measurement for $[Co(NH_3)_5CN]^{2+}$ is consistent with that reported by Espenson and Birk[16] at 15°. Their value of 61 ± 6 M^{-1} sec^{-1} in combination with ours leads to $\Delta H^* \approx 9$ kcal mole^{-1} and $\Delta S^* \approx -30$ eu.

It is clear that acetonitrile, acrylonitrile, and pyridine as heteroligands lead to much lower rates of reduction than does a typical carboxylate, such as acetate. The nitrogen bound to the Co(III) center is less open to attack by Cr^{2+} than is at least one of the oxygens in the carboxylate complex. The spectra of the Cr(III) products in fact suggest that the ligand is not transferred in the case of the three nitrogen-containing ligands just mentioned. Though we are probably dealing there with an outer-sphere reaction, the rate is somewhat higher than it is for [Co-$(NH_3)_6]^{3+}$. For the latter ion k has been reported[17] as 0.9×10^{-4} M^{-1} sec^{-1} at $\mu = 0.4$ and 25°.

(16) J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965).

The reduction of the complex with malonodinitrile as the ligand is very rapid, and the reduction phase is followed by at least two other processes, as judged by the changes in extinction with time. That the initial rapid phase corresponds to reduction was proven by quenching the reaction mixture with air quickly after mixing, whereupon analysis showed Co^{2+} to be present in substantial amounts. Ligand transfer does occur in this case. We do not understand the nature of the subsequent changes, but the system seems particularly interesting to us because there is the possibility of attack by Cr^{2+} at the carbon of the ligand.

(17) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

Oxygen Tracer Studies on the Reaction of Cyanate Ion with Aquo and Diaquo Cobalt Ammines, and on the Nitrosation of Carbamatopentaamminecobalt(III)

BY ALAN M. SARGESON AND HENRY TAUBE

The reaction of $Co(NH_3)_5OH_2^{3+}$ with NCO^- takes place to form the carbamato complex as an intermediate. Oxygen tracer studies on the reaction of the carbamato complex with nitrous acid prove that the Co–O bond remains intact in the reaction of the aquopentaammine complex with NCO^-. The mechanism of the nitrosation of the carbamato complex is such that it leads to 80% Co–O bond rupture. The competition of Cl^- and H_2O for the presumed intermediate $Co(NH_3)_5^{3+}$ is discussed. The reaction of NCO^- with $Co(en)_2(OH_2)_2^{3+}$ leads to $Co(en)_2CO_3^+$ as product. Oxygen tracer studies on the reaction of this product with acid show that one of the two oxygen atoms in the chelate ring is derived from NCO^-, the other from the aquo complex, and the remaining oxygen in the complex is derived from the solvent.

Introduction

The substitution of NCO^- in cobalt(III) ammine complexes has been examined previously by Linhard and Flygare[1] in the course of an extensive study of the spectral properties of the halo and pseudo-halo Co(III) ammine compounds. These authors noted that the spectra of the supposed cyanato compounds were not related to those of the halogen compounds and that NCO^- was not detected when the Co(III) complexes were decomposed. They suggested from these results and their analytical data that NCO^- substituted by addition to the coordinated water or more likely by the addition of HNCO to the hydroxo complex, giving the corresponding carbamato complex. In this way Co-$(NH_3)_5O_2CNH_2^{2+}$ and $Co(NH_3)_4(OH_2)O_2CNH_2^{2+}$ were prepared; the latter ion, however, eventually hydrolyzes to the $Co(NH_3)_4CO_3^+$ ion.

The present investigation was carried out to test these proposals and to attempt to establish the mechanism of the reactions by means of tracer experiments. Nitrosation suggested itself as a convenient possibility for the workup of the carbamate complex. It proved

(1) M. Linhard and H. Flygare, *Z. Anorg. Chem.*, **251**, 25 (1943).

to be well suited to our needs and the interest in the reaction itself grew so that it became the dominant theme of this part of our work.

The experiments divided naturally into two parts: (a) those concerning the pentaammine complex and (b) those dealing with a tetraammine system and its subsequent hydrolysis, and they will be dealt with in that order.

A. The Reaction of NCO^+ with $Co(NH_3)_5OH_2^{3+}$; Mechanism of Nitrosation of the Carbamato Complex

Experimental Section

Preparations.—$[Co(NH_3)_5O_2CNH_2](ClO_4)_2$ was prepared essentially by the method of Linhard and Flygare.[1] $[Co(NH_3)_5-OH_2](ClO_4)_3$ (14 g) added to water (40 ml at 60°) was stirred rapidly until the complex dissolved.

NaNCO (2 g) was added and the mixture cooled to 25° over 30 min. The complex which formed was recrystallized rapidly from warm water with NaClO$_4$. The salt was collected and washed with methanol and dried in a vacuum desiccator for 12 hr. The extinction coefficient ϵ was 60 at 505 mμ. *Anal.* Calcd for $[Co(NH_3)_5O_2CNH_2](ClO_4)_2$: C, 2.98; H, 4.25; N, 20.85; ClO$_4$, 49.4. Found: C, 3.15; H, 4.16; N, 20.98; ClO$_4$, 50.5.

The sparingly soluble dithionate salt was prepared by dissolving the perchlorate in a minimum of water and adding excess

Na$_2$S$_2$O$_6$. The dithionate which crystallized was washed with water and methanol and dried in a vacuum desiccator for 12 hr.

Anal. Calcd for [Co(NH$_3$)$_5$O$_2$CNH$_2$]S$_2$O$_6$: C, 3.30; H, 4.71; N, 23.08. Found: C, 3.15; H, 4.57; N, 22.74.

The infrared spectrum of the complex dithionate (KBr pellet) showed a peak at 1560 cm^{-1} attributed to the C=O stretching mode of the coordinated carbamate. This is to be compared with an expected[2] frequency of ~2100 cm^{-1} for coordinated NCO$^-$.

The complex carbamate where the bridging oxygen was enriched was prepared from [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ of known enrichment, by the procedure above using normal NaNCO and normal water. A preparation using enriched aquo, normal NaNCO, and enriched water gave some enrichment in the carboxyl oxygen as well as in the bridging oxygen, Table Ib (run 21).

The NaNCO was fractionally recrystallized from water with methanol and dried in a vacuum desiccator. A substantial first fraction was discarded to remove Na$_2$CO$_3$.

Nitrosation Reactions.—The carbamate (1.0 mmole) was suspended or dissolved in water (9 ml) and NaNO$_2$ solid (1.4 mmoles) was added. The solution was flushed with helium (0.5 l./min) to remove dissolved CO$_2$. The mixture was then treated with either HCl or HClO$_4$ (1 ml of 10 N) and the gases evolved were carried by the He through a Cr^{2+} solution (~3 M in 3 M HClO$_4$) to remove the nitrogen oxides and through two methanol–solid CO$_2$ traps to remove water. The resulting CO$_2$ was trapped with liquid N$_2$. The CO$_2$ was distilled into a Urey tube and its isotopic composition was determined in an Atlas M 86 mass spectrometer.

The water from the solution was also sampled (~0.5 g) and equilibrated with CO$_2$ of normal isotopic composition (~0.2 mmole for 10 hr at 70°), and the composition of the enriched CO$_2$ was determined as above. The remaining solution, cooled and filtered to remove the precipitated [Co(NH$_3$)$_5$Cl]Cl$_2$, was treated with cold concentrated HBr. The [Co(NH$_3$)$_5$OH$_2$]Br$_3$ which precipitated was collected and washed with cold HBr and then methanol and dried in a vacuum desiccator for 10 hr and then for 2 hr under high vacuum. The aquo bromide was heated at 100° for 5 hr under vacuum, and the water evolved was collected in a break-seal tube and treated by the Anbar and Guttman method.[3] The CO$_2$ formed was separated from other gases by passing the mixture through a chromatographic column (10 ft × 0.25 in.) containing *sec*-butyl phthalate on Chromosorb P (80–100 mesh). The CO$_2$ was trapped and the isotope composition determined as above.

For NH$_4$O$_2$CNH$_2$ and C$_2$H$_5$O$_2$CNH$_2$, where a minimum time of contact with the solvent was required, the deaerated solvent was added to the compound and NaNO$_2$ at the same time as the HCl.

The [Co(NH$_3$)$_5$Cl]Cl$_2$ collected was washed with a small amount of cold HCl (5 N) and methanol and dried and weighed (~0.2 mmole). *Anal.* Calcd for [Co(NH$_3$)$_5$Cl]Cl$_2$: N, 27.97; H, 6.04. Found: N, 28.5; H, 5.7. The extinction coefficients for this product were 49.3 at 520 mμ and 65 at 325 mμ compared with the values of Linhard and Weigel,[4] 50 at 520 mμ and 53 at 325 mμ. The high extinction coefficient at 325 mμ was attributed to the presence of some [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ in the chloro chloride, ~4% (calculated from the values of Linhard, *et al.*,[5] ϵ 100 at 458 mμ and ϵ 1660 at 325 mμ). This result was consistent with the analytical result above. When excess NaNO$_2$ was used (3.0 mmoles) considerably more [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ was formed, and for the [Co(NH$_3$)$_5$Cl]Cl$_2$ plus [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ product, the values of ϵ were 37 at 530 mμ, 48 at 460 mμ, and 475 at 325 mμ. The mixture contained approximately 30% of the nitro and 70% of the chloro complex.

In one instance the chloro chloride containing nitro chloride was redissolved immediately and treated with NaN$_3$ and HClO$_4$

with no change in the extinction coefficients. This experiment showed that the NO$_2^-$ was bonded to cobalt through the N atom.[6]

Effect of Cr^{2+} on the Enrichment in CO$_2$.—A sample of enriched NaHCO$_3$ was treated with acid and the CO$_2$ collected (a) after bubbling through Cr^{2+} and (b) in the absence of the Cr^{2+} scrubber. Approximately 3% of the enrichment in (b) was lost in the passage through the Cr^{2+} solution and the CO$_2$ values in Table I have been corrected where necessary.

Later in the investigation the CO$_2$ was trapped by a mixture of liquid N$_2$ and isopentane (−135°). In these experiments (runs 4, 12–18, 20, and 21) the Cr^{2+} solution was not used.

Acid Hydrolysis.—Either the carbamate was treated with deaerated acid (10 ml of 1 M) or HCl or HClO$_4$ (1 ml of 10 M) was added to the carbamate in deaerated water (9 ml).

Stoichiometry.—(a) Normal CO$_2$ from the nitrosation reaction was collected and mixed with a sample of enriched CO$_2$ obtained by heating a known quantity of enriched Ag$_2$C$_2$O$_4$. The isotopic dilution was then measured in the mass spectrometer. If the stoichiometry of the reaction was assumed to be

$$Co(NH_3)_5OCNH_2{}^{2+} + NO^+ \longrightarrow Co(NH_3)_5OH_2{}^{3+} + CO_2 + N_2$$
$$\underset{\parallel}{}\underset{O}{}$$
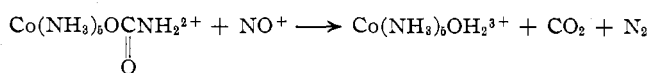
then 90% of the CO$_2$ was recovered.

(b) A solution of [Co(NH$_3$)$_5$O$_2$CNH$_2$](ClO$_4$)$_2$ (0.40 g) and NaNO$_2$ (0.070 g) in water (9 ml deaerated with He) was treated with HCl (1 ml of 10 N) and the He flow stopped. The gases evolved were injected into the gas chromatograph and the peak height ratio determined: N$_2$/CO$_2$ = 1.6. This is to be compared with the ratio for equal volumes of CO$_2$ and N$_2$ when N$_2$/CO$_2$ = 1.4. The slightly high value in the first instance was probably due to the higher solubility of CO$_2$ in aqueous solution. The measured ratio corresponds to 53% N$_2$ and 47% CO$_2$.

(c) The gas collected was composed primarily of species of mass numbers 28 and 44. The latter value does not distinguish between N$_2$O and CO$_2$ but the 45/44 ratio showed that the gas sample contained CO$_2$ and not N$_2$O.

All three experiments are consistent with the stoichiometry given above; a number of causes, other than deviations from it, can account for the deficiency in CO$_2$ recovered.

Results

The distribution of the tracer O^{18} for the reaction

$$(NH_3)_5CoOH_2{}^{3+} + N_2 + CO_2$$
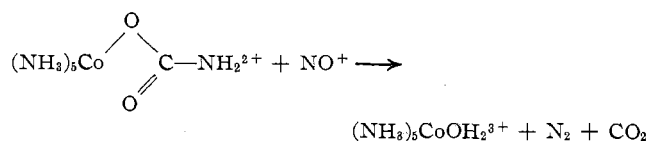
under various conditions is given in Table I (a, b). The nitrosation was carried out (a) with the solvent enriched (and the NO$_2^-$ necessarily also enriched because the exchange of NO$_2^-$ with H$_2$O in acidic solution is rapid[7]) and (b) with the carbamate complex prepared from O^{18}-enriched aquo ion, but the nitrosation carried out in solvent of normal isotopic composition. Stoichiometry requires that the products must contain at least one oxygen atom derived from the solvent or the nitrite; solvent oxygen content in the products in excess of this will then indicate exchange of complex before or during reaction.

Examination of the results of expt 1–12 shows that the reaction takes place with very little oxygen exchange. For most of the experiments, specifically from 5 to 12, the products between them show only a single oxygen atom derived from the solvent (though

(2) A. Maki and J. C. Decius, *J. Chem. Phys.*, **28**, 1003 (1958).

(3) M. Anbar and S. Guttman, *J. Appl. Rad. Isotopes*, **5**, 223 (1959).

(4) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 49 (1951).

(5) M. Linhard, H. Siebert, and M. Weigel, *ibid.*, **278**, 287 (1955).

(6) F. Seel and R. Wölfle, *ibid.*, **308**, 305 (1961).

(7) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **77**, 2993 (1955).

TABLE I

OXYGEN ISOTOPE EXPERIMENTS ON THE NITROSATION
AND ACID HYDROLYSIS OF CARBAMATES[a]

$$\text{(a)} \quad (NH_3)_5Co \overset{O}{\underset{O}{\diagdown}} C—NH_2{}^{2+} + N\otimes^+ + H_2\otimes$$

| Run no. | Enrichment ratio[b] | | | % enriched O in | | Fraction of Co(III) as chloro complex |
	Solvent[d]	Aquo product	CO₂[c]	Aquo	CO₂	
1	6.28	5.17	2.00	78.8	19.0	0.17
2	6.00	4.88	1.88	77.4	17.5	0.16
3	6.78	5.48	1.80	77.5	13.7	...
4	6.58	5.28	2.02	76.7	17.0	0.15
5	7.06	5.82	1.67	78.2	10.8	0.15
6	8.34	...	1.74	...	10.1	...
7	7.98	...	1.68	...	9.7	...
8	7.87	...	1.69	...	9.9	0.18
9	7.75	...	1.80	...	11.8	0.20
10	7.16	...	1.62	...	9.9	0.15
11	7.16	...	1.67	...	10.8	...
12	7.86	...	1.67	...	9.6	...
13	6.68	5.22	1.99	74.2	17.3	0.19
14	7.54	5.81	2.00	73.6	15.1	0.07
15	8.07	6.23	2.00	74.1	14.0	...
16	6.72	4.86	1.79	67.5	13.7	0.21
17	6.77	4.83	1.72	66.4	12.3	0.22

$$\text{(b)} \quad (NH_3)_5Co \overset{\otimes}{\underset{O}{\diagdown}} CNH_2{}^{2+} + NO^+ + H_2O$$

18	3.92	1.57	2.12	19.4	38.4	...
19	6.76	2.04	3.42	18.0	42.0	0.17
20	7.28	...	3.65	...	42.1	0.16
21	3.37	1.47	2.17	19.4	49.1	...

$$\text{(c)} \quad NH_2CO_2{}^- + N\otimes^+ + H_2\otimes$$

| 22 | 4.14 | ... | 1.37 | ... | 11.5 | ... |
| 23 | 4.16 | ... | 1.40 | ... | 12.5 | ... |

$$\text{(d)} \quad C_2H_5—O \underset{O}{\diagdown} C—NH_2 + N\otimes^+ + H_2\otimes$$

24	6.66	...	1.71	...	12.4	...
25	4.83	...	1.33	...	8.4	...
26	4.11	...	1.26	...	8.4	...

$$\text{(e)} \quad NH_2CO_2{}^- + H_3\otimes^+$$

| 27 | 4.10 | ... | 1.01 | ... | 0 | ... |

$$\text{(f)} \quad (NH_3)_5Co \overset{O}{\underset{O}{\diagdown}} C—NH_2{}^{2+} + H_3\otimes^+$$

| 28 | 6.64 | 4.32 | 2.20 | 58.9 | 21.2 | ... |

[a] Temperature 25° except in expt 16 and 17 where it was 5°; reaction medium, 1 M HCl except in expt 14 (0.42 M HCl), 15 (1.0 M HClO₄), and 25 and 26 (2 M HCl); NO₂⁻ used in 1.4-fold excess except in expt 25 and 26 where equivalent amounts were used; 1 mmole of salt used except in expt 25 and 26 where 20 mmoles was used; reactant complex added as perchlorate salt (if cation) or ammonium salt (if anion) except in expt 4 (S₂O₈²⁻ salt); contact time of the carbamate with the solvent before nitrosation was 5 min except in expt 1 and 2 where it was 1 min, expt 3 where it was 30 min, and in expt 22 to 26 where it was zero min. [b] Mole fraction of O¹⁸ in species under consideration compared to a sample of normal isotopic composition. [c] Corrected where applicable for exchange in passing through Cr²⁺(aq). [d] In part (b) this column represents the isotopic composition of water in the aquo complex from which the carbamato was prepared.

the isotopic composition of the aquo products in expt 6–12 was not determined, the enriched oxygen content can fairly confidently be taken the same as the average of expt 1–5 since the same conditions were used) for each molecule of complex which reacts. The apparent exchange indicated by expt 1 and 2 can probably be attributed to the fact that for these the reactant solutions were not completely purged of CO₂ before reaction. This leaves only a single experiment in this group, namely expt 4, indicating substantial exchange, and although no explanation for the apparent exchange can be offered, the other experiments constitute overwhelming evidence for the conclusion that the results are not complicated by significant exchange. All the experiments agree in showing that reaction takes place with 79 ± 2% bond rupture at the Co–O position.

The experiments in part (b) of Table I lead to the same conclusions and furthermore prove that the aquo oxygen is retained bound to the cobalt in the formation of the carbamato complex. This conclusion follows because the products Co(NH₃)₅OH₂³⁺ and CO₂ between them contain just the same amount of enriched oxygen as was present in the O¹⁸-enriched aquo ion used to prepare the carbamato complex. The excess content of enriched oxygen shown in expt 21 probably is a result of the fact that the carbamato complex was prepared in O¹⁸-enriched solvent, and oxygen exchange took place in the formation of the carbamato complex.

Experiments 13–15 were performed with a preparation that contained some aquo salt, and it is for this reason that the enriched oxygen content of the aquo product is found to be less than in expt 1–12. Though the experiments are imperfect also in showing an enriched oxygen content in the CO₂ which is too high, they serve to prove that the bond-breaking pattern is not altered by replacing 1 M HCl by 0.4 M HCl or by 1 M HClO₄. The results of expt 16 and 17 compared to others in the table suggest that slightly less Co–O bond breaking relative to C–O bond breaking takes place at 5° compared to 25°. However, in view of the fact that not enough enriched oxygen is shown in the product CO₂ to meet the requirements of stoichiometry this conclusion cannot be insisted upon.
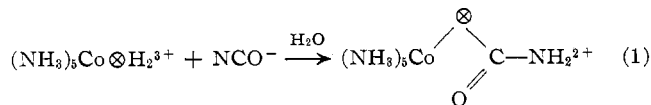
In commenting on the results of the nitrosation experiments, attention should also be directed to the fact that when HCl is present in the reaction medium, the chloro complex constitutes a significant component of the products.

Part (c) of Table I shows that nitrosation of carbamate ion also places solvent oxygen in the CO₂, and part (d) that the same conclusion obtains with ethyl carbamate as reactant. It is astonishing that incorporation of solvent (or nitrite) oxygen is so nearly the same for all three nitrosation reactions and particularly that as much as 80% C₂H₅–O bond rupture takes place in the nitrosation of ethyl carbamate. As judged by the odor, some C₂H₅Cl and/or C₂H₅ONO appears to form in the latter reaction. No attempts were made to determine the amount quantitatively. An attempt was made to determine the O¹⁸ content of the alcohol

presumed to be a product of the reaction, but it was unsuccessful.

Discussion

Since the original purpose of this part of the study was to learn the mechanism of the reaction of NCO^- with $Co(NH_3)_5OH_2{}^{3+}$, it seems appropriate at the outset to repeat the conclusions on this point made in passing in the preceding section. Experiments 18–20 prove the isotopic course of the reaction to be

$$(NH_3)_5Co\otimes H_2{}^{3+} + NCO^- \xrightarrow{H_2O} (NH_3)_5Co \begin{smallmatrix} \otimes \\ O \end{smallmatrix} C\!-\!NH_2{}^{2+} \quad (1)$$

The partition of the labeled oxygen between the products CO_2 and $(NH_3)_5CoOH_2{}^{3+}$ taken in conjunction with the results of expt 5–12 proves conclusively that in the carbamate complex it is in the position indicated in eq 1.

It is not possible on the basis of the present evidence to decide whether the nitrosation occurs by the reaction of NO^+ or $H_2NO_2{}^+$ with the carbamate ion, but the composition of the intermediate exclusive of the water content follows from the rate law established for the nitrosation reaction[8]

$$R = k(\text{complex})(NO_2{}^-)(H^+)$$

and we will take its structure to be

$$^{2+}(NH_3)_5Co\!-\!O \begin{smallmatrix} N=O \\ | \\ N \\ C \quad H \\ \| \\ O \end{smallmatrix}$$
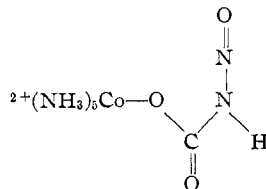
This structure is supported by evidence obtained for analogous reactions with organic amides where the

The tracer results show that nearly 80% bond breaking takes place at Co–O and 20% occurs at C–O–. It is conceivable that the intermediate I decomposes in the manner shown in Scheme I through the two paths A and B. The intermediate A may first decompose to the pentaammine carbonato complex, which is known to lose CO_2 without rupture of the Co–O bond in H^+ media.[9] This mode of decomposition leads to 20% of the total CO_2 having one oxygen atom with the same enrichment as the solvent and is consistent with the observed result (recorded as 10% of the total oxygen content of the CO_2 having the solvent enrichment). The aquo product from this path contains oxygen with the normal isotopic composition.

Path B leads ultimately to the $(NH_3)_5CoCO_2{}^{3+}$ complex, which would be expected to be short-lived, and dissociation of the CO_2 of normal composition leads to the aquo product with the same enrichment as the solvent.

Many of the results might equally well be understood on the basis that $(NH_3)_5CoO\!=\!C\!=\!O^{3+}$ forms as an intermediate for both paths and this species reacts either by Co–O bond rupture or by hydration to $CO_3{}^{2-}$. This explanation, however, does not accommodate the fact that the solvent content of the CO_2 formed is the same for the nitrosation of three different species.

For the reaction path which occurs by 80% Co–O fission either CO_2 or $\begin{smallmatrix} O \\ \diagdown \\ C\!-\!N\!=\!N \\ \diagup \\ O \end{smallmatrix}$ is a good leaving group and there is a possibility that the five-coordinate intermediate $Co(NH_3)_5{}^{3+}$ is formed. Under these circumstances $(NH_3)_5CoCl^{2+}$ should form in addition to $(NH_3)_5CoOH_2{}^{3+}$ if Cl^- is present. In 1 M HCl within a minute of adding the reagents, $[Co(NH_3)_5Cl]$-

SCHEME I
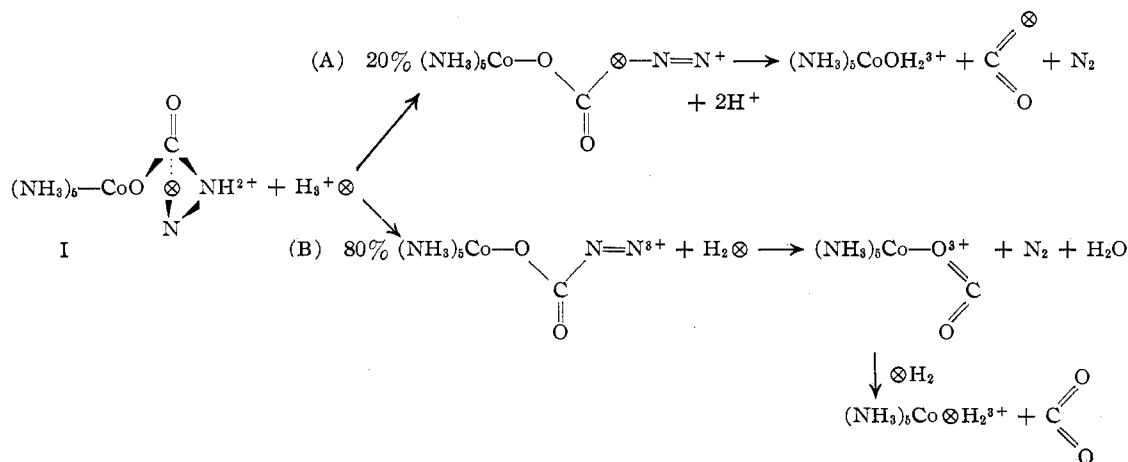

nitroso derivative can at times be isolated. It should be mentioned that the aquation of $(NH_3)_5CoO_2CNH_2{}^{2+}$ is so slow (the half-life at 25° and 1 M H^+ is 3.5 × 10^4 sec) compared to nitrosation that the results on the latter reaction are not complicated by the former.

Cl_2 precipitates, and it constitutes 20% of the total product or 25% of the product derived from the Co–O fission. The competition ratio for Cl^- and H_2O for the supposed intermediate $Co(NH_3)_5{}^{3+}$ has been as-

(8) A. M. Sargeson and H. Satrapa, to be published.

(9) J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Am. Chem. Soc.*, **74**, 268 (1952).

sessed by Haim and Taube[10] as $k_x/k_{H_2O} = 0.32$. The present experiments show $k_x/k_{H_2O} = 0.31$, in excellent agreement with the previous result. Moreover, in the two instances the leaving groups are vastly different, N_2 or N_2O in the former and CO_2 in the latter. These facts are consistent with the same intermediate being involved in both reactions.[11] It should be noted, in addition, that the precipitated $[Co(NH_3)_5Cl]Cl_2$ contains some

$$\left[(NH_3)_5Co{-}N\underset{O}{\overset{O}{\diagup\diagdown}} \right] Cl_2$$
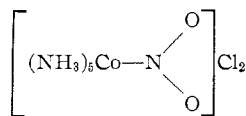
This result is significant because NO_2^- normally coordinates by adding NO^+ to the coordinated water and the $(NH_3)_5Co{-}O{-}N{=}O^{2+}$ formed rearranges slowly to the nitro complex intramolecularly.[12] That the N atom coordinates directly in this instance is conclusive evidence that another mechanism for coordinating NO_2^- is involved and is consistent with the proposal that $Co(NH_3)_5{}^{3+}$ is attacked directly by the NO_2^- ion or N_2O_3 or NO^+. When excess NO_2^- was added the concentration of $[(NH_3)_5CoNO_2]Cl_2$ increased considerably.

The fact that no solvent oxygen is incorporated into the CO_2 evolved when $NH_2CO_2^-$ decomposes in acid proves that carbonate is not formed as an intermediate product. A reasonable form for the activated complex is

$$\left[\underset{H}{\overset{+}{H}} \quad \underset{H}{\overset{H}{N}}{-}\underset{O}{\overset{O}{C}} \right]^-$$
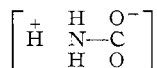
B. The Isotopic Course of the Reaction of NCO^- with cis-$Co(en)_2(OH_2)_2{}^{3+}$

In the experiments described in this section NCO^- was brought into reaction with cis-$Co(en)_2(OH_2)_2{}^{3+}$ and with the complex, the solvent, or both enriched in O^{18}. Since the isotopic course of the reaction of $Co(en)_2CO_3{}^+$ with H^+ is known,[13] the release of CO_2 by acid is a convenient method of isotopic analysis of the product complex, and this procedure was adopted for the present experiments.

Experimental Section

(1) cis-$[Co(en)_2(OH_2)_2](ClO_4)_3$ (0.515 g) was dissolved in O^{18}-enriched water (10 ml, 1.5 atom %) containing NaOH (0.040 g). The solution was allowed to stand at 25° for 3.5 hr, at which stage both coordinated water molecules were equilibrated with the solvent.[14] Perchloric acid (0.1 ml of 10 M) was then added to re-form the diaquo complex followed by NaNCO (0.65 g), and the mixture was allowed to stand at 25°. After 30 min the $[Co(en)_2CO_3]ClO_4$ salt commenced to crystallize (ϵ 132 at 515

(10) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(11) The experiments of R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964), taken together with Haim and Taube's results[10] prove conclusively and contrary to the conclusion reached by H. and T. that the nitrosation of the azide complex and the spontaneous aquations do not involve the same intermediates. They do not prove, however, that a genuine five-coordinate intermediate is not formed when a good leaving group is generated on the Co(NH₃)₅³⁺ residue.

(12) R. G. Pearson, P. M. Henry, J. G. Bergman, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954).

(13) F. A. Posey and H. Taube, *ibid.*, **75**, 4099 (1953).

(14) W. Kruse and H. Taube, *ibid.*, **83**, 1280 (1961).

mμ) and more was obtained on adding $NaClO_4$. The isolated carbonato complex (0.1–0.2 g) was dissolved in water (10 ml) and deaerated with He, and $HClO_4$ (1 ml of 10 M) was added. The CO_2 formed was flushed out of solution continuously with He (0.5 l./min), collected in a trap cooled with liquid N_2, and finally distilled into a Urey tube. The isotope ratio was measured in an Atlas M86 mass spectrometer. Little or no exchange occurs between CO_2 and water in the time it takes to remove CO_2 with He.[13]

Two additional traps cooled with methanol and solid CO_2 were inserted between the reactor and the trap cooled by liquid N_2 to collect water vapor carried by the He stream. *Anal.* Calcd for $CoC_4H_{16}N_4CO_3ClO_4$: C, 17.73; H, 4.76; N, 16.55. Found: C, 17.85; H, 4.83; N, 16.81.

(2) $[Co(en)_2CO_3]ClO_4$ (0.34 g) was dissolved in O^{18}-enriched water (10 ml, 1.5 atom %) and $HClO_4$ (0.2 ml of 10 M) added. The mixture was refluxed for 12 hr to equilibrate the coordinated water with the solvent, then NaNCO (0.65 g) was added and the solution was allowed to stand for 5 hr. The $[Co(en)_2CO_3]$-ClO_4 was collected, dried, and allowed to react with $HClO_4$; the CO_2 was collected and the isotope ratio measured, as before.
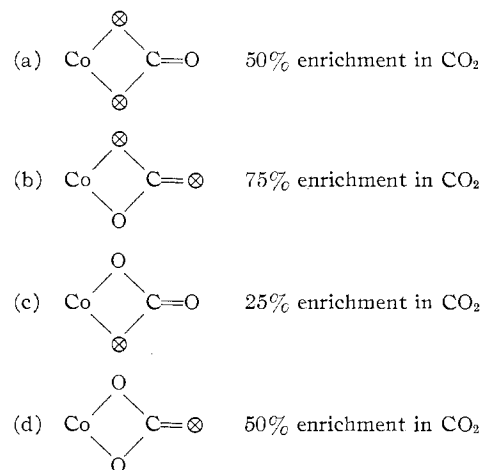
(3) cis-$[Co(en)_2(O^{18}H_2)_2](ClO_4)_3$ was prepared as in method 2 and the solution was then evaporated in a vacuum desiccator to dryness when the diaquo perchlorate crystallized out. The solid enriched complex was dissolved in normal H_2O and treated with normal NaNCO and the carbonato complex so formed analyzed as before.

(4) Normal cis-$[Co(en)_2(OH_2)_2](ClO_4)_3$ (1 g), prepared and isolated as in method 3, was dissolved in H_2O^{18} (1.5 atom %) and treated with NaNCO (1.3 g). The $[Co(en)_2CO_3]ClO_4$ was collected and analyzed as before.

The enrichment in the complexes was determined by sampling the solution after equilibration and heating a sample of normal CO_2 with the enriched solvent at 70° for 10 hr.

Results

The O^{18} tracer experiments[13] on the acid hydrolysis of the $Co(NH_3)_4CO_3{}^+$ ion show that only one Co–O bond is broken for each CO_2 molecule lost. This is significant for the present investigation since the enrichment in the CO_2 will depend on where the enriched oxygen resides. The possible products are given in the following scheme, assuming, as was the case, that the reaction with acid is carried out in solvent of normal isotopic composition.

The results of the tracer experiments are shown in Table II. Only (b) is consistent with the observations for expt 1 and 2 of the table. It follows then that the result shown for (c) should be observed in expt 3. The low value in the enrichment of the CO_2 for

TABLE II

OXYGEN TRACER RESULTS ON THE REACTION OF
NCO^- WITH $Co(en)_2(OH_2)_2^{3+}$

Expt No.	Enrichment[a] ratio of—		CO_2	% of enriched O in CO_2
	Solvent[b]	Aquo ion[c]		
1	5.33[d]	5.33[d]	4.36	77
2	6.64[d]	6.64[d]	5.12	73
3a	1.00	6.00	1.42	9
3b	1.00	8.65	1.54	7
4	8.65	1.00	5.91	64

[a] In each case NCO^- and the solvent used for decomposition of the carbonato complex were of normal isotopic composition, that is, the enrichment ratio was 1.00. [b] Refers to the solvent used for the reaction of NCO^- with $Co(en)_2(H_2O)_2^{3+}$. [c] For the aquo ion used in the preparation of the carbonato complex. [d] No account has been taken of the fact that the equilibrium constant for the reaction $H_2O^{16}_h + H_2O^{18}_l = H_2O^{18}_l + H_2O^{16}_h$ is about 1.020. Subscripts h and l refer to hydrate and liquid, respectively.

expt 3 is attributed to exchange between the enriched complex and normal solvent in the time for reaction; in expt 1 and 2 this process cannot affect the result as both solvent and complex were enriched to the same extent. Experiment 4 should give the enrichment in (d) unless exchange takes place, and the observed enrichment of 64% allowing for exchange of the complexed water with normal solvent as in expt 3 is consistent with this. Since the limiting enrichment in the CO_2 for complete exchange between the aquo ion and the solvent would be 75% in expt 4, the extents of exchange in expt 3 and 4 are in fact roughly comparable.

Discussion

The mechanism outlined in eq 2–4 accommodates the tracer results and is consistent with the proposal by Linhard and Flygare[1] that NCO^- adds to coordinated water. The carbamato complex so formed then chelates by displacing the other coordinated water molecule and subsequently hydrolyzes to the carbonate. When solvent and aquo ion are enriched these events lead to the isotopic distribution shown in the reaction scheme below
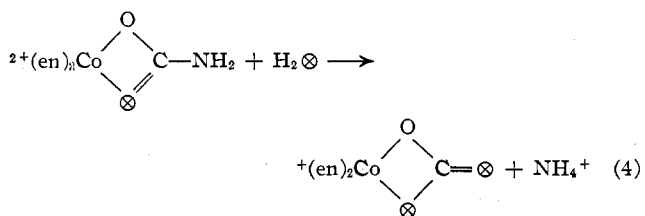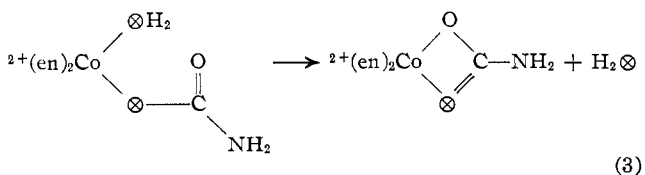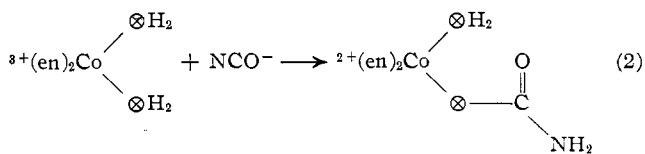
Reaction 2 in the above scheme is entirely analogous to reaction 1 of the previous section. Reaction 3 is the analog of the carbonate–diaquo complex reaction.[12] The tracer results show that hydrolysis of NH_2 does not take place while the carbamate is in the monodentate form. If the hydrolysis were complete at this stage 62.5% enrichment of the CO_2 obtained in expt 1 and 2 would be observed as indicated in the reaction sequence, eq 5 and 6. The fact that $Co(NH_3)_5$-
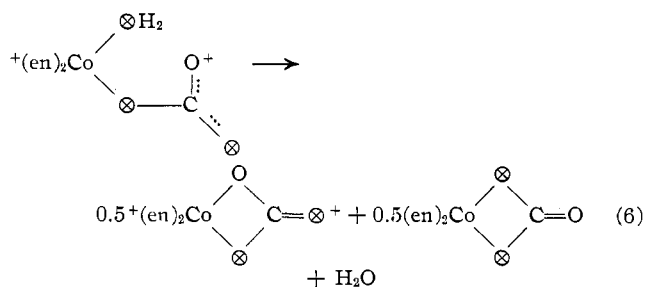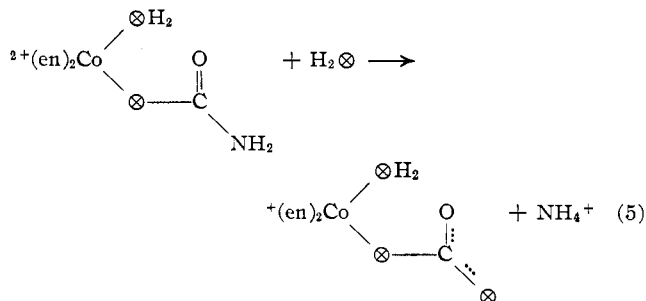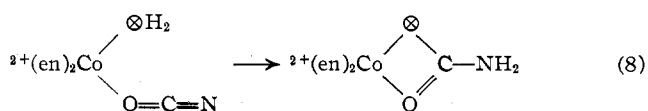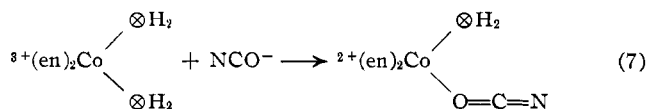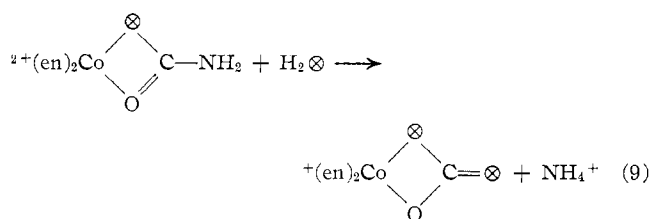
$O_2CNH_2^{2+}$ hydrolyzes slowly is further evidence against reaction 5 as being a significant process in our experiments.

Since this point is not developed explicitly by eq 2–4, nor is demonstrated by expt 1 and 2 of Table II, it should be mentioned that our results show that the bound carbonate contains oxygen derived from three sources: aquo ion, NCO^-, and solvent. Even with the limitation imposed by the occurrence of exchange, expt 3 and 4 in conjunction with expt 1 and 2 show that both aquo complex oxygen and solvent oxygen are present in the resulting complex.

The mechanism shown in eq 2–4 makes no assertions about the location of protons in the activated complex. Our results will affect the conclusions to be reached on this aspect of the mechanisms of reaction but do not define the role of the protons uniquely.

The tracer results do not exclude the possibility that NCO^- coordinates directly and then reacts with coordinated water as shown in reactions 7–9. However, preliminary rate studies show that the half-life for the formation of the carbonato complex was ~14 min at 25°, whereas the water exchange process for the *cis*-

$$^{2+}(en)_2Co \overset{\otimes}{\diagup}\overset{\diagdown}{\underset{O}{\diagdown}}C-NH_2 + H_2\otimes \longrightarrow$$

$$^{+}(en)_2Co \overset{\otimes}{\diagup}\overset{\diagdown}{\underset{O}{\diagdown}}C=\otimes + NH_4^+ \quad (9)$$

hydroxyaquo ion has a half-life of about 25 min at 25°. It seems unlikely that the NCO⁻ ion will greatly accelerate the water exchange rate, and the latter figure probably imposes a maximum rate on the entry of NCO⁻ by the anation mechanism. At the same time it requires NCO⁻ to be an unusually good competitor for the coordination position to be vacated; water usually competes about three times as well as a mononegative anion under similar circumstances[9] (1 M NCO⁻ and 55 M H_2O). Both the rate and competition factor militate against the anation mechanism. In addition it has been shown unequivocally that NCO⁻ adds to the coordinated water in the $Co(NH_3)_5OH_2^{3+}$ ion.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

The Kinetics of Protonation of Nickel and Chromium Hexaaquo Cations in Aqueous Solution

By T. J. SWIFT AND T. A. STEPHENSON

A detailed study of the kinetics of acid dissociation of $Cr(H_2O)_6^{3+}$ in aqueous solution was performed by the application of proton magnetic resonance. The rate constant for the transfer of protons from $Cr(H_2O)_6^{3+}$ ions to bulk water was found to be of the form $k = k_1 + k_2[H^+]$. Further investigation revealed that this is also the form of the rate constant for proton transfer involving $Ni(H_2O)_6^{2+}$ in aqueous solution. The rate constants, k_1 and k_2, were found to be $7.0 \pm 0.1 \times 10^4$ sec⁻¹ and $5.0 \pm 0.2 \times 10^4$ M^{-1} sec⁻¹, respectively, for chromic ion at 298°K. The values of k_1 and k_2 for nickelous ion at the same temperature were found to be $9 \pm 1 \times 10^4$ sec⁻¹ and $1.3 \pm 0.2 \times 10^6$ M^{-1} sec⁻¹, respectively. A mechanism is proposed for the acid-dependent proton-transfer process revealed by these studies, and this mechanism involves the protonation of the hexaaquo cations as the principal step.

Introduction

It has recently been demonstrated that the exchange of water molecules between the bulk of an aqueous solution and the primary hydration sphere of manganous ion in solution may be used to study the primary hydration of cations in solution. At least in principle other reactions exist which may be employed in a similar manner as independent checks on the results obtained by Swift and Sayre.[1] One such reaction of some promise has been reported previously by Bloembergen and Morgan.[2] The authors have studied the temperature and frequency dependences of proton relaxation in aqueous solutions containing each of several paramagnetic cations.

The relaxation produced by one of the ions, $Cr(H_2O)_6^{3+}$, appears to be controlled at lower temperatures by the rate of a chemical-exchange process. Since the rate of water molecule exchange between the bulk and the primary hydration sphere of a $Cr(H_2O)_6^{3+}$ ion is relatively slow at these temperatures,[3] the authors[2] concluded that the exchange process revealed by their studies is

$$Cr(H_2O)_6^{3+} + H_2O \xrightarrow{k_1} Cr(H_2O)_5OH^{2+} + H_3O^+ \quad (1)$$
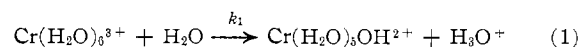
This reaction and the line broadening produced by it form exactly the type of basis sought for the hydration number technique. Water molecules are directly involved in the reaction, kinetic distinguishability may be realized through the anticipated difference in basicity between bulk water molecules and waters in the primary hydration spheres of cations, and the reaction is directly and simply related to a precisely measurable line width.

Because of this potentially important application the detailed investigation of the line-broadening effect of $Cr(H_2O)_6^{3+}$ was undertaken in this laboratory.

Experimental Section

Stock solutions of Cr³⁺ and Ni²⁺ were prepared from analytical grade nitrate salts, and these stock solutions were subsequently analyzed for the metal ions. Solutions of various concentrations of acid were prepared in the following manner. Those solutions in which the acid concentration was less than 10^{-1} M were prepared by dropwise addition of dilute HNO_3, and the pH was measured with a Beckman pH meter. Those solutions in which

(1) T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).
(2) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).
(3) J. P. Hunt and H. Taube, *ibid.*, **18**, 757 (1950).