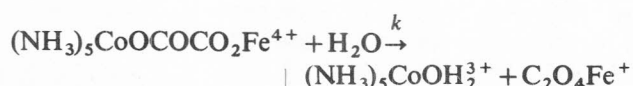
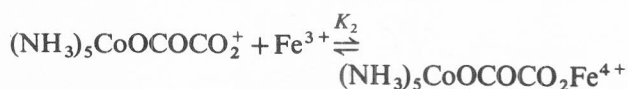
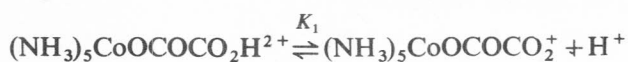


Table 1—Rate Data for Fe(III) Catalysed Aquation of Oxalatopentaamminecobalt(III) in Methanol-Water Media
 {[Complex]_T = (5.0 ± 0.1) × 10⁻⁴ mol dm⁻³ (10-30% MeOH) or (2.0 ± 0.2) × 10⁻⁴ mol dm⁻³ (40-50% MeOH); I = 0.3 mol dm⁻³; [H⁺]_T = 0.1 mol dm⁻³}

MeOH (%)	[Fe ³⁺] _T (mol dm ⁻³)	10 ⁵ k at 40°C		10 ⁵ k at 45°C		10 ⁵ k at 50°C	
		Obs (s ⁻¹)	Calc* (s ⁻¹)	Obs (s ⁻¹)	Calc* (s ⁻¹)	Obs (s ⁻¹)	Calc* (s ⁻¹)
10	0.005	3.10	3.00	5.55	5.46	8.40	8.30
	0.0075	3.60	3.70	7.00	7.00	—	—
	0.01	4.05	4.21	7.77	8.16	13.90	14.30
	0.0125	4.50	4.57	—	—	—	—
	0.015	5.00	4.85	9.10	9.79	18.38	18.70
	0.02	5.50	5.26	11.00	10.80	21.00	22.20
	0.025	—	—	12.80	11.60	25.00	25.00
	0.03	—	—	—	—	30.50	27.20
20	0.005	4.15	4.01	6.10	5.90	9.00	9.00
	0.0075	4.80	5.13	7.25	7.66	—	—
	0.01	5.70	5.96	8.40	9.00	15.30	15.10
	0.0125	6.40	6.62	10.23	10.00	—	—
	0.015	8.10	7.13	12.00	10.90	20.00	19.50
	0.02	—	—	—	—	22.00	22.80
30	0.005	5.10	5.25	7.20	7.26	10.80	10.50
	0.006	6.40	6.08	8.50	8.39	—	—
	0.0075	7.25	7.23	10.00	9.93	13.30	14.08
	0.01	8.71	8.92	12.00	12.16	16.50	16.90
	0.0125	—	—	—	—	19.20	19.30
40	0.002	3.20	3.20	4.10	4.00	4.50	4.50
	0.003	4.48	4.48	5.10	5.60	6.63	6.53
	0.004	5.71	5.56	7.50	7.05	7.80	8.43
	0.005	6.66	6.51	8.50	8.30	11.12	10.20
	0.0075	8.00	8.42	11.00	11.00	14.00	14.20
50	0.002	3.50	3.50	—	—	—	—
	0.003	5.10	5.00	—	—	—	—
	0.004	6.40	6.38	—	—	—	—
	0.005	7.40	7.57	—	—	—	—

*Calculated by Eq. (1) using the values of the rate and equilibrium parameters given in Table 2.

methanol-water media at 40°, 45° and 50°C, I = 0.3 mol dm⁻³ (ClO₄⁻) and [H⁺] = 0.1 mol dm⁻³. Independent studies also confirmed that aquation of the oxalate complex in methanol-water media in the absence of Fe(III) but under identical acidity, ionic strength and at the temperature range studied, is negligible. The various steps of the reaction may be represented as follows^{1,2}:



where K_1 is acid dissociation constant of the oxalato complex and K_2 , k are the stability constant and the rate constant of aquation of the binuclear species respectively. Under pseudo-first order conditions of

constant [Fe³⁺] and [H⁺], the rate law of aquation is given by

$$\frac{-d\ln C_t}{dt} = k_{\text{obs}} = \frac{kK_1K_2[\text{Fe}^{3+}]/[\text{H}^+]}{1 + K_1/[\text{H}^+] + K_1K_2[\text{Fe}^{3+}]/[\text{H}^+]}$$

... (1)

where C_t = [oxalato complex]_T. The acid dissociation constants, K_1 , at different temperatures and solvent compositions were obtained from our earlier work¹². The correction of [Fe³⁺] due to hydrolysis was considered negligible at the experimental acidity¹². The values of k and K_2 were calculated from the intercept and slope of the least square best line plot of k_{obs}^{-1} versus [Fe³⁺]⁻¹ as it can be easily shown that Eq. (1) transforms to the form:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k} + \left(\frac{1}{kK_2} \right) \frac{([\text{H}^+] + K_1)}{K_1} \frac{1}{[\text{Fe}^{3+}]}$$

... (2)

Values of k and the associated activation parameters at different solvent compositions are summarised in Table 2.

In the present context it is worth examining the solvent effect on the Hg(II) catalysed aquation of haloaminocobalt(III) complexes. Unfortunately in most of such studies the haloaminocobalt(III) substrates used do not exhibit strong associative propensity for Hg(II), and the rate data have been collected in different solvent media of varying water-organic solvent compositions under second order conditions. Burgess and Price³ reported that the pseudo-first order rate constants for Hg(II) catalysed aquation of $(\text{NH}_3)_5\text{CoCl}^{2+}$ and $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$ increased with the addition of ethanol in aqueous-ethanol medium. The slopes of the Grunwald-Winstein plots of logarithms of rate constant against solvent Y -values (0-25% v/v, ethanol-water medium) turned out to be -0.35 for $(\text{NH}_3)_5\text{CoCl}^{2+}$ and -0.25 for $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$. Similarity in m -values was ascribed to similarity in the mechanism (S_N1 limit) and similar solvation requirements for the $(\text{NH}_3)_5\text{M}^{n+}$ [$\text{M} = \text{Co(III)}$ or Rh(III)] moieties. In another study of the mercury(II) induced aquation of *trans*-chloroamine-bis-(dimethylglyoximate)cobalt(III) complex Chan and Tan⁸ could determine the stability constant of the Cl-bridged binuclear complex, $[\text{Co}(\text{dmgh})(\text{NH}_3)\text{Cl-Hg}]^{2+}$ and its rate constant of aquation both in aqueous and aqueous ethanol (1:5.1) media. These data show that on changing the solvent from water to ethanol-water, the stability constant of the binuclear species increases 64-fold whereas the rate constant of aquation of such a species decreases only 5-fold. Combination of these two effects, however, is reflected as 4 to 8-fold increase in the apparent second order constant of Hg(II) catalysed aquation of this substrate. In a subsequent study Blandamer *et al.*⁹, have attempted to explain the solvent effect on the rate of Hg(II) catalysed aquation of chloroamine-metal complexes using a variety of aquo-organic solvent mixtures considering the initial state and transition state solvation effects of this reaction. They again used $(\text{NH}_3)_5\text{CoCl}^{2+}$ and (*trans*) $\text{Co}(\text{en})_2\text{Cl}_2^+$ as substrates for which Hg(II) catalysed reactions are strictly second

order. As such the observed solvent effect on the second order rate constant could not be split into individual components for the initial equilibrium process to form the presumed binuclear complex, i.e. $(\text{NH}_3)_5\text{Co-Cl-Hg}^{4+}$ and for its aquation. But one notes from their data in aqueous methanol media (10-40% v/v) that the second order rate constant for the Hg(II) catalysed aquation increases only slightly (from 0.095 to $0.112 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C). For oxalatopentamminecobalt(III) the apparent second order rate constant for the Fe(III) catalysed aquation ($k_{\text{app}} = kK$) increases with increasing methanol percentage. As for instance, k_{app} increases from 0.12 to $0.52 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 40°C ($I = 0.3 \text{ mol dm}^{-3}$) when MeOH is varied from 10 to 50%. It is, however, interesting to note that this effect is predominantly due to increase of the stability constant (K_2) of the binuclear species $(\text{NH}_3)_5\text{CoC}_2\text{O}_4\text{Fe}^{4+}$ with increase in methanol content (see Table 2). The plot of aquation rate constants of the binuclear species against solvent Y -values¹³ shows a maximum in 30% MeOH at 40° and 45°C (see Fig. 1). However, at 50°C the rate constants appear to be virtually independent of solvent composition. It is worth noting that the first order rate constants of aquation of the binuclear complex at 40° and 45°C show a definite trend, i.e. these increase with methanol content (or decrease in water content) up to 30% MeOH. This argues against S_N2 mechanism (acyl cleavage) involving rate-controlling nucleophilic attack of water at the acyl carbon of the bridging carboxyl group followed by C-O bond fission.

The observed trend in rate can be more realistically accommodated by the difference in solvation pattern of the initial and S_N1 (limit) transition state for the aquation process of the binuclear species. This is further supported by the analysis of ΔH^\ddagger data (Table 3).

The activation free energy (ΔG^\ddagger) appears to be almost independent of solvent. But on splitting it into ΔH^\ddagger and ΔS^\ddagger (see Fig. 2) the solvent dependence is evident. It appears that both ΔH^\ddagger and ΔS^\ddagger decrease to

Table 2—Calculated Rate and Equilibrium Parameters*

MeOH (%)	40°C		45°C		50°C	
	$10^4 k$ (s^{-1})	K_2^\ddagger ($\text{dm}^3 \text{ mol}^{-1}$)	$10^4 k$ (s^{-1})	K_2^\ddagger ($\text{dm}^3 \text{ mol}^{-1}$)	$10^4 k$ (s^{-1})	K_2^\ddagger ($\text{dm}^3 \text{ mol}^{-1}$)
10	0.70 ± 0.04	1776 ± 112	1.60 ± 0.10	1202 ± 97	5.0 ± 0.50	472 ± 47
20	1.20 ± 0.20	1674 ± 331	1.90 ± 0.40	1455 ± 276	4.7 ± 0.40	780 ± 57
30	3.00 ± 1.30	805 ± 360	3.70 ± 0.7	912 ± 169	4.4 ± 0.80	1200 ± 220
40	2.00 ± 0.20	2038 ± 232	3.00 ± 1.20	1652 ± 646	6.7 ± 3.60	776 ± 420
50	3.20 ± 0.60	1618 ± 281				

*Based on temperature independent values of $10^3 K_1$ (mol dm^{-3}) = 9.3, 6.6, 5.6, 4.85, 3.93, at 10, 20, 30, 40 and 50% MeOH respectively (ref. 12).

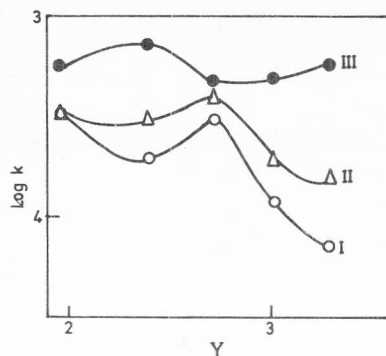


Fig. 1—Plot of $\log k$ versus Y for the aquation of $(\text{NH}_3)_5\text{CoO}_2\text{CCO}_2\text{Fe}^{4+}$ [I-40°, II-45° and III-50°C]

minimum values in 30% MeOH, corresponding to the maximum in the rate profile at 40–45°C. The highly negative value of ΔS^\ddagger and low positive value of ΔH^\ddagger in 30% MeOH probably reflect greater stability of the transition state in relation to the ground state due to solvation interaction with the medium. A near constancy of ΔG^\ddagger , and strong dependence of ΔH^\ddagger and ΔS^\ddagger on solvent composition clearly indicates that both enthalpy and entropy effects are mutually compensatory. This could be an indication of constancy of the mechanism (mostly S_N1 limit) over the solvent composition range studied. Similar observation has been made by Holba *et al.*¹⁴ in the aquation of $[\text{CoNH}_3\text{Br}(\text{en})_2]^{2+}$ in aquo-organic solvent mixtures.

At this stage it appears relevant to mention about the solvated Fe^{3+} species involved in the process. Absorbance measurements of Fe(III) perchlorate solution in methanol/water media indicate that absorbance of Fe^{3+} at 380 nm is strongly sensitive to methanol content of the medium. This, in fact, causes serious problem in the choice of the range of $[\text{Fe}^{3+}]$ in the aquation study. Similar observation has also been reported by Kunimura *et al.*¹⁵ Although there is evidence that the aquo ligands in the coordination sphere of Fe^{3+} are partially replaced by MeOH, our kinetic data, however, do not differentiate between the catalytic behaviour of $\text{Fe}(\text{OH})_2^{3+}$ and $\text{Fe}(\text{OH})_2(\text{MeOH})_3^{3-m}$.

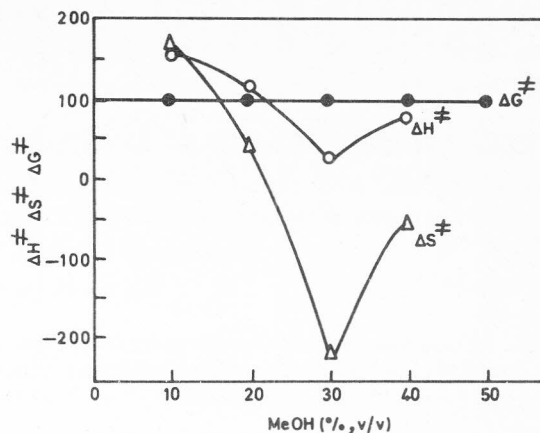


Fig. 2—Plot showing the sensitivity of the activation parameters to the solvent composition [Units; kJ mol^{-1} for ΔH^\ddagger , ΔG^\ddagger and $\text{JK}^{-1} \text{mol}^{-1}$ for ΔS^\ddagger]

Table 3—Activation Parameter Data (40°C)

MeOH (%)	ΔG^\ddagger (kJ mol^{-1})	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)
10	101.7	156.1 ± 43.1	171.6 ± 134
20	100.3	114.7 ± 31.4	46.0 ± 96.2
30	97.95	29.3 ± 7.1	-217.6 ± 23
40	99.0	82.4 ± 16.7	-54.0 ± 50
50	97.8	—	—

References

- Dash A C & Nanda R K, *Inorg Chem*, **13** (1974) 655.
- Dash A C & Harris G M, *Inorg Chem*, **21** (1982) 1265.
- Burgess J & Price M G, *J chem Soc (A)*, (1971) 3108.
- Madan S K & Peone (Jr) J, *Inorg Chem*, **7** (1968) 824.
- Reynolds W L, Birus M & Asperger S, *J chem Soc Dalton Trans*, (1974) 716.
- Glavas M & Reynolds W L, *J chem Soc Dalton Trans*, (1975) 1706.
- Grancicova O & Holba V, *Colln Czech chem Commun*, **43** (1978) 2152.
- Chan S F & Tan S L, *Aust J Chem*, **28** (1975) 1133.
- Blandamer M J, Burgess J & Haines R I, *J chem Soc Dalton Trans*, (1980) 607.
- Blandamer M J & Burgess J, *J Coord Chem Rev*, **31** (1980) 93.
- Saffir P & Taube H, *J Am chem Soc*, **82** (1960) 13.
- Dash A C, Khatoun S & Nanda R K, *Indian J Chem*, **21A** (1982) 891.
- Grunwald E & Winstein S, *J Am chem Soc*, **70** (1948) 846.
- Holba V & Grancicova O, *J inorg nucl Chem*, **43** (1981) 2071.
- Ohashi K, Yamamoto K, Suzuki T & Kurimura T, *Bull chem Soc (Japan)*, **44** (1971) 3363.