The Radiolysis of Cobaltammine Complexes

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It has been found that the recoil and subsequent reactions in cobaltammine complexes irradiated with thermal neutrons are greatly influenced by such chemical factors as the chemical composition and stability as ligand of the outer anion.[1] Although a systematic study of the stability with regard to the ionizing radiations of these complex is also needed for the purpose of elucidating the intricate mechanism of such reactions, very few investigations have so far been made of the radiolysis of cobalt complexes in the solid state.[2,3] Therefore, the present authors have studied the radiolysis of the 23 kinds of crystalline cobaltammine complexes listed in Table I.

The cobaltammine complexes were irradiated with Co-60 gamma rays at an ambient temperature and at a dose rate of about 1.6×10^5 r./hr., up to a total dose of about 2×10^8 r., in

TABLE I. $G(\mathrm{Co}^{2+})$ VALUES OF COBALTAMMINE COMPLEXES

No.	Complex	$G(\mathrm{Co}^{2+})$
1	$[\mathrm{Co(NH_3)_6}]\mathrm{F_3}$	3.65 ± 0.30
2	$[\mathrm{Co(NH_3)_6}](\mathrm{NO_3})_3$	2.73 ± 0.40
3	$[\mathrm{Co(NH_3)_6}](\mathrm{NO_2})_3$	1.52 ± 0.22
4	$[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$	0.82 ± 0.02
5	$[\mathrm{Co(NH_3)_6}]\mathrm{Br_3}$	0.32 ± 0.06
6	$[\mathrm{Co(NH_3)_6}]\mathrm{I_3}$	0.21 ± 0.07
7	$[\mathrm{Co(NH_3)_5NO_2}](\mathrm{NO_3})_2$	1.39 ± 0.17
8	$[\mathrm{Co(NH_3)_5NO_2}](\mathrm{NO_2})_2$	0.93 ± 0.12
9	$[\mathrm{Co(NH_3)_5NO_2}]\mathrm{Cl_2}$	0.48 ± 0.02
10	$[\mathrm{Co(NH_3)_5NO_2}]\mathrm{Br_2}$	0.16 ± 0.04
11	*cis*-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{NO_3}$	0.59 ± 0.07
12	*trans*-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{NO_3}$	0.22 ± 0.03
13	*cis*-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{Cl}$	0.30 ± 0.04
14	*trans*-$[\mathrm{Co(NH_3)_4(NO_2)_2}]\mathrm{Cl}$	0.30 ± 0.03
15	$[\mathrm{Co(NH_3)_3(NO_2)_3}]$	0.37 ± 0.05
16	$\mathrm{NH_4}[\mathrm{Co(NH_3)_2(NO_2)_4}]$	0.26 ± 0.04
17	$[\mathrm{Co(NH_3)_5NO_3}]\mathrm{Br_2}$	0.48 ± 0.04
18	$[\mathrm{Co(NH_3)_5F}]\mathrm{Br_2}$	1.28 ± 0.10
19	$[\mathrm{Co(NH_3)_5Cl}]\mathrm{Br_2}$	0.65 ± 0.04
20	$[\mathrm{Co(NH_3)_5Br}]\mathrm{Br_2}$	2.43 ± 0.18
21	$[\mathrm{Co(NH_3)_5I}]\mathrm{Br_2}$	4.05 ± 0.30
22	$[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$	2.13 ± 0.08
23	$[\mathrm{Co(NH_3)_5Br}]\mathrm{Cl_2}$	3.05 ± 0.25

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[1] N. Saito, T. Tominaga and H. Sano, This Bulletin, **35**, 365 (1962); ibid., **36**, 230, 232 (1963); *J. Inorg. & Nucl. Chem.*, **24**, 1539 (1962).

[2] A. Sugimori and G. Tsuchihashi, This Bulletin, **34**, 449 (1961).

[3] N. Saito, H. Sano and N. Matsubara, paper presented at the 7th Symposium on Radiochemistry, Sendai, October, 1963.

the presence of air. After irradiation, each complex was dissolved in water, and the cobalt(II) present in the solution was determined spectrophotometrically, by means of solvent extraction into chloroform, as β-nitroso-α-naphtholato-complex. The $G(Co^{2+})$ values obtained are shown in Table I. For convenience of comparison, the $G(Co^{2+})$ values of nitroamminecobalt complexes are plotted against the number of NO_2 groups contained in ligands of a complex in Fig. 1, while the $G(Co^{2+})$ values of pentamminecobalt complexes are plotted against the frequency of the maximum in the first absorption band in Fig. 2.

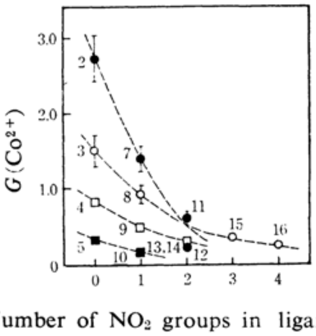

Fig. 1. The $G(Co^{2+})$ value of nitroammine complexes.
-●- Nitrates ; -○- Nitrites ;
-□- Chlorides ; -■- Bromides
(Numbers in Figs. 1 and 2 correspond to those in Table I.)

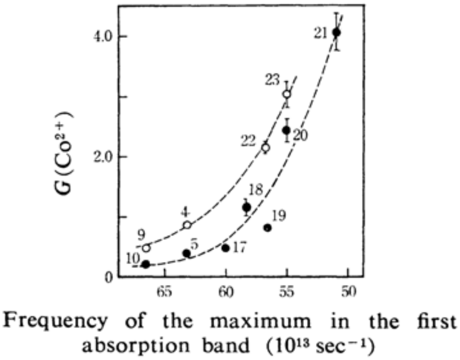

Fig. 2. The $G(Co^{2+})$ value of pentammine complexes.
-●- $[Co(NH_3)_5X]Br_{2,3}$
-○- $[Co(NH_3)_5X]Cl_{2,3}$

The following conclusions may be drawn from the experimental results:

1) For a series of nitroammine complexes which contain the same outer anion (those plotted on the curves in Fig. 1), the $G(Co^{2+})$ value decreases with the increase in the number of NO_2 groups in the ligands. Hence, it may be tentatively assumed that the stability of nitroammine complexes towards gamma irradiation increases with the increase in the thermodynamic stability of these complexes.[4]

2) For a series of pentammine complexes containing the same outer anion and a different acidic ligand, X ($[Co(NH_3)_5X]Br_{2,3}$ and $[Co(NH_3)_5X]Cl_{2,3}$), the $G(Co^{2+})$ value decreases with the increase in the stability in the spectrochemical series.

3) In a group of salts composed of the same complex cation and a different outer anion, the $G(Co^{2+})$ value is greatly affected by the kind of outer anion. For hexammine complex salts, the $G(Co^{2+})$ value increases with the variation in the outer anion in the order: $I < Br < Cl < NO_2 < NO_3 < F$. For nitropentammine and other complex salts, the $G(Co^{2+})$ value increases in a similar order.

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[4] M. Mori, R. Tsuchiya and H. Fukuda, This Bulletin, 33, 1503 (1960).