Studies of Halogenoacetato Cobalt(III) Complexes.* I. The Preparation and Some Properties of Bromoacetato Cobalt(III) Complexes

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Although several species of fluoroacetato and chloroacetato ammine cobalt(III) complexes have been prepared and their chemical and physical properties studied,[1-6] bromoacetato and iodoacetato ammine cobalt(III) complexes have not yet been isolated. Riolo and Soldi[4] attempted to prepare $[Co(CH_2BrCO_2)(NH_3)_5]X_2$ and $[Co(CH_2ICO_2)(NH_3)_5]X_2$ by the reaction between $[CoCO_3(NH_3)_5]NO_3$ and CH_2BrCO_2H or CH_2ICO_2H in carbon tetrachloride, but they could not isolate the desired compounds. The difficulty in making such a preparation has been attributed to the instability of the bromoacetate and iodoacetate ions at high temperatures, which must be maintained during the reaction period since halogenoacetate ions do not coordinate rapidly enough with cobalt at room temperature. However, the higher the temperature, the larger the danger of the decomposition and/or the hydrolysis of the halogenoacetate ions. Despite the possibility of many side reactions occurring, bromoacetate ions are not so unstable[7,8] as to deter entirely the formation of their complexes. It was, therefore, considered that the desired compound must be present in the reaction products of a carbonato-complex with bromoacetic acids, and that by regulating the reaction temperature, time, and concentration of the reactants and by applying fractional extraction and precipitation, the complexes could be isolated with a high level of purity. Accordingly, after many attempts, several new species of monobromoacetato- and dibromoacetato-complexes were isolated.

The group of halogenoacetato complexes is of especial interest because, since the atomic and/or electronic configuration around the coordination bond is the same in all of the complexes, and since the basicity and the volume of the ligands change regularly with the increase in the number of halogen atoms in the halogenoacetato ligands, one is able to examine the influence of these factors on the physical and chemical properties of the complexes. This standpoint will be maintained throughout this series of studies.

Experimental

Materials.—Monochloroacetic acid, dichloroacetic acid and trichloroacetic acid (Fisher Scientific Co.), monobromoacetic acid (Eastman Organic Chemicals), dibromoacetic acid, tribromoacetic acid (K & K Laboratories, Inc.), and all other reagent-grade chemicals were used without further purification.

Analysis.—Cobalt was analyzed by a direct EDTA titration, using murexide as an indicator,[9] after the decomposition of a complex with hot concentrated sulfuric and nitric acid. The other elements were analyzed microquantitatively by the Schwarzkopf Microanalytical Laboratory.** An indication of the degree of purity of the complexes was also

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* The most part of this research was done in the laboratory of Department of Chemistry, Fordham University, New York 58, N. Y., U. S. A., during the period in which the former of the authors was a visiting chemist to the University.

[1] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1949); **264**, 321 (1951).

[2] M. Linhard and G. Stirn, ibid., **268**, 105 (1952).

[3] M. Linhard and B. Rau, ibid., **271**, 121 (1953).

[4] C. B. Riolo and T. Soldi, *Gazz. chim. ital.*, **86**, 282 (1956).

[5] F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

[6] K. Kuroda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 572 (1961).

[7] H. Brooke and H. M. Dawson, *J. Chem. Soc.*, **1936**, 497.

[8] F. Kunze and H. Merkader, *Z. physik. Chem.*, **A187**, 285 (1940).

** Schwarzkopf Microanalytical Laboratory, Woodside, New York, U. S. A.

[9] H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, **39**, 38 (1952).

TABLE I. ABSORPTION SPECTRA OF $[Co(halac)(NH_3)_5](ClO_4)_2$, *cis*-$[Co(halac)_2(NH_3)_4]ClO_4$ AND *cis*-$[Co(halac)_2(en)_2]ClO_4$

	1st band		2nd band		3rd band	
	ν(10^{13}/sec.)	log ε	ν(10^{13}/sec.)	log ε	ν(10^{13}/sec.)	log ε
$[Co(halac)(NH_3)_5](ClO_4)_2$						
CH_3CO_2	59.7	1.877	85.2	1.774	—	—
CH_2ClCO_2	59.7	1.869	85.5	1.766	—	—
$CHCl_2CO_2$	59.8	1.850	85.8	1.750	—	—
CCl_3CO_2	59.8	1.857	85.9	1.756	—	—
CH_2BrCO_2	59.7	1.875	85.5	1.778	—	—
$CHBr_2CO_2$	59.7	1.860	85.7	1.751	—	—
cis-$[Co(halac)_2(NH_3)_4]ClO_4$						
CH_3CO_2	57.3	2.050	82.2	1.808	133	4.27
CH_2ClCO_2	57.4	2.003	82.6	1.794	133	4.24
$CHCl_2CO_2$	57.9	1.985	82.8	1.791	134.5	4.28
CCl_3CO_2	58.4	1.929	83.1	1.775	135	4.28
CH_2BrCO_2	57.5	2.018	82.6	1.802	134.5	4.16
$CHBr_2CO_2$	57.8	2.003	82.9	1.814	136	4.31
cis-$[Co(halac)_2(en)_2]ClO_4$						
CH_3CO_2	59.3	2.175	82.9	1.980	132	4.29
CH_2ClCO_2	59.8	2.134	83.0	1.955	131.5	4.30
$CHCl_2CO_2$	60.2	2.090	83.1	1.935	133	4.32
CCl_3CO_2	60.3	2.101	83.1	1.944	132.5	4.34
CH_2BrCO_2	(not obtained)					
$CHBr_2CO_2$	60.1	2.147	83.1	1.984	133	4.37

Ionization constants of the halogenoacetic acids:

CH_3CO_2H	CH_2ClCO_2H	$CHCl_2CO_2H$	CCl_3CO_2H
1.75×10^{-5}	1.4×10^{-3}	5×10^{-2}	2×10^{-1}
	CH_2BrCO_2H	$CHBr_2CO_2H$	
	1.38×10^{-3}	?	

obtained by converting the perchlorate to other salts, and by using equivalent weights, comparing the molar extinction coefficients at their maxima in the visible region.

Apparatus and Spectral Measurements.—The visible and ultraviolet absorption spectra of the complexes were measured with a Cary 15 spectrophotometer using a pair of 1 cm. quartz cells; in some cases the maxima in the absorption bands were confirmed using a Beckman DU spectrophotometer. The concentrations were 0.005 mol./l., except in the case of *cis*-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$, where a 0.0025 mol./l. solution was used because of the solubility limitation. The complexes were dissolved in 0.01 N and 0.04 N perchloric acid in order to avoid the possibility of a rapid base hydrolysis; it was confirmed that a difference in the acid concentration does not change the spectra in most cases. However, where the acidity accelerates the aquation of the complexes, i. e., in *cis*-$[Co(CH_3CO_2)_2(NH_3)_4]^+$ and *cis*-$[Co(CH_3CO_2)_2(en)_2]^+$, the spectra of aqueous solutions were measused. Infrared spectra were also taken with a Perkin-Elmer Infracord in order to verify the composition of the compounds. All of them showed absorptions characteristic of NH_3, CO, and ClO_4 groups. The results are shown in Table I and in Figs. 1 and 2.

The Assignment of the Configuration.—For complexes of the Coa_4b_2 type it has been established,

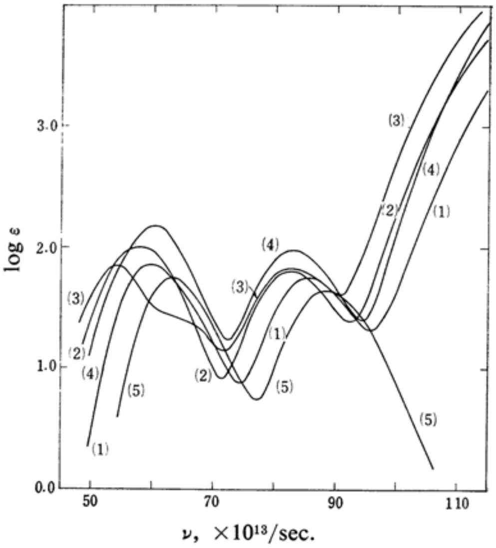

Fig. 1. Absorption spectra of dibromoacetatocobalt(III) complexes.
(1) $[Co(CHBr_2CO_2)(NH_3)_5](ClO_4)_2$
(2) *cis*-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$
(3) *trans*-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$
(4) *cis*-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$
(5) $[Co(NH_3)_6](ClO_4)_3$

TABLE II. SOLUBILITIES AND PRECIPITATION REACTIONS OF THE PERCHLORATES OF HALOGENOACETATO COBALT(III) COMPLEXES

Complex	HCl 6 N	NH_4Cl 2 N	HNO_3 6 N	NH_4NO_3 2 N	$HClO_4$ 6 N	$NaClO_4$ 2 N	NaBr 2 N	KI 2 N	$Na_2S_2O_3$ N	KSCN N	$Na_2C_2O_4$ sat.	K_2CrO_4 N	$K_2Cr_2O_7$ sat.	Solubility ml. H_2O/g.
$[Co(CH_3CO_2)(NH_3)_5]^{2+}$	—	—	4	4	4	4	—	3	—	—	—	—	4	65
$[Co(CH_2ClCO_2)(NH_3)_5]^{2+}$	—	—	4	3	4	3	—	1	—	—	—	2	4	55
$[Co(CHCl_2CO_2)(NH_3)_5]^{2+}$	—	—	2	—	4	4	—	—	—	—	—	4	2	70
$[Co(CCl_3CO_2)(NH_3)_5]^{2+}$	—	—	—	—	3	2	—	—	—	—	—	—	2	120
$[Co(CH_2BrCO_2)(NH_3)_5]^{2+}$	—	—	2	2	4	4	—	—	—	—	—	4	4	63
$[Co(CHBr_2CO_2)(NH_3)_5]^{2+}$	—	—	—	—	4	4	—	4	3	3	—	4	—	26
cis-$[Co(CH_3CO_2)_2(NH_3)_4]^+$	—	—	—	—	—	—	—	—	—	—	—	—	—	vs
cis-$[Co(CH_2ClCO_2)_2(NH_3)_4]^+$	—	—	1	—	3	1	—	—	—	—	—	—	—	24
cis-$Co(CHCl_2CO_2)_2(NH_3)_4]^+$	—	—	—	—	2	4	2	3	—	—	—	—	—	25
cis-$[Co(CCl_3CO_2)_2(NH_3)_4]^+$	1	1	—	1	3	4	—	—	—	—	—	—	1	56
cis-$[Co(CH_2BrCO_2)_2(NH_3)_4]^+$	—	—	—	—	3	2	—	—	—	—	—	—	—	10
cis-$[Co(CHBr_2CO_2)_2(NH_3)_4]^+$	1	1	1	1	4	4	4	4	—	1	—	—	4	50
cis-$[Co(CH_3CO_2)_2(en)_2]^+$	—	—	—	—	—	—	—	—	—	—	—	—	—	vs
cis-$[Co(CH_2ClCO_2)_2(en)_2]^+$	—	—	—	—	—	2	—	1	—	—	—	—	—	62
cis-$[Co(CHCl_2CO_2)_2(en)_2]^+$	—	—	—	—	2	3	—	—	—	—	—	—	—	89
cis-$[Co(CCl_3CO_2)_2(en)_2]^+$	1	—	1	1	3	4	1	—	—	2	2	—	—	280
cis-$[Co(CHBr_2CO_2)_2(en)_2]^+$	—	—	—	—	3	4	3	3	—	1	1	—	—	160

—: No precipitation
1: A small amount of deposit observable on the surface of the test tube
2: A small amount of precipitate
3: A large amount of precipitate (the liquid phase still has the color of the complex)
4: Almost complete precipitation (the liquid phase is almost colorless)
vs: Very soluble

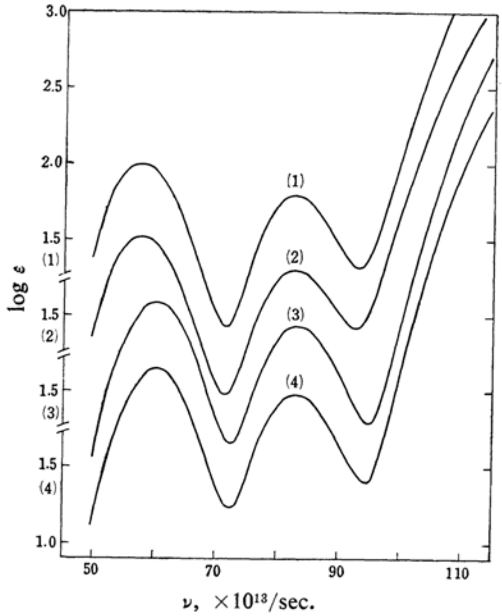

Fig. 2. Absorption spectra of some *cis*-bis-(halogenoacetato)-cobalt(III) complexes.
(1) *cis*-$[Co(CH_2ClCO_2)_2(NH_3)_4]ClO_4$
(2) *cis*-$[Co(CH_2BrCO_2)_2(NH_3)_4]ClO_4$
(3) *cis*-$[Co(CHCl_2CO_2)_2(en)_2]ClO_4$
(4) *cis*-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$

experimentally[1,10] and theoretically[11,12], that the first band of the trans-isomer splits significantly into two parts, whereas that of the cis-isomer does not. In addition, the third band (the charge-transfer band) of the trans-isomer appears at a low frequency than that of the cis-isomer.[13-15] In all the cases studied here, the corresponding isomers showed these spectral characteristics, as the figures show.

Some Physical and Chemical Properties.—Solubilities were measured semiquantitatively by the following method: A definite amount (0.1—1.0 g.) of a complex was placed in a 50 ml. flask; water was then added in 1 ml. increments until the solid was completely dissolved. The temperature was maintained at 20±1°C. The solubility data are, therefore, not equilibrium values; however, because all complexes were powdery or fine crystalline, the data are fairly accurate.

In the precipitation tests, 1 ml. of a reagent was added to 1 ml. of a saturated solution of the complex which had been obtained from the solubility test and cooled to 0°C. In several cases, where the complexes were very soluble, 0.05 molar solutions were tested. The results are summarized in Table II.

Preparations.—*1) Monobromoacetato-pentammine-cobalt(III) Perchlorate,* $[Co(CH_2BrCO_2)(NH_3)_5](ClO_4)_2$.—Ten grams of $[CoCO_3(NH_3)_5]NO_3$ was suspended in 20 ml. of water, and a solution was added which contained 30 g. of CH_2BrCO_2H in 30 ml. of water. The solution was heated for one hour at 70°C, and then cooled to 0°C. After the violet residue which had formed had been removed, 10 ml. of a 25 per cent ammonium nitrate solution was added to the filtrate, and the resulting reddish-orange precipitate was also filtered off. Then 30 ml. of ethanol was added to the cold filtrate with continuous stirring. After the mixture had stood in an ice-water bath for an hour, a reddish-white precipitate formed; this was collected and washed with ethanol and ether. The nitrate, the bromine content of which was a little low, was purified by transformation to the perchlorate. To a saturated solution of the nitrate (one gram of it dissolves in 100 ml. of water at room temperature), concentrated perchloric acid was added. After the mixture had stood at 0°C, the pinkish-orange precipitate was collected, washed with ethanol and ether, and then dried in a desiccator. Yield, ca. 2 g.

Found: Co, 12.15; C, 5.13; H, 3.77; N, 14.67; Br, 16.91. Calcd. for $[Co(CH_2BrCO_2)(NH_3)_5](ClO_4)_2$: Co, 12.25; C, 4.99; H, 3.56; N, 14.56; Br, 16.62%.

2) Dibromoacetato-pentammine-cobalt(III) Perchlorate, $[Co(CHBr_2CO_2)(NH_3)_5](ClO_4)_2$.—Seven grams of $[CoCO_3(NH_3)_5]NO_3$ was suspended in 10 ml. of water, and then a solution of $CHBr_2CO_2H$ (20 g.) in 30 ml. of water was added. The solution was heated for one hour and then cooled in an ice bath. The residue which formed was collected on a glass-filter, and an extract was obtained by washing the residue with 100 ml. of a 50 per cent ethanol - water mixture, A 25 per cent ammonium nitrate solution was added to the extract until precipitation was almost complete. The reddish-white nitrate was isolated and washed with ethanol and ether. The nitrate, the bromine content of which was a little low, was transformed to the perchlorate. The nitrate (ca. 5 g.) was dissolved in 125 ml. of water, and 15 ml. of concentrated perchloric acid was added. The precipitate formed was washed with ethanol and ether. Yield, 5 g.

Found: Co, 10.38; C, 4.38; H, 2.77; N, 12.77; Br, 28.80. Calcd. for $[Co(CHBr_2CO_2)(NH_3)_5](ClO_4)_2$: Co, 10.53; C, 4.29; H, 2.88; N, 12.51; Br, 28.55%.

3) cis-Bis(acetato)-tetrammine-cobalt(III) Perchlorate, *cis*-$[Co(CH_3CO_2)_2(NH_3)_4]ClO_4$.—Although this compound was originally prepared by Linhard and Weigel,[1] the following procedure was found to be much simpler. To 3 g. of $[CoCO_3(NH_3)_4)ClO_4$, a 30 per cent perchloric acid at 50°C was added until the evolution of CO_2 ceased. Sodium acetate (1.7 g.) was added to the solution, which was then evaporated to almost complete dryness at ca. 60°C. Ten milliliters of absolute alcohol was stirred into the product, and the residue which had collected on a filter was washed with absolute alcohol and ether. This perchlorate (3 g.) was dissolved in 60 ml. of an 85 per cent alcohol - water mixture, and, after filtration, 90 ml. of ether was added. The

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[10] Y. Shimura, This Bulletin, **25**, 49 (1952).
[11] C. J. Ballhausen and C. K. Jörgensen, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.*, **29** (14) (1955).
[12] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).
[13] H. Kuroya and R. Tsuchida, This Bulletin, **15**, 427 (1940).
[14] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).
[15] Y. Shimura, ibid., **73**, 5079 (1951).

reddish-purple crystals formed were washed with a 50 per cent ethanol - ether mixture and ether. Yield, 2 g.

Found: Co, 17.08. Calcd. for *cis*-$[Co(CH_3CO_2)(NH_3)_4]ClO_4$: Co, 17.10%.

4) cis - Bis(monobromoacetato) - tetrammine - cobalt(III) Perchlorate, cis-$[Co(CH_2BrCO_2)_2(NH_3)_4]ClO_4$.—A mixture of $[CoCO_3(NH_3)_4]ClO_4$ (3 g.), CH_2BrCO_2H (3.2 g.), and water (4 ml.) was evaporated to almost complete dryness at 50—55°C. The product was then dissolved in 20 ml. of a very dilute perchloric acid solution at 40°C and filtered. Five milliliters of concentrated perchloric acid was added to the filtrate, which was then cooled to 0°C. The resulting reddish-purple crystals were washed with ethanol and ether. The crude perchlorate, the yield of which was ca. 3 g., was recrystallized from 20 ml. of a slightly acidified water with perchloric acid at 40°C. Yield, 2.0 g.

Found: Co, 11.61; C, 9.79; H, 3.23; N, 11.46; Br, 32.02. Calcd. for *cis*-$[Co(CH_2BrCO_2)_2(NH_3)_4]ClO_4$: Co, 11.73; C, 9.56; H, 3.21; N, 11.15; Br, 31.81%.

5) cis-Bis(dibromoacetato)-tetrammine - cobalt(III) Perchlorate, cis-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$. — A solution of $CHBr_2CO_2H$ (4.8 g.) and $[CoCO_3(NH_3)_4]ClO_4$ (3 g.) in 4 ml. of water was evaporated to dryness at 50—55°C. After the addition of a dilute perchloric acid and filtration, the residue on the filter was extracted with 50 ml. of warm water. The extract was cooled, and several drops of perchloric acid were added. The resulting reddish-purple crystals were recrystallized in the same way as 4). Yield, 3.5 g.

Found: Co, 8.95; C, 7.49; H, 2.22; N, 8.67; Br, 48.50. Calcd. for *cis*-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$: Co, 8.93; C, 7.28; H, 2.14; N, 8.49; Br, 48.41%.

6) cis - Bis(dibromoacetato) - bis(ethylenediamine) - cobalt(III) Perchlorate, cis-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$.—A mixture of $[CoCO_3(en)_2]ClO_4$ (2 g.), $CHBr_2CO_2H$ (2.7 g.) and water (3 ml.) was evaporated at ca. 60°C until the mixture nearly solidified. The product was then mixed with 20 ml. of dilute perchloric acid; the reddish precipitate which formed was washed with alcohol and ether. The crude perchlorate, the yield of which was 1.5 g., was dissolved in 40 ml. of warm water and recrystallized in a way similar to that used in 4). Yield, 1.5 g.

Found: Co, 8.12; C, 13.58; H, 2.71; N, 8.05. Calcd. for *cis*-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$: Co, 8.27; C, 13.49; H, 2.55; N, 7.87%.

7) cis-Bis(acetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, cis-$[Co(CH_3CO_2)_2(en)_2]ClO_4$.—This compound has already been prepared,[2)] but it was found that the following procedure was simpler and gave a high yield. To 3 g. of $[CoCO_3(en)_2]ClO_4$, a 30 per cent solution of perchloric acid at 50°C was added until the evolution of carbon dioxide ceased. Sodium acetate (1.5 g.) was then added to the mixture, and it was evaporated to almost complete dryness at 60—65°C. The product was thoroughly mixed with 10 ml. of alcohol, and the resulting precicipitate was washed several times with alcohol and finally with ether. The bright red crystals thus obtained were the double salt, *cis*-$[Co(CH_3CO_2)_2(en)_2]ClO_4 \cdot NaClO_4$, judging from the analytical results and the spectra of its solution. Yield, 3.5 g. The neutral perchlorate is very soluble in water and unobtainable by usual methods. It was isolated as follows: To a mixture of 30 ml. of alcohol and the double salt, water was slowly added, drop by drop, by continuous stirring, until the color suddenly changed to violet. At this point a few extra drops of water were added, and the precipitate was collected and washed with alcohol several times and finally with ether. The filtrate also contained a large amount of the complex, and upon the addition of ether, additional perchlorate was obtained in a pure state. Yield, 3 g. Although the perchlorate and the double salt are different colors in the solid state, the absorption spectra of their solutions were exactly identical.

Found: Co, 14.73. Calcd. for *cis*-$[Co(CH_3CO_2)_2(en)_2]ClO_4$: Co, 14.86%.

8) cis - Bis(chloroacetato) - tetrammine - cobalt(III) Perchlorate, cis-$[Co(clac)_2(NH_3)_4]ClO_4$ *and cis-Bis(chloroacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, cis-*$[Co(clac)_2(en)_2]ClO_4$, where clac = CH_2ClCO_2, $CHCl_2CO_2$, CCl_3CO_2. These complexes were prepared by the method of Linhard and Weigel.[1)]

Results and Discussion

Preparations.—The usual procedure for the preparation of $[Co(X)(NH_3)_5]^{n+}$-type complexes[16)] requires that the mixture of $[Co(H_2O)(NH_3)_5]^{3+}$ and X be kept at a temperature (usually higher than room temperature) for a suitable period in an acidic solution. This approach was used for the preparation of $[Co(CH_2BrCO_2)(NH_3)_5]^{2+}$ and $[Co(CHBr_2CO_2)(NH_3)_5]^{2+}$. However, unlike many other ligands, the bromoacetate ions are relatively unstable at high temperatures and yet do not rapidly coordinate at low temperatures. It was, therefore, observed, from the color and absorption spectra of the by-products, that at higher temperatures and for longer periods than those described in the Experimental section, the yield of the desired complexes became lower as a result of the decomposition and/or hydrolysis of the ligands, whereas at lower temperatures the main product was the unreacted aquo-complex.

The preparation of $[Co(CBr_3CO_2)(NH_3)_5]X$ was also attempted in a similar way. In this case, however, the tribromoacetate of the aquo-complex, $[Co(H_2O)(NH_3)_5](CBr_3CO_2)_3$, precipitates immediately after the starting materials are mixed. When the temperature is elevated, the tribromoacetate ion decomposes to an oily material, and the desired complex is not obtained.

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16) J. C. Bailar, Jr., "Inorganic Syntheses," Vol. IV, 171 (1953).

Linhard and his co-workers[1-3] studied the $[Co(clac)_2(NH_3)_4]X$ complexes and found that cis-isomers were obtained when $[CoCO_3(NH_3)_4]ClO_4$ and an equivalent amount of chloroacetic acid were evaporated at a relatively low temperature, whereas trans-isomers were obtained when a large excess of acids was used and the evaporation occurred at a higher temperature. This principle was used for the preparation of the cis-isomers of the bromoacetato complexes, and the desired complexes, except for *cis*-$[Co(CH_2BrCO_2)_2(en)_2]ClO_4$, were obtained with comparative ease. The preparation of *cis*-$[Co(CH_2BrCO_2)_2(en)_2]ClO_4$ was attempted, with varying temperatures, solvents and starting materials. However, the resulting reaction products were always extremely hygroscopic and no definite solid material was obtained, although the spectra of solutions of some products showed fairly satisfactory features.

Solubilities.—Although several reversed cases may be noted, there are definite trends in the solubilities of the complexes. That is, the larger the halogen content of the ligands, the less soluble they are in water and the more soluble they are in ethanol, especially when the compound is slightly moist.

Precipitation Reactions.—In addition to the anions shown in Table II, it was observed that a 1 N solution of sodium carbonate, sodium acetate, sodium nitrite and sodium sulfite, and a saturated solution of sodium hydrogen phosphate, 6 N sulfuric acid and 2 N ammonium sulfate did not precipitate any of the complexes. This table may prove useful for the transformation of the anion of the complexes, and it suggests the possibility of utilizing the complexes for the analysis of anions. For example, $[Co(CHBr_2CO_2)(NH_3)_5]^{2+}$ precipitates with iodide but not with bromide and chloride. Therefore, the complex presents the possibility of detecting the I^- ion in the presence of Br^- and Cl^- ions.

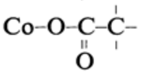
Visible and Ultraviolet Absorption Spectra.—As may be seen in Table I, in the case of pentammine complexes the maxima of the first band appear at almost identical frequencies, and those of the second band are also very close to each other. However, in the tetrammine series, obvious differences in the maxima are observable; that is, the larger the halogen content in the halogenoacetato ligand, the larger the frequencies of both the first and the second bands. The same order exists in the bis-(ethylenediamine) series. It has been pointed out[17] that if the ligand "a" is replaced in a complex Ma_6 by a ligand "b", the shift of the maxima is approximately as represented by the following equation:

$$\nu(Ma_{6-n}b_n)=\frac{6-n}{6}\,\nu(Ma_6)+\frac{n}{6}\nu(Mb_6)$$

Therefore, the difference in ν between Ma_4b_2 and $Ma_4b'_2$ should be twice as large as that between Ma_5b and Ma_5b'. This relation holds in the present complexes. Thus, the relative position of the ligands in the spectrochemical series is determined to be:

$$I<\cdots<CH_3CO_2<\left\{\begin{array}{l}CH_2ClCO_2<CHCl_2CO_2<CCl_3CO_2\\ \quad\wr\qquad\qquad\wr\\ CH_2BrCO_2<CHBr_2CO_2<(CBr_3CO_2)\end{array}\right\}<\cdots<CN$$

from the data of bis-(halogenoacetato) as well as mono-(halogenoacetato) series.

Now, since all the complexes have the  $Co{-}O{-}\underset{\underset{O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}$ atomic arrangement, it may be said that the factors which may influence the spectra are: (1) the polarity of the cobalt-halogenoacetato bond, (2) the volume of the ligands, and (3) the chemical (especially the oxidation-reduction) property of halogens. We shall now consider these factors.

Previously, Linhard and his co-workers[1-3] measured the absorption spectra of $[Co(RCO_2)(NH_3)_5]^{2+}$ and *cis*-$[Co(RCO_2)_2(NH_3)_4]^+$ where R=alkyl, and found that in each case the absorption maxima of both the first and the second bands appear at almost identical frequencies, with a variety of R. This indicates that the volume of a ligand is a minor factor in the spectral characteristics of complexes. The same situation exists in the present case, since there is little shift in the absorption maxima with the variety of halogen species, and chlorine and bromine have fairly different atomic radii.

It is well-known that, when halogens coordinate to the central atom directly, the corresponding halogeno-complexes (e.g., $[CoCl(NH_3)_5]^{2+}$ and $[CoBr(NH_3)_5]^{2+}$) have greatly different spectral features. This phenomena have been attributed to the different oxidation-reduction properties of halogens. On the contrary, corresponding chloroacetato- and bromoacetato-complexes show identical features, as may be seen in Figs. 1 and 2. Furthermore, the halogen-carbon bondings have no absorption in the visible and near ultraviolet region. Thus, it is clear that the differences in the chemical property of halogens in the ligands are also a minor factor in affecting the positions of the first and the second absorptions.

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[17] Y. Shimura and R. Tsuchida, This Bulletin, 28, 572 (1955).

(Since carbon-halogen bondings have a slight absorption in far ultraviolet region, the third band may be influenced by the variety of halogen.)

The first factor, the polarity of Co–O bonds, is not known exactly, but it may be assumed that it parallels the polarity of the H–O bonds of the halogenoacetic acids, which can be placed in a qualitative order by the dissociation constant of each acid, or by the basicity of each halogenoacetate ion. The experimental results show that the smaller the basicity of the halogenoacetato ligand, the larger the frequencies of the absorption maxima, as may be seen in Table I. That the polarity of central atom - ligand bonding is the predominant factor in the energy splitting of the d-electrons in a complex is a fundamental assumption of the recent ligand field theory of complex compounds; this assumption has been experimentally verified by the present results.

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