Steric effects on the anation reactions of pentaamine complexes of Co(III)

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Abstract

The kinetics of the anation reactions of $[Co(MeNH_2)_5H_2O]^{3+}$ with $H_3PO_4/H_2PO_4^-$, $H_3PO_3/H_2PO_3^-$, Br^-, Cl^- and CF_3OO^- and those of $[Co(NH_3)_5H_2O]^{3+}$ with Br^-, Cl^- and CF_3COO^- (for the sake of comparison) have been studied at different temperatures and at $I=1.0$ M ($LiClO_4$). This is the first study on the effects of the size of the amines on anation reactions of these complexes. All results are interpreted on the basis of an I_d mechanism. The span of Kk values for different entering ligands, decreases slightly on going from NH_3 to $MeNH_2$, and this is interpreted as the maintenance of a dissociatively activated interchange mechanism on going from NH_3 to $MeNH_2$ complexes. Activation enthalpy values decrease for each ligand (CF_3COO^- excepted) on going from NH_3 to $MeNH_2$. This is interpreted on the basis of a weaker ground state $Co-OH_2$ bond for the $MeNH_2$ complex, as compared to the NH_3 analogue, that needs less energy to be stretched to the transition sate. The variation of the activation entropy values for the same entering ligand on increasing the amine size confirms this assumption. The overall activation free energies also confirm a greater steric relief, on H_2O dissociation, for the $MeNH_2$ complexes.

Introduction

Substitution reactions on $[Co(NH_3)_5H_2O]^{3+}$ have been thoroughly studied for many years [1]. There is no doubt, contrary to the $[Cr(NH_3)_5H_2O]^{3+}$ systems, about the intimate mechanism of these reactions: a dissociatively activated one, with no lower coordination number intermediate, I_d, is operative [2]. However, only a few aquation and base hydrolysis studies have been carried out on the same type of complexes with bulkier amine ligands (RNH_2) [3]. From the results obtained it seems clear that the same mechanism, I_d, operates for the aquation reactions of $[Co(RNH_2)_5Cl]^{3+}$ complexes, both with R=H and with R=Me, Et, Pr or Bu [4].

The crystal structures of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(MeNH_2)_5Cl](NO_3)_2$ have been determined and the Co–Cl distance shown to be the same for both complexes within experimental error [5, 6]. This indicates that the reason for the observed rate increase in the hydrolysis reaction on going from NH_3 to the bulkier amines is a lowering of the free energy of the activated state caused by the greater steric relief on Cl dissociation for the $[Co(RNH_2)_5Cl]^{2+}$ complex as compared to the less sterically hindered $[Co(NH_3)_5Cl]^{2+}$ [3, 4].

In this paper we present a study of the anation reactions of $[Co(RNH_2)_5H_2O]^{3+}$ (R = Me) by a series of entering ligands, namely, $H_3PO_4/H_2PO_4^-$, $H_3PO_3/H_2PO_3^-$, Br^-, Cl^- and CF_3COO^-, and those of $[Co(NH_3)_5H_2O]^{3+}$ by Br^-, Cl^- and CF_3COO^-. This will enable, for the first time, a comparison of the span of rate constant values obtained for different entering ligands with the span of the anation reactions when R=H. The maintenance or decrease of the span on going from R=H to R=Me should indicate that the mechanism is maintained on increasing the steric hindrance caused by the amine ligands. Moreover, the differences in the activation enthalpy values on going from NH_3 to $MeNH_2$ in the pentaaminecobalt(III) complexes should also indicate the difference in the strength of the $Co-OH_2$ bond on increasing the size of the amine and/or the greater steric relief produced in the dissociation of the H_2O ligand in the transition state.

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Experimental

Reagents

$[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared according to a literature method [7] and characterized by its electronic spectrum [8]. The new complex $[Co(MeNH_2)_5H_2O](ClO_4)_3$ was prepared by addition of an excess (10%) of $AgClO_4$ to a stirred solution of the corresponding chlorocomplex, $[Co(MeNH_2)_5Cl]Cl_2$ [9], at *c.* 40 °C ($[H^+]=0.1$ M $HClO_4$). After stirring for *c.* 4–5 h, the solution was filtered to eliminate the precipitated AgCl, and concentrated at 40 °C in a vacuum-line to a small volume. Caution: special care must be exercised on manipulating organic amines in concentrated perchloric acid medium. Storage of the resulting solution for several days at *c.* −30 °C produced the desired solid.

Anal. Calc. for $[Co(MeNH_2)_5H_2O](ClO_4)_3$: C, 11.3; H, 5.1; N, 13.2. Found: C, 11.5; H, 4.9; N, 13.4%. Electronic spectra at 25 °C, $[H^+]=0.1$ M ($HClO_4$): 512 nm (71.0 M^{-1} cm^{-1}), 362 nm (72.5 M^{-1} cm^{-1}).

Solutions of LiBr, LiCl, LiH_2PO_4, LiH_2PO_3, $LiClO_4$ and $LiCF_3COO$ were prepared by carefully mixing the equivalent volumes of LiOH and HBr, HCl, H_3PO_4, H_3PO_3, $HClO_4$ and HCF_3COO solutions [10]. All solutions were checked for any resulting acidity and standardized by Li^+/H^+ exchange on an Amberlite IR 120(H) column followed by acid–base titration. All the other chemicals were reagent grade and were used as provided.

Kinetics

UV–Vis spectra were recorded on an HP-8452A instrument equipped with a thermostated (±0.2 °C) multicell transport. Reactions were followed in the full 600–325 nm range. Observed rate constants were derived from the absorbance versus time traces at the wavelengths where the difference between initial and final products was largest. The increase in absorbance values was *c.* $5\text{–}10\times10^{-2}$ for the $MeNH_2$ complexes and $15\text{–}20\times10^{-2}$ for the NH_3 complexes. Good retention of isosbestic points was observed during the time in which reactions were monitored (2–3 half lives).

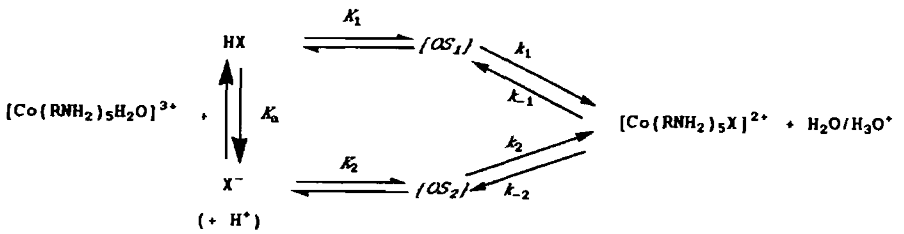
All kinetic runs were performed under pseudo first-order conditions. Observed rate constants were obtained by an exponential fitting Marquardt algorithm. Errors in k_{obs} were always in the range 3–10% of the plot-fitted values. Solutions for the kinetic runs were prepared and adjusted to $I=1.0$ M ($LiClO_4$) as previously described [11]. The values of the acidity constants of H_3PO_4 and H_3PO_3 at $I=1.0$ M used for the corresponding anation reactions were those determined in previous works under the same conditions [12, 13].

All the k_{obs} versus total ligand concentration plots were adjusted by a $1/k_{obs}^2$ weighted Marquardt algorithm; typical errors were in the 5–10% range for the slopes and in the 10–20% range for the intercepts. For the *A* and *C* terms of the derived rate law and for the Eyring plots, a weight of (standard deviation)$^{-2}$ was used. When the standard deviation was not known a percentage error was used.

Results

The processes studied follow, in principle, Scheme 1, a reaction scheme already proved for similar systems [10–16].

Table 1 gives the observed rate constants for all the $[Co(RNH_2)_5H_2O]^{3+}$ (R = Me) systems studied ($H_3PO_4/H_2PO_4^-$, $H_3PO_3/H_2PO_2^-$, Br^-, Cl^- and CF_3COO^-), as a function of the entering ligand concentration, acidity and temperature. Table 2 gives the observed rate constants for the $[Co(RNH_2)_5H_2O]^{3+}$ (R = H) systems studied (Br^-, Cl^- and CF_3COO^-), also as a function of the entering ligand concentration, acidity and temperature. These R = H systems have been studied at three temper-



$os_1 = \{[Co(RNH_2)_5H_2O]^{3+};H_3PO_4\}$

$os_2 = \{[Co(RNH_2)_5H_2O]^{3+};H_2PO_4^-\}$

Scheme 1.

TABLE 1. Observed rate constants for the anation reactions of the $[Co(MeNH_2)_5H_2O]^{3+}$ complex with different ligands as a function of ligand concentration, acidity and temperature. $I = 1.0$ M ($LiClO_4$)

Temperature (°C)	Entering ligand (X)	$[X]_T$ (M)	$[H^+]$ (M)	$10^4\ k_{obs}$ (s^{-1})
40	$H_3PO_4/H_2PO_4^-$	0.400	0.006	2.20
		0.600	0.006	3.34
		0.700	0.006	3.61
		0.800	0.006	4.03
		0.400	0.010	2.15
		0.600	0.010	2.73
		0.700	0.010	3.47
		0.800	0.010	3.80
		0.400	0.050	1.21
		0.600	0.050	1.45
		0.700	0.050	2.19
		0.800	0.050	2.22
50		0.100	0.001	3.49
		0.200	0.001	4.79
		0.500	0.001	9.13
		0.700	0.001	11.9
		0.800	0.001	14.0
		0.100	0.005	2.03
		0.200	0.005	4.52
		0.300	0.005	6.10
		0.500	0.005	8.61
		0.700	0.005	11.1
		0.800	0.005	12.7
		0.100	0.010	1.55
		0.200	0.010	3.03
		0.300	0.010	5.48
		0.500	0.010	8.04
		0.700	0.010	10.2
		0.800	0.010	12.0
		0.100	0.025	1.47
		0.200	0.025	2.46
		0.300	0.025	3.65
		0.500	0.025	6.30
		0.700	0.025	8.34
		0.800	0.025	8.98
		0.100	0.050	1.44
		0.200	0.050	2.53
		0.300	0.050	3.43
		0.500	0.050	5.84
		0.600	0.050	6.73
		0.700	0.050	8.00
		0.800	0.050	8.83
		0.300	0.075	3.65
		0.500	0.075	5.26
		0.700	0.075	7.98
		0.800	0.075	8.73
60		0.200	0.001	8.02
		0.300	0.001	14.7
		0.500	0.001	19.9
		0.700	0.001	30.1
		0.100	0.005	5.61
		0.200	0.005	10.6
		0.300	0.005	15.5
60	$H_3PO_4/H_2PO_4^-$	0.500	0.005	22.0
		0.700	0.005	33.0
		0.800	0.005	39.9
		0.100	0.010	5.27
		0.200	0.010	15.2
		0.300	0.010	15.0
		0.500	0.010	21.5
		0.700	0.010	29.8
		0.800	0.010	37.1
		0.100	0.025	6.27
		0.200	0.025	9.90
		0.300	0.025	14.2
		0.500	0.025	19.9
		0.700	0.025	26.7
		0.800	0.025	33.9
		0.100	0.050	3.84
		0.200	0.050	11.0
		0.300	0.050	12.1
		0.500	0.050	16.4
		0.700	0.050	23.2
		0.800	0.050	26.6
		0.200	0.075	8.17
		0.500	0.075	14.7
		0.700	0.075	20.9
		0.800	0.075	25.2
		0.100	0.100	6.23
		0.200	0.100	7.99
		0.300	0.100	11.2
		0.500	0.100	15.5
		0.700	0.100	21.5
		0.800	0.100	26.7
40	$H_3PO_3/H_2PO_3^-$	0.100	0.030	0.681
		0.200	0.030	1.06
		0.300	0.030	1.39
		0.400	0.030	1.83
		0.500	0.030	2.14
		0.600	0.030	2.52
		0.200	0.050	0.985
		0.300	0.050	1.29
		0.400	0.050	1.66
		0.500	0.050	2.03
		0.600	0.050	2.32
		0.100	0.070	0.700
		0.200	0.070	0.935
		0.300	0.070	1.23
		0.400	0.070	1.63
		0.500	0.070	1.90
		0.600	0.070	2.28
		0.100	0.100	0.686
		0.200	0.100	0.908
		0.300	0.100	1.23
		0.400	0.100	1.58
		0.500	0.100	1.89
		0.600	0.100	2.16
		0.200	0.150	0.893
		0.300	0.150	1.13

(*continued*)

TABLE 1. (*continued*)

Temperature (°C)	Entering ligand (X)	$[X]_T$ (M)	$[H^+]$ (M)	$10^4\ k_{obs}$ (s^{-1})
40	$H_3PO_3/H_2PO_3^-$	0.400	0.150	1.45
		0.500	0.150	1.75
		0.600	0.150	1.97
50		0.100	0.030	2.73
		0.200	0.030	4.52
		0.300	0.030	6.11
		0.400	0.030	7.23
		0.500	0.030	9.03
		0.600	0.030	12.0
		0.100	0.050	2.82
		0.200	0.050	4.29
		0.300	0.050	5.49
		0.400	0.050	7.12
		0.600	0.050	10.4
		0.100	0.070	2.58
		0.200	0.070	4.01
		0.300	0.070	5.71
		0.400	0.070	6.92
		0.500	0.070	8.34
		0.600	0.070	9.44
		0.200	0.100	3.88
		0.300	0.100	5.36
		0.400	0.100	6.48
		0.500	0.100	8.19
		0.600	0.100	9.28
		0.100	0.150	2.76
		0.200	0.150	3.81
		0.300	0.150	4.85
		0.400	0.150	6.02
		0.500	0.150	7.55
		0.600	0.150	8.64
		0.100	0.200	2.33
		0.200	0.200	3.72
		0.300	0.200	4.41
		0.400	0.200	5.63
		0.500	0.200	6.78
		0.600	0.200	7.79
60		0.200	0.030	12.7
		0.400	0.030	26.7
		0.500	0.030	28.4
		0.100	0.050	8.34
		0.200	0.050	12.8
		0.300	0.050	19.8
		0.400	0.050	21.3
		0.500	0.050	24.9
		0.600	0.050	29.8
		0.100	0.070	9.37
		0.300	0.070	18.4
		0.400	0.070	21.4
		0.500	0.070	25.6
		0.600	0.070	30.4
		0.100	0.100	11.4
		0.200	0.100	11.4
		0.300	0.100	15.4
		0.400	0.100	18.1
		0.500	0.100	24.0
		0.600	0.100	26.5

(*continued*)

TABLE 1. (*continued*)

Temperature (°C)	Entering ligand (X)	$[X]_T$ (M)	$[H^+]$ (M)	$10^4\ k_{obs}$ (s^{-1})
60	$H_3PO_3/H_2PO_3^-$	0.100	0.150	6.81
		0.200	0.150	12.7
		0.300	0.150	16.9
		0.400	0.150	19.2
		0.500	0.150	22.9
		0.600	0.150	24.5
		0.100	0.200	12.1
		0.200	0.200	11.7
		0.300	0.200	15.4
		0.500	0.200	22.6
		0.600	0.200	26.7
40	Br^-	0.100	0.100	18.1
		0.200	0.100	20.3
		0.300	0.100	23.4
		0.400	0.100	26.2
		0.500	0.100	29.0
		0.600	0.100	32.1
50		0.100	0.100	48.9
		0.200	0.100	55.7
		0.300	0.100	61.8
		0.400	0.100	68.8
		0.500	0.100	77.5
		0.600	0.100	86.7
60		0.100	0.100	114
		0.200	0.100	129
		0.300	0.100	147
		0.400	0.100	168
		0.500	0.100	181
		0.600	0.100	205
40	Cl^-	0.100	0.100	3.68
		0.200	0.100	5.22
		0.300	0.100	7.51
		0.400	0.100	9.31
		0.600	0.100	13.5
50		0.100	0.100	12.6
		0.200	0.100	16.7
		0.300	0.100	24.0
		0.400	0.100	31.5
		0.500	0.100	36.1
		0.600	0.100	41.9
60		0.100	0.100	37.9
		0.200	0.100	57.4
		0.300	0.100	82.1
		0.400	0.100	105
		0.500	0.100	120
		0.600	0.100	144
		0.200	0.300	54.6
		0.300	0.300	70.7
		0.400	0.300	103
		0.600	0.300	144
40	CF_3COO^-	0.100	0.100	7.72
		0.300	0.100	17.3
		0.400	0.100	24.0
		0.500	0.100	30.6
		0.600	0.100	36.6
50		0.100	0.100	26.6
		0.200	0.100	46.9

(*continued*)

TABLE 1. (*continued*)

Temperature (°C)	Entering ligand (X)	$[X]_T$ (M)	$[H^+]$ (M)	$10^4\ k_{obs}$ (s^{-1})
50	CF_3COO^-	0.300	0.100	67.0
		0.400	0.100	96.7
		0.500	0.100	116
		0.600	0.100	133
60		0.100	0.100	99.6
		0.200	0.100	163
		0.300	0.100	256
		0.400	0.100	349
		0.500	0.100	435
		0.600	0.100	494

atures for the first time, in order to obtain the thermal activation parameters, as well as the first- and second-order rate constants at the same temperature and conditions as for the R = Me systems. The values of the second-order rate constants obtained indicate a good agreement with previously published data [17–19].

The rate law derived from Scheme 1 is [11]:

$$k_{obs}=\frac{A}{[H^+]+K_a+B[\text{ligand}]_T}[\text{ligand}]_T+C \qquad (1)$$

with

$$A=K_1k_1[H^+]+K_2K_ak_2 \qquad (2)$$

$$B=K_1[H^+]+K_2K_a \qquad (3)$$

$$C=k_{-1}[H^+]+k_{-2} \qquad (4)$$

From the plots of k_{obs} versus the total ligand concentration, the values of A, B and C can be obtained. In all the systems studied no curvature in these plots has been observed, indicating that the term B is negligible. This fact has already been observed for nearly all systems with R = H, and it can be related to the $t_{2g}{}^6$ configuration of the Co(III) metal ion, which causes a rather small outer-sphere equilibrium constants when compared to the analogous Cr(III) systems, for which this equilibrium constant is not negligible [11, 12, 20]. For the systems where K_a is very large (HBr, HCl and HCF_3COO) the term $([H^+]+K_a)$ can be taken as K_a and then $A=(K_1/K_a)k_1[H^+]+K_2k_2$. Inspection of the observed rate constants at different acidities indicates, as expected, that only for the ligands derived from acids with a sufficiently small K_a to be measurable (H_3PO_4 and H_3PO_3), is an acid-dependent path (K_1k_1) detected. All the remaining ligands have an $[H^+]$-independent observed rate constant, as shown in Fig. 1. Figures 2 and 3 show the acid dependence of the A values obtained from the slopes of the k_{obs} versus [phosphorus oxoanion]$_T$ plots when R = Me. The values of K_1k_1 and K_2k_2 are obtained from these plots and the known K_a. For all the other ligands the slope of the k_{obs} versus [ligand]$_T$ plots gives the value of K_2k_2 directly. Table 3 shows all the forward second-order rate constants for the systems studied. It should

TABLE 2. Observed rate constants for the anation reactions of the $[Co(NH_3)_5H_2O]^{3+}$ complex with different ligands as a function of ligand concentration, acidity and temperature. I = 1.0 M ($LiClO_4$)

Temperature (°C)	Entering ligand (X)	$[X]_T$ (M)	$[H^+]$ (M)	$10^4\ k_{obs}$ (s^{-1})
60	Br^-	0.100	0.100	28.8
		0.200	0.100	30.3
		0.300	0.100	34.9
		0.400	0.100	40.6
		0.500	0.100	45.4
		0.600	0.100	50.5
70		0.100	0.100	88.4
		0.200	0.100	91.4
		0.300	0.100	107
		0.400	0.100	126
		0.500	0.100	136
		0.600	0.100	154
80		0.100	0.100	223
		0.200	0.100	246
		0.300	0.100	280
		0.400	0.100	329
		0.500	0.100	359
		0.600	0.100	408
60	Cl^-	0.100	0.100	11.8
		0.200	0.100	12.1
		0.300	0.100	15.8
		0.400	0.100	20.7
		0.500	0.100	23.1
70		0.100	0.100	32.0
		0.200	0.100	40.7
		0.300	0.100	52.6
		0.400	0.100	63.6
		0.500	0.100	75.3
		0.600	0.100	85.2
80		0.100	0.100	79.7
		0.200	0.100	113
		0.300	0.100	162
		0.400	0.100	196
		0.500	0.100	223
		0.600	0.100	261
60	CF_3COO^-	0.100	0.100	2.05
		0.300	0.100	4.63
		0.400	0.100	6.22
		0.500	0.100	7.36
		0.600	0.100	8.96
70		0.100	0.100	7.97
		0.200	0.100	11.1
		0.300	0.100	15.3
		0.400	0.100	20.6
		0.500	0.100	25.5
		0.600	0.100	30.7
80		0.200	0.100	36.6
		0.300	0.100	52.2
		0.400	0.100	66.1
		0.500	0.100	79.8
		0.600	0.100	94.9

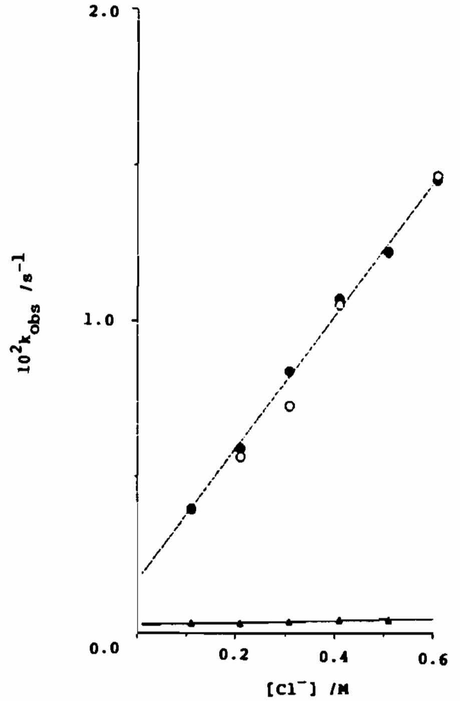


Fig. 1. Plot of the observed rate constants, k_{obs}, in front of the total ligand concentration for the anation reactions of $[Co(RNH_2)_5H_2O]^{3+}$ (R=H, ▲; R=Me, ○) by Cl^- at 60 °C and I=1.0 M ($LiClO_4$). Full points $[H^+]$=0.1 M, empty points $[H^+]$=0.3 M.

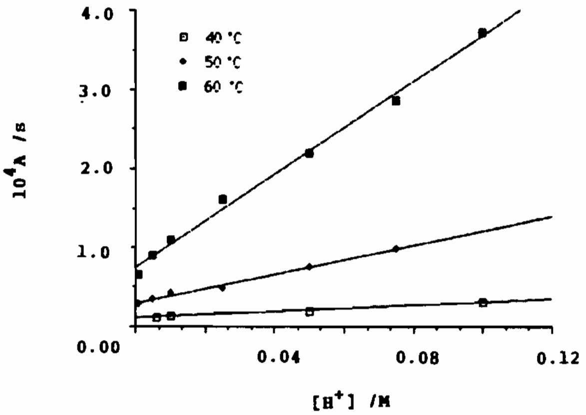


Fig. 2. Plot of the parameter A values (see eqn. (2)) vs. $[H^+]$ for the $[Co(MeNH_2)_5H_2O]^{3+}+H_2PO_4^-$ anation reaction. I=1.0 M ($LiClO_4$).

be noted that for R=H no K_1k_1 path is detected for the $H_3PO_4/H_2PO_4^-$ and $H_3PO_3/H_2PO_3^-$ systems [13, 14], but for R=CH_3 this reaction path is clearly present.

For all the systems studied an intercept of the k_{obs} versus $[ligand]_T$ plots, C term, was detected, indicating a back reaction. None of these systems show any $[H^+]$-dependence on those reverse rate constants, which means that, under the experimental conditions of these studies, the k_{-1} term in eqn. (4) should be negligible for all entering ligands. Table 4 shows the acidity-independent reverse rate constants (k_{-2}) for the systems studied as a function of the temperature.

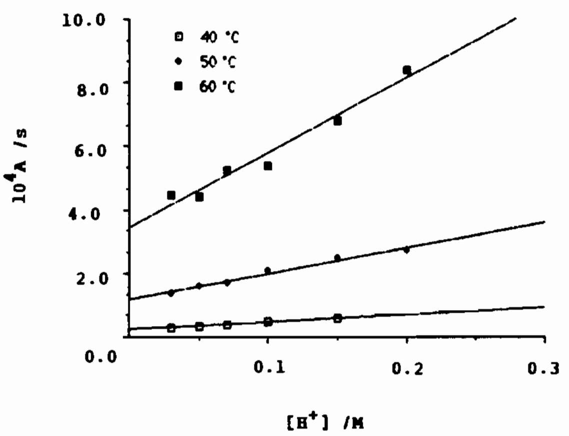


Fig. 3. Plot of the parameter A values (see eqn. (2)) vs. $[H^+]$ for the $[Co(MeNH_2)_5H_2O]^{3+}+H_2PO_3^-$ anation reaction. I=1.0 M ($LiClO_4$).

From the temperature dependence of all the determined rate constants the values of the thermal activation parameters can be obtained by Eyring plots. Table 5 collects all these parameters for the forward and reverse rate constants.

Discussion

Inspection of the data in Table 3 indicates, in agreement with a dissociatively activated mechanism, a general acceleration in the rate of the anation of the $[Co(RNH_2)_5H_2O]^{3+}$ for each ligand on increasing the size of the R substituent; at the same temperature, on going from R=H to R=Me the rate constant increases by a factor of 30–100 (depending on the ligand). From these data, and the published values for acid and base hydrolysis reactions of the corresponding chloro and bromo complexes, it is clear that the extent of dissociative activation is less for the anation and spontaneous aquation reactions than for the base hydrolysis, where the increase in rate constant values on going also from R=H to Me is of c. 1000 [18, 21]. That is, the life-span of the penta-coordinate transition state for a conjugated-base mechanism is longer than for an anation or aquation reaction; nevertheless, even for a base hydrolysis reaction, the existence of a genuine intermediate, long lived enough to change its solvation sphere, has not been proved [22].

TABLE 3. Formation rate constants for the anation reactions of the $[Co(RNH_2)_5H_2O]^{3+}$ complexes as a function of amine, entering ligand and temperature. $I = 1.0$ M ($LiClO_4$), $Kk = K_1k_1$ for acid forms and K_2k_2 for the anionic form

R	Entering ligand	T (°C)	10^4 Kk (M^{-1} s^{-1})
H	$H_2PO_4^-$ [14]	50	0.450
		60	1.54
		70	5.39
	$H_2PO_3^-$ [15]	60	0.620
		70	1.38
		80	7.33
	H_3PO_2 [11]	60	0.410
		70	2.49
		80	6.12
	$H_2PO_2^-$ [11]	60	1.79
		70	4.48
		80	8.65
	Br^-	60	4.40
		70	13.3
		80	36.3
	Cl^-	60	2.90
		70	10.7
		80	37.2
	CF_3COO^-	60	1.36
		70	4.32
		80	14.5
CH_3	H_3PO_4	40	1.37
		50	9.31
		60	23.8
	$H_2PO_4^-$	40	5.83
		50	15.1
		60	52.7
	H_3PO_3	40	2.14
		50	8.30
		60	32.6
	$H_2PO_3^-$	40	4.58
		50	21.3
		60	51.5
	Br^-	40	27.9
		50	72.8
		60	179
	Cl^-	40	19.2
		50	59.6
		60	212
	CF_3COO^-	40	5.51
		50	21.9
		60	80.6

TABLE 4. Inverse rate constants (i.e. aquation rate constants) for the anation ractions of the $[Co(RNH_2)_5H_2O]^{3+}$ complexes as a function of amine, leaving ligand and temperature. $I = 1.0$ M ($LiClO_4$)

R	Leaving ligand	T (°C)	10^4 k_{-2} (s^{-1})
H	H_3PO_2 [11]	60	0.711[a]
		70	3.62[a]
		80	13.2[a]
	$H_2PO_2^-$ [11]	60	0.290
		70	1.10
		80	3.91
	Br^-	60	2.29
		70	7.02
		80	18.0
	Cl^-	60	0.780
		70	2.06
		80	4.24
	CF_3COO^-	60	0.068
		70	0.321
		80	0.781
CH_3	$H_2PO_4^-$	40	0.350
		50	0.52
		60	2.22
	$H_2PO_3^-$	40	0.321
		50	1.31
		60	4.51
	Br^-	40	15.1
		50	41.0
		60	94.7
	Cl^-	40	1.65
		50	6.16
		60	15.1
	CF_3COO^-	40	0.210
		50	0.430
		60	1.55

[a] 10^4 k_{-1} (M^{-1} s^{-1}) in this case.

The span of second-order rate constants (Kk) for anating systems of the same charge (i.e. those with comparable outer-sphere equilibrium constants (K) [23]) decreases slightly from the R = H to the R = Me systems (7-fold and 4-fold, respectively). If we take the magnitude of the span as a measure, in a way, of the extent of dissociative activation, the anations for R = Me system would have a slightly 'more dissociative' character. Nevertheless, the difference should not be very important. As for the thermal activation parameters, although the span of values, especially those of activation entropy, could indicate the contrary, good isokinetic plots are obtained for both R = Me and R = H complexes, indicating a constant mechanism for each one. Figure 4 shows the isokinetic plots for the two substrates. It is clear from these that for R = Me the reactions are genuinely faster. The isokinetic temperature for both systems is the same, so making all comparisons of the span of rate constant values more reliable. Table 5 shows that there is a general decrease of the activation parameters for the forward reaction (although not very important) on going from NH_3 to $MeNH_2$ for all the anating ligands studied (CF_3COO^- excepted). These decreases could be explained in two ways: (i) a weaker Co–OH_2 bond in the ground state for the $MeNH_2$ complex and (ii) a transition state with lower energy caused by the greater steric relief on dissociation from a highly crowded ground state.

TABLE 5. Thermal activation parameters for all the forward (+) and reverse (−) reaction rate constants of the anation reactions of $[Co(RNH_2)_5H_2O]^{3+}$ as a function of the anating species and the amines. $I = 1.0$ M ($LiClO_4$)

R	Anating species	$\Delta H_+^{\neq}$ (kJ mol^{-1})	$\Delta S_+^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H_-^{\neq}$ (kJ mol^{-1})	$\Delta S_-^{\neq}$ (J K^{-1} mol^{-1})
H	$H_2PO_4^{-}$[a]	112 ± 3	18 ± 9		
	$H_2PO_3^{-}$[b]	137 ± 4	80 ± 12		
	H_3PO_2[c]	96 ± 18	-37 ± 52[d]	141 ± 3	98 ± 10
	$H_2PO_2^{-}$[c]	77 ± 8	-86 ± 23	125 ± 1	42 ± 1
	Br^-	100 ± 1	-10 ± 3	97 ± 3	-23 ± 8
	Cl^-	123 ± 1	57 ± 2	74 ± 7	-101 ± 21
	CF_3COO^-	114 ± 1	21 ± 4	116 ± 9	4 ± 25[d]
CH_3	H_3PO_4	97 ± 26	-3 ± 81[d]		
	$H_2PO_4^-$	89 ± 8	-22 ± 26[d]	80 ± 16	-76 ± 48
	H_3PO_3	115 ± 2	53 ± 5		
	$H_2PO_3^-$	115 ± 13	58 ± 41	113 ± 2	29 ± 6
	Br^-	78 ± 1	-45 ± 1	77 ± 2	-53 ± 8
	Cl^-	102 ± 5	28 ± 14	95 ± 9	-15 ± 28[d]
	CF_3COO^-	113 ± 1	55 ± 1	81 ± 15	-76 ± 48

[a]Recalculated from ref. 14 by weighted least-squares. [b]Recalculated from ref. 13 by weighted least-squares. [c]Recalculated from ref. 11 by weighted least-squares. [d]Error too large for any good estimation.

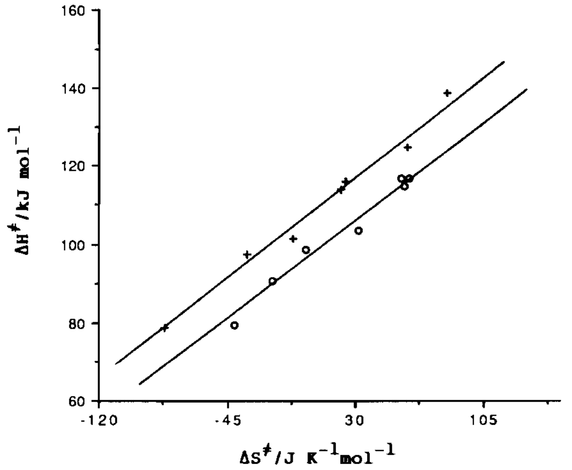


Fig. 4. Isokinetic plots for the two $[Co(RNH_2)_5H_2O]^{3+}$ systems studied (R = H, +; R = Me, ○) ($I = 1.0$ $LiClO_4$).

Nevertheless, for CF_3COO^- as entering ligand the activation parameters decrease is non-existent, and any further information in this respect should be drawn from the knowledge of the crystal structure of these complexes. In relation to this, the structures of $[Co(NH_3)_5Cl]Cl_2$ and $[Co(MeNH_2)_5Cl](NO_3)_2$ have been determined, and, although the Co–Cl distance has been found to be the same within experimental error [5, 6], the Co–N bonds are longer for the methylamine complexes, probably indicating a general decrease in the bond strength, as shown in the position of the maxima of the electronic spectra [19, 24]. If this effect held for the aqua complexes the reasoning should be directed directly to activation free energy values, enthalpy values alone being much less informative. Activation free energy differences for R = Me and R = H reactions, as shown in Fig. 1, are of *c.* −10 kJ mol^{-1}, that is, we could associate an increase on steric relief of *c.* 2 kJ mol^{-1} per Co–N bond on going from the methylamine to the ammonia complexes.

Any discussion on the activation entropies alone is less reliable given the fact of the large errors involved in their determination by Eyring plots, and all the solvent interactions that are included in this term [1]. The different geometry, size and capacity of hydrogen bonding with the solvent — or the amines — of the entering ligand should contribute largely to the entropy values determined.

Nevertheless, there is a small decrease on activation entropies on going from R = H to R = Me. If the ground state Co–OH_2 bond is stronger for the NH_3 complex, it should be more stretched on going to the transition state as compared to the $MeNH_2$ complex, so the activation entropy should be more positive for the anation reactions of the $[Co(NH_3)_5H_2O]^{3+}$ complex, since there has had to be a larger bond stretching for R = H as compared with R = Me. Again, the anation reactions with CF_3COO^- do not show this trend; it seems that the special geometric and electronic features of this anion produce some differences when compared with the others.

With respect to the reverse (i.e. aquation) rate constants, inspection of Table 4 shows a general increase of *c.* 20–40-fold, depending on the ligand, on going from NH_3 to $MeNH_2$, for leaving groups of the same charge, also in agreement with a dissociatively activated mechanism. This acceleration has to take into account not only transition state energies, but ground state effects that weaken the different Co–X bonds due to steric clashes when R moves from H to Me. On the other hand, any discussion on the activation enthalpy and entropy values for the reverse rate constants, determined in this work as intercepts of the k_{obs} versus $[\text{ligand}]_T$ plots, would be presumptuous, the errors involved in the values of C (eqn. (1)), and especially those of activation enthalpies and entropies, being, *de facto*, much larger than the actual standard deviation of the mathematical fitting.

References

1 T. W. Swaddle, *Coord. Chem. Rev., 14* (1974) 217; *Inorganic Reaction Mechanisms,* Vol. 7, Royal Society of Chemistry, Specialist Periodical Reports, London 1981; R. van Eldik (ed.), *Inorganic High Pressure Chemistry: Kinetics and Mechanisms,* Elsevier, Amsterdam, 1986, Ch. 3; L. Mönsted and O. Mönsted, *Coord. Chem. Rev., 94* (1989) 109.

2 R. G. Wilkins, *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes, Allyn and Bacon, Boston, MA, 1974; T. W. Swaddle, Adv. Inorg. Bioinorg. Mech., 2* (1983) 1.

3 D. A. Buckingham, B. M. Foxman and A. M. Sargeson, *Inorg. Chem., 9* (1970) 1790; T. W. Swaddle, *Can. J. Chem., 55* (1977) 3166; G. A. Lawrance, K. Schneider and R. van Eldik, *Inorg. Chem., 23* (1984) 3922; G. A. Lawrance and R. van Eldik, *J. Chem. Soc., Chem. Commun.,* (1987) 1105; N. J. Curtis, G. A. Lawrance and R. van Eldik, *Inorg. Chem., 28* (1989) 329.

4 P. A. Lay, *J. Chem. Soc., Chem. Commun.,* (1986) 1422; P. A. Lay, *Inorg. Chem., 26* (1987) 2144.

5 G. G. Messmer and E. L. Amma, *Acta Crystallogr., Sect. B, 24* (1968) 217.

6 B. M. Foxman, *Inorg. Chem., 17* (1978) 1936.

7 R. S. Splinter, S. J. Harris and R. S. Tobias, *Inorg. Chem., 7* (1968) 897.

8 J. C. Sullivan and J. E. French, *Inorg. Chem., 3* (1964) 832; M. Green and A. G. Sykes, *J. Chem. Soc. A,* (1970) 3209.

9 R. Mitzner, P. Blakenburg and W. Depkat, *Z. Chem., 9* (1969) 68.

10 M. Martinez and M. Ferrer, *Inorg. Chim. Acta, 69* (1983) 123.

11 M. Ferrer, G. Gonzalez and M. Martinez, *J. Chem. Soc., Dalton Trans.,* (1990) 2597.

12 M. Ferrer and A. G. Sykes, *Inorg. Chem., 18* (1979) 3345.

13 M. Martinez and M. Ferrer, *Transition Met. Chem. (Weinheim Ger.), 9* (1984) 395.

14 J. M. Coronas, R. Vicente and M. Ferrer, *Inorg. Chim. Acta, 49* (1981) 259.

15 M. Ferrer, M. Martinez and M-A. Pitarque, *J. Chem. Soc., Dalton Trans.,* (1990) 1629.

16 M. Martinez and M. Ferrer, *Inorg. Chem., 24* (1985) 792.

17 R. van Eldik, D. A. Palmer and H. Kelm, *Inorg. Chem., 18* (1979) 1520.

18 A. W. Adamson and F. Basolo, *Acta Chem. Scand., 9* (1955) 1261.

19 S. C. Chan and K. Y. Hui, *Aust. J. Chem., 20* (1967) 2529.

20 T. Ramasami and A. G. Sykes, *Inorg. Chem., 15* (1975) 2885.

21 S. C. Chan, K. Y. Hui, J. Miller and W. S. Tsang, *J. Chem. Soc.,* (1965) 3207.

22 D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *J. Am. Chem. Soc., 88* (1966) 5443; W. G. Jackson, B. C. McGregor and S. S. Jurisson, *Inorg. Chem., 26* (1987) 1286; F. P. Rotzinger, *Inorg. Chem., 27* (1988) 772.

23 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions: A Study of Metal Ions in Solution,* Wiley, New York, 1967.

24 M. Linhard and M. Weigel, *Z. Phys. Chem. (Frankfurt am Main), 11* (1957) 308.