Effects of Solvent on the Reactions of Coordination Complexes. Part 24. Kinetics of Base Hydrolysis of Some (Aminomonocarboxylato)(Tetraethylenepentamine)Cobalt(III) Complexes in Methanol + Water Media: The Role of Substrate Hydrophobicity and Solvent Structure

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ABSTRACT: The kinetics of base hydrolysis of some (aminomonocarboxylato)(tetraethylenepentamine)cobalt(III) complexes, $[(tetren)CoO_2CR]^{2+}$ (R = —NH_2CH_2, pyridine-2—, —$NH_2CH_2CH_2$, —$NH_2CH(CH_3)$ ($\alpha\beta$S isomer); R = —$NH_2CH(CH_3)$ ($\alpha\beta$R isomer)), have been investigated in methanol–water media (0–80 vol % MeOH) at $15.0 \leq t°C \leq 40.0$ (0.02 mol dm^{-3} NaOH). The second-order rate constant at zero ionic strength, $k_2°$, increases

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nonlinearly with X_{MeOH}. The transfer free energy of the initial state and the transition state of the amido conjugate base ($|\Delta_t G(i)|_{(s\leftarrow w)}$) for the glycinato- and pyridine-2–carboxylato complexes have been calculated using the solubility data of their picrate salts, pK_{NH} date of their N-protonated forms, and the $k_2°$ values in mixed solvent media. The kinetic solvent effects have been interpreted in terms of preferential solvation of the initial state, transition state, and the solvent structure. The activation enthalpies and entropies varied nonlinearly with X_{MeOH} displaying extrema, which is attributable to the solvent structural effects on these thermodynamic parameters. It is also evident that the mutation process, $\alpha\beta$R → $\alpha\beta$S isomer for the α-alaninato complex, where this isomerisation refers to the arrangement of the tetren skeleton around the planar secondary NH is sensitive to the nature of the cosolvent molecules and solvent structure. The mutation process is generally more favorable for the five coordinate amido conjugate bases than the initial state. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 55–64, 1999

INTRODUCTION

A recent study of the base-catalyzed hydrolysis of a series of halogeno amine cobalt(III) complexes, *cis*-$[Co(en)_2(B)(X)]^{2+}$ (X = Cl, Br, B = a monodentate amine of varying structure and hydrophobicity; en = 1,2 diaminoethane) in methanol + water media [1] demonstrated that the reactivities of these substrates are grossly influenced by the preferential solvation, solvent structure, and hydrophobic interaction. These substrates, however, undergo ligand substitution in basic medium via SN_1cb mechanism. Stereochemical changes at the cobalt(III) center (*cis* → *trans* isomerization) occur during the base hydrolysis, due to the fact that the octahedral amido conjugate base assumes a transition state that is essentially a five-coordinate one with trigonal bipyramidal (TBP) geometry. This stereochemical change at the cobalt(III) center can be prevented in the base hydrolysis of (tetren)CoX^{n+} (*tetren* = tetraethylenepentamine) due to the rigidity of the *tetren* ligand. It is our hope that the kinetic solvent effects can be better understood in the absence of the complexity due to stereochemical changes at the cobalt(III) center.

Our recent investigations on the base-catalyzed hydrolysis of the substrates, $[(tetren)CoO_2CR]^{2+}$ (R = —CH_2NH_2, —$CH_2CH_2NH_2$, —$CH(CH_3)NH_2$, pyridine-2— (I–IV) in CH_3CN + water [2] and DMSO + water [3] media reinforced our views that the chemical potentials of the initial states and transition states of these substrates are grossly affected by the solvent acidities (α), basicities (β), polarizabilities) (π^*), and the structure of the mixed solvents. Our earlier work on the base hydrolysis of $\alpha\beta$S-(*o*-methoxy benzoato)(tetren)cobalt(III) [4] and $\alpha\beta$S-(salicylato)(tetren) cobalt(III) [5,6] in different aquo-organic solvent media also indicated that the relative stabilities of the initial state and transition state are cosolvent specific and governed by preferential solvation. It was apparent that the hydrophobicities of the substrates and the cosolvent molecules play a specific role in mediating the reactivities of the substrates. We now report a thorough and extensive study in methanol + water media to further elucidate the role of hydrophobic interactions and solvent structure on the kinetics of the base-catalyzed hydrolysis of (aminomonocarboxylato)(tetren)cobalt(III). MeOH was chosen, as it is a protic hard electron-pair-donor capable of influencing the structure of water and associated with the substrates through hydrogen bonding. Besides, it can also undergo hydrophobic association with substrates due to the favorable interaction of the CH_3 group with the apolar segments of the latter.

EXPERIMENTAL

The complexes $[(tetren)CoO_2CR](ClO_4)_n$ [R = pyridine-2—(n = 2, $\alpha\beta$S isomer); R = $^+NH_3(CH_2$—, $^+NH_3CH_2CH_2$— (n = 3, $\alpha\beta$S isomer); R = $^+NH_3CH(CH_3)$— (n = 3, $\alpha\beta$S and $\alpha\beta$R isomers) and the picrate salts, $[(tetren)CoO_2CCH_2NH_3](Pic)_3$, $2H_2O$; $[(tetren)CoO_2CPy(-2-)](Pic)_2$, $2H_2O$, were received from our earlier work [2,3]. The relatively more reactive isomer of the α-alaninato complex was assigned as the $\alpha\beta$R configuration.

Analar grade reagents were used. MeOH (Qualigens, purity > 99.9% by G.C.) was further dried over molecular sieve (4 Å) and distilled; the middle fraction (b.p. 64.8°C) was used. Distilled water was redistilled over alkaline $KMnO_4$ in an all glass distillation apparatus. Solvent mixtures were prepared in volume percent, conversion to mol fraction was done by using density data. The pH measurements were made with an ELICO digital pH meter model LI 120 using a combined glass–Ag/AgCl, Cl^-(2 mol dm^{-3} NaCl) electrode CL 51. The electrode system was calibrated with standard aqueous buffers of pH 4.01, 6.86, and 9.2. The observed pH values (pH_{obs}) of the experimental

solutions in MeOH + H_2O media were corrected using the reported values of the correction factor δ for different solvent compositions (pH = $pH_{obs} - \delta$) [7a] and the corrected pH data were converted to $[H^+]$ $(= 10^{-pH}/\gamma_{H^+})$ by γ_{H^+} calculated using the Davies equation [7b]. The UV-visible sectra were recorded on a JASCO 7800 spectrophotometer using 10-mm matched quartz cells.

p*K* Measurements

The p*K* of the N-protonated pyridine-2−carboxylato complex in MeOH + H_2O was determined spectrophotometrically at 25°C. The absorbances (260 nm) of a known concentration of the complex at $1 \leq pH \leq 6$ were measured. The pH adjustments were done with standard $HClO_4$ or NaOH. The molar extinction coefficients of the unprotonated (ϵ_1) and N-protonated forms (ϵ_2) were taken to be the observed values (ϵ_{obs}) at pH 6 and 1, respectively, ϵ_1 and ϵ_2 were also solvent composition independent. The ϵ_{obs} data at pH = 3.5−4.5 ($\epsilon_{obs} = \epsilon_1[C^{2+}] + \epsilon_2[CH^{3+}]$. $[C]_T = [C^{2+}] + [CH^{3+}]$, where C^{2+} and CH^{3+} denote an unprotonated and N-protonated complex, respectively) were used to calculate K_{NH} $\{= [C^{2+}]\ [H^+]/[CH^{3+}]\}$. The acid dissociation of the N-protonated glycinato and alaninato complexes did not result in significant spectral changes. Hence, pH titration was adopted to determine their pK_{NH}. The effect of ionic strength on pK_{NH} (25.0°C) was studied for the pyridine-2−carboxylato complex at 0, 20, and 80% (v/v) MeOH + H_2O; ionic strength (adjusted with $NaClO_4$) was varied as 0.010, 0.020, 0.050, 0.10 and 0.15 mol dm^{-3}. The values of $pK_{NH}{}^0$ (i.e., pK_{NH} at zero ionic strength) were calculated by eq. (1) based on the Davies Equation [7b] for the activity coefficients of ions.

$$pK_{NH} = pK_{NH}{}^0 + S\,A\,\{1^{1/2}/(1.0 + 1^{1/2}) - 0.21\} \quad (1)$$

Note that the values of the slope ($S\,A$) of the plots of pK_{NH} vs. $[1^{1/2}/(1.0 + 1^{1/2}) - 0.21]$ yielded + 2.5 as the effective charge of the N-protonated complex (CH^{3+}); the values of the Debye-Huckel constant $A(= 1.824 \times 10^6/(D_sT)^{3/2}$, D_s is the dielectric constant of the medium) were calculated using the value of D_s reported by Akerlof [8]. This is understandable, as the 2+ and 1+ charge centers are well separated in the N-protonated complex. Similar behavior was shown in the CH_3CN + H_2O media. For all other complexes pK_{NH} was measured at $I = 0.1$ mol dm^{-3} and corrected for the ionic strength effect using eq. (1) and the same value of the slope parameter (S). $pK_{NH}{}^0$ values are collected in Table I.

Solubility Measurements

The sparingly soluble picrate salts of the N-protonated glycinato and pyridine-2−carboxylato complexes were equilibrated in MeOH + H_2O media at 25.0 ± 0.1°C in a water thermostat for 1 week. However, the solutions attained saturation within 48−72 h. The complexes are virtually inert to aquation (i.e., substitution of the bound carboxylate by H_2O) under the

Table I Solubilities (*s*) of Picrate (Pic) Salts and $pK_{NH}°$ of $\alpha\beta$S-[Tetren)CoO_2CR]$^{n+}$ Ions in Methanol + Water Media at 25°C[a,b]

	$s/(10^{-4}$ dm^3 mol$^{-1})$[c]		$pK_{NH}°$ [d]	
X_{MeOH}	I	II	I	II
0.0	6.11 ± 0.10	4.10 ± 0.10	8.26 ± 0.05	4.03 ± 0.07
0.047	6.73 ± 0.08	3.58 ± 0.11	8.19 ± 0.01	3.93 ± 0.04
0.10	5.94 ± 0.05	3.76 ± 0.09	8.12 ± 0.03	3.86 ± 0.02
0.16	6.28 ± 0.16	4.45 ± 0.04	7.94 ± 0.05	3.70 ± 0.07
0.227	6.49 ± 0.04	3.20 ± 0.16	7.87 ± 0.02	3.60 ± 0.06
0.306	7.69 ± 0.07	3.02 ± 0.12	7.82 ± 0.03	3.44 ± 0.08
0.398	8.72 ± 0.04	3.86 ± 0.05	7.70 ± 0.02	3.35 ± 0.03
0.507	8.19 ± 0.08	3.69 ± 0.09	7.61 ± 0.06	3.27 ± 0.06
0.64	7.91 ± 0.12	4.02 ± 0.04	7.49 ± 0.05	3.18 ± 0.02

[a] R = —CH_2NH_3 (n = 3) (I) and —(-2-)C_5H_4N (n = 2) (II).

[b] X_{MeOH} = 0.023, 0.047, 0.10, 0.16, 0.227, 0.306, 0.398, 0.507, and 0.64 are for (v/v)% MeOH, 5.2, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, and 80.0, respectively.

[c] Solubilities of $IPic_3$ and $IIPic_2$.

[d] $pK_{NH}° = 7.48 \pm 0.08$, 9.0 ± 0.1, and 8.83 ± 0.05 (25°C) for N-protonated ($\alpha\beta$R), ($\alpha\beta$S), and ($\alpha\beta$S) isomers of α- and β-alaninato complexes in aqueous medium, respectively.

condition of the solubility measurements. The concentrations of the complexes in their saturated solutions were computed from the absorbances (A_{obs}) at 355 nm. A calibration curve {$A_{obs} = (\epsilon_1 + n\epsilon_2)[\text{complex}]_T$ where ϵ_1 and ϵ_2 denote the molar extinction coefficients of $[(\text{tetren})CoO_2CR]^{n+}$ and Pic^-, respectively} was used. It was assumed that the picrate (Pic^-) and the complex ions did not undergo association in the saturated solution, and the solid phase did not change its state of hydration in the mixed solvent media. The solubility equilibria for the pyridine-2−carboxylato and glycinato complexes may be defined as given in eqs. (2) and (3), for which the solubility product may be defined by eqs. (4) and (5), respectively.

$$CPic_{2(\text{hydrated solid})} = C^{2+}{}_{(\text{solvated})} + 2\ Pic^-{}_{(\text{solvated})} \quad (2)$$

$$CHPic_{3(\text{hydrated solid})} == CH^{3+}{}_{(\text{solvated})} + 3\ Pic^-{}_{(\text{solvated})} \quad (3)$$

$$K_{sp}{}^0 = 4s^3\ \gamma^2_{Pic^-} \cdot \gamma_{C}{}^{2+} \quad (4)$$

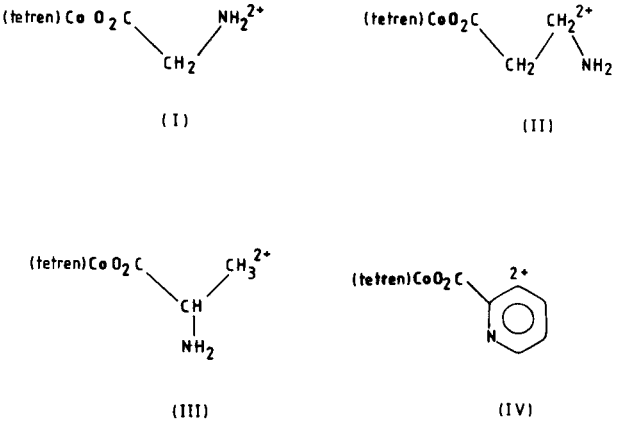
$$K_{sp}{}^0 = 27s^4\ \gamma^3_{Pic^-} \cdot \gamma_{CH}{}^{3+} \quad (5)$$

The solubility products ($K_{sp}{}^0$) were calculated from the solubility data (s) using the activity coefficients computed from the Davies Equation [7b]; the effective charge of CH^{3+} was taken to be +2.5, as mentioned earlier. These data are also collected in Table I.

Kinetic Measurements

The base-catalyzed hydrolysis of the complexes was studied in MeOH + H_2O ($0 \le$ v/v% MeOH ≤ 80) at $20.0 \le t/°C \le 40.0$ (± 0.1°C) under pseudofirst-order conditions with $[\text{complex}]_T = (2-8) \times 10^{-4}$ and $[NaOH]_T = 0.02$ mol dm^{-3}. The reaction was monitored at 260 nm using a stopped flow spectrophotometer (SF51, M/s HITECH, UK) interfaced with an APPLE II GS PC. The decrease of absorbance with time for any run was a single exponential curve characteristic of the first-order kinetics. The values of k_{obs} and $\sigma(k_{obs})$ were calculated from at least seven replicate measurements for any run.

All other calculations were done on an IBM 486 PC. A weighted least-squares program was used and the dependent variable was weighted as the inverse of its variance.



Structures I—[(tetren)Co(glycinato)]$^{2+}$, II—[(tetren)Co(β-alaninato)]$^{2+}$ III—[(tetren)Co(α-alaninato)]$^{2+}$, IV—[(tetren)CoO_2C(-2-)Py]$^{2+}$.

RESULTS AND DISCUSSION

The base hydrolysis reaction in methanol−water media may be represented by eq. (6)

$$(\text{tetren})CoO_2CR^{2+} + S^- \underset{(C^{2+})}{\overset{K_{CB}{}^{app}}{\rightleftharpoons}} \{(\text{tetren}).\cdots\cdots HS\}$$

$$CoO_2CR\}^+ \xrightarrow[(\text{C. B.})]{K_{CB}{}^{app}} (\text{tetren})CoS^{2+} + RCO_2- \quad (6)$$

where S^- is the lyate ion ($[S^-]_T = [OH^-]_T = [OH^-] + [^-OMe]$), K_{CB}^{app} is the apparent equilibrium constant of the formation of the reactive amido conjugates base {$K_{CB}^{app} = [CB^+]/([C^{2+}][S^-]_T)$}, and k_{cb} is the first-order dissociation rate constant of the carboxylate ion (RCO_2^-) from the conjugate base. The conjugate base equilibrium is rapidly established and it is essentially shifted to the reactant side due to the high pK of the coordinated amine ($pK_{NH} > 15$). Note that *SH* liberated in the conjugate-base equilibrium is hydrogen bonded to the strongly basic amido base. The reaction obeys second-order kinetics (first order in both [complex] and $[OH^-]_T$). Accordingly the second-order rate constant ($k_2 = k_{obs}/[OH^-]_T$) is given by eq. (7)

$$k_2 = k_{cb}K_{CB}{}^{app} \quad (7)$$

where

$$K_{CB}^{app} = K_{CB}^{OMe}\ K_{CB}^{OH}/(K_{CB}^{OH} + K_{CB}^{OMe}); \quad (8)$$

K_{CB}^{OH} and K_{CB}^{OMe} are the equilibrium constants for the formation of the reactive amido conjugate base by OH^- and MeO^-, respectively [see eq. (6); $1/K_{CB}^{app} = 1/K_{CB}^{MeO} + 1/K_{CB}^{OH}$]. The overall second-order rate constant (k_2) was corrected to zero ionic strength ($k_2{}^0$)

assuming that the ionic strength effect on k_2 at the low ionic strength used was due to the same on the equilibrium constant, K_{CB}^{app}, and $\gamma_S^- = \gamma_{OH}^- = \gamma_{OMe}^-$. The k_2^0 ($= k_2$ at I = 0) values were calculated using the relationship [see eq. (9)]

$$\log k_2 = \log k_2^0 - 2 z_A A 1^{1/2}/(1 + 1^{1/2}) \qquad (9)$$

where z_A is the charge of the complex ion, and A is the Debye-Huckel constant as defined earlier. The values of k_2^0 and associated activation parameters are collected in Table II.

Effect of Solvent Composition on the Reactivities of the Complexes

It is observed that k_2^0 increases nonlinearly with increasing mol fraction of the cosolvent (see Fig. 1). This trend is similar to those observed for CH_3CN + H_2O [2] and DMSO + H_2O [3] media. The rate-accelerating effect of this dipolar protic cosolvent is, however, less than the same for the other two dipolar aprotic cosolvents under comparable conditions of dielectric permitivity. We believe that this differential behavior at least partly arose due to the solvation stabilisation of OH^- by MeOH through hydrogen bonding, which is not possible for DMSO or CH_3CN. Unlike the two dipolar aprotic cosolvents, both MeO^- and OH^- are likely to set up the conjugate base equilibrium for the complex in MeOH + H_2O. This is more significant at relatively high value of X_{MeOH} (X denotes mol fraction). It is, however, possible to evaluate the OH^- component rate constant at zero ionic strength, $k_2^{OH\ O,S}$. Combining eqs. (7) and (8), $k_2^{OH\ O,S}$ can be expressed as in eq. (10)

$$k_2^{O,S} = k_{cb}\bullet\ (K_{CB}^{OH})^0/[1 + (K_{CB}^{OH})^0/(K_{CB}^{MeO})^0] = k_2^{OH\ O,S}/(1 + a_{MeO^-}/a_{OH^-}) \qquad (10)$$

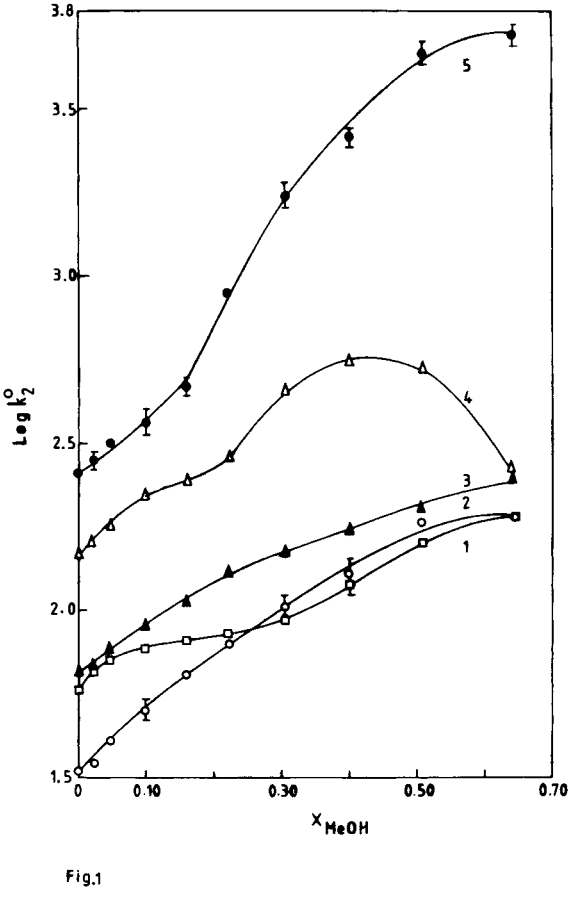


Figure 1 Plot of log $k_2°$ vs. X_{MeOH} for base hydrolysis of $[(tetren)CoO_2CR]^{2+}$ complexes at 25°C: R = —CH_2CH_2-NH_2($\alpha\beta$S)(**1**), —$CH(CH_3)NH_2$($\alpha\beta$S)(**2**), —CH_2NH_2 ($\alpha\beta$S)(**3**), —(-2-)Py($\alpha\beta$S)(**4**), —$CH(CH_3)NH_2$($\alpha\beta$R)(**5**).

In eq. (10) $k_2^{O,S}$ and $k_2^{OH\ O,S}$ denote the overall second-order rate constant and its OH^- component (i.e., $(tetren)CoO_2CR^{2+} + OH^- \rightarrow (tetren)CoOH^{2+} + RCO_2^-$; $k_2^{OH\ O,S}$) in the mixed solvent (s) and at zero ionic strength, respectively, and the activity ratio a_{MeO}^-/a_{OH}^- refer to the same solvent composition as the rate constants. The values of a_{MeO}^-/a_{OH}^- can be calculated from the ratio of ionic product of water $K_{IP}^{H_2O}$) and ionic product of methanol (K_{IP}^{MeOH}) in the same solvent composition as $a_{MeO}^-/a_{OH}^- = K_{IP}^{MeOH}/K_{IP}^{H_2O}$. Using the values of K_{IP}^X (X = H_2O, MeOH) reported by Rochester [9], the values of a_{MeO}^-/a_{OH}^- turned out to be 0.041, 0.086, 0.193, 0.358, 0.574, 0.879, 1.320, 2.042, and 3.529 for 5.2, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70,0 and 80.0 (v/v)% MeOH, respectively at 25°C. An attempt is made here to elucidate the solvent effects on the OH^- catalyzed hydrolysis of the complexes by considering the transfer Gibbs free energies of the initial state, transition state, and OH^-, and the solvent structure.

The Gibbs excess free energy (G^E) of the mixed solvent may be taken as an indicator of solvent structure. The solvent effect on the stability of the transition state relative to that of the initial state can be judged from the relative transfer free energy P' as defined by eq. (11)[1]

$$P' = [\Delta_t G(t.s.) - \Delta_t G(i.s.)]_{(s\leftarrow w)} = RT \ln (k_2^{OH\ O,W}/k_2^{OH\ O,S}) + [\Delta_t \overline{G}^0(OH^-)]_{(s\leftarrow w)} \qquad (11)$$

where *t.s.* {$= [(tetren\ ..\ HOH)Co^{2+} \ldots . {}^-O_2CR]^+$ *} is the dissociative transition state of the conjugate

Table II Rate Constants (k_2^0) and Associated Activation Parameters ($\Delta H^{\#}$) and $\Delta S^{\#}$) for Base Hydrolysis of $[(Tetren)CoO_2CR]^{2+}$ in MeOH + Water Media[a]

	$10^{-2}\ k_2^0$/ dm^3 mol^{-1} s^{-1}				$\Delta H^{\#}$/ kJ mol^{-1}	$\Delta S^{\#}$/ JK^{-1} mol^{-1}
X_{MeOH}	20.0 ± 0.1	25.0 ± 0.1	35.0 ± 0.1	40.0 ± 0.1°C		
			R = CH_2NH_2[b]			
0.0	0.33 ± 0.01	0.65 ± 0.02	2.49 ± 0.07	4.20 ± 0.20	97 ± 2	115 ± 7
0.023	0.37 ± 0.02	0.68 ± 0.05	2.67 ± 0.05	5.25 ± 0.25	99 ± 2	121 ± 7
0.047	0.39 ± 0.02	0.78 ± 0.08	3.07 ± 0.07	6.18 ± 0.13	103 ± 2	138 ± 6
0.10	0.47 ± 0.02	0.89 ± 0.04	3.77 ± 0.06	7.36 ± 0.19	104 ± 2	140 ± 6
0.16	0.53 ± 0.04	1.05 ± 0.05	4.51 ± 0.10	9.53 ± 0.26	110 ± 3	162 ± 9
0.227	0.63 ± 0.06	1.26 ± 0.06	5.52 ± 0.15	11.4 ± 0.3	110 ± 1	163 ± 5
0.306	0.73 ± 0.04	1.48 ± 0.10	6.86 ± 0.42	14.1 ± 1.3	111 ± 2	168 ± 6
0.398	0.91 ± 0.07	1.72 ± 0.10	7.28 ± 0.58	13.4 ± 0.8	102 ± 2	140 ± 7
0.507	0.96 ± 0.06	1.94 ± 0.15	8.17 ± 0.71	15.2 ± 0.7	103 ± 1	146 ± 3
0.64	1.27 ± 0.07	2.50 ± 0.16	10.1 ± 0.9	19.0 ± 1.6	101 ± 1	141 ± 2
			R = —$CH_2CH_2NH_2$[b]			
0.0	0.28 ± 0.01	0.58 ± 0.02	2.08 ± 0.12	3.82 ± 0.07	97 ± 1	112 ± 3
0.023	0.33 ± 0.02	0.66 ± 0.02	2.51 ± 0.07	4.59 ± 0.20	99 ± 1	120 ± 3
0.047	0.37 ± 0.02	0.71 ± 0.03	2.67 ± 0.07	5.21 ± 0.29	98 ± 1	119 ± 5
0.10	0.37 ± 0.02	0.76 ± 0.03	3.14 ± 0.09	6.15 ± 0.42	105 ± 1	144 ± 2
0.16	0.39 ± 0.02	0.81 ± 0.02	3.58 ± 0.10	7.19 ± 0.63	110 ± 1	160 ± 4
0.227	0.42 ± 0.02	0.85 ± 0.03	3.78 ± 0.22	7.35 ± 0.55	108 ± 2	154 ± 6
0.306	0.45 ± 0.02	0.93 ± 0.03	4.01 ± 0.07	8.08 ± 0.55	109 ± 1	157 ± 3
0.398	0.51 ± 0.02	1.20 ± 0.08	4.68 ± 0.32	9.27 ± 0.68	108 ± 2	156 ± 8
0.507	0.73 ± 0.03	1.59 ± 0.10	5.90 ± 0.22	10.9 ± 0.7	101 ± 2	136 ± 5
0.64	1.16 ± 0.07	1.90 ± 0.09	9.59 ± 0.50	17.6 ± 1.4	107 ± 8	158 ± 26
			R = —$CH(CH_3)NH_2$[c]			
0.0	1.40 ± 0.03	2.56 ± 0.13	8.80 ± 0.71	14.6 ± 1.4	88 ± 1	96 ± 4
0.023	1.50 ± 0.07	2.79 ± 0.19	9.02 ± 0.91	16.1 ± 1.6	88 ± 0.3	96 ± 1
0.047	1.64 ± 0.14	3.15 ± 0.20	10.0 ± 0.5	18.5 ± 1.3	89 ± 1	100 ± 5
0.10	2.03 ± 0.11	3.63 ± 0.36	12.4 ± 1.1	21.8 ± 2.1	88 ± 1	100 ± 3
0.16	2.42 ± 0.20	4.68 ± 0.34	19.2 ± 1.9	35.4 ± 2.5	101 ± 1	145 ± 5
0.227	4.63 ± 0.11	8.84 ± 0.35	32.7 ± 1.6	55.6 ± 5.5	94 ± 1	128 ± 4
0.306	9.66 ± 0.20	17.3 ± 1.5	54.6 ± 4.3	93.1 ± 8.0	84 ± 0.3	99 ± 1
0.398	13.1 ± 1.1	26.0 ± 1.7	87.3 ± 8.6	127 ± 11	85 ± 4	105 ± 14
0.507	25.1 ± 1.5	46.3 ± 3.7	159 ± 16	254 ± 25	87 ± 2	118 ± 6
0.64	30.9 ± 3.2	52.6 ± 3.8	206 ± 20	410 ± 41	98 ± 4	156 ± 15
			R = —$CH(CH_3)NH_2$[b]			
0.0	0.19 ± 0.01	0.33 ± 0.02	1.33 ± 0.05	2.60 ± 0.07	99 ± 3	117 ± 9
0.023	0.20 ± 0.01	0.35 ± 0.01	1.39 ± 0.04	2.70 ± 0.20	99 ± 4	117 ± 13
0.047	0.23 ± 0.02	0.41 ± 0.02	1.54 ± 0.04	3.13 ± 0.13	99 ± 4	119 ± 12
0.10	0.28 ± 0.02	0.50 ± 0.04	1.85 ± 0.09	3.94 ± 0.15	100 ± 4	122 ± 14
0.16	0.33 ± 0.03	0.65 ± 0.02	2.67 ± 0.24	4.74 ± 0.30	101 ± 2	128 ± 6
0.227	0.39 ± 0.02	0.79 ± 0.04	3.63 ± 0.13	6.77 ± 0.57	109 ± 2	158 ± 8
0.306	0.48 ± 0.04	1.02 ± 0.07	4.46 ± 0.19	8.68 ± 0.38	108 ± 1	157 ± 3
0.398	0.58 ± 0.05	1.28 ± 0.12	5.43 ± 0.35	10.5 ± 0.38	107 ± 1	155 ± 3
0.507	0.86 ± 0.03	1.82 ± 0.06	8.01 ± 0.41	15.7 ± 1.3	109 ± 1	164 ± 3
0.64	1.21 ± 0.13	1.92 ± 0.15	9.77 ± 0.50	20.2 ± 1.5	111 ± 7	172 ± 23
			R = —(-2-)C_6H_4N[b]			
0.0	0.77 ± 0.03	1.50 ± 0.07	5.90 ± 0.20	11.0 ± 0.07	100 ± 1	131 ± 3
0.023	0.87 ± 0.01	1.62 ± 0.07	6.08 ± 0.50	12.5 ± 0.6	98 ± 2	127 ± 7
0.047	0.93 ± 0.01	1.81 ± 0.08	7.33 ± 0.26	13.8 ± 0.6	100 ± 1	135 ± 4
0.10	1.03 ± 0.03	2.19 ± 0.09	9.14 ± 0.14	18.5 ± 0.8	107 ± 1	159 ± 2
0.16	1.14 ± 0.06	2.40 ± 0.12	10.5 ± 0.4	21.2 ± 2.4	109 ± 1	167 ± 2
0.227	1.37 ± 0.06	2.86 ± 0.10	12.5 ± 0.3	24.9 ± 2.2	109 ± 1	167 ± 3
0.306	1.96 ± 0.13	4.51 ± 0.42	20.2 ± 1.2	36.8 ± 3.9	112 ± 3	181 ± 9
0.398	2.55 ± 0.07	5.53 ± 0.32	26.6 ± 2.7	54.7 ± 3.4	115 ± 1	192 ± 3
0.507	2.80 ± 0.08	5.33 ± 0.34	26.2 ± 2.2	53.8 ± 4.1	110 ± 3	176 ± 12
0.64	1.55 ± 0.10	2.64 ± 0.19	15.6 ± 1.5	29.4 ± 1.7	113 ± 6	182 ± 21

[a] $[complex]_T = (2.0–8.0) \times 10^{-4}$ mol dm^{-3}; $\lambda = 260$ nm. (b) $\alpha\beta$S isomer. (c) $\alpha\beta$R isomer.

base) and *i.s.* is the initial state of the complex, $[(\text{tetren})CoO_2CR]^{2+}$; $[\Delta_t\overline{G}^0(OH^-)]_{(s\leftarrow w)}$ denotes the transfer free energy of OH^-, the transfer of species being considered from water (*w*) to the mixed solvent (*s*) and $k_2^{OH\ O,W}$ denotes the second-order rate constant at zero ionic strength for aqueous medium. The $[\Delta_t\overline{G}^0(OH^-)]_{(s\leftarrow w)}$ data reported by different workers [10–12] are based on diffrent extrathermodynamic assumptions (see Table II of [1]) and, hence, do not show good agreement so far as the absolute values are concerned. However, the trend is similar. The values given by Abraham et al. [11] cover the widest range of the solvent composition ($0 \leq$ vol % MeOH ≤ 90). Using their values after due correction for the desired solvent composition the P' values (molar scale) were calculated [see eq. (11)]. It is at once evident (see Fig. 2) that the unipositive and expanded transition state is stabilized to a greater extent than the dipositive and more compact initial state when transfer occurs from water to MeOH + H_2O media ($\Delta_tG(t.s.) < \Delta_tG(i.s.)$). A minimum is discernible in the P' vs. X_{MeOH} plots (see Fig. 2) around $X_{MeOH} \sim 0.35$. The relative transfer free energy (P') is clearly substrate specific beyond $X_{MeOH} = 0.1$. The *tetren* envelope of cobalt(III) and the apolar skeleton of the amino acids remarkably influence the solvation of the initial state and the transition state. The role of the conformational arrangement of *tetren* around cobalt(III) on the solvation of the substrates is also clearly evident in the observed trend in the variation of P' with X_{MeOH} for the $\alpha\beta$S and $\alpha\beta$R isomers of the α-alaninato complex (P' ($\alpha\beta$R) < P' ($\alpha\beta$S)) at $X_{MeOH} > 0.2$ (see Fig. 2, curves 1 and 2). We are, thus, led to believe that these substrates, both in the initial state and transition state, tend to discriminate the solvent molecules in their solvation sphere that results in the preferential solvation. The nature of variation of the gradient ($\delta P'/\delta X_{MeOH}$) around the minimum of the P' vs. X_{MeOH} plots may be taken to indicate that the species (i.e., *i.s.* or *t.s.*) are preferentially solvated by H_2O at $X_{MeOH} < 0.32$ and by MeOH at $X_{MeOH} > 0.32$. This effect is relatively sharply defined for the pyridine-2–carboxylate (see Fig. 2), thus indicating the specific role of the pyridine moiety. Also, a clear indication of the marked preferential solvation by H_2O upto $X_{MeOH} \sim 0.5$ for the $\alpha\beta$R isomer of α-alaninato complex demonstrates that the preferential solvation is also solute structure mediated. It is quite likely that both structure and hydrophobicity of the substrates and solvent media play a dominant role in the preferential solvation, which is a marker of molecular recognition.

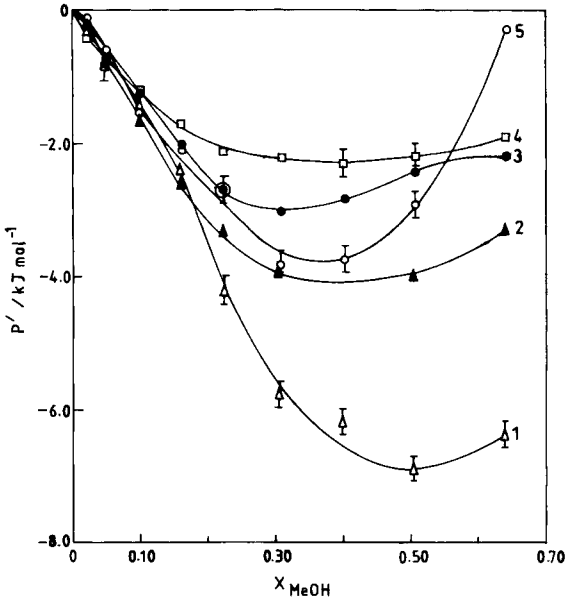


Fig. 2

Figure 2 $P'I$ kJ mol^{-1} vs. X_{MeOH} plot for base hydrolysis of $[(\text{tetren})CoO_2CR]^{2+}$ complexes at 25°C: R = —$CH(CH_3)NH_2$($\alpha\beta$R)(**1**), —$CH(CH_3)NH_2$($\alpha\beta$S(**2**), —CH_2NH_2 ($\alpha\beta$S) (**3**), —$CH_2CH_2NH_2$($\alpha\beta$S)(**4**), —(-2-)Py($\alpha\beta$S)(**5**)

A preferential solvation model as discussed in our earlier work [1] may be used to interpret the transfer free energies according to which the Gibbs excess free energy of transfer is given by eq. (12)

$$[\Delta_tG^E(i)]_{(s\leftarrow w)} = gRT\,X_{MeOH}(1 - X_{MeOH}) = [\Delta_tG(i)]_{(s\leftarrow w)} - X_{MeOH}[\Delta_tG(i)]_{(MeOH\leftarrow w)} \quad (12)$$

where *i* denotes the species (initial state or the transition state) transferred, and *g* is a dimensionless preferential solvation parameter. Taking account of the solvent structural effects and preferential solvation and combining eqs. (11) and (12), P' can be expressed by eq. (13)

$$P' = a\,X_{MeOH} + b\,X_{MeOH}^{\ 2} + c\,G^E \quad (13)$$

where $a = \Delta gRT + h$, $b = -\Delta gRT$, $\Delta g = g(t.s.) - g(i.s.)$, *and c* is a constant. The values of G^E were taken from the literature [13] and P' data were fitted to eq. (13). The $b\,X_{MeOH}^2$ term turned out statistically insignificant. Setting $b = 0$, the values of *a* and *c* were recalculated, which are collected in Table III. As G^E is positive (see footnote a of Table III), the negative value of its coefficient (*c*) point to the fact that solvent structural perturbation tends to make P' negative and, hence, it has rate accelerating effect. Burgess et al. [14,15] reported similar correlation in the substitution reaction of pentacyanoferrate(II) com-

Table III Calculated Values of *a* and *c* for Base Hydrolysis of $[(Tetren)CoO_2CR]^{2+}$ Complexes at 25° C[a]

R	*a*/kJ mol^{-1}	*c*
—CH(CH_3)NH_2	3.0 ± 0.8	−18.9 ± 1.3
	[−3.3 ± 1.1][b]	[−16.9 ± 1.7][b]
—CH_2NH_2	3.7 ± 1.1	−16.1 ± 1.7
—$CH_2CH_2NH_2$	2.2 ± 0.8	−12.0 ± 1.3
—(-2-)C_5H_4N	9.9 ± 0.5	−25.8 ± 0.9

[a] See eq. (13) G^E/kJ mol^{-1} used are 0.02, 0.04, 0.10, 0.149, 0.20, 0.255, 0.29, 0.30, 0.260, at X_{MeOH}, 0.023, 0.047, 0.10, 0.16, 0.227, 0.306, 0.398, 0.507, and 0.64, respectively [13].

[b] Values in the parentheses are for $\alpha\beta$R isomer and unparenthesized values are for $\alpha\beta$S isomer.

plexes in aqueous alcoholic media. The sign and magnitude of "a" (see Table III) suggest that Δg and "*h*" might be sensitive to the solute hydrophobicity and conformational arrangement of *tetren* around cobalt(III) center. Also the positive value of a (i.e., the coefficient of X_{MeOH}) shows that preferential solvation results in destabilization of the transition state relative to the initial state and, hence, has a rate retardation effect. Interestingly for the $\alpha\beta$R isomer of the α-alaninato complex, both the effects are favorable for rate enhancement.

A further detailed analysis of the solvent effects on the initial state and transition state for pyridine-2−carboxylato and glycinato complexes is possible by combining the pK_{NH} and solubility data with the rate constants. It is possible to calculate the transfer free energies of the unprotonated (C^{2+}), N-protonated (CH^{3+}), complexes and their transition states (25°C) as given below using the transfer free energies of picrate (Pic^-) and H^+ ions [11].

$$RT \ln K_{sp}^{O,W}/K_{sp}^{O,S} = [\Delta_t G^0(i)]_{(s\leftarrow w)} + n[\Delta_t \overline{G}^0(Pic^-)]_{(s\leftarrow w)} \quad (14)$$

$$2.303RT(pK_{NH}^{O,W} - pK_{NH}^{O,S}) = [\Delta_t G^0(C^{2+})]_{(s\leftarrow w)} + \Delta_t \overline{G}^0(H^+)]_{(s\leftarrow w)} - [\Delta_t G^0(CH^{3+})]_{(s\leftarrow w)} \quad (15)$$

Note that K_{sp}^0 denotes the solubility product of the picrate salt of a complex at I = 0 (25°C) and $n = 2$ and 3 for the pyridine-2−carboxylato and N-protonated glycinato complexes respectively; *i* denotes [(tetren)CoO_2C(-2-)Py]$^{2+}$ (C^{2+}) and [(tetren)$CoO_2CCH_2NH_3$]$^{3+}$ (CH^{3+}). Then combining the P' data with those for $[\Delta_t G^0(C^{2+})]_{(s\leftarrow w)}$ it is possible to calculate $[\Delta_t G(t.s.)]_{(s\leftarrow w)}$. Figure 3 depicts the solvent and substrate dependence of $[\Delta_t G(i)]_{(s\leftarrow w)}$ ($i = C^{2+}$, CH^{3+}, and *t.s.*). Extrema are discernible, which presumably reflect the solvent structural effect on the transfer free energies. The sequence $[\Delta_t G(CH^{3+})]_{(s\leftarrow w)} > [\Delta_t G(C^{2+})]_{(s\leftarrow w)} > [\Delta_t G(t.s.)]_{(s\leftarrow w)}$ is maintained over the entire composition range for the pyridine-2−carboxylato complex. Note that the transfer free energies are positive and increase with increasing X_{MeOH} for the C^{2+} and CH^{3+} species of this complex while $[\Delta_t G(t.s.)]_{(s\leftarrow w)}$ is close to zero upto $X_{MeOH} \sim 0.16$ and thereafter it increases nonlinearly with increasing X_{MeOH}. A similar trend is also evident for the glycinato complex beyond $X_{MeOH} \sim 0.18$, but the effect is relatively less pronounced compared to that for the pyridine-2−carboxylato complex. It is thus evident that the solvent acceleration of the rate of base hydrolysis is partly attributable to the fact that the transition state is more stabilized than the initial state when transfer occurs from water to MeOH + H_2O ($[\Delta_t G(t.s.)]_{(s\leftarrow w)} < [\Delta_t G(C^{2+})]_{(s\leftarrow w)}$).

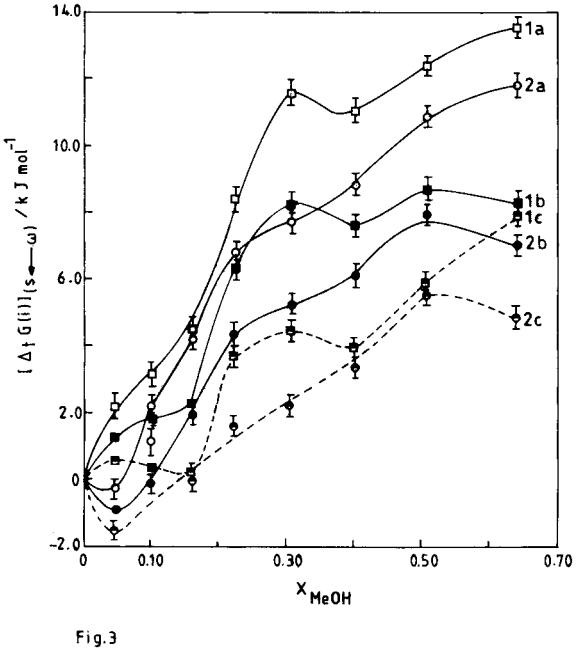


Fig.3

Figure 3 Plot of $[\Delta_t G(i)_{(s\leftarrow w)}/k$ mol^{-1} vs. X_{MeOH} for different species of $\alpha\beta$S-[(tetren)$CoO_2CR]^{n+}$ complexes at 25°C: R = —(-2-(Py(**1**), —CH_2NH_2(**2**): (**a**) CH^{3+}; (**b**) C^{2+}; (**c**) **t.s.** The Gibbs transfer free energy data used for H^+, OH^- and Pic^- ions are in molar scale at 25°C [11]. [$\Delta_t = G°(i)]_{(s\leftarrow w)}$/kJ mol^{-1} for $i = H^+$ (OH^-) [Pic^-] are 0.27 (−0.08) [−0.15], 0.39 (−0.17) [−0.56], 0.44 (−0.08) [−1.27], 0.35 (0.17) [−2.20], −0.01 (1.05) [−2.85], −0.45 (2.68) [−3.36], −0.70 (4.81) [−3.67], and 0.44 (7.44) [−3.69] for X_{MeOH} of 0.047, 0.10, 0.16, 0.227, 0.306, 0.398, 0.507, and 0.64, respectively.

Medium Effect on the Mutation Process, $\alpha\beta$R Isomer $\rightarrow$ $\alpha\beta$S Isomer, for the α-Alaninato Complex

The rate constants for the ($\alpha\beta$R) and ($\alpha\beta$S) isomers of the α-alaninato complex, [(tetren)$CoO_2CCH(CH_3)NH_2]^{2+}$, can be used to calculate the free energy change associated with the mutation process, $\alpha\beta R \rightarrow \alpha\beta S$, which is due to the conformational change of the coordinated *tetren* ligand. As discussed in our earlier article [2,3], a paramter Z' may be defined by eq. (16)

$$\begin{aligned} Z' = & \\ & -RT \ln \{k_2^{OH\ O,S}(\alpha\beta R)/k_2^{OH\ O,S}(\alpha\beta S)\} \\ & = \Delta G^{02+}_{CB}(\alpha\beta R \leftarrow \alpha\beta S) \\ & - \Delta G^{02+}_{C}(\alpha\beta R \leftarrow \alpha\beta S) \end{aligned} \quad (16)$$

where ΔG^{02+}_{CB} and ΔG^{02+}_{C} denote mutational Gibbs free energy changes for the five coordinate amido conjugate-base intermediate {CB^{2+} = [(tetren-HOH)Co$)^{2+}$} and its six coordinate conjugate acid analog {C^{2+} = [(tetren)$CoO_2CR]^{2+}$}, respectively. This anlaysis is based on the limiting SN_1cb mechanism so that the Gibbs free energy of the transition state is considered to be additive {i.e., *G(t.s.)* = G(CB^{2+}) + $G^0(-O_2CCH(CH_3)NH_2)$}. The calculated values of Z' for MeOH + H_2O, CH_3CN + H_2O [2] and DMSO + H_2O [3] are compared in Figure 4 using the data for the last two solvents from our earlier work. It is clear that the mutation ($\alpha\beta R \rightarrow \alpha\beta S$) is more favorable for the five coordinate amido base (CB^{2+} = [(tetren-HOH)Co$]^{2+}$) than for the initial state C^{2+} ($\Delta G(CB^{2+}) < \Delta G(C^{2+})$). However, both the nature of the cosolvent and composition of the mixed solvents influence this process. The dipolar protic methanol favor this process with increasing methanol content beyond X_{MeOH} = 0.15, while the dipolar aprotic cosolvents tend to show opposite trend at high cosolvent contents. At mol fractions greater than 0.2, the trend for the isomerization ($\alpha\beta R \leftarrow \alpha\beta S$), is MeOH > CH_3CN > DMSO. This specificity of the solvent effect is closely an indication of the role of preferential solute–solvent interaction, which might be linked with solvent structure and hydrophobic interaction. Note that the hydrophobic interaction of the cosolvent molecules with the substrate is likely to follow the sequence: DMSO > CH_3CH > CH_3OH.

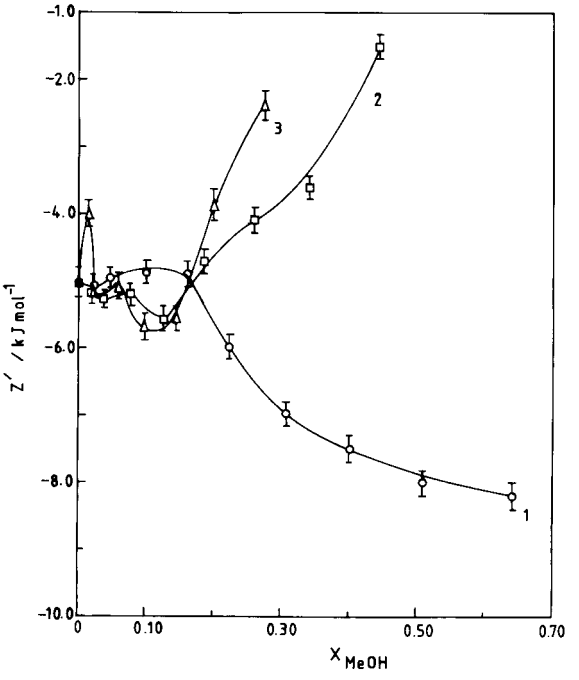


Fig.4

Figure 4 Plot of Z'/kJ mol^{-1} vs. X_{MeOH} for base hydrolysis of [(tetren)$CoO_2CCH(CH_3)NH_2]^{2+}$ complexes at 25°C: **1**—MeOH + H_2O, **2** —CH_3CH + H_2O, **3** —DMSO + H_2O. Data for CH_3CN + H_2O and DMSO + H_2O were taken from refs. [2] and [3], respectively.

Variation of $\Delta H^{\#}$ and $\Delta S^{\#}$ with X_{MeOH}

Data in Table II depict the variation of activation enthalpies and entropies ($\Delta H^{\#}$, $\Delta S^{\#}$) with X_{MeOH}. The clear contrasting feature is shown in the plots of $\Delta H^{\#}$ ($\Delta S^{\#}$) vs. X_{MeOH} for the two isomers of the α-alaninato complex; extrema being evident for the $\alpha\beta$R isomer. For all other complexes the trend is similar to that observed for the $\alpha\beta$S isomer of the α-alaninato complex. It is thus clear that the geometrical arrangement of the *tetren* ligand strongly influence the solvent structural perturbations in the cospheres of the initial state and the transition state for which the solvation components of the observed $\Delta H^{\#}$ and $\Delta S^{\#}$ are most likely influenced by the solvent structure. However, a linear correlation, $\Delta H^{\#}$ (kJ $mol^{-}1$) = (53.7 ± 1.6) + (0.340 ± 0.013) $\Delta S^{\#}$ (J $K^{-}1$ $mol^{-}1$) (corr. coeff. = 0.931) suggests that the effect of solvent on these thermodynamic parameters is mutually compensatory. This can only be true if the intimate mechanism is insensitive to the solvent variations.

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