32. *Exchange Reactions of Co-ordinated Ammonia: Isotopic Study of the Lability of Ammines of Copper*(II), *Nickel*(II), *Platinum*(II), *Chromium*(III), *and Cobalt*(III) *in Aqueous Solution.*

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Exchange of [^{15}N]ammonia with some transition-metal ammines in aqueous solution has been studied. It has been shown that the complexes, $[Pt(NH_3)_4]^{2+}$, $[Cr(NH_3)_6]^{3+}$, and $[Co(NH_3)_6]^{3+}$, and a number of substituted cobalt(III) ammines, undergo no exchange, or only a very slow exchange, though the ammines $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ undergo complete exchange within the time of separation. When two or more NO_2 ligands are substituted in a cobalt(III) ammine they appear to exert a labilising influence on *trans*-NH_3 ligands.

CO-ORDINATION compounds of transition elements of the type MA_n undergo replacement reactions which are usually either very fast or very slow, and this has given rise to the classification of such complexes in two groups called " labile " and " inert." In studying this property the exchange reaction of an isotopically labelled ligand has many advantages over other types of replacement. Such exchange has been studied for complex cyanides,[1] for complex oxalates by using labelled carbon and oxygen,[2] and for hydrated metal cations by using $H_2{}^{18}O$.[3] Two studies have been reported of exchange reactions of complex

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[1] Grinberg and Nikol'skaya, *Zhur. priklad. Khim.*, 1951, **24**, 893; Adamson, Welker, and Volpe, *J. Amer. Chem. Soc.*, 1950, **72**, 4030; Long, *ibid.*, 1951, **73**, 537; Adamson, Welker, and Wright, *ibid.*, p. 4786; Adamson, *ibid.*, p. 5710; MacDiarmid and Hall, *ibid.*, 1954, **76**, 4222; Goodenow and Garner, *ibid.*, 1955, **77**, 5268; Baadsgaard and Treadwell, *Helv. Chim. Acta*, 1955, **38**, 1669; Clark, Curtis, and Odell, *J.*, 1954, 63.

[2] Long, *J. Amer. Chem. Soc.*, 1939, **61**, 570; 1941, **63**, 1353; Haenny and Wickler, *Helv. Chim. Acta*, 1949, 2444; Kant and Kohman, 118th Meeting Amer. Chem. Soc., 1950; Bunton, Bishop, Carter, Llewellyn, Odell, Olliff, and Yih, Austral. Atomic Energy Symp., 1958; Graziano and Harris, *J. Phys. Chem.*, 1959, **63**, 330; Barton and Harris, *J. Chem. Phys.*, 1961, **34**, 71; Barton and Harris, *Inorg. Chem.*, 1962, **1**, 251.

[3] Hunt and Taube, *J. Chem. Phys.*, 1950, **18**, 757; Friedman, Taube, and Hunt, *ibid.*, p. 759; Hunt and Taube, *ibid.*, 1951, **19**, 602; Rutenberg and Taube, *ibid.*, 1952, **20**, 825; Plane and Taube, *J. Phys. Chem.*, 1952, **56**, 33; Hunt and Plane, *J. Amer. Chem. Soc.*, 1954, **76**, 5960.

ammines with the solvent ammonia,[4] and Ishimori[5] has shown that in aqueous solution the ions $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$, and $[Ag(NH_3)_2]^{2+}$ belong to the labile class as they show rapid exchange with $[^{15}N]$ammonia.

The present Paper describes some experiments on the exchange of isotopically labelled ammonia in aqueous solution with some complexes in the inert class, as well as with two in the labile class.

The complex ammines of copper and nickel underwent complete exchange within the time of separation and so fall into the " labile " class. All the complexes listed in Table 1 showed little exchange in many days and are therefore classified as " inert."

TABLE 1.

Experiments demonstrating lack of exchange in " inert " complexes.

Complex	Temp.	No exchange in days	Complex	Temp.	No exchange in days
$[Pt(NH_3)_4]Cl_2$	24·8°	217	*trans*-$NH_4[Co(NH_3)_2(NO_2)_4]$	24·8°, 34·7	142, 259
$[Cr(NH_3)_6](NO_3)_3$	24·8	0·3 *		These compounds are " inert," but the exchange results are difficult to interpret because of extraneous substitution.	
$[Co(NH_3)_6]Cl_3$	24·8	162	*cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$		
$[Co(NH_3)_4(C_2O_4)]Cl$	24·8	120	*trans*-$[Co(NH_3)_3(NO_2)_3]$		
$[Co(NH_3)_5(NO_2)]Cl_2$	24·8, 34·7	183, 99	*cis*-$[Co(NH_3)_3(NO_2)_3]$		
trans-$[Co(NH_3)_4(NO_2)_2]Cl$	24·8, 34·7	203, 259			

* This compound could not be investigated beyond 8 hours because of rapid aquation.

The hexamminechromium(III) ion suffers considerable aquation in 8 hours but the absence of isotopically labelled ammonia in the unchanged complex shows that the aquation has an irreversible first step.

The absence of exchange in the case of the hexamminecobalt(III) ion is of special interest. Bjerrum[6] has given values for the stepwise formation constants of this ion at 30°, his value for the final step being log $K_6 = 4{\cdot}41$. If the equilibrium $[Co(NH_3)_6]^{3+} + H_2O \rightleftharpoons [Co(NH_3)_5H_2O]^{3+} + NH_3$, were established in aqueous solution at room temperature, one would expect to find dilution of the isotopic label in the free ammonia, but we have shown that dilution is negligible after 162 days at pH 2·4 or 9·9.

A more sensitive method of detecting the presence of free ammonia is by isotopic dilution analysis. If labelled ammonia is added to the solution of dissociating complex in an amount to make its concentration equal to that expected for the free ammonia, one would expect a 50% change in isotopic abundance. $[^{15}N]$Ammonium nitrate ($2{\cdot}93 \times 10^{-3}$M) was added to an aqueous hexamminecobalt(III) chloride solution (0·22M) which had been set aside for 162 days at 24·8°. (The concentration of dissociated ammonia in such a solution may be calculated, by using the value of k_6 above, to be $2{\cdot}93 \times 10^{-3}$.) The free ammonia was then separated by vacuum-distillation and assayed for nitrogen-15. The initial abundance of ^{15}N was 3·32%; that calculated for equilibrium aquation was 1·64%; that observed was 3·15%. Thus dissociation of the complex in 162 days is not greater than 10% of the value required by the value for k_6.

Bjerrum evaluated the constant k_6 by measuring the hydrolysis constant for the reaction, $[Co(NH_3)_6]^{3+} + H_2O \rightleftharpoons [Co(NH_3)_5OH]^{2+} + NH_4^+$, and then measuring the acid dissociation constant for aquopentamminecobalt(III). The hydrolytic equilibrium was established by shaking the hexammine complex with dilute ammonia and charcoal or colloidal platinum. We have repeated this procedure, using isotopically labelled ammonia and sugar charcoal. Shaking was continued until the optical density between 481 and 590 mμ became constant, which corresponds, as Bjerrum has shown, to the production of a steady concentration of hydroxopentamminecobalt(III). The free ammonia was then

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[4] Weisendanger, Jones, and Garner, *J. Chem. Phys.*, 1957, **27**, 668; Sutter and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 6420.

[5] Ishimori, *Bull. Chem. Soc. Japan*, 1960, **33**, 520.

[6] Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941, p. 285.

separated by distillation and assayed for nitrogen-15. The isotopic abundance corresponds to the value calculated for complete exchange.

Successful attempts to establish the equilibrium were made by using activated charcoal and platinum black as heterogeneous catalysts. Silica gel and activated alumina were not effective. Even with an efficient catalyst, equilibrium could not be established in the absence of ammonia or ammonium ions; *e.g.*, no hydrolysis took place in 10^{-3}M-sodium hydroxide in 3 days at 24·8°.

The hydrolytic reaction does represent a true equilibrium, because the same value for the equilibrium constant was obtained by observing the fall in molar extinction coefficient when a solution of $[Co(NH_3)_5(H_2O)]Cl_3$ was shaken with ammonia in the presence of activated charcoal. Under the conditions in which the heterolytic equilibrium was established, *e.g.*, in 3 days at 24·8° in a solution (" complexed " ammonia = 0·05M, " free " ammonia = 0·30M) containing 0·02 g. of charcoal in 10 ml., the complex ion $[Co(NH_3)_6]^{3+}$ exchanged all its ammonia with $[^{15}N]$ammonia. It is conceivable that this exchange took place as the result of electron transfer involving the cobaltous ion. Hoshowsky *et al.*[6a] have shown that $Co(NH_3)_6{}^{3+}$ and Co^{2+} in ammoniacal solution undergo some 5·6% electron transfer in 17 days. We have found approximately 2·5% exchange of $[^{15}N]$ammonia in 13 days in the presence of the cobaltous ion, so that this route for ligand exchange remains a possibility.

It was difficult to study the exchange of amminenitro-complexes of cobalt(III) because hydrolysis is much faster than exchange. However, it was possible to relate qualitatively the stability of the complexes with respect to substitution, to the number and relative positions of the various nitro and ammonia groups. With one nitro-group, as in $[Co(NH_3)_5NO_2]^{2+}$, or with an even number *trans* to each other, as in *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ and *trans*-$[Co(NH_3)_2(NO_2)_4]^-$, there was no uptake of $[^{15}N]$ammonia from solution. However, with more than one nitro-group and at least one *trans* to an NH_3 group, as in *cis*-$[Co(NH_3)_4(NO_2)_2]^+$ and *trans*-$[Co(NH_3)_3(NO_2)_3]$, $[^{15}N]$ammonia was taken into the complex. The same effect is probably operative with the ammine, *cis*-$[Co(NH_3)_3(NO_2)_3]$, for which a fairly rapid migration of NH_3 groups from the complex to the solution was observed. Thus it seems that the nitro-ligands labilise the complex.

For the nitrate, *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$ at 24·8°, a slight increase in atom % abundance of nitrogen-15 was observed in samples of complex precipitated over a period of 82 days. This effect was enhanced at 34·7°. A typical result is shown in Table 2. The results indicate that direct exchange (if any) is not the only process taking place. The results in excess of the calculated value (0·63) for complete exchange can not readily be accounted for. That other substitutions are occurring is indicated by the ammonia : nitrogen dioxide ratio in the precipitate obtained by adding propan-2-ol after the nitro-ammine complex had been kept at 90° in concentrated aqueous ammonium nitrate for 2 hours. The ratio $NH_3 : NO_2$ originally 2 : 1 had changed to 2·9 : 1.

TABLE 2.

" Complexed " ammonia = 0·1023M. " Free " $[^{15}N]$ammonia = 0·0245M.
Nitrogen-15 = 3·28 atom % excess abundance.
Calc. value for complete exchange = 0·63 atom % excess abundance of ^{15}N.

Time (days)	0	18	42	60	99	116
^{15}N (atom % excess)	0·08	0·28	0·59	0·61	1·03	1·19

When the ion *cis*-$Co(NH_3)_4(NO_2)_2$ is allowed to react with both oxalate and $[^{15}N]$-ammonia, no nitrogen-15 appears in the complex. This observation and the changes in the characteristic absorption peak are in accord with the view that the oxalate ions replace the nitro-groups and that this process is faster than the substitution of nitro by ammonia.

[6a] Hoshowsky *et al.*, *Canad. J. Res.*, 1945, **27**, *B*, 285.

TABLE 3.

Temp. = 25·0°. " Complexed " ammonia = 0·0247M. " Free " [^{15}N]ammonia = 0·0249M.
Nitrogen-15 = 3·28 atom % excess abundance.
Calc. value for complete exchange = 1·63 atom % excess abundance of ^{15}N.

Time (days)		0	4	48	60	265
^{15}N (atom % excess)	" Complexed "	0·30	0·23	0·37	0·47	0·91
	" Free "	3·06	3·11	2·59	2·54	1·97

In the case of the complex *trans*-$Co(NH_3)_3(NO_2)_3$ there was extensive decomposition, as shown by the gradual appearance of a brown precipitate. The relative importance of such decomposition and reactions incorporating labelled ammonia into the complex was evaluated by observing both the rate of isotopic dilution of the [^{15}N]ammonium ions and the rate of appearance of [^{15}N]ammonia in the complex. A typical result is shown in Table 3. Although there is some scatter in these results, it is apparent that the abundance of nitrogen-15 in the " free " ligand decreases faster than that in the " complexed " ligand increases. It appears that some exchange and/or substitution of nitro by ammonia does occur, but this is accompanied by considerable aquation.

When the exchange reaction was carried out in diethylene glycol no precipitate was formed. In dry ethylene glycol the atom % abundance of nitrogen-15 as " free " ammonia decreased only slightly in 383 days. Since there was no visible decomposition within this time, the observed decrease probably represented a true exchange reaction. In a mixture (1 : 1) of diethylene glycol and water the rate of decrease in abundance of nitrogen-15 in the " free " ligand was 1/5 of that in water.

The ion, *cis*-$[Co(NH_3)_3(NO_2)_3]^+$, is much less stable in aqueous solution than its *trans*-isomer. Visible decomposition to cobaltic hydroxide was much more obvious for the *cis*-compound. The atom % abundance of nitrogen-15 in the " free " ligand also decreased much faster. A typical result is in Table 4. The rate of decrease of atom % abundance of nitrogen-15 in the " free " ligand was much reduced if the decomposition was depressed by addition of diethylene glycol; in 50% aqueous diethylene glycol it was 50 times slower than in water.

TABLE 4.

Temp. = 25·0°. " Complexed " ammonia = 0·0248M. " Free " [^{15}N]ammonia = 0·246M.
Nitrogen-15 = 3·27 atom % excess abundance.
Calc. value for complete exchange = 1·63 atom % excess abundance of ^{15}N.

Time (days)	0	2	4	7	9	11
^{15}N (atom % excess)	2·97	2·75	2·58	2·61	2·43	2·28

EXPERIMENTAL

Materials.—The following ammines were prepared by standard methods and characterised by analysis: $[Pt(NH_3)_4]Cl_2$,[7] $[Co(NH_3)_6]Cl_3$,[8] $[Ni(NH_3)_6]Br_2$,[9] $[Cr(NH_3)_6](NO_3)_3$,[10] $[Co(NH_3)_4C_2O_4]Cl$,[11a] $[Co(NH_3)_5(NO_2)]Cl_2$,[11b] *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$,[11b] *trans*-$[(Co(NH_3)_4(NO_2)]Cl$,[11b] *trans*-$[Co(NH_3)_3(NO_2)_3]$,[11b] $NH_4[Co(NH_3)_2(NO_2)_4]$,[11b] and *cis*-$[Co(NH_3)_3(NO_2)_3]$.[12]

Exchange.—The exchange medium was a solution of [^{15}N]ammonium nitrate containing *ca.* 3 atoms % excess abundance of nitrogen-15. Solutions were kept in stoppered bottles, enclosed in metal containers, before immersion in a thermostat-bath. At intervals, samples (sufficient to yield 1 ml. of nitrogen at N.T.P.) were removed and either the " free " or the " complexed " ligand was converted through ammonia into ammonium sulphate, which was treated with sodium hypobromite to liberate nitrogen for analysis in a mass-spectrometer (Metropolitan Vickers M.S.3).

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[7] Keller, *Inorg. Synth.*, 1946, **2**, 250.
[8] Bjerrum and McReynolds, *Inorg. Synth.*, 1946, **2**, 216.
[9] Watt, *Inorg. Synth.*, 1950, **3**, 194.
[10] Christensen, *Z. anorg. Chem.*, 1893, **4**, 229.
[11] Jörgensen, *Z. anorg. Chem.*, (*a*) 1896, **11**, 429; (*b*) 1898, **17**, 455.
[12] Sueda, *Bull. Chem. Soc. Japan*, 1938, **13**, 450.

Separation.—In the exchange solutions of ions $[Cu(NH_3)_4]^{2+}$, $[Cr(NH_3)_6]^{3+}$, and $[Co(NH_3)_6]^{3+}$ the samples were frozen in liquid air after addition of a few drops of N-alkali, and were distilled in an evacuated, inverted U tube, the receiver being cooled in liquid air. This liberated " free " ligand and did not decompose the complex.

In solutions of the complex $NH_4[Co(NH_3)_3(NO_2)_3]$ the free ammonium ions were precipitated with an excess of sodium nitritocobalt(III), and the ammonia of the complex was obtained by decomposing the filtrate with sodium hydroxide.

The other complexes were isolated in solid form before decomposition. The following precipitants were used: for $[Ni(NH_3)_6]Br$ and *cis*-$[Co(NH_3]_4(NO_2)_2]NO_3$, propan-2-ol; for $[Pt(NH_3)_4]Cl_2$, acetone; for *trans*-$NH_4[Co(NH_3)_2(NO_2)_4]$, silver nitrate; for $[Co(NH_3)_5NO_2]Cl_2$, potassium oxalate (precipitates the oxalate); and for $[Co(NH_3)_4C_2O_4]Cl$, sodium perchlorate (precipitates the perchlorate).

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Added in Proof. Since this report was submitted, Ruterberg and Drury (*Inorg. Chem.*, 1963, **2**, 219) have reported that $Co(NH_3)_6^{3+}$ undergoes a very slow exchange reaction with [^{15}N]ammonium ions.

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