solution does not give rise to a marked decrease in the dielectric increment; on the contrary the value at −5° is larger than that of 25°.

The dipole moments were calculated as described in the preceding paper, and listed in Table I. It is assumed that the axial ratio of both proteins

TABLE I

THE COMPARISON OF THE CALCULATION AND OBSERVED DIPOLE MOMENT OF EGG AND SERUM ALBUMINS

Temp., °C.	μ_{obs} Egg alb.	μ_{obs} Serum alb.	μ_{cal} Egg alb.	μ_{cal} Serum alb.
− 5	270	360	330	320
−10	210	300	(sphere)	(sphere)
−20	..	220	460	510
−30	180		(ellipsoid)	(ellipsoid)
−40	150			
−60	120			
Soln.(25°)	250	700		

is 5:1. As can be seen from the table, the dipole moment of egg albumin in the frozen state is of the same order of magnitude as that of the solution; however, the dipole moment of serum albumin drops considerably on freezing. The results on egg albumin may be interpreted in two ways: (1) the molecule has the same freedom of orientation in ice as in solution; or (2) the dielectric polarization of this protein is entirely due to the sorbed water or to mobile proton fluctuation in solution as well as in ice. The asymptotic decrease of the dipole moment below −10° to a lower value favors explanation (1). However the dimensions of the molecule and its shape indicate that orientation of the whole molecule in ice will require a large heat of activation, since the orientation might accompany the breaking of the directed hydrogen bonds of ice. However, the temperature dependence of the relaxation time which is shown in Fig. 4 gives the heat of activation as about 1 kcal., which indicates that orientation of the whole molecule in ice may not be the case.

As in the case of hemoglobin, the dipole moments calculated from the data on the albumins are not far from the theoretical values of Kirkwood; see Table I. This strongly suggests that proton fluctuation is a possible mechanism for the dielectric polarization of these proteins.

Bayley[2] who worked with dry albumin crystals observed a very small dielectric constant, but he also found that the presence of excess moisture increased the dielectric constant and dielectric loss. However, as mentioned in the preceding paper, it is obvious that the polarization which was observed in the present experiment cannot be attributed merely to the polarization of sorbed water. The polarization may be due partly to the dielectric polarization of the sorbed water itself, but there is the possibility that water increases the dissociation of polar groups and thus may enhance the fluctuation of protons.

The quantitative interpretation of the anomalous dispersion of the solid sample requires further study, particularly to explain the shift of the dispersion curve and its shape between −20 and −30°.

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PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SYDNEY]

The Resolution of the Quinquedentate Cobalt(III) Complexes with Ethylenediaminetetraacetic Acid

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The resolution of the quinquedentate cobalt(III) complexes with ethylenediaminetetraacetic acid with nitro, chloro and bromo groups occupying the sixth coördination position has been effected with optically active *cis*-dinitrobis-(ethylenediamine)-cobalt(III) chloride. Treatment of the active bromo and chloro complexes with mercury(II) nitrate solution or solid silver oxide caused a quantitative transformation to the sexadentate complex with complete retention of configuration. When the optically active sexadentate complex was treated with concentrated hydrochloric acid, it was converted to the quinquedentate complex in which a chlorine is attached to the central metal ion, with some retention of configuration. On reaction with ethylenediamine, all of the complexes exchanged to give tris-(ethylenediamine)-cobalt(III) ion. Only the nitro complex yielded an inactive product.

Introduction

The sexadentate function of ethylenediaminetetraacetic acid, (H_4Y), in the anion, (ethylenediaminetetraacetato)-cobaltate(III),[2] has been established by the infrared studies of Busch and Bailar.[3] The complex ion also has been separated into the optical forms.[3-5] Quinquedentate Co(III) complexes in which one carboxyl group of the organic moiety is not attached to the metal have been obtained as the acid salts [Co (HY) X]$^-$, (X = Br, NO_2) by Schwarzenbach,[6] who reported that when the sexadentate anion, [Co(Y)]$^-$, was

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(2) It is considered desirable with organic molecules capable of multidentate chelate function that the nomenclature applied to the metal complex should distinguish clearly between groups or atoms that are coördinated and those that are unattached, especially when the stereochemistry of the complex has been established. The name, potassium (ethylenediaminetetraacetato)-cobaltate(III) implies coördination of all carboxyl groups; whereas potassium chloro-(ethylenediaminetriacetatoacetic acid)-cobaltate(III), implies coördination of the chlorine and three of the carboxyl groups, with the fourth carboxyl group unattached to the octahedral sphere of the complex.

(3) D. H. Busch and J. C. Bailar, THIS JOURNAL, **75**, 4574 (1953).

(4) F. P. Dwyer, E. C. Gyarfas and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(5) F. P. Dwyer and F. L. Garvan, "Inorganic Syntheses," H. Rochow, Ed., Vol. VI, in publication.

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

treated with hydrochloric acid, the chloro complex was not formed but merely decomposition ensued. Recently[7] the blue anion $[Co(HY)Cl]^-$ was obtained by the chlorination of the Co(II) complex. The normal salts $[Co(Y)\ X]^=$ also were described. Infrared studies[3,7] show that in the quinquedentate derivatives one carboxyl group is, in fact, uncoordinated.

Contrary to the previous report[6] it has been found that the chloro complex is conveniently prepared in high yield by the reaction between the violet sexadentate anion and concentrated hydrochloric acid at 90°. Evidently one carboxyl group can be detached more easily than the others. This group becomes protonated in the presence of the strong acid, and then the chlorine can bond to the cobalt.

The nitro compound also was prepared by a new method which gave much higher yields than those reported earlier.[6] The hexanitro-cobaltate(III) anion readily reacts with the disodium salt of ethylenediaminetetraacetic acid at 80° whereupon the nitro groups are replaced as the complexing acid enters the coördination sphere of the cobalt, until only one of the nitro groups remains and the ethylenediaminetetraacetic acid is acting as a quinquedentate.

The quinquedentate complexes are capable of existence in isomeric forms depending on whether the unique group occupying the sixth coördination position is *cis* to both nitrogen atoms or *trans* to one of them. Assuming that the "*trans* effect" operates in octahedral complexes, the unique substituent might be expected to occupy one of the polar (1,6)-positions. Neither in the previous nor the present work is there any evidence to suggest that more than one isomer is present. It is possible that the properties of both isomers—if both are formed—are not sufficiently dissimilar to be detected easily. Both forms lack a center and a plane of symmetry and hence exist in optical forms. A partial resolution of the bromo complex has been effected[3] with optically active quartz and the transformation to the sexadentate complex by means of silver oxide has been reported to occur without total loss of the activity.

The complete resolution of the nitro, bromo and chloro complexes can be effected conveniently and rapidly with *d*- and *l*-*cis*-dinitrobis-(ethylenediamine)-cobalt(III) chloride.[5] In aqueous solution at 25° the bromo complex in a day and the chloro complex in three days, lose the halogen atoms and the violet sexadentate results with complete retention of configuration. Reaction apparently occurs by a slow dissociation step leaving an active 5-covalent intermediate, followed by rapid coördination of the free carboxylate group. The reaction is strongly catalyzed by heavy metal ions such as Hg^{+2}, Ag^+, Cd^{+2}, Zn^{+2} and Fe^{+3}, especially the first two ions. It is probable that a metal ion–halogen bond is responsible for rapid detachment of the halogen. By the use of silver oxide, it has been possible to effect transformation to the sexadentate complex which could be isolated quantitatively in the optically pure state.

When the active isomer of the violet sexadentate complex (*d*-form) was treated on the water-bath at 90° with concentrated hydrochloric acid, it was converted to the chloro complex without total loss of optical activity. During the transformation the chloro complex produced has the opposite rotation to the sexadentate used. The crude chloro salt (without any purification) gave a specific rotation of −400° at the green line of mercury. This represents 75% retention of configuration. However, the exact proportion of retention of configuration cannot be determined as there is reduction of the cobalt(III) to cobalt(II) during the transformation. Furthermore, analysis of the crude product proved that it was not pure.

It can be seen that as a result of this reaction an asymmetric nitrogen is produced that did not previously exist in the complex. It is interesting to observe that it does not matter which acetate group is detached from the cobalt as the same *optical* isomer of the chloro complex is produced. This means that there should be 100% retention of configuration in the transformation provided that no decomposition takes place.

The nitro complex is quite stable at room temperature, and solutions retain their activity for several weeks. A solution of the disodium salt which initially had a specific rotation at +700° changed its rotation to +500° after two months. At elevated temperatures, when dissociation of the nitro group occurs, conclusions as to the retention of configuration are invalid because racemization of the sexadentate complex proceeds simultaneously.

The chloro and bromo complexes, like the sexadentate complex,[4,8] reacted with 50% ethylenediamine at 25°, to yield partly active tris-(ethylenediamine)-cobalt(III) ion. However, the nitro complex reacted to give an inactive product. Furthermore, when the sexadentate complex and the chloro complex were treated with anhydrous ethylenediamine, the rotations observed were almost double the figure when 50% ethylenediamine was used. With anhydrous ethylenediamine, the nitro complex still gave racemic tris-(ethylenediamine)-cobalt(III) ion. At present we prefer to offer no explanation to account for the formation of inactive material with the nitro complex, nor for the fact that the sexadentate yields a purer optical specimen when anhydrous ethylenediamine is used.

The complexes of *d* and *l*-propylenediaminetetraacetic acid and of rhodium with polyaminocarboxylic acids will be described in a subsequent communication.

Experimental

Unless otherwise stated, all rotations were measured in a one dm. polarimeter tube at 25°.

dl-**Potassium Chloro-(ethylenediaminetriacetatoacetic acid)-cobaltate Dihydrate K[Co(HY)Cl]·2H$_2$O.**—*dl*-Potassium (ethylenediaminetetraacetato)-cobaltate(III) dihydrate,[4] (10 g.) was stirred with concentrated hydrochloric acid, (5 ml.) in an evaporating dish until a uniform mixture was obtained. This was heated on a boiling water-bath, stirring constantly until most of the acid had evaporated. The resulting blue-green mass was cooled, broken up and stirred for a few minutes with cold water (15 ml.), followed by

(7) M. L. Morris and D. H. Busch, THIS JOURNAL, **78**, 5178 (1956).

(8) S. Kirschner, Yung-Kang Wei and J. C. Bailar, *ibid.*, **79**, 5877 (1957).

ethanol (50 ml.). After filtration the crude salt (9.3 g.) was washed well with ethanol to remove hydrochloric acid. It was purified by suspension in cold water (50 ml.) to which was then added potassium acetate (7.5 g.). Dissolution was effected by stirring and to the filtered dark blue solution hydrochloric acid (10 *N*) was added to *p*H 1. The blue plates that separated on standing were collected and washed with 50% aqueous ethanol, ethanol and acetone in that order and air-dried (yield 7.5 g.).

Anal. Calcd. for $K[Co(C_{10}H_{13}N_2O_8)Cl]\cdot 2H_2O$: C, 26.56; H, 3.78; N, 6.19. Found: C, 26.26; H, 3.8; N, 6.1.

The *sodium salt* was prepared in a similar manner from $Na[Co(Y)]\cdot 4H_2O$ using sodium acetate for purification.

Anal. Calcd. for $Na[Co(C_{10}H_{13}N_2O_8)Cl]\cdot 2H_2O$: C, 27.14; H, 3.87; N, 6.33. Found: C, 27.1; H, 4.0; N, 6.3.

***dl*-Dipotassium Chloro-(ethylenediaminetriacetatoacetate)-cobaltate(III) Trihydrate, $K_2[Co(Y)Cl]\cdot 3H_2O$.**—The salt $K[Co(HY)Cl]\cdot 2H_2O$ above (5 g.) was suspended in cold water (50 ml.), potassium acetate (15 g.) added and dissolution effected by stirring. On the addition of ethanol (250 ml.) and scratching of the sides of the vessel, the deep blue dipotassium salt separated in almost quantitative yield. It was recrystallized from water by the addition of ethanol.

Anal. Calcd. for $K_2[Co(C_{10}H_{12}N_2O_8)Cl]\cdot 3H_2O$: C, 23.32; H, 3.53; N, 5.45; Cl, 6.90. Found: C, 23.3; H, 3.5; N, 5.6; Cl, 7.0.

***l*-Dipotassium Chloro-(ethylenediaminetriacetatoacetate)-cobaltate(III) Trihydrate, *d*-$K_2[Co(Y)Cl]\cdot 3H_2O$.**—The resolution was performed *via* the salt $K[Co(HY)Cl]\cdot 2H_2O$ which was obtained in a suitable form for rapid dissolution by the addition of 1 *N* hydrochloric acid (10 ml.) to a solution of $K_2[Co(Y)Cl]\cdot 3H_2O$ (5 g.) in 50 ml. of water. The very fine precipitate was collected, washed with ice-water and then acetone and air-dried. *d-cis*-Dinitrobis-(ethylenediamine)-cobalt(III) bromide[5] (0.9 g.) was suspended in water (60 ml.) at 60° and shaken for three minutes with freshly precipitated silver chloride (2 g.). The silver halides were filtered off and washed with 10 ml. of warm water. The combined filtrate and wash liquid were heated to 65° and the finely divided $K[Co(HY)Cl]\cdot 2H_2O$ (2.3 g.) added. On vigorous shaking the solid dissolved and almost immediately the green diastereoisomer separated. The mixture was cooled rapidly to room temperature and then allowed to stand in an ice-bath for 0.2 hr. The crystals were collected, washed with ice-cold 50% aqueous ethanol, ethanol and then acetone; yield (air-dried), 1.45 g. The blue filtrate was reserved for recovery of the *d*-isomer. A 0.025% solution of the diastereoisomer in water gave α_{5461} −0.12°, whence $[\alpha]^{25}_{5461}$ −480°.

Anal. Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]\cdot[Co(C_{10}H_{13}N_2O_8)Cl]\cdot 3H_2O$: C, 23.73; H, 4.98; N, 15.82. Found: C, 23.95; H, 4.6; N, 15.4.

The diastereoisomer (1.4 g.), potassium acetate (2 g.), potassium iodide (5 g.) and water (10 ml.) were ground up in a mortar for a few minutes. The sparingly soluble *d*-[Co $en_2(NO_2)_2$] I separated and was filtered off. Immediately ethanol (20 ml.) was added to the filtrate which deposited the *l*-isomer on scratching the sides of the vessel. It was recrystallized from water (10 ml.) by addition of ethanol; yield 0.85 g. A 0.02% solution gave α_{5461} −0.14°, whence $[\alpha]_{5461}$ −700°.

Anal. Calcd. for $K_2[Co(C_{10}H_{12}N_2O_8)Cl]\cdot 3H_2O$: C, 23.32; H, 3.53; N, 5.45. Found: C, 23.1; H, 3.3; N, 5.7.

***d*-Dipotassium Chloro-(ethylenediaminetriacetatoacetate)-cobaltate(III) Trihydrate.**—Potassium acetate (2 g.) was added to the filtrate from the separation of the diastereoisomer above, followed by ethanol (200 ml.). The *d*-form crystallized on cooling in an ice-bath for 0.5 hr. It was recrystallized from water (10 ml.) containing potassium acetate (1 g.) by the gradual addition of ethanol. The first fraction containing racemate was rejected (yield 0.7 g.). A 0.02% solution gave α_{5461} 0.14°, whence $[\alpha]_{5461}$ +700°.

Anal. Calcd. for $K_2[Co(C_{10}H_{12}N_2O_8)Cl]\cdot 3H_2O$: C, 23.32; H, 3.53; N, 5.45. Found: C, 23.3; H, 3.4; N, 5.7.

***d*- and *l*-Potassium Chloro-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III) Monohydrate.**—The active salts $K_2[Co(Y)Cl]\cdot 3H_2O$ (0.5 g.) above were dissolved in water (2 ml.) and 1 *N* hydrochloric acid (0.9 ml.) added. The active potassium acid salts crystallized on cooling in ice. Alternatively, they could be prepared from the crude active isomers obtained during the resolution of $K[Co(HY)Cl]$. These were dissolved in water (5 ml.) containing potassium acetate (1 g.). Concentrated hydrochloric acid was added to *p*H 1 whereupon small amounts of racemate separated almost at once. The pure optical forms separated on standing and cooling. A 0.02% solution gave α_{5461} ±0.16°, whence $[\alpha]_{5461}$ ±800°.

Anal. Calcd. for $K[Co(C_{10}H_{13}N_2O_8)Cl]\cdot H_2O$: C, 27.26; H, 3.44; N, 6.36. Found *d*-form: C, 27.2; H, 3.4; N, 6.4. *l*-Form: C, 27.3; H, 3.5; N, 6.3.

***l*-Potassium Chloro-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III) Monohydrate from *d*-Potassium (ethylenediaminetetraacetato)-cobaltate(III) Dihydrate.**—The latter salt (0.4 g., $[\alpha]_{5461}$ +1000°) was moistened with two drops of concentrated hydrochloric acid and heated at 80 to 90° for five minutes. The residue was cooled, dissolved in water (5 ml.) and ethanol (20 ml.) added. The blue solid gave $[\alpha]_{5461}$ −400°. Purification was effected by dissolution in 2 ml. of water containing potassium acetate (0.3 g.), followed by concentrated hydrochloric acid (0.1 ml.). The solid that separated on standing for 10 min. at 20° had a small activity, $[\alpha]_{5461}$ −200°. The mother liquor was treated with a further 0.1 ml. of hydrochloric acid and cooled in ice. The blue crystals gave $[\alpha]_{5461}$ −800°.

Anal. Found: C, 27.2; H, 3.7; N, 6.2.

Transformation of *l*-Potassium Chloro-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III) Monohydrate to *d*-Potassium (Ethylenediaminetetraacetato)-cobaltate Dihydrate with Complete Retention of Configuration.—(1) A 0.01% solution of *l*-$K[Co(HY)Cl]\cdot H_2O$ in 0.05 *N* nitric acid gave α_{5461} −0.08°. Addition of a small crystal of mercury(II) nitrate changed the color from blue to violet, due to the $[Co(Y)]^-$ ion, and this gave α_{5461} +0.09°. The expected rotation was +0.09$_5$°.

(2) Four tenths of a gram of *l*-$K[Co(HY)Cl]\cdot H_2O$ suspended in water (5 ml.) was shaken with freshly precipitated silver oxide (1 g.) for three minutes. The color changed to deep violet and silver chloride separated. The silver salts were removed and washed with water (2 ml.). Potassium iodide (0.3 g.) was added to the filtrate and then ethanol in small portions until micaceous plates separated on scratching the sides of the vessel. Finally, sufficient ethanol was added to precipitate the whole of the substance, leaving the mother liquor nearly colorless. The solid was washed with ethanol and acetone and air-dried. It was optically pure, $[\alpha]_{5461}$ +1000°.

Anal. Calcd. for $K[Co(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$: C, 28.45; H, 3.82; N, 6.64. Found: C, 28.8; H, 3.8; N, 6.7.

***d*-Disodium Bromo-(ethylenediaminetriacetatoacetate)-cobaltate(III) Tetrahydrate.**—The resolution was performed through the sodium acid salt *dl*-$Na[Co(HY)Br]\cdot H_2O$ prepared by the method of Schwarzenbach. *l-cis*-Dinitrobis-(ethylenediamine)-cobalt(III) bromide (1.1 g.) was converted to the chloride by shaking with an aqueous suspension of silver chloride at 60°. The final volume of solution with the washings of the silver halide precipitate was 30 ml. To the cooled solution was added sodium acetate trihydrate (1.1 g.) and then *dl*-$Na[Co(HY)Br]\cdot H_2O$ (2.3 g.). Dissolution was effected rapidly by shaking and then hydrochloric acid (1.00 *N*, 5.4 ml.) was added. The green solution on cooling in ice and scratching the sides of the vessel yielded the crystalline diastereoisomer *l*-[Co $en_2(NO_2)_2$]·*d*-[Co(HY)Br]. This was collected and washed with a little ice-cold water and then ethanol (yield 1.4 g.). A 0.025% solution gave α_{5461} +0.11°, whence $[\alpha]_{5461}$ +440°.

Anal. Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]\cdot[Co(C_{10}H_{13}N_2O_8)Br]$: C, 24.03; H, 4.18; N, 16.04. Found: C, 24.0; H, 4.3; N, 15.4.

The diastereoisomer in water (10 ml.) was treated with sodium acetate (1 g.), and the resolving agent eliminated as the sparingly soluble perchlorate by the addition of sodium perchlorate (7 g.). After filtration, the *d*-salt was crystallized by the addition of sufficient ethanol. It was recrystallized from a little water by the addition of ethanol (yield 0.7 g.). A 0.02% solution gave α_{5461} +0.14°, whence $[\alpha]_{5641}$ +700°.

Anal. Calcd. for $Na_2[Co(C_{10}H_{17}N_2O_8)Br]\cdot 4H_2O$: C, 22.06; H, 3.70; N, 5.14. Found: C, 22.3; H, 4.1; N, 5.4.

***l*-Disodium Bromo-(ethylenediaminetriacetatoacetate)-cobaltate(III) Tetrahydrate.**—Sodium acetate (1 g.) was added

to the filtrate from the separation of the diastereoisomer above and then sodium perchlorate (7 g.). After cooling in ice for ten minutes the mixture was filtered and ethanol (250 ml.) added to the blue-green filtrate. The crude *l*-salt that separated was purified by recrystallization from water by the addition of ethanol. The small amount of racemic impurity remained in solution, though there is little difference in the solubilities of the active forms, and the racemate. A 0.02% solution gave α_{5461} −0.14°, whence $[\alpha]_{5461}$ −700°.

Anal. Found: C, 22.2; H, 4.1; N, 5.2.

Active Sodium Bromo-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III), Na[Co(HY)Br] and Hydrogen Bromo-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III) H[Co(HY)Br].—The former was prepared by dissolution of the respective active disodium salt (0.56 g.) in water (2 ml.), followed by the addition of hydrochloric acid (1.00 N, 0.9 ml.). The crystals that separated on cooling were washed with aqueous ethanol. The *dl*-form was much less soluble than either optical form. Aqueous solutions (0.02%) gave α_{5461} ±0.16°, whence $[\alpha]_{5461}$ ±800°.

Anal. Calcd. for $Na[Co(C_{10}H_{13}N_2O_8)Br]$: C, 26.63; H, 2.91; N, 6.21. Found (*d*-form): C, 26.8; H, 3.1; N, 6.1, (*l*-form): C, 26.6; H, 3.3; N, 6.1.

The free acids were obtained by dissolution of the respective impure disodium salts (0.9 g.) in water (6 ml.), followed by concentrated hydrochloric acid (1 ml.). The small fraction that separated at once was rejected. The pure optical forms separated as sparkling granules on the addition of ethanol (4 ml.). Aqueous solutions (0.02%) gave α_{5461} ±0.17°, whence $[\alpha]_{5461}$ ±850°.

Anal. Calcd. for $H[Co(C_{10}H_{13}N_2O_8)Br]\cdot{}^1/_2H_2O$: C, 27.42; H, 3.22; N, 6.40. Found (*d*-form): C, 27.4; H, 3.1; N, 6.4. (*l*-form): C, 27.1; H, 3.3; N, 6.3.

Transformation of *d*-Hydrogen Bromo-(ethylenediaminetriacetatoacetic acid)-cobaltate(III) to *l*-Hydrogen (Ethylenediaminetetraacetato)-cobaltate(III) with Retention of Configuration.—(1) A 0.01% solution of the bromo complex in 0.05 *N* nitric acid had a rotation, α_{5461} +0.08$_5$°. On the addition of a crystal of mercury(II) nitrate the color changed from green to violet and the rotation to −0.09°. The expected rotation was −0.09$_6$°.

(2) The pure *d*-isomer (0.4 g.) was treated with silver oxide as for the chloro compound above. The whole of the potassium (ethylenediaminetetraacetato)-cobaltate(III) was precipitated with ethanol. The substance was analytically pure and had $[\alpha]_{5461}$ −1000°.

Anal. Calcd. for $K[Co(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$: C, 28.45; H, 3.82; N, 6.64. Found: C, 28.5; H, 4.0; N, 6.66.

***dl*-Sodium Nitro-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III) Dihydrate, Na[Co(HY)NO$_2$]·2H$_2$O.**—The oxidation of ethylenediaminetetraacetato cobaltate(III) ion with nitrous acid, described by Schwarzenbach, gave yields of 40–48%. The present method gave yields of 70%.

Sodium hexanitrocobaltate(III) (20 g.) in 60 ml. of water was treated with disodium ethylenediaminetetraacetic acid dihydrate (18.4 g.) and heated with stirring at 50° for 0.25 hr. The temperature was then raised to 90° for 0.5 hr.; the mixture was then cooled and filtered. The dark violet-brown solution was treated with 12 *N* sulfuric acid (10 ml.), when a large amount of solid crystallized. The crude product was collected, washed with ice-cold 50% aqueous ethanol and purified in the manner of the chloro compound above (yield 16 g., 70%).

Anal. Calcd. for $Na[Co(C_{10}H_{13}N_2O_8)NO_2]\cdot 2H_2O$: C, 26.50; H, 3.78; N, 9.27. Found: C, 26.4; H, 4.2; N, 9.2.

The disodium salt, $Na_2[Co(Y)NO_2]\cdot 3H_2O$, was obtained by dissolution of the sodium acid salt above in 10% aqueous sodium acetate and precipitated by the addition of ethanol. The substance separated in brown-violet plates.

Anal. Calcd. for $Na_2[Co(C_{10}H_{12}N_2O_8)NO_2]\cdot 3H_2O$: C, 24.35; H, 3.68; N, 8.52. Found: C, 24.7; H, 3.8; N, 8.3.

***l*-Disodium Nitro-(ethylenediaminetriacetatoacetate)-cobaltate(III) Trihydrate.**—The resolution was effected through the sodium acid salt Na[Co(HY)NO$_2$] and *d-cis*-dinitro-bis-(ethylenediamine)-cobalt(III) bromide, as for the bromo complex above except that 1.0 g. of sodium acetate was used instead of 1.1 g. A 0.05% solution of the gold-colored diastereoisomer gave α_{5461} −0.22°, whence $[\alpha]_{5461}$ −440° (yield 1.4 g.).

Anal. Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]\cdot[Co(C_{10}H_{13}N_2O_8)\cdot H_2O]$: C, 24.6; H, 4.58; H, 18.46. Found: C, 24.7; H, 4.6; N, 18.4.

The diastereoisomer (1.4 g.) was ground up in a mortar with water (10 ml.), sodium acetate (1 g.) and sodium iodide (5 g.). The sparingly soluble iodide of the resolving agent was removed and ethanol added gradually to the filtrate, whereupon the *l*-form of the complex separated as violet-brown plates. The substance was recrystallized from cold water by the addition of ethanol (yield 0.9 g.).

A 0.02% solution in water gave α_{5461} −0.14°, whence $[\alpha]_{5461}$ −700°.

Anal. Calcd for $Na_2[Co(C_{10}H_{12}N_2O_8)NO_2]\cdot 3H_2O$: C, 24.35; H, 3.68; N, 8.52. Found: C, 24.4; H, 3.8; N, 8.4.

***d*-Disodium Nitro-(ethylenediaminetriacetatoacetate)-cobaltate(III) Trihydrate.**—The filtrate from the separation of the diastereoisomer above was treated with sodium acetate (1 g.) and sodium iodide (6 g.) and cooled in ice whereupon the resolving agent in excess crystallized as the iodide. This was removed and the crude active disodium salt precipitated by the addition of ethanol. After recrystallization from water by the addition of ethanol it gave lustrous plates, $[\alpha]_{5461}$ +700° (yield 0.9 g.).

Anal. Found: C, 24.3; H, 3.8; N, 8.4.

***d*- and *l*-Sodium Nitro-(ethylenediaminetriacetatoacetic Acid)-cobaltate(III).**—The active disodium salts (0.5 g.) were each dissolved in water (2 ml.) acidified with hydrochloric acid (1.00 *N*, 1 ml.) and crystallization brought about by the addition of ethanol. The active forms were more soluble than the racemate. Aqueous solutions (0.125%) gave α_{5461} ±0.10°, whence $[\alpha]_{5461}$ ±800°.

Anal. Calcd. for $Na[Co(C_{10}H_{13}N_2O_8)NO_2]$: C, 28.79 H, 3.15; N, 10.08. Found (*d*-form): C, 29.1; H, 3.3; N, 10.0; (*l*-form): C, 28.8; H, 3.2; N, 10.3.

Reaction of the Active Isomers with Ethylenediamine.—One tenth of a gram of the pure optical isomer of the chloro, bromo and nitro quinquedentate chelates and the sexadentate chelate was stirred with 50% aqueous ethylenediamine (1.5 ml.) at 25°. When the pure orange-yellow color of the tris-(ethylenediamine)-cobalt(III) ion had developed the volume of the solution was adjusted to 25 ml. and the rotation measured in a 2-dm. tube.

Initial complex	α_D (found)	α_D (for full retention of configuration)
l-K[Co(Y)]·2H$_2$O	−0.15°	−1.15°
l-Na[Co(HY)Br]	+ .11°	+1.08°
l-K[Co(HY)Cl]·H$_2$O	+ .11°	+1.10°
d-Na$_2$[Co(Y)NO$_2$]·3H$_2$O	± .00°	+0.98°
l-K$_2$[Co(Y)Cl]·3H$_2$O	+ .09°	+0.94°

This transformation was repeated on the nitro complex, the chloro complex and the sexadentate complex using 1 ml. of anhydrous ethylenediamine. The time for complete reaction was 3 to 4 hr.

Initial complex	α_D found	α_D (for full retention of configuration)
l-K[Co(Y)]·2H$_2$O	−0.30°	−1.15°
d-Na$_2$[Co(Y)NO$_2$]·3H$_2$O	± .00°	+0.98°
l-K$_2$[Co(Y)Cl]·3H$_2$O	+ .16°	+0.94°

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