936. *The Preparation and Properties of Some Azidobis(ethylenediamine)cobalt*(III) *Salts.*

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Two isomeric series of salts have been characterised for each of the following complex cations, $[Co\ en_2(N_3)_2]^+$, $[Co\ en_2N_3Cl]^+$, and $[Co\ en_2N_3H_2O]^{2+}$. One isomeric form of each of these cations has been resolved into an optically active enantiomorph and, on this basis, has been assigned the *cis*-configuration. The near-ultraviolet and visible absorption spectra of all these complex ions are reported together with some of the infrared absorption bands. Evidence supports a linear arrangement of the three nitrogen atoms in the co-ordinated azide group.

IN recent investigations of the replacement of chloride by azide in dichlorobis(ethylenediamine)cobalt(III) cations,[1-3] it became apparent that a knowledge of the properties of the products is very necessary. Furthermore, it was desirable to examine the effect of a co-ordinated azide group upon the lability of other ligands in the complex and upon the steric course of any resulting substitution reaction.

A number of azido-cobaltammine complexes have already been described, *e.g.*, $[Co(NH_3)_5N_3]X_2$, *cis*- and *trans*-$[Co(NH_3)_4(N_3)_2]X$, and $[Co(NH_3)_3(N_3)_3]$ [4] and their spectra and reactivity reported in many cases. Strecker and Oxenius [5] described both the *cis*- and the *trans*-isomer of the $[Co\ en_2(N_3)_2]^+$ cation but they did not use any satisfactory criteria in their assignment of configuration. There is much disagreement between their observations and those reported in this paper. The $[Co\ en_2N_3Cl]^+$ and $[Co\ en_2N_3H_2O]^{2+}$ salts are now reported.

The main methods for the preparation of the diazido- and chloroazido-complexes use the ready replacement of the chlorine in *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride by azide ions in aqueous solution. This reaction takes place in two stages:

(1) *trans*-$[Co\ en_2Cl_2]^+ + N_3^- \longrightarrow$ *cis*- and *trans*-$[Co\ en_2N_3Cl]^+ + Cl^-$

(2) *cis*- and *trans*-$[Co\ en_2N_3Cl]^+ + N_3^- \longrightarrow$ *cis*- and *trans*-$[Co\ en_2(N_3)_2]^+ + Cl^-$

These two reactions proceed at similar rates and it is possible that step (2) is faster than step (1).

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride reacts with an excess of sodium azide to give a mixture of *cis*- and *trans*-$[Co\ en_2(N_3)_2]N_3$, which can be readily separated owing to differences in solubility of the other salts in the series. The chloroazido-complexes, $[Co\ en_2N_3Cl]^+$ are prepared in poor yield by reaction of *trans*-$[Co\ en_2Cl_2]Cl$ with

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[1] Brown and Ingold, *J.*, 1953, 2680.

[2] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379.

[3] Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5382.

[4] Linhard and Flygare, *Z. anorg. Chem.*, 1950, **262**, 328; Linhard, Weigel, and Flygare, *ibid.*, **263**, 233; Linhard and Weigel, *ibid.*, p. 245.

[5] Strecker and Oxenius, *Z. anorg. Chem.*, 1934, **218**, 151.

one equivalent of sodium azide. As the chlorine in the chloroazido-complex is readily replaced by water and by azide, the main components of the mixture at the completion of reaction are unchanged dichloro-complex, the two diazido-isomers, and the two aquo-azido-isomers. The main difficulty, therefore, was the isolation of the small amount of the required compound from large amounts of impurity.

cis-Diazidobis(ethylenediamine)cobalt(III) nitrate has been prepared almost quantitatively by passing air through an aqueous solution of cobalt nitrate containing ethylenediamine and sodium azide. No *trans*-isomer was detected, and the very short time required for the reaction to take place indicates that the *cis*-isomer is formed directly by the oxidation. It is noteworthy that *trans*-dinitrobis(ethylenediamine)cobalt(III) nitrate is formed in a very few minutes when air is blown through an aqueous solution of cobalt nitrate containing ethylenediamine and sodium nitrite,[6] and that *trans*-di-isothiocyanatobis(ethylenediamine)cobalt(III) thiocyanate can be prepared analogously.[7] The stereospecificity of these oxidations presents problems of considerable interest, and Watts [8] has recently shown that, if the air oxidation of a mixture of cobalt(II) nitrate, ethylenediamine, and sodium azide is carried out in suspension in methanol, instead of in aqueous solution, *trans*-diazidobis(ethylenediamine)cobalt(III) azide is obtained in almost theoretical yield.

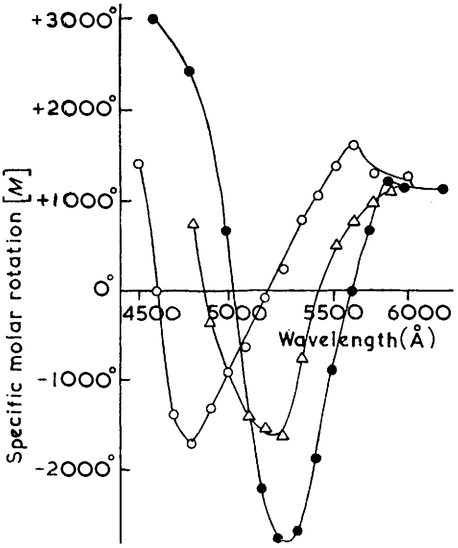

FIG. 1. Rotatory dispersion curves for: *d-cis*-[Co $en_2(N_3)_2$] antimonyl-(+)-tartarate, ●; *d-cis*-[Co en_2N_3Cl] (+)-α-bromocamphorsulphonate, ○; *d-cis*-[Co $en_2N_3H_2O]^{2+}$, △.

The *cis*- and *trans*-aquoazidobis(ethylenediamine)cobalt(III) salts were obtained from the corresponding chloroazido-salts. It has been shown that the *cis*- and the *trans*-[Co $en_2N_3H_2O]^{2+}$ cation isomerise to an equilibrium mixture containing 73% of *cis*- and 27% of *trans*-isomer, and that the rate of this isomerisation is not much slower than the rate at which the aquo-complexes are formed from the corresponding chloro-complexes,[9] so that, although aquation proceeds with considerable retention of configuration, extensive rearrangement takes place before the aquation is complete. If, however, an excess of mercuric perchlorate is added to the solution of the chloroazido-complex, the co-ordinated chlorine is removed in a few minutes and is replaced by water. The co-ordinated azide is unaffected in the time required to complete this reaction. A spectrophotometric study of the products of the mercury(II)-catalysed aquation showed that the configuration is fully retained in the product. It is of interest that *trans*-chloroazidobis(ethylenediamine)-cobalt(III) salts yield 20% of the *cis*-product when they are aquated in the absence of

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[6] Holtzclaw, Sheetz, and McCarty, *Inorg. Synth.*, 1953, **4**, 177.

[7] Groszman and Schuck, *Ber.*, 1906, **39**, 1897.

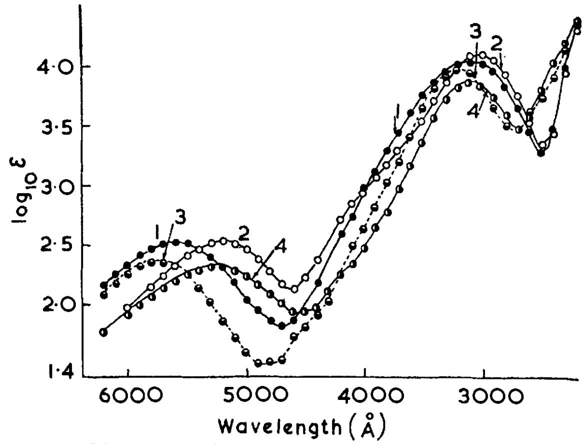
[8] Watts, personal communication.

[9] Staples and Tobe, preceding paper.

mercuric ions.[9] Until now, the mercuric ion-induced aquation has been studied only in systems that either cannot indicate their steric course, *e.g.*, $[Co(NH_3)_5Br]^{2+}$,[10,11] or whose uncatalysed aquation also proceeds with complete retention of configuration, *e.g.*, *cis*- and *trans*-$[Co\ en_2(NH_3)Br]^{2+}$, *trans*-$[Co\ en_2(NO_2)Br]^{+}$, and *cis*- and *trans*-$[Co\ en_2(NO_2)Cl]^{+}$.[12,13] In these latter compounds the mercuric-induced aquation proceeds with complete retention of configuration.[14]

It was possible to obtain crystalline, optically active salts of the red diazidobis(ethylenediamine)cobalt(III) series and also of the red chloroazido-series, thus proving their configuration to be *cis*. The purple diazido- and blue chloroazido-series therefore have the *trans*-configuration. It was not possible to obtain sufficient of the aquoazido-complexes to attempt their resolution directly, but it was shown that, when an optically active solution of *cis*-chloroazidobis(ethylenediamine)cobalt(III) (+)-bromocamphorsulphonate was treated with excess of mercuric perchlorate the solution produced was still optically active, possessed a rotation–dispersion curve that was quite different from that of the chloroazido-complex, and had a visible absorption spectrum that was almost identical with that of the red aquoazido-complex. The rotation–dispersion curves for all three *cis*-species are given in Fig. 1.

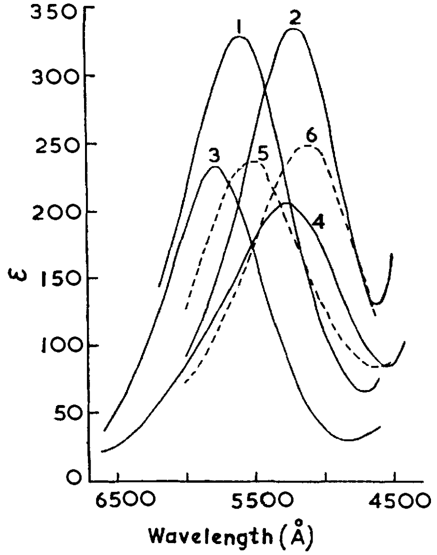
FIG. 2.



Near ultraviolet and visible absorption spectra of:

(1) *trans*-$[Co\ en_2(N_3)_2](ClO_4)$, ●.
(2) *cis*-$[Co\ en_2(N_3)_2](ClO_4)$, ○.
(3) *trans*-$[Co\ en_2N_3Cl](ClO_4)$, ◒.
(4) *cis*-$[Co\ en_2N_3Cl](ClO_4)$, ◑.

FIG. 3.



Visible absorption spectra of:

(1) *trans*-$[Co\ en_2(N_3)_2](ClO_4)$.
(2) *cis*-$[Co\ en_2(N_3)_2](ClO_4)$.
(3) *trans*-$[Co\ en_2N_3Cl](ClO_4)$.
(4) *cis*-$[Co\ en_2N_3Cl](ClO_4)$.
(5) *trans*-$[Co\ en_2N_3H_2O](ClO_4)_2$.
(6) *cis*-$[Co\ en_2N_3H_2O](ClO_4)_2$.

The visible and near-ultraviolet absorption spectra were measured with a Unicam S.P. 500 Quartz spectrophotometer. The visible absorption spectra of all the salts of a particular complex ion were identical, and this was taken as evidence for isomeric purity. The visible and near-ultraviolet spectra of some of the complexes are plotted in Fig. 2 and

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[10] Brönsted and Livingston, *J. Amer. Chem. Soc.*, 1927, **49**, 435.
[11] Posey and Taube, *J. Amer. Chem. Soc.*, 1957, **79**, 255.
[12] Tobe, *J.*, 1959, 3776.
[13] Asperger and Ingold, *J.*, 1956, 2862.
[14] Tobe, unpublished work.

the visible absorption band is given in more detail in Fig. 3. It will be seen that replacement of chlorine by azide shifts the longest-wavelength peak towards shorter wavelengths and considerably increases the molar extinction coefficients.

The characteristic infrared absorption frequencies of the co-ordinated azide group were measured and are reported in Table 1, where they are compared with the frequencies assigned to similar vibrations in ionic azides of other cobaltammines, alkali-metal azides, and typically covalent azides. All measurements were made on the solid complex, which was ground to a mull with Nujol and placed between potassium bromide or sodium chloride plates. Spectra were measured with a Grubb-Parsons GS 2A spectrometer. The two frequencies reported are assigned to the bending mode of the azide group and to its asymmetric stretch.

TABLE 1. *Some characteristic frequencies (in cm.$^{-1}$) for infrared absorption by some azido-cobaltammine complexes.*

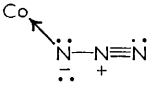
Assignment	$\underset{\downarrow\quad\downarrow}{N{-}\overset{\uparrow}{N}{-}N}$	$\overset{\rightarrow\ \leftarrow\ \rightarrow}{N{-}N{-}N}$
Compound		
NaN_3 [15]	639	2128
KN_3 [15]	645	2041
$Ca(N_3)_2$ [15]	638	2114
NH_4N_3 [15]	650, 661	2041
HN_3 [16]		2140 (gas) 2169 (solid)
CH_3N_3 [17]		2143 (gas)
cis-$[Co\ en_2Cl_2]N_3$	626, 634	2037
trans-$[Co\ en_2Cl_2]N_3$	626, 633	2033
cis-$[Co\ en_2N_3Cl]_2(S_2O_6)$		2037
cis-$[Co\ en_2N_3Cl](ClO_4)$		2041
trans-$[Co\ en_2N_3Cl](ClO_4)$		2033
trans-$[Co\ en_2N_3Cl](BF_4)$		2033
cis-$[Co\ en_2(N_3)_2]Br$	657, 677	
cis-$[Co\ en_2(N_3)_2](NO_3)$		2024, 2092
cis-$[Co\ en_2(N_3)_2](ClO_4)$		2028, 2075
trans-$(Co\ en_2(N_3)_2]I$	667, 677	
trans-$[Co\ en_2(N_3)_2](ClO_4)$		2020

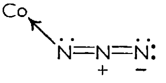
DISCUSSION

Although there is considerable information in the literature on the structure of the azide ion in ionic compounds [18] and the structure of covalent azides, there is no report of any *X*-ray diffraction studies of the co-ordinated azide group. In the absence of such evidence any conclusions regarding the structure of that group must be deduced by analogy and considered to be rather speculative.

The azide ion in ionic crystals has been shown to be linear with the two N–N bonds of equal length. When this group is co-ordinated to a metal ion there ought to be some electron shift towards the positive charge on the metal so that a contribution from the form (I) would be expected in addition to the form (II). It is not possible at this stage, especially in the absence of any N–N bond-distance data, to assess the relative contributions of these two canonical forms to the actual structure but in both cases the three nitrogen atoms will be linear and the Co–N–N bond will be bent, the final angle being somewhere between 108° and 120°. Covalent azides, such as hydrazoic acid and the organic azides, have been shown to have such structures with a significant difference between the two N–N bond lengths.

(I)





(II)

There are no structural data in the literature for azide compounds containing some

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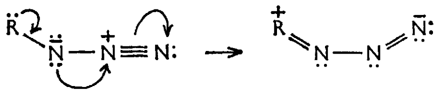
[15] Gray and Waddington, *Trans. Faraday Soc.*, 1957, **53**, 901.

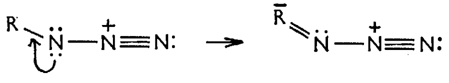
[16] Dows and Pimentel, *J. Chem. Phys.*, 1955, **23**, 1258.

[17] Eyster and Gillette, *J. Chem. Phys.*, 1940, **8**, 369.

[18] Evans, Yoffe, and Gray, *Chem. Revs.*, 1959, **59**, 515.

double-bond character in the bond joining the azide group to the rest of the molecule. In principle, two possible extreme structures can be visualised, one in which the electrons are displaced towards the azide group, and the other in which they are withdrawn from it:





At first sight, it would seem that the first structure might contribute to the bonding in azido-cobalt(III) complexes, where a pair of d_ϵ electrons from the cobalt ion might participate in back donation. However, a comparison of the σ- and π-bonded structures indicates that, as a result of the radically different bond angle requirements of the central nitrogen atom, there can be little, if any, mixing of the two canonical forms and the co-ordinated azide group must either by strongly double-bonded or else not double-bonded at all. The infrared and visible absorption spectra indicate quite definitely that there is no evidence for double-bonding in the ground state of these complexes and that the three nitrogen atoms are linear.

The wave-numbers of the asymmetric stretching of the azide group and of its bending mode cannot be used as criteria for assessing covalent character in the metal ligand bond, since differences in crystal structures of the proven ionic azides can cause shifts comparable to those due to covalent-bond formation. An increase in the multiplicity of the metal–ligand bond as a result of back donation from the cobalt to the nitrogen atom would lead to a decrease in the total multiplicity of the N–N bonds in the azide group and should lead to a very significant decrease of the frequencies of both the asymmetric stretching and the bending mode. This is not observed, nor is an absorption found that can be assigned to the symmetrical stretching mode which should be active in the infrared region if the N–N–N bonds are bent.

It is noteworthy that there is a splitting of the absorption band assigned to the asymmetric stretching of the azide group in the *cis*-diazidobis(ethylenediamine)cobalt(III) salts that does not appear in any of the other azido-complexes. A similar splitting has been observed for the *cis*-dinitrobis(ethylenediamine)cobalt(III) salts, where the 820 cm.$^{-1}$ band, assigned to the bending of the nitro-group, is split. This is said to be due to both the in-phase and the out-of-phase vibrations of the two *cis*-nitro-groups being active in the infrared region.[19]

The evidence from the visible absorption spectra is in accord with the conclusions drawn from the infrared spectra, although the interpretation is, by itself, less reliable. If we consider a complex ion of the type, *trans*-$[\text{Co en}_2\text{X}_2]^{n+}$, the cobalt ion can be looked upon as experiencing a tetragonally distorted cubic field. The distortion will be greatest when the effective field of the ligand X is most different from that of ethylenediamine. The longest-wavelength peak in the visible region corresponds to the lowest-energy *d–d* transition, and if the frequency of this transition is considered it is possible to obtain a crude spectrochemical series:

$$NO_2 > NH_3 > NCS > OH > OH_2 > N_3 > F > Cl > Br$$

This series reflects the effective field produced by the ligand. It will be seen that the azide group is considerably removed from the other ligands that have nitrogen as the donor atom. Many factors will influence the position of a ligand in the spectrochemical series, but two of the most important are expected to be (i) the polarisability of the lone pair of electrons forming the σ metal–ligand bond, and (ii) the capacity of the ligand as a whole to accept back donation from the metal in a π-bond. The presence of other lone pairs of electrons on the donor atom will decrease the effectiveness of the lone pair pointing

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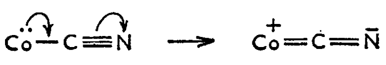
[19] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

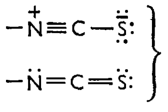
towards the cobalt atom, while the possibility of d_π–p_π back donation will increase the overall effective field strength, *e.g.*:

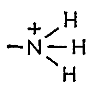
and

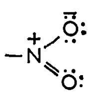


In both these cases the bond-angle requirements of the σ-bonded structure allow the appropriate overlap for the π bond and will allow some mixing to take place.

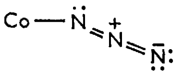
Considering the ligands of the above series where nitrogen is the donor atom, and omitting azide in the first instance, we find that NCS < NH_3 < NO_2 in terms of ligand field strength. The common structures written for these ligands are,



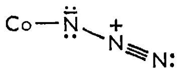




Neither NCS nor NH_3 has any easily accountable way of accepting back donation from the cobalt, whereas NO_2 has. Neither NO_2 nor NH_3 has an extra lone pair of electrons on the donor nitrogen atom whereas one of the canonical forms of the NCS ligand has. It remains to be seen to what extent mixing can occur between the two forms of thiocyanate because a fully covalent Co–N bond would lead to a Co–N–C bond angle of 180° in the first case and 120° in the second. The azide group seems to produce a lower effective field than any of the other ligands that have a nitrogen donor atom that have been considered. If we apply the above reasoning to the azide group, it would appear that there is at least one extra lone pair of electrons associated with the donor nitrogen, suggesting that the azido-



and



group, when co-ordinated to cobalt(III), is a mixture of the two canonical forms, but it is not possible to assess their relative contributions. There is no evidence for a significant contribution from a double-bonded form involving back donation from the cobalt to the nitrogen.

EXPERIMENTAL

Preparations.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) azide was precipitated from a cold aqueous solution of the chloride by adding the appropriate amount of sodium azide solution. The pale green precipitate was washed with water and left damp. The small specimen required for the infrared measurements was washed with alcohol and ether and dried in a desiccator.

cis-*Diazidobis*(*ethylenediamine*)*cobalt*(III) *nitrate*. Method 1. *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride (14·3 g.) was dissolved in water (30 ml.) and a solution of sodium azide (10 g.) in water (20 ml.) was added. A dull, pale green precipitate of the *trans*-dichloro-azide was formed, and the mixture was stirred and heated gently until all the precipitate had dissolved, yielding a deep purple solution. The hot solution was filtered and, on cooling, a dark purple crystalline solid crystallised. Examination showed this to be a 1 : 1 mixture of *cis*- and *trans*-diazidobis(ethylenediamine)cobalt(III) azides which retains its composition on recrystallisation. The mixture was separated into its components by dissolving it in the minimum amount of cold water and adding an excess of solid ammonium nitrate to the filtered solution. After a few minutes, deep red crystals of the *cis*-diazidobis(ethylenediamine)cobalt(III) nitrate were filtered off, washed with alcohol and ether, and dried ($CaCl_2$). After a few hours, the mother-liquor deposited a second crop of *cis*-nitrate which was also filtered off. The filtrate contained *trans*-diazidobis(ethylenediamine)cobalt(III) salts and served as the starting material for the preparation of the salts of the *trans*-series.

The *cis*-nitrate was recrystallised by adding solid ammonium nitrate to a saturated lukewarm aqueous solution of the crude salt.

Method 2. A mixture of ethylenediamine (5 g.) and water (2 ml.), partly neutralised with concentrated nitric acid (3 ml.), was added to a solution of cobalt(II) nitrate hexahydrate (11·5 g.) and sodium azide (6 g.) in water (50 ml.). Air was then bubbled through the solution, and after 30 min. the crop of deep red crystals was filtered off, washed with alcohol and ether, and dried over $CaCl_2$; the yield was 12·0 g. (95%). The spectrum of this compound is identical with that of all the proved *cis*-diazido-complexes.

cis-*Diazidobis(ethylenediamine)cobalt*(III) *perchlorate.* A filtered saturated solution of the *cis*-diazido-nitrate was treated with an excess of solid sodium perchlorate. After a short while, dark red crystals of *cis*-diazidobis(ethylenediamine)cobalt(III) perchlorate were filtered off, washed with alcohol and ether, and dried (P_2O_5). The *compound* was recrystallised by adding solid sodium perchlorate to its saturated aqueous solution (Found: N_3^-, 23·1. $[Co(C_2H_8N_2)_2(N_3)_2]ClO_4$ requires N_3, 23·2%). By the use of the appropriate sodium salt, the following salts were prepared: *iodide* (Found: N_3^-, 21·5; I^-, 31·6. $[Co(C_2H_8N_2)_2(N_3)_2]I$ requires N_3^-, 21·5; I^-, 31·6%); *bromide* (Found: N_3^-, 24·5; Br^-, 23·3. $[Co(C_2H_8N_2)_2(N_3)_2]Br$ requires N_3^-, 24·6; Br^-, 23·3%); *thiocyanate* {Found: N_3^-, 26·0; SCN^-, 18·2. $[Co(C_2H_8N_2)_2(N_3)_2](SCN)$ requires N_3^-, 26·2; SCN^-, 18·1%}; *dithionate* {Found: N_3^-, 24·6. $[Co(C_2H_8N_2)_2(N_3)_2]_2(S_2O_6)$ requires N_3^-, 24·6%}.

(+)-cis-*Diazidobis(ethylenediamine)cobalt*(III) *antimonyl-(+)-tartrate.* A cold saturated solution of *cis*-diazidobis(ethylenediamine)cobalt(III) bromide was mixed with a concentrated solution of potassium antimonyl-(+)-tartrate. Almost immediately, fine red crystals separated and were filtered off, washed with alcohol and ether, and dried. Measurement of the rotatory dispersion of an aqueous solution showed that it was, at least partially, resolved. The antimonyl (+)-tartrate was converted into the active perchlorate by adding perchloric acid to its aqueous solution and then precipitating the perchlorate with alcohol and ether. The perchlorate was converted into the bromide by adding solid sodium bromide to its aqueous solution, and the bromide was once again converted into the antimonyl (+)-tartrate. The rotatory-dispersion of this compound was found to be identical with that of the first crop, indicating that the *complex* had been fully resolved at the first attempt (Found: N_3^-, 15·3. $[Co(C_2H_8N_2)_2(N_3)_2]C_4H_4O_7Sb$ requires N_3^-, 15·3%).

trans-*Diazidobis(ethylenediamine)cobalt*(III) *perchlorate.* The filtrate from the precipitation of *cis*-diazidobis(ethylenediamine)cobalt(III) nitrate in the preparation starting from *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride was treated with solid sodium perchlorate. In a few minutes the impure *trans*-diazido-perchlorate was precipitated as brownish-purple crystals. These were filtered off and washed with alcohol and ether, and the *perchlorate* was purified by reprecipitating it four times from its saturated aqueous solution by adding solid sodium perchlorate. The crystals were dried (P_2O_5) (Found: N_3^-, 23·0. $[Co(C_2H_8N_2)_2(N_3)_2]ClO_4$ requires N_3^-, 23·2%). The corresponding *iodide* was prepared by treating a saturated solution of the foregoing perchlorate with solid sodium iodide. The brownish-purple crystals were filtered off, washed with alcohol and ether, dried, and purified by reprecipitation from aqueous solution with sodium iodide (Found: N_3^-, 21·5; I^-, 31·6. $[Co(C_2H_8N_2)_2(N_3)_2]I$ requires N_3^-, 21·5; I^-, 31·6%). The *thiocyanate* was prepared by an analogous method (Found: N_3^-, 26·1; SCN^-, 18·2. $[Co(C_2H_8N_2)_2(N_3)_2]SCN$ requires N_3^-, 26·2; SCN^-, 18·1%).

trans-*Chloroazidobis(ethylenediamine)cobalt*(III) *perchlorate.* *trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride (14·3 g.) was dissolved in water (30 ml.), and a solution of sodium azide (3·25 g.) in water (10 ml.) added. A dull, pale green precipitate of the *trans*-dichloro-azide was formed, and the mixture was stirred and heated gently until all this precipitate had redissolved to form a deep purple solution which was filtered while still hot. Solid sodium dithionate was added to the filtrate which was then rapidly cooled to 0° in ice and the walls of the beaker were scratched vigorously with a glass rod for 2—3 min. The resulting considerable purplish precipitate was filtered off; it consisted of *cis*- and *trans*-diazido-dithionates, unchanged *trans*-dichloro-dithionate, sodium dithionate, and *cis*-chloroazido-dithionate, but it was not possible to isolate useful amounts of the last salt. The filtrate was treated with concentrated perchloric acid (5 ml.), and after about 15 min. a bluish-green solid was filtered off and extracted with several small portions (5 ml.) of ice-cold water until the insoluble residue of *trans*-dichlorobis(ethylenediamine)cobalt(III) perchlorate was bright green. The combined extracts were treated with a large quantity of alcohol and ether, and a blue powder was precipitated and filtered off. The trans-*chloroazido-perchlorate* was purified by precipitating it from its aqueous solution with solid sodium perchlorate. The extreme lability of this complex makes it necessary for this procedure to be carried out as quickly as possible in ice-cold water. The compound was recrystallised in this way until its absorption spectrum was reproducible (Found: N_3^-, 11·7; total Cl, 10·0; ionic Cl^-, 0·0. $[Co(C_2H_8N_2)_2N_3Cl]ClO_4$ requires N_3^-, 11·8; total Cl, 10·0; ionic Cl^-, 0·0%).

trans-*Chloroazidobis(ethylenediamine)cobalt*(III) *thiocyanate.* A saturated solution of the foregoing perchlorate in cold water was treated with an excess of solid sodium thiocyanate and the walls of the vessel were scratched with a glass rod. After a few minutes, blue crystals of the *thiocyanate* were filtered off, washed with alcohol and ether, and dried (P_2O_5) (Found: N_3^-, 13·2; total Cl, 11·3; total SCN^- = ionic SCN^-, 18·6; ionic Cl^-, 0·0. $[Co(C_2H_8N_2)N_3Cl]SCN$ requires N_3^-, 13·4; Cl^-, 11·3; SCN^-, 18·4%).

cis-*Chloroazidobis(ethylenediamine)cobalt*(III) *dithionate.* *trans*-Dichlorobis(ethylenediamine)-cobalt(III) azide (30 g. of the damp compound) was stirred with water (25 ml.) and carefully heated until all the solid had dissolved to give a very deep purple solution that was filtered and treated with solid sodium fluoroborate (10 g.). A purplish-blue precipitate, containing unwanted diazido-, dichloro-, and *trans*-chloroazido-fluoroborates formed on cooling and was filtered off. The filtrate was ground with a large excess of powdered sodium dithionate, and a red precipitate containing *cis*-chloroazidobis(ethylenediamine)cobalt(III) dithionate and undissolved sodium dithionate was obtained. The sodium dithionate was removed by successive extractions with very small amounts of ice-cold water. The residual *dithionate* was washed with alcohol and ether and dried (P_2O_5) {Found: N_3^-, 12·5; total Cl, 10·5; ionic Cl^-, 0·0. $[Co(C_2H_8N_2)_2N_3Cl]_2(S_2O_6)$ requires N_3^-, 12·5; Cl, 10·5%}.

To obtain the corresponding *perchlorate*, the above dithionate was ground with concentrated perchloric acid for 3 min. until all the solid had dissolved. Alcohol and ether were added, and the precipitate was immediately washed with alcohol, ether, and light petroleum to prevent it from liquefying. The dried powder was dissolved in the minimum amount of water and the filtered solution was treated with solid sodium perchlorate. After several minutes, dark-red crystals of the perchlorate were filtered off, washed with alcohol and ether, and dried (P_2O_5) (Found: N_3^-, 11·8; total Cl, 10·0. $[Co(C_2H_8N_2)_2N_3Cl]ClO_4$ requires N_3^-, 11·8; total Cl, 10·0%).

The (+)-α-bromocamphor-π-sulphonate could not be prepared by adding ammonium (+)-α-bromocamphor-π-sulphonate to a solution of the racemic bromide and so the following procedure was adopted. A freshly prepared, damp specimen of *trans*-dichlorobis(ethylenediamine)-cobalt(III) azide (30 g.) was suspended in water and carefully heated until all the green solid had dissolved to form a deep purple solution. The hot solution was filtered on to solid ammonium (+)-α-bromocamphor-π-sulphonate (20 g.) and the solution was cooled. Crystallisation was induced by scratching for 2—3 min. and the pinkish-red crystals were filtered off, washed with alcohol and ether and dried (P_2O_5). Further batches of the salt were obtained from the mother-liquor and were similarly treated. The rotatory-dispersion of an aqueous solution of each batch was measured. Because of the fairly rapid mutarotation it was necessary to prepare a fresh solution for each wavelength. The rotatory-dispersion curves of each batch were the same within the wide limits of experimental error and the curves indicated that the complex ion was, at least, partially resolved. As it has not yet been possible to convert this salt into the perchlorate or to convert the perchlorate into the diastereoisomer, it is not possible to say whether the *complex* is fully resolved (Found: N_3^-, 7·4; Cl^-, 6·25. $[Co(C_2H_8N_2)_2N_3Cl]C_{10}H_{14}BrO_4S$ requires N_3^-, 7·4; Cl^-, 6·25%).

trans-*Aquoazidobis(ethylenediamine)cobalt*(III) *perchlorate.* *trans*-Chloroazidobis(ethylenediamine)cobalt(III) perchlorate (0·4 g.) was ground with a little cold water and a few drops of 0·1M-mercuric perchlorate solution until all the solid had dissolved to form a violet solution. This was filtered and passed down a column of Amberlite IRA-400 anion-exchange resin in the hydroxide form. The effluent contained only *trans*-hydroxoazidobis(ethylenediamine)cobalt-(III) hydroxide and was neutralised to pH 4 with dilute perchloric acid. An excess of solid lithium perchlorate was added and the solution was cooled. After about 10 minutes' scratching violet crystals of the trans-*aquoazido-perchlorate* were precipitated and were filtered off, washed with alcohol and ether and dried {Found: N_3^-, 9·7. $[Co(C_2H_8N_2)_2N_3,H_2O](ClO_4)_2$ requires N_3^-, 9·6%. Ionic and co-ordinated chloride were shown to be absent}. A solution of the perchlorate gave insoluble precipitates with sodium reineckate, potassium mercuri-iodide, and sodium tetraphenylborate.

cis-*Aquoazidobis(ethylenediamine)cobalt*(III) *perchlorate*. *cis*-Chloroazidobis(ethylenediamine)-cobalt(III) dithionate (0·25 g.) was ground with a little water and a few drops of 0·1M-mercuric perchlorate solution until all the solid had dissolved. The filtered solution was passed down a column of Amberlite IRA-400 anion-exchange resin (hydroxide form). All anionic species were replaced by hydroxide ions and the mercuric species were retained on the column as insoluble mercuric hydroxide. The effluent containing only *cis*-$[Co\ en_2N_3OH]OH$ was neutralised to pH 4 with dilute perchloric acid, and an aqueous solution of sodium tetraphenylborate was then added. A pink precipitate of *cis*-aquoazidobis(ethylenediamine)cobalt(III) tetraphenylborate was filtered off, washed with water, dried (P_2O_5) and then dissolved in a little ethanol. A saturated solution of lithium perchlorate in ethanol was added and the solution set aside for 5 min. Red crystals of cis-*aquoazidobis(ethylenediamine)cobalt*(III) *perchlorate* were filtered off, washed with alcohol and ether, and dried {Found: N_3^-, 9·5. $[Co(C_2H_8N_2)_2(N_3)_2H_2O](ClO_4)$ requires N_3^-, 9·6%}. An aqueous solution of this salt gave insoluble precipitates with potassium mercuri-iodide and sodium reineckate.

Analyses.—The halogens and thiocyanate were estimated by potentiometric titrations with silver nitrate solution by using a silver-wire electrode, an agar–potassium nitate salt bridge, and a calomel reference electrode. Azide ions could also be determined by this method provided the solution was buffered to pH 5 with acetic acid and sodium acetate. Ionic halide and " halogenoid " ions were determined by dissolving a sample of the complex in ice-cold water and then carrying out the titration as rapidly as possible. The total halogen or " halogenoid " content was determined by first breaking up the complex with alkali, acidifying it with a little acetic acid, and titrating the acidified solution. Prolonged treatment of the azido-complexes with alkali seemed to lead to low results for the analyses, possibly as a result of hydrolysis of the free azide ion. Such vigorous conditions, however, were not necessary for breaking up the complex.

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