Kinetics of the Solvolysis of *trans*-Dichlorotetra(4-methylpyridine)-cobalt(III) Ions in Water + t-Butyl Alcohol Mixtures

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The solvolysis of a cobalt complex presenting a largely hydrocarbon outer surface to the solvent, *trans*-$[Co(4Me\text{-}py)_4Cl_2]^+$ (4Me-py = 4-methylpyridine), has been investigated with solvents consisting of mixtures of water with the co-solvent Bu^{t}OH, which possesses a high structure-inducing capacity in water. Extrema found in the variation of the enthalpy and entropy of activation with solvent composition correlate very well with extrema in the variation of the physical properties of the mixture which relate to sharp changes in the solvent structure. Using a free-energy cycle and solubility measurements on salts of *trans*-$[Co(4Me\text{-}py)_4Cl_2]^+$, values for the free energy of transfer of the cation in the transition state, $\Delta G_t^\ominus[Co(4Me\text{-}py)_4Cl^{2+}]$, have been obtained. These are compared with the free energies of transfer of this complex in the initial and transition states in water + Pr^{i}OH and for other cobalt complexes in the initial and transition states in mixtures of water with various alcohols.

Following a survey of the kinetic data relating to the solvolysis of transition-metal complexes in water + co-solvent mixtures,[1] the kinetics of the solvolysis of several cobalt(III) complexes have been investigated in mixtures of water with co-solvents which at low concentrations cause marked changes in the structure of water. Isopropyl and t-butyl alcohols have been used as co-solvents, as the physical properties of mixtures of alcohols with water show [2] that these are the most effective of all the simple alcohols in inducing such changes in the water structure. The solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ (py = pyridine) has been compared in water + methanol,[3] water + Pr^{i}OH[4] and water + Bu^{t}OH[5] and the solvolysis of *cis*-$[Co(en)_2(N_3)Cl]^+$,[6] *trans*-$[Co(en)_2Cl_2]^+$,[7] and *trans*-$[Co(en)_2(N_3)Cl]^+$ (en = ethylenediamine) [8] have been examined in water + Pr^{i}OH.

It has long been recognised that such solvolysis reactions have I_d mechanisms involving the rate-determining loss of a Cl^-. However, no reverse step has been detected for the above complexes as all the rates remain independent of chloride ions added to the reaction mixtures. Moreover, in general, they give good linear plots for log(rate constant) against the Grünwald–Winstein Y factor [9] for these mixtures, suggesting that the effect of solvent on these solvolyses is mechanistically similar to that on the solvolysis of t-butyl chloride. Although the $C^{\delta+}$–$Cl^{\delta-}$ charge separation in the transition state for the solvolysis of t-butyl chloride in water and alcohols and their mixtures approaches *ca.* 90%,[10] it has been suggested that the solvent molecules may be involved in direct nucleophilic attack on t-butyl chloride.[11] However, the linear plots of log(rate constant) with slope m *ca.* 1 for the solvolysis of 1-adamantyl (tricyclo[3.3.1^{3,7}]decyl) bromide [12,13] and chloride [13] in water + co-solvent (co-solvent = ethanol, acetone, methanol, dimethyl sulphoxide, or dioxane) against the Y factor, together with the linear plots of log(relative rate constant) in such aqueous mixtures for the solvolysis of t-butyl bromide against log(relative rate constant) for the solvolysis of 1-adamantyl bromide [11] and for log(relative rate constant) for the solvolysis of t-butyl chloride in water + ethanol against log(relative rate constant) for the solvolysis of 2-methyl-2-adamantyl chloride,[11] both the latter plots having a slope of *ca.* 1, suggest, as the adamantyl system is not susceptible to nucleophilic attack, that direct nucleophilic attack of solvent molecules need not be considered for t-butyl halides in aqueous alcohols; this also removes the possibility that elimination reactions are involved. All this suggests that the transition state for the cobalt complexes in these mixtures is similar to that for t-butyl chloride with a long Co–Cl bond extension. The real extent of the bond fission in the transition state is revealed by a comparison [14,15] of the volumes of activation with the overall volume changes for related cobalt(III) complexes which suggests that such solvolyses are D reactions with the chloride ion completely removed from the Co in the transition state and with the ions independently solvated. This latter evidence allows the application of a free-energy cycle relating the process initial state ⟶ transition state for the solvolysis of the six-co-ordinated complex $[CoL_5Cl]^+$ to give the five-co-ordinated ion $[CoL_5]^{2+}$ together with the chloride ion in the transition state in water (w) and in the mixed solvent (s).[1-8]

Initial state   Transition state

$$\begin{tikzcd}
{[CoL_5Cl]^+(w)} \arrow[r, "\Delta G_w^{*\ddagger}"] & {[CoL_5]^{2+}(w)} \arrow[d, "\Delta G_t^\ominus(CoL_5^{2+})"'] & + & {Cl^-(w)} \arrow[d, "\Delta G_t^\ominus(Cl^-)"'] \\
{[CoL_5Cl]^+(s)} \arrow[u, "-\Delta G_t^\ominus(CoL_5Cl^+)"] \arrow[r, "\Delta G_s^{*\ddagger}"] & {[CoL_5]^{2+}(s)} & + & {Cl^-(s)}
\end{tikzcd}$$

Equation (1) results from this cycle, where $\Delta G_t^\ominus$(i) is the free energy of transfer for species i between water and the mixture.

$$\Delta G_s^\ddagger = \Delta G_w^\ddagger + \Delta G_t^\ominus(CoL_5^{2+}) + \Delta G_t^\ominus(Cl^-) - \Delta G_t^\ominus(CoL_5Cl^+) \quad (1)$$

Converting free energies of activation, $\Delta G^\ddagger$, into first-order rate constants, equation (1) can be rearranged to (2). Values

$$2.303RT\log(k_w/k_s) - \Delta G_t^\ominus(Cl^-) = \Delta G_t^\ominus(CoL_5^{2+}) - \Delta G_t^\ominus(CoL_5Cl^+) \quad (2)$$

for k can be determined experimentally and values for $\Delta G_t^\ominus(Cl^-)$ are available [16] for mixtures of water with a range of co-solvents enabling the left-hand side of equation (2) to be calculated, thereby giving a measure of the difference in the free energy of the cobalt ion in the transition and initial states; $-\Delta G_t^\ominus(M^{2+}) > -\Delta G_t^\ominus(M^+)$ for ions of similar size,[16,17] and the solvent structure has a dominating effect in determining the size of $\Delta G_t^\ominus$(i) for i = a cation.[16,17] Therefore, a positive value of the left-hand side of equation (2) means that the effect of solvent structure on the ion in the initial state dominates over that on the ion in the transition state and a negative value indicates the opposite: usually it is found that the solvent structure has a dominating effect on the ion in the

Table 1. Values of the first-order rate constant, $10^4k/\mathrm{s}^{-1}$ for various solvent compositions and temperatures

Bu^{t}OH		θ_c/°C			
wt. %	Mol fraction	40.0	45.0	50.0	55.0
7.99	0.021	0.48	0.82	1.72	3.00
7.99	0.021	0.45	0.85	1.57	3.07
16.35	0.045	0.305	0.59	1.54	3.19
16.35	0.045	0.311	0.66	1.39	3.30
25.10	0.075	0.290	0.67	1.38	3.04
25.10	0.075	0.315	0.67	1.39	3.31
34.27	0.113	0.38	0.75	1.54	3.33
34.27	0.113	0.35	0.73	1.51	3.19
43.88	0.160	0.338	0.73	1.42	3.45
43.88	0.160	0.333	0.69	1.52	3.36

transition state for such solvolyses.[1-8] Moreover, if values can be determined for $\Delta G_t^{\ominus}(\mathrm{CoL_5Cl^+})$ from solubility measurements on a suitable salt,[17] the free energy of transfer of the five-co-ordinated cobalt ion in the transition state can be evaluated using equation (2).

We now report the results of a kinetic investigation of the solvolysis of $[\mathrm{Co(4Me\text{-}py)_4Cl_2}]^+$ (4Me-py = 4-methylpyridine) in water with added t-butyl alcohol which causes greater changes in solvent structure at lower mol fractions than does the Pr^{i}OH used previously with this complex.[18] We also compare these results with those for *trans*-$[\mathrm{Co(py)_4Cl_2}]^+$ in water + Bu^{t}OH [5] to discover the effect on $\Delta G_t^{\ominus}(\mathrm{CoL_5}^{2+})$ of increasing the 'hydrocarbon content' at the outer edge which the complex presents to the solution.

Experimental

The salt *trans*-$[\mathrm{Co(4Me\text{-}py)_4Cl_2]ClO_4}$ was prepared from the chloride by a similar procedure to that described for the preparation of the nitrate for the analogous pyridine complex:[19] *trans*-$[\mathrm{Co(4Me\text{-}py)_4Cl_2]Cl}$ was prepared in a similar manner to that described for the analogous pyridine complex.[3,19] Water was distilled once in an all-glass still; Bu^{t}OH was fractionally distilled. Spectra and rates of solvolysis were measured as described previously.[18]

Results and Discussion

Rates in Water + t-Butyl Alcohol.—In common with water and water + Pr^{i}OH mixtures,[18] the spectrum has a maximum at 233 nm and a small flat maximum at *ca.* 300 nm. As before, the product has a minimum at 233 nm and the solvolysis of *trans*-$[\mathrm{Co(4Me\text{-}py)_4Cl_2]ClO_4}$ followed at 233 nm produced linear plots of $\log(\mathrm{O.D.}_t - \mathrm{O.D.}_\infty)$ against time (O.D. = optical density). The final optical density, $\mathrm{O.D.}_\infty$, was measured after leaving the reaction mixture overnight and accepted as $\mathrm{O.D.}_\infty$ only if it agreed with a measurement after a further 24 h. As the rate is independent of pH in the range 1—8.5,[20] no adjustment was made to the acidity of the reaction mixtures.

The values of the first-order rate constant for any concentration of Bu^{t}OH are given in Table 1 for the range 10—50% v/v Bu^{t}OH at 40.0, 45.0, 50.0, and 55.0 °C. For each concentration of Bu^{t}OH a linear plot was obtained of log(mean rate constant) against the reciprocal of the absolute temperature. Values for the enthalpy, $\Delta H^\ddagger$, and entropy, $\Delta S^\ddagger$, of activation were determined using a least-squares procedure with all the individual values of the rate constants: these values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are given with their standard errors in Table 2.

Table 2. Variation of transition-state parameters with solvent composition

Bu^{t}OH				
wt. %	Mol fraction	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$ (25 °C)/ J K^{-1} mol^{-1}	$\Delta G^\ddagger$ (25 °C)/ kJ mol^{-1}
7.99	0.021	105 ± 2	7.2 ± 7.6	103 ± 5
16.35	0.045	133 ± 3	92 ± 11	105 ± 7
25.10	0.075	131 ± 3	85 ± 8	105 ± 5
34.27	0.113	122 ± 2	59 ± 7	104 ± 4
43.88	0.160	129 ± 3	80 ± 9	105 ± 5

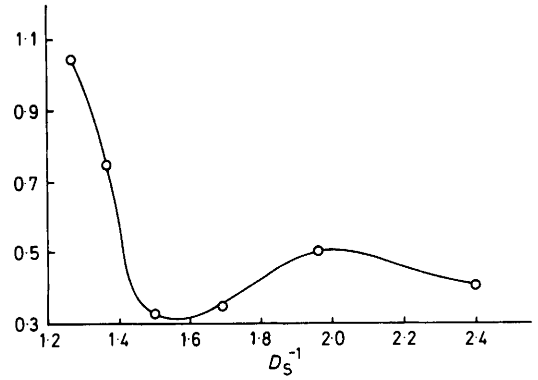

Figure 1. Plot of log k against the reciprocal of the dielectric constant at 25 °C for water + Bu^{t}OH

The Laidler–Landskroener equation,[21] based on a purely electrostatic consideration of the rate of dissociation of a complex C^{Z_C} into a metal M^{Z_M} and a ligand X^{Z} in a dielectric continuum, requires log(rate constant) to vary linearly with the reciprocal of the dielectric constant (D_s) of the medium. Figure 1 shows that values of log(rate constant) at 25 °C calculated from the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 2 do not vary linearly with D_s^{-1} and it is therefore concluded that the free energy of transfer terms in the extended [1-8,18] Laidler–Landskroener equation (3) make significant contributions to the variation in rate with solvent composition. In equation (3),

$$2.303RT\log\frac{k_w}{k_s} = \frac{Ne^2}{2}\left(\frac{1}{D_s} - \frac{1}{D_w}\right)\left[\frac{Z_M{}^2}{r_M} + \frac{Z_X{}^2}{r_X} - \frac{Z_C{}^2}{r_C} + \frac{3}{2}\left(\frac{G_M}{r_M{}^3} + \frac{G_X}{r_X{}^3} - \frac{G_C}{r_C{}^3}\right)\right] + \Delta G_t^{\ominus}(\mathrm{M})_n + \Delta G_t^{\ominus}(\mathrm{X})_n - \Delta G_t^{\ominus}(\mathrm{C})_n \quad (3)$$

k is the rate constant, N is Avogadro's number, e is the electronic charge, r is the radius, G is related to dipole moment, and $\Delta G_t^{\ominus}(\mathrm{i})_n$ is the free energy of transfer of i from water into the mixture excluding the contribution from the electrostatic term already present on the right-hand side. Values of D_s were interpolated from the data of Brown and Ives [22] and Broadwater and Kay; [23] the value for the rate constant in water was that determined previously.[18]

Values for the Grünwald–Winstein Y factor [9] have been calculated [24] for water + Bu^{t}OH using the only kinetic data available, that from Robertson and Sugamori,[25] for the solvolysis of t-butyl chloride in these mixtures. Figure 2 shows that a curve is obtained for the plot of log(rate constant) against these values of Y: this is perhaps not surprising as a non-linear plot was obtained using the same Y values for water + Bu^{t}OH in the solvolysis of *trans*-$[\mathrm{Co(py)_4Cl_2}]^+$.[5]

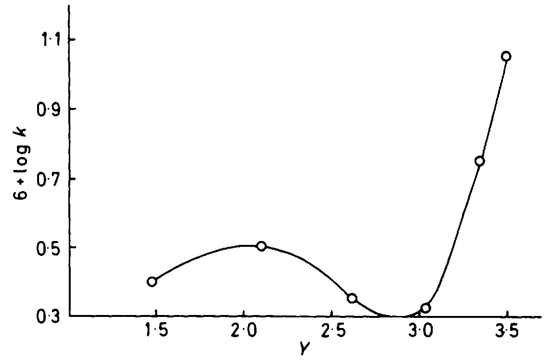

Figure 2. Plot of log k against the Grünwald-Winstein Y factor at 25 °C for water + Bu^{t}OH

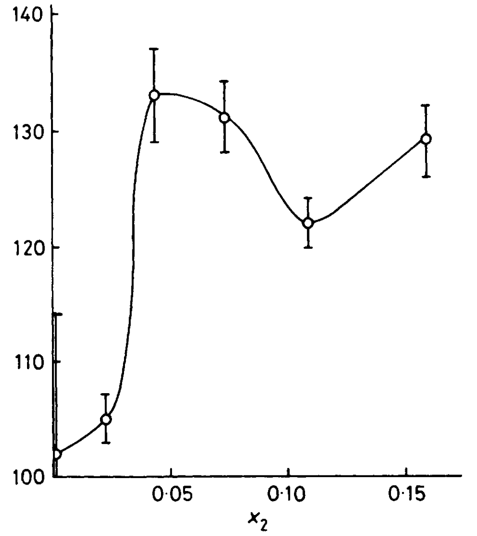

Figure 3. Plot of the enthalpy of activation against the mol fraction of Bu^{t}OH, x_2

Also non-linear plots have been obtained for the solvolysis of several complexes [4,6–8,18] in water + Pr^{i}OH using Y values, calculated from rate data from the same source,[25] whereas linear plots are usually obtained [4,6,8] for these complexes using Y values for water + Pr^{i}OH calculated [7] from a different source of kinetic data, excluding *trans*-[Co(4Me-py)$_4$Cl$_2$]$^+$.[18]

Variation of Transition-state Parameters with Solvent Composition.—Figures 3 and 4 show that both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ vary in an irregular manner with solvent composition, as found for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the solvolysis of several complexes in water + co-solvent mixtures.[3–8,18] However, a plot of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ for the solvolysis of *trans*-[Co(4Me-py)$_4$Cl$_2$]$^+$ in water + Bu^{t}OH is linear. The maxima at mol fraction x_2 *ca.* 0.04—0.05 and the minima at x_2 *ca.* 0.10—0.11 are well outside the possible deviations of individual determinations. They contrast with the single broad maximum found for *trans*-[Co(py)$_4$Cl$_2$]$^+$ in water + Bu^{t}OH,[4] but they compare well with the maximum at x_2 *ca.* 0.05 and the minimum at x_2 *ca.* 0.15 found for *trans*-[Co(4Me-py)$_4$Cl$_2$]$^+$ in water + Pr^{i}OH.[18]

In all the earlier cases [3–8,18] it was found that the extrema in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ correlate with the physical properties of the mixture. In the present case, the maxima occur in the same region as the minimum found at x_2 *ca.* 0.04 for $\bar{V}_2 - V_2^\circ$ in water + Bu^{t}OH,[26,27] and the minima are in the same region as x_2 *ca.* 0.1 where the minimum in the excess enthalpy of mixing, ΔH^E,[26] and the maximum in the ultrasonic absorption [28] occur for water + Bu^{t}OH. These relationships between the extrema in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ and the extrema in the physical properties of the mixtures compare well with the same relationships found with the same complex in water + Pr^{i}OH.[18] These extrema in physical properties at low x_2 in water + co-solvent are associated with sharp changes in solvent structure and show clearly the specific influence which solvent structure has on the transition-state parameters. It is suggested [29] that the extrema described for the lower x_2 (0.04) correspond to the exertion of maximum strain by the branched-chain alkyl groups lying in the cavities between the 'flickering clusters' of water [30] on the 'clusters' of structured water, and that the extrema at the higher x_2 (0.1) correspond to the beginning of the breakdown of the structure of the 'clusters' due to the increasing stress within them.

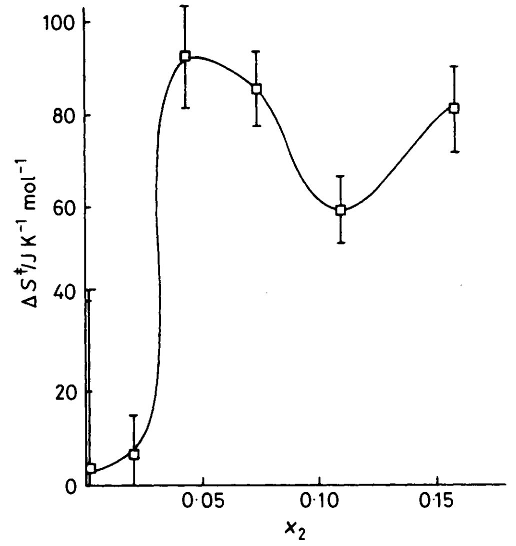

Figure 4. Plot of the entropy of activation against the mol fraction of Bu^{t}OH, x_2

Application of the Free-energy Cycle.—The free-energy cycle discussed above can be applied to the rate constants at 25 °C calculated from the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 2, with [CoL$_5$Cl]$^+$ = [Co(4Me-py)$_4$Cl$_2$]$^+$ and [CoL$_5$]$^{2+}$ = [Co(4Me-py)$_4$Cl]$^{2+}$. To complete the data needed to calculate the left-hand side of equation (2), the values for ΔG_t°(Cl$^-$) used have been derived from ΔG_t°(HCl) and values for ΔG_t°(H$^+$) calculated by the solvent-sorting method.[16] Small corrections have been applied [31] to the published data [16] for ΔG_t°(Cl$^-$) arising from the inclusion of a scale correction to the small Born contribution to ΔG_t°(H$^+$) to adjust to the mol fraction scale, the re-calculation of [H$_2$O] used in the evaluation of ΔG_t°(H$^+$), and the inclusion of new electrochemical data for ΔG_t°(HCl) from Smits *et al.*[32] and Elsemongy:[33] the new values have been reported.[5,31] Figure 5 shows that $-\Delta G_t^\circ$[Co(4Me-py)$_4$Cl^{2+}] > $-\Delta G_t^\circ$[Co(4Me-py)$_2$Cl$_2$$^+$], in agreement with the findings for these cations in water + Pr^{i}OH.[18] This order conforms with the general observation in water + co-solvent mixtures for simple cations of similar size,[16,17] $-\Delta G_t^\circ(M^{2+}) > -\Delta G_t^\circ(M^+)$, and for complex cations of similar size,[1,3–8,17] $-\Delta G_t^\circ(\text{CoL}_5{}^{2+}) > -\Delta G_t^\circ(\text{CoL}_5\text{Cl}^+)$.

In Figure 5 the left-hand side of equation (2) is plotted for the solvolysis of all the pyridinecobalt(III) complexes [3–5,18]

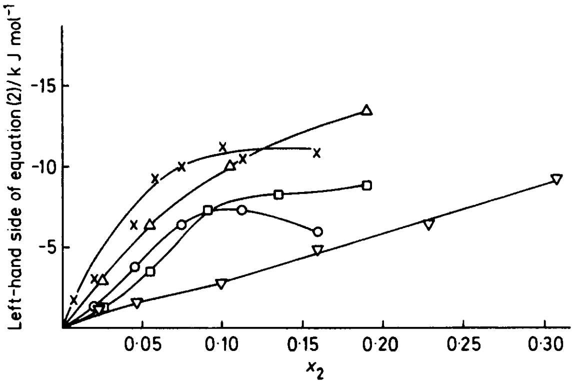

Figure 5. Comparison of the variation of the left-hand side of equation (2) for the solvolysis of $[Co(4Me\text{-}py)_4Cl_2]^+$ in water + Bu^{t}OH (○) with that for the solvolysis of chloropyridinecobalt(III) complexes in mixtures of water and co-solvent at 25 °C: □ $[Co(4Me\text{-}py)_2Cl_2]^+$ in water + Pr^{i}OH; △ $[Co(py)_4Cl_2]^+$ in water + Pr^{i}OH; ▽ $[Co(py)_4Cl_2]^+$ in water + methanol; × $[Co(py)_4Cl_2]^+$ in water + Bu^{t}OH

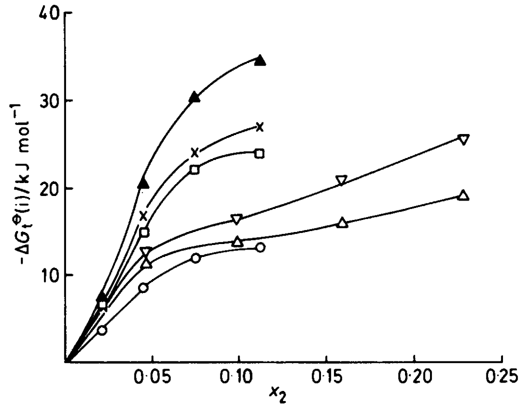

Figure 6. Comparison of the free energies of transfer, $\Delta G_t^{\ominus}(i)$, for i = $[Co(4Me\text{-}py)_4Cl_2]^+$ (×) and $[Co(4Me\text{-}py)_4Cl]^{2+}$ (▲) in water + Bu^{t}OH with those for i = $[Co(py)_4Cl_2]^+$ and $[Co(py)_4Cl]^{2+}$ in water + co-solvent mixtures at 25 °C: ○ $[Co(py)_4Cl_2]^+$ in water + Bu^{t}OH; □ $[Co(py)_4Cl]^{2+}$ in water + Bu^{t}OH; △ $[Co(py)_4Cl_2]^+$ in water + methanol; ▽ $[Co(py)_4Cl]^{2+}$ in water + methanol

Table 3. Values for the free energies of transfer from water to mixture, $\Delta G_t^{\ominus}(i)$, at 25 °C

Bu^{t}OH		$\Delta G_t^{\ominus}(i)$/kJ mol^{-1}	
wt. %	Mol fraction	i = $[Co(4Me\text{-}py)_4Cl_2]^+$	i = $[Co(4Me\text{-}py)_4Cl]^{2+}$
7.99	0.021	−6.3	−7.5
16.35	0.045	−16.6	−20.3
25.10	0.075	−24.0	−30.3
34.27	0.113	−26.7	−33.3

using the new values[31] for $\Delta G_t^{\ominus}(Cl^-)$ for each water + co-solvent mixture. The mutual similarity of these plots, conforming to $-\Delta G_t^{\ominus}(M^{2+}) > -\Delta G_t^{\ominus}(M^+)$ and very similar to those found for the complexes $[Co(en)_2Cl_2]^+$ in water + co-solvent,[7,34] supports the assumption in the above cycle that the extension of the Co–Cl bond in the transition state for the pyridinecobalt(III) complexes corresponds as closely to complete dissociation as found from data on $\Delta V^{\ddagger}$ specifically for $[Co(en)_2Cl_2]^+$ [15,35] and in general for other complexes $[CoL_5Cl]^{2+}$ and $[CoL_4Cl_2]^+$ where L is co-ordinated through N atoms.[15,35]

Free Energies of Transfer for Complexed Cobalt(III) *Ions*.— Values for $\Delta G_t^{\ominus}[Co(4Me\text{-}py)_4Cl_2^+]$ have been determined[17] from the solubilities of $[Co(4Me\text{-}py)_4Cl_2]_2[ReCl_6]$ [17] and $Cs_2[ReCl_6]$ [36] and the values of $\Delta G_t^{\ominus}(Cs^+)$ [16] in water + Bu^{t}OH. As the values of $\Delta G_t^{\ominus}(Cs^+)$ ultimately depend on the values of $\Delta G_t^{\ominus}(H^+)$ determined by the spectrophotometric solvent-sorting method,[16] the small corrections discussed above have also been applied to $\Delta G_t^{\ominus}(Cs^+)$.[5,31] The corrected values for $\Delta G_t^{\ominus}[Co(4Me\text{-}py)_4Cl_2^+]$ are given in Table 3 together with the values derived for $\Delta G_t^{\ominus}[Co(4Me\text{-}py)_4Cl^{2+}]$ by using the former in equation (2).

Figure 6 shows that, for the pyridinecobalt(III) complexes in water + alcohol mixtures, the cobalt cation with the highest charge and the greatest hydrocarbon content at its outer edge is stabilized the most in water + Bu^{t}OH relative to pure water, as expected from the high values obtained for $-\Delta G_t^{\ominus}$(cation) for cations containing hydrocarbon groups.[16,31] However, the difference in the stabilization between the cation in the initial and transition states is greatest for $[Co(py)_4Cl_2]^+$ and $[Co(py)_4Cl]^{2+}$ in water + Bu^{t}OH, in conformity with the large negative values in Figure 5. For $[Co(4Me\text{-}py)_4Cl_2]^+$ and $[Co(4Me\text{-}py)_4Cl]^{2+}$, Figure 5 shows that the difference in stabilization varies little between Pr^{i}OH and Bu^{t}OH as co-solvent at low x_2. To a first approximation, $-\Delta G_t^{\ominus}[Co(py)_4Cl_2^+]$ is the same in water + Bu^{t}OH and in water + methanol at low x_2 and, therefore, the order for $-\Delta G_t^{\ominus}[Co(py)_4Cl^{2+}]$, water + Bu^{t}OH > water + methanol, suggests that the principal effect of the greater structure-inducing co-solvent occurs in the transition state rather than the initial state. This is in agreement with the general observation of negative values for the left-hand side of equation (2) when applied[1] to a wide range of published rate data for cobalt complexes and to our own rate data.[3–8,18]

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