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## Activated Ligand Substitution in Bridged Complexes. 1. Base Hydrolysis and Structure of $(\pm)$ - $(\mu$ -Amido)-*cis,cis*-tetrakis(1,2-ethanediamine)diamminedicobalt(III) Pentanitrate Dihydrate

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The title compound has been prepared from the known  $(\mu$ -amido)( $\mu$ -sulfato)tetrakis(ethanediamine)dnicobalt(III) ion in several steps. It crystallizes in the orthorhombic space group *Pbca* with  $a = 17.791$  (6) Å,  $b = 17.859$  (6) Å,  $c = 18.382$  (8) Å, and  $Z = 8$ . The complex cation has *cis*-1,2-ethanediamine ligands and is racemic. A near-twofold axis lies perpendicular to the Co-Co distance, going through the NH<sub>2</sub> bridge. Co-N distances in the NH<sub>2</sub> bridge are 2.049 (6) and 2.032 (7) Å, respectively, and the Co-N distances to the nonbridging nitrogen atoms range between 1.966 (7) and 1.983 (7) Å. The Co-N-Co angle is 143.8 (3)°. The title compound is kinetically stable in acid with a spontaneous aquation rate constant  $k_{\text{OH}_2} = (5.0 \pm 1.4) \times 10^{-6} \text{ s}^{-1}$  at 25 °C,  $\mu = 0.1$  (HClO<sub>4</sub>), but decomposes rapidly in alkaline aqueous solution. The kinetics of base hydrolysis follow a complex rate law:  $-d[\text{complex}]/dt = kK_b[\text{OH}^-][\text{complex}]/(1 + K_b[\text{OH}^-] + \beta_2[\text{OH}^-]^2)$  with  $k = 1.54 \pm 0.22 \text{ s}^{-1}$ ,  $K_b = 88 \pm 18 \text{ dm}^3 \text{ mol}^{-1}$ , and  $\beta_2 = (4.0 \pm 0.2) \times 10^3 \text{ dm}^6 \text{ mol}^{-2}$  at 25 °C,  $\mu = 0.1$  (NH<sub>4</sub>ClO<sub>4</sub> or KClO<sub>4</sub>/KOH). This is interpreted as the effect of amine deprotonation ( $\text{p}K_a = 11.7 \pm 0.1$ ) and ion pairing with OH<sup>-</sup> in the reactant. In the presence of coordinating anions (Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>), the empirical rate law contains anion-dependent terms that are taken to reflect anion association preequilibria. Quantitative material balances of the base hydrolysis reaction products provide evidence for two parallel reaction pathways: (1) The  $\mu$ -NH<sub>2</sub> bridge is cleaved (75–90% at 25 °C) to form 1 mol of *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> and 1 mol of a mixture of *cis*- and *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)OH]<sup>2+</sup> (along with *cis*- and *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)N<sub>3</sub>]<sup>2+</sup> in azide medium (1 mol dm<sup>-3</sup>)). The azido complexes arise from scavenging of N<sub>3</sub><sup>-</sup> by a coordinatively unsaturated intermediate state arising after cleavage of the amido bridge. (2) Coordinated ammonia is lost to give [(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>Co(OH)(en)<sub>2</sub>]<sup>4+</sup> (10–25%). This pathway is about as fast as the loss of NH<sub>3</sub> in *trans*-[(en)<sub>2</sub>NH<sub>3</sub>CoSO<sub>3</sub>]<sup>+</sup>. Part of this rate enhancement is accounted for by the high N-H acidity of the 5+-charged reactant. The ratio of cleavage to NH<sub>3</sub> elimination products is independent of [OH<sup>-</sup>] at constant ionic strength but depends on the nature of the supporting electrolyte.

### Introduction

The polymerization of metal aqua ions is of fundamental interest and has practical importance in many fields of natural science.<sup>2</sup> Nevertheless, the mechanisms of these highly complex reaction networks are as yet little understood.

We have therefore searched for models for elementary steps of polynuclear complex formation and cleavage. Clearly, these processes involve ligand substitution, and some characteristics of buildup and cleavage of hydrolytic polymers could be related to special features of substitution processes in polynuclear species. We have chosen to study such substitution reactions in some detail, using dimeric compounds of a kinetically inert metal center, viz. Co(III). In  $(\mu$ -amido)bis(pentaamine)cobalt(III) cations,  $\mu$ -NH<sub>2</sub> and NH<sub>3</sub> or aliphatic amine ligands are in the place of isoelectronic  $\mu$ -OH and H<sub>2</sub>O ligands in hydrolytic dimers. The ligand sphere of such Co(III) model compounds may be varied widely and can be tailor-made to answer mechanistic questions such as "Are some or all of the nonbridging ligands in a binuclear species more labile than in mononuclear analogues?" or "Is bridge splitting competing with nonbridging ligand substitution?" This paper reports the synthesis and structure of the  $(\pm)$ - $(\mu$ -amido)bis[*cis*-bis(ethylenediamine)aminocobalt](5+) ion (**1**) (Scheme I) and the kinetics and mechanism of its reactions in alkaline aqueous solution.

### Results

**Preparation and Physical Properties of 1.** The synthetic route to this new  $\mu$ -amido decaamine species is represented in Scheme I. The individual steps in this synthesis have precedent in known transformations in the analogous octaamine series.<sup>3</sup>

Table I. <sup>13</sup>C NMR Data for [(en)<sub>2</sub>NH<sub>3</sub>CoX]<sup>n+</sup> Compounds

compd	$\delta^a$
<i>cis</i> -[Co(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>3+</sup>	44.2, 44.0 <sup>b</sup>
<i>trans</i> -[Co(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>3+</sup>	43.8 <sup>b</sup>
$(\pm)$ - <i>cis,cis</i> -[(en) <sub>2</sub> (NH <sub>3</sub> )Co] <sub>2</sub> NH <sub>2</sub> ] <sup>5+</sup>	44.9, 44.2, 43.8 [1:2:1] <sup>c</sup>
<i>cis</i> -[Co(en) <sub>2</sub> (NH <sub>3</sub> )OH] <sup>2+</sup>	44.5, 43.7, 42.7 [1:2.1:1] <sup>b,d</sup>
<i>trans</i> -[Co(en) <sub>2</sub> (NH <sub>3</sub> )OH] <sup>2+</sup>	44.0 <sup>b,d</sup>

<sup>a</sup> Relative to external Me<sub>4</sub>Si. <sup>b</sup> In Na<sub>2</sub>CO<sub>3</sub>/D<sub>2</sub>O. <sup>c</sup> In Me<sub>2</sub>SO-d<sub>6</sub>. <sup>d</sup> *cis/trans* isomer mixture from base hydrolysis of **1**. Peak intensity ratio 44.5:44.0:43.7:42.7 = 1.05:2.6:2.1:1.

The UV-vis spectrum of (1)(NO<sub>3</sub>)<sub>5</sub>·2H<sub>2</sub>O in water at pH 4 shows the following features ( $\lambda$ , nm [ $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]): 499 [380] (max), 418 [62] (min), 355 [714] (max), 334 [585] (min). Data for the analogous decaamine ion [(H<sub>3</sub>N)<sub>5</sub>Co]<sub>2</sub>NH<sub>2</sub>]<sup>5+</sup>: 505 [428] (max), 420 [57] (min), 360 [708] (max), 331 [457] (min). In **1**, the  $\mu$ -amido bridge links two Co(III) centers that may each adopt a *trans* or a  $\Delta$ - or  $\Lambda$ -*cis* configuration, and six nonsuperimposable configurations are possible. The <sup>13</sup>C NMR spectrum of **1** (Table I) is consistent with the absence ( $\leq 5\%$ ) of *trans*-[Co(en)<sub>2</sub>NH<sub>3</sub>NH<sub>2</sub>]<sup>2+</sup> moieties in the purified compound since their four carbons are expected to give rise to a single line at a different resonant frequency.<sup>6</sup>

**Crystal and Molecular Structure of  $(\pm)$ -[*cis*-((en)<sub>2</sub>NH<sub>3</sub>Co)<sub>2</sub>NH<sub>2</sub>](NO<sub>3</sub>)<sub>5</sub>·2H<sub>2</sub>O.** The crystal data are summarized in Table II. The fractional positional parameters are given in Table III. Perspective views of the dimeric cation are shown in Figure 1. The binuclear cation is present as the racemic  $\Delta\Delta$ ,  $\Lambda\Lambda$  pair, and its stereochemistry is therefore analogous to that of all other  $(\mu$ -amido)tetrakis(1,2-ethane-

(1) To whom correspondence should be addressed at the University of Neuchâtel.

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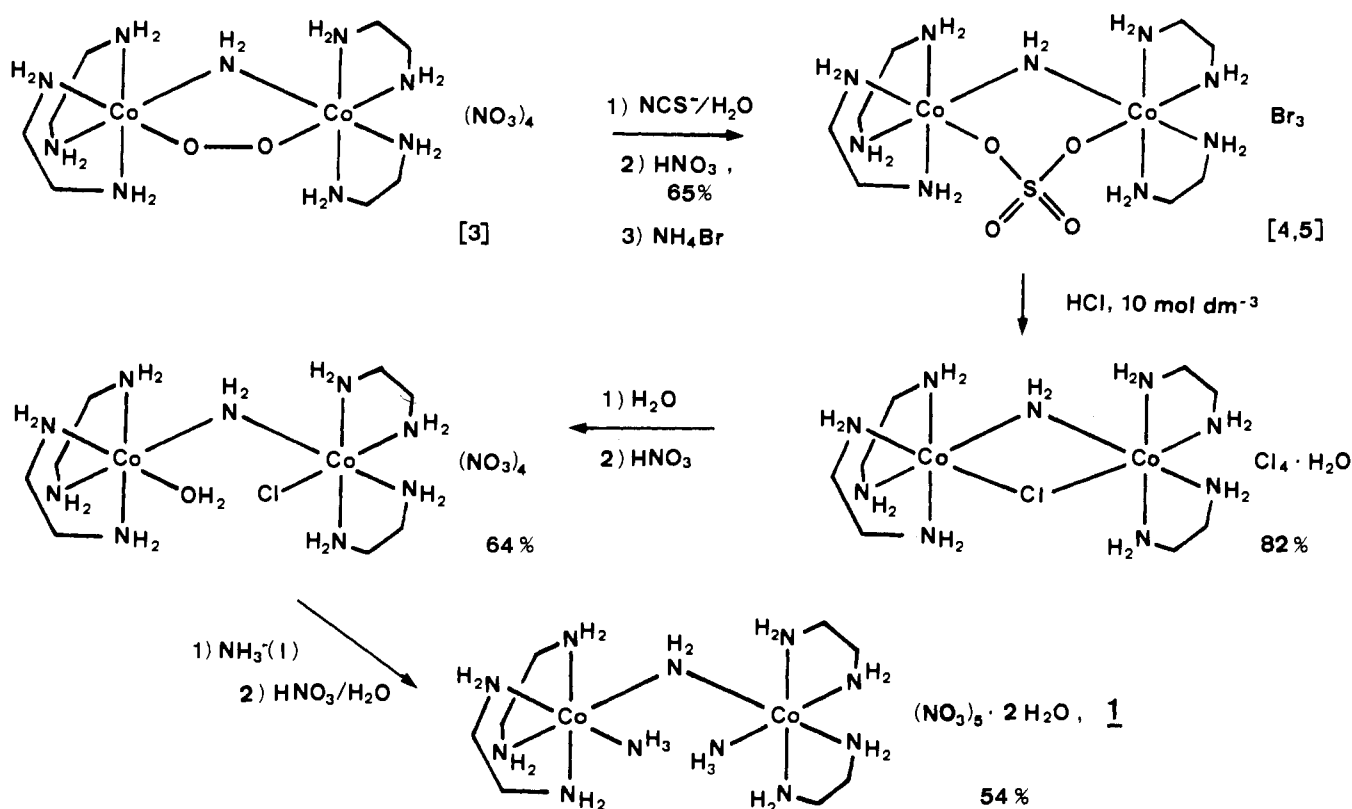
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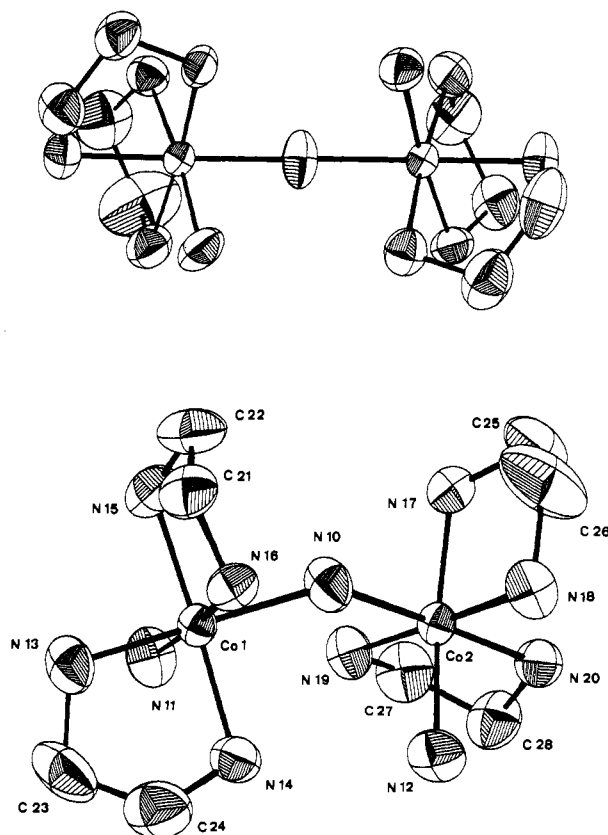
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Scheme I

**Table II.** Summary of Crystal Data, Intensity Collection, and Refinement

formula	(±)- <i>cis,cis</i> - [(en) <sub>2</sub> NH <sub>3</sub> CoNH <sub>2</sub> CoNH <sub>3</sub> (en) <sub>2</sub> ](NO <sub>3</sub> ) <sub>5</sub> ·2H <sub>2</sub> O
fw	754.4
source and appearance of crystals	red needles, grown from H <sub>2</sub> O/HNO <sub>3</sub>
dimens, mm	0.5 × 0.2 × 0.2
cryst class	orthorhombic
a, Å	17.791 (6)
b, Å	17.859 (6)
c, Å	18.382 (8)
V, Å <sup>3</sup>	5840.5
Z	8
d <sub>calcd</sub> , g/cm <sup>3</sup>	1.716
F <sub>000</sub>	3152
space group	<i>Pbca</i>
syst absences	0kl (k = 2n + 1), h0l (l = 2n + 1), hk0 (h = 2n + 1)
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromator
scan method	ω-2θ scan, 1.5°, 60-s measuring time/reflection
((sin θ)/λ) <sub>max</sub>	0.595
no. of unique reflns	5088 (1 octant)
no. of reflns with F <sub>o</sub> ≥ σ <sub>F</sub>	3861
refinement method	block-matrix least squares
function minimized	Σw( F <sub>o</sub>   -  F <sub>c</sub>  ) <sup>2</sup>
w <sup>4s</sup>	(1/σ <sub>F</sub> ) <sup>2</sup> exp [15((sin θ)/λ) <sup>2</sup> ]
R <sub>w</sub>	Σw( F <sub>o</sub>   -  F <sub>c</sub>  )/ΣwF <sub>o</sub> = 0.069
av shift/error in last cycle of refinement	0.028

diamine)dnicobalt(III) species of known structure:  
((en)<sub>2</sub>Co)<sub>2</sub>{NH<sub>2</sub>,O<sub>2</sub>}(SCN)<sub>3</sub>·H<sub>2</sub>O,<sup>7</sup> ((en)<sub>2</sub>Co)<sub>2</sub>{NH<sub>2</sub>,OH}-

**Figure 1.** Molecular structure of the (±)-*cis,cis*-[(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>CoNH<sub>3</sub>(en)<sub>2</sub>]<sup>5+</sup> ion, viewed along the near-twofold axis (top), and atom-numbering scheme (bottom).

(NO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O,<sup>8</sup> ((en)<sub>2</sub>Co)<sub>2</sub>{NH<sub>2</sub>,NO<sub>2</sub>}(NO<sub>3</sub>)<sub>4</sub>,<sup>9</sup> ((en)<sub>2</sub>Co)<sub>2</sub>-  
{NH<sub>2</sub>,O<sub>2</sub>}(NO<sub>3</sub>)<sub>4</sub>·H<sub>2</sub>O,<sup>10,11</sup> ((en)<sub>2</sub>Co)<sub>2</sub>{NH<sub>2</sub>,O<sub>2</sub>H}(NO<sub>3</sub>)<sub>4</sub>.

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Table III. Fractional Atomic Coordinates with Standard Deviations and Equivalent Isotropic Thermal Parameters<sup>a</sup>

atom	x	y	z	$B_{eq}, \text{\AA}^2$	molecule or fragment
Co1	0.17533 (5)	0.31231 (5)	0.21869 (4)	1.49	} H <sub>2</sub> O of crystallization
Co2	0.20180 (4)	0.44507 (5)	0.38377 (4)	1.43	
O1	0.5013 (5)	0.2640 (6)	0.0677 (5)	5.7	
O2	0.0885 (9)	0.1130 (7)	0.2049 (8)	8.9	
N1	0.2576 (3)	0.0528 (4)	0.1401 (3)	2.4	
O11	0.2671 (4)	0.0528 (5)	0.2071 (3)	4.7	
O12	0.2706 (4)	-0.0037 (4)	0.1040 (4)	3.9	
O13	0.2343 (4)	0.1104 (4)	0.1098 (4)	4.0	
N2	0.1930 (4)	0.1889 (5)	0.4570 (3)	3.1	
O21	0.1747 (6)	0.1860 (8)	0.3921 (3)	6.6	
O22	0.1922 (5)	0.2511 (4)	0.4883 (4)	4.5	
O23	0.2100 (5)	0.1317 (4)	0.4908 (4)	4.4	
N3	0.3716 (4)	0.2001 (5)	0.4106 (5)	3.7	
O31	0.3347 (6)	0.1598 (6)	0.3689 (6)	6.4	
O32	0.3698 (6)	0.2675 (5)	0.4018 (8)	7.3	
O33	0.4061 (9)	0.1697 (8)	0.4581 (8)	9.1	
N4	0.4649 (5)	0.0892 (6)	0.1589 (6)	4.7	
O41	0.427 (1)	0.081 (2)	0.108 (1)	16.1	
O42	0.4759 (7)	0.0386 (6)	0.2020 (7)	7.2	
O43	0.488 (1)	0.1516 (8)	0.175 (1)	10.2	
N5	0.4375 (4)	0.4232 (5)	0.1997 (4)	3.3	
O51	0.4544 (6)	0.3734 (5)	0.2450 (6)	5.8	
O52	0.3737 (3)	0.4493 (4)	0.1999 (4)	4.1	
O53	0.4843 (5)	0.4434 (6)	0.1552 (5)	5.6	
N10	0.2238 (3)	0.3735 (4)	0.3005 (3)	2.5	
N11	0.0962 (3)	0.2735 (4)	0.2837 (4)	2.5	
N12	0.1343 (4)	0.5060 (4)	0.3231 (3)	2.7	
N13	0.1281 (3)	0.2531 (4)	0.1397 (3)	2.6	
C23	0.0562 (5)	0.2922 (6)	0.1179 (5)	3.9	
C24	0.0723 (5)	0.3738 (6)	0.1152 (5)	3.8	
N14	0.1109 (3)	0.3954 (4)	0.1839 (3)	2.4	
N15	0.2410 (4)	0.2272 (4)	0.2432 (4)	2.7	
C21	0.3186 (5)	0.2425 (5)	0.2157 (5)	3.3	
C22	0.3105 (4)	0.2787 (5)	0.1422 (4)	2.8	
N16	0.2558 (3)	0.3418 (3)	0.1509 (3)	2.1	
N17	0.2755 (3)	0.3937 (3)	0.4463 (3)	2.1	
C25	0.3458 (5)	0.4388 (6)	0.4510 (5)	3.8	
C26	0.3588 (5)	0.4740 (9)	0.3815 (7)	5.4	
N18	0.2817 (4)	0.5095 (4)	0.3549 (3)	2.6	
N19	0.1198 (3)	0.3820 (4)	0.4212 (3)	2.0	
C27	0.0934 (5)	0.4108 (5)	0.4939 (4)	2.8	
C28	0.0996 (5)	0.4930 (5)	0.4931 (5)	2.9	
N20	0.1776 (4)	0.5124 (3)	0.4658 (3)	2.2	

$$^a B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_j \cdot a_i^{47}$$

### 2H<sub>2</sub>O,<sup>10</sup> and ((en)<sub>2</sub>Co)<sub>2</sub>[NH<sub>2</sub>SO<sub>4</sub>]Br<sub>3</sub>.<sup>5</sup>

The conformation of the binuclear cation is characterized by a near-twofold axis going through the bridging nitrogen atom and bisecting the Co-Co distance. The distances Co-N (nonbridging) vary within the range of 1.966–1.982 Å, and their average is 0.068 Å shorter than the mean Co-(μ-NH<sub>2</sub>) distance of 2.04 (1) Å (Table IV). The Co-NH<sub>3</sub> distances (average 1.970 (3) Å) are not significantly shorter than the Co-NH<sub>2</sub>(en) distances (1.974 (6) Å). No ground-state cis or trans influence of the amido bridge becomes apparent from these bond lengths and thermal motion ellipsoids. The bond lengths within the coordinated 1,2-ethanediamine molecules are normal except for the distance C25–C26.<sup>46</sup> The conformations of the chelate rings are δ,λ at each Co unit.

The angle at the NH<sub>2</sub> bridge, Co-N-Co, is 143.8 (3)°. This value is significantly larger than that for an sp<sup>3</sup> nitrogen, which would correspond to the simplest valence-bond description of the formally (1-) charged NH<sub>2</sub> bridge. The N-Co-N angles range from 85.2 to 94.6° and fall into the same range as those in the previously known dinuclear Co(III) species.

**Product Analysis and Reaction Stoichiometry of 1 in Alkaline Solution.** In acidic solution, cation 1 undergoes very slow

Table IV. Selected Bond Lengths and Bond Angles in ΔΔ,ΛΛ-cis-cis-[((en)<sub>2</sub>NH<sub>3</sub>Co)<sub>2</sub>NH<sub>2</sub>]<sup>5+</sup>

Bond Lengths, Å			
Co1-N10	2.049 (6)	N13-C23	1.51 (1)
Co1-N11	1.972 (6)	N14-C24	1.49 (1)
Co1-N13	1.983 (7)	N23-C24	1.49 (2)
Co1-N14	1.981 (6)	N15-C21	1.49 (1)
Co1-N15	1.969 (7)	N16-C22	1.50 (1)
Co1-N16	1.970 (6)	C21-C22	1.51 (1)
Co2-N10	2.032 (7)	N17-C25	1.49 (1)
Co2-N12	1.966 (7)	N18-C26	1.51 (1)
Co-N17	1.970 (6)	C25-C26	1.44 (2)
Co-N18	1.976 (7)	N19-C27	1.51 (1)
Co-N19	1.967 (6)	N20-C28	1.51 (1)
Co-N20	1.976 (6)	C27-C28	1.47 (1)

Bond Angles, deg			
Co1-N10-Co2 <sup>a</sup>	143.8 (3)	N10-Co2-N12 <sup>c</sup>	92.2 (3)
N10-Co1-N13 <sup>b</sup>	179.8 (2)	N10-Co2-N17 <sup>c</sup>	91.1 (2)
N10-Co2-N20 <sup>b</sup>	178.0 (3)	N10-Co2-N18 <sup>c</sup>	40.9 (3)
N10-Co1-N11 <sup>c</sup>	92.5 (3)	N10-Co2-N19 <sup>c</sup>	92.6 (2)
N10-Co1-N14 <sup>c</sup>	94.6 (3)	N11-Co1-N16 <sup>d</sup>	174.9 (3)
N10-Co1-N15 <sup>c</sup>	89.7 (3)	N12-Co2-N17 <sup>d</sup>	174.0 (3)
N10-Co1-N16 <sup>c</sup>	90.9 (2)		

<sup>a</sup> Bridging angle. <sup>b</sup> N trans to the bridge. <sup>c</sup> N cis to the bridge. <sup>d</sup> N trans to ammonia.

spectral change. At λ = 355 nm, the optical density of a solution (5.6 × 10<sup>-4</sup> mol dm<sup>-3</sup>) in perchloric acid (0.1 mol dm<sup>-3</sup>) decreased according to a first-order rate law for 2–3

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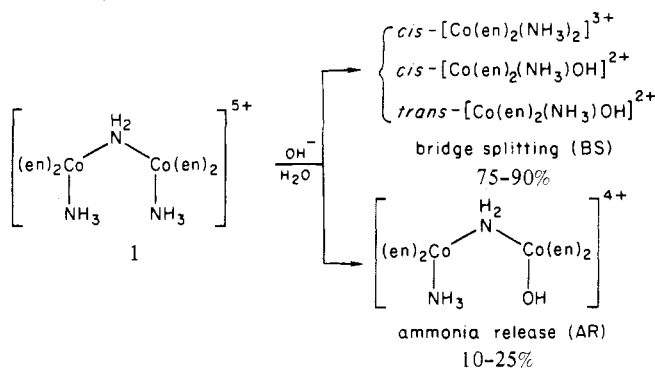
(11) Thewalt, U.; Marsh, R. E. *Inorg. Chem.* 1972, 11, 351.

Table V. Material Balance of Base Hydrolysis Reaction Products<sup>a</sup>

expt	medium		pH	[OH <sup>-</sup> ], mol dm <sup>-3</sup>	% reaction product <sup>b</sup>			% re- covery
	electrolyte	μ			Co(en) <sub>2</sub> NH <sub>3</sub> OH <sup>2+</sup>	Co(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	(en) <sub>2</sub> NH <sub>3</sub> CoNH <sub>2</sub> CoOH(en) <sub>2</sub> <sup>4+</sup>	
1	NaClO <sub>4</sub>	1.0	9.38 <sup>c</sup>		<i>f</i>	45	10	100
2	NaClO <sub>4</sub>	1.0	10.24 <sup>d</sup>		<i>f</i>	45	11	101
3	NaClO <sub>4</sub>	1.0	11.43 <sup>e</sup>		<i>f</i>	45	11	101
4	NaClO <sub>4</sub>	1.0		0.1	44	45	11	101
5	NaOH	1.0		1.0	38	37	25	98
6	NaN <sub>3</sub>	1.1		0.1	23 (+15% <i>cis</i> - and <i>trans</i> - [Co(en) <sub>2</sub> NH <sub>3</sub> N <sub>3</sub> ] <sup>2+</sup> )	42	20	101
					24 (+15% <i>cis</i> - and <i>trans</i> - [Co(en) <sub>2</sub> NH <sub>3</sub> N <sub>3</sub> ] <sup>2+</sup> )	40	21	94
7	NaCl	1.0		0.1	41	40	19	100
8	NaOH	0.1		0.1	41	41	18	101
					41	42	17	99
9	NaClO <sub>4</sub>	0.1		0.01	44	43	13	99
					43	44	13	101
10	NaOH	0.2		0.2	<i>f</i>	40	<i>f</i>	<i>f</i>
11	NaOH	low		0.01	39	41	20	102
12	CAPS	low	9.8		<i>f</i>	43	15	101
13	CAPS	low	10.5		<i>f</i>	43	14	100
14	CAPS	low	10.6		<i>f</i>	43	13	99

<sup>a</sup> See Experimental Section for reaction conditions. <sup>b</sup> Normalized to 100%, on the basis of total cobalt; accuracy ±1% absolute. <sup>c</sup> Di-ethanolamine/HClO<sub>4</sub> buffer, 0.05 mol dm<sup>-3</sup>. <sup>d</sup> Ethanolamine/HClO<sub>4</sub> buffer, 0.05 mol dm<sup>-3</sup>. <sup>e</sup> Piperidine/HClO<sub>4</sub> buffer, 0.1 mol dm<sup>-3</sup>. <sup>f</sup> Not determined. For calculation of recovery, the amount of [Co(en)<sub>2</sub>NH<sub>3</sub>OH]<sup>2+</sup> was supposed the same as that of [Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>.

## Scheme II



half-lives and the corresponding rate constant,  $k_{\text{H}_2\text{O}} = (5.0 \pm 1.4) \times 10^{-6} \text{ s}^{-1}$ , was determined at 25 °C. This value may be compared to that for  $[(\text{H}_3\text{N})_5\text{Co}]_2\text{NH}_2^{5+}$  aquation, which is estimated as  $\sim 2 \times 10^{-7} \text{ s}^{-1}$  at 25 °C from known activation parameters.<sup>12</sup> The product analyses carried out on alkaline reaction mixtures will therefore exclusively represent the base hydrolysis pathways (see below).

Reaction of **1** in aqueous alkaline solution is greatly accelerated and gives a mixture of products that were separated by ion-exchange chromatography and characterized by UV-vis spectroscopy and cobalt determinations (Table V). In one case, <sup>13</sup>C NMR spectra served as an independent check of the results (Table I). The data support the reaction stoichiometry in Scheme II. The relative contribution of the two pathways is independent of [OH<sup>-</sup>] in a constant medium but depends on both the ionic strength and the nature of the supporting electrolyte (Table V). The kinetics (see below) are consistent with irreversible, parallel pathways for NH<sub>2</sub> bridge cleavage and ammonia release. Detectable amounts of [Co(en)<sub>2</sub>(OH)<sub>2</sub>]<sup>+</sup> isomers (≥1%) were not found in the reaction products; these tetraamines would have been easily detected as a fast eluting band in the beginning of the ion-exchange chromatographic procedure. It follows that all *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> formed must arise from cleavage of **1** as its formation from the very stable [(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>(OH)(en)]<sup>4+</sup><sup>13</sup> would require formation of 1 equiv of [Co(en)<sub>2</sub>(OH)<sub>2</sub>]<sup>+</sup>.

The *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> fraction was examined in detail because determination of its isomeric composition could serve as an independent check of the isomeric purity of the starting material, **1**. Furthermore, the amount of hexamine formed corresponds to the amount of **1** reacting by the bridge-splitting pathway.

Formation of the pure *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> ion on base hydrolysis was confirmed by <sup>13</sup>C NMR spectroscopy (Table I), but the use of published molar extinction coefficients<sup>14</sup> for its spectrophotometric determination suggested unreasonably high yields that were at variance with atomic absorption determinations of cobalt in the solutions. *cis*- and *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> salts of checked isomeric purity and composition were therefore prepared and their molar absorptivities (λ, nm [ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]) redetermined: *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, 469 [79.1] (max), 387 [9.8] (min), 339 [70.2] (max), 287 [7.0] (min); *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, 465 [60.7] (max), 385 [7.8] (min), 336 [53.6] (max), 289 [7.5] (min). The [Co(en)<sub>2</sub>(NH<sub>3</sub>)OH]<sup>2+</sup> isomer mixture was determined by using known extinction coefficients.<sup>15</sup>

The dimeric product, [(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>OH(en)]<sup>5+</sup>, remained near the top of the ion-exchange column after removal of all mononuclear species. This purple band was not properly eluted from the Dowex 50W-X2 resin by perchloric acid. Elution with HCl (4 mol dm<sup>-3</sup>) was successful since under these conditions, possibly already upon elution of the mononuclear fragments, the aqua complex was converted into the corresponding chloro complex. The last was eluted as one band with no further species remaining on the column. Since known mononuclear [(en)<sub>2</sub>CoL<sub>2</sub>]<sup>3+</sup> species are eluted by ≤2 mol dm<sup>-3</sup> hydrochloric acid, we conclude that this new species must be a binuclear ion of charge ≥4+. This chloride anion product, viz. (±)-*cis,cis*-[(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>CoCl(en)]<sup>4+</sup>, has the following UV-vis spectrum (λ, nm [ε, dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]): 510 [338] (max), 436 [128] (min), 367 [851] (max), 351 [810] (min). These values have been confirmed independently by recording the solution spectrum of authentic [(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>CoCl(en)]<sub>2</sub>I<sub>4</sub> and by recording the spectrum

(13) Rotzinger, F. P.; Rickli, D.; Marty, W., unpublished work.

(14) (a) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc.* **1965**, 5094. (b) Basolo, F. *J. Am. Chem. Soc.* **1950**, *72*, 4393.(15) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6654.

of the chloro complex generated from the solid bromo analogue by base hydrolysis with subsequent  $\text{Cl}^-$  anation.<sup>13</sup>

This spectrum closely resembles that of the analogous enneaammine  $(\text{H}_3\text{N})_5\text{CoNH}_2\text{Co}(\text{NH}_3)_4\text{Cl}^{4+}$  ( $\lambda$  518 nm [ $\epsilon$  305] (max), 437 [108] (min), 367 [745] (max), 345 [674] (min))<sup>16</sup> but is distinctly different from that of  $[(\text{en})_2\text{Co}]_2[\text{NH}_2\text{Cl}]^{4+}$  or its solvolysis product(s) in hydrochloric acid (4 mol  $\text{dm}^{-3}$ ) which has  $\lambda(\text{max})$  at 533 nm and  $\lambda(\text{min})$  at 448 nm with two shoulders at  $\sim 500$  and  $\sim 367$  nm. Attempts at converting the chloride anation product into the aqua ion by  $\text{Ag}^+$ - or  $\text{Hg}^{2+}$ -induced aquation revealed its inertness against these electrophilic catalysts. This can be accounted for by the high charge of these complex ions suppressing preequilibrium adduct formation with these positively charged species. The same inertness toward electrophiles has been observed for  $[(\text{H}_3\text{N})_5\text{CoNH}_2\text{CoCl}(\text{NH}_3)_4]^{4+}$ .<sup>16</sup>

### Stereochemistry and Anion Scavenging

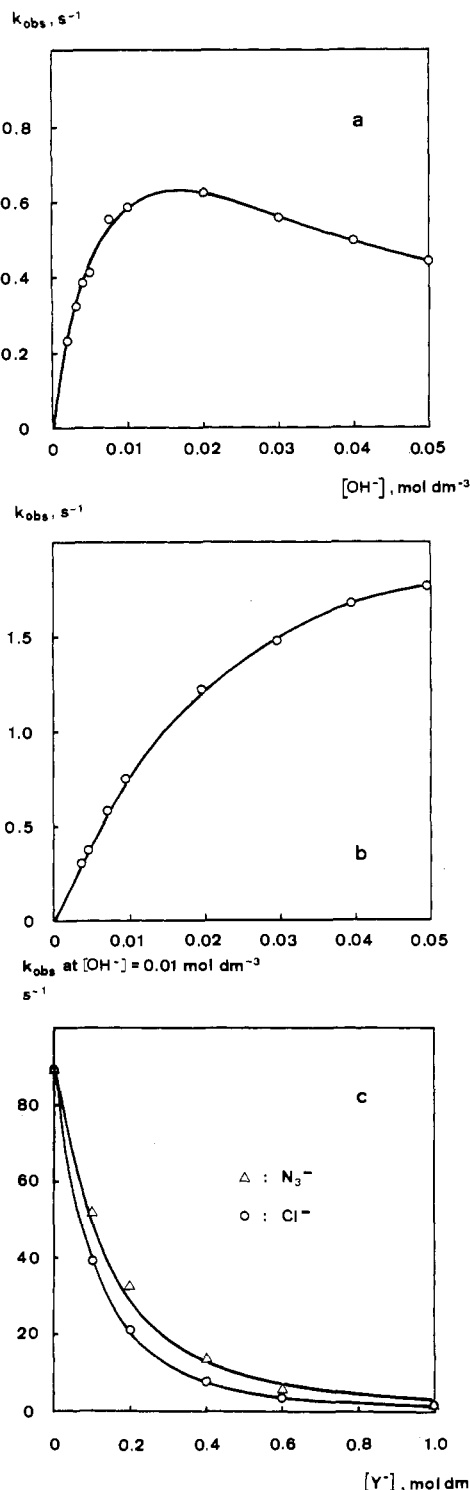
The stereochemical course of the base hydrolysis reaction has been determined at the Co(III) center, which loses the *cis*- $[(\text{en})_2\text{NH}_3\text{CoNH}_2]^{2+}$  leaving group (Table V). The stereochemistry of the  $[(\text{en})_2\text{NH}_3\text{CoOH}]^{2+}$  fraction in the cleavage products was determined by UV-vis spectroscopy following the literature procedure<sup>15,17</sup> whenever its concentration was sufficient to obtain good precision of the *cis/trans* isomer ratio. The isomer distribution was checked by  $^{13}\text{C}$  NMR and agreed within the larger limit of error of this method (Table I). There is extensive *cis* to *trans* rearrangement.

Formation of *cis*- and *trans*- $[(\text{en})_2\text{NH}_3\text{CoN}_3]^{2+}$  in the base hydrolysis reaction in azide medium (1 mol  $\text{dm}^{-3}$ ) was observed on cursory examination and is explained by azide scavenging by a coordinatively unsaturated intermediate state following splitting of the  $\text{NH}_2$  bridge and preceding entry of a new ligand. Compound **1** does not react with azide unless activated by hydroxide ion, and there is no kinetic evidence for associative substitution in **1** by azide ion (see below). Substitution of  $\text{OH}^-$  by  $\text{N}_3^-$  in *cis*- and *trans*- $[(\text{en})_2\text{NH}_3\text{CoOH}]^{2+}$  is much slower<sup>15</sup> than base hydrolysis of e.g. *cis*- $[(\text{en})_2\text{NH}_3\text{CoCl}]^{2+}$  ( $k_{\text{OH}} \approx 1\text{--}4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )<sup>18</sup> and does not interfere in the present product analysis. Clearly, these preliminary experiments need to be complemented by studies of the  $\text{OH}^-$  and  $\text{N}_3^-$  dependence and of the stereochemistry of the competition products. Similar anion scavenging in the  $\text{NH}_3$ -release pathway is likely but cannot presently be distinguished from anation of  $[(\text{en})_2\text{NH}_3\text{CoNH}_2\text{Co}(\text{OH})(\text{en})_2]^{4+}$  on the cation-exchange column.

**Base Hydrolysis Kinetics of 1.** The base hydrolysis reaction (Scheme II) was followed spectrophotometrically at 355 nm either in  $\text{NH}_3/\text{NH}_4^+$  buffers or in KOH solutions. Linear plots of  $\ln(D_t - D_\infty)$  vs.  $t$  were observed for at least 90% of the reaction, which is therefore considered uniphase. In the ammonia buffers, the reaction order in  $\text{NH}_3$  is zero (Table VIa (supplementary material)). The rate dependence on  $[\text{OH}^-]$

$$-\frac{d[\mathbf{1}]}{dt} = \frac{kK_b[\text{OH}^-][\mathbf{1}]}{1 + K_b[\text{OH}^-] + \beta_2[\text{OH}^-]^2} \quad (1)$$

obtains (Table VIb (supplementary material), Figure 2a) with values of the parameters  $k = 1.54 \pm 0.22 \text{ s}^{-1}$ ,  $K_b = 88 \pm 18 \text{ dm}^3 \text{ mol}^{-1}$ , and  $\beta_2 = (4.0 \pm 0.2) \times 10^3 \text{ dm}^6 \text{ mol}^{-2}$  at 25 °C and  $\mu = 0.1$  ( $\text{NH}_4\text{ClO}_4$  or  $\text{KOH}/\text{KClO}_4$ ). In these experiments, potassium ion was substituted for  $\text{NH}_4^+$  to attain the



**Figure 2.** Base hydrolysis kinetics of  $1^{5+}$ : (a)  $k_{\text{obs}}$  vs.  $[\text{OH}^-]$  at low ionic strength ( $\mu = 0.1$ ); (b)  $k_{\text{obs}}$  vs.  $[\text{OH}^-]$  at high ionic strength ( $\mu = 1.0$ ); (c) anion dependence of the rate at constant  $[\text{OH}^-]$ ,  $k_{\text{obs}}$  at  $[\text{OH}^-] = 0.01 \text{ mol dm}^{-3}$  vs.  $[\text{Y}^-]$  ( $\text{Y}^- = \text{Cl}^-, \text{N}_3^-$ ).  $T = 25$  °C.

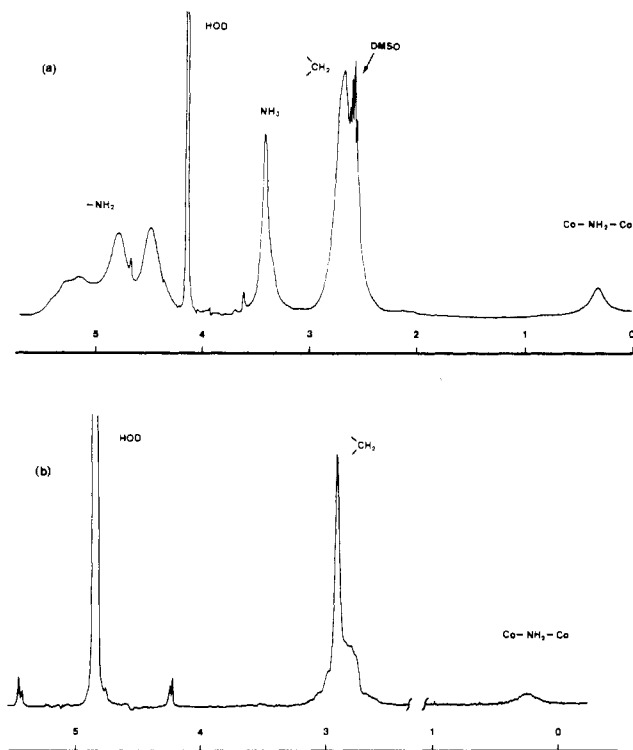
ionic strength. The empirical parameters  $K_b$  and  $\beta_2$  will be interpreted in the Discussion. The study of the rate dependence on anions (see below) required estimates of some of the kinetic parameters at higher ionic strength. At  $\mu = 1.0$  ( $\text{NaClO}_4$ ), the empirical rate law was determined up to  $0.05 \text{ mol dm}^{-3}$   $\text{NaOH}$  and these limited data fit the rate law (2) with parameters  $k = 2.7 \pm 0.1 \text{ s}^{-1}$  and  $K_b = 41 \pm 4 \text{ dm}^3 \text{ mol}^{-1}$  at 25 °C (Table VIc (supplementary material), Figure 2b).

$$-\frac{d[\mathbf{1}]}{dt} = \frac{kK_b[\text{OH}^-][\mathbf{1}]}{1 + K_b[\text{OH}^-]} \quad (2)$$

(16) Rotzinger, F. P.; Marty, W., unpublished results.

(17) Buckingham, D. A.; Clark, C. R.; Lewis, T. W. *Inorg. Chem.* **1979**, *18*, 1985.

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**Figure 3.**  $^1\text{H}$  NMR spectra of  $(1)(\text{NO}_3)_5$ . (a) Fresh solution in  $\text{Me}_2\text{SO}/\text{D}_2\text{O}/\text{DCI}$  ( $3 \text{ mol dm}^{-3}$ ). In this solvent mixture, both slow proton exchange and sufficient solubility are achieved. (b) Solution in pure  $\text{D}_2\text{O}$  after 1 day. All amine protons, except those of the  $\text{NH}_2$  bridge, are exchanged. Abscissa: chemical shifts ( $\delta$ ), relative to external TSP reference.

As the base hydrolysis gives rise to scavenging of anions, the kinetics were also followed in the presence of  $\text{Y}^- = \text{Cl}^-$ ,  $\text{N}_3^-$  ( $1 \text{ mol dm}^{-3}$ ). In order to determine whether reactive aggregates with  $\text{Y}^-$  exist, measurements were made at one hydroxide ion concentration ( $0.01 \text{ mol dm}^{-3}$ ), supposing the same  $[\text{OH}^-]$  dependence as in rate law (2). The good fit to the rate laws and the independence of the product distribution on  $[\text{OH}^-]$  in a constant medium are consistent with this assumption. Series of measurements at different  $[\text{Y}^-]$  were made spectrophotometrically at  $355 \text{ nm}$ ,  $26^\circ\text{C}$ , and  $\mu = 1.0$  ( $\text{NaY}/\text{NaClO}_4$ ). The results (Table VI d (supplementary material), Figure 2c) fit the empirical rate law (3) with the

$$-\frac{d[1]}{dt} = \frac{kK_b[\text{OH}^-][1]}{1 + K_b[\text{OH}^-] + K_Y[\text{Y}^-] + K_YK_{Y_2}[\text{Y}^-]^2} \quad (3)$$

parameters for  $\text{Y}^- = \text{Cl}^-$  of  $k = 3.07 \pm 0.05 \text{ s}^{-1}$ ,  $K_{\text{Cl}} = 12 \pm 3 \text{ dm}^3 \text{ mol}^{-1}$ , and  $K_{\text{Cl}_2} = 5.3 \pm 2.5 \text{ dm}^3 \text{ mol}^{-1}$ , with those for  $\text{Y}^- = \text{N}_3^-$  of  $k = 3.06 \pm 0.15 \text{ s}^{-1}$ ,  $K_{\text{N}_3} = 6.4 \pm 3.5 \text{ dm}^3 \text{ mol}^{-1}$ , and  $K_{(\text{N}_3)_2} = 5.4 \pm 5.7 \text{ dm}^3 \text{ mol}^{-1}$ , and with the previously determined value  $K_b = 41 \pm 4 \text{ dm}^3 \text{ mol}^{-1}$ . Although no corrections for activity coefficient differences for the different anions and for medium dependence of  $K_b$  were made, the fit is acceptable particularly at  $[\text{Y}^-] < 0.5 \text{ mol dm}^{-3}$ . In conclusion, there is no detectable numerator term proportional to  $[\text{OH}^-]$  and  $[\text{Y}^-]$ , and this is consistent with the supposed  $[\text{OH}^-]$  dependence also in the presence of  $\text{Y}^-$ .

**Proton Exchange.** The study of the  $^1\text{H}$  NMR spectrum and of the amine proton exchange was complicated by the generally limited solubility of salts of 1. Figure 3 shows the spectrum of a freshly prepared solution in  $0.15 \text{ M DCI}$  (a) and of a solution after standing for several hours at room temperature in  $\text{D}_2\text{O}$  (b). The first spectrum shows the known<sup>19</sup> pattern of

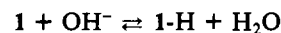
a  $\text{cis}-[\text{Co}(\text{en})_2(\text{amine})\text{X}]^{m+}$  moiety. The broad resonances are attributed to the  $\text{CH}_2$  protons ( $2.3\text{--}2.9 \text{ ppm}$ ,  $8 \text{ H}$ ),  $\text{NH}_3$  protons ( $3.4 \text{ ppm}$ ,  $3 \text{ H}$ ), and  $\text{NH}_2$  protons of ethylenediamine ( $4.2\text{--}5.5 \text{ ppm}$ ,  $8 \text{ H}$ ). The  $\text{NH}_2$  protons of the bridging ligand give rise to one broad signal ( $0.3 \text{ ppm}$ ,  $13\text{-Hz}$  half-width). Its peak area corresponds to ca. one proton in both spectra, relative to the  $\text{CH}_2$  protons of the ethylenediamine ligands (see below). After several hours in  $\text{D}_2\text{O}$  (unbuffered solution), all signals downfield of  $3 \text{ ppm}$  have disappeared, thus supporting their assignment as  $\text{NH}$  protons. However, the amido bridge proton signal retains a similar position and the same intensity, relative to the  $\text{CH}_2$  proton signals. Since a change in peak area of  $20\%$  in  $24 \text{ h}$  would have been detected, a second-order proton-exchange rate constant  $\leq 3 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is estimated. This value is lower than the base hydrolysis rate constant, and the amido bridge is thus not the site of deprotonation in the conjugate base.

### Discussion

The synthesis of 1 relies on established methods in  $\text{Co(III)}$  chemistry, most of which had already been developed by Werner. The configuration of the pure product  $(1)(\text{NO}_3)_5 \cdot 2\text{H}_2\text{O}$  was established by single-crystal X-ray diffraction. A distinctive feature of the cation structure is the large  $\text{Co-N-Co}$  angle ( $143.8 (3)^\circ$ ). An even larger angle ( $152.9^\circ$ )<sup>20</sup> is found in the similar compound  $[(\text{H}_3\text{N})_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5]^{5+}$ .

Base hydrolysis of 1 proceeds through two parallel pathways (Scheme II) both of which represent quite unprecedented reactions in  $\text{Co(III)}$  chemistry and which are fundamentally interesting. At  $25^\circ\text{C}$ , base-catalyzed splitting of an amido bridge is the predominant pathway. It can be regarded as a substitution process at a  $\text{Co(III)}$  pentaamine with a doubly positively charged leaving group,  $\text{cis}-[(\text{en})_2\text{NH}_3\text{CoNH}_2]^{2+}$ . As this leaving group will be protonated in water at a nearly diffusion-controlled rate, a presently indistinguishable alternative is cleavage with concerted protonation of the leaving group, which thus would be  $3+$  charged. The minor pathway corresponds to strong labilization of coordinated ammonia, which is one of the most inert ligands in  $\text{Co(III)}$  amine chemistry. In this paper, we focus on the bridge-splitting pathway but wish to point out that the ammonia-release pathway appears to be the only major pathway in the base hydrolysis of the related  $[(\text{H}_3\text{N})_5\text{CoNH}_2\text{Co}(\text{NH}_3)_5]^{5+}$  ion.<sup>16</sup>

The product analyses in conjunction with the rate law suggest two parallel, base-catalyzed pathways. Both pathways thus have a complex  $[\text{OH}^-]$  dependence (rate laws 1 and 2) in common. The  $\text{OH}^-$ -catalyzed acceleration is interpreted by an amine deprotonation preequilibrium.<sup>21</sup> The observed empirical rate laws (1) and (2) are uncommon in the base hydrolysis of  $\text{Co(III)}$  pentaamines,<sup>21</sup> but (2) has been observed recently in a hexaamine  $\text{Co(III)}$  complex.<sup>22</sup> We shall only discuss rate law (1), which is observed at ionic strength  $\mu = 0.1$ .<sup>48</sup> It shows two opposing effects of  $[\text{OH}^-]$  on the rate: a net acceleration at lower  $[\text{OH}^-]$  that is reduced and partly reversed at high  $[\text{OH}^-]$  (Figure 2a).  $K_b$  is taken as the equilibrium constant of the reaction



$$K_b = \frac{[1\text{-H}]}{[1][\text{OH}^-]} = \frac{K_a}{K_w} \quad (4)$$

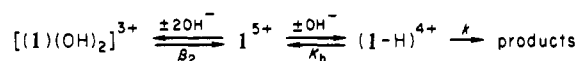
(20) Schaefer, W. P.; Cordes, A. W.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1968**, *B24*, 283.

(21) (a) Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527. (b) Tobe, M. L. *Acc. Chem. Res.* **1970**, *3*, 377. (c) Poon, C. K. *Inorg. Chim. Acta, Rev.* **1970**, *12*. (d) Sargeson, A. M.; Jackson, W. G. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, London, 1980; Vol. 2, p 273.

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

(19) See: Buckingham, D. A.; Davis, C. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 6159.

## Scheme III



and the corresponding  $\text{p}K_a$  value is  $11.7 \pm 0.1$  at  $25^\circ\text{C}$ ,  $\mu = 0.1$ .

This value is characteristically lower than those for the lower charged, mononuclear species  $[(\text{H}_3\text{N})_5\text{CoNO}_2]^{2+}$  (16.8),<sup>23</sup>  $[(\text{en})_3\text{Co}]^{3+}$  (14.9),<sup>23</sup> and  $ap-[[\text{Me}(\text{tren})]\text{Co}(\text{NH}_3)_2]^{3+}$  (14.1).<sup>22</sup> Considering that the 5+ charge on **1** is distributed over two metallic centers, the decrease of 2–3  $\text{p}K$  units relative to the 3+-charged species appears reasonable. A similar  $\text{p}K_a$  reduction has been found for a pair of analogous Cr(III) aqua complexes  $[(\text{H}_3\text{N})_5\text{CrOH}_2]^{3+}$  ( $\text{p}K_a = 5.0$ ,<sup>24</sup>  $\mu = 0.1$ ,  $20^\circ\text{C}$ ) and  $[(\text{H}_3\text{N})_5\text{CrOHCr}(\text{NH}_3)_4\text{OH}_2]^{5+}$  ( $\text{p}K_a = 2.8$ ,<sup>25</sup>  $\mu = 0.14$ ,  $20^\circ\text{C}$ ; the aqua ligand is deprotonated). At  $\mu = 1$ , the  $\text{p}K_a$  value of **1** is  $12.1 \pm 0.1$ . This increase fits into the general pattern of increasing  $\text{p}K_a$  values as the ionic strength increases.

The term  $\beta_2[\text{OH}]^2$  in the denominator of rate law (1) is taken to reflect formation of an unreactive ion aggregate with  $\text{OH}^-$ . This hypothesis is certainly in keeping with the observed reactivity pattern in the presence of other anions ( $\text{Y} = \text{Cl}^-$ ,  $\text{N}_3^-$ ) where unreactive ion aggregates are inferred from the kinetics. However, this term may be interpreted alternatively as the medium effect of replacing  $\text{ClO}_4^-$  by  $\text{OH}^-$  or as a second deprotonation preequilibrium. If rate law (1) is interpreted in terms of double deprotonation, a value of  $\text{p}K_{a2} = 12.0 \pm 0.1$  is derived. The difference  $\text{p}K_{a2} - \text{p}K_{a1} \approx 0.3$  is much smaller than that in diaqua(tetraamine)- and triaqua(triamine)cobalt(III) species ( $\Delta\text{p}K_a = 1.8\text{--}2.5$ ). The small difference found favors the ion-pairing hypothesis. Indeed, it is difficult to see why **1-2H** should be much less reactive than **1-H**. We therefore propose an unreactive ion triplet,  $[(1)(\text{OH})_2]^{3+}$ , instead of a doubly deprotonated reactant,  $(\text{1-2H})^{3+}$ , and the empirical constant  $\beta_2$  in rate law (1) is therefore interpreted as the cumulative ion triplet formation constant of  $\text{I}^{5+}$  with two  $\text{OH}^-$ :  $\beta_2 = \frac{[(1)(\text{OH})_2]^{3+}}{[\text{I}^{5+}][\text{OH}^-]^2}$ . The corresponding reaction scheme (Scheme III) leads to the rate law

$$-\frac{d[\text{I}^{5+}]}{dt} = \frac{kK_b[\text{OH}^-][\text{I}^{5+}]}{1 + K_b[\text{OH}^-] + \beta_2[\text{OH}^-]^2}$$

Product analyses have been carried out at different hydroxide concentrations and at different ionic strengths made up by different electrolytes. The results (Table V) allow the following conclusions:

(a) At a given ionic strength ( $\mu = 1.0$ ) in sodium perchlorate medium, the ratio of bridge splitting to ammonia elimination ( $\approx 9$ ) is constant up to  $[\text{OH}^-] = 0.1 \text{ mol dm}^{-3}$  (experiments 1–4).

(b) At the same ionic strength,  $\mu = 1.0\text{--}1.1$ , achieved with other electrolytes, viz.  $\text{NaOH}$ ,  $\text{NaN}_3$ , or  $\text{NaCl}$  (experiments 5–7), this ratio is smaller ( $\sim 4\text{--}5$ ) for all three anions. The ratio for  $\text{NaOH}$  is the smallest.

(c) At  $\mu = 0.1$ , the product ratio was different for  $\text{NaOH}$  and  $\text{NaClO}_4$  media (experiments 8 and 9). The pH range in which this change occurs is ca. 1 unit lower than at  $\mu = 1$ . A medium effect is therefore suggested rather than a deprotonation equilibrium. The ratios at  $\mu = 0.1$  are different from those at  $\mu = 1.0$ , but for pure  $\text{NaOH}$  media, the ratio remains essentially constant from  $\mu = \text{ca. } 0.01\text{--}0.2$  (experiments 8–10).

(d) Experiments in 3-(cyclohexylamino)propanesulfonate (CAPS) buffers (experiments 12–14) at low  $\mu$  gave product ratios different from those at similar pH but at  $\mu = 1$ , confirming strong medium effects in the product-determining step.

While parallel pathways undoubtedly exist in product formation, their point of bifurcation remains uncertain. All amine protons except for the bridge  $\text{NH}_2$  protons are sufficiently acidic to form a conjugate base, but ammonia release is unlikely if the leaving group  $\text{NH}_3$  affords the conjugate base.

The following rate law is derived under the two assumptions (1) that abstraction of the most acidic proton affords the most reactive conjugate base and (2) that one common conjugate base pathway obtains for the ammonia-release and bridge-splitting pathways:

$$-\frac{d[\text{I}]}{dt} = \frac{(k_{\text{AR}} + k_{\text{BS}})K_aK_w^{-1}[\text{I}][\text{OH}^-]}{1 + K_aK_w^{-1}[\text{OH}^-] + \beta_2[\text{OH}^-]^2}$$

where  $K_a = [\text{H}^+][\text{1-H}^{4+}]/[\text{I}^{5+}]$  and  $K_w = [\text{H}^+][\text{OH}^-]$ .

From the product analyses, we find the following expression, which is  $[\text{OH}^-]$  independent at least for  $\mu = 1.0$  ( $\text{NaClO}_4$ ):

$$\frac{[\text{dimer}]_\infty}{[\text{cis-}[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}]_\infty} = \frac{11}{89} = \frac{k_{\text{AR}}}{k_{\text{BS}}}$$

At  $25^\circ\text{C}$  and  $\mu = 1.0$  ( $\text{NaClO}_4$ ),  $k = k_{\text{AR}} + k_{\text{BS}} = 2.7 \text{ s}^{-1}$  from the kinetics. Thus,  $k_{\text{AR}} = 0.30 \text{ s}^{-1}$  and  $k_{\text{BS}} = 2.40 \text{ s}^{-1}$ . At  $25^\circ\text{C}$  and  $\mu = 0.1$  ( $\text{NaClO}_4$ ),  $k_{\text{AR}} = 0.20 \text{ s}^{-1}$  and  $k_{\text{BS}} = 1.34 \text{ s}^{-1}$ .

Base hydrolysis of **1** affords the two unusual leaving groups  $\text{NH}_3$  and  $[(\text{en})_2\text{NH}_3\text{CoNH}_2]^{2+}$  (or  $[(\text{en})_2\text{NH}_3\text{CoNH}_3]^{3+}$ ). So far, these are the only leaving groups known for our binuclear substrate and we cannot characterize them but by comparison with mononuclear analogues. Such comparison requires correction for the large acidity difference between **1** and its 2+-charged mononuclear analogues. For the latter, we take  $\text{p}K_a = 16.8$  for  $(\text{H}_3\text{N})_5\text{CoNO}_2^{2+}$  as a guide.<sup>23</sup> In order to compare the unimolecular rate constants  $k_{\text{AR}}$  and  $k_{\text{BS}}$  with the second-order rate constants  $k_{\text{OH}}$  of  $\text{cis-}[(\text{en})_2\text{NH}_3\text{CoX}]^{2+}$  ions, we consider that in  $1 \text{ mol dm}^{-3} \text{ OH}^-$  ca.  $1/1000$ th of these complexes are present as the conjugate bases. On this basis,  $\text{NH}_3$  and  $\text{cis-}[(\text{en})_2\text{NH}_3\text{CoNH}_2]^{2+}$  are seen to be intermediate leaving groups between the classes of mononuclear compounds  $\text{cis-}[(\text{en})_2\text{NH}_3\text{CoX}]^{2+}$  with  $\text{X} = \text{Cl}^-$ ,<sup>18</sup>  $\text{Br}^-$ ,<sup>27</sup>  $\text{Me}_2\text{SO}$ ,<sup>27</sup> and  $\text{TMP}$ <sup>27</sup> ( $k_{\text{OH}} = 1\text{--}2500 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) and  $\text{X} = \text{NH}_3$  in  $(\text{H}_3\text{N})_5\text{CoNO}_2^{2+}$  ( $k_{\text{OH}} = 2.7 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $62.9^\circ\text{C}$ ,  $\mu = 1.0$ ;<sup>28</sup> estimate for  $20^\circ\text{C}$ ,  $k_{\text{OH}} < 10^{-9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )<sup>29</sup> and in  $\text{Co}(\text{NH}_3)_6^{3+}$  ( $k_{\text{OH}} = 9.6 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).<sup>28</sup> The reactivity of **1** is similar to that of  $[(\text{en})_2\text{NH}_3\text{CoSO}_3]^{3+}$  ( $k_{\text{AR}} = 2 \times 10^{-2} \text{ s}^{-1}$ ),<sup>29</sup> which is subject to the strong trans-labilizing effect of  $\text{SO}_3^{2-}$ .<sup>29</sup> Other examples of ammonia labilization involve imine nitrogen donors in sterically crowded macrocyclic ligands<sup>31</sup> and are less pertinent to our comparison. Despite the similar reactivity of the sulfito and related S-donor complexes, we do not consider a similar trans effect in **1** as there is no structural evidence for a ground-state trans influence as in the sulfur-donor complexes.

The two reaction pathways of **1** are both greatly accelerated relative to mononuclear analogues. Part of this acceleration ( $\sim 10^3\text{--}10^5$  times) reflects the  $\text{p}K_a$  difference between mononuclear and dinuclear species. We attribute the remaining, intrinsic rate acceleration for the loss of ammonia in the conjugate base  $(\text{1-H})^{4+}$  ( $\geq 10^3$  times higher than in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  or  $[(\text{H}_3\text{N})_5\text{CoNO}_2]^{2+}$ ) to the steric effect of the

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linking of two hexacoordinate units by one bridging atom. The structural effects of nonbonded interactions become indeed apparent from the structure of cation **1**; the evidence for strain around the bridging ligand has been presented above. Base hydrolysis of Co(III) amines is particularly sensitive to steric acceleration effects, which supports the dissociative character of this reaction.<sup>32</sup> Strain relief by formation of an intermediate state of reduced coordination number should be effective both in the bridge-splitting pathway and in ammonia release.

The kinetics of the base hydrolysis of **1** in azide and chloride media show a nonlinear rate decrease with increasing anion concentration (Figure 2c). We interpret the rate effect of the added anions by ion association to form unreactive ion pairs ( $K_Y$ ) and ion triplets ( $K_{Y_2}$ ). One important consequence of ion aggregate formation is the lowering of the deprotonation constant  $K_b$  for electrostatic reasons. The calculated stabilities for the ion aggregates (relative to the perchlorate reference medium) are as expected,  $K_Y > K_{Y_2}$  for both anions. The larger standard deviations of the parameters in rate law (3) for  $Y^- = N_3^-$  may be caused by specific activity effects of the nonspherical azide ion. Formation of unreactive ion aggregates has previously been found in acid-induced and spontaneous aquation of the "mono-ol" cation  $[(H_3N)_5CoOHCo(NH_3)_5]^{5+}$ .<sup>33</sup> While the stereochemistry and anion-scavenging properties of ammonia release have not so far been explored, the bridge-splitting pathway has been found to proceed with extensive *cis* to *trans* rearrangement at the center of substitution. Configurational rearrangement is commonly found in the base hydrolysis of *cis*- and *trans*- $[(en)_2NH_3CoX]^{n+}$  ions. The data in Table VII show insignificantly small variation (75.5 ( $\pm 1.5$ )%) in the extent of rearrangement across the series of 2+-, 3+-, and 5+-charged species. However, the latter should be regarded as preliminary. Across this series of *cis*- $[(en)_2NH_3CoX]^{n+}$  species, there is also an impressive variation of the bulk of the leaving group from simple anions such as  $Cl^-$  to the  $[(en)_2(NH_3)_2Co]^{3+}$  or  $[(en)_2NH_3CoNH_2]^{2+}$  moiety, respectively.

In contrast, azide scavenging increases significantly with increasing charge of the reactant: 25% (2+), 30 ( $\pm 1$ )% (3+), and 38% (5+). Such dependence on the charge of the leaving group may appear inconsistent with the existence of an intermediate of discrete lifetime. Concerted, dissociative interchange of leaving and entering groups ( $I_d$ ) has been postulated for such situations.<sup>34,35</sup> However, the criteria of concertedness are incompletely fulfilled, as the extent of stereochemical rearrangement is rather constant for differently charged substrates and leaving groups with different steric requirements. A similar, charge-dependent anion-scavenging pattern for  $[(H_3N)_5CoX]^{n+}$  substrates with  $n = 1, 2, \text{ or } 3$  has been interpreted in terms of coordinatively unsaturated intermediates under the influence of the ionic atmosphere of the starting complex.<sup>36</sup> The lifetime of these intermediates is thus shorter than, or comparable with, relaxation of the ionic atmosphere surrounding the conjugate base of the starting material.

In conclusion, the bridge-splitting pathway of the base hydrolysis of **1** shares the main characteristics of product formation with mononuclear analogues. Anion scavenging is higher than for lower charged substrates, but no evidence for anion entry with concerted loss of the leaving group is found.

The kinetics at low ionic strength allowed observation of an unreactive ion pair of  $OH^-$  with the complex, and ion pairs with other anions are also unreactive. The high acidity of the coordinated amine functions as well as steric strain at the bridging ligand explains the high rates observed in base.

Both bridge splitting and monodentate ligand release could constitute models of elementary steps following dimer formation in metal ion hydrolysis if  $NH_2^-$  and  $NH_3$  are good analogues of  $OH^-$  and  $OH_2$ . The rapid bridge-splitting pathway suggests the possibility of rapid base-catalyzed depolymerization steps, at least involving singly bridged intermediates. The rapid loss of  $NH_3$  may find a parallel in water lability in hydrolytic dimers. Further work,<sup>16</sup> including X-ray structural studies, suggests an important steric contribution in the acceleration of both pathways, and this could operate generally in singly bridged moieties of hydrolytic polymers.

Clearly, care must be exercised in generalizing these results to hydrolytic species of other metallic centers, given the special features of low-spin  $3d^6$  Co(III), particularly its distinct preference for dissociative activation in its substitution reactions. However, we wish to point out that the two main factors recognized in the accelerated substitution at Co(III) amine dimers (viz. electrostatically enhanced ligand acidity and steric strain at the bridging ligand) are rather general ones. While their influence is likely to vary considerably from one metal center to the other, we nevertheless expect them to operate in most cases. This view finds support in several hydroxo-bridge formation reactions of  $[L_4Cr(OH)(\mu-OH)(OH_2)CrL_4]^{4+}$  species ( $L = 1/2 en, NH_3, H_2O$ ).<sup>37</sup> The unimolecular rate constant of formation of the  $(\mu-OH)_2$  species is some 7–140 times larger than that of formation of the  $(\mu-H_2O)(\mu-OH)$  dibridged species from  $[L_4Cr(OH_2)(\mu-OH)(OH_2)CrL_4]^{5+}$ . These latter species are all strong acids ( $pK_a = 0.5-1.6$ ) as expected. The observed accelerations for the dinuclear monohydroxo species are similar to or larger than those for dissociatively activated  $[(H_2O)_5CrOH]^{2+}$  relative to associatively activated  $[Cr(OH_2)_6]^{3+}$  (60 times).<sup>40</sup>

Steric acceleration does not clearly emerge from these data as expected from the positive bond length difference between Cr–O and Co–N bonds. However, the electrostatic acidity effect of the Cr(III) dimers is manifested by a high efficiency of the conjugate base pathway, already at low pH.

## Experimental Section

**Physical Measurements.** UV-vis spectra and conventional kinetics were measured on a Varian Techtron 635 instrument thermostated to  $25.0 \pm 0.1$  °C by a Lauda thermostat.  $^{13}C$  and  $^1H$  NMR spectra were recorded on Bruker HX-90 or WM-250 instruments in the FT mode at 22.63 and 90 or 250 MHz, respectively. pH values of the  $NH_3/NH_4^+$  buffers were measured at 25 °C with a combined-glass (Ag/AgCl) electrode filled with  $KClO_4$  ( $0.09 \text{ mol dm}^{-3}$ )/KCl ( $0.01 \text{ mol dm}^{-3}$ ) reference electrolyte. The electrode was calibrated by titrations of  $HClO_4$  ( $2 \times 10^{-3} \text{ mol cm}^{-3}$ ) in  $KClO_4$  ( $0.1 \text{ mol dm}^{-3}$ ) with standard KOH ( $0.1 \text{ mol dm}^{-3}$ ).  $pK_w$  was determined as  $13.69 \pm 0.01$  in this medium.

**Materials.** All chemicals used were of purissimum or analytical reagent grade quality. Water was deionized and distilled before use.

**Preparations.**  $(\pm)$ - $(\mu$ -Amido) $(\mu$ -chloro)tetrakis(1,2-ethanediamine)dibromide Tetrachloride Hydrate.  $(\mu$ -Amido) $(\mu$ -sulfato)tetrakis(1,2-ethanediamine)dibromide<sup>3,4</sup> (0.62 g, 0.87 mmol) was dissolved and stirred in hydrochloric acid ( $10 \text{ mol dm}^{-3}$ ,  $1.24 \text{ cm}^3$ , 48 h at 25 °C). Slow addition of ethanol to the cooled solution (0 °C) precipitated the desired product, which was filtered off, washed (ethanol), and dried. Recrystallization was achieved by dissolving

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Table VII. Stereochemical Course and Azide Scavenging in Base Hydrolysis of  $[(en)_2CoNH_3X]^{2+}$  Complexes at 25 °C

complex	medium		products <sup>a</sup>					
	anion	concn, mol dm <sup>-3</sup>	$[(en)_2CoNH_3N_3]^{2+}$			$[(en)_2CoNH_3OH]^{2+}$		
			$\Lambda$ -cis	$\Delta\Lambda$ -cis	trans	$\Lambda$ -cis	$\Delta\Lambda$ -cis	trans
$X = Cl^-, Br^-, NO_3^-^{15}$								
$\Lambda$ -cis	$N_3^-$	1.0	9	9	7	35	23	17
	$ClO_4^-$	1.0				46	31	23
trans	$N_3^-$	1.0		16	8		49	27
	$ClO_4^-$	1.0					64	36
$X = (CH_3)_2SO^{17}$								
$\Lambda$ -cis	$N_3^-$	1.0	13.3	6.9	9.6	36.2	18.0	16.0
	$ClO_4^-$	1.0				51.3	25.6	23.1
$X = (CH_3O)_3PO^{17}$								
$\Lambda$ -cis	$N_3^-$	1.0	14.4	6.2	10.5	37.4	16.0	15.5
	$ClO_4^-$	1.0				54.3	23.2	22.5
$X = (en)_2NH_3CoNH_2^{2+}$								
1	$N_3^-$	1.0		38 <sup>b</sup>			62 <sup>b</sup>	
		$\mu$ low					74 <sup>b</sup>	26 <sup>b</sup>

<sup>a</sup> Data normalized to 100% product recovery. <sup>b</sup> Bridge-splitting pathway only.

the crude product in the minimum of concentrated hydrochloric acid and addition of ethanol; yield 0.41 g (82%). Anal. Calcd for  $C_8H_{36}Cl_3Co_2N_9O$ : C, 16.87; H, 6.37; N, 22.13. Found: C, 17.0; H, 6.5; N, 21.6.

**( $\pm$ )-( $\mu$ -Amido)chloroaquatetakis(1,2-ethanediamine)dicalcobalt Tetranitrate.** The ( $\mu$ -amido)( $\mu$ -chloro) compound (0.42 g, 0.74 mmol) was dissolved in water (10 cm<sup>3</sup>, 0 °C) with vigorous stirring. As soon as dissolution was complete, nitric acid (65%, 3.5 cm<sup>3</sup>) was added at once. A precipitate formed, which was filtered off and washed with ethanol and diethyl ether; yield 0.32 g (64%). Anal. Calcd for  $C_8H_{36}ClCo_2N_{13}O_{13}$ : C, 14.22; H, 5.37; N, 26.94. Found: C, 14.5; H, 5.6; N, 26.5.

**( $\pm$ )-( $\mu$ -Amido)tetrakis(1,2-ethanediamine)diamminedicalcobalt Pentanitate Dihydrate (1).** The chloro aqua complex (0.25 g, 0.37 mmol) was placed in a predried Schlenk tube (50 cm<sup>3</sup>) with a gas inlet tube. Enough sodium-dried liquid ammonia was evaporated from a reservoir and condensed in the Schlenk tube to just cover the solid. This was completely dissolved by gentle shaking of the tube. Most of the ammonia evaporated during the dissolution process. After all liquid ammonia had disappeared, the reaction vessel was connected to an oil-pump vacuum for at least 2 h. Thus, the material was exposed to ammonia for 7–15 min. The tarry residue was then dissolved in dilute nitric acid (1%, 40 °C), and from the filtered solution was precipitated 1 with nitric acid (65%) at 0 °C. The compound was filtered off, washed (ethanol, diethyl ether), and dried in a stream of air. Pure, light red product was obtained by at least one recrystallization from water/nitric acid; yield 0.15 g (54%). Anal. Calcd for  $C_8H_{44}Co_2N_{16}O_{17}$ : C, 12.74; H, 5.88; N, 29.71. Found: C, 12.7; H, 5.6; N, 29.0.

**trans-Bis(1,2-ethanediamine)diamminedicalcobalt Trichloride Hydrate.<sup>14</sup>** Finely ground ( $\pm$ )-*cis*-dichlorobis(1,2-ethanediamine)cobalt chloride<sup>41</sup> (4 g, 0.014 mol) was dissolved in liquid ammonia (ca. 300 cm<sup>3</sup>). The ammonia was then evaporated overnight with stirring under an atmosphere that excluded air. The residue was dissolved in the minimum of water (20 °C). Sodium dithionite (5.1 g, 0.02 mol) was added to crystallize the *trans*-diammine compound. (The mother liquor contains the *cis* isomer.) The solid *trans* isomer was filtered off, washed (ethanol, diethyl ether), and air-dried; yield 1 g (15%) of *trans*- $[(en)_2Co(NH_3)_2(S_2O_6)_3 \cdot 4H_2O]$ . This product was dissolved in water, adsorbed on Dowex 50W-X2 cation-exchange resin (200–400 mesh, H<sup>+</sup> form), washed with water to remove dithionite, and eluted with hydrochloric acid (3 mol cm<sup>-3</sup>). The eluate was evaporated to small volume. On addition of ethanol, crystals of the chloride salt separated, which were recrystallized from hot hydrochloric acid (4 mol cm<sup>-3</sup>)/ethanol; yield 0.63 g of *trans*- $[(en)_2Co(NH_3)_2]Cl_3 \cdot H_2O$ . Anal. Calcd for  $C_8H_{24}Cl_3CoN_6O$ : C, 14.23; H, 7.17; N, 24.90; Cl, 31.51. Found: C, 14.7; H, 7.3; N, 24.4; Cl, 31.6.

**( $\pm$ )-*cis*-Bis(1,2-ethanediamine)diamminedicalcobalt Trichloride Dihydrate.<sup>14</sup>** The mother liquor of the preceding preparation was treated with potassium iodide (7 g, 0.042 mol). The resulting precipitate of potassium dithionite was filtered off, and the filtrate was evaporated until crystals of the product formed, which were recrystallized three times from water/potassium iodide; yield 3.2 g (38%) of *cis*- $[(en)_2Co(NH_3)_2]I_3$ . A 1-g sample of this product was converted into the chloride as described for the *trans* isomer to yield 0.35 g of *cis*- $[(en)_2Co(NH_3)_2]Cl_3 \cdot 2H_2O$ . Anal. Calcd for  $C_8H_{26}Cl_3CoN_6O_2$ : C, 13.51; H, 7.37; N, 23.63; Co, 16.57. Found: C, 13.9; H, 6.9; N, 23.4; Co, 16.7. The product was shown to contain 5 ( $\pm$ 2)% *trans* isomer by <sup>13</sup>C NMR spectroscopy. Since the molar absorptivities of the two diastereoisomers are similar at the chosen wavelengths, this impurity will not influence the spectral parameters beyond the error.

**Kinetics. (a) [OH<sup>-</sup>] Dependence of the Base Hydrolysis of 1.** For the runs in  $NH_3/NH_4^+$  buffers, samples of 1 (ca. 2 mg) were directly dissolved in prethermostated spectrophotometric cells (1 cm) containing the buffer. The reaction was then immediately followed at 355 nm for 4–10 half-lives, and the pH was measured after the reaction. The rapid reactions in KOH/KClO<sub>4</sub> ( $\mu = 0.1 \pm 0.005$ ) or NaOH/NaClO<sub>4</sub> ( $\mu = 1.0 \pm 0.05$ ) were also followed at 355 nm on a Durrum D-110 stopped-flow spectrophotometer. Plots of  $\ln |D_t - D_\infty|$  vs. time were linear for at least 3–4 half-lives.  $[Co]_t$  was within  $(1-1.6) \times 10^{-3}$  mol dm<sup>-3</sup>.

**(b) Anion Dependence.** A solution of NaOH (0.02 mol dm<sup>-3</sup>) with  $[NaClO_4] + [NaY] = 1$  mol dm<sup>-3</sup> was rapidly mixed with another solution containing 1 ( $[Co]_t = (1-2.8) \times 10^{-4}$  mol dm<sup>-3</sup>) and electrolytes ( $[NaClO_4] + [NaY] = 1$  mol dm<sup>-3</sup>) in the stopped-flow spectrophotometer. Plots of  $\ln |D_t - D_\infty|$  vs.  $t$  were linear for at least 3–4 half-lives.

**Product Analysis.** A 46–70-mg sample ( $(6.1-9.3) \times 10^{-5}$  mol) of 1 was treated with NaOH (0.01 mol dm<sup>-3</sup>, 40 cm<sup>3</sup>) at 25 °C for 5 min. The reaction mixture was then acidified with HCl (1 mol dm<sup>-3</sup>, 1–2 cm<sup>3</sup>) and sorbed on a column of Dowex 50W-X2 (200–400 mesh, H<sup>+</sup> form, (5–7)  $\times$  (0.8–1) cm). In the reactions with alkaline azide medium (1 mol dm<sup>-3</sup> NaN<sub>3</sub>, 0.1 mol dm<sup>-3</sup> NaOH, 25 cm<sup>3</sup>), the same procedure was followed except that the mixture was quenched with acetic acid (1 cm<sup>3</sup>, 100%) and diluted to 200 cm<sup>3</sup> with water before adsorption on the column. The products were separated on the column and eluted first with NH<sub>4</sub>Cl (1 mol dm<sup>-3</sup>, pH 3) to give *cis*- and *trans*- $[(en)_2NH_3CoN_3]^{2+}$  and then with NH<sub>4</sub>Cl/NH<sub>3</sub> (1 mol dm<sup>-3</sup>, pH 9) to remove *cis*- and *trans*- $[(en)_2NH_3CoOH]^{2+}$ , which was acidified after elution (HClO<sub>4</sub>). The  $[(en)_2NH_3CoOH]^{2+}$  band was not preceded by detectable amounts of  $[(en)_2Co(OH)_2]^{2+}$ . *cis*- $[(en)_2Co(NH_3)_2]^{3+}$  was eluted with HCl (2 mol dm<sup>-3</sup>). The remaining dimer fraction was removed by HCl (4 mol dm<sup>-3</sup>). The concentrations of the complex species in the eluate fractions were determined by atomic absorption for Co in the azido and aqua complexes and the dimer fraction. Spectrophotometry was used as a complementary or alternative method for the aqua complexes and  $(en)_2Co(NH_3)_2^{3+}$ , using published extinction coefficients<sup>15</sup> for *cis*- $[(en)_2NH_3CoOH]^{2+}$  ( $\epsilon_{485} = 67.9$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) and *trans*- $[(en)_2NH_3CoOH]^{2+}$  ( $\epsilon_{485} = 45.5$

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$\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ) and the redetermined value for *cis*-[(en)<sub>2</sub>Co(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> ( $\epsilon_{469} = 79.1 \text{ mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ ). For the determination of the *cis*/*trans* ratio in [(en)<sub>2</sub>NH<sub>3</sub>CoOH]<sup>2+</sup> by <sup>13</sup>C NMR, the NH<sub>4</sub>Cl eluates were adsorbed once again on the resin, eluted with HCl (3 mol dm<sup>-3</sup>), and evaporated to dryness at room temperature. Spectra were recorded on solutions of the dry residues in D<sub>2</sub>O with a small amount of Na<sub>2</sub>CO<sub>3</sub> for complete amine proton exchange.

**Crystal Structure Determination.** The space group was determined by using a Charles Supper Co. precession camera with Cu K $\alpha$  radiation. Precise determination of the cell parameters and data collection were carried out on an automated CAD-4 (Enraf-Nonius) diffractometer at room temperature. The cobalt atoms were found in an initial Patterson synthesis, and the further non-hydrogen atoms in a subsequent Fourier synthesis. Refinement was made for all non-hydrogen atoms by the method of least squares with scattering factors from the literature.<sup>43,44</sup> Three positional and six thermal

parameters were determined for each refined atom.

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**Registry No.** 1(NO<sub>3</sub>)<sub>5</sub>·2H<sub>2</sub>O, 87393-35-9; [(en)<sub>2</sub>Co]<sub>2</sub>[NH<sub>2</sub>Cl]Cl<sub>4</sub>, 87420-78-8; [(en)<sub>2</sub>Co]<sub>2</sub>[NH<sub>2</sub>SO<sub>4</sub>]Br<sub>3</sub>, 87420-79-9; *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 36883-69-9; ( $\pm$ )-*cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>, 52021-81-5;  $\Lambda$ -*cis*-[(en)<sub>2</sub>CoNH<sub>3</sub>OH]<sup>2+</sup>, 45837-83-0;  $\Delta$  $\Lambda$ -*cis*-[(en)<sub>2</sub>CoNH<sub>3</sub>OH]<sup>2+</sup>, 38246-61-6; *trans*-[(en)<sub>2</sub>CoNH<sub>3</sub>OH]<sup>2+</sup>, 38246-62-7;  $\Lambda$ -*cis*-[(en)<sub>2</sub>CoNH<sub>3</sub>N<sub>3</sub>]<sup>2+</sup>, 46139-34-8;  $\Delta$  $\Lambda$ -*cis*-[(en)<sub>2</sub>CoNH<sub>3</sub>N<sub>3</sub>]<sup>2+</sup>, 36501-76-5; *trans*-[(en)<sub>2</sub>CoNH<sub>3</sub>N<sub>3</sub>]<sup>2+</sup>, 46139-36-0; [(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>Co(OH)(en)<sub>2</sub>]<sup>4+</sup>, 87372-44-9; ( $\pm$ )-*cis*, *cis*-[(en)<sub>2</sub>NH<sub>3</sub>CoNH<sub>2</sub>CoCl(en)<sub>2</sub>]<sup>4+</sup>, 87372-45-0; ( $\pm$ )-( $\mu$ -amido)aquachlorotetakis(1,2-ethanediamine)dichlorobis(1,2-ethanediamine)cobalt tetranitrate, 87420-81-3; ( $\pm$ )-*cis*-dichlorobis(1,2-ethanediamine)cobalt chloride, 14040-32-5.

**Supplementary Material Available:** Listings of observed and calculated structure factors, temperature factors, and rate data in aqueous solution (Table VI) (17 pages). Ordering information is given on any current masthead page.

- (43) Co: "International Tables for X-Ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1968; Vol. III.  
 (44) C, N, O: Cromer, D.; Mann, J. *Acta Crystallogr., Sect. A* 1968, A24, 321.  
 (45) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B* 1972, B29, 589.  
 (46) This short bond length coincides with a large thermal motion ellipsoid of C26 and one could suspect the presence of two disordered conformers. However, in a Fourier map at 0.1-Å resolution with C26 omitted, two maxima were not seen up to 1 Å around the idealized position of C26. Furthermore, the calculated N-C-C-N torsion angle in this chelate ring (47.2°) agrees reasonably with the experimental values of 50.3, -49.3, and -49.1°, respectively, for the other three en rings. Much larger deviations are expected if two disordered conformers were present. The carbon atoms of en chelate rings are basically quite mobile, but their motion is usually restricted by the proximity of other atoms in the lattice.

- (47) Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 509.  
 (48) Rate law (2) is probably observed because of the more restricted range of [OH<sup>-</sup>].

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## Preparation, Characterization, and Chromium(II) Reduction Kinetics of Tetrazole Complexes of Pentaamminecobalt(III)

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The synthesis and characterization of several pentaamminecobalt(III) complexes of 5-substituted tetrazoles are reported: 5-cyanotetrazole, 5-methyltetrazole, 5-carbamoyltetrazole, and unsubstituted tetrazole. Characterization by proton, carbon-13, and nitrogen-15 NMR and by ultraviolet-visible spectroscopy established that bonding between cobalt(III) and the tetrazole ring occurs at the nitrogen at ring position 2 in agreement with previous crystal structure determinations on the 5-methyl and 5-cyanotetrazole complexes. Kinetics of the hexaaquachromium(II) reduction of these various cobalt(III) complexes is reported as well as the reduction kinetics for the N-1-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex, the linkage isomer of the N-2-bonded 5-methyl complex. All reductions proceed principally by an inner-sphere electron-transfer process with reduction pathways appearing for both the protonated (3+) and deprotonated (2+) complexes characterized by rate constants  $k_0$  and  $k_1$ , respectively. A mechanistic scheme common to all five complexes is proposed that predicts the operation of two limiting forms of the rate law governed by the  $pK_a$ 's of the five complexes. At 25 °C,  $k_0$  values are  $19 \pm 2$ ,  $0.15 \pm 0.08$ , and  $2.4 \pm 0.3 \text{ L mol}^{-1} \text{ s}^{-1}$  for the tetrazole, N-2-bonded 5-methyltetrazole, and N-1-bonded 5-methyltetrazole complexes, respectively. The  $k_1$  values are  $3.3 \pm 0.3$ ,  $0.41 \pm 0.02$ , and  $0.83 \pm 0.02 \text{ s}^{-1}$  for these same three complexes at 25 °C. Separation of the observed rate constants into the two components was not possible for the 5-cyanotetrazole and 5-carbamoyltetrazole complexes.

### Introduction

Compared to the wealth of literature to be found for inner-sphere electron-transfer reactions involving bridging six-membered nitrogen heterocycles, relatively few studies utilizing

five-membered heterocyclic bridges are available. This is indeed unfortunate considering the importance of five-membered nitrogen heterocycles in biological systems, e.g., imidazole, benzimidazole, the purines, proline, and tryptophan. The concentration of effort on the six-membered nitrogen heterocycles probably reflects expediency since numerous substituted pyridines, pyrazines, and pyrimidines are commercially available. The literature that does exist concerning the electron-transfer involvement of five-membered nitrogen heterocycles is somewhat confusing. Understandably, studies

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