

^{17}O NMR Study of Solvent Exchange in Some Aqueous $[\text{Co}(\text{tren})(\text{X})(\text{OH}_2/\text{OH})]^{n+}$, $[\text{Co}(\text{cyclen})(\text{X})(\text{OH}_2/\text{OH})]^{n+}$, and $[\text{Co}(\text{N-Mecyclen})(\text{X})(\text{OH}_2/\text{OH})]^{n+}$ Systems ($\text{X} = \text{NH}_3$, OH_2/OH ; $n = 3, 2, 1$)¹

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A ^{17}O NMR study ($I = 1.0 \text{ M}$, NaClO_4 or $\text{NaOSO}_2\text{CF}_3$, $25.0 \text{ }^\circ\text{C}$) of solvent exchange in labeled p - and t - $[\text{Co}(\text{tren})(\text{NH}_3)\text{OH}_2]^{3+}$, $[\text{Co}(\text{tren})(\text{OH}_2)_2]^{3+}$, $[\text{Co}(\text{cyclen})(\text{OH}_2)_2]^{3+}$, and $[\text{Co}(\text{N-Mecyclen})(\text{OH}_2)_2]^{3+}$ ions (ca. 30% ^{17}O) in aqueous solution has shown that loss of coordinated OH_2 is slow for all of the complexes ($k_{\text{ex}}/\text{s}^{-1} = 1.1 \times 10^{-5}$, 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 $[\text{Co}(\text{tren})(\text{OH}_2)_2]^{3+}$ have been determined as $9.7 \times 10^{-5} \text{ s}^{-1}$ (p -site) and $2.2 \times 10^{-7} \text{ s}^{-1}$ (t -site). Coordinated OH^- in both p - and t - $[\text{Co}(\text{tren})(\text{NH}_3)\text{OH}]^{2+}$ also exchanges only slowly with solvent ($k_{\text{ex}}/\text{s}^{-1} = 1.7 \times 10^{-4}$, and $< 1 \times 10^{-6}$, respectively), whereas exchange of coordinated solvent in the aqua-hydroxo complexes $[\text{Co}(\text{tren})(t\text{-OH}_2)(p\text{-OH})]^{2+}$, $[\text{Co}(\text{cyclen})(\text{OH}_2)\text{OH}]^{2+}$, and $[\text{Co}(\text{N-Mecyclen})(\text{OH}_2)\text{OH}]^{2+}$ is much more rapid ($k_{\text{ex}}/\text{s}^{-1} = 0.03$ (p -site)/ 0.01 (t -site), 12 and 15, respectively). Ligand- OH^- exchange in these latter systems is interpreted as occurring via (indirect) $\text{S}_{\text{N}}1(\text{CB})$ -type processes on the corresponding aqua complexes: $[\text{Co}(\text{amine})\text{OH}]^{2+} \rightleftharpoons [\text{Co}(\text{amine-H})\text{OH}_2]^{2+} \rightarrow \text{exchange}$. 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 NH 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 $\text{Co}(\text{III})$ 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-cobalamin⁹ and its $\text{Co}(\text{III})$ mimics,¹⁰ and in the cyclen and tren $\text{Co}(\text{III})$ 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 $\text{Co}(\text{III})$ 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 $\text{Co}(\text{III})$ -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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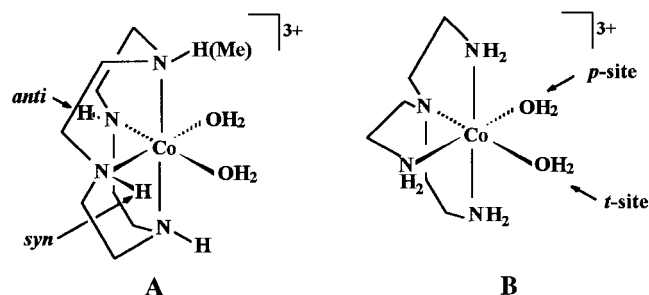


Figure 1. Representations designating (A) the syn- and anti *sec*-NH protons in $[\text{Co}(\text{cyclen})(\text{OH}_2)_2]^{3+}$ and $[\text{Co}(\text{N-Mecyclen})(\text{OH}_2)_2]^{3+}$ and (B) the *p*- and *t*-sites in $[\text{Co}(\text{tren})(\text{OH}_2)_2]^{3+}$.

± 0.5 °C) probe and external 5 mm CD₃OD lock and reference (δ ¹⁷O –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 μ s, SW = 10⁵ 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 N₂. ¹⁷O-Enriched (~30 atom % ¹⁷O) and depleted (~0.007 atom % ¹⁷O) 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)(NH₃OH₂)(NO₃)₂ClO₄] were prepared from *p*- and *t*-[Co(tren)(NH₃Cl)(ClO₄)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)(NH₃OH₂)(CF₃SO₃)₃].** A solution of *p*-[Co(tren)(NH₃-Cl)(ClO₄)Cl]¹³ (0.84 g, 2.6 mmol) in aqueous Hg(CF₃SO₃)₂/CF₃SO₃H (5.0 mL, 0.74 M Hg²⁺ (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 HgCl₂) and the filter washed with a little MeOH. Solid NaCF₃SO₃ (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 H₂O (2 mL), and additional NaCF₃SO₃ (0.5 g) and *i*-PrOH (2 mL) were added, whereupon additional HgCl₂ 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)(NH₃-Cl)]²⁺ as demonstrated by RP-HPLC.¹⁴

***p*-[Co(tren)(NH₃)(OSO₂CF₃)](CF₃SO₃)₂.** This mauve-colored complex was prepared by heating (100 °C) the above complex under vacuum (120 Pa) for 3 days.

***p*-[Co(tren)(NH₃)(¹⁷OH₂)](CF₃SO₃)₃.** Freshly prepared *p*-[Co(tren)(NH₃)(OSO₂CF₃)](CF₃SO₃)₂ (~0.3 g) was dissolved in ~30% H₂¹⁷O (~2 mL) by warming, and the solvent was then removed by freeze-drying under vacuum (120 Pa, with recovery of residual H₂¹⁷O). The recovered solid was stored in an airtight container.

***t*-[Co(tren)(NH₃)(OSO₂CF₃)](CF₃SO₃)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)(NH₃Cl)(ClO₄)Cl]¹³ (0.93 g, 2.8 mmol) suspended in cold (–15 °C, ice–salt bath) CF₃SO₃H (4.6 mL) contained in a centrifuge tube was added dropwise a cream suspension of Hg(CF₃SO₃)₂ in CF₃SO₃H (prepared by

dissolving 0.3 g of yellow HgO in 6 mL of CF₃SO₃H by stirring and warming (50 °C) overnight). The transfer of Hg²⁺ was completed by using a further 2 mL of CF₃SO₃H. 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)(NH₃)(¹⁷OH₂)](CF₃SO₃)₃.** This was prepared (0.3 g) as above for the *p*-isomer.

[Co(tren)(OSO₂CF₃)₂](CF₃SO₃)₃. [Co(tren)Cl₂]Cl¹³ (1.0 g, 3.2 mmol) was dissolved in fresh concentrated CF₃SO₃H (7.5 mL) with the evolved HCl gas being removed using a stream of dry N₂. 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)(¹⁷OH₂)](CF₃SO₃)₃. This complex was prepared by adding the above complex (0.3 g) to ~30% H₂¹⁷O (2 mL) at ambient temperature, and excess solvent was removed by freeze-drying (120 Pa).

[Co(cyclen)(OH₂)₂](ClO₄)₃. To a slurry of [Co(cyclen)O₂CO]ClO₄·H₂O¹⁵ (3 g) in water (5 mL) was added 2 molar equiv of 1 M HClO₄ (14.7 mL), and the solution was stirred for 1.5 h at 40 °C under a stream of N₂ 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 P₂O₅. (This complex could be readily crystallized from aqueous solution as its bis perchlorate nitrate salt¹⁶ but for our purpose we wished coordinating anions such as NO₃[–] 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-Mecyclen)(OH₂)₂](ClO₄)₃. To a slurry of [Co(N-Mecyclen)-O₂CO]ClO₄·2H₂O¹⁵ (2 g) in water (5 cm³) was added 2 molar equiv of HClO₄ (1 M, 9.1 cm³), and the mixture was left for 1 h at ambient temperature under a stream of N₂. 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.

¹⁷O-Labeled Cyclen/Mecyclen Complexes. The above freshly prepared diqua complexes (1–2 g) were dissolved in ~30% H₂¹⁷O (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 P₂O₅.

Acidity Constant (*K*_a) Determinations. Values of *K*_a are given as mixed constants, i.e., $K_a = a_{\text{H}^+}[\text{A}^-]/[\text{HA}]$; $[\text{H}^+] = a_{\text{H}^+}/\gamma_{\pm}$, $\gamma_{\pm} = 0.58$ (1.0 M NaClO₄).¹⁷ Potentiometric titration data were obtained as follows: 20.00 mL of a stock solution of the appropriate isolated aqua or triflate complex (3–5 mM, in *I* = 1.0 M electrolyte; NaCF₃SO₃ for tren complexes, NaClO₄ 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 ¹⁷O NMR titration data were obtained as follows. To a solution of [Co(tren)(OSO₂CF₃)₂](CF₃SO₃) (150 mg) in 2.3 mL of 30% H₂¹⁷O (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 ¹⁷O NMR spectrum recorded.

Rates of ¹⁷O Exchange. When “normal” H₂O solvent was used (0.037 atom % ¹⁷O; *I* = 1.0 M in NaCF₃SO₃ or NaClO₄; 25.0 °C), the decay of the ¹⁷O signal for the enriched complex was followed. However, on a limited number of occasions when ¹⁷O-depleted solvent was used (0.007 atom %), the increase in solvent signal intensity was also monitored. Peak areas of expanded spectra (PA_o, former method)

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

complex	δ/ppm ^a (Δν/Hz)	pK _a
<i>p</i> -[Co(tren)(NH ₃)OH ₂] ³⁺	-100 (340 ± 30)	5.82
<i>t</i> -[Co(tren)(NH ₃)OH ₂] ³⁺	-134 (290 ± 30)	6.33
<i>p</i> -[Co(tren)(NH ₃)OH] ²⁺	-120 (800 ± 100)	
<i>t</i> -[Co(tren)(NH ₃)OH] ²⁺	-172 (900 ± 100)	
[Co(tren)(OH ₂) ₂] ³⁺	-95 (<i>p</i>) (380 ± 30)	5.89(<i>p</i>)
	-131 (<i>t</i>) (300 ± 30)	6.40(<i>t</i>)
[Co(tren)(<i>t</i> -OH ₂)- <i>p</i> -OH] ²⁺	-112 (<i>p</i>) ^d	8.17(<i>p</i>)
	-134 (<i>t</i>) ^d	8.68(<i>t</i>)
[Co(tren)(OH) ₂] ⁺	-109 (<i>p</i>) (1000 ± 200)	
	-162 (<i>t</i>) (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-Mecyclen)(OH ₂) ₂] ³⁺	-106 (400 ± 40 ^c)	5.28, 8.03

^a ppm from solvent H₂¹⁷O 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 ¹⁷O from *p*- and *t*-[Co(tren)(NH₃)OH₂/OH]^{3+/2+} (*I* = 1.0 M, NaCF₃SO₃, 25 °C)

complex	conditions	k _{obs} /s ^{-1 a}
<i>p</i>	0.40 M CF ₃ SO ₃ H	1.16 × 10 ^{-5 b}
	0.20 M CF ₃ SO ₃ H	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}
<i>t</i>	0.35 M NaOH	1.72 × 10 ^{-4 c}
	0.50 M CF ₃ SO ₃ H	8.70 × 10 ^{-6 b}
	0.42 M CF ₃ SO ₃ H	1.36 × 10 ^{-5 b}
	0.30 M CF ₃ SO ₃ H	1.28 × 10 ^{-5 b}
	0.22 M NaOH	<5 × 10 ^{-6 b,d}
	0.01 M NaOH	<1 × 10 ^{-6 b,d}

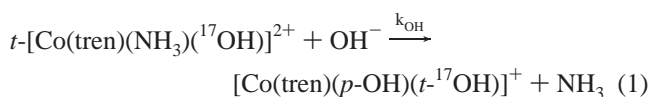
^a The relatively large errors in these values (10–25%) derive both from variation in probe temperature (±0.5 °C) and from significant background “noise” during the limited time available for spectrum accumulation. ^b Normal H₂O; complex signal monitored. ^c ¹⁷O-Depleted H₂O; both complex and solvent signal monitored. ^d *p*-NH₃ ligand lost (see text).

or peak heights (PH_i, latter method) were used to evaluate exchange rates. Values of k_{obs} were obtained from linear plots of ln(PA_i) or ln(PH_∞ - PH_i) 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 CF₃SO₃H). Data collection was begun within 2 min. Depending on reaction rate, spectra were acquired at intervals of 15 min (4.5 × 10³ transients) to 4 h (7.2 × 10⁴ transients). For pH 5.80 data with [Co(tren)(¹⁷OH₂)₂](CF₃SO₃)₃, aliquots (0.76 mL) were removed from the bulk solution (5 mL, *I* = 1.0 M NaCF₃SO₃) 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 OH₂/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 γ_± = 0.58 (1.0 M electrolyte)¹⁷ and K_w = 1.00 × 10⁻¹⁴ M².

Results

The *p*- and *t*-[Co(tren)(NH₃)(OH₂/OH)]^{3+/2+} System. Potentiometric titration (1.0 M NaCF₃SO₃, 25.0 °C) using the isolated aqua complexes as their nitrate–perchlorate salts (4 mM) gave K_a(*p*) = (1.5 ± 0.1) × 10⁻⁶ M, K_a(*t*) = (4.7 ± 0.2) × 10⁻⁷ M, respectively. Thus, the *p*-aqua isomer is slightly more acidic (3×) than the *t*-isomer.

Solvent exchange was followed by ¹⁷O NMR spectroscopy (*I* = 1.0 M (NaCF₃SO₃), 25 ± 0.5 °C) using either natural abundance or ¹⁷O-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_{H₂O}(*p*) = (1.1 ± 0.1) × 10⁻⁵ s⁻¹, k_{H₂O}(*t*) = (1.2 ± 0.3) × 10⁻⁵ s⁻¹, Table 2. For loss of label from *p*-[Co(tren)(NH₃)¹⁷OH]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 ± 0.1) × 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 × 10⁻⁵ s⁻¹, agrees well with that calculated (2.1 × 10⁻⁵ s⁻¹) using pK_a(*p*) = 5.82 and the above rate constants. For *t*-[Co(tren)(NH₃)¹⁷OH]²⁺ no measurable loss of label occurred over a 9 h period in 0.22 M NaOH (*I* = 1.0 M, NaCF₃SO₃, 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)(¹⁷OH)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*-NH₃ ligand, eq 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 × 10⁻⁴ (0.20); 2.80 × 10⁻⁵ (0.05); 6.0 × 10⁻⁶ (0.01) giving k_{OH-}(*p*-NH₃) = (6.0 ± 0.4) × 10⁻⁴ M⁻¹ s⁻¹ at *I* = 1.0 M NaCF₃SO₃ and 25.0 °C. It is important to note that the *t*-¹⁷OH resonance was retained throughout this process in 0.01 M alkali, implying that hydroxo ligand exchange in *t*-[Co(tren)(NH₃)OH]²⁺ is very slow, k_{OH}(*t*) < 1 × 10⁻⁶ s⁻¹. This is at least 10 times slower than exchange of the aqua ligand in *t*-[Co(tren)(NH₃)OH₂]³⁺ and more than 100-fold slower than hydroxo exchange in *p*-[Co(tren)(NH₃)OH]²⁺.

The [Co(tren)(OH₂/OH)]^{3+/2+} System. Potentiometric titration of an acidic aqueous solution (5 mM) prepared by dissolution of [Co(tren)(OSO₂CF₃)₂](CF₃SO₃) in water (1.0 M NaCF₃SO₃, 25.0 °C) gave K_{a1}(obs) = (1.7 ± 0.1) × 10⁻⁶ M (pK_{a1}(obs) = 5.77), K_{a2}(obs) = (8.8 ± 0.4) × 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 NaClO₄ (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 ¹⁷O 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)(NH₃)OH₂/OH]^{3+/2+}, whereas that at highest field (b) corresponds to that for *t*-[Co(tren)(NH₃)OH₂/OH]^{3+/2+} (cf. Table 1). Titration of [Co(tren)(¹⁷OH₂)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

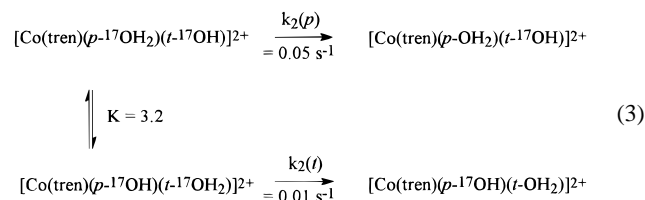
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signal a position (−112 ppm) remains unchanged. Both major shifts ($\delta(\text{obs})$) can be fitted to an expression of the type

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

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 $K_{\text{a}1} = 2.8 \times 10^{-6}$ M ($\text{p}K_{\text{a}1} = 5.6$), $K_{\text{a}2} = 8.09 \times 10^{-9}$ M ($\text{p}K_{\text{a}2} = 8.1$). These values are in good agreement with those obtained by the more accurate potentiometric method, but more importantly they assign $K_{\text{a}1}$ mainly to ionization of the *p*-site water molecules, and $K_{\text{a}2}$ 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 $[\text{Co}(\text{tren})(p\text{-OH}_2)(t\text{-OH})]^{2+}$). Taking into account this overlap in ionization constants, and using the relative acidities of *p*- and *t*- $[\text{Co}(\text{tren})(\text{NH}_3)\text{OH}_2]^{3+}$ as a guide ($K_{\text{a}}(p)/K_{\text{a}}(t) = 3.2$), gives $\text{p}K_{\text{a}1}(p) = 5.89$, $\text{p}K_{\text{a}1}(t) = 6.40$, and $\text{p}K_{\text{a}2}(p) = 8.17$, $\text{p}K_{\text{a}2}(t) = 8.68$ 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 $[\text{Co}(\text{tren})(\text{OH}_2)\text{OH}/\text{H}]^{3+/2+}$ and $[\text{Co}(\text{tren})(\text{NH}_3)\text{OH}/\text{H}]^{3+/2+}$ ions is not guaranteed. The above values were used when rates of exchange were calculated for particular coordination positions (cf. below).

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 H_2O as solvent (1.0 M 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 $\text{CF}_3\text{SO}_3\text{H}$). The data (Table 3) clearly show a pH-independent exchange in acid ($k_{\text{H}_2\text{O}}(p) = 3.7 \times 10^{-5}$ s $^{-1}$; $k_{\text{H}_2\text{O}}(t) = 8.7 \times 10^{-6}$ s $^{-1}$) and alkali ($k_{\text{OH}}(p) = 9.7 \times 10^{-5}$ s $^{-1}$; $k_{\text{OH}}(t) = 2.2 \times 10^{-7}$ 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 $[\text{Co}(\text{tren})(\text{OH}_2)\text{-OH}]^{2+}$ (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 basis²⁰ 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 $[\text{Co}(\text{tren})(p\text{-OH})(t\text{-OH}_2)]^{2+}$ isomer (i.e., *p*-OH exchange is preferred over *p*-OH $_2$

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

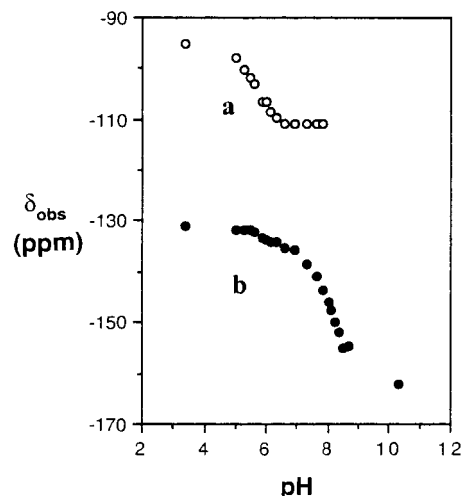
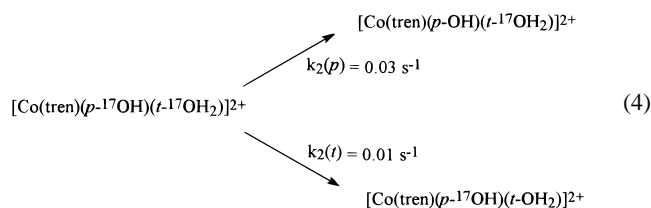


Figure 2. Plot of ^{17}O chemical shifts (signals a and b, see text) vs pH for the resonances of $[\text{Co}(\text{tren})(\text{OH}_2/\text{OH})_2]^{3+/2+/+}$ (0.10 M in ca. 30% H_2^{17}O , $I = 1.0$ M, NaCF_3SO_3).

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.



The $[\text{Co}(\text{cyclen})(\text{OH}_2/\text{OH})_2]^{3+/2+/+}$ and $[\text{Co}(\text{N-Mecyclen})(\text{OH}_2/\text{OH})_2]^{3+/2+/+}$ 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, 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 $K_{\text{a}1} = (1.51 \pm 0.07) \times 10^{-6}$ M ($\text{p}K_{\text{a}1} = 5.82$), $K_{\text{a}2} = (6.3 \pm 0.6) \times 10^{-9}$ M ($\text{p}K_{\text{a}2} = 8.20$) and $K_{\text{a}1} = (5.25 \pm 0.3) \times 10^{-6}$ M ($\text{p}K_{\text{a}1} = 5.28$), $K_{\text{a}2} = (9.3 \pm 0.6) \times 10^{-9}$ M ($\text{p}K_{\text{a}2} = 8.03$) for the two complexes, respectively (cf. Table 1). Thus N-methylation at the apical position²² 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-NH* and the other *cis* to *anti-NH*.²³ The above $\text{p}K_{\text{a}}$ values are in good agreement with those given for a cyclen complex of less certain origin in 0.1 M NaClO_4 , $\text{p}K_{\text{a}1} = 5.6$, $\text{p}K_{\text{a}2} = 8.0$.²⁴

^{17}O -Exchange kinetics for the labeled complexes (1.0 M 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 $[\text{H}^+]^{-1}$ in Figure 4. Again, the water molecules *cis* to the

(21) Calculated by fitting data to the expressions $k_{\text{obs}}(p) = (k_1(p)a_{\text{H}^+} + k_2(p)K_{\text{a}1}(p)a_{\text{H}^+} + k_3(p)K_{\text{a}1}(p)K_{\text{a}2}(p))/(a_{\text{H}^+} + a_{\text{H}^+}K_{\text{a}1}(p)(1 + 1/K) + K_{\text{a}1}(p)K_{\text{a}2}(p))$, using $K = 3.2$, K_{a} values given in Table 1, $k_1(p) = 3.7 \times 10^{-5}$ s $^{-1}$, and $k_3(p) = 9.7 \times 10^{-5}$ s $^{-1}$; $k_{\text{obs}}(t)$ 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.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186.

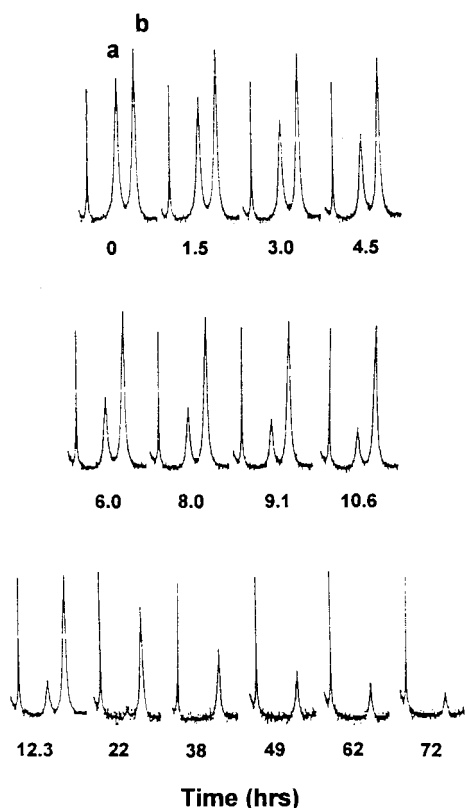


Figure 3. ¹⁷O NMR spectra showing loss of label from [Co(tren)-(¹⁷OH₂)₂]³⁺ (signals a and b) into 0.30 M CF₃SO₃H, *I* = 1.0 M, NaCF₃SO₃, 25 °C. MeOH (external reference, δ = -35 ppm) signal at left.

Table 3. Observed and Calculated Rate Constants^a for Loss of ¹⁷O from [Co(tren)(¹⁷OH₂/¹⁷OH)₂]^{3+/2+/+} Species (*I* = 1.0 M NaCF₃SO₃, 25 °C; Normal H₂O Solvent)

condition	<i>p</i> -exchange			<i>t</i> -exchange	
	10 ⁵ <i>k</i> _{obs}	10 ⁵ <i>k</i> _{calc} ^b	10 ⁵ <i>k</i> _{calc} ^c	10 ⁶ <i>k</i> _{obs}	10 ⁶ <i>k</i> _{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*-¹⁷OH₂)(*t*-¹⁷OH)]²⁺ using p*K*_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*-¹⁷OH)(*t*-¹⁷OH₂)]²⁺ using p*K*_a values given in Table 1, and *k*₂(*t*) = 0.01 s, *k*₂(*p*) = 0.03 s⁻¹.

syn- and *anti*-NH 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*_{H₂O} = 2 × 10⁻⁴ s⁻¹ (per H₂O molecule). The slopes may be related either to spontaneous (i.e., uncatalyzed) exchange in the hydroxo-aqua complexes giving *k*' = 2 slope γ_±/*K*_{a1} = 12 and 15 s⁻¹, respectively (slope = 1.6 × 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 γ_±/2/*K*_w = 1.1 × 10⁹ and 4.6 × 10⁹ M⁻¹ s⁻¹, respectively (the

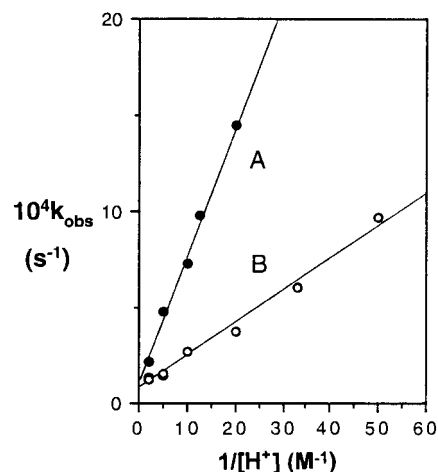


Figure 4. Plot of *k*_{obs} vs [H⁺]⁻¹ for ¹⁷O exchange in [Co(N-Mecyclen)(¹⁷OH₂)₂]³⁺ (A, closed circles) and [Co(cyclen)(¹⁷OH₂)₂]³⁺ (B, open circles); 25 °C.

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.

Discussion

The spontaneous (uncatalyzed) loss of H₂O 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} ~ 32 h, 25 °C) for exchange in [Co(NH₃)₅OH₂]³⁺,²⁵ and Kruse and Taube found not too different values for exchange in *cis*- and *trans*-[Co(en)₂(OH₂)₂]³⁺ (7.5 × 10⁻⁶ s⁻¹, 1.1 × 10⁻⁵ s⁻¹, 25 °C, 0.8 M HClO₄).²⁶ There appears to be little difference whether one or two H₂O 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)(NH₃)OH₂]³⁺, [Co(tren)(OH₂)₂]³⁺, *k*_{H₂O} = (1-4) × 10⁻⁵ s⁻¹). Exchange in the cyclen/N-Mecyclen complexes is somewhat faster (*k*_{H₂O} ≈ 2 × 10⁻⁴ s⁻¹), as it is for [Co(NH₂CH₃)₅OH₂]³⁺ (Table 4), but the overall inference is that saturated amine systems will all exhibit slow, uncatalyzed exchange rates for coordinated H₂O (with half-lives of hours). Unsaturation, such as in the planar ring system of vitamin-B₁₂,⁹ 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_N1(CB) mechanism, below).

The loss of coordinated OH⁻ provides much more interesting data. For example, OH⁻ exchange in *p*-[Co(tren)(NH₃)OH]²⁺ is some 100 times faster than that in *t*-[Co(tren)(NH₃)OH]²⁺ (1.7 × 10⁻⁴ s⁻¹ vs 1 × 10⁻⁶ s⁻¹) even though the former is somewhat less basic (p*K*_a = 5.82, 6.33 respectively). On the basis of ligand field strengths, OH⁻ loss would be expected to be much slower than H₂O loss, and previous work on purely metal-aqua systems attributes faster exchange in M(OH₂)₅OH²⁺ compared to M(OH₂)₆³⁺ (M = Ga, Fe, Cr, Ru, Rh) to the stronger electron-donating property of OH⁻ weakening M-OH₂ bonds.²⁷ Certainly *t*-OH loss in *t*-[Co(tren)(NH₃)OH]²⁺ and [Co(tren)(OH)₂]⁺ is slower than *t*-OH₂ loss in their acid

(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		
[Co(NH ₃) ₅ OH ₂] ³⁺	6×10^{-6}	25
[Co(NH ₂ CH ₃) ₅ OH ₂] ³⁺	7×10^{-4}	b
<i>cis</i> -[Co(en) ₂ (NH ₃)OH ₂] ³⁺	1.1×10^{-6}	c
<i>p</i> -[Co(tren)(NH ₃)OH ₂] ³⁺	1.1×10^{-5}	d
<i>t</i> -[Co(tren)(NH ₃)OH ₂] ³⁺	1.2×10^{-5}	d
[Co(cyclen)(NH ₃)OH ₂] ³⁺	$<1 \times 10^{-4}$	29
Diaqua Systems		
<i>cis</i> -[Co(en) ₂ (OH ₂) ₂] ³⁺	7.5×10^{-6}	26, e
<i>trans</i> -[Co(en) ₂ (OH ₂) ₂] ³⁺	1.1×10^{-5}	26
[Co(tren)(OH ₂) ₂] ³⁺	3.7×10^{-5} (<i>p</i>), 8.7×10^{-6} (<i>t</i>)	d
[Co(cyclen)(OH ₂) ₂] ³⁺	2×10^{-4}	d
[Co(N-Mecyclen)(OH ₂) ₂] ³⁺	2×10^{-4}	d
Monohydroxo Systems		
[Co(NH ₃) ₅ OH] ²⁺	$<1.4 \times 10^{-7}$	25
<i>p</i> -[Co(tren)(NH ₃)OH] ²⁺	1.7×10^{-4}	d
<i>t</i> -[Co(tren)(NH ₃)OH] ²⁺	$<1 \times 10^{-6}$	d
[Co(cyclen)(NH ₃)OH] ²⁺	8	29
Dihydroxo Systems		
<i>cis</i> -[Co(en) ₂ (OH) ₂] ⁺	3.0×10^{-5}	26
<i>trans</i> -[Co(en) ₂ (OH) ₂] ⁺	2.3×10^{-6}	26
[Co(tren)(OH) ₂] ⁺	9.7×10^{-5} (<i>p</i>), 2.2×10^{-7} (<i>t</i>)	d
Aqua–Hydroxo Systems		
<i>cis</i> -[Co(en) ₂ (OH ₂)OH] ²⁺	9.3×10^{-4}	26
<i>trans</i> -[Co(en) ₂ (OH ₂)OH] ²⁺	1.2×10^{-3}	26
[Co(tren)(<i>p</i> -OH ₂)(<i>t</i> -OH)] ²⁺	0.05 (<i>p</i>)	d
[Co(tren)(<i>t</i> -OH ₂)(<i>p</i> -OH)] ²⁺	0.03 (<i>p</i>), 0.01 (<i>t</i>)	d
[Co(cyclen)(OH ₂)OH] ²⁺	12	d
[Co(N-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.

conjugates, as is OH[−] loss in [Co(NH₃)₅OH]²⁺. Hunt and Taube²⁵ made the interesting suggestion that ligand–OH[−] exchange could result from an indirect process involving amine deprotonation and loss of H₂O, viz., eq 5, that is via an S_N1-



(CB) process on the aqua complex, and this allows for the rate of OH[−] exchange to exceed that of H₂O exchange depending on the values of K and k'_{OH} . The unusually rapid substitution reactions of the [Co(dien)(dapo)OH]²⁺ ion have similarly been interpreted as involving deprotonation at the dien *sec*-NH site in the conjugate acid, followed by water exchange in the resulting aqua–amido intermediate.²⁸ Also, in the *p*-[Co(tren)(NH₃)OH/H]^{2+/3+} system coordinated OH[−] exchanges faster than coordinated OH₂ (15-fold; cf. Table 4), and a similar case can be made for [Co(tren)(*t*-OH₂)(*p*-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 H₂O ($k_{\text{H}_2\text{O}} = (1-2) \times 10^{-4} \text{ s}^{-1}$), loss of OH[−] is extremely rapid, 8 s^{−1} for [Co(cyclen)(NH₃)OH]²⁺, 12 s^{−1} for [Co(cyclen)(OH₂)OH]²⁺, and 15 s^{−1} for [Co(N-Mecyclen)(OH₂)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 $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, 1.1×10^9

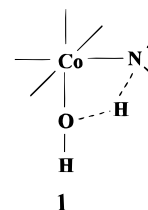
Table 5. k_{OH} Values (M^{−1} s^{−1}, 25 °C) for Base Hydrolysis in some *p*- and *t*-[Co(tren)(NH₃)X]^{3+/2+} ^a and Some [Co(cyclen)(A)X]^{3+/2+} ^b Systems

X	k_{OH} (M ^{−1} s ^{−1})	
	<i>p</i> -[Co(tren)(NH ₃)X] ^{3+/2+} loss of X	<i>t</i> -[Co(tren)(NH ₃)X] ^{3+/2+} loss of <i>t</i> -X
OH ₂ (OH [−])	1.5×10^4 ($1.7 \times 10^{-4} \text{ s}^{-1}$)	$<27^c$ ($<1 \times 10^{-6} \text{ s}^{-1}$)
NH ₃	5.4×10^{-2}	5.4×10^{-2}
Cl [−]	4×10^2	2×10^{-2}
SCN [−]	1.1×10^4	2.1×10^{-2}
NCS [−]	3.4×10^{-2}	2.5×10^{-3}
N ₃ [−]	0.44	1.2×10^{-3}
Br [−]		0.24
NO ₃ [−]		0.24
Me ₂ SO		3.7
MeSO ₃ [−]		10.0

[Co(cyclen)(A)X] ^{3+/2+} (Loss of X)		
A	X	k_{OH}
NH ₃	NH ₃	2×10^4
NH ₃	OH ₂	4.5×10^8
NH ₃	OH	4×10^4
NH ₃	Cl	4×10^6 (<i>syn</i>), 3×10^5 (<i>anti</i>)
NH ₃	N ₃	4×10^4
OH	NH ₃	1.0
OH ₂	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; $k_{\text{OH}} = kK_a\gamma_{\pm}/K_w$ using $\gamma_{\pm} = 0.58$, $K_w = 1.0 \times 10^{-14} \text{ M}^2$.

M^{−1} s^{−1}, and $4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Such values are very large indeed. Similar calculations lead to values of $27 \text{ M}^{-1} \text{ s}^{-1}$ and $1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for OH[−]-catalyzed exchange in the *t*- and *p*-[Co(tren)(NH₃)OH₂]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 H₂O compared to NH₃ (or Cl[−]), and we suggest that instead of the sequence of protonation (of coordinated OH), deprotonation (of amine), and loss of OH₂ in the mechanism of Hunt and Taube²⁵ (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*-NH proton, and as discussed elsewhere²⁹ 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)(NH₃)OH]²⁺, [Co(NH₃)₅OH]²⁺, and [Co(tren)(*p*-OH₂)(*t*-OH)]²⁺ (*t*-OH exchange) systems. This is presumably related to both diminished *NH* acidity and stereochemical availability. With [Co(tren)(OH₂)OH]²⁺ the data best fit both *p*- and *t*-exchanges occurring in the more dominant [Co(tren)-(*p*-OH)(*t*-OH₂)]²⁺ isomer (Table 3), eq 4, and this supports the above mechanism for exchange of the *p*-OH ligand, but a more conventional route²⁷ for exchange of the *t*-OH₂ 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)(OH₂)₂]³⁺ and [Co(tren)(OH)₂]⁺ in normal H₂O and Table S1 giving spectroscopic constants for the [Co(cyclen)(OH₂/OH)₂]^{3+/2+/+} and [Co(N-Mecyclen)(OH₂/OH)₂]^{3+/2+/+} ions (2 pages). Ordering information is given on any current masthead page.

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