^{17}O NMR Study of Solvent Exchange in Some Aqueous [Co(tren)(X)(OH$_2$/OH)]$^{n+}$, [Co(cyclen)(X)(OH$_2$/OH)]$^{n+}$, and [Co(N-Mecyclen)(X)(OH$_2$/OH)]$^{n+}$ Systems (X = NH$_3$, OH$_2$/OH; *n* = 3, 2, 1)[1]

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A ^{17}O NMR study (I = 1.0 M, NaClO$_4$ or NaOSO$_2$CF$_3$, 25.0 °C) of solvent exchange in labeled *p*- and *t*-[Co(tren)(NH$_3$)OH$_2$]$^{3+}$, [Co(tren)(OH$_2$)$_2$]$^{3+}$, [Co(cyclen)(OH$_2$)$_2$]$^{3+}$, and [Co(N-Mecyclen)(OH$_2$)$_2$]$^{3+}$ ions (ca. 30% ^{17}O) in aqueous solution has shown that loss of coordinated OH$_2$ is slow for all of the complexes (k_{ex}/s^{-1} = 1.1 × 10^{-5}, 1.2 × 10^{-5}, 3.7 × 10^{-5} (*p*-site)/8.7 × 10^{-6} (*t*-site), 2 × 10^{-4}, and 2 × 10^{-4}, respectively). Values of k_{ex} for solvent exchange in [Co(tren)(OH)$_2$]$^{+}$ have been determined as 9.7 × 10^{-5} s^{-1} (*p*-site) and 2.2 × 10^{-7} s^{-1} (*t*-site) Coordinated OH^{-} in both *p*- and *t*-[Co(tren)(NH$_3$)OH]$^{2+}$ also exchanges only slowly with solvent (k_{ex}/s^{-1}= 1.7 × 10^{-4}, and <1 × 10^{-6}, respectively), whereas exchange of coordinated solvent in the aqua−hydroxo complexes [Co(tren)(*t*-OH$_2$)(*p*-OH)]$^{2+}$, [Co(cyclen)(OH$_2$)OH]$^{2+}$, and [Co(N-Mecyclen)(OH$_2$)OH]$^{2+}$ is much more rapid (k_{ex}/s^{-1} = 0.03 (*p*-site)/0.01 (*t*-site), 12 and 15, respectively). Ligand−OH^{-} exchange in these latter systems is interpreted as occurring via (indirect) S$_N$1(CB)-type processes on the corresponding aqua complexes: [Co(amine)OH]$^{2+}$ $\rightleftharpoons$ [Co(amine-H)OH$_2$]$^{2+}$ → exchange. This type of pathway is seen to be more efficient when leaving-group departure is synchronous with proton transfer, and this appears to be more important for exchange in the cyclen and N-Mecyclen complexes where a reasonably acidic, adjacent syn N*H* proton is involved.

Introduction

Rates of solvent exchange provide perhaps our best guide to the ability of a metal complex to undergo substitution in aqueous solution.[2−4] Water is a particularly good ligand and, being the solvent, is immediately available at the reaction site. Other variables such as diffusion, stereochemical positioning, and stability of the resultant encounter complex do not complicate the interpretation. Substitution of a ligand L$_1$ by L$_2$ invariably proceeds via an MOH$_2$ complex, and this species may undergo many acts of water exchange before L$_2$ entry. The observed substitution rate is thus dictated both by the underlying solvent exchange rate and by the ability of L$_2$ to be in the right place at the right time during this process.[5,6]

Considering the vast literature available on substitution in octahedral Co(III) complexes,[7] relatively little information on exchange rates in these systems is available. In particular, there are few examples where rates of solvent exchange have been determined in the presence of L$_2$.[8] This limits our knowledge of substitution in the more labile complexes such as aqua−cobalamin[9] and its Co(III) mimics,[10] and in the cyclen and tren Co(III) systems which have recently been used to catalyze the hydrolysis of dialkyl phosphates (as mimics for DNA hydrolysis).[11]

In this study we examine in detail the rates of exchange of aqua and hydroxo ligands coordinated to Co(III) amine systems containing the cyclen, N-Mecyclen, and tren quadridentates (see Figure 1 for stereochemical designations). We show that stereochemical location is important, that exchange without OH^{-} catalysis is slow, but that the OH^{-}-catalyzed reaction is rather rapid and seems to be controlled by the ability of the hydroxo complex to undergo internal protonation in the transition state by making use of a specific NH residue. This mechanism may well be widespread among Co(III)−amine systems and is deserving of special attention.

Experimental Section

Apparatus and Reagents. UV−vis spectrophotometric measurements were carried out using a Cary 219 spectrophotometer. ^{17}O NMR spectra were recorded on a Varian VXR 300 MHz spectrometer operating at 40.662 MHz equipped with a 10 mm thermostated (25.0

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[7] For the most recent summary account (and references) on Co(III) substitution, see: Tobe, M. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, U.K., 1987; Vol. 1, Section 7.1.5, p 300.

[8] In a recent study (Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Simpson, J. *Inorg. Chem.* **1996**, *35*, 7728) Cl^{-} anation of *p*-[Co(tren)(NH$_3$)OH$_2$]$^{3+}$ via a specific ion pair has been discussed in relation to H$_2$O exchange.

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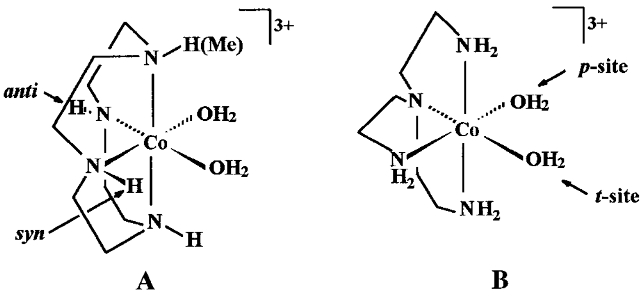

Figure 1. Representations designating (A) the syn- and anti *sec*-N*H* protons in $[Co(cyclen)(OH_2)_2]^{3+}$ and $[Co(N\text{-}Mecyclen)(OH_2)_2]^{3+}$ and (B) the *p*- and *t*-sites in $[Co(tren)(OH_2)_2]^{3+}$.

± 0.5 °C) probe and external 5 mm CD_3OD lock and reference (δ ^{17}O −35 ppm). For measurements in alkaline solution the NMR tube was fitted with a Teflon liner. Recording parameters were usually AT = 0.15 s, D1 = 0.05 s, D2 = 0 s, PW = 16.0 μs, SW = 10^5 Hz. pH was measured using a PHM 62 standard pH meter equipped with G2020B/K4040 or Ingold 6030-02 electrodes (for NMR measurements). Measurement in alkaline solution was carried out under N_2. ^{17}O-Enriched (~30 atom % ^{17}O) and depleted (~0.007 atom % ^{17}O) water was obtained from Yeda Research and Development Co., Rehovot, Israel. All other reagents were AR grade.

CAUTION: Although no problems were encountered in the synthesis and handling of the complexes described below, those containing perchlorate are potentially explosive and should be handled with great care!

Synthesis. ***p*- and *t*-$[Co(tren)(NH_3)OH_2](NO_3)_2ClO_4$** were prepared from *p*- and *t*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$ as reported previously.[12] Anal. Calcd: C, 15.54; H, 5.00; N, 21.15; Cl, 7.65. Found: for the *p*-isomer, C, 15.4; H, 5.0; N, 20.8; Cl, 8.2; for the *t*-isomer, C, 15.4; H, 5.0; N, 21.0; Cl, 7.8.

***p*-$[Co(tren)(NH_3)OH_2](CF_3SO_3)_3$.** A solution of *p*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$[13] (0.84 g, 2.6 mmol) in aqueous $Hg(CF_3SO_3)_2/CF_3SO_3H$ (5.0 mL, 0.74 M Hg^{2+} (3.7 mmol), 0.4 M H^+) was left at ambient temperature for 5 min and stirred occasionally. The mixture was then cooled in ice and filtered through Celite (to remove $HgCl_2$) and the filter washed with a little MeOH. Solid $NaCF_3SO_3$ (1 g) was then added to the filtrate, followed by *i*-PrOH (40 mL) and ether (300 mL) while cooling was maintained. The precipitated solid was collected, washed with ether, and air-dried. This material was then dissolved in H_2O (2 mL), and additional $NaCF_3SO_3$ (0.5 g) and *i*-PrOH (2 mL) were added, whereupon additional $HgCl_2$ precipitated and was removed as before. Addition of further *i*-PrOH (3 mL) and ether (200 mL) resulted in precipitation of the orange product. This was collected, washed with ether, dried, and stored under vacuum: Anation of this material in concentrated HCl, ~ 80 °C, gave only *p*-$[Co(tren)(NH_3)Cl]^{2+}$ as demonstrated by RP-HPLC.[14]

***p*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$.** This mauve-colored complex was prepared by heating (100 °C) the above complex under vacuum (120 Pa) for 3 days.

***p*-$[Co(tren)(NH_3)(^{17}OH_2)](CF_3SO_3)_3$.** Freshly prepared *p*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$ (~0.3 g) was dissolved in ~30% $H_2{}^{17}O$ (~2 mL) by warming, and the solvent was then removed by freeze-drying under vacuum (120 Pa, with recovery of residual $H_2{}^{17}O$). The recovered solid was stored in an airtight container.

***t*-$[Co(tren)(NH_3)(OSO_2CF_3)](CF_3SO_3)_2$.** This isomer could not be prepared as above because partial isomerization to the *p*-isomer occurred when the aqua triflate salt was heated. To *t*-$[Co(tren)(NH_3)Cl](ClO_4)Cl$[13] (0.93 g, 2.8 mmol) suspended in cold (−15 °C, ice−salt bath) CF_3SO_3H (4.6 mL) contained in a centrifuge tube was added dropwise a cream suspension of $Hg(CF_3SO_3)_2$ in CF_3SO_3H (prepared by dissolving 0.3 g of yellow HgO in 6 mL of CF_3SO_3H by stirring and warming (50 °C) overnight). The transfer of Hg^{2+} was completed by using a further 2 mL of CF_3SO_3H. After 15 min at −15 °C the mixture was centrifuged, and the red supernatant liquid was transferred to rapidly stirred cold (−15 °C) dry ether (300 mL), whereupon the desired complex precipitated. This was collected, washed with ether, dried, and stored under vacuum.

***t*-$[Co(tren)(NH_3)(^{17}OH_2)](CF_3SO_3)_3$.** This was prepared (0.3 g) as above for the *p*-isomer.

$[Co(tren)(OSO_2CF_3)_2](CF_3SO_3)$. $[Co(tren)Cl_2]Cl$[13] (1.0 g, 3.2 mmol) was dissolved in fresh concentrated CF_3SO_3H (7.5 mL) with the evolved HCl gas being removed using a stream of dry N_2. After 6 h the red-violet solution was added dropwise to rapidly stirred dry ether (500 mL) at 0 °C. After 2 h the pink product was collected, washed with ether, and stored under vacuum.

$[Co(tren)(^{17}OH_2)_2](CF_3SO_3)_3$. This complex was prepared by adding the above complex (0.3 g) to ~30% $H_2{}^{17}O$ (2 mL) at ambient temperature, and excess solvent was removed by freeze-drying (120 Pa).

$[Co(cyclen)(OH_2)_2](ClO_4)_3$. To a slurry of $[Co(cyclen)O_2CO]ClO_4\cdot H_2O$[15] (3 g) in water (5 mL) was added 2 molar equiv of 1 M $HClO_4$ (14.7 mL), and the solution was stirred for 1.5 h at 40 °C under a stream of N_2 before filtration and reduction of the filtrate volume (rotavap). The resultant red oil in acetone (3 mL) was added dropwise to rapidly stirred dry ether (0.5 L), giving a pink precipitate. This material was collected, washed with ether, and stored under vacuum over P_2O_5. (This complex could be readily crystallized from aqueous solution as its bis perchlorate nitrate salt[16] but for our purpose we wished coordinating anions such as NO_3^- to be absent.) Anal. Calcd: C, 16.99; H, 4.28; N, 9.91; Cl, 18.80. Found: C, 17.1; H, 4.5; N, 9.6; Cl, 18.6.

$[Co(N\text{-}Mecyclen)(OH_2)_2](ClO_4)_3$. To a slurry of $[Co(N\text{-}Mecyclen)O_2CO]ClO_4\cdot 2H_2O$[15] (2 g) in water (5 cm^3) was added 2 molar equiv of $HClO_4$ (1 M, 9.1 cm^3), and the mixture was left for 1 h at ambient temperature under a stream of N_2. Following filtration the dark red solution was taken to dryness under vacuum. Anal. Calcd: C, 18.65; H, 4.52; N, 9.67; Cl, 18.35. Found: C, 18.8; H, 4.6; N, 9.7; Cl, 18.1.

^{17}O-Labeled Cyclen/Mecyclen Complexes. The above freshly prepared diaqua complexes (1−2 g) were dissolved in ~30% $H_2{}^{17}O$ (2 mL), and after ~1 h at ambient temperature the solvent was slowly removed under vacuum (120 Pa, 24 h). The anhydrous solids were stored over P_2O_5.

Acidity Constant (K_a) Determinations. Values of K_a are given as mixed constants, i.e., $K_a = a_{H^+}[A^-]/[HA]$; $[H^+] = a_{H^+}/\gamma_\pm$, $\gamma_\pm = 0.58$ (1.0 M $NaClO_4$).[17] Potentiometric titration data were obtained as follows: 20.00 mL of a stock solution of the appropriate isolated aqua or triflato complex (3−5 mM, in $I = 1.0$ M electrolyte; $NaCF_3SO_3$ for tren complexes, $NaClO_4$ for cyclen complexes) under nitrogen was titrated with 0.0500 or 0.100 M NaOH (0.100, 0.200 mL aliquots) at 25 °C using a precision buret. The pH was recorded after each addition and the data treated according to the method of Albert and Serjeant.[18] ^{17}O NMR titration data were obtained as follows. To a solution of $[Co(tren)(OSO_2CF_3)_2](CF_3SO_3)$ (150 mg) in 2.3 mL of 30% $H_2{}^{17}O$ (10 mm NMR tube) were added small increments (microliter additions) of ~4 M NaOH. After each addition the pH was measured (Ingold 6030-02 pH electrode) and the ^{17}O NMR spectrum recorded.

Rates of ^{17}O Exchange. When "normal" H_2O solvent was used (0.037 atom % ^{17}O; I = 1.0 M in $NaCF_3SO_3$ or $NaClO_4$; 25.0 °C), the decay of the ^{17}O signal for the enriched complex was followed. However, on a limited number of occasions when ^{17}O-depleted solvent was used (0.007 atom %), the increase in solvent signal intensity was also monitored. Peak areas of expanded spectra (PA_t, former method)

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Table 1. ^{17}O Chemical Shifts (Bandwidths) and pK_a Data for Some Co(III) Complexes at 25 °C

complex	δ/ppm[a] ($\Delta\nu$/Hz)	pK_a
p-$[Co(tren)(NH_3)OH_2]^{3+}$	−100 (340 ± 30)	5.82
t-$[Co(tren)(NH_3)OH_2]^{3+}$	−134 (290 ± 30)	6.33
p-$[Co(tren)(NH_3)OH]^{2+}$	−120 (800 ± 100)	
t-$[Co(tren)(NH_3)OH]^{2+}$	−172 (900 ± 100)	
$[Co(tren)(OH_2)_2]^{3+}$	−95 (p) (380 ± 30)	5.89(p)
	−131 (t) (300 ±30)	6.40(t)
$[Co(tren)(t\text{-}OH_2)p\text{-}OH]^{2+}$	−112 (p)[d]	8.17(p)
	−134 (t)[d]	8.68(t)
$[Co(tren)(OH)_2]^+$	−109 (p) (1000 ± 200)	
	−162 (t) (1000 ± 200)	
$[Co(cyclen)(NH_3)OH_2]^{3+}$	−115[b] (380 ± 40[c])	6.02[b]
$[Co(cyclen)(OH_2)_2]^{3+}$	−110 (400 ± 40[c])	5.82, 8.20
$[Co(N\text{-}Mecyclen)(OH_2)_2]^{3+}$	−106 (400 ± 40[c])	5.28, 8.03

[a] ppm from solvent H_217O signal (MeOH (ref), −35 ppm). [b] Mixture of syn(N), anti(O) and syn(O), anti(N) isomers. [c] Broadness of signal prevents distinction between syn(O) and anti(O) absorptions. [d] Observed values for the two sites at pH 6.9.

Table 2. Rate Data for Loss of ^{17}O from p- and t-$[Co(tren)(NH_3)OH_2/OH]^{3+/2+}$ (I = 1.0 M, $NaCF_3SO_3$, 25 °C)

complex	conditions	k_{obs}/s^{-1} [a]
p	0.40 M CF_3SO_3H	1.16×10^{-5} [b]
	0.20 M CF_3SO_3H	1.09×10^{-5} [b]
	pH 4.63	2.25×10^{-5} [b]
	0.11 M NaOH	1.64×10^{-4} [b]
	0.20 M NaOH	1.64×10^{-4} [c]
	0.35 M NaOH	1.72×10^{-4} [c]
t	0.50 M CF_3SO_3H	8.70×10^{-6} [b]
	0.42 M CF_3SO_3H	1.36×10^{-5} [b]
	0.30 M CF_3SO_3H	1.28×10^{-5} [b]
	0.22 M NaOH	$<5 \times 10^{-6}$ [b,d]
	0.01 M NaOH	$<1 \times 10^{-6}$ [b,d]

[a] The relatively large errors in these values (10−25%) derive both from variation in probe temperature (±0.5 °C) and from significant background "noise" during the limited time available for spectrum. accumulation. [b] Normal H_2O; complex signal monitored. [c] ^{17}O-Depleted H_2O; both complex and solvent signal monitored. [d] p-NH_3 ligand lost (see text).

or peak heights (PH_t, latter method) were used to evaluate exchange rates. Values of k_{obs} were obtained from linear plots of ln(PA_t) or ln($PH_\infty - PH_t$) vs time. For most exchange reactions sufficient complex (0.2−0.5 mmol) was dissolved in the appropriate solvent (2.3 mL) and the solution pH was rapidly adjusted to the required value (microliter additions of ~1 M NaOH or 2 M CF_3SO_3H). Data collection was begun within 2 min. Depending on reaction rate, spectra were acquired at intervals of 15 min (4.5×10^3 transients) to 4 h (7.2×10^4 transients). For pH 5.80 data with $[Co(tren)(^{17}OH_2)_2](CF_3SO_3)_3$, aliquots (0.76 mL) were removed from the bulk solution (5 mL, I = 1.0 M $NaCF_3SO_3$) every 30 s, quenched into NaOH (1.5 mL, 0.50 M), and stored at −18 °C prior to spectrum acquisition (30 min). Normally, ca. 10 spectra were acquired over the course of a run. Errors in the values of the observed rate constants (k_{obs}) ranged from 10% to 25%. They derived principally from broadness in the signals of coordinated OH_2/OH (cf. Table 1) and from the relatively short times available for data acquisition (unfavorable signal-to-noise levels). Values of rate constants for reaction of particular species were calculated from k_{obs} values using $\gamma_\pm = 0.58$ (1.0 M electrolyte)[17] and $K_w = 1.00 \times 10^{-14}$ M^2.

Results

The p- and t-$[Co(tren)(NH_3)(OH_2/OH)]^{3+/2+}$ System. Potentiometric titration (1.0 M $NaCF_3SO_3$, 25.0 °C) using the isolated aqua complexes as their nitrate−perchlorate salts (4 mM) gave $K_a(p) = (1.5 \pm 0.1) \times 10^{-6}$ M, $K_a(t) = (4.7 \pm 0.2) \times 10^{-7}$ M, respectively. Thus, the p-aqua isomer is slightly more acidic (3×) than the t-isomer.

Solvent exchange was followed by ^{17}O NMR spectroscopy (I = 1.0 M ($NaCF_3SO_3$), 25 ± 0.5 °C) using either natural abundance or ^{17}O-depleted solvent. Both complexes showed well-characterized absorptions in both acid and alkaline solution (cf. Table 1), and loss of label from the enriched materials (ca. 0.08−0.10 M) in acid solution gave good first-order plots over at least 2−3 $t_{1/2}$. These corresponded to $k_{H_2O}(p) = (1.1 \pm 0.1) \times 10^{-5}$ s^{-1}, $k_{H_2O}(t) = (1.2 \pm 0.3) \times 10^{-5}$ s^{-1}, Table 2. For loss of label from p-$[Co(tren)(NH_3)^{17}OH]^{2+}$ in alkali it was found preferable to follow the increase in solvent signal intensity, due to broadness of the coordinated OH signal (cf. Table 1). This gave the $[OH^-]$-independent rate constant: $k_{OH}(p) = (1.7 \pm 0.1) \times 10^{-4}$ s^{-1}. Thus the hydroxo form of the p-isomer exchanges some 15 times faster than the aqua form. One measurement at pH 4.63, $k_{obs} = 2.25 \times 10^{-5}$ s^{-1}, agrees well with that calculated (2.1×10^{-5} s^{-1}) using p$K_a(p)$ = 5.82 and the above rate constants. For t-$[Co(tren)(NH_3)^{17}OH]^{2+}$ no measurable loss of label occurred over a 9 h period in 0.22 M NaOH (I = 1.0 M, $NaCF_3SO_3$, 25 °C), but instead the absorption slowly moved downfield from −172 to −162 ppm, suggesting that a slow chemical change was taking place. One of the two absorptions in $[Co(tren)(^{17}OH)_2]^+$ occurs at −162 ppm (cf. Table 1), and UV−vis spectra confirmed that the reaction being followed was indeed the loss of the p-NH_3 ligand, eq 1.

$$t\text{-}[Co(tren)(NH_3)(^{17}OH)]^{2+} + OH^- \xrightarrow{k_{OH}} [Co(tren)(p\text{-}OH)(t\text{-}^{17}OH)]^+ + NH_3 \quad (1)$$

Spectroscopic rate data (430 nm) established the second-order rate law $k_{obs} = k_{OH}[OH^-]$ with $k_{obs}/s^{-1}([OH^-]/M) = 1.26 \times 10^{-4}$ (0.20); 2.80×10^{-5} (0.05); 6.0×10^{-6} (0.01) giving $k_{OH}(p\text{-}NH_3) = (6.0 \pm 0.4) \times 10^{-4}$ M^{-1} s^{-1} at I = 1.0 M $NaCF_3SO_3$ and 25.0 °C. It is important to note that the t-^{17}OH resonance was retained throughout this process in 0.01 M alkali, implying that hydroxo ligand exchange in t-$[Co(tren)(NH_3)OH]^{2+}$ is very slow, $k_{OH}(t) < 1 \times 10^{-6}$ s^{-1}. This is at least 10 times slower than exchange of the aqua ligand in t-$[Co(tren)(NH_3)OH_2]^{3+}$ and more than 100-fold slower than hydroxo exchange in p-$[Co(tren)(NH_3)OH]^{2+}$.

The $[Co(tren)(OH_2/OH)_2]^{3+/2+/+}$ System. Potentiometric titration of an acidic aqueous solution (5 mM) prepared by dissolution of $[Co(tren)(OSO_2CF_3)_2]CF_3SO_3$ in water (1.0 M $NaCF_3SO_3$, 25.0 °C) gave $K_{a1}(obs) = (1.7 \pm 0.1) \times 10^{-6}$ M (pK_{a1}(obs) = 5.77), $K_{a2}(obs) = (8.8 \pm 0.4) \times 10^{-9}$ M (pK_{a2}(obs) = 8.06), where K_{a1}(obs) represents ionization of the first water molecule and K_{a2}(obs) ionization of the second. These values are not too different from those reported previously in 1.0 M $NaClO_4$ (pK_{a1} = 5.80 ± 0.04; pK_{a2} = 8.23 ± 0.03).[19] The p- and t-coordination positions are not distinguished by this type of measurement but are by NMR titration. Figure S1 (Supporting Information) shows ^{17}O spectra for the complex in acidic (A) and alkaline (B) solution, with two signals being evident under both sets of conditions, but being somewhat broader in alkali. The signal at lowest field (a) corresponds closely in chemical shift to that found for p-$[Co(tren)(NH_3)OH_2/OH]^{3+/2+}$, whereas that at highest field (b) corresponds to that for t-$[Co(tren)(NH_3)OH_2/OH]^{3+/2+}$ (cf. Table 1). Titration of $[Co(tren)(^{17}OH_2)_2]^{2+}$ gave the chemical shift data shown in Figure 2. As the pH is raised from 3.3 to 6.9, signal a undergoes a large shift (from −95 to −112 ppm) while signal b moves only slightly (−3 ppm). Increasing the pH beyond 6.9 produces a major shift in the b signal (from −134 to −162 ppm), but the

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signal a position (−112 ppm) remains unchanged. Both major shifts (δ(obs)) can be fitted to an expression of the type

$$\delta(\mathrm{obs}) = (\delta_{\mathrm{HA}}a_{\mathrm{H^+}} + \delta_{\mathrm{A}}K_{\mathrm{a}})/(K_{\mathrm{a}} + a_{\mathrm{H^+}}) \qquad (2)$$

where K_a, δ_{HA}, and δ_A respectively represent the ionization constant and the chemical shift values of the conjugate acid and base forms of the complex in the two situations (i.e., diaqua to aqua−hydroxo ionization and aqua−hydroxo to dihydroxo ionization). Using the δ_{HA}, δ_A data of Table 1 gives $K_{a1} = 2.8 \times 10^{-6}$ M (pK_{a1} = 5.6), $K_{a2} = 8.09 \times 10^{-9}$ M (pK_{a2} = 8.1). These values are in good agreement with those obtained by the more accurate potentiometric method, but more importantly they assign K_{a1} mainly to ionization of the *p*-site water molecules, and K_{a2} mainly to ionization of the *t*-site water molecules. The small shift in the b signal during the first ionization (Figure 2) can be attributed to some concomitant ionization at the *t*-site (i.e., to the presence of some $[\mathrm{Co(tren)}(p\text{-}\mathrm{OH_2})(t\text{-}\mathrm{OH})]^{2+}$). Taking into account this overlap in ionization constants, and using the relative acidities of *p*- and *t*-$[\mathrm{Co(tren)(NH_3)OH_2}]^{3+}$ as a guide ($K_a(p)/K_a(t)$ = 3.2), gives p$K_{a1}(p)$ = 5.89, p$K_{a1}(t)$ = 6.40, and p$K_{a2}(p)$ = 8.17, p$K_{a2}(t)$ = 8.68 for the separate site acidities. It appeared to us that this was the best type of approach when making these assignments, but an exact parallel in behavior between the $[\mathrm{Co(tren)(OH_2)OH/H}]^{3+/2+}$ and $[\mathrm{Co(tren)(NH_3)OH/H}]^{3+/2+}$ ions is not guaranteed. The above values were used when rates of exchange were calculated for particular coordination positions (cf. below).

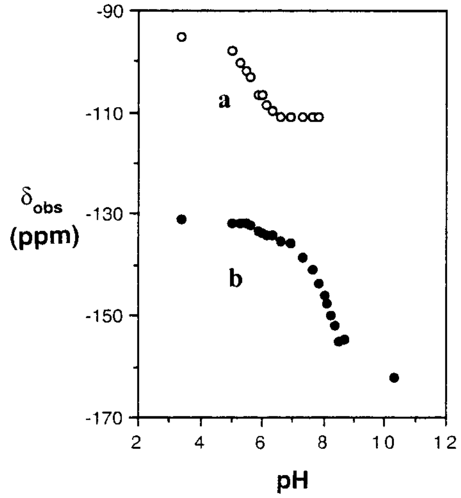

Figure 2. Plot of ^{17}O chemical shifts (signals a and b, see text) vs pH for the resonances of $[\mathrm{Co(tren)(OH_2/OH)_2}]^{3+/2+/+}$ (0.10 M in ca. 30% $\mathrm{H_2{}^{17}O}$, I = 1.0 M, $\mathrm{NaCF_3SO_3}$).

Solvent exchange was followed by ^{17}O NMR using labeled complexes and with decay of the a and b absorptions (Figure 3) being used to follow exchange at the *p*- and *t*-sites, respectively. Good first-order plots were again obtained over 2−3 $t_{1/2}$ using normal $\mathrm{H_2O}$ as solvent (1.0 M $\mathrm{NaCF_3SO_3}$, 25 °C) with the a signal decaying faster than the b signal under all conditions (cf. Figure 3 for exchange in 0.30 M $\mathrm{CF_3SO_3H}$). The data (Table 3) clearly show a pH-independent exchange in acid ($k_{\mathrm{H_2O}}(p) = 3.7 \times 10^{-5}\ \mathrm{s^{-1}}$; $k_{\mathrm{H_2O}}(t) = 8.7 \times 10^{-6}\ \mathrm{s^{-1}}$) and alkali ($k_{\mathrm{OH}}(p) = 9.7 \times 10^{-5}\ \mathrm{s^{-1}}$; $k_{\mathrm{OH}}(t) = 2.2 \times 10^{-7}\ \mathrm{s^{-1}}$), with *p*-exchange being some 4-fold faster than *t*-exchange in acid, and almost 500-fold faster in alkali. These differences will be discussed below. At intermediate pH the much faster observed exchange can be attributed to that occurring in $[\mathrm{Co(tren)(OH_2)OH}]^{2+}$ (approximately 75% (*p*-OH)(*t*-OH$_2$), 25% (*p*-OH$_2$)(*t*-OH)), and two approaches were adopted when these data were analyzed. If exchange of coordinated OH$_2$ is always preferred over exchange of coordinated OH$^-$ (eq 3), then first-order rate constants calculated on this basis[20] indicate that *p*-OH$_2$ exchange is some 5-fold faster than *t*-OH$_2$ exchange. On the other hand, if both exchanges occur in the more dominant $[\mathrm{Co(tren)}(p\text{-}\mathrm{OH})(t\text{-}\mathrm{OH_2})]^{2+}$ isomer (i.e., *p*-OH exchange is preferred over *p*-OH$_2$ exchange), then eq 4 follows.[21] Again, if this mechanism holds, then exchange occurs more rapidly at the *p*-site than at the *t*-site.

$$\begin{tikzcd}
{[\mathrm{Co(tren)}(p\text{-}^{17}\mathrm{OH_2})(t\text{-}^{17}\mathrm{OH})]^{2+}} \arrow[r, "k_2(p)", "= 0.05\ \mathrm{s^{-1}}"'] \arrow[d, shift left] & {[\mathrm{Co(tren)}(p\text{-}\mathrm{OH_2})(t\text{-}^{17}\mathrm{OH})]^{2+}} \\
{[\mathrm{Co(tren)}(p\text{-}^{17}\mathrm{OH})(t\text{-}^{17}\mathrm{OH_2})]^{2+}} \arrow[u, shift left, "K = 3.2"] \arrow[r, "k_2(t)", "= 0.01\ \mathrm{s^{-1}}"'] & {[\mathrm{Co(tren)}(p\text{-}^{17}\mathrm{OH})(t\text{-}\mathrm{OH_2})]^{2+}}
\end{tikzcd} \qquad (3)$$

$$\begin{tikzcd}
 & {[\mathrm{Co(tren)}(p\text{-}\mathrm{OH})(t\text{-}^{17}\mathrm{OH_2})]^{2+}} \\
{[\mathrm{Co(tren)}(p\text{-}^{17}\mathrm{OH})(t\text{-}^{17}\mathrm{OH_2})]^{2+}} \arrow[ur, "k_2(p) = 0.03\ \mathrm{s^{-1}}"'] \arrow[dr, "k_2(t) = 0.01\ \mathrm{s^{-1}}"] & \\
 & {[\mathrm{Co(tren)}(p\text{-}^{17}\mathrm{OH})(t\text{-}\mathrm{OH_2})]^{2+}}
\end{tikzcd} \qquad (4)$$

The $[\mathrm{Co(cyclen)(OH_2/OH)_2}]^{3+/2+/+}$ and $[\mathrm{Co(N\text{-}Mecyclen)(OH_2/OH)_2}]^{3+/2+/+}$ Systems. UV−vis spectra for the isolated complexes in acid (pH < 4), neutral (pH ∼ 7), and alkaline (pH ∼ 10) solutions gave the absorption maxima and extinctions listed in Table S1 (Supporting Information) for I = 1.0 M, $\mathrm{NaClO_4}$, 25 °C. As with all such diaqua complexes, successive ionizations result in red shifts and lower extinctions in the visible. Potentiometric titrations gave $K_{a1} = (1.51 \pm 0.07) \times 10^{-6}$ M (pK_{a1} = 5.82), $K_{a2} = (6.3 \pm 0.6) \times 10^{-9}$ M (pK_{a2} = 8.20) and $K_{a1} = (5.25 \pm 0.3) \times 10^{-6}$ M (pK_{a1} = 5.28), $K_{a2} = (9.3 \pm 0.6) \times 10^{-9}$ M (pK_{a2} = 8.03) for the two complexes, respectively (cf. Table 1). Thus N-methylation at the apical position[22] results in slightly more acidic water molecules. The broadness of the ^{17}O resonances in acidic solution (cf. Table 1) did not allow distinction of the two water molecules, one of which will almost certainly be cis to *syn*-N*H* and the other cis to *anti*-N*H*.[23] The above pK_a values are in good agreement with those given for a cyclen complex of less certain origin in 0.1 M $\mathrm{NaClO_4}$, pK_{a1} = 5.6, pK_{a2} = 8.0.[24]

^{17}O-Exchange kinetics for the labeled complexes (1.0 M $\mathrm{NaClO_4}$, 25.0 °C) gave excellent linear first-order traces over at least 2 $t_{1/2}$ under acidic conditions, and the k_{obs} data are plotted vs $[\mathrm{H^+}]^{-1}$ in Figure 4. Again, the water molecules cis *to* the

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(20) Calculated by fitting data to the expressions $k_{\mathrm{obs}}(p) = (k_1(p)a_{\mathrm{H^+}}{}^2 + k_2(p)K_{a1}(t)a_{\mathrm{H^+}} + k_3(p)K_{a1}(t)K_{a2}(p))/(a_{\mathrm{H^+}}{}^2 + a_{\mathrm{H^+}}K_{a1}(t)(1 + 1/K) + K_{a1}(t)K_{a2}(p))$; $k_{\mathrm{obs}}(t) = (k_1(t)a_{\mathrm{H^+}}{}^2 + k_2(t)K_{a1}(p)a_{\mathrm{H^+}} + k_3(p)K_{a1}(p)K_{a2}(t))/(a_{\mathrm{H^+}}{}^2 + a_{\mathrm{H^+}}K_{a1}(p)(1 + 1/K) + K_{a1}(p)K_{a2}(t))$ using K = 3.2, K_a values given in Table 1, and $k_1(p) = 3.7 \times 10^{-5}\ \mathrm{s^{-1}}$, $k_3(p) = 9.7 \times 10^{-5}\ \mathrm{s^{-1}}$, $k_1(t) = 8.7 \times 10^{-6}\ \mathrm{s^{-1}}$, and $k_3(t) = 2.2 \times 10^{-7}\ \mathrm{s^{-1}}$.

(21) Calculated by fitting data to the expressions $k_{\mathrm{obs}}(p) = (k_1(p)a_{\mathrm{H^+}}{}^2 + k_2(p)K_{a1}(p)a_{\mathrm{H^+}} + k_3(p)K_{a1}(p)K_{a2}(t))/(a_{\mathrm{H^+}}{}^2 + K_{a1}(p)(1 + 1/K) + K_{a1}(p)K_{a2}(t))$, using K = 3.2, K_a values given in Table 1, $k_1(p) = 3.7 \times 10^{-5}\ \mathrm{s^{-1}}$, and $k_3(p) = 9.7 \times 10^{-5}\ \mathrm{s^{-1}}$; $k_{\mathrm{obs}}(t)$ calculated as given in ref 20.

(22) Buckingham, D. A.; Clark, C. R.; Rogers, A. J.; Simpson, J. *Inorg. Chem.* **1995**, *34*, 3646.

(23) Buckingham, D. A.; Clark, C. R.; Rogers, A. J. *Inorg. Chim. Acta* **1995**, *240*, 125.

(24) Chin, J.; Banaszezyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186.

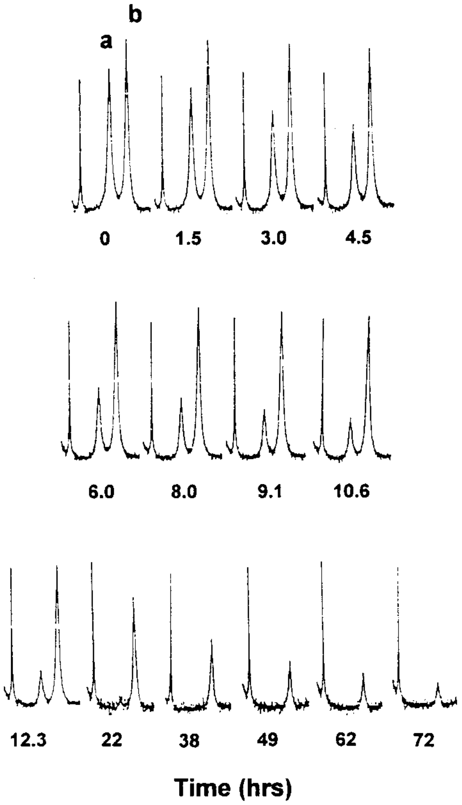

Figure 3. ^{17}O NMR spectra showing loss of label from [Co(tren)(^{17}OH$_2$)$_2$]$^{3+}$ (signals a and b) into 0.30 M CF$_2$SO$_3$H, $I = 1.0$ M, NaCF$_3$SO$_3$, 25 °C. MeOH (external reference, $\delta = -35$ ppm) signal at left.

Table 3. Observed and Calculated Rate Constants[a] for Loss of ^{17}O from [Co(tren)(^{17}OH$_2$/^{17}OH)$_2$]$^{3+/2+/+}$ Species ($I = 1.0$ M NaCF$_3$SO$_3$, 25 °C; Normal H$_2$O Solvent)

	p-exchange			*t*-exchange	
condition	10^5k_{obs}	10^5k_{calc}[b]	10^5k_{calc}[c]	10^6k_{obs}	10^6k_{calc}[c]
0.50 M CF$_3$SO$_3$H	3.8				
0.40 M CF$_3$SO$_3$H				8.6	
0.30 M CF$_3$SO$_3$H	3.6			8.8	
0.20 M CF$_3$SO$_3$H	3.8				
pH 3.24	13	7	10	25	23
pH 3.50	18	10	16	40	50
pH 3.72	42	14	24	89	89
pH 5.80	>1100	950	1200	3900	3900
pH 10.50	36	310	44	45	150
0.10 M NaOH	9.70, 9.64			0.22	

[a] Units, s^{-1}. [b] Calculated values for *p*-exchange in [Co(tren)(*p*-^{17}OH$_2$)(*t*-^{17}OH)]$^{2+}$ using pK_a values given in Table 1, and $k_2(p) = 0.05$ s^{-1}. [c] Calculated values for *p*- and *t*-exchange in [Co(tren)(*p*-^{17}OH)(*t*-^{17}OH$_2$)]$^{2+}$ using pK_a values given in Table 1, and $k_2(t) = 0.01$ s, $k_2(p) = 0.03$ s^{-1}.

syn- and *anti*-N*H* sites could not be distinguished, probably because of interconversion via the water exchange process (vide infra).[25] The plotted data (Figure 4) have slopes of 1.6×10^{-5} M s^{-1} (cyclen complex) and 6.6×10^{-5} M s^{-1} (N-Mecyclen complex) and indistinguishable intercepts, 1.0×10^{-4} s^{-1}, the latter giving $k_{H_2O} = 2 \times 10^{-4}$ s^{-1} (per H$_2$O molecule). The slopes may be related either to spontaneous (i.e., uncatalyzed) exchange in the hydroxo−aqua complexes giving $k' = 2$ slope $\gamma_{\pm}/K_{a1} = 12$ and 15 s^{-1}, respectively (slope $= 1.6 \times 10^{-5}$ M s^{-1}, cyclen; 6.6×10^{-5} M s^{-1}, N-Mecyclen), or to OH$^-$-catalyzed exchange in the diaqua ions giving $k_{OH} = 2$ slope $\gamma_{\pm}2/K_w = 1.1 \times 10^9$ and 4.6×10^9 M^{-1} s^{-1}, respectively (the factor of 2 is again a statistical correction assuming equivalence of the two water molecules). The merits of these two interpretations will be discussed below.

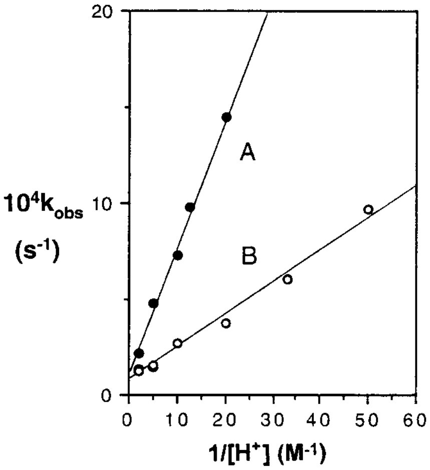

Figure 4. Plot of k_{obs} vs [H$^+$]$^{-1}$ for ^{17}O exchange in [Co(N-Mecyclen)(^{17}OH$_2$)$_2$]$^{3+}$ (A, closed circles) and [Co(cyclen)(^{17}OH$_2$)$_2$]$^{3+}$ (B, open circles); 25 °C.

Discussion

The spontaneous (uncatalyzed) loss of H$_2$O is usually slow (25 °C, hours) for all Co(III)−amine complexes, whereas OH$^-$-catalyzed exchange, in appearance apparently involving the loss of coordinated OH$^-$, is highly variable in rate and often dominates well into the acidic region. The rate at which this reaction occurs seems to depend both on the location of the OH$^-$ ligand and on amine stereochemistry. Available data for water exchange in Co(III) systems are listed in Table 4.

In the earliest study on aqua systems, Hunt and Taube report a value of 6×10^{-6} s^{-1} ($t_{1/2} \sim 32$ h, 25 °C) for exchange in [Co(NH$_3$)$_5$OH$_2$]$^{3+}$,[25] and Kruse and Taube found not too different values for exchange in *cis*- and *trans*-[Co(en)$_2$(OH$_2$)$_2$]$^{3+}$ (7.5×10^{-6} s^{-1}, 1.1×10^{-5} s^{-1}, 25 °C, 0.8 M HClO$_4$).[26] There appears to be little difference whether one or two H$_2$O molecules are present, or whether the *p*- or *t*-sites are involved for exchange in the tren complexes (i.e., *p*- and *t*-[Co(tren)(NH$_3$)OH$_2$]$^{3+}$, [Co(tren)(OH$_2$)$_2$]$^{3+}$, $k_{H_2O} = (1-4) \times 10^{-5}$ s^{-1}). Exchange in the cyclen/N-Mecyclen complexes is somewhat faster ($k_{H_2O} \approx 2 \times 10^{-4}$ s^{-1}), as it is for [Co(NH$_2$CH$_3$)$_5$OH$_2$]$^{3+}$ (Table 4), but the overall inference is that saturated amine systems will all exhibit slow, uncatalyzed exchange rates for coordinated H$_2$O (with half-lives of hours). Unsaturation, such as in the planar ring system of vitamin-B$_{12}$,[9] seems necessary in order to produce significantly faster rates of uncatalyzed exchange, and this is possibly due to the greater availability of electrons on the coordinated N-centers (cf. S$_N$1(CB) mechanism, below).

The loss of coordinated OH$^-$ provides much more interesting data. For example, OH$^-$ exchange in *p*-[Co(tren)(NH$_3$)OH]$^{2+}$ is some 100 times faster than that in *t*-[Co(tren)(NH$_3$)OH]$^{2+}$ (1.7×10^{-4} s^{-1} vs 1×10^{-6} s^{-1}) even though the former is somewhat less basic (pK_a = 5.82, 6.33 respectively). On the basis of ligand field strengths, OH$^-$ loss would be expected to be much slower than H$_2$O loss, and previous work on purely metal−aqua systems attributes faster exchange in M(OH$_2$)$_5$OH^{2+} compared to M(OH$_2$)$_6$$^{3+}$ (M = Ga, Fe, Cr, Ru, Rh) to the stronger electron-donating property of OH$^-$ weakening M−OH$_2$ bonds.[27] Certainly *t*-OH loss in *t*-[Co(tren)(NH$_3$)OH]$^{2+}$ and [Co(tren)(OH)$_2$]$^+$ is slower than *t*-OH$_2$ loss in their acid

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(25) Hunt, J. P.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.

(26) Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280.

Table 4. First-Order Rate Constants for Solvent Exchange in Some Co(III)−Aqua/Hydroxo Complexes[a]

complex	k/s^{-1} (25 °C)	ref
Monaqua Systems		
$[\mathrm{Co(NH_3)_5OH_2}]^{3+}$	6×10^{-6}	25
$[\mathrm{Co(NH_2CH_3)_5OH_2}]^{3+}$	7×10^{-4}	*b*
cis-$[\mathrm{Co(en)_2(NH_3)OH_2}]^{3+}$	1.1×10^{-6}	*c*
p-$[\mathrm{Co(tren)(NH_3)OH_2}]^{3+}$	1.1×10^{-5}	*d*
t-$[\mathrm{Co(tren)(NH_3)OH_2}]^{3+}$	1.2×10^{-5}	*d*
$[\mathrm{Co(cyclen)(NH_3)OH_2}]^{3+}$	$<1 \times 10^{-4}$	29
Diaqua Systems		
cis-$[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$	7.5×10^{-6}	26, *e*
trans-$[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$	1.1×10^{-5}	26
$[\mathrm{Co(tren)(OH_2)_2}]^{3+}$	3.7×10^{-5} (*p*), 8.7×10^{-6} (*t*)	*d*
$[\mathrm{Co(cyclen)(OH_2)_2}]^{3+}$	2×10^{-4}	*d*
$[\mathrm{Co(N\text{-}Mecyclen)(OH_2)_2}]^{3+}$	2×10^{-4}	*d*
Monohydroxo Systems		
$[\mathrm{Co(NH_3)_5OH}]^{2+}$	$<1.4 \times 10^{-7}$	25
p-$[\mathrm{Co(tren)(NH_3)OH}]^{2+}$	1.7×10^{-4}	*d*
t-$[\mathrm{Co(tren)(NH_3)OH}]^{2+}$	$<1 \times 10^{-6}$	*d*
$[\mathrm{Co(cyclen)(NH_3)OH}]^{2+}$	8	29
Dihydroxo Systems		
cis-$[\mathrm{Co(en)_2(OH)_2}]^{+}$	3.0×10^{-5}	26
trans-$[\mathrm{Co(en)_2(OH)_2}]^{+}$	2.3×10^{-6}	26
$[\mathrm{Co(tren)(OH)_2}]^{+}$	9.7×10^{-5} (*p*), 2.2×10^{-7} (*t*)	*d*
Aqua−Hydroxo Systems		
cis-$[\mathrm{Co(en)_2(OH_2)OH}]^{2+}$	9.3×10^{-4}	26
trans-$[\mathrm{Co(en)_2(OH_2)OH}]^{2+}$	1.2×10^{-3}	26
$[\mathrm{Co(tren)}(p\text{-}\mathrm{OH_2})t\text{-}\mathrm{OH}]^{2+}$	0.05 (p)	*d*
$[\mathrm{Co(tren)}(t\text{-}\mathrm{OH_2})p\text{-}\mathrm{OH}]^{2+}$	0.03 (*p*), 0.01 (*t*)	*d*
$[\mathrm{Co(cyclen)(OH_2)OH}]^{2+}$	12	*d*
$[\mathrm{Co(N\text{-}Mecyclen)(OH_2)OH}]^{2+}$	15	*d*

[a] Most rate constants refer to $I = 1.0$ M. [b] González, G.; Moullet, B.; Martinez, M.; Merbach, A. E. *Inorg. Chem.* **1994**, *33*, 2330. [c] Martin, D. F.; Tobe, M. L. *J. Am. Chem. Soc.* **1962**, *84*, 1388. [d] This work. [e] Aygen, S.; Hanssam, H.; van Eldik, R. *Inorg. Chem.* **1985**, *24*, 2853.

Table 5. k_{OH} Values (M^{-1} s^{-1}, 25 °C) for Base Hydrolysis in some *p*- and *t*-$[\mathrm{Co(tren)(NH_3)X}]^{3+/2+\,a}$ and Some $[\mathrm{Co(cyclen)(A)X}]^{3+/2+\,b}$ Systems

X	*p*-$[\mathrm{Co(tren)(NH_3)X}]^{3+/2+}$ loss of X	*t*-$[\mathrm{Co(tren)(NH_3)X}]^{3+/2+}$ loss of *t*-X	loss of *p*-$\mathrm{NH_3}$
$\mathrm{OH_2}$ ($\mathrm{OH^-}$)	$1.5 \times 10^{4\,c}$ (1.7×10^{-4} s^{-1})	$<27^c$ ($<1 \times 10^{-6}$ s^{-1})	(6×10^{-4})
$\mathrm{NH_3}$	5.4×10^{-2}		5.4×10^{-2}
$\mathrm{Cl^-}$	4×10^{2}	2×10^{-2}	
$\mathrm{SCN^-}$	1.1×10^{4}	2.1×10^{-2}	
$\mathrm{NCS^-}$	3.4×10^{-2}		2.5×10^{-3}
$\mathrm{N_3}$-	0.44		1.2×10^{-3}
$\mathrm{Br^-}$		0.24	
$\mathrm{NO_3}$-		0.24	
$\mathrm{Me_2SO}$		3.7	
$\mathrm{MeSO_3}$-		10.0	

$[\mathrm{Co(cyclen)(A)X}]^{3+/2+}$ (Loss of X)

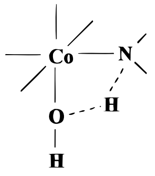
A	X	k_{OH}
$\mathrm{NH_3}$	$\mathrm{NH_3}$	2×10^{4}
$\mathrm{NH_3}$	$\mathrm{OH_2}$	4.5×10^{8}
$\mathrm{NH_3}$	OH	4×10^{4}
$\mathrm{NH_3}$	Cl	4×10^{6} (syn), 3×10^{5} (anti)
$\mathrm{NH_3}$	$\mathrm{N_3}$	4×10^{4}
OH	$\mathrm{NH_3}$	1.0
$\mathrm{OH_2}$	$\mathrm{OH_2}$	1.1×10^{9}
Cl	Cl	2×10^{7}

[a] Data from this work, refs 12 and 13, and Buckingham et al.: Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041. [b] Data from this work and ref 29. [c] Calculated from spontaneous rate for X = OH$^-$ complex; $k_{\mathrm{OH}} = kK_a\gamma_\pm/K_w$ using $\gamma_\pm = 0.58$, $K_w = 1.0 \times 10^{-14}$ M^2.

conjugates, as is OH$^-$ loss in $[\mathrm{Co(NH_3)_5OH}]^{2+}$. Hunt and Taube[25] made the interesting suggestion that ligand−OH$^-$ exchange could result from an indirect process involving amine deprotonation and loss of $\mathrm{H_2O}$, viz., eq 5, that is via an S_N1-

$$[\mathrm{Co(amine)OH}]^{2+} \overset{K}{\rightleftharpoons} [\mathrm{Co(amine\text{-}H)OH_2}]^{2+} \xrightarrow{k'_{\mathrm{OH}}} \text{exchange} \tag{5}$$

(CB) process on the aqua complex, and this allows for the rate of OH$^-$ exchange to exceed that of $\mathrm{H_2O}$ exchange depending on the values of K and k'_{OH}. The unusually rapid substitution reactions of the $[\mathrm{Co(dien)(dapo)OH}]^{2+}$ ion have similarly been interpreted as involving deprotonation at the dien *sec*-N*H* site in the conjugate acid, followed by water exchange in the resulting aqua−amido intermediate.[28] Also, in the *p*-$[\mathrm{Co(tren)(NH_3)OH/H}]^{2+/3+}$ system coordinated OH$^-$ exchanges faster than coordinated $\mathrm{OH_2}$ (15-fold; cf. Table 4), and a similar case can be made for $[\mathrm{Co(tren)}(t\text{-}\mathrm{OH_2})(p\text{-}\mathrm{OH/H})]^{2+/3+}$ (vide infra), so that the Hunt and Taube suggestion has considerable merit. It takes on even greater weight when exchange in the cyclen/N-Mecyclen systems is considered. Here, compared to the slow replacement of $\mathrm{H_2O}$ ($k_{\mathrm{H_2O}} = (1-2) \times 10^{-4}$ s^{-1}), loss of OH$^-$ is extremely rapid, 8 s^{-1} for $[\mathrm{Co(cyclen)(NH_3)OH}]^{2+}$, 12 s^{-1} for $[\mathrm{Co(cyclen)(OH_2)OH}]^{2+}$, and 15 s^{-1} for $[\mathrm{Co(N\text{-}Mecyclen)(OH_2)OH}]^{2+}$. If reaction occurs via OH$^-$-catalyzed exchange in the aqua complexes, the conventional second-order rate constant (k_{OH}) takes on values of 4.5×10^8 M^{-1} s^{-1}, 1.1×10^9 M^{-1} s^{-1}, and 4.6×10^9 M^{-1} s^{-1}, respectively. Such values are very large indeed. Similar calculations lead to values of 27 M^{-1} s^{-1} and 1.5×10^4 M^{-1} s^{-1} for OH$^-$-catalyzed exchange in the *t*- and *p*-$[\mathrm{Co(tren)(NH_3)OH_2}]^{3+}$ complexes. These are compared with other base hydrolysis rate constants in Table 5 where amine deprotonation is involved.[7] The surprising, and difficult to reconcile, comparison here is the enhanced rate for loss of $\mathrm{H_2O}$ compared to $\mathrm{NH_3}$ (or Cl$^-$), and we suggest that instead of the sequence of protonation (of coordinated OH), deprotonation (of amine), and loss of $\mathrm{OH_2}$ in the mechanism of Hunt and Taube[25] (i.e., eq 7), intramolecular partial transfer of a proton takes place in the transition state for cleavage of the Co−OH bond. This avoids the higher energy required for stepwise proton transfer (K values for eq 5 are generally of the order of 10^{-8}−10^{-9}) and provides a more reasonable explanation for the wide variation in k_{OH} values. This type of mechanism would seem to require an adjacent *syn*-N*H* proton, and as discussed elsewhere[29] this is readily available in the cyclen/N-Mecyclen systems by way of a reasonably acidic meridional *sec*-NH residue. Such proton transfer may occur directly (cf. **1**) or via participation of an intervening water molecule. The



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present results suggest that the mechanism is less available in the *p*-tren(OH) systems, and less again (or not available) in the *t*-$[Co(tren)(NH_3)OH]^{2+}$, $[Co(NH_3)_5OH]^{2+}$, and [Co(tren)(*p*-OH_2)(*t*-OH)]$^{2+}$ (*t*-OH exchange) systems. This is presumably related to both diminished N*H* acidity and stereochemical availability. With $[Co(tren)(OH_2)OH]^{2+}$ the data best fit both *p*- and *t*-exchanges occurring in the more dominant [Co(tren)(*p*-OH)(*t*-OH_2)]$^{2+}$ isomer (Table 3), eq 4, and this supports the above mechanism for exchange of the *p*-OH ligand, but a more conventional route[27] for exchange of the *t*-OH_2 ligand. The respective rate constants 0.03 s^{-1} ($k_2(p)$) and 0.01 s^{-1} ($k_2(t)$) imply that the two pathways are of near equal efficiency for this complex.

Supporting Information Available: Figure S1 showing ^{17}O spectra for labeled $[Co(tren)(OH_2)_2]^{3+}$ and $[Co(tren)(OH)_2]^{+}$ in normal H_2O and Table S1 giving spectroscopic constants for the $[Co(cyclen)(OH_2/OH)_2]^{3+/2+/+}$ and $[Co(N\text{-}Mecyclen)(OH_2/OH)_2]^{3+/2+/+}$ ions (2 pages). Ordering information is given on any current masthead page.

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