Solvent-interchange Reactions of the Penta-amminecobalt(III) Ions † $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_5(dmf)]^{3+}$ in Dimethylformamide (dmf)–Water Media

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The rate law for aquation of $[Co(NH_3)_5(dmf)][ClO_4]_3$ is first order with respect to the concentration of the cobalt(III) complex and independent of aluminium(III) or perchloric acid concentration, contrary to a previous report. Tracer experiments have shown more than 95% cobalt(III)–oxygen bond fission, and chromatographic analyses for the formato-complex indicated less than 1% carbon–nitrogen bond fission. It is concluded that aquation proceeds by water molecules replacing intact dimethylformamide (dmf) molecules. Solvent interchange between the aqua- and dimethylformamide complexes has been studied in dmf–water mixtures at 25, 45, and 65 °C. The activation enthalpy for aquation of the dmf complex is independent of the composition of the solvation shell of the complex. The dependence of rate and equilibrium constants on dmf concentration is interpreted in terms of a free dmf-co-ordinated dmf interaction at small dmf contents which decreased the aquation rate constants at a more rapid rate at small dmf contents than at larger dmf contents at all temperatures. This same interaction increased the equilibrium concentration of the dmf complex more rapidly at small dmf than at larger dmf contents at 65 and probably at 45 °C also. Other explanations for preferential solvation of the complexes are considered and rejected. The rate law for aquation is $R_{aq} = k_{aq}'[Co(NH_3)_5(dmf)^{3+}]x_{H_2O}$. The activation parameters for k_{aq}' are satisfactorily constant over the range 0—0.7 mol fraction dmf, *viz.* $\Delta H^‡ = 105 \pm 2$ kJ mol^{-1} and $\Delta S^‡ = -3 \pm 7$ J K^{-1} mol^{-1}. The rate law for ligation is expressed as $R_{lig} = k_{lig}'[Co(NH_3)_5(OH_2)^{3+}]x_{dmf}$. The activation parameters for k_{lig}' are not constant; $\Delta H^‡_{lig}$ and $\Delta S^‡_{lig}$ both decrease with increasing dmf content (x_{dmf}).

THE study of substitution reactions of penta-ammine-anionocobalt(III) complexes has revealed some very interesting details. It is generally agreed [1-3] that the unassisted substitution reactions proceed by the dissociative interchange, I_d,[4] mechanism and that the second-order rate constants, k_{lig}, for ligation of $[Co(NH_3)_5(OH_2)]^{3+}$ by various ligands Y^-, as in reaction (1), are independent of the nature of the entering ligand Y^-. If K_f is the complex-formation constant equal to k_{lig}/k_{aq} for a given ionic strength and temperature, then

$$[Co(NH_3)_5(OH_2)]^{3+} + Y^- \underset{k_{aq}}{\overset{k_{lig}}{\rightleftharpoons}} [Co(NH_3)_5Y]^{2+} + H_2O;\ K_f \quad (1)$$

it follows that a plot of log k_{aq} against log K_f for the various Y^- must be linear with a gradient of -1 as has been shown.[5] The indicated lack of bond formation between Co^{III} and Y^- in the transition state is further supported by the fact that the quotient k_{ip}/k_{ex}, where k_{ip} is the first-order rate constant for interchange of ligands within an ion pair and k_{ex} is the first-order water-exchange rate constant, seems to be determined by the relative abundance [2] of Y^- and H_2O in the second co-ordination, or solvation, shell of the reactant and by the fact that k_{lig}/k_{ex} can approach unity in at least one case for a neutral ligand [6] when the ligand completely displaces the water from the solvation shell of $[Co(NH_3)_5(OH_2)]^{3+}$. (However, the relative distribution of ligand and solvent in this solvation shell of the reactant complex is at least as important as their relative abundance in this shell as will be discussed in the next paragraph.) The lack of bonding between Co^{III} and leaving or entering ligands in base-catalyzed substitution reactions of $[Co(NH_3)_5X]^{(3-x)+}$ complexes proceeding by an I_d mechanism has also been shown recently.[7] Specifically, when $Y^- = Cl^-$ in reaction (1) the lack of bonding between Co^{III} and Cl^- and between Co^{III} and H_2O in the transition state does not lead to a D mechanism [4] since this mechanism has been quantitatively invalidated [8] in certain media subject to the assumption that k_{ex} is independent of ion-pair formation. This assumption is currently under investigation for dimethyl sulphoxide (dmso) exchange.

Furthermore, the aquation of $[Co(NH_3)_5(dmso)]^{3+}$ in water + non-aqueous solvent + perchlorate-ion solutions containing very weakly (if at all) complexing non-aqueous components has shown [9-11] that k_{aq} is not dependent on solvent structure but does decrease with increasing perchlorate-ion concentration and with increasing non-aqueous solvent content, presumably because of increasing displacement of water from the solvation shell of the reactant. The increasing displacement of water from this shell by species which do not compete effectively with dmso for the vacated co-ordination site apparently increases the ' internal return ' of dmso in the transition state with consequent decrease of k_{aq}. If the water which remained in the solvation shell of the octahedral reactant had preferentially solvated the dmso ' corner ' of the complex (say by occupying the centres of the four adjacent triangular faces of the octahedron) there would have been little decrease in k_{aq} because the remaining water could then have competed as effectively with the dmso molecule in the presumed 1,4,2 geometry of the transition state as it would have in a more fully hydrated state. Apparently, the remaining water was more randomly distributed in the solvation shell because k_{aq} did decrease. Thus the subject of preferential solvation is an interesting one and here we report a study of solvent interchange between $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_5(dmf)]^{3+}$ in water–dimethylformamide (dmf) media.

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† Aquapenta-amminecobalt(III) and penta-ammine(dimethylformamide)cobalt(III).

EXPERIMENTAL

Chemicals.—The complexes $[Co(NH_3)_5(dmf)][ClO_4]_3$,[12] $[Co(NH_3)_5([^2H_7]dmf)][ClO_4]_3$,[12] $[Co(NH_3)_5(OH_2)][ClO_4]_3$,[13] and $[Co(NH_3)_5(O_2CH)][ClO_4]_2$ [14] were prepared as described in the literature. The 42.1 atom % $H_2{}^{18}O$ was obtained from Prochem. Stock solutions of $Al[ClO_4]_3$ were standardized with quinolin-8-ol. Deionized water was used throughout. Other solvents and reagents were reagent grade and were used without further purification.

Procedures.—The tracer experiments with $[Co(NH_3)_5([^2H_7]dmf)][ClO_4]_3$ were performed as described earlier with a Finnigan 4000 chemical-ionization mass spectrometer being used to record spectra. Appropriate blanks containing $[^2H_7]$dmf and the product $[Co(NH_3)_5(OH_2)]^{3+}$ and containing $[Co(NH_3)_5([^2H_7]dmf)]^{3+}$ and ordinary water were prepared and compared with the reaction mixture.

In some reaction mixtures providing evidence on the site of bond fission in the aquation of the dmf complex, the complexes were separated chromatographically on AG 50W-X4 resin (200—400 mesh) using 3 mol dm^{-3} HCl to elute the aqua-complex and 4 mol dm^{-3} HCl to elute the dmf complex. When the formato-complex was also present in simulated reactions mixtures it was first separated on the column from the dmf and aqua-complexes using 1.5 mol dm^{-3} $Na[ClO_4]$, then rapidly eluted with 2.0 mol dm^{-3} $Na[ClO_4]$.

In the solvent-interchange studies the amount of dmf complex in an equilibrium mixture was determined spectrophotometrically at 280 nm, where the aqua-complex has a very small absorbance, after correcting for the absorbance of the latter by successive approximations. The amounts of aqua-complex were then determined by difference since the initial amount of complex used was accurately known.

Absorbance measurements were made with Beckman DU or Unicam SP 500 spectrophotometers. The temperature of the Beckman DU cell compartment was controlled at 45.0 ± 0.1 °C. The temperature of the water-bath was maintained within ±0.05 °C of the selected temperature.

RESULTS AND DISCUSSION

$[Co(NH_3)_5(dmf)]^{3+}$ *Aquation in Aqueous Media*.—The rate of aquation of this complex has been studied [12] in aqueous $Li[ClO_4]$, $Na[ClO_4]$, and $Mg[ClO_4]_2$ solutions at perchloric acid concentrations up to 1.00 mol dm^{-3} and found to be first order in the concentration of the complex. It was reported elsewhere [15] that the mechanism of aquation changed in 0.35 mol dm^{-3} $Al[ClO_4]_3$ solutions and in perchloric acid solutions containing more than 1.0 mol dm^{-3} perchloric acid because the rate law for aquation was not first order in the complex concentration. It was decided to investigate this report before starting the non-aqueous solvent studies to ascertain whether or not mechanism changes would be likely. Rate constants and activation parameters were determined for various concentrations of $Al[ClO_4]_3$ and $HClO_4$ and are listed in Table 1. No deviation from first-order kinetics was observed.

The tracer experiments conducted with $[Co(NH_3)_5([^2H_7]dmf)]^{3+}$ in 42.1 atom % $H_2{}^{18}O$ to determine the point of bond breaking contained 0.35 mol dm^{-3} $Al[ClO_4]_3$ but otherwise were done as already described.[16] The liberated $[^2H_7]$dmf did not contain more than 5% oxygen-18 so that aquation occurred mainly, if not exclusively, through cobalt(III)–oxygen bond fission. Furthermore, if carbon–nitrogen bond fission had occurred the formato-complex would have been formed as an intermediate. Qualitative experiments showed that the latter complex aquates very slowly compared to aquation of the dmf complex. Hence this intermediate would have accumulated in solutions and traces of it could have been detected and determined. When reaction mixtures containing 0.35 mol dm^{-3} $Al[ClO_4]_3$ were placed on the column at 0.5, 1, and 3 half-lives, and 1.5 and 2.0 mol dm^{-3} $Na[ClO_4]$ passed through the column, no formato-complex could be detected in the colourless eluant prior to the elution of a 3+ species. Consequently, it was very unlikely that as much as 1% of formato-complex was formed and that as much as 1% of carbon–nitrogen bond fission occurred. It was concluded that the mechanism for $[Co(NH_3)_5(dmf)]^{3+}$ aquation was unchanged in these media.

$[Co(NH_3)_5(OH_2)]^{3+}$ *and* $[Co(NH_3)_5(dmf)]^{3+}$ *Solvent Interchange*.—Absorbance–time data for various dmf–water mixtures gave linear $\ln(A_t - A_\infty)$–time plots. A_∞ values were obtained at ⩾10 half-lives. The plots

TABLE 1

Values of k_{aq}, $\Delta H^‡$, and $\Delta S^‡$ for $[Co(NH_3)_5(dmf)]^{3+}$ aquation in aqueous perchlorate-ion solutions

$[Al(ClO_4)_3]$ / mol dm^{-3}	$[HClO_4]$ / mol dm^{-3}	θ_c [a] / °C	10^5k_{aq} [b] / s^{-1}	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol^{-1}	n [c]
0.340	0.100	25.0	0.0863			3
		45.0	1.60			2
		65.0	21.6	113	35	3
0.500	0.100	25.0	0.0745			3
		45.0	1.35			4
		65.0	17.3	111	28	3
0.700	0.100	25.0	0.0557			3
		45.0	1.075			4
		65.0	14.6	114	35	3
	1.00	25.0	0.0873			3
		65.0	21.9	113	35	3
	2.00	25.0	0.0578			3
		45.0	1.17			4
		65.0	15.3	114	36	3
	3.00	25.0	0.0416			3
		45.0	0.810			4
		65.0	12.4	117	39	3

[a] Standard deviation *ca.* 0.1 °C. [b] Standard deviation *ca.* 1%. [c] Number of separate kinetic runs for the given conditions.

TABLE 2

Values of Q_e, $k_{obs.}$, k_{aq}, and k_{lig} at various solvent compositions and at 25, 45, and 65 °C. Total cobalt(III) complex concentration = 1.00 × 10^{-3} mol dm^{-3}; $[HClO_4]$ = 0.010 mol dm^{-3}

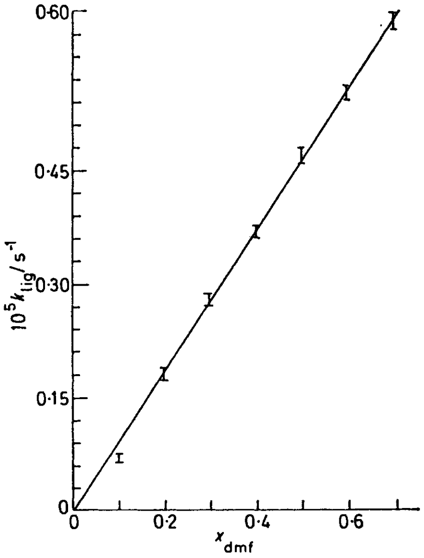
x_{dmf} [a]	θ_c [b] / °C	Q_e	$10^5k_{obs.}$ / s^{-1}	10^5k_{aq} / s^{-1}	10^5k_{lig} / s^{-1}	n [c]
0.00	25.0	0	0.196	0.196		3
	45.0	0	2.85	2.85		3
	65.0	0	36.4	36.4		3
0.10	25.0	0.492	0.215	0.145	0.0708	4
	45.0	1.03	4.24	2.10	2.14	4
	65.0	1.07	55.3	26.7	28.6	4
0.20	25.0	1.51	0.299	0.119	0.180	4
	45.0	1.71	4.75	1.74	3.01	4
	65.0	2.25	65.0	20.0	45.0	4
0.30	25.0	2.90	0.375	0.096	0.279	4
	45.0	2.81	5.39	1.42	3.97	4
	65.0	3.01	73.2	18.3	54.9	4
0.40	25.0	4.55	0.451	0.081	0.370	4
	45.0	4.31	5.96	1.12	4.84	4
	65.0	4.80	80.7	14.0	66.7	4
0.50	25.0	6.75	0.538	0.070	0.468	4
	45.0	5.57	6.55	1.00	5.55	4
	65.0	6.61	87.4	11.5	75.9	4
0.60	25.0	9.09	0.613	0.061	0.552	4
	45.0	8.03	7.07	0.784	6.29	4
	65.0	8.42	94.8	10.1	84.7	4
0.70	25.0	12.5	0.701	0.052	0.649	4
	45.0	11.7	7.71	0.610	7.10	4
	65.0	11.5	105	8.41	96.6	4

[a] Calculated on the basis of the weights of dmf and H_2O only. [b] Temperature variation was ±0.10 °C. [c] Number of rate experiments for a given set of conditions.

were linear to at least 3 half-lives. The pseudo-first-order rate constant, $k_{obs.}$, for the observed approach to equilibrium was equal to $(k_{aq} + k_{lig})$, where k_{aq} and k_{lig} are defined by reaction (1) when $Y^- =$ dmf, and was obtained from the slope of the $\ln(A_t - A_\infty)$–time plot. Individual values of k_{aq} and k_{lig} were obtained from the

$$Q_e = \frac{k_{lig}}{k_{aq}} = \frac{[Co(NH_3)_5(dmf)^{3+}]_e}{[Co(NH_3)_5(OH_2)^{3+}]_e} \qquad (2)$$

experimental $k_{obs.}$ values with the aid of the relationship in equation (2) where the equilibrium concentrations of the two complexes in a final reaction mixture are designated by the subscript e. The equilibrium concentrations were determined spectrophotometrically. Values of Q_e, $k_{obs.}$, k_{aq}, and k_{lig} obtained for various solvent mixtures at 25, 45, and 65 °C are listed in Table 2. The standard deviation of Q_e for a given set of conditions was *ca.* 7% whereas those of $k_{obs.}$, k_{aq}, and k_{lig} were *ca.* 1, 7, and 1.5%, respectively. The standard deviation of k_{lig} is considerably less than that of k_{aq} because, for most of the media, k_{lig} contributes much more to $k_{obs.}$ than does k_{aq}. The data for 0.8 and 0.9 mol fraction dmf are not given because solubility problems gave unreliable data.



Ligation rate constant for $[Co(NH_3)_5(OH_2)]^{3+}$ as a function of the mol fraction of dmf at 25 °C. The vertical bars mark the ranges of the rate constant

A plot of k_{lig} against x_{dmf}, the mol fraction of dmf, at 25 °C as in the Figure shows that k_{lig} was proportional to x_{dmf}, *i.e.* as in (3) where k_{lig}' is the rate constant for

$$k_{lig}' = k_{lig}/x_{dmf} \qquad (3)$$

the rate law:

$$R_{lig} = \frac{d[Co(NH_3)_5(dmf)^{3+}]}{dt} = k_{lig}'x_{dmf}[Co(NH_3)_5(OH_2)^{3+}]$$

From equations (2) and (3) it is readily shown that (4) is

$$k_{lig}' = Q_ek_{aq}/x_{dmf} = \frac{Q_ex_{H_2O}}{x_{dmf}} \cdot \frac{k_{aq}}{x_{H_2O}} = K_ek_{aq}' \qquad (4)$$

applicable where K_e, defined' by equation (5), is the equilibrium constant for reaction (1) when $Y^- =$ dmf

$$K_e = \frac{k_{lig}'}{k_{aq}'} = \frac{[Co(NH_3)_5(dmf)^{3+}]_ex_{H_2O}}{[Co(NH_3)_5(OH_2)^{3+}]_ex_{dmf}} \qquad (5)$$

and the dmf and water contents are expressed in mol fractions, and k_{aq}' is defined as in (6). Since the equality in equation (4) requires only that the product K_ek_{aq}' be

$$k_{aq}' = k_{aq}/x_{H_2O} \qquad (6)$$

TABLE 3

Values of K_e, k_{aq}', and k_{lig}' at different x_{dmf} and temperatures

x_{dmf} *	θ_c * / °C	K_e	$10^5 k_{aq}'$ / s^{-1}	$10^5 k_{lig}'$ / s^{-1}	n *
0.00	25.0		0.196		3
	45.0		2.85		3
	65.0		36.4		3
0.10	25.0	4.4	0.16	0.708	4
	45.0	9.3	2.3	21.4	4
	65.0	9.0	30	286	4
0.20	25.0	6.0	0.15	0.900	4
	45.0	6.8	2.2	15.1	4
	65.0	9.0	25	225	4
0.30	25.0	6.8	0.14	0.930	4
	45.0	6.6	2.0	13.2	4
	65.0	7.0	26	183	4
0.40	25.0	6.8	0.14	0.25	4
	45.0	6.5	1.6	12.1	4
	65.0	7.2	23	167	4
0.50	25.0	6.8	0.14	0.936	4
	45.0	5.6	2.0	11.1	4
	65.0	6.6	23	152	4
0.60	25.0	6.1	0.15	0.920	4
	45.0	5.4	2.0	10.5	4
	65.0	5.6	25	141	4
0.70	25.0	5.4	0.17	0.927	4
	45.0	5.0	2.0	10.1	4
	65.0	4.9	28	138	4

* See footnotes to Table 2.

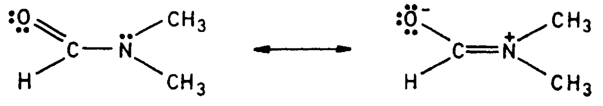
constant it is not necessary that the individual values of K_e and k_{aq}' be constant. The values of K_e, k_{aq}', and k_{lig}' are listed in Table 3. It is seen that k_{aq}' is approximately constant over the range $0.1 \leqslant x_{dmf} \leqslant 0.7$ at all three temperatures; the average values of k_{aq}' and their standard deviations for a single measurement are $(0.15 \pm 0.01) \times 10^{-5}$ s^{-1} at 25 °C, $(2.0 \pm 0.2) \times 10^{-5}$ s^{-1} at 45 °C, and $(25 \pm 2) \times 10^{-5}$ s^{-1} at 65 °C. The average value of K_e and its standard deviation at 25 °C is 6.0 ± 0.9. At 45 °C, K_e shows a downward trend but if this is ignored its value is 6.5 ± 1.4. At 65 °C, K_e shows a distinct downward trend with increasing x_{dmf} and cannot be considered constant. The average value of k_{lig}' and its standard deviation at 25 °C is $(0.923 \pm 0.014) \times 10^{-5}$ s^{-1}. At 45 °C, k_{lig}' shows a downward trend but if this is ignored $k_{lig}' = (13.4 \pm 4.0) \times 10^{-5}$ s^{-1}. At 65 °C there is a marked downward trend of k_{lig}' with increasing x_{dmf}.

At 25 °C the lack of dependence of k_{lig}' on x_{dmf} is readily explained if it is assumed that the composition of the solvation shell of $[Co(NH_3)_5(OH_2)]^{3+}$ is the same as the composition of the bulk solvent and that the chances of the reactant capturing a water or a dmf molecule from this solvation shell are in direct proportion to their numbers in this shell. In regard to the latter assumption it should be remembered that there is no bond formed between Co^{III} and the entering ligand in the transition state. Hence the reactant cannot select between different entering ligands on the basis of bonding interactions between metal and the different ligand choices and a random selection of entering ligands seems to be a reasonable possibility. On this basis of random selection of ligand from the solvation shell of the reactant, k_{lig}' will be proportional to the mol fraction of dmf in the solvation shell which is, by the first assumption, equal to x_{dmf} in the bulk solvent.

The value of k_{aq} reported in Table 2 for purely aqueous media at 45 °C is in excellent agreement with the value of $(2.67 \pm 0.20) \times 10^{-5}$ s^{-1} reported by Reynolds and Knoll.[12] The real but small decrease in k_{aq}' at all temperatures for $[Co(NH_3)_5(dmf)]^{3+}$ on going from purely aqueous media to 0.1 mol fraction dmf could be due to preferential solvation of this complex by dmf at small x_{dmf} but not at x_{dmf} much greater than 0.1 or 0.2. This preferred solvation by dmf could arise in three ways: (*a*) from specific dmf–dmf intermolecular interaction (see below); (*b*) as the result of a decrease in the total number of solvent molecules in the solvation shell as dmf occupies some solvation-shell sites so that one dmf molecule in effect displaces more than one water molecule; or (*c*) the number of solvent molecules in the solvation shell may remain constant with randomly distributed dmf present at a larger mol fraction than exists in the bulk solvent.

The second explanation seems to be inadequate because if the entrance of a dmf molecule into the solvation shell crowded out more than one water molecule so as to effectively increase the dmf : H_2O ratio in the solvation shell over that in the bulk solvent one would expect k_{lig}' at 25 °C as well as k_{aq}' at 25 °C to be dependent on x_{dmf} over the same range of solvent composition. The third explanation also seems to be inadequate because if $[Co(NH_3)_5(dmf)]^{3+}$ randomly but preferentially takes dmf into its solvation shell at constant solvation number then $[Co(NH_3)_5(OH_2)]^{3+}$ would be expected to do the same since both complexes would look the same to free dmf molecules except in the near vicinity of the bound dmf and H_2O ligands. If free dmf can distinguish between $[Co(NH_3)_5(dmf)]^{3+}$ and $[Co(NH_3)_5(OH_2)]^{3+}$ only when in the near vicinity of the co-ordinated dmf then this may be termed dmf–dmf interaction and is the first explanation advanced above for preferential solvation of $[Co(NH_3)_5(dmf)]^{3+}$ by dmf.

The dmf–dmf interaction might arise as follows. It is well known that resonance-structure II contributes sufficiently to the electronic structure of dmf so that n.m.r. spectra of both free and co-ordinated dmf show a doublet for the methyl-proton resonance which does not coalesce until *ca.* 372 K,[17] that dmf bonds almost exclusively to Co^{III} through the oxygen atom in the penta-ammine complex, and that the dmf molecule is essentially planar because of sp^2 hybridization at the C and N atoms. The partially negative O atom of a free dmf is very likely to interact more strongly with a partially positive N atom of a co-ordinated dmf than with the NH_3 ligands. Once this dmf–dmf interaction is nearly saturated further increase in x_{dmf} provides



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increase of randomly located dmf, not specifically located dmf near the substitution site. Location of the first dmf to enter the solvation shell at the substitution site could cause a greater decrease in k_{aq} than random location of dmf elsewhere in the solvation shell. Consequently early addition of dmf to the solvation shell can cause larger decreases in k_{aq} at low x_{dmf} than the later additions do, as observed.

Furthermore, the reason for the early extra-large decrease in k_{aq} does not appear to agree with the reason advanced by Frankel *et al.*[18] for the preferred solvation of tris(pentane-2,4-dionato)cobalt(III) in CH_3OH–$CHCl_3$ mixtures. They reasoned that, at low $CHCl_3$ mol fractions, the CH_3OH prefers the hydrogen-bonded bulk-solvent structure and $CHCl_3$ is 'squeezed out' of the bulk phase and preferentially taken into the solvation shell. At sufficiently large $CHCl_3$ mol fraction the hydrogen-bonded structure of bulk CH_3OH is disrupted and CH_3OH is preferred in the solvation shell. If dmf in water behaved as $CHCl_3$ in CH_3OH one might reasonably expect $[Co(NH_3)_5(OH_2)]^{3+}$ to prefer dmf at small x_{dmf} as $[Co(NH_3)_5(dmf)]^{3+}$ appears to. Preference for dmf by the aqua-complex at small x_{dmf} could be expected to lead to a more rapidly increasing k_{lig} at small x_{dmf} than at large x_{dmf}. This was not observed as the Figure shows.

Although k_{lig}' is independent of x_{dmf} at 25 °C it is not at 65 °C and probably not at 45 °C. At 65 °C there is a distinct decrease of k_{lig}' with increasing x_{dmf}. The large values of k_{lig}', and hence of k_{lig}, result from large values of K_e and Q_e, respectively, because $k_{lig}' = K_e k_{aq}'$ and $k_{lig} = Q_e k_{aq}$ and k_{aq}' is independent of x_{dmf} from 0.1 to 0.7 at 65 °C. The values of Q_e at small x_{dmf} are larger than expected from the values of Q_e at the larger x_{dmf}. From equation (2) it can be seen that these larger-than-expected values of Q_e at small x_{dmf} arise from equilibrium concentrations of $[Co(NH_3)_5(dmf)]^{3+}$ being larger at small x_{dmf} than expected from comparison with the equilibrium concentrations at large x_{dmf}. These unexpectedly higher concentrations can arise from the free dmf–bound dmf interaction already postulated for the initial rapid decrease of k_{aq}' at small x_{dmf}. This one interaction can decrease the rate constant for aquation and increase the equilibrium concentration of the dmf complex. When the interaction is largely saturated at small x_{dmf} further increases of x_{dmf} will not succeed in increasing the interaction proportionately.

TABLE 4

Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_{aq}' and k_{lig}' at various x_{dmf}

x_{dmf}	$\Delta H^{\ddagger}_{aq}$ [a] / kJ mol^{-1}	$\Delta S^{\ddagger}_{aq}$ [b] / J K^{-1} mol^{-1}	$\Delta H^{\ddagger}_{lig}$ [a] / kJ mol^{-1}	$\Delta S^{\ddagger}_{lig}$ [b] / J K^{-1} mol^{-1}
0.00	107	3.3		
0.10	107	1.5	123	70
0.20	105	5.8	113	19
0.30	108	2.0	108	21
0.40	105	−5.2	106	14
0.50	104	−7.4	104	6
0.60	104	−7.0	103	3
0.70	104	−8.4	102	−0.4

[a] Standard deviation not more than 2%. [b] Standard deviation *ca.* ±7 J K^{-1} mol^{-1}.

The values of the activation parameters for k_{aq}' and k_{lig}' in each reaction medium are listed in Table 4. The values of $\Delta H^{\ddagger}_{aq}$ are satisfactorily constant at 105 ± 2 kJ mol^{-1}. The standard deviation of ± 2 kJ mol^{-1} in $\Delta H^{\ddagger}_{aq}$ gives rise to a standard deviation of ± 7 J K^{-1} mol^{-1} in $\Delta S^{\ddagger}_{aq}$. Consequently the drift in the latter is not significant and the average $\Delta S^{\ddagger}_{aq} = -3 \pm 7$ J K^{-1} mol^{-1}. These values are in good agreement with the literature[12] values of 110 ± 4 kJ mol^{-1} and $+16 \pm 8$ J K^{-1} mol^{-1} for 0.01 mol dm^{-3} aqueous perchloric acid. Therefore $\Delta H^{\ddagger}_{aq}$ is, to a very good approximation, independent of the composition of the solvation shell of $[Co(NH_3)_5(dmf)]^{3+}$. This result supports the assumption of Reynolds and Barber[8] that the rate of Co^{III}–OH_2 bond breaking in the anation of $[Co(NH_3)_5(OH_2)]^{3+}$ by Cl^- was not dependent on the composition of the solvation shell of the aqua-complex; the validity of this assumption was crucial in quantitatively invalidating the *D* mechanism for this reaction.

The downward trends of $\Delta H^{\ddagger}_{lig}$ and $\Delta S^{\ddagger}_{lig}$, however, appear to be outside experimental error and real. As is very frequently the case when solvent exchange is involved,[19] the trends in the two parameters tend to compensate each other in their effect on the rate constant.

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