although these ligands are of different structural types, there is a rough relationship between the k_{H1}/k_0 and K_{A1} ratios. The larger K_{A1} produces the larger enhancement in k_{H1}/k_0. This is in line with the view that the stronger the association of a proton with the ligand in the complex, the weaker becomes the Co^{III}–O (carboxylate) bond.[6,13] The pK_1 values of the corresponding carboxylic acids [13] [4.76 (acetic), 4.10 (*o*-methoxybenzoic), at $I = 0$, 25 °C] are also in the same order as the K_{A1} values for these complexes.

With regard to the complexes containing dicarboxylate ligands, the first four in Table 4 are fairly closely related which might justify using the information for the malonato- and succinato-complexes to estimate the undetermined K_{A2} and k_{H2} values for the oxalato- and tartrato-species. The

' slopes ' given by the data in Table 4 are the function K_{A2}-($k_{H2} - k_{H1}$); if the K_{A2} values for the succinato- and malonato-forms are plotted against these ' slopes ' using the origin as a third point (' slope ' = 0 at $K_{A2} = 0$) a slight curve is obtained. From the ' slope ' for the oxalato-complex, interpolation gives $K_{A2} \simeq 0.03$ and similarly $K_{A2} \simeq 0.15$ for the tartrato-complex. (The data for the *o*-phthalato-complex fit this curve and a similar plot for the acetato- and *o*-methoxybenzoato-complexes gives, with the origin, a straight line lying below that described above.) Also, from these estimates of K_{A2} and the k_{H1} values determined, the corresponding k_{H2} values can be estimated (*ca.* 4×10^{-5} s^{-1} for both the oxalato- and the tartrato-complex).

This order of K_{A2} for the oxalato-, malonato-, and succinato-series suggests that as the chain length of the $-R-CO_2H$ group of  $Cp-O-\overset{\overset{\displaystyle O}{\|}}{C}-R-CO_2H$ increases the degree of second protonation (at the O atom of $Cp-O^-$) is rendered easier by distancing the H atom attached to $-CO_2H$. The pK_1 values of the corresponding carboxylic acids (which correspond to the association of a second proton to the acids) also increase from oxalate to succinate (1.3, 2.85, and 4.2 at [14] $I = 0$, 25 °C). Also, the decrease in the K_{A2} value of the tartrato-complex compared with that of the succinato-complex is similar to the influence of the OH groups upon the pK_1 values of the acids (3.0 and 4.2 respectively).

As to the unprotonated forms of the dicarboxylato-complexes, the only direct determination in the present work is for the oxalato-complex at $I = 0.5$ mol dm^{-3} and 60 °C. The ratio of k_{H1}/k_0 is 5.8, the same order as that found by Dash and Nanda,[12] namely 5.3 at $I = 0.3$ mol dm^{-3}, 55 °C, and although K_{A1} is large the firmly attached proton of the first $-CO_2H$ group has little kinetic effect. Also, if our values at $I = 0.5$ mol dm^{-3} are used as a rough guide, k_0 at $I = 2.0$ mol dm^{-3} and 40 °C would be about 3×10^{-7} s^{-1} and since the pK_1 values for the other dicarboxylato-complexes are about 3.1—3.9,[13] the k_0 values for these could be still smaller.

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