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### The Reactions of Iodopentamminecobalt(III) with Various "One-electron" Oxidation-Reduction Reagents

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The reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with Ce(IV) perchlorate or sulfate and with Co(III) perchlorate yields, over a wide range of concentrations, almost equimolar mixtures of Co(II) and pentamminecobalt(III). When Ce(IV) perchlorate or sulfate is added to a mixture of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and free iodide ion, the yield of Co(II) is close to 100%. The photochemical decomposition of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  at 2537 Å. to form Co(II) and  $\text{I}_2$  proceeds with a quantum yield of 1.94. These results suggest that Ce(IV) reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to give  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  and iodine atoms, and that iodine atoms react efficiently with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to yield Co(II) and  $\text{I}_2$ . The ratio of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  to Co(II) formed when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts with Fe(II)- $\text{H}_2\text{O}_2$  mixtures depends upon the concentrations of the three reactants, and yields of Co(II) varying between 65 and 92% have been obtained. The reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{O}_2$ -Fe(II) and  $\text{S}_2\text{O}_8^{2-}$ -Fe(II) mixtures result, at the concentrations used, in yields of Co(II) higher than 90%. These results provide some evidence on the nature of the reaction intermediates present in the three systems, and for the occurrence of a reaction between hydroxyl radicals and  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to form Co(II) and HOI. An exploratory study with *tert*-butylhydroperoxide-Fe(II) mixtures indicates that when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ ,  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  and  $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$  react with methyl radicals, reduction of the Co(III) center occurs. It is suggested that the difference in the behavior of iodine atoms, hydroxyl and methyl radicals on one hand, and Ce(IV), Co(III) on the other, depends on the ability of the external oxidation-reduction reagent to form a bond with the iodine in the coordination sphere of the cobalt complex.

The effect of ligands on the rates and stoichiometries of oxidation-reduction reactions between metal ions in aqueous solution has been investigated extensively.<sup>1</sup> In the majority of these studies no net change in the oxidation state of the ligands takes place. Recently, interest has arisen in the reactions of coordinated ligands,<sup>2</sup> and, in particular, a few studies have been concerned with oxidation-reduction changes of ligands coordinated to substitution-inert complexes.<sup>3,4</sup>

In the present paper we report the results obtained when iodopentamminecobalt(III) in aqueous solution reacts with various "one-electron" oxidation-reduction reagents—cerium(IV), cobalt(III), iodine atoms, hydroxyl radicals and methyl radicals. The cobalt-containing products derived from the iodopentamminecobalt(III) ion are aquopentamminecobalt(III), sulfatopentamminecobalt(III), cobalt(II) or mixtures of these species. The retention of the oxidation state of the cobalt(III) center or its reduction to cobalt(II) as the coordinated iodide ion reacts with the external oxidation-reduction reagent is an important feature of the present investigation. As discussed below, it appears that bonding of the iodine to the external "one-electron" oxidation-reduction reagent is a necessary condition for the reduction of the cobalt(III) center. Thus, the possible distinction between "one-electron" oxidation-reduction reagents such as cerium(IV) and cobalt(III) which yield aquopentamminecobalt(III) and "one-electron" oxidation-reduction reagents such as

iodine atoms, hydroxyl radicals and methyl radicals which yield cobalt(II) has been exploited to yield evidence on the nature of the products formed in the primary step of the reaction between iron(II) and hydrogen peroxide. The discovery of a very efficient reaction between iodopentamminecobalt(III) and iodine atoms provides the possibility, which has not yet been exploited, of using this reaction as a diagnostic for the presence of iodine atoms in other systems.

### Experimental

**Materials.**—The cerium(IV) perchlorate solution was obtained from the G. F. Smith Chemical Co. Iron(II) perchlorate solutions were prepared by dissolving analytical grade iron wire in excess perchloric acid. Cobalt(III) perchlorate solutions were prepared by the method of Welser.<sup>5</sup> *tert*-Butylhydroperoxide was supplied by the courtesy of Professor H. Mosher of this department. All other chemicals were reagent grade. The water used for some experiments was redistilled from alkaline permanganate in an all-Pyrex still.

**Preparation of Complexes.**— $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$  prepared according to Basolo and Murmann<sup>6</sup> was the source of most of the complexes. Treatment with perchloric acid and recrystallization from perchloric acid solution yielded  $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_2$ . Treatment with hydrochloric or hydrobromic acids yielded  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ , respectively. These were transformed into the corresponding perchlorates by treatment with perchloric acid followed by recrystallization from perchloric acid solutions.  $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{OCHO}](\text{ClO}_4)_2$  were prepared according to Linhard.<sup>7,8</sup> In our hands the synthesis of iodopentamminecobalt(III) salts presented some difficulties. Although  $[\text{Co}(\text{NH}_3)_5\text{OH}_2]\text{I}_2$  was obtained readily following the procedure of Basolo and Murmann, the preparation of  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{I}_2$  by heating  $[\text{Co}(\text{NH}_3)_5\text{OH}_2]\text{I}_2$  at 60° during 8 hours resulted in partial decomposition (with forma-

(1) See the review by H. Taube in "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959, chapter 1.

(2) Symposium on Homogeneous Catalysis and the Reactions of Coordinated Ligands, 141st Natl. Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(3) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, **82**, 13 (1960).

(4) R. T. M. Fraser and H. Taube, *ibid.*, **82**, 4152 (1960).

(5) D. W. Welser, Ph.D. Dissertation, University of Chicago, 1955.

(6) J. C. Bailar, Jr., "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 171.

(7) M. Linhard and H. Flygare, *Z. anorg. u. allgem. Chem.*, **262**, 328 (1950).

(8) M. Linhard and B. Ran, *ibid.*, **271**, 120 (1953).

tion of  $I_2$  and  $[Co(NH_3)_5I]Cl_2$ .  $[Co(NH_3)_5I]Cl_2$  prepared following Yalman's<sup>9</sup> method was contaminated by  $[Co(NH_3)_5]Cl_2$ . However, if sufficient water was added to dissolve all the ammonium chloride (70 ml. instead of 40 ml. as recommended by Yalman), no  $Co(NH_3)_5^{++}$  was detected in the  $[Co(NH_3)_5I]Cl_2$  product. The chloride was transformed into the perchlorate and recrystallized from perchloric acid as described by Yalman,<sup>9</sup> except that the dissolution of the complex was carried out in water at 25° instead of 40–45°. In all instances the mother liquor contained some iodine, as judged from the color. Even after three recrystallizations the  $[Co(NH_3)_5I](ClO_4)_2$  product was contaminated by  $[Co(NH_3)_5OH_2](ClO_4)_3$ . Cobalt was determined spectrophotometrically at 692  $m\mu$  as  $CoCl_4^-$  in 9.6  $M$  hydrochloric acid. Iodine was determined iodimetrically after oxidation to iodate.<sup>10</sup>

*Anal.* Calcd. for  $[Co(NH_3)_5I](ClO_4)_2$ : Co, 12.54; I, 27.01. Found: Co, 12.46; I, 24.90.

The absorption spectrum of a solution of the impure  $[Co(NH_3)_5I](ClO_4)_2$  after induced aquation by silver perchlorate and removal of the silver iodide formed agreed quantitatively with that calculated if all the cobalt were present as  $Co(NH_3)_5OH_2^{+3}$ ; observed optical densities at 492 and 345  $m\mu$  were 0.517 and 0.495, respectively, to be compared with the calculated values 0.516 and 0.490. The preparation of iodopentamminecobalt(III) perchlorate was therefore contaminated by 8% of  $[Co(NH_3)_5OH_2](ClO_4)_3$ . Since the aquopentamminecobalt(III) ion appears to be inert in all the systems we studied, the salt was used without further purification.

**Procedure.**—Solutions of the complex ion and the oxidation-reduction reagent under study were pipetted into volumetric flasks with vigorous manual shaking and any volume defect was made up by adding solvent. In the experiments with cerium(IV) and cobalt(III) the excess oxidizing agent was destroyed with hydrogen peroxide. Iodine was extracted with carbon tetrachloride, and aliquots from the aqueous layer were withdrawn to determine the reaction products. Cobalt(II) was determined spectrophotometrically from the optical density at 692  $m\mu$  of the  $CoCl_4^-$  ion in 9.6  $M$  hydrochloric acid.  $Co(NH_3)_5OH_2^{+3}$  was determined spectrophotometrically at 492  $m\mu$  after correction for the small light absorption of cobalt(II). Absorption spectra were obtained with a Cary Model 14PM recording spectrophotometer. All the experiments were carried out at room temperature. The order of mixing, concentrations and other experimental conditions will be given below. The experiments involving  $Co(NH_3)_5I^{++}$  were performed in semi-darkness to avoid photochemical decomposition. In all cases the sum of the cobalt(II) and  $Co(NH_3)_5OH_2^{+3}$  products agreed within 2% with the cobalt initially present in the solution. The results reported below have been corrected for the initial amount of  $Co(NH_3)_5OH_2^{+3}$  present in the preparation of  $[Co(NH_3)_5I](ClO_4)_2$ .

**Photochemical Experiments.**—Three ml. of a solution of  $Co(NH_3)_5I^{++}$  in 0.1  $M$   $HClO_4$  was pipetted into a 1 cm. silica cell and irradiated with the 2537 Å. radiation of a Mineralight lamp. Quantum yields were measured using the uranyl oxalate actinometer as described by Pitts, *et al.*<sup>11</sup>

### Results

**The Reaction with Cerium(IV) and Cobalt(III).**—At the concentrations used in the experiments reported in Table I, the reaction between Ce(IV) and  $Co(NH_3)_5I^{++}$  in perchloric acid solutions is complete within 2–3 minutes. The values listed in column 5 of Table I are the mole per cent of Co(II) formed, the remaining product being  $Co(NH_3)_5OH_2^{+3}$ . Experiments 1–6 of Table I indicate that the ratio of the two products is close to unity and fairly insensitive to concentrations and order of mixing of the reagents within a wide range. However, when  $Co(NH_3)_5I^{++}$  is added slowly to a large excess of Ce(IV) the yield of Co(II) decreases appreciably below the 50% value, as shown by experiments 7, 8 of Table I. The products of the oxidation of iodide ion are molecular iodine and iodate, the latter no doubt being formed by reaction of molecular iodine with excess cerium(IV). Experiment 10 of Table I was performed in the presence of carbon tetrachloride, and the iodine extracted was titrated with thiosulfate. The ratio of  $I_2$  to  $IO_3^-$  was 0.64, indicating that 61% of the iodide originally present in the com-

plex ended up as  $IO_3^-$ . Experiment 9 of Table I was performed to find out whether the iodine formed during the reaction would alter the stoichiometry, and it is seen that the presence of an amount of iodine equal to 1.5 times the iodide present in the complex increases the yield of Co(II).

The reaction of  $Co(NH_3)_5I^{++}$  with Ce(IV) in sulfuric acid solution, although slower than in perchloric acid solutions, is still very rapid. As shown by the values listed in column 5 of Table II, the yield of Co(II) is again very close to 50%.<sup>12</sup> In the sulfuric acid solutions the oxidation of molecular iodine by Ce(IV) is much slower than in perchloric acid solutions, and experiment 4 of Table II shows that in the sulfuric acid solutions the presence of iodine does not alter the yield of Co(II).

The reaction of  $Co(NH_3)_5I^{++}$  with Co(III) in 1  $M$  perchloric acid again results in a yield of Co(III) (derived from the  $Co(NH_3)_5I^{++}$ ) very close to 50%, as shown in the last two experiments of Table II.

TABLE I

STOICHIOMETRY OF THE  $Co(NH_3)_5I^{++}$ -Ce(IV) REACTION, 1.2  $M$   $HClO_4$ , ROOM TEMPERATURE

Expt.	(Ce <sup>IV</sup> ), M	(Ce <sup>IV</sup> )/ (Co- (NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> )	Order of mixing	% Co(II)
1	0.05	7.4	$Co(NH_3)_5I^{++}$ added to Ce(IV)	48 <sup>a</sup>
2	.05	4.75	$Co(NH_3)_5I^{++}$ added to Ce(IV)	46
3	.10	7.3	$Co(NH_3)_5I^{++}$ added to Ce(IV)	45
4	.10	12.2	$Co(NH_3)_5I^{++}$ added to Ce(IV)	48
5	.10	15.6	$Co(NH_3)_5I^{++}$ added to Ce(IV)	46
6	.10	15.6	Ce(IV) added to $Co(NH_3)_5I^{++}$	49, 46
7	.20 <sup>b</sup>	150	$Co(NH_3)_5I^{++}$ added to Ce(IV)	26 <sup>c</sup>
8	.20 <sup>b</sup>	150	$Co(NH_3)_5I^{++}$ added to Ce(IV)	11 <sup>d</sup>
9	.03	23.5	Ce(IV) added to $Co(NH_3)_5I^{++}$	68 <sup>e</sup>
10	.10	15.5	Ce(IV) added to $Co(NH_3)_5I^{++}$	42 <sup>f</sup>

<sup>a</sup> Redistilled water was used. <sup>b</sup> 2.4  $M$   $HClO_4$ . <sup>c</sup> 0.013  $M$   $Co(NH_3)_5I^{++}$  added to Ce(IV). <sup>d</sup> 0.0065  $M$   $Co(NH_3)_5I^{++}$  added to Ce(IV). <sup>e</sup>  $10^{-3}$   $M$   $I_2$  present. <sup>f</sup> In the presence of carbon tetrachloride.

TABLE II

STOICHIOMETRY OF THE  $Co(NH_3)_5I^{++}$ -Ce(IV) REACTION, 1.0  $N$   $H_2SO_4$ , ROOM TEMPERATURE

Expt.	(Ce <sup>IV</sup> ), M	(Ce <sup>IV</sup> )/ (Co- (NH <sub>3</sub> ) <sub>5</sub> - I <sup>++</sup> )	Order of mixing	% Co(II)
1	0.0153	11.8	$Co(NH_3)_5I^{++}$ added to Ce(IV)	48
2	.0306	22	$Co(NH_3)_5I^{++}$ added to Ce(IV)	45
3	.00306	2.2	Ce(IV) added to $Co(NH_3)_5I^{++}$	46
4	.00306	2.2	Ce(IV) added to $Co(NH_3)_5I^{++}$	47 <sup>a</sup>
5	.00765	7.0	$Co(NH_3)_5I^{++}$ added to Ce(IV)	49 <sup>b</sup>
6	.00765	7.0	$Co(NH_3)_5I^{++}$ added to Ce(IV)	49 <sup>c</sup>
7	.02 <sup>d</sup>	2	Co(III) added to $Co(NH_3)_5I^{++}$	49 <sup>e</sup>
8	.008 <sup>d</sup>	2	$Co(NH_3)_5I^{++}$ added to Co(III)	50 <sup>e</sup>

<sup>a</sup>  $10^{-3}$   $M$   $I_2$  present. <sup>b</sup> 0.063  $N$   $H_2SO_4$ . <sup>c</sup> 0.20  $N$   $H_2SO_4$ . <sup>d</sup> Co(III) in 1.0  $M$   $HClO_4$ . <sup>e</sup> Co(II) derived from  $Co(NH_3)_5I^{++}$ .

**The Reaction with Iodine Atoms.**—The reaction between  $Co(NH_3)_5I^{++}$  and iodide ion at the concentrations used in the present work is sufficiently slow<sup>13</sup> to make feasible the addition of cerium(IV) to a mixture of  $Co(NH_3)_5I^{++}$  and  $I^-$  before much direct reaction takes place. Two ml. of 0.05  $M$  Ce(IV) and 0.6  $M$   $HClO_4$  were added to 8 ml. of  $8.65 \times 10^{-3}$   $M$   $Co(NH_3)_5I^{++}$  and 0.0125  $M$  KI; the yield of Co(II) was 98%. Increasing the concentrations of Ce(IV) and  $I^-$  by a factor of two resulted in a 97% yield of Co(II). Addition of 2

(12) In these experiments, in addition to  $Co(NH_3)_5OH_2^{+3}$ ,  $Co(NH_3)_5SO_4^{+3}$  is also a reaction product. This observation will be discussed in a future publication.

(13) R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

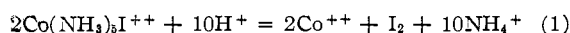
(9) R. G. Yalman, *J. Am. Chem. Soc.*, **77**, 3219 (1955).

(10) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957, p. 249.

(11) J. N. Pitts, J. P. Margerum, R. P. Taylor and W. Prim, *J. Am. Chem. Soc.*, **77**, 5499 (1955).

ml. of 0.05 *M* Ce(IV) and 1.0 *N* H<sub>2</sub>SO<sub>4</sub> to 8 ml. of 8.65 × 10<sup>-3</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and 0.0125 *M* KI under the same conditions resulted in a 98% yield of Co(II). Addition of 2 ml. of 0.05 *M* Ce(IV) perchlorate and 0.6 *M* HClO<sub>4</sub> to 8 ml. of 0.0125 *M* iodide ion and 0.010 *M* Co(NH<sub>3</sub>)<sub>5</sub>-Cl<sup>++</sup> or Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> resulted in no reaction for the chloro complex and in the disappearance of 5.3% of the bromo complex, with formation of the equivalent amount of Co(II).

**Photolysis of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>.**—With the geometrical arrangement used the light flux arriving at the 1 cm. silica cell was 9.3 × 10<sup>-5</sup> einstein/min./l. The extinction coefficients of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and I<sub>2</sub> at 2537 Å. are such that even after 80% disappearance of the complex 90% of the light is absorbed by the unreacted Co(NH<sub>3</sub>)<sub>5</sub>-I<sup>++</sup>. Photolysis of 3.46 × 10<sup>-3</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> in 0.1 *M* HClO<sub>4</sub> yielded, after 25 minutes, a solution 1.69 × 10<sup>-3</sup> *M* in I<sub>2</sub><sup>14</sup> (measured spectrophotometrically at 460 mμ) and 3.48 × 10<sup>-3</sup> *M* in Co(II), a result that indicates that the photochemical reaction proceeds according to the stoichiometry given by equation 1. By



following the decrease in optical density at 580 mμ (where Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> has an absorption maximum) it was established that the photochemical reaction obeys zero order kinetics, up to 80% reaction. The quantum yield, measured by determining the concentration of Co(II) after 10 minutes of irradiation, was 1.94.

**The Reaction with Fe(II)-H<sub>2</sub>O<sub>2</sub>.**—When hydrogen peroxide is added to a solution of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> is formed quantitatively at a measurable rate.<sup>15</sup> However, in the presence of iron(II) the reaction appears to be complete upon mixing the reagents and the stoichiometry is drastically altered,<sup>16</sup> with large amounts of Co(II) being formed. The experiments were performed by adding 5 ml. of a solution of hydrogen peroxide of the desired concentration to a 50-ml. volumetric flask containing 40 ml. of a solution of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, Fe(II) and HClO<sub>4</sub> of the desired concentrations. Thiosulfate was added to reduce the iodine formed, the solution was made up to volume and examined spectrophotometrically to determine the reaction products. The optical density at 388 mμ (where Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> has a maximum with extinction coefficient 2700, as compared to extinction coefficients 11 and 0.16 for Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> and Co(II), respectively) indicated that in all instances the Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> has reacted completely. The results are summarized in Table III, where columns 2, 3 and 4 represent the initial concentrations of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, Fe(II), and H<sub>2</sub>O<sub>2</sub>, respectively, calculated if reaction did not occur. Experiments 1, 2 and 3 show that increasing the Fe(II) concentration increases the yield of Co(II). Experiments 2 and 6 show that decreasing the Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> concentration increases the yield of Co(II). Experiment 8 shows that in the presence of added Br<sup>-</sup>, Co(II) is the only reaction product.

A few experiments were performed to learn whether other pentammine cobalt(III) complexes would react with Fenton's reagent: 1 ml. of 1 *M* Fe(II) perchlorate in 2 *M* HClO<sub>4</sub> was added to 5 ml. of 0.020 *M* Co(NH<sub>3</sub>)<sub>5</sub>-OCHO<sup>++</sup> and 0.2 *M* H<sub>2</sub>O<sub>2</sub>.<sup>17</sup> The solution was diluted

(14) This concentration exceeds the solubility of iodine in water, indicating that the solution is supersaturated.

(15) A. Haim and H. Taube, to be published.

(16) The reaction between Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and Fe<sup>++</sup> at the concentrations used is sufficiently slow to allow a study of the reaction with Fenton's reagent by adding hydrogen peroxide to a mixture of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and Fe(II). At 0.36 *M* Fe(II), 1.0 *M* HClO<sub>4</sub> and 4.3 × 10<sup>-3</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> the half-life for the disappearance of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> is approximately 30 minutes at room temperature.

(17) Unpublished experiments indicate that Co(NH<sub>3</sub>)<sub>5</sub>OCHO<sup>++</sup> and H<sub>2</sub>O<sub>2</sub> do not react, even in the presence of molybdate ion.

TABLE III  
STOICHIOMETRY OF THE Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>-H<sub>2</sub>O<sub>2</sub>-Fe(II) REACTIONS,  
1.0 *M* HClO<sub>4</sub>, ROOM TEMPERATURE

Expt.	(Co(NH <sub>3</sub> ) <sub>5</sub> I <sup>++</sup> ) (Fe <sup>++</sup> ) × 10 <sup>3</sup> , (H <sub>2</sub> O <sub>2</sub> ) × 10 <sup>4</sup> ,			% Co(II)
	× 10 <sup>3</sup> , <i>M</i> <sup>a</sup>	<i>M</i> <sup>a</sup>	<i>M</i> <sup>a</sup>	
1	1.00	0.40	2.0	65
2	1.00	1.00	2.0	73
3	1.00	2.00	2.0	81
4	1.00	2.00	10.0	91
5	1.00	1.00	8.0	83
6	0.26	1.00	2.0	87
7	1.00	10.0	20.0	92
8	1.00	2.00	10.0	101 <sup>b</sup>

<sup>a</sup> Initial concentrations calculated assuming that reaction did not occur. <sup>b</sup> 1.25 × 10<sup>-2</sup> *M* NaBr present.

to 10 ml. and examined spectrophotometrically to determine the reaction products: 38% of the Co(NH<sub>3</sub>)<sub>5</sub>-OCHO<sup>++</sup> was left unreacted and 62% was converted to Co<sup>++</sup>. Under the same experimental conditions, Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> and Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> were unchanged. The experiment with Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> serves in addition as a blank to show that Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> is compatible with H<sub>2</sub>O<sub>2</sub>-Fe(II) mixtures.

**The Reaction with Fe(II)-S<sub>2</sub>O<sub>8</sub><sup>=</sup>.**—The reaction of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> with S<sub>2</sub>O<sub>8</sub><sup>=</sup> is complete within 25 min. in 0.05 *M* S<sub>2</sub>O<sub>8</sub><sup>=</sup> and yields Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> quantitatively.<sup>15</sup> In this instance again, the reaction stoichiometry is drastically altered by the presence of Fe(II); 5 ml. of 0.040 *M* S<sub>2</sub>O<sub>8</sub><sup>=</sup> was added to 40 ml. of 1.02 × 10<sup>-3</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, 0.025 *M* Fe(II) and 1.25 *M* HClO<sub>4</sub>. Thiosulfate was added to reduce the iodine formed, the solution was diluted to 50 ml. and its absorption spectrum was measured. From the optical density at 388 mμ, it was found that 4.60 × 10<sup>-4</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> was left unreacted. The Co(II) concentration was 3.5 × 10<sup>-4</sup> *M*, indicating that 97% of the Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> that had disappeared ended up as Co(II). In another experiment, 5 ml. of 0.42 *M* S<sub>2</sub>O<sub>8</sub><sup>=</sup> was added to 40 ml. of 0.125 *M* Fe(II), 8.2 × 10<sup>-4</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> and 1.25 *M* HClO<sub>4</sub>. Under these conditions all of the Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> reacted and the yield of Co(II) was 91%. A blank experiment indicated that Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> survives treatment with Fe(II)-S<sub>2</sub>O<sub>8</sub><sup>=</sup> mixtures.

**The Reaction with Fe(II)-O<sub>3</sub>.**—The reaction of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> with ozone yields Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> rapidly and quantitatively.<sup>15</sup> However, when oxygen containing 2% ozone was bubbled through a solution 8.2 × 10<sup>-4</sup> *M* in Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, 0.02 *M* in Fe(II) and 1.0 *M* in HClO<sub>4</sub>, the yield of Co(II) was 94%. Blank experiments indicated that Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> survives treatment with ozone in the presence of Fe(II).

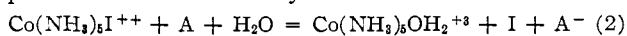
**The Reaction with Fe(II)-(CH<sub>3</sub>)<sub>3</sub>COOH.**—The reactions of various pentamminecobalt(III) complexes with Fe(II)-*tert*-butylhydroperoxide mixture were explored: 2 ml. of 0.15 *M* (CH<sub>3</sub>)<sub>3</sub>COOH was added to 40 ml. of 1.0 × 10<sup>-3</sup> *M* Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup>, 0.025 *M* Fe(II) and 1.25 *M* HClO<sub>4</sub>. The yield of Co(II) was 98%. Under the same conditions, Co(NH<sub>3</sub>)<sub>5</sub>Br<sup>++</sup> and Co(NH<sub>3</sub>)<sub>5</sub>N<sub>3</sub><sup>++</sup> yielded 80 and 20% of Co(II), respectively, with the remaining being unreacted complex, whereas Co(NH<sub>3</sub>)<sub>5</sub>OCHO<sup>++</sup> and Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> did not react. Experiments with Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> were performed at various acidities, but even at pH 6.0, where more than 50% of the complex is present as Co(NH<sub>3</sub>)<sub>5</sub>OH<sup>++</sup>, no Co(II) was detected.<sup>18</sup>

### Discussion

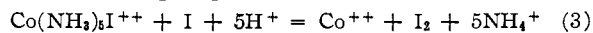
The formation of Co(II) and Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>+3</sup> (or Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub><sup>+</sup>) in the reaction of Co(NH<sub>3</sub>)<sub>5</sub>I<sup>++</sup> with Ce(IV) or Co(III) raises the question as to whether the Co-

(18) At pH higher than 6.0, the direct reduction of Co(NH<sub>3</sub>)<sub>5</sub>OH<sup>++</sup> by Fe(II) becomes too rapid.

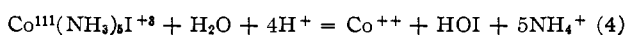
(II) and Co(III) products are formed in parallel or consecutive steps. The fact that the different oxidizing agents, Ce(IV) in perchloric acid, Ce(IV) as the sulfate complex and Co(III), give the same ratio of Co(II) to Co(III) products shows that a common process leading to a common intermediate occurs in all three systems, and also that the succeeding steps are not strongly affected by the identity of the oxidizing agent. This common process is almost certainly reaction 2.



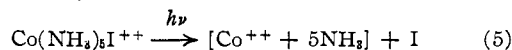
If the succeeding step is taken to be



the observed 1:1 ratio of Co(II) to  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  is explained readily. An alternative to reactions 2 and 3, namely, that the intermediate  $[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{I}]^{+3}$  is generated, which can react to give the products shown in reaction 2 or as shown in reaction 4

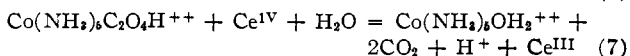
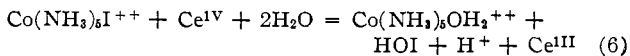


is not nearly as attractive for it would require the 1:1 product ratio to be merely the result of coincidence. Reaction 3 appears to be extremely efficient since the ratio of Co(II) to  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  is close to unity and quite insensitive to the concentration, the order of mixing of the reagents and the nature of the oxidizing agent. However, when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  is added to an excess of Ce(IV) perchlorate the yield of Co(II) decreases appreciably below the 50% value, indicating that under these conditions the iodine atoms formed in reaction 2 are oxidized by Ce(IV). Furthermore, in the presence of added iodine (expt. 9, Table I) the yield of Co(II) increases above the 50% value, indicating that the reaction of Ce(IV) with iodine produces an intermediate, perhaps iodine atoms, capable of reducing the Co(III) center. Independent evidence for the occurrence of reaction 3 is the very high yield (98%) of Co(II) when Ce(IV) is added to  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ -I<sup>-</sup> mixtures. It is suggested that the reaction of Ce(IV) with free iodide ions generates iodine atoms which react with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  according to equation 3.<sup>19</sup> The results obtained in the photochemical decomposition of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  also point to an efficient reaction between  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and iodine atoms. The quantum efficiency of 1.94 at 2537 Å. is understood readily if the primary photochemical act given by equation 5 is followed rapidly by reaction 3. If all the iodine atoms



generated in reaction 5 react with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , the primary quantum yield is 0.97.<sup>20</sup>

The retention of the oxidation state of the cobalt center in the reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with Ce(IV) is to be contrasted with the reduction of cobalt(III) when  $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_4^{+}$  reacts with Ce(IV).<sup>3</sup> From a consideration of the appropriate oxidation-reduction potentials, it can be shown that reactions 6 and 7 are thermo-



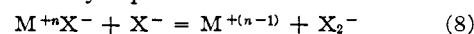
dynamically favorable. Assuming that in each case the external oxidizing agent brings about a one-electron oxidation of the ligand and that intermediates with the corresponding radicals in the coordination sphere of Co(III) are formed, the difference between the two systems indicates that the oxidation of the oxalate

(19) In the early stages of the reaction, when free iodide is still present in the solution, I<sub>2</sub><sup>-</sup> may be formed. It is not known whether I<sub>2</sub><sup>-</sup> reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to form Co(III).

(20) A. W. Adamson, *Discussions Faraday Soc.*, **29**, 163 (1960), reports quantum yields of 0.66 and 0.10 at 370 and 550 mμ, respectively.

radical-ion by the Co(III) center is favored over its expulsion from the coordination sphere of Co(III) whereas the opposite situation prevails for an iodine atom in the coordination sphere of Co(III). The difference in behavior of the two intermediates may be ascribed to the reducing power of the two radicals. Whereas  $\text{C}_2\text{O}_4^{--}$  can be oxidized by simple electron abstraction, the oxidation of I to HOI is at least kinetically less favorable for it requires an I-O bond to be formed, and it may even be thermodynamically unfavorable. It is not known whether water enters the coordination sphere of Co(III) as the iodine atom leaves, or whether an intermediate of coordination number 5 is formed as the iodine atom is expelled from the coordination sphere of Co(III). O<sup>18</sup> isotope discrimination studies and a comparison with the results obtained by Posey and Taube<sup>21</sup> in the metal ion catalyzed aquations of halogenopentamminecobalt(III) complexes might shed some light on this question. No conclusion on the formation of an intermediate can, at the present stage of development of the subject, be drawn from the fact that some of the Co(III) appears as the sulfato complex when  $\text{SO}_4^{--}$  is present.

A type of reaction which appears to have some generality is described by equation 8. For a substitution-



inert oxidizing agent such as was used in the present study, this reaction is exemplified by  $\text{M}^{+n} = \text{Co}(\text{NH}_3)_5^{+3}$  and  $\text{X}^- = \text{I}^-$ .<sup>22</sup> In labile systems, greater freedom in specifying the geometry of the activated complex remains, but for  $\text{M}^{+n} = \text{Ce}^{+4}$  and  $\text{X}^- = \text{Br}^-$ ,<sup>23</sup> and for  $\text{M}^{+n} = \text{Fe}^{+3}$  and  $\text{X}^- = \text{I}^-$ ,  $\text{SCN}^-$ ,<sup>24,26</sup> such a reaction path is consistent with the experimental results and appears to be the most reasonable. The reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with iodine atoms is of the type of reaction 8, and it is interesting to note that a similar reaction in a labile system, the reaction of  $\text{FeN}_3^{+2}$  with azide radicals to give Fe(II) and nitrogen, has been postulated recently.<sup>26</sup> The small yield of Co(II) obtained in the reaction of  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  with iodine atoms indicates that  $\text{Co}(\text{NH}_3)_5\text{Br}^{++}$  does not compete as favorably as  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  against recombination of iodine atoms, and the failure of atomic iodine to react with  $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$  is therefore not unexpected.<sup>27</sup>

The much higher yield of Co(II) in the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{H}_2\text{O}_2$ ,  $\text{S}_2\text{O}_8^{--}$  and  $\text{O}_3$  in the presence of Fe(II), as compared to that observed in its absence, shows that at least one intermediate capable of producing Co(II) from  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  is formed in the reactions of the oxidizing agents with Fe(II). That different intermediates are formed in the reactions of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{--}$  with Fe(II) is shown by the comparison of the results obtained when either peroxide is added to a solution containing the same concentrations of Fe(II) and  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . As indicated above, at  $1.00 \times 10^{-3} M$   $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $0.020 M$  Fe(II), addition of  $2 \times 10^{-3} M$   $\text{H}_2\text{O}_2$  results in the complete disappearance of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , whereas addition of  $4 \times 10^{-3} M$   $\text{S}_2\text{O}_8^{--}$  causes the disappearance of only 44% of the Co-

(21) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

(22) R. G. Yalman, *ibid.*, **75**, 1842 (1953), writes the rate determining step of the reaction as  $\text{Co}(\text{NH}_3)_5\text{I}^{++} + \text{I}^- = \text{Co}(\text{NH}_3)_5\text{I}^+ + \text{I}$ . However, on energetic grounds, it would appear that the formulation given by equation 8 is more favorable.

(23) E. L. King and M. L. Pandow, *ibid.*, **75**, 3063 (1953).

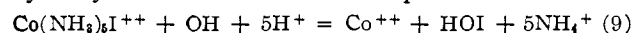
(24) A. J. Fudge and K. F. Sykes, *J. Chem. Soc.*, 119 (1952).

(25) R. H. Betts and F. S. Dainton, *J. Am. Chem. Soc.*, **75**, 5021 (1953).

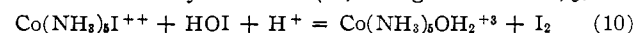
(26) Unpublished results by F. S. Dainton and D. G. L. James, quoted in *Trans. Faraday Soc.*, **57**, 1131 (1961).

(27)  $\Delta F^\ddagger$  for the reaction  $\text{Co}(\text{NH}_3)_5\text{X}^{++} + \text{I} + \text{H}_2\text{O} = \text{Co}(\text{NH}_3)_5\text{OH}_2^{++} + \text{XI}$  has been estimated from the oxidation-reduction potentials  $-0.33$  v. for the  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{++}$ - $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  couple<sup>19</sup> and  $-1.27$  v. for the  $\text{I}^-$ (aq.) couple. The values for X = I, Br and Cl are  $-12$ ,  $-4$  and  $+0.5$  kcal., respectively.

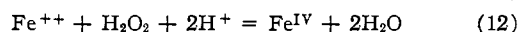
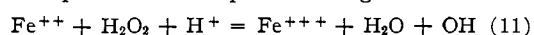
$(\text{NH}_3)_5\text{I}^{++}$ . These results further indicate that  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts very efficiently with the intermediate(s) formed in the  $\text{H}_2\text{O}_2$ - $\text{Fe}(\text{II})$  reaction, even in the presence of excess  $\text{Fe}(\text{II})$ , and that the competition of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{Fe}(\text{II})$  for reaction with the intermediate(s) is less favorable in the  $\text{S}_2\text{O}_8^{2-}$  system.<sup>28</sup> Various items of evidence indicate that the primary products of the  $\text{Fe}(\text{II})$ - $\text{S}_2\text{O}_8^{2-}$  reactions are  $\text{Fe}(\text{III})$  and  $\text{SO}_4^-$ ,<sup>29</sup> and the formation of  $\text{Co}(\text{II})$  could be ascribed to the reaction of  $\text{SO}_4^-$  with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . However, in view of the rapid  $\text{SO}_4^-$ - $\text{OH}$  interconversion,<sup>29</sup> the intermediate that reacts with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  may be the hydroxyl radical as indicated in equation 9.



Although the nature of the intermediates present in the  $\text{Fe}(\text{II})$ - $\text{H}_2\text{O}_2$ - $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  system has not been established definitely, the variation in the yield of  $\text{Co}(\text{II})$  with the concentrations of the reactants (see Table III) clearly indicates the presence of at least two intermediates, differing in yields of  $\text{Co}^{++}$  or  $\text{Co}(\text{III})$  which they produce. The identification of the intermediate that yields  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  is relevant to the question of the products formed in the initial step of the  $\text{Fe}(\text{II})$ - $\text{H}_2\text{O}_2$  reaction.<sup>30,31</sup> If it is assumed that these products are  $\text{Fe}(\text{III})$  and  $\text{OH}$  radicals, the formation of  $\text{Co}(\text{II})$  is ascribed to reaction 9<sup>32</sup> followed by reaction 10. Since the yield of  $\text{Co}(\text{II})$  is higher than 50%, there



must be another path for the disappearance of hypoiodous acid, and a reasonable reaction is its reduction by  $\text{Fe}(\text{II})$ . The observed increase in the yield of  $\text{Co}(\text{II})$  with decreasing  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  concentration and increasing  $\text{Fe}(\text{II})$  concentration is compatible with such a mechanism. However, other evidence argues against the participation of reaction 10 when  $\text{Fe}^{++}$  is present. First, the increase in the yield of  $\text{Co}(\text{II})$  with increasing  $\text{H}_2\text{O}_2$  concentration is incompatible with the mechanism represented by equations 9, 10 and 11. Second, the formation of iodine in the reactions of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{O}_3$  or  $\text{H}_2\text{O}_2$  in the absence of  $\text{Fe}(\text{II})$ <sup>15</sup> indicates that the hypoiodous acid formed in the primary steps reacts efficiently with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , even in the presence of  $\text{O}_3$  or  $\text{H}_2\text{O}_2$ ; but since in the presence of  $\text{Fe}(\text{II})$  a yield as high as 95% of  $\text{Co}(\text{II})$  can be obtained using  $\text{O}_3$ , most of the hypoiodous ion formed in reaction 9 must be destroyed by oxidizing  $\text{Fe}(\text{II})$ .<sup>33</sup> A mechanism compatible with the experimental results features two initiation steps.<sup>31</sup> The steps following are reaction 9



and reaction 13 which is entirely analogous to that of  $\text{Fe}^{\text{IV}} + \text{Co}(\text{NH}_3)_5\text{I}^{++} + \text{H}_2\text{O} = \text{Fe}^{+3} + \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3} + \text{I}$  (13)

$\text{Ce}(\text{IV})$  or  $\text{Co}(\text{III})$ . The details of the subsequent steps have not been established, but it is necessary to include a reaction between  $\text{Fe}(\text{IV})$  and  $\text{H}_2\text{O}_2$  to account

(28) These observations parallel the results obtained by I. M. Kolthoff and co-workers (*J. Am. Chem. Soc.*, **71**, 3777 (1949); **73**, 1733 (1951)) in the induced oxidation of ethanol. They found that  $\text{Fe}(\text{II})$ - $\text{S}_2\text{O}_8^{2-}$  mixtures induce the oxidation to a smaller extent than  $\text{Fe}(\text{II})$ - $\text{H}_2\text{O}_2$  mixtures.

(29) For a summary see W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms," edited by J. O. Edwards, Interscience Publishers, New York, N. Y., 1962, p. 175.

(30) J. H. Baxendale in "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 367.

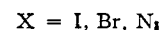
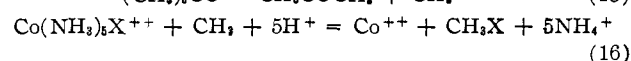
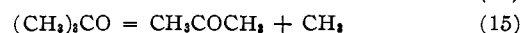
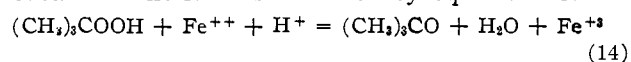
(31) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952).

(32) A reaction of  $\text{OH}$  radicals with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  to form  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  and iodine atoms, followed by reaction 3, can be ruled out since according to this sequence the yield of  $\text{Co}(\text{II})$  never could be higher than 50%.

(33) A direct test, which we have been unable to carry out because we have failed in our attempts to prepare a solution of hypoiodous acid, involves the addition of hypoiodous acid to a mixture of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{Fe}(\text{II})$ .

for the increase in the yield of  $\text{Co}(\text{II})$  with increasing  $\text{H}_2\text{O}_2$  concentration. If the interpretation advanced is correct, the quantitative formation of  $\text{Co}(\text{II})$  in the presence of bromide ion (expt. 8, Table III) shows that bromide ion is a good scavenger for  $\text{Fe}(\text{IV})$  and that atomic bromine reacts efficiently with  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ . Experiment 1 of Table III yields the upper limit 0.43 for the ratio of the rate constants for reactions 11 and 12, a value compatible with the results obtained in isotope discrimination studies.<sup>30</sup>

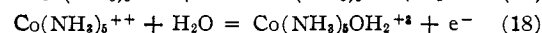
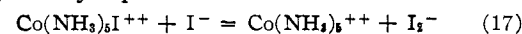
The study of the reactions of various pentamminecobalt(III) complexes with *tert*-butylhydroperoxide- $\text{Fe}(\text{II})$  mixtures, although of an exploratory nature, clearly indicates that an intermediate capable of reducing  $\text{Co}(\text{III})$  is present in these systems. It is suggested that methyl radicals<sup>34</sup> formed by reactions 14 and 15 or methyl radical-iron complexes<sup>35</sup> react with the cobaltamine ions as indicated by equation 16.



Here again, as observed in the reactions with iodine atoms and hydroxyl radicals,  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  is the most reactive of the complexes.

The reduction of the  $\text{Co}(\text{III})$  center when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts with iodine atoms, hydroxyl radicals and methyl radicals is to be contrasted with the retention of the oxidation state of the  $\text{Co}(\text{III})$  center when  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  reacts with  $\text{Ce}(\text{IV})$ ,  $\text{Co}(\text{III})$  and, perhaps,  $\text{Fe}(\text{IV})$ . The distinction between two typical "one-electron" oxidizing agents such as  $\text{Ce}(\text{IV})$  and  $\text{OH}$  is noteworthy, and it is suggested that the difference depends on the ability of the external oxidation-reduction reagent to form a bond with the iodine in the coordination sphere of  $\text{Co}(\text{III})$ .

In view of the numerous examples of reduction of  $\text{Co}(\text{III})$  complexes observed in the present work and elsewhere, and of the scarcity of energy data relative to such reductions, it is of interest to estimate the "kinetic" oxidizing power of the  $\text{Co}(\text{III})$  center in ammine complexes. Using the free energy of activation of 19 kcal. for the reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  and  $\text{I}^-$ ,<sup>13</sup> the value 1.04 v. for the  $\text{I}_2^-$ - $\text{I}^-$  couple, the value 0.12<sup>13</sup> for the equilibrium constant for the formation of  $\text{I}^- + \text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  from  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$ , and assuming that the rate-determining step is given by equation 17, where  $\text{Co}(\text{NH}_3)_5^{++}$  represents a spin-paired  $\text{Co}(\text{II})$  ion, the maximum oxidation-reduction potential of the couple given by equation 18 is calculated as -0.27 v.



Considering that the oxidation-reduction potential of the  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$ - $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+3}$  couple is -0.33 v.,<sup>13</sup> and that the spin-free  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{++}$  is more stable than the spin-paired  $\text{Co}(\text{NH}_3)_5^{++}$ , the oxidation-reduction potential of the couple given by equation 18 probably is very close to -0.27 v.

The calculation shows that if spin-paired  $\text{Co}(\text{II})$  is the primary product of the reaction of  $\text{Co}(\text{NH}_3)_5\text{I}^{++}$  with  $\text{I}^-$ , it differs little in energy from the spin-free pentammine  $\text{Co}(\text{II})$ . However, there is no proof that the spin-paired complex is in fact the primary product of the reduction process, and the close correspondence of the oxidation-reduction potentials referred to above may

(34) See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(35) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

simply mean that spin-free Co(II) is produced directly when  $I^-$  reacts with  $Co(NH_3)_5I^{++}$ .

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## Coördination Compounds of Trivalent Metals with Unsymmetrical Bidentate Ligands. II. Trifluoroacetylacetonates<sup>1</sup>

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The preparation and characterization of trifluoroacetylacetonates of a variety of trivalent metals is reported. *cis* and *trans* geometrical isomers of the inert complexes ( $M = Cr, Co, Rh$ ) were separated by chromatography on alumina. Only the *trans* isomer was isolated in the solid state in the case of the labile complexes ( $M = Al, Ga, In, Mn, Fe$ ). Vibration and electronic spectra of the isomers are nearly identical. The geometrical configuration of the isomers was established by proton and fluorine n.m.r. spectra and X-ray powder patterns. The n.m.r. chemical shifts are discussed in terms of electronic structure. Equilibrium constants for isomerization of the cobalt, aluminum, and gallium compounds in chloroform solution were evaluated at several temperatures by fluorine n.m.r. spectra. The free energy for *trans* to *cis* isomerization is slightly less than 1 kcal./mole, to which the heat and entropy terms contribute about equally.

### Introduction

Coördination of three unsymmetrical bidentate ligands to a trivalent metal ion offers the possibility of two geometric isomers. Recently, by means of n.m.r. spectroscopy a number of trivalent metal benzoylacetonates have been shown to exhibit *cis-trans* isomerism.<sup>3</sup> The present work reports the preparation, separation, and determination of configuration of isomeric complexes of a variety of trivalent metals with 1,1,1-trifluoro-2,4-pentanedione [hereafter often referred to as  $M(tfac)_3$  and called metal trifluoroacetylacetonates]. The trifluoroacetylacetonates were of particular interest because fluorine resonance could be observed. In addition to establishing the configuration of the isomers, the n.m.r. studies provide useful information about electronic structure and equilibria in solution.

### Experimental

With the exception of the aluminum and iron<sup>4,5</sup> compounds, methods for the preparation of trifluoroacetylacetonates of trivalent metals have not been previously reported. The methods of preparation reported here are similar to those which have been employed for the simple metal acetylacetonates.<sup>6-9</sup> 1,1,1-Trifluoro-2,4-pentanedione was used as obtained from Columbia Organic Chemicals Co., Inc.

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-chromium(III).**—A mixture of chromium chloride hexahydrate (2.66 g., 0.0100 mole), 1,1,1-trifluoro-2,4-pentanedione (5.17 g., 0.0345 mole), and urea (20 g.) in 100 ml. of water was heated on the steam bath for 7 hr. with stirring. The olive-drab product was collected, washed with water, and air dried. After purification by chromatography on alumina, the yield was 2.23 g. (44%).

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-cobalt(III).**—1,1,1-Trifluoro-2,4-pentanedione (4.63 g., 0.030 mole) was dissolved in 50 ml. of aqueous alcohol (40% ethanol).  $Na_3[Co(CO_3)_3] \cdot 3H_2O$ <sup>10</sup> (3.62 g., 0.010 mole) and 5 ml. of 6 *N*  $HNO_3$  were added,

and the mixture was allowed to reflux for 0.5 hr. The resulting green precipitate was then collected, washed with water, air dried, and purified by chromatography on alumina. The yield was 1.45 g. (28%).

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-rhodium(III).**—A solution of rhodium nitrate (0.0114 mole), prepared as described previously,<sup>3</sup> was treated with solid sodium bicarbonate until pH 4 was attained. 1,1,1-Trifluoro-2,4-pentanedione (5.28 g., 0.0342 mole) was added, and the mixture was allowed to reflux for 0.5 hr. After readjusting the pH to 4.5-5 with more sodium bicarbonate, refluxing was continued for 15 min. longer. Finally an additional 1.00 g. of 1,1,1-trifluoro-2,4-pentanedione was added, and the mixture was refluxed for 0.5 hr. longer. The orange-yellow product was collected and purified by chromatography. The yield of purified product was 3.21 g. (50%).

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-aluminum(III).**—1,1,1-Trifluoro-2,4-pentanedione (9.45 g., 0.0614 mole) was added to a solution of aluminum isopropoxide (4.16 g., 0.0204 mole) in 40 ml. of benzene. The resulting solution was allowed to stand for 2 hr. The benzene and 2-propanol which were produced were removed by vacuum distillation at room temperature. The yield of the white crystalline product was 8.9 g. (91%).

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-gallium(III).**—Gallium metal (0.78 g., 0.0112 mole) was dissolved in aqua regia and the solution evaporated nearly to dryness. After solution of the residue in 25 ml. of water, 25 ml. of an aqueous solution containing 1,1,1-trifluoro-2,4-pentanedione (5.18 g., 0.0336 mole) and 7 ml. of conc.  $NH_4OH$  was added. The white precipitate which formed immediately was collected, washed with water, and air dried. Extraction of the solid with benzene and subsequent vacuum distillation of the solvent yielded 0.48 g. (8%) of  $Ga(tfac)_3$ .

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-indium(III).**—Indium trifluoride 9-hydrate (2.25 g., 0.00675 mole) was converted to the water soluble chloride by evaporation with 6 *N*  $HCl$ . The chloride was taken up in 25 ml. of water, and 25 ml. of an aqueous solution containing 1,1,1-trifluoro-2,4-pentanedione (3.12 g., 0.0202 mole) and conc.  $NH_4OH$  (3 ml.) was added. The product was purified in the same manner as the gallium compound. The yield of the ivory-colored  $In(tfac)_3$  was 1.2 g. (31%).

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-manganese(III).**—A solution of potassium permanganate (0.32 g., 0.0020 mole) in 25 ml. of water was added to a solution of manganese(II) sulfate monohydrate (1.35 g., 0.0080 mole) in 25 ml. of water. Immediately 1,1,1-trifluoro-2,4-pentanedione (9.5 g., 0.062 mole) was added, and the mixture was heated on the steam bath. During the first 5 min. of heating, 10 ml. of 6 *N*  $NH_4OH$  was added slowly. After digesting for 10 min. longer, the mixture was cooled, and the dark brown precipitate was collected and air dried. The yield of crude product, after separation from unreacted manganese(III) hydroxide by extraction with acetone, was 3.25 g. (63%). Since the product was still contaminated with manganese(II) trifluoroacetylacetonate, the  $Mn(tfac)_3$  was concentrated by extraction with 20 ml. of benzene. Recrystallization from hot benzene-pentane yielded large clumps of badly twinned  $Mn(tfac)_3$  and a few fine yellow crystals of the manganese(II) complex. The latter could be readily removed by washing with ethanol. The yield of purified product was 0.8 g.

**Tris-(1,1,1-trifluoro-2,4-pentanedione)-iron(III).**<sup>5</sup>—An aqueous solution (100 ml.) containing iron(III) chloride hexahydrate

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