PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA CITY, A. C. T., AUSTRALIA]

Mechanism of the Inversion Reaction between d,cis-Dichlorobis-(ethylenediamine)-cobalt(III) Ion and Silver Carbonate

BY FRANCIS P. DWYER,[1] ALAN M. SARGESON AND IAN K. REID

It has been concluded that the predominant formation of *levo* carbonatobis-(ethylenediamine)-cobalt(III) ion by the reaction between silver carbonate and *dextro* cis-dichloro bis-(ethylenediamine)-cobalt(III) ion is due to a *trans* displacement process involving both hydroxyl and silver ions followed by the addition of bicarbonate ion to the dihydroxo complex. By trying each intermediate in the reaction sequence separately the predominant inversion was found to occur with the release of the first chloride ion which gave 34% inversion, 14% retention and 52% isomerization to the *trans* product. The inverted chloro hydroxo complex proceeded *via* the dihydroxo to the carbonato complex with retention of configuration.

Introduction

In a series of papers,[2,3] Bailar and co-workers have shown that the substitution of the carbonato group for the chloride ions of d,cis-dichlorobis-(ethylenediamine)-cobalt(III) ion[4] may yield either predominantly the d or the l isomer of the resulting carbonatobis-(ethylene-diamine)-cobalt(III) ion, depending on the reaction conditions. Substitution with aqueous potassium carbonate, as found by Werner and McCutcheon,[5] or with a suspension of mercurous carbonate yielded a dextro-rotatory product, but when freshly wetted cis-dichloro salt was ground up with silver carbonate, the levorotatory carbonato complex resulted. Since the reaction of d-[Coen$_2$ClH$_2$O]$^{2+}$ ion with silver carbonate gave the *dextro* carbonato complex, it was concluded that the production of the *levo* complex necessitated direct replacement of the chloride ions without prior aquation. With potassium carbonate solution, rapid base hydrolysis preceded substitution by the carbonato group, leading to the *dextro* form. Mathieu[6] deduced from rotatory dispersion studies that the cations [Coen$_2$Cl$_2$]$^+$, [Coen$_2$ClH$_2$O]$^{2+}$ and [Coen$_2$CO$_3$]$^+$ that are dextrorotatory in the Na$_D$ line have the same configuration, and this has been confirmed by recent work[7,8]; hence the direct replacement reaction must have involved inversion of configuration. It has been pointed out[9,10] that inversion can only occur by a *trans* displacement process, and the necessary bimolecular reaction[9] might well proceed in the solid phase between the insoluble

(1) Deceased.

(2) (a) J. C. Bailar and R. W. Auten, *J. Am. Chem. Soc.*, **57**, 774 (1934); (b) J. C. Bailar and J. P. McReynolds, *ibid.*, **61**, 3199 (1939).

(3) J. C. Bailar and D. F. Peppard, *ibid.*, **62**, 820 (1940).

(4) Some confusion about the sign of the rotation in the Na$_D$ line has been resolved by the work of B. E. Douglas and W. C. Erdman, *ibid.*, **79**, 3012 (1957).

(5) A. Werner and McCutcheon, *Ber.*, **45**, 3284 (1912).

(6) J. P. Mathieu, *Bull. Soc. Chim.*, [5] **3**, 476 (1936); [5] **4**, 678 (1937).

(7) R. D. Archer and J. C. Bailar, *J. Am. Chem. Soc.*, **83**, 812 (1961).

(8) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, in press.

(9) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, pp. 235-237.

(10) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

silver carbonate and the d-[Coen$_2$Cl$_2$]$^+$ ion adsorbed on its surface. Some support for this suggestion might be adduced from the slight inversion observed when the substance is ground up for some time with solid potassium carbonate before the addition of water.[3]

Under all experimental conditions the reaction with silver oxalate was found to proceed with preponderant retention of configuration, yielding the *dextro* [Coen$_2$-C$_2$O$_4$]$^+$ ion.[2a,3] Unlike silver oxalate, which is the salt of a relatively strong acid, suspensions of silver carbonate have an alkaline reaction, and the saturated solution contains in addition to silver and carbonate ions, hydroxyl and bicarbonate ions. The observations made by Bailar and co-workers can be rationalized by the proposition that the inversion reaction involves *both* silver and hydroxyl ions, and the carbonato complex results not from direct substitution by carbonate ion but by the reaction of bicarbonate ion with the products of the silver ion–hydroxyl ion reaction. The release of the first chlorine atom must occur with a preponderant inversion over retention and subsequent reactions of the cis-chlorohydroxo enantiomers must occur with substantial retention of configuration.

The fast base hydrolysis of cis-[Coen$_2$Cl$_2$]$^+$ ion with one equivalent of hydroxyl ion has been found to lead to isomerization, and the products to consist of dihydroxo and chlorohydroxo complexes as well as a portion of unreacted cis dichloro complex.[11] With two equivalents of hydroxyl ion, cis and trans dihydroxo complexes should result as before, though the presence of silver ion may affect their relative proportions, and if the reaction is carried out at low temperatures and for a short time some isomeric chlorohydroxo species may remain. Reaction of the products of base hydrolysis with bicarbonate ion is useful in determining the proportion of inversion to the over-all reaction, because of the very large specific rotation of the [Coen$_2$CO$_3$]$^+$ ion, but does not permit an assessment of the proportions of inversion to retention and isomerization. The

(11) R. G. Pearson, R. E. Meeker and F. Basolo, *J. Am. Chem. Soc.*, **78**, 2673 (1956).

racemic $[Coen_2CO_3]^+$ ion arises not only from *trans* products, but from equal amounts of the *cis* optical antipodes. However, the reaction products can be determined quantitatively subject to the condition that the *cis* and *trans* diaquo complexes (formed by adding acid to the dihydroxo complexes and known to isomerize only slowly in acid solution[12]) as well as residual chloroaquo species react with nitrite ion to give complete retention of configuration. It has been shown already that 97.5% retention of configuration occurs when *cis*-$[Coen_2(H_2O)_2]^{3+}$ ion reacts with nitrite ion,[13] and that the conversion of optically active $[Coen_2-NO_2H_2O]^{2+}$ ion to the $[Coen_2(NO_2)_2]^+$ ion[14] occurs without racemization. Similar exchange studies have not been carried out with the *trans* diaquo complex. In addition, it is probable from acid decomposition studies with the carbonato-pentaammine[15] and tetraammine[16] cobalt(III) complexes which showed retention of the Co–O bond that the reverse reaction (substitution of a carbonato for a *cis* diaquo group), should occur with complete retention of configuration.

Results

Carbonatobis-(ethylenediamine)-cobalt(III) chloride has been obtained in high yield by oxidizing a mixture of cobalt(II) chloride (1 mole) and ethylenediamine monohydrochloride (2 moles) with lead(IV) oxide, and then heating the resulting mixture of diaquo complexes with lithium carbonate. Resolution through the *d*-ethylenediaminebis-(oxalato)-cobaltate(III) anion[17] gave the optically pure antipodes, $[\alpha]D \pm 1250°$ for the iodides. Values reported previously for material prepared from *d*-$[Coen_2Cl_2]Cl$ with potassium carbonate[5] ($[\alpha]D +250°$), and with silver carbonate[3] ($[\alpha]D +740°$ for the carbonate), show that substantial racemization accompanied substitution. Optically pure *l*-$[Coen_2(H_2O)_2](NO_3)_3$, $[\alpha]_{5461} -300°$, was isolated from the reaction of *l*-$[Coen_2CO_3]NO_3$ with dilute nitric acid. No rotational change occurred when *d*-$[Coen_2CO_3]ClO_4$ was decomposed with dilute perchloric acid, and then regenerated by the addition of a little solid sodium bicarbonate, thus demonstrating complete retention in the removal and re-addition of the carbonato group.[18]

The reaction sequence at 20° *d*-$[Coen_2CO_3]^+ \xrightarrow{H^+} d$-$[Coen_2(H_2O)_2]^{3+} \xrightarrow{NO_2^-} d$-$[Coen_2(NO_2)_2]^+$ was found to proceed with complete retention of configuration, confirming the previous studies,[15,16] and the exchange of water by nitrite ion in *trans*-$[Coen_2(H_2O)_2]^{3+}$ ion to take place at 20° with 95–100% retention. *trans*-$[Coen_2(NO_2)_2]NO_3$ was isolated quantitatively and the above limit fixed by the failure to detect any *cis*-$[Coen_2(NO_2)_2]I$ when a saturated solution at 20° was treated with sodium iodide (2 moles).[19]

Inversion Reaction with Silver and Hydroxyl Ions (*d*-$[Coen_2Cl_2]^+$ + 2Ag$^+$ + 2OH$^-$).—This was carried out at 1° by the addition of silver nitrate solution (2 moles) to a solution of *d*-$[Coen_2Cl_2](CH_3CO_2)$, followed at once by sodium hydroxide (2 moles). Silver chloride precipitated instantly on the addition

of the alkali, and after 20 seconds nitric acid was added to convert the dihydroxo to the diaquo complexes. From the rotation of the solution ($\alpha D -0.27°$) measured 5 minutes after the addition of solid sodium bicarbonate it was estimated that the carbonato complex consisted of 20 ± 2% of the *levo* isomer, and 80% racemate. Similarly, after reaction of the diaquo complexes with sodium nitrite at 20° for 48 hours, the rotation ($\alpha D -0.14°$) indicated 20 ± 2% of the *levo* *cis*-dinitro complex. The *cis* and *trans*-dinitro complexes were isolated almost quantitatively (93%) as the nitrates, converted to the iodides and fractionally crystallized. The less soluble[19] *cis*-dinitro iodides, (*l* and *dl*) accounted for 60% of the product and the *trans*, 40%, whence the over-all reaction yielded 20% *l*-isomer, 40% racemate and 40% *trans* complex. Pure *l*-$[Coen_2(NO_2)_2]I$ ($[\alpha]D -35°$) was obtained from the less soluble material. A more accurate assessment of the amounts of the dinitro complexes was made by means of paper chromatography using aqueous *sec*-butyl alcohol–acetic acid as eluent. The two bands, containing the *cis* and *trans* isomers, respectively, were eluted from the paper and estimated spectrophotometrically to give *cis* isomer, 61%, *trans* isomer, 39%.

d-$[Coen_2Cl H_2O]^{2+}$ + Ag$^+$ + 2OH$^-$.—The products formed by the release of chloride ion from the chlorohydroxo intermediates have been investigated by treating the corresponding chloroaquo complexes with silver nitrate (1 mole) and sodium hydroxide (2 moles) at 1° for 20 seconds. Subsequent to the very fast deprotonation reaction which consumes one equivalent of alkali and involves no configurational change the situation approximates closely to the intermediate stage in the over-all reaction with the *cis*-dichloro complex. The cation *d*-$[Coen_2ClH_2O]^{2+}$ was found to be converted through the dihydroxo and diaquo complexes to the cations *d*-$[Coen_2CO_3]^+$, $[Coen_2(NO_2)_2]^+$ with probably complete retention of configuration (*cf*. Table I). A slight loss of the complex occurs by adsorption on the silver halide. Direct substitution with bicarbonate ion proceeded with complete retention, but the slower direct reaction with nitrite ion led to partial racemization and isomerization (*cf*. Table I). Inversion must therefore occur with the loss of the first chlorine atom, and *cis* products formed in this process retain their identity completely in subsequent reactions

trans-$[Coen_2ClH_2O]^{2+}$ + Ag$^+$ + 2OH$^-$.—*trans*-$[Coen_2ClH_2O]SO_4$ has been synthesized from *trans*-$[Coen_2Cl_2]Cl$ and mercuric acetate (1 mole) in dilute sulfuric acid and freedom from the *cis* isomer confirmed spectrophotometrically. The pure *cis* isomer could be prepared in a similar manner from *cis*-$[Coen_2Cl_2]Cl$. Little release of chloride ion was found to occur when the *trans*-chloroaquo complex was allowed to react with silver nitrate (1 mole) and sodium hydroxide (2 moles) at 1° for 20 seconds. Most of the substance was regenerated when the mixture was brought to pH 6, prior to the addition of sodium nitrite. After two days at 20°, when all of the coördinated chloride ion had separated as the silver salt, the mixture of dinitro complexes was separated chromatographically to give *trans*, 75 ± 2%, and *cis*, 25 ± 2%. Much of the isomerization probably occurred in the reaction *trans*-$[Coen_2-ClH_2O]^{2+} \rightleftarrows cis$-$[Coen_2ClH_2O]^{2+}$ contemporaneous[11,20] with the rather slow formation of the dinitro complexes. Isomerization that occurred during the incomplete reaction with hydroxyl ion is, of course, taken

(12) T. Uemura and N. Hirosawa, *Bull. Chem. Soc. Japan*, **13**, 377 (1938); F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950); J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952); J. Y. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).

(13) R. K. Murmann and H. Taube, *ibid.*, **78**, 4886 (1956).

(14) R. K. Murmann, *ibid.*, **77**, 5190 (1955).

(15) J. P. Hunt, A. C. Rutenberg and H. Taube, *ibid.*, **74**, 268 (1952).

(16) F. A. Posey and H. Taube, *ibid.*, **75**, 4099 (1953).

(17) F. P. Dwyer, I. K. Reid and F. L. Garvan, *ibid.*, **83**, 1285 (1961).

(18) Acceleration of the rather slow rates of racemization of the *d*-$[Coen_2(H_2O)_2]^{3+}$ and *l*-$[Coen_2CO_3]^+$ ions takes place in the presence of each other, presumably by carbonato group exchange.

(19) Abegg, "Handbuch der anorg. Chem.," IV, S. Hirzel, Leipzig, 1953, 3, pp. 750–752.

(20) At equilibrium (25°) 73% of the *cis* form is present, and for the forward reaction $k = 7.3 \times 10^{-3}$ min.$^{-1}$; $E_a = 27.1$ kcal.; $\Delta S^{\mp} = 3$ e.u.; A. M. Sargeson, Australian and New Zealand Association for the Advancement of Science Conference, Brisbane, Australia, May, 1961, Paper No. 11, 4; M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

TABLE I

SUMMARY OF REACTIONS TAKING PLACE WITH PREDOMINANT RETENTION OR INVERSION

Reactant	Conditions	Product	d%	l%	d,l%	trans, %
$(+)[Coen_2Cl_2]^+$	HCO_3^-	$Coen_2CO_3^+$	60		40	
	$2Ag^+ + 2OH^- + HCO_3^-$	$Coen_2CO_3^+$		20	80	
	$1Ag^+ + 2OH^- + HCO_3^-$	$Coen_2CO_3^+$		20	80	
	$1Ag^+ + 1OH^- + HCO_3^-$	$Coen_2CO_3^+$		4	96	
	$10Ag^+ + 2OH^- + HCO_3^-$	$Coen_2CO_3^+$		20	80	
	$2[Ag(NH_3)_2]^+ + 2OH^- + HCO_3^-$	$Coen_2CO_3^+$		7	93	
	$2OH^- + HCO_3^-$	$Coen_2CO_3^+$	8		92	
$(+)[Coen_2ClH_2O]^{2+}$	HCO_3^-	$[Coen_2CO_3]^+$	100			
	$1Ag^+ + HCO_3^-$	$[Coen_2CO_3]^+$	96^a			
	$1Ag^+ + 2OH^- + HCO_3^-$	$[Coen_2CO_3]^+$	94^a			
$(+)_{5461}[Coen_2(H_2O)_2]^{3+}$	HCO_3^-	$[Coen_2CO_3]^+$	100			
	$1Ag^+ + HCO_3^-$	$[Coen_2CO_3]^+$	92^a			
$(+)[Coen_2Cl_2]^+$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$	37		63	
	$Ag^+ + 2NO_2^-$	$[Coen_2(NO_2)_2]^+$	59		41	
	$2Ag^+ + 2OH^- + 2NO_2^-$	$[Coen_2(NO_2)_2]^+$		20	40	40^b
$(+)[Coen_2ClH_2O]^{2+}$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$	71		29	
$(\pm)[Coen_2ClH_2O]^{2+}$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$			85	15^b
$(+)[Coen_2ClH_2O]^{2+}$	$Ag^+ + 2NO_2^-$	$[Coen_2(NO_2)_2]^+$	51		49	
$trans-[Coen_2ClH_2O]^{2+}$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$			3	97^b
	$Ag^+ + 2OH^- + 2NO_2^-$	$[Coen_2(NO_2)_2]^+$			25	75^c
$(+)_{5461}[Coen_2(H_2O)_2]^{3+}$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$	100 (97.5 ref. 13)			
$trans-[Coen_2(H_2O)_2]^{3+}$	$2NO_2^-$	$[Coen_2(NO_2)_2]^+$				100^c

^{a} Some $[Coen_2CO_3]^+$ lost on the silver halide precipitate. ^{b} Chromatographic analysis. ^{c} Solubility separation.

into account in the dinitro complexes, and the over-all isomeric ratio determined represents the fate of trans chlorohydroxo complex formed with the release of the first chlorine atom.

The series of reactions involved in the transformation of the cis-dichloro to the dinitro complexes are summarized in Fig. 1.

$[Coen_2Cl_2]Cl$ at $-50°$ which yields a predominance of the levo isomer of the $[Coen_2(NH_3)_2]^{3+}$ ion over the dextro form.[21] In considering the formation of the 7-covalent intermediate, the stereochemistry of which follows previous suggestions,[10,11,22] it has been proposed that repulsive interaction between the lone pair of the attacking ammonia molecule and a chlorine atom directs
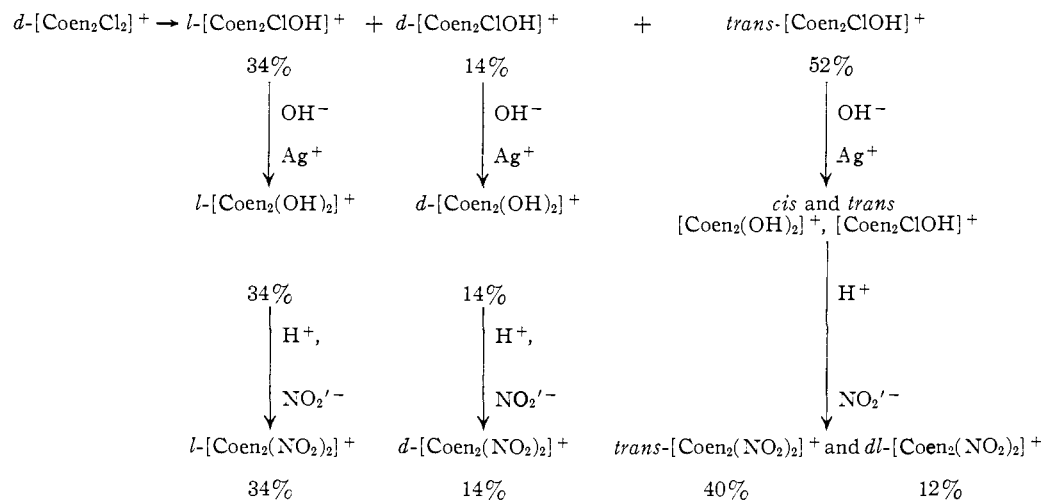
Fig. 1.—The isomeric products in the reaction $cis-(Coen_2Cl_2)^+ + 2Ag^+ + 2OH^-$.

The results of quantitative experiments used to define the reaction conditions have been summarized in Table I. Whereas no advantage accrues from the use of more than one equivalent of silver ion for each equivalent of the $cis-[Coen_2Cl_2]^+$ ion, its role in promoting the trans displacement (inversion) reaction will be evident. Diammine silver ion had a lowered efficiency because of the low concentration of silver ion, but there is no possibility of precipitation of silver oxide, and hence the experiment demonstrates that the proposed "solid state" reaction[9] is not an essential mechanism.

Recently Archer and Bailar[7] have carried out a detailed study of the reaction between ammonia and d-

the attack away from the adjacent cis octahedral faces (cis reaction with retention) toward the two faces in the trans relationship to the chlorine atom. Inversion occurs with the formation of the chloroammino complex at the release of the first chlorine atom.

The mechanism and stereochemistry of the present reaction is essentially similar, Fig. 2, save that the attack of hydroxyl ion at one or the other of the trans octahedral faces is promoted by the silver ion attached to one or both of the chlorine atoms, i.e., a push–pull mechanism. The nature of the silver–chlorine bond

(21) J. C. Bailar, J. H. Haslam and E. M. Jones, J. Am. Chem. Soc., 58, 2226 (1936).

(22) Ref. 9, pp. 213–224.

is not known, but it is possibly a weak polar association with the negative chlorine atoms. The visible spectrum of [Coen$_2$Cl$_2$]ClO$_4$ is unaltered in the presence of silver ion, and conductimetric tests also showed that any complex must be weak. The formation of 1:1 silver ion complexes with cis and trans-[Coen$_2$(NCS)$_2$]$^+$ ions has been established, however, by potentiometric and infrared studies.[23] The silver ion increases the electron density in the vicinity of the chloride ions, thus inhibiting cis attack, and at the same time predisposes trans attack by increasing the positive charge on the remote side of the complex. In the absence of silver ion, the ratio of cis to trans attack is such that the mixture of products has a slight dextro-rotation. The mechanism for the reaction in the presence of Ag$^+$ ion is schematically represented in Fig. 2. Efforts to
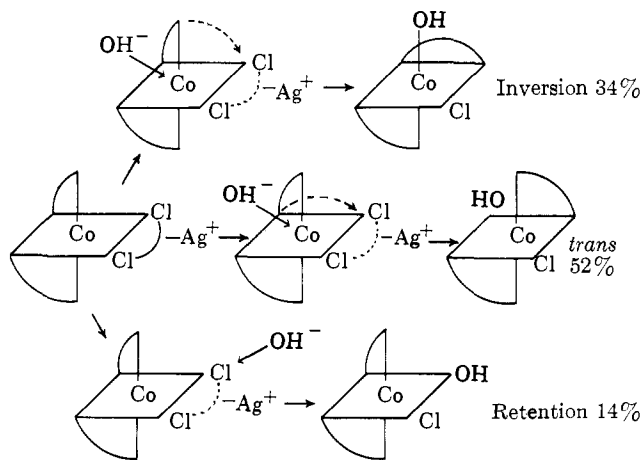

Fig. 2.—The mechanism of the inversion reaction.

substitute other metal ions such as Hg^{2+}, Pb^{2+} or Tl$^+$ for silver ion were unsuccessful. One factor, undoubtedly, is the low solubility of their hydroxides. Similarly, the supposedly strongly nucleophilic nitrite and azide ions could not be used in place of hydroxyl ion. As pointed out by Archer and Bailar[7] the conditions necessary for a preponderance of trans over cis attack are extremely critical and rarely achieved in practice.

Both cis- and trans-[Coen$_2$Cl$_2$]Cl can be prepared in much better yield than the usual method[24] by decomposition of the carbonato complex with two and five moles of hydrochloric acid, respectively. The hydrogen chloride adduct of the latter is decomposed conveniently by means of calcium acetate. The cis complex can be resolved more easily through the d-[Coen(C$_2$O$_4$)$_2$]$^-$ anion[17] than through the bromocamphorsulfonate.[24]

Experimental

d,l-Carbonatobis-(ethylenediamine)-cobalt(III) Chloride.—A solution of cobalt(II) chloride 6-hydrate (80 g.) in water (100 ml.) and hydrochloric acid (667 ml., 1.00 N) was de-aerated by a continuous stream of carbon dioxide for 10 minutes at room temperature and anhydrous ethylenediamine (40 ml.) added slowly. The mixture was heated rapidly to 80° while being stirred mechanically, lead dioxide (60 g.) added, and the carbon dioxide gas stopped. The stirring was maintained for 3 hr. at 80° sufficiently vigorously to prevent the lead dioxide from caking. The hot solution then was filtered and lithium carbonate (48 g.) added to the filtrate, which was stirred occasionally and maintained at 80–90° on a water-bath for 0.5 hr. The strongly alkaline red mixture was filtered, and the filtrate evaporated in a stream of air at 60° to a volume of 480 ml. Free carbonate ion was removed by the addition of calcium chloride 6-hydrate (20 g.), and the calcium carbonate filtered off. Twice the volume of ethanol was added to the warm solution, which deposited fine red crystals on cooling (yield 66 g.). The product

was freed from a little tris-(ethylenediamine)-cobalt(III) chloride impurity by dissolution in water (310 ml.) at 40°, and adding ethanol (620 ml.) while stirring. The substance was washed with 80% alcohol and air-dried (yield 62 g., 70%).

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$CO$_3$]Cl: C, 21.87; H, 5.87; N, 20.41. Found: C, 21.98; H, 5.97; N, 20.1.

Resolution of Carbonatobis-(ethylenediamine)-cobalt(III) Ion. —A solution of the d,l salt above, (27.5 g.) in water (150 ml.) was cooled to 5°, and d-sodium ethylenediaminebis-(oxalato-cobaltate(III) 1-hydrate (17 g.) stirred in. The diastereoisomer, d-[Coen$_2$CO$_3$]d-[Coen(C$_2$O$_4$)$_2$]·3H$_2$O, that separated was collected, washed with ice water (50 ml.), alcohol and acetone in that order, and air dried (yield 25.7 g., 88%). It then was ground up in a cold mortar with sodium perchlorate (60 g.) and ice water (40 ml.). The perchlorate of the complex was filtered off, washed with a little ice water, and transformed to the iodide by grinding in a mortar with sodium iodide (60 g.) and ice water (40 ml.). The iodide was collected, washed with ethanol, and the grinding with sodium iodide repeated (yield, 16.4 g.). A 0.1% aqueous solution gave [α]D +1250°.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$CO$_3$]I: C, 16.40; H, 4.41; N, 15.31. Found: C, 16.56; H, 4.33; N, 15.29

The filtrate from the separation of the diastereoisomer above was fractionally precipitated by adding 20% sodium iodide. The first fractions (4 g.) were impure ([α]D −400°) but the most soluble material (12.7 g.) was the pure levo isomer, ([α]D −1250°).

Anal. Found: C, 16.40; H, 4.59; N, 15.1.

Resolution of cis-Dichlorobis-(ethylenediamine)-cobalt(III) Ion. —The d,l complex was prepared from d,l-[Coen$_2$CO$_3$]Cl (27.5 g.) which was added with stirring to hydrochloric acid (200 ml., 1.00 N) and the mixture then evaporated to dryness on the water bath. The purple residue was washed with ice water (50 ml.), and the washings again evaporated to dryness to yield a second crop of crystals (27 g., 90%).

Anal. Calculated for [Co(C$_2$H$_8$N$_2$)$_2$Cl$_2$]Cl·H$_2$O: C, 15.83; H, 5.97; N, 18.46. Found: C, 15.88; H, 5.81; N, 18.36.

The finely divided solid (18.2 g.) suspended in water (100 ml., 4°) was shaken with silver acetate (10.0 g.) and the silver chloride removed by means of a large centrifuge. Solid l-Na[Coen(C$_2$O$_4$)$_2$]·H$_2$O (10 g.) was stirred into the cold solution, and the diastereoisomer d-[Coen$_2$(Cl$_2$)]l-[Coen(C$_2$O$_4$)$_2$]·H$_2$O separated. After 5 min. at 4° the diastereoisomer was collected, washed with ice water, alcohol and then acetone and air-dried (yield 14 g.). The resolving agent was eliminated by grinding with cold 40% sodium iodide, and the active [Coen$_2$Cl]I collected and washed with ice water and acetone (yield, 10.2 g., [α]D +660°). The filtrate from the separation of the diastereoisomer above gave four fractions on fractional precipitation with sodium iodide. All had the same specific rotation, [α]D −640° (yield, 6 g.).

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$Cl$_2$]I: C, 12.74; H, 4.28; N, 14.87. Found: d-isomer, C, 12.72; H, 4.39; N, 14.6; l-isomer, C, 12.90; H, 4.19; N, 14.5.

cis-Chloroaquobis-(ethylenediamine)-cobalt(III) Sulfate and Chloride.—Low yields are obtained by direct aquation of the cis-dichloro complex, described by Werner.[25] Mercuric acetate (31.8 g.) in water (100 ml.) was added slowly to cis-[Coen$_2$Cl$_2$]Cl·H$_2$O (30.3 g.) suspended in sulfuric acid (100 ml., 2 N) at 4°, with vigorous stirring. After 3 min. the mixture was filtered, and the [Coen$_2$ClH$_2$O]SO$_4$ caused to crystallize by the addition of ethanol. The substance (25 g.) was recrystallized from water by adding alcohol. The blue-green filtrates contained the more soluble trans isomer.

Anal. Calcd. for [Co(C$_2$H$_8$N$_2$)$_2$ClH$_2$O]SO$_4$·2H$_2$O: C, 13.17; H, 6.08; N, 15.36. Found: C, 13.17; H, 6.09; N, 15.27.

The above sulfate (13.7 g.) was converted to the chloride by stirring with concentrated hydrochloric acid (17 ml.) at 4°. The product was washed with an ethanol–ether mixture, then ether, and dried in vacuo (yield, 10.6 g., 90%). Resolution of the latter salt was effected by the method of Werner[25] through bromcamphorsulfonate. The bromide gave [α]D +220°.

trans-Chloroaquobis-(ethylenediamine)-cobalt(III) Sulfate.— A solution of [Coen$_2$CO$_3$]Cl (5.5 g.) in water (100 ml.) was treated with hydrochloric acid (10 N, 15 ml.), evaporated to dryness on the steam bath, and the green solid washed with alcohol. It was suspended in cold water (20 ml.), solid calcium acetate 1-hydrate (1.8 g.) added, then cold alcohol, 400 ml., and cooled in ice. The green needles were washed with alcohol and air-dried (yield 4.5 g., 70%).

trans-[Coen$_2$Cl$_2$]Cl (28.5 g.) suspended in sulfuric acid (100 ml., 2 N) was treated with a solution of mercuric acetate (31.9 g.) in water (100 ml.) added over 1 min. with vigorous stirring. Ethanol (100 ml.) was added, the sides of the vessel were scratched to induce crystallization of the cis chloroaquo sulfate, which then

(23) M. M. Chamberlain and J. C. Bailar, J. Am. Chem. Soc., 81, 6412 (1959).

(24) J. C. Bailar and C. L. Rollinson, Inorg. Syntheses, 22, 222 (1946).

(25) A. Werner, Helv. Chim. Acta, 4, 113 (1921); Ann., 386, 122 (1911).

was filtered off, and the filtrate poured slowly into cold alcohol (1.5 l.) while stirring. The mushroom colored product was collected and washed copiously with alcohol and acetone to remove mercuric chloride, and air-dried (yield, 16 g.). Recrystallization from aqueous alcohol eliminated the less soluble cis isomer and the final traces of mercuric chloride. Solutions of the substance were gray-green in color, ϵ 11.2 (510 mμ, 20°) compared with ϵ 91 for the cis complex at the same wave length.

Anal. Calcd. for [Co(C₂H₈N₂)₂Cl·H₂O]SO₄: C, 14.61; H, 5.52; N, 17.05. Found: C, 14.39; H, 5.55; N, 16.9.

l-cis-Diaquobis-(ethylenediamine)-cobalt(III) Nitrate.—A suspension of l-[Coen₂CO₃]I (4 g.) in water (30 ml.) was shaken for 5 min. with silver nitrate (1.86 g.) in water (20 ml.). The silver iodide was removed, alcohol added to the filtrate, and l-[Coen₂CO₃]NO₃ crystallized. This was collected, washed with alcohol and dried. The dry salt (3 g.) was added gradually to ice-cold nitric acid (15 ml., 3 N) and when evolution of carbon dioxide was complete, a mixture of equal volumes of ethanol, acetone and ether was added. The resultant red oil which crystallized on the addition of methanol was collected, washed with acetone and dried over calcium chloride. A 0.1% aqueous solution gave $[\alpha]_{5461}$ −300°.

Anal. Calcd. for [Co(C₂H₈N₂)₂(H₂O)₂](NO₃)₃: C, 12.00; H, 5.02; N, 24.44. Found: C, 12.20; H, 4.90; N, 24.46.

Transformation of d-[Coen₂Cl₂]I to l-[Coen₂(NO₂)₂]I.—A mixture of dry d-[Coen₂Cl₂]I·H₂O (9.04 g.) and silver acetate (4 g.) was ground up finely in a mortar and then added to water (100 ml.) at 1° and shaken vigorously for exactly one minute to precipitate silver iodide. At once, silver nitrate (8.2 g.) in water (40 ml.) at 1°, followed immediately by sodium hydroxide solution (56 ml., 1.00 N) at 1°. The mixture was shaken vigorously for 20 seconds, and then nitric acid (57 ml., 1.00 N) at 1° was added. To the bright red diaquo complex was added sodium nitrite (8 g.) and urea (3.0 g.) to destroy nitrous acid. The mixture then was allowed to stand at room temperature in the dark to form the cis-dinitro complex, and allow any nitrito complex to isomerize. The silver halide was collected, washed with warm water to extract as much adsorbed dinitro complex as possible and the volume of filtrate and washings adjusted to 500 ml. The yellow solution gave α_D −0.14° in a 1 dm. tube; 20% of the total dinitro complexes was l-[Coen₂(NO₂)₂]NO₃.

After addition of glacial acetic acid (5 ml.) the solution was evaporated in a current of air at room temperature to yield a mixture of cis and $trans$-[Coen₂(NO₂)₂]NO₃ (6.75 g.). Addition of sodium iodide to the filtrate gave a further 0.6 g. as [Coen₂(NO₂)₂]I. Addition of hydrogen peroxide (2 ml., 10%) gave a precipitate of the triiodide, and an additional 0.4 g. of iodide was obtained by reduction with sulfur dioxide in ethanol (total yield, calculated as [Coen₂(NO₂)₂]I, 7.6 g., theory, 8.0 g.).

The product was converted wholly to the iodide with concentrated sodium iodide solution, and then fractionally crystallized in such a way as to obtain the whole of the much less soluble cis-[Coen₂(NO₂)₂]I in the head fractions. In this way was obtained 4.5 g. of material, *i.e.*, 60% cis (l + dl); the $trans$ isomer (by difference) represented 40% of the total. From the specific rotation of the original mixture it follows that the composition was 40% dl, 20% l, 40% $trans$-[Coen₂(NO₂)₂]I. Repetitions of the procedure gave the same composition ±5%. Two recrystallizations of the dl-l mixture from hot water gave the pure *levo* iodide (0.8 g., $[\alpha]_D$ −35°).

Anal. Calcd. for [Co(C₂H₈N₂)₂(NO₂)₂]I·0.5H₂O: C, 11.80; H, 4.21; N, 20.64. Found: C, 11.82; H, 4.18; N, 20.7.

The chromatographic separation on paper was done with a portion of solution from another preparation as above. Elution was carried out with a mixture of sec-butyl alcohol (70%), acetic acid (10%) and water (20%). The two bands (the cis complex moved most) were eluted from the paper with water and estimated spectrophotometrically. Found: cis, 61%; $trans$, 39%.

Transformation of d-[Coen₂Cl₂]I to l-[Coen₂CO₃]ClO₄.—This was carried out in the same manner as for the l-[Coen₂(NO₂)₂]⁺ ion, using half amounts of material, but perchloric acid (28.5 ml., 1.00 N) was added to form the diaquo complex. Sodium bicarbonate (3 g.) then was stirred in to yield the carbonato complex quantitatively. The cold, deep red solution was evaporated in a strong stream of air, and the crystalline material collected from time to time: (1) 30 min., 1.5 g., $[\alpha]_D$ −100°; (2) 2 hr., 0.45 g., $[\alpha]_D$ −230°; (3) 9 hr., 0.7 g., $[\alpha]_D$ −1200°. The specific rotation of the last fraction is close to that of the optically pure carbonato perchlorate ($[\alpha]_D$ −1300°).

Anal. Calcd. for [Co(C₂H₈N₂)₂CO₃]ClO₄·0.5H₂O: C, 17.28; H, 4.93; N, 16.12. Found: C, 17.57; H, 4.97; N, 16.04.

Reaction of d-[Coen₂ClH₂O]²⁺ **Ion with Silver and Hydroxyl Ions.**—Silver nitrate (1.02 g.) in water (10 ml.) was added to a solution of d-[Coen₂ClH₂O]Br₂·H₂O (0.82 g.) in water (6 ml., 1°) and the mixture shaken for 0.5 min. Sodium hydroxide (1 N, 4 ml.) at 1° was added with vigorous shaking for 20 sec.,

followed by perchloric acid (1 N, 4.5 ml.). Sodium bicarbonate (1 g.) was added to the red solution of the diaquo complex, and after 10 min. the rotation determined with a portion of the filtered solution. The value $[\alpha]_D$ +1300° calculated as [Coen₂CO₃]ClO₄ showed that the reaction had occurred with complete retention. By evaporation in a stream of air at 20°, 0.6 g. of the salt above was obtained (yield, 85%, $[\alpha]_D$ +1300°).

Anal. Found: C, 17.32; H, 4.99; N, 16.10.

Reaction of $trans$-[Coen₂ClH₂O]²⁺ **Ion with Silver and Hydroxyl Ions.**—Silver nitrate (2.55 g.) in water (20 ml.) at 1° was added to a solution of $trans$-[Coen₂ClH₂O]SO₄ (4.92 g.) in water (50 ml.) at 1°, followed immediately by sodium hydroxide solution (1 N, 30 ml.) at 1°. After 20 sec., nitric acid (0.936N, 32.5 ml.) was added. The brown precipitate of silver oxide which separated on the addition of the alkali had not changed appreciably in the reaction time, and on acidification a suspension of mostly silver sulfate remained. The color of the mixture reverted to the gray-green of $trans$-chloroaquo solution. Urea (1.5 g.) and sodium nitrite (4 g.) were added, and the mixture kept for 2 days with occasional shaking. The yellow solution was then filtered from the precipitate of silver chloride, which was washed well with water, and the combined filtrates evaporated at 20° in a stream of air to a volume of 50 ml. Repetition of the reaction at one-third the above concentration showed that a slight (5%) release of chloride ion occurred as a result of hydroxyl ion attack in the 20 sec. reaction time. A portion of the solution containing the dinitro complexes was separated by partition chromatography on paper as before. Two bands only were obtained, and the spectrophotometric estimation, which gave cis, 25 ± 2%, $trans$, 75 ± 2%, also showed that chloronitro complexes were absent.

Retention Reactions.—(1) d-[Coen₂ClH₂O]²⁺ + HCO₃'⁻ → d-[Coen₂CO₃]⁺.—Sodium bicarbonate (0.5 g.) and d-[Coen₂H₂O-Cl]Br₂·H₂O (0.5 g.) each in water (5 ml.) were mixed at 20° and after 0.5 hr. the resulting carbonate complex was precipitated with sodium iodide (2 g.). The red product after washing with cold 10% sodium iodide solution, acetone, and drying, gave $[\alpha]_D$ +1250° (yield, 0.42 g.); theoretical, 0.44).

Anal. Calcd. for [Co(C₂H₈N₂)₂CO₃]I: C, 16.40; H, 4.41; N, 15.31. Found: C, 16.49; H, 4.43; N, 15.35.

(2) d-[Coen₂(H₂O)₂]³⁺ + HCO₃'⁻ → d-[Coen₂CO₃]⁺.—The diaquo complex was prepared by dissolution of d-[Coen₂CO₃]I ($[\alpha]_D$ +1250°, 0.5 g.) in perchloric acid (1 N, 3 ml.) at 10°. Sodium bicarbonate (1.0 g.) in water (10 ml.) was added and the carbonato complex isolated as above, yield, 0.45 g., theoretical 0.5 g.; $[\alpha]_D$ +1200°).

Anal. Found: C, 16.46; H, 4.51; N, 15.25.

(3) d-[Coen₂(H₂O)₂]³⁺ + 2NO₂'⁻ → d-[Coen₂(NO₂)₂]⁺.—A solution of the diaquo complex, from d-[Coen₂CO₃]ClO₄ (3.5 g.) and perchloric acid (1 N, 21 ml.) was treated with sodium nitrite (2 g.) and kept at 20° for 2 days. The product was precipitated by the addition of sodium iodide (5 g.) and washed with acetone (yield, 4.1 g., theoretical, 4.2 g.; $[\alpha]_D$ +35°). It was optically pure.

Anal. Calcd. for [Co(C₂H₈N₂)₂(NO₂)₂]I·0.5H₂O: C, 11.80; H, 4.21; N, 20.64. Found: C, 11.87; H, 4.18; N, 20.85.

(4) $trans$-[Coen₂(H₂O)₂]³⁺ + 2NO₂'⁻ → $trans$-[Coen₂(NO₂)₂]⁺.—Sodium nitrite (2 g.) and $trans$-[Coen₂(H₂O)₂](NO₃)₃ (4.7 g.), prepared by the method of Werner,[26] in water (50 ml.) were allowed to stand at 20° for 2 days, and the solution then was evaporated to a small volume in a rapid current of air. The product was collected and washed with alcohol (yield, 3.75 g., theoretical, 3.9 g.). A saturated solution in water (100 ml.) at 20° gave no precipitate of the cis iodide on the addition of sodium iodide (3 g.); 5% cis isomer was present. This experiment repeated with authentic $trans$ (3 g.) and cis (0.15 g.) iodides gave a trace of cis-iodide precipitate.

Anal. Calcd. for [Co(C₂H₈N₂)₂(NO₂)₂]NO₃: C, 14.42; H, 4.84; N, 29.43. Found: C, 14.46; H, 5.07; N, 29.45.

(5) d-[Coen₂Cl₂]⁺ + 2NO₂'⁻ → d-[Coen₂(NO₂)₂]⁺.—A suspension of d-[Coen₂Cl₂]I (0.5 g.) in water (20 ml.) containing sodium nitrite (0.5 g.) was shaken for 18 hr. and then allowed to stand at 20° for 2 days. The solution ($[\alpha]_D$ +13°) was evaporated to a small volume and the product collected ($[\alpha]_D$ +13°). From the reaction stoichiometry and the specific rotation of the pure material, the substitution occurred with 37 ± 5% retention. The same reaction in the presence of silver nitrate (0.67 g.) was complete in 0.5 hr. After 2 days, the solution ($[\alpha]_D$ +20.5°) was evaporated as before; retention in reaction, 59 ± 2%.

Anal. Found: C, 11.90; H, 4.13; N, 20.53; and C, 12.07; H, 4.21; N, 20.5.

(26) A. Werner, *Ber.*, **40**, 272 (1907).