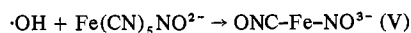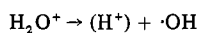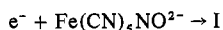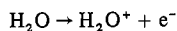on annealing species IV, we must conclude that this complex is unstable.

Radical Pairs. We have previously shown that a range of radical-pair "triplet-state" species are formed during room-temperature irradiation of $Na_2Fe(CN)_5NO\cdot2H_2O$.[9] We have searched for similar pair trapping during radiolysis of all of the new salts studied, but only in the case of the sodium hydrate have the characteristic features been obtained. We therefore tentatively postulate that these pairs arise as a consequence of initial damage to the hydrate water

$$H_2O \rightarrow H_2O^+ + e^-$$

$$e^- + Fe(CN)_5NO^{2-} \rightarrow I$$

$$H_2O^+ \rightarrow (H^+) + \cdot OH$$

$$\cdot OH + Fe(CN)_5NO^{2-} \rightarrow ONC\text{-}Fe\text{-}NO^{3-} \quad (V)$$

Species V would be expected to have properties very similar to those for I_{nonax}. Provided electron capture is efficient, this could lead to pair trapping of species I as observed.

The Ag(II) Center. Our results demonstrate that electron loss from Ag^+ competes favorably with loss from the nitrosylferrate ion. The spectra are clearly caused by d^9 Ag(II) centers having four strongly coupled nitrogen ligands. Just this situation was observed for metal(II) pentacyanonitrosylferrate salts doped with Cu^{2+} ions.[18] In both cases the unpaired electron occupies a b_{2g} level which is σ antibonding with respect to four isocyanide ligands in the $x-y$ plane and mainly $d_{x^2-y^2}$ on the metal.

The large value for $g_{\parallel}$ indicates strong coupling between the $d_{x^2-y^2}$ and d_{xy} orbitals on silver and is quite normal for Ag(II) complexes. The far smaller shift for $g_{\perp}$ is again quite normal and arises because of the larger separation between the $d_{x^2-y^2}$ and filled $d_{xz,yz}$ orbitals on silver. The factors controlling the g values and $A(^{109}Ag, ^{107}Ag)$ coupling constants are discussed in depth for the copper complexes.[18]

There is an appreciable increase in the $A_{\parallel}$ and $A_{\perp}$ (^{14}N) coupling constants relative to the Cu^{2+} complexes. These are compared in Table II. We stress that the "parallel" features for the silver A- and g-tensor components display the "perpendicular" coupling to ^{14}N. The "perpendicular" g and A features then display a nitrogen coupling equal to $[A_{\parallel}(^{14}N) + A_{\perp}(^{14}N)]/2$.[19] This increase corresponds to an increase in both 2s and 2p character on nitrogen, relative to the copper

complex. This can be understood in terms of the greater polarizability of silver. Thus, the σ-bonding level gains more silver character, and the σ^*-orbital gains more ligand character.

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Contribution from the Department of Inorganic Chemistry, Free University, De Lairessestraat 174, Amsterdam, The Netherlands

Competition between Ammonia and the Nitrite Ion as Leaving Groups in Cobalt(III) Complexes. I. Hydrolysis of the Nitropentaamminecobalt(III) Ion in Ammonia Buffers

S. BALT* and C. DEKKER

Kinetic measurements are reported on the base hydrolysis and the spontaneous aquation of the nitropentaamminecobalt(III) cation in weakly alkaline ammoniacal solutions, at a constant ionic strength. The results are at variance with the generally accepted picture of the inert $Co^{III}(NH_3)_n$ frame. On the basis of kinetic evidence for the occurrence of the *trans*-hydroxonitrotetraamminecobalt(III) ion as an intermediate in the aquation of nitropentaammine, a novel mechanism is presented for the hydrolysis reaction: in the aquation the first step is loss of the trans NH_3 group, whereas in base hydrolysis NO_2^- is the first group to leave. Numerical values of activation parameters agree with published results.

Introduction

The hydrolysis of the nitropentaamminecobalt(III) ion has been widely investigated. Roughly there are three independent reaction paths: base hydrolysis, acid-catalyzed hydrolysis, and a spontaneous reaction of the complex. Of these, especially the acid-catalyzed reaction has been thoroughly studied.[1-4]

Much less is known about the base hydrolysis reaction of the complex.[5,6] The mechanism of the spontaneous reaction seems to present some difficulties. There are indications[2] that a direct aquation is not involved.

An additional disturbing aspect appears to be that extrapolation of hydrolysis rates measured in acid solutions under

different circumstances gives different rates for the spontaneous reaction.[1-3] To avoid these difficulties we have studied the hydrolysis of the nitropentaamminecobalt(III) ion in weakly alkaline solutions. To do this we have used ammonia–ammonium perchlorate buffers, for the following reason. If activation parameters for the hydrolysis reactions of the hexaammine[7,8] and the nitropentaamminecobalt(III) ions are compared (brought together in the last table of this paper), it will become clear that the values reported are of comparable magnitude. This may mean that the first step in the hydrolysis of both complexes is the same: loss of ammonia. In fact this assumption explains the absence of either the aquo- or the acetatopentaammine complex as a reaction product in the hydrolysis of the nitropentaamminecobalt(III) acetate studied by Banerjea.[2]

We have investigated the assumed mechanism of primary loss of ammonia in the hydrolysis of the nitropentaammine complex by studying this reaction in ammonia-containing solutions, as this medium can prevent degradation of the complex, making it possible to separate this reaction path from other reactions.[9,10]

Experimental Part

Chemicals. [Co(NH₃)₅(NO₂)](ClO₄)₂ was prepared by recrystallization of the nitrate salt[11] from sodium perchlorate–perchloric acid solutions, followed by a final recrystallization from water. The absence of impurities was checked by uv and ir spectroscopy.

trans-[Co(NH₃)₄(NO₂)(H₂O)](ClO₄)₂. Preparation of the perchlorate from the nitrate according to Poon[12] was abandoned in view of the low yield, resulting from the high solubility of the perchlorate in water. Better yields were obtained by grinding together in a mortar [Co(NH₃)₄(NO₂)(Cl)]Cl (5.4 g, 22.1 mmol) and AgClO₄·H₂O (10.0 g, 44.4 mmol) in 15 ml of acidified water for 10 min. The mixture was then filtered by suction and the cooled filtrate was saturated with solid sodium perchlorate. The orange-brown crystals of *trans*-[Co(NH₃)₄(NO₂)(H₂O)](ClO₄)₂ which separated out were filtered off and washed several times with small amounts of cold ethanol and ether. The product was dried at 50 °C (yield 3.2 g, 37%). The generally assumed trans structure of the complex has recently been confirmed by us, using ¹H NMR spectroscopy.[13] Anal. Calcd for [Co(NH₃)₄(NO₂)(H₂O)](ClO₄)₂: Co, 15.1; NH₃, 17.5; NO₂, 11.8; ClO₄, 51.0. Found: Co, 14.8; NH₃, 17.0; NO₂, 10.7; ClO₄, 50.0. The low values found may be due to water, retained in the crystals. The other chemicals used were of reagent grade.

Kinetics. All solutions were made up at room temperature from ammonia–ammonium perchlorate buffers. The concentrations were corrected for the differences between room and cell temperatures. The ionic strength (1.00 M) was fixed by adding sodium perchlorate. The usual precautions were taken to exclude carbon dioxide.[10]

The reactions were monitored spectrophotometrically on a Beckman Acta C III spectrophotometer, equipped with a timer device to measure the absorptions at different wavelengths at fixed time intervals. To examine the influence of the light beam from the spectrophotometer passing through the solution on the rate of the reaction, solutions of the complexes kept continuously in the light beam of the spectrophotometer were compared with identical solutions kept in the dark. The extent of the reaction was the same in the two types of solution at all times. We used a closed cell (optical path length 10 mm), specially designed to resist the buildup of pressure resulting from warming the solutions to the high temperature necessary to attain a measurable reaction rate. The kinetic runs were started by quickly raising the temperature of the cell. Temperature constancy (±0.20 °C) was attained by circulating thermostated water around the optical cell. The temperature was measured with the internal Pt resistor of the spectrophotometer, calibrated with an iron–constantan thermocouple and a Leeds and Northrup millivolt potentiometer. In the case of the nitropentaamminecobalt(III) complex the optical density of the solution was recorded at 29200 and 31500 cm⁻¹, 31500 cm⁻¹ giving the maximum difference between the extinction coefficients of the nitropentaammine and the hydroxonitrotetraamminecobalt(III) complexes. No wavelength dependence was observed. On varying the complex concentration from 4 × 10⁻⁴ to 10 × 10⁻⁴ M, no concentration dependence was found. The reaction was followed up to 4 half-lives. In all cases the absorbance as a function of time obeyed

a first-order rate law. The (pseudo-) first-order rate constant k(obsd) was obtained from a computer fit as described below. For the analysis of the medium dependence we have used the value averaged over the two wavelengths. In the case of the hydroxonitrotetraamminecobalt(III) ion the reaction was monitored at two wavelengths: (a) 35500 cm⁻¹, where $\epsilon\{[Co(NH_3)_4(NO_2)(OH)]^+\} > \epsilon\{[Co(NH_3)_5(NO_2)]^{2+}\} > \epsilon\{[Co(NH_3)_5(OH)]^{2+}\}$, to guarantee an appreciable change of absorbance; complex concentration 5 × 10⁻⁴ M; (b) 26110 cm⁻¹, the isosbestic point of [Co(NH₃)₅(NO₂)]²⁺ and [Co(NH₃)₅OH]²⁺, where a complex concentration of 5 × 10⁻³ M was employed. At this concentration the absorbance of the solution after reaction was also measured at 21000, 21500, 22000, 22500, and 23000 cm⁻¹. From the values obtained, the relative amounts of nitropentaammine and hydroxopentaammine as reaction products have been calculated. The absorbance as a function of time obeyed a first-order rate law, when following the reaction up to 3 half-lives. At longer reaction times the reaction of nitropentaammine to hydroxopentaammine interfered. Neither wavelength nor concentration dependence was observed, so for k(obsd) the mean of the two rate constants has been used.

pH Measurements. As a consequence of using ammonia buffers the pH dependence of our rate constants is expressed in the ratio (NH₄⁺)/(NH₃). To compare the present results with other experiments using sodium hydroxide, it is necessary to convert values of (NH₄⁺)/(NH₃) into concentrations of sodium hydroxide. To do this the pH of a number of ammoniacal solutions was measured at four temperatures (56.1, 64.8, 71.3, 77.5 °C), using an Electrofact 36200 pH meter with an Electrofact 7G111 glass electrode and a calomel Hg–HgCl₂–KCl reference electrode, connected to the solution by a sodium nitrate bridge.

The pH of the ammonical solutions (I = 1.00 M) was reproduced by adding NaOH to a 1.00 M solution of NaClO₄, giving the desired correlation, expressed in the dissociation constant K

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

Within the experimental error no temperature dependence of the dissociation constant has been observed. The average dissociation constant was found to be $K = 6.52 \times 10^{-5}$ M.

Calculations

The absorbance of the reacting solutions was analyzed with the help of a computer program (LSKIN1 from DeTar[14]) using the formula

$$\ln [(A_\infty - A_t)/(A_\infty - A_0)] = -k(\text{obsd})t \tag{2}$$

in an iterative fit for the parameters A_0, A_∞ (absorbances at zero and hundred percent reaction), and k(obsd) (the observed rate constant).

The rate constants have been fitted to equations expressing the medium dependence, with the help of programs from the "IBM Scientific Subroutine Package" and by a steepest descent computer program.[10]

The activation parameters $\Delta S^\ddagger$ ((pseudo) entropy of activation) and $\Delta H^\ddagger$ ((pseudo) enthalpy of activation) have been obtained from the temperature dependence of the rate constants, using a computerized least-squares analysis,[15] on the basis of the Eyring formula.[16]

All calculations were performed in the SARA computer center in Amsterdam.

Results

In alkaline medium the hydrolysis (whether spontaneous or base catalyzed) of the nitropentaamminecobalt(III) ion (compound I) may take two different routes, involving as first steps (a) loss of the nitro group to give the hydroxopentaamminecobalt(III) ion (compound III) or (b) loss of a coordinated ammonia to give the (*cis*- and/or *trans*-) hydroxonitrotetraamminecobalt(III) ion (compound II).

Under alkaline conditions the reaction generally does not stop at the first step but proceeds further (at increasing rates) down to cobalt(III) hydroxide.[7,17] However, the reaction may be stopped at the hydroxopentaammine (III), if the buffer
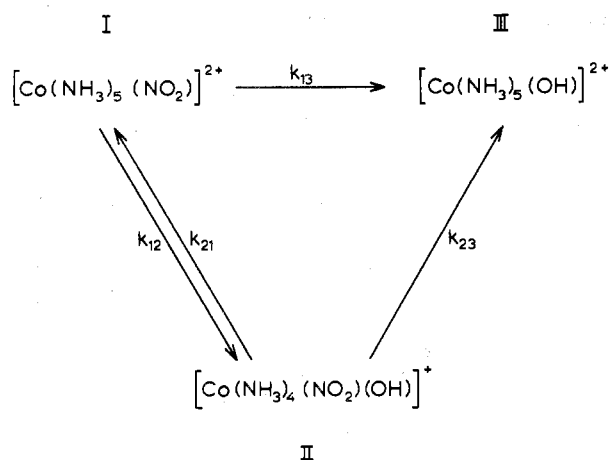
Figure 1. Reaction scheme for the nitropentaamminecobalt(III) ion in ammoniacal solutions.

system ammonia–ammonium perchlorate is used at the right concentrations. We were able to select conditions at which the nitropentaammine (I) showed a first-order reaction with the hydroxopentaammine as end product; at the same time the supposed intermediate hydroxonitrotetraammine (II) (prepared in the trans form, but see also below) showed a much faster (2 orders) reaction to form a mixture of I and III. We may then formulate the reaction scheme in Figure 1 (for the present leaving open the geometry of complex II).

We have verified spectrophotometrically that under the circumstances employed in this study, no aquo complexes are present besides the hydroxo complexes. We have studied independently the reactions of both nitropentaammine and *trans*-hydroxonitrotetraamminecobalt(III) in the medium mentioned, in order to obtain unequivocal evidence for the importance of loss of ammonia in the hydrolysis of the nitropentaammine.

The results obtained for the *trans*-hydroxonitrotetraamminecobalt(III) ion will be described first, followed by those for the nitropentaamminecobalt(III) ion.

Kinetic Studies of the *trans*-Hydroxonitrotetraamminecobalt(III) Ion. The reactions have been studied at four temperatures (58–76 °C). The kinetic results obtained for one representative temperature are listed in Table I. As already stated the primary reaction products on dissolving this complex in aqueous ammonia at elevated temperatures are nitropentaammine (I) and hydroxopentaammine (III), whereafter the nitropentaammine undergoes a much slower hydrolysis to the hydroxopentaammine (III). The presence of isosbestic points in the absorbance spectrum during the first stage of the reaction and the fact that the spectrum could be reproduced by assuming the presence of only the starting product and the two reaction products I and III were taken as proof that no prior cis–trans rearrangement of the tetraammine (II) occurred.

Referring to the reaction scheme given above, we now have

$$k(\text{obsd}) = k_{21} + k_{23} \tag{3}$$

Further the ratio of the two constants follows from product analysis of the reaction. We define

$$\alpha = \frac{(\text{III})}{(\text{I}) + (\text{III})} = \frac{k_{23}}{k_{21} + k_{23}} \tag{4}$$

where (I) and (III) stand for the concentrations of nitropentaammine and hydroxopentaammine.

The value of α was determined spectrophotometrically after 3 or more half-lives of the reaction, applying a correction for

Table I. Observed and Calculated Constants for the Reaction of the *trans*-Hydroxonitrotetraamminecobalt(III) Ion, as a Function of the Medium, at 70.8 °C and at a Constant Ionic Strength (1.00 M)

(NH$_3$), M	(NH$_4$), M	α	$10^6 k$-(obsd), s^{-1}	$10^6 k$(calcd), s^{-1}	
				a	*b*
0.64	0.10	0.62	266	276	270
1.02	0.10	0.62	272	280	275
1.62	0.10	0.62	289	286	284
2.57	0.10	0.61	305	296	298
0.64	0.16	0.50	318	331	323
1.02	0.16	0.50	333	337	332
1.62	0.16	0.51	353	347	346
2.57	0.16	0.50	371	362	369
0.64	0.25	0.41	396	412	403
1.02	0.25	0.41	414	422	417
1.62	0.25	0.41	444	438	440
2.57	0.25	0.40	471	462	475
0.64	0.40	0.31	538	549	537
1.02	0.40	0.30	567	564	560
1.62	0.40	0.31	601	589	595
2.57	0.40	0.30	646	628	652

a Obtained by applying eq 3, 5, and 6 and the parameter values in Table II. *b* Obtained by applying eq 7 and the parameter values in Table II.

incompleteness of the reaction. Then k_{21} and k_{23} were calculated from eq 4 and k(obsd). The ensuing value of k_{23} was found to be independent of the medium. This constant value will be denoted as k^0_{23}. It will be clear that

$$k_{23} = k^0_{23} = \overline{\alpha k(\text{obsd})} \tag{5}$$

in which $\overline{\alpha k(\text{obsd})}$ is the averaged value over the product $\alpha k(\text{obsd})$. The calculated value of k_{21} was found to be dependent on the concentrations of both ammonia (NH$_3$) and ammonium ion (NH$_4$). It appeared that the concentration dependence of k_{21} could be described by

$$k_{21} = k^0_{21} + k^1_{21}(\text{NH}_4) + k^2_{21}(\text{NH}_3)(\text{NH}_4) \tag{6}$$

A least-squares fit (better than 4%) of the values of the rate constant k_{21} to eq 6 proved the contribution of the first and third term to be small compared to that of the second term $k^1_{21}(\text{NH}_4)$. The parameter values as a function of temperature are listed in Table II. The average standard deviation of the parameter k^0_{23} is 1.5%, of k^0_{21} is 30%, of k^1_{21} is 1.5%, and of k^2_{21} is 6%. Table I gives a final comparison between observed and calculated (using the parameter values of Table II) rate constants.

Alternatively, without using the spectrophotometrically determined ratio α, we may write the complete $k(\text{obsd})$ as (neglecting the small contribution of k^0_{21})

$$k(\text{obsd}) = k^0_{23} + k^1_{21}(\text{NH}_4) + k^2_{21}(\text{NH}_3)(\text{NH}_4) \tag{7}$$

A least-squares fit of the observed rate constants to eq 7 resulted in the parameter values given in Table II. The fit achieved was better than 2%. The average deviation of the parameter k^0_{23} is 4%, of k^1_{21} is 3%, and of k^2_{21} is 7.5%. Again the agreement between observed and calculated values for the rate constants is good (Table I).

As Table II shows, there is indeed excellent agreement between the two sets of rate parameters. Finally we have applied a least-squares activaton analysis to the parameter values (cf. eq 7) in Table II. The activation plots did not show curvature, as a comparison between input and calculated values in Table II will show. (The values of the activation parameters are collected in Table V.)

Table II. Rate Parameters Describing the Medium Dependence of the Rate Constants of the Reactions of the *trans*-Hydroxonitrotetraamminecobalt(III) Ion in Ammoniacal Solutions at Constant Ionic Strength (1.00 M)
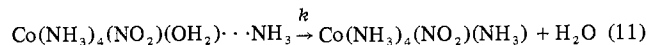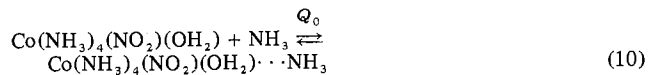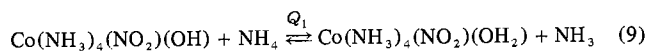
Temp, °C	$10^6 k^0_{23}$, s^{-1}			$10^6 k^0_{21}$, s^{-1}	$10^6 k^1_{21}$, M^{-1} s^{-1}			$10^6 k^2_{21}$, M^{-2} s^{-1}		
	Eq 5[a]	Eq 7[a]	Activ anal.[b]	Eq 6[a]	Eq 6[a]	Eq 7[a]	Activ anal.[b]	Eq 6[a]	Eq 7[a]	Activ anal.[b]
58.6	34.68	37.55	34.2	4.07	188.7	178.0	186	32.13	43.18	43.0
64.8	81.35	82.28	84.8	9.53	375.3	388.8	388	55.43	72.00	80.7
70.8	175.5	180.5	198	9.72	842.7	796.7	770	103.0	148.2	145
76.0	371.5	417.8	402	69.2	1303	1318	1369	168.2	226.3	238
62.9[c]			64.4				310			66.7
69.2[c]			158				642			124
75.3[c]			366				1268			223
80.0[c]			686				2108			345

[a] Obtained by applying the equation indicated. [b] Calculated values resulting from a least-squares activation analysis of the figures in the preceding column (Table V). [c] Temperatures used for the study of the nitropentaamminecobalt(III) ion.

The rate equations (6) and (7) refer to a rate proportional to the concentration of the ammonium ion. This cannot in itself have direct mechanistic significance, so we have rewritten eq 6 as (with $k^0_{21} = 0$)

$$k_{21} = (NH_4)(NH_3)^{-1}[k^1_{21}(NH_3) + k^2_{21}(NH_3)^2] \qquad (8)$$

This medium dependence is consistent with a reaction sequence according to a dissociative interchange mechanism (omitting charges)

$$Co(NH_3)_4(NO_2)(OH) + NH_4 \overset{Q_1}{\rightleftharpoons} Co(NH_3)_4(NO_2)(OH_2) + NH_3 \quad (9)$$

$$Co(NH_3)_4(NO_2)(OH_2) + NH_3 \overset{Q_0}{\rightleftharpoons}$$
$$Co(NH_3)_4(NO_2)(OH_2)\cdots NH_3 \qquad (10)$$

$$Co(NH_3)_4(NO_2)(OH_2)\cdots NH_3 \overset{k}{\to} Co(NH_3)_4(NO_2)(NH_3) + H_2O \quad (11)$$

If we put

$$k^1_{21} = Q_1 Q_0 k \qquad (12)$$

This explains the first term of eq 8. The second term containing $(NH_3)^2$ represents a small part of the reaction rate and has been proved[18] for a similar case to be a consequence of the change of dielectric constant of the solvent caused by substituting ammonia for water.

The assumption implicit in reactions 9–11 that the aquo complex is more reactive to ammonia substitution than the hydroxo complex is a general feature of aquoammine complexes.[9,10,19]

The fact that we have found one principal reaction route for the uptake of ammonia by the hydroxonitrotetra-amminecobalt(III) ion means that the reverse reaction (rate constant k_{12}) will also take one main route, the spontaneous loss of ammonia.[20,21] We shall use this result in the next section.

Kinetic Studies of the Nitropentaamminecobalt(III) Ion. The reaction has been studied at four temperatures (60–80 °C). The kinetic results for one representative temperature are listed in Table III. The absence of appreciable amounts of the hydroxonitrotetraamminecobalt(III) ion (compound II) in the hydrolysis reaction mixture of the nitropentaammine means that we may apply a steady-state treatment to the reaction scheme of Figure 1. From this

$$k(obsd) = k_{13} + \alpha k_{12} \qquad (13)$$

(with α defined as in eq 4) assuming that no *cis*-hydroxo-nitrotetraammine is formed in the reaction. We shall come back to this assumption later. Further we have seen from the tetraammine reaction results that k_{12} will be medium independent ($k_{12} = k^0_{12}$). We may expect k_{13} to contain con-

Table III. Observed and Calculated Rate Constants for the Hydrolysis of the Nitropentaamminecobalt(III) Ion as a Function of the Medium, at 75.3 °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), s^{-1}	
			a	b
0.63	0.10	15.0	14.8	14.8
1.26	0.10	17.7	17.5	17.4
1.89	0.10	19.8	20.2	20.0
2.53	0.10	22.8	22.9	22.6
0.63	0.13	13.1	13.3	13.2
1.26	0.13	15.2	15.3	15.2
1.89	0.13	16.7	17.2	17.1
2.53	0.13	19.2	19.2	19.2
0.63	0.20	10.6	10.9	10.7
1.26	0.20	12.0	12.0	12.0
1.89	0.20	12.9	13.1	13.2
2.53	0.20	14.7	14.3	14.6
0.63	0.40	6.86	7.49	7.03
1.26	0.40	7.92	7.88	7.68
1.89	0.40	8.31	8.28	8.32
2.53	0.40	9.05	8.74	8.98

[a] Obtained by applying eq 15 and the parameter values in Tables II and IV. [b] Obtained by applying eq 17 and the parameter values in Tables II and IV.

tributions from spontaneous hydrolysis and from base hydrolysis

$$k_{13} = k^0_{13} + k^1_{13}(NH_3)(NH_4)^{-1} \qquad (14)$$

Equation 13 can then be written as

$$k(obsd) = k^0_{13} + k^1_{13}(NH_3)(NH_4)^{-1} + k^0_{12}\alpha \qquad (15)$$

Equation 15 expresses k(obsd) for the hydrolysis of the nitropentaammine as a function of the buffer medium and the ratio α, calculated from eq 4 and 6 using the parameter values in Table II. Application of a least-squares fitting procedure of the rate constants of Table III to eq 15 resulted in the parameter values of Table IV. Table III gives a comparison between the observed rate constants and the ones calculated from the least-squares parameters.

An important result of this analysis is that the parameter k^0_{13} represents only a negligible fraction of the observed rate and moreover is zero within the experimental error. This may be reformulated as the important result that in the hydrolysis of the nitropentaamminecobalt(III) ion the first step of the spontaneous reaction is loss of NH$_3$ whereas loss of NO$_2^-$ is only relevant for the base-catalyzed reaction. To test the assumptions inherent in the treatment of the rate constants given above, we have applied a general fitting procedure to the observed rate constants of Table III, without introducing numerical results from the analysis of the kinetics of the

Table IV. Rate Parameters Describing the Medium Dependence of the Hydrolysis Rate Constants of the Reactions of the Nitropentaamminecobalt(III) Ion in Ammoniacal Solutions at Constant Ionic Strength (1.00 M)

Temp, °C	$10^6 k^0_{13}$, s^{-1} Eq 15[a]	$10^6 k^1_{13}$, s^{-1} Eq 16, 17[a]	Eq 15[a]	Activ anal.[b]	$10^6 k^0_{12}$, s^{-1} Eq 16, 17[a]	Eq 15[a]	Activ anal.[b]	$k^1_{21} k^0_{23}{}^{-1}$, M^{-1} Eq 16, 17[a]
62.9	0.18 ± 0.25	0.050	0.062 ± 0.003	0.063	3.13	2.70 ± 0.17	2.61	5.74
69.2	0.38 ± 1.07	0.165	0.187 ± 0.013	0.182	5.99	5.35 ± 0.75	6.51	4.41
75.3	0.6 ± 1.0	0.410	0.473 ± 0.013	0.493	17.6	15.6 ± 0.7	15.3	4.39
80.0	3.3 ± 3.9	0.917	1.02 ± 0.05	1.035	34.0	28.7 ± 2.7	28.8	3.35

[a] Obtained by applying the equation indicated. [b] Calculated values resulting from a least-squares activation analysis of the figures in the preceding column (Table V).

trans-hydroxonitrotetraamminecobalt(III) ion. In this case eq 15, after writing the medium dependence of $\alpha = k_{23}/(k_{21} + k_{23})$ by using eq 5 and 6 (with $k^0_{21} = 0$), becomes

$$k(\text{obsd}) = k^0_{13} + k^1_{13}(\text{NH}_3)(\text{NH}_4)^{-1} +$$
$$k^0_{12}k^0_{23}[k^0_{23} + k^1_{21}(\text{NH}_4) + k^2_{21}(\text{NH}_3)(\text{NH}_4)]^{-1} \quad (16)$$

The rate constants of Table III have been fitted to eq 16 with the help of a steepest descent routine using a least-squares criterion. Successively all parameter terms of eq 16 have been tested for significance by using the criterion of the F ($P = 0.99$) test.[22]

In this way only a part of eq 16 has been retained

$$k(\text{obsd}) = k^1_{13}(\text{NH}_3)(\text{NH}_4)^{-1} +$$
$$k^0_{12}k^0_{23}[k^0_{23} + k^1_{21}(\text{NH}_4)]^{-1} \quad (17)$$

Table III contains a typical comparison between observed and calculated (with the help of eq 17) rate constants for one temperature. The values of the final set of significant parameters for each temperature are listed in Table IV. The procedure leading to eq 17 yields larger values of the standard deviations of the parameters, but the results agree well with the more direct application of eq 15. As a consequence of the smaller accuracy inherent in using the extended equation, the medium correction term containing k^2_{21} is not significant in this analysis.

The agreement between both modes of analysis proves that the hydroxonitrotetraammine complex in the trans configuration occurs as an intermediate in the hydrolysis of the nitropentaamminecobalt(III) ion. The significant parameter values obtained by the least-squares procedure (eq 15), with their standard errors listed in Table IV, were used for a least-squares activation analysis. As a comparison between the input and calculated values in Table IV shows, no curvature was found in the activation plot. The values of the activation parameters are collected in Table V.

For a more general discussion of activation parameters the rate constant for base hydrolysis k^1_{13} has been converted to an equivalent sodium hydroxide concentration before applying the activation analysis.

Discussion

A most important and, in view of the literature, rather unexpected result of the present study is that the first step in the aquation of the nitropentaamminecobalt(III) ion is loss of ammonia to form the *trans*-nitroaquotetraamminecobalt-(III) ion. It appears that in the nitropentaammine at least one of the coordinated ammine ligands leaves the complex more readily than the nitro group. The reason may be that the leaving ammine is labilized by the trans NO_2^- group. At the moment we are investigating this labilization more extensively by studying other nitroamminecobalt(III) complexes.

On the contrary, base hydrolysis of the nitropentaammine takes the conventional route via loss of the nitro group. It must be emphasized that the mechanism of loss of ammonia could only be detected by our kinetic method, using ammonia buffers.

Table V. Activation Parameters for the Different Rate Parameters

Reaction	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	Comment	Ref
		[Co(NH$_3$)$_5$(NO$_2$)]$^{2+}$		
Base hydr ($k^1_{13}K^{-1}$)	158.7 ± 2	168.6 ± 6	Ammonia soln	This work
Base hydr	156	177	$I = 0$ M (extrap) (NaOH)	5
Base hydr	153 ± 1	149 ± 4	$I = 1.00$ M (NaOH)	6
Aquation (k^0_{12})	135.7 ± 6	51.0 ± 18	Ammonia soln	This work
Aquation	124	19	$I = 0.12$ M (HClO$_4$)	1
Redox	131	27	$I = 1.00$ M (acetic acid)	2
		trans-[Co(NH$_3$)$_4$(NO$_2$)(OH)]$^+$		
k^0_{23}	133.6 ± 8	71.4 ± 24	Ammonia soln	This work
k^1_{21}	107.7 ± 4	7.4 ± 12	Ammonia soln	This work
k^2_{21}	91.9 ± 5	−52.4 ± 16	Ammonia soln	This work
		[Co(NH$_3$)$_6$]$^{3+}$		
Aquation	153	45	$I = 0.16$ M (HClO$_4$)	7
Base hydr	144	114	NaOH, 1.4 M	8

It is therefore understandable that other authors have not mentioned this mechanism. On the other hand our values for rate and activation parameters, apart from their mechanistic interpretation, should not differ significantly from the ones previously reported (Table V). In the following paragraphs we will discuss previous work on the basis of our mechanism.

A. When we compare the activation parameters of base hydrolysis of the nitropentaamminecobalt(III) ion reported by Lalor and Lang[5] with our values for concentrated sodium hydroxide[6] or the present ones for ammoniacal solutions, an excellent agreement for the activation enthalpy is observed. The values of the activation entropy differ slightly, which is acceptable in view of the different composition of the media employed.

B. Lalor also studied the aquation of the nitropenta-amminecobalt(III) ion in dilute perchloric acid.[1] He did not investigate the reaction product but assumed a complete conversion to aquopentaamminecobalt(III). His rate constants and activation parameters are also compatible with our results.

C. Further the results obtained by Banerjea[2] in weakly acidic media and our results in ammoniacal solutions should agree. Banerjea studied the decomposition of nitropenta-ammine in acetic acid–acetate buffers. He found a transformation to cobalt(II) species, without any apparent formation as intermediates of the expected acetato- or aquo-pentaamminecobalt(III) that would be formed after prior loss of NO$_2^-$. His conclusion is that the reaction takes place by an intramolecular electron transfer from the bound NO$_2^-$ to the Co^{3+} in the complex. The activation parameters found for this reaction (Table V) agree very well with the values for our k^0_{12}, the aquation in ammoniacal solutions, when the activation enthalpy is considered. Again the difference be-

tween the values of the activation entropy may be regarded to stem from the different composition of the media employed. It is evident that primary loss of ammonia, followed by the predicted spontaneous redox reaction[23] of the nitroaquotetraammine complex, can also explain Banerjea's results.

Banerjea also studied the reaction in nitric acid media. In this solution he found a much larger acid-independent rate. We do not agree with Banerjea, who called this reaction an aquation, as this would imply that the same reaction could have two widely differing rates. It is not contradictory to describe this reaction as part of an acid-catalyzed reaction in a saturation region. In this connection it is important to note that also Jolly and co-workers[3] found a constant rate in acid solutions, up to 55 wt % H_2SO_4, this rate being an order of magnitude larger than the rate in neutral solutions.

The final conclusion is then that our detailed analysis of the medium dependence in which all assumptions have been tested and the comparison with previously reported results together give a firm support to the postulated mechanism.

In order to get more detailed information on this mechanism, we are now extending our study to other nitroamminecobalt(III) complexes.

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Contribution from the Christopher Ingold Laboratories,
University College, London WC1H OAJ, England

Resonance Raman Spectra of the Mixed-Valence Compounds Pd2(NH3)4Cl6 and PdPt(NH3)4Cl6

ROBIN J. H. CLARK* and WILLIAM R. TRUMBLE

Resonance Raman spectra have been observed for the two mixed-valence compounds PdPt(NH3)4Cl6 and Pd2(NH3)4Cl6, using a variety of exciting lines. For the former compound resonance progressions involving the three Raman-active metal–chlorine stretching vibrations are observed, compatible with the assignment of the resonant electronic transition to a metal–metal mixed-valence transition. For the latter, the spectra are found to depend markedly on the exciting line used and they indicate the presence of two allowed transitions in the visible region. The spectra differ from those of PdPt(NH3)4Cl6; they exhibit overtones and combination tones involving several stretching and bending fundamentals of the Pd(IV) constituent complex. For Pd2(NH3)4Cl6, the resonance effects are attributed to excitation within ligand → Pd(IV) charge-transfer bands. The analogous mixed-valence transition is inferred to lie in the infrared region, contrary to a previous report. Far-infrared spectra of the compounds are also reported.

Introduction

Compounds containing atoms of the same metallic element in more than one oxidation state have been broadly classified by Robin and Day.[1] They proposed essentially three categories of mixed-valence compounds, depending on the degree of electronic interaction between the valence sites. In class I compounds the valences are firmly "trapped" at markedly different coordination sites, with no significant electronic interaction between them. At the other extreme, in class III compounds, valence delocalization is essentially complete and no distinction can be made between valence sites. Class II compounds comprise those materials with intermediate properties. Valences remain quite firmly trapped and the sites distinguishable, but there is sufficient overlap between orbitals on adjacent metal atoms to permit electron transfer between

the two sites. Such materials typically exhibit intense, broad absorption in the visible region due to intervalence charge-transfer transitions.

The resonance Raman (RR) spectra of many simple compounds[2] and biological materials[3] possessing electronic transitions in the visible region have been extensively studied. Mixed-valence compounds so far have not, despite the fact that in several respects those of class II are potentially extremely interesting candidates for investigation by this technique. Our earlier report[4] indicated that such compounds (specifically mixed-valence antimony compounds) may display striking RR effects.

While the theoretical study of the RR effect is currently in a state of active development, most treatments agree that, at least qualitatively, the resonance enhancement of modes in