the minor species, $Co(NH_3)_4(OH)_2^+$, one obtains

$$R_O = \frac{k_1[Co(NH_3)_5OH^{2+}]k_2[OH^-]}{k_{-1}[NH_3] + k_2[OH^-]}$$

If $k_{-1}[NH_3] > k_2[OH^-]$ this reduces to

$$R_O = \frac{k_1k_2[Co(NH_3)_5OH^{2+}][OH^-]}{k_{-1}[NH_3]}$$

In our experiments the ratio $[OH^-]/[NH_3]$ was held constant, leading to the apparent first-order rate law. The lower rate for oxygen exchange would then be due to low hydroxide ion concentration. Using the rate ratios, R_N/R_O, a calculation of the ratio k_2/k_{-1} at 35.5° gives a value of *ca.* 4×10^4.

If the major species, H_2O, is considered in place of OH^- in the previous mechanism, a similar calculation gives $k_{-1} \approx 300k_2$. Why water should be less reactive than ammonia is not clear to us, but if oxygen exchange is due only to the reaction of the intermediate with water, this is the apparent conclusion.

The above rate law for oxygen exchange is consistent with the difference in activation enthalpy for oxygen and nitrogen exchange and some curvature in the Arrhenius plot of the oxygen data.

It would be desirable to obtain more data on the oxygen-exchange reaction for the pentaammine as well as for nitrogen and oxygen exchange in the tetraammine.

Nitrogen and Oxygen Exchange between Hydroxopentaamminecobalt(III) and Solvent Species in Aqueous Ammonia. II. Cobalt(II)-Catalyzed Exchange[1]

Theodore J. Williams and John P. Hunt[2]

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received July 29, 1968*

Abstract: The effect of the electron-transfer reaction between $Co(NH_3)_5OH^{2+}$ and cobaltous ammines on the nitrogen and oxygen exchange between the cobaltic pentaammine and solvent species was observed by measuring these exchange rates in aqueous solutions of ammonia and Co(II). Previously measured electron-transfer rates were also remeasured using a different experimental technique. The rates of electron transfer and catalyzed nitrogen exchange were shown to follow the rate law, rate = $k[Co(NH_3)_5OH^{2+}][Co(NH_3)_5^{2+}]$. The lack of catalysis of oxygen exchange by Co(II) demonstrated a hydroxo-bridged mechanism for electron transfer. The rates of catalyzed nitrogen exchange were slower, relative to the electron-exchange rates, than expected for a simple hydroxo-bridged mechanism. This suggested the possibility of multiple bridging in the activated complex.

The electron-transfer reaction between $Co(NH_3)_5OH^{2+}$ and cobaltous ammine species, $Co(NH_3)_n^{2+}$, in aqueous ammonia solutions has been studied briefly using ^{60}Co as a tracer to measure the rates of cobalt exchange for various conditions.[3] A comparison of this reaction with the electron-transfer behavior in the $Co(NH_3)_6^{3+}$–$Co(NH_3)_n^{2+}$ system under similar conditions[4] suggests that it might proceed through a bridged intermediate in which the proposed activated complex is the symmetrical species, $(NH_3)_5Co–OH–Co(NH_3)_5^{4+}$. In support of this hypothesis, the rate law for the electron-transfer reaction appeared to have the form

$$\text{rate} = k[Co(NH_3)_5OH^{2+}][Co^{2+}][NH_3]^5$$

To more clearly elucidate aspects of the mechanism for electron exchange in this system, a study was made of the effect of the electron-exchange reaction on the exchange of the ammonia and hydroxide ligands in the cobaltic complex. The rates of nitrogen and oxygen exchange promoted by the electron transfer were found using the data in part I of this work.[5] The previously measured rates of cobalt exchange were also checked using a different method of removing oxygen from the reaction solution and a different separation procedure.

Experimental Section

Spectrophotometric Studies and Solution Composition. Spectra were taken in an attempt to detect any species formed by the combination of the cobaltic and cobaltous complexes. In an apparatus similar to that described in part I for preparing reaction solutions, solutions were prepared by separately degassing ammonia and $Co(NO_3)_2 \cdot 6H_2O$ and/or $[Co(NH_3)_5H_2O](ClO_4)_3$ solutions. The solutions were then mixed and transferred to an attached, evacuated, quartz 1-mm cell obtained from the Pyrocell Manufacturing Co. The cobaltous nitrate was a commercial product and the cobaltic complex was the same as that used in part I. The 1-mm cell was purchased with quartz to Pyrex sealed tubing to which a stopcock and taper joint were added. The spectra of solutions containing both Co(II) and $Co(NH_3)_5OH^{2+}$ were compared to the sum of absorbances of the analogous solutions containing either only Co(II) or $Co(NH_3)_5OH^{2+}$. The spectra were measured with a Cary Model 14 spectrophotometer.

Spectral experiments were done on acidified reaction solutions to observe changes in the solution as a result of the electron-transfer reaction. A reaction carried out at 35.5° and 0.33 *M* NH_3 was acidified at 80% exchange, and its spectrum was compared with the sum of the absorbances of analogous acidified solutions containing

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[1] This work supported by U. S. AEC Contract AT-(45-1)-2040 and is report No. RLO-2040-6.

[2] To whom inquiries should be addressed.

[3] E. Appelman, M. Anbar, and H. Taube, *J. Phys. Chem.*, **63**, 126 (1959).

[4] N. S. Biridar, D. R. Stranks, and M. S. Vaidya, *Trans. Faraday Soc.*, **58**, 2421 (1962).

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Table I. Cobalt-Exchange Results[a]

Expt no.	Temp, °C	$[NH_3]$,[b] M	$[R^{2+}]$,[c] M	$[ROH^{2+}]$,[c] M	Rate[d] $\times 10^4$ M/hr	Rate $\times 10^4$ M/hr	k[f] $\times 10^3$ M^{-1} sec^{-1}
1	35.5	0.127	0.0027	0.042	3.1	1.56 ± 0.12	0.38
2	35.5	0.429	0.0154	0.043	10.6	11.2 ± 2.6	0.47
3	35.5	0.672	0.0217	0.043		15.5 ± 0.4	0.46
4	35.5	7–8	~0.021	0.043		12.0[e]	~0.37
5	44.4	0.131	0.0023	0.042	5.8	4.6 ± 1.0	1.35
6	55.2	0.137	0.0019	0.041	13.0	8.3 ± 2.8	2.95

[a] For all samples $[Co(III)] = 0.043\ M$, $[Co(II)] = 0.0535\ M$, $[NH_4^+] = 0.98\ M$, and the ionic strength was 2.28 M. [b] Calculated free ammonia concentration. [c] R represents $Co(NH_3)_5$. Concentrations are calculated by the approximation method mentioned in the Experimental Section. [d] Rates previously measured (ref 3). [e] Only one experimental point was taken for these conditions. [f] Calculated from rate = $k[Co(NH_3)_5OH^{2+}][Co(NH_3)_5^{2+}]$.

the initial amounts of $Co(NH_3)_n^{2+}$ or $Co(NH_3)_5OH^{2+}$. In this case the absorbances were measured with a Beckman Model DU spectrophotometer.

The distribution of cobaltous amine species and the concentrations of the other species were calculated for the various initial conditions using literature values for the concentration product constants as a function of temperature and ionic strength for the following equilibria.

	Ref
$K_w = [H^+][OH^-]$	6, 7
$K_a = [NH_3][H^+]/[NH_4^+]$	8
$K_{5A} = [Co(NH_3)_5OH^{2+}][NH_4^+]/[Co(NH_3)_5H_2O^{3+}][NH_3]$	8
$k_n = [Co(NH_3)_n^{2+}]/[Co(NH_3)_{n-1}^{2+}][NH_3]$	8
$n = 1–6$	

The resulting 12 nonlinear equations needed to describe the system were solved by a computer-programmed approximation method.[9]

Nitrogen and Oxygen Exchange. The rates of nitrogen and oxygen exchange in the presence of cobaltous amines were measured by the same procedures used in part I with the exception that cobaltous nitrate was added to the reaction solutions. The degassing procedure was carried out before the Co(II) and ammonia solutions were mixed to remove oxygen from the solutions and to prevent the air oxidation of Co(II) which is easily accomplished in basic solution.

Cobalt Exchange. The exchange reaction was begun and quenched by the same procedure used for nitrogen exchange with a very dilute solution of ^{60}Co tracer added to the Co(II) stock solution. The precipitated $[Co(NH_3)_5H_2O]Br_3$ was heated overnight and weighed as $[Co(NH_3)_5Br]Br_2$. The weighed sample was suspended in a small amount of water in standard sample bottles. The activity of each sample was then measured by counting emitted γ rays. In most cases three experimental points were taken for each set of conditions. The rates were calculated by using the McKay treatment to find the half-time, $t_{1/2}$, which gives the rate as

$$\text{rate} = \frac{[Co(III)][Co(II)]0.693}{([Co(III)] + [Co(II)])t_{1/2}}$$

Results

Spectral Studies. The comparison of spectra showed that within the limits of spectrophotometric detection no new species are formed as a result of mixing Co(II) and $Co(NH_3)_5OH^{2+}$ in aqueous ammonia solution. The spectra taken after electron exchange showed that no change occurred in the reaction solution during the time for 80% exchange at 0.33 M NH_3. The previous work indicated by a similar experiment that 0.69 M NH_3 reaction solutions do not change during the course of the electron-transfer reaction.[3]

Cobalt Exchange. The results of the cobalt-exchange experiments are presented in Table I along with those rates previously found for the same conditions. The rates measured previously are in general somewhat higher than those found in this work. This may be because of a small but continuous supply of oxygen in the earlier experiments which used a nitrogen atmosphere to prevent air oxidation. It has been shown that small amounts of oxygen may catalyze the rate of electron transfer in this system.[10] Rather large deviations in the half-times were found as indicated by the errors, 2σ, listed in Table I. This is thought to be the result of the procedure used for preparing the samples for counting.

The rate constants in Table I indicate that the electron-transfer reaction most closely follows the rate law

$$\text{rate} = k[Co(NH_3)_5OH^{2+}][Co(NH_3)_5^{2+}]$$

Experiments 3–4 in Table I show that the $Co(NH_3)_6^{2+}$ is not utilized in the mechanism for electron exchange since the rate appears to decrease while the concentration of the cobaltous hexaammine species increases from 0.003 to *ca.* 0.033 M.

The activation parameters were calculated by the method of least squares and found to be $\Delta H^{\ddagger} = 20 \pm 4$ kcal mole^{-1} and $\Delta S^{\ddagger} = -7.3 \pm 12$ eu. The parameters previously given are $\Delta H^{\ddagger} = 15.6$ kcal mole^{-1} and $\Delta S^{\ddagger} = -8.0$ eu.[3]

Oxygen Exchange. As shown by the McKay plot in Figure 1, the presence of Co(II) in the reaction solution does not affect the rate of exchange found for the same solutions not containing Co(II). Within experimental error the points for the four sets of conditions give the same half-time (*i.e.*, the same rate).

Nitrogen Exchange. The exchange of ammonia is significantly catalyzed by the presence of Co(II) in the reaction solution. This is demonstrated by the data given in Table II. The rate of exchange due to the electron-transfer reaction, the "catalyzed rate," is assumed to be the difference between the observed rate of exchange in the presence of Co(II) and the rate in the same solutions not containing Co(II) given in the

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(7) H. S. Harned and B. B. Owen, "Electrolytic Solution," Reinhold Publishing Corp., New York, N. Y., 1958, pp 752–754.

(8) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, pp 180–190, 278–285.

(9) Address inquiries concerning computer program to T. J. Williams, Department of Chemistry, University of California, Los Angeles, Calif. 90024.

(10) W. B. Lewis, C. D. Coryell, and J. W. Irvine, *J. Chem. Soc.*, S386 (1949).

Table II. Nitrogen-Exchange Results

Expt[a] no.	Obsd rate, *M*/hr	Uncatalyzed rate,[b] *M*/hr	Catalyzed rate, *M*/hr	Catalyzed $k \times 10^3$ M^{-1} sec^{-1} [c]
1	8.0×10^{-4}	3.2×10^{-4}	4.8×10^{-4}	1.2
2	46.0×10^{-4}	3.2×10^{-4}	42.8×10^{-4}	1.8
3	63.6×10^{-4}	3.2×10^{-4}	60.4×10^{-4}	1.8
5	26.1×10^{-4}	14.4×10^{-4}	11.7×10^{-4}	3.4
6	111×10^{-4}	78×10^{-4}	33×10^{-4}	11.8

[a] The conditions of the experiments are the same as those for the corresponding experiment numbers in Table I. [b] Taken from part I (ref 5). [c] Found from rate = $k[\mathrm{Co(NH_3)_5OH^{2+}}][\mathrm{Co(NH_3)_5{}^{2+}}]$.

uncatalyzed exchange paper.[5] The error in the observed rates appeared to be less than ±5% of their values.

The rate constants fit the rate law given for electron transfer. The activation parameters for catalyzed nitrogen exchange were calculated to be $\Delta H^{\ddagger} = 22 \pm 1$ kcal mole^{-1} and $\Delta S^{\ddagger} = -1 \pm 7$ eu.

Discussion

The data for cobalt exchange confirm the earlier work done on this reaction. The rate law found for electron transfer indicates that the initial step in the mechanism involves the combination of $\mathrm{Co(NH_3)_5OH^{2+}}$ and $\mathrm{Co(NH_3)_5{}^{2+}}$. This does not necessitate a bridged structure for the activated complex, and an outer-sphere mechanism such as that discussed in the hexaamminecobalt(III) work[4] could be operative. The enthalpy of activation is in the range normally found for bridged mechanisms.[11]

The observation that the electron-transfer reaction does not catalyze the rate of oxygen exchange demonstrates that the hydroxo ligand acts as a bridge between the metal ions in the activated complex. Since only the solvent species are initially enriched with the oxygen isotope, the mechanism of electron transfer does not allow free hydroxide to enter the complex. The bridged mechanism is given by the scheme

$$\mathrm{Co(NH_3)_5OH^{2+} + {*Co}(*NH_3)_5{}^{2+} \rightleftharpoons (NH_3)_5Co{-}OH{-}{*Co}(*NH_3)_5{}^{4+}}$$

$$\mathrm{Co(NH_3)_5{}^{2+} + {*Co}(*NH_3)_5OH^{2+} \rightleftharpoons (NH_3)_5Co{-}OH{-}{*Co}(*NH_3)_5{}^{4+}}$$

In this mechanism the hydroxo ligand is always involved in an inert Co(III)–OH bond preventing exchange with hydroxide in solution. Since the cobaltous ammines exchange ligands very rapidly in solution, an outer-sphere or nonbridged exchange would occur by the mechanism

$$\mathrm{Co(NH_3)_5OH^{2+} + {*Co}(NH_3)_5{*OH}^{+} \rightleftharpoons Co(NH_3)_5OH^{+} + {*Co}(NH_3)_5{*OH}^{2+}}$$

where the cobaltous ammine would initially be enriched with the oxygen isotope, *O. The isotope would then be retained in the cobaltic complex formed by electron transfer.

The similarity in both the activation parameters and the fit of the data to the proposed rate law for cobalt and catalyzed nitrogen exchange indicate that both are the result of the same mechanism. The proposed bridged mechanism would cause the observed catalysis of nitrogen exchange since the initial cobaltous pentaammine would be enriched with the ^{15}N isotope.

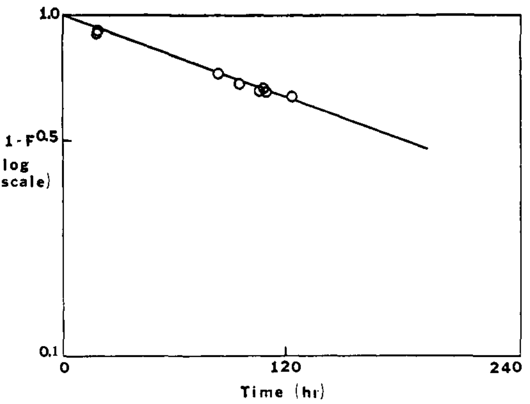

Figure 1. Comparison of McKay plots for oxygen exchange at 35.5°. The plot includes experimental points for each of the initial conditions: 0.69 *M* $\mathrm{NH_3}$ and 0.0535 *M* Co(II), 0.69 *M* $\mathrm{NH_3}$ and 0.0 *M* Co(II), 0.33 *M* $\mathrm{NH_3}$ and 0.0535 *M* Co(II), and 0.33 *M* $\mathrm{NH_3}$ and 0.0 *M* Co(II). All other initial conditions are the same for all four cases.

The simple bridged mechanism which has been given would be expected to result in the exchange of five ammine ligands for each electron exchange. Therefore, the rates or the rate constants from the given rate law for catalyzed nitrogen exchange are expected to be five times the rates or rate constants for electron transfer. Where possible, comparisons gave the ratio of the rate constant for nitrogen exchange to the rate constant for electron exchange as 3.2, 3.8, 3.9, 2.5, and 4.0. These ratios strongly suggest that less than five ammine ligands are exchanged per electron transfer. Since it was the nitrogen-containing species in solution which were initially enriched, the ratios further suggest that some of the unenriched ammonia on the initial cobaltic pentaammine is somehow transferred to the cobaltic complex resulting from electron exchange. According to Taube's classification of bridged and nonbridged mechanisms,[12] this experimentally defines bridging in the activated complex by at least one of the ammine ligands originating from the initial Co(III). Ammonia-bridged activated complexes are, however, difficult to imagine, particularly since the electron-transfer data indicate that the rate is not pH dependent[3] and that ten ammonia molecules are in the activated complex. Possibly the distortions in the hydroxo-bridged structure needed to match the energies of the electronic sites used for the electron transfer are such that after electron exchange an ammine ligand on the initial Co(III) is in the position of an entering group of the newly formed Co(III) while an ammonia molecule initially on Co(II) acts as a leaving group. The distinction between this idea and actual bridging is slight. The previous data on electron transfer showed a deviation in the rate law from fifth order in free ammonia when $[\mathrm{NH_3}] < 0.3$ *M*.[3] The order dropped as low as two for low ammonia concentrations. This observation also supports the possibility of multiple bridging or transfer in the mechanism. More studies along these lines would seem to be in order to see if some general phenomenon is involved.

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