Hot-atom Chemistry of Radiocobalt in Nitro-ammine Cobalt Complex Salts[*]

By Nobufusa SAITO, Takeshi TOMINAGA
and Hirotoshi SANO

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The present authors had previously reported[1,2] that radiobromine recoil atoms arising from thermal neutron capture in outer anions of various cobaltammine bromides could substitute in the cobalt coordination sphere to form ^{80m}Br- or ^{82}Br-labeled complex cations. In this investigation they found that outer anions of nitroammine cobalt(III) nitrates and nitrites could replace ligand NH_3 groups in the radiocobalt coordination sphere when cobalt atom was activated by slow neutron bombardment.

Seven kinds of crystalline complex salts listed in Table I were irradiated in an experimental hole in JRR-1 reactor for one to six hours at pile temperature. Thermal neutron flux was approximately 3×10^{11} n/cm^2 sec. After standing for one day at room temperature, the irradiated salts were dissolved in water and ^{60}Co-labeled species were separated by procedures involving paper electrophoresis[3], paper chromatography[4],

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[1] N. Saito, H. Sano and T. Tominaga, This Bulletin, 33, 20 (1960).

[2] N. Saito, T. Tominaga, and H. Sano, ibid., 33, 120 (1960).

[3] M. Maki, *Japan Analyst*, 4, 217 (1955).

[4] Y. Yamamoto, A. Nakahara and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 75, 114 (1954).

TABLE I. PERCENTAGE DISTRIBUTION OF ^{60}CO-LABELED SPECIES AFTER THE DISSOLUTION OF IRRADIATED NITROAMMINE COMPLEXES

Target	^{60}Co-labeled species, %*						R**
	CoA_6^{3+}	CoA_5-$NO_{2,3}^{2+}$	CoA_4-$(NO_{2,3})_2^+$	CoA_3-$(NO_{2,3})_3$	CoA_2-$(NO_{2,3})_4^-$	Co^{2+}	
$[Co(NH_3)_6](NO_2)_3$	0.9	17	38	13.5	9	19	19
$[Co(NH_3)_6](NO_3)_3$	4.5	11.5	26	<1.7	<0.8	58	3
$[Co(NH_3)_5NO_2](NO_2)_2$	≤ 0.6	39	18	3.9	1.4	38	0.5
$[Co(NH_3)_5NO_2](NO_3)_2$	≤ 0.7	34	23	4.0	1.1	37	0.7
cis-$[Co(NH_3)_4(NO_2)_2](NO_3)$	~0	<1.4	cis: 47 trans: 4	4.2	0.9	43	0.08
trans-$[Co(NH_3)_4(NO_2)_2](NO_3)$	~0	0.5	cis: 4.6 trans: 45	3.1	0.4	46	0.07
$[Co(NH_3)_3(NO_2)_3]$	~0	~0	0.5	55	~0	44	0

* "A" denotes an NH_3 group in most cases. However, it is possible that small amounts of species with one or two of A's being H_2O may also be present in some cases.

** $R = \dfrac{\text{Percentage of labeled species containing one more anionic ligand than the target complex}}{\text{Percentage of labeled species containing the same number of anionic ligands as the target complex}}$

ion exchange, or precipitation. The results are summarized in Table I.

As shown in Table I, substitution of ligand NH_3 groups by outer anions (NO_2^- or NO_3^-) was observed** in most complex salts whenever the substitution product was considerably stable in aqueous solutions. On the contrary, labeled complexes containing less anions in ligands than the target complex were not found in practice after dissolution of almost all the irradiated salts. The factor, *R*, in Table I is the ratio of percentage of labeled species containing one more anionic ligand than the target complex to percentage of labeled species containing the same number of anionic ligands as the target complex. It is interesting that this ratio increases with the increase in electric charge on the target complex ion, or with the increase in number of neighboring outer anions. The results may be generally explained by assuming the electrostatic interaction between the outer anions and the complex ions fragmented more or less during recoil reactions.

It is worth mentioning that cis-trans isomerization of dinitrotetrammine complexes occurs during recoil processes. Cis isomer was found with an enrichment factor of 23±5 in the irradiated *trans*-$[Co(NH_3)_4(NO_2)_2](NO_3)$, while trans isomer with an enrichment factor of 80±10 in the irradiated cis salt.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo

** This shwos a similarity to the well-known thermal transformation reactions of nitroammine cobalt(III) nitrites.