praseodymium compound was white, but the cerium compound was yellow. This would indicate oxidation of some Ce(III) to Ce(IV). Since in these structures the cations are located in only partially filled tunnels or cages formed by $TaO_6$ octahedra,[8] charge compensation is most likely achieved by an increase in cation vacancies, either K(I) or Ce(III). However, the deficiency was less than the precision (about 5%) of our fluorescence analysis,[9] which gave a 1:1:4 ratio for K:Ce:Ta.

[9] We wish to thank Mr. J. H. Richardson of this organization for carrying out our quantitative X-ray fluorescence analyses.

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Contribution from the Department of Chemistry,
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# The Mechanism of the Reaction of Carbonatopentaamminecobalt(III) with Divalent Ions

By R. B. Jordan, A. M. Sargeson, and H. Taube

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The investigation to be described arose from the observation that the reaction of $(NH_3)_5CoCO_3^+$ with $Pb^{2+}(aq)$ or $Hg^{2+}(aq)$ gives an almost immediate precipitate of the metal ion carbonate leaving $(NH_3)_5CoOH_2^{3+}$ in solution, while the reaction with $Ba^{2+}(aq)$

$$(NH_3)_5CoCO_3^+ + M^{2+} + H_2O \longrightarrow (NH_3)_5CoOH_2^{3+} + MCO_3 \quad (1)$$

is at least one hundred times slower. Of interest in these systems is the position of bond rupture—a question that can be settled by oxygen tracer experiments—and the difference in rates for different ions—a question that is not at all easily settled.

## Experimental Section

(1) **Tracer Studies on the Position of Bond Rupture.**—The reactant solutions made up in $O^{18}$-enriched water were initially ~0.1 *M* in $(NH_3)_5CoCO_3NO_3$[1] and with $Hg(OAc)_2$, $Pb(NO_3)_2$, or $Ba(NO_3)_2$ at equivalent concentrations. The reaction time, 4 min for the first two reagents, was sufficient to ensure complete reaction in these cases. In the case of $Ba^{2+}$ as reactant the reaction time was 2 hr and the reaction was only 30% complete in this time.

After reaction, the carbonates (in the case of $Hg^{2+}$ as reactant, the product was probably the basic carbonate) were separated by filtration; the precipitates were washed lightly with water, then with methanol, and dried in a vacuum desiccator for 2 days. The precipitates were then treated with acid, the $CO_2$ formed being flushed out with He. Under these conditions very little exchange with the solvent takes place.

The filtrates resulting from the separation of the insoluble carbonates were immediately acidified with excess cold concentrated HBr; the solid aquo bromide was collected, washed with a small amount of water, then with methanol, and dried for 12 hr in a vacuum desiccator. The contained water was liberated by heating the solid. The water-oxygen was converted to $CO_2$ following the Anbar–Gutman[2] procedure, and the resulting $CO_2$ was purified by gas chromatography.

It should be recognized that the HBr treatment converts $(NH_3)_5CoCO_3^+$ to $(NH_3)_5CoOH_2^{3+}$. Thus in the case of the $Ba^{2+}$ system, 70% of the aquo bromide results from the release by acid of $CO_2$ from the unreacted carbonato complex. The reaction of the carbonato complex with acid is known[3] to take place leaving the bridging oxygen in the aquo product. To determine the isotopic composition only of the aquo product resulting from the reaction of the complex ion with $Ba^{2+}$, an aliquot of the filtrate was taken and treated with LiBr. This treatment leaves $(NH_3)_5CoCO_3^+$ intact and in solution.

(2) **Exchange of Oxygen between $(NH_3)_5CoCO_3^+$ and $H_2O$.**—The reaction of $(NH_3)_5CoCO_3^+$ with $Ba^{2+}$ is so slow that exchange of oxygen between the complex and solvent may affect the results. An experiment was undertaken to measure the rate of exchange, mildly alkaline conditions being chosen to avoid a contribution to the reaction by a hydrogen ion catalyzed path. The reactant solution, 0.10 *M* $(NH_3)_5CoCO_3^+$, was made up in $O^{18}$-enriched water, and the pH was adjusted to 9.6 using NaOH. Aliquots were taken at intervals and treated with cold concentrated HBr. The $CO_2$ was collected using a continuous stream of He, and the aquo complex formed was treated as described above.

For all experiments the isotopic composition of the solvent was determined by equilibrating it with $CO_2$; all isotopic compositions were determined by readings on $CO_2$ using an Atlas M 86 mass spectrometer; the temperature was 25°.

## Results

The results of the tracer experiments are summarized in Table I, and of the exchange experiment in Table II.

Table I

Tracer Results on the Reaction of $Hg^{2+}$, $Pb^{2+}$, and $Ba^{2+}$ with $(NH_3)_5CoCO_3^+$
(Complex of normal isotopic composition)

| | Enrichment ratio[a] | | | % oxygen from solvent in | |
|---|---|---|---|---|---|
| Ion | Solvent | $MCO_3$ | $(NH_3)_5$-$CoOH_2^{3+}$ | $MCO_3$ | $(NH_3)_5$-$CoOH_2^{3+}$ |
| $Hg^{2+}$ | 8.85 | 3.67 | 1.57 | 34 | 7.3 |
| $Pb^{2+}$ | 7.40 | 2.90 | 1.02 | 30 | 0.3 |
| $Ba^{2+}$ | 7.41 | 3.52 | 1.52[b] | 39 | 8.0 |
| | | | 3.06[c] | 39 | 32 |

[a] Isotopic ratio compared to that of a standard sample of $CO_2$. [b] Aquo derived by treating product solution with HBr. [c] Aquo precipitated with LiBr.

Table II

Oxygen Exchange between Solvent and $(NH_3)_5CoCO_3^+$
(pH 9.6; 25°)

| | % exchange | |
|---|---|---|
| Time, min | $CO_2$[a] | $(NH_3)_5CoOH_2^{3+}$[b] |
| 15 | 9.8 | 0 |
| 45 | 13.9 | 0 |
| 75 | 20.1 | 0 |
| 200 | 31.2 | 0.3 |
| 1080 | 68.2 | 3.3 |

[a] As found in the $CO_2$ formed when the reactant solution was treated with HBr. [b] As found in the aquo formed on treatment as above.

## Discussion

Two facts emerge from the results for the $Hg^{2+}$ and $Pb^{2+}$ reactions: there is little or no enrichment in the

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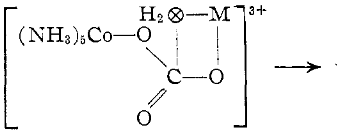
[1] Prepared by the method of A. B. Lamb and K. J. Mysels, *J. Am. Chem. Soc.*, **67**, 468 (1945).

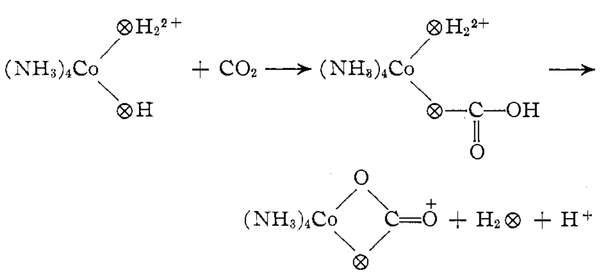
[2] M. Anbar and S. Gutman, *J. Appl. Rad. Isotopes*, **5**, 223 (1959).

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

resulting aquo complex and only one oxygen atom in the metal ion carbonate is enriched. These facts show that under the influence of the metal ion, the carbon-bridging oxygen bond breaks and that an oxygen derived from solvent takes the place on C(IV) of the oxygen lost to Co(III). The detailed mechanism expressed by eq 2 is consistent with all the facts, though it is of course not proven that the oxygen atom incorporated into $CO_3^{2-}$ comes directly from the coordination sphere of $M^{2+}$ rather than from the solvent. This mechanism is partly analogous to the formation of the carbonatotetraamminecobalt(III) ion from hydroxyaquotetraamminecobalt(III), *i.e.*



$$MCO_2\otimes + (NH_3)_5CoOH_2^{3+} \quad (2)$$



(3)

where $CO_2$ adds to one coordinated oxygen and subsequently one coordinated water is lost.[4]

The fact that $CO_2$ rather than $CO_3^{2-}$ is removed from the carbonato complex is consistent with the speed of the reactions with $Hg^{2+}$ and $Pb^{2+}$. Substitution at Co(III) in the ammine complexes is usually slow and thus Co–O bond fission in the present reaction might be expected to be slow. In the presence of $H^+$, the release of $CO_2$ from the carbonato complex takes place rapidly, with retention of the Co–O bond, as in the present system. The analogy between the reaction with $H^+$ and with $Pb^{2+}$ or $Hg^{2+}$ is by no means complete, however. With $H^+$ as reactant, $H_2CO_3$ is *not* formed as an intermediate; *i.e.*, the coordination number 3 for C(IV) is not maintained as it is when $Pb^{2+}$ or $Hg^{2+}$ react.

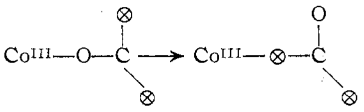
At least one oxygen derived from the solvent must appear in the products $MCO_3$ and $(NH_3)_5CoOH_2^{3+}$ between them. When $Pb^{2+}$ is a reactant, the one solvent oxygen is accounted for without complication, but when $Hg^{2+}$ reacts, more than one solvent oxygen appears in the products. Exchange must occur in the course of the reaction, but whether it is between the carbonato complex and solvent, induced by $Hg^{2+}$, or between the product aquo ion and solvent catalyzed by $Hg^{2+}$, or even between the mercuric carbonate and solvent, is not settled by the present observations. The spontaneous exchange between the aquo product and solvent is far too slow to account for the excess solvent oxygen in the products. If exchange between the carbonato complex or mercuric carbonate and solvent accounts for the excess incorporation of solvent oxygen, we would be admitting that some Co–O bond breaking occurs and would need to assume that the defect in solvent oxygen in the carbonate is exactly made up by exchange. The alternatives featuring carbonate exchange seem less likely than direct exchange between the aquo product and solvent catalyzed by mercuric ion. An interesting but unproven possibility for an effect of $Hg^{2+}$ is that it associates with an amido group formed by the loss of a proton from a coordinated ammonia.

The interpretation of the results of the reaction with $Ba^{2+}$ is by no means simple. No unambiguous conclusion about mechanism can be based on the 39% incorporation of solvent oxygen into $BaCO_3$; the precipitate was in contact with the solvent so long that exchange with solvent oxygen may have occurred. The 32% enrichment in the aquo sample obtained by using LiBr as precipitant does suggest that although most of the reaction takes place by C–O fission, Co–O fission is competitive with it. Here too, spontaneous exchange between the product aquo ion and solvent cannot account for the effects observed; the half-time for the exchange reaction is 32.7 hr at 25°.[5] It should be noted that the results obtained for the two aquo samples are in good agreement; the labeled aquo (30%) in the HBr case is diluted by normal aquo (70%) formed in the decomposition of $(NH_3)_5CoCO_3^+$ by acid. The results obtained with $Ba^{2+}$ as reactant show excess incorporation of solvent oxygen to the extent of 0.49 atom per act of hydrolysis. Just where the exchange occurs is not settled by our work. If it takes place between the product aquo and solvent catalyzed by $Ba^{2+}$, then our conclusion that there is a dual mechanism for bond breaking is unjustified, but a catalyzed exchange seems to be a very unlikely possibility in this case.

The extent of net dissociation in the exchange experiment cannot have been large. The reaction

$$(NH_3)_5CoCO_3 + OH^- = (NH_3)_5CoOH^{2+} + CO_3^{2-}$$

consumes $OH^-$ and complete consumption of $OH^-$ would account for only a small fraction of the complex ion. The interesting result is that there is exchange of coordinated oxygen and that this exchange proceeds much more rapidly for the singly ligated oxygens than for that which is ligated both to C and to Co. The interchange process



thus has a half-life well in excess of 18 hr at 25°. The exchange is rapid enough that it may account for the excess incorporation of solvent oxygen into the products in the case of the $Ba^{2+}$ system.

While the tracer experiments establish an important feature of the mechanism and thus provide a basis for discussing the rate differences, they do not explain them. Removal of $CO_2$ as $CO_3^{2-}$ by Co–O---C bond rupture is

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[4] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953).

[5] H. R. Hunt and H. Taube, *ibid.*, **80**, 2642 (1958).

much slower when $Ba^{2+}$ is a reactant than it is when $Pb^{2+}$ or $Hg^{2+}$ react. The difference is in line with the greater capacity $Hg^{2+}$ or $Pb^{2+}$ have compared to $Ba^{2+}$ in polarizing associated ligands. Some related observations are these: $Ag^+$ reacts rapidly with $(NH_3)_5CoCO_3^+$; the reactions of $Ni^{2+}$, $Cu^{2+}$, or $Co^{2+}$ with the carbonato complex are even slower than that of $Ba^{2+}$; $Pb^{2+}$ reacts with $en_2CoCO_3^+$ to form $PbCO_3$, but the reaction is slower than that with the pentaammine.

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Contribution from Hynes Chemical Research
Corporation, Durham, North Carolina

# The Addition of Chlorine Monofluoride to Fluorinated Nitriles

By John B. Hynes and Thomas E. Austin

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Fluorinated analogs of the alkyl dichloramines have received only cursory attention in the recent literature and the two known examples, $CF_3NCl_2$ and $C_2F_5NCl_2$, were prepared by rather difficult routes. For example, the high-pressure reaction of silver(I) fluoride and chlorine with ClCN or $CF_3CN$ produced $CF_3NCl_2$ and $C_2F_5NCl_2$ in low yields.[1] The reaction of ClCN with silver(II) fluoride and excess chlorine resulted in an improved yield of $CF_3NCl_2$ (30%).[2]

We wish to report a general synthesis of fluorinated aliphatic dichloramines which involves the low-temperature addition of chlorine monofluoride to fluorinated nitriles. Using this technique, $C_2F_5NCl_2$, $C_3F_7NCl_2$, $CClF_2CF_2NCl_2$, and $NCl_2CF_2CF_2CF_2NCl_2$ have been prepared in 65 to 75% yield with only a very small percentage of by-product formation accompanying the reactions. The generalized equation for this transformation is

$$RCN + 2ClF \longrightarrow RCF_2NCl_2$$

Although these compounds rapidly oxidize aqueous potassium iodide solutions, they were found not to be appreciably impact sensitive.

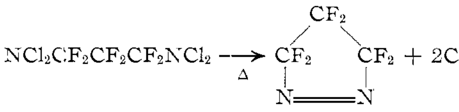
Two observations help to elucidate the mechanism of this reaction. First, when a 1:1 molar ratio of the reactants was employed, no RCF=NCl compounds were detected. This result was not unexpected, however, since the imine should be considerably more susceptible to addition than the corresponding nitrile, as has been observed in a number of fluorination studies. Secondly, evidence for the imine intermediate is furnished by the fact that no azo compounds of the type $RCF_2N{=}NCF_2R$ were formed in any of the experiments. This fact seems to preclude the path whereby chlorine monofluoride fluorinates the nitrile carbon to produce a nitrene intermediate, $RCF_2\ddot{N}$, and chlorine. This latter process always occurs to an appreciable extent when fluorinated nitriles are allowed to react with silver(II) fluoride or with elemental fluorine.[2-5]

In an attempt to compare the reactivity of chlorine monofluoride with that of fluorine, an analogous experiment was performed using fluorine and $CF_3CN$. Almost complete fluorinolysis of the C–N bond occurred, with $C_2F_6$ and $NF_3$ being the major components of a very complex reaction product. Thus, it is apparent that chlorine monofluoride is a considerably less energetic reagent than fluorine when employed at low temperatures in a closed system.

The thermal decomposition of the fluorinated dichloramines proceeded cleanly in the neighborhood of 200° producing chlorine and a symmetrical azo compound in high yield. For example, $CClF_2CF_2NCl_2$ decomposed as follows yielding the known azo compound, $CClF_2CF_2N{=}NCF_2CClF_2$.[3]

$$2CClF_2CF_2NCl_2 \xrightarrow[\Delta]{} CClF_2CF_2N{=}NCF_2CClF_2 + 2Cl_2$$

Under similar conditions the bis(dichloramine) produced the cyclic azo compound, hexafluoro-1-pyrazoline, which was recently prepared in low yield by the action of silver(II) fluoride on $CF_2(CN)_2$.[3] The related four-membered heterocyclic compound, $CF_2N{=}NCF_2$, was prepared by the action of silver(II) fluoride on cyanogen.[6]



In addition to providing further structural corroboration for the new dichloramines, this pyrolytic reaction provides a convenient route to otherwise difficultly accessible azo compounds and a potential route to new unsymmetrical and cyclic systems. Further work in these areas is presently in progress.

## Experimental Section

**Apparatus and Materials.**—The addition reactions were conducted in a 150-cc Monel cylinder which was equipped with an M440 Hoke valve and was silver soldered directly to an all-metal vacuum system. Infrared spectra were determined using a Beckman IR-8 spectrophotometer while the ultraviolet absorption spectra were measured with a Beckman DB spectrophotometer. The $F^{19}$ nmr spectra were measured with a Varian high-resolution spectrometer, Model V-4300-2, employing a probe frequency of 56.4 Mc. The chemical shifts are reported in ppm relative to $CCl_3F$ which was used as an internal standard and solvent. Chromatographic separations were made using a Micro-Tek 1500 gas chromatograph. Unless stated otherwise, all analytical separations were made at ambient temperature with a 6 ft ×

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[1] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 2337 (1962).

[2] J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *J. Org. Chem.*, in press.

[3] J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *ibid.*, **28**, 2811 (1963).

[4] J. A. Young, W. S. Durrell, and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 4553 (1960).

[5] J. A. Attaway, R. H. Groth, and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

[6] H. J. Emeléus and G. L. Hurst, *J. Chem. Soc.*, 3276 (1962).