dentate ligand in the monosulfatopentaaquochromium(III) ion. Because of the many lines due to water vibrations in the 400-700 cm.$^{-1}$ region,[9] no attempt was made to determine the degree of splitting of ν_4.

Barraclaugh and Tobe[10] have reported the preparation of salts containing the $CoSO_4H_2O(C_2H_8N_2)_2{}^+$ ion. From infrared studies of these salts the sulfate was found to be a monodentate ligand. Upon heating, a conversion to salts containing $CoSO_4(C_2H_8N_2)_2{}^+$ took place, and the sulfate was found to be bidentate. When dissolved in water, $CoSO_4(C_2H_8N_2)_2{}^+$ was found to revert to $CoSO_4H_2O(C_2H_8N_2)_2{}^+$, indicating that the monodentate form is the more stable of the two. It would be interesting to determine if a chromium species containing sulfate as a bidentate ligand could be prepared in a similar fashion.

The knowledge that sulfate behaves as a monodentate ligand should be of use in investigating the kinetics of chromium(III) reactions. Most ligands of -2 or -3 charge are multidentate and attempts to distinguish effects due to ligand charge are obscured by the multidentate character of the ligands. Straightforward investigation of ligand charge effects should be possible by comparing monodentate sulfate to ligands of -1 and 0 charge.

The monodentate nature of the sulfate in the monosulfatopentaaquochromium(III) ion can be rationalized by consideration of bond distances and angles. The Cr–O bond distances in *trans*-dioxalatodiaquochromate(III)[11] and trisoxalatochromate(III)[12] range from 1.92 to 2.02 Å. If one assumes the Cr–O distance to be about 1.97 Å. in a bidentate sulfatochromium(III) species, and, further, that the O–Cr–O angle would be 90°, the distance between the two oxygen atoms is 1.39 Å. The S–O bond distance in sulfate is 1.44 Å.[13] Assuming that the oxygen atoms are arranged tetrahedrally around the sulfur, the distance between two oxygen atoms is 1.17 Å. Thus, if the sulfate is to be a bidentate ligand one or more of the following must occur: the S–O bond must be stretched, the O–S–O bond angle increased, the Cr–O bond shrunk, or the O–Cr–O bond angle decreased. The idea that geometrical factors prevent sulfate from acting as a bidentate ligand with chromium(III) would be supported if a bidentate selenatochromium(III) species could be prepared. The Se–O distance is 1.61 Å. in selenate,[14] so much less distortion would be required for the selenate to act as a bidentate ligand than for the sulfate.

Acknowledgments.—We wish to thank Dr. Stuart Tobias of the University of Minnesota for help in obtaining the infrared spectra. We also wish to thank the Research Corporation and the National Science Foundation, Undergraduate Research Participation Program, for financial support of this work.

[9] G. Blyholder and S. Vergez, *J. Phys. Chem.*, **67**, 2146 (1963).

[10] C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

[11] J. N. van Nieckerk and F. R. Schoening, *Acta Cryst.*, **5**, 196, 499 (1952).

[12] J. N. van Nieckerk and F. R. Schoening, *ibid.*, **4**, 35 (1951).

[13] F. Mazzi, *ibid.*, **8**, 137 (1955).

[14] M. Bailey and A. F. Wells, *J. Chem. Soc.*, 968 (1951).

CONTRIBUTION FROM THE UNIT OF BIOLOGICAL INORGANIC CHEMISTRY,
THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA

The Absolute Configurations of Disubstituted Cobalt(III) Triethylenetetramine Complexes

BY A. M. SARGESON AND G. H. SEARLE

Received May 11, 1964

The rotatory dispersion and circular dichroism curves for the following complex ions are recorded[1]: (+)-α-$[Co(trien)Cl_2]^+$, (+)-α-$[Co(trien)ClOH_2]^{+2}$, (+)-α-$[Co(trien)CO_3]^+$, $(+)_{546}$-α-$[Co(trien)(OH_2)_2]^{+3}$, $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$, (+)-β-$[Co(trien)Cl_2]^+$, (+)-β-$[Co(trien)ClOH_2]^{+2}$, (+)-β-$[Co(trien)CO_3]^+$, $(+)_{546}$-β-$[Co(trien)(OH_2)_2]^{+3}$, and $(+)_{546}$-$[Co(trien)(NO_2)_2]^+$. The relative and absolute configurations of the complex ions are discussed in the light of recent advances in the interpretation of circular dichroism curves and in conjunction with reactions which interrelate the compounds and are known to occur with retention of configuration.

Introduction

The absolute and relative configurations of a series of optically active disubstituted bis(ethylenediamine)-cobalt(III) complexes have been assessed by an analysis of their rotatory dispersion (RD) curves, correlated with kinetic and mechanistic evidence which interrelates the configurations of the compounds independently of rotatory dispersion.[2] The present paper is concerned with a similar series of complexes containing the quadridentate ligand triethylenetetramine (trien) which may be regarded as two ethylenediamine (en) molecules linked by an ethylene bridge. The distinction between the $[Co(en)_2X_2]^{+n}$ and $[Co(trien)X_2]^{+n}$ complexes arises from the manner in which the quadridentate can attach to the cobalt. Whereas $[Co(en)_2X_2]^{+n}$

[1] The optical isomers are denoted by the sign of rotation in the Na D or if another wave length is used then the wave length appears as a subscript, *e.g.*, $(+)_{546}$.

[2] T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

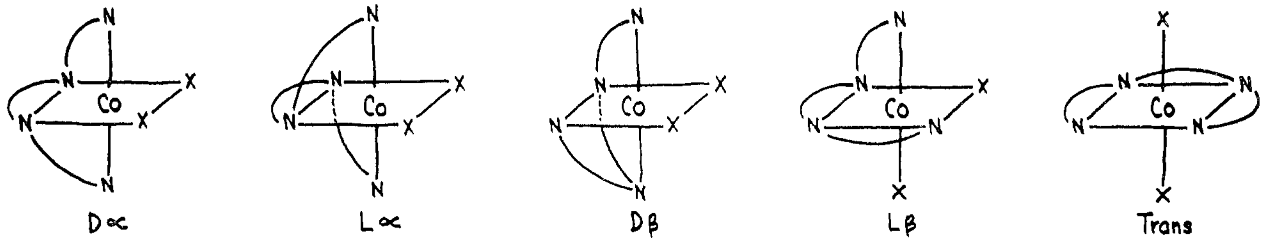


Figure 1.—The optical and geometrical isomers of $[Co(trien)X_2]^{+n}$.

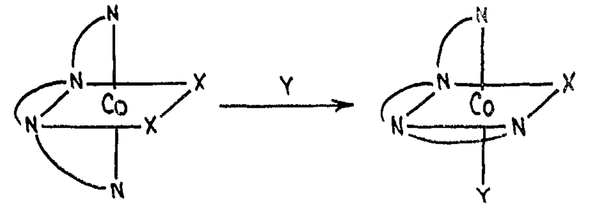


Figure 2.—The inversion reaction for Dα-$[Co(trien)X_2]$ → Lβ-$[Co(trien)XY]$.

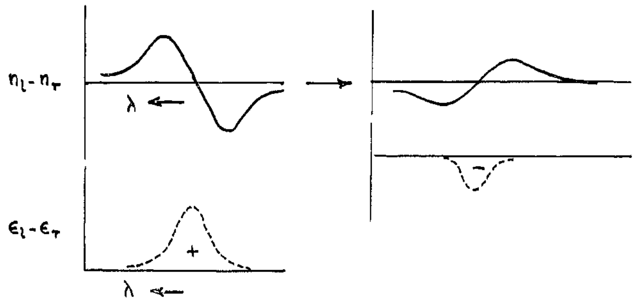
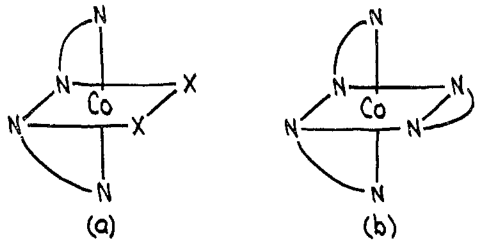


Figure 3.—The relation between rotatory dispersion and circular dichroism for an isolated transition for the change of D → L.



(a) (b)

Figure 4.—The structures of D-$[Co(en)_2X_2]^{+n}$ and D(+)-$[Co(en)_3]^{+3}$.

has three possible isomers; D, L, and *trans*, the trien complexes have five, Figure 1. The two *cis* geometrical forms are denoted α and β and by eliminating the central ethylene bridges in Figure 2 it can be seen that they are related as are the D- and L-$[Co(en)_2X_2]^{+n}$ isomers. This is significant because in the course of a reaction such as in Figure 2 a change from α to β, essentially an inversion, would be reflected by a change in shape of the RD curves, and a change in sign of the associated circular dichroism CD band (Cotton effect), Figure 3. In this way stereochemical changes involving displacement of the terminal NH_2 group in the trien complexes may be followed during substitution reactions and the technique will be used in this and a subsequent series of papers to follow the stereochemical course of the hydrolysis of the dichloro complexes.

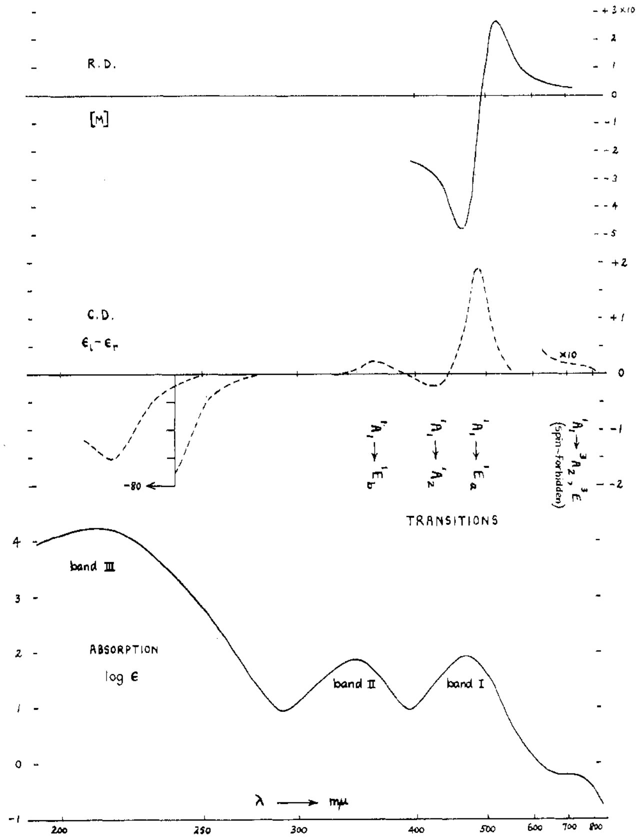


Figure 5.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-$[Co(en)_3](ClO_4)_3$.

It is assumed that a secondary N atom would not be involved in a displacement since the rearrangement necessary for this process to occur would be excessive.

Mason[3] has proposed that the *cis* complexes $[Co(en)_2X_2]^{+n}$ with the configuration, Figure 4 (a), closely related to the dihedral ion (+)-$[Co(en)_3]^{+3}$, Figure 4 (b), of known absolute configuration should give a transition (in the long wave length region, band I) of A symmetry with a positive rotational strength (positive Cotton effect). This transition is derived from the transition of E_a symmetry in the dihedral ion and has been approximated to the $^1A_1 \rightarrow {}^1E_a$ transition by some authors.[4] Using this theoretical background it is possible to relate the configurations of the *cis*-$[Co(en)_2X_2]^{+n}$ and *cis*-$[Co(trien)X_2]^{+n}$ ions to the absolute configuration of the D(+)-$[Co(en)_3]^{+3}$ ion.

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(3) S. F. Mason, *Quart. Rev.* (London), **17**, 20 (1963).

(4) J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Am. Chem. Soc.*, **84**, 3227 (1962).

Results and Discussion

It seems clear that the E_a (positive CD) and A (negative CD) transitions in (+)-$[Co(en)_3]^{+3}$ are superimposed partly[3] and that a similar situation exists for the (+)-$[Co(en)_2(NH_3)_2]^{+3}$ ion. However in the latter instance the E_a transition has split into two levels A and B both giving positive CD bands and the A transition has transformed to one of B symmetry with a negative CD band. Moreover since there is no mixing of the E_a and A transitions in the $[Co(en)_3]^{+3}$ ion and as the essential field is unchanged in (+)-$[Co(en)_2(NH_3)_2]^{+3}$ the A and B transitions derived from E_a do not mix with the B transition derived from the A transition in $[Co(en)_3]^{+3}$. This is borne out by the similarity of the RD and CD curves in Figures 5 and 6 and it is evident that these complexes have the same configuration and that the dominant transition in (+)-$[Co(en)_2(NH_3)_2]^{+3}$ is that of A symmetry derived from the E_a transition in D(+)-$[Co(en)_3]^{+3}$. It follows that the D-bis(ethylenediamine)cobalt(III) complexes with C_2 symmetry and those which approximate to C_2 symmetry, (+)-$[Co(en)_2Cl_2]^+$, (+)-$[Co(en)_2ClOH_2]^{+2}$, (+)-$[Co(en)_2CO_3]^+$, (+)-$[Co(en)_2NH_3Cl]^{+2}$, (+)-$[Co(en)_2(OH_2)_2]^{+3}$, (+)-$[Co(en)_2(NO_2)_2]^+$, (+)-$[Co(en)_2NH_3H_2O]^{+3}$, and (+)-$[Co(en)_2NH_3NO_2]^{+2}$, which have been related to (+)-$[Co(en)_2(NH_3)_2]^{+3}$ in an earlier communication[2] all have a predominant optically active transition of A symmetry in the visible region (band I) which gives rise to the major part of the rotation of the complexes in this region. Gillard[5] has also proposed that the major CD band in the visible in these complexes has A symmetry.

The spectra, RD, and CD curves for the ions (+)-α-$[Co(trien)Cl_2]^+$, (+)-α-$[Co(trien)ClOH_2]^{+2}$, (+)-α-$[Co(trien)CO_3]^+$, $(+)_{546}$-α-$[Co(trien)(OH_2)_2]^{+3}$, and $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$ are given in Figures 7–11. The ions all have C_2 symmetry except for the chloroaquo complex and it is assumed that this approximates to C_2. The predominant CD band (A symmetry) in band 1 is positive for all the complexes shown and this transition gives rise to the major part of the RD curve in the visible region (Mathieu's "principal absorption band"),[6] and correspondence between the shapes of all the RD curves[2] is also observed. It would seem then that these complexes have a common configuration which can be related to the analogous bis(ethylenediamine) complexes and through D(+)-$[Co(en)_2(NH_3)_2]^{+3}$ to the dihedral D(+)-$[Co(en)_3]^{+3}$ ion. Some comment on the minor structure of the CD curves is required to support the argument above. The (+)-α-$[Co(trien)Cl_2]^+$ ion shows initially a weaker negative transition in the CD while (+)-$[Co(en)_2(NH_3)_2]^{+3}$ and $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$ both have initially a dominant positive CD band in the visible region. This behavior merely reflects the average ligand field in the horizontal plane and apical positions in the ion. Since in $[Co(en)_3]^{+3}$ the A level lies slightly higher in energy than E[4] the same distribution could be ex-

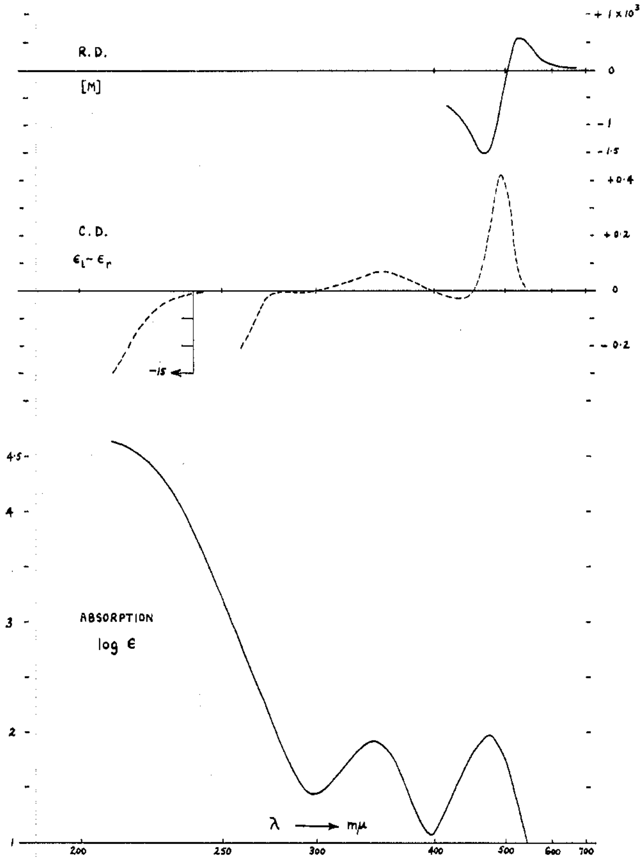

Figure 6.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-$[Co(en)_2(NH_3)_2](ClO_4)_3$.

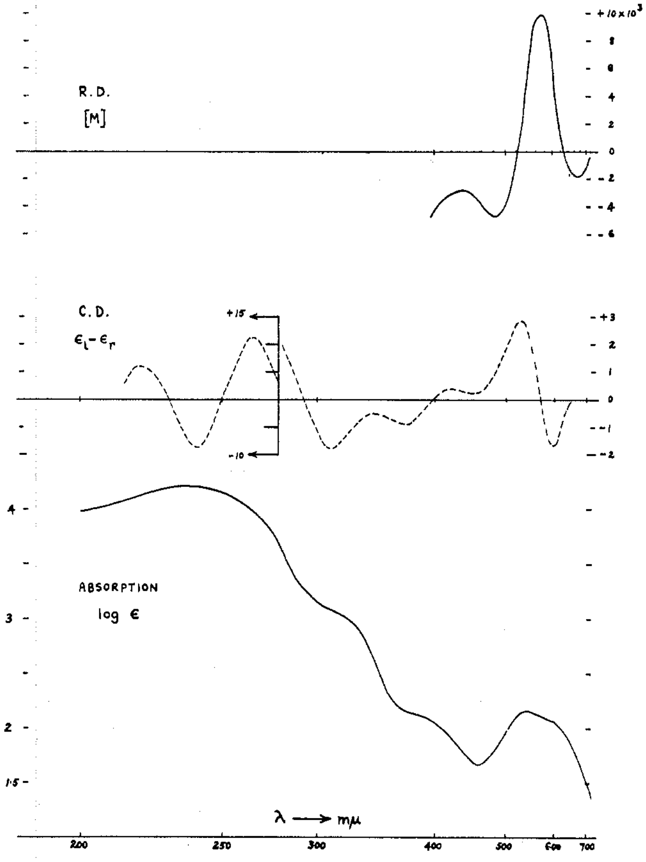

Figure 7.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-α-$[Co(trien)Cl_2]ClO_4$.

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(5) R. D. Gillard, *Proc. Chem. Soc.*, in press.
(6) J. P. Mathieu, *Bull. soc. chim. France*, [5] **6**, 873 (1939).

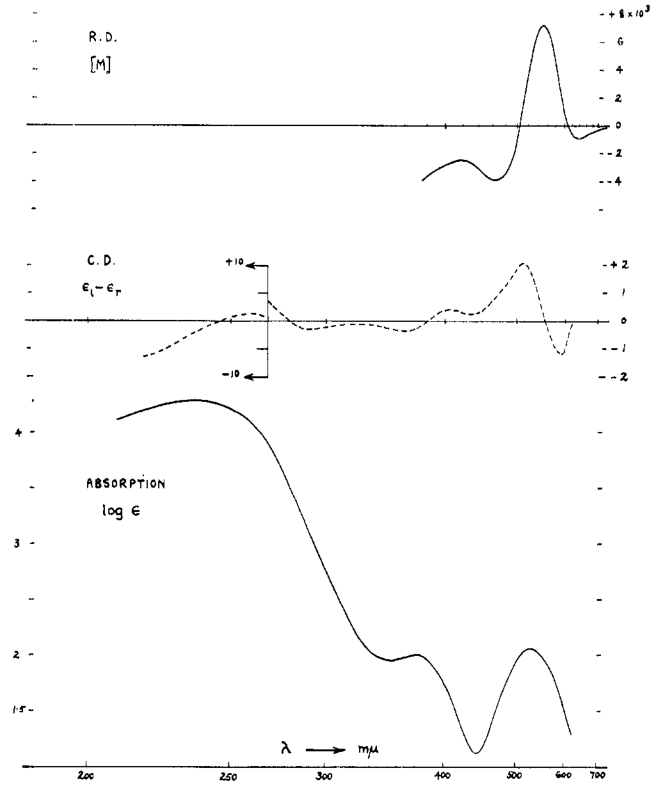

Figure 8.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-α-$[Co(trien)Cl(H_2O)]^{+2}$.

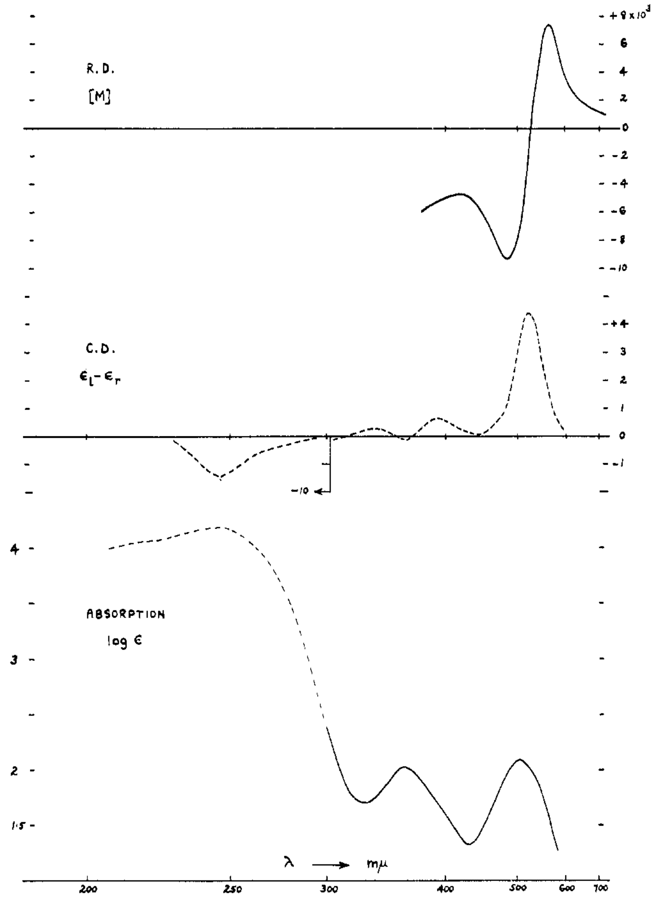

Figure 9.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-α-$[Co(trien)CO_3]ClO_4 \cdot H_2O$.

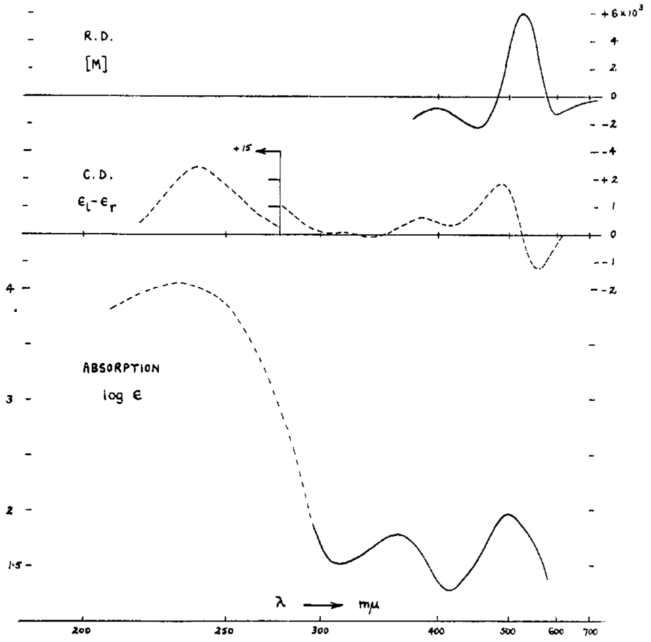

Figure 10.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)$_{546}$-α-$[Co(trien)(H_2O)_2](ClO_4)_3$.

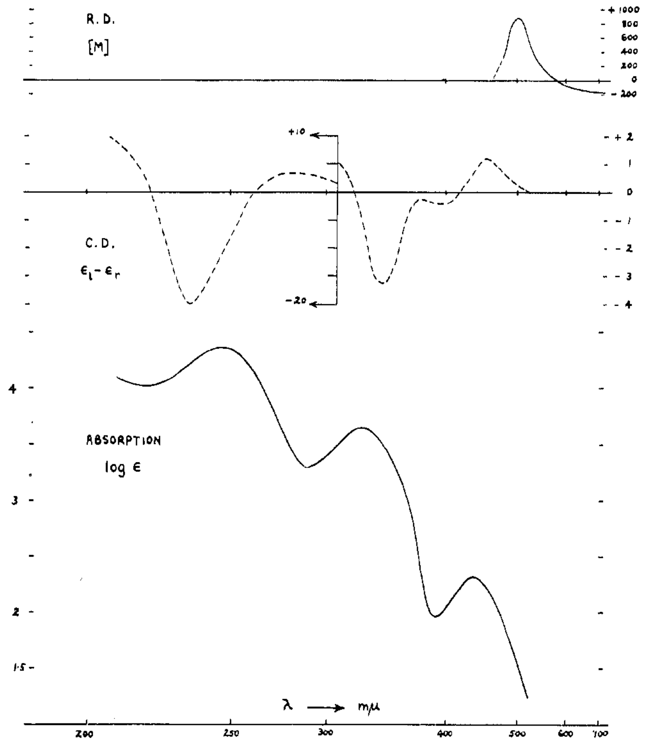

Figure 11.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)$_{546}$-α-$[Co(trien)(NO_2)_2]ClO_4$.

pected in (+)-$[Co(en)_2(NH_3)_2]^{+3}$ where the field is essentially unaltered, *i.e.*, A and B (positive) are lower in energy than B (negative). For α-$[Co(trien)Cl_2]^+$ the field in the plane is less than in the apical positions and the B (negative) transition should now be lower in energy than the A and B (positive) transitions. Alternatively the α-$[Co(trien)(NO_2)_2]^+$ ion has a stronger field in the plane than in the apical positions and hence B (negative) should be higher in energy than

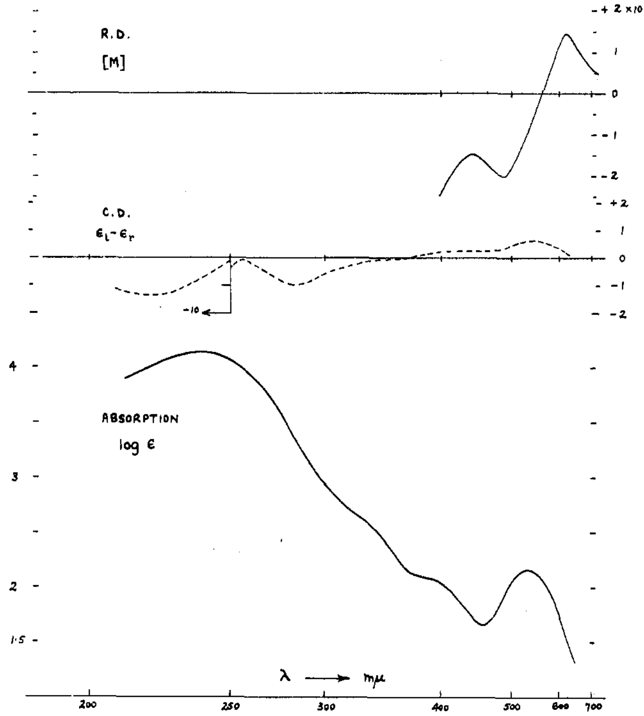

Figure 12.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-β-[Co(trien)Cl_2]ClO_4.

the two positive transitions. These trends are observed in the CD curves.

The corresponding data for the ions (+)-β-[Co(trien)Cl_2]$^+$, (+)-β-[Co(trien)$ClOH_2$]$^{+2}$, (+)-β-[Co(trien)CO_3]$^+$, $(+)_{546}$-β-[Co(trien)$(OH_2)_2$]$^{+3}$, and (+)-β-[Co(trien)$(NO_2)_2$]$^+$ are given in Figures 12–16. Although the ions no longer have C_2 symmetry the same general pattern is observed as for the α series and for the bis(ethylenediamine) complexes, and for this reason it is assumed that the complexes approximate to C_2 symmetry. The intensities of the CD bands in the visible are considerably less than the α series which is consistent with the lower symmetry order, but the major band is still positive for the series shown and it is proposed that the D(+)-β complexes described have the same configuration as the Dα complexes and the D-[Co(en)$_2$X$_2$]$^{+n}$ complexes.

The configurations were also correlated by the following reactions.

$$\underset{[M]_D\ +8750°}{(+)\text{-}\alpha\text{-}[Co(trien)Cl_2]^+} \xrightarrow{H_3O^+} \underset{[M]_D\ +2400°}{(+)\text{-}\alpha\text{-}[Co(trien)ClOH_2]^{+2}} \xrightarrow{HCO_3^-}$$

$$\underset{[M]_D\ +4730°}{(+)\text{-}\alpha\text{-}[Co(trien)CO_3]^+} \xrightarrow{H_3O^+} \underset{[M]_{546}\ +4700°}{(+)_{546}\text{-}\alpha\text{-}[Co(trien)(OH_2)_2]^{+3}}$$

$$\xrightarrow{NO_2^-} \underset{[M]_{546}\ +210°}{(+)_{546}\text{-}\alpha\text{-}[Co(trien)(NO_2)_2]^+}$$

The aquation of the dichloro to the chloroaquo complex in aqueous solution at pH <3 occurred at the same rate as the mutarotation[7] and in this respect it was similar to the (+)-[Co(en)$_2$Cl$_2$]$^+$ ion except that no subsequent isomerization of the chloroaquo ion occurred.

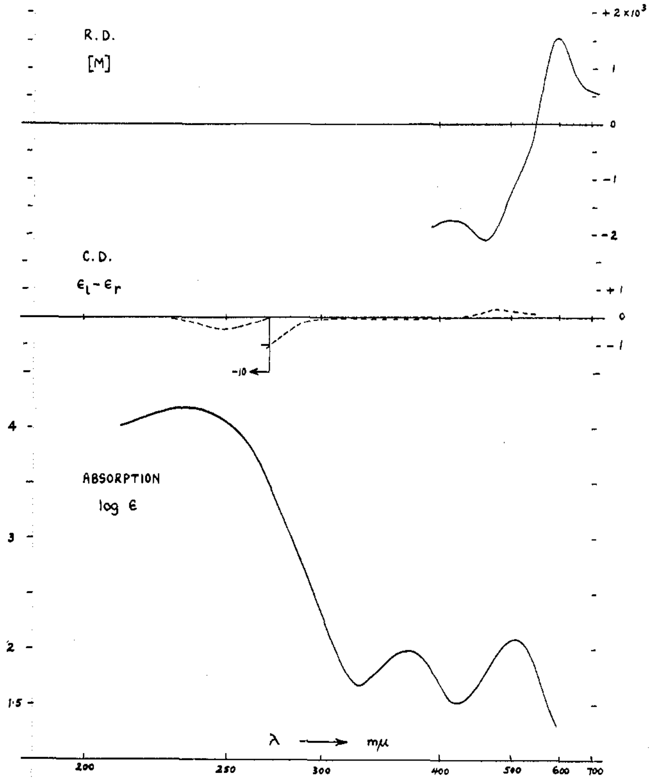

Figure 13.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-β-[Co(trien)Cl(H_2O)]$^{+2}$.

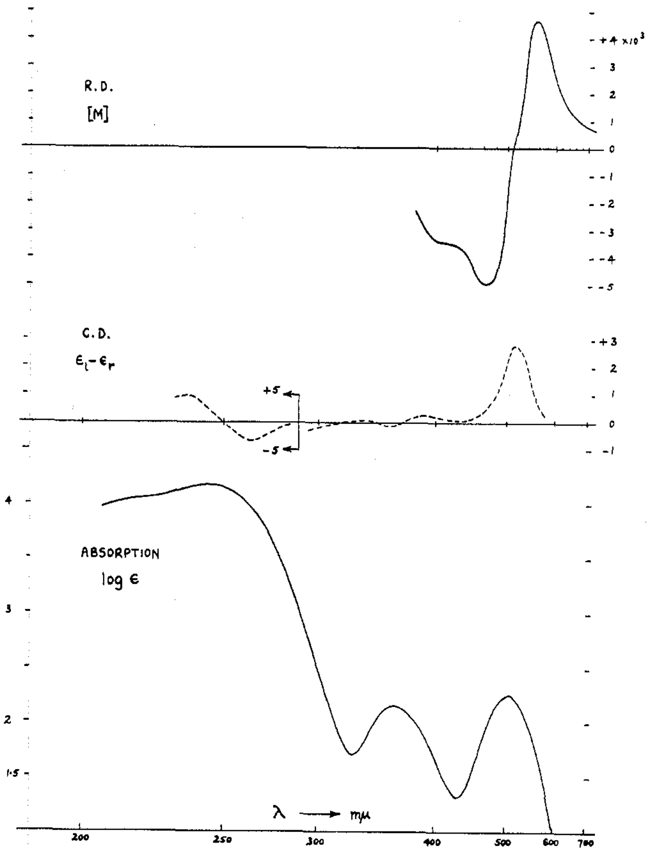

Figure 14.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)-β-[Co(trien)CO_3]$ClO_4 \cdot H_2O$.

The chloroaquo ion was converted to the carbonato complex with full retention of configuration and the

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[7] A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).

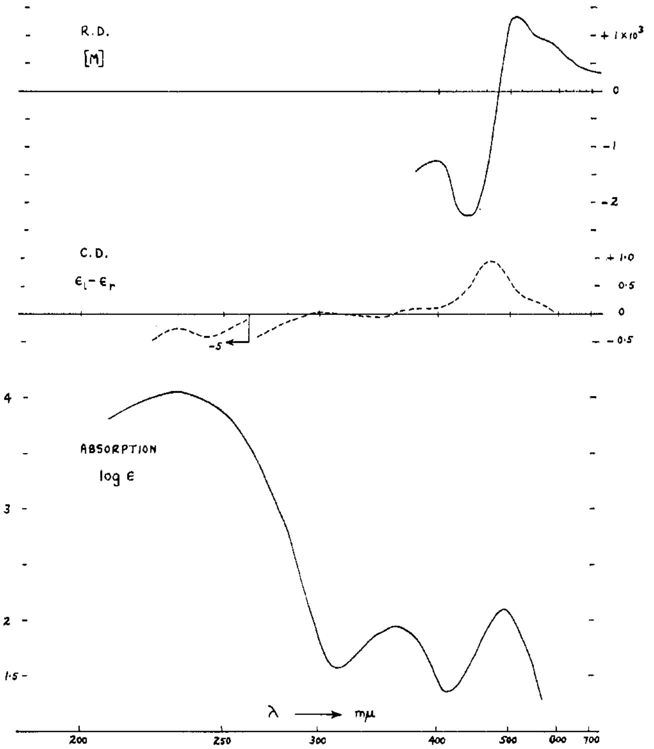


Figure 15.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)$_{546}$-β-[Co(trien)(H$_2$O)$_2$](ClO$_4$)$_3$.

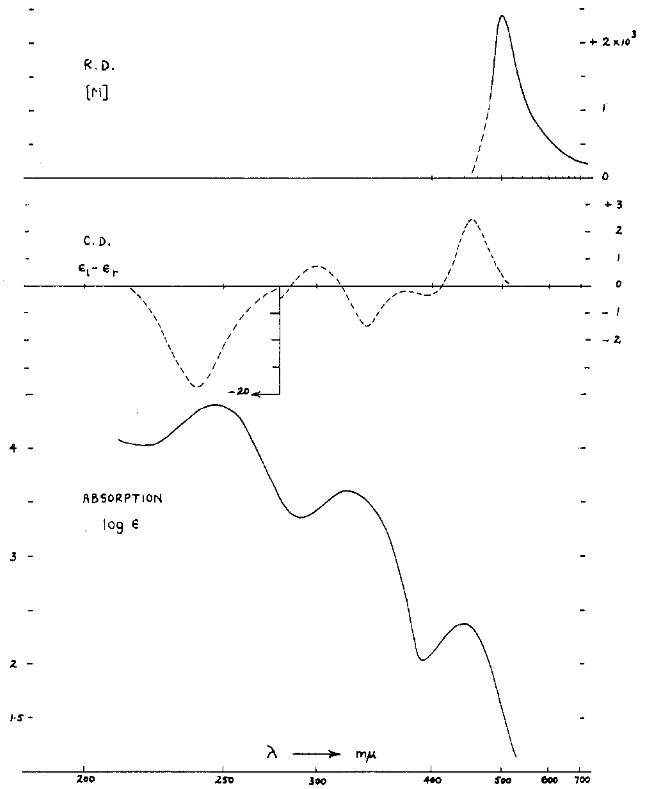


Figure 16.—Rotatory dispersion, circular dichroism, and absorption spectrum of D(+)$_{546}$-β-[Co(trien)(NO$_2$)$_2$]ClO$_4$.

rotation observed, [M]D +4700°, was essentially the same as that obtained for the fully resolved isomer, [M]D +4730°. This reaction takes place by the fast addition of CO$_2$ to the coordinated water molecule without Co–O bond cleavage, followed by the dissociation of the Cl$^-$ ion with retention of configuration, Figure 17. The two steps in the reaction were identified clearly by acidifying the solution after the CO$_2$ addition was complete ($T_{1/2} \approx 6$ sec.) when practically all the Cl$^-$ ion was still coordinated.[8]

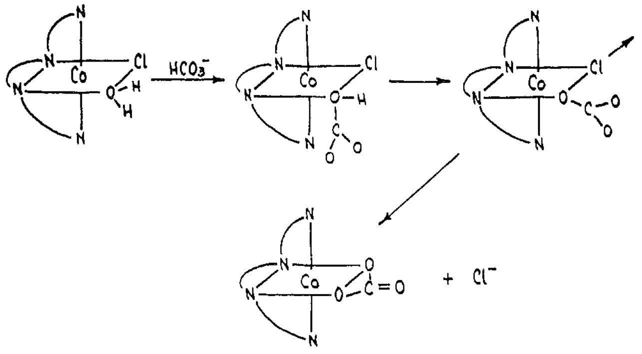
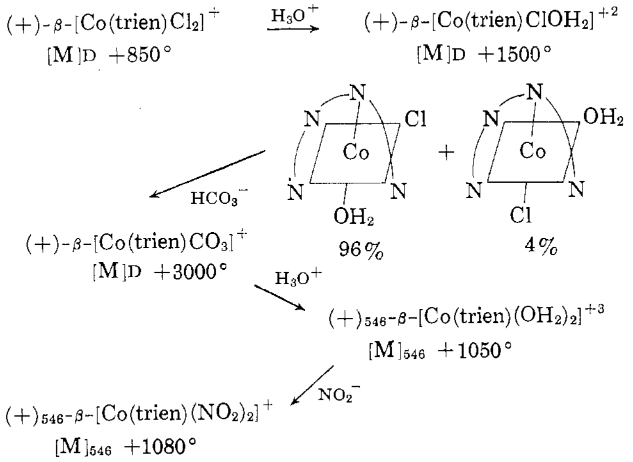


Figure 17.—The mechanism of the conversion of D(+)-α-[Co(trien)ClOH$_2$]$^{2+}$ to D(+)-α-[Co(trien)CO$_3$]$^+$.

Acidification of the carbonato complex gave the diaquo ion also with full retention of configuration and subsequent addition of NaNO$_2$ gave the (+)$_{546}$-α-[Co(trien)(NO$_2$)$_2$]$^+$ ion with better than 90% retention of configuration. The rotation observed for the isolated dinitro isomer, [M]$_{546}$ +220° (±20°), agreed with that obtained by resolving the racemic compound, [M]$_{546}$ +200° (±20°).

The mechanism proposed for the fission of the carbonato group in [Co(NH$_3$)$_4$CO$_3$]$^{+}$[9] is consistent with the observed retention of configuration in the trien complexes while the addition of nitrite ion to coordinated water is known to occur without Co–O bond fission initially.[10] The N is coordinated subsequently by an intramolecular rearrangement which also occurs with full retention of configuration.

The β complexes showed essentially the same pattern as the α complexes for the stereochemical course of their reactions.



The β-dichloro ion aquated to give two β-chloroaquo isomers and from the rates of the subsequent aquation

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(8) H. Amling, F. Dwyer, Jr., and A. M. Sargeson, to be published.

(9) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **75**, 4099 (1953).

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

of the second Cl^- ion it was estimated that 96% of one form occurred and 4% of the other.[9] The conversion of both to the same carbonato complex ion gave a rotation ($[M]_D$ +3000°) equivalent to that obtained by resolving the racemic β-carbonato complex ($[M]_D$ +2990°). The conversion of the carbonato compound to the diaquo and then to the dinitro complex occurred with full retention of activity in the first instance and better than 90% in the second. The rotation of the β-dinitro isomer isolated from the transformation, $[M]_{546}$ +1080°, agreed with that obtained by resolving the racemic β-dinitro complex, $[M]_{546}$ +1120°, within the experimental error. The diaquo complex was also reconverted to the carbonato complex with full retention of activity using $NaHCO_3$.

The detection of the two β-chloroaquo isomers identified the geometrical structure of the β-dichloro isomer, Figure 1, and this was supported by Mason's suggestion[11] that the β isomer with less symmetry should have a smaller CD in absolute magnitude than the α isomer, particularly in the charge-transfer region.

The transformation of resolved α- and β-dichloro complexes to the dinitro compounds without appreciable loss of activity showed that the complexes were optically pure, since the possibility that the dichloro, carbonato, and dinitro isomers were all resolved to the same degree of impurity is remote. The purity of the geometrical, α- and β-dinitro, isomers was established by chromatographing them on paper with 1-butanol–pyridine–acetic acid–H_2O (40:30:10:20) as eluent.

From the CD and RD curves and the full retention of activity involved in the transformations of the dichloro to the dinitro compounds it is evident that negligible geometrical isomerization occurred. However, the possibility that the Dα complex can invert to the Lα form or Dβ → Lβ with full retention of activity in the course of reaction has to be considered. Two general routes are available for the stereochange, intramolecular rearrangement and substitution, but neither can account for the inversion simply. Trigonal or rhombic twists[12] are excluded by the restrictions enforced by the multidentate. If both ends of the ligand dissociate then 50% of the L form might be obtained when the ligand recoordinates but the process cannot occur with total inversion. Only multiple substitutions can lead from Dα → Lα and the possibility of all these occurring stereospecifically is negligible. Similar considerations apply to the β isomer.

It would seem then that the reactions involved in the reaction sequence are certain to take place with retention of configuration as well as retention of activity and the common configuration of the complexes in each set of transformations is established independently of the RD and CD evidence. Thus all three methods agree and the absolute configurations of the α and β dextro isomers described are shown as Dα and Dβ in Figure 1 related to the analogous D-bisethylenediamine-cobalt(III) complexes in Figure 4 (a) and the D(+)-$[Co(en)_3]^{+3}$ ion in Figure 4 (b).

In addition (+)-$[Co(en)_2Cl_2]^+$, $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$, (+)-α-$[Co(trien)Cl_2]^{+2}$, and (+)-β-$[Co(trien)Cl_2]^+$ all crystallized as the least soluble diastereoisomer in the form $[CoN_4X_2]\{(-)\text{-}[Co(en)(C_2O_4)_2]\}\cdot H_2O$ and this also indicates that they have the same configuration and is consistent with the conclusion above.

Several other reactions with these compounds are of interest. The (+)-β-chloroaquo complexes were converted to the $(+)_{546}$-β dinitro isomer with excess $NaNO_2$ and approximately 70% retention of activity. Similarly the (+)-α-chloroaquo isomer was converted to the $(+)_{546}$-dinitro compound with about 80% retention of activity and the addition of acid to $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$ slowly gave the $(+)_{546}$-α-$[Co(trien)(OH_2)_2]^{+3}$ ion largely with retention of configuration.

Experimental

The complexes used in this investigation were optically and analyticaly pure and their preparation and resolution will be published shortly.

Optical rotations were measured with a Bellingham and Stanley polarimeter (visually), and a Shimadzu photoelectric polarimeter attached to a Shimadzu spectrophotometer (QR-50) or a Perkin-Elmer polarimeter (141) coupled with a Zeiss monochromator. All rotations were measured in a 1-dm. tube unless otherwise stated. The CD curves were measured with a Dichrograph under the same conditions as the RD measurements.

(+)-β-$[(Co(trien)Cl_2]^+$ → (+)-β-$[Co(trien)ClOH_2]^{+2}$.—Optically pure (+)-β-$[Co(trien)Cl_2]ClO_4$, $[\alpha]_D$ +230° (0.0150 g.), was dissolved in cold perchloric acid (20 ml. of 0.01 N) and the solution (2.0×10^{-3} M) was added to a thermostated polarimeter tube (10°). The half-life for the aquation of the dichloro to the chloroaquo ion was ~12 min. at 20° so that several solutions prepared in this way were used to obtain the complete RD curve given in Figure 12.

The dichloro solution above was allowed to stand at 20° for 70–80 min., and at this stage the concentration of β-chloroaquo was maximum, ~93%. The RD curve of this solution was then measured since the chloroaquo isomers were not isolated, Figure 13.

(+)-β-$[Co(trien)ClOH_2]^{+2}$ → (+)-β-$[Co(trien)CO_3]^+$.—When the aquation of the β-dichloro to chloroaquo was complete (90 min. at 20°) excess $NaHCO_3$ (0.05 g.) was added to the solution and the β-$[Co(trien)CO_3]^+$ complex formed immediately. The RD curve, Figure 14, was measured after 30 min. and both the spectra and rotations were unaffected by excess $NaHCO_3$. The (+)-β-$[Co(trien)CO_3]^+$ ion was optically stable in aqueous solution and the observed rotation, $[M]_D$ +3000°, agreed with that of the resolved isomer, $[M]_D$ +2990°. The rotation of a solution at 50° fell 7% after 14 hr.

(+)-β-$[Co(trien)CO_3]^+$ → $(+)_{546}$-β-$[Co(trien)(OH_2)_2]^{+3}$.—$HClO_4$ (11.6 N) was added dropwise to the solution of (+)-β-$[Co(trien)CO_3]^+$ (2.0×10^{-3} M) until the pH of the solution was ~2. The RD curve of the diaquo complex so formed was measured after 15 min. and the result is given in Figure 15.

A solution of fully resolved (+)-β-$[Co(trien)CO_3]ClO_4\cdot H_2O$ ($[\alpha]_D$ +770°) (2.0×10^{-3} M in 0.1 N $HClO_4$) gave an RD curve for the diaquo complex identical with that in Figure 15.

The conversion of the β-diaquo to the β-carbonato complex with excess $NaHCO_3$ also occurred with full retention of activity. $(+)_{546}$-β-$[Co(trien)(OH_2)_2](ClO_4)_3$ (3.78×10^{-3} M) in $HClO_4$ (0.01 N) (α_D +0.32°, $[M]_D$ +850°, $[M]_{546}$ + 1050°) was treated with $NaHCO_3$ until the solution was faintly alkaline and the rotation of the carbonato complex then was measured, α_D +1.12° when $[M]_D$ +2970°. For the optically pure carbonato complex $[M]_D$ +3000°.

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$(+)_{546}$-β-[Co(trien)(OH$_2$)$_2$]$^{+3}$ → $(+)_{546}$-β-[Co(trien)(NO$_2$)$_2$]$^{+}$. (a).—Optically pure $(+)_{546}$-β-[Co(trien)(OH$_2$)$_2$](ClO$_4$)$_3$ (3.78×10^{-3} *M*) in $HClO_4$ (0.01 *N*) was treated with excess $NaNO_2$. The orange diaquo complex changed to the yellow dinitro compound in about 10 min. and the following rotations were measured subsequently: 0.25 hr. $[M]_{546}$ +1540°, 0.5 hr. $[M]_{546}$ +1480°, 15 hr. $[M]_{546}$ +1060°. The rotation at 15 hr. corresponded to that for the fully resolved $(+)_{546}$-β-[Co(trien)(NO$_2$)$_2$-ClO$_4$, $[M]_{546}$ +1120°. The change in rotation was attributed to nitrito–nitro isomerization.

(b).—$(+)$-β-[Co(trien)CO$_3$]ClO$_4 \cdot$H$_2$O, $[M]_D$ +2890° (0.38 g.) was dissolved in water (5 ml.) and $HClO_4$ (2.1 ml. of 1 *N*) was added. After 20 min. excess $NaNO_2$ (0.4 g.) was added to form the dinitro complex which began to crystallize from the orange solution (pH 4) (10 min.), and the product was filtered off after 1.5 days. The orange filtrate was acidified with 1 drop of glacial acetic acid and $NaClO_4$ (0.07 g.) was added. Evaporation of this solution to 3 ml. gave a further yield of dinitro product. The combined fractions were washed with methanol and acetone and dried in air; total yield 0.36 g. (91%). A 0.195% solution gave α_{546} +0.53° when $[M]_{546}$ was +1080° and the visible absorption spectrum corresponded to that of the pure β-dinitro isomer. *Anal.* Calcd. for [CoC$_6$H$_{18}$N$_4$(NO)$_2$]ClO$_4$: C, 18.2; H, 4.6; N, 21.2. Found: C, 18.3; H, 4.7; N, 21.3. The RD curves for the solution and isolated sample were identical, Figure 16.

$(+)$-α-[Co(trien)Cl$_2$]$^{+}$ → $(+)$-α-[Co(trien)ClOH$_2$]$^{+2}$.—The half-life of aquation of α-[Co(trien)Cl$_2$]ClO$_4$, $[\alpha]_D$ +2330°, was 80 min. at 25° in $HClO_4$ (0.01 *N*) so that its RD curve was measured quickly at 20° in 2.0×10^{-3} *M* solution and is given in Figure 7. The α-dichloro solution above was allowed to stand for 10 hr. at 20°. At this stage the maximum amount (97%) of chloroaquo ion was present and the rotations remained constant for 40 hr. The RD curve of this solution was measured since the chloroaquo salt could not be isolated, and the result is given in Figure 8.

$(+)$-α-[Co(trien)ClOH$_2$]$^{+}$ → $(+)$-α-[Co(trien)CO$_3$]$^{+}$.—This transformation was carried out as described for the β isomer. $(+)$-α-[Co(trien)Cl$_2$]ClO$_4$ aquated for 16 and 43 hr. gave the same rotation for the carbonato salt after treatment with NaHCO$_3$, $[M]_D$ +4700°, and no further change in rotation occurred in 24 hr. at 20°. The RD curve is given in Figure 9.

$(+)$-α-[Co(trien)Cl$_2$]ClO$_4$, $[\alpha]_D$ +2330° (0.1 g.), was dissolved in $HClO_4$ (0.01 *M*) and after 15 hr. at 20° $NaHCO_3$ (0.06 g.) and $NaClO_4$ (0.05 g.) were added. The red solution, evaporated at 20°, gave a total yield of carbonatoperchlorate of 0.093 g. (92%) which was washed with methanol and acetone and dried in air. A 0.0792% aqueous solution gave α_D +0.96°, α_{578} +1.18°, α_{546} +1.25°, when $[M]_D$ +4630°, $[M]_{578}$ +5700°, $[M]_{546}$ +6030°. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)CO$_3$]ClO$_4 \cdot$H$_2$O: C, 22.0; H, 5.3; N, 14.6. Found: C, 21.8; H, 5.3; N, 14.7. Fractional recrystallization of the carbonato complex from water gave maximum rotations of $[M]_D$ +4730°, $[M]_{578}$ +5920°, and $[M]_{546}$ +6170°.

The carbonato complex was also isolated as the tetraphenylborate $(+)$-α-[Co(trien)CO$_3$][B(C$_6$H$_5$)$_4$]$\cdot$2H$_2$O, $[M]_D$ +4730°. It was insoluble in water but dissolved in aqueous acetone. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)CO$_3$][B(C$_6$H$_5$)$_4$]$\cdot$2H$_2$O: C, 60.1; H, 6.8; N, 9.0. Found: C, 60.8; H, 6.7; N, 8.9.

$(+)$-α-[Co(trien)CO$_3$]$^{+}$ → $(+)_{546}$-α-[Co(trien)(OH$_2$)$_2$]$^{+3}$.—$(+)$-α-[Co(trien)CO$_3$]ClO$_4 \cdot$H$_2$O, $[M]_D$ +4630° (2.0×10^{-3} *M* aqueous solution from the transformation above), was converted to the α-diaquo complex with $HClO_4$ as described for the β isomer. The carmine solution gave the rotations $[M]_D$ −950° (α_D −0.19°), $[M]_{578}$ −300°, $[M]_{546}$ +4700°, and the RD curve is given in Figure 10.

The isolated $(+)$-α-[Co(trien)CO$_3$]ClO$_4 \cdot$H$_2$O, $[\alpha]_D$ +1200° (10 ml. of 2.14×10^{-3} *M* solution) was also converted to the diaquo ion with 1 drop of concentrated $HClO_4$ and the following rotations were measured after 20 min., $[M]_D$ −930° (α_D −0.20°), $[M]_{578}$ −190°, $[M]_{546}$ +4750°. The diaquo complex was also isolated from more concentrated solutions containing excess perchloric acid.

$(+)_{546}$-α-[Co(trien)(OH$_2$)$_2$]$^{+3}$ → $(+)_{546}$-α-[Co(trien)(NO$_2$)$_2$]$^{+}$.—$(+)$-α-[Co(trien)Cl$_2$]ClO$_4$, $[\alpha]_D$ +2250° (1.00 g. in $HClO_4$, 50 ml. of 1.2×10^{-3} *M*), was aquated for 12 hr. at 20° and excess $NaHCO_3$ (0.46 g.) was added followed by excess $HClO_4$ (7.8 ml. of 1.0 *M*) after a further 30 min. The resulting diaquo solution was then treated (50 min.) with excess $NaNO_2$ (1.8 g.). The $(+)_{546}$-α-[Co(trien)(NO$_2$)$_2$]ClO$_4$ slowly crystallized and three fractions were obtained which were washed with $NaClO_4$ solution, alcohol, and ether and dried. Each fraction had the same rotation, $[M]_{546}$ +220° (α_{546} +0.11° for 0.2% aqueous solution), $[M]_D$ −20° (±20°), $[M]_{578}$ +20° (±20°); yield 0.95 g., 90%. The RD curve is given in Figure 11. *Anal.* Calcd. for [Co(C$_6$H$_{18}$N$_4$)(NO$_2$)$_2$]ClO$_4$: C, 18.2; H, 4.6; N, 21.2. Found: C, 18.1; H, 4.6; N, 20.5.

This transformation was repeated using $(+)$-α-[Co(trien)Cl$_2$]-ClO$_4$, $[\alpha]_D$ +2300° (0.100 g.). The dinitro product was not isolated but the final volume was adjusted to 50 ml. and the rotation, measured after 2 days, was α_{546} +0.11°, $[M]_{456}$ +210°. The RD curve was also similar to that of the isolated sample. The formation of the yellow α-dinitro complex was considerably slower than for the β isomer.

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Reactions of Hexafluorocyclobutanone with Metalloid Compounds

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Hexafluorocyclobutanone, a highly polarized ketone, reacts with boron halides to give esters of 1-halohexafluorocyclobutanol. Similarly, silanes add to the ketone to give hexafluorocyclobutoxy derivatives. Phosphines add in the opposite direction to give 1-hydroxyhexafluorocyclobutylphosphines.

Hexafluorocyclobutanone (1) is one of the most reactive ketones ever reported.[1] The exceptional reactivity may be attributed to a combination of ring strain and the electron-withdrawing influence of the fluorine atoms. Both forces tend to reinforce the normal

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