The possibility that the discrepancies are primarily due instead to unexpectedly large atom polarizations seems unlikely for two reasons. First, with compounds, such as *p*-benzoquinone, which do have large atom polarizations, the sum A of the electronic and atom polarizations is essentially independent of solvent[16]; with 1,1-bis-(*p*-chlorophenyl)-cyclopropane, on the other hand, A is 18.4 cc. per mole greater in *p*-xylene than it is in tetrachloroethylene (Table IV). Second, the atom polarizations of several closely analogous compounds, such as *p*-bromophenyl ether, are evidently small since, with these substances, the sums of the atom plus orientation polarizations have been found to be of the order of only 10 cc. per mole.[17] For these reasons, the optical values will be accepted in preference to the temperature variation ones, and the dipole moment of 1,1-bis-(*p*-chlorophenyl)-cyclopropane will be taken as 2.02 ± 0.03 D.

The phenyl–carbon–phenyl angle, θ, may be calculated in the manner previously described[9] by Sutton and his co-workers. If it is assumed that the optical-solution value of the dipole moment of chlorobenzene[14] is 1.57 D, and that the cyclopropylidene–phenyl and phenyl–chlorine bond moments are in the same direction, the angle θ is found to be equal to 116 ± 10°. If it is instead assumed that these bond moments are in opposite directions, the angle is found to be 81 ± 10°. A value of θ which is almost 30° less than the normal tetrahedral angle is improbable. It is therefore considered that θ is equal to 116 ± 10°; this conclusion supports the value, 112 ± 4°, assigned by electron diffraction to the Cl–C–Cl angle[8] in 1,1-dichlorocyclopropane. (The limits of error cited above are based merely on the internal consistency of the optical measurements reported in this paper. The true limits of error, as in all analogous measurements of bond angles, must be somewhat greater when allowance is made for the uncertainty in the value of the atom polarization and in the moment of chlorobenzene, and for the possibility of variations in bond angles, in bond moments, and in the solvent effect.)

Acknowledgments.—The authors are indebted to Messrs. P. R. Bell, Jr.,[18] and P. Shevick[19] for the design and construction of the heterodyne beat apparatus, and to Mr. W. Saschek and Mr. D. E. Mann of this Laboratory for their aid and suggestions.

Summary

The dipole moments of 1,1-bis-(*p*-chlorophenyl)-cyclopropane and 1,1-diphenylcyclopropane have been measured.

The phenyl–carbon–phenyl angle in 1,1-diphenylcyclopropane has been estimated as 116 ± 10°.

CHICAGO, ILLINOIS RECEIVED MARCH 18, 1948

[16] *Cf.* Finn, Hampson and Sutton, *J. Chem. Soc.*, 1254 (1938); Hammick, Hampson and Jenkins, *ibid.*, 1263 (1938); Coop and Sutton, *ibid.*, 1269 (1938).

[17] Coop and Sutton, *J. Chem. Soc.*, 1869 (1938).

[18] Present address: Clinton Laboratories, Oak Ridge, Tenn.

[19] Nuclear Physics Institute, University of Chicago.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Quadridentate Amines. I. Some Coördination Compounds of Cobalt(III) and Triethylenetetramine[1]

BY FRED BASOLO

It was first shown by Mann[2] and later by Morgan and Burstall[3] that certain tetramines are capable of behaving as quadridentate donors to form complex inorganic compounds of cobalt(III). Mann[2] used β,β',β''-triaminotriethylamine and obtained *cis*-[Co tren$(SCN)_2$]SCN. Because of the structure of this amine, the corresponding *trans*-salt is sterically too unstable to exist. The amine used by Morgan and Burstall[3] was 2,2′,2″,2‴-tetrapyridyl and yielded *trans*-[Co tetrpyCl_2]Cl. They point out that the pyridine rings of the coördinated tetrapyridyl must remain in the same plane, and therefore the chloro groups must be in *trans*-positions. In both of these investigations the analyses of the resulting compounds agreed with those calculated for the respective compounds, but in neither case was any attempt made to establish conclusively the configuration of the complex cation.

More recently, Jonassen, Dexter and Douglas[4] have studied the complexes formed between triethylenetetramine and copper(II) and nickel(II) ions in water solution. They found that triethylenetetramine behaves as a quadridentate amine. The present work was undertaken to determine whether coördination compounds of triethylenetetramine and cobalt(III) can be isolated and also to study the configuration and stability of these compounds.

The dichlorotriethylenetetraminecobalt(III) ion can theoretically exist in three stereoisomeric forms

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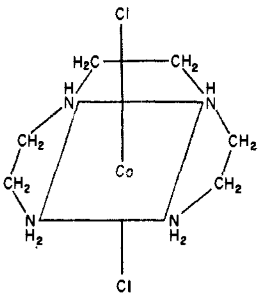
[1] Presented before the Physical and Inorganic Division at the 113th meeting of the American Chemical Society, Chicago, Ill., April 19–23, 1948.

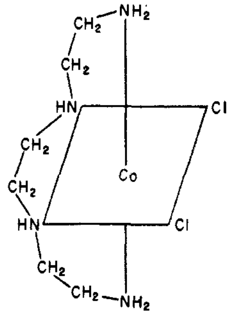
[2] Mann, *J. Chem. Soc.*, 409 (1929).

[3] Morgan and Burstall, *ibid.*, 1672 (1938).

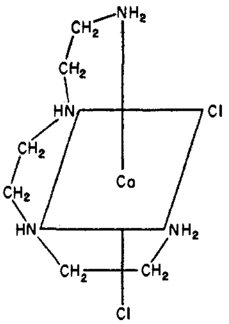
[4] Reported by Jonassen, Dexter and Douglas at the 112th meeting of the American Chemical Society.



I



II



III

The salt, [Co trien Cl_2]Cl, was prepared by the air oxidation of a reaction mixture containing cobalt(II) chloride and triethylenetetramine. This cation has been assigned a *cis*-configuration, II or III, because the salt obtained is purple, which is a characteristic color for *cis*-dichlorotetrammine compounds of cobalt(III) and chromium(III). Additional indication that the salt has the *cis*-configuration was obtained by comparing the ultraviolet absorption spectrum (Fig. 1) of this salt with those for the corresponding ethylenediamine salts, *cis*- and *trans*-[Co en_2 Cl_2]Cl. The ions II and III are asymmetric and an attempt was made to resolve the purple salt by the method[5] used for the corresponding complex, *cis*-[Co en_2 Cl_2]Cl, but this was not successful. It would be extremely difficult to distinguish between II and III and, since it does not appear important, this was not done.

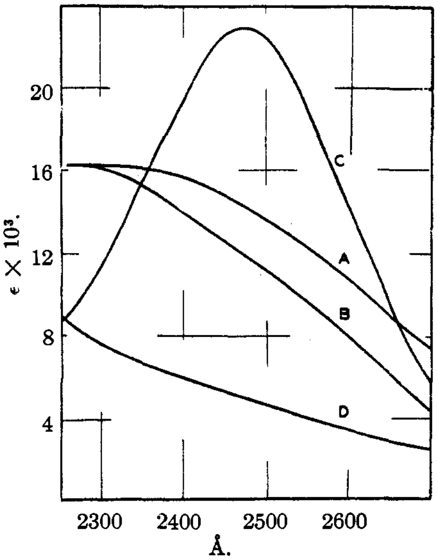


Fig. 1.—Absorption spectra of dichlorotetramminecobalt(III) chlorides: A, [Co trien Cl_2]Cl; B, *cis*-[Co en_2 Cl_2]Cl; C, *trans*-[Co en_2 Cl_2]Cl; D, unidentified mixture.

Although a study of molecular models indicates that I may exist, several attempts to prepare the *trans*-salt were unsuccessful. No rearrangement of the *cis*-salt occurred in concentrated hydrochloric acid, as is generally true of similar salts.[6] The reactions of both *cis* and *trans*-dinitrotetramminecobalt(III) chloride with triethylenetetramine in absolute alcohol gave the *cis*-salt [Co trien $(NO_2)_2$]Cl. This *cis*-configuration of this salt was indicated by its reaction with concentrated hydrochloric acid and by a comparison of its ultraviolet absorption spectrum (Fig. 2) with the spectra of the corresponding ethylenediamine salts, *cis* and *trans*-[Co en_2 $(NO_2)_2$]Cl, and also of the salt, [Co trien $(NO_2)_2$]Cl, obtained from the reaction of II or III with sodium nitrite. A third attempt was made by a slight modification of the method used by Morgan and Burstall[3] and a green product was obtained. This material dissolved in water to give an orange solution and did not have an absorption spectrum (Fig. 1) similar to that of the complex, *trans*-[Co en_2 Cl_2]Cl. The behavior of this unidentified substance suggests it may be a mixture of cobalt(II) chloride (blue)

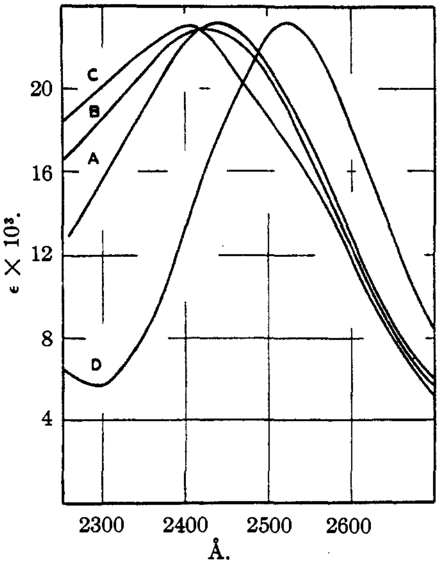


Fig. 2.—Absorption spectra of dinitrotetramminecobalt(III) chlorides: A, [Co trien $(NO_2)_2$]Cl obtained from *cis* or *trans* [Co $(NH_3)_4$ $(NO_2)_2$]Cl; B, [Co trien $(NO_2)_2$]Cl obtained from II or III; C, *cis*-[Co en_2 $(NO_2)_2$]Cl; D, *trans*-[Co en_2 $(NO_2)_2$]Cl.

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[5] Bailar, *Inorg. Syntheses*, **2**, 223 (1946).

[6] Jörgensen, *Z. anorg. Chem.*, **14**, 415 (1897).

and tris(triethylenetetramine) dicobalt(III) chloride (orange).

The fact that many inorganic complex compounds have been resolved is a good indication of the firmness with which the donor molecule is held or, in other words, of the stability of the coordination compound. The resolution of certain asymmetric complexes of cobalt(III) containing triethylenetetramine would conclusively show that the tetramine behaves as a strong quadridentate donor. Compounds similar to tris(ethylenediamine)cobalt(III) chloride were prepared and the method used by Werner[7] and also by Jaeger[8] for the resolution of this type of a cation was studied. These hexammine salts are all extremely soluble and could not be resolved by the methods employed. All of these salts, however, are highly crystalline and stable at temperatures as high as 150°.

The ultraviolet absorption spectrum obtained, particularly with the dinitrotetrammine series of compounds, is of interest. Shibata[9] showed that in addition to the two absorption bands always observed in the cobalt ammines, certain of these compounds have an additional absorption band in the shorter ultraviolet region which he designated as the "third band." A much more extensive study has been made by Tsuchida[10] who concludes that any two negative ligands, when in *trans*-positions to each other, cause a third absorption band at approximately 2500 Å., whereas if they occupy *cis*-positions, the third band is absent. Contrary to this, however, the ultraviolet absorption spectra (Fig. 2) obtained for some *cis*-dinitrotetrammine salts show very definite absorption bands at approximately 2425 Å. Although these results are not conclusive, they indicate that some cobalt(III) ammines with two negative ligands in the *cis*-positions also have additional absorption bands but in the shorter ultraviolet region. A more thorough investigation of this phenomenon is now in progress.

Experimental[11]

Reagents.—The cobalt(II) chloride hexahydrate was Merck reagent grade. The triethylenetetramine was obtained from Carbide and Carbon Chemicals Corporation. This amine was refluxed for six hours in presence of metallic sodium and then distilled *in vacuo* over sodium. The fraction collected had a boiling point range of 128–131° at 3 mm.

Spectral Measurements.—Ultraviolet absorption spectra were measured with the Beckman quartz spectrophotometer, using 1 cm. silica cells. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10}(I_0/I)$$

where I_0 is the intensity of the light passing through the solvent, I, the intensity of the light passing through the solution, c, the concentration of solute in moles per liter, and d, the thickness of the cell in centimeters.

Aqueous solutions (1.0×10^{-5} molar) of the complex salts were used and measurements were made at room temperature as rapidly as possible (total operation time less than twenty minutes) to keep the reaction of the complex with water at a minimum.

cis-Dichlorotriethylenetetraminecobalt(III) Chloride, (II) or (III).[12]—The procedure described by Bailar[5] for the preparation of *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride was slightly modified. A solution of 75 g. (0.50 mole) of triethylenetetramine in 525 cc. water was added, with stirring, to a solution of 160 g. (0.67 mole) of cobalt(II) chloride hexahydrate in 500 cc. of water contained in a two-liter flask. A vigorous stream of air, previously washed with a dilute solution of sodium hydroxide, was passed through the solution for approximately eleven hours. After 350 cc. of concentrated hydrochloric acid was added, the solution was concentrated on a steam-bath until finely divided crystals began to separate (650 cc.). Upon standing overnight at room temperature the bluish-purple crystalline product was collected on a filter and washed with a small amount of cold water followed by alcohol and ether. The salt was dried at 110° and 86 g. of material was obtained. Further concentration (400 cc.) of the combined filtrate and washings from this salt gave an additional 40 g. of product. This preparation was carried out six times and found to progress smoothly to give an over-all yield of 80% of crude dichlorotriethylenetetraminecobalt(III) chloride based on triethylenetetramine. The crude salt was recrystallized twice from dilute hydrochloric acid and dried at 110° for two days.

Anal. Calcd. for [Co trien Cl$_2$]Cl: C, 23.12; H, 5.82; N, 18.03; Co, 18.91; Cl, 34.13. Found: C, 23.42; H, 5.85; N, 18.18; Co, 18.68; Cl, 34.04.

The salt is purple in color, which is characteristic of the *cis*-dichlorotetrammine compounds of cobalt and chromium, indicating a *cis* configuration represented either by II or III. Additional indication for a *cis* structure was obtained from the fact that the ultraviolet spectrum (Fig. 1) of this salt closely resembles that of *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride.

The procedure described by Bailar[5] for the resolution of *cis*-[Co en$_2$ Cl$_2$]Cl was followed with *cis*-[Co trien Cl$_2$]Cl, but did not yield any crystals of the complex *dextro*-α-bromocamphor-π-sulfonate. The salt was obtained, however, by adding 15 cc. of a solution containing 9 g. (0.028 mole) of ammonium *dextro*-α-bromocamphor-π-sulfonate to 25 cc. of a solution containing 5 g. (0.016 mole) of *cis*-[Co trien Cl$_2$]Cl and immediately cooling the mixture in an ice–salt-bath. The crystals which separated were collected on a filter and washed with a very small amount of ice-water followed by alcohol and ether. A 0.32% solution of the air-dried crystals had a stable optical rotation of 0.18°, $[\alpha]^{25}_{\text{D}}$ +55.6. One gram of the salt was ground in an ice-cold mortar with 10 cc. of an ice-cold mixture (1:1:1) of concentrated hydrochloric acid, alcohol, and ether. The purple residue was then collected on a filter and washed with absolute alcohol and ether. A 0.25% solution of this substance was immediately prepared and found to have no optical activity at the D line of sodium.

An attempt was made to effect the rearrangement of *cis*-[Co trien Cl$_2$]Cl to the *trans* configuration by the method which Jörgensen[6] used for the preparation of *trans*-[Co (NH$_3$)$_4$ Cl$_2$]HSO$_4$. Five grams of the *cis*-dichloro complex, II or III, was dissolved in 25 cc. of concentrated sulfuric acid and the solution was allowed to stand six hours at room temperature. The solution was then surrounded by an ice–salt bath and 25 cc. of concentrated hydrochloric acid was added dropwise with vigorous stirring. After standing for three days the well-defined purple crystals, which separated from the dark purple solution, were collected on a sintered glass filter and washed with dilute sulfuric acid, cold water, alcohol and ether. There were no signs of the *cis* (purple) salt rearranging to

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[7] Werner, *Ber.*, **45**, 121 (1912).

[8] Jaeger, *Rec. trav. chim.*, **38**, 185 (1919).

[9] Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, **37**, 1–18 (1915).

[10] Tsuchida, *Bull. Chem. Soc. Japan*, **11**, 785 (1936).

[11] Carbon, hydrogen and nitrogen analyses by Miss Patricia Craig and Miss Margaret Hines.

[12] Preliminary preparation by Miss Ruth Slaton.

the *trans* (green) configuration. This salt was dried at 110° overnight.

Anal. Calcd. for [Co trien Cl_2]HSO_4: C, 19.00. Found: Cl, 19.21.

The method used by Morgan and Burstall[8] for the preparation of *trans*-dichloro-(2,2′,2″,2‴-tetrapyridyl)-cobalt(III) chloride was modified in another attempt to obtain I. A solution which contained 10 g. (0.042 mole) of cobalt(II) chloride hexahydrate and 6 g. (0.041 mole) of triethylenetetramine in 10 cc. of water was kept on a steam-bath under an atmosphere of nitrogen for four hours. At the end of this time an excess of alcohol and ether was added and the reddish-brown oil which separated was washed three times with absolute alcohol. This oil was finally dried in a vacuum over sulfuric acid; analysis of the brown residue for chlorine checked favorably with that calculated for the cobalt(II) complex, [Co trien $(H_2O)_2$]Cl_2.

Anal. Calcd. for [Co trien $(H_2O)_2$]Cl_2: Cl, 22.72. Found: Cl, 22.97.

Three grams of this residue, ground to a fine powder and suspended in 50 cc. of absolute ethyl alcohol, was treated with an excess of dry chlorine. Almost immediately the brown particles became a bright green. This product was collected on a filter, washed with absolute alcohol and dried at 110° for two days. The green product appeared to be a mixture of the hexammine cobalt(III) chloride and unchanged cobalt(II) chloride. This was indicated by the fact that it dissolved to give an orange colored solution and the analysis for chlorine was consistently high. The ultraviolet spectrum of the green material (Fig. 1) showed no signs of any *trans*-salt.

Diammine-(triethylenetetramine)-cobalt(III) Chloride.—A solution of 3.2 g. (0.022 mole) of triethylenetetramine in 25 cc. of absolute ethanol was added to 5 g. (0.017 mole) of finely ground *trans*-dichlorotetramminecobalt-(III) hydrogen sulfate. The flask was equipped with a reflux condenser fitted with a calcium oxide drying tube, and the mixture was allowed to reflux on the steam-bath for five days. Ammonia was liberated and even after refluxing for five days traces of ammonia could still be detected. The grayish-orange reaction mixture was collected on a filter and washed with absolute alcohol and ether. A portion of this material was added to cold water and a small amount of slightly soluble violet-red residue was removed on a filter leaving an orange filtrate. An excess of alcohol and ether was added to the filtrate, causing an orange precipitate to separate. This precipitate was collected on a filter and washed with alcohol and ether and then dried at 110°.

Anal. Calcd. for [Co trien $(NH_3)_2$]Cl_3: Cl, 30.78. Found: Cl, 30.93.

cis-Dinitrotriethylenetetraminecobalt(III) Chloride.—A solution of 2.9 g. (0.020 mole) of triethylenetetramine in 25 cc. of absolute ethanol was added to 5 g. (0.020 mole) of finely ground *trans*-dinitrotetramminecobalt-(III) chloride. The flask was equipped with a reflux condenser fitted with a calcium oxide drying tube, and the mixture was allowed to reflux on the steam-bath for two days. A small amount of ammonia was still being liberated at the end of this time and the reaction mixture had not changed noticeably in appearance. The orange residue, which gave a qualitative test for ammonia, was purified by recrystallization from water. The crystals were washed successively with a small amount of cold water, alcohol and ether, and dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co trien $(NO_2)_2$]$Cl \cdot H_2O$: C, 20.60; H, 5.76; N, 24.03; Cl, 10.14; Co, 16.85. Found: C, 20.64; H, 5.79; N, 24.18; Cl, 9.98; Co, 16.93.

The *cis* configuration of this dinitro salt was suggested by the fact that boiling it with concentrated hydrochloric acid liberated nitrogen dioxide and formed a red solution which quickly turned purple. This is a qualitative test commonly used to distinguish between *cis*- and *trans*-dinitrotetramminecobalt(III) salts, the *trans*-salt forming a red precipitate of the corresponding chloronitro complex. No such precipitate separated from the purple hydrochloric acid solution even after prolonged standing at room temperature. It was likewise found that the ultraviolet spectrum (Fig. 2) of this salt is similar to that obtained for *cis*-dinitro-bis-(ethylenediamine)cobalt(III) chloride.

The same results were obtained when the experiment was repeated starting with the corresponding *cis*-salt, [Co $(NH_3)_4$ $(NO_2)_2$]Cl.

Anal. Found: C, 20.72; H, 5.80; N, 24.21; Cl, 10.05; Co, 16.89.

cis-Dinitrotriethylenetetraminecobalt(III) chloride prepared from II or III was found to have properties similar to the salt obtained from the *cis*- or *trans*-dinitrotetrammine complex. Six grams (0.019 mole) of II or III was mixed with 20 g. (0.218 mole) of sodium nitrite and 40 cc. of water. This mixture was heated to boiling and then cooled in an ice-salt-bath. The orange crystals which separated were collected on a filter and washed with a small amount of cold water followed by alcohol and ether. The ultraviolet absorption spectrum (Fig. 2) of this salt and its reaction with concentrated hydrochloric acid indicate the presence of the ion, *cis*-[Co trien $(NO_2)_2$]$^+$.

Carbonatotriethylenetetraminecobalt(III) dextro-Camphor-π-sulfonate.—Forty grams (0.129 mole) of II or III and 61 g. (0.219 mole) of freshly precipitated moist silver carbonate were ground in a mortar for two hours. The mixture was extracted with 200 cc. of distilled water and analysis of the filtrate revealed that it was free of chloride ion and contained 30 g. (0.051 mole) of the carbonate complex. It was mixed with a solution of 0.051 mole of barium *dextro*-camphor-π-sulfonate and the barium carbonate was removed on a filter. A portion of the filtrate was slowly concentrated in a drying oven at 40°. Crystals of the complex *dextro*-camphor-π-sulfonate were not obtained because the salt is extremely water soluble.

Oxalatotriethylenetetraminecobalt(III) dextro-Camphor-π-sulfonate.—The second portion of the carbonatotriethylenetetraminecobalt(III) *dextro*-camphor-π-sulfonate solution was allowed to react with 4.6 g. (0.051 mole) of oxalic acid. Carbon dioxide was liberated and the resulting solution was concentrated to 150 cc. This concentrate was cooled in an ice-bath and the pink crystals which separated were collected, washed with a small amount of cold water followed by alcohol and ether and the ether was removed at room temperature by a stream of air. A 1% solution of air-dried salt was immediately prepared and found to have an optical rotation of +0.12°, $[\alpha]^{25}_{D}$ +12. The optical rotation of this solution had not changed after one week at 50°.

Two grams of this salt was also immediately ground, in an ice-cold mortar, with 30 cc. of an ice-cold mixture of concentrated hydrochloric acid, alcohol, and ether (1:1:1). After approximately ten minutes of constant grinding, the residue was collected on a filter and washed with cold alcohol and ether. A solution of a portion of this residue exhibited no optical activity at the D line of sodium. A major portion of the salt was dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co trien C_2O_4]Cl: Cl, 10.79. Found: Cl, 10.86.

Careful recrystallization of the oxalatotriethylenetetraminecobalt(III) *dextro*-camphor-π-sulfonate gave no indication of any separation of the optically active antipodes of the complex cation.

Ethylenediamine(triethylenetetramine)cobalt(III) Chloride.—Thirty grams (0.096 mole) of finely ground II or III, 12.8 g. (0.147 mole) of 69% ethylenediamine, and 500 cc. of absolute ethyl alcohol were placed in a three-necked round-bottomed flask containing some glass beads and equipped with an agitator and reflux condenser. The mixture was allowed to reflux with vigorous agitation for eight hours. The orange residue which formed was freed from any excess amine by washing with alcohol and ether. The theoretical yield of crude product was obtained and some of it was purified for analysis by recrystallization from water and drying at 110°.

Anal. Calcd. for [Co en trien]Cl$_3$: C, 25.84; H, 7.05; N, 22.64; Cl, 28.61; Co, 15.85. Found: C, 25.63; H, 6.98; N, 22.42; Cl, 28.57; Co, 15.93.

The salt can be purified more easily by conversion to the much less soluble iodide. Five grams (0.013 mole) of the salt in 20 cc. of water and 5 g. (0.033 mole) of sodium iodide in 10 cc. gave a crystalline iodide which was washed with cold water, recrystallized from 20 cc. of distilled water and dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co en trien]I$_3$: I, 58.92. Found: I, 58.67.

Attempts to resolve the ion, [Co en trien]$^{+++}$, from the bromide *dextro*-tartrate[7] and *dextro*-α-bromocamphor-π-sulfonate were not successful. The difficulty encountered was largely due to the extreme solubility of these salts.

Tetrakis-(ethylenediamine)-triethylenetetraminedicobalt(III) Chloride.—Thirty grams (0.105 mole) of finely ground *cis* or *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) chloride, 11.5 g. (0.079 mole) of triethylenetetramine, and 500 cc. of absolute alcohol were allowed to react as described for the preparation of [Co en trien]Cl$_3$. An orange residue was formed, in practically theoretical amount. It was recrystallized from water and dried at 110°.

Anal. Calcd. for [Co$_2$ en$_4$ trien]Cl$_6$: C, 23.43; H, 7.02; N, 23.46; Cl, 29.65; Co, 16.43. Found: C, 23.23; H, 6.89; N, 23.58; Cl, 29.43; Co, 16.35.

Preparation and purification of the much less soluble iodide was accomplished by the method outlined for the corresponding [Co en trien]I$_3$.

Anal. Calcd. for [Co$_2$ en$_4$ trien]I$_6$: I, 60.14. Found: I, 59.93.

The resolution of this ion, [Co$_2$ en$_4$ trien]$^{+6}$, was not accomplished using the bromide *dextro*-tartrate[7] and the *dextro*-α-bromocamphor-π-sulfonate.

tris-(Triethylenetetramine)-dicobalt(III) Chloride.—Twenty grams (0.064 mole) of finely ground II or III, 9.6 g. (0.065 mole) of triethylenetetramine, and 300 cc. of absolute ethyl alcohol were allowed to react as described for the preparation of [Co en trien]Cl$_3$. A portion of the orange product was recrystallized from water and dried at 110°.

Anal. Calcd. for [Co$_2$ trien$_3$]Cl$_6$: C, 28.09; H, 7.07; N, 21.87; Cl, 27.64; Co, 15.32. Found: C, 27.87; H, 6.97; N, 21.93; Cl, 27.39; Co, 15.47.

The complex iodide was obtained by the addition of a small excess of sodium iodide solution to a solution of the complex chloride. This slightly soluble iodide was purified by recrystallization from water and dried in a vacuum over sulfuric acid.

Anal. Calcd. for [Co$_2$ trien$_3$]I$_6$:, I, 58.92. Found: I, 58.67.

Again all efforts to resolve this ion, [Co$_2$ trien$_3$]$^{+6}$, from the bromide *dextro*-tartrate[7] and *dextro*-α-bromocamphor-π-sulfonate were without avail.

Summary

Salts of the following cations containing triethylenetetramine and cobalt(III) have been prepared and some of their properties are described: [Co trien Cl$_2$]$^+$, [Co trien (NO$_2$)$_2$]$^+$, [Co trien CO$_3$]$^+$, [Co trien C$_2$O$_4$]$^+$, [Co trien (NH$_3$)$_2$]$^{+3}$, [Co en trien]$^{+3}$, [Co$_2$ en$_4$ trien]$^{+6}$, and [Co$_2$ trien$_3$]$^{+6}$.

A *cis*-configuration seems to be indicated for the ions, [Co trien Cl$_2$]$^+$ and [Co trien (NO$_2$)$_2$]$^+$.

An absorption band was obtained at approximately 2425 Å. for several *cis*-dinitrotetramminecobalt(III) compounds and this same band was less clearly shown by the corresponding *cis*-dichloro compounds.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 20, 1948

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Determination of Position of Tracer Atom in a Molecule: Mass Spectra of Some Deuterated Hydrocarbons[1]

BY JOHN TURKEVICH,[2] LEWIS FRIEDMAN,[2] ERNEST SOLOMON AND FRANCES M. WRIGHTSON[3]

The problem of determining the position of a tracer atom in a complex molecule arose during the study of the mechanism of catalytic reduction of acetone to propane with deuterium. Since the mass spectrum of a molecule consists of fragment ions obtained by rupture of valence bonds it was thought that the relative abundance of appropriate ions would indicate the position of an isotopic atom. Thus C$_3$H$_7$D-1 should give among others, ions of mass 16 and 15.

$$H_3C{-}CH_2{-}CH_2D \longrightarrow C_2H_5 + \underset{16}{CH_2D^+} + E$$

$$C_2H_4D + \underset{15}{CH_3{}^+} + E$$

While C$_3$H$_7$D-2 should give no ions of mass 16.

$$CH_3{-}CH_2D{-}CH_3 \longrightarrow C_2H_4D + \underset{15}{CH_3{}^+} + E$$

The purpose of this study was to establish the validity of this approach and to study in general the changes in the mass spectrographic pattern of hydrocarbons produced by replacing some of the hydrogens with deuterium. With this in mind monodeuteromethane, tetradeuteromethane, monodeuteroethane, monodeuteropropane-1 and monodeuteropropane-2 were prepared and studied on two standard mass spectrographs, that of Nier and the one of the Consolidated Engineering Corporation.

A mass spectrometric study of dideuteroethylene has been made by Delfosse and Hipple.[4] More recently Evans, Bauer and Beach[5] have investigated the mass spectrum of monodeuteromethane and Mohler and Dibeler,[6] mono- and dideuteroacetylenes. These studies show that the

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[1] Presented at the meeting of the American Chemical Society in Atlantic City, April 15, 1947.

[2] Princeton University.

[3] M. W. Kellogg Co.

[4] J. Delfosse and J. A. Hipple, *Phys. Rev.*, **54**, 1060 (1938).

[5] M. Evans, N. Bauer and J. Y. Beach, *J. Chem. Phys.*, **14**, 701 (1946).

[6] F. L. Mohler and V. Dibeler, *Phys. Rev.*, **72**, 158A (1947).