# Studies of Halogenoacetato Cobalt(III) Complexes. III.*,1) The Preparation and Some Properties of Trifluoroacetato Cobalt(III) Complexes

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In the preceding communications[1,2] the present authors have reported on the preparation of and some properties of pentammine-, tetrammine- and bis(ethylenediamine)-cobalt(III) complexes with chloroacetato and bromoacetato ligands—$[Co(halac)(NH_3)_5]X_2$, *cis-* and *trans-*$[Co(halac)_2(NH_3)_4]X$ and *cis-* and *trans-*$[Co(halac)_2(en)_2]X$, where halac$=CH_3CO_2$, $CH_2ClCO_2$, $CHCl_2CO_2$, $CCl_3CO_2$, $CH_2BrCO_2$ and $CHBr_2CO_2$. There we pointed out several regularities found in their properties. It was there considered to be very interesting that in each series of complexes the basicity of the halogenoacetato ligands is the main factor determining the maxima of their absorption spectra, and that the volume of the ligands and the sort of halogen in the halac's are minor ones.

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* This work was mostly done in the laboratory of Chemistry Department, Fordham University, New York 58, N. Y., U. S. A., when the former of the authors was a visiting chemist to the university.

[1] Parts I and II of this series: K. Kuroda and P. S. Gentile, This Bulletin, **38**, 1362, 1368 (1965).

[2] K. Kuroda and P. S. Gentile, *J. Inorg. Nucl. Chem.*, **27**, 155 (1965).

Although the trifluoroacetato-pentammine-cobalt(III) complex, $[Co(CF_3CO_2)(NH_3)_5]X_2$, has previously been studied,[3,4] bis(trifluoroacetato)-cobalt(III) complexes have so far not been prepared. Since trifluoroacetic acid is a stronger acid than any other halogenoacetic acid (it is virtually a strong electrolyte), the basicity of the trifluoroacetato ligand is the smallest among all of the halogenoacetato ligands, the spectral features of trifluoroacetato complexes should be the most extreme in each member of the above series. With such an expectation, several new cobalt complexes with trifluoroacetato ligand, *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]ClO_4$, *trans*-$[Co(CF_3CO_2)_2(NH_3)_4]Cl$, *cis*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$ and *trans*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$, have been prepared, and some physical and chemical properties have been examined. In consequence, the expected results have been obtained, and also a few special noteworthy phenomena have been observed.

## Experimental

**Materials.** — Trifluoroacetic acid (K & K Laboatories, Inc.) and all the other reagent-grade chemicals were used without further purification.

**Analysis.**—Cobalt was analyzed by EDTA direct titration, using murexide as an indicator,[5] after a complex had been decomposed with hot concentrated sulfuric and nitric acids. The other elements were analyzed microquantitatively by the Schwarzkopf Microanalytical Laboratory (Woodside, New York, U. S. A.).

**Apparatus and Measurements.**—The visible and ultraviolet absorption spectra of the complexes were measured with a Cary 15 spectrophotometer, using a pair of one-cm. quartz cells. The measurements were carried out in a way which has been described previously.[1] The infrared spectra were also taken with a Perkin-Elmer Infracord in order to help verify the composition of the compounds. All of the complexes showed the characteristic absorptions of CO and $ClO_4$ (except for 3) below). The procedure of the solubility measurement, as well as that of the precipitation test, have also been described previously.[1]

**The Assignment of Configuration.**—It has been settled both experimentally[6,7] and theoretically[8,9] that the 1st band of a trans-isomer splits much more significantly than that of the corresponding cis-isomer. As may be seen in Fig. 1, two isomers exhibited such absorption curves; by this means geometrical configurations were assigned.

**Preparations.** — *1) Trifluoroacetato-pentammine-cobalt(III) Perchlorate,* $[Co(CF_3CO_2)(NH_3)_5](ClO_4)_2$.—The nitrate was prepared by a procedure similar to that used for the acetato-complex described in "Inorganic Syntheses."[10] The nitrate was transformed to the perchlorate by the addition of perchloric acid to its solution.

*2) cis-Bis(trifluoroacetato)-tetrammine-cobalt(III) Perchlorates, cis-*$[Co(CF_3CO_2)_2(NH_3)_4]ClO_4$.—A mixture of $[CoCO_3(NH_3)_4]ClO_4$ (2 g.), $CF_3CO_2H$ (1.7 g.) and water (2 ml.) was evaporated to almost complete dryness at 65°C. To the reaction product was then added 5 ml. of a 20% sodium perchlorate solution; the precipitate thus formed was collected and washed with the sodium perchlorate solution. The product was recrystallized from 20 ml. of warm (~40°C) water, and the resulting crystals were collected on a glass filter and washed with ether in order to remove the attached aqueous phase mechanically as completely as possible, and then with an ethanol (80%) - ether mixture and with ether. (The complex is very soluble in ethanol, especially when it is wet.) Yield: 0.5 g.

Found: Co, 12.76; C, 10.85; H, 2.83; N, 12.14. Calcd. for *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]ClO_4$: Co, 13.02; C, 10.62; H, 2.67; N, 12.38%.

*3) trans-Bis(trifluoroacetato)-tetrammine-cobalt(III) Chloride, trans-*$[Co(CF_3CO_2)_2(NH_3)_4]Cl$.—A product was obtained by the evaporation of a mixture of $[CoCO_3(NH_3)_4]ClO_4$ (3 g.), $CF_3CO_2H$ (9.5 g.) and water (5 ml.) at 75—80°C. Ten milliliters of a 20% sodium perchlorate solution was added to the cooled product, and the precipitate formed was separated and extracted by 10 ml. of warm water. After combining the extracted solution with the first filtrate, 20 ml. of a 6 N hydrochloric acid was added and the mixture was kept at 0°C for an hour. The light brownish-violet crystals which formed, which were the acidic chloride of the complex *trans*-$[Co(CF_3CO_2)_2(NH_3)_4]Cl\cdot HCl$, were then washed with a cold 6 N hydrochloric acid until the filtrate became colorless. To convert to a neutral salt, the crystals were dissolved in 10 ml. of ethanol containing a few drops of water; then 10 ml. of ether was added to the solution. The resulting pale violet precipitate was washed with an ethanol (50%) - ether mixture and with ether. The neutral salt can also be obtained if the *dry* acidic chloride is treated with absolute ethanol, but the *wet* one is very soluble in ethanol. Yield: 0.5 g.

Found: Co, 14.94; C, 12.23; H, 3.46; N, 14.07. Calcd. for *trans*-$[Co(CF_3CO_2)_2(NH_3)_4]Cl$: Co, 15.17; C, 12.36; H, 3.34; N, 14.42%.

*4) cis-Bis(trifluoroacetato)-bis(ethylenediamine)-cobalt-(III) Perchlorate, cis-*$[Co(CF_3CO_2)_2(en)_2]ClO_4$. — This complex was prepared by a procedure similar to 2). The yield of the recrystallized product was 1 g. from 2 g. of $[CoCO_3(en)_2]ClO_4$.

Found: Co, 11.50; C, 18.91; H, 3.66; N, 10.93. Calcd. for *cis*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$: Co, 11.68; C, 19.04; H, 3.20; N, 11.10%.

*5) trans-Bis(trifluoroacetato)-bis(ethylenediamine)-cobalt-(III) Perchlorate, trans-*$[Co(CF_3CO_2)_2(en)_2]ClO_4$.—A mixture of $[CoCO_3(en)_2]ClO_4$ (3 g.), $CF_3CO_2H$ (10 g.) and water (5 ml.) was evaporated at 75°C to a small volume; the solution was then carefully boiled for a few minutes with a small flame until the color suddenly changed from dark red to deep reddish-violet. As soon as this process had finished, the mixture was

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

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

[5] H. Flaschka, *Microchemie ver. Microchim. Acta*, **39**, 38 (1952).

[6] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1952).

[7] Y. Shimura, This Bulletin, **25**, 49 (1952).

[8] C.J. Ballhausen and C.K. Jørgensens, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.*, **29**, No. 14 (1955).

[9] H. Yamatera, This Bulletin, **31**, 95 (1958).

[10] J. C. Bailar, "Inorganic Syntheses," Vol. IV, 175 (1953).

cooled. The resulting solid was crushed, and 20 ml. of a dilute sodium perchlorate solution was added and thoroughly mixed in. The precipitate which formed, after being washed with a cold sodium perchlorate solution, was recrystallized from 40 ml. of warm water. A concentrated solution which contained 2 g. of sodium perchlorate was added in order to complete the precipitation. The pale violet crystals which formed were washed with ethanol and ether. Yield: 1.5 g.

Found: Co, 11.64; C, 18.84; H, 2.86; N, 11.45. Calcd. for *trans*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$: Co, 11.68; C, 19.04; H, 3.20; N, 11.10%.

## Results and Discussion

Table I shows the solubilities of the complexes prepared and their precipitation reactions with various common anions. The salts are, in general, readily soluble in water; this is in contrast to the corresponding trichloroacetato-complexes.[1] On the other hand, they are soluble in ethanol or even in an ethanol-ether mixture, especially when they are wet, as are the trichloroacetato-complexes.[1] One must take remember this quality in washing the complexes in preparing them.

Among the reactions with various anions, the precipitation of *cis*-$[Co(CF_3CO_2)_2(en)_2]^+$ with acetate ions is considered to be the most important, because there is as yet no precipitant for acetate ions. It has already been reported[11] that this reaction may be used as a new method for detecting acetate in the qualitative analysis of anions. The reactions in which trichloroacetic acid makes precipitates with the trans-isomers but not with the cis-isomers are similar to those with other halogenoacetato-complexes already reported.[1]

Table II and Fig. 1 show the absorption spectra of the complexes. Previously,[1] it has been pointed out that, in the absorption spectra of each series of halogenoacetato-complexes—the pentammine-, *cis*- and *trans*-tetrammine- and *cis*- and *trans*-bis-(ethylenediamine)-series of complexes—, the basicity of halogenoacetato ligands is the predominant factor in determining spectral characteristics, and that the other factors—the volume of the ligands and the oxidation-reduction property of halogen atoms—are minor.

Thus, the relative position of $CF_3CO_2$ in the spectrochemical series is expected to be:

$$I < \cdots < CH_3CO_2 < \left\{\begin{array}{ccccc} & & & & CF_3CO_2 \\ & & & & \vee \\ CH_2ClCO_2 & < & CHCl_2CO_2 & < & CCl_3CO_2 \\ \wr & & \wr & & \\ CH_2BrCO_2 & < & CHBr_2CO_2 & & \end{array}\right\} < \cdots < CN$$

(increasing ligand field)

since the basicity of $CF_3CO_2^-$ is the smallest of

TABLE I. SULUBILITIES AND PRECIPITATION REACTIONS OF TRIFLUOROACETATO COBALT(III) COMPLEXES

| | HCl<br>6 N | $NH_4Cl$<br>2 N | $HNO_3$<br>6 N | $NH_4NO_3$<br>2 N | KI<br>2 N | $CH_3CO_2Na$<br>N | $K_2Cr_2O_7$<br>sat | $CCl_3CO_2H$<br>2 N | Solubility<br>ml. $H_2O$/g. |
|---|---|---|---|---|---|---|---|---|---|
| $[Co(CF_3CO_2)(NH_3)_5](ClO_4)_2$ | — | — | 3 | 1 | 2 | — | 4 | 1 | 153 |
| *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]ClO_4$ | — | — | — | — | — | — | — | — | ~10 |
| *trans*-$[Co(CF_3CO_2)_2(NH_3)_4]Cl$ | 4 | — | — | — | — | — | — | 1 | v.s. |
| *cis*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$ | — | — | — | — | — | 4 | — | — | ~18 |
| *trans*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$ | — | — | — | — | 1 | — | 3 | 4 | 25 |

| | |
|---|---|
| — | 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 has still the color of the complex) |
| 4 | Almost complete precipitation (the liquid phase is almost colorless) |
| v.s. | Very soluble |

The following reagents do not precipitate with any of the above complexes: 6 N $H_2SO_4$, 2 N $(NH_4)_2SO_4$, 2 N NaBr, N $Na_2SO_3$, N $Na_2S_2O_3$, N $NaNO_2$, N $Na_2CO_3$, sat-$Na_2C_2O_4$, N KSCN, N $K_2CrO_4$, sat-$Na_2HPO_4$.

TABLE II. ABSORPTION SPECTRA OF TRIFLUOROACETATO COBALT(III) COMPLEXES

| | 1st band | | | | 2nd band | |
|---|---|---|---|---|---|---|
| | Ia | | Ib | | | |
| | $\nu_{1a}$ ($10^{13}$/sec.) | $\log \varepsilon_{1a}$ | $\nu_{1b}$ ($10^{13}$/sec.) | $\log \varepsilon_{1b}$ | $\nu_2$ ($10^{13}$/sec.) | $\log \varepsilon_2$ |
| $[Co(CF_3CO_2)(NH_3)_5]^{2+}$ | 60.1 | 1.799 | | | 86.2 | 1.697 |
| *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]^+$ | 58.5 | 1.894 | | | 83.5 | 1.713 |
| *trans*-$[Co(CF_3CO_2)_2(NH_3)_4]^+$ | 53.7 | 1.672 | 66.0 | 1.40 | 84.5 | 1.702 |
| *cis*-$[Co(CF_3CO_2)_2(en)_2]^+$ | 60.6 | 2.061 | | | 83.3 | 1.903 |
| *trans*-$[Co(CF_3CO_2)_2(en)_2]^+$ | 54.5 | 1.650 | 68.6 | 1.49 | 85.2 | 1.728 |

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[11] K. Kuroda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **85**, 515 (1964).

all of the halogenoacetate ions. This expectation was statisfactorily verified by the experimental results that the absorption maxima of the present complexes (except for the split 1st bands of the trans-isomers) were found at the highest frequencies in each series of complexes.[1]

The splitting of the 1st bands of the *trans*-isomers is worth noticing because of its magnitude. As may be clear from a comparison of Fig. 1 and Figs. 1 and 2 in Part II (Ref. 1), the degree of the splitting of the present trans-isomers is rather larger than that of trichloroacetato complexes. This result confirms the previous suggestion that the distance in the spectrochemical series between the "a" and "b" of a complex *trans*-$[Coa_4b_2]$ is not the sole factor determining the magnitude of the splitting.

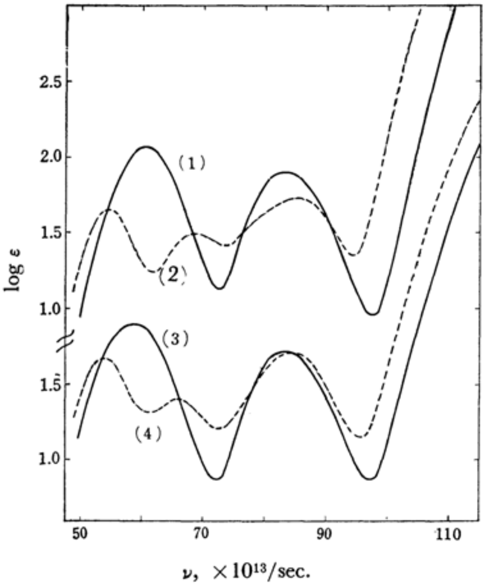

Fig. 1. Absorption spectra of trifluoroacetato cobalt(III) complexes.

(1) *cis*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$
(2) *trans*-$[Co(CF_3CO_2)_2(en)_2]ClO_4$
(3) *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]ClO_4$
(4) *trans*-$[CO(CF_3CO_2)_2(NH_3)_4]Cl$

The shape of the 2nd band of *trans*-$[Co(CF_3CO_2)_2(en)_2]^+$ is considered to be noteworthy. It is well known[12] that, in a pure single band, the half-width of the left branch, $\delta$-, is usually about 10% smaller than that of the right branch, $\delta_+$; this generality is preserved in the lst and 2nd bands of $[Co(CF_3CO_2)(NH_3)_5]^{2+}$, *cis*-$[Co(CF_3CO_2)_2(NH_3)_4]^+$, and *cis*-$[Co(CF_3CO_2)_2(en)_2]^+$ and in Ia bands of the trans-isomers, as in the bands of many other cobalt complexes. Contrary to this rule, however, the 2nd band of *trans*-$[Co(CF_3CO_2)_2(en)_2]^+$ is abnormally asymmetric in a direction the reverse of the ordinary cases, as may be observed in Fig. 1. Indeed, the right branch of the Ib band might influence the left branch of the 2nd band, but because Ib is so small and so separated from the 2nd that it is not possible to deform for it the band to such a large extent. A similar deformation can be observed in the spectra of the *trans*-$[Co(halac)_2(en)_2]^+$ series previously reported[1]; that is, the left branch of the 2nd band broadens steadily with an increase in the chlorine content of the halac-ligands, and the deformation of *trans*-$[Co(CCl_3CO_2)_2(en)_2]^+$ is as large as that of *trans*-$[Co(CF_3CO_2)_2(en)_2]^+$. The same trend, but to a lesser degree, is also observable in the *trans*-$[Co(halac)_2(NH_3)_4]^+$ series. These facts may indicate a splitting of the 2nd bands.

It has been pointed out[13] that the 2nd band of a *trans*-$[Coa_4b_2]$-type complexes should split into two parts by the tetragonal distortion of the ligand field, as the 1st band does. However, no cobalt complex has ever been found which exhibits such splitting in the band. The reasons for this are considered to be that, in many cases, the 2nd band is greatly influenced by adjacent bands and/or ligand specific bands; there have been very few examples in which both the branches of the band could be compared over a sufficient frequency range free from the influence of other bands. Fortunately, the 2nd bands of the present complexes are satisfactorily pure and can be examined with accuracy. A precise analysis of the spectral curves is undoubtedly necessary for a decision on the splitting phenomena; this research will be reported on shortly in a separate paper.

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[12] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

[13] J. S. Griffith and L. E. Orgel, *J. Chem. Soc.*, **1956**, 4981.