1136. *Optically Active Co-ordination Compounds. Part I. The Optical Configurations of Bisethylenediamine Complexes of Cobalt*(III)

By K. GARBETT and R. D. GILLARD

Reactions which proceed without metal–ligand bond breakage occur without change of optical configuration in resolved complexes. Such reactions have been applied to correlate a substantial number of optical configurations of complexes of the type [Co $en_2XY]^{n+}$.

A number of isothiocyanato-complexes [Co $en_2(NCS)X]^{n+}$ have been correlated chemically with the analogous ammine complexes [Co $en_2(NH_3)X]^{(n+1)+}$. Resolutions of the cations *cis*-isothiocyanatonitrobisethylenediaminecobalt(III), *cis*-isothiocyanatoamminebisethylenediaminecobalt(III), and *cis*-di-isothiocyanatobisethylenediaminecobalt(III) by means of their (+)-bromocamphorsulphonate salts are described. The absolute configuration D(+)-di-isothiocyanatobisethylenediaminecobalt(III) is established spectroscopically through its adduct with mercuric ion.

A number of optically active aquo-complexes have been converted into the corresponding hydroxo-complexes, and into the corresponding nitrito-complexes, which form without rupture of the cobalt–oxygen bond. These nitrito-complexes then isomerise by an intramolecular mechanism to the nitro-compound.

A proof is given that the aquation of halogeno-complexes occurs through a common optical mechanism; a similar proof of the common optical mechanism of ammonation of halogeno-complexes is also given.

Results are discussed in relation to other methods which have been used to deduce relative configurations. A summary of results on the interconversions and the relative and absolute optical configurations of complexes of the type [Co $en_2XY]^{n+}$ is presented. An empirical rule is given for deducing absolute configurations of complexes [Co $en_2XY]^{n+}$ from rotatory dispersion curves, where X and Y are not halide ions.

THE relationship between optical configuration and signs of rotational strengths of electronic transitions has received much attention particularly for the dihedral co-ordination compounds. One major difficulty, however, has been the lack of knowledge of optical configurations, relative and absolute, in complex compounds, particularly the absence of unequivocal correlations of optical configurations of reactant and product. Such chemical relationships of optical configurations are possible in organic nucleophilic substitutions of known mechanism, but this has not yet been true of octahedral complexes.

Many compounds containing the *cis*-bisethylenediaminecobalt(III) moiety, of the type [Co $en_2XY]^{n+}$, are readily resolvable, and there have been several attempts [1-3] to correlate their optical configurations. Such attempts have rested on comparisons either of signs of Cotton effects or of the less soluble diastereoisomers formed with a given resolving agent, usually (+)-bromocamphorsulphonate ion for the particular cations treated here. The lack of agreement of these two methods, and the internal inconsistency of both methods, will be illustrated in this work.

There are a few complexes of the type [Co $en_2XY]^{n+}$ whose absolute configurations are known [4] from considerations of stereospecific induction in analogous complexes of optically active diamines. Those which have the absolute configuration (D) derived from that of the D(+)-[Co $en_3]^{3+}$ (I) ion by opening one chelate ring are:[5] D(+)-[Co $en_2Cl_2]^+$ (II),

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[1] J. P. Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.
[2] T. E. Macdermott and A. M. Sargeson, *Austral. J. Chem.*, 1963, **16**, 334.
[3] J. G. Brushmiller, E. L. Amma, and B. E. Douglas, *J. Amer. Chem. Soc.*, 1962, **84**, 3227.
[4] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1368.
[5] R. D. Gillard, *Nature*, 1964, **201**, 989.

D(+)-$[\mathrm{Co\,en_2(H_2O)_2}]^{3+}$ (III), D(+)-$[\mathrm{Co\,en_2CO_3}]^{+}$ (IV), D(+)-$[\mathrm{Co\,en_2(C_2O_4)}]^{+}$ (V), and D(+)-$[\mathrm{Co\,en_2(NO_2)_2}]^{+}$ (VI). These serve as reference points in the present correlation.

Aquations of *cis*-halogeno-complexes of cobalt(III) occur with retention of *geometric* configuration (*i.e.*, the aquo-product is also *cis*), but there is no rigorous basis for the suggestion that *optical* configuration is also retained in reactions where metal–ligand bonds are broken, such as

$$\mathrm{D(+)\text{-}[Co\,en_2Cl_2]^{+}} \dashrightarrow \mathrm{(+)\text{-}[Co\,en_2(H_2O)Cl]^{2+}} \dashrightarrow \mathrm{D(+)\text{-}[Co\,en_2(H_2O)_2]^{3+}}$$

Inversion in each step is as consistent with observation as is retention. We represent reactions of unproved optical mechanism by the broken arrow shown. For reactions where optical configuration is quite certainly retained, we employ a full arrow, and for those where configuration is inverted, we use the symbol for a Walden inversion, though we suggest the name Bailar inversion because, mechanistically, the two types of inversion are unrelated.

A possible means of relating optical configurations depends on the small class of reactions in which no metal–ligand bond is broken. These reactions occur within the ligand, and the optical configuration of the complex is unaffected by the resultant change in the nature of the ligand. Such reactions are not common, and have, till now, been studied only for racemic complexes. They include:

(*a*) Isothiocyanato–ammine conversions, *e.g.*,

$$cis\text{-}\mathrm{[Co\,en_2(NCS)X]}^{n+} \longrightarrow cis\text{-}\mathrm{[Co\,en_2(NH_3)X]}^{(n+1)+}$$

(*b*) Aquo–hydroxo conversions and *vice versa*, *e.g.*,

$$cis\text{-}\mathrm{[Co\,en_2(H_2O)X]}^{(n+1)+} \longleftrightarrow cis\text{-}\mathrm{[Co\,en_2(OH)X]}^{n+}$$

(*c*) Formation of nitrito- (O-bonded) complexes from aquo-complexes, *e.g.*,

$$cis\text{-}\mathrm{[Co\,en_2(H_2O)X]}^{(n+1)+} \longrightarrow cis\text{-}\mathrm{[Co\,en_2(ONO)X]}^{n+}$$

We have used reactions of all these types, and discuss them in turn.

(*a*) *Isothiocyanato–ammine Conversions*.—Reactions of this class were discovered by Werner and Braunlich,[6] who used such oxidants as hydrogen peroxide and chlorine. We have now demonstrated that such conversions can be quantitatively achieved by the use of a carefully chosen oxidant. This establishes the isothiocyanate nature of the ligand in the complexes used, since exchange of the thiocyanate ion in such complexes is known [7] to be extremely slow, and so oxidation must occur *in situ*.

It was noticed by Schug and Gilmore [8] in the course of work on the conversion of isothiocyanatopentamminecobalt(III) cation into the hexamminecobalt(III) cation that of all the oxidants tried (including Werner's orginal hydrogen peroxide or chlorine) only iodate ion, in acid solution, formed no cobalt(II) species as by-products Since racemisation of cobalt(III) complexes is said to occur rapidly through electron transfer labilisation by cobalt(II), it is essential in oxidising optically active isothiocyanato-complexes to the corresponding optically active ammine that no cobalt(II) be formed. When *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) perchlorate $[\mathrm{Co\,en_2(NCS)Cl}](\mathrm{ClO_4})$ is treated with an acid solution of potassium iodate, oxidation occurs rapidly at room temperature, iodine being formed. This may be removed either by solvent extraction or by titration with sodium thiosulphate. The cobalt is then found spectroscopically to be entirely in the form of *cis*-chloroamminebisethylenediaminecobalt(III) cation, $[\mathrm{Co\,en_2(NH_3)Cl}]^{2+}$. Other racemic isothiocyanato-complexes can be converted into the corresponding ammine in this way.

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[6] A. Werner and F. Braunlich, *Z. anorg. Chem.*, 1900, **22**, 147.

[7] A. W. Adamson and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1954, **76**, 3379.

[8] K. Schug and M. D. Gilmore, Proc. 7th Int. Conf. Coord. Chem., Stockholm, 1962, 274.

When the chloroisothiocyanato-complex dextrorotatory at the mercury green line was treated in the same way, the product was the dextrorotatory chloro-ammine

$$\underset{\text{(VIII)}}{(+)_{5461}\text{-}[\mathrm{Co\,en_2(NCS)Cl}]^+} \longrightarrow \underset{\text{(IX)}}{(+)\text{-}[\mathrm{Co\,en_2(NH_3)Cl}]^{2+}}$$

These species therefore have the same optical configurations. That the reaction can be performed with retention of optical activity suggests that no cobalt(II) is formed, so that the mechanism of the iodate oxidation obviously differs from that of oxidation by other agents, where cobalt(II) is a significant product.

It has been said [2] that the optical rotatory dispersion curve in the visible region arises largely from the contribution of the principal absorption band, and provides a means of comparing the configurations of all complexes of cobalt(III). While the Cotton effect gives a reliable correlation for very closely similar complexes, such as trisethylenediamine-cobalt(III) and tris-(+)-propylenediaminecobalt(III) cations,[9] or for $[\mathrm{Co\,en_2CO_3}]^+$ and $[\mathrm{Co\,en_2(C_2O_4)}]^+$,[5] where relative spectroscopic energy levels are similar, it is a dangerous procedure for complexes as dissimilar as (VIII) and (IX).

The rotatory dispersion curve of (VIII) in the region of the longest wavelength absorption band ($'T_{1g} \longleftarrow {}'A_{1g}$ in the notation appropriate to complexes with O_h symmetry) is made up of two overlapping Cotton effects of opposite sign (with the negative inverse curve centred at longer wavelengths). The point is more directly established for the circular dichroism spectrum,[1] where, for the region of Band I ($'A + {}'A + {}'A \longleftarrow {}'A$ in the C_1 symmetry appropriate to the complex), $\varepsilon_e - \varepsilon_d = 0{\cdot}432$ at 578 mμ, and $+0{\cdot}415$ at 505 mμ. For (IX), which we have shown to have the same optical configuration as (VIII), the rotatory dispersion curve shows a positive Cotton effect, and the circular dichroism spectrum shows $\varepsilon_e - \varepsilon_d = +0{\cdot}318$ at 554 mμ, and $+0{\cdot}017$ at 478 mμ. There is no obvious correlation between the Cotton effects in (VIII) and (IX); this is a very direct proof that comparisons of configurations for complexes of the type $[\mathrm{Co\,en_2XY}]^{n+}$ by means of the Cotton effects in the visible region may be unreliable,[2] in the absence of other evidence.

The method of less soluble diastereoisomers has often been used, *faute de mieux*, to relate optical configurations for complexes (+)- or (—)-$[\mathrm{Co\,en_2XY}]^{n+}$. Werner [10] suggested that the less soluble diastereoisomer of similar complexes with the same resolving agent contained complex enantiomers which were configurationally related, as in the cases of (+)-$[\mathrm{Co\,en_3}]\mathrm{Cl}$ (+)-tartrate,$5\mathrm{H_2O}$ and (—)-$[\mathrm{Rh\,en_3}]\mathrm{Cl}$ (+)-tartrate,$4\mathrm{H_2O}$, where (+)-$[\mathrm{Co\,en_3}]^{3+}$ and (—)-$[\mathrm{Rh\,en_3}]^{3+}$ were said to have the same optical configuration. The method has been criticised, and is certainly unreliable, as will be shown later. However, it so happens that the rule holds for (VIII) and (IX), where the less soluble diastereoisomers with (+)-bromocamphorsulphonate ion, (+)-BCS, are $(+)_{5461}$-(VIII) (+)-BCS and (+)-(IX) (+)-BCS.

The one known case [1] of a complex $[\mathrm{Co\,en_2XY}]^{n+}$ where the method using rotatory dispersion and the method of less soluble diastereoisomers led to opposite conclusions was that of the less soluble diastereoisomer (—)-$[\mathrm{Co\,en_2(NH_3)(NO_2}]$ (+)-BCS, which contained the complex enantiomer giving a negative Cotton effect. We have obtained this enantiomer from the analogous (—)-isothiocyanato-complex by oxidation with acid iodate.

$$\text{(X)}\ (-)\text{-}[\mathrm{Co\,en_2(NCS)(NO_2)}]^+ \longrightarrow (-)\text{-}[\mathrm{Co\,en_2(NH_3)(NO_2)}]^{2+}\ \text{(XI)}$$

Rather surprisingly, the isothiocyanatonitro-compound had not previously been resolved directly. We resolved it by means of the (+)-bromocamphorsulphonate, when the less soluble diastereoisomer was (—)-$[\mathrm{Co\,en_2(NCS)\ (NO_2)}]$ (+)-BCS, which gave a negative Cotton effect in the region of the longest-wavelength absorption band. This is another example of contradiction between the two empirical rules, although both rules are self-consistent between (X) and (XI). This is shown in Table 1, with some other compounds for comparison. The two methods do not correlate as well as had previously been thought.

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[9] J. H. Dunlop, R. D. Gillard, and G. Wilkinson, *J.*, 1964, 3160.

[10] A. Werner, *Bull. Soc. chim. France*, 1912, **11**, 1.

TABLE 1

Less soluble diastereoisomers and the Cotton effect

Complex	Less soluble (+)-BCS [a]	Positive Cotton effect [b]
$[Co\,en_2(NO_2)_2]^+$ (VI)	(+)	(+)
$[Co\,en_2(NCS)(NO_2)]^+$ (XI)	(−)	(+)
$[Co\,en_2(NCS)_2]^+$ (XV)	(−)	(+)
$[Co\,en_2(NH_3)(NO_2)]^{2+}$ (XI)	(−)	(+)
$[Co\,en_2(NH_3)(NCS)]^{2+}$ (XVI)	(+)	(+)

[a] This is that enantiomer of the complex which forms the less soluble diastereoisomer. [b] This is that enantiomer which gives a positive Cotton effect.

Previous methods [11] of obtaining optically active samples of the isothiocyanatonitro-complex involved the reactions:

$$\begin{tikzcd} \text{(XII)}\ (+)\text{-}[Co\,en_2(NO_2)Cl]^+ \arrow[dr, dashed] & & (-)\text{-}[Co\,en_2(NCS)Cl]^+\ \text{(VIII)} \arrow[dl, dashed] \\ & (+)\text{-}[Co\,en_2(NCS)(NO_2)]^+\ \text{(X)} & \end{tikzcd}$$

We have allowed the chloroisothiocyanato-complex to aquate, confirming earlier results:[12]

$$\underset{\text{(VIII)}}{(+)_{5461}\text{-}[Co\,en_2(NCS)Cl]^+} \dashrightarrow \underset{\text{(XIII)}}{(+)\text{-}[Co\,en_2(NCS)(H_2O)]^{2+}}$$

The aquoisothiocyanato-complex was then oxidised to the aquo-ammine complex with retention of optical configuration.

$$\text{(XIII)}\ (+)\text{-}[Co\,en_2(NCS)(H_2O)]^{2+} \longrightarrow (+)\text{-}[Co\,en_2(NH_3)(H_2O)]^{3+}\ \text{(XIV)}$$

While neither (XIII) nor (XIV) has been resolved directly, both show positive Cotton effects in the region of the longest-wavelength absorption band.

We have also studied the series (XV), (XVI), and (XVII):

$$\underset{\text{(XV)}}{(+)\text{-}[Co\,en_2(NCS)_2]^+} \longrightarrow \underset{\text{(XVI)}}{(+)\text{-}[Co\,en_2(NCS)(NH_3)]^{2+}} \longrightarrow \underset{\text{(XVII)}}{(+)\text{-}[Co\,en_2(NH_3)_2]^{3+}}$$

Both (XV) and (XVI) have been resolved for the first time, by means of (+)-BCS; the less soluble diastereoisomers contain the (−)-$[Co\,en_2(NCS)_2]^+$ and the (+)-$[Co\,en_2(NH_3)(NCS)]^{2+}$ ions. On oxidation, (−)-(XV) gives (−)-(XVII) and (+)-(XVI) gives (+)-(XVII).

The D configuration of (+)-(XV) has been established by the following spectroscopic method. The transitions under Band I of a trigonal cobalt(III) complex are $'E_a + {}'A_2 \longleftarrow {}'A_1$. It is known that D(+)-$[Co\,en_3]$ gives a positive rotational strength for the E_a transition (perpendicular to the three-fold axis). When the symmetry is lowered to C_2, the transition with trigonal E_a parentage will also have a positive Cotton effect. In other words, the transition parallel to the two-fold axis will show positive rotational strength for those complexes called D here. It has not previously been possible to assign this transition with certainty. In the case of *cis*-$[Co\,en_2(NCS)_2]^+$, however, we now find that the relevant transition can readily be distinguished through the adduct [13] formed with mercuric ion, where the mercuric ion lies on the two-fold axis of the complex. The transition which will be severely modified by this addition of mercury is that parallel to the two-fold axis which concerns us. When the mercuric adduct (+)-$[Co\,en_2(NCS)_2Hg]^{3+}$ is formed, the positive component of the Cotton effect of (+)-$[Co\,en_2(NCS)_2]^+$ exhibits a blue shift. The transition along the two-fold axis thus shows a positive Cotton effect, proving that (+)-$[Co\,en_2(NCS)_2]^+$ has the D configuration.

Clearly, since (+)-(XVI) and (+)-(XVII) are derived from D(+)-(XV) without bond

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[11] C. E. Wood and S. D. Nicholas, *J.*, 1928, 1727.

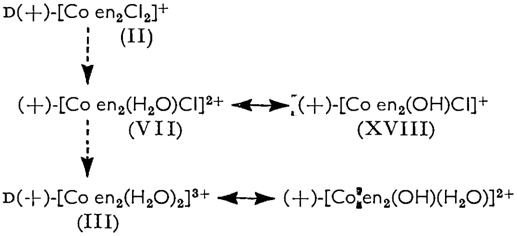
[12] J. P. Mathieu, *Bull. Soc. Chim. France*, 1937, **4**, 687.

[13] W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Amer. Chem. Soc.*, 1959, **81**, 2958.

breakage, they too have the D configuration. The configuration D(+)-[Co $en_2(NH_3)_2]^{3+}$ is established. This assignment had tentatively been made [2,4] on the basis of the similar rotatory dispersion curves of this cation and D(+)-[Co $en_3]^{3+}$, where the ligand fields about cobalt are extremely similar. Whereas the rule using the sign of the Cotton effect in rotatory dispersion holds in this case [(+)-(XV), (+)-(XVI), and (+)-(XVII) all show positive Cotton effects], the method of less soluble diastereoisomers breaks down, since it suggests that (—)-(XV) and (+)-(XVI) have related configurations, which is wrong.

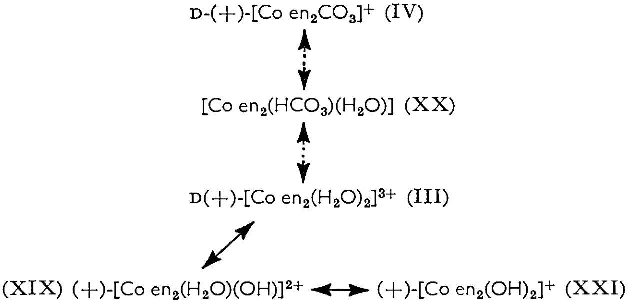
(*b*) *Aquo–Hydroxo Conversions.*—Some reactions of the ion D(+)-[Co $en_2Cl_2]^+$ are shown in Scheme 1.

In aquo–hydroxo conversions (VII) ⟷ (XVIII) and (III) ⟷ (XIX) optical configuration is retained so (XIX) has the same optical configuration as (III) (*i.e.*, D). While (VII) and (XVIII) have related optical configurations, their absolute configurations are not known. The less soluble diastereoisomers are for (II) [14] (+)-[Co en_2Cl_2] (+)-BCS, and for (VII) either (—)-[Co $en_2(H_2O)Cl$] (+)-BCS,[15] or (+)-[Co $en_2(H_2O)Cl$] (+)-BCS_2,[1] though Mathieu [1] had difficulty with the resolution. We established that the earlier directions [15] give a good yield of quite well resolved (+)-[Co $en_2(H_2O)Cl]^{2+}$ salt. The enantiomers having rotatory dispersion curves dominated by positive contributions are (+)-(II) and (+)-(VII), so that for the method of less soluble diastereoisomers to agree with the method using the Cotton effect, the less soluble diastereoisomer should contain (+)-[Co $en_2(H_2O)Cl]^{2+}$. Our result, which confirms this, removes one contradiction between the two classical methods of configurational assignment, though others remain.



Scheme 1

The complex (III) can be prepared by the aquation of (II) as shown above, or by treating D(+)-carbonatobisethylenediaminecobalt(III) chloride (IV) with dilute acid. The sequence of reactions shown in Scheme 2 has been established.



Scheme 2

The conversion of (III) into (IV) and *vice versa* is known, and was said [2,5] to prove the configurational relationship. However, it is not a one-step reaction, and the conversion of

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[14] J. C. Bailar, *Inorg. Synth.*, 1942, **2**, 222.

[15] A. Werner, J. E. Schwyzer, and W. Karrer, *Helv. Chim. Acta*, 1921, **4**, 113.

(IV) into (III) involves [16] the rupture of one of the two cobalt–oxygen bonds of the carbonato-species. We have represented this by means of the uncharacterised intermediate (XX). That (III) and (IV) have the D configuration is of course known from the method [4] using optically active ligands.

From the reactions shown in Scheme 2, (+)-(III), (+)-(XIX), and (+)-(XXI) all have the D configuration, since they are interconvertible without cobalt–oxygen bond breakage. The conversions in the corresponding racemic system containing (±)-(III), -(XIX), and -(XXI) were studied by Bjerrum and Rasmussen,[17] who found that *cis*-(XIX) very rapidly formed the equilibrium mixture of *cis*- and *trans*-(XIX). This rapid conversion is very obvious in the present work on the optically active complexes. Both (+)-(III) and (+)-(XXI) [formed from (+)-(III) in the presence of excess of hydroxyl ions] are optically rather stable, as shown by the constancy of their rotatory dispersion curves over a period of a few hours. Further, on re-acidification of (+)-(XXI), (+)-(III) with its original rotatory dispersion curve is re-formed. However, when (+)-(III) was treated with sufficient hydroxide ion to convert it into (+)-(XIX) (pH 6—8), and the resulting solution was made acid after a few minutes, thereby producing (II) once more, the original optical activity had decreased considerably. (+)-(XIX) readily loses activity, probably through isomerisation to the *trans*-isomer.

A point of some interest in this sytem is that the amplitude of the rotatory dispersion curve for (+)-(XIX) is much larger (*ca.* three times) than that for either (+)-(III) or (+)-(XXI). This may be attributed to the lower symmetry of (XIX), which belongs to point group C_1, (III) and (XXI) having C_2 symmetry. The important conclusion is that rather small changes in substitution at the cobalt atom can engender surprisingly large effects on the optical rotatory power.

Other hydroxo–aquo coversions which have been studied are those of the complexes $[\mathrm{Co\ en_2X(H_2O)}]^{n+}$, where X = NO_2, NCS, and NH_3. The conversions shown in Scheme 3 have been demonstrated.

$$\begin{array}{ccccc}
(+)\text{-}[\mathrm{Co\ en_2(NO_2)Cl}] & \dashrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NO_2)(H_2O)}] & \longleftrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NO_2)(OH)}] \\
\text{(XII)} & & \text{(XXII)} & & \text{(XXIII)} \\
(+)_{5461}\text{-}[\mathrm{Co\ en_2(NCS)Cl}] & \dashrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NCS)(H_2O)}] & \longleftrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NCS)(OH)}] \\
\text{(VIII)} & & \text{(XIII)} & & \text{(XXIV)} \\
(+)\text{-}[\mathrm{Co\ en_2(NH_3)Cl}] & \dashrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NH_3)(H_2O)}] & \longleftrightarrow & (+)\text{-}[\mathrm{Co\ en_2(NH_3)(OH)}] \\
\text{(IX)} & & \text{(XIV)} & & \text{(XXV)}
\end{array}$$

Scheme 3

In each case, the rotatory dispersion curves of the hydroxo-products, (+)-(XXIII) to (+)-(XXV), are of the same positive type as those of the parent aquo-complexes, (+)-(XXII), (+)-(XIII), and (+)-(XIV).

(*c*) *Aquo–nitrito–nitro Conversions.*—The third type of reaction which we have used to establish configurational relationships is the conversion of complexes of the type $[\mathrm{Co\ en_2X(H_2O)}]^{n+}$ with nitrite ion at pH 4 in the cold into $[\mathrm{Co\ en_2X(ONO)}]^{(n-1)+}$. It has been shown [18] in such reactions that the cobalt–oxygen bond is retained, so that optical configuration is also retained. It is further known that the nitrito-complex isomerises *via* an intramolecular mechanism to the corresponding N-bonded nitro-complex, and it has been suggested [18] that this step proceeds with retention of optical configuration.

We have studied a number of such systems. The most informative is the conversion of the bisaquo-complex, D(+)-$[\mathrm{Co\ en_2(H_2O)_2}]^{3+}$ (III) into D(+)-$[\mathrm{Co\ en_2(NO_2)_2}]^{+}$ (VI). The details are given in Scheme 4.

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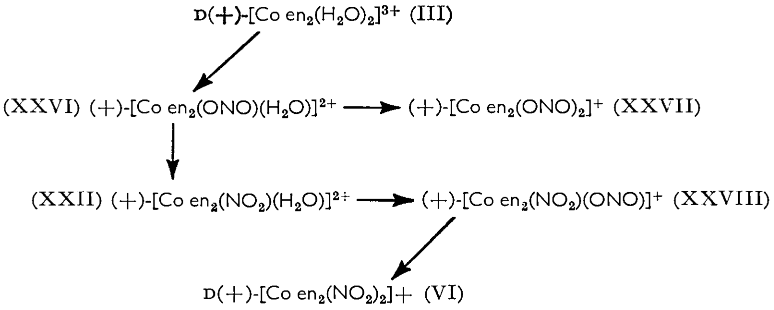
[16] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 1953, **75**, 4099.

[17] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.

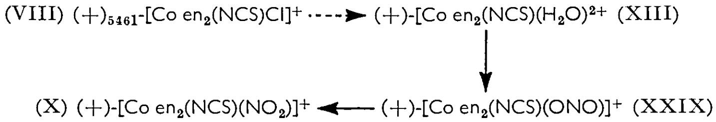
[18] R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, 1956, **78**, 4886.



Scheme 4

All these conversions were effected without loss of optical activity. (III) and (VI) were known to have the D configuration, so that all the intermediate compounds, (+)-(XXVI), (+)-(XXVII), (+)-(XXII), and (+)-(XXVIII) may be assigned also to the D configuration. (+)-(XXII) has previously been shown to give (+)-(XXIII), so that this also has the D configuration. All the complexes in Scheme 4 have positive Cotton effects for their longest-wavelength absorption bands in rotatory dispersion. (+)-(VI) and (+)-(XXVIII) were previously known [19] to form the less soluble diastereoisomers with (+)-bromocamphorsulphonate. The reactions shown in Scheme 4 have also been carried out at room temperature (*ca.* 20°) and the optical rotations of the final products were essentially identical with those of the products of the reactions in the cold, though, of course, the intermediate nitrito-complexes isomerised much more rapidly at the higher temperature.

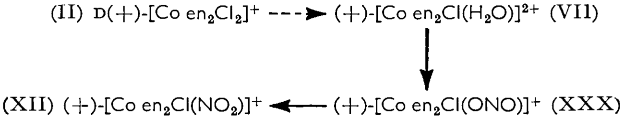
The isothiocyanatonitrobisethylenediaminecobalt(III) cation has also been obtained in a similar fashion shown in Scheme 5.



Scheme 5

This relates the optical configurations of (XIII), (XXIX), and (X). (XII) had previously been related to its hydroxy-derivative (XXIV). All show positive Cotton effects for the longest-wavelength absorption band in rotatory dispersion.

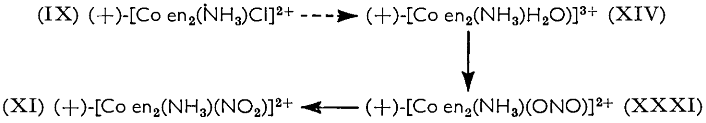
We have also studied the aquo–nitrito–nitro conversions shown in Scheme 6



Scheme 6

This series relates the configurations of (VII), (XXX), and (XII). It is again found that the rotatory dispersion curves of these three enantiomers show positive Cotton effects in the region of the longest-wavelength *d–d* absorption band.

Finally, we have established the similar cycle of reactions for the chloro-ammine complex shown in Scheme 7.



Scheme 7

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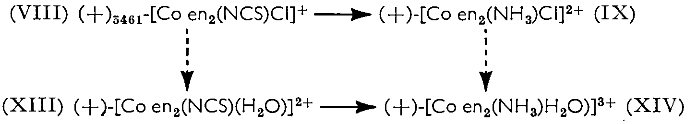
[19] R. K. Murmann, *J. Amer. Chem. Soc.*, 1955, **77**, 5190.

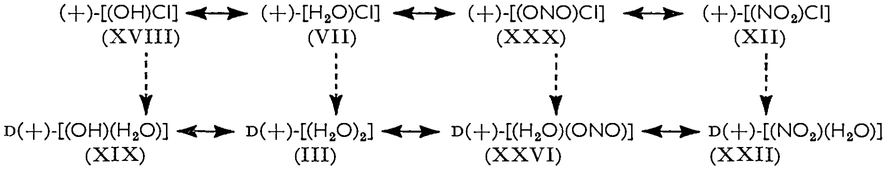
This relates the configurations of (+)-(XIV), (+)-(XXXI), and (+)-(XI), and, by the earlier relationship of (+)-(XXV) to (+)-(XIV), (+)-(XXV) also. The lack of agreement in recorded values of absorption maxima for (±)-(IX) was pointed out [20] by Archer and Bailar, values from 512 to 527 mμ being available. We find, as they did, that, after resolution, the longest-wavelength band occurs at 528 mμ. This agrees well with other values [1,20] for the complex after resolution, when it is free from the aquo-contaminant, $[Co\,en_2(NH_3)(H_2O)]^{3+}$ cation, whose (+)-bromocamphorsulphonate, like those of other aquo-cations, is extremely soluble in water. The value for the absorption wavelength found here, 528 mμ, is close to that for the very similar chloropentamminecobalt(III) cation, at 529 mμ. It appears that several studies of the chloroamminebisethylenediaminecobalt(III) cation may have used partly aquated samples.

Although nothing is known about the optical mechanisms of aquation reactions from $[Co\,en_2XCl]^{n+}$ to $[Co\,en_2X(H_2O)]^{(n+1)+}$, it is readily proved from some results already mentioned that the optical mechanism is common to all halogeno-complexes, *i.e.*, that if a Bailar inversion occurs in one such aquation, it must also occur in all others. One proof is summarised in Scheme 8.



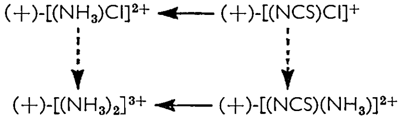
Scheme 8

(VIII) and (IX) have related configurations, and the products of their aquations (XIII) and (XIV) also have related configurations. Both aquations therefore occur with either retention or inversion of configuration. A similar proof is possible from a second range of complexes studied in this work; this is summarised in Scheme 9. Here only the ligands X and Y in the complexes $[Co\,en_2XY]^{n+}$ are given.



Scheme 9

This proof of common optical mechanism for aquation relies on the conversion of aquo- into nitro-complexes without bond breakage. Using the conversion of isothiocyanate to ammonia without bond breakage, we can demonstrate similarly the ammonation of chloro-complexes by liquid ammonia. This is shown in Scheme 10, from which it is clear that the replacement of chloride by ammonia occurs through a common optical mechanism.



Scheme 10

Conclusion.—Table 2 offers proof that, for the limited range of eight complexes covered, the sign of the Cotton effect in rotatory dispersion is directly related to relative configuration; all eight cations which have the same optical configurations give Cotton effects of the same sign. The rule of less soluble diastereoisomers is consistent for the only two compounds in Table 2 which have been resolved. However, in the more general classifications which

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[20] R. D. Archer and J. C. Bailar, *J. Amer. Chem. Soc.*, 1961, **83**, 812.

TABLE 2

Properties of complex enantiomers with related optical configurations

Complex	Less soluble (+)-BCS	Positive o.r.d.	Isomers with same configurations
[Co $en_2(NCS)(H_2O)]^{2+}$ (XIII) ...		(+)	(+)
[Co $en_2(NCS)(OH)]^+$ (XXIV) ...		(+)	(+)
[Co $en_2(NCS)(ONO)]^+$ (XXIX)		(+)	(+)
[Co $en_2(NCS)(NO_2)]^+$ (X)	(−)	(+)	(+)
[Co $en_2(NH_3)(H_2O)]^{2+}$ (XIV) ...		(+)	(+)
[Co $en_2(NH_3)(OH)]^+$ (XXV) ...		(+)	(+)
[Co $en_2(NH_3)(ONO)]^+$ (XXXI)		(+)	(+)
[Co $en_2(NH_3)(NO_2)]^+$ (XI)	(−)	(+)	(+)

have been based on extended series of complexes [Co $en_2XY]^{n+}$, the less soluble diastereoisomer has been said to contain that cation which gives a positive Cotton effect. This contradiction emphasises the danger of arguments based on less-soluble diastereoisomers.

From Table 3, it is clear that the complexes D-[Co $en_2XY]^{n+}$, where X and Y are not halides, give positive rotatory dispersion curves. The deductions from Tables 2 and 3 may be used to formulate an empirical rule for relating optical configurations: if a resolved complex ion, [Co $en_2XY]^{n+}$ where X and Y are not halides, gives a single observable longest-wavelength absorption band and a single positive Cotton effect in rotatory dispersion, then it has the D configuration, related to that of (+)-[Co $en_3]^{3+}$

TABLE 3

Properties of complexes D[Co $en_2XY]^{n+}$

Complex	Less soluble (+)-BCS [a]	Rotatory dispersion: Band I [b]
D(+)-[Co $en_3]^{3+}$ (I)		(+)
D(+)-[Co $en_2Cl_2]^+$ (II)	(+)	(−) (+)
D(+)-[Co $en_2(H_2O)_2]^{3+}$ (III)		(+)
D(+)-[Co $en_2CO_3]^+$ (IV)		(+)
D(+)-[Co $en_2(C_2O_4)]^+$ (V)		(+)
D(+)-[Co $en_2(NO_2)_2]^+$ (VI)	(+)	(+)
D(+)-[Co $en_2(H_2O)(OH)]^{2+}$ (XIX)		(+)
D(+)-[Co $en_2(OH)_2]^+$ (XXI)		(+)
D(+)-[Co $en_2(NO_2)(H_2O)]^{2+}$ (XXII)		(+)
D(+)-[Co $en_2(NO_2)(OH)]^+$ (XXIII)		(+)
D(+)-[Co $en_2(ONO)(H_2O)]^{2+}$ (XXVI)		(+)
D(+)-[Co $en_2(ONO)_2]^+$ (XXVII)		(+)
D(+)-[Co $en_2(NO_2)(ONO)]^+$ (XXVIII) ...	(+)	(+)
D(+)-[Co $en_2(NCS)_2]^+$ (XV)	(−)	(+)
D(+)-[Co $en_2(NCS)(NH_3)]^{2+}$ (XVI)	(+)	(+)
D(+)-[Co $en_2(NH_3)_2]^{3+}$ (XVII)		(+)

[a] The enantiomer of the complex ion forming the less soluble diastereoisomer. [b] The Cotton effects of the D complexes given in Column 1.

Halogeno-complexes are excluded from this rule because of two cases. First, all but one of the complexes studied which have the D configuration (Table 3) have a very obviously single positive Cotton effect. The exception, D-(II), has a rotatory dispersion curve made up of an overlapping negative component (at longer wavelength) and a positive component (at shorter wavelength), the resultant curve having the characteristic humped shape shown in Figure 1. All the other non-halide complexes with the D configuration have the single positive Cotton curve shown for D(+)-[Co $en_2(H_2O)_2]^{3+}$ (III) also in Figure 1. In the second exceptional case involving a halogeno-complex, $(+)_{5461}$-[Co $en_2(NCS)Cl]^+$ (VII) has a humped rotatory dispersion curve shown in Figure 2; however, (+)-[Co $en_2(NH_3)Cl]^{2+}$ (IX), with the configuration related to that of (VII), has a distinctly different curve, also in Figure 2.

Comparisons of configurations by using rotatory dispersion curves for complexes containing halogeno-ligands are not justified. The point is even more strongly brought out in the circular dichroism data in Table 4.

A spectroscopic explanation can be given for the deviations of chloro-complexes from

TABLE 4

Properties of complexes [Co $en_2XCl]^{n+}$

Less soluble (+)-BCS	O.r.d. (Band I)	Circular dichroism				
		λ	$\varepsilon_e - \varepsilon_d$	λ	$\varepsilon_e - \varepsilon_d$	
(+)-[Co $en_2(NH_3)Cl]^{2+}$ (IX)	(+)	554	0·318	478	0·017	*a*
$(+)_{5461}$-[Co $en_2(NCS)Cl]^{+}$ (VIII)	(−) (+)	578	−0·432	505	0·415	*a*
(+)-[Co $en_2(NO_2)Cl]^{+}$ (XII)	(+)	545	0·346	445	0·204	*b*
(+)-[Co $en_2(ONO)Cl]^{+}$ (XXX)	(+)	—	—	—	—	*b*
(+)-[Co $en_2(H_2O)Cl]^{2+}$ (VII)	(+)	566	0·743	—	—	*b*
(+)-[Co $en_2(OH)Cl]^{+}$ (XVIII)	(+)	—	—	—	—	*b*

[a] These are known to have related configurations. [b] These four cations also have related configurations.

the regular behaviour of other complexes. In a complex of C_2 or C_1 symmetry, the $'T_{1g} \longrightarrow 'A_{1g}$ transition of cobalt(III) in a ligand field of regular octahedral symmetry splits into $'A + 'B + 'B \longleftarrow 'A_1$. The size of the splitting is a function of the departure from octahedral symmetry of the ligand field, and consequently of the differences in ligand field strength between X and Y and the ethylenediamine in complexes [Co $en_2XY]^{n+}$. This difference in ligand field strength is normally not large enough for the component transitions to be resolved in solution absorption spectra. However, in compounds containing halide ions, which are much weaker ligands than ethylenediamine, the separated components can often be observed. This is the case for complexes (II) and (VIII) [and, incidentally, for the other halogeno-complexes (VII) and (IX)]. The transition $'A \longleftarrow 'A_1$ in complexes [Co $en_2XY]^{n+}$ with the D configuration should have a positive rotational strength. It is evidently this transition which is largely responsible for the rotatory dispersion curves of most complexes D-[Co $en_2XY]^{n+}$. It is only in the two halogeno-complexes (II) and (VIII) that the *A* and *B* levels are sufficiently different in energy to

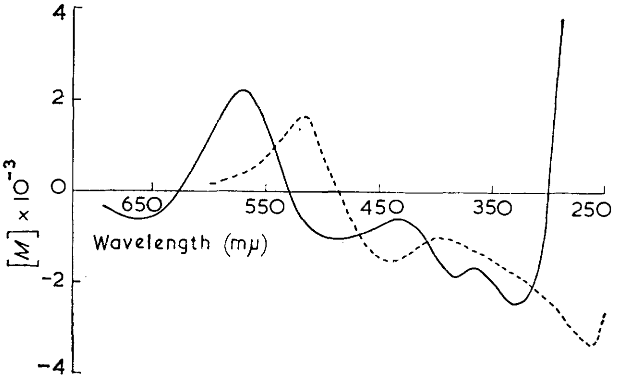


FIGURE 1. Rotatory dispersion curve of —— D(+)-[Co $en_2Cl_2]^{+}$; - - - - D(+)-[Co $en_2(H_2O)_2]^{3+}$

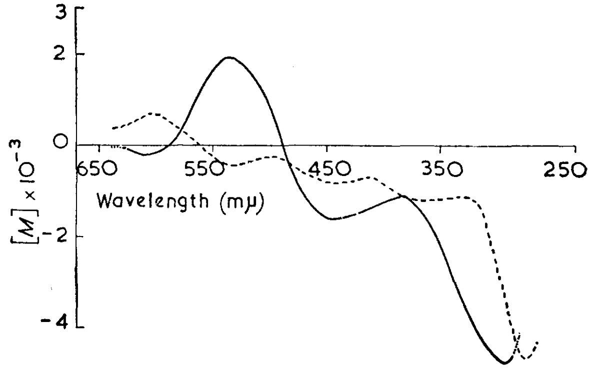
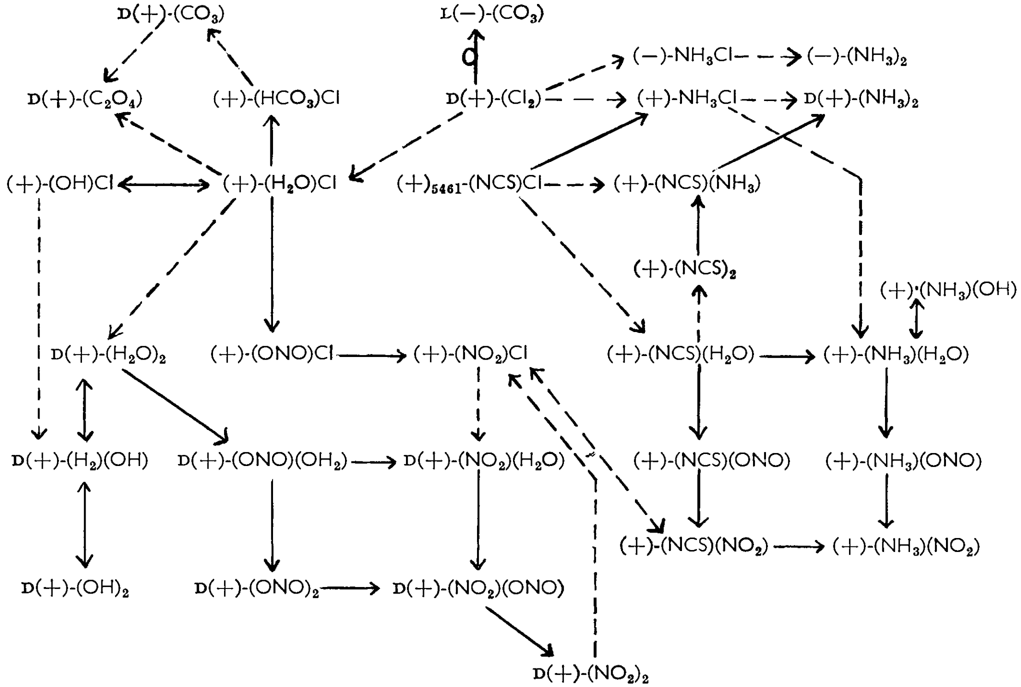


FIGURE 2. Rotatory dispersion curve of —— $(+)_{5461}$-[Co $en_2(NCS)Cl]^{+}$; - - - - (+)-[Co $en_2(NH_3)Cl]^{2+}$

give separable contributions of opposite sign to the resultant Cotton effect. For halogeno-complexes therefore, in the absence of independent spectroscopic data on the ordering of *A* and *B* levels, configurational comparisons are not possible on the basis of rotatory dispersion curves.

Tables 1, 2, and 3 also make it quite clear that the method of less soluble diastereoisomers often contradicts the Cotton effect method; it has been said [12] that the less soluble diastereoisomers with (+)-bromocamphorsulphonate contain the cations $[\mathrm{Co\,en_2XY}]^{n+}$ which give a positive Cotton effect. Of the ten cations studied in this work which have been resolved by means of (+)-BCS, no less than three contradict this statement, and the two chloro-complexes (II) and (VIII) do not agree completely.

Finally, as a summary of the position resulting from the present work, the known transformations within the series of complexes $[\mathrm{Co\,en_2XY}]^{n+}$ studied here are collected in Scheme 11.



Scheme 11. Interconversions between optically active complexes of the series $[\mathrm{Co\,en_2XY}]^{n+}$

EXPERIMENTAL

Electronic spectra were obtained on a Unicam S.P. 700 spectrophotometer, or for routine experiments, a Perkin-Elmer Ultracord spectrophotometer. Optical rotatory dispersion curves were obtained on a Bendix spectropolarmatic 62 spectropolarimeter with a direct read-out *X–Y* plotter. Rotatory dispersion values are quoted as pairs of simple numbers (λ, $[M]$) where λ is the wavelength in millimicrons and $[M]$ is the rotation in molecular degrees.

In the resolutions no attempt was made to achieve optical purity. The optical purities quoted for the compounds are referred to the best available literature values, usually those of Mathieu,[1] except where noted.

Resolutions.—The following compounds were obtained in a resolved form.

$(+)_{5461}$-*Chloroisothiocyanatobisethylenediaminecobalt*(III) *perchlorate* (VIII). The less soluble diastereoisomer [21a] was $(+)_{5461}$-$[\mathrm{Co\,en_2Cl(NCS)}]$ (+)-BCS. The derived perchlorate had: λ 504 mμ, ε 166; the rotatory dispersion curve showed: 625; 0; 610, −124; 395; 0; 535, +1160; 495; 0, 444, −956; 380, −660; 334, −2220; optical purity 60%.

[21] A. Werner, *Annalen*, 1912, **386**, (*a*) 143; (*b*) 252; (*c*) 165; (*d*) 206.

(+)-*Chloronitrobisethylenediaminecobalt*(III) *chloride* (XII). The less soluble diastereoisomer [21b] was (+)-[Co en$_2$Cl(NO$_2$)] (+)-BCS. The chloride had: λ 505 mμ, ε 90; the rotatory dispersion curve showed: 605, +81·6; 572, +224; 540, 0; 500, −490; 475, −439; 420, −1215; 394, −1348; 380, 908; optical purity 50%.

D(+)-*Dichlorobisethylenediaminecobalt*(III) *chloride* (II). The less soluble diastereoisomer [14] was D(+)-[Co en$_2$Cl$_2$] (+)-BCS. The chloride derived from the first fraction of diastereoisomer had: λ 537·5 mμ, ε 84·5; the rotatory dispersion curve showed: 629, 0; 572, +1295; 528, 0; 487, −636; 435, −344; 383, −1098; 365, −971; 329, −1458; 302, 0; 282, +4400; optical purity 58·6%. This agrees fairly well, except in the low-wavelength region, with that given.[22]

D(+)-*Carbonatobisethylenediaminecobalt*(III) *iodide* (IV). The less soluble diastereoisomer [23] was D(+)-[Co en$_2$CO$_3$] (+)-BCS. The derived iodide had: λ 510 mμ, ε 135; the rotatory dispersion curve showed; 590, 3220; 565, +4120; 532, 0; 495, −7330; 410, −4470; 383, −6080; 354, −5730; 300, −12,520; optical purity 94·5% (from ref. 23).

(+)-*Chloroamminebisethylenediaminecobalt*(III) *sulphate* (IX). The racemic complex was prepared as described [21c] and recrystallised from dilute hydrochloric acid, and resolved by adding to a concentrated aqueous solution one quarter of the amount of solid ammonium (+)-bromocamphorsulphonate necessary to completely precipitate the complex as (+)-[Co en$_2$Cl(NH$_3$)] (+)-BCS$_2$. The solution was cooled and stirred for 30 min., then the precipitate was collected and washed with ethanol and ether.

To a concentrated aqueous solution of the (+)-[Co en$_2$Cl(NH$_3$)] (+) bromocamphorsulphonate was added a slight excess of ammonium sulphate, then ethanol until the complex was completely precipitated as its sulphate. This removed the ammonium (+)-bromocamphorsulphonate which remained in solution, together with small amounts of [Co en$_2$(NH$_3$)H$_2$O]$^{3+}$ salts. The sulphate was reprecipitated to free it from ammonium sulphate. (−)-[Co en$_2$Cl(NH$_3$)]SO$_4$ was recovered from the filtrate following removal of the (+)-[Co en$_2$Cl(NH$_3$)] (+)-bromocamphorsulphonate similarly.

Before resolution, the chloride had λ 523 mμ. After resolution the derived sulphate had: λ 528 mμ, ε 68, and the rotatory dispersion curve showed: 625, +303; 602, +428; 584, 0; 535, −252; 493, −126; 430, −529; 408, −428; 384, −756; 350, −700; 333, −656; 286, −2825; 278, −2770; optical purity 60% referred to that of Mathieu whose complex had λ 525 mμ. The shape of the optical rotatory dispersion curve agrees well with that reported in ref. 1.

(+)-*Chloroaquobisethylenediaminecobalt*(III) *sulphate* (VII). The racemic complex [15] was resolved using the same method as for [Co en$_2$Cl(NH$_3$)]SO$_4$ (IX). The less soluble diastereoisomer was (+)-[Co en$_2$Cl(H$_2$O)] (+)-BCS, which was converted into the sulphate. (−)-[Co en$_2$Cl(H$_2$O)]SO$_4$ was recovered from the filtrate. The sulphate had: λ 517 mμ, ε 88; λ 375 mμ, ε 102; the rotatory dispersion curve showed: 605, +152·3; 555, +406; 520, 0; 472, −418; 464, −390; 455, −499; 416, −363; 345, −535; 286, −1560; 278, −1295; optical purity 25·7% from Mathieu's values.[1] From the results of the reactions with nitrite this appears low, and a better agreement is obtained using more recent values.[23] These give an optical purity of 29%.

(−)-*Isothiocyanatonitrobisethylenediaminecobalt*(III) *perchlorate* (X). The racemic complex was prepared as its chloride using the literature method.[24] Attempts to resolve the complex by the usual methods gave racemic precipitates. To achieve a partial resolution the following method of fractional crystallisation was used. The complex (1 g.) in water (8 ml.) was treated with solid ammonium (+)-bromocamphorsulphonate (1·5 g.), and heated on the steam-bath until all had dissolved. On standing an orange precipitate of (−)-[Co en$_2$(NCS)NO$_2$] (+)-BCS was obtained, which was collected, dried, and ground with 60% perchloric acid. From this a pink precipitate of (−)-[Co en$_2$(NCS)H$_2$O](ClO$_4$)$_2$ was obtained initially, formed by acid catalysed aquation of the nitro-complex. This pink precipitate was removed. On standing, the filtrate gave crystals of (−)-[Co en$_2$(NCS)NO$_2$]ClO$_4$ of 24% apparent optical purity.

The complex was also prepared in an optically active form as described below.

(−)-[Co en$_2$(NCS)NO$_2$]Cl was prepared by heating an aqueous solution of (−)-[Co en$_2$(NO$_2$)(H$_2$O)]Cl of 27% optical purity with excess of potassium thiocyanate for 20 min.

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[22] Y. Shimura, *Bull. Chem. Soc. Japan*, 1958, **31**, 315.

[23] F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, 1963, **85**, 1215.

[24] A. Werner and R. Klein, *Z. anorg. Chem.*, 1900, **22**, 111.

on a steam-bath. The resulting thiocyanate was converted into its chloride which was of 30% apparent optical purity.

(+)-[Co $en_2(NCS)NO_2$]Cl was prepared by treating an aqueous solution of (+)-[Co $en_2Cl(NCS)$]Cl of 22·2% optical purity with excess of sodium nitrite and converting the nitrite obtained into its chloride. This had λ 474 mμ, ε 262; and the rotatory dispersion curve showed; 590, +94; 532, +371; 495, 0; 457, −574; 385, −130; apparent optical purity 46%.

(+)-*Isothiocyanatoamminebisethylenediaminecobalt*(III) *sulphate* (XVI). This was prepared optically active from the reaction of (+)-[Co $en_2Cl(NCS)$]Cl of 24% optical purity with liquid ammonia following the literature method.[21d] The residue after evaporating off the ammonia was dissolved in a little water, made slightly alkaline and first ammonium sulphate, then ethanol added. (+)-[Co $en_2(NCS)NH_3$]SO_4 was precipitated whilst salts of the ions (+)-[Co $en_2Cl(NCS)$]$^+$ and (+)-[Co $en_2(OH)NCS$]$^+$ remained in solution. The precipitate was collected and recrystallised from water. The sulphate had: λ 485 mμ, ε 114; the rotatory dispersion curve showed; 590, +17·4; 544, +72·6; 515, 0; 466, −308; 416, −244; 384, −327; 370, −268; 302, −634; optical purity 22%.

The racemic complex was also prepared and purified in a similar way. It was converted into its chloride and resolved and isolated in the same way as for the chloro-ammine complex (IX). The less soluble diastereoisomer was (+)-[Co $en_2(NCS)NH_3$] (+)-bromocamphorsulphonate. The optical purity of the sulphate derived from the first crop of diastereoisomer was 13%.

A partial resolution was also obtained using (+)-tartrate ion, the less soluble diastereoisomer being (−)-[Co $en_2(NCS)NH_3$] (+)-tartrate.

(−)-*Di-isothiocyanatobisethylenediaminecobalt*(III) *nitrate* (XV). The racemic nitrate was prepared by the literature method.[6] Attempts to resolve the nitrate were unsuccessful except on slow crystallisation of a concentrated solution containing a large excess of ammonium (+)-bromocamphorsulphonate. The racemic complex was therefore converted into its chloride. To a concentrated solution of this chloride was added sufficient solid ammonium (+)-bromocamphorsulphonate to precipitate half the complex, and the solution allowed to evaporate. The initial crystalline fractions were of inactive chloride; however at a later stage, the less soluble diastereoisomer, (−)-[Co $en_2(NCS)_2$] (+)-bromocamphorsulphonate separated. This was removed, washed with ether, and dried. The resolved complex was obtained as its nitrate by treating an aqueous solution of the diastereoisomer with an excess of solid ammonium nitrate. The recrystallised nitrate had: λ 493 mμ, ε 250; λ 311 mμ, ε 2010; the rotatory dispersion curve showed; 590, −23·4; 526, −386; 498, 0; 436, 562; 386, 339; 345, 926; 316, 0; 305, −128·5; 299, 0; 261, 2410; 256, 2360. From the results of the oxidation to (−)-[Co $en_2(NH_3)_2$]$^{3+}$ the optical purity is estimated as 64%.

(+)-[Co $en_2(NCS)_2$]$^+$ can also be prepared in solution by heating either (+)-[Co $en_2Cl(NCS)$]$^+$ or (+)-[Co $en_2(NCS)H_2O$]$^{2+}$ with excess of potassium thiocyanate on the steam-bath for *ca.* 30 min.

(+)-[Co $en_2(NCS)(H_2O)$]$^+$ of 38·5% apparent optical purity gave (+)-[Co $en_2(NCS)_2$]$^+$ of 28·5% optical purity; and (+)-[Co $en_2Cl(NCS)$]ClO_4 of 22·2% optical purity gave a product of 20% optical purity.

Preparations of Aquo-complexes.—D(+)-*Diaquobisethylenediaminecobalt*(III) *perchlorate* (III). The complex was prepared in solution by the action of perchloric acid (1N) on D(+)-[Co en_2CO_3] (I) of 94·5% optical purity. In the following experiments it was found necessary to use completely fresh alkali to raise the pH from 1 to 5, otherwise the carbonate complex was partially re-formed. The solution had: λ 495 mμ, ε 71·5; λ 355 mμ, ε 66; and the rotatory dispersion curve showed: 610, +193; 519, +1550; 478, 0; 442, −1410; 394, −1040; 329, −1760; 268, −3095; 364, −2900; optical purity 94%.

(+)-*Isothiocyanatoaquobisethylenediaminecobalt*(III) *perchlorate* (XIII). The complex was prepared [12] in solution by allowing (+)-[Co $en_2Cl(NCS)$]ClO_4 of 60% optical purity to aquate for seven days. The final solution had: λ 497 mμ, ε 216; the rotatory dispersion curve showed: 590, +119; 520, +876; 480, 0; 446, −559; 389, −398; 345, −1195; apparent optical purity 41·6%.

(+)-*Aquoamminebisethylenediaminecobalt*(III) *chloride* (XIV). The complex was prepared in solution by warming an aqueous solution of (+)-[Co $en_2Cl(NH_3)$]SO_4 of 60% optical purity with silver nitrate, precipitating silver chloride. A concentrated solution of ammonium chloride was then added to precipitate the remaining silver ions, and the precipitate then removed by filtration. The filtrate gave: λ 485 mμ, ε 65; λ 340 mμ, ε 72·5; and the rotatory dispersion curve showed: 605, +304; 564, +362; 526, 0; 500, −333; 476, −570; 440, −704; 398, −599; 359, −800; 330, −608; 313, −1250; optical purity 49%.

L(−)-*Nitroaquobisethylenediaminecobalt*(III) *chloride* (XXII). The complex was prepared in solution from the filtrate of (−)-$[Co\,en_2Cl(NO_2)]Cl$ obtained in the resolution of that complex. Traces of ammonium (+)-bromocamphorsulphonate were removed by means of an anion exchange resin. The resultant aquated solution racemised and allowance was made for this. The solution with 20% optical purity had: λ 455 mμ, ε 100; and the rotatory dispersion curve showed: 590, −51·4; 547, −140; 523, 0; 435, +584; 400, +640.

Isothiocyanate Oxidations.—Solutions of the complexes were oxidised under the conditions indicated by Schug and Gilmore,[8] namely using a slight excess of potassium iodate in a solution of the complex ($\sim 10^{-2}$M) in perchloric acid (0·01—0·05M), the reaction being complete in all cases within 1—2 hr. The iodine formed did not affect the measurement of the rotatory dispersion curves. To determine the absorption spectra of the products, iodine was removed either by extracting five times with carbon tetrachloride or by titration with sodium thiosulphate solution.

It seems from our work likely that many resolutions in the literature have been incomplete. We indicate this by using the term " apparent optical purity " for such cases. In these cases the results presented have been verified by varying the reaction conditions, namely the molarity of the perchloric acid and the excess of potassium iodate.

The results for the products have been estimated from the final oxidised solutions obtained, which agree well with those calculated using known extinction coefficients.

Conversion of (−)-$[Co\,en_2(NCS)_2]NO_3$ (XV) *into* (−)-$[Co\,en_2(NH_3)_2]ClO_4$ (XVII). The nitrate resolved as described earlier gave the perchlorate in solution which had: λ 470 mμ, ε 62; and whose rotatory dispersion curve showed: 593, +28·4; 526, +397; 503, 0; 467, −1015; 410, −558; 357, −695; 303, −1415; 278, −1950; optical purity 64% ± 1%.

Conversion of (+)-$[Co\,en_2(NCS)NH_3]SO_4$ (XVI) *into* (+)-$[Co\,en_2NH_3)_2]ClO_4$ (XVII). The sulphate (22% optical purity) gave the perchlorate in solution; optical purity 19·7 ± 1%.

Conversion of (+)-$[Co\,en_2(NCS)NO_2]Cl$ (X) *into* (+)-$[Co\,en_2(NO_2)NH_3]ClO_4$ (XI). The chloride (46% apparent optical purity) gave the perchlorate in solution which had: λ 454 mμ, ε 89; and whose rotatory dispersion curve showed 593, +52·3; 513, +167; 474, 0; 441, −345; 391, −89; 365, −130; apparent optical purity 20·5 ± 1%.

Conversion of (+)-$[Co\,en_2(NCS)H_2O]ClO_4$ (XIII) *into* (+)-$[Co\,en_2(H_2O)NH_3]ClO_4$ (XIV). The perchlorate (41·6% apparent optical purity) gave the product, in solution, of 25 ± 2% optical purity.

Conversion of (+)-$[Co\,en_2Cl(NCS)]ClO_4$ (VIII) *into* (+)-$[Co\,en_2Cl(NH_3)]ClO_4$ (IX). Although (+)-$[Co\,en_2Cl(NCS)]^+$ aquates only slowly in perchloric acid solutions of the strengths used in the oxidation experiments the products of the oxidations in all cases consisted of a mixture of (+)-$[Co\,en_2(NH_3)Cl]^{2+}$ and (+)-$[Co\,en_2(H_2O)NH_3]^{3+}$, typically with λ 505—510 mμ and rotatory dispersion curves with a maximum ~575 mμ and minimum ~470. When oxidation was done in a solution saturated with sodium chloride, the product had $\lambda_{\text{max.}}$ 518 mμ; rotatory dispersion maximum, 590 mμ, $M = +452$; minimum 497 mμ, $M = -423$. This corresponds approximately to 33% aquo-complex being present. After seven days, this solution gave: λ 485 mμ, ε = 66; rotatory dispersion maximum 567, +147 and minimum 440, −275; corresponding to (+)-$[Co\,en_2(H_2O)NH_3]^{2+}$ of *ca.* 20% optical purity. The initial optical purity of the (+)-$[Co\,en_2Cl(NCS)]ClO_4$ used in this case was 60%.

(−)-*Mercuric Di-isothiocyanatobisethylenediaminecobalt*(III) *Perchlorate* (XXXII).—The 1 : 1 complex between mercuric ion and (−)-$[Co\,en_2(NCS)_2]NO_3$ of the same optical purity as above was prepared in a solution of perchloric acid at pH 3 by addition of mercuric chloride.[13] This solution had: λ 488 mμ, ε 190; λ 302 mμ, ε 1720; the rotatory dispersion curve showed: 590, +71·3; 529, +617; 496, 0; 433, −1460; 427, −1448; 394, −1520; 383, −1400; 336, −2565; 302, −1120; 256, −5370; 250−3680.

Aquo–Hydroxo Interconversions.—In all systems studied an equilibrium exists between the *cis-* and *trans*-hydroxo-species; the rate of attaining this equilibrium increases with increasing concentration of hydroxide ions. Although the amplitude of the rotatory dispersion curve provides a sensitive method for determining the activity remaining, we have not attempted to attain the equilibrium conditions, but only to proceed to a point where the rotatory dispersion curve is changing slowly enough to make the readings accurate.

L(−)-*Hydroxonitrobisethylenediaminecobalt*(III) *chloride* (XXIII). The complex was prepared by adding sodium hydroxide to a solution of L(−)-$[Co\,en_2(NO_2)H_2O]Cl_2$ of 20% optical purity until the pH was 8. The absorption spectrum was measured immediately. The product had; λ 463 mμ, ε 107; the rotatory dispersion curve showed: 590, −60; 562, −92·2; 534, 0; 461, +463; 398, +126; 370, +270. On reacidification immediately after measuring the rotatory dispersion curve, the L(−)-$[Co\,en_2(NO_2)H_2O]^{2+}$ regenerated was 17·4% optically pure.

(+)-*Hydroxoisothiocyanatobisethylenediaminecobalt*(III) *chloride* (XXIV). The complex was prepared by adding sodium hydroxide to a solution of (+)-$[Co\,en_2(NCS)H_2O]Cl_2$ of 41·6% optical purity until the pH was 8. On reacidification immediately after measuring the rotatory dispersion curve, the aquo-complex regenerated still had an optical purity of 41·6%. The hydroxo-complex had λ 502 mμ, ε 151; and its rotatory dispersion curve showed: 590, +204; 550, +204; 550, +484; 489, 0; 468, −455; 435, −348; 345, −847

(+)-*Hydroxoamminebisethylenediaminecobalt*(III) *nitrate* (XXV). The complex was prepared in solution by adding sodium hydroxide to (+)-$[Co\,en_2(H_2O)NH_3]Cl_3$ of 33·5% optical purity until the pH was 8. After 2 hr., on reacidification the resultant solution had lost 10% of the initial optical activity. At pH 12 a similar solution had lost 40% of its optical activity after 45 min. The hydroxo-complex had: λ 495 mμ, ε 73·7; λ 360 mμ, ε 79·5; the rotatory dispersion curve showed: 590, +232; 546, +298; 485, 0; 451, −547; 384, −475; 336, −216; 333, −249. On reacidification immediately after determining the rotatory dispersion curve, the (+)-$[Co\,en_2(H_2O)NH_3]^{2+}$ regenerated was 27·7% optically pure.

D(+)-*Hydroxoaquobisethylenediaminecobalt*(III) *perchlorate* (XIX). The complex was prepared in solution from D(+)-$[Co\,en_2(H_2O)_2](ClO_4)_3$ of 94% optical purity. The monohydroxo-complex, which is the stable species between pH 6 and 8, undergoes a very rapid *cis–trans* isomerisation as found by Bjerrum and Rasmussen.[17] A solution which had been kept for 45 min. at pH 6 was brought to pH 1; the resultant diaquo-complex was 52% optically pure. At pH ~8 the isomerisation was extremely rapid, the solution regenerating only 35% of the initial optical activity on acidifying after 10 min. The monohydroxo-complex had: λ 512 mμ, ε 86; λ 367 mμ, ε 93; the rotatory dispersion curve showed: 605, +626; 553, +2740; 532, 0; 486, −4060; 463, −3370; 410, −2310; 389, −2940; 358, −2810; 278, −9470. On reacidification this solution regenerated (+)-$[Co\,en_2(H_2O)_2]^{3+}$ of 52% optical activity.

D(+)-*Dihydroxobisethylenediaminecobalt*(III) *perchlorate* (XXI). The complex was prepared from D(+)-$[Co\,en_2(H_2O)_2](ClO_4)_3$ of 82% optical purity above pH 8. The *cis–trans* isomerisation was slow, no change in optical purity having occurred on regeneration of D(+)-$[Co\,en_2(H_2O)_2]^{3+}$.

The dihydroxo-complex had λ 518 mμ, ε 90; λ 370 mμ, ε 105; the rotatory dispersion curve showed: 605, +172·5; 575, +431; 546, 0; 508, −948; 478, −562; 417, −604; 400, −431; 358, −1038.

(−)-*Chlorohydroxobisethylenediaminecobalt*(III) *chloride* (XVIII). The complex was prepared in solution from (−)-$[Co\,en_2(H_2O)]Cl_2$ of 4·1% optical purity which had been prepared by allowing the filtrate from the resolution of $[Co\,en_2Cl_2]Cl$ to aquate overnight. Ammonium (+)-bromocamphorsulphonate was removed by anion exchange. The aquo-complex is stable up to pH 7. The hydroxo-complex undergoes very rapid base-catalysed hydrolysis; between pH 7 and 8 (−)-$[Co\,en_2(OH)H_2O]^{2+}$ was formed and above pH 8, (−)-$[Co\,en_2(OH)_2]^+$.

Measurements on the chlorohydroxo-complex were only possible at a pH just above pH 7 when the rate of hydrolysis was comparatively slow. On reacidification after measuring the rotatory dispersion curve, (−)-$[Co\,en_2Cl(H_2O)]$ was almost completely regenerated, very little diaquo-complex being present.

The chlorohydroxo-complex had: λ 530 mμ, ε 104; and its rotatory dispersion curve showed: 590, −33·7; 568, −63·3; 520, 0; 479, +81·8; 555, +51·6.

Aquo–Nitrito–Nitro Interconversions.—The reactions were carried out by adding a slight excess of sodium nitrite to an aqueous solution of the aquo-complex at 0—5°. The solution was then brought to pH 4 by adding perchloric acid. The spectra and optical rotatory dispersion curves were measured after reaction in the cold for 10—15 min. Measurements after this time did not differ greatly from measurements taken after 30 min. although after 1 hr. an appreciable shift to shorter wavelengths could be observed, showing that nitrito–nitro isomerisation takes place even in the cold.

The spectra and optical rotatory dispersion curves given were calculated from the initial concentrations of aquo-complex, complete conversion into nitrito-complex being assumed. The results agree well {except for (+)-$[Co\,en_2Cl(H_2O)]^{2+}$} with those calculated from the final solutions which contain nitro-complexes of known extinction coefficient. There is therefore 100% retention of geometric configuration in all these reactions.

In a number of cases comparative experiments were carried out at room temperature where the nitrito–nitro isomerisation is much more rapid. In all cases the optical purity of the final nitro-complex was the same as that obtained by carrying out the reaction in the cold.

Because of the lack of knowledge of rotations of 100% optically pure complexes, it has been difficult to correlate the optical purities of the initial and final complexes, though repeated experiments give consistent results which correlate well with those obtained in the isothiocyanate oxidations.

D(+)-*Dinitritobisethylenediaminecobalt*(III) *perchlorate* (XXVII).

$$\text{D(+)-}[Co\,en_2(H_2O)_2]^{3+} \longrightarrow \text{D(+)-}[Co\,en_2(ONO)_2]^{+} \longrightarrow \text{D(+)-}[Co\,en_2(NO_2)_2]^{+}$$

D(+)-$[Co\,en_2(H_2O)_2](ClO_4)_3$ of 94% optical purity was prepared in solution as described above. Before reaction the pH was adjusted from pH 1 to 5 with *fresh* sodium hydroxide solution to avoid formation of carbonato-complex. After this partial neutralisation the optical purity was 71·8% owing to the *cis–trans* isomerisation of the aquo-hydroxo-complex formed locally during the addition of the sodium hydroxide. After 10 min. the solution had: λ 494 mμ, ε 83; the optical rotatory dispersion curve showed: 590, +242; 518, +1260; 489, 0; 449, −1480; 400, −1115; 385, −1165. After 36 hr. the solution had $\lambda_{max.}$ 438 mμ, ε 188, owing to complete isomerisation to (+)-$[Co\,en_2(NO_2)_2]^+$ which was 70 ± 2% optically pure. Identical final results were obtained from reactions carried out in the cold or at room temperature. The electronic spectrum given for the dinitrito-complex does not agree with that obtained by Adell [25] on isolated solid samples of dinitrito-complex (λ 456 mμ, ε 135). When however the reaction mixture was allowed to stand in the cold, the following values of λ (ε) were obtained: initial, 495 (71·5); after 11 min., 494 (83); after +1 hr., 482 (124); after 3 hr., 458 (136); after 14 hr. (dinitro), 438 (188). It is probable therefore that the solids which Adell obtained were partly isomerised.

D(+)-*Nitritoaquobisethylenediaminecobalt*(III) *perchlorate* (XXV).

$$\text{D(+)-}[Co\,en_2(H_2O)_2]^{3+} \longrightarrow \text{D(+)-}[Co\,en_2(ONO)H_2O]^{2+} \longrightarrow \text{D(+)-}[Co\,en_2(NO_2)H_2O]^{2+}$$

The diaquo-complex used was of 71·8% optical purity. A slight excess of sodium nitrite over that calculated to give D(+)-$[Co\,en_2(ONO)H_2O]^{2+}$ was employed so that a mixture of this and the dinitrito-complex was obtained. On standing the rotatory dispersion curve showed that a mixture of D(+)-$[Co\,en_2(NO_2)H_2O]^{2+}$ and D(+)-$[Co\,en_2(NO_2)_2]^+$ was obtained. The former was allowed to racemise completely and from the residual optical activity due to the dinitro-complex the concentration and rotatory dispersion curve of the dinitrito-complex initially formed were calculated. This permitted the properties of D(+)-$[Co\,en_2(ONO)H_2O]^{2+}$ to be obtained. These are: λ 495 mμ, ε 75; λ 362 mμ, ε 166: and the rotatory dispersion curve; 590, +48; 519, +964; 483, 0; 440, −1260; 400, −940; 385, −1015.

(+)-*Isothiocyanatonitritobisethylenediaminecobalt*(III) *perchlorate* (XXIX).

$$\text{(+)-}[Co\,en_2(NCS)H_2O]^{2+} \longrightarrow \text{(+)-}[Co\,en_2(NCS)ONO]^{+} \longrightarrow \text{(+)-}[Co\,en_2(NCS)NO_2]$$

The aquo-complex was obtained from the chloro-complex as previously described. The initial apparent optical purity of the aquo-complex was 29%. The ion (+)-$[Co\,en_2(NCS)NO_2]^+$ finally obtained had an optical purity of 48 ± 1% whether the reaction was carried out in the cold or at room temperature (λ 472 mμ, ε 262).

After 10 min. the solution of the nitrito-complex had: λ 494 mμ, ε 222; and the rotatory dispersion curve showed: 575, +314; 518, +679; 486, 0; 451, −554; 416, −428; 400, −453.

(+)-*Nitritoamminebisethylenediaminecobalt*(III) *perchlorate* (XXX).

$$\text{(+)-}[Co\,en_2(H_2O)NH_3]^{3+} \longrightarrow \text{(+)-}[Co\,en_2(ONO)NH_3]^{2+} \longrightarrow \text{(+)-}[Co\,en_2(NO_2)NH_3]^{2+}$$

The aquo-complex was obtained from the chloro-complex. The initial optical purity was 49%. The ion (+)-$[Co\,en_2(NO_2)NH_3]^{2+}$ finally obtained had an optical purity of 66 ± 1% from the reaction in the cold (λ 454 mμ, ε 89), whilst for the experiments at room temperature a somewhat lower optical purity of 62 ± 2% was obtained.

[25] B. Adell, *Acta Chem. Scand.*, 1951, **5**, 941.

After 10 min. the solution containing the nitrito-complex had: λ 482 mμ, ε 81 and the rotatory dispersion curve showed: 590, +265; 556, +367; 512, 0; 449, −622; 384, −498; 378, −550.

L(−)-*Nitritonitrobisethylenediaminecobalt*(III) *perchlorate* (XXVIII).

$$\text{L}(-)\text{-}[\text{Co en}_2\text{NO}_2\text{H}_2\text{O}]^{2+} \longrightarrow (-)\text{-}[\text{Co en}_2\text{NO}_2(\text{ONO})]^{+} \longrightarrow \text{L}(-)\text{-}[\text{Co en}_2(\text{NO}_2)_2]^{+}$$

The aquo-complex was obtained from the chloro-complex. The initial optical purity of the aquo-complex was 34%. The ion (+)-[Co $\text{en}_2(\text{NO}_2)_2]^+$ finally obtained had an optical purity of 33 ± 1% (λ 438 mμ, ε 186).

After 15 min. the solution of the nitrito-complex had: λ 448 mμ, ε 130 and its rotatory dispersion curve showed: 590, −16; 538, −95; 507, 0; 425, +620; 400, +526.

(+)-*Chloronitritobisethylenediaminecobalt*(III) *perchlorate* (XXX).

$$(+)\text{-}[\text{Co en}_2\text{Cl}(\text{H}_2\text{O})]^{2+} \longrightarrow (+)\text{-}[\text{Co en}_2\text{Cl}(\text{ONO})]^{+} \longrightarrow (+)\text{-}[\text{Co en}_2\text{Cl}(\text{NO}_2)]^{+}$$

The resolved chloroaquo-complex of 25·7% optical purity was used. From the results it is clear that the initial reaction in the cold is the formation of the chloronitrito-complex, the chloride group not being replaced by nitrite. However at an intermediate state of the reaction at room temperature the optical rotatory dispersion curve reveals the presence of a mixture of dinitro- and chloronitro-complex.

The final spectra and rotatory dispersion curves of these systems after 66 hr. show that the optical purity of the D(+)-[Co $\text{en}_2(\text{NO}_2)_2]^+$ complex formed is 29 ± 1%. This suggests that the rotations for (+)-[Co $\text{en}_2\text{Cl}(\text{H}_2\text{O})$] given by Mathieu[1] may be too high and that more recent figures[23] are better ($[M]_\text{D} = +820$; Mathieu[1] gave $[M]_\text{D}$ +900); using the value $[M]_\text{D} = +820$, the chloroaquo-complex is 29·2% optically pure.

For the reactions both in the cold and at room temperature the percentage of D(+)-[Co $\text{en}_2(\text{NO}_2)_2]^+$ present in the final solution was 63 ± 5% which is in fairly good agreement with earlier results,[23] *i.e.*, 71% D(+)-*cis*- and 29% *trans*-[Co $\text{en}_2(\text{NO}_2)_2]^+$. It is probable that this isomerisation occurs in the aquation of the (+)-[Co $\text{en}_2(\text{NO}_2)\text{Cl}]^+$ formed.

After 10 min. the solution of the chloronitrito-complex had λ 515 mμ, ε 90; the rotatory dispersion curve was: 590, +123; 541, +315; 580, 0; 448, −447; 427, −342; 379, −561.

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