Studies on the Synthesis of Metal Complexes. II. Synthesis and Absorption Spectra of Hydrogen Ethylenediaminetetraacetato-cobaltate (III) and Sodium-hydrogen Chloro-ethylenediaminetetraacetato-cobaltate (III)*

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The common cobalt (III) complex in which ethylenediaminetetraacetic acid is hexadentate was first prepared by Brintzinger, Thiele and Mueller[1], and nitro-(ethylenediaminetetraacetato)-cobaltate (III) and bromo-(ethylenediaminetetraacetato-cobaltate (III) were later synthesized by Schwarzenbach[2]. Hereafter, ethylenediaminetetraacetic acid, quadrivalent ethylenediaminetetraacetate anion and tervalent anion will be denoted by EDTA, edta and edtaH respectively.

In the present study, free acid of the common complex, H[Coedta]·$4H_2O$ and sodium salt of the chloro-complex, Na[Co(Cl) (edtaH)]·$2H_2O$ were newly synthesized, and absorption spectra of all Co(III)-EDTA complexes including older ones were also measured. The geometrical configuration of the complexes is also discussed in this paper.

Experimental

Synthesis of H[Coedta]·$4H_2O$.—Ten grams of EDTA($edtaH_4$) and about the same amount of freshly prepared cobaltic hydroxide were introduced into 200 cc. of water, and the mixture was heated on a water-bath for about one hour until the completion of the reaction. After cooling, the solution was filtered and then the filtrate was poured into a column of cation exchanger Amberlite IR-120 which had been converted into H-form. By this operation the alkali ions contained in the cobaltic hydroxide were completely removed. The solution passing through the exchanger was collected and then concentrated by means of vacuum distillation. On cooling the residual solution in an ice-bath, crystals were deposited, which were filtered by suction and recrystallized from the aqueous solution by adding dil. hydrochloric acid in the cold. Yield, about 65%

Anal. Found: H_2O, 17.1; Co, 14.30. Calcd.: H_2O, 17.0; Co, 14.15%.

The crystals obtained were deep lavender in color like the common complex, Na[Coedta]·$4H_2O$, but less soluble than the latter. The pH of a 10^{-3} M aqueous solution was found to be 2.80.

Synthesis of Na[Co(Cl) (edtaH)]·$2H_2O$.—This compound was prepared as blue crystals by the following method. To a conc. solution prepared by dissolving 10 g. of Na[Co(edta)]·$4H_2O$ in water was added 40 cc. of conc. hydrochloric acid, and the solution was evaporated nearly to dryness on a water-bath. After cooling, the blue residue was washed several times with a little water until the washings did not show any reddish-violet color. By this treatment the unchanged salt, Na[Co(edta)], was removed from the complex aimed at. The remainder was dissolved in water containing a small amount of sodium acetate, and then pure alcohol was added to this solution until blue crystals separated out. They were dissolved again in water containing sodium acetate and then recrystallized by adding dil. hydrochloric acid to the cooled solution. Yield, about 45%.

Anal. Found: H_2O, 8.0; Co, 13.08; Cl, 10.0%. Calcd: H_2O, 7.95; Co, 13.02; Cl, 7.84%.

The complex was readily soluble in water containing an acetate and was converted to the common complex when the aqueous solution was heated for a long time or some silver nitrate or an acid was added to it. The pH of a 10^{-3} M aqueous solution was found to be 2.91.

The same complex was synthesized alternatively by using Na[Co(Br) (edtaH)]·$2H_2O$ or Na[Co(NO_2) (edtaH)]·H_2O in place of Na[Coedta]·$4H_2O$. Free acid of the chloro-complex, H[Co(Cl) (edtaH]·$2H_2O$ was prepared by using H[Coedta]·$4H_2O$ in place of Na[Coedta]·$4H_2O$. It came in blue crystals like the sodium salt and the yield was about 50%.

Formation of Blue Co-EDTA Complex.—To an alkaline solution of EDTA prepared by dissolving the disodium salt ($Na_2H_2edta·2H_2O$) in dil. aqueous solution of sodium hydroxide, an aqueous solution of cobalt sulfate was added and the mixture was inserted in an ice-bath. On adding 10% solution of hydrogene peroxide, the reaction mixture changed from pink to blue in color. Attempts to isolate crystals from this solution ended in failure. This blue solution was very unstable and was converted to the violet solution of common complex with elevation of temperature or by acidification of the solution.

Other Complexes.—Na[Coedta]·$4H_2O$, Na[Co(NO_2) (edtaH)]·H_2O and Na[Co(Br) (edtaH)]·$2H_2O$ were synthesized by the methods reported by Schwarzenbach[2].

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1) H. Brintzinger, H. Thiele and U. Mueller, *Z. anorg. Chem.*, **251**, 285 (1943).

2) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

Analysis.—The water of crystallization was determined from the loss of weight of samples at 130°C by means of a Shimazu Thermano Balance, and it was also found that the samples could be dehydrated by the drying with no change in their chemical properties. The cobalt contents were iodometrically determined for samples treated by bisulfate fusion. The chlorine content was determined by Volhard's method.

Measurement.—The visible and ultraviolet absorption spectra were measured by using a Beckman Model DU Spectrophotometer, and the infrared absorption spectrum, by a Hilger Model 800 Recording Spectrophotometer. Potentiometric titration was carried out by a Shimazu Model MT-3 Electronic Titrimeter.

Results and Discussion

The titration curves of the complexes and the infrared spectrum of chloro-complex are shown in Fig. 1 and Fig. 2 respectively. All the absorption curves of the aqueous solution of the complexes are shown in Figs. 3 and 4, and their absorption maxima are given in Table I.

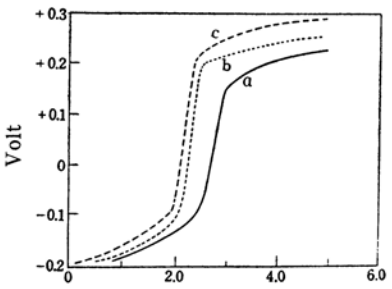


Fig. 1. Titration curves of 10^{-3} M complexes (20 cc) with 10^{-2} N sodium hydroxide.
a. $H[Coedta]\cdot 4H_2O$
b. $Na[Co(Cl)(edtaH)]\cdot 2H_2O$
c. $Na[Co(NO_2)(edtaH)]\cdot H_2O$

TABLE I
ABSORPTION MAXIMA OF Co (III)-EDTA COMPLEXES

Complexes	First Band ν_1	First Band log ε_1	Second Band ν_2	Second Band log ε_2	Third Band ν_3	Third Band log ε_3	Specific Band ν_s	Specific Band log ε_s
Common complex $Na[Coedta]\cdot 4H_2O$	55.9	2.51	78.5	2.34	132.16	4.34	—	—
Blue Complex [Coedta]⁻ ?..	51.7	2.47	77.9	2.37	135.14	4.25	—	—
Free Acid of Common Complex $H[Coedta]\cdot 4H_2O$	55.9	2.55	78.5	2.38	133.33	4.45	—	—
Nitro-Complex $Na[Co(NO_2)(edtaH)]\cdot H_2O$.....	53.0 60.6	2.03 2.33	—	—	120.00 133.33	4.26 4.26	88.24	3.52
Bromo-complex $Na[Co(Br)(edtaH)]\cdot 2H_2O$.....	50.9	2.37	75.0 ?	2.39	111.11 130.43	4.18 4.22	—	—
Chloro-complex $Na[Co(Cl)(edtaH)]\cdot 2H_2O$.....	51.3	2.38	74.6	2.31	111.52 132.74	4.18 4.43	—	—

Chemical Formulae of the Synthesized Compounds.—As will be seen in Fig. 1, the titration curve of our chloro-complex is very similar to that of the nitro-complex, and both complexes act as monobasic acids. A like behavior is observed in the free acid of common complex. Further, the two carbonyl bands shown by the infrared spectrum of the chloro-complex are strong evidence for the existence of a free carboxyl group in the coordination sphere of the complex (Fig. 2). The stronger band, which appears at 1610 cm^{-1}, is attributed to the presence of coordinated carboxyl groups. The weaker band, at 1724 cm^{-1}, is associated with the free carboxyl group. Incidentally, the bands for corresponding bromo-complex appear at 1628 cm^{-1} and 1723 cm^{-1} [3]. Thus, in view of the information obtained from the chemical analysis, titration and infrared spectrum measurement, it is reasonable to give our compounds such formulae as given in the experimental section.

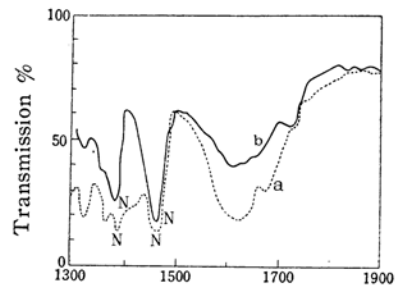
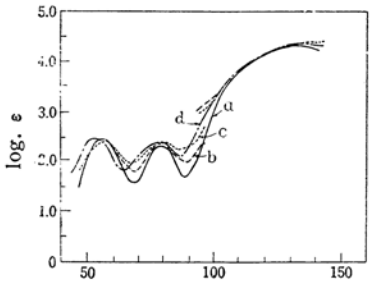


Fig. 2. Infrared absorption spectra of:
a. $Na_2H_2edta\cdot 2H_2O$
b. $Na[Co(Cl)(edtaH)]\cdot 2H_2O$
N. Nujol.

3) D.H. Bush and J.C. Bailar, *J. Am. Chem. Soc.*, **75**, 4574 (1953).

Absorption Spectra of [Coedta] and Blue Co-EDTA Species.—Although the absorption spectrum of the common violet complex had already been measured by Y. Shimura and R. Tsuchida[4], the present workers made new measurements to investigate the pH effect on the absorption spectrum. As is seen in Fig. 3, the absorption curves of buffer solutions prepared in the pH range 2 to 4 are exactly identical with that of an aqueous solution, while those of alkaline solution prepared in the pH range 8 to 10 are different, and further the variation of the optical density shows appreciable deviation from that predicted by Beer's law.

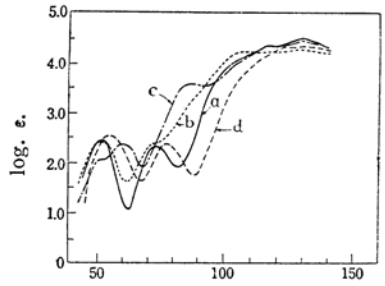
The blue-Co-EDTA complex species described in the experimental section may be identical with the blue complex species regarded as hydroxo-complex, $[Co(OH)(edtaH)]^-$, by Schwarzenbach[2]. The absorption curve of this complex is given in the same figure (Fig. 3d). Discussion of the configuration of species will be given later.



Frequency, 10^{13}/sec.

Fig. 3. Absorption spectra of $[Coedta]^-$:
- a. in aqueous sol. (pH 6.9), acid sols. (pH>2).
- b. in pH 9.5.
- c. in pH 10.3.
- d. blue Co-EDTA complex species.

Absorption Spectra of [Co(X) (edtaH)].—Although the absorption spectra of nitro-and bromo-complex had already been measured by Y. Shimura and R. Tsuchida*, the same thing was attempted by the present workers in relation to the chloro-complex. As is seen in Fig. 4, the absorption curves of bromo- and chloro-complex are similar to each other in appearance, and the maxima of the first and second bands both show a bathochromical shift from the corresponding maxima of the common complex. A little difference between the two, however, is clearly to be seen from Table I, that is, the maximum of the first band for the bromo-complex is shifted to a slightly longer wave-length than that for chloro-complex. The reason for these bathochromic effects of the ligands may be explained by the familiar empirical rule that the bromide and chloride ions are more bathochromic ligands than the oxalate ion, and the bromide ion is slightly more bathochromic than the chloride ion as ligand. The same relation probably holds for the second set of bands, but it is still uncertain since the absorption curve of bromo-complex does not show a well-defined maximum in the second band.



Frequency, 10^{13}/sec.

Fig. 4. Absorption spectra of:
- a. $Na[Co(Cl)(edtaH)]\cdot 2H_2O$
- b. $Na[Co(Br)(edtaH)]\cdot 2H_2O$
- c. $Na[Co(NO_2)(edtaH)]\cdot H_2O$
- d. $Na[Coedta]\cdot 4H_2O$.

As is seen in the same figure, the first band of nitro-complex clearly splits into two components, and this interesting fact will be reported shortly by other workers*. Inspection of the absorption spectra in the ultraviolet region reveals the interesting fact that there are two absorption maxima in the region. For nitro-complex they appear at 120.00 ($\times 10^{13}$/sec.) and 133.33, for bromo-complex, at 111.11 and 130.43, and for chloro-complex, at 111.52 and 132.74 (Table I). In contrast, the common complex shows a single maximum at 132.16. Accordingly, the appearance of two maxima in the longer wave-lengths may be attributed to the entrance of ligand X into the coordination sphere.

Configuration of the Complexes.—Now, we are in a position to discuss the configuration of the complexes. So far as the absorption spectrum of the blue Co-EDTA complex is concerned, the maximum of the first band is shifted bathochromically to a considerable degree as is seen in Fig. 3d. If the complex in question is hydroxo- or aquo-complex including ethylenediaminetetraacetate anion as a pentadentate ligand, the absorption maximum will be shifted hypsochromically from the maximum of common complex according to the empirical rule of "spectrochemical series". Therefore we regard this blue

4) Y. Shimura and R. Tsuchida, This Bulletin, 28, 572 (1955).

* Private information from Dr. Y. Shimura.

complex as a modification of Co(III)-EDTA complexes in which ethylenediaminetetraacetate anion acts as a hexadentate ligand.

In a previous paper[5], the authors reported the synthesis of a blue and a violet variety of $K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$ and assumed *cis*-form for the former and *trans*-form for the latter. Comparison of the absorption spectra of these complexes with those of the complexes obtained in the present work showed that the maxima of the first and second bands of the two blue complexes occupied similar positions and that the same thing was true about the two violet complexes (for blue Co (III)-EDTA; 51.7 ($\times 10^{13}$/sec.), 77.9; for blue-$[Co(NH_3)_2(CO_3)_2]$, 52.2, 76.8; for violet-[Coedta], 55.9, 78.5; for violet-$[Co(NH_3)_2(CO_3)_2]$, 55.5, 80.2).

By this analogy of the absorption maxima, therefore, it may be assumed that the blue complex has one configuration in which the two nitrogen atoms span in *cis*-positions of octahedron and the violet common complex has another configuration in which the two nitrogen atoms span in *trans*-positions. Of course, the regular octahedron will suffer considerable distortion in the latter configuration. Such hypothesis about the configuration of the common complex, however, gives us a convenient explanation for the origin of the absorption band in the ultraviolet region. Provided that the absorption band in the ultraviolet region—"the third band"—is due to negative ions coordinated in trans-positions, the appearance of two maxima in the absorption spectra of [Co(X) (edtaH)] can be understood by taking into consideration such configuration as is indicated in Fig. 5.

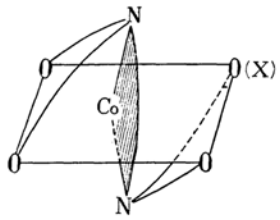


Fig. 5. Assumed configuration.

The present discussion of the configuration of "hexadentate" and "pentadentate" complexes is based on the assumption that the blue Co(III)-EDTA complex is a modification of "hexadentate" complex in spite of our failure to isolate this complex. Furthermore the dimentional restriction of the EDTA molecule makes it appear unnatural that the nitrogen atoms should span in trans-positions. Consequently, further studies must be carried out.

5) M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, 29, 883 (1956).

Summary

Two new compounds, $H[Coedta]\cdot 4H_2O$ and $Na[Co(Cl)(edtaH)]\cdot 2H_2O$ were synthesized, and their chemical formulae were confirmed by means of potentiometric titration and by examination of the infrared spectrum.

The absorption spectrum of $Na[Coedta]\cdot 4H_2O$ in solution was measured to investigate the pH effect. The absorption curves in acid solutions ($pH>2$) were wholly identical with that in aqueous solution of the salt, but those of alkaline solutions ($pH<10$) were not identical and further showed deviation from Beer's law.

The absorption curves of $Na[Co(NO_2)(edtaH)]\cdot H_2O$, $Na[Co(Br)(edtaH)]\cdot 2H_2O$ and $Na[Co(Cl)(edtaH)]\cdot 2H_2O$ were also measured. The first band for the chloro-complex and that for the bromo-complex occupied the similar position and shifted bathochromically as compared with the corresponding maximum for the common complex [Coedta]. These results may be explained on the basis of the so-called "spectrochemical series". The absorption spectra of the complexes [Co(X) (edtaH)] were found to have two absorption maxima in the ultraviolet region. This phenomenon may be attributed to the "trans effect" of negative ions.

By oxidation of an alkaline solution containing cobaltous and edta ions with hydrogen peroxide, a blue complex was produced. Although an attempt to isolate it ended in failure, existence of cobalt (III) complex containing hexadentate EDTA was assumed on the basis of the absorption spectrum.

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