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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. 11. Synthesis, Characterization, and Reaction Kinetics of Some *cis*-Chlorobis(1,3-diaminopropane)(alkylamine)cobalt(III) Complexes

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The *cis*-$CoCl(tmd)_2(A)^{2+}$ cation (A = NH_3, $MeNH_2$, $EtNH_2$, *n*-$PrNH_2$, *n*-$BuNH_2$, *i*-$BuNH_2$, and $BzNH_2$) is produced when *trans*-$[CoCl_2(tmd)_2](ClO_4)$, dissolved in dimethylacetamide (DMA), is reacted with aqueous, alcoholic, or DMA solutions of the amine. Tetrachlorozincate(II) and perchlorate salts have been isolated and characterized by analysis and ^{13}C NMR spectra. The cis configuration has been established by resolution of the complexes with A = $MeNH_2$ and $BzNH_2$. Rates of both acid and base hydrolysis are about 100 times faster than their bis(ethylenediamine) analogues due to a decrease of about 10 kJ mol^{-1} in the activation energies. The activation parameters for both reactions show the same trends with variation in A. Second-order rate constants for the Hg^{2+}-assisted aquation and Fe^{2+} reduction of this series of complexes have also been measured.

Introduction

Considerable reaction rate data have been accumulated for *cis*-$CoCl(en)_2(A)^{2+}$ complexes, where A is an aliphatic primary or aromatic heterocyclic tertiary amine.[1,2] However, the influence of the diamine on the kinetic parameters has not been investigated to any great extent.[1] In this paper, we describe the synthesis of some *cis*-$CoCl(tmd)_2(A)^{2+}$ (A = aliphatic primary amine) complexes.[3] We are thus able to study the influence of the six-membered chelate rings on the rates of acid and base hydrolysis for these chloropentaaminecobalt(III) systems. In addition, these complexes allow a comparison of the visible absorption and chiroptical parameters with their bis(ethylenediamine) analogues.

Experimental Section

The commercially available amines were used without further purification. Ammonia was used as an aqueous solution ($\rho = 0.880$), methylamine as a 40% aqueous solution, ethylamine as a 33% alcoholic solution, and the other amines as pure liquids. All other chemicals were AR or the best Reagent Grade available.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these complexes should be treated as potentially explosive and handled with care.

***trans*-Dichlorobis(1,3-diaminopropane)cobalt(III) Perchlorate,[4] *trans*-$[CoCl_2(tmd)_2]ClO_4$.** A solution of 1,3-diaminopropane (62 g) in water (200 mL) was quickly added (over 1–2 min) to a solution of $CoCl_2 \cdot 6H_2O$ (100 g) in water (200 mL) which was stirred with a good stream of oxygen gas. A green precipitate formed but this slowly dissolved as the reaction proceeded and a dark brown solution was obtained after 1 h of oxygenation. Hydrochloric acid (150 mL, 12 M) and perchloric acid (50 mL, 72%) were separately added, and the solution was warmed on a steam bath for 10 min. Green crystals of the desired product deposited from the hot solution which was rapidly cooled to room temperature in ice before filtration. The product (60 g, 62%) was washed with 2-propanol and then ether and air-dried.

In certain cases, the mother liquor slowly deposited a mixture of green and red crystals, but the nature of this latter product has not yet been established.

***cis*-Chlorobis(1,3-diaminopropane)(amine)cobalt(III) Salts, *cis*-$[CoCl(tmd)_2(amine)]ZnCl_4$.** *trans*-$[CoCl_2(tmd)_2]ClO_4$ (10 g) was stirred into 40 mL of DMA to give a green solution. Amine, 1.5 times the theoretical amount, was added as quickly as possible. (The green starting material seems to recrystallize from the initial green solution after about 5 min at room temperature.) The color changed to violet and this color change was accelerated by heating. (Heating should not be excessive as most of the amines are low boiling liquids.) After overnight stirring at room temperature (17–20 h) the solution was filtered from a small amount of unreacted starting material and HCl (5 mL, 12 M), $ZnCl_2$ (15 g), and 2-propanol (80 mL) were successively added. The purple-red $ZnCl_4^{2-}$ salt (often contaminated with green starting material) usually crystallized within 30 min and was collected by filtration (8–12 g). One recrystallization from the minimum volume of 60 °C 0.1 M HCl (50–100 mL), with HCl (10 mL, 12 M) and $ZnCl_2$ (15 g) added after filtration of small traces of undissolved solid, gave 4.5–5 g of pure *cis*-$[CoCl(tmd)_2(amine)]ZnCl_4$. Tetrachlorozincate(II) salts for amine = $MeNH_2$, $EtNH_2$, *n*-$PrNH_2$, *n*-$BuNH_2$, and *i*-$BuNH_2$ were anhydrous while those of amine = NH_3 and $BzNH_2$ crystallized as monohydrates.

With amine = *i*-$PrNH_2$, *sec*-$BuNH_2$, and 3,5-dimethylpyridine, the reaction did not appear to take place, while with amine = cyclohexylamine, a favorable color change took place, but only unreacted starting material was recovered in the workup.

***cis*-$[CoCl(tmd)_2(amine)](ClO_4)_2$.** The appropriate tetrachlorozincate(II) salt (2 g) was dissolved in 20–40 mL of warm 0.1 M HCl. $HClO_4$ (5 mL, 72%) and $NaClO_4 \cdot H_2O$ (3 g) were added, and the solution was allowed to cool slowly to room temperature and then in ice. About 1–1.3 g (60–70%) of the diperchlorate salts was collected by filtration and washed with 2-propanol and then ether and air-dried.

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Table I. ^{13}C NMR Spectral Data (DMF or H_2O) for Some *cis*-$CoCl(tmd)_2(A)^{2+}$ Complexes[a]

	NH_3		$MeNH_2$		$EtNH_2$	*n*-$PrNH_2$	*n*-$BuNH_2$	*i*-$BuNH_2$	$BzNH_2$	
Assignment[b]	DMF	H_2O	DMF	H_2O	DMF	DMF	DMF	DMF	DMF	H_2O
Aromatic C									139.01 129.63 129.10 128.30	137.59 130.01 129.50 129.30
C(1)			28.84	28.91	39.13(?)	45.53	43.49	30.29	47.50	47.45
C(2)					16.52	24.89	33.85	51.09		
C(3)						11.27	20.29	20.30		
C(4)							13.78			
C(B)	39.22	39.56 39.37 39.06 38.79 38.58	39.05 38.70 38.43	39.27 38.98 38.37	39.13(?) 38.92 38.78 38.52	39.00 38.77 38.36	39.02 38.82 38.38	39.17 38.51	38.99 38.91 38.59	39.28 39.13 38.64 38.31
C(A)	26.09	26.18 25.89 25.50 24.72	25.82 25.27	25.82 25.49	25.96 25.42	25.81 25.27	25.82 25.31	25.93 25.40	25.84 25.48	25.82 25.48

[a] At ~25 °C, ppm relative to dioxane = 67.4 ppm. [b] Assignments in the order NH_2–CH_2(1)-CH_2(2)–CH_2(3)–CH_3(4) and NH_2–CH_2(B)–CH_2(A)–CH_2(B)–NH_2 for the aliphatic carbon atoms. Doubtful assignments are indicated (?).

Table II. Analytical Data and Visible Absorption Spectral Parameters for Some *cis*-[$CoCl(tmd)_2(A)$] Y Salts

A	Y^{2-}	Formula wt	Ionic Cl^- Calcd	Ionic Cl^- Found	Non-ClO_4^- Cl^- Calcd	Non-ClO_4^- Cl^- Found	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{min}, nm (ϵ, M^{-1} cm^{-1})	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	λ_{min}, nm (ϵ, M^{-1} cm^{-1})
NH_3	$ZnCl_4 \cdot H_2O$	486.6	29.2	29.3	36.4	37.8	548 (47.6)[a,c]	425 (15.2)	370 (64.1)	338 (36.9)
	$(ClO_4)_2$	459.5			7.7	7.8	548 (47.9)[b]	425 (16.0)	370 (64.6)	338 (36.1)
$MeNH_2$	$ZnCl_4$	481.4								
	$(ClO_4)_2 \cdot H_2O$	490.5			7.24	7.27	540 (51.2)[b]	427 (13.0)	370 (63.7)	336 (33.2)
$EtNH_2$	$ZnCl_4$	495.4			35.8	35.1				
	$(ClO_4)_2 \cdot H_2O$	505			7.03	6.90	540 (54.4)[b]	430 (14.9)	373 (66.0)	338 (36.2)
n-$PrNH_2$	$ZnCl_4$	509.4			34.9	34.5				
	$(ClO_4)_2$	501			7.08	6.91	540 (53.4)[b]	430 (12.6)	372 (63.6)	338 (31.9)
n-$BuNH_2$	$ZnCl_4$	523.4			33.9	33.7				
	$(ClO_4)_2$	515			6.89	6.91	532 (55.4)[b]	430 (13.7)	372 (65.3)	338 (35.8)
i-$BuNH_2$	$ZnCl_4$	523.4			33.9	33.0				
	$(ClO_4)_2 \cdot {}^1/_2H_2O$	524			6.77	6.77	532 (55.2)[b]	428 (12.5)	372 (66.1)	338 (34.6)
$BzNH_2$	$ZnCl_4 \cdot H_2O$	574.6	24.7	24.6	30.9	31.3	535 (61.0)[a]	432 (14.9)	370 sh (84.5)	
							535 (59.0)[b]	432 (14.4)	370 sh (81.8)	
	$(ClO_4)_2$	548.5			6.47	6.43	534 (61.2)[b]	432 (14.9)	365 sh (86.1)	

[a] In 1.0 M $HClO_4$. [b] In 0.1 M $HClO_4$. [c] There is a pronounced shoulder at ~480 nm on the low-wavelength side of this band.

The salts are readily soluble in dimethylformamide. Anhydrous salts were obtained for A = NH_3, *n*-$PrNH_2$, *n*-$BuNH_2$, and $BzNH_2$ while the others were hemi- (A = *i*-$BuNH_2$) or monohydrates (A = $MeNH_2$, $EtNH_2$).

Resolution of *cis*-[CoCl(tmd)$_2$(BzNH$_2$)]ZnCl$_2$. The racemic salt (5 g) was dissolved in 80 mL of warm 0.01 M HCl and 3 g of solid NH_4-(+)-BCS[3] was stirred in. A purple precipitate deposited over several days and was collected in crops. After 2.0 g (four crops) of the less soluble diastereoisomeride had been collected, HCl (10 mL, 12 M) and $ZnCl_2$ (10 g) were added to give a $ZnCl_4^{2-}$ salt (crop 5). The CD spectrum of the products was recorded in 0.1 M $HClO_4$ and the data are, in order, crop number, weight (g), $\Delta\epsilon$ (470 nm, M^{-1} cm^{-1}): 1, 0.13, +0.098; 2, 0.61, +0.104; 3, 1.27, +0.114; 4, 0.044, +0.122; 5, 0.82, just negative. Crops 1–4 were combined and dissolved in 20 mL of 12 M HCl. Solid $ZnCl_2$ (10 g) was stirred in and the $(+)_{589}$-$ZnCl_4^{2-}$ salt deposited (0.78 g). Chiroptical properties are $[M]_{589} = +12$, $[M]_{529} = +76$, $[M]_{450} = 0$, and $[M]_{410} = +20$ (sh) deg mol^{-1} m^{-1}. $\Delta\epsilon(568) = -0.102$, $\Delta\epsilon(528) = 0$, $\Delta\epsilon(468) = +0.168$, $\Delta\epsilon(360) = 0$, $\Delta\epsilon(350) = -0.007$, and $\Delta\epsilon(340) = 0$ M^{-1} cm^{-1}. Treatment of the (+)-chloro complex with excess Hg^{2+} rapidly produces $(+)_{589}$-$Co(tmd)_2(BzNH_2)(OH_2)^{3+}$ with the following chiroptical parameters: $[M]_{589} = +5$, $[M]_{515} = +93$, $[M]_{460} = 0$, $[M]_{442} = -13$, $[M]_{414} = 0$ deg mol^{-1} m^{-1}. $\Delta\epsilon(550) = -0.123$, $\Delta\epsilon(515) = 0$, $\Delta\epsilon(468) = +0.228$, $\Delta\epsilon(368) = 0$, $\Delta\epsilon(355) = -0.013$, $\Delta\epsilon(340) = 0$ M^{-1} cm^{-1}.

Resolution of *cis*-[CoCl(tmd)$_2$(MeNH$_2$)](ClO$_4$)$_2$·H$_2$O. The racemic salt (2 g) was dissolved in 40 mL of 60 °C aqueous 0.1 M tartaric acid and 2 g of solid Na-(+)-AsOT[3] was stirred in. Crops of the less soluble diastereoisomeride were collected after 3 and 20 h at room temperature. Circular dichroism parameters for samples dissolved in 3 M $HClO_4$ are the following: crop 1 $\Delta\epsilon(570) = +0.066$, $\Delta\epsilon(530) = 0$, $\Delta\epsilon(485) = -0.091$, $\Delta\epsilon(425) = 0$; crop 2 (same wavelengths) $\Delta\epsilon = +0.057, 0, -0.090, 0$, respectively.

Kinetic Data. Rates of acid hydrolysis (1.0 M $HClO_4$) were measured by Cl^- titration and by spectrophotometry,[5,6] while base hydrolysis rates (0.1 M NaCl) were measured using a pH-Stat.[7–9] Appropriate rate constants were calculated from the extent of reaction vs. time data using the previously described equations.[5–9a]

Mercury(II)-assisted aquation rate constants (μ = 1.0 M, 298 K) were obtained using a hand-powered double syringe stopped-flow system coupled to a 5.0-cm flow-through spectrophotometer cell. Pseudo-first-order rate constants were calculated using the half-life method as the $[Hg^{2+}]$ was always >10 times the complex ion concentration.

Second-order rate constants for the iron(II) reduction reactions were obtained spectrophotometrically by use of the repetitive scan technique or at 535 nm. The complex, as the tetrachlorozincate salt, was added to 5 mL of $NaClO_4$ (0.6 M in 0.1 M $HClO_4$) to form a ca. 10^{-3} M solution. Standardized ($KMnO_4$) $FeSO_4$ (5 mL, 0.7 M in 0.1 M $HClO_4$) was added and the solutions were mixed before transferring to a 5.0-cm jacketed spectrophotometer cell. Reactions were followed for at least 7 half-lives.

Spectral Measurements. Visible absorption spectra (three determinations, 320–650 nm) were recorded in 0.1 M $HClO_4$ using matched 5.00-cm cells, while IR spectra were run in Nujol mulls. ^{13}C NMR spectra (in DMF) and CD spectra (in 0.1 M $HClO_4$) were obtained as previously described.[9b]

Results and Discussion

Characterization of the Complexes. Seven *cis*-[$CoCl(tmd)_2(A)$][$ZnCl_4^{2-}$ or $2ClO_4^-$] salts have been synthesized by reaction of the amine (A = NH_3, $MeNH_2$, $EtNH_2$, *n*-

$PrNH_2$, n-$BuNH_2$, i-$BuNH_2$, $BzNH_2$)[3] with *trans*-$[CoCl_2(tmd)_2]ClO_4$ in dimethylacetamide. The presence of the amine (except NH_3) has been confirmed by ^{13}C NMR (Table I) and the cis configuration of the product by optical resolution (attempted only for A = $MeNH_2$ and $BzNH_2$). In our hands, the synthetic reaction was only successful for amines of the NH_2CH_2R type.

The visible absorption spectra of these chloropentaamine complexes are characterized by two maxima at 532–548 and 370–372 nm with molar extinction coefficients of 48–60 and 64–66 M^{-1} cm^{-1}, respectively (Table II). The analogous *cis*-$CoCl(en)_2(A)^{2+}$ complexes have maxima in similar positions (525, 368 nm) but with distinctly increased molar extinction coefficients (ϵ 75–80, 85–90 M^{-1} cm^{-1}, respectively).[10] This decrease in intensity for AA = tmd is also reflected in a decrease in $\Delta\epsilon$ for the circular dichroism spectra. ($\Delta\epsilon_{max}(475) = \pm 0.286$ M^{-1} cm^{-1} for AA = en, A = $BzNH_2$[11] while $\Delta\epsilon_{max}(470) = \pm 0.168$ M^{-1} cm^{-1} for AA = tmd, A = $BzNH_2$). A similar decrease in CD intensity has been observed for the $Co(en)_x(tmd)_{3-x}{}^{3+}$ complexes as x decreases,[12] although this decrease is not observed in the *uns-cis*-$Co(trien)(AA)^{3+}$ (AA = en, tmd) series.[13]

There are three possible arrangements of *cis*-$(tmd)_2$ rings in the chair conformation[14,15] but only one isomer was detected for any particular complex synthesized here. Strain energy minimization calculations[14] show the energy differences between the three arrangements to be small and thus the one found in the solid state may depend largely on the requirements of the crystal lattice. On the basis of the ^{13}C NMR spectral analysis of the bis((*R*,*S*)-2,4-pentanediamine)cobalt(III) complexes by Boucher and Bosnich[15] we would expect a *cis*-(C_2)-*syn*[15] (or A,B type[14]) configuration for most of the complexes isolated here, as we observe a ^{13}C doublet for the central methylene carbon atom (atom A, Table I). For A = NH_3, the ^{13}C NMR in DMF would suggest a *cis*-(C_2)-*anti*[15] (or B,B type[14]).

Kinetic Data. Table III presents the pseudo-first-order rate constants, k_H, defined by the equation

$$-d[\text{complex}]/dt = k_H[\text{complex}]$$

for the disappearance of *cis*-$CoCl(tmd)_2(A)^{2+}$ in 1.0 M $HClO_4$ solution at various temperatures. Excellent isosbestic points were observed in the spectrophotometric scans for each of the complexes in the 300–700-nm range and these were in good agreement with those predicted for the reaction

$$cis\text{-}CoCl(tmd)_2(A)^{2+} + H_2O = cis\text{-}Co(tmd)_2(A)(OH_2)^{3+} + Cl^-$$

Rate constants calculated from chloride release measurements agreed well with those determined spectrophotometrically. Although $ZnCl_4{}^{2-}$ salts were used, there was no evidence for the reverse reaction and the spectrum of the product after 10 half-lives agreed well with the spectrum of the corresponding aqua complex produced by Hg^{2+}-assisted aquation of the chloro ligand. The above observations suggest that isomerization to a trans configuration plays no significant role in the aquation process.

Table IV presents the second-order rate constants, k_{OH}, defined by the equation

$$-d[\text{complex}]/dt = k_{OH}[\text{complex}][OH^-]$$

for the reaction

$$cis\text{-}CoCl(tmd)_2(A)^{2+} + OH^- = cis\text{-} + trans\text{-}CoOH(tmd)_2(A)^{2+} + Cl^-$$

in 0.1 M NaCl at various temperatures. These rate constants were determined for the perchlorate salts using the pH-Stat technique described previously.[8] Acidification of the product after complete hydrolysis and measurement of the visible absorption spectrum of the aqua ion so produced indicates some isomerization (see ref 16 for the technique used), but

Table III. Pseudo-First-Order Rate Constants (10^4k_H, s^{-1}) for the Aquation of Some *cis*-$CoCl(tmd)_2(A)^{2+}$ Complexes in 1.0 M $HClO_4$ [a]

NH_3	1.69 ± 0.08^b (1.69) [324.2], 3.23 ± 0.15^b (3.16) [329.7], 4.38 ± 0.22^a (4.56) [333.0], 6.81 ± 0.34^a (6.73) [336.6], 8.39 ± 0.42^b (8.32) [338.6], 10.8 ± 0.5^a (10.93) [341.2]
$MeNH_2$	3.50 ± 0.03^a (3.49) [318.9], 4.62 ± 0.05^a (4.58) [321.8], 5.87 ± 0.07^a (5.92) [324.6], 8.32 ± 0.13^a (8.34) [328.4], 12.21 ± 0.25^b (12.16) [332.7]
$EtNH_2$	4.39 ± 0.08^b (4.34) [318.9], 5.74 ± 0.05^a (5.83) [321.8], 7.76 ± 0.07^b (7.73) [324.6], 11.26 ± 0.10^a (11.24) [328.4], 17.00 ± 0.18^b (16.98) [332.7]
n-$PrNH_2$	4.52 ± 0.07^c (4.51) [318.9], 6.22 ± 0.08^b (6.25) [321.8], 8.59 ± 0.57^a (8.51) [324.6], 12.64 ± 0.15^a (12.82) [328.4], 20.32 ± 0.53^a (20.18) [332.7]
n-$BuNH_2$	5.00 ± 0.11^c (4.95) [318.9], 6.77 ± 0.18^b (6.80) [321.8], 9.06 ± 0.28^a (9.19) [324.6], 13.85 ± 0.28^d (13.73) [328.4], 21.41 ± 0.43^b (21.38) [332.7]
i-$BuNH_2$	5.05 ± 0.17^a (4.84) [318.9], 6.52 ± 0.18^a (6.70) [321.8], 8.82 ± 0.23^a (9.14) [324.6], 13.83 ± 0.48^a (13.81) [328.4], 22.22 ± 0.65^b (21.77) [332.7]
$BzNH_2$	2.23 ± 0.12^b (2.35) [317.4], 4.76 ± 0.28^e (4.36) [324.2], 5.99 ± 0.30^b (5.62) [326.2], 7.85 ± 0.39^a (8.30) [330.3], 9.68 ± 0.50^b (10.09) [332.4]

[a] Rate constants determined spectrophotometrically by either spectral scan or fixed-wavelength techniques. The rate constants for A = $BzNH_2$ include five determinations from released Cl^- data (titrimetric). Values in parentheses are calculated from the activation parameters cited in Table VII. The superscripts a–e indicate 1–5 determinations at the cited temperature (in square brackets), respectively. The numbers quoted for the rate constants are the mean ± the standard deviation of 7–12 point-by-point calculations, for each run, spanning at least 2 half-lives.

Table IV. Second-Order Rate Constants (M^{-1} s^{-1}) for the Reaction of *cis*-[CoCl(tmd)$_2$(A)]Y$_2$ with OH^- in 0.1 M NaCl

		Temperature,[b] K					
		273.7		287.7		298.2	
Complex[a]	Formula wt used	k_{OH}(obsd)[c]	k_{OH}(calcd)[d]	k_{OH}(obsd)[c]	k_{OH}(calcd)[d]	k_{OH}(obsd)[c]	k_{OH}(calcd)[d]
[M(NH$_3$)](ClO$_4$)$_2$	460	22.6 ± 2.2	22.1	137 ± 6	141	505 ± 42	508
[M(MeNH$_2$)](ClO$_4$)$_2$·H$_2$O	491	61.0 ± 3.5	60.3	269 ± 23	272	777 ± 87	765
[M(EtNH$_2$)](ClO$_4$)$_2$·H$_2$O	505	49.7 ± 3.8	47.6	267 ± 34	281	933 ± 72	952
[M(*n*-PrNH$_2$)](ClO$_4$)$_2$	501	47.3 ± 4.6	45.7	275 ± 25	284	1024 ± 117	997
[M(*n*-BuNH$_2$)](ClO$_4$)$_2$	515	40.3 ± 3.3	40.6	266 ± 8	257	902 ± 43	916
[M(*i*-BuNH$_2$)](ClO$_4$)$_2$·$^1/_2$H$_2$O	524	78.4 ± 2.3		Not determined	445	1470 ± 144	
[M(BzNH$_2$)](ClO$_4$)$_2$	549	82.8 ± 5.8	79.2	421 ± 65	434	1492 ± 116	1397

[a] M = *cis*-CoCl(tmd)$_2$. [b] At temperatures of 273.7, 287.7, and 298.2 K, the pH ranges of 10.6–10.8, 8.8–9.5, and 8.2–8.5, respectively, gave half-lives of 3.5–6 min using 0.117 M NaOH. [c] Mean ± the standard deviation of at least three determinations. [d] Calculated from the activation parameters cited in Table VIII.

Table V. Second-Order Rate Constants for the Hg^{2+}-Assisted Aquation of Some *cis*-CoCl(tmd)$_2$(A)$^{2+}$ Complexes at 298.2 K (μ = 1.0 M)[a,b]

A	[Hg^{2+}], M	$t_{1/2}$,[c] s	10^2k_1, s^{-1}	k_{Hg}, M^{-1} s^{-1}	10^2k_{Hg},[d] M^{-1} s^{-1}
NH$_3$	0.0372	153 ± 1.0	0.453 ± 0.003	0.122 ± 0.001	0.566
MeNH$_2$	0.0398	10.4 ± 0.7	6.68 ± 0.4	1.70 ± 0.11	1.46
EtNH$_2$	0.0372	8.93 ± 0.6	7.76 ± 0.5	2.09 ± 0.14	0.883
n-PrNH$_2$	0.0398	8.17 ± 0.4	8.49 ± 0.4	2.13 ± 0.10	1.02
n-BuNH$_2$	0.0398	8.44 ± 0.4	8.21 ± 0.4	2.06 ± 0.09	1.20
i-BuNH$_2$	0.0372	9.37 ± 0.6	7.39 ± 0.5	1.98 ± 0.13	1.19
BzNH$_2$	0.0372	25.3 ± 1.6	2.73 ± 0.17	0.74 ± 0.05	

[a] Complexes used as $ZnCl_4^{2-}$ salts. [b] [$HClO_4$] = 0.4 M, [Co(III)] ~ 2 × 10^{-3}, [NO_3^-] ~ 0.08 M. [c] Mean of four determinations. [d] Data[1] for *cis*-CoCl(en)$_2$A^{2+} analogues (μ = 0.2 M).

Table VI. Second-Order Rate Constants for the Fe^{2+} Reduction of Some *cis*-CoCl(AA)$_2$(A)$^{2+}$ Complexes (μ = 2.0 M)[a]

		10^4k_{Fe},[b] M^{-1} s^{-1}					
		298.2 K		303.2 K		308.2 K	
A	AA	Obsd	Calcd[c]	Obsd	Calcd[c]	Obsd	Calcd[c]
NH$_3$	tmd	10.1 ± 0.09	10.2	15.9 ± 0.11	16.2	25.4 ± 0.4	25.3
		10.5 ± 0.14				25.7 ± 0.2	
MeNH$_2$	tmd	10.2 ± 0.04	10.0	15.1 ± 0.44	16.2	26.0 ± 0.4	25.7
		10.2 ± 0.09		16.4 ± 0.15		26.2 ± 0.3	
EtNH$_2$	tmd	10.8 ± 0.09	10.8	17.2 ± 0.18	17.0	26.8 ± 0.5	26.4
		10.5 ± 0.18		18.0 ± 0.18		25.1 ± 0.5	
n-PrNH$_2$	tmd	10.1 ± 0.01	10.3	17.9 ± 0.32	17.5	28.8 ± 0.3	29.0
		10.2 ± 0.01		18.0 ± 0.18		28.5 ± 0.4	
n-BuNH$_2$	tmd	8.96 ± 0.04	9.31	15.0 ± 0.18	15.4	25.7 ± 0.2	25.2
		9.47 ± 0.09		16.6 ± 0.18		24.2 ± 0.2	
i-BuNH$_2$	tmd	11.7 ± 0.3	11.5	18.8 ± 0.14	18.4	28.9 ± 0.3	29.0
		11.3 ± 0.1		18.2 ± 0.18		29.4 ± 0.4	
		11.4 ± 0.6					
BzNH$_2$	tmd	14.9 ± 0.09	15.0	23.8 ± 0.4	23.4	35.8 ± 0.5	36.0
		15.1 ± 0.09		23.1 ± 0.3		36.3 ± 0.4	
MeNH$_2$	en	0.761 ± 0.028					
n-BuNH$_2$	en	0.722 ± 0.023					

[a] [$FeSO_4$] ~ 0.4 M, [$HClO_4$] = 0.1 M, [$NaClO_4$] ~ 0.3 M, [Co^{3+}] ~ 10^{-3} M as $ZnCl_4^{2-}$ salts. [b] Errors cited are the standard deviations from the mean of 8–16 point-by-point calculations over 3 half-lives. [c] Calculated using the activation parameters cited in Table IX.

the actual amount of trans hydroxo produced cannot be estimated at this stage. First, we do not know the spectral parameters for the *trans*-Co(tmd)$_2$(A)(OH$_2$)$^{3+}$ species and, second, we do not know the rate of trans hydroxo to cis hydroxo isomerization, although it cannot be greater than the rate of base hydrolysis. Starting with (+)$_{589}$-CoCl(tmd)$_2$(BzNH$_2$)$^{2+}$, there is 50% optical retention found in the resultant aqua complex (after acidification). Consequently 50% trans can be considered as an upper limit (assuming 0% racemization) but this is bound to be high.

Analysis of the change in stereochemistry for the *cis*-bis(ethylenediamine) analogues[16] (A = RNH$_2$) gives the amount of trans hydroxo product as 10–20%. Our results suggest that a similar figure for the *cis*-CoCl(tmd)$_2$(A)$^{2+}$ complexes would be reasonable.

The second-order rate constants (k_{Hg}) obtained at 298 K (μ = 1.0 M) for the mercury(II)-assisted aquation reactions are given in Table V and the rate constants (k_{Fe}) for the Fe^{2+} reduction reactions are listed in Table VI.

Activation parameters, E_a, log (PZ), and $\Delta S^{\ddagger}_{298}$ (Tables VII, VIII, and IX) have been calculated from the temperature dependence of k_H, k_{OH}, and k_{Fe} using the standard methods and equations.[6,7]

Comparison with CoCl(en)$_2$(A)$^{2+}$ Systems. The replacement of a five-membered ethylenediamine ring by a six-membered trimethylenediamine ring in an octahedral cobalt(III) complex generally results in the labilization of a coordinated aniono ligand. Most studies have involved aquation or mercury(II)-assisted aquation kinetics[1,5,9a,17–20] but base hydrolysis rates also appear to follow similar trends.[9a]

The complexes used in this work also follow the above generalization and have aquation, Hg^{2+}-assisted aquation and base hydrolysis rates about 2 orders of magnitude faster than their bis(ethylenediamine) analogues. The increase in rate for

Table VII. Kinetic Parameters for the Aquation of Some *cis*-$CoCl(AA)_2(A)^{2+}$ Complexes at 298.2 K

A	AA	μ, M	$10^6k_H(298)$, s^{-1}	log (*PZ*), s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$, J K^{-1} mol^{-1}	Ref
NH_3	tmd	1.0	6.5	12.47	101 ± 1.4	−14 ± 3	*a*
$MeNH_2$	tmd	1.0	43.5	9.586	79.6 ± 0.6	−70 ± 2	*a*
$EtNH_2$	tmd	1.0	44.3	10.92	87.1 ± 1.0	−44 ± 2	*a*
n-$PrNH_2$	tmd	1.0	36.7	12.33	95.7 ± 1.0	−17 ± 2	*a*
n-$BuNH_2$	tmd	1.0	42.8	12.01	93.5 ± 1.0	−23 ± 2	*a*
i-$BuNH_2$	tmd	1.0	39.0	12.43	96.1 ± 3.0	−15 ± 6	*a*
$BzNH_2$	tmd	1.0	29.0	10.38	85 ± 4.0	−58 ± 8	*a*
NH_3	en	Var	0.42	11.20	100.4	−33.7	*b*
$MeNH_2$	en	Var	0.16		114	0	*b*
$EtNH_2$	en	Var	0.21		109	−14	*b*
n-$PrNH_2$	en	H_2O	0.31		106	−23	*b*
n-$BuNH_2$	en	Var	0.47		100	−40	*b*
i-$BuNH_2$	en	H_2O	0.45		101	−36	*b*
$BzNH_2$	en	Var	0.14		112	−9	*b*

[a] This research. [b] Data from ref 1.

Table VIII. Activation Parameters of the Base Hydrolysis of Some *cis*-$CoCl(AA)_2(A)^{2+}$ Complexes (μ = 0.1 M) at 298.2 K

A	AA	$k_{OH}(298)$, M^{-1} s^{-1}	log (*PZ*), M^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$, J K^{-1} mol^{-1}	Ref
NH_3	tmd	508	17.915	86.8 ± 0.7	+90 ± 1.5	*a*
$MeNH_2$	tmd	765	15.213	70.4 ± 1.1	+38 ± 2	*a*
$EtNH_2$	tmd	951	17.508	82.9 ± 1.6	+82 ± 3	*a*
n-$PrNH_2$	tmd	997	17.951	85.4 ± 1.6	+90 ± 3	*a*
n-$BuNH_2$	tmd	916	18.084	86.3 ± 0.9	+93 ± 2	*a*
i-$BuNH_2$	tmd	1470	17.388	81.2	+80	*a,b*
$BzNH_2$	tmd	1397	17.070	79.5 ± 1.8	+74 ± 4	*a*
NH_3	en	8.1				*c*
$MeNH_2$	en	7.3		98	+100	*d*
		13				*c*
$EtNH_2$	en	6.5		98	+120	*d*
		12		106	+133	*e*
n-$PrNH_2$	en	11		98	+104	*d*
		13				*c*
n-$BuNH_2$	en	6.5		98	+104	*d,f*
		13				*c*
i-$BuNH_2$		11		98	+104	*d,f*

[a] This research. [b] Only two temperatures. [c] R. W. Hay and P. L. Cropp, *J. Chem. Soc. A*, 42 (1969). [d] S. C. Chan, C. Y. Chang, and F. Leh, *J. Chem. Soc. A*, 1586 (1967). [e] V. D. Panasyuk and L. G. Reiter *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 10, 1316 (1965). [f] R. W. Hay and D. J. Barnes, *J. Chem. Soc. A*, 3337 (1970).

Table IX. Kinetic Parameters for the Fe^{2+} Reduction of Some *cis*-$CoCl(AA)_2(A)^{2+}$ Complexes at 298.2 K

A	AA	μ, M	$10^4k_{Fe}(298)$, M^{-1} s^{-1}	log (*PZ*), s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$, J K^{-1} mol^{-1}	Ref
NH_3	tmd	2.0	10.2	9.090	68.9 ± 1.7	−79 ± 3	*a*
$MeNH_2$	tmd	2.0	10.0	9.570	71.7 ± 2.9	−70 ± 6	*a*
$EtNH_2$	tmd	2.0	10.8	8.955	68.0 ± 3.1	−82 ± 6	*a*
n-$PrNH_2$	tmd	2.0	10.3	10.842	78.9 ± 1.8	−45 ± 4	*a*
n-$BuNH_2$	tmd	2.0	9.31	10.303	76.1 ± 3.8	−56 ± 8	*a*
i-$BuNH_2$	tmd	2.0	11.5	9.449	70.7 ± 1.5	−72 ± 3	*a*
$BzNH_2$	tmd	2.0	15.0	8.912	67.0 ± 1.0	−82 ± 2	*a*
NH_3	en	1.0	0.18				*b*
$MeNH_2$	en	1.0	0.272		58	−137	*c*
		2.0	0.761				*a*
$EtNH_2$	en	1.0	0.270		58	−138	*c*
n-$PrNH_2$	en	1.0	0.258		56	−144	*c*
n-$BuNH_2$	en	1.0	0.203		58	−141	*c*
		2.0	0.722				*a*

[a] This research. [b] P. Bensen and A. Haim, *J. Am. Chem. Soc.*, 87, 3826 (1965). [c] Y. Kurimura and K. Ohashi, *Bull Chem. Soc. Jpn.*, 44, 1797 (1971).

aquation is reflected in a decrease in activation energy of about 10 kJ mol^{-1} relative to the ethylenediamine systems, but for base hydrolysis, both activation energy and entropy are lower (Tables VII and VIII).

Rather less data are available for Fe^{2+} reduction reactions. A study of the Fe^{2+} reduction of some $CoCl(N_5)^{2+}$ systems[21,22] has shown that increasing five-membered ring chelation results in a decrease in reaction rate, but, unfortunately, the isomeric purity of the complexes used was not well established. These same workers have measured the reduction rates of some *cis*-$CoCl(en)_2(A)^{2+}$ complexes in a slightly different medium from ours (Table IX). The medium change appears to contribute a rate increase of about 3 and the *cis*-$CoCl(tmd)_2(A)^{2+}$ complexes thus react about 15 times faster than the bis(ethylenediamine) complexes. The activation parameters suggest that this rate increase is due mainly to a decrease in the entropy of activation, as the activation energy actually increases for the bis(trimethylenediamine) systems (Table IX).

Mechanistic Implications. Plots of E_a and ΔS^{*}_{298} for both aquation and base hydrolysis vs. formula weight of the amine, A, are shown in Figure 1. The trends in the homologous series

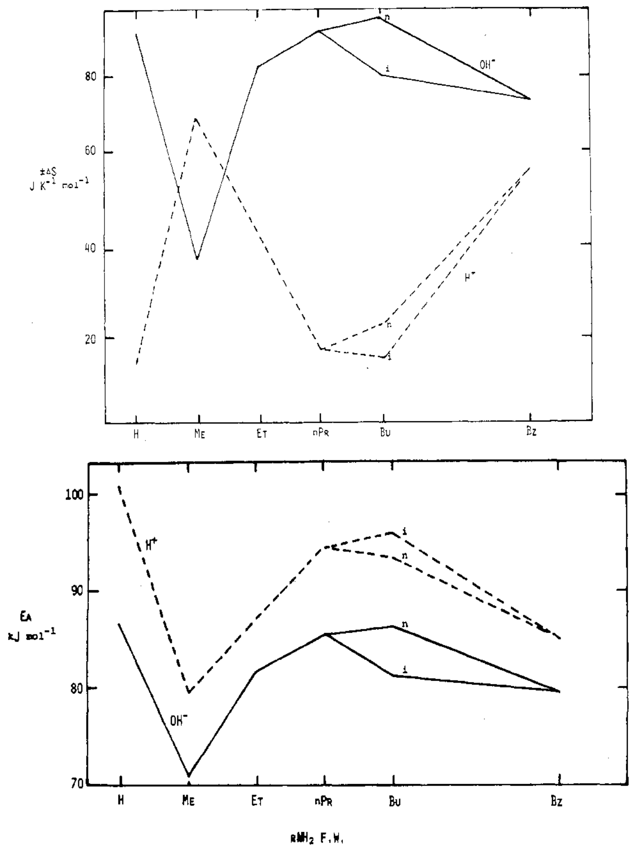

Figure 1. Plots of E_a (kJ mol^{-1}) and $\Delta S^{‡}_{298}$ (J K^{-1}mol^{-1}) vs. amine formula weight for the aquation (H$^+$) and base hydrolysis (OH$^-$) reactions of some *cis*-CoCl(tmd)$_2$(amine)$^{2+}$ complexes.

A = NH_3 to *n*-$BuNH_2$ appear to be remarkably uniform and similar for both reactions. The analogous data for the *cis*-CoCl(en)$_2$(A)$^{2+}$ systems are not complete, but the $\Delta S^{‡}_{298}$ values obtained for the aquation of CoBr(RNH$_2$)$_5$ show a similar pattern.[23]

The generally accepted mechanism for the base hydrolysis of chloropentaaminecobalt(III) complexes is via a conjugate base involving deprotonation of a coordinated NH group and the development of a five-coordinate trigonal-bipyramid transition state.[1,2] Such a mechanism readily accounts for the stereochemical changes observed in the base hydrolysis of *cis*-CoCl(en)$_2$(A)$^{2+}$ systems.[16,24]

The stereochemistry of the transition state involved in the aquation of chloropentaaminecobalt(III) complexes is less certain. A dissociative mechanism is favored[1,2,25] and the lack of isomerization observed in the aquation of *cis*-CoCl(en)$_2$(A)$^{2+}$ complexes has been explained in terms of a square-pyramidal transition state, although the trigonal-bipyramid form cannot be excluded.[26] It has proved difficult to explain the influence of the nonreplaced amine ligands on the kinetic parameters for aquation using a square-pyramidal transition state, and a distortion theory has recently been postulated.[9a] Here, the driving force in the aquation of CoCl(N$_5$)$^{2+}$ systems is thought to be related to the ease of distortion to a five-coordinate trigonal-bipyramid transition state with the flexible diamine systems such as trimethylenediamine or two NH_3 groups twisting more readily than the rigid ethylenediamine systems.[4]

The data in this work also support a trigonal-bipyramid transition state for aquation insofar as the kinetic parameters for both aquation and base hydrolysis show similar trends. The fact that cis → trans isomerization is not observed in the aquation is possibly due to a less well developed trigonal bipyramid than that stabilized by the amido group[27] in the base hydrolysis reaction.

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Registry No. *cis*-[CoCl(tmd)$_2$(NH$_3$)]ZnCl$_4$, 66417-05-8; *cis*-[CoCl(tmd)$_2$(NH$_3$)](ClO$_4$)$_2$, 66417-06-9; *cis*-[CoCl(tmd)$_2$(MeNH$_2$)]ZnCl$_4$, 66417-08-1; *cis*-[CoCl(tmd)$_2$(MeNH$_2$)](ClO$_4$)$_2$, 66417-09-2; *cis*-[CoCl(tmd)$_2$(EtNH$_2$)]ZnCl$_4$, 66417-11-6; *cis*-[CoCl(tmd)$_2$(EtNH$_2$)](ClO$_4$)$_2$, 66417-12-7; *cis*-[CoCl(tmd)$_2$(PrNH$_2$)]ZnCl$_4$, 66417-14-9; *cis*-[CoCl(tmd)$_2$(PrNH$_2$)](ClO$_4$)$_2$, 66417-15-0; *cis*-[CoCl(tmd)$_2$(BuNH$_2$)]ZnCl$_4$, 66417-17-2; *cis*-[CoCl(tmd)$_2$(BuNH$_2$)](ClO$_4$)$_2$, 66417-18-3; *cis*-[CoCl(tmd)$_2$(*i*-BuNH$_2$)]ZnCl$_4$, 66417-20-7; *cis*-[CoCl(tmd)$_2$(*i*-BuNH$_2$)](ClO$_4$)$_2$, 66417-21-8; *cis*-[CoCl(tmd)$_2$(BzNH$_2$)]ZnCl$_4$, 66417-23-0; *cis*-[CoCl(tmd)$_2$(BzNH$_2$)](ClO$_4$)$_2$, 66417-24-1; *cis*-CoCl(en)$_2$(MeNH$_2$)$^{2+}$, 17631-61-7; *cis*-CoCl(en)$_2$(BuNH$_2$)$^{2+}$, 31102-25-7; *trans*-[CoCl$_2$(tmd)$_2$]ClO$_4$, 59598-02-6; (+)$_{589}$-[CoCl(tmd)$_2$(BzNH$_2$)]ZnCl$_4$, 66537-30-2; (+)$_{589}$-Co(tmd)$_2$(BzNH$_2$)(OH$_2$)$^{3+}$, 66495-41-8; Hg^{2+}, 14302-87-5; Fe^{2+}, 15438-31-0; OH$^-$, 14280-30-9.

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(3) Abbreviations used: MeNH$_2$ = methylamine, EtNH$_2$ = ethylamine, *n*-PrNH$_2$ = *n*-propylamine, *n*-BuNH$_2$ = *n*-butylamine, *i*-BuNH$_2$ = isobutylamine = (CH$_3$)$_2$CHCH$_2$NH$_2$, BzNH$_2$ = benzylamine, en = 1,2-diaminoethane, tmd = 1,3-diaminopropane, NH$_4$-(+)-BCS = ammonium α-bromo-(+)-camphorsulfonate, Na-(+)-AsOT = sodium (+)-arsenic(III) tartrate, trien = NH$_2$(CH$_2$)$_2$NH(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$.
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