CONTRIBUTION NO. 1935 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Transition Metal Complexes of Tetraethylenepentamine. I. Preparation, Properties, and Geometric Configuration of α- and β-Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II) and the α Chromium(III) Analog[1]

BY D. A. HOUSE AND CLIFFORD S. GARNER

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Two (α and β) of the four possible geometric isomers of [Co(tetren)Cl]$ZnCl_4$ have been isolated and characterized by infrared and visible absorption spectra. The β form has been resolved *via* the *d*-antimony(III) oxytartrate salt to give (−)-β-[Co(tetren)Cl]$ZnCl_4$; its optical rotatory dispersion curve suggests that the absolute configuration is L. The α form of [Cr(tetren)Cl]$ZnCl_4$ has also been prepared. The possible geometric configuration of the quinquedentate tetraethylenepentamine (tetren) ligand in these complexes is discussed in terms of spectral, optical activity, ring strain, and aquation and oxidation–reduction kinetics considerations. Evidence is presented that in the methods described for synthesis of α- and β-[Co(tetren)Cl]$ZnCl_4$ from commercial tetren containing ethylenediamine, diethylenetriamine, triethylenetetramine, tetren, and an isomeric pentamine, plus several higher polyamines, the ligand amine of the precipitated complex is exclusively tetren.

Several recent publications have discussed the occurrence of geometric and optical isomerism in diacidochromium(III)[2] and diacidocobalt(III)[3,4] complexes of the straight-chain quadridentate ligand, triethylenetetramine (trien).[5]

In this paper we report the occurrence of geometric and optical isomerism in complexes of the straight-chain quinquedentate ligand, tetraethylenepentamine. The chlorotetraethylenepentaminecobalt(III) cation, Co(tetren)Cl^{2+}, has been previously reported[6,7] only as poorly characterized materials admittedly mixtures, perhaps containing unknown geometric isomers of this ion or complexes with structural isomers of the ligand. Chromium(III) analogs have not been reported. We describe here the synthesis of [Co(tetren)Cl]$ZnCl_4$ in two isomeric forms by a variety of methods and the synthesis of [Cr(tetren)Cl]$ZnCl_4$ in one isomeric form. For the former, infrared and visible absorption spectra have enabled us to distinguish two different forms, α and β, which can be chemically readily interconverted and which correspond to two (probably I and II, respectively) of the four possible geometric isomers of the Co(tetren)Cl^{2+} ion (Figure 1). Comparison of the infrared spectra shows that the chromium(III) analog corresponds to the α cobalt(III) isomer. In addition, β-[Co(tetren)Cl]$ZnCl_4$ has been resolved *via* the *d*-antimony(III) oxytartrate salt to give (−)-β-[Co(tetren)Cl]$ZnCl_4$[8] and the optical rotatory dispersion (ORD) curve recorded.

Experimental Section

Commercial tetraethylenepentamine [Matheson Coleman and Bell, Practical, bp 165–175° (5 torr)] was used without purification. Anhydrous $CrCl_3$, *d*-$K(SbO)(C_4H_4O_6)\cdot 0.5H_2O$, and $VOSO_4\cdot 2H_2O$ were obtained from Riedel de Haën AG, Fisher Scientific Co., and Fairmount Chemical Co., respectively.

Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—Five different methods of synthesis were used which produced mixtures of the α and β isomers; one method each was developed for synthesis of these isomers in pure form from the isomeric mixtures. In methods A–E equimolar amounts of the starting cobalt salt and the amine (assuming the commercial amine to be 100% pure) were taken. Yields given are based on the weight of cobalt salt used and are probably low in part because the commercial tetren was later found to contain only about 20% tetren (*vide infra*). Methods A, B, and C were on a 0.1-mole scale and methods D and E on a 0.04-mole scale. The infrared spectrum of the recrystallized [Co(tetren)Cl]$ZnCl_4$ was examined for isomeric composition in each case.

Method A.—An aqueous solution of 24 g of $CoCl_2\cdot 6H_2O$ in 75 ml of water and 20 ml of 30% H_2O_2 was added dropwise over 20 min to a stirred solution of 19 g of tetren in 50 ml of water, with cooling in an ice bath. The mixture was then allowed to stand at room temperature for 30 min and then 75 ml of 12 *F* HCl and 30 g of $ZnCl_2$ were added. The solution was heated at 80–90° for 1–2 hr (maintaining the volume at about 200 ml with the addition of water) until the product commenced to crystallize. The crude product was collected by filtration from the cooled mixture, and the crystals were washed with 95% ethanol, then with methanol, and air dried. The rose-red product was recrystallized by dissolving it in the minimum amount of hot 0.1 *F* HCl (5 g/150 ml) and adding 20 ml of a 10% solution of $ZnCl_2$ in 12 *F* HCl. The crystals obtained from the cooled solution were washed and dried as above. The recrystallized material was a mixture of the α and β isomers, with the α isomer predominating; yield 15%.

If the oxidation is performed without cooling, the solution becomes hot and the pure α isomer is obtained.

Method B.—Tetren (19 g) was added to 24 g of $CoCl_2\cdot 6H_2O$ dissolved in 75 ml of water. While the solution was still warm,

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[1] Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P12-49 to the A.E.C.

[2] D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, **88**, 2156 (1966), and the references cited therein.

[3] E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120 (1966).

[4] E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1125 (1966).

[5] Abbreviations used: en = ethylenediamine, $H_2N(CH_2)_2NH_2$; dien = diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; trien = triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; tren = 2,2′,2″-triaminotriethylamine, $N[(CH_2)_2NH_2]_3$; tetren = tetraethylenepentamine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; pren = N,N′-bis(2-aminoethyl)-diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2N[(CH_2)_2NH_2]_2$.

[6] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[7] R. T. M. Fraser, *Proc. Chem. Soc.*, 262 (1963).

[8] The optical enantiomers are denoted by the sign of rotation at the Na D wavelength.

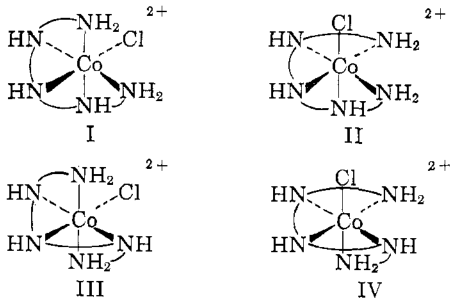

Figure 1.—Possible geometric isomers of $Co(tetren)Cl^{2+}$.

2.5 g of $NaClO_2$ was added in small portions[9] and the reaction mixture became hot as the oxidation proceeded. When all the $NaClO_2$ had dissolved, the solution was allowed to stand for 20 min and then the tetrachlorozincate(II) salt was obtained and recrystallized as in method A. The material was mainly the α isomer; yield 15%.

Method C.—Tetren (19 g) was added to 40 g of $Na_3[Co(NO_2)_6]$ dissolved in 100 ml of water, and the brown mixture was boiled gently under reflux for 8 hr.[10] Concentrated HCl (100 ml) was then cautiously added, followed by 30 g of $ZnCl_2$. The reaction mixture was heated at 80–90° for 3–5 hr until $[Co(tetren)Cl]ZnCl_4$, along with some NaCl, crystallized from the hot solution. The crystals were washed and recrystallized as in method A, giving mainly the β isomer; yield 15%.

Method D.—Tetren (8 g) was added to a suspension of 10 g of $Co(NH_3)_3(NO_2)_3$[11] in 50 ml of water.[6] The solution was heated on a steam bath for 60–80 min, until all the solid had reacted and the color was a clear yellow. The solution was then boiled for 10 min, and 25 ml of 12 *F* HCl and 15 g of $ZnCl_2$ were added. The $[Co(tetren)Cl]ZnCl_4$ was obtained as in C and in this case was an approximately equimolar mixture of the α and β isomers; yield 15%.

Method E.—Tetren (12 g) was added to an aqueous suspension of 20 g of $Na_3[Co(CO_3)_3]\cdot 3H_2O$[12] in 50 ml of water. A clear orange solution formed on heating for 10 min. Concentrated HCl (40 ml) and $ZnCl_2$ (20 g) were cautiously added and $[Co(tetren)Cl]ZnCl_4$ was obtained and recrystallized as in method A. The product was the α and β isomers in approximately equal amounts; yield 15%.

Method F (Pure β Isomer).—Pure β-$[Co(tetren)Cl]ZnCl_4$ was obtained from any of the above isomeric mixtures *via* β-$[Co(tetren)NO_2]ZnCl_4$, as follows.

One gram of β-$[Co(tetren)NO_2]ZnCl_4$ (see below for preparation) was warmed at 80–90° with 15 ml of 10% $ZnCl_2$ in 12 *F* HCl. Pure β-$[Co(tetren)Cl]ZnCl_4$ crystallized from the hot solution, then was washed as in method A; yield 80–90% from the isomeric mixture.

Method G (Pure α Isomer).—Pure α-$[Co(tetren)Cl]ZnCl_4$ was obtained from any of the above isomeric mixtures by base hydrolysis, as follows.

One gram of $[Co(tetren)Cl]ZnCl_4$ was dissolved in 20 ml of 2 *F* NaOH and heated 10 min at 80° until hydrolytic removal of the chloro ligand was essentially complete. The pure α isomer was obtained by adding 15 ml of 10% $ZnCl_2$ in 12 *F* HCl to the orange α-$Co(tetren)OH^{2+}$ and heating at 80° for *ca.* 30 min until crystals formed, which were washed as in method A.

Anal. Calcd for $[Co(tetren)Cl]ZnCl_4$: C, 19.57; H, 4.72; N, 14.26; Co, 12.0; Cl, 36.1. Found, α isomer (method G): C, 19.57; H, 4.80; N, 14.40; Co, 12.0; Cl, 36.0. Found, β isomer (method F): C, 19.60; H, 4.66; N, 14.30; Co, 12.1; Cl, 36.2.

β-Nitrotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—An isomeric mixture of 2 g of $[Co(tetren)Cl]ZnCl_4$ was dissolved in 50 ml of 0.2 *F* HCl and 8 g of $NaNO_2$ added. The solution was heated at 80° for 30 min. Mild effervescence occurred and the color changed from red to bright yellow. After addition of 2 g of $ZnCl_2$, the solution was cooled and 150–200 ml of a 1:1 mixture of methanol and 2-propanol was added. Small yellow crystals of β-$[Co(tetren)NO_2]ZnCl_4$ were precipitated and, after filtration, were washed with methanol. The product was recrystallized from 100 ml of 0.2 *F* HCl containing 5 g of $ZnCl_2$ by addition of 300 ml of a 1:1 mixture of methanol and 2-propanol.

Anal. Calcd for $[Co(tetren)NO_2]ZnCl_4$: C, 19.24; H, 4.64; Co, 11.8; Cl, 28.4. Found: C, 19.24; H, 4.88; Co, 11.7; Cl, 28.4.

Selbin[10] has prepared and described other salts of this cation. The properties of the above material and other acidotetren cobalt(III) complexes will be described in detail in a future publication.

(−)-β-Chlorotetraethylenepentaminecobalt(III) *d*-Antimony(III) Oxytartrate.—Three grams of β-$[Co(tetren)Cl]ZnCl_4$ was dissolved in 100 ml of 60° 0.1 *F* HCl and 10 g of solid *d*-$K(SbO)C_4H_4O_6\cdot 0.5H_2O$ was stirred in. After 5 min at 70° the insoluble material was removed by filtration and the filtrate left overnight at room temperature. The well-formed rose-red rod-shaped crystals that were deposited were collected and washed once with ice water and then with methanol; yield 2.5 g.

Anal. Calcd for $[Co(tetren)Cl][(SbO)C_4H_4O_6]_2$: C, 22.5; H, 3.7; Co, 6.89; Cl, 4.12. Found: C, 22.9; H, 3.8; Co, 7.00; Cl, 4.32.

(−)-β-Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—The antimony(III) oxytartrate salt (1 g) from the above synthesis was warmed with 12 *F* HCl until it dissolved, then 2 g of $ZnCl_2$ was added to the red solution. The product crystallized spontaneously and was collected from the cooled solution and washed with methanol. The substance was characterized by its visible absorption and infrared spectra and by its optical activity.

Partially Resolved (+)-β-Chlorotetraethylenepentaminecobalt(III) Tetrachlorozincate(II).—The filtrate from the synthesis of the optically active antimony(III) oxytartrate salt was heated with 10 g of $ZnCl_2$ and 50 ml of 12 *F* HCl until crystallization commenced. The product was collected from the cooled solution, washed with methanol, and characterized by the visible absorption and infrared spectra. Comparison of the ORD curve with that of the pure (−) isomer showed the (+) product to be 49% optically pure.

The α-$[Co(tetren)Cl]ZnCl_4$ could not be resolved under similar conditions.

α-Chlorotetraethylenepentaminechromium(III) Tetrachlorozincate(II).—Anhydrous $CrCl_3$ (10 g) and tetren (14 g) were mixed in 150–200 ml of anhydrous methanol and 50 mg of Zn powder was added as a reducing catalyst. Reaction was initiated by gentle warming and then allowed to proceed spontaneously for 5 min. The hot solution was filtered through a 1-cm bed of Celite and then concentrated by evaporation in an air stream. The pink crystals of the chloride salt that separated (*ca.* 3.5 g) were dissolved in 12 *F* HCl (30 ml) and poured into a solution of $ZnCl_2$ (10 g) in methanol (300 ml) containing a few drops of 12 *F* HCl. The orange-red crystals were washed with methanol and air dried; yield 15%.

Anal. Calcd for $[Cr(tetren)Cl]ZnCl_4$: C, 27.63; H, 6.67; Cr, 15.0; Cl, 30.6. Found: C, 27.63; H, 6.66; Cr, 14.9; Cl, 30.7.

Amine Characterization.—Elemental analysis indicates an empirical formula $MC_8H_{23}N_5ZnCl_5$ (M = Co, Cr) for the tetrachlorozincate(II) complexes isolated and the visible absorption spectra support a MN_5Cl chromophore (Table II). However, in view of the low yields of the cobalt(III) complexes obtained in methods A–E, the commercial amine was checked for purity using an Aerograph gas chromatograph, Model A-90-P.

With a 50-cm silicone rubber column at 225°, at least eight species were detected. The first four compounds to come through the column were lower polyamines (5% en plus dien and

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[9] See P. Spacu, C. Gheorghiu, M. Brezianu, and S. Popescu, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **3**, 127 (1958), for the use of $NaClO_2$ in other Co(II) oxidations.

[10] J. Selbin, *J. Inorg. Nucl. Chem.*, **17**, 84 (1961); the procedure was used in the preparation of $Co(tetren)NO_2^{2+}$.

[11] Prepared according to G. Schlessinger, *Inorg. Syn.*, **6**, 189 (1960).

[12] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

10% trien plus tren, positions checked using commercially available amines), followed by pentamine (20% tetren, 30% pren) and then two higher polyamines (30%). Aqueous and ethereal solutions of the commercial tetren (10% amine) also gave the same chromatographic pattern of products, except that the en and dien bands were obscured by the strong solvent water band.

Because the commercial amine used in the above syntheses was a complex mixture of amines, one needs to distinguish among three possible alternatives for the structure of the α and β cobalt isomers; namely, the two forms are: (a) geometric isomers of a tetren complex, (b) geometric isomers of a pren complex, or (c) one isomer of a tetren complex and one isomer of a pren complex.

Methods F and G outlined for the conversion of mixtures to the pure α and β isomer show that the α and β forms can be readily chemically interconverted, which effectively rules out possibility (c). To decide between alternatives (a) and (b) the structure of the amine coordinated to the cobalt(III) was investigated. Samples of α- and β-[Co(tetren)Cl]ZnCl$_4$ (0.5 g) were dissolved in 20 ml of water containing 2 g of KCN and heated on a steam bath for 15 min until the solutions became yellow. Saturated KOH (25 ml) was added, and the solution was cooled and extracted with ether or CCl$_4$.

The CCl$_4$ extract was dried with Na$_2$SO$_4$ and the nuclear magnetic resonance proton spectrum taken, giving a spectrum with the CH protons to the NH protons in a ratio of about 16:8 (theory for tetren or pren is 16:7), but the NH and NH$_2$ protons could not be differentiated.

Gas chromatography of the ether extract showed only one sharp amine band which corresponded to the first portion of the broad tetren–pren band appearing after the trien plus tren band in chromatography of the commercial tetren. Assuming that tetren will pass through the column faster than the branched-chain isomer pren (a supposition supported by the fact that trien appears before tren in chromatography of the commercial trien), then the pentamine obtained from the cobalt(III) complex is indeed tetren.

Kinetic Measurements.—Vanadium(II) solutions were prepared by dissolving VOSO$_4$·2H$_2$O in 0.5 *F* H$_2$SO$_4$ under a H$_2$ atmosphere and reducing with 2% amalgamated zinc prepared by the method of Schlessinger.[13] Rates of reduction were measured spectrophotometrically at 480 mμ and the concentrations were chosen such that the cobalt(III) complex was always in excess.

The cobalt(III) complex was dissolved in O$_2$-free 1 *F* HClO$_4$ or H$_2$O at 25° in a 10.00-cm quartz cell and V(II) solution was added with a syringe. The cell was then filled with O$_2$-free 1 *F* HClO$_4$ or H$_2$O, shaken, and placed in the spectrophotometer cell compartment thermostated at 25°. From the initial and final optical absorbancies, the initial and final Co(tetren)Cl^{2+} concentrations could be calculated; the initial V(II) concentration was assumed to be the difference between these two (the absorbancies of Co(II) and V(III) formed are negligible here). From these values and the values of the absorbancy measured at intermediate time intervals, the rate constants for the reduction were calculated using the method of Sebera and Taube.[14]

Spectral Measurements.—The visible absorption spectra and spectra used in the cobalt analyses and vanadium(II) reduction kinetic runs were obtained with a Cary Model 15 recording spectrophotometer. Data for the molar absorbancy indices were obtained in 0.1 *F* HClO$_4$ at 20–25° using matched 10.00-cm quartz cells with the reference cell filled with water. A Beckman DU spectrophotometer was used for the chromium analyses. The infrared spectra were determined in KBr disks using a Perkin-Elmer Model 421 spectrophotometer. The ORD spectra were recorded in 0.1 *F* HClO$_4$ with a Cary Model 60 spectropolarimeter, using a 10.00-cm quartz cell.

Chemical Analyses.—Chromium, chlorine, carbon, and hydrogen were determined as described previously.[2] The complex cobalt cations were decomposed by boiling in peroxydisulfate solution. Cobalt was determined spectrophotometrically by adapting the method of Zvenigorodskaya[15–17] and measuring the optical absorbancy of the cobalt thiocyanate complex at 620 mμ in aqueous acetone.

Results

Properties of the Complexes.—The tetrachlorozincate(II) salts of the cobalt(III) and chromium(III) chlorotetraethylenepentamine complexes are readily soluble in water and dilute acid to give red and orange solutions, respectively, but are only sparingly soluble in 12 *F* HCl and insoluble in the lower aliphatic alcohols. The coordinated chloride is only very slowly aquated from the cobalt(III) complex in dilute aqueous acid at 25°, but base hydrolysis is rapid. The chromium(III) complex appears from spectral evidence to undergo slow decomposition (rupture of Cr–N bonds) in acid solution which complicates chloride aquation studies. Further acidotetraethylenepentaminecobalt(III) and chromium(III) salts, derived from these chloro complexes, will be described in a later paper, as will aquation kinetic studies of these complexes.

Spectra.—Infrared frequencies of α- and β-[Co(tetren)Cl]ZnCl$_4$ and the α chromium(III) analog are given in Table I. Maxima and minima in the visible absorption spectra of the M(tetren)Cl^{2+} (M = Co, Cr) cations, together with those reported for the analogous chloropentaammine complexes, are given in Table II. The previously unreported visible absorption spectra of the α- and β-Co(tetren)Cl^{2+} and α-Cr(tetren)Cl^{2+} and the ORD curve of (–)-β-Co(tetren)Cl^{2+} are shown in Figure 2.

Kinetics.—The rate constants for the reduction of α- and β-Co(tetren)Cl^{2+} with vanadium(II) at 25° are given in Table III. Our rate plots gave good second-order kinetics to at least 50–80% reaction.

Discussion

Spectra.—The most noticeable differences in the infrared spectra of α- and β-[Co(tetren)Cl]ZnCl$_4$ (Table I) are the presence of a single band at 1565 cm^{-1} (NH$_2$ bending) for the α isomer, which band is split into two bands at 1589 and 1560 cm^{-1} in the β isomer, and the presence of four sharp bands in the region of 3200 cm^{-1} (N–H stretching) in the α isomer, which appear in the β isomer as one sharp band plus a broad band having shoulders. The existence of two bands at 1111 and 1123 cm^{-1} for the β isomer (absent in the spectrum of the α isomer), the presence of a band at 590 cm^{-1} in the α form (absent in the β form), as well as other smaller differences further permit differentiation between these two isomers. These differences (which are much more obvious from the actual spectra than from the data tabulated), especially the splitting of the 1565 cm^{-1} band in the β isomer, serve to detect the presence of isomeric mixtures in any

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(13) G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 202.

(14) D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).

(15) V. M. Zvenigorodskaya, *Zavodskaya Lab.*, **7**, 1350 (1938); *Chem. Abstr.*, **33**, 4900 (1939).

(16) V. M. Zvenigorodskaya, *ibid.*, **11**, 1022 (1945); *Chem. Abstr.*, **40**, 7052 (1946).

(17) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, 3rd ed, D. Van Nostrand Co., Princeton, N. J., 1949, p 362.

TABLE I

INFRARED FREQUENCIES[a] (CM^{-1}) OF α-[Cr(tetren)Cl]ZnCl$_4$, α-[Co(tetren)Cl]ZnCl$_4$, AND β-[Co(tetren)Cl]ZnCl$_4$ (KBr DISK)

α-Cr	α-Co	β-Co	α-Cr	α-Co	β-Co
			1173 m	1183 m	1188 m
		3270 sh		1159 s	1165 w
3260 s	3255 s	3250 sh			1150 m
3215 s	3215 s	3230 s	1143 s		1143 m
3175 s	3165 s	3180 s	1120 m		1123 m
3125 s	3130 s	3135 s			1111 m
		3110 m			1098 w
	3000 w			1082 w, sh	1086 s
2995 w	2995 w	2995 w	1078 m	1070 s	1068 s
2980 w	2960 w	2975 m	1060 s	1064 w, sh	
2935 w	2935 w	2920 w	1050 s	1043 s	1048 s
2880 w	2875 w	2885 w		1032 m	1037 m
		1589 m	1027 s	1027 m	1024 w
1555 s	1565 s	1560 s		1015 w, sh	1010 m
1473 m	1487 m	1482 m	1004 s	1000 m	1000 m
1462 m	1465 m	1470 m	990 w		
1450 w, sh	1450 m	1450 sh	957 m	976 m	970 m
1444 m	1441 w	1444 m	915 w	920 w	925 w
		1437 m	898 m	905 w	892 w
1428 m	1425 m	1428 w	868 w	873 w	884 m
1405 m	1401 m	1411 s	859 m	864 m	864 m
1393 w				831 m	846 s
1388 w	1385 m	1388 w	822 m	823 m	
1372 w	1372 w	1373 w	813 m		
1360 m	1361 m	1364 m			788 m
1347 m	1342 m	1346 s	768 m	773 m	771 w
1325 m	1323 m	1321 w		724 m	723 m
1313 m	1313 w	1313 w		695 m	
1305 m	1301 w	1304 m	673 s	669 m	673 m
1284 m	1281 m	1288 w	640 m		638 m
		1277 m	620 m	620 w	
	1266 w	1268 w		590 m	
1251 m	1247 m	1255 m			570 m
1235 w	1232 w	1228 m	560 m, br		560 w
1208 m	1209 m	1198 w			

[a] Estimated intensities: s, strong; m, medium; w, weak; br, broad; sh, shoulder; doublets are bracketed; pairing of Cr with Co frequencies is somewhat arbitrary, since former are often displaced to smaller wavenumbers by *ca.* 15–50 cm^{-1}.

particular preparation. The spectra of synthetic mixtures of the pure isomers show that from the infrared spectrum it is possible to detect 5–10% of one isomer in the presence of the other.

The infrared spectrum of [Cr(tetren)Cl]ZnCl$_4$ is very similar to that of α-[Co(tetren)Cl]ZnCl$_4$, and on this basis the former is assigned to the α configuration. The visible absorption spectra (Figure 2) of the α and β cobalt(III) isomers (synthesized using methods G and F, respectively, and isomerically pure according to the infrared spectra) differ in the band intensities and intensity ratios as well as in the degree of splitting of the 480–520 mμ bands. The visible absorption spectrum of α-Cr(tetren)Cl^{2+} exhibits a suggestion of a shoulder in the 520–550 mμ region (Figure 2), presumably related to the presence of the 522–525 mμ band in α- and β-Co(tetren)Cl^{2+}. Comparison of the visible absorption spectra of all three chlorotetren complexes with the spectra of the chloropentaammine complexes (Table II) indicates a MN$_5$Cl chromophore (M = Co, Cr) with all five nitrogens of the quinquedentate ligand coordinated to the central metal atom.[18]

TABLE II

VISIBLE ABSORPTION MAXIMA AND MINIMA OF α- AND β-M(tetren)Cl^{2+} AND M(NH$_3$)$_5$Cl^{2+} (M = Co, Cr) IN 0.1 *F* HClO$_4$ AT 20–25°

Complex	λ, mμ	a_M,[a] M^{-1} cm^{-1}
α-Co(tetren)Cl^{2+}	328 (min)	43.6
	362 (max)	103
	417 (min)	37.5
	480 (sh)	105
	522 (max)	109
β-Co(tetren)Cl^{2+} [b]	332 (min)	64.5
	360 (max)	107
	415 (min)	37.2
	480 (max)	101
	508 (min)	97.3
	525 (max)	98.6
α-Cr(tetren)Cl^{2+} [b]	375 (max)	82.0
	422 (min)	45.4
	495 (max)	118
Co(NH$_3$)$_5$Cl^{2+} [c,d]	364 (max)	46.8
	467 (sh)	11.0
	534 (max)	50.1
Cr(NH$_3$)$_5$Cl^{2+} [d,e]	375 (max)	43.7
	515 (max)	38
Cr(NH$_3$)$_5$Cl^{2+} [d,f]	375 (max)	39
	512 (max)	36

[a] Molar absorbancy index (extinction coefficient ϵ), defined by the relation $A = \log(I_0/I) = a_Mcd$. [b] This research. [c] M. Linhard and M. Weigel, *Z. Physik. Chem.*, **11**, 308 (1957). [d] Medium not reported. [e] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266,** 49 (1951). [f] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83,** 2453 (1961).

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE REDUCTION OF Co(tetren)Cl^{2+} COMPLEXES BY V^{2+} IN HClO$_4$ AT 25°

Complex	HClO$_4$, F^a	10^4(complex)$_0$, M^b	10^4 (V^{2+})$_0$, M^b	k, M^{-1} sec^{-1}
α-Co(tetren)Cl^{2+}	~0.01	10.9	3.70	15.4
		15.7	3.10	14.2
	1.0	19.2	6.55	5.1
		18.7	7.00	4.7
β-Co(tetren)Cl^{2+}	~0.01	10.3	4.19	21.0
		9.0	3.63	21.4
	1.0	16.6	5.13	8.4
		13.4	8.94	8.1
"Co(tetren)Cl^{2+}"[c]				
"Slow"	1[d]			1.1[e]
"Fast"	1[d]			6.5[e]

[a] Ionic strength same. [b] Initial concentrations. [c] Ref 7. [d] Ionic strength given in ref 7 as 1.0, apparently as HClO$_4$. [e] Extrapolated to 25° from 10 and 21° data of ref 7, assuming Arrhenius *T* dependence.

Optical Activity.—Considerable confusion exists in the literature with regard to the asymmetry or otherwise of the four geometric isomers of M(tetren)Cl^{2+} in an octahedral complex (Figure 1). Selbin[10] and Goodwin[19] state that all four isomers are asymmetric and this is also suggested by Fernelius and Bryant.[20] Fraser,[7] however, correctly states that one isomer will be optically inactive but does not indicate which one.

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(18) See ref 10 for a further discussion of this point, made with reference to the Co(tetren)NO$_2$$^{2+}$ cation.

(19) H. A. Goodwin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, p 169.

(20) W. C. Fernelius and B. E. Bryant, *J. Am. Chem. Soc.*, **75**, 1735 (1953), Table III, isomer ABCBA d.

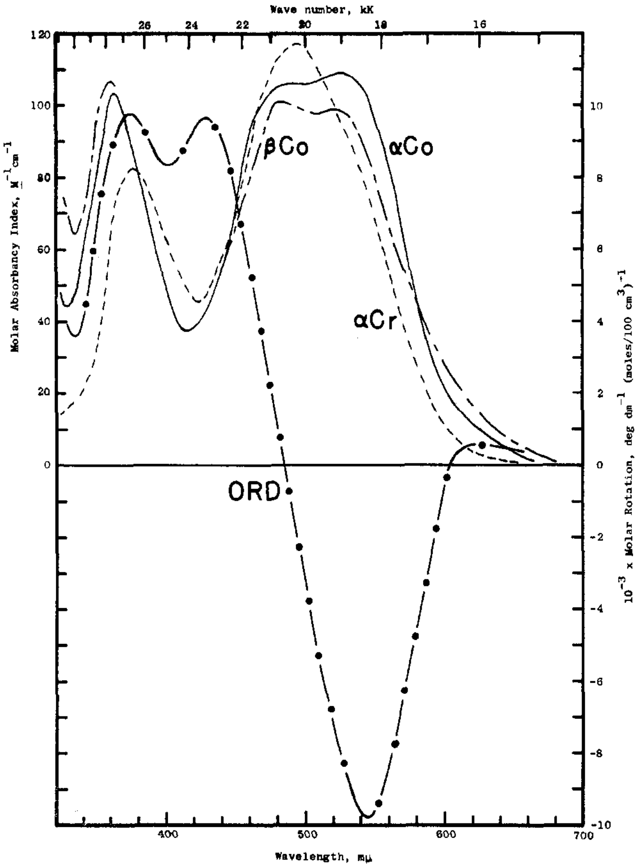

Figure 2.—Visible absorption spectra of chlorotetren complexes of cobalt(III) and chromium(III) and optical rotatory dispersion of (−)-β-Co(tetren)Cl^{2+} in 0.1 *F* $HClO_4$ at 20–25°: αCo, α-Co(tetren)Cl^{2+}; βCo, β-Co(tetren)Cl^{2+}; αCr, α-Cr(tetren)-Cl^{2+}; ORD, ORD of (−)-β-[Co(tetren)Cl]$ZnCl_4$; the molar absorbancy index a_M (extinction coefficient ε) and molar rotation [M] are defined by the relations $\log (I_0/I) = A = a_M cd$ and $[M] = 100\alpha/cd$, where *d* is the optical path length in centimeters, α is the angle of rotation in degrees, and *c* is the molar concentration of the complex ion.

Examination of the structures given in Figure 1 shows that only isomer I has a plane of symmetry (passing through the Cl, Co, and N *trans* to the Cl and bisecting the primary amine N–Co–N angle) and thus will be optically inactive.

The isomers in the configuration pair I–II are related to each other by a shift of one primary amine group, and the same is true for the configuration pair III–IV. Thus, because of the ready chemical interconversion observed, it is probable that α- and β-Co(tetren)Cl^{2+} are related to one another as either I and II or III and IV.

The resolution of the β isomer shows that it is not I, and its resolution and the nonresolution of the α isomer under the same experimental conditions suggest that the α and β forms are I and II, respectively. However, our failure to achieve resolution of the α form in no way indicates the cation is optically inactive, and other evidence is necessary to support this conclusion.

Assignment of the absolute configuration of the β isomer (relative to the absolute configuration of D-(+)-Co(en)$_3{}^{3+}$) is speculative at this stage. Nevertheless, absolute configurations have been assigned[21] to D-(+)- and L-(−)-*cis*-α-Co(trien)$Cl_2{}^+$, and we may imagine the formal conversion of each of these ions to α and β forms of Co(tetren)Cl^{2+} by replacing one of the chloro ligands and one of the primary amine hydrogen atoms with the $H_2N(CH_2)_2$– bridging group, thus permitting the (−)- and (+)-β-Co(tetren)Cl^{2+} configurations to be related to the known D and L configurations of *cis*-α-Co(trien)$Cl_2{}^+$, as shown in Figure 3. Comparison of the ORD of (−)-β-Co(tetren)Cl^{2+} (Figure 2) with the ORD reported[21] for D-(+)-*cis*-α- and D-(+)-*cis*-β-Co(trien)$Cl_2{}^+$ (the latter can be imagined to form Co(tetren)Cl^{2+} in configurations II, III, and IV by substitution of a $H_2N(CH_2)_2$– bridging group for a chloro ligand and a primary amine hydrogen atom) shows that the shapes of the ORD curves are similar (when allowing for the change expected in going from the D-(+) to the L-(−) isomers) and suggests that (−)-β-Co(tetren)Cl^{2+} has the L configuration. Circular dichroism measurements would be required to support this tentative assignment.

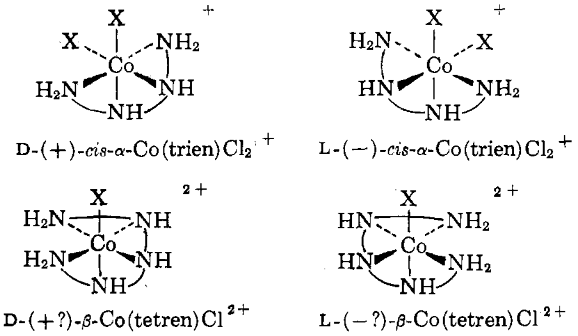

Figure 3.—Relation between D- and L-*cis*-α-Co(trien)$Cl_2{}^+$ and D- and L-β-Co(tetren)Cl^{2+} configurations.

Ring Strain.—Inspection of Figure 1 shows that in isomers I and II, respectively, none and only one of the coordinated secondary amine groups needs to be strained from the normal tetrahedral angle, whereas III and IV contain one and two strained secondary amine groups, respectively. Fisher–Hirschfelder–Taylor molecular models indicate that all four isomers should be structurally capable of existing, but Sargeson[22] has pointed out that nonbonding interactions are probably important in assessing the relative stability of any particular M(tetren)Cl^{2+} configuration.

Our previous work with *cis*-α-Cr(trien)$Cl_2{}^+$ complexes[2] indicates that only the unstrained α configuration is formed under synthetic conditions similar to those used by us to make the Cr(tetren)Cl^{2+} cation. By analogy the [Cr(tetren)Cl]$ZnCl_4$ isolated would be expected to have the symmetric unstrained configuration I (Figure 1). Inasmuch as [Cr(tetren)Cl]-$ZnCl_4$ has an infrared spectrum very similar to that of α-[Co(tetren)Cl]$ZnCl_4$ (Table I and actual spectra)

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(21) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(22) A. M. Sargeson, ref 19, p. 192.

these facts further support an assignment of the α form of these chlorotetraethylenepentamine complexes to I and the β form to II.

Additional evidence comes from the shapes of the bands associated with NH_2 bending modes (1550–1600 cm^{-1}) in the infrared spectra of α- and β-[Co(tetren)Cl]$ZnCl_4$. These bands are very similar to the analogous bands from the α- and β-[Co(trien)Cl_2]Cl isomers[23] in this region. In the latter compounds, the amine configuration is changed from an unstrained conformation (α isomer) to one containing both strained and unstrained secondary amines (β isomer). This results in a splitting of the NH_2 bending vibration by about 30 cm^{-1}. A similar splitting of about 30 cm^{-1} for the α- and β-[Co(tetren)Cl]$ZnCl_4$ isomers suggests a similar configuration change and further supports our assignment of the α and β isomers to I and II, respectively.

Kinetics Interpretation.—Using a synthetic method similar to our method C, Pearson, Boston, and Basolo[6] have prepared a noncrystalline material which had a chlorine analysis agreeing with the formula [Co(tetren)Cl]Cl_2 within 1–2%. They deduced from a study of the aquation kinetics that the material was 51% a "slow" component which they took to be one isomer of the above compound (later[24] written without comment as isomer I) and 49% a "fast" component which they assumed was either one of the other three isomers or more likely a "dichloro tertiary pentamine complex." The ratio of the first-order rate constants for the "fast" and "slow" components at 35° and pH 1 was about 500.

We have made preliminary measurements of the rates of aquation of our α and β forms at 35° in 0.1 *F* $HClO_4$ and find that the β isomer aquates less than twice as fast as the α form. Our α isomer appears to aquate at 35° approximately two times as fast as the "slow" component of Pearson, Boston, and Basolo.[6] This is about the order of rate difference we would expect if the α and β isomers are related as I and II, where the coordinated chloride ion is *trans* to an unstrained coordinated secondary amine in both cases. A much larger rate difference would be expected if the isomers were related as III and IV because in III the coordinated chloride is *trans* to the strained coordinated secondary amine whereas in IV the coordinated chloride is *trans* to an unstrained coordinated primary amine. A full kinetic study of these aquation reactions is underway and will be reported later.

Using a synthesis similar to that of Pearson, Boston, and Basolo,[6] but with purified tetren,[25] Fraser[7] obtained a "[Co(tetren)Cl]$(ClO_4)_2$" (no analytical data given) which, on reduction with V^{2+} or Cr^{2+} (apparently in 1 *F* $HClO_4$), gave rate plots showing a "fast" and a "slow" component present in approximately equal amounts and with a ratio of second-order rate constants of about 6.4 at 21°. By comparison with similar kinetic data for *cis*- and *trans*-$Co(en)_2(NH_3)Cl^{2+}$, Fraser suggested that if his "fast" and "slow" components are $Co(tetren)Cl^{2+}$ isomers, they may be isomers III and IV, respectively. Fraser also reported obtaining a partial resolution of his "slow" component after aging out the "fast" component. Thus if his "slow" component is one of the four $Co(tetren)Cl^{2+}$ isomers in pure form and if the apparent partial resolution was real, his "slow" component would not be isomer I.

We have examined the kinetics of reduction of our α and β isomers with V^{2+} under conditions similar to those apparently used by Fraser and find that the β isomer reacts in 1 *F* $HClO_4$ at 25° about 1.7 times as fast as the α form and with a rate constant of the same order of magnitude as for Fraser's "fast" component (Table III). The ratio of oxidation–reduction rate constants we find is essentially the same as we find for aquation of the α and β isomers (*vide ante*). Thus Fraser's "fast" component may be the same as our β isomer, or possibly it is a mixture of our α and β isomers; in the latter case, his "fast" component would have been only partly removed in his aging experiment and the partial optical resolution he reported for the "slow" component could actually have been a resolution of the β isomer left in the aged mixture. His "slow" component would appear not to be either our α or β isomer because of the difference in oxidation–reduction rate constants.

A further source of differences between our α and β isomers and the impure materials studied by the earlier workers could be associated with the synthetic methods used. Our method of synthesis involves precipitation of α- and β-$Co(tetren)Cl^{2+}$ cations from the reaction mixtures as the tetrachlorozincate(II) salts. There could be considerable solubility differences between these two compounds and the other two isomeric forms (III and IV) of this compound. If such were true, isomers III and IV, present in low yield if at all, would remain in solution. Isomers III and IV, however, could conceivably have been obtained in the procedures used by the earlier workers, although we would expect isomers III and IV to react faster than I and II from ring-strain considerations, rather than slower. Pearson, Boston, and Basolo[6] obtained their "[Co(tetren)Cl]Cl_2" by extraction of an oil with absolute ethanol and drying the extract at 110° to get a hygroscopic residue; if all isomers formed, they would have been included in the material so obtained. Fraser[7] stated he used the same method of synthesis, except with tetraethylenepentamine purified differently, and with precipitation of a perchlorate salt.

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[23] D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

[24] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 117.

[25] H. B. Jonassen, F. W. Frey, and A. Schaafsma, *J. Phys. Chem.*, **61**, 504 (1957). The tetren used in the synthesis given in ref 6 was purified by Prof. Jonassen after the method of E. H. Gause, T. B. Crumpler, and H. B. Jonassen, *J. Am. Chem. Soc.*, **73**, 5457 (1951), and was stated in ref 6 to be contaminated with an isomeric tertiary pentamine.