595. *Triethylenetetramine Complexes of Cobalt*(III) *and Rhodium*(III).

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The preparation and characterisation of new complexes of triethylenetetramine with cobalt(III) and rhodium(III) are described. Spectral and other measurements are used to relate this series of complexes to the analogous bisethylenediamine compounds. Interconversions within the series and some stereochemical studies are also described.

TRIETHYLENETETRAMINE (trien) $(\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2)_2$ forms complexes with several metal ions. Selbin [1] surveyed the literature up to 1960 and since then dichlorotriethylenetetraminechromium(III) chloride has been prepared.[2] We have prepared the *cis*-dichloro-complex of rhodium(III) as well as some new cobalt(III) derivatives. The relation of the present work on the cobalt compounds to previous studies is outlined in the Chart. The major difference between the triethylenetetraminecobalt(III) and the similar bisethylenediaminecobalt(III) system of complexes is the instability of the *trans*-isomer in the former.

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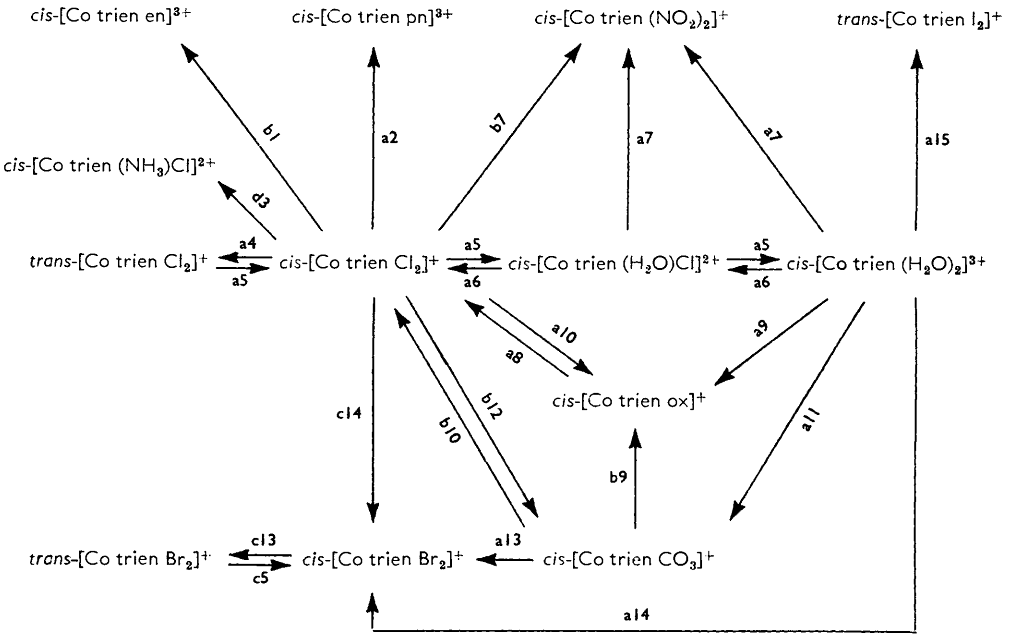
[1] Selbin, *J. Inorg. Nuclear Chem.*, 1961, **17**, 84.

[2] Kling and Schläfer, *Z. anorg. Chem.*, 1961, **313**, 187.



The cobalt(III)*-triethylenetetramine system*, [Co trien AB].

References: (a) This work; (b) Basolo, *J. Amer. Chem. Soc.*, 1948, **70**, 2634; (c) Bailar and Selbin, *J. Amer. Chem. Soc.*, 1955, **77**, 5480; (d) Pearson, Boston, and Basolo, *J. Phys. Chem.*, 1955, **59**, 304.

Reagents:
1, en.
2, pn.
3, NH_3.
4, Heat.
5, H_2O.
6, Cl^-.
7, NO_2^-.
8, NH_4 ox.
9, H_2 ox.
10, HCl.
11, CO_2.
12, Ag_2CO_3.
13, HBr.
14, Br^-.
15, I^-.

cis-*Dichlorotriethylenetetraminerhodium*(III) *Salts*.—The ion *cis*-[Rh trien Cl_2]$^+$ is formed by the prolonged interaction of the tetramine with the hexachlororhodate(III) ion in aqueous solution. It may be isolated as its yellow perchlorate which is diamagnetic in common with other compounds of rhodium(III). Although resolution of the complex has not been possible owing to the high solubilities of the diastereoisomers, a comparison of the electronic spectrum in aqueous solution (Table 1) and of the infrared spectrum (Table 2)

TABLE 1.

Absorption spectra (mμ) of rhodium complexes as perchlorate salts.

cis-[Rh en$_2$Cl$_2$]		*trans*-[Rh en$_2$Cl$_2$]		[Rh trien Cl$_2$]	
λ	ε	λ	ε	λ	ε
—	—	407	75	—	—
350	130	—	—	350	101
292	170	289	130	304	198
—	—	240	1510	—	—

TABLE 2.

Infrared spectra (cm.$^{-1}$) of dichlorotetramine-cobalt(III) and -rhodium(III) tetraphenylborate.

cis- [Co trien Cl$_2$]	1032	—	926	—	849
[Rh trien Cl$_2$]	1026	—	920	—	854
cis-[Rh en$_2$Cl$_2$]	1042	—	980	—	850
trans-[Rh en$_2$Cl$_2$]	1050	1021	—	868	850
trans-[Co trien Cl$_2$] *	1052	1004	—	—	841

* As chloride.

with corresponding spectra of analogous ethylenediaminerhodium or trien–cobalt complexes in the characteristic regions [3] shows that it is the *cis*-isomer.

Although nucleophilic displacement of the chloride in *cis*-[Rh trien Cl_2]$^+$ ion can occur rapidly on treatment with solutions of sodium borohydride, as will be discussed in a later paper, other nucleophilic displacements are exceedingly slow as is well known to be the case for other rhodium(III) compounds.[4] Thus, when the perchlorate solution is treated with oxalate ion under the conditions which, in the case of *cis*-[Co trien Cl_2]$^+$ cause displacement of both chloride ions by $C_2O_4^{2-}$, there is no reaction, as shown by the lack of change in the absorption spectrum and by isolation of the tetraphenylborate whose infrared spectrum was identical with that of the original complex. There is also no reaction between oxalate and the *cis*- or *trans*-[Rh en_2Cl_2]$^+$ ions; further, neither of these isomers nor *cis*-[Rh trien Cl_2]$^+$ reacts with nitrite ion or aquates readily. Addition of sodium tetraphenylborate to aged solutions of these species gives always the dichloro-compound, although traces of rhodium, probably as the aquo-species, can be detected in the filtrates.

trans-*Dichlorotriethylenetetraminecobalt*(III) *Chloride*.—The *trans*-[Co trien Cl_2]$^+$ ion has not previously been prepared although the bromo-analogue, which we have also obtained by a different procedure, has been made; [5] Jørgensen [6] mentioned that he would later discuss a blue *trans*-dichloro-isomer, but nothing further has appeared.

The acid mother-liquors from the preparation [7] of the complex *cis*-[Co trien Cl_2]$^+$, on evaporation to dryness at room temperature, deposit a greenish powder, which on being heated to 110° loses hydrogen chloride but remains green. The product gives incorrect analyses and its infrared spectrum shows bands found in both *cis*- and *trans*-dibromotriethylenetetraminecobalt(III) chloride. It thus appears to be a mixture of isomers contaminated with a triethylenetetrammonium salt of the tetrachlorocobaltate(II) ion. Some enrichment of the *trans*-isomer can be obtained by dissolution of the crude material in dimethylformamide and partial precipitation with dichloromethane. Extremely low yields can also be obtained by treating a dry methanolic suspension of the salt *cis*-[Co trien Cl_2]Cl with anhydrous hydrogen chloride; the methanol solution of the *cis*-isomer forms an equilibrium mixture of *cis*- and *trans*-isomers,[8] but evaporation of the solution gives crystals only of the pure *cis*-isomer. The hydrogen chloride treatment gives a green solution and slow evaporation in a vacuum deposits a mixture of green and purple crystals. The green crystals, separated manually, are instantly attacked by water to give *cis*-[Co trien (H_2O)Cl]$^{2+}$. However, their solution in dimethylformamide has a visible spectrum very similar indeed to that of a freshly made solution of *trans*-[Co en_2Cl_2]Cl in the same solvent. The colour of the solution of the trien compound does not change in a week, whereas the solution of the bisethylenediamine compound slowly becomes blue through formation of cobalt(II) tetrahedral complexes and a pale green solid deposits. The *trans*-dichlorotriethylenetetraminecobalt(III) chloride is best made simply by heating either moist *cis*-[Co trien Cl_2]Cl or *cis*-[Co trien (H_2O)Cl]Cl to 180°, whereupon the *trans*-compound is quantitatively and rapidly formed. With water this product gives an orange solution and in methanol an equilibrium (*ca.* 1 : 1) between the *cis*- and the *trans*-dichloro-compound is established. The compound is virtually insoluble in ethanol. Absorption spectra are given in Table 3. The infrared spectrum of the *trans*-compound is very similar to that of the *trans*-[Co trien Br_2]$^+$ ion.

Aquation of the cis-*Dichlorotriethylenetetraminecobalt*(III) *Ion*.—The kinetics of replacement [9] of chloride ion by water in the complex *cis*-[Co trien Cl_2]$^+$ indicated the presence of

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[3] Baldwin, *J.*, 1960, 4369.

[4] See, *e.g.*, Johnson, Thesis, Northwestern University, 1961, and Basolo and Pearson in *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 32.

[5] Bailar and Selbin, *J. Amer. Chem. Soc.*, 1960, **82**, 1524.

[6] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

[7] Basolo, *J. Amer. Chem. Soc.*, 1948, **70**, 2634.

[8] Sarma and Bailar, *J. Amer. Chem. Soc.*, 1955, **77**, 5480.

[9] Pearson, Boston, and Basolo, *J. Phys. Chem.*, 1955, **59**, 304.

TABLE 3.

Electronic spectra of complex cobalt(III) chlorides.

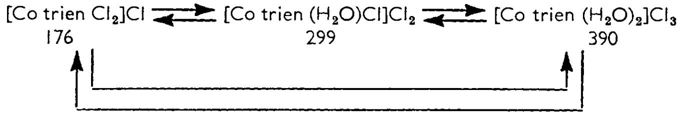
Complex	Solvent *	λ	log ε	λ	log ε	λ	log ε	λ	log ε
cis-[Co trien Cl_2]Cl	H_2O	620 †	2·01	540	2·31	384	2·31	242	4·1
	DMF	610 †	1·93	532	2·08				
cis-[Co en_2Cl_2]Cl	H_2O	605 ‡	1·7	540 ‡	2·0	390 §	1·89	240 §	4·28
	DMF	606	1·86	530	2·11				
trans-[Co trien Cl_2]Cl	DMF	615	1·56	454	1·53				
trans-[Co en_2Cl]Cl	DMF	615	1·76	452	1·42				
	H_2O ¶	625	1·54	450	1·40	385	1·64	252	4·31
cis-[Co trien $(H_2O)Cl$]Cl_2	H_2O			536	2·18	392	2·15		
cis-[Co $en_2(H_2O)Cl$]Cl_2 ...	H_2O			523 ‡	1·92	378	—		
trans-[Co $en_2(H_2O)Cl$]Cl_2	H_2O			523	2·03	390 †	—		
cis-[Co trien $(H_2O)_2$]Cl_3 ...	H_2O **			492	2·11	362	1·93		
cis-[Co $en_2(H_2O)_2$]Cl_3	H_2O ¶			495	1·90	360	1·81		
trans-[Co $en_2(H_2O)_2$]Cl_3 ...	H_2O ¶	540	1·54	440	1·58	340	1·74		

* DMF is dimethylformamide. † Observed as shoulder. ‡ Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476. § Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393. ¶ Bjerrum and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265. ** The spectrum recorded here was found for the compound prepared as described in the text, and for the compounds prepared by acid hydrolysis of both *cis*-dichlorotriencobalt(III) chloride and *cis*-chloroaquotriencobalt chloride.

an intermediate monoaquo-species. We have been able to isolate this and to show that on acid hydrolysis it forms the bisaquo-ion. On keeping *cis*-[Co trien Cl_2]Cl in aqueous solution containing a trace of hydrochloric acid at 65° for an hour, *cis*-[Co trien$(H_2O)Cl$]Cl_2 can be obtained as red-purple crystals from the cooled solution by addition of ethanol. Control experiments showed that even a large excess of ethanol does not affect either complex ion. When perchloric acid was added to the aged solution, only a small amount of unchanged starting material was precipitated as its perchlorate.

The monoaquo-ion was also obtained by fractionally crystallising a solution of the dichloro-compound in dilute hydrochloric acid at 25°. The first crops were pure dichloro-compound, but subsequent crops had the red tinge of the aquo-ion and finally pure *cis*-[Co trien $(H_2O)Cl$]Cl_2 was obtained.

The molar conductivities of the ions in aqueous solution (10^{-3}M) support the scheme (Λ in mhos):



The rather high value for [Co trien Cl_2]Cl is due to the rapid aquation. The same bisaquo-ion [Co trien $(H_2O)_2$]$^{3+}$ is obtained directly from the bis-chloride or from the intermediate chloro-aquo-ion, as shown by the identity of absorption spectra. The reactions are reversible and when solutions of the bisaquo- or monoaquo-chloride are concentrated either *in vacuo* at 5° or by evaporation at 100°, the sole product is *cis*-[Co trien Cl_2]Cl.

In contrast to the above behaviour of *cis*-[Co trien Cl_2]Cl, if the chloride ion is removed, for example as silver chloride, the cherry-red bisaquo-ion is formed readily. The salts of *cis*-[Co trien $(H_2O)_2$]$^{3+}$ are extremely soluble in water; the nitrate was obtained only as a red gum, while with bromide and iodide ion the substituted species *cis*-[Co trien X_2]$^+$ are rapidly formed. A small quantity of crystalline *cis*-[Co trien $(H_2O)_2$]$(ClO_4)_3$ was finally obtained after prolonged storage of a concentrated solution of the nitrate to which concentrated perchloric acid had been added. The bisaquo-ion can also be precipitated as the insoluble red-orange tetraphenylborate.

cis-*Oxalatotriethylenetetraminecobalt*(III) *Salts*.—The red ion *cis*-[Co trien ox]$^+$ has been obtained[7] by the action of oxalic acid on carbonatotriethylenetetraminecobalt(III) carbonate. We have obtained the ion by the interaction of *cis*-[Co trien Cl_2]Cl with ammonium oxalate, a method used by Werner[10] for the preparation of *cis*-[Co $en_2ox]^+$ ion where the *trans*-compound can also be used as a source because of the rapid *trans–cis*-isomerisation in hot water. In all these preparations some cobalt(II) oxalate is also formed.

The *cis*-oxalatotriethylenetetraminecobalt(III) chloride hydrate is extremely soluble in water and is very deliquescent; when heated with an excess of hydrochloric acid, it reverts to the *cis*-dichloro-compound (as does the analogous ethylenediamine complex[11]). The bromide is also very soluble but the iodide can be obtained as brick-red crystals. Other salts are readily obtained from this by trituration with the appropriate silver salt. Absorption spectra are given in Table 3. The infrared spectrum of the iodide (Experimental section) is similar to those of $[Co(NH_3)_4ox]Cl$,[12] and $K_3[Co\ ox_3]$;[13] the chloride shows additional water bands at *ca.* 3450 and 1600 cm.$^{-1}$.

Carbonatotriethylenetetraminecobalt(III) *Ion.*—The carbonate of the ion [Co trien $CO_3]^+$ has been obtained by several methods.[5,7,8] A much simpler preparation of this ion is to treat a solution of the nitrate [Co trien $(H_2O)_2](NO_3)_3$ with carbon dioxide until acid. Addition of sodium tetraphenylborate gives an orange precipitate which is not deliquescent.

cis-(*Propylenediamine*)*triethylenetetraminecobalt*(III) *Iodide.*—Cobalt(III) complexes containing different co-ordinated polyamines are uncommon. The salts of *cis*-[Co trien en]$^{3+}$ have been obtained[7] by refluxing *cis*-[Co trien Cl_2] salts with ethylenediamine in ethanol. The propylenediamine compound can be made similarly. The crude product was purified by dissolving it in water, running the solution through an alumina column, which removes any [Co trien $(H_2O)Cl]Cl_2$ (formed by traces of water) and unchanged dichloro-compound. Addition of potassium iodide to the resultant yellow-brown solution gave the complex iodide which can be crystallised from water. When *cis*-[Co trien pn]I_3 is treated with sodium sulphide [a valuable method of recovering polyamines from their complexes with cobalt(III)], the distillate contains a 1 : 1 mixture of the two bases.

Stereochemical Studies.—Optically active derivatives of the type [Co trien X_2] have been made[8] by treating the (±)-dichloro-compound with (+)-antimonyltartrate and converting the product through the *cis*-bisaquo-complex into the carbonato-complex. The latter with hydrogen chloride gave an optically active *cis*-dichloro-cation. We have confirmed these reactions and shown that the dichloro-complex, on treatment with nitrite ion, gives an optically active dinitrotriethylenetetraminecobalt(III) ion. We have shown[14] that (+)-[Co $en_2Cl_2]^+$ and (+)-[Co $en_2(NO_2)_2]^+$ ions have the same configuration; in view of the great similarity between corresponding *cis*-ethylenediamine and *cis*-triethylenetetraminecobalt-(III) systems, it appears that the reaction

$$(+)\text{-[Co trien Cl}_2]^+ + 2NO_2^- = (+)\text{-[Co trien (NO}_2)_2]^+ + 2Cl^-$$

goes with retention of configuration. It may be noted also that the *cis*-dinitro-compound, when treated with hydrochloric acid, undergoes a marked change in colour but we have been unable to isolate a chloro-nitro-complex ion.

EXPERIMENTAL

Analyses were by the Microanalytical Laboratory, Imperial College. Infrared spectra were taken on a Perkin-Elmer model 21 instrument with calcium fluoride and sodium chloride optics, electronic spectra on a Perkin-Elmer model 4000 spectrophotometer, and reflectance spectra of solids (with the reflectance attachment to the Unicam S.P. 500 spectrophotometer). Proton resonance spectra were taken at 56·43 Mc./sec. on a Varian V-4310 instrument. Optical rotations were measured by using a Schmidt and Haensch polarimeter with 40-cm. tube and Na_D radiation.

cis-*Dichlorotriethylenetetraminerhodium*(III) *Perchlorate.*—Sodium hexachlororhodate(III) (2·0

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[10] Werner, *Ber.*, 1912, **45**, 3281.
[11] Bushra and Johnson, *J.*, 1939, 1937.
[12] Nakamotor, Fujikta, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[13] Fujita, Nakamoto, and Kobayashi, *J. Phys. Chem.*, 1957, **61**, 1014.
[14] Gillard and Wilkinson, unpublished work.

g., 5×10^{-3} mole) in water (10 ml.) was treated with triethylenetetramine (0·75 g., 5×10^{-3} mole) freshly distilled from sodium. The red solution soon became yellow and was heated under reflux for 2 hr. After concentration nearly to dryness, ethanol (20 ml.) was added and the mixture cooled to 0°, whereupon sodium chloride (0·84 g., 95%) separated and was removed and washed with ethanol. The combined filtrate and washings were evaporated *in vacuo* at 40° and the gummy residue was treated with water (5 ml.) and 70% perchloric acid (2 ml.). After 2 days' refrigeration (*ca.* 10°) the yellow crystals of the *product* (1—3 g., 72%) were collected and dried in a vacuum-desiccator over silica gel (Found: C, 17·3; H, 4·5; N, 13·3. $C_6H_{18}Cl_3N_4O_4Rh$ requires C, 17·1; H, 4·3; N, 14·3%). The conductivity in water, Λ (10^{-3}M) = 117 mhos, supports the formulation as a 1 : 1 electrolyte. The compound has the strong perchlorate band at 1100 cm.$^{-1}$.

The yellow *tetraphenylborate* obtained by addition of a solution of sodium tetraphenylborate to the perchlorate solution can be crystallised from aqueous acetone. It has $\nu_{\text{max.}}$ 3201 1572 (N–H); 3013, 1962, 1894, 1836, 1758, 1426, 1389, 744 (BPh_4); 1182, 1152, and 719 cm.$^{-1}$; *cis*-[Co en_2Cl_2][BPh_4] has an almost identical spectrum. The tetraphenylborate in acetone has absorption bands at 349 and 304 mμ.

trans-*Dichlorotriethylenetetraminecobalt*(III) *Chloride.*—*cis*-Chloroaquotriethylenetetraminecobalt(III) chloride (1·65 g.) was heated on a flat dish at 180° until no further change in weight occurred. The residue is the pure trans-*chloride* (1·56 g.) (Found: C, 23·0; H, 5·9; N, 18·0. $C_6H_{18}Cl_3CoN_4$ requires C, 23·1; H, 5·8; N, 18·0%). The compound is quite deliquescent.

cis-*Chloroaquotriethylenetetraminecobalt*(III) *Chloride.*—A solution of *cis*-dichlorotriethylenetetraminecobalt(III) chloride [7] (1·56 g., 5×10^{-3} mole) in water (10 ml.) containing one drop of concentrated hydrochloric acid was kept at 65° for 1 hr., cooled rapidly, and treated slowly with ethanol (25 ml.). When the sides of the vessel were scratched, red-purple crystals of the *aquo-compound* separated (1·4 g., 85%). The salt was crystallised by dissolving it in water (8 ml.) and slowly adding ethanol (20 ml.); it was washed with ethanol and dried (Found: C, 21·7; H, 6·2; N, 17·4. $C_6H_{20}Cl_3CoN_4O$ requires C, 21·8; H, 6·0; N, 17·0%). Infrared maxima were at 3502, 3411sh (O–H str.); 3230, 3180, 3101 (N–H str.); 1635 (O–H def.); 1590, 1554 cm.$^{-1}$ (N–H def.). The reflectance spectrum had a maximum at 536 mμ (cf. value for *cis*-[Co trien Cl_2]Cl at 545 mμ).

Fractional Crystallisation of cis-*Dichlorotriethylenetetraminecobalt*(III) *Chloride.*—The compound (15·6 g., 5×10^{-2} mole) was dissolved in 2N-hydrochloric acid (100 ml.) at 65° and the solution set aside to crystallise at 25°. The progress of the crystallisation is set out in Table 4 where X = [Co trien Cl_2]Cl and Y = [Co trien (H_2O)Cl]Cl_2.

cis-*Diaquotriethylenetetraminecobalt*(III) *Tetraphenylborate.*—*cis*-Dichlorotriethylenetetraminecobalt(III) chloride (1·56 g., 5×10^{-3} mole) in water (10 ml.) was treated with a solution of silver nitrate (2·55 g., $1·5 \times 10^{-2}$ mole) in water (15 ml.). The mixture was digested on the steam-bath for 1 hr. The precipitated silver chloride (2·15 g.) was removed and the filtrate evaporated to dryness, leaving a gum. To an aliquot part in water was added a solution of sodium tetraphenylborate; a cherry-red precipitate of the *diaquo-compound* was obtained. It was collected, washed with ice–water, air-dried, and crystallised from water (Found: C, 79·5; H, 6·7; N, 4·3. $C_{78}H_{82}B_3CoN_4O_2$ requires C, 78·1; H, 6·9; N, 4·6%). The infrared spectrum showed strong bands at 3603 (O–H str.) and 1627 (O–H def.), 3247 and 3182 (N–H str.) and 1556 (N–H def.), with other bands due to (BPh_4). The reflectance spectrum had a maximum at 495 mμ. The dry solid decomposes under nitrogen during a week to leave a brown solid which contains much free phenol.

trans-*Dibromotriethylenetetraminecobalt*(III) *Bromide.*—While this salt has been prepared by Bailar and Selbin,[5] a much easier preparation is merely to treat *cis*-[Co trien $(H_2O)_2$]$^+$ with hydrobromic acid. On evaporation of the solution, the required compound is obtained as green needles whose properties are identical with those reported.

cis-*Oxalatotriethylenetetraminecobalt*(III) *Iodide.*—*cis*-Dichlorotriethylenetetraminecobalt(III) chloride (1·56 g., 5×10^{-3} mole) and ammonium oxalate (0·6 g., 5×10^{-3} mole) in water (25 ml.) were treated at 65° for 1 hr. The pink precipitate of cobalt(II) oxalate (0·08 g.) was removed and to the filtrate was added concentrated hydrochloric acid (3 ml.). After concentration to 5 ml., the solution was cooled and red crystals of deliquescent oxalatotriethylenetetraminecobalt(III) chloride hydrate (*ca.* 1·5 g., 70%) were collected. It was dissolved in water (3 ml.), and the solution was saturated with potassium iodide; after 1 hr., red-brown crystals of the *oxalato-compound* were obtained which were collected, washed with ice–water, and air-dried

TABLE 4.

Fractional crystallisation of *cis*-[Co trien Cl_2]Cl.

Time (days)	Crop (g.)	C	H	N	Cl	I.R. H_2O bands	
Calc. for $C_6H_{18}CoCl_3N_4$		23·13	5·84	17·98	34·14		*x*
Calc. for $C_6H_{20}CoCl_3ON_4$		21·86	6·12	17·00	32·09		*y*
0·5	5	23·0	5·7			None	*x*
1	1·2	23·0	5·6	18·1	34·3	None	*x*
2	3·8	—			33·0	Weak	$x + y$
3	1·8	21·8	5·9	17·0	32·2	Strong	*y*
4	0·3	21·6	6·1			,,	*y*
7	0·5	21·9	6·1			,,	*y*

(Found: C, 22·8; H, 4·3; I, 30·0. $C_8H_{18}ClIN_4O_4$ requires C, 22·85; H, 4·3; I, 30·2%). Infrared maxima (with assignments given in irreducible representation in C_{2v}) were: 1700 (ν_{CO}, b_1); 1678, 1658 (ν_{CO}, a_1); 1400 (ν_{CO}, a_1); 1262 (ν_{CO}, b_1); 878 (ν_{C-C}); 810 ($\nu_{asymm.\ O-C-O}$). The reflectance spectrum of the iodide showed a maximum at 498 mμ (cf. [Co en_2ox] 500 mμ) and an aqueous solution of the chloride had $\lambda_{max.}$ 501 (log ε 2·12) and 352 mμ (log ε 2·30), comparable with our new measurement of [Co en_2ox]Cl which had, in aqueous solution, $\lambda_{max.}$ 500 (log ε 2·05) and 352 (log ε 2·18).

Carbonatotriethylenetetraminecobalt(III) *Nitrate*.—An aqueous solution of diaquotriethylenetetraminecobalt(III) nitrate was treated at room temperature with solid carbon dioxide in small pieces until the solution was acid. Evaporation of the solution gave red crystals of the *carbonato-compound* (Found: C, 25·5; H, 5·6. $C_7H_{18}CoN_5O_6$ requires C, 25·69; H, 5·55%). The tetraphenylborate can be precipitated from solution as a pink solid; the infrared has bands at: 1030m (ν_1); 844m (ν_2); 1574s, 1261s (ν_3); 748 (ν_4); these can be assigned by comparison with the spectrum of $[Co(NH_3)_4CO_3]$;[12] and at 1605 (NH_2 asymm. def.) in addition to (BPh_4) bands.

Stereochemical Studies.—(−)-Dichlorotriethylenetetraminecobalt(III) chloride[8] (1·6 g., 5×10^{-3} mole) was treated with sodium nitrite (2 g.) in water (15 ml.). The mixture was warmed to 40°. After 3 min. the resultant orange solution had $[\alpha]_D^{20}$ about −50° when diluted to 0·1% and an absorption spectrum identical with that of authentic (±)-[Co trien $(NO_2)_2]^+$. Results of rotation measurements, $[\alpha]_D^{20}$, are as follows:

(−)-[Co trien(D-SbO-tart)$_2$] ⟶ (−)-[Co trien CO_3] ⟶
[0·1%, −118°, *ca.* −120°][8] [0·1%, −88°, −85°][8]
(−)-[Co trien Cl_2] ⟶ (−)[Co trien $(NO_2)_2$]
[0·05%, −85°, −90°][8] [0·1%, −50°]

Isomers of cis-*Dichlorotriethylenetetraminecobalt*(III) *Ion*.—The relative simplicity of the infrared spectrum of salts of *cis*-[Co trien Cl_2] in the N–H stretching region supports Basolo's tentative assignment[7] that the ion has the 1236 arrangement rather than the 1234 arrangement.

TABLE 5.

d-Spacings for *cis*-dichloro-(1,2,3,6)-tetraminecobalt(III) chlorides.

cis-[Co en_2Cl_2]	4·16	3·88	3·45	3·25	3·06	2·90	2·80	2·67
cis-[Co trien Cl_2] *	4·21	3·88	3·41	3·20		2·90	2·76	
cis-[Co en_2Cl_2]	2·61	2·53	2·457	2·355	2·277	2·212	2·160	
cis-[Co trien Cl_2] ...	2·61	2·55	2·451	2·344			2·155	
cis-[Co en_2Cl_2]	2·074	2·028	1·878	1·801	1·766	1·718	1·696	
cis-[Co trien Cl_2] ...	2·073				1·770		1·692	
cis-[Co en_2Cl_2]	1·624	1·577	1·524	1·292	1·272			
cis-[Co trien Cl_2] ...	1·623			1·293	1·277			

* The shorter exposure in this case led to some of the very weak reflections not being observed.

X-Ray powder photographs (Table 5) show that *cis*-[Co trien Cl_2]Cl and *cis*-[Co en_2Cl_2]Cl are isomorphous, suggesting that in the tetramine complex the nitrogen atoms are again 1,2,3,6.

Proton resonance studies at 40 Mc./sec. of ethylenediamine complexes[15] showed merely a

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[15] Powell and Sheppard, *J.*, 1959, 791.

rather broad hump, presumably because the rapid inversion of the chelate rings gives rise to effectively *cis*-conformation. Studies on several of the triethylenetetramine complexes in H_2O and D_2O gave similar broad peaks except for the case of *cis*-[Co trien Cl_2]Cl where two proton resonance peaks at 1·5 and 2 p.p.m. on the high-field side of water were observed. This suggests some fixing of the conformations of the chelate rings in this case since the virtually spherical symmetry of the cobalt(III) atom should not give rise to anisotropy in shielding.

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