the relative rates have been shown to be affected both by steric and electronic effects.[37] In cluster chemistry, however, intramolecular mechanisms are possible involving intermediates with one metal coordinatively unsaturated: the break of a Re(μ-H)Re interaction, for instance, would make a rhenium atom pentacoordinate and therefore stereochemically nonrigid. The isomerization rate would therefore be related to the cis-labilizing power of the phosphine, which is expected to increase not only with the size of the ligand but also with its donor ability.

No definite mechanistic conclusion, however, can be drawn from the data concerning the isomerization. A theoretical approach, based on MO and molecular mechanic computations, is on schedule, in order to better understand electronic and steric properties of the two ground states and their possible interconversion paths.

Acknowledgment. We are indebted to Prof. Angelo Sironi for many helpful discussions and suggestions.

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(37) See, for instance: Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307.

Contribution from the Institut de Chimie Physique,
Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Base Hydrolysis of Acidato Pentakis(methylamine) Complexes of Cobalt(III): Evidence for the Pentacoordinated Intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ Exhibiting a Lifetime of ≈1 ns

François P. Rotzinger

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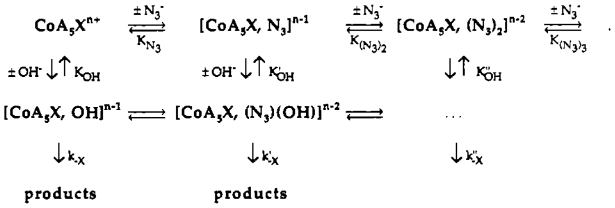
The kinetics and products of the base hydrolysis of two $Co(NH_2CH_3)_5X^{n+}$ complexes ($X = Cl^-$, DMF) have been studied at 25 °C in 0.02–1.0 M azide and $\approx(0.2–8) \times 10^{-3}$ M hydroxide (at variable ionic strength). The products, $Co(NH_2CH_3)_5OH^{2+}$ and $Co(NH_2CH_3)_5N_3{}^{2+}$, are formed via the genuine pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ and its ion-aggregates with azide, viz. $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$ and $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$. The free intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ collapses with water, whereas both the ion aggregates collapse exclusively with azide to form $Co(NH_2CH_3)_5N_3{}^{2+}$. The intermediates are not at equilibrium with azide from the bulk solution because of their fast collapse rates. The lifetime of the pentacoordinated intermediate is ≈1 ns. Base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ has also been studied at 25 °C and $I = 1$ M in the presence of competitors other than azide, and competition ratios have been obtained via a new method. Interestingly, fluoride competes efficiently for the pentacoordinated intermediate, but not for the hexacoordinated ones.

Introduction

Base hydrolysis[1] of acidato pentaammine complexes of cobalt(III), $Co(NH_3)_5X^{n+}$, has been shown[2,3] to proceed via hexacoordinated intermediates. The reactions presented in Scheme I (A_5 is equal to $(NH_3)_5$ in this case) did not allow us to rationalize both kinetic[2] and competition[3] data obtained at variable ionic strength. Scheme I—being consistent with the kinetics[2]—turns out incomplete, since the kinetically predicted competition ratios (R) are much larger than the measured ones. This apparent discrepancy has been suggested[2,3] to be due to the existence of intermediates arising *after* the activation of the Co–X bond (i.e. the rate-determining step). They escape kinetic detection and exhibit[3] a sufficiently long lifetime to establish ion-aggregation equilibria with anions from the bulk solution. These intermediates are hexacoordinated, because the ionic strength dependence of the competition ratios showed unambigously[3] that the leaving group is present in the first coordination sphere during the product formation step. The facts presented above[2,3] as well as a quantum mechanical study[4] support the existence of hexacoordinated intermediates in the base hydrolysis of the $Co(NH_3)_5X^{n+}$ complexes. The latter are the least strained and constrained (acidato)pentaaminecobalt(III) compounds.

The more strained $Co(NH_2CH_3)_5X^{n+}$ complexes are well-known[1,5] for their enhanced sensitivity to base hydrolysis. This effect is known[5] as steric acceleration. It was expected that strain in the ligand sphere would destabilize the weak[4] Co–X bond of hypothetical hexacoordinated intermediates and favor the formation of pentacoordinated ones. This study reports on the kinetics and reaction products of the base hydrolysis of two $Co(NH_2CH_3)_5X^{n+}$ complexes ($X = Cl^-$, DMF). Various models for product formation involving either intermediates or just transition states are discussed in detail.

Scheme I[a]



[a] A_5 = pentaamine ligand, i.e. $(NH_3)_5$ or $(NH_2CH_3)_5$.

Experimental Section

Physical Measurements. The equipment and the general procedures have been described previously.[2,3]

Synthesis. $[Co(NH_2CH_3)_5Cl]Cl_2$ and $[Co(NH_2CH_3)_5DMF](CF_3SO_3)_3$ were prepared as described in the literature.[6-8] $[Co(NH_2CH_3)_5N_3](NO_3)_2 \cdot {}^1/_2H_2O$ was prepared by adding 200 mg of $[Co(NH_2CH_3)_5Cl]Cl_2$ dissolved in 10 mL of 2 mM $HClO_4$ to a solution containing 10 mL of 5 M NaN_3 and 2 mL of 0.4 M KOH. After about 5 s, 15 mL of 4 M $HClO_4$ was added and the solution diluted 10 times and adsorbed on an ion-exchange column (Dowex 50W-X2 200–400 mesh, H^+ form) under exclusion light. The desired product was eluted with 1 M NH_4Cl at pH = 2 (HCl), the eluent evaporated, and the NH_4Cl removed by washing with ethanol. The crude chloride was dissolved in water and precipitated with $NaNO_3$. Finally, the crude nitrate was redissolved in water, the solution filtered to remove solid impurities, and the product precipitated by adding a saturated $NaNO_3$ solution. The crystals were filtered off, washed with ethanol, and air-dried. Anal.

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Table I. Extinction Coefficients of $Co(NH_2CH_3)_5OH^{2+}$ (**1**) and $Co(NH_2CH_3)_5N_3^{2+}$ (**2**) Used for the Product Analysis

λ, nm	ε, M^{-1} cm^{-1} **1**	 **2**
416	46.6	277
446	23.6 (min)	98.6
462	30.1	74.9 (min)
492	61.8	147
522	80.9 (max)	296
538	75.6	334 (max)
580	40.9	185

Calcd: C, 15.43; H, 6.73; N, 35.98. Found: C, 15.65; H, 6.48; N, 36.07.

Product Analysis. Since both products, $Co(NH_2CH_3)_5N_3^{2+}$ and $Co(NH_2CH_3)_5OH^{2+}$, are unstable under the experimental conditions ($[Co]_0 \approx 5$ mM, $[OH^-]_0 \approx 7$ mM, 25 °C), the UV–vis spectrum of the product mixture was measured immediately after the end of the reaction (after $8\text{-}10t_{1/2}$) with a diode-array spectrophotometer. This was performed by reacting a solution of ≈10 mM $Co(NH_2CH_3)_5X^{n+}$ (X = Cl^- or DMF) in 1–2 mM $HClO_4$ with one containing 0–2 M NaN_3 (≈15 mM in KOH) in a 1:1 ratio using a HI-TECH SFA-11 rapid-mixing device. In order to minimize the losses due to spontaneous aquation, the freshly prepared $Co(NH_2CH_3)_5X^{n+}$ solutions were used within ≈2 min. The individual concentrations of the products were determined as described.[3] The UV-vis spectrum of $Co(NH_2CH_3)_5OH^{2+}$ was obtained via base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the absence of azide as described above. The extinction coefficients used for the spectrophotometric analysis are presented in Table I. The concentration of the $Co(NH_2CH_3)_5X^{n+}$ reactants agreed well with the sum of the analyzed products (error ≲2%).

Base hydrolysis of $Co(NH_2CH_3)_5DMF^{3+}$ leads exclusively to $Co(NH_2CH_3)_5OH^{2+}$; viz., no $Co(NH_2CH_3)_5(HCOO)^{2+}$ is formed. This was verified as follows: 17 mg of $[Co(NH_2CH_3)_5DMF](CF_3SO_3)_3$ was dissolved in 20 mL of water at pH = 3 ($HClO_4$). Then, 0.25 mL of 0.4 M KOH were added. After about 10 s, the solution was acidified with 0.25 mL of 1 M $HClO_4$, and the product was adsorbed on a Sephadex SP C-25 column (Na^+ form) and eluted first with 0.2 M $NaClO_4$, pH = 3, and then with 0.5 M $NaClO_4$, pH = 3. The product, $Co(NH_2CH_3)_5OH_2^{3+}$, identified by its UV–vis spectrum,[9] was eluted as a single band—no species exhibiting a 2+ charge was detected.

Results and Discussion

Kinetics. A detailed analysis of the product-forming reactions should be based on precise knowledge of the (preceding) rate-determining steps. To this end, the kinetics of base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ (reaction 1) have been studied in detail in the presence of 0–1 M azide by stopped-flow spectrophotometry at variable ionic strength and 25 °C.

$$Co(NH_2CH_3)_5Cl^{2+} + \nu OH^- + (1-\nu)N_3^- \xrightarrow{k} \nu Co(NH_2CH_3)_5OH^{2+} + (1-\nu)Co(NH_2CH_3)_5N_3^{2+} + Cl^- \quad (1)$$

The kinetic traces, monitored at 522 nm, were analyzed by least-squares fits to eq 2, where $[OH]_0$ is the initial OH^- concentration (usually 7.5 mM), $[Co]_0$ the initial $Co(NH_2CH_3)_5Cl^{2+}$ concentration (≈5 mM), and d the path length of the cell. The parameters $|\Delta\epsilon|$, k, and ν were optimized. It should be noted that ν does not depend on the extinction coefficients of reactant and products; i.e. *ν is available even if the UV-vis spectra of reactant and products are unknown.* The competition ratio R (eq 3) is related to the stoichiometric factor ν (eq 4), and in principle, eqs 2 and 4 allow one to also obtain competition ratios of unstable products exhibiting unknown or not precisely measurable extinction coefficients, provided that ν is not too close to 1 (i.e. ≲0.95). This method has the advantage that rate constants and competition ratios are available in a single experiment, and furthermore, a preceding preparation and characterization of the products is not required. Remarkably, the UV-vis spectra of the products need not be different. Of course, whenever applicable, the in situ spectrophotometric analysis is more precise, but also more laborious (see below and ref 3).

$$|D - D_\infty| = \frac{d|\Delta\epsilon|([OH]_0 - \nu[Co]_0)}{\dfrac{[OH]_0}{[Co]_0}\exp\{([OH]_0 - \nu[Co]_0)kt\} - \nu} \quad (2)$$

$$R = \frac{[Co(NH_2CH_3)_5N_3^{2+}]_\infty}{[Co(NH_2CH_3)_5OH^{2+}]_\infty[N_3^-]} \quad (3)$$

$$R = \frac{1-\nu}{\nu[N_3^-]} \quad (4)$$

Table II. Kinetic Data for the Base Hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the Presence of Azide at 25 °C

$[N_3^-]$, M	I, M	ν	k_{obsd}, M^{-1} s^{-1}	k_{calcd}, M^{-1} s^{-1} [a]
0.0	0.0229	1.07 ± 0.02	4740 ± 60	4870
		1.05 ± 0.02	4730 ± 50	
		1.07 ± 0.02	4790 ± 50	
0.01	0.0316	1.02 ± 0.03	4570 ± 70	4420
		1.02 ± 0.02	4660 ± 60	
		1.03 ± 0.02	4610 ± 60	
0.025	0.0477	0.99 ± 0.02	3950 ± 30	3870
		0.96 ± 0.02	3900 ± 40	
		1.03 ± 0.01	3840 ± 30	
0.05	0.0727	0.93 ± 0.02	3360 ± 20	3320
		0.92 ± 0.01	3340 ± 20	
		0.95 ± 0.01	3320 ± 20	
0.10	0.123	0.92 ± 0.01	2700 ± 10	2690
		0.93 ± 0.01	2650 ± 10	
		0.92 ± 0.01	2680 ± 10	
0.25	0.273	0.77 ± 0.02	1850 ± 10	1860
		0.77 ± 0.02	1850 ± 10	
0.50	0.522	0.65 ± 0.04	1320 ± 20	1330
		0.68 ± 0.03	1350 ± 10	
		0.67 ± 0.02	1360 ± 10	
0.80	0.823	0.62 ± 0.03	1030 ± 10	1030
		0.63 ± 0.02	1050 ± 10	
		0.57 ± 0.04	1040 ± 10	
		0.56 ± 0.05	1060 ± 10	
1.00	1.022	0.55 ± 0.05	906 ± 10	903
		0.46 ± 0.07	882 ± 14	
		0.49 ± 0.03	880 ± 6	

[a] Fit according to eq 5 with $k_{-Cl} = 1580 \pm 30$ s^{-1}, $k'_{-Cl} = 1520 \pm 140$ s^{-1}, and $r = 4.92 \pm 0.22$ Å.

Table III. Comparison of Kinetically and Spectrophotometrically Determined Competition Ratios

$[N_3^-]$, M	I, M	R, M^{-1} kinetically[a]	 spectrophotometrically[b]
0.25	0.27	1.20 ± 0.04	1.26[c]
0.50	0.52	0.98 ± 0.07	1.05
0.80	0.82	0.86 ± 0.13	0.93
1.00	1.02	1.01 ± 0.19	0.93

[a] Calculated by using eqs 2 and 4. [b] Average of the corresponding values from Table Va. [c] Obtained by interpolation.

The experimental rate constants and ν values are summarized in Table II. The slightly too large ν values (in the absence of azide ν should be equal to 1 and not ≈1.06), arise from systematic errors originating from the decomposition of the products (≲5%) and perhaps also from imperfections of the stopped-flow traces. Notwithstanding, the kinetically determined R values (Table III) agree reasonably well with those obtained by the intrinsically more accurate in situ spectrophotometric analytical method (see below). The accuracy of the k values, however, was less sensitive to secondary reactions.

The experimental rate constants (k) were fitted to rate law 5, derived from Scheme I[2]. The introduction of further species and reactions did not improve the fit as in the case of the previously[2] studied $Co(NH_3)_5NO_3^{2+}$ complex. The ion triplets $[Co(NH_3)_5NO_3,(N_3)_2]$, $[Co(NH_3)_5NO_3,(ClO_4)_2]$, and $[Co(NH_2CH_3)_5Cl,(N_3)_2]$ turn out to be quite unreactive, because aggregation of these uncharged species with hydroxide is unfavorable, and consequently, only insignificant amounts of (very reactive) con-

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Table IV. Molar Mean Activity Coefficients of Three Selected NaX Salts[a]

(a) X = Cl

I, M	$f_\pm$(obsd)	$f_\pm$(calcd) eq 6a[b]	$f_\pm$(calcd) eq 6b[c]
0.0997	0.778	0.7853	0.7784
0.199	0.735	0.7418	0.7340
0.298	0.710	0.7164	0.7093
0.397	0.693	0.6987	0.6931
0.495	0.681	0.6855	0.6817
0.593	0.673	0.6749	0.6734
0.690	0.667	0.6662	0.6672
0.787	0.662	0.6589	0.6625
0.884	0.659	0.6525	0.6589
0.981	0.657	0.6470	0.6562

(b) X = Br

I, M	$f_\pm$(obsd)	$f_\pm$(calcd) eq 6a[d]	$f_\pm$(calcd) eq 6b[e]
0.0996	0.782	0.7940	0.7816
0.199	0.741	0.7542	0.7402
0.297	0.719	0.7315	0.7187
0.395	0.704	0.7158	0.7056
0.493	0.697	0.7039	0.6972
0.590	0.692	0.6945	0.6919
0.687	0.689	0.6868	0.6888
0.783	0.687	0.6804	0.6871
0.879	0.687	0.6748	0.6866
0.974	0.687	0.6700	0.6870

(c) X = NCS

I, M	$f_\pm$(obsd)	$f_\pm$(calcd) eq 6a[f]	$f_\pm$(calcd) eq 6b[g]
0.0994	0.787	0.8030	0.7878
0.198	0.750	0.7669	0.7501
0.296	0.731	0.7464	0.7312
0.393	0.720	0.7324	0.7205
0.489	0.715	0.7221	0.7144
0.584	0.712	0.7139	0.7111
0.679	0.710	0.7072	0.7097
0.772	0.710	0.7016	0.7098
0.865	0.711	0.6968	0.7109
0.958	0.712	0.6926	0.7129

[a] Data from ref 12. Molal concentrations have been converted to the molar scale. [b] $r = 5.11 \pm 0.07$ Å. [c] $r = 4.22 \pm 0.03$ Å; $C = 0.030 \pm 0.001$ M^{-1}. [d] $r = 5.82 \pm 0.15$ Å. [e] $r = 4.15 \pm 0.03$ Å; $C = 0.052 \pm 0.001$ M^{-1}. [f] $r = 6.59 \pm 0.20$ Å. [g] $r = 4.50 \pm 0.03$ Å; $C = 0.059 \pm 0.001$ M^{-1}.

jugate base is formed. Since $[OH^-]_0$ was always <0.01 M, terms containing $[OH^-]$ in the denominator were negligible.

$$k = \frac{k_{-Cl}K_{OH} + k'_{-Cl}K'_{OH}K_{N_3}[N_3^-]}{1 + K_{N_3}[N_3^-] + K_{N_3}K_{(N_3)_2}[N_3^-]^2} \qquad (5)$$

In previous work,[2] it has been shown that the aggregation constants K are predictable by the Fuoss equation.[10] They depend on the ionic strength, the temperature, the charge of the ions, and the distance of closest approach (see Appendix). On the basis of a concept developed in previous work,[3] the average distance of closest approach (r) within contact ion-aggregates (e.g. $[Co(NH_2CH_3)_5Cl,N_3]^+$) was estimated to be 5.14 Å. The internal rotations of the $Co-NH_2-CH_3$ fragments, however, may give rise to a different average contact distance. In order to check this point, the fit of the experimental rate constants according to eq 5 was performed by optimizing the three parameters k_{-Cl}, k'_{-Cl} and r—all the K values depend on r (see Appendix). The k_{-Cl} and k'_{-Cl} values are equal, i.e. 1580 ± 30 and 1520 ± 140 s^{-1}, respectively, as are k_{-NO_3} and k'_{-NO_3} for the previously[2] studied $Co(NH_3)_5NO_3^{2+}$ complex. The optimized distance of closest approach, $r = 4.92 \pm 0.22$ Å, compares well with that predicted for contact ion aggregates. The concept previously[3] used to estimate contact distances appears to remain valid for the present compounds.

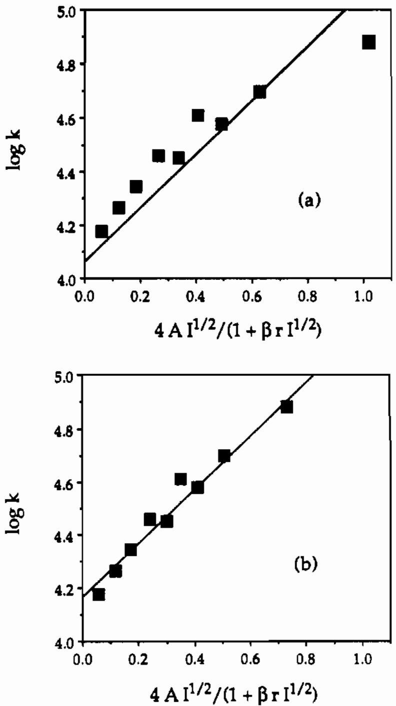

Figure 1. Linearized plots of equation $k = k_0 \times 10^{4AI^{1/2}/(1+\beta rI^{1/2})}$, with data from refs 13 and 14: (a) $\beta r = 1.00$ $M^{-1/2}$ and $k_0 = (1.16 \pm 0.11) \times 10^4$ M^{-1} s^{-1}; (b) $\beta r = 1.77 \pm 0.18$ $M^{-1/2}$ and $k_0 = (1.47 \pm 0.07) \times 10^4$ M^{-1} s^{-1}.

Calculated and observed rate constants agree well (Table II), although ionic strengths up to 1 M have been used. It will be shown that the Debye–Hückel law[11] (eq 6a) predicts activity coefficients (f_i) of aqueous NaX solutions up to $I \approx 1$ M within an error of less than 3%. Although eq 6a is not expected to yield the best activity coefficients for such high ionic strengths, it has the advantage that A and β are physical constants[2,11] and r is the distance of closest approach of cation and anion of the ion aggregate. Extended expressions for the activity coefficients such as eq 6b[11] cannot be applied, because they involve two empirical parameters (r and C) that are not available for the $Co(NH_2CH_3)_5Cl^{2+}/N_3^-$ or OH^- system; r no longer represents the distance of closest approach. Since no activity coefficients for

$$\log f_i = -Az_i^2I^{1/2}/(1 + \beta rI^{1/2}) \qquad (6a)$$

$$\log f_i = -Az_i^2I^{1/2}/(1 + \beta rI^{1/2}) + CI \qquad (6b)$$

aqueous NaN_3 solutions are available from the literature, they are assumed to resemble those of NaCl, NaBr, or NaNCS being similar in terms of atomic weight, size, or shape, respectively. The activity coefficients of the above salts,[12] fitted according to eq 6a, deviate from the experimental ones by <3% in the worst cases (Table IV), and the extended expression (6b) reproduces the experimental activity coefficients exactly. For Cl^-, Br^-, and NCS^-, respectively, the r values are expected to increase with increasing size of the anion. Equation 6a reproduces this trend correctly in contrast to eq 6b (Table IV). This is not surprising, since r and C are empirical constants without physical meaning.

Activity coefficients of pentaamine complexes of cobalt(III) are not available from the literature. The rate of the $Co(NH_3)_5Cl^{2+} + Cu^+$ reaction, however, has been measured[13] at variable ionic strength, and the data have been discussed[13,14] by

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Table V. Competition Data for the Base Hydrolysis of $Co(NH_2CH_3)_5X^{n+}$ Complexes in the Presence of Azide at 25 °C

$[N_3^-]$, M	$[OH]_{av}$, M[a]	I, M	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[b]	$[N_3^-]$, M	$[OH]_{av}$, M[a]	I, M	R_{obsd}, M^{-1}	R_{calcd}, M^{-1}[b]
				(a) X = Cl					
0.01	4.03×10^{-3}	0.0291	2.01 ± 0.08	2.15				1.24 ± 0.02	
			2.01 ± 0.03		0.30	4.54×10^{-3}	0.319	1.20 ± 0.04	1.18
			2.02 ± 0.09					1.20 ± 0.03	
0.02	4.07×10^{-3}	0.0391	1.98 ± 0.06	2.01				1.21 ± 0.03	
			1.95 ± 0.05		0.40	4.75×10^{-3}	0.418	1.13 ± 0.04	1.11
			1.97 ± 0.03					1.13 ± 0.03	
0.05	$\approx 2 \times 10^{-4}$[c]	0.0775	1.71 ± 0.06	1.69				1.12 ± 0.04	
			1.67 ± 0.04			8.04×10^{-3}	0.423	1.08 ± 0.02	1.10
			1.69 ± 0.04					1.10 ± 0.02	
	4.14×10^{-3}	0.0691	1.73 ± 0.01	1.75				1.10 ± 0.03	
			1.75 ± 0.02		0.50	4.80×10^{-3}	0.518	1.05 ± 0.06	1.06
			1.75 ± 0.01					1.07 ± 0.06	
	7.56×10^{-3}	0.0728	1.65 ± 0.04	1.72				1.05 ± 0.06	
			1.68 ± 0.03		0.60	4.87×10^{-3}	0.618	1.01 ± 0.06	1.03
			1.65 ± 0.04					1.02 ± 0.05	
0.10	$\approx 2 \times 10^{-4}$[c]	0.128	1.62 ± 0.06	1.48				1.01 ± 0.05	
			1.55 ± 0.04		0.70	8.24×10^{-3}	0.723	0.96 ± 0.04	1.00
			1.60 ± 0.04					0.96 ± 0.04	
	4.27×10^{-3}	0.119	1.50 ± 0.01	1.52				0.97 ± 0.04	
			1.56 ± 0.01		0.80	4.94×10^{-3}	0.818	0.92 ± 0.07	0.98
			1.55 ± 0.01					0.93 ± 0.08	
	7.69×10^{-3}	0.123	1.50 ± 0.02	1.50				0.93 ± 0.08	
			1.51 ± 0.03		1.00	5.05×10^{-3}	1.018	0.92 ± 0.10	0.96
			1.51 ± 0.02					0.94 ± 0.10	
0.20	4.40×10^{-3}	0.219	1.31 ± 0.02	1.29				0.93 ± 0.10	
			1.32 ± 0.02			8.38×10^{-3}	1.023	0.86 ± 0.07	0.96
			1.33 ± 0.03					0.89 ± 0.06	
	7.81×10^{-3}	0.223	1.29 ± 0.01	1.29				0.89 ± 0.06	
			1.28 ± 0.01						
				(b) X = DMF					
0.05	$\approx 5 \times 10^{-3}$	0.0772	1.84 ± 0.04	1.91				1.21 ± 0.05	
			1.84 ± 0.04		0.60	$\approx 5 \times 10^{-3}$	0.624	1.06 ± 0.09	1.14
			1.85 ± 0.04					1.05 ± 0.10	
0.10	$\approx 5 \times 10^{-3}$	0.127	1.72 ± 0.03	1.67				1.05 ± 0.09	
			1.71 ± 0.03		0.80	$\approx 5 \times 10^{-3}$	0.824	1.09 ± 0.08	1.09
			1.67 ± 0.02					1.05 ± 0.08	
0.20	$\approx 5 \times 10^{-3}$	0.226	1.43 ± 0.03	1.43				1.05 ± 0.08	
			1.44 ± 0.03		1.00	$\approx 5 \times 10^{-3}$	1.024	1.05 ± 0.10	1.07
			1.47 ± 0.03					1.07 ± 0.09	
0.40	$\approx 5 \times 10^{-3}$	0.426	1.23 ± 0.05	1.23				1.03 ± 0.10	
			1.22 ± 0.04						

[a] $[OH]_{av} = [OH]_0 - {}^1/_2[Co(NH_2CH_3)_5OH^{2+}]_\infty$. [b] Calculated by using the parameters from fit 4 (Table VI). [c] 0.04 M 2-amino-2-methyl-1-propanol buffer.

using simplified expressions of eq 6a. For ionic strengths up to 1 M, the weighted ($1/k^2$) least-squares fit using the best reported[14] model (eq 6a with βr fixed at 1.0 $M^{-1/2}$) shows systematic deviations (Figure 1a). Application of eq 6a including an optimized distance of closest approach (r = 5.4 ± 0.5 Å) leads to a significantly improved fit—the experimental rate constants are now reproduced within the experimental limit (Figure 1b). Furthermore, the optimized r value is in agreement with the expected Co–Cu distance, since this electron-transfer reaction proceeds via the inner-sphere pathway involving a (most likely bent) Co···Cl···Cu transition state.

The validity of eq 6a for ionic strengths up to 1 M is further corroborated by the present analysis of the kinetic data, since a physically meaningful distance of closest approach has been obtained (see above).

Spectrophotometric Product Analysis. Two $Co(NH_2CH_3)_5X^{n+}$ complexes (X = Cl^-, DMF), representing two different charge types, were reacted in the presence of 0.02–1.0 M (sodium) azide[15] and ≈(0.2–8) × 10^{-3} M hydroxide at 25 °C and variable ionic strength. The products,[16] $Co(NH_2CH_3)_5N_3^{2+}$ and $Co(NH_2CH_3)_5OH^{2+}$, were analyzed spectrophotometrically[3] immediately after completion of the reaction ($8-10t_{1/2}$); both products are less stable in base than the analogous pentaammine complexes.[3] Since spontaneous aquation of the $Co(NH_2CH_3)_5X^{n+}$ complexes

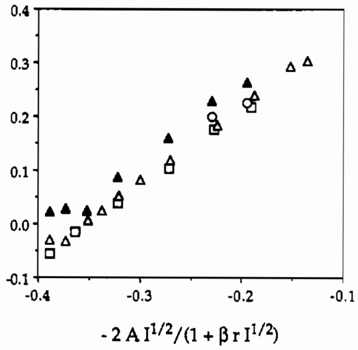

Figure 2. Plots of log R vs $-2AI^{1/2}/(1 + \beta r I^{1/2})$: filled symbols, $Co(NH_2CH_3)_5DMF^{3+}$; open symbols, $Co(NH_2CH_3)_5Cl^{2+}$; circles, $[OH]_{av} \approx 2 \times 10^{-4}$ M; triangles, $[OH]_{av} \approx (4-5) \times 10^{-3}$ M; squares, $[OH]_{av} \approx 8 \times 10^{-3}$ M.

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(14) Espenson, J. H. *Chemical Kinetics and Reactions Mechanisms*; McGraw-Hill: New York, St. Louis, San Francisco, Auckland, Bogota, Hamburg, London, Madrid, Mexico, Montreal, New Delhi, Panama, Paris, Sao Paulo, Singapore, Sydney, Tokyo, Toronto, 1981; pp 173–174.

(15) The contribution of HN_3 to product formation is negligible (<10 ppm), since the pH of the solution was always ≥10, i.e., more than 5 orders of magnitude larger than the pK_a of HN_3.

(16) Base hydrolysis of $Co(NH_2CH_3)_5DMF^{3+}$ does not lead to detectable amounts of $Co(NH_2CH_3)_5(HCOO)^{2+}$ (Experimental Section) in contrast[17] to the more substitution-inert $Co(NH_3)_5DMF^{3+}$ reactant.

(17) Buckingham, D. A.; Harrowfield, J. MacB; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726.

Table VI. Summary of the Weighted Least-Squares Fits of the Competition Data

fit no.	comments	optimized param	eq	std dev
1	$Co(NH_2CH_3)_5Cl^{2+}$ data only	$K'_{OH}(I \to 0) = 3.34 \pm 0.04\ M^{-1}$ $z_I = 1.53 \pm 0.02$	8	0.026 48
2	$Co(NH_2CH_3)_5Cl^{2+}$ data only	$x_{OH} = 0.291 \pm 0.014$ $K'_{OH}(I \to 0) = 3.9 \pm 0.1\ M^{-1}$	9	0.034 85
3	$Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$ data simulataneously, $k'_{H_2O} = k''_{H_2O} = 0$	$k_{H_2O}/k^I_{-1} = 0.228 \pm 0.031$ $k'_{N_3}/k_{H_2O} = 0.799 \pm 0.009$ $k''_{N_3}/k^I_{-2} = -0.057 \pm 0.098$ $k''_{N_3}/k_{H_2O} = 0.575 \pm 0.061$	3, 16, 19, 20	0.032 66
4	$Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$ data simultaneously, $k'_{H_2O} = k''_{H_2O} = 0$ and $k''_{N_3}/k^I_{-2} = 0$	$k_{H_2O}/k^I_{-1} = 0.214 \pm 0.017$ $k'_{N_3}/k_{H_2O} = 0.796 \pm 0.006$ $k''_{N_3}/k_{H_2O} = 0.602 \pm 0.040$	3, 16, 19, 20	0.032 51
5	$Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$ data simultaneously	$k_{H_2O}/k^I_{-1} = 0.198 \pm 0.026$ $k'_{N_3}/k_{H_2O} = 0.621 \pm 0.011$ $k''_{N_3}/k^I_{-2} = 0.057 \pm 0.095$ $k'_{H_2O}/k_{H_2O} = -0.944 \pm 0.040$ $k''_{H_2O}/k_{H_2O} = 0.118 \pm 0.029$ $k''_{N_3}/k_{H_2O} = -1.20 \pm 0.14$	3, 16, 19, 20	0.027 86
6	$Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$ data simultaneously, $k'_{H_2O} = k''_{H_2O}$	$k_{H_2O}/k^I_{-1} = 0.202 \pm 0.033$ $k'_{N_3}/k_{H_2O} = 0.995 \pm 0.124$ $k''_{N_3}/k^I_{-2} = 0.008 \pm 0.145$ $k'_{H_2O}/k_{H_2O} = 1.38 \pm 0.95$ $k''_{N_3}/k_{H_2O} = 4.47 \pm 2.99$	3, 16, 19, 20	0.029 90
7	$Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$ data simultaneously, $k_{H_2O} = k'_{H_2O} = k''_{H_2O}$	$k_{H_2O}/k^I_{-1} = 0.209 \pm 0.027$ $k'_{N_3}/k_{H_2O} = 0.945 \pm 0.028$ $k''_{N_3}/k^I_{-2} = -0.022 \pm 0.101$ $k''_{N_3}/k_{H_2O} = 3.34 \pm 0.29$	3, 16, 19, 20	0.029 74

is quite fast,[8] the most inert anionic and neutral leaving groups, Cl^- and DMF, were chosen in order to minimize decomposition of the reactants prior to base hydrolysis. Before the present results (Figure 2 and Table V) are discussed, some comments on the previously[3] studied $Co(NH_3)_5X^{n+}$ complexes are appropriate. The competition data of these latter have been interpreted by using eq 7,[3] where $R(I \to 0)$ is the competition ratio at zero ionic

$$R = R(I \to 0) \times 10^{-2Az_I I^{1/2}/(1+\beta r I^{1/2})} \qquad (7)$$

strength, r is the distance of closest approach, A and β are physical constants, and z_I is the charge of the intermediate. For the leaving groups X = SO_4^{2-}, NO_3^-, and $OS(CH_3)_2$, z_I values of 0, 1, and 2, respectively, have been found. Equation 7, where $R(I \to 0) = k'_{N_3}K^I_{N_3}(I \to 0)/k_{H_2O}$, applies[3] to the $Co(NH_3)_5X^{n+}$ complexes under three conditions. (i) r represents the distance of closest approach for *contact ion pairs*. (ii) The major amount of products is formed via two intermediates: free $Co(NH_3)_4(NH_2)\cdots X^{n-1}$ forms exclusively $Co(NH_3)_5OH^{2+}$ and the ion pair $[Co(NH_3)_4(NH_2)\cdots X,N_3]^{n-2}$ exclusively $Co(NH_3)_5N_3^{2+}$. (iii) The equilibration of the ion aggregates of the intermediates with azide is much faster than the reaction with nucleophiles.

In the following sections, the competition data arising from the base hydrolysis of the two presently studied $Co(NH_2CH_3)_5X^{n+}$ complexes (X = Cl^-, DMF) are analyzed in detail.

(a) Models That Do Not Involve Product Formation via Intermediates. Intermediates are considered to be species whose decomposition rates are not faster than the fastest chemical reactions in the system of interest. In this particular case, the fastest reactions are the formation and dissociation of ion aggregates. They occur on the time scale of ≈100 ps. On the basis of the kinetically thoroughly studied $Co(NH_2CH_3)_5Cl^{2+}$ reactant (Scheme I), two such models will be discussed. In the first and most simple one the product $Co(NH_2CH_3)_5OH^{2+}$ is formed via the k'_{-X} pathway and $Co(NH_2CH_3)_5N_3^{2+}$ is formed via the k'_{-X} pathway, respectively (Scheme I). Since k_{-X} and k'_{-X} (see Kinetics section), as well as K_{OH} and K_{N_3} (see Appendix) are equal, the competition data (Table Va) should follow eq 8, with $K'_{OH}(I \to 0) \approx 1.4\ M^{-1}$ (calculated according to the Fuoss equation[10]) and $z = 1$. Although the weighted $(1/\sigma^2)$ least-squares fit is good (Table VI, fit 1), this model cannot apply, since the calculated parameters deviate too much from the expected ones. This model,

$$R = K'_{OH}(I \to 0) \times 10^{-2AzI^{1/2}/(1+\beta r I^{1/2})} \qquad (8)$$

however, may be extended to allow $Co(NH_2CH_3)_5OH^{2+}$ formation via a fraction (x_{OH}) of the k'_{-X} path; $Co(NH_2CH_3)_5N_3^{2+}$ would then be formed via the remaining fraction $(1 - x_{OH})$ of the k'_{-X} path. *This is the only alternative model for product formation consistent with the kinetics that does not involve intermediates.* In this case, the competition ratio would be predicted by eq 9 (derived by setting $k_{-X} = k'_{-X}$ and $K_{N_3} = K_{OH}$).

$$R = \frac{(1 - x_{OH})K'_{OH}(I \to 0) \times 10^{-2AI^{1/2}/(1+\beta r I^{1/2})}}{1 + x_{OH}[K'_{OH}(I \to 0)][N_3^-] \times 10^{-2AI^{1/2}/(1+\beta r I^{1/2})}} \qquad (9)$$

The weighted $(1/\sigma^2)$ least-squares fit of the $Co(NH_2CH_3)_5Cl^{2+}$ data (Table Va) according to eq 9 is worse than that of the previous model and yields $0 < x_{OH} < 1$ as expected, but again, $K'_{OH}(I \to 0)$ (Table VI, fit 2) is larger than the value of ≈1.4 M^{-1} predicted by the Fuoss equation.[10]

The example of the $Co(NH_2CH_3)_5Cl^{2+}$ reactant shows, that models involving only the reactions presented in Scheme I do not allow one to rationalize the competition data. *In fact, product formation is not—at least not in a simple way—directly related to the rate-determining steps* and are therefore determined by species arising *after* the rate-determining steps. These species must have a sufficiently long lifetime to undergo chemical reactions other than a collapse with their immediate environment—otherwise, the competition data could be rationalized by one of the models discussed above. In fact, this is known from earlier work[2,3,18] involving $Co(NH_3)_5X^{n+}$ complexes.

(b) Models Where Product Formation Occurs via Intermediates. The competition data of both of the investigated complexes, $Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$, are summarized in Table V, and plots corresponding to the linearized expression of eq 7 are presented in Figure 2. The competition ratios exhibit a pronounced dependence on the ionic strength, but they are independent of $[OH^-]$. This establishes that, in agreement with earlier findings,[3,19-21] OH^- does not act as a competitor. In contrast to the $Co(NH_3)_5X^{n+}$ complexes,[3] the competition ratios are larger and the slopes *nonintegral* numbers (≈1.4–1.5) and *equal in spite*

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(18) Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473.

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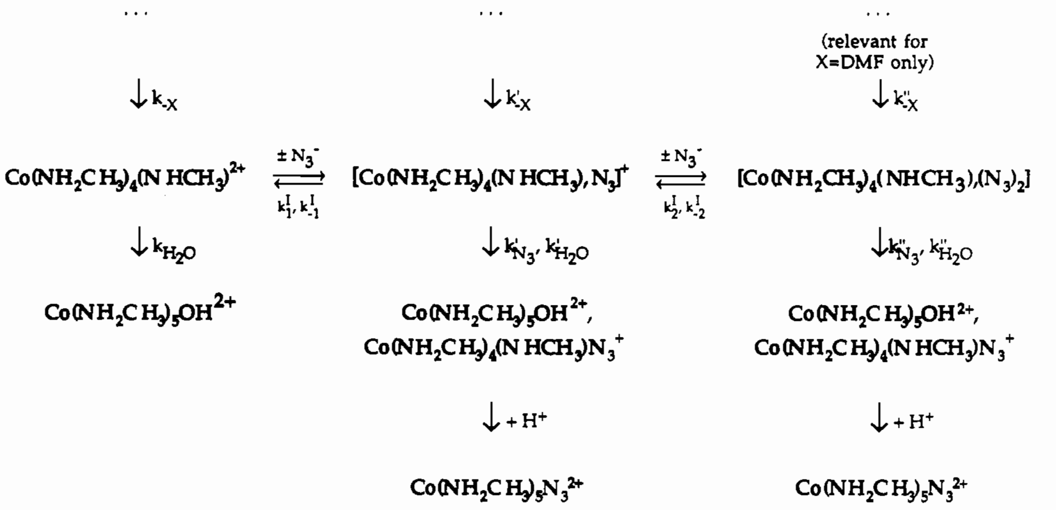
(20) Green, M.; Taube, H. *J. Phys. Chem.* **1963**, *67*, 1565.

(21) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.

Scheme II[a]



[a] With $k_1^I/k_{-1}^I = K_1^I$ and $k_2^I/k_{-2}^I = K_2^I$.

of the different charges of the leaving group. For the $Co(NH_2CH_3)_5X^{n+}$ reactants, condition i of eq 7 is fulfilled, since the kinetic study (see Kinetics section) established that contact ion aggregates are formed. It will be shown below, however, that conditions ii and iii do not apply to the $Co(NH_2CH_3)_5X^{n+}$ reactants.

For the $Co(NH_3)_5X^{n+}$ complexes, it has been shown previously[3] that the slope of the log R vs. $-2AI^{1/2}/(1 + \beta rI^{1/2})$ plots is identical with the charge of the free intermediate, $Co(NH_3)_4(NH_2)\cdots X^{n-1}$ and that $Co(NH_3)_5N_3^{2+}$ formation occurs exclusively via the ion pair of the latter with azide, $[Co(NH_3)_4(NH_2)\cdots X,N_3]^{n-2}$. The presently observed nonintegral slopes of 1.4–1.5 (Figure 2) may be considered as an average of slopes 1 and 2, respectively. This indicates that two intermediates exhibiting charges of 1+ and 2+ are responsible for product formation. The two reactants ($Co(NH_2CH_3)_5Cl^{2+}$ and $Co(NH_2CH_3)_5DMF^{3+}$) with *different* charges give rise to intermediates of the *same* charges, because of the equal slopes of the log R plots (Figure 2). Therefore, the (differently charged) leaving groups DMF and Cl^- have to be *absent* from the first coordination sphere of the intermediates during product formation. The intermediate with a 2+ charge must be the pentacoordinated species $Co(NH_2CH_3)_4(NHCH_3)^{2+}$. It may collapse with water to form $Co(NH_2CH_3)_5OH^{2+}$ or react reversibly with azide to form an ion pair, $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$. The latter, identical with the above postulated singly charged intermediate, may collapse with nucleophiles (i.e. N_3^- or H_2O) to yield the products or react again reversibly with another azide anion to form the ion-triplet $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$, which may also collapse to form the products. It will be shown below (section b2) that the ion aggregates of the intermediate do not collapse with water to form $Co(NH_2CH_3)_5OH^{2+}$ and that the proposed composition of the intermediates and their reactions—summarized in Scheme II, the continuation of Scheme I—are consistent with the experimental competition data (Table V and Figure 2).

Slightly, but significantly larger competition ratios (Table V and Figure 2) have been measured for the $Co(NH_2CH_3)_5DMF^{3+}$ reactant exhibiting a higher charge than $Co(NH_2CH_3)_5Cl^{2+}$. Since for both of the reactants a common mechanism involving the same intermediates (Scheme II) is likely to operate, the slightly different competition ratios of the two reactants are assumed to be due to the relatively high collapse rates (i.e. k_{H_2O} and k'_{N_3}), which prevent complete equilibration of the intermediates with azide from the bulk solution. Then, in contrast to the $Co(NH_3)_5X^{n+}$ complexes,[3] the species $Co(NH_2CH_3)_4(NHCH_3)^{2+}$, $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$, and $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$ are never at equilibrium. In this situation, the competition ratios are expected to be influenced *also* by the rate-determining steps. For example, the reactant with the lower charge, $Co(NH_2CH_3)_5Cl^{2+}$, forms less ion aggregates with azide than the $Co(NH_2CH_3)_5DMF^{3+}$ reactant. Therefore, for $Co(NH_2CH_3)_5Cl^{2+}$ the k_{-X} pathway leads to more $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ and consequently also more $Co(NH_2CH_3)_5OH^{2+}$ is formed at the expense of $Co(NH_2CH_3)_5N_3^{2+}$. Moreover, in contrast to $Co(NH_2CH_3)_5DMF^{3+}$, the less charged $Co(NH_2CH_3)_5Cl^{2+}$ complex does not form $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$ directly (via the k''_{-X} pathway), since the ion triplet $[Co(NH_2CH_3)_5Cl,(N_3)_2]$ is quite unreactive (see Kinetics section). In other words, the steady-state concentration of $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ is higher for the reactant with a lower charge. In my opinion, this is the only explanation for the slight dependence of the competition ratio on the charge of the leaving group. The numerical analysis of the competition data supports this hypothesis (section b2).

Incomplete equilibration of the intermediate with the nucleophile has previously been postulated[22] in order to explain the slightly leaving-group-dependent competition ratios observed in the base hydrolysis of $Co(NH_3)_5X^{n+}$ complexes (at $I = 1$ M). This hypothesis, however, was based on the existence of the $Co(NH_3)_4NH_2^{2+}$ intermediate—an incorrect assumption, since base hydrolysis of $Co(NH_3)_5X^{n+}$ complexes was shown[2,3] to proceed via the relatively long-lived hexacoordinated intermediates $Co(NH_3)_4(NH_2)\cdots X^{n-1}$. It is of course not surprising that (in a hexacoordinated intermediate still carrying the leaving group) product formation is influenced[3,22,23] by charge and the nature of the leaving group.

In principle, dissociation of the Co–Cl bond is expected to lead to aggregates of the intermediate with chloride, viz. $[Co(NH_2CH_3)_4(NHCH_3),Cl]^+$ and $[Co(NH_2CH_3)_4(NHCH_3),(Cl)(N_3)]$, which subsequently equilibrate *partially* with azide. From the numerical analysis of the competition data (section b2) it is known that the ion-pair would dissociate to $\gtrsim$80% in the worst case ($k_{H_2O}/k_{-1}^I \approx 0.2$), and that even >90% of the ion triplet would lose Cl^- from the second coordination sphere ($k''_{N_3}/k_{-2}^I \lesssim 0.1$) prior to nucleophile scavenging. Furthermore, a part of the ion pair possibly re-forms the reactant (see the section Base Hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the Presence of Various Competing Anions and ref 25). Therefore, the contribution of the ion aggregates with chloride to product formation is negligible.

(b1) Mathematical Description of the System. The rate-determining steps of the base hydrolysis of $Co(NH_2CH_3)_5X^{n+}$ complexes are summarized in Scheme I, and the subsequent product-determining ones are summarized in Scheme II. Product formation is described by eqs 10–14, where $[Co(NH_2CH_3)_5X^{n+}]$ represents the concentration of the free $Co(NH_2CH_3)_5X^{n+}$ species

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(22) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.

(23) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. *Inorg. Chem.* **1989**, *28*, 4567.

(excluding the ion aggregates with azide). Since the intermediates are always present at a very low concentration, the steady-state approximation was applied to the intermediate concentrations (abbreviations: CoX = $Co(NH_2CH_3)_5X^{n+}$; CoN_3 = $Co(NH_2CH_3)_5N_3^{2+}$; CoOH = $Co(NH_2CH_3)_5OH^{2+}$; I = $Co(NH_2CH_3)_4(NHCH_3)^{2+}$; I,N_3 = $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$; $I,(N_3)_2$ = $[Co(NH_2CH_3)_4(NHCH_3),(N_3)_2]$). For the Co-

$$d[I]/dt = k_{-X}K_{OH}[OH][CoX] + k^{I}_{-1}[I,N_3] - (k_{H_2O} + k^{I}_{1}[N_3])[I] = 0 \quad (10)$$

$$d[I,N_3]/dt = k'_{-X}K'_{OH}K_{N_3}[OH][N_3][CoX] + k^{I}_{1}[N_3][I] + k^{I}_{-2}[I,(N_3)_2] - (k^{I}_{2}[N_3] + k^{I}_{-1} + k'_{H_2O} + k'_{N_3})[I,N_3] = 0 \quad (11)$$

$$d[I,(N_3)_2]/dt = k''_{-X}K''_{OH}K_{N_3}K_{(N_3)_2}[OH][N_3]^2[CoX] + k^{I}_{2}[N_3][I,N_3] - (k^{I}_{-2} + k''_{H_2O} + k''_{N_3})[I,(N_3)_2] = 0 \quad (12)$$

$$d[CoN_3]/dt = k'_{N_3}[I,N_3] + k''_{N_3}[I,(N_3)_2] \quad (13)$$

$$d[CoOH]/dt = k_{H_2O}[I] + k'_{H_2O}[I,N_3] + k''_{H_2O}[I,(N_3)_2] \quad (14)$$

$(NH_2CH_3)_5Cl^{2+}$ reactant $k_{-X} = k'_{-X}$ was found (see Kinetics section). By analogy, $k_{-X} = k'_{-X} = k''_{-X}$ is expected to hold for $Co(NH_2CH_3)_5DMF^{3+}$. The rate constants k^{I}_{1} and k^{I}_{2} were substituted using the relations $K^{I}_{1} = k^{I}_{1}/k^{I}_{-1}$ and $K^{I}_{2} = k^{I}_{2}/k^{I}_{-2}$. Equations 10–12 were combined and solved for $[I,N_3]$ (eqs 15 and 16). Rearrangement of eqs 10 and 12 lead to the corresponding expressions for [I] and $[I,(N_3)_2]$ (eqs 17 and 18).

$$[I,N_3] = \frac{\alpha}{k_{H_2O}}k_{-X}[OH][CoX] \quad (15)$$

$$\alpha = \{K'_{OH}K_{N_3}[N_3] + K^{I}_{1}K_{OH}[N_3]/(k_{H_2O}/k^{I}_{-1} + K^{I}_{1}[N_3]) + K''_{OH}K_{N_3}K_{(N_3)_2}[N_3]^2/(1 + k''_{H_2O}/k^{I}_{-2} + k''_{N_3}/k^{I}_{-2})\}/ \{k'_{H_2O}/k_{H_2O} + k'_{N_3}/k_{H_2O} + 1/(k_{H_2O}/k^{I}_{-1} + K^{I}_{1}[N_3]) + K^{I}_{2}[N_3](k''_{H_2O}/k_{H_2O} + k''_{N_3}/k_{H_2O})/ (1 + k''_{H_2O}/k^{I}_{-2} + k''_{N_3}/k^{I}_{-2})\} \quad (16)$$

$$[I] = \frac{k_{-X}K_{OH}[OH][CoX] + k^{I}_{-1}[I,N_3]}{k_{H_2O} + k^{I}_{-1}K^{I}_{1}[N_3]} \quad (17)$$

$$[I,(N_3)_2] = \frac{k_{-X}K''_{OH}K_{N_3}K_{(N_3)_2}[OH][N_3]^2[CoX] + k^{I}_{-2}K^{I}_{2}[N_3][I,N_3]}{k^{I}_{-2} + k''_{H_2O} + k''_{N_3}} \quad (18)$$

Calculation of the competition ratio *R* (eq 3) requires $[CoN_3]_\infty$ and $[CoOH]_\infty$, which were obtained by integration of eqs 13 and 14. The solutions are represented by eqs 19 and 20. The integrals need not to be calculated, because they cancel in the ratio $[CoN_3]_\infty/[CoOH]_\infty$. The base hydrolysis reaction must not be pseudo first order, since the integral is taken over the product of [CoX][OH]. A numerical analysis of the competition data is now available via eqs 3, 16, 19, and 20. The ion-aggregation constants (i.e. K_{OH}, K_{N_3}, and K^{I}_{1}) were calculated based on the Fuoss equation[10] (see Appendix). Equal distances of the closest approach for the aggregates with azide and hydroxide were used. For $Co(NH_2CH_3)_5Cl^{2+}$, $Co(NH_2CH_3)_5DMF^{3+}$, and $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ contact distances of 5.14, 5.34, and 4.95 Å, respectively, were estimated.[3] The competition ratios depend on six parameters (see eqs 16, 19, and 20), namely k_{H_2O}/k^{I}_{-1}, k'_{N_3}/k_{H_2O}, k''_{N_3}/k^{I}_{-2}, k'_{H_2O}/k_{H_2O}, k''_{H_2O}/k_{H_2O}, and k''_{N_3}/k_{H_2O}, since $k''_{H_2O}/k^{I}_{-2} = (k''_{N_3}/k^{I}_{-2}) \times (k''_{H_2O}/k_{H_2O})/(k''_{N_3}/k_{H_2O})$.

$$[CoN_3]_\infty = \left(\frac{k'_{N_3}}{k_{H_2O}}\alpha + \frac{k''_{N_3}}{k^{I}_{-2}}\,\frac{K''_{OH}K_{N_3}K_{(N_3)_2}[N_3]^2}{1 + k''_{H_2O}/k^{I}_{-2} + k''_{N_3}/k^{I}_{-2}} + \frac{k''_{N_3}}{k_{H_2O}}\,\frac{K^{I}_{2}[N_3]^2}{1 + k''_{H_2O}/k^{I}_{-2} + k''_{N_3}/k^{I}_{-2}}\alpha\right)\int_0^\infty k_{-X}[OH][CoX]\,dt \quad (19)$$

$$[CoOH]_\infty = \left(\frac{K_{OH}}{1 + k^{I}_{-1}K^{I}_{1}[N_3]/k_{H_2O}} + \frac{\alpha}{k_{H_2O}/k^{I}_{-1} + K^{I}_{1}[N_3]} + \frac{k'_{H_2O}}{k_{H_2O}}\alpha + \frac{\frac{k''_{H_2O}}{k^{I}_{-2}}K''_{OH}K_{N_3}K_{(N_3)_2}[N_3]^2 + \frac{k''_{H_2O}}{k_{H_2O}}\alpha K^{I}_{2}[N_3]}{1 + k''_{H_2O}/k^{I}_{-2} + k''_{N_3}/k^{I}_{-2}}\right) \times \int_0^\infty k_{-X}[OH][CoX]\,dt \quad (20)$$

(b2) Numerical Analysis of the Competition Data. First, the model was considered where the ion aggregates of the intermediate with azide were assumed to collapse exclusively with azide, i.e. $k'_{H_2O} = k''_{H_2O} = 0$ (Scheme II). Then, the competition ratios depend on four parameters only. The corresponding weighted $(1/\sigma^2)$ least-squares fit of the data for both of the investigated reactants (Table V) yielded a meaningful set of parameters (Table VI, fit 3). The rate constants for nucleophile scavenging follow the order $k''_{N_3} < k'_{N_3} < k_{H_2O}$. A stabilization of the coordinatively unsaturated pentacoordinated intermediate is indeed expected with compensation of the 2+ charge through aggregation with anions. The parameter $k''_{N_3}/k^{I}_{-2} \lesssim 0.1$ is not well determined (Table VI, fit 3). Nevertheless, its value is in agreement with expectation, since $k^{I}_{-2} > k^{I}_{-1}$ (for electrostatic reasons dissociation of an anion from an ion triplet is more favorable than the corresponding process from an ion pair) and, therefore $k''_{N_3}/k^{I}_{-1} = (k''_{N_3}/k_{H_2O})(k_{H_2O}/k^{I}_{-1}) = 0.13 \pm 0.02 > k''_{N_3}/k^{I}_{-2}$. A least-squares fit with the restriction $k''_{N_3}/k^{I}_{-2} = 0$ leads to the same result, but more precisely defined parameters (Table VI, fit 4).

In the alternative model, water scavenging by the ion aggregates of the intermediate was assumed to be relevant (i.e. k'_{H_2O}, $k''_{H_2O} \neq 0$). Two of the six parameters obtained by the corresponding weighted least-squares fit were significantly negative and therefore physically meaningless (Table VI, fit 5).

A five-parameter fit with the restriction $k'_{H_2O} = k''_{H_2O}$ led to positive, but poorly determined parameters (Table VI, fit 6). In particular, the parameter $k'_{H_2O}/k_{H_2O} = k''_{H_2O}/k_{H_2O}$ could be insignificant—this case would lead us to the already discussed first model where $k'_{H_2O} = k''_{H_2O} = 0$ (see above)—or equal to one. The latter possibility was checked by performing another weighted least-squares fit with the restriction $k_{H_2O} = k'_{H_2O}$. The parameter set thus obtained (Table VI, fit 7) is physically not meaningful, since the ratio $k''_{N_3}/k'_{N_3} = (k''_{N_3}/k_{H_2O})/(k'_{N_3}/k_{H_2O}) = 3.5 \pm 0.3$ is too large. A value of 2 would be acceptable, because the probability for azide scavenging within the ion triplet could be twice as large as that for the ion pair. There is no other reason for the ion triplet to be more reactive—on the contrary, the uncharged ion triplet is expected to be more stable and hence less reactive than the charged ion pair. Other fits were also attempted, but none of them led to a physically meaningful set of parameters.

The least-squares fits according to the first model (Table VI, fits 3 and 4; no water scavenging by ion aggregates of the intermediate) are marginally poorer than those for the second one (Table VI, fits 5–7) due to their slightly higher standard deviations. On the basis of statistical criteria such as the *F* test, the first model cannot be rejected in favor of the second one. Remarkably, only the fits based on the first model gave rise to a set of physically meaningful parameters. Therefore, models involving water scavenging by ion aggregates of the intermediate are rejected. The slightly larger standard deviations for the first model could arise from systematic errors of the competition ratios (≲5% of the products decompose; see Kinetics section).

Like the hexacoordinated intermediates, the pentacoordinated ones exhibit a very pronounced selectivity for azide, since the ion aggregates of the intermediate do not react with water to a significant extent.

(b3) Lifetime of the Pentacoordinated Intermediate. The competition ratios are determined by ratios of rate constants (eqs 16, 19, and 20). If a single rate constant is known, all the others can be calculated. For the present system, it is possible to calculate for example the rate constant (k^{I}_{-1}) for the dissociation of the ionpair $[Co(NH_2CH_3)_4(NHCH_3),N_3]^+$ by using the relation k^{I}_{-1}

Table VII. Kinetic and Competition Data for the Base Hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the Presence of Various Anions at I = 1 M and 25 °C

anion[a]	k, M^{-1} s^{-1}	ν	R, M^{-1}
	(a) Unidentate Anions		
F^- [b]	920 ± 10	1.24 ± 0.01	*c*
	900 ± 7	1.25 ± 0.01	*c*
	900 ± 7	1.27 ± 0.01	*c*
	884 ± 7	1.26 ± 0.01	*c*
Cl^-	840 ± 6	1.07 ± 0.01	*d*
	819 ± 9	1.00 ± 0.02	*d*
	811 ± 9	1.00 ± 0.02	*d*
Br^-	918 ± 12	1.05 ± 0.02	*d*
	878 ± 10	0.95 ± 0.02	*d*
	904 ± 11	1.00 ± 0.02	*d*
	885 ± 11	1.04 ± 0.02	*d*
NO_3^-	955 ± 12	0.93 ± 0.02	*d*
	1010 ± 10	1.07 ± 0.02	*d*
	1000 ± 10	1.01 ± 0.02	*d*
	965 ± 11	0.96 ± 0.02	*d*
ClO_4^-	1230 ± 20	1.03 ± 0.03	*d*
	1170 ± 20	1.01 ± 0.04	*d*
	1200 ± 20	1.05 ± 0.03	*d*
	1190 ± 20	1.01 ± 0.03	*d*
N_3^-	906 ± 10	0.55 ± 0.05	0.81 ± 0.17
	882 ± 14	0.46 ± 0.07	1.19 ± 0.35
	880 ± 6	0.49 ± 0.03	1.02 ± 0.12
CH_3COO^-	1140 ± 20	0.99 ± 0.03	*c*
	1090 ± 10	0.93 ± 0.03	*c*
	1150 ± 10	1.00 ± 0.02	*c*
SO_4^{2-} [e]	673 ± 6	1.02 ± 0.02	*c*
	680 ± 4	1.02 ± 0.01	*c*
	680 ± 4	1.02 ± 0.01	*c*
	671 ± 6	0.98 ± 0.02	*c*
$C_2O_4^{2-}$ [b,e]	867 ± 9	0.95 ± 0.02	0.16 ± 0.06
	869 ± 10	0.95 ± 0.02	0.15 ± 0.07
	876 ± 8	0.93 ± 0.02	0.23 ± 0.06
	887 ± 9	0.91 ± 0.02	0.31 ± 0.07
	(b) Ambidentate Anions		
CN^- [b]	1420 ± 30	0.49 ± 0.04	1.04 ± 0.18
	1460 ± 30	0.48 ± 0.05	1.08 ± 0.22
	1480 ± 30	0.52 ± 0.04	0.91 ± 0.15
SCN^-	1050 ± 10	0.62 ± 0.02	0.61 ± 0.05
	1070 ± 10	0.66 ± 0.02	0.52 ± 0.04
	1060 ± 10	0.66 ± 0.01	0.51 ± 0.03
NO_2^-	1060 ± 20	0.63 ± 0.03	0.58 ± 0.09
	1070 ± 10	0.60 ± 0.03	0.66 ± 0.08
	1100 ± 10	0.61 ± 0.03	0.63 ± 0.08
	1080 ± 10	0.71 ± 0.02	0.41 ± 0.05
$S_2O_3^{2-}$ [e]	576 ± 5	0.88 ± 0.02	0.40 ± 0.07
	562 ± 5	0.86 ± 0.02	0.49 ± 0.07
	571 ± 6	0.86 ± 0.02	0.49 ± 0.08

[a] Sodium salt unless stated otherwise. [b] Potassium salt. [c] See text. [d] No competition observed. [e] $^1/_3$ M.

$= k_1^{\mathrm{I}}/K_1^{\mathrm{I}}$, since k_1^{I} and K_1^{I} are available from the Debye[24] and Fuoss[10] equations, respectively. From $k_{-1}^{\mathrm{I}} \approx 5 \times 10^9$ s^{-1}, the collapse rate $k_{H_2O} \approx 10^9$ s^{-1} is calculated, and therefore, the lifetime of the intermediate, $\tau \approx 1/k_{H_2O} \approx 1$ ns, is obtained. This value might be correct within a factor of 2.

Base Hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the Presence of Various Competing Anions. The kinetics of reaction 1 have also been investigated in the presence of anions (Y^{m-}) other than azide at I = 1 M and 25 °C. The results are summarized in Table VII. The small variation of the rate constants[25] is due to the relative amount of uncharged and unreactive ion aggregate formed.[2] If—in analogy with the above results (see Kinetics section)—the doubly charged anions forming uncharged ion pairs with the reactant are assumed to be rather unreactive, rate constants on the order of ≈700–800 $M^{-1}s^{-1}$ are predicted. This assumption seems correct, since the experimental values are close to the predicted ones (Table VII). As expected for a dissociative substitution process, no correlation between the rate constants and the nucleophilicity of the anions becomes apparent (the origin of the slightly higher rate constants in the presence of CN^- is discussed below).

The measurements in azide media have shown that competition ratios were also available via eqs 2 and 4, if ν was not too close to 1. Although this method gave less accurate R values (Table III), it allows one to distinguish poor and good competitors readily. It should be noted, however, that experimental ν values of 1 do not necessarily imply that no or almost no anion scavenging occurs, since reaction 1 might be followed by a very fast consumption of OH^- due to NH_2CH_3 loss (reaction 21 with $\mu = 1$), which would lead to an overall ν value of 1.

$$Co(NH_2CH_3)_5Y^{n+} + \mu OH^- \rightarrow Co(NH_2CH_3)_{5-\mu}(OH)_\mu Y^{n-\mu} + \mu NH_2CH_3 \quad (21)$$

The pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ scavenges F^-, N_3^-, $C_2O_4^{2-}$, NO_2^-, CN^-, NCS^-, and $S_2O_3^{2-}$ efficiently and perhaps also CH_3COO^- and SO_4^{2-} to a small extent (Table VII). In the presence of fluoride, a ν value of 1.26 was found, although also this reaction was uniphasic. Since on the time scale of the stopped-flow experiments, no appreciable (≲5%) decomposition of $Co(NH_2CH_3)_5OH^{2+}$ occurred (base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the presence of Cl^-, Br^-, NO_3^-, and ClO_4^- is a uniphasic reaction with $\nu = 1$), $Co(NH_2CH_3)_5F^{2+}$ is expected to be formed as an unstable intermediate that very rapidly loses more than one NH_2CH_3 ligand (reaction 21 with $\mu > 1$); loss of only one NH_2CH_3 ligand would give rise to $\nu = 1$. This reaction was not investigated further; it should be pointed out that the pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ obviously scavenges fluoride in contrast[26] to the hexacoordinated intermediates $Co(NH_3)_4(NH_2)\cdots X^{n-1}$.

Acetate and sulfate are weak competing anions toward the $Co(NH_3)_4(NH_2)\cdots X^{n-1}$ intermediates.[21,22,26,27] Since oxalate competes for the $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ intermediate, the similar acetate anion (coordinating also through a $-COO^-$-donating group) and possibly also sulfate might be scavenged to a small extent as well.

Base hydrolysis of $Co(NH_3)_5X^{n+}$ complexes in the presence of ambidentate anions is a two-step process whose kinetics and products have been studied extensively[22,28-32] (reactions 22 and 23; $Co(NH_2CH_3)_5AB^{3-m}$ represents the stable isomer).

$$Co(NH_2CH_3)_5X^{n+} + \nu OH^- + (1-\nu)AB^{m-} \xrightarrow{k_1} \nu Co(NH_2CH_3)_5OH^{2+} + (1-\nu)\{Co(NH_2CH_3)_5AB^{3-m}, Co(NH_2CH_3)_5BA^{3-m}\} + X^{n-3} \quad (22)$$

$$Co(NH_2CH_3)_5BA^{3-m} + \mu OH^- \xrightarrow{k_2} \mu Co(NH_2CH_3)_5OH^{2+} + (1-\mu)Co(NH_2CH_3)_5AB^{3-m} + \mu AB^{m-} \quad (23)$$

The ambidentate anions CN^-, NO_2^-, NCS^-, and $S_2O_3^{2-}$ all reacted efficiently with the pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ (Table VIIb); the kinetics were uniphasic. The reactivity of the $Co(NH_3)_5BA^{n+}$ complexes[28,30,32] increases

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[24] Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

[25] The lowest rate constant (5–10% lower than those in F^-, Br^-, or N_3^- media) measured in the presence of singly charged anions (1 M) was found in chloride media. It cannot be excluded that the pentacoordinated intermediate reacts with chloride to re-form the reactant. This would indeed retard the reaction.

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

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in the order $Co(NH_3)_5ONO^{2+} < Co(NH_3)_5SCN^{2+} \approx Co(NH_3)_5OS_2O_2^{+}$, whereas the latter two complexes exhibit a reactivity similar to that of $Co(NH_3)_5Cl^{2+}$. By analogy to the reactivity of the $Co(NH_3)_5X^{n+}$ complexes, it was expected that for the base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in the presence of SCN^-, $S_2O_3^{2-}$ and perhaps CN^-—the isomerization of the recently[33] characterized $Co(NH_3)_5NC^{2+}$ complex has not been studied so far[34]—reactions 22 and 23 were not resolved, if significant amounts of the unstable isomers are formed at all. In these cases, most likely overall rate constants and ν values for the two processes would have been obtained. As an artifact, unexpectedly large (for $Y^{m-} = CN^-$) or small ($Y^{m-} = S_2O_3^{2-}$) rate constants were observed in these media (Table VII). Alternatively, decomposition of the products could be responsible for these deviating rate constants. In the presence of NO_2^- mainly (if not exclusively), reaction 22 is likely[35] to operate, because $Co(NH_3)_5ONO^{2+}$ is about 2 orders of magnitude less reactive than $Co(NH_3)_5Cl^{2+}$, and the observed rate constant (Table VIIb) compares well with those obtained in the presence of other singly charged anions (Table VIIa).

The Present Results in Relation to Work from the Literature. For the $Co(NH_3)_5X^{n+}$ complexes, the competition ratios depend[3,22,23] on the charge of the leaving group X, and for a given charge type of X, slight, but significant variations of R with the *nature* of leaving group are known to exist.[22,23] The present study shows that the competition ratios of the $Co(NH_2CH_3)_5X^{n+}$ complexes are also slightly sensitive to the charge of the leaving group (Figure 2). In this respect, these two types of reactants behave similarly, although the origin of this feature is fundamentally different.

Alkaline hydrolysis of $Co(NH_3)_5X^{n+}$ was shown[2,3] to proceed via hexacoordinated intermediates exhibiting the same charge as the corresponding conjugate base. In other words, the charge of the intermediate $[Co(NH_3)_4(NH_2)\cdots X]^{n-1}$ is related to the charge of the leaving group. The dependence of R on the charge of X—being very pronounced[3] at low ionic strengths—arises therefore from the charge sensitive stability of the ion pairs (or ion aggregates) involving the intermediate and the competing nucleophile, e.g. azide. (The ion aggregates are always at equilibrium with azide from the bulk solution.) The slopes of the log R vs $-2AI^{1/2}/(1 + \beta rI^{1/2})$ plots[3] reflect precisely this effect. For the $Co(NH_2CH_3)_5X^{n+}$ complexes, however, these *slopes* are independent of the charge of X (Figure 2), proving the absence of X from the—necessarily—pentacoordinated intermediate, but the slight sensitivity of the *magnitude* of R on the charge of the leaving group is due to the short lifetime of the intermediate preventing complete equilibration of the latter with azide from the bulk solution.

For the $Co(NH_3)_5X^{n+}$ reactants, the product-formation step corresponds to a *displacement* of the leaving group by the nucleophiles within the hexacoordinated intermediate. The competition ratio reflects[3] the ratio of the individual displacement rates of the respective nucleophiles (water and, e.g., azide). It is not surprising at all that this ratio depends on the nature of, also equally charged, X—on the contrary, the dependence[22,23] of R on the *nature* of X (for a given charge of X) supports the existence of hexacoordinated intermediates.

The aggregates of the hexacoordinated intermediates are always at equilibrium with azide from the bulk solution. From this observation, a *lower limit* for their lifetime has been estimated[3] to be $\gtrsim 1$ ns. The pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ exhibits a shorter lifetime (see the section Spectrophotometric Product Analysis and section b3), since it equilibrates only *partially* with azide due to its fast collapse with nucleophiles (sections b and b2). The lifetime of an intermediate is in fact determined by the energy of activation for product formation: *displacement* of a—although weakly bound—leaving group in a hexacoordinated intermediate is expected to require a higher energy of activation than a "simple" *addition* to a pentacoordinated species.

The above considerations show that the *selectivity* (magnitude of R) of an intermediate is not related to its lifetime but to its structural and electronic properties, since these two features determine its affinity toward nucleophiles. The pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$, in spite of its shorter lifetime, gives rise to much higher azide competition than the equally charged hexacoordinated intermediate $[Co(NH_3)_4(NH_2)\cdots OS(CH_3)_2]^{2+}$. Interestingly, comparably high competition ratios have also been observed[36] for the trigonal-bipyramidal intermediate *mer*-Co(dien-H)(dapo)$^{2+}$. In fact, trigonal-bipyramidal pentacoordinated and hexacoordinated intermediates exhibit[4] very different electronic structures: the $Co(NH_3)_4(NH_2)\cdots X^{n-1}$ species are low-spin cobalt(II) complexes, i.e. $Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots X^{n-1}$, and the trigonal-bipyramidal ones exhibit a cobalt(III) center with a triplet electronic ground state. From the similarity of the competition ratios of $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ and *mer*-Co(dien-H)(dapo)$^{2+}$, the former is likely to be also trigonal bipyramidal; square-pyramidal pentacoordinated intermediates are unlikely to exist.[4]

Both types of intermediates exhibiting different lifetimes and structural and electronic properties distinguish good (e.g. N_3^- and NCS^-) and poor (e.g. CH_3COO^- and SO_4^{2-}) nucleophiles. Interestingly, the "hard" fluoride anion competes efficiently for the "hard" pentacoordinated intermediate, but not for the "soft" hexacoordinated ones. By analogy, the pentacoordinated intermediate is expected to scavenge mainly the "hard" end of ambidentate nucleophiles (e.g. *N*CS$^-$, *N*O$_2^-$, ...) whereas the hexacoordinated ones are known to prefer[22,28-31] the "soft" end of the latter (e.g. *S*CN$^-$, *O*NO$^-$, ...). There is some evidence that the above statement could be true, since the extinction coefficient of a $Co(NH_2CH_3)_5NCS^{2+}/Co(NH_2CH_3)_5SCN^{2+}$ mixture (generated by immediate acidification of a solution produced by base hydrolysis of $Co(NH_2CH_3)_5Cl^{2+}$ in 1 M NCS^-) is about 2700 M^{-1} cm^{-1} at 300 nm. At this wavelength, the extinction coefficients[28] of $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5SCN^{2+}$ are $\approx$1400 and $\approx$14000 M^{-1} cm^{-1}, respectively. The present experimental values indicate (provided that the extinction coefficients of $Co(NH_2CH_3)_5CNS^{2+}$ complexes are not too different from the above values) that $Co(NH_2CH_3)_5SCN^{2+}$ is a minor product, whereas, for the $Co(NH_3)_5X^{n+}$ reactants, the opposite was observed.[22,28,29] The possibility that some $Co(NH_2CH_3)_5SCN^{2+}$ has isomerized cannot be excluded, but the extinction coefficient of $\approx$140 M^{-1} cm^{-1} at 522 nm, obtained from the stopped-flow experiments, also indicates that $Co(NH_2CH_3)_5NCS^{2+}$ is the major product.

The alkaline hydrolysis reaction is triggered by deprotonation of the reactant and therefore ultimately involves a back-protonation. The hexacoordinated intermediates $Co(NH_3)_4(NH_2)\cdots X^{n-1}$ are not protonated, since they exhibit the same charge as their conjugate base precursors.[3] For the $Co(NH_3)_5X^{n+}$ reactants, protonation takes place *after* azide entry, but water addition might be a concerted process where the proton is supplied by the entering water ligand. Also the pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ is unlikely to be protonated, since no species with a 3+ charge (i.e. $Co(NH_2CH_3)_5^{3+}$) has been detected. Its presence would produce (at least at low $[N_3^-]$) slopes of the log R vs $-2AI^{1/2}/(1 + \beta rI^{1/2})$ plots (Figure 2) greater than 2.

Summary

Base hydrolysis of $Co(NH_2CH_3)_5X^{n+}$ complexes proceeds via the—most likely trigonal bipyramidal[4,36]—genuine pentacoordinated intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ exhibiting a shorter lifetime, higher competition ratios for azide, and a

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(33) Jackson, W. G.; Rahman, F. F. M. M. *Inorg. Chem.* **1990**, *29*, 3247.

(34) To my knowledge, no competition experiments in the presence of cyanide have been reported thus far.

(35) Furthermore, reaction 23 is retarded by almost a factor of 2 with respect to reaction 22 under the present experimental conditions ($[OH]_0 \approx 7$ mM and $[Co(NH_2CH_3)_5Cl^{2+}]_0 \approx 5$ mM), because the first reaction occurs at a higher average hydroxide concentration than the second one.

(36) Comba, P.; Jackson, W. G.; Marty, W.; Zipper, L. Submitted for publication.

pronounced selectivity for fluoride in contrast to the hexacoordinated intermediates,[3] $Co(NH_3)_4(NH_2)\cdots X^{n-1}$.

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Appendix

The ion-aggregation constant K_Y at $I \to 0$ for the example $A^{z+} + Y^- \rightleftarrows [A,Y]^{z-1}$ is given[10] by

$$K_Y(I \to 0) = \frac{4\pi N_A r^3}{3000} \exp\left\{\frac{ze^2N_A}{DrRT}\right\}$$

with N_A, e, D, R, r, and T being Avogadro's number, the elementary charge, the dielectric constant of water, the gas constant, the distance of closest approach, and the absolute temperature, respectively.

The ionic strength dependence of K_Y was calculated by using the Debye–Hückel equation[11] (eq 6a) for the activity coefficients:

$$K_Y = K_Y(I \to 0) \times 10^{-2zAI^{1/2}/(1+\beta rI^{1/2})}$$

Contribution from the Departments of Chemistry, Canisius College,
Buffalo, New York 14208, and York University, Downsview, Ontario, Canada M3J 1P3

Near-Infrared Spectra of $BaCl_2{\cdot}2D_2O$ at 10 K. A Local-Mode Approach

Paul J. McCarthy*,† and Ian M. Walker‡

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The polarized crystal spectra of $BaCl_2{\cdot}2D_2O$ and of several partially deuterated crystals have been measured at 10 K in the near-infrared region. The O–D stretching bands have been analyzed by using local-mode theory, and the calculated parameters are compared with those derived from $BaCl_2{\cdot}2H_2O$. The anharmonicities are smaller than those observed for O–H oscillators in bound H_2O; this trend follows that found in the gas-phase molecules. The local-mode parameters for O–H oscillators in HOD are not the same as those in H_2O. Some possible explanations for this are presented.

Introduction

Recently, we have begun to apply local-mode theory to the vibrational overtone-combination spectra of oriented water molecules in single crystals.[1,2] These spectra occur in the near-infrared (near-IR) region, and the use of low temperature and polarized light insures optimum resolution of the vibrational bands in this region. Most recently we have measured the near-IR spectra of single crystals of $BaCl_2{\cdot}2H_2O$, and have derived local-mode parameters for water in these crystals.[2] The present study is a corollary to that report, and in it we calculate local-mode parameters for O–D oscillators in $BaCl_2{\cdot}2D_2O$ and try to assess the effect of deuteration on the local-mode parameters for O–H oscillators.

Barium chloride dihydrate (BCD) belongs to space group $P2_1/c$ (C^5_{2h}, $Z = 4$)[3] in which the formula units have a layered arrangement with the layers stacked along the crystal *b* axis. All atom positions have been determined by neutron diffraction,[4] and the angles and distances associated with the various hydrogen bonds have been codified by Brink,[5] whose numbering system we use in this work (see Figure 1). The lattice contains two crystallographically distinct water molecules on general positions. The spectra are therefore the superposition of features expected for two different water molecules. Oscillators 1 and 2 on water(I) and oscillator 3 on water(II) are engaged in strong hydrogen bonding to neighboring chloride ions. Oscillator 4 on water(II), on the other hand, forms weaker, bifurcated hydrogen bonds to neighboring chlorides. The local-mode parameters that we derived for these four oscillators are all different from one another. We were able to provide assignments for most of the strong bands in the spectra and also to correlate the local-mode parameters with hydrogen-bond distances and/or angles.

Experimental Section

Single crystals of BCD with varying degrees of deuteration were grown by recrystallization from aqueous solutions containing about 25%, 50%, 75%, 94%, and 98% D_2O. The solutions were slowly evaporated over concentrated H_2SO_4 in a desiccator. The crystals form as large rectangular plates showing the [010] face.[6]

Spectra were recorded at 10 K on a Varian-2300 spectrophotometer by using a Displex cryogenic refrigerator to cool the sample. Polarized light was provided by a pair of matched Glan-Thompson prisms. The incident light was perpendicular to the prominent [010] face of the crystal, and so was parallel to the crystal *b* axis (C_2). Two orthogonal polarizations were recorded with the electric vector of the light along the crystal extinction directions, one of which is about 8° from the *a* axis. Both polarizations are accordingly perpendicular to C_2. The water molecules lie in such a way that the two polarizations contain various mixtures of absorptions parallel and perpendicular to the O–H or O–D bonds. The bands differ in intensity and also are slightly different in energy in the two polarizations, the latter being due to factor-group splitting. The observed absorptions listed in this paper are the average energies of the two polarizations.

Results and Discussion

The most complete study of the fundamental vibrations of BCD and its deuterio analogue has been made by Lutz et al.,[7] and it is their 95 K data that we use in the following discussion. Our assignments differ in some instances from theirs, as we have noted previously.[2]

Spectra of $BaCl_2{\cdot}2D_2O$. The near-IR spectra of $BaCl_2{\cdot}2D_2O$ are rich in detail, but less so than those of the non-deuterated crystal. The lower frequency of the absorptions in the deuterated compound places many of the combinations outside the range of the spectrophotometer. The assignments are also less certain for the deuterated crystal, since even the most highly deuterated sample contains some HOD. This adds some weak features, which complicate the assignments. Furthermore, we were unable to grow thick crystals of $BaCl_2{\cdot}2D_2O$, which are needed to observe all of the weak 3ν overtones.

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† Canisius College.
‡ York University.

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