nitude of tensor components of the shielding tensor from the spinning sidebands give the approximate orientation of the ^{113}Cd shielding tensor without single-crystal NMR data.

It is clear from these two examples that the isotropic chemical shifts in the liquid and the solid state are misleading as to environmental differences but the components of the chemical shift do reflect subtle differences, specifically, the differences between σ_{33} of +31 ppm for A and +12 ppm for B. Therefore, at this time the best structural probe seems to be the combination of solid-state MAS/CP ^{113}Cd NMR data utilizing the spinning sidebands. X-ray crystallography will point the way toward the correct interpretations along with single-crystal ^{113}Cd NMR.

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Supplementary Material Available: Observed and simulated MAS/CP ^{113}Cd NMR spectra and Tables SI and SII, listing thermal parameters and hydrogen positions (13 pages); tables of calculated and observed structure factors (106 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratorium für Anorganische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland, and Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Activated Ligand Substitution in Bridged Complexes. 2.[1] Base Hydrolysis of the (μ-Amido)decaamminedicobalt(5+) Ion. Synthesis and Structure of the (μ-Amido)chloroenneaamminedicobalt(4+) Ion

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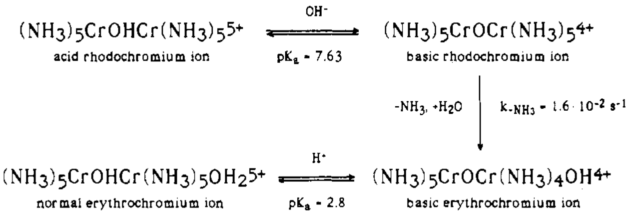
Deprotonation of the (μ-amido)decaamminedicobalt(III) ion (**1**) at one of the ammine ligands ($K_b = 89 \pm 19\ M^{-1}$, $pK_a = 11.7 \pm 0.1$, 25 °C, $I = 0.1$ ($KClO_4/NH_4ClO_4$)) is followed by rapid ammonia loss ($k_{-NH_3} = (4.6 \pm 1.0) \times 10^{-2}\ s^{-1}$). The thus formed intermediate reacts either with water (k_{H_2O}) to form $(NH_3)_5CoNH_2Co(OH)(NH_3)_4{}^{4+}$ (**2**) or with ammonia (k_{NH_3}) to re-form the (deprotonated) reactant ($R = k_{NH_3}/k_{H_2O} = 0.135 \pm 0.011\ M^{-1}$). The substitution of the first ammonia is followed by a series of further ammonia substitution and amido bridge cleavage steps. The first two reactions of **1** were retarded in aqueous ammonia. Product analyses under different conditions have established the absence of $(NH_3)_5CoOH^{2+}$ as a primary cleavage product of **1**. Thus, loss of the first ammonia is not accompanied by cleavage of **1** in a parallel pathway. Two of the observed reaction products, $(NH_3)_4Co(OH)_2{}^+$ and $Co(NH_3)_6{}^{3+}$, must arise in a later phase of the reaction, e.g. by cleavage of **2**. Kinetic studies have established conditions for the efficient synthesis of the "μ-amido–chloro–erythrocobalt" complex *cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4{\cdot}H_2O$. This compound crystallizes in the orthorhombic space group *Pcmn* with $a = 10.079$ (5) Å, $b = 12.382$ (8) Å, $c = 14.57$ (4) Å, and $Z = 4$. The molecules occupy special positions, and the two Co atoms and the Cl, N1, N2, N6, and N7 atoms as well as the oxygen atom of the water of crystallization lie on a mirror plane. The Co–N bond trans to Cl is slightly shortened (1.947 (9) Å); all others fall within the normal range (1.97–1.98 Å). The N1–Co2–Cl angle is distorted (97.2°). From the angle at the bridge, Co1–N1–Co2 = 140°, the cation appears strained, even in the most favorable, "staggered", conformation of the two octehedra that is adopted in the lattice. In acidic solution, *cis*-$(NH_3)_5CoNH_2CoCl(NH_3)_4{}^{4+}$ (**3**) first loses chloride ($k_{fast} = (6 \pm 2) \times 10^{-5}\ s^{-1}$, 25 °C, $I = 0.1$ ($HClO_4$)) and then cleaves into monomers ($k_{slow} = (1.4 \pm 0.9) \times 10^{-6}\ s^{-1}$).

Introduction

A little more than a century ago, Jørgensen prepared the rhodo- and erythrochromium complexes.[3] Since then, their structure and optical and magnetic properties as well as the unusual, fast formation of the erythrochromium ion by release of ammonia from the basic rhodochromium ion (Scheme I) have attracted continued interest.[4–9] In their classical paper (which established many of the important features of Scheme I), Schwarzenbach and Magyar[10] attributed the high reactivity of the basic rhodochromium ion to the trans labilizing effect of the μ-oxo ligand.

Scheme I



The cobalt(III) analogue of the acid rhodochromium ion, the so-called monool $(NH_3)_5CoOHCo(NH_3)_5{}^{5+}$, has been prepared by Siebert and Feuerhake.[11] The monool is unstable in aqueous solution at pH ≤4: 2 mol of aquapentaamminecobalt(III) is formed by acid-catalyzed and spontaneous bridge cleavage.[12–14] At pH >4 the monool decomposes rapidly, forming a dark brown solid.[12]

The (isoelectronic) μ-amido analogue of the monool, $(NH_3)_5CoNH_2Co(NH_3)_5{}^{5+}$ (**1**), has already been prepared by Werner.[15] This ion as well as the recently[1] prepared (±)-*cis*,*cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2{}^{5+}$ ion is stable in acid.

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Therefore, workup of the products formed by base hydrolysis is always possible by acidification, since under such conditions the rapid base hydrolysis reactions do not take place.

A previous study on the (±)-*cis,cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2^{5+}$ ion has shown that the μ-NH_2 bridge is *not* deprotonated in the formation of the conjugate base,[1] and this is also likely to be the case for complex **1**. Thus, possible acceleration of NH_3 substitution cannot follow the same mechanism as in the rhodochromium ion. Accelerated NH_3 release was indeed found in the base hydrolysis of the above μ-amido en dimer, although this was only a minor pathway (10–25 %). Most of the complex was cleaved into monomers.[1]

This work reports the kinetics and reaction products of base hydrolysis of **1** and the synthesis and crystal structure of an erythro-type cobalt(III) complex, $[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4{\cdot}H_2O$.

Experimental Section

Physical Measurements. UV–vis spectra and spectrophotometric kinetics were measured as described previously.[1] ^1H NMR spectra were recorded on a Bruker HX-90 or WM-250 instrument in the FT mode. pH measurements and pK_w determinations were made at 25 °C as in ref 1. pH stat kinetics were run on a Mettler titrator equipped with a potentiostat.

Materials. $[(NH_3)_4Co(OH_2)_2](ClO_4)_3$ was prepared according to ref 16. Anal. Calcd for $H_{16}N_4Cl_3CoO_{14}$: Co, 12.77. Found: Co, 12.56. A solution of this compound was equilibrated (cis and trans isomers) in CF_3SO_3H (0.1 M) at 25 °C. A solution of NH_4Cl was then added to make up $[Cl^-] = 0.9$ M. The UV–vis spectrum was then recorded immediately in $HClO_4$ (1 M): $\epsilon_{519} = 48.3$ (max), $\epsilon_{430} = 12.6$ (min), $\epsilon_{380} = 65.2$ (max), $\epsilon_{352} = 42.6$ (min) $M^{-1}\ s^{-1}$. The spectrum changed somewhat with time but remained unchanged after 12 h to give $\epsilon_{523} = 46.7$ (max), $\epsilon_{431} = 18.9$ (min), $\epsilon_{384} = 72.3$ (max), $\epsilon_{350} = 65.3$ (min) $M^{-1}\ s^{-1}$. These last extinction coefficients were used in calculating the amounts of $(NH_3)_4Co(OH)_2^+$ formed (Table II).

Preparation of $[(NH_3)_5CoNH_2Co(NH_3)_5](ClO_4)_5{\cdot}H_2O$. The nitrate salt[17] was dissolved in a minimum amount of acidified ($HClO_4$) water, treated with excess $NaClO_4$ and some ethanol, and cooled to −5 °C. The crude perchlorate salt precipitated and was purified as described previously.[17] However, in the last crystallization, the compound was precipitated with $HClO_4$ (60%). The crystals were washed with ethanol and ether and dried in air. Anal. Calcd for $H_{34}N_{11}O_{21}Cl_5Co_2$: H, 4.18; N, 18.80; Cl, 21.63. Found: H, 4.13; N, 18.82; Cl, 21.62. UV–vis spectrum is in accord with ref 17.

Preparation of *cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4{\cdot}H_2O$. A 0.7-g (1.2-mmol) sample of $[(NH_3)_5CoNH_2Co(NH_3)_5](NO_3)_5$[17] was dissolved in water (ca. 75 mL). To this solution was added a mixture of 25% ammonia (10 mL) and NaOH (1 M, 7.5 mL) at room temperature. After 3 min, HCl (2 M, ca. 90 mL, 0 °C) was added. The reaction mixture was diluted (400 mL) and sorbed onto Dowex 50W-X2, 200–400 mesh, 10 × 1 cm (H^+ form). Elution with HCl (2 M) removed the mononuclear complexes as well as a small amount of brown polymer. When the eluate was colorless, the $(NH_3)_5CoNH_2CoCl(NH_3)_4^{4+}$ ion was eluted with HCl (4 M). This fraction was evaporated on rotary evaporator (40 °C bath temperature) to incipient crystallization. Addition of ethanol completed the crystallization. The crude product was recrystallized from water/concentrated HCl/ethanol, filtered out, washed (ethanol, ether), and air-dried. Yield: 0.3 g (50%). Anal. Calcd for $H_{31}N_{10}OCl_5Co_2$: H, 6.48; N, 29.03; Cl, 36.74. Found: H, 6.34; N, 28.08; Cl, 36.35.

Kinetics. For the pH stat kinetics, the pH values were determined by using a combined glass electrode (Ag/AgCl reference). Samples of 27–40 mg ($(4.4–6.5) \times 10^{-5}$ mol) of **1** (as the pentanitrate) were dissolved in $KClO_4$ (0.1 M) at 25 °C. Nitrogen was bubbled through the solutions during the additions of base (KOH, 0.1 M), and the volumes of base were recorded as a function of time.

In the spectrophotometric runs at 330 nm, 1.5–1.9-mg samples of **1** (pentanitrate salt) were rapidly dissolved in the reaction medium (Table I) in a thermostated 1-cm quartz cell (ca. 3 mL).

Product Analysis. Complex **1** as the nitrate or perchlorate salt (30–100 mg) was dissolved in water. The reaction was then immediately started by adding a solution of KOH or of a mixture of NH_3 and KOH containing enough electrolyte to make up the final ionic strength. The reactions were quenched with HCl, and the mixtures were diluted to a total electrolyte concentration of <0.2 M and adsorbed on Dowex 50W-X2, 200–400 mesh, 10 × 1 cm (H^+ form). The separation was carried out in two steps. First, elution with HCl (2 M) gave a fraction containing mononuclear species and brown, higher polynuclear aggregates. Subsequently, HCl (4 M) eluted $(NH_3)_5CoNH_2CoCl(NH_3)_4^{4+}$ and unreacted starting material as separate bands. The fraction containing the mononuclear species was then diluted 10-fold, adsorbed, and separated as follows: $(NH_3)_4Co(OH_2)_2^{3+}$ was eluted with NaCl or NH_4Cl (1 M, pH 4–5), and $(NH_3)_5CoOH_2^{3+}$ was eluted as the hydroxo complex by using NaCl or NH_4Cl (1 M, pH 8–10). These fractions were often contaminated by small amounts of brown, higher polymers. The remaining part of this polymer was eluted along with $Co(NH_3)_6^{3+}$ by using HCl (2 M). Quantitative determination of the fractions was made spectrophotometrically by using $\epsilon_{510} = 55.3$ for the equilibrium mixture of *trans*- and *cis*-$(NH_3)_4Co(OH_2)_2^{3+}$, $\epsilon_{492} = 47.9$[18] for $(NH_3)_5CoOH_2^{3+}$, $\epsilon_{479} = 57.6$[18] for $Co(NH_3)_6^{3+}$, $\epsilon_{512} = 306$ for $(NH_3)_5CoNH_2CoCl(NH_3)_4^{4+}$, and $\epsilon_{507} = 413\ M^{-1}\ cm^{-1}$ for $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$. No correction was made for the variable amounts of brown, higher polymer.

The nitrogen-containing (<9%), insoluble "$Co(OH)_3{\cdot}2H_2O$" fraction was obtained as the end product in the absence of excess ammonia. Solutions containing this material, along with soluble species (viz. largely $Co(NH_3)_6^{3+}$), were treated by one of the following methods: (i) filtration of the insoluble material and separation of the soluble species by the above procedure; (ii) treating the suspension with acids (HCl, $HClO_4$, H_2SO_4) at 20–60 °C, diluting, and separating the fragments as above; (iii) removal of the soluble fraction by dialysis through a collodium membrane. All the three procedures gave very nearly the same amounts of $Co(NH_3)_6^{3+}$. Procedure ii gave $Co(NH_3)_6^{3+}$ and Co^{2+} as the only products.

Crystal Structure Determination. The space group was determined photographically on a Charles Supper Co. precession camera using Cu Kα radiation. Precise determination of the cell parameters and data collection were carried out on an automated four-circle diffractometer (CAD-4; Enraf-Nonius) at room temperature. The Patterson function was difficult to interpret, but the Co atoms were found by using direct methods (Multan-77).[19] Isotropic refinement of the Co atoms and subsequent Fourier synthesis gave all non-hydrogen atom positions in the noncentrosymmetric space group $Pc2_1n$ ($Z = 4$). However, anisotropic refinement of the N atoms failed, and the parameters of the Cl and N atoms were highly correlated. The phases of most reflections were near 0 or 180°. Thus, the centrosymmetric space group $Pcmn$ ($Z = 4$) was chosen. In this space group, anisotropic refinement of all non-hydrogen atoms was successful with the atoms Co1, Co2, N1, N2, N6, N7, and O in a special position (mirror plane: $y = 0.25$). The parameters were not significantly correlated. Smaller standard deviations in the bond lengths and angles were found than in the noncentrosymmetric space group $Pc2_1n$. A difference Fourier synthesis showed the hydrogen positions to be somewhat disordered. No hydrogen atoms were therefore considered in the refinement. A high-order refinement according to Seiler and Dunitz[20] was performed to compensate for this omission and to determine precise positions of the electron core containing non-H atoms. Scattering factors from the literature[21,22] were used in the refinement, and three positional and six thermal parameters were determined for each non-hydrogen atom. All the calculations were done using the programs of Stewart et al.[23]

Results and Discussion

The $(NH_3)_5CoNH_2Co(NH_3)_5^{5+}$ Ion (1). This dimer was synthesized by the published method.[17] Its ^1H NMR spectra measured in D_2O/DCl and D_2O/CF_3COOD, respectively, show similar high-field resonances for the bridging NH_2 group ($\delta(\mu$-$NH_2)$ ~1 ppm, ~1 H, $\Delta\nu_{1/2} = 100$ Hz) as (±)-*cis,cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2^{5+}$.[1] The μ-NH_2 protons did not show any exchange against deuterium within 30 min in neutral D_2O. The

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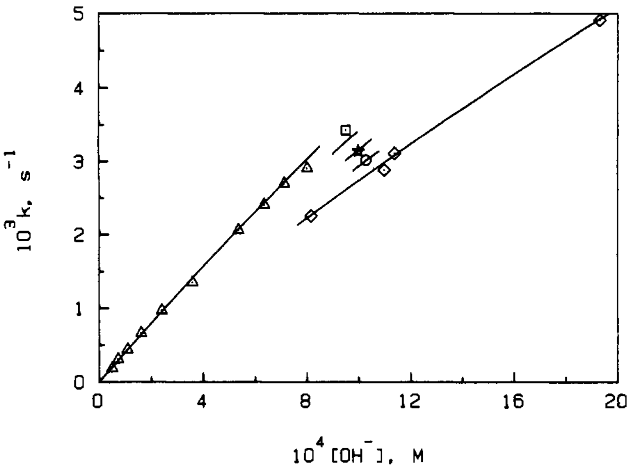

Figure 1. Base hydrolysis kinetics of **1** at 25 °C and $I = 0.1$ ($KClO_4$/NH_4ClO_4). [NH_3] (M): triangles, 0.0; square, 0.66; star, 1.32; circle, 1.98; diamonds, 2.64. Solid line was calculated according to rate law I.

NH_3 protons exchanged much faster (by $>10^4$ times), and compound **1** resembles the ethylenediamine analogue in this respect.

Reactivity in Acid and in Base. While quite inert in acidic solution ($k \approx 2 \times 10^{-7}$ s^{-1}, by extrapolation to 25 °C[24]), **1** decomposes more rapidly in alkaline solution. The reactivity of **1** can be illustrated by the following, qualitative observations: in dilute NaOH (pH ~11–12) the dimer remains unchanged for a few minutes and then turns purple and eventually brown. As soon as the color changes occur, free ammonia is detected. From the brown solution separates an olive brown, flocculent precipitate within a few minutes to hours. In the presence of excess ammonia, however, no precipitate is formed even after several days and the brown color develops much more slowly.

The nature of this precipitate has not been established. Its cobalt content (~41%) is similar to that of "$Co(OH)_3 \cdot 2H_2O$", but it contains nitrogen in variable amounts (4–9%), depending on the method of preparation and workup. Its formation probably implies cleavage of the μ-NH_2 bridge in **1** at some stage of the reaction sequence, since hexaamminecobalt(III) was found in the supernatant liquid of the resulting precipitate. $Co(NH_3)_6^{3+}$ does not, however, arise from direct cleavage of deprotonated **1** (see below).

Kinetics of Base-Catalyzed Decomposition of 1. In a first set of experiments, the reaction of **1** in aqueous solution was followed by pH stat titration with KOH at 25 °C and $I = 0.1$ ($KClO_4$). The volume of base consumed at constant [OH$^-$] followed nearly uniphasic kinetics. The pseudo-first-order rate constants k_1 were obtained from Guggenheim plots. The values of k_1 (Table I, Figure 1) show small, but distinct, deviations from a perfectly linear dependence on [OH$^-$]. This indicates that some NH protons of **1** are quite acidic.

In these runs, the total base consumption was ~0.8–1.6 mol OH$^-$/mol of **1**, and the values increased nonlinearly as a function of pH. However, no attempt has been made thus far to establish the net stoichiometry of this reaction and its dependence on [OH$^-$].

In a second set of experiments, the kinetics were measured spectrophotometrically in aqueous ammonia. This prevented the formation of the "$Co(OH)_3 \cdot 2H_2O$" precipitate. The kinetics were followed at 330 nm (25 °C, $I = 0.1$). At least three reaction phases were observed in contrast to the pH stat runs. We assume that the consecutive steps escaped detection on the pH stat because these reactions consume small amounts of base. The optical density D as a function of time was fitted to a sum of three exponentials: $D = A \exp(-k_1 t) + B \exp(-k_2 t) + C \exp(-k_3 t) + E$. The third exponential was included in order to obtain reasonable k_2 values. The most rapid first phase (k_1) contributed most to the optical density change and was thus determined with greater precision than k_2 and especially k_3. The first phase was accompanied by a large increase in optical density; the others caused a comparatively small decrease.

Table I. Kinetics of Base Hydrolysis of **1** at $I = 0.1$ ($KClO_4$/NH_4ClO_4) and 25 °C

		$10^3 k_1$, s^{-1}		
10^4[OH$^-$], M	[NH_3], M	obsd	calcd[a]	k_1/k_2
0.486	0.0	0.183[b]	0.196	
0.711		0.305[b]	0.287	
1.07		0.437[b]	0.430	
1.59		0.660[b]	0.636	
2.39		0.969[b]	0.950	
3.58		1.35[b]	1.41	
5.34		2.06[b]	2.07	
6.33		2.41[b]	2.43	
7.12		2.70[b]	2.72	
8.01		2.91[b]	3.03	
9.51	0.66	3.43 ± 0.12 (4)[c]	3.27	7.1
10.0	1.32	3.15 ± 0.08 (3)[c]	3.16	9.8
10.3	1.98	3.03 ± 0.10 (4)[c]	3.02	9.3
8.15	2.64	2.26 ± 0.04 (4)[c]	2.27	7.3
11.0		2.89 ± 0.18 (3)[c]	2.99	9.4
11.4		3.12 ± 0.06 (4)[c]	3.09	10.1
19.3		4.91 ± 0.09 (4)[c]	4.92	15.1

[a] $k_{1,\mathrm{calcd}} = k_{-NH_3} K_b[OH^-]/[(1 + K_b[OH^-])(1 + R[NH_3])]$; $k_{-NH_3} = (4.6 \pm 1.0) \times 10^{-2}$ s^{-1}; $K_b = 89 \pm 19$ M^{-1}; $R = 0.135 \pm 0.011$ M^{-1}. [b] A 5% error was assumed ($s_{k_1} = 0.05\ k_1$). [c] Errors are standard deviations. Number of determinations are given in parentheses.

A common reversible substitution of ammonia by e.g. water *in one step* would be accelerated in aqueous ammonia, since the equilibrium would be reached faster; viz., $k = k_f + k_r[NH_3]$ would apply. Surprisingly, we observed a *retardation* of the first, fast, reaction due to ammonia (Table I, Figure 1). This behavior can only be explained by a *two-step mechanism*. According to the currently accepted[25] D_{cb} mechanism, ammonia loss leads to a pentacoordinated intermediate that scavenges water and ammonia. The product of the first ammonia substitution is $(NH_3)_5CoNH_2Co(OH)(NH_3)_4^{4+}$ (**2**), a hydroxo–erythro complex. Hydroxide is a very poor leaving group, and therefore, the dissociatively activated back-reaction of **2** with ammonia is certainly very slow. An associative back-reaction with ammonia can be excluded because it would proceed in one and not two steps.

On the basis of the observations presented above, we propose that, in the first reaction phase (k_1), $(NH_3)_5CoNH_2Co(OH)(NH_3)_4^{4+}$ (**2**) is formed via reactions 1–3. Retardation by ammonia is due to scavenging of ammonia by the intermediate and re-formation of the deprotonated reactant. This behavior supports the D_{cb} mechanism.

$$\mathbf{1} + OH^- \overset{\text{fast}}{\rightleftharpoons} (NH_3)_5CoNH_2Co(NH_2)(NH_3)_4^{4+} + H_2O \quad K_b \qquad (1)$$

$$(NH_3)_5CoNH_2Co(NH_2)(NH_3)_4^{4+} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} (NH_3)_5CoNH_2Co(NH_2)(NH_3)_3^{4+} + NH_3 \quad k_{-NH_3}, k_{NH_3} \qquad (2)$$

$$(NH_3)_5CoNH_2Co(NH_2)(NH_3)_3^{4+} + H_2O \xrightarrow{\text{fast}} \mathbf{2} \quad k_{H_2O} \qquad (3)$$

The experimental data (Table I, Figure 1) are in excellent agreement with the values calculated by a weighted least-squares fit to rate law I, which was derived from the mechanism presented

$$\begin{gathered} -d[\mathbf{1}]/dt = d[\mathbf{2}]/dt = k_1[\mathbf{1}] \\ k_1 = k_{-NH_3} K_b[OH^-]/[(1 + K_b[OH^-])(1 + R[NH_3])] \end{gathered} \qquad (I)$$

above (steady-state was assumed for $(NH_3)_5CoNH_2Co(NH_2)(NH_3)_3^{4+}$). The parameters $R = k_{NH_3}/k_{H_2O} = 0.135 \pm 0.011$ M^{-1}, $k_{-NH_3} = (4.6 \pm 1.0) \times 10^{-2}$ s^{-1}, and $K_b = 89 \pm 19$ M^{-1} were found. The rate constants k_1 obtained from two different kinds of experiments produced uniform data. No discontinuity between the

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Table II. Approximate Amounts of Reaction Products in the Alkaline Hydrolysis of **1**

			% products^b					
no.	reacn medium^a	reacn time	polymer^c	**1**	**2**	$(NH_3)_4$-$Co(OH)_2^+$	$(NH_3)_5$-$CoOH^{2+}$	$Co(NH_3)_6^{3+}$
1	NH_3 (1.5)/OH^- (0.1)	3 min	yes	0	48		0	~46
2	NH_3 (1.32)/OH^- (10^{-3})	15 min		yes	yes	trace	0	trace
3	NH_3 (1.98)/OH^- (10^{-3})	71 min		3	23	12	0	46
4	NH_3 (0.66)/OH^- (10^{-3})	1 day	yes	0	5	15		50
5	NH_3 (1.98)/OH^- (10^{-3})	28 h	yes	0	3	32	19	46
6	NH_3 (1.32)/OH^- (10^{-3})	2 days	yes	0	0	large amt	0	large amt
7	NH_3 (2.64)/OH^- (10^{-3})	3 days	yes	0	0	10	33	56
8	OH^- (10^{-3})^d	40 min	yes	1	13		0	74
9	OH^- (10^{-4}–10^{-3})^d	>1 month	*e*	0	0	0	0	60–70
10	OH^- (0.1)	25 s	trace	yes	46		0	~18
11	OH^- (0.1)	25 s	trace	yes	46		0	~10
12	OH^- (0.1)	3 min	yes	0	20		0	~57

^{a} In parentheses: molar concentration. ^{b} Per mole of **1**. No entry: product not sought or determined. ^{c} Polymer in homogeneous solution. ^{d} pH maintained by pH stat. ^{e} Insoluble "$Co(OH)_3 \cdot 2H_2O$".

rate constants obtained on the pH stat and those obtained by UV–vis spectroscopy becomes apparent. Possible medium effects from high ammonia concentrations appear to be small if not negligible. The postulated intermediate of reduced coordination number has a high mole per mole selectivity for NH_3 relative to H_2O whereas <1% ammonia is scavenged during base hydrolysis of mononuclear pentaammines under similar conditions.[26]

The second reaction phase (k_2) is interesting for preparative purposes: high yields of **2** are expected for large k_1/k_2 ratios. The latter are not affected very much by $[NH_3]$ but depend strongly on $[OH^-]$ (Table I). Also, the small base consumption due to this reaction suggests that large amounts of **2** are cleaved.[27]

Isolation of a μ-Amido–Erythrocobalt(III) Complex. The kinetics in ammoniacal potassium hydroxide solution suggested an efficient preparative procedure for the so far unknown μ-amido Co(III) analogues of the erythrochromium ions.[28] The decaammine complex **1** was treated with ammonia and NaOH for a defined time. The kinetics led to the conclusion that the ratio of the rates of formation and decay of **2** is largest at $[OH^-] \approx 0.05$ M. The product mixture obtained under these conditions was separated by ion-exchange chromatography. Elution with HCl (4 M) afforded the homogeneous anation product *cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$, which was crystallized in ca. 50% yield. Its UV–vis spectrum has a shoulder near 580–590 nm ($\epsilon_{512} = 306$ (max), $\epsilon_{437} = 108$ (min), $\epsilon_{367} = 745$ (max), and $\epsilon_{345} = 674$ (min) M^{-1} cm^{-1}). It thus resembles the analogous compound (±)-*cis,cis*-$(en)_2(NH_3)CoNH_2CoCl(en)_2^{4+}$.[1]

Product Analysis for the Alkaline Hydrolysis of 1 under Different Conditions. Samples of **1** were treated with KOH in the presence and absence of NH_3, the reaction mixture was acidified, and the products were separated, as far as possible, by ion-exchange chromatography after defined reaction times. From such experiments (Table II) was sought independent confirmation for the conclusions drawn from the kinetics and information on the steps subsequent to the first NH_3 release. Except in some experiments, where the reaction was quenched long before completion (experiments 2 and 3), a soluble (possibly colloidal) brown polymer was observed, which spread out on the column during adsorption and which eluted continuously, thus contaminating slightly most or all other fractions. This polymer lacks distinct spectral features in the vis range but shows an almost continuous increase in absorptivity between 650 and 350 nm. In most cases, it was therefore impossible to establish accurate material balances, and these experiments are therefore only qualitative; the quantities given in Table II are approximate. Thus, the determined amounts of hexaammine are probably systematically too high by up to 20% when soluble polymer had formed.

In NH_3/OH^- and pure OH^- media, **2** was present after short reaction times and was recovered as the anation product $(NH_3)_5CoNH_2CoCl(NH_3)_4^{4+}$ (**3**). At the same time, no $(NH_3)_5CoOH^{2+}$ was found (experiments 1 and 2). Also in the absence of excess NH_3, **3** was formed in major amounts after acidification with HCl and detected after short reaction times, and again, no $(NH_3)_5CoOH^{2+}$ was formed. However, in the last experiments (experiments 10–12), polymer was formed at least in traces. As $(NH_3)_5CoOH^{2+}$ is not converted into $Co(NH_3)_6^{3+}$ under the conditions of these experiments,[29,30] its absence suggests that there is no cleavage pathway (<5%) parallel to the NH_3 release in **1**.

After long reaction times in NH_3/OH^- media, soluble and insoluble brown polymers are formed along with $(NH_3)_4Co(OH)_2^+$ and $(NH_3)_5CoOH^{2+}$ (experiment 3). Cleavage of **2** leads to equal amounts of dihydroxotetraammine- and hexaamminecobalt(III) or all hydroxopentaamminecobalt(III), depending on which of the two Co–μ-NH_2 bonds is broken. However, the pentaammine may also rise from subsequent reaction of the tetraammine with ammonia. This reaction is reversible and fast enough to account for the occurrence of $(NH_3)_5CoOH^{2+}$[29,30] under the experimental conditions (experiments 4–7). In the absence of excess ammonia, no tetraammine or pentaammine is isolated after 40 min at pH ~11 and quenching (experiment 8), and apart from a trace of unreacted **1** and some **3**, polymer and hexaammine were the only products. This result is consistent with the interpretation that under the conditions of the pH stat kinetics (i.e. in pure KOH) less NH_3 release from **2** than cleavage takes place. Also, the presence of small amounts of **1** but large amounts of **3** indicates that **2** is more stable in base than **1**; i.e., $k_2 < k_1$ at a given pH >7. Finally, after long reaction times in alkali-metal hydroxide solution, hexaammine and insoluble "$Co(OH)_3 \cdot 2H_2O$" polymer were the only products.

Hexaammine cannot arise from cleavage from **1**, as no pentammine is formed in parallel as a primary product, but it must be formed in subsequent steps. This step may largely be cleavage of **2**, since the sum of tetraammine and pentaammine is nearly equivalent to the amount of hexaammine in experiments 5 and 7. Furthermore, we know from the pH stat kinetics that the second reaction (k_2) consumes only small amounts of base.[27] However, in the presence of excess NH_3, cleavage of **2** cannot account for the polymer formed, since $(NH_3)_4Co(OH)_2^+$ does not form polymers at $[NH_3] > 1$ M but rather reacts with NH_3 to form

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(26) Jackson, W. G.; Begbie, C. M.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7.

(27) The proton balance for the decomposition of **2** is presently unknown. Cleavage of **2** (and, for that matter, of **1**) into monomers does not lead to net base consumption, as one OH^- is consumed (to form a hydoxo complex) simultaneously with one H^+ (to protonate the very basic (pK_a ≈ 15), leaving $(NH_3)_5CoNH_2^{2+}$ moiety).

(28) We have, in fact, first studied the kinetics and then developed the synthetic procedure on this basis. This is thus one of the perhaps rare examples of a planned synthetic procedure based on a detailed kinetic study. The quantity of **1** used in the complete study of the spectrophotometric kinetics was much smaller than the quantity engaged in a single preparation (see Experimental Section). This is not a negligible advantage, since six or seven steps are required to prepare **1**.

(29) Balt, S. *Inorg. Chim. Acta* **1974**, *8*, 159.

(30) Balt, S.; Bohte, E. G. A. M. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 178.

Table III. Summary of Crystal Data, Intensity Collection, and Parameter Refinement

formula	*cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$
fw	482.44
appearance of crystals; source	purple needles; grown from $H_2O/HCl/CH_3OH$
dimens, mm	ca. 0.2 × 0.2 × 0.3
cryst class	orthorhombic
a, Å	10.079 (5)
b, Å	12.382 (8)
c, Å	14.57 (4)
V, Å^3	1818.3
Z	4
d_{calcd}, g cm^{-3}	1.762
F_{000}	992
space group	*Pcmn*
syst absences	$0kl$ ($l = 2n + 1$), $hk0$ ($h + k = 2n + 1$)
radiation	Mo Kα (λ = 0.71069 Å; graphite monochromator)
temp	room temp
scan method	ω–2θ scan (1.5°, 60 s measuring time/reflcn)
$2\theta_{max}$, deg	60
data collcd	$+h,+k,+l$
no. of reflcns collcd	2295 (one octant)
no. of indep reflcns ($\lvert F_o\rvert \geq \sigma_F$)	1658
abs cor	not applied
extinction cor	not applied
refinement method	full-matrix least squares
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
w[20]	$[1/(\sigma_F)^2] \exp[20((\sin\theta)/\lambda)^2]$
R_w	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)/\sum wF_o = 0.053$
R	0.080
av shift/error in last cycle of refinement	0.0013

Table IV. Fractional Atomic Coordinates of Independent Atom Positions and Equivalent Isotropic Thermal Parameters[a]

atom	x	y	z	B_{eq},[b] Å^2
Co1	0.2506 (2)	0.25[c]	0.06153 (9)	0.95
Co2	0.5766 (1)	0.25[c]	0.18139 (8)	0.92
Cl	0.4282 (3)	0.25[c]	0.3012 (2)	1.9
Cl-1[d]	0.0908 (2)	0.5508 (1)	0.8458 (2)	2.9
Cl-2[d]	0.1204 (2)	0.5814 (1)	0.5730 (1)	2.9
O	0.0561 (9)	0.25[c]	0.3119 (8)	3.4
N1	0.4440 (8)	0.25[c]	0.0804 (5)	1.4
N2	0.0572 (9)	0.25[c]	0.0373 (7)	2.3
N3	0.2285 (6)	0.3634 (4)	0.1564 (4)	1.9
N4	0.2699 (6)	0.3621 (4)	−0.0336 (4)	1.9
N5	0.5792 (6)	0.4098 (4)	0.1824 (5)	2.1
N6	0.7132 (8)	0.25[c]	0.0870 (6)	1.7
N7	0.7193 (10)	0.25[c]	0.2746 (6)	2.7

[a] Anisotropic temperature factors: see supplementary material (Table S2). [b] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_j$.[31] [c] Special position. [d] Chloride anions.

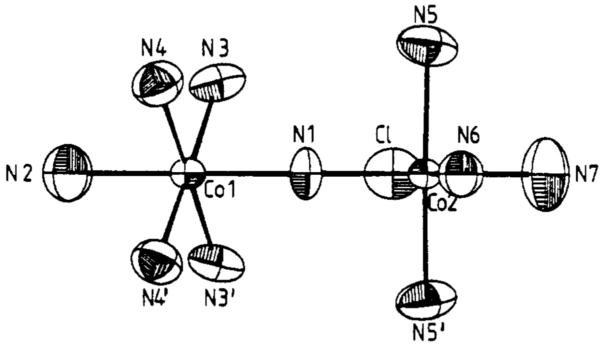

Figure 2. ORTEP drawing[32] of the molecular structure of the *cis*-$(NH_3)_5CoNH_2CoCl(NH_3)_4{}^{4+}$ ion and atom-numbering scheme.

Table V. Selected Bond Lengths and Bond Angles in *cis*-$(NH_3)_5CoNH_2CoCl(NH_3)_4{}^{4+}$

	Bond Lengths, Å		
Co1–N1	1.969 (8)	Co2–Cl	2.298 (5)
Co1–N2	1.981 (9)	Co2–N1	1.988 (9)
Co1–N3	1.983 (6)	Co2–N5	1.979 (5)
Co1–N4	1.971 (6)	Co2–N6	1.947 (9)
		Co2–N7	1.979 (10)
	Bond Angles, deg		
Co1–N1–Co2	140.2 (4)	N1–Co2–Cl	97.2 (3)
N1–Co1–N2	177.7 (4)	N1–Co2–N5	90.8 (2)
N1–Co1–N3	90.8 (2)	N1–Co2–N6	87.2 (4)
N1–Co1–N4	90.0 (2)	N1–Co2–N7	175.6 (4)
N2–Co1–N3	90.8 (3)	Cl–Co2–N5	90.2 (2)
N2–Co1–N4	88.4 (3)	Cl–Co2–N6	175.6 (3)
N3–Co1–N3′	90.2 (3)	Cl–Co2–N7	87.2 (3)
N3–Co1–N4	90.2 (3)	N5–Co2–N5′	178.2 (3)
N3–Co1–N4′	179.1 (3)	N5–Co2–N6	89.8 (2)
N4–Co1–N4′	89.5 (3)	N5–Co2–N7	89.1 (2)
		N6–Co2–N7	88.3 (4)
	Dihedral Angles, deg		
Cl–Co2–N1–Co1	0.0	Co2–N1–Co1–N3	−45.0

hydroxopentaamminecobalt(III).[29,30] On the other hand, the amount of $Co(NH_3)_6{}^{3+}$ was always inferior to the quantity anticipated for 100% cleavage of **2**. By inference, some of the $(NH_3)_5CoNH_2$ fragments in **2** also lose ammonia, and the nitrogen-containing "$Co(OH)_3 \cdot 2H_2O$" polymer could result from this pathway by a series of subsequent steps.

Structure of *cis*-$[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$. The crystal data are summarized in Table III. Table IV lists the fractional positional coordinates. Perspective views of the cation are shown in Figure 2 along with the atom numbering. Selected bond lengths and angles are shown in Table V.

The Cl^- ligand is in a cis position with respect to the μ-NH_2 bridge. The cation lies on a symmetry plane of the space group, going through Co1, Co2, Cl, N1, N2, N6, N7, and the oxygen atom of the water molecule. The NH_3 trans to Cl has a slightly shorter bond to Co (1.947 Å) than all others (1.97–1.98 Å). The two octahedra of coordination, which are linked through the amido bridge, are in a staggered conformation. The Co–N–Co angle is 140°, i.e. 32° larger than in an sp^3 nitrogen, and the Cl–Co–N1 angle (97.2°) is deformed such that the Cl^- ligand bends away from the neighboring $(NH_3)_5Co$ fragment. All other angles are normal.

The Cl ligand is H-bonded[33] to the two N3 and N3′ atoms with (equal) Cl–N3 and Cl–N3′ distances of 3.24 (1) Å. These hydrogen bonds favor the staggered conformation of **3**, which is responsible for the strain release at the bridge. H-bonding of this kind is absent in cation **1**, thus exhibiting a large Co–N–Co bridging angle (153°[34]) and also unusually long Co–N bridging distances (2.06 Å[34]) compared to those of **3**.

Similar structural changes have been noticed in the rhodo- and erythrochromium compounds: the angle Cr–O–Cr in $(NH_3)_5CrOHCr(NH_3)_5{}^{5+}$ (166°)[7] decreases in going to *trans*-$(NH_3)_5CrOHCr(OH)(NH_3)_4{}^{4+}$ (155°)[8] and to *cis*-$(NH_3)_5CrOHCr(OH)(NH_3)_4{}^{4+}$ (143°).[9] The decrease of the angle at the bridge upon substitution of NH_3 by OH^- is paralleled by the NH_3/Cl^- substitution in compounds **1** and **3**, and it appears that NH_3 exerts a rather large cone angle.

Acid Hydrolysis of the *cis*-$(NH_3)_5CoNH_2CoCl(NH_3)_4{}^{4+}$ Ion (3). This reaction was examined cursorily in $HClO_4$ (0.1 M) at 25 °C. Repetitive spectral scans showed an increase in optical density, followed by a slower decrease near the long-wavelength maximum (512 nm). Decreasing optical density was noted in the region of the long-wavelength shoulder (~580 nm). The kinetics were

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(32) Johnson, C. K. "ORTEP"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(33) This suggestion made by a reviewer is acknowledged.

(34) Schaefer, W. P.; Cordes, A. W.; Marsh, R. E. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 283. Vannerberg, N.-G. *Acta Chem. Scand.* **1963**, *17*, 79.

measured at 510 nm and were found to be biphasic and first order in the complex concentration. The fast rate was attributed to aquation with loss of chloride, and the slower rate, to cleavage into mononuclear fragments. The rate constants were calculated by a nonlinear least-squares fitting procedure: $k_{fast} = (6 \pm 2) \times 10^{-5}$ s^{-1} (hydrolysis of Cl^-) and $k_{slow} = (1.4 \pm 0.9) \times 10^{-6}$ s^{-1} (cleavage into monomers).

Conclusions

This work focuses on the initial step of the alkaline hydrolysis of **1** and the isolation of **2** as the anation product **3**, whose crystal structure has been determined by X-ray diffraction. Deprotonation of an NH_3 ligand (but not of the μ-NH_2 bridge) of **1**, followed by rapid elimination of one NH_3 ligand (presumably on the Co(III) center carrying the deprotonated ammine ligand), leads to a pentacoordinated intermediate (reactions 1–3). Interestingly, this intermediate scavenges not only water but also ammonia to restore the deprotonated reactant although ammonia is a poor nucleophile. For the first time, ***retardation*** of base hydrolysis in the presence of an excess of the leaving group has been observed. This is taken as strong evidence for the D_{cb} mechanism. Bridge cleavage was not detected at this stage.

The fast rate of NH_3 release ($k_{-NH_3} = 4.6 \times 10^{-2}$ s^{-1}) relative to that of mononuclear analogues, e.g. $Co(NH_3)_6^{3+}$, is due to steric acceleration. The pK_a of $Co(en)_3^{3+}$ was estimated[35] as 14.9. We assume that the pK_a of $Co(NH_3)_6^{3+}$ is approximately equal or lower, e.g. ~14. On the basis of the published[36] second-order rate constant for base hydrolysis of $Co(NH_3)_6^{3+}$, $k_{OH} = 9.6 \times 10^{-7}$ M^{-1} s^{-1}, we estimate k_{-NH_3} for this complex as $\sim 10^{-6}$ s^{-1}. This value is smaller than the corresponding value of **1** by a factor of ~50 000. Such a large steric acceleration may indicate that an ammonia ligand cis to the μ-NH_2 bridge is eliminated. The isolated chloride anation product of **2**, $[(NH_3)_5CoNH_2CoCl(NH_3)_4]Cl_4 \cdot H_2O$, is also present in the cis configuration. The enhanced acidity of **1** (pK_a = 11.7) compared to e.g. that of $Co(NH_3)_6^{3+}$ is due to the high charge of **1**.

The dimer **1** resembles the $(\pm)$-*cis,cis*-$(en)_2(NH_3)CoNH_2Co(NH_3)(en)_2^{5+}$ ion in its reactivity, but the en compound reacts in base with only 10–25% ammonia release to give the corresponding μ-amido–erythro compound. The major part of the starting material is cleaved into monomers. It may be speculated that the cleavage pathway occurs via the species where deprotonation is at the most acidic site, presumably the NH_3 ligand. The resulting coordinated NH_2 cannot act as a leaving group, and an $(en)_2(NH_3)CoNH_2$ moiety is substituted, as the en nitrogens are even poorer leaving groups. The amount of NH_3 release would thus arise from deprotonation of a somewhat less acidic en–NH_2 function.

Both **1** and the acid rhodochromium ion undergo fast ammonia release. However, the mechanism of activation is different: the Cr(III) compound is deprotonated at the bridge and can thereby adopt a linear Cr–O–Cr geometry that gives rise to special electronic effects. Ammonia is released from the compound in this configuration. In contrast, the cobalt compound is deprotonated at one ammonia ligand (presumably because the filled d_π orbitals of Co(III) cannot stabilize p orbitals of the bridge). The pK_a of **1** is much higher, but the resulting conjugate base is very reactive due to steric acceleration.

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Registry No. **1**·$5NO_3^-$, 15363-12-9; **1**·$5ClO_4$, 31151-80-1; **2**, 110795-80-7; **3**·$4Cl^- \cdot H_2O$, 110795-81-8; $(NH_3)_4Co(OH)_2^+$, 38467-93-5; $(NH_3)_5CoOH^{2+}$, 16632-75-0; *trans*-$(NH_3)_4Co(OH_2)_2^{3+}$, 19394-99-1; *cis*-$(NH_3)_5Co(OH_2)_2^{3+}$, 18460-36-1; $(NH_3)_5Co(OH_2)^{3+}$, 14403-82-8; $Co(NH_3)_6^{3+}$, 14695-95-5.

Supplementary Material Available: Table S2, listing anisotropic thermal parameters (1 page); Table S1, listing observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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[36] Balt, S.; Breman, J.; Dekker, C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2023.

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Ligand Substituent Contributions to the Rotational Strengths in Cyano(ethylenediamine-*N*,*N*,*N'*-triacetato)cobaltate(III) Type Complexes. Crystal Structures of Rb-$(-)_{546}$-*cis*-*eq*-$[Co(ed3a)CN] \cdot 2H_2O$ and K-$(-)_{546}$-*cis*-*eq*-$[Co(hed3a)CN] \cdot 1.5H_2O$

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Circular dichroism spectra are reported for K-*cis-eq*-[Co(ed3a)CN], K-*cis-eq*-[Co(med3a)CN], K-*cis-eq*-[Co(hed3a)CN], and K-*trans-eq*-[Co(ed3a)CN]. Structures and absolute configurations were determined for Rb-$(-)_{546}$-*cis-eq*-$[Co(ed3a)CN] \cdot 2H_2O$ (**1**) (orthorhombic, $C222_1$, with the cell dimensions a = 6.600 (7) Å, b = 14.243 (8) Å, and c = 30.76 (1) Å; eight molecules in the unit cell) and K-$(-)_{546}$-*cis-eq*-$[Co(hed3a)CN] \cdot 1.5H_2O$ (**2**) (monoclinic, $C2$, with the cell dimensions a = 14.546 (7) Å, b = 7.219 (1) Å, c = 19.78 (1) Å, and β = 130.09 (3)°; four molecules in the unit cell). For the *cis-eq*-$[Co(ed3a)CN]^-$ type complexes an alkyl substituent on the ethylenediamine nitrogen, compared to the case of the unsubstituted ed3a, reverses the sign of the circular dichroism peaks in the region of the lower energy absorption band. As for the corresponding nitro complexes, *cis-eq*-$[Co(ed3a)CN]^-$ and *trans-eq*-$[Co(ed3a)CN]^-$ show very similar CD curves.

Introduction

Absorption spectra of transition-metal complexes are insensitive to changes in stereochemistry except for great effects such as for cis and trans isomers involving ligands differing greatly in field strength. Circular dichroism (CD) spectra reveal smaller splittings in energy levels and often reflect the true molecular symmetry. For chelate complexes the contributions to the rotational strength (or CD intensity) are the chirality and conformation of the chelate rings and the vicinal effect of asymmetric ligand atoms. These contributions have been shown to be additive.[2] Generally, the

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