

# Kinetics of aquation of *trans*-dichlorobis(*N,N'*-dimethylethylenediamine)cobalt(III) ion in water–methanol and in water–propan-2-ol media

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## Summary

The complex *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]Cl (dmen=*N,N'*-dimethylethylenediamine) has been prepared and characterized by elemental analysis, u.v.-vis. and i.r. spectra. The kinetics of the primary aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in H<sub>2</sub>O, H<sub>2</sub>O–MeOH and H<sub>2</sub>O–*i*-PrOH have been examined over a wide range of solvent compositions and temperatures (40–55 °C). Plots of rate constants (log *k*) versus the reciprocal of the dielectric constant of the medium (*D*<sub>s</sub><sup>−1</sup>) and Grunwald–Winstein values of the solvent (*Y*) were found to be non-linear. The variation of enthalpies (Δ*H*<sup>‡</sup>) and entropies (Δ*S*<sup>‡</sup>) of activation with solvent composition has been determined. Plots of Δ*H*<sup>‡</sup> or Δ*S*<sup>‡</sup> versus the mole fraction of each solvent exhibit extrema at *x*<sub>2</sub> = *ca.* 0.16 and 0.27 for MeOH and at *x*<sub>2</sub> = *ca.* 0.03 and 0.14 for *i*-PrOH. Furthermore, the cycle relating the free energy of activation in H<sub>2</sub>O to that in H<sub>2</sub>O–co-solvent shows that the stabilizing influence of the changes in the solvent structure is greater on the emergent five-coordinate cation in the transition state than that on the complex ion in the initial state, with the difference becoming greater as the mole fraction of the co-solvent increases.

## Introduction

The solvolyses of octahedral halopentaamine- and dihalotetraamminecobalt(III) complexes of general formulae [Co(N)<sub>5</sub>X<sub>1</sub>]<sup>2+</sup> and [Co(N)<sub>4</sub>X<sub>1</sub>X<sub>2</sub>]<sup>+</sup>, respectively, where (N)<sub>5</sub> and (N)<sub>4</sub> refer to any combination of uni-, bi-, tri-, tetra- or pentadentate amines, and X<sub>1</sub> and X<sub>2</sub> represent Cl<sup>−</sup> or Br<sup>−</sup>, has been the subject of numerous studies<sup>(1–4)</sup> and has been extensively reviewed recently by Wells<sup>(5)</sup>. The mechanistic information obtained from high pressure kinetic studies dealing with the aquation/solvolysis reactions at the cobalt(III) centre<sup>(6)</sup> and the constancy of the *cis/trans* ratios in the products<sup>(7)</sup> with various leaving groups. X<sub>2</sub> and the same X<sub>1</sub> are consistent with Co<sup>3+</sup> ..... Cl<sup>−</sup> bond cleavage in line with an *I*<sub>a</sub> mechanism. For most of the complexes investigated in water–co-solvent mixtures, the plot of log(rate constant) versus the reciprocal of the dielectric constant (*D*<sub>s</sub>) is non-linear<sup>(1–3)</sup>, strongly suggesting a free energy contribution arising from the influence of changes in the solvent structure on the process initial state → transition state<sup>(8)</sup>.

Recently, we have reported the effect of organic solvents on the aquation of *trans*-[Co(meen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, where meen = *N*-methylethylenediamine<sup>(1,9)</sup>. Following this work, the present study was undertaken to explore the steric effects of the (N)<sub>4</sub> ligands by the use of *N,N'*-di-

methylethylenediamine (dmen), in which methyl substituents are introduced on the coordinated nitrogens of ethylenediamine ligands. With the exception of the kinetic data reported for the aquation of [Co(dmen)<sub>2</sub>(CO<sub>3</sub>)]<sup>+</sup> ion<sup>(10)</sup>, almost no information is available about the reactivity of dmen-Co<sup>III</sup> systems. Therefore, the aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> was conducted in methanol and in *i*-propanol (methanol has a relatively low hydrophobic effect, whereas *i*-propanol has a greater effect on the structure of water) to determine the influence of changes in solvent structure on changes in the activation parameters.

## Experimental

### Materials and physical measurements

MeOH and *i*-PrOH (BDH) were purified as described elsewhere<sup>(1,9)</sup>. *N,N'*-Dimethylethylenediamine was purchased from Fluka. All other chemicals were reagent grade. The mixtures were prepared using double distilled H<sub>2</sub>O. Methods for u.v.-vis. and i.r. spectra, determination of the Cl<sup>−</sup> released from the hydrolysis and kinetic measurements for the aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> were the same as described for the aquation of *trans*-[Co(meen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> in MeOH<sup>(1)</sup>. Elemental analyses were performed at the microanalytical laboratory, Chemistry Department, Faculty of Science, Alexandria University, Egypt.

### Preparation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]Cl

*Trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]Cl was prepared essentially as described for *trans*-[Co(meen)<sub>2</sub>Cl<sub>2</sub>]Cl by oxidation in air of an aqueous solution of CoCl<sub>2</sub>·6H<sub>2</sub>O and two equimolar amounts of dmen. The green product was recrystallized from 5 M HCl in *ca.* 20% yield. The complex was dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. (Found: C, 28.3; H, 6.8; N, 16.5. C<sub>8</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>3</sub>Co; calcd.: C, 28.1; H, 7.1; N, 16.4%.)

## Results and discussion

### Structural aspects of the complexes

It has been shown that the number and positions of the i.r. bands in the CH<sub>2</sub> rocking region (910–800 cm<sup>−1</sup>) can be used to distinguish between *cis* and *trans* isomers in [Co(N)<sub>4</sub>X<sub>1</sub>X<sub>2</sub>]<sup>+</sup> complexes<sup>(1,11)</sup>. In general, these studies have shown that the *cis* compounds exhibit more bands than *trans* compounds. Also, the intensities of the bands are somewhat weaker in the case of *cis* complexes<sup>(11,12)</sup>. The i.r. spectral bands in the CH<sub>2</sub> rocking region for [Co(dmen)<sub>2</sub>Cl<sub>2</sub>]Cl display only one band at 860 cm<sup>−1</sup> of medium intensity, consistent with a *trans* geometry.

A *trans* geometry for the complex under investigation was also supported by the electronic spectrum; a fresh

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solution of the complex in HClO<sub>4</sub> (0.01 M) displayed maxima at 643, 488 and 410 nm with molar absorptivity values of 20, 21 and 31 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, respectively. These are in agreement with the assigned *trans* geometry<sup>(11,13)</sup>. The electronic spectra of low-spin six-coordinate *trans* cobalt(III) complexes, [Co(N)<sub>4</sub>X<sub>1</sub>X<sub>2</sub>]<sup>n+</sup> exhibit more bands with low intensities than those of the corresponding *cis*-isomers<sup>(13)</sup>. The observed absorption bands arise from the electronic transitions <sup>1</sup>E<sub>g</sub> ← <sup>1</sup>A<sub>1g</sub>(D<sub>4h</sub>), <sup>1</sup>A<sub>2g</sub> ← <sup>1</sup>A<sub>1g</sub>(D<sub>4h</sub>) and <sup>1</sup>T<sub>2g</sub> ← <sup>1</sup>A<sub>1g</sub>(D<sub>4h</sub>), respectively. The N-alkyl substitution of ethylenediamine leads to a reduction in ligand field strength in *trans*-[Co(N)<sub>4</sub>Cl<sub>2</sub>]<sup>2+</sup>; i.e. the position of the low energy absorption band {<sup>1</sup>E<sub>g</sub> ← <sup>1</sup>A<sub>1g</sub>(D<sub>4h</sub>)} decreases in the order: dmen (643 nm) > meen (625 nm)<sup>(1)</sup> > en (617 nm)<sup>(14)</sup>.

Similarly, the aquation product of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> exhibits three maxima at ca. 635, 490 and 402 nm, showing that the complex is aquated to the corresponding aqua-chloro species with retention of configuration.

#### Variation of the rate constant with temperature and composition

The kinetics of aquation conversion of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> into *trans*-[Co(dmen)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> were followed spectrophotometrically at 565 nm; at this wavelength, a substantial difference in absorbance was observed between reactants and products. The final solution spectrum of *trans*-[Co(dmen)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> was stable and did not show any sign of isomerization. Also, the study was not complicated by any interference from a second aquation step. Back-titration of the released chloride with standard NH<sub>4</sub>SCN<sup>(1,15)</sup> gave 2.07 ± 0.05 mol of chloride released per mole of [Co(dmen)<sub>2</sub>Cl<sub>2</sub>]Cl, corresponding to the displacement of one chloro ligand from the complex cation.

The kinetics of conversion of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> into *trans*-[Co(dmen)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> were determined in water and water-alcohol mixtures containing 10–60 % v/v co-solvent at 40.0, 45.0, 50.0 and 55.0 °C.

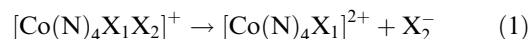
The first-order rate constants, *k*, collected in Table 1, were evaluated from the slopes of the plots of ln(A<sub>∞</sub> - A<sub>t</sub>) versus *t* by linear-least squares analysis. These plots were linear for at least two half-lives of the reaction. The values of A<sub>∞</sub> were measured when no further changes in absorbance were detected. The aquation rates were unaffected

by changing the HClO<sub>4</sub> concentration from 1.0 × 10<sup>-3</sup> to 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

In general, it was observed that at a given temperature and for the same solvent composition, the aquation rate of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> in H<sub>2</sub>O–MeOH or in H<sub>2</sub>O–*i*-PrOH mixtures is much faster than that for *trans*-[Co(meen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup><sup>(1,9)</sup>. This may be attributed to the increase in steric crowding at the coordinated nitrogens of dmen in dissociative reactions<sup>(16)</sup>.

The activation parameters were evaluated for each solvent composition from the linear Eyring plots of ln*k*/T versus 1/T. The values of Δ*H*<sup>‡</sup>, Δ*S*<sup>‡</sup> and Δ*G*<sup>‡</sup> with their standard deviations were calculated for each mole fraction of co-solvent using a computer program; the values are collected in Table 2. Also, the rate constants at 25 °C were calculated using Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> values.

A linear variation of log *k* versus D<sub>s</sub><sup>-1</sup> (D<sub>s</sub> = dielectric constant of the solvent mixture) would be expected from the Laidler–Landskroener equation<sup>(17)</sup> in I<sub>d</sub> reactions involving a nearly full extension of the Co<sup>3+</sup> ..... X<sub>2</sub><sup>-</sup> bond in the transition state, as illustrated by Equation 1.



A linear variation of log *k* versus D<sub>s</sub><sup>-1</sup> requires that Equation 2 holds;

$$\Delta G_t^\ominus([\text{Co}(\text{N})_4\text{X}_1\text{X}_2]^+) = \Delta G_t^\ominus([\text{Co}(\text{N})_4\text{X}_1]^{2+}) + \Delta G_t^\ominus(\text{X}_2^-) \quad (2)$$

where Δ*G*<sub>t</sub><sup>⊖</sup>(*i*)<sub>n</sub> is the free energy of transfer of species *i* from water into the mixture, excluding electrostatic contributions. This behaviour has been noticed in some reactions<sup>(4)</sup>.

In fact, plots of log *k* versus D<sub>s</sub><sup>-1</sup> at 25 °C, interpolated for each co-solvent using Akerlöf's data<sup>(18)</sup> for the aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> in H<sub>2</sub>O–MeOH and H<sub>2</sub>O–*i*-PrOH were non-linear. Similar plots for log *k* versus the interpolated Grunwald–Winstein *Y*-values<sup>(19,20)</sup> were also obtained and found to be far from linear. The lack of linearity in these plots represents no exception to the general observation found in the solvolysis for a large number of cobalt(III) complexes<sup>(1–3,5,9)</sup>. This non-linearity may arise from the differential effects in solvent structure and solvation with changes in solvent composition between the initial state, *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup>, and the transition state, [(dmen)<sub>2</sub>ClCo<sup>III</sup> ..... Cl]<sup>+</sup>.

**Table 1.** First-order rate constants (10<sup>4</sup> s<sup>-1</sup>) for the aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>2+</sup> in H<sub>2</sub>O–MeOH and H<sub>2</sub>O–*i*-PrOH mixtures with varying temperature and solvent composition

Co-solvent	W(%)	Mole fraction	Temp. (°C)			
			45.0	50.0	55.0	60.0
MeOH	0.00	0.000	2.43	5.28	11.19	23.19
MeOH	8.17	0.048	3.32	6.13	11.10	19.74
MeOH	16.54	0.100	3.61	6.55	11.68	20.45
MeOH	25.36	0.160	9.15	12.71	17.48	23.81
MeOH	34.58	0.229	9.81	15.92	25.43	40.06
MeOH	44.22	0.308	17.54	27.93	43.85	67.89
MeOH	54.32	0.401	41.88	48.89	56.80	65.69
<i>i</i> -PrOH	8.04	0.026	3.35	7.64	17.01	36.97
<i>i</i> -PrOH	16.44	0.056	2.72	6.06	13.19	28.02
<i>i</i> -PrOH	25.44	0.092	5.99	10.97	19.70	34.78
<i>i</i> -PrOH	34.41	0.136	8.31	13.13	20.44	31.39
<i>i</i> -PrOH	44.04	0.191	11.72	22.33	41.71	76.43
<i>i</i> -PrOH	54.15	0.261	8.29	17.78	37.25	76.30

**Table 2.** Variation of  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  with mole fraction of MeOH and *i*-PrOH for the aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  in  $\text{H}_2\text{O}$ –MeOH and  $\text{H}_2\text{O}$ –*i*-PrOH mixtures, respectively

Co-solvent	Wt(%)	Mole fraction	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ (25 °C) (kJ mol <sup>-1</sup> )
MeOH	0.00	0.000	126 ± 6	88 ± 20	100 ± 13
MeOH	8.17	0.048	99 ± 8	4 ± 24	98 ± 15
MeOH	16.54	0.100	96 ± 8	-4 ± 25	97 ± 16
MeOH	25.36	0.160	52 ± 7	-137 ± 21	93 ± 13
MeOH	34.58	0.229	78 ± 8	-55 ± 24	94 ± 15
MeOH	44.22	0.308	75 ± 11	-60 ± 36	92 ± 22
MeOH	54.32	0.401	23 ± 2	-217 ± 7	88 ± 4
<i>i</i> -PrOH	8.04	0.026	134 ± 8	117 ± 25	99 ± 15
<i>i</i> -PrOH	16.44	0.056	130 ± 10	103 ± 32	100 ± 20
<i>i</i> -PrOH	25.44	0.092	98 ± 13	5 ± 40	96 ± 25
<i>i</i> -PrOH	34.41	0.136	73 ± 12	-71 ± 37	94 ± 23
<i>i</i> -PrOH	44.04	0.191	104 ± 4	32 ± 13	95 ± 8
<i>i</i> -PrOH	54.15	0.261	124 ± 6	92 ± 18	97 ± 11

### Influence of solvent structure on aquation

The differential effect of solvent structure between the initial and transition states is illustrated in Figures 1 and 2 by the variation of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  with the mole fraction of each co-solvent,  $x_2$  (all plots obtained in this work are the best fits through the experimental data points). Table 2 shows that as with the solvolysis of other complexes<sup>(1,21)</sup>, within the error-limits,  $\Delta G^\ddagger$  for the aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  varies little with solvent composition due to the considerable compensating effects of the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values. The isokinetic temperatures,  $\beta$ , were estimated from the slopes of the linear plots of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$ , giving 337 and 323 K for MeOH and *i*-PrOH, respectively. The latter temperature is very close to the experimental one, whereas the former temperature, which is comparable to that found in

the aquation of  $\text{trans}[\text{Co}(\text{meen})_2\text{Cl}_2]^+$  in  $\text{H}_2\text{O}$ –MeOH<sup>(1)</sup>, indicates that the aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  in the same co-solvent is primarily entropy controlled. This reflects the importance of solute–solvent interactions.

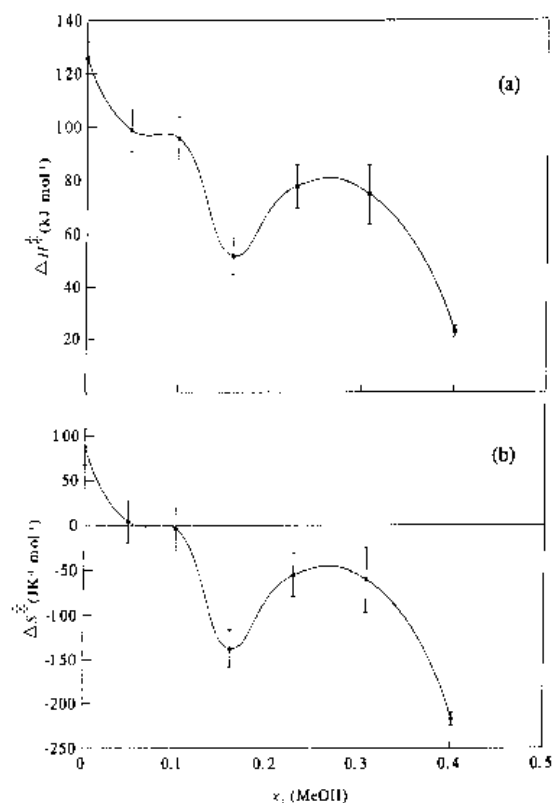
The aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  in  $\text{H}_2\text{O}$ –MeOH mixtures shows a minimum for both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  at  $x_2 = \text{ca. } 0.16$  and a maximum at  $x_2 = \text{ca. } 0.27$  (Figure 1). These extrema are very close to those observed for the solvolysis of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  and  $\text{trans}[\text{Co}(\text{R-py})_4\text{Cl}_2]^+$  (R-py = substituted alkyl pyridine)<sup>(1,21)</sup> and they occur roughly in the same composition region, where the physical properties of MeOH indicate changes in the solvent structure.

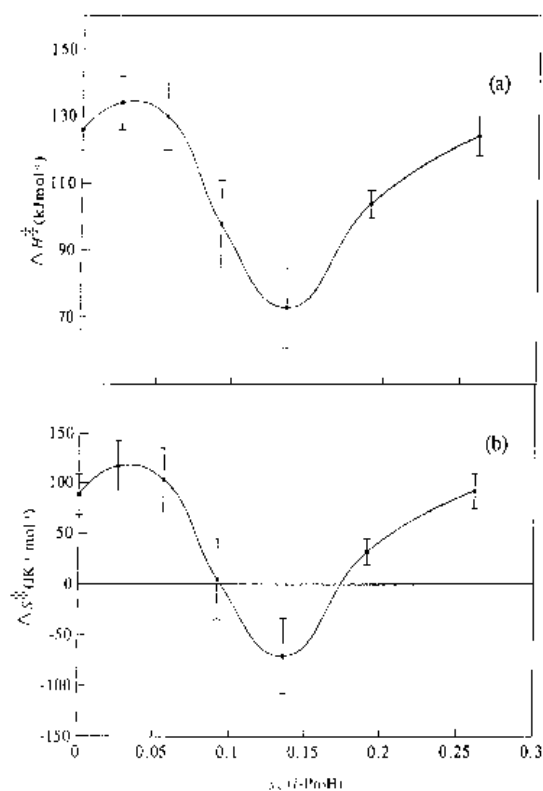
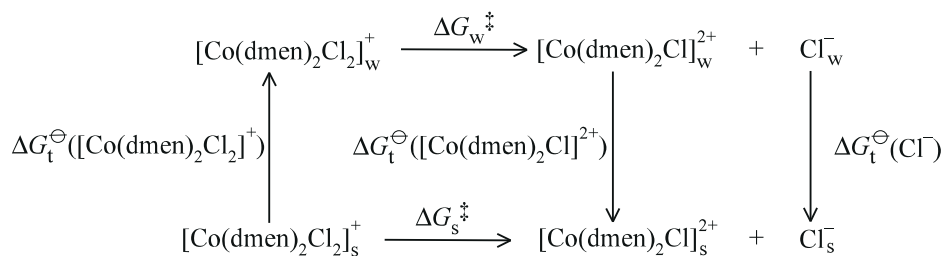
In the aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  in  $\text{H}_2\text{O}$ –*i*-PrOH mixtures, both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  exhibit extrema at  $x_2 = \text{ca. } 0.03$  and  $0.14$  (Figure 2). These mole fractions roughly correlate with the physical properties of  $\text{H}_2\text{O}$ –*i*-PrOH mixtures. A plot of the decrease in the partial molar volume of propan-2-ol,  $\bar{V}_2 - V_2^\circ$ , has a deep minimum<sup>(22)</sup> at  $x_2 = \text{ca. } 0.04$  and the excess enthalpy of mixing,  $\Delta H^E$ , has a maximum<sup>(23)</sup> at  $x_2 = \text{ca. } 0.1$ . The former minimum is thought to correspond to the composition range where the alkyl chain of the co-solvent induces maximum structure formation within the surrounding flickering “icebergs” of structured water<sup>(24,25)</sup>. With further additions of *i*-PrOH, a situation is reached<sup>(24)</sup> at  $x_2 = 0.10$ – $0.15$  [the same region of the extremum in  $\Delta H^E$  (the ultrasonic absorption of  $\text{H}_2\text{O}$ –*i*-PrOH mixtures has a maximum at  $x_2 = \text{ca. } 0.15$ )<sup>(26)</sup>] where the cavities between the structured “icebergs” of water<sup>(25)</sup> are completely filled by alkyl groups, resulting in the onset of the breakdown of one water structure.

The solvolysis of  $\text{trans}[\text{Co}(\text{N})_4\text{Cl}_2]^+$  ions in  $\text{H}_2\text{O}$ –*i*-PrOH mixtures where (N)<sub>4</sub> = (en)<sub>2</sub> and (meen)<sub>2</sub>, show extrema in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  at  $x_2 = \text{ca. } 0.04$  and  $0.05$ , respectively<sup>(3,9)</sup>. Thus, these extrema probably derive from the sharp changes in the solvent structure in the mixture.

### The free-energy cycle

The lack of linearity in the plots of  $\log k$  versus  $D_s^{-1}$  implies a differential effect of changes in solvent structure with changes in solvent composition between the initial state,  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$ , and the long extension of  $[(\text{dmen})_2\text{ClCo}^{\text{III}} \cdots \text{Cl}]^+$  bond in the transition state. This requires the application of the free-energy cycle to the free energy of activation in water and in the mixtures using the free energies of transfer,  $\Delta G_t^\ominus(i)$ , of ionic species *i* between water, w, and the mixed solvent, s:

**Figure 1.** Plots of (a)  $\Delta H^\ddagger$  and (b)  $\Delta S^\ddagger$  versus mole fraction of MeOH for the aquation of  $\text{trans}[\text{Co}(\text{dmen})_2\text{Cl}_2]^+$  ion in  $\text{H}_2\text{O}$ –MeOH



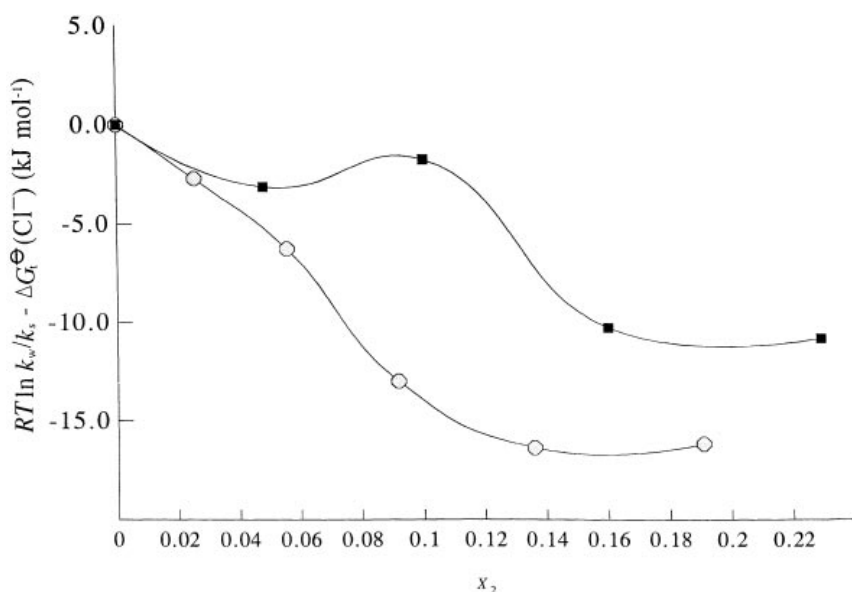
**Figure 2.** Plots of (a)  $\Delta H^\ddagger$  and (b)  $\Delta S^\ddagger$  versus mole fraction of *i*-PrOH for the aquation of *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ion in H<sub>2</sub>O–*i*-PrOH

For this cycle, it is not difficult to correlate rate constants  $k_{\text{w}}$  and  $k_{\text{s}}$  to the free energy of transfer,  $\Delta G_{\text{t}}^\ominus(i)$  by the following Equation<sup>(8)</sup>:

$$RT \ln k_{\text{w}}/k_{\text{s}} - \Delta G_{\text{t}}^\ominus(\text{Cl}^-) = \Delta G_{\text{t}}^\ominus([\text{Co(dmen)}_2\text{Cl}]^{2+}) - \Delta G_{\text{t}}^\ominus([\text{Co(dmen)}_2\text{Cl}_2]^+) \quad (3)$$

where  $k_{\text{w}}$  and  $k_{\text{s}}$  have been calculated at 25 °C from  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values listed in Table 2, and  $\Delta G_{\text{t}}^\ominus(\text{Cl}^-)$  values were interpolated from the spectrophotometric solvent sorting method<sup>(27,28)</sup>. Figure 3 shows that the plots of the left-hand side of Equation (3) versus the mole fraction of each co-solvent mixtures are all negative values with  $-\Delta G_{\text{t}}^\ominus([\text{Co(dmen)}_2\text{Cl}]^{2+}) > -\Delta G_{\text{t}}^\ominus([\text{Co(dmen)}_2\text{Cl}_2]^+)$ .

It is evident from the results presented in Figure 3 that the stabilizing influence of the changes in solvent structure is greater on the emergent cation in the transition state than that on the complex ion in the initial state, with the difference becoming greater as  $x_2$  increases in water-rich conditions for each of the water–co-solvent mixtures. The conclusion reached here is parallel to the general conclusion observed in the solvolysis of many complex cations of the type *trans*-[Co(N)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> in water–co-solvent mixtures<sup>(1–3, 8,9,29)</sup>. In addition, the stabilizing influence of changes in solvent structure is greater in H<sub>2</sub>O–*i*-PrOH mixtures than in H<sub>2</sub>O–MeOH mixtures. This again confirms the fact that *i*-PrOH has more effect on the structure of water than methanol, which in turn affects the solvation and the stability in this  $I_{\text{d}}$  process.



**Figure 3.** Plots of the left-hand side of Equation (3) versus mole fraction of MeOH for the aquation of the *trans*-[Co(dmen)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ion at 25 °C in H<sub>2</sub>O–MeOH (■) and in H<sub>2</sub>O–*i*-PrOH (○)

## References

- (1) G. M. El-Subruiti, S. S. Massoud and A. Z. Chehata, *Transition Met. Chem.*, **21**, 437 (1996)
- (2) G. M. El-Subruiti, I. M. Sidahmed and C. F. Wells, *Transition Met. Chem.*, **18**, 323 (1993) and refs cited therein.
- (3) G. S. Groves and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **78**, 619 (1982); **81**, 2475 (1985).
- (4) Sh. A. El-Shazly, S. S. Massoud, A. A. Zaghloul, M. T. Mohamed and M. F. Amira, *Bull. Soc. Chim. Fr.*, **6**, 780 (1989) and refs cited therein.
- (5) C. F. Wells, *Prog. React. Kinet.*, **20**, 1 (1995).
- (6) M. Kotowski and R. van Eldik, *Coord. Chem. Rev.*, **93**, 19 (1989); R. van Eldik, *Inorganic High Pressure Chemistry*, Elsevier, Amsterdam 1986, pp. 139–63.
- (7) W. G. Jackson and C. M. Begbie, *Inorg. Chim. Acta*, **60**, 115 (1982); W.G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **17**, 1348 (1978).
- (8) C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1851 (1977).
- (9) G. M. El-Subruiti, submitted, *Transition Met. Chem.*
- (10) S. S. Massoud, and R. B. Jordan, *Inorg. Chim. Acta*, **221**, 9 (1994).
- (11) S. S. Massoud *Polyhedron*, **13**, 1467, 3127 (1994).
- (12) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edit., Wiley, New York, 1986, Ch. 3.
- (13) C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw - Hill, New York, 1962.
- (14) C. K. Jorgensen, *Adv. Chem. Phys.*, **5**, 33 (1963).
- (15) S. S. Massoud and R. M. Milburn, *Inorg. Chim. Acta*, **148**, 233 (1988).
- (16) R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).
- (17) K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).
- (18) G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).
- (19) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
- (20) P. R. Wells, *Linear Free Energy Relationships*, Academic Press, London, 1986, p. 60.
- (21) A. E. Eid and C. F. Wells, *Int. J. Chem. Kinet.*, **18**, 215 (1986) and refs cited therein.
- (22) K. Nakanishi, *Bull. Chem. Soc. Jpn.*, **33**, 793 (1960).
- (23) R. F. Lama and B.C.-T. Lu, *J. Chem. Eng. Data*, **10**, 216 (1965).
- (24) C. F. Wells, *Trans Faraday Soc.*, **66**, 204 (1970); *J. Chem. Soc., Faraday Trans.*, **1**, **70**, 694 (1974).
- (25) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1974); N. Laiden and G. Némethy, *J. Phys. Chem.*, **74**, 3501 (1970).
- (26) M. J. Blandamer, *Introduction to Chemical Ultrasonics*, Academic Press, London, 1973, Ch. 11.
- (27) C. F. Wells, *J. Chem. Soc. Faraday Trans. 1*, **69**, 984 (1973).
- (28) C. F. Wells, *Aust. J. Chem.*, **36**, 1739 (1983); I.M. Sidahmed and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **82**, 257 (1986).
- (29) G. M. El-Subruiti, I. M. Sidahmed and C. F. Wells, *J. Solution Chem.*, **22**, 883 (1993); **20**, 403 (1991).

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TMC 3738