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Competition between Ammonia and the Nitrite Ion as Leaving Groups in Cobalt(III) Complexes. 3. Hydrolysis of Nitroamminecobalt(III) Complexes

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A kinetic study is reported on the spontaneous aquation of nitroamminecobalt(III) complexes in weakly alkaline ammoniacal solutions using a spectrophotometric technique. The results could be interpreted by the assumption of a duality of mechanism for the aquation: loss of NH$_3$ or NO$_2^-$. Independent measurements of liberated NH$_3$ and NO$_2^-$ by way of gas-detecting electrodes have confirmed the photometric results. The determining factor for the mechanism in this class of complexes is suggested to be a trans-labilizing effect of the NO$_2^-$ group.

Introduction

In the preceding parts[1,2] of the present series on the competition between ammonia and the nitrite ion as leaving groups in cobalt(III) complexes a dual mechanism has been proposed for the spontaneous aquation of the nitroamminecobalt(III) complexes. It has been shown[1] that the spontaneous aquation of the nitropentaamminecobalt(III) ion involves as the first step the loss of the ammine group trans to the nitro group to form the *trans*-aquo(hydroxo)nitrotetraamminecobalt(III) ion. Further we have found indications[2] that the same mechanism is operative for some of the remaining nitroamminecobalt(III) complexes.

To test the proposed mechanism experiments are reported on the *cis*- and *trans*-dinitrotetraamminecobalt(III), the *mer*-trinitrotriamminecobalt(III), and the *trans*-tetranitrodiamminecobalt(III) complexes in the ammonia/ammonium perchlorate buffer system. The reason for choosing this medium is that it can stop further degradation of the complexes in alkaline solution after the first hydrolysis step. In this way the route via loss of an ammine group can be separated from other reaction paths.[3,4] Apart from the mechanistic criterion the aquation rate obtained by extrapolation from weakly alkaline conditions is more reliable than the one obtained from the extrapolation of acid-catalyzed rate values. In this series we have discussed this problem in relation to the fact that the values for the aquation of nitropentaamminecobalt(III)[5] and *trans*-tetranitrodiamminecobalt(III)[6] obtained as the acid-independent part of the rate in strongly acidic solutions are not in agreement with the values in slightly acidic to alkaline media.[1,2,7,8] As a probable cause for this discrepancy we have suggested the presence of a saturation effect with regard to the hydrogen ion concentration for the acid-catalyzed hydrolysis. The conclusion reached by a kinetic analysis of the hydrolysis rates in the ammonia buffers has been tested in-

dependently in a more direct way by monitoring the loss of ammonia and nitrite during the reaction with the help of gas-detecting electrodes.

Experimental Part

Chemicals. The preparation, recrystallization, and analysis of the compounds used has been described.[1,2]

In this paper previously introduced[2] abbreviations will be used: [Co(NH$_3$)$_5$(NO$_2$)][ClO$_4$]$_2$, A5N; *cis*-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$, *cis*-A4N2; *trans*-[Co(NH$_3$)$_4$(NO$_2$)$_2$]ClO$_4$, *trans*-A4N2; *mer*-[Co(NH$_3$)$_3$(NO$_2$)$_3$], *mer*-A3N3; *trans*-K[Co(NH$_3$)$_2$(NO$_2$)$_4$], *trans*-A2N4.

The other chemicals used were of reagent grade.

Spectrophotometric Measurements of the Reaction Rate. The solutions were made up at room temperature from ammonia/ammonium perchlorate buffers at a constant ionic strength (1.00 M) obtained by adding sodium perchlorate. Concentrations will refer to the temperature at which the reaction was followed. The reacting solutions were monitored spectrophotometrically, using the procedure described in our study of the nitropentaamminecobalt(III) ion.[1] The reactions are not photosensitive as far as the amount of irradiation inherent in the photometric measurements is concerned.

Product Analysis with Gas-Detecting Electrodes. A direct determination of the concentrations of the leaving groups was performed with a nitrogen oxide electrode (Model 95-46, Orion) and an ammonia probe (Model 8002-2, E.I.L.) connected to an Electrofact 36200 pH meter. The pH was measured with Electrofact 7G111 or 7G112 glass electrodes and a Hg/HgSO$_4$/Na$_2$SO$_4$ reference electrode (E.I.L. 33-1352-330).

Solutions were prepared by dissolving the required amount of the complex (concentration 0.01 M) in a sodium perchlorate solution at a fixed ionic strength (0.10 M). The use of this value for the ionic strength is imperative from the composition of the internal solutions of the electrodes which is about 0.10 M. The neutral (unbuffered) perchlorate solutions were brought into a darkened thermostated bath and allowed to equilibrate to the bath temperature before addition of the complex. At appropriate time intervals aliquot portions of the reacting solution were withdrawn and cooled in ice to quench the

reaction. The concentrations of ammonia and nitrite were then determined in separate experiments at 10.9 °C. For the ammonia measurements the solution was brought to pH 11 and for the nitrogen oxide measurements a pH of 2 was used.

Calculations. The absorbance as a function of time was analyzed with the help of a computer program (LSKIN1 from DeTar[9]). The medium dependence of the observed rate constants was fitted by a steepest descent computer program.[4]

The activation parameters $\Delta S^{\ddagger}$ ((pseudo) entropy of activation) and $\Delta H^{\ddagger}$ ((pseudo) enthalpy of activation) were obtained from a least-squares computer analysis,[10] based on the Eyring formula.[11] Further details can be found in ref 1.

The calculations were executed in the SARA computer center in Amsterdam.

Results and Discussion

General Considerations. The values of the overall rate constants for base hydrolysis and spontaneous aquation of the nitroamminecobalt(III) complexes have been determined in sodium hydroxide containing aqueous solution.[2] To permit a comparison with the present experiments in ammonia buffers we use a conversion from sodium hydroxide concentration to $(NH_4^+)/(NH_3)$ via the previously determined[1] dissociation constant K

$$K = (NH_4^+)(OH^-)/(NH_3) \tag{1}$$

From the values of the rate constants for aquation and for base hydrolysis calculated from the activation parameters found in sodium hydroxide solutions[2] it is expected that under the circumstances used in this study base hydrolysis will not give a significant contribution to the overall rate constant.

In this study the buffer system has been used in the concentration range employed for the study of the nitropentaamminecobalt(III) ion and the *trans*-hydroxonitrotetraamminecobalt(III) ion.[1] The latter ion in this buffer forms a mixture of A5N and hydroxopentaammine at a rate which is large compared to the subsequent reaction of A5N to the hydroxopentaammine. The complexes under study in the present paper also were found to show a relatively fast reaction up to a mixture of A5N and hydroxopentaammine. This reaction path is possible due to the lability of the complexes in which a nitro or ammine group is substituted by water. However it must be noted that for *mer*-A3N3 and *trans*-A2N4 the possibility of forming the relatively stable *cis*-A4N2 as preliminary end product of a side reaction cannot be completely excluded due to the close similarity of the electronic spectra of the relevant products. The identity of the final products on the time scale of the reaction had no effect on the order of the reaction. In spite of several complications to be discussed below, the absorbances as a function of time in all cases obeyed a first-order rate law up to 3 half-lives. The accuracy of the fits achieved was better than 0.3%.

Neither wavelength nor complex concentration dependence of the observed rate constants has been found. All this together is a strong indication that the reaction rates are governed by one principal unidirectional change which must be the first hydrolysis step. This assumption can be tested from a comparison of activation parameters for this step (vide infra). As explained previously[1] ammonia will introduce the reversible route for the first aquation step via loss of NH_3; in this way the ammonia dependence of the rate constant will give the contribution of this route to the overall reaction.

Photometric Study of the *cis*-Dinitrotetraamminecobalt(III) Ion. The absorbance of the reacting solution was monitored at 22 500 cm^{-1} (the absorbance maximum) and at 26 110 cm^{-1} (the isosbestic point of A5N and $[Co(NH_3)_5(OH)]^{2+}$); the complex concentration was varied from 2.0×10^{-3} to 3.9×10^{-3} M. Neither wavelength nor concentration dependence was observed. Since the standard error of the first-order fit at 26 110 cm^{-1} was 5 or more times larger than the standard

Table I. Observed and Calculated Rate Constants for the Aquation of the *cis*-Dinitrotetraamminecobalt(III) Ion, as a Function of the Medium, at 77.2 °C and at a Constant Ionic Strength (1.00 M)

(NH_3), M	(NH_4), M	$10^6 k$(obsd) s^{-1}	$10^6 k$(calcd),^{a} s^{-1}
0.16	0.10	80.4	79.3
0.32	0.10	69.4	70.5
0.63	0.10	64.6	64.7
1.26	0.10	60.9	61.2
0.25	0.16	66.7	65.5
0.50	0.16	56.4	56.2
0.63	0.16	53.1	53.9
1.00	0.16	52.1	50.3
1.26	0.16	47.2	48.9
2.00	0.16	47.8	46.9
0.40	0.25	51.1	51.4
0.63	0.25	43.4	45.3
0.79	0.25	41.1	42.8
1.26	0.25	37.5	39.0
1.59	0.25	38.1	37.6
3.17	0.25	33.8	34.7
1.26	0.40	32.4	30.8
2.52	0.40	28.0	26.5
5.04	0.40	25.7	24.3

^{a} The calculated values of the rate constant have been obtained by applying eq 6 and the parameter values in Table II.

error at 22 500 cm^{-1}, the following experiments were only performed at the latter wavelength. During the reaction the spectrum showed an isosbestic point at 20 200 cm^{-1} that started to shift outside the experimental error after 3 half-lives, which indicates that the initial reaction product is a mixture of fixed composition, spectrophotometrically identified as A5N and $[Co(NH_3)_5(OH)]^{2+}$ (as stated above). The reaction was studied at five temperatures (61.4–85.3 °C). The kinetic results obtained for one representative temperature (77.2 °C) are listed in Table I. No cis–trans rearrangement prior to the hydrolysis was observed. The remaining possibility that the observed hydrolysis rate is determined by a cis–trans rearrangement is excluded from the observation that the hydrolysis rates measured for *cis*-A4N2 and *trans*-A4N2 differ less than 1 order of magnitude,[2] which would bring about a deviation from first-order behavior. Moreover the observed medium dependence contradicts the explanation of a cis–trans rearrangement that can be expected to be medium independent. Table I shows the rate constant to decrease with increasing ammonia (NH_3) and ammonium perchlorate (NH_4) concentration. This (NH_3) and (NH_4) dependence of the rate constant indicates a reaction mechanism in which the complex ion loses its coordinated ammonia, as observed for A5N. The two cases are not completely analogous. This is only partly due to the fact that base hydrolysis is negligible for *cis*-A4N2 but not for A5N. The concentration dependence found makes it necessary to formulate for *cis*-A4N2 a slightly different reaction scheme, assuming the following steps (omitting charges and configurations): (a) the irreversible loss of the nitro group

$$Co(NH_3)_4(NO_2)_2 \xrightarrow[+H_2O, -NO_2^-]{k_{13}} Co(NH_3)_4(NO_2)(OH_2) \tag{2}$$
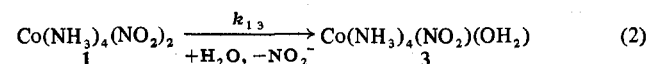
and (b) the reversible loss of the ammine group according to a dissociative interchange mechanism. The rate-determining step is

$$Co(NH_3)_4(NO_2)_2 + H_2O \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Co(NH_3)_3(OH_2)(NO_2)_2 \cdots NH_3 \tag{3}$$
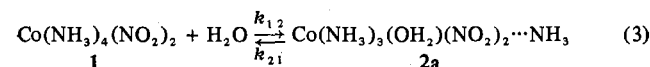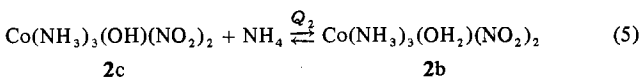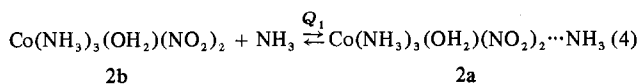
We also introduce a relatively fast equilibrium for the formation of the outer-sphere complex 2a from NH_3 and 2b (Q_1)

Table II. Rate Parameters Describing the Medium Dependence of the Rate Constants of the Aquation of the cis-Dinitrotetraamminecobalt(III) Ion in Ammoniacal Solutions at Constant Ionic Strength (I = 1.00 M)

Temp, °C	$10^6 k_{12}$, s⁻¹			a_1,[a] M⁻¹	a_2[a]
	a	b	c		
61.4	10.66	11.9	10.6	9.21	3.31
67.0	26.26	27.5	23.7	10.2	3.03
71.9	65.81	56.2	47.1	11.1	0.95
77.2	124.3	119	96.6	11.7	1.70
85.3	321.7	358	279	8.87	1.65

[a] Obtained from applying eq 6. [b] Calculated values resulting from a least-squares activation analysis of the figures in the preceding column. [c] Values calculated from the activation parameters obtained in sodium hydroxide aqueous solutions.[2]

and the acid—base equilibrium for **2b** and its conjugated base **2c** (Q_2).

$$\text{Co(NH}_3)_3(\text{OH}_2)(\text{NO}_2)_2 + \text{NH}_3 \overset{Q_1}{\rightleftarrows} \text{Co(NH}_3)_3(\text{OH}_2)(\text{NO}_2)_2\cdots\text{NH}_3 \quad (4)$$

$$\qquad\qquad \textbf{2b} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{2a}$$

$$\text{Co(NH}_3)_3(\text{OH})(\text{NO}_2)_2 + \text{NH}_4 \overset{Q_2}{\rightleftarrows} \text{Co(NH}_3)_3(\text{OH}_2)(\text{NO}_2)_2 \quad (5)$$

$$\qquad \textbf{2c} \qquad\qquad\qquad\qquad\qquad \textbf{2b}$$

Compounds **2b** and **2c** will react further under loss of NO_2^- (rate constants k_{2b} and k_{2c}, respectively) and eventually form the mixture of hydroxopentaammine and A5N in the reaction with ammonia. This mechanism differs from the one proposed for A5N in the assumption of an appreciable concentration of the aquo complex **2b**, which seems reasonable in view of the decreased positive charge of the complex and inferences from literature comparison.[12] The finding of a first-order rate law for the hydrolysis means that we may apply a steady-state treatment, giving

$$k(\text{obsd}) = k_{13} + k_{12}[1 + a_2(\text{NH}_4)/(\text{NH}_3)]/[1 + a_1(\text{NH}_4) + a_2(\text{NH}_4)/(\text{NH}_3)] \quad (6)$$

where

$$a_1 = Q_1 Q_2 k_{21}/k_{2c} \quad (7)$$

$$a_2 = Q_2 k_{2b}/k_{2c} \quad (8)$$

Equation 6 was fitted to the rate constants of Table I with the help of a steepest descent routine using a least-squares criterion. Successively all parameter terms of eq 6 were tested for significance by using the criterion of the F (P = 0.99) test.[13] In this way the medium independent k_{13} term was found not to be significant. The same is true for terms describing base hydrolysis (for the sake of clearness not mentioned in eq 6). An important result of this analysis is that direct loss of NO_2^- (described by k_{13}) does not give any significant contribution to the overall rate constant. This means that in the hydrolysis of the cis-dinitrotetraamminecobalt(III) ion the first step in the spontaneous aquation is only loss of NH_3.

The values of the significant parameters of eq 6 are presented in Table II. The fitting error is generally better than 10%. Table I contains the comparison between observed and calculated (with the help of eq 6 and the parameter values of Table II) rate constants for one representative temperature. The temperature dependence of the values for the aquation parameter k_{12} has been fitted with a least-squares activation analysis. As discussed previously[1] the application of a many-parameter equation yields large values of the standard deviation of the parameters. Consequently it will be clear that also the activation parameters do show large values of the standard deviation (Table V). In Table II the value of the aquation parameter k_{12} obtained from the steepest descent routine is compared to the value of this rate parameter cal-

Table III. Observed Rate Constants for the Hydrolysis of trans-Dinitrotetraamminecobalt(III) (trans-A4N2), mer-Trinitrotriamminecobalt(III) (mer-A3N3), and trans-Tetranitrodiamminecobalt(III) (trans-A2N4) as a Function of the Medium, at a Constant Ionic Strength (I = 1.00 M)

(NH₃), M	(NH₄), M	$10^6 k$(obsd), s⁻¹		
		trans-A4N2 77.2 °C	mer-A3N3 47.7 °C	trans-A2N4 47.7 °C
0.16	0.10	470	54.6	160
0.32	0.10	463	54.9	161
0.63	0.10	480	55.9	157
1.26	0.10		55.9	150
0.25	0.16	462	62.6	171
0.50	0.16	463	62.7	169
1.00	0.16	481	61.7	163
2.00	0.16		60.3	151
0.40	0.25	472	62.6	178
0.79	0.25	478	61.8	172
1.59	0.25	492	59.4	160
3.17	0.25		56.1	140
0.63	0.40	484	66.6	180
1.26	0.40	497	64.5	170
2.52	0.40	509	60.7	155
5.04	0.40		51.3	118

culated from the activation parameters in Table V and the ones calculated from the activation parameters determined for sodium hydroxide solution (from 30 to 62 °C). Differences between the sets are within the experimental error. This is a final proof that the present results pertain to the first rate-determining hydrolysis step.

Photometric Study of the trans-Dinitrotetraamminecobalt(III) Ion. During the hydrolysis of trans-A4N2 the electronic spectrum initially showed isosbestic points that started to move when the reaction proceeded. This behavior can be ascribed to the appearance of the hydroxonitrotetraamminecobalt(III) as intermediate, because the reaction of this ion to A5N and the hydroxopentaammine is not so much faster than the reaction under study that this interference can be ruled out.[1] Therefore only the first part of the hydrolysis reaction was considered, resulting in a lesser accuracy of the rate constant. In spite of this the reaction still showed first-order behavior, also witnessed by the absence of a concentration dependence (varied between 3.9 × 10⁻⁴ and 2.0 × 10⁻³ M).

The absorbance of the reacting solutions was monitored at 22 750 cm⁻¹ (the absorbance maximum) and at 26 110 cm⁻¹ (the isosbestic point of A5N and $[\text{Co(NH}_3)_5(\text{OH})]^{2+}$). The first-order fits for the two wavelengths were equal within 10%; the most accurate data have been obtained at 26 110 cm⁻¹. The reaction has been studied at five temperatures (56.5–77.2 °C). The observed rate constants as a function of the buffer composition have been listed for one representative temperature (77.2 °C) in Table III. Although a slight dependence of the observed rate constants on the ammonia (NH₃) and ammonium perchlorate (NH₄) concentration is seen, the total difference between minimum and maximum k(obsd) is less than 10%. The same trend has been observed at all five temperatures; in all cases the difference between the minimum and maximum k(obsd) is about 10%. We may assume that these small medium effects (almost within the experimental error) are caused by deviations from real first-order behavior described above, that should be a function of the buffer composition.[1] The essential medium independence can be stated as the conclusion that addition of ammonia cannot reverse the reaction: the rate-determining step does not involve a splitting off of NH₃.

The averaged values of the observed rate constants (in this case equal to the rate parameter k_{aq} of the aquation) for the five temperatures have been collected in Table IV. To obtain

Table IV. Parameter Values Describing the Aquation of the *trans*-Dinitrotetraamminecobalt(III), the *mer*-Trinitrotriamminecobalt(III), and the *trans*-Tetranitrodiamminecobalt(III) Complexes as a Function of Temperature, at a Constant Ionic Strength ($I = 1.00$ M)

trans-A4N2				*mer*-A3N3				*trans*-A2N4			
Temp, °C	$10^6 k_{aq}$, s^{-1}			Temp, °C	$10^6 k_{aq}$, s^{-1}			Temp, °C	$10^6 k_{aq}$, s^{-1}		
	a	b	c		a	b	c		a	b	c
56.5	29.4 ± 1.1	29.9	27.9	42.7	27.3 ± 0.5	27.9	17.8	42.7	84.0 ± 3.7	83.4	93.6
61.4	57.9 ± 1.7	60.0	57.6	47.7	55.3 ± 0.7	56.2	36.7	47.7	160 ± 8	163	181
67.0	127 ± 6	130	128	53.0	120 ± 1	116	77.2	53.0	328 ± 14	324	354
71.9	248 ± 7	249	253	57.9		221	151	57.9	604 ± 28	600	648
77.2	479 ± 15	496	518	63.8	459 ± 6	469	328	63.8	1200 ± 130	1230	1310

[a] Obtained from averaging k(obsd). [b] Calculated values resulting from a least-squares activation analysis of the figures in the preceding column (Table V). [c] Calculated values from the activation parameters obtained in sodium hydroxide aqueous solutions[2] (Table V).

Table V. Activation Parameters for the Aquation of the Nitroamminecobalt(III) Complexes

Complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	Comment	Ref
cis-A4N2	139.2 ± 7	75.9 ± 20	Ammonia soln	This work
	133.6 ± 6	58.2 ± 18	NaOH	2
trans-A4N2	127.4 ± 1	54.1 ± 3	Ammonia soln	This work
	132.6 ± 4	69.3 ± 12	NaOH	2
mer-A3N3	115.7 ± 2	33.7 ± 7	Ammonia soln	This work
	119.6 ± 1	42.3 ± 3	NaOH	2
trans-A2N4	110.2 ± 1	25.4 ± 3	Ammonia soln	This work
	108.0 ± 3	19.4 ± 9	NaOH	2
	101	-4.6	Buffer	8

the values for the activation parameters the temperature dependence of this parameter has been subjected to a least-squares analysis. The activation parameters have been listed in Table V. In this table the values for the activation parameters obtained in sodium hydroxide aqueous solution[2] have also been listed and are seen to be compatible with the present values showing the validity of our approximation and the identity of the two reactions.

Photometric Study of *mer*-Trinitrotriamminecobalt(III). The absorbance of the reacting solution was monitored at 29 260 cm^{-1} (the absorbance maximum) for a complex concentration of 3.9×10^{-4} M. The wavelength and complex concentration independence was verified by comparing 23 000 cm^{-1} and a complex concentration of 4.0×10^{-3} M. The random differences were within 5%. During the hydrolysis reaction the only products observed are A5N and the hydroxopentaammine, no intermediates being detected. The reaction was studied at four temperatures (42.7–63.8 °C). The observed rate constants as a function of the buffer concentration for one representative temperature (47.7 °C) have been collected in Table III. This table shows the difference between maximum and minimum rate constant to be 25%. The changes in rate constant observed on varying (NH3) and (NH4) do not show a general trend and moreover are often opposed to the effects encountered for A5N[1] and *cis*-A4N2. The small variations in rate constant (small compared to the large medium variations) show a similar trend and must probably have the same causes as noted for *trans*-A4N2 (vide supra). If these conclusions are accepted, the present reaction will also involve as the rate-determining aquation step loss of NO2$^-$. The same pattern of (NH3) and (NH4) dependence has been found at 53.0 °C. At the other temperatures the reaction was performed at a single (NH4) = 0.10 M and varying (NH3) (0.16–1.29 M); the averaged value was used as the parameter value for the aquation (k_{aq}). The temperature dependence of the parameters formed the basis of a least-squares activation analysis. In Table V the activation parameters obtained in ammoniacal solution are compared to the activation parameters obtained in sodium hydroxide aqueous solution.[2] Table IV gives the corresponding comparison of calculated rate constants. Although relatively small, the differences are beyond the experimental error. These differences are un-

doubtedly due to the complicated mechanism of the reaction in ammoniacal solutions involving consecutive steps that cannot be completely approached as infinitely fast compared to the first step. In spite of this the two sets of figures in Tables IV and V certainly represent the same reaction.

Photometric Study of the *trans*-Tetranitrodiamminecobalt(III) Ion. The absorbance of the reacting solution was monitored at 28 650 cm^{-1} (the absorbance maximum) and the wavelength dependence was checked at 24 000 cm^{-1} (the same value for the rate constant has been observed in both cases). The complex concentration was varied from 4.0×10^{-4} to 4.0×10^{-3} M. No concentration dependence was found. The reaction was studied at five temperatures (42.7–63.8 °C). The observed rate constants for one temperature (47.7 °C) have been collected in Table III. The difference between maximum and minimum rate constant is 40%. Although the difference is larger than in the preceding case (*mer*-A3N3), the observed picture is the same and so will be the explanation. Indeed more interference from consecutive reactions may be feared as the reaction route to the end products A5N and hydroxopentaammine is longer. Again for one other temperature (57.9 °C) a similar picture has been obtained. The medium independence excludes the loss of NH3 in the rate-determining step of the aquation. For the other temperatures the value of the rate constant for the medium-independent aquation (k_{aq}) is the averaged value for the observed rate constant acquired at (NH4) = 0.10 and 0.16 M and varying (NH3) from 0.16 to 2.00 M. The values for the activation parameters have been listed in Table V and an excellent agreement with the values obtained in sodium hydroxide[2] is found. Also the values given by Zsako et al.[8] in buffered media are compatible. The comparison (Table IV) of the rate constants calculated from the activation parameters obtained in the different media employed shows an excellent agreement (deviation about 10%). This makes it certain that the same reaction has been studied in both media.

Direct Measurement of NH3 and NO2$^-$ Concentrations. For all complexes the increase of ammonia and nitrite concentrations during the hydrolysis in a neutral nonbuffered aqueous solution ($I = 0.10$ M (sodium perchlorate)) was monitored by gas-detecting electrodes. In these experiments the ratio (NO2$^-$)/(NH3) as a function of time is illustrative for the mechanism of the first step.

For *cis*-A4N2 reacting solutions immediately became cloudy with cobalt(III) hydroxide (72.6 °C) making the use of the electrode system impossible. For *trans*-A4N2 the reaction was followed at 65.4 °C, up to 10 800 s, when at last the solution became cloudy with cobalt hydroxide. For *mer*-A3N3 the solution was prepared at 49.3 °C and the reaction followed until the solution became cloudy at 18 000 s. Finally the solution of *trans*-A2N4 was prepared at 49.9 °C and the reaction followed up to turbidity at 15 000 s. In all cases (except the *cis*-A4N2, for which no results were obtained) the ratio (NO2$^-$)/(NH3) decreased in time, while the pH of the solutions increased. The results have been collected in Table

Table VI. Results Obtained with the Gas-Detecting Electrodes for the Determination of the Ammonia and the Nitrite Concentrations (in Units of 10^{-4} M) during Hydrolysis

Time, s	trans-A4N2 (65.4 °C)			mer-A3N3 (49.3 °C)			trans-A2N4 (49.9 °C)		
	(NH_3)	(NO_2^-)	$(NO_2^-)/$ (NH_3)	(NH_3)	(NO_2^-)	$(NO_2^-)/$ (NH_3)	(NH_3)	(NO_2^-)	$(NO_2^-)/$ (NH_3)
1 800	1.2	6.9	5.8	2.1	6.4	3.0	3.1	20	6.5
3 000							5.0	31	6.2
3 600	5.1	9.0	1.8	4.0	9.8	2.5			
6 000							10	43	4.3
7 200	19	20	1.1	8.5					
10 800	37	30	0.8	18	28	1.6	28	61	2.2
12 000							35	76	2.2
15 000				30	45	1.5			

VI. Both *trans*-A4N2 and *trans*-A2N4 show in the initial stage of the reaction a high ratio $(NO_2^-)/(NH_3)$ indicating that for the first step loss of NO_2^- dominates. This ratio rapidly decreases to the ratio expected for the total decomposition of the complex. The same conclusion is true for *mer*-A3N3, but for this complex loss of NH_3 could play a larger role in the initial stage.

Conclusion

The most striking result of the present study on the hydrolysis of nitroamminecobalt(III) complexes is that a duality of mechanism exists for the first aquation step. In this report and in the preceding parts of this series evidence has been presented to show that the aquation of A5N and *cis*-A4N2 starts with the loss of an ammine group, followed by a rapid degradation up to cobalt(III) hydroxide. On the other hand, for the complexes *trans*-A4N2, *mer*-A3N3, and *trans*-A2N4, the first aquation step is loss of NO_2^-, followed by a stepwise degradation. The latter fact enabled us to deduce confirmation for the mechanism developed from the kinetics in ammonia buffers, by monitoring the liberation of NO_2^- and NH_3 with the use of gas-detecting electrodes.

The existence of two mechanisms of aquation for this class of complexes is also displayed in the entropy pattern for the aquation reactions, deduced from experiments performed in sodium hydroxide aqueous solutions.[2] It can also be pointed out that another empirical fact noted is illustrative for the difference in mechanism: the group of complexes losing NH_3 in the first step (including the hexaammine) shows a rapid complete degradation up to cobalt(III) hydroxide, following the first step, whereas the other group shows an overlap of the first and the second step. The latter fact may be explained from the view developed above that these complexes (*trans*-A4N2, *mer*-A3N3, and *trans*-A2N4) lose NO_2^- in the first step, thus retaining their $Co(NH_3)_n$ "skeleton", whereas it is an empirical fact that cobalt(III) complexes become more reactive on substituting NH_3 by other ligands.[14,15] If a distinction of two aquation mechanisms for the class of nitroamminecobalt(III) complexes is accepted, we may ask for the factors responsible for the duality of mechanism. Inspection of the geometry of the complexes concerned makes it obvious that the mechanistic difference developed here can be explained from a kinetic trans effect exerted by the nitro group. The ions *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ and *trans*-$[Co(NH_3)_2(NO_2)_4]^-$, which have no NH_3 trans to an NO_2^- group, lose NO_2^- (trans to another NO_2^-) in the first aquation step, whereas $[Co(NH_3)_5(NO_2)]^{2+}$ only loses NH_3 in the trans NO_2^- position.[1] *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ has no opposite trans NO_2^- groups and also retains NO_2^- but splits off NH_3.

Then from a very simple model assuming equal trans-labilizing influences from each NO_2^- group, the *mer*-$[Co(NH_3)_3(NO_2)_3]$ compound will be expected to show a probability ratio for loss of NO_2^- vs. NH_3 of 2:1. Indeed for this complex we have found indications that loss of NO_2^- is prominent but loss of NH_3 in the first step is not excluded. Unfortunately the *fac*-$[Co(NH_3)_3(NO_2)_3]$ complex, which on

the basis of the proposed model will only contain labilized NH_3 groups, could not be prepared by us. There is no agreement in the literature whether the *fac* isomer has been prepared[16,17] or cannot be prepared by the published procedures.[18-20] Favoring our model are the reports that a proposed synthesis leading to *fac*-$[Co(NH_3)_3(NO_2)_3]$ yields a very unstable product.[17,20]

At present the possibility of giving a structural or electronic explanation of the phenomenon of trans labilization by the NO_2^- group must be rated rather low. A survey of the literature ascertains that comparison with other systems is difficult. This is undoubtedly due to the fact that trans influences for cobalt(III) complexes depend so much on the type of complex used,[21] which prohibits the development of a predictive theory.[21,22] Llewellyn et al.[23] have obtained some qualitative evidence from $^{15}NH_3$ exchange on nitroamminecobalt(III) complexes which is in the line of our observations. These authors have formulated the conclusion that two or more nitro ligands, substituted in a cobalt(III) ammine, appear to exert a kinetic labilization influence on trans NH_3 ligands. In line with this conclusion is the interpretation of the results of a ^1H NMR study on the rate of hydrogen–deuterium exchange of a number of cobalt(III)–ammine complexes.[24] The observed decelerating effect of the NO_2^- group on the trans hydrogens has been interpreted as partially due to a ground-state weakening of the trans (to NO_2^-) Co–N bonds.

On the other hand, Pratt and Thorp[25] could summarize the results of the normal-coordinate analysis of Nakagawa and Shimanouchi[26-28] in the conclusion that there are no great differences between NH_3 and NO_2^- in their cis and trans effects.[29] However it must be noted that here a ground-state effect is discussed, which can probably better be called a trans influence.[22] Nevertheless, surveying kinetic results, Pratt and Thorp could find no systematic difference between NH_3 and NO_2^- in labilizing power.[30]

In view of the ambiguity in the experimental results pertaining to the supposed trans-labilizing effect of the nitro group it seems to be premature to try to interpret our results in terms of an electronic theory.

Registry No. *cis*-A4N2, 15040-55-8; *trans*-A4N2, 58749-15-8; *mer*-A3N3, 20749-21-7; *trans*-A2N4, 22337-74-2.

Supplementary Material Available: A table containing the observed and calculated rate constants for the hydrolysis of the *cis*-dinitrotetraamminecobalt(III) ion as a function of the medium and the five temperatures (3 pages). Ordering information is given on any current masthead page.

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Methylation of Zinc(II), Cadmium(II), and Lead(II) by a *trans*-Dimethylcobalt Complex

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The methylation reactions of Zn^{2+}, Cd^{2+}, and Pb^{2+} by the *trans*-dimethylcobalt complex $(CH_3)_2Co(BDM1,3pn)$ in 2-propanol are discussed (BDM1,3pn is a mononegative tetradendate dioxime–diimine ligand formed by the condensation of 2 mol of 2,3-butanedione monoxime and 1,3-propanediamine). The products of the 1:1 reactions are $CH_3Co^{III}(BDM1,3pn)^+$ and unstable CH_3Zn^+, CH_3Cd^+, and CH_3Pb^+. Kinetic studies were carried out on the decomposition of the CH_3M^+ intermediates resulting in the relative rates $CH_3Zn^+ \gg CH_3Cd^+ \sim CH_3Pb^+$, with half-lives of 1.5, 52.6, and 60.1 h, respectively. A kinetic study of the demethylation of $(CH_3)_2Co(BDM1,3pn)$ by Zn^{2+} and Cd^{2+} revealed the presence of binuclear intermediates of the type $M^{2+}\cdot R_2Co(BDM1,3pn)$.

Introduction

The dealkylation reactions of organocobalt chelates of the type $RCo(chel)^{30}$ (R = CH_3, C_2H_5, n-C_3H_7, etc.) by the Hg(II) electrophile has been a subject of considerable interest in recent years. The Co–Hg transalkylation reactions of cobaloximes have been extensively investigated, and a wealth of kinetic and stereochemical data has been accumulated for this system.[1-9] More recently, the reactions of [RCo-(BDM1,3pn)H$_2$O]$^+$ [10,11] and of $CH_3Co(chel)$ (chel = tim, salen, and saloph)[12] with Hg(II) were studied in detail. These reactions invariably exhibit a 1:1 stoichiometry and result in the products shown in eq 1. The effect of the R group and

$$RCo(chel) + Hg^{2+} \rightarrow RHg^+ + Co^{III}(chel)^+ \qquad (1)$$
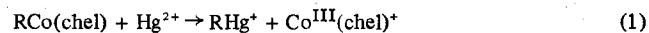
of the chelating ligand on the rates of these reactions support a bimolecular electrophilic substitution (SE2) mechanism.

Of principal interest to our work are the reactions of alkylcobalt complexes with metal ions other than Hg^{2+}. Perhaps the most interesting reactions studied in this respect are the reactions of methylcobalamin with Cr^{2+} [13] and Tl^{3+} [9] to yield CH_3Cr^{2+} and CH_3Tl^{2+}, respectively. Analogous reactions of alkylcobaloximes with Cr^{2+} [14] and Tl^{3+} [5] to yield RCr^{2+} and RTl^{2+} were reported. Other metal ions including Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, and In^{3+} were shown to be unreactive toward monoalkylcobalt chelates.[9,15]

We are presently engaged in a comprehensive study of the cobalt–carbon bond reactivity in a series of *trans*-dialkylcobalt chelates toward metal ions and metalloids. Complexes of this type $R_2Co(chel)$ (chel = BDM1,3pn, tim, cr) remain relatively unstudied presumably because of their high reactivity. The

Co–C bond of the $R_2Co(BDM1,3pn)$ complexes is readily cleaved by electrophiles such as ICl^{16} or $Co^{III}(chel)$.[17] In addition, these complexes are extremely unstable to light as exemplified by the photolytic reactions of $(CH_3)_2Co$-(BDM1,3pn) (structure I) in methanol, ethanol, and 2-propanol.[18]

In this paper we will discuss the dealkylation reactions of I by Zn^{2+}, Cd^{2+}, and Pb^{2+} in i-C_3H_7OH. These metal ions were previously shown to be unreactive toward a variety of organocobalt species.[9,15] This study involves the elucidation of some very surprising reactions in which I is unusually effective among methylcobalt complexes as a carbanion donor. In addition, our data support the formation of relatively stable organometallic products of the type CH_3M^+ which is entirely unexpected in view of the protic solvent employed.

I
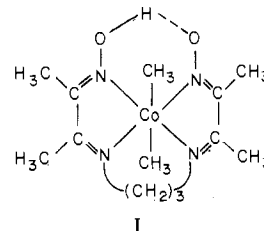
Results and Discussion

Stoichiometry and Products. In contrast to the reactions of the monoalkyl derivatives $RCo(chel)$ with Hg^{2+} which demonstrate a simple 1:1 stoichiometry (eq 1), the reactions of I with Zn^{2+}, Cd^{2+}, and Pb^{2+} are unique. The demethylation of I by all three metal ions can be obtained with two different