[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XVII. The Stereochemistry of Hexadentate Ethylenediaminetetraacetic Acid Complexes

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The existence of a cobalt(III) complex containing hexadentate ethylenediaminetetraacetic acid was confirmed by examination of infrared spectra. Resolution of the hexadentate complex was attained by fractionation of the strychnine salt and by preferential adsorption on optically active quartz. Elimination of the second substituent from an optically active ion containing pentadentate ethylenediaminetetraacetic acid demonstrated that this reaction proceeds without loss of optical activity.

Two types of chelating agents are known which are capable of occupying six positions in a coördination sphere. These are ethylenediaminetetraacetic acid and 3,6-dithia-1,8-bis-(salicylideneamino)-octane and its derivatives. Complex compounds containing the latter substance have been studied extensively by Dwyer and Lions and their associates.[1-5] The cobalt(III) complex has been proven to exist in two enantiomorphic forms. Although the literature on the behavior of the metal complexes of ethylenediaminetetraacetic acid (hereafter denoted by EDTA) is extensive, there has been little work which serves to elucidate the structures of these interesting chemical species, and optical resolution of complex ions containing EDTA has not been reported. Pfeiffer[6] attempted without success to resolve the calcium complex into its optical antipodes.

The Hexadentate Cobalt(III) Complex.—In general, it has been assumed that EDTA acts as a hexadentate donor molecule when coördinated to metal ions which are commonly hexacoördinate, and tetradentate with metals which are normally tetracovalent. Some question has been raised as to the ability of an EDTA anion to occupy six positions in the coördination sphere[7]; however, a number of types of evidence for the hexadentate nature of the cobalt EDTA complex may be cited. Brintzinger, Thiele and Muller[8] obtained the sodium salt of the cobalt(III) EDTA complex as a 4-hydrate and found that this compound could be dehydrated by drying at 150° with no change in its properties or appearance. Since the cobalt(III) ion is commonly six-coördinate, the EDTA molecule is apparently hexadentate in this species. Schwarzenbach[9] prepared a number of cobalt(III) complex ions containing pentadentate EDTA and a second substituent. Removal of this second group yielded a hydrate of the "hexadentate" complex. It was demonstrated that when a water molecule is actually coördinated, $[Co(EDTA)H_2O]^-$, a reversible color change from red to blue takes place as the *p*H is increased. This is attributed by Schwarzenbach[9] to conversion of the monoaquo complex to the monohydroxy complex. The monoaquo species may be converted into the red hexadentate species by boiling, as evidenced by the fact that the reversible color change no longer occurs.

Perhaps the best evidence for the existence of a cobalt(III) complex in which EDTA is hexadentate has now been found in the infrared spectra of the "pentadentate" and the "hexadentate" species and is reported in this paper. The pentadentate complexes, bromo-(ethylenediaminetetraacetato)-cobaltate(III) and nitro-(ethylenediaminetetraacetato)-cobaltate(III), were synthesized in this Laboratory by the methods reported by Schwarzenbach.[9] The hexadentate complex was prepared from the bromo complex by triturating with silver oxide.[9] *Anal.* Calcd. for $Na[Co(C_{10}H_{13}N_2O_8)NO_2]\cdot H_2O$: C, 27.60; H, 3.48; N, 9.66. Found: C, 28.01; H, 3.90; N, 9.61. Calcd. for $Ba[Co(C_{10}H_{12}N_2O_8)]_2\cdot 4H_2O$: C, 26.58; H, 3.57; N, 6.20. Found: C, 26.54; H, 3.33; N, 5.89. The infrared absorption spectra were obtained with a Perkin–Elmer Model 21 Recording Spectrophotometer using sodium chloride prisms and a Nujol suspension of the compound in question. The infrared spectra for complexes containing pentadentate EDTA show two carbonyl bands (Fig. 1). The stronger band, which appears at 1635 and 1628 cm.$^{-1}$ for the nitro and bromo complexes, respectively, is attributed to the presence of three coördinated carboxyl groups. The weaker band, at 1740 and 1723 cm.$^{-1}$, is associated with the free carboxyl group. Only one carbonyl band appears in the infrared spectrum of the hexadentate species, thus indicating the equivalence of the four carboxyl groups. This single band appears at 1638 cm.$^{-1}$. Comparison of the spectra of the complex compounds with that of the free acid (maximum absorption at 1697 cm.$^{-1}$) is also enlightening. Complexing of the carboxyl groups shifts the carbonyl band toward the lower frequencies, while the band associated with a single free carboxyl group is shifted toward the higher frequencies. These observations are compatible with the assumption that the carboxyl groups in ethylenediaminetetraacetic acid are normally associated through hydrogen bonding. Complex formation results in a greater localization of electrons in the carbonyl group and in this manner imparts single bond character to the group, thereby shifting the characteristic infrared absorption band toward longer wave lengths. Such phenomena should be anticipated as a result of the partial ionic character of the coördinate link. In the case of the free carboxyl

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[1] F. P. Dwyer and F. Lions, THIS JOURNAL, **69**, 2917 (1947).

[2] F. P. Dwyer and F. Lions, *ibid.*, **72**, 1545 (1950).

[3] F. P. Dwyer, F. Lions and D. P. Mellor, *ibid.*, **72**, 5037 (1950).

[4] F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **74**, 4188 (1952).

[5] F. P. Dwyer and E. C. Gyarfas, *Nature*, **168**, 29 (1951).

[6] P. Pfeiffer and H. Simons, *Ber.*, **76**, 847 (1943).

[7] R. L. Pecsok, *J. Chem. Ed.*, **29**, 597 (1952).

[8] H. Brintzinger, H. Thiele and U. Müller, *Z. anorg. Chem.*, **251**, 285 (1943).

[9] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

group in a pentadentate complex, the possibility of intramolecular hydrogen bonding has been obviated through the involvement of three of the four carboxyl groups in the formation of coördinate bonds.

Resolution of Ethylenediaminetetraacetatocobaltate(III) Ion.—Two facts support the possibility that the hexadentate cobalt(III) complex partakes of sufficient configurational stability to facilitate the isolation of its stereoisomers. The cobalt atom in the complex is diamagnetic[8] and does not exchange with cobalt(II) ions in solution.[10] Resolution was accomplished by fractionation of the strychnine salt and by preferential adsorption on optically active quartz.

Preparation of the Strychnine Salt, $(C_{21}H_{22}N_2O_2)\cdot H[Co(C_{10}H_{12}N_2O_8)]$.—Ten grams of strychnine sulfate 5-hydrate (0.012 mole) was ground with 10.8 g. of barium ethylenediaminetetraacetatocobaltate(III) (0.012 mole) in a mortar. The mixture was transferred to a beaker and heated to boiling with 300 ml. of water. The precipitated barium sulfate was recovered by filtration and weighed. Calcd. wt. of $BaSO_4$, 2.72 g.; found, 2.72 g. The strychnine salt was recovered by evaporating the solution to dryness with a stream of air.

Resolution of Strychnine Salt.—Because of the extreme solubility of the compound in water, the fractionation was carried out in mixed solvents. Ten grams of the strychnine salt was dissolved in 50 ml. of water and added to 500 ml. of ethanol, whereupon the first fraction crystallized out. The ethanol–water solution was then cooled in a solid carbon dioxide–ethanol bath and a second fraction was obtained. The third fraction formed when 150 ml. of diethyl ether was added to the solution. Upon concentration of the filtrate from the third fraction, decomposition occurred.

Samples of the three fractions, each weighing 0.116 mg. (1.7×10^{-4} mole), were dissolved in 100 ml. of water and the optical activity was measured. The high dilution at which the optical activity was measured was dictated by the optical density of the solution. A Schmidt and Haensch Polarimeter (No. 9143) was used and all readings were made at the D-line of sodium. The rotations given represent the average of at least ten settings of the instrument. The average deviation experienced in reading the instrument varied from ±0.003 to ±0.007°, depending on the optical density of the solution in the polarimeter tube.

The first fraction of the strychnine salt gave an observed rotation of −0.023 ± 0.004°, from which a specific rotation of −100° and a molecular rotation of −68,400° were calculated. The rotation which might have been expected from the strychnine alone is −0.005°. The second and third fractions were inactive.

The strychnine was removed from the active fraction by dissolving 0.116 g. of the strychnine ethylenediaminetetraacetatocobaltate(III) (1.7×10^{-4} mole) in 25 ml. of water and adding 0.077 g. of potassium iodide (4.65×10^{-4} mole). The potassium iodide dissolved completely and, after a short time, strychnine iodide precipitated. The potassium ethylenediaminetetraacetatocobaltate(III) solution was filtered directly into a volumetric flask. The strychnine iodide was washed with a small amount of cold water and the washings added to the solution containing the complex. This solution was then diluted to 100 ml. The resulting 1.7×10^{-4} *M* solution gave an observed rotation of −0.022 ± 0.003°, and a specific rotation of −158°.

Resolution with Optically Active Quartz.—Twenty-five milliliters of solution containing 0.836 g. of sodium ethylenediaminetetraacetatocobaltate(III) (2.26×10^{-3} mole) was stirred with 1 g. of powdered dextro quartz for 15 minutes. The solution was filtered directly into a volumetric flask and made up to 100 ml. The optical rotation was then measured at three concentrations as shown below. (Concentrations are not accurate but are given as they would have been, had none of the complex been adsorbed.)

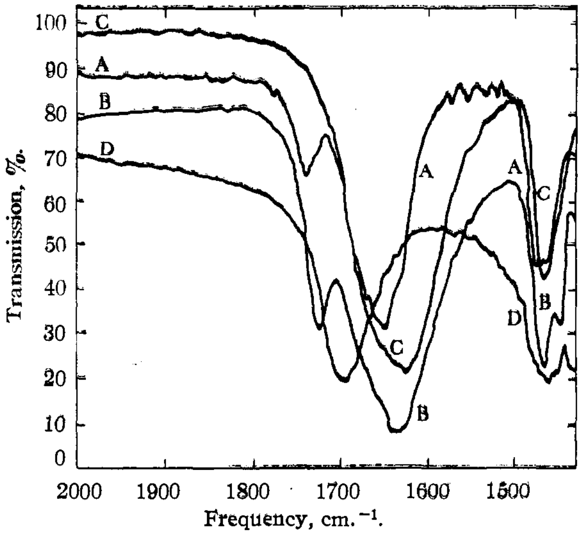

Fig. 1.—Infrared absorption spectra of ethylenediaminetetraacetic acid and some of its cobalt(III) complexes (in nujol emulsion): A, $Na[Co(C_{10}H_{13}N_2O_8)NO_2]\cdot H_2O$; B, $Ba[Co(C_{10}H_{13}N_2O_8)Br]_2\cdot 9H_2O$; C, $Ba[Co(C_{10}H_{12}N_2O_8)]_2\cdot 4H_2O$; D, $C_{10}H_{16}N_2O_8$.

Molarity	α	[α]	[M]
1.13×10^{-3}	−0.063 ± 0.007°	−75	−27,800
5.65×10^{-4}	−0.031 ± 0.005°	−74	−27,400
2.26×10^{-4}	−0.012 ± 0.003°	−72	−26,600

Preparation of the Active Hexadentate Complex from Active Bromo-(ethylenediaminetetraacetato)-cobaltate (III).—Since the hexadentate complex which was the subject of the above investigations was prepared by the reaction of barium bromo-(ethylenediaminetetraacetato)-cobaltate(III) with silver oxide, it appeared cogent to demonstrate that the configuration of the complex was not affected by this simple reaction. This was realized by attaining partial resolution of the bromo complex through adsorption on optically active quartz, and then converting the optically active ion to the hexadentate form. It is not feasible to attempt resolution of the bromo complex by a fractionation technique because of its tendency to hydrolyze.

One hundred forty-four milligrams of barium bromo-(ethylenediaminetetraacetato)-cobaltate(III) (1.35×10^{-4} mole) was dissolved in 25 ml. of water and stirred with 0.5 g. of dextro quartz for 18 minutes. The solution showed a rotation of −0.018 ± 0.006° at a concentration of 6.8 $\times 10^{-5}$ *M*. An aliquot of this optically active solution was then treated with a slight excess of silver nitrate. It may be inferred that the precipitation of silver bromide is not preceded by any extensive dissociation of the bromide ion from the fact that the blue color of the bromo complex remained unchanged until the silver nitrate was added. The addition of silver nitrate was followed by the immediate separation of the silver bromide which was accompanied by a change in the color of the solution from blue to pink. The new complex was also optically active with a rotation of −0.026 ± 0.004° at 6.8×10^{-5} *M* concentration. The compound in solution was assumed to be the hexadentate complex since it did not exhibit the reversible red to blue color change upon addition of base, which is attributed to the presence of an aquo complex. It appears that the dextro form of the bromo complex is preferentially adsorbed on dextro quartz and that the conversion of this complex to the hexadentate complex proceeds wihout racemization or inversion, although the last possibility "t" is not obviated.

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[10] F. A. Long, S. S. Jones and M. Burke, Brookhaven Conf. Rept. BNL-C-8, Isotopic Exchange Reactions and Chem. Kinetics, Chem. Conf., No. 2, 106 (1948).