7728 *Inorg. Chem.* **1996,** *35,* 7728−7734

Reactivity of a Regiospecific Ion Pair. Comparisons of Cl^- and H_2O Entry into the Five-Coordinate Intermediate Generated from *p*-$[Co(tren)(NH_3)OH_2]^{3+}\cdot Cl^-$

Nicola E. Brasch, David A. Buckingham,* Charles R. Clark, and Jim Simpson

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

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Equilibration in the system : *p*-$[Co(tren)(NH_3)OH_2]^{3+} + Cl^- \rightleftarrows$ *p*-$[Co(tren)(NH_3)Cl]^{2+} + H_2O$ (*p*-stereochemistry has the labile group (OH_2, Cl^-) trans to a tren NH_2) in aqueous solution of variable ($I = 0-2.0$ M) and constant ($I = 2.0$ M, $NaClO_4$) ionic strength at 37.5 °C is described by the following rate law: $k_{obs} = k_{aq} + k_{an}K_{Cl}[Cl^-]/(1 + K_{Cl}[Cl^-] + K_{ClO_4}[ClO_4^-])$; K_{Cl} ($0.64\ M^{-1}$) and K_{ClO_4} ($0.21\ M^{-1}$) correspond to ion pairing of Cl^- and ClO_4^- to the aqua complex and k_{aq} ($1.4 \times 10^{-5}\ s^{-1}$) and k_{an} ($1.2 \times 10^{-4}\ s^{-1}$) to the rate constants for aquation of the chloro complex and anation of the ion-paired (Cl^-) aqua complex respectively. The rate constant for loss of coordinated $^{17}OH_2$ from the labeled aqua complex is the same ($k_{OH_2} \sim 1.2 \times 10^{-4}\ s^{-1}$) irrespective of the presence (2.0 M) or absence of $NaClO_4$ ($[H^+] = 0.10$ M, 37.5 °C) but increases with increasing $[Cl^-]$ to reach a limit ($\sim 2.4 \times 10^{-4}\ s^{-1}$) at high concentrations (range 0−1.90 M; $I = 2.0$ M, $NaClO_4$). Water exchange in the *p*-$[Co(tren)(NH_3)OH_2]^{3+}\cdot Cl^-$ ion pair ($k'_{OH_2} = 1.2 \times 10^{-4}\ s^{-1}$) occurs just as readily as anation. A mechanism for anation is suggested whereby entry of Cl^- ion and OH_2 molecules from positions adjacent to the *p*-site affects reentry of the original OH_2 ligand such that all processes are partly rate determining. A combination of 1D nOe and 2D COSY spectroscopy (DMSO-d_6 solvent) has allowed all the H atoms in *p*-$[Co(tren)(NH_3)OH_2]^{3+}$ and *p*-$[Co(tren)(NH_3)Cl]^{2+}$ to be assigned. Added Cl^- ion strongly influences the chemical shifts of the O*H*$_2$, N*H*$_3$, and N*H* hydrogens in the aqua complex (in decreasing order of importance) and appears to associate more strongly than ClO_4^-. Anation in DMSO occurs without the intermediacy of the DMSO complex. The crystal structure of *p*-$[Co(tren)(NH_3)OH_2]Cl_3$, orthorhombic, $Pmn2_1$, $a = 11.689(6)$ Å, $b = 8.215(3)$ Å, $c = 6.878(2)$ Å, $Z = 2$, and $R = 0.0490$ shows one unique Cl^- ion (Cl(1)) H-bonded to the OH_2 and NH_3 ligands of the complex cation (distances 2.89 and 3.96 Å respectively). Heating the crystalline solid results in rapid Cl^- entry.

Introduction

The essential idea for this study arose out of an earlier investigation into the isomerization reaction $(NH_3)_5CoSCN^{2+} \rightarrow (NH_3)_5CoNCS^{2+}$ in which small amounts of solvent (H_2O) as well as added $N^{14}CS^-/S^{14}CN^-$ became coordinated in addition to the large amount of isomerized ligand (∼90%).[1] It was shown that all entering groups competed for the same site. Furthermore, the amounts of $N^{14}CS/S^{14}CN^-$ entry compared favorably with those found for other spontaneous reactions, $(NH_3)_5CoX^{2+} \rightarrow (NH_3)_5CoOH_2^{3+} + X^-$, in which excellent leaving groups were involved ($X = OClO_3^-, OSO_2CF_3^-$),[2] and this suggested that entry was dependent on site location in the five-coordinate intermediate rather than on subsequent behavior of the original ligand. It also suggested that Co−X bond breaking may not be entirely rate determining, with reentry of the original ligand being preferred in those cases where the leaving group was also a good entering group. Could we confirm this by studying a more conventional reaction such as anation of a Co(III)−aqua complex, where the leaving group is H_2O? Water is also a "good" ligand in Co(III) substitution chemistry even when its local concentration in the solvation shell is taken into account, and reentry of the original H_2O molecule is a distinct possibility. A study of this meant choosing both a complex cation where association with the entering anion X^- is appreciable in aqueous solution (so that its extent can be measured) and one where the anion is localized at a site immediately adjacent to the coordinated water molecule. Rate constants obtained for anation and water exchange might then be attributed predominantly to those for reaction of this one ion pair.

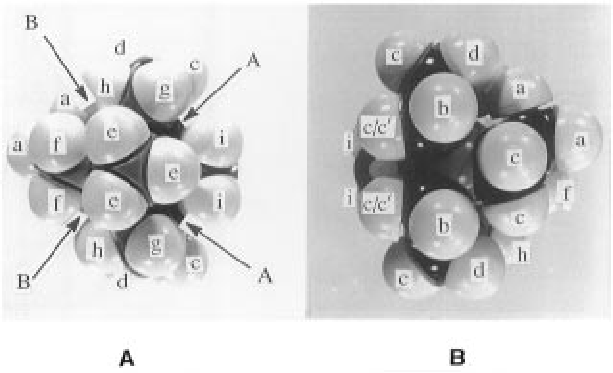

Figure 1. Space-filling molecular model of the *p*-$CoOH_2^{3+}$ ion. A: "front face" view down the NH_3−*tert*-N axis showing the coordinated H_2O molecule to the right and the *trans*-NH_2 group (f) to the left. Three-fold sites for ion-pairing are shown by A (no stereochemical change required on substitution) and B (*p* to *t* stereochemical change on substitution). B: opposite "back-face" view down the *tert*-N−NH_3 axis showing the coordinated H_2O molecule (i) to the left. No sites are available for ion-pairing. Individual H atoms are labeled (a−i) using the assignments given in Table 4.

The *p*-$[Co(tren)(NH_3)OH_2]^{3+}$ ion is one with the desired properties. Figure 1 shows H-bonding to Cl^- (or any potential entering anion) is possible only on the "front face" (sites A and B, Figure 1A) adjacent to the NH_3 and OH_2 ligands (*H* atoms **e** and **i** respectively) and to the three terminal NH_2 groups of tren (f + f, g + h, g + h). The reverse "back face" centered about the tertiary N center has no N-*H* hydrogens available for hydrogen bonding (Figure 1B). Two of the "front face" sites

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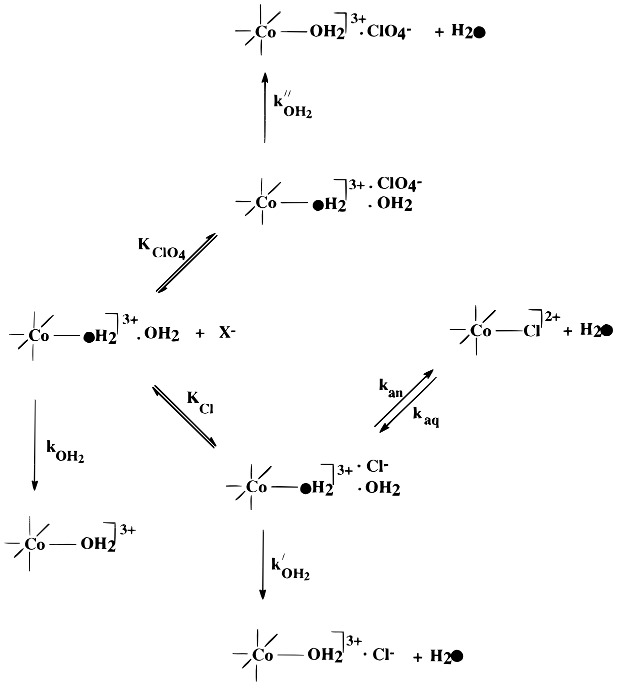
Scheme 1



are adjacent to the OH_2 ligand and these would lead directly to Cl^- insertion (or H_2O entry/reentry) without stereochemical change (sites A), whereas sites B are somewhat further removed and would necessarily involve stereochemical change *p* to *t* if involved in substitution. As we shall see no such stereochemical change is observed, so that these B sites, if occupied, remain unreactive as far as anation and water exchange are concerned.

Scheme 1 sets out our model of pathways for anation (k_{an}), hydrolysis of the $CoCl^{2+}$ product (k_{aq}) and water exchange into the ion-paired, and non-ion-paired, reactant k'_{OH_2}, k''_{OH_2}; k_{OH_2}). Specific ion pairs with Cl^- and $ClO_4^-$are represented by K_{Cl} and K_{ClO_4} with anation by Cl^- occurring via K_{Cl}. The K_{ClO_4} path is also likely to lead to some ClO_4^- entry, but the $CoOClO_3^{2+}$ product would rapidly hydrolyze to regenerate $CoOH_2^{3+}$, which is then available for further anation by Cl^- (but not for H_2O exchange). Ion pairing with Cl^- in the $CoCl^{2+}$ product (at the same location) cannot lead directly to $CoOH_2^{3+}$ (microscopic reversibility) and in any event is unlikely to be of major importance for this complex (for the same reasons as those outlined above); it is therefore omitted from the model. It is to be emphasised that all estimates of rate and ion pair constants given in this article are in no way to be taken as thermodynamic values since no attempt was made to achieve constancy of ionic strength or to take variation in activity coefficients into account.[3] The ion pair constants simply provide a measure of the extent of ion association under a particular condition, and the rate constants quoted give an indication of limiting rates for reaction of ion-paired species.

Experimental Section

Materials. ^{17}O-enriched H_2O (~40 atom %) and ^{17}O-depleted H_2O (~0.007 atom %) were obtained from Yeda Research and Development Co, Ltd., Rehovot, Israel. A solution of $Hg(CF_3SO_3)_2$ (0.74 M) was prepared by dissolving HgO (yellow) in excess aqueous CF_3SO_3H. D_2O, DMSO-d_6, methanol-d_4, and DCl (37%) were supplied by Aldrich. Sodium chloride and sodium perchlorate were of AR grade. Their solutions were filtered through Celite (BDH) prior to use.

Complexes. *p*-$[Co(tren)(NH_3)OH_2](NO_3)_2ClO_4$ and *p*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$ were prepared as described elsewhere.[4,5] [***Caution***! Although we have not experienced difficulties with these materials, perchlorate salts are potentially explosive and should be handled with care.] *p*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as follows.[6] A solution of *p*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$ (0.84 g) in aqueous $Hg(CF_3SO_3)_2$ (5 mL, 0.74 M in 0.4 M CF_3SO_3H) was left to stand at room temperature for 5 min, with occasional stirring. The mixture was then cooled in ice and filtered through Celite. The material on the filter ($HgCl_2$) was then washed with a small volume of MeOH and $NaCF_3SO_3$ (1g) added to the combined filtrate and washings followed by 2-propanol (~40 mL) and ether (~300 mL), while cooling was maintained. The precipitate was recovered on a glass filter, washed with ether, and air-dried. This material was redissolved in H_2O (~2 mL) and addition of $NaCF_3SO_3$ (~0.5 g) and 2-propanol (~2 mL) resulted in further $HgCl_2(s)$, which was removed. Addition of further 2-propanol (3 mL) and ether (~200 mL) then gave *p*-$[Co(tren)(NH_3)OH_2](CF_3SO_3)_3$ as an orange powder which was collected and washed with ether and dried in a dessicator under vacuum. Heating this material at 100 °C under vacuum (120 Pa) for 1 day gave mauve *p*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$. *p*-$[Co(tren)(NH_3)OH_2](ClO_4)_3$ was prepared by passing a solution of the nitrate-perchlorate salt through an Amberlite IRA 400 anion exchange column (ClO_4^- form) and taking the aqueous solution to dryness on a rotary evaporator at below room temperature. *p*-$[Co(tren)(NH_3)OH_2]Cl_3$ was prepared by dissolving the nitrate−perchlorate salt (0.31 g) in ice-cold 5 M HCl (5 mL) and slowly adding acetone with scratching. The recovered yellow powder was redissolved in ice-cold H_2O (5 drops), MeOH was added (3 mL), and then acetone was added with scratching. The product was collected, washed with acetone, and air-dried. Crystals suitable for X-ray analysis formed as yellow plates on dissolving 50 mg of this material in H_2O (2 drops), adding MeOH (2 drops) and then acetone (4 drops), and allowing this to stand overnight in a refrigerator.

^{17}O-Labeled Complexes. *p*-$[Co(tren)(NH_3)OH_2]X_3$ ($X_3 = (ClO_4)_3$, $(NO_3)_2ClO_4$)) was dissolved in ~30 atom % $H_2{}^{17}O$ and left to stand overnight at ~45 °C. The labeled complex was then recovered by removing $H_2{}^{17}O$ on the vacuum line. *p*-$[Co(tren)(NH_3)(^{17}OH_2)](CF_3SO_3)_3$ was prepared by dissolving *p*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$ (0.3 g) in 30 atom % $H_2{}^{17}O$ (2 mL) and removing the water on the vacuum line at room temperature.

NMR studies were carried out on a Varian VXRS 300 MHz spectrometer using 5−50 mg of complex and 0.6−0.7 mL of DMSO-d_6 as solvent. It was found necessary to add ~1 μL of concentrated acid (H/$DClO_4$ (***Caution***!), H/DCl, or CF_3SO_3H) to the DMSO solvent **before** adding the complex to avoid rapid proton exchange of the coordinated H_2O group, or base-catalyzed solvolysis of coordinated Cl^- (apparently the DMSO-d_6 used was slightly basic).

Loss of coordinated $^{17}OH_2$ was followed at 40.662 MHz at constant temperature (37.5, 29.6, and 22.1 to 31.3 °C) using a 10 mm probe (with 2.3 mL of solvent, prepared using either ^{17}O depleted or normal H_2O) fitted with a 5 mm insert containing CD_3OD for locking and referencing purposes ($CD_3{}^{17}OD$, −35.0 ppm vs $H_2{}^{17}O$).

Rates of Equilibration. Rate data (k_{obs}) were collected on a Varian Cary 219 spectrophotometer equipped with a thermostated rotary cell holder (five 1 cm cells, 37.5 ± 0.3 °C). Two sets of measurements were made, one used varying concentrations of NaCl (0−2.0 M) in media 0.1 M in $HClO_4$, and the other used constant ionic strength conditions ($I = 1.94$ M) for media also 0.1 M in $HClO_4$. For Cl^- concentration > 0.4 M *p*-$[Co(tren)(NH_3)OH_2](NO_3)_2ClO_4$ was used as the starting material, and for Cl^- concentrations < 0.4 M *p*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$ was used. The solutions (12.5 mM in complex) were left in the thermostated cell for ~30 min before beginning data collection (376 nm).

Equilibrium Constant (K_{an}). Two sets of solutions were prepared containing NaCl (0−4.0 M); the first containing no added $NaClO_4$ and the second being made up to $I = 3.72$ M with $NaClO_4$. To 4.00 mL

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[3] Burnett, M. G. *J. Chem. Soc. A* **1970,** 2480.

[4] Buckingham, D. A.; Creswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485.

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[6] This complex could not be prepared in the usual way by treating the chloro complex with concentrated CF_3SO_3H. Even in the cold this procedure gave substantial amounts of *t*-$[Co(tren)(NH_3)CF_3SO_3](CF_3SO_3)_2$.

Table 1. Crystal Data and Structure Refinement for p-[Co(tren)(NH$_3$)OH$_2$]Cl$_3$

empirical formula: $C_6H_{23}Cl_3CoN_5O$
fw: 346.57
temp: 158(2) K
wavelength: 0.710 73 Å
cryst syst: orthorhombic
space group: $Pmn2_1$
unit cell dimens: $a = 11.689(6)$, $b = 8.215(3)$, $c = 6.878(2)$ Å
volume: 660.5(4) Å^3
Z: 2
density: not measured
density (calcd): 1.743 Mg/m^3
abs coeff: 1.895 mm^{-1}
F(000): 360
cryst size: 0.4 × 0.3 × 0.1 mm
θ range for data collcn: 3.44−25.00°
index ranges: $-1 \le h \le 13$, $-9 \le k \le 0$, $-8 \le l \le 0$
no. of reflcns collcd: 695
no. of independent reflcns: 630 ($R_{int} = 0.0896$)
refinement method: full-matrix least-squares on F^2
data/params: 630/89
goodness-of-fit on F^2: 0.926
final R indices [$I > 2\sigma(I)$]^a: R1 = 0.0490, wR2 = 0.1129
R indices (all data)^a: R1 = 0.0710, wR2 = 0.1204
absolute struct param: 0.05(7)
largest diff. peak and hole: +0.486 and −0.628 e Å^{-3}

[a] $R1 = (\Sigma|F_o| - |F_c|/\Sigma|F_o|)$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

of this solution was added 4.00 mL of a solution containing p-[Co(tren)(NH$_3$)OH$_2$](NO$_3$)$_2$ClO$_4$ (13 mM) in 0.20 M HClO$_4$. Each solution was left to equilibrate at 37.5 °C for 4 days before the absorbance was recorded.

Loss of Coordinated H$_2$^{17}O. Rates of loss of the ^{17}O label from p-[Co(tren)(NH$_3$)^{17}OH$_2$]X$_3$ (X$_3$ = (NO$_3$)$_2$ClO$_4$, (ClO$_4$)$_3$, (CF$_3$SO$_3$)$_3$; concentrations varied from 0.030 to 0.089 M) into ^{17}O-depleted or normal 0.10 M HX (2.3 mL) containing varying concentrations of electrolyte (NaX = 0−1.80 M; I = 0.11−2.0 M) were obtained by observing the increase in height of the solvent H$_2$^{17}O signal (0.0 ppm) and/or by following the loss of enrichment through observation of the coordinated H$_2$^{17}O absorption (−100.1 ppm). Peak areas used in the latter analysis were determined by cutting and weighing expanded spectra.

Reaction Products. Reversed phase ion pair chromatography[7] (C-18 μ-Bondapak columns) was used to quantify the reaction products; (λ = 500 nm; aqueous 25 mM p-tolyl dihydrogen phosphate containing 25 mM Et$_3$N and 10% V/V MeOH at pH 3.5 (isocratic) was used as eluant; 2.0 mL min^{-1}). Reaction products were also separated on, and then eluted from, short cation ion-exchange columns (Dowex 50W-X2 resin). The CoCl^{2+} eluate (1M HCl) was immediately taken to dryness at below room temperature while the CoOH$_2$$^{3+}$ eluate (4 M HCl) was warmed to ∼50 °C to convert it to CoCl^{2+} before being evaporated to dryness.

X-ray Data Collection, Reduction, and Structure Solution for p-[Co(tren)(NH$_3$)(OH$_2$)]Cl$_3$. Diffraction data were collected on orange/red crystals of p-[Co(tren)(NH$_3$)(OH$_2$)]Cl$_3$ using a Nicolet R3M diffractometer at 158(2) K, with graphite monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using SHELXTL.[8] Analysis of systematic absences in the data was consistent with the space group $Pmn2_1$ (No 31).[9] Details of the crystal, data collections and refinements are summarised in Table 1.

The structure was solved using SHELXS-86.[10] The Co atom, the aqua O , ammine N, and two N atoms and one C atom from the tren ligand lie on a mirror plane (a in Wycoff notation for the space group $Pmn2_1$), and their coordinates were restrained appropriately. The second C atom from this five-membered ring of the tren ligand is thus disordered over two positions above and below the crystallographic mirror plane. Weighted full matrix refinement of the structures on F^2 was performed with SHELXL-93,[11] with all non-hydrogen atoms assigned anisotropic temperature factors. Hydrogen atoms for the tren and ammine ligands were included in calculated positions. Examination of difference Fourier maps did not reveal the location of the H atoms on the aqua ligand, and these were not included in the final refinement. Calculation of the Flack absolute structure parameter[12] for the non-centrosymmetric structure gave −0.05(6) in the final cycle, confirming that the chosen coordinates represented the correct structure. The final difference Fourier map was essentially flat with the highest peak at 0.51 e Å^{-3}. Final positional and equivalent thermal parameters, anisotropic displacement parameters, hydrogen and isotropic displacement parameters and important interionic contacts are listed in Tables S1−S4, respectively of the Supporting Information.

Results

1. Rates of Equilibration. Figure S1 (Supporting Information) gives visible−UV spectra of freshly prepared acidified aqueous solutions of p-[Co(tren)(NH$_3$)OH$_2$]$^{3+}$ (p-CoOH$_2$$^{3+}$) and p-[Co(tren)(NH$_3$)Cl]$^{2+}$ (p-CoCl^{2+}). The absorbance difference is at a maximum at 376 nm, and this wavelength was chosen for data collection for the equilibrium process

$$p\text{-CoOH}_2{}^{3+} + \text{Cl}^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} p\text{-CoCl}^{2+} + \text{H}_2\text{O} \tag{1}$$

Experiments were carried out at both constant (I = 2.0 M, Cl$^-$ and ClO$_4$$^-$ both present) and variable (I = 0.12−2.0 M, Cl$^-$ only present) ionic strengths and at 37.5 °C (at 25 °C the reaction was found to be inconveniently slow). Initial experiments established that k_{obs} was the same irrespective of starting complex (p-CoOH$_2$$^{3+}$ or p-CoCl^{2+}) and the former was routinely used for [Cl$^-$] ≥ 0.4 M and the latter for [Cl$^-$] < 0.4 M. Absorbance vs time traces gave excellent first-order fits over the time of data collection (usually $\ge 3t_{1/2}$). Values of k_{obs} are given in Table 2.

2. Reaction Products. Reversed phase ion pair chromatography (RP-IPC[7]) established that the reaction products were exclusively p-CoCl^{2+} and p-CoOH$_2$$^{3+}$ independent of starting complex. RP-IPC using the p-tolyl phosphate ion-pair reagent allows ready separation of p-CoCl^{2+} from t-CoCl^{2+} and the latter was not detected in the CoCl^{2+} eluate or in the anated (HCl) CoOH$_2$$^{3+}$ fraction recovered following ion exchange separation of equilibrium mixtures (<1% of Co$_T$). Loss of coordinated NH$_3$ was not detected.

3. Equilibrium Position (K_{an}). Table S5 (Supporting Information) lists absorbance data (376 nm) for various reaction mixtures following equilibration at 37.5 °C (6.5 × 10^{-3} M complex); both variable and constant I data are given. The variation in the observed absorbance follows eq 2, where A_{CoCl}

$$A_{obs} = (A_{CoCl}K_{an}[\text{Cl}^-] + A_{CoOH_2})/(1 + K_{an}[\text{Cl}^-]) \tag{2}$$

and A_{CoOH_2} represent the absorbances of p-CoCl^{2+} and p-CoOH$_2$$^{3+}$ respectively, and K_{an} is the equilibrium constant for eq1 ($K_{an} = k_f/k_r$). It can be seen that the full range of the equilibrium process given by eq 1 is covered by this data. This treatment assumes that ion pairing by Cl$^-$ and ClO$_4$$^-$ does not

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Table 2. Rate Data (k_{obs}/s^{-1}) for the Equilibration of p-$CoOH_2^{3+}$ and p-$CoCl^{2+}$ (12.5 mM) at Variable and Constant ($I = 2.0$ M ($NaClO_4$) Ionic Strengths (37.5 °C, $HClO_4 = 0.10$ M)

	Variable I (Cl^- only)		const I ($[Cl^-] + [ClO_4^-] = 2.0$ M)	
$[Cl^-]$/M	$10^5k_{obs}/s^{-1}$	$10^5k_{calc}{}^a/s^{-1}$	$10^5k_{obs}/s^{-1}$	$10^5k_{calc}{}^b/s^{-1}$
0	1.49	1.4	1.23	1.4
	1.51		1.23	
	1.49			
0.10	2.56	2.1	1.83	1.9
	2.62		1.85	
	2.28			
	2.37			
	2.44			
0.20	3.06	2.8	2.32	2.4
	3.05		2.44	
0.40	3.92	3.8	3.42	3.3
	3.92		3.36	
0.80	5.11	5.5	5.10	4.9
	5.14		4.92	
	5.19			
1.20	6.11	6.6	6.33	6.2
			6.65	
1.60	7.53	7.5	7.61	7.2
2.00[c]	8.11	8.1	8.11	8.1
	8.13		8.13	

[a] Calculated using eq 4 and $k_{aq} = 1.4 \times 10^{-5}$ s^{-1}, giving $k_{an} = 1.2 \times 10^{-4}$ s^{-1} and $K_{Cl} = 0.64$ M^{-1}. [b] Calculated using eq 3 and $k_{aq} = 1.4 \times 10^{-5}$ s^{-1} and $K_{Cl} = 0.64$ M^{-1}, giving $k_{an} = 1.2 \times 10^{-4}$ s^{-1} and $K_{ClO_4} = 0.21$ M^{-1}. [c] $I = 2.16$ M.

Table 3. Rate Constants (k_{OH_2}/s^{-1}) for Loss of Coordinated $H_2{}^{17}O$ from p-$Co^{17}OH_2^{3+}$ in the Presence of NaCl and Other Electrolytes and Temperature Variation

Co(III) salt[a]	electrolyte/M	T/°C	$10^4k_{OH_2}/s^{-1}$
$(ClO_4)_3$	0[b]	37.5	1.3
$(NO_3)_2ClO_4$	0[c]	37.5	1.3
$(ClO_4)_3$	0.50 NaCl[c]	37.5	1.6
$(NO_3)_2ClO_4$	1.00 NaCl[c]	37.5	2.0
$(NO_3)_2ClO_4$	1.50 NaCl[c]	37.5	2.2
$(NO_3)_2ClO_4$	1.80 NaCl[c]	37.5	2.4
$(NO_3)_2ClO_4$	1.90 NaCl[c]	37.5	2.4
$(CF_3SO_3)_3$	0[d]	29.6	0.38
$(CF_3SO_3)_3$	0.84 $NaCF_3SO_3$[d]	29.6	0.42
$(CF_3SO_3)_3$	0.84 NaCl[d]	29.6	0.51
$(CF_3SO_3)_3$	0.80 NaCl[e]	22.1	0.15
$(CF_3SO_3)_3$	0.80 NaCl[e]	25.0	0.26
$(CF_3SO_3)_3$	0.80 NaCl[e]	28.0	0.38
$(CF_3SO_3)_3$	0.80 NaCl[e]	29.7	0.51
$(CF_3SO_3)_3$	0.80 NaCl[e]	31.3	0.73

[a] $Co^{17}OH_2^{3+}$ concentration varied from 0.030 to 0.089 M; normally ~0.05 M. [b] 0.10 M $HClO_4$ only. [c] 0.10 M $HClO_4$ plus added $NaClO_4$ to $I = 2.0$ M. [d] 0.01 M in CF_3SO_3H. [e] 0.05 M in HCl.

affect the absorbances of either complex (at 376 nm), and this was confirmed by experiment. If we set $A_{CoOH_2} = 0.300$, the data gives best fit K_{an} and A_{CoCl} values of 6.8 M^{-1}, 0.58 (variable I) and 5.0 M^{-1}, 0.60 ($I = 2.16$ M), respectively. The A_{CoCl} value of 0.60 was confirmed by experiment ($I = 2.0$, $NaClO_4$).

4. Loss of Coordinated Water. Figure 2SA (Supporting Information) gives 17O NMR spectra showing loss of label from p-$Co^{17}OH_2^{3+}$ (signal c) into ^{17}O-depleted water in the presence of 0.50 M Cl^- ($I = 2.0$ M ($NaClO_4$), 37.5 °C) together with the associated increase in solvent ^{17}O (signal a). Figure 2SB (Supporting Information) gives the 1n(ΔA) vs t plot ($\Delta A = A_\infty - A_t$) with slope $k_{OH_2} = 1.6 \times 10^{-4}$ s^{-1}. Table 3 lists k_{OH_2} data at varying Cl^- concentrations (0−1.9 M, $I = 2.0$ M ($NaClO_4$)). Additional experiments (not given) indicated a maximum error of ±20% in these rate constants. The table also gives data at 29.6 °C collected in the absence and presence of $NaCF_3SO_3$ and NaCl electrolyte and a set of measurements in 0.85 M Cl^- at different temperatures. The latter data gives an excellent Arrhenius plot, $E_a = 120 \pm 10$ kJ mol^{-1} (this data was collected using normal water, and the rate constants were obtained by estimating areas of expanded $Co^{17}OH_2^{3+}$ spectra). The k_{OH_2} value at 29.6 °C in 0.84 M NaCl is in excellent agreement with that in 0.85 M Cl^- at 29.7 °C ($k_{obs} = 5.1 \times 10^{-4}$ s^{-1}), and the E_a value predicts $k_{OH_2} = 1.7 \times 10^{-4}$ s^{-1} at 37.5 °C which is in good agreement with the Cl^- variation data. k_{OH_2} clearly shows an electrolyte, but not an ionic strength, dependence. Thus the presence of 2.0 M ClO_4^- has no effect on the rate, whereas $CF_3SO_3^-$has a small effect, and Cl^- has a large effect. The significance of these observations will be considered below.

Table 4. NOe and COSY Assignments for C−H and N−H Hydrogens of p-$CoOH_2^{3+}$ and p-$CoCl^{2+}$

^{1}H	nOe		COSY		
(δ/ppm)[a]	N−H	C−H	N−H	C−H	assignment
		p-$CoOH_2^{3+}$ [b]			
a (2.56)	f, h	c, d	f	c	CH_2 (*trans* OH_2)
b (2.95)		c, d		c, d	CH (*anti* OH_2)
c (3.2)	g, i	a, b, d	g	a, b, d	CH_2 (*trans* OH_2); CH (*syn* OH_2)
d (3.5)	h	a, b, c	g, h	b, c	CH (*anti* OH_2)
e (3.88)	f, g, h	i			NH_3
f (4.55)	e, h	a		a	NH_2 (*trans* OH_2)
g (4.78)	i, h, e	c	h	c, d	NH (*syn* OH_2)
h (5.14)	e, f, g	a, d	g	d	NH (*anti* OH_2)
i(j)(6.15, 6.25)	e, g	c	j(i)		OH_2 (OHD)
		p-$CoCl^{2+}$ [c]			
a (2.66)	f, h	c, d	f, h	c	CH_2 (*trans* Cl)
b (2.87)		c, d, c′		d, c′	CH (*anti* Cl)
c (3.15)	g, h	a, b, d, c′	g	a, d, c′	CH_2 (*trans* Cl), CH (*syn* Cl)
d (3.4)	h	a, b, c	g,h	b, c, c′	CH (*anti* Cl)
c′ (3.7)		c, b		b, c, d	CH (*syn* Cl)
e (3.84)	f, g, h				NH_3
g (4.90)	e, h	c	h	c, d	NH (*syn* Cl)
f (5.74)	e, h	a		a	NH_2 (*trans* Cl)
h (5.83)	e, f, g	a, d	g	d	NH (*anti* Cl)

[a] Values in parentheses represent chemical shifts (δ, ppm) referenced to NaTPS. [b] $(ClO_4)_3$ salt in d_6-DMSO (700 mL) containing 1 μL of concentrated $DClO_4$. [c] $Cl(ClO_4)$ salt in d_6-DMSO (700 mL) containing 1 μL of concentrated DCl.

5. ^{1}H NMR Experiments. Figure S3 (Supporting Information) gives ^{1}H NMR spectra of p-$CoOH_2^{3+}$ (as its Cl^- (Figure 3SA) and ClO_4^- (Figure 3SB) salt respectively) in DMSO-d_6 containing 1 μL of DCl or $DClO_4$ to sharpen the coordinated OH_2 signal; this addition results in the appearance of an extra downfield signal due to coordinated OHD.[13] The various absorptions labeled $a-i$ (higher to lower field) represent C−H hydrogens (a (2H), b (2H), c (6H), d (2H)), the NH_3 ligand (e (3H)), three distinguishable N−H hydrogens (f (2H), g (2H), h (2H)) and coordinated OH_2 (i (2H)). A combination of 1D nOe and 2D COSY spectroscopies resulted in all H atoms being assigned;[14] Table 4 summarizes this data. Figure 1 gives labels

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(13) It was shown that addition of DX (X = Cl, ClO_4) gave an excellent measure of the amount of residual H_2O in the DMSO-d_6 solvent. Complete equilibration between H and D for coordinated and solvent H_2O/HDO occurs in this type of experiment, but the rate of equilibration is slow on the NMR time scale (for water concentrations <17%); thus separate coordinated H_2O (i), coordinated HDO (j) and solvent H_2O/HDO (*) signals are observed under this condition (cf. Figure S3 (Supporting Information)), The signals are very sharp for H_2O concentrations of <1%.

(14) A recent article (Buckingham, D. A.; Clark, C. R.; Rogers, A. J. *Inorg. Chim. Acta* **1995**, *240*, 125) outlines how this was done.

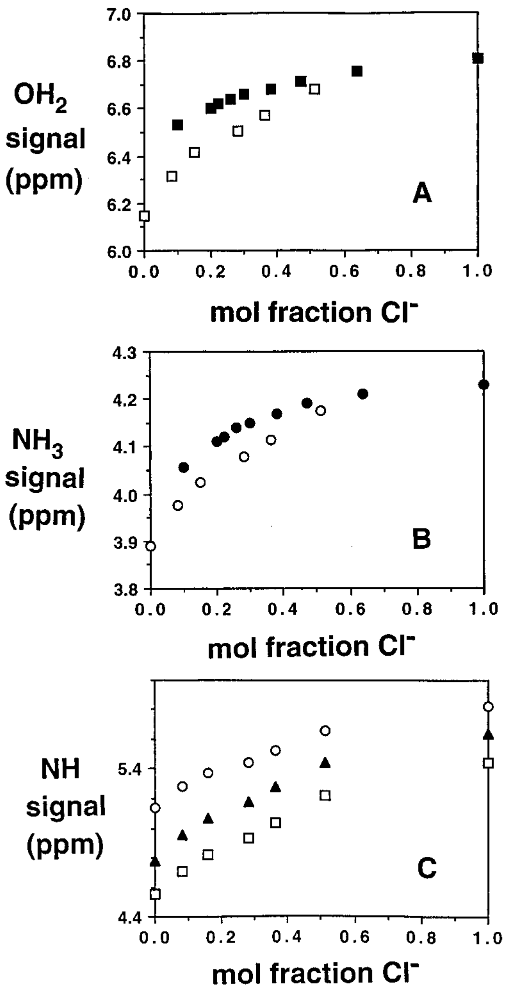

Figure 2. Chemical shift (δ, ppm) vs mol fraction of Cl^- ($n_{Cl^-}/(n_{Cl^-} + n_{ClO_4^-})$) on titrating either *p*-$[CoOH_2](ClO_4)_3$ (40 mg) or *p*-$[CoOH_2]Cl_3$ (8.6 mg) in DMSO-d_6 (0.60 mL with 0.020 mL of added water) with either 5 M HCl or 11.3 M $HClO_4$ (plus solid $NaClO_4$) respectively. (A) Chemical shift of coordinated OH_2 (*i*): open squares, data for ClO_4^- salt; closed squares, data for Cl^- salt. (B) Chemical shift of coordinated NH_3 (*e*): open circles, data for ClO_4^- salt, closed circles: data for Cl^- salt. (C) Chemical shift of coordinated NH for ClO_4^- salt: open squares (*f*), solid triangles (*g*), open circles (*h*). Data at mole fraction $Cl^- = 1.0$ are for *p*-$[CoOH_2]Cl_3$ in the absence of added ClO_4^-.

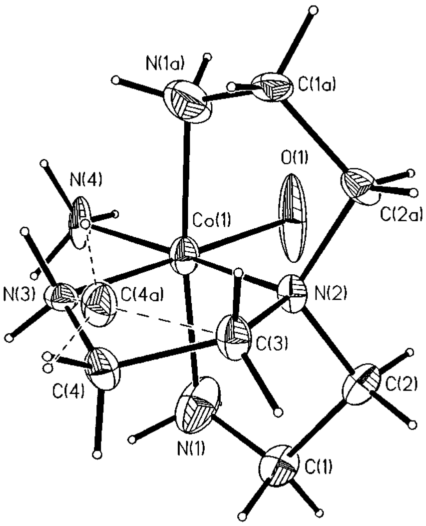

Figure 3. Perspective view of the *p*-$[Co(tren)(NH_3)OH_2]^{3+}$ cation showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

to the various H atoms. Likewise all H atoms in *p*-$CoCl^{2+}$ were assigned (absorptions *a*−*h*, Table 4), and the ^1H NMR spectrum of this complex is given in Figure 3SC (Supporting Information).

Three observations of particular significance to this study can be made from consideration of these spectra. First, the chemical shifts (δ, Table 4) of all the C*H* hydrogens in *p*-$CoOH_2^{3+}$ show little or no difference between the Cl^- and ClO_4^- salts; only the c manifold shows small changes, and four of the six hydrogens responsible for this signal lie in the vicinity of the coordinated OH_2 molecule (cf. Figure 1B). Second, differences between the C*H* hydrogens of *p*-$CoOH_2^{3+}$ and *p*-$CoCl^{2+}$ are seen only in the c region, with a two proton absorption of $CoCl^{2+}$ being moved to lower field. This is labeled c′ in Figure 3SC (Supporting Information) and results from hydrogens which lie immediately adjacent to coordinated Cl^- (cf. Figure 1B). Likewise the resonances of the *trans* NH_2 hydrogens (f) and the *anti* Cl hydrogens (h) move to substantially lower field in the *p*-$CoCl^{2+}$ complex (compared to the ClO_4^- salt of *p*-$CoOH_2^{3+}$). Third, the OH_2 (i) and N*H* (e,f,g,h) hydrogens are **very sensitive** to the anion present (Cl^- or ClO_4^-), and this is particularly so for the $CoOH_2^{3+}$ complex. It was shown that these resonances were essentially independent of complex concentration (0.02 and 0.10 M), so that ion association appears to be complete in DMSO under such conditions.[15] The presence of small amounts of added H_2O (up to 4%) had little effect on the chemical shifts, but larger amounts (to 22% V/V) resulted in progressive upfield shifts (OH_2, N*H* hydrogens, but not C*H* hydrogens) with the OH_2 signal broadening appreciably at 17% due to rapid H-exchange with the solvent and disappearing at higher H_2O concentrations. No coordinated OH_2 absorption was observed in acidified H_2O (or D_2O) solvent irrespective of acid concentration (to 2 M), and the chemical shift differences between the various N*H* hydrogens (f, g, h) largely disappeared in acidified H_2O (or D_2O). Warming the NMR tube (DMSO-d_6 solvent) to 80 °C, or leaving it for several days at ambient temperature, changed the *p*-$CoOH_2^{3+}$ spectrum (Cl^- salt) progressively to that of *p*-$CoCl^{2+}$ **without** the appearance of signals due to $CoDMSO^{3+}$. Similar treatment of $CoOH_2^{3+}$ (ClO_4^- salt) resulted in only $CoDMSO^{3+}$ absorptions.

Changes in the OH_2 (i), NH_3 (e), and N*H* (f, g, h) chemical shifts were followed for *p*-$CoOH_2^{3+}$ (ClO_4^- and Cl^- salts) on titration with HCl and $HClO_4$ + $NaClO_4$ respectively in 3% aqueous DMSO-d_6 solutions. Figure 2 shows these data plotted against mole fraction of Cl^-. The significance of this data for interpreting the site location of ion pairs will be taken up below, but it is very clear from the nature of the curves that Cl^- ion pairs with *p*-$CoOH_2^{3+}$ much more strongly than does ClO_4^-. Even under the condition $ClO_4^-:Cl^- = 30:3$ (mol fraction $Cl^- = 0.091$) ClO_4^- has only a small effect on the spectrum of the Cl^- salt, compared to that seen on addition of small amounts of Cl^- to *p*-$[CoOH_2](ClO_4)_3$. Finally, it was noted that the N*H* shifts (e, g, f, h) of $CoCl^{2+}$ were less sensitive to the identity of the accompanying anion, and appeared to be somewhat dependent on the concentration of the complex.

6. Structure of the Complex *p*-[Co(tren)(NH$_3$)(OH$_2$)]Cl$_3$. The molecular structure and numbering scheme used for the *p*-$[Co(tren)(NH_3)(OH_2)]^{3+}$ cation is illustrated in Figure 3, with bond distances and angles detailed in Table 5. The structure of *p*-$[Co(tren)(NH_3)(OH_2)]Cl_3$ comprises discrete *p*-$[Co(tren)(NH_3)(OH_2)]^{3+}$ cations and chloride anions held together by electrostatic forces and a network of hydrogen bonds, *vide infra* (Figure 4). The cobalt(III) atom adopts distorted octahedral coordination with the tren ligand bound in a quadridentate

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Table 5. Bond Lengths [Å] and Angles [°] for p-[Co(tren)(NH$_3$)OH$_2$]Cl$_3$

Co(1)−N(1)	1.970(9)	Co(1)−N(1)#1[a]	1.970(9)
Co(1)−N(2)	1.940(10)	Co(1)−N(3)	1.951(10)
Co(1)−N(4)	1.957(10)	Co(1)−O(1)	1.922(10)
N(1)−C(1)	1.450(13)	C(1)−C(2)	1.521(14)
C(2)−N(2)	1.472(10)	N(2)−C(2)#1	1.472(10)
N(2)−C(3)	1.503(14)	C(3)−C(4)	1.51(2)
C(4)−N(3)	1.46(2)		
N(2)−Co(1)−N(1)	86.1(3)	N(3)−Co(1)−N(1)	90.4(4)
N(4)−Co(1)−N(1)	93.9(3)	O(1)−Co(1)−N(1)	89.6(4)
N(2)−Co(1)−N(1)#1	86.1(3)	N(3)−Co(1)−N(1)#	190.4(4)
N(4)−Co(1)−N(1)#1	93.9(3)	O(1)−Co(1)−N(1)#	189.6(4)
N(1)−Co(1)−N(1)#1	172.1(5)	O(1)−Co(1)−N(2)	93.9(4)
N(2)−Co(1)−N(3)	86.4(4)	O(1)−Co(1)−N(3)	179.7(5)
N(2)−Co(1)−N(4)	176.9(4)	N(3)−Co(1)−N(4)	90.5(4)
O(1)−Co(1)−N(4)	89.2(4)	C(1)−N(1)−Co(1)	109.9(6)
N(1)−C(1)−C(2)	110.0(9)	N(2)−C(2)−C(1)	106.9(7)
C(2)−N(2)−C(2)#1	113.0(10)	C(2)−N(2)−C(3)	109.5(6)
C(2)#1−N(2)−C(3)	109.5(6)	C(2)−N(2)−Co(1)	106.3(6)
C(2)#1−N(2)−Co(1)	106.3(6)	C(3)−N(2)−Co(1)	112.4(7)
N(2)−C(3)−C(4)	110.9(10)	N(3)−C(4)−C(3)	111.1(12)
C(4)−N(3)−Co(1)	111.7(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1, −x, y, z.

fashion through its four N atoms. The aqua and ammine ligands fill the remaining *cis* coordination positions in the coordination sphere with normal Co−N and Co−O bond distances. The mean Co−N(tren) distance is 1.96(1) Å and the mean N(tren)−Co−N(tren) angle 88(2)°, which are comparable to corresponding values in other tren complexes of Co(III).[16−19] Other bond lengths and angles for the tren ligand are unremarkable. The conformations of the two 5-membered chelate rings generated by the crystallographic mirror plane [Co(1)−N(1)−C(1)−C(2)−N(2)] are δ and λ, respectively. The third ring has the C(4) atom disordered with respect to the mirror plane to give both δ and λ conformations.

Discussion

The ^{1}H NMR data for CoOH$_2^{3+}$ in DMSO strongly suggest that ion association in aqueous solution will occur preferentially at a position adjacent to the aqua ligand, and that this will be more pronounced for Cl$^-$ than for ClO$_4^-$. Thus the NMR data (Figure 2) shows that the presence of Cl$^-$ strongly influences the chemical shifts of the OH_2, NH_3 and NH hydrogens (in order of diminishing importance), but not the CH hydrogens. This is most obvious for the ClO$_4^-$ salt, where the addition of **one** molar equivalent of Cl$^-$ has a large effect compared to the addition of a further two. The addition of ClO$_4^-$ to the Cl$^-$ salt on the other hand (up to a mole ratio of 10:1) has a very much smaller effect on the chemical shifts. Clearly the presence of a single Cl$^-$ ion is sufficient to cause substantial displacement of ClO$_4^-$ from the vicinity of these hydrogens, and in particular from the vicinity of the OH$_2$ hydrogens. Also, warming the Cl$^-$ salt of p-CoOH$_2^{3+}$ in DMSO results **directly** in p-CoCl^{2+} without the production of any CoDMSO^{3+}. This is additional evidence that ion association occurs adjacent to the OH$_2$ ligand, and shows that DMSO does not compete with Cl$^-$ entry in this solvent. Further consideration of this aspect will be taken up below.

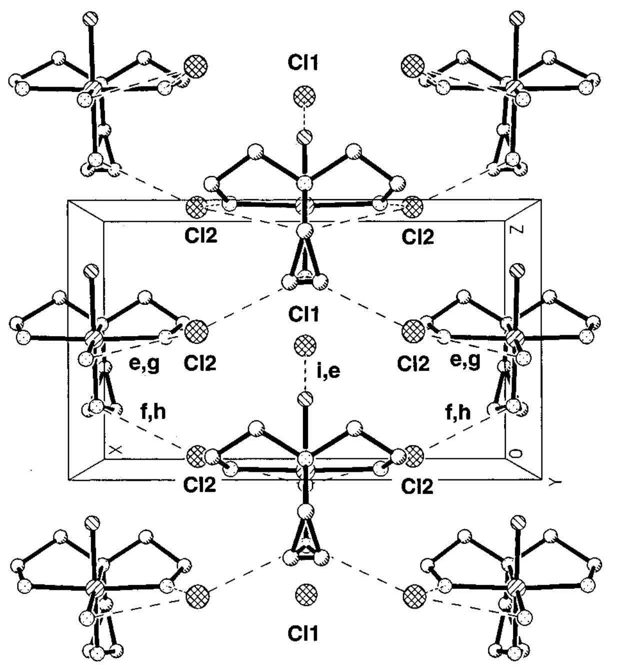

Figure 4. View of the unit cell contents of p-[Co(tren)(NH$_3$)OH$_2$]Cl$_3$ viewed down the b axis. Possible H-bonds are represented by dotted lines. Cross-hatched spheres represent Cl$^-$ ions (**1**,**2**), hatched spheres represent coordinated OH$_2$, and dotted spheres represent amine centers.

The crystal structure of p-[CoOH$_2$]Cl$_3$ (Figure 4) shows one **unique** Cl$^-$ anion (Cl(1)) H-bonded to the OH$_2$ and NH$_3$ ligands in a intramolecular fashion (distances of 2.89 and 3.96 Å respectively) such that it is in an ideal position for substitution of the aqua ligand. Heating this crystalline material to 100 °C resulted in rapid anation. The other two identical Cl$^-$ anions (C1(2)) are involved in intermolecular H-bonding between sheets of cations. This latter network ties up the two g and the two f NH hydrogens of a particular cationic unit (cf. Figure 1), and two out of the three **e** hydrogens of the NH$_3$ ligand (the third is involved intramolecularly with C1(1)). All three Cl$^-$ ions are on the "open face" of the molecule, one in a position intermediate between "sites A" of Figure 1 (Cl(1)) and the other two (Cl(2)) close to the 3-fold "sites B". In aqueous solution competitive H-bonding to solvent H$_2$O molecules will also occur so that the detailed picture will almost certainly be different, but it is likely that the positioning of the unique Cl$^-$ in the ion pair will remain close to that given by Cl(1) in the crystal.

Figure S4 (Supporting Information) gives a plot of $k_{\rm obs}$ vs Cl$^-$ concentration for the anation rate data (Table 4). It shows that, at low [Cl$^-$], $k_{\rm obs}$ is slightly larger in the absence of ClO$_4^-$ than when it is present, but neither plot is linear with curvature being particularly noticeable at low and high Cl$^-$. The [Cl$^-$] = 0 intercept gives the rate constant for aquation of p-CoCl^{2+} ($k_{\rm r}$, eq 1), and the difference between the two values, 1.23×10^{-5} s^{-1} (in 2.0 M ClO$_4^-$) and 1.50×10^{-5} s^{-1} (in the absence of ClO$_4^-$), is small compared to the overall effect of added Cl$^-$. In what follows this effect of ionic strength on the rate of aquation will be ignored;[20−23] $k_{\rm r} = k_{\rm aq} = (1.4 \pm 0.2) \times 10^{-5}$ s^{-1} at 37.5 °C.

Scheme 1 relates the rate constant for anation to the ion pair constants $K_{\rm Cl}$ and $K_{\rm ClO_4}$ as follows

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$$k_{obs} = k_{aq} + k_{an}K_{Cl}[Cl^-]/(1 + K_{Cl}[Cl^-] + K_{ClO_4}[ClO_4^-]) \quad (3)$$

where k_{an} represents the rate constant for anation within the ion pair with Cl^-. For the data in the presence of Cl^- alone, this reduces to

$$k_{obs} = k_{aq} + k_{an}K_{Cl}[Cl^-]/(1 + K_{Cl}[Cl^-]) \quad (4)$$

and least-squares fitting (using $k_{aq} = 1.4 \times 10^{-5}$ s^{-1}) gives k_{an} and K_{Cl} values of 1.2×10^{-4} s^{-1} and 0.64 M^{-1} respectively. Calculated fits are given in Table 3. Likewise the data at constant ionic strength (ClO_4^- also present) can be fitted to eq 3 ($k_{aq} = 1.4 \times 10^{-5}$ s^{-1}, $K_{Cl} = 0.64$ M^{-1} fixed), giving $k_{an} = 1.2 \times 10^{-4}$ s^{-1}, and $K_{ClO_4} = 0.21$ M^{-1}. The agreement between the two k_{an} values, one at variable *I* and the other at constant *I*, supports the treatment taken. Thus ion association between *p*-$CoOH_2^{3+}$ and ClO_4^- appears to be less important than that between *p*-$CoOH_2^{3+}$ and Cl^- ($K_{ClO_4} = 0.21$ M^{-1}, $K_{Cl} = 0.64$ M^{-1}) but neither is complete at the 2.0 M condition. It appears that H-bonding with solvent H_2O decreases ion association in aqueous solution compared to that in DMSO (*vide supra*).

The equilibrium data (Table S5, Supporting Information) gives K_{an} values of 6.8 and 5.0 M^{-1} at variable *I* and constant *I*, respectively. The error in these values is estimated to be 10%. The rate and equilibrium data can also be related

$$K_{an} = K_{Cl}k_{an}/k_{aq} \quad (5)$$

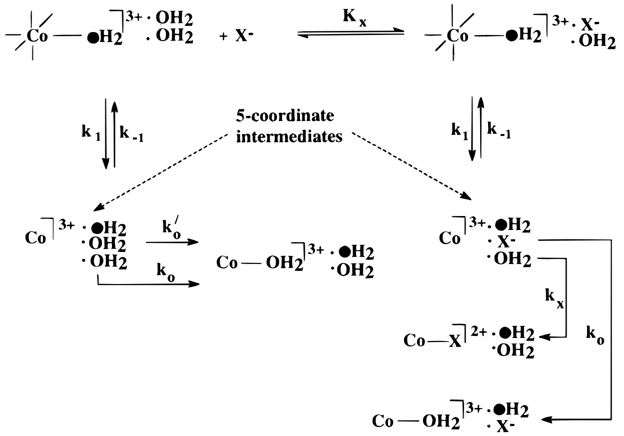
and substituting the appropriate k_{an}, k_{aq}, and K_{Cl} values from Table 2 gives $K_{an} = 5.5$ M under the two sets of conditions. This value agrees with those obtained from the equilibrium data.

Let us now examine the rate data for loss of coordinated $^{17}OH_2$ (Table 3). The presence (2.0 M) or absence (0.1M $HClO_4$ only) of $NaClO_4$ does not affect k_{OH_2} but the presence of $NaCF_3SO_3$ and NaCl (0.84 M) does, and to increasing extents. The Cl^- data (37.5 °C) appears to approach a limiting value of k_{OH_2} $\sim 2.4 \times 10^{-4}$ s^{-1} (1.9 M Cl^-) and we attribute this to loss of coordinated water from the ion pair *p*-$CoOH_2^{3+}.Cl^-$. Comparison with the rate constant for anation within the ion pair shows that water exchange occurs just as readily as anation, $k'_{OH_2} = k_{an} = 1.2 \times 10^{-4}$ s^{-1} ($k_{OH_2} = k_{an} + k'_{OH_2}$), Scheme 1. This contrasts with DMSO solution, where only Cl^- entry occurs from within the ion pair (vide supra).

How can loss of coordinated OH_2 from the Cl^- ion pair in aqueous solution be affected (by a factor of almost 2 when comparing the rate constants for the free ion and Cl^- ion pair) when bond breaking is considered to be entirely dissociative? We believe this means that entry of Cl^- and adjacent H_2O molecules affects reentry of the original $^{17}OH_2$ ligand such that all processes are partly rate determining. The alternative explanation is that the presence of Cl^- adjacent to the leaving OH_2 molecule affects the rate of bond cleavage. Scheme 2 outlines the first proposal. The two most likely entering sites adjacent to the leaving group (labeled A in Figure 1A) will be occupied by H_2O molecules in the free ion and by X^- (Cl^- or ClO_4^-) and by H_2O in the ion pair.

The equivalence of k'_{OH_2} and k_{an} (for $X^- = Cl^-$) means that OH_2 and Cl^- enter equally well into the five-coordinate intermediate generated from the ion pair, $k_o = k_x$. We[1] and others[2] have argued that the lifetime of such intermediates is so short that they must accept entering groups **immediately** available to them. In the present case this includes the original $^{17}OH_2$ ligand. If reacceptance of this group occurs in competition with entry of a new ligand, then clearly bond breaking is not entirely rate determining. Treating the five-coordinate intermediate as steady state gives **for the ion pair** (Scheme 2)

Scheme 2



$$k_{OH_2} = \frac{k_1(k_o + k_x)}{k_{-1} + k_o + k_x} \quad (6)$$

$$k_{an} = \frac{k_1k_x}{k_{-1} + k_o + k_x} \quad (7)$$

$$k_{OH_2}/k_{an} = (k_o + k_x)/k_x \quad (8)$$

The same equations relate to H_2O entry into the non-ion-paired complex ($k_x = k'_o$), but the experimental data then requires $k'_o = 0$. If return of the same $H_2{}^{17}O$ molecule is favored in the ion-pair, as we think is very likely, ($k_{-1} > k_o$, k_x), then

$$k_{OH_2} = k_1(k_o + k_x)/k_{-1} \quad (9)$$

$$k_{an} = k_1k_x/k_{-1} \quad (10)$$

and both k_{OH_2} and k_{an} should show an X^- dependence. The non-entry of DMSO, and the exchange data in ClO_4^- media are in agreement with this. In future studies it will be of interest to determine the influence of other X^- anions on k_{OH_2}, k_{an} for reaction of this *p*-$CoOH_2^{3+}$ ion and similar complexes in which specific X^- association can be identified.

Acknowledgment. We thank Professor W. T. Robinson, University of Canterbury, for the X-ray data collection.

Supporting Information Available: Figures showing UV−vis spectra of *p*-$CoCl^{2+}$ and *p*-$CoOH_2^{3+}$, ^{17}O NMR spectra for loss of label out of *p*-$Co^{17}OH_2^{3+}$, ^1H NMR spectra of *p*-$CoOH_2^{3+}$ and *p*-$CoCl^{2+}$ in DMSO-d_6, and plots of k_{obs} vs [Cl^-] for equilibration and tables giving atomic coordinates and equivalent isotropic displacement parameters, anisotropic thermal parameters, hydrogen positional and thermal parameters, important interionic contacts, and equilibrium absorbance data (9 pages). Ordering information is given on any current masthead page.

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