

Kinetic Origin of the Chelate Effect. Base Hydrolysis, H-Exchange Reactivity, and Structures of *syn,anti*-[Co(cyclen)(NH₃)₂]³⁺ and *syn,anti*-[Co(cyclen)(diamine)]³⁺ Ions (diamine = H₂N(CH₂)₂NH₂, H₂N(CH₂)₃NH₂)

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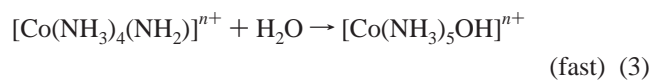
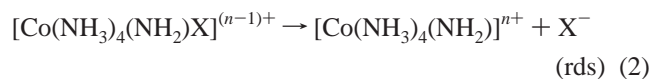
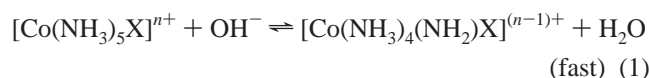
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The synthesis of *syn,anti*-[Co(cyclen)en](ClO₄)₃ (**1**(ClO₄)₃) and *syn,anti*-[Co(cyclen)tn](ClO₄)₃ (**2**(ClO₄)₃) is reported, as are single-crystal X-ray structures for *syn,anti*-[Co(cyclen)(NH₃)₂](ClO₄)₃ (**3**(ClO₄)₃): orthorhombic, *Pnma*, *a* = 17.805(4) Å, *b* = 12.123(3) Å, *c* = 9.493(2) Å, $\alpha = \beta = \gamma = 90^\circ$, *Z* = 4, *R*₁ = 0.030. **1**(ClO₄)₃: monoclinic, *P2*(1)/*n*, *a* = 8.892(2) Å, *b* = 15.285(3) Å, *c* = 15.466(3) Å, $\alpha = 90^\circ$, $\beta = 91.05(3)^\circ$, $\gamma = 90^\circ$, *Z* = 4, *R*₁ = 0.0657. **2**Br₃: orthorhombic, *Pca*2(1), *a* = 14.170(4) Å, *b* = 10.623(3) Å, *c* = 12.362(4) Å, $\alpha = \beta = \gamma = 90^\circ$, *Z* = 4, *R*₁ = 0.0289. Rate constants for H/D exchange (D₂O, *I* = 1.0 M, NaClO₄, 25 °C) of the *syn* and *anti* NH protons (rate law: $k_{\text{obs}} = k_0 + k_{\text{H}}[\text{OD}^-]$) and the apical NH, and the NH₃ and NH₂ protons (rate law: $k_{\text{obs}} = k_{\text{H}}[\text{OD}^-]$) in the **1**, **2**, and **3** cations are reported. Deprotonation constants ($K = [\text{Co}(\text{cyclen-H})(\text{diamine})^{2+}]/[\text{Co}(\text{cyclen})(\text{diamine})^{3+}][\text{OH}^-]$) were determined for **1** ($5.5 \pm 0.5 \text{ M}^{-1}$) and **2** ($28 \pm 3 \text{ M}^{-1}$). In alkaline solution **1**, **2**, and **3** hydrolyze to [Co(cyclen)(OH)₂]⁺ via [Co(cyclen)(amine)OH]²⁺ monodentates. Hydrolysis of **3** is two step: $k_{\text{obs}(1)} = k_{\text{OH}(1)}[\text{OH}^-]$, $k_{\text{obs}(2)} = k_0 + k_{\text{OH}(2)}[\text{OH}^-]$ ($k_{\text{OH}(1)} = (2.2 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_0 = (5.1 \pm 1.2) \times 10^{-4} \text{ s}^{-1}$, $k_{\text{OH}(2)} = 1.0 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$). Hydrolysis of **2** is biphasic: $k_{\text{obs}(1)} = k_1 K[\text{OH}^-]/(1 + K[\text{OH}^-])$ ($k_1 = 5.0 \pm 0.2 \text{ s}^{-1}$, $K = 28 \text{ M}^{-1}$), $k_{\text{obs}(2)} = k_2 K_2[\text{OH}^-]/(1 + K_2[\text{OH}^-])$ ($k_2 = 3.5 \pm 1.2 \text{ s}^{-1}$, $K_2 = 1.2 \pm 0.8 \text{ M}^{-1}$). Hydrolysis of **1** is monophasic: $k_{\text{obs}} = k_1 k_2 K K_2 [\text{OH}^-]^2 / (1 + K[\text{OH}^-])(k_{-1} + k_2 K_2 [\text{OH}^-])$ ($k_1 = 0.035 \pm 0.004 \text{ s}^{-1}$, $k_{-1} = 2.9 \pm 0.6 \text{ s}^{-1}$, $K = 5.5 \text{ M}^{-1}$, $k_2 K_2 = 4.0 \text{ M}^{-1} \text{ s}^{-1}$). The much slower rate of chelate ring-opening in **1**, compared to loss of NH₃ from **3**, is rationalized in terms of a reduced ability of the former system to allow the bond angle expansion required to produce the S_N1CB trigonal bipyramidal intermediate.

Introduction

With a view toward exploring how rates of NH exchange and chelate ring-opening and closure in Co(III) chelates are correlated with complex structure and NH acidity, three [Co(cyclen)diamine](ClO₄)₃ complexes (diamine = (NH₃)₂, en, tn)¹ have been prepared and characterized. In alkaline solution these species undergo rapid hydrolysis to [Co(cyclen)(OH)₂]⁺ via processes involving formation of [Co(cyclen)(monodentate-amine)OH]²⁺ intermediates. It is well-known that base hydrolysis of acido-Co(III) amines proceeds via S_N1CB mechanisms² (eqs 1–3 for [Co(NH₃)₅X]^{*n*+}), and several previous studies



involving various (N)₅Co systems have endeavored to identify

the kinetically important NH deprotonation site (cf. eq 1)³ and probe the nature of the 5-coordinate intermediate (cf. eq 2).^{3,4} It is generally agreed that deprotonation at a *cis* NH site leads to the most reactive conjugate base.^{2d} The relatively high charge (3+) carried by the Co(III)–cyclen complexes should result in enhanced NH acidity compared to related 1+ and 2+ charged species,^{5,6} and the *sec*-NH sites (*syn*, *anti*, and *ap* (*ap* = apical)

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(1) en = ethylenediamine, tn = 1,3-trimethylenediamine.

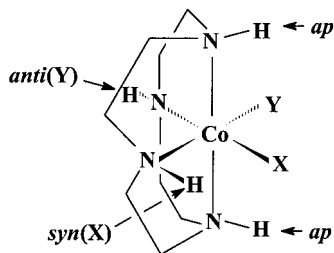


Figure 1. Representation of a $[\text{Co}(\text{cyclen})\text{XY}]^{n+}$ ion showing the syn, anti, and ap configurations for the *sec-NH* centers. This example has syn(X),anti(Y) stereochemistry.

cf. Figure 1) are able to be distinguished by NOE methods.⁷ In what follows we identify the critical NH site and directly measure its acidity. We further explore whether the reactivity of the conjugate base is altered when Co–N bond cleavage results in opening of a chelate ring, rather than in loss of a monodentate ligand, and whether these two processes are discernibly different in a mechanistic sense. Jordan⁸ has recently commented on the unexpectedly slow rates of chelate ring-opening in exchange labile systems.

Experimental Section

CAUTION! The potentially explosive qualities of perchloric acid and perchlorate salts mean that these should be treated with great care at all times. No problems were encountered during the synthesis and use of the complexes described below.

syn,anti-[Co(cyclen)en](ClO₄)₃ and syn,anti-[Co(cyclen)tn](ClO₄)₃·H₂O. Ethylenediamine or trimethylenediamine (98–99%, 1.50 cm³) and finely powdered [Co(cyclen)Cl₂]Cl⁹ (1.0 g) were ground to a smooth paste for 30 s. To the semisolid was added HCl (3.0 M, 50 cm³) and water (200 mL), and the solution was sorbed onto Dowex 50W × 2 IE resin. The orange product was removed on elution with 3.0 M HCl and recovered by evaporation. The residue in HCl (1.0 M, 5 cm³) was treated with excess LiClO₄. Storage at 4 °C gave orange crystals, which were filtered off, washed with ethanol, and air-dried. Found for the en complex: C, 20.40; H, 4.69; N, 14.11. CoC₁₀H₂₈N₆Cl₃O₁₂ requires: C, 20.37; H, 4.79; N, 14.25. ¹H NMR in ca. 1 M DCl: δ = 7.26 (1H, s, br), 7.13 (1H, s, br), 6.13 (2H, s, br), 5.35 (2H, s, br), 4.94 (2H, s, br), 3.9–2.7 (20H, m) ppm. UV–vis in 1 M HClO₄: λ_{max}, ε (M⁻¹ cm⁻¹) = 487 nm, 205; 342 nm 156. Found for the tn complex: C, 21.45; H, 5.38; N, 13.57; Cl, 17.37. CoC₁₁H₃₀N₆Cl₃O₁₂·H₂O requires: C, 21.25; H, 5.19; N, 13.52; Cl, 17.11. ¹H NMR in acidified (ca. 3 M) DCl: δ = 7.20 (1H, s, br), 6.93 (1H, s, br), 6.50 (2H, s, br), 4.98 (2H, s, br), 4.65 (2H, s, br), 3.7–2.7 (20H, m), 2.10 (2H, m) ppm.

Reagents were of AR grade. Anhydrous NaClO₄ was obtained from the monohydrate by drying under vacuum (0.05 mmHg, 85 °C). D₂O (isotopic purity 99.9 atom %) was obtained from Aldrich. *syn,anti*-[Co(cyclen)(NH₃)₂](ClO₄)₃ was prepared from the reaction of [Co(cyclen)Cl₂]Cl⁹ with NH₃(g) in acetone.⁷

Zero time absorbance data (25.0 °C, *I* = 1.0 M, NaClO₄) were obtained using Durrum D-110 and Olis USA stopped-flow spectrophotometers. Measurements were obtained within 10 ms of mixing equal volumes of the complex in NaClO₄ solution and NaOH solution of the required concentration. Rates of alkaline hydrolysis (25.0 °C, *I* = 1.0 M, NaClO₄) were measured using a Cary 219 UV–vis spectrophotometer for [Co(cyclen)en](ClO₄)₃, and either the Durrum or Olis for [Co(cyclen)tn](ClO₄)₃, [Co(cyclen)(NH₃)₂](ClO₄)₃, and [Co(cyclen)(NH₃)OH](ClO₄)₂. Rapid scan spectra were obtained using the Durrum in conjunction with a Harrick rapid-scan spectrometer. H–D exchange data were obtained using a Varian VXR300 MHz or Inova 500 MHz NMR spectrometer for the complex (3–4 mg) in HCOOD buffer (0.05 M) or DClO₄ solution (0.80 mL, *I* = 1.0 M NaClO₄).

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Reactions were monitored over at least three half-lives and peak areas obtained by integration. DClO₄ concentrations were determined by titration (standard NaOH), and measurements of pD were made using a Radiometer PHM 82 pH meter equipped with G2040B and K4040 electrodes. Standardization was carried out using 0.05 M potassium tetroxalate (pH 1.679), 0.05 M potassium hydrogen phthalate (pH 4.008), and 0.025 M KH₂PO₄/0.025 M Na₂HPO₄ (pH 6.865) buffers at 25.0 °C.¹⁰ pD was obtained from the relationship pD = meter reading + 0.40,¹¹ and concentrations of OD⁻ were calculated from pD or [D⁺] using pK_w(D₂O) = 14.95¹² and γ_± = 0.67 (*I* = 1.0 M NaClO₄).¹³ First-order rate constants were obtained by least-squares analysis¹⁴ of peak area vs time data (exchange reactions) or absorbance vs time data (hydrolysis reactions). The biphasic reaction of [Co(cyclen)tn]³⁺ in alkaline solution was monitored at a wavelength either in the range 500–580 nm (absorbance decrease followed by increase) or at 356 nm (continuous decrease), with the wavelength selected being the one that gave best definition to the fast and slow processes at a particular [OH⁻]. Values of the rate constants were obtained by least-squares analysis using the appropriate double-exponential expression.¹⁵ UV–vis spectra were recorded using the Cary.

Diffraction quality crystals of [Co(cyclen)en](ClO₄)₃ were obtained on leaving a concentrated solution (weakly acidified D₂O) in an NMR tube. [Co(cyclen)tn](ClO₄)₃ was converted to the Br⁻ salt by anion exchange chromatography on Amberlite IRA 400 resin, and crystals were obtained on layering a 1 M HBr solution with EtOH. [Co(cyclen)(NH₃)₂](ClO₄)₃ crystallized as orange blocks on diffusion of ethanol vapor into a weakly acidic aqueous solution. X-ray data were collected on a Siemens Smart diffractometer with graphite-monochromated Mo Kα radiation and a CCD detector, with exposures over 0.3°. Data were processed, empirical corrections were applied, and space groups were assigned using programs from the SHELXTL package.¹⁶ Choice of the correct space groups were confirmed by subsequent solution and refinement of the structures. The structures were solved using SHELXS-97,¹⁷ with the resulting Fourier map revealing the location of all non-hydrogen atoms. Weighted full-matrix refinement on *F*² was carried out using SHELXL-97¹⁸ with all non-hydrogen atoms being refined anisotropically. Hydrogen atoms were included in calculated positions and refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters. The large thermal parameters of the perchlorate oxygen atoms bonded to Cl1 in [Co(cyclen)en](ClO₄)₃ suggested that some disorder was present, and this was modeled as 2-fold rotational disorder about the Cl1–O14 bond, giving occupancies of 63:37 for the two conformations.

Results and Discussion

The formation of [Co(cyclen)en]³⁺ or [Co(cyclen)tn]³⁺ occurs rapidly (within seconds) on treating [Co(cyclen)Cl₂]Cl with the neat diamine. The products are easily isolated from acidic

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(13) Data for activity coefficients of salts in normal water are given by Latimer (Latimer, W. M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*; Prentice-Hall: New York, 1953) and quoted in the following: *pH Measurements in Theory and Practice*; Linnert, N. Radiometer: Copenhagen, 1970. Marshall and Katz (Marshall, P. R.; Katz, J. J. *Inorg. Nucl. Chem.* **1974**, *36*, 1589) have shown that these are not too different for D₂O solution.

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solution as ClO_4^- or Br^- salts, and crystal structures (see below) show *syn,anti* configurations for the equatorial *NH* protons in both complexes. In the ^1H NMR spectrum (acidified D_2O) these give rise to the signals at lowest field (7.26, 7.13 ppm, respectively, *en* complex, 1 M DCl; 7.20, 6.93 ppm, respectively, *tn* complex, 3 M DCl), and the assignments were confirmed by NOE spectroscopy. The *ap-NH* protons of both complexes give rise to a single resonance in the vicinity of 6–6.5 ppm, while the NH_2 protons in the diamine chelates are distinguished and appear in the region 4.5–5.5 ppm. We could find no evidence for isomerization in either complex (by IE chromatography and reversed-phase HPLC, *syn, syn* and *anti, anti* isomers absent), and this was also the case for *syn, anti*-[Co(cyclen)(NH_3) $_2$]-(ClO_4) $_3 \cdot \text{H}_2\text{O}$,⁷ where the configuration was assigned by a combination of NOE and COSY spectroscopies and confirmed by a crystal structure.

1. *NH* Proton Exchange. In all three complexes the equatorial *NH* centers are the most labile and these undergo H/D exchange even under acidic conditions. Figure S1 (Supporting Information) shows this for [Co(cyclen)] $^{3+}$ at $[\text{D}^+] = 0.0535 \text{ M}$ and 25°C with the *syn*- and *anti-NH* signals decaying at identical rates, $k_{\text{obs}} = (1.08 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$. In less acidic solution the other amine signals (*ap*, NH_2) also decay, and Tables S1, S2, and S3 (Supporting Information) give rate data for all three complexes. Exchange at the *syn*- and *anti-NH* sites follows the two-term rate law:

$$k_{\text{obs}} = k_0 + k_{\text{H}}[\text{OD}^-] \quad (4)$$

with, for the *en* complex, $k_0 = (8 \pm 3) \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{H}} = (3.0 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Exchange of the *ap* and primary amine protons follows strictly first-order kinetics in OD^- catalysis, with $k_{\text{H}} = (1.6 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for *ap-NH* and $k_{\text{H}} = (8.3 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for both ethylenediamine NH_2 centers. The latter rate is not too different from that observed for [Co(en) $_3$] $^{3+}$, $k_{\text{H}} = 2.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ The *syn*- and *anti-NH* protons in [Co(cyclen)tn] $^{3+}$ are distinguished by differing exchange rates, and with $k_0^{\text{syn}} = (3.7 \pm 0.4) \times 10^{-4} \text{ s}^{-1}$, $k_{\text{H}}^{\text{syn}} = (3.3 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_0^{\text{anti}} = (1.1 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$, $k_{\text{H}}^{\text{anti}} = (6.2 \pm 0.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (cf. eq 4) indicating somewhat faster processes than those observed for [Co(cyclen)-en] $^{3+}$. This is also true for *ap* proton exchange: $k_{\text{H}} = (7.8 \pm 0.8) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. No attempt was made to obtain rate data for exchange of the primary amine protons (partially obscured by the HOD signal) in the *tn* complex. The data for [Co(cyclen)-(NH_3) $_2$] $^{3+}$ show that decay of the lowest field signal (6.7 ppm, 2H) follows eq 4 with $k_0 = 1.5 \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{H}} = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($I = 1.0 \text{ M}$, 25°C). This process involves both the *syn*- and *anti-NH* protons, as shown by an experiment in 0.035 M DClO_4 , where acid quenching after ca. $1 \times t_{1/2}$, recovery of unreacted starting material as the ClO_4^- salt, and examination of this in d_6 - Me_2SO showed both the *syn* (7.30 ppm) and *anti* (7.12 ppm) *NH* protons at ca. 50% exchange when compared to the *ap-NH* signal (6.76 ppm, 2H). The *ap* and NH_3 protons showed no exchange over 2 days under this condition, nor were they found to have exchanged in the [Co(cyclen)(NH_3) OH_2] $^{3+}$ product following acid quenching after 1 min at pD 7.62. Therefore, they cannot be involved in the OH^- -catalyzed hydrolysis reaction.

OD^- -catalyzed exchange at *syn*- and *anti-NH* sites in the complexes ($k_{\text{H}} = (3-7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) occurs with rates either close to or at (for the *tn* complex) the diffusion limit (ca. $10^{10} \text{ M}^{-1} \text{ s}^{-1}$). This is in accord with these centers having $\text{p}K_{\text{a}}$ values

Table 1. Rate Data^a for the OH^- -Catalyzed Loss of NH_3 from *syn*(NH_3),*anti*(NH_3)-[Co(cyclen)(NH_3) $_2$] $^{3+}$ and [Co(cyclen)(NH_3) OH] $^{2+}$ ($I = 1.0 \text{ M}$, NaClO_4 ; 25°C)

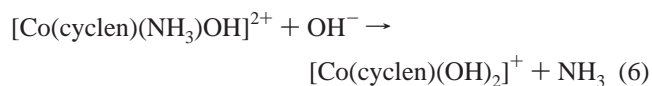
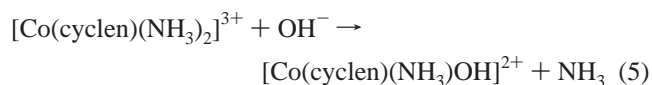
pH (or[OH^-]) [Co(cyclen)(NH_3) $_2$] $^{3+}$	[OH^-]/M	$k_{\text{obs}(1)}/\text{s}^{-1}$	$k_{\text{calc}}^g/\text{s}^{-1}$
7.66 ^c	6.82×10^{-7}	0.0163	0.0150
8.09 ^c	1.84×10^{-6}	0.0384	0.0405
8.82 ^c	9.86×10^{-6}	0.277	0.217
9.07 ^d	1.75×10^{-5}	0.437	0.385
9.30 ^d	2.98×10^{-5}	0.648	0.656
9.92 ^{b,e}	1.24×10^{-4}	2.75	2.73
10.42 ^e	3.93×10^{-4}	7.43	8.65
10.79 ^e	9.20×10^{-4}	20.1	20.2

[Co(cyclen)(NH_3) OH] $^{2+}$ (isomeric mixture)	[OH^-]/M	$10^4 k_{\text{obs}(2)}/\text{s}^{-1}$	$10^4 k_{\text{calc}}^h/\text{s}^{-1}$
8.68 ^c	7.14×10^{-6}	5.14	5.47
9.07 ^d	1.75×10^{-5}	5.26	5.57
9.37 ^d	3.50×10^{-5}	5.46	5.74
9.92 ^{b,e}	1.24×10^{-4}	7.28	6.62
10.42 ^e	3.93×10^{-4}	9.59	9.28
10.79 ^e	9.20×10^{-4}	15.2	14.5
0.1 ^f	0.1	995	994
0.25 ^f	0.25	2470	2470
0.50 ^f	0.50	4950	4950

^a $\lambda = 523 \text{ nm}$ for [Co(cyclen)(NH_3) $_2$] $^{3+}$; 570 nm for [Co(cyclen)-(NH_3) OH] $^{2+}$; [buffer] = 0.1 M unless stated otherwise. ^b [Buffer] = 0.2 M. ^c Tris. ^d Ches. ^e Caps. ^f NaOH solution. ^g $k_{\text{calc}} (\text{s}^{-1}) = (2.2 \pm 0.4) \times 10^4 [\text{OH}^-]$. ^h $k_{\text{calc}} (\text{s}^{-1}) = (5.1 \pm 1.2) \times 10^{-4} + (1.0 \pm 0.1) [\text{OH}^-]$.

≤ 14 ,²⁰ which is consistent with the observation of “spontaneous” pathways (i.e., water catalyzed, $k_0 = 8 \times 10^{-5}$ to $1.1 \times 10^{-3} \text{ s}^{-1}$) for exchange. Only for an acid of $\text{p}K_{\text{a}} \leq 14$ in water will H_2O be a sufficiently strong base to abstract the proton at a measurable rate. In contrast, most other Co(III)-amines have $\text{p}K_{\text{a}}$ values in well in excess of 14.²¹

2. Acidity Measurements and Hydrolysis in Alkaline Solution. OH^- -catalyzed loss of the NH_3 ligands in [Co(cyclen)-(NH_3) $_2$] $^{3+}$ occurs in two stages, eqs 5 and 6. The first reaction



shows strict OH^- catalysis, i.e., $k_{\text{obs}(1)} = k_{\text{OH}(1)}[\text{OH}^-]$ with $k_{\text{OH}(1)} = (2.2 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, while the second reaction follows a two-term rate law: $k_{\text{obs}(2)} = k_0 + k_{\text{OH}(2)}[\text{OH}^-]$ with $k_0 = (5.1 \pm 1.2) \times 10^{-4} \text{ s}^{-1}$, $k_{\text{OH}(2)} = 1.0 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$ ($I = 1.0 \text{ M}$, NaClO_4 , 25°C), Table 1. The first reaction gives an equilibrium mixture of the two [Co(cyclen)(NH_3) OH] $^{2+}$ isomers (75% *syn*(NH_3),*anti*(OH) + 25% *syn*(OH),*anti*(NH_3)).²² This was established by quenching experiments (pH 8.0; 2, 5, 10 min) followed by IE chromatography, anation of recovered [Co(cyclen)(NH_3) OH_2] $^{3+}$ (HCl, 55°C), and HPLC estimation of resulting [Co(cyclen)(NH_3)Cl] $^{2+}$. The [Co(cyclen)(NH_3) OH_2] $^{3+}$ isomers rapidly isomerize under the pH 8 condition, but anate with full retention of configuration.²² Thus the identity (*syn* or *anti*) of the first NH_3 ligand lost and the stereochemistry of the

(20) Eigen, M.; Kruse, W.; Maass, G.; De Maeyer, L. *Prog. React. Kinet.* **1963**, *2*, 308.

(21) Reference 2b, pp 33, 183.

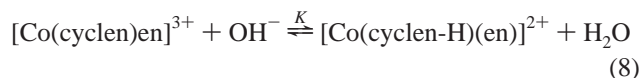
(22) Buckingham, D. A.; Clark, C. R.; Rogers, A. J.; Simpson, J. *Inorg. Chem.* **1998**, *37*, 3497.

first formed $[\text{Co}(\text{cyclen})(\text{NH}_3)\text{OH}]^{2+}$ product remain unknown. Likewise, since eq 6 refers to the reaction of the equilibrated mixture, the stereochemistry of release of the second NH_3 ligand is also unknown. The final $[\text{Co}(\text{cyclen})(\text{OH})_2]^+$ product was characterized as $[\text{Co}(\text{cyclen})\text{Cl}_2]^+$ following workup from HCl solution.²³

In alkaline solution both chelates also hydrolyze rapidly to $[\text{Co}(\text{cyclen})(\text{OH})_2]^+$ (λ_{max} , ϵ ($\text{M}^{-1} \text{cm}^{-1}$) = 547 nm, 188; 358 nm, 166⁶), but stopped-flow mixing allowed absorbances to be determined before hydrolysis was appreciable. Initial absorbances (A_{in}) for $[\text{Co}(\text{cyclen})\text{en}]^{3+}$ are plotted versus $[\text{OH}^-]$ (0.10–1.0 M, $[\text{Co}]_{\text{T}} = 8.24 \times 10^{-4} \text{ M}$) in Figure S2 (Supporting Information). These follow eq 7, with A_{lim} , K , $A_0 = 0.884$, 5.9

$$A_{\text{in}} = (A_{\text{lim}}K[\text{OH}^-] + A_0)/(1 + K[\text{OH}^-]) \quad (7)$$

M^{-1} , 0.097 (360 nm data) and 1.053, 5.1 M^{-1} , 0.419 (495 nm data). The constant, K , is interpreted as arising from deprotonation at an NH site in the cyclen ligand (cf. eq 8), and the



data correspond to $\text{p}K_{\text{a}}^{\text{c}} = 12.92 \pm 0.04$ ($K_{\text{a}}^{\text{c}} = KK_{\text{w}}/\gamma_{\pm}^2 = (1.2 \pm 0.2) \times 10^{-13} \text{ M}$). Parallel measurements on $[\text{Co}(\text{cyclen})\text{tn}]^{3+}$ (495 nm, $[\text{Co}]_{\text{T}} = 1.46 \times 10^{-3} \text{ M}$) established $K = 28 \pm 3 \text{ M}^{-1}$ ($\text{p}K_{\text{a}}^{\text{c}} = 12.21 \pm 0.05$), but a direct acidity determination for $[\text{Co}(\text{cyclen})(\text{NH}_3)_2]^{3+}$ was precluded owing to its enhanced base hydrolysis reactivity. However, the similar H/D exchange rates of the diammine and chelate complexes would suggest very similar $\text{p}K_{\text{a}}$ values. The exchange data ($k_{\text{H}}^{\text{syn}}$, $k_{\text{H}}^{\text{anti}} = (3-7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are clearly in accord with deprotonation at equatorial NH , proven in the case of the diammine, but the results do not distinguish whether exclusive syn or anti deprotonation is involved, or whether the conjugate base is a combination of syn- and anti-deprotonated forms. Deprotonation in the $(\text{N})_6\text{Co}^{3+}$ ions coincides with a color change from orange to red and is distinguished from ion association, $(\text{N})_6\text{Co}^{3+} \cdot \text{OH}^-$, which gives spectral changes only below 300 nm.^{4c}

Rate data for hydrolysis of the chelate complexes were obtained under conditions where $[\text{OH}^-]$ was in large excess over $[\text{Co}]_{\text{T}}$. For $[\text{Co}(\text{cyclen})\text{en}]^{3+}$ only one process was observable using rapid-scan spectrophotometry, and values of k_{obs} were obtained at 320 nm (cf. Table S4, Supporting Information). These are plotted against $[\text{OH}^-]$ in Figure 2A giving a clear sigmoidal variation. This behavior contrasts with that of $[\text{Co}(\text{cyclen})\text{tn}]^{3+}$ where two processes were evident (500–580, 356 nm data; $k_{\text{obs}(1)}$, $k_{\text{obs}(2)}$, cf. Table S5, Supporting Information). Both increased in rate as the OH^- concentration increased, and approached limiting rates at high concentrations, Figure 2B.

The data for both chelate complexes are interpreted in terms of the processes shown in Scheme 1. For $[\text{Co}(\text{cyclen})\text{tn}]^{3+}$ this involves initial rapid deprotonation of the cyclen ligand (K), with ring opening (k_1) in the resultant conjugate base being essentially irreversible ($k_1 \gg k_{-1}$) and corresponding to the faster of the two observed processes. Thus:

$$k_{\text{obs}(1)} = k_1K[\text{OH}^-]/(1 + K[\text{OH}^-]) \quad (9)$$

and least-squares fitting using $K = 28 \text{ M}^{-1}$ (see above) gave good correspondence between observed and calculated data for

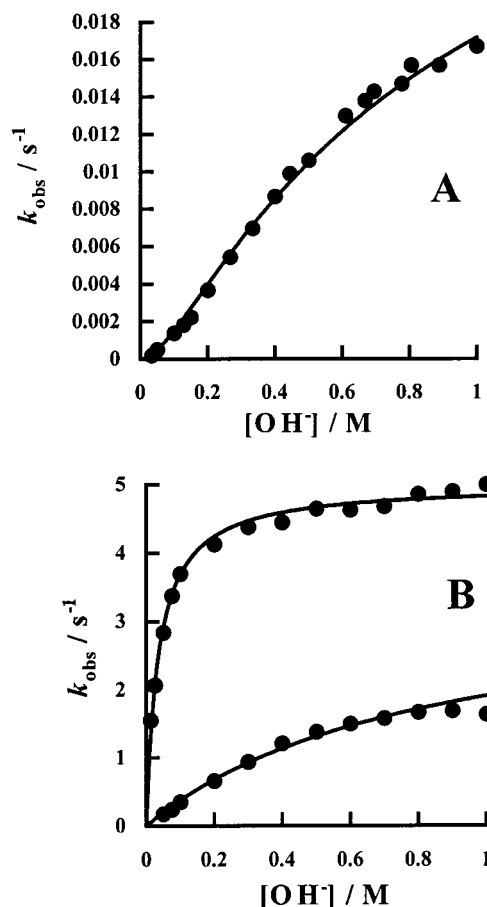
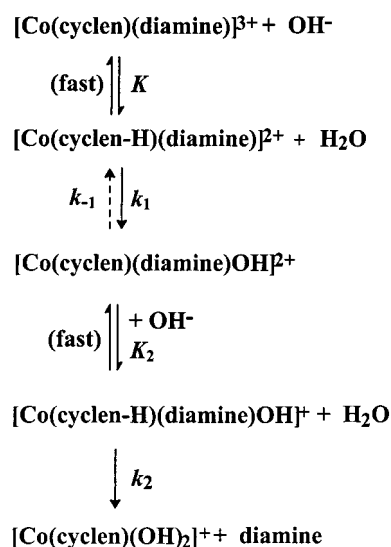


Figure 2. Plots of k_{obs} versus $[\text{OH}^-]$ for alkaline hydrolysis of $[\text{Co}(\text{cyclen})\text{en}]^{3+}$ (A), and for the two processes observed on alkaline hydrolysis of $[\text{Co}(\text{cyclen})\text{tn}]^{3+}$ (B) at $25.0 \text{ }^\circ\text{C}$ and $I = 1.0 \text{ M}$. The fitted curves are drawn using eq 11 and eqs 9 and 10, respectively, and the values of the constants given in the text.

Scheme 1



$k_1 = 5.0 \pm 0.2 \text{ s}^{-1}$. The slower process corresponds to loss of monodentate tn from $[\text{Co}(\text{cyclen})(\text{tn})\text{OH}]^{2+}$. This varied in rate according to eq 10, and data fitting gave $k_2 = 3.5 \pm 1.2 \text{ s}^{-1}$ and $K_2 = 1.2 \pm 0.8 \text{ M}^{-1}$ (see Table S5).

$$k_{\text{obs}(2)} = k_2K_2[\text{OH}^-]/(1 + K_2[\text{OH}^-]) \quad (10)$$

Table 2. Crystallographic Data for [Co(cyclen)(diamine)]X₃ Complexes (diamine = en, tn, (NH₃)₂)

chemical formula	C ₁₀ H ₂₈ Cl ₃ CoN ₆ O ₁₂	C ₁₁ H ₃₀ Br ₃ CoN ₆	C ₈ H ₂₆ Cl ₃ CoN ₆ O ₁₃
fw	589.66	545.07	579.63
T (K)	149(2)	168(2)	163(2)
λ (Å)	0.71073	0.71073	0.71073
cryst syst	P2(1)/n	Pca2(1)	Pnma
space group	monoclinic	orthorhombic	orthorhombic
a (Å)	8.892(2)	14.170(4)	17.805(4)
b (Å)	15.285(3)	10.623(3)	12.123(3)
c (Å)	15.466(3)	12.362(4)	9.493(2)
β (deg)	91.05(3)	90	90
V (Å ³)	2101.7(7)	1860.8(10)	2049.1(8)
Z	4	4	4
ρ _{calcd} (g cm ⁻³)	1.864	1.946	1.827
μ (mm ⁻¹)	0.954	7.387	1.300
R1 ^a [I > 2σ(I)]	0.0657	0.0289	0.0300
wR2 ^b (all data)	0.1666 ^c	0.0780 ^d	0.0861 ^e

^a R1 = Σ||F_o| - |F_c||/Σ|F_o|. ^b wR2 = [Σ[w(F_o² - F_c²)²]/Σ[(wF_o²)²]]^{1/2}. ^c w = 1/[σ²(F_o²) + (0.0707P)² + 6.5695P] where P = (F_o² + 2F_c²)/3. ^d w = 1/[σ²(F_o²) + (0.0477P)² + 4.5410P] where P = (F_o² + 2F_c²)/3. ^e w = 1/[σ²(F_o²) + (0.0553P)² + 2.6980P] where P = (F_o² + 2F_c²)/3.

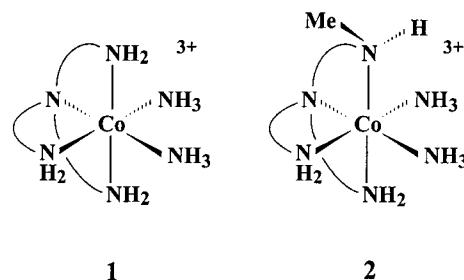
On the premise that ring opening in the en chelate conjugate base is reversible and assuming steady-state conditions in [Co(cyclen)(en)OH²⁺], then eq 11 follows. The hydrolysis data (cf.

$$k_{\text{obs}} = k_1 k_2 K K_2 [\text{OH}^-]^2 / (1 + K[\text{OH}^-])(k_{-1} + k_2 K_2 [\text{OH}^-]) \quad (11)$$

Table S4) were fitted to eq 11 by setting the value of $k_2 K_2$ equal to that determined for [Co(cyclen)(tn)OH]²⁺ (4.0 M⁻¹ s⁻¹, near identity in the base hydrolysis rates would be expected), and with use of the known value of the deprotonation constant (5.5 M⁻¹, see above). This approach gave excellent agreement between observed and calculated data for $k_1 = 0.035 \pm 0.004$ s⁻¹ and $k_{-1} = 2.9 \pm 0.6$ s⁻¹ (Table S4, Figure 2A). Because the reaction is dissociative, cyclization in the [Co(cyclen)(en)-OH]²⁺ ion ($t_{1/2} \sim 0.2$ s) is controlled, at least in part, by the rate of ligand OH⁻/solvent exchange. This should be similar to that for [Co(cyclen)(NH₃)OH]²⁺ ($k_{\text{ex}} = 8$ s⁻¹, 25 °C, I = 1.0 M NaClO₄²⁴), which implies an efficient mechanism for re-entry of the dangling NH₂ group; identity in the exchange rates would correspond to one cyclization event occurring for every two or three acts of ligand OH⁻ exchange. Cyclization in the [Co(cyclen)(tn)OH]²⁺ cation is likely to be substantially slower than in [Co(cyclen)(en)OH]²⁺ since the entering group is further removed from the Co(III) center, but ligand OH⁻/solvent exchange rates for these two intermediates will be similar.

Base hydrolysis reactivity in the Co(III)-cyclen system is very sensitive to the nature of the non-cyclen amine ligand(s), with relative rates for [Co(cyclen)(NH₃)₂]³⁺, [Co(cyclen)tn]³⁺, and [Co(cyclen)en]³⁺ lying in the order 10⁵:(7 × 10²):1. [Co(cyclen)(NH₃)₂]³⁺ ($k_{\text{OH}} = k_1 K = 2.2 \times 10^4$ M⁻¹ s⁻¹) undergoes base hydrolysis 4 × 10⁵ times faster than does [Co(tren)(NH₃)₂]³⁺ (**1**, $k_{\text{OH}} = 0.054$ M⁻¹ s⁻¹), but only 2 × 10² times faster than does *anti-p*-[Co(metren)(NH₃)₂]³⁺ (**2**, $k_{\text{OH}} = 100$ M⁻¹ s⁻¹).²⁵ This emphasizes both the labilizing influence of the cyclen ligand and the importance of a *cis sec-NH* site to enhanced reactivity. We were unable to detect appreciable hydrolysis (< 1% [Co(NH₃)₅OH]²⁺ production) for [Co(NH₃)₆]³⁺ in 1.0 M NaOH at 25 °C after 5 h. Thus, k_{OH} for this substrate must be ≤ 6 × 10⁻⁷ M⁻¹ s⁻¹, which indicates that [Co(cyclen)(NH₃)₂]³⁺ is at least 3 × 10¹⁰ (= 2 × 10⁴/6 × 10⁻⁷) more labile

than [Co(NH₃)₆]³⁺. This enhancement appears to be the largest yet observed in Co(III) substitution chemistry.



3. Structure and Reactivity. Table 2 gives crystal and structure refinement details for [Co(cyclen)(NH₃)₂](ClO₄)₃, [Co(cyclen)en](ClO₄)₃ and [Co(cyclen)tn]Br₃, and the structures of the three cations are shown in Figure 3. Bond length and bond angle data are listed in Tables S8, S12, and S16 (Supporting Information). The Co-N bond lengths all lie within the range considered normal for Co(III)-amines, with those involving *syn*- and *anti-NH* centers being somewhat shorter than those involving *ap*-NH, NH₂R, or NH₃. There are significant differences in the geometry of the *sec* amine centers, with the C-N-C bond angles for *syn*-NH (C1-N1-C8: 118.3–118.7°) being consistently larger than those for *anti*- (C4-N3-C5: 114.0–115.8°) and *ap*- (C2-N2-C3, C6-N4-C7: 88.9–94.8°) NH sites, as is usually observed in Co(III)-cyclen complexes.^{5,26} Also, the bond angles do not differ greatly from those for comparable sites in complexes of reduced overall charge (2+,

(26) X-ray structures have been reported for the following. (a) *syn*(N),*anti*(N)-[Co(cyclen)(NO₂)₂]Cl: Iitaka, Y.; Shina, M.; Kimura, E. *Inorg. Chem.* **1974**, *13*, 2886. (b) *syn*(N),*anti*(O)[Co(cyclen)((S)-Ala)]I₂·H₂O, *syn*(O),*anti*(N)[Co(cyclen)((S)-Ala)](ClO₄)₂·H₂O, and *syn*(N),*syn*(O)-[Co(cyclen)((S/R)-Ala)]ZnBr₄, see ref 5. (c) [Co(cyclen)(O₂CO)ClO₄·H₂O: Loehlin, J. H.; Fleischer, E. B. *Acta Crystallogr.* **1976**, *B32*, 3063. (d) [Co(cyclen)(acac)](ClO₄)₂·H₂O and [Co(cyclen)(Br-acac)](ClO₄)₂·0.5H₂O: Matsumoto, N.; Hirano, A.; Hara T.; Ohyoshi, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2405. (e) *syn*(S),*anti*(N)-[Co(cyclen)((S)-NH₂CH₂CH(CH₃)S)]ZnCl₄·H₂O (green isomer): Kojima, M.; Nakabayashi, K.; Ohba, S.; Okumoto, S.; Saito, Y.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 277. (f) *syn*(NH₃),*anti*(N₃)[Co(cyclen)-(NH₃)N₃]Cl_{0.5}(ClO₄)_{1.5}·H₂O, see ref 24. (g) *syn*(OH₂),*anti*(OP(H)O₂)-[Co(cyclen)(OH₂)OP(H)O₂](ClO₄): Carrington, S. J.; Buckingham, D. A.; Simpson, J.; Blackman, A. G.; Clark, C. R. *J. Chem. Soc., Dalton Trans.* **1999**, 3809. The structures of a number of alkyl-substituted cyclen complexes have also been reported, see: Buckingham, D. A.; Clark, C. R.; Rogers, A. J.; Simpson, J. *Inorg. Chem.* **1995**, *34*, 3646. Buckingham, D. A.; Clark, C. R.; Rogers, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 4050 and references therein.

(24) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Rogers, A. J. *Inorg. Chem.* **1998**, *37*, 4865.

(25) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 2041.

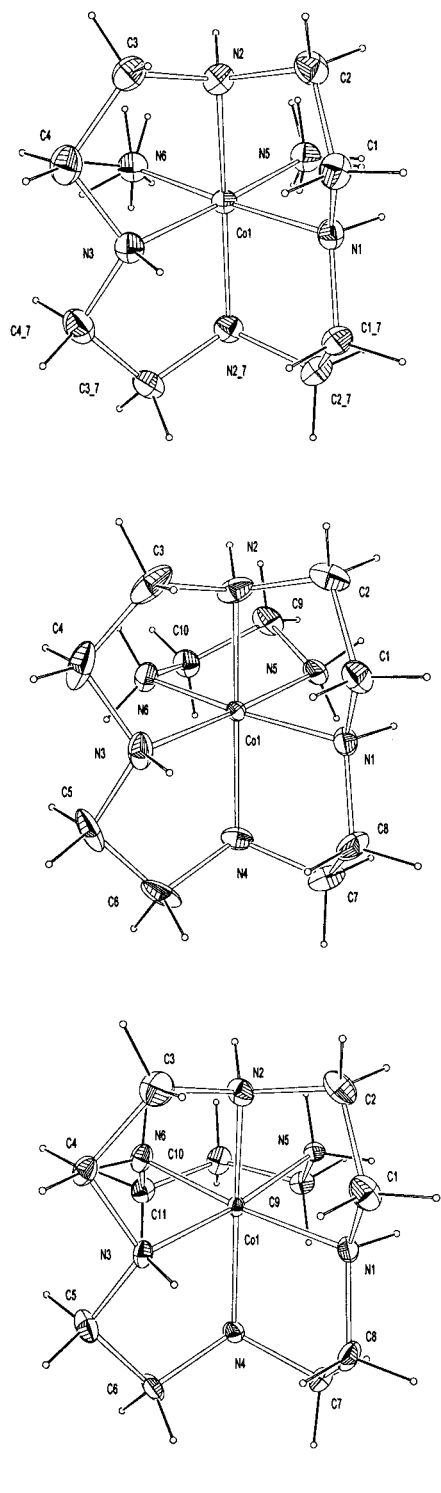
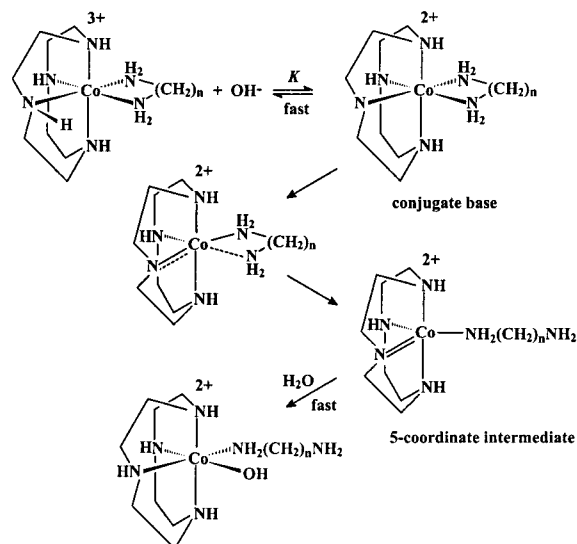


Figure 3. ORTEP diagrams for the $[\text{Co}(\text{cyclen})(\text{NH}_3)_2]^{3+}$ (A), $[\text{Co}(\text{cyclen})\text{en}]^{3+}$ (B), and $[\text{Co}(\text{cyclen})\text{tn}]^{3+}$ (C) cations. Thermal ellipsoids are drawn at the 50% confidence level.

1+).^{5,26a-d} The structural differences between *syn* and *anti* sites in the 3+ charged complexes are not reflected in their essentially identical *NH* exchange rates, but the slower to exchange *ap-NH* centers are distinctly less strained. The bite angles for the *en* (83.2°) and *tn* (83.6°) chelate rings are remarkably similar and are not too different from the corresponding angle in the diammine complex ($\text{N5-Co1-N6} = 84.2^\circ$). Clearly, the conformation of the macrocyclic ligand controls this angle to a considerable degree.

Scheme 2

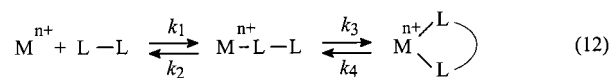


Previously, we argued²² that the positioning of a *cis-NH* proton in the parent acido-Co(III) complex was crucial to high base hydrolysis reactivity, with repulsive overlap between the lone pair in the amido base derived from *syn-NH* and the filled bonding and nonbonding orbitals of the leaving group assisting its departure.²⁷ However, the leaving groups in the present complexes are not too different in basicity,²⁸ the complexes possess essentially the same geometry, and each has a comparably acidic *syn-NH* proton in the correct orientation. This makes it all the more surprising that the rates of first Co–N bond cleavage should differ so widely. Clearly the energy barrier for formation of the dissociative 5-coordinate intermediate is significantly higher for the $[\text{Co}(\text{cyclen})(\text{diamine})]^{3+}$ ions than it is for $[\text{Co}(\text{cyclen})(\text{NH}_3)_2]^{3+}$. We interpret this in terms of retention of diamine chelate character in the transition state for ring opening, cf. Scheme 2, where rate-determining Co–N bond cleavage and concomitant production of the trigonal bipyramidal intermediate become increasingly more difficult the greater the degree of structural restriction imposed by the diamine chelate. Formation of the intermediate requires expansion of the bond angles in the equatorial plane from ca. 90° to ca. 120°, and the in-plane bidentate ligand will hinder expansion provided the Co–N bond is not fully broken in the transition state. Loss of NH_3 from the $[\text{Co}(\text{cyclen-H})(\text{NH}_3)_2]^{2+}$ conjugate base is not restricted in this way, and the more rapid ring opening of $[\text{Co}(\text{cyclen-H})\text{tn}]^{2+}$ compared to $[\text{Co}(\text{cyclen-H})\text{en}]^{2+}$ ($k_1 = 5.0$ versus 0.035 s^{-1} , respectively) is in accord with the *tn* chelate ring having the greater flexibility.

The formation constant of a metal–chelate complex is related to the rate constants for the separate bond-making and bond-breaking steps by the expression $K_f = k_1 k_3 / k_2 k_4$ (eq 12), and there is increasing evidence from studies on exchange labile

(27) Sargeson et al. (ref 3e) interpret data for base hydrolysis of $[\text{Co}(\text{ditame})\text{Cl}]^{2+}$ (ditame = 2,2'-dimethyl-2,2'-iminodimethylene-bis(1,3-propanediamine)) in terms of *trans sec-NH* deprotonation and reaction via a stabilized square pyramidal intermediate. The base hydrolysis rate constant ($k_{\text{OH}} = 68 \text{ M}^{-1} \text{ s}^{-1}$) is 250-fold greater than that for $[\text{Co}(\text{NH}_3)_3\text{Cl}]^{3+}$. Such observations suggest that reacting $(\text{N})_5\text{CoX}^{n+}$ systems have a range of options, depending on the nature of $(\text{N})_5$, both as to *NH* deprotonation site (or sites) and as to 5-coordinate intermediate geometry.

(28) $\text{p}K_a$ values for NH_4^+ , tnH_2^{2+} , and enH_2^{2+} are 9.50, 9.12, and 7.49, respectively (25 °C, $I = 1.0 \text{ M}$ (KNO_3)), see ref 16. Substitution of a $(\text{N})_5\text{Co}^{\text{III}}$ center for H^+ in enH_2^{2+} does not appreciably change its acidity (<0.1 p*K* unit): Clark, C. R., unpublished data.



systems^{2a} indicating that the processes of metal–ligand bond formation (k_1 , k_3) and loss of monodentate ligand (k_2) are not the principal factors in determining heightened stability; the slowness of the ring-opening reaction (k_4) accounts for the high formation constants of Co(II) and Ni(II) chelates.^{8,29,30} These species also react via dissociative pathways, and it seems likely that chelate ring-opening rates are similarly controlled by the ability of the complex to adapt its geometry in the drive to produce an intermediate of reduced coordination number. We

(29) Aizawa, S.; Iide, S.; Matsuda, K.; Funahashi, S. *Inorg. Chem.* **1996**, *35*, 1338.

(30) Soyama, S.; Ishii, M.; Funahashi, S.; Tanaka, M. *Inorg. Chem.* **1992**, *31*, 536.

suggest that this is limited more by the nature of the L–L bidentate than by intrinsic differences in M–L bond strength.

Supporting Information Available: Tables listing H/D exchange data as a function of pD for *syn,anti*-[Co(cyclen)(NH₃)₂]³⁺, *syn,anti*-[Co(cyclen)en]³⁺, and *syn,anti*-[Co(cyclen)tn]³⁺ in D₂O, and rate constants as a function of [OH[−]] for hydrolysis of *syn,anti*-[Co(cyclen)en]³⁺ and *syn,anti*-[Co(cyclen)tn]³⁺ (*I* = 1.0 M (NaClO₄), 25.0 °C); detailed crystallographic data, bond lengths and angles, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for *syn,anti*-[Co(cyclen)(NH₃)₂](ClO₄)₃·H₂O, *syn,anti*-[Co(cyclen)en](ClO₄)₃, and *syn,anti*-[Co(cyclen)tn]Br₃. Figures showing ¹H NMR spectra for decay of the *syn* and *anti* *sec*-NH protons and time-zero absorbances versus [OH[−]] for [Co(cyclen)en]³⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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