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Acidopentaminecobalt(III) Complexes with Polyamine Ligands. II. The Four Geometric Isomers of the Chloro(ethylenediamine) (diethylenetriamine)cobalt(III) Ion [1]

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Received, May 31, 1969

Tetrachlorozincate(II) salts of the four (ω, κ, π *and* ε) *possible geometric isomers of the Co(en)(dien)Cl^{2+} have been synthesised. The* π *and* ε *forms contain the dien ligand in the facial* (cis) *configuration with the cloro ligand* trans *to the NH$_2$ and NH groups of the dien respectively. The* ω *and* κ *forms contain the dien ligand in the peripherial* (trans) *configuration with the NH hydrogen of the dien ligand adjacent to and remote from the chloro ligand, respectively. Chemical interconversions of the isomers and their infrared and visible absorption spectra are described.*

Introduction

As part of a continuing investigation of acidopentaminecobalt(III) complexes with mixed diamine-triamine ligands, we describe here the preparation, properties, stereochemistry and interconversions of the four possible isomers of the Co(en)(dien)Cl^{2+} ion.[2]

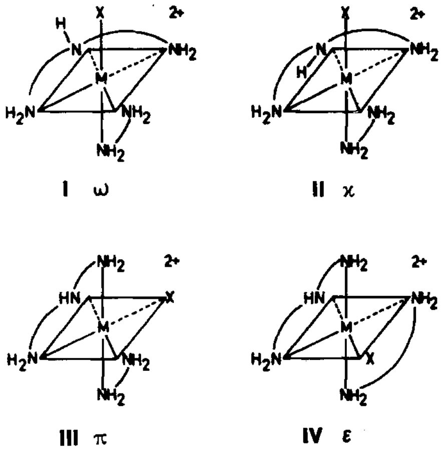

Figure 1. Possible geometric isomers of the Co(en)(dien)X^{2+} ion (X = Cl).

Salts of the Co(en)(dien)Cl^{2+} ion have been described previously[3-6] but only in the case of Bosnich and Dwyer's work[5] was there more than one (*viz.* two) isomer detected.

Using a variety of synthetic methods, we have prepared tetrachlorozincate(II) salts of the four Co(en)(dien)Cl^{2+} isomers and have assigned them to the configurations shown in Figure 1.

The ω and κ isomers can be regarded as *cis* and *trans* forms differing only in the position of the NH proton. The π, κ and ε isomers are related by edgewise displacements of the dien and en respectively.

Experimental Section

The commercial amines were used without further purification. All other chemicals were of reagent grade quality. [$Co_2(en)_2(dien)_2O_2$](ClO_4)$_4$. 2H_2O,[7] Na_3[Co(CO_3)$_3$] . 3H_2O[8] and *trans*–Co(dien)(NO_2)$_3$[5,9] were prepared by the literature methods. Infrared spectra of the $ZnCl_4^{2-}$ salts were used to determine the isomeric composition of the chloro complexes.

Isomers of Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). Method A: [$Co_2(en)_2(dien)_2O_2$](ClO_4)$_4$. 2H_2O (30 g) was added to a solution of 12 F HCl (85 ml) in water (170 ml) containing $ZnCl_2$ (50 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (0.5 hr) during which time a red crystalline material was deposited. The solution was cooled to room temperature and the product was collected, washed with 2-propanol and then ether; yield 13 g. The crude product was recrystallised by dissolving it in the minimum volume of 0.2 F HCl at 50° (ca. 150 ml) and then adding 12 F HCl (50 ml) and $ZnCl_2$ (25 g). The product from the cooled solution was collected and washed as above. Losses were mechanical and the product was a π–κ mixture in a 42% yield.

The original mother liquor (orange-brown) was again heated at 80° and after 0.5 hr a further 50 ml portion of 12 F HCl was added to the solution. An orange-red product slowly deposited and this was

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(1) Part I, *Inorg. Chim. Acta*, 3, 33 (1969).
(2) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.
(3) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955).
(4) G. G. Schlessinger, *Gannon Coll. Chem. J.*, 2, 20 (1965).
(5) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 19, 2045 (1966).
(6) B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 19, 2051 (1966).
(7) D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, in press.
(8) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, 82, 5031 (1960).
(9) P. H. Crayton, *Inorg. Synth.*, 7, 211 (1963).

collected and washed as above. The product was recrystallised as above but using a corresponding reduction in volumes and weights of reagents. The yield was 1.5 g of the pure κ isomer. The total yield of chloropentamine complex was 47%.

Method B. $Co(dien)(NO_2)_3$[9] (15 g) was suspended in water (30 ml) and ethylenediamine (3.3 ml, 100%) was added. The solution was stirred and allowed to digest on a steam bath for 1 hr. The filtered solution was heated to 80° and 12 F HCl (30 ml) was cautiously added. Heating was continued for a further hour, during which time the evolution of nitrogen oxides subsided, and a deep red color was produced. $ZnCl_2$ (15 g) and 12 F HCl (5 ml) were then added and after heating for a further 30 min, the product commenced to crystallise. The product was collected in about 2g fractions, which were washed with 2-propanol and ether. Each fraction was recrystallised by dissolving the crude complex in the minimum volume of 0.2 F HCl at 25° (1 g/50 ml) and then adding 12 F HCl (25 ml/1 g) and $ZnCl_2$ (5 g/1 g). The products were again collected in fractions and were collected and washed as above. The isomeric composition of the fractions are tabulated below.

Crude Crop No.	Recrytallised Crop No.	Isomeric Composition	Yield (g) of Recrytallised Product
1	1, 2, and 3	ε	2.3
2	1 and 2	ε	2.3
3	1	ω	0.6
	2	ω+ε	0.5
4	1	ε+κ	0.6
	2	ε+ω+κ	0.7
	3	ε+κ	0.7

The total yield was 7.7 g or 36% and fractions after the 4th crop increasingly contaminated with yellow hexamine salts.

Method C. The procedure of Bosnich and Dwyer[5] was followed on a 1/20 scale. The crude product was converted to the tetrachlorozincate(II) salt by dissolving it in the minimum volume of 50° 0.1 F HCl and then adding excess 12 F HCl and $ZnCl_2$. The material that deposited on cooling in an ice bath was collected in fractions, washed with 2-propanol and then ether (Crops 1-4). The original mother liquor was heated to 50° and 10 g of $ZnCl_2$ in 20 ml of 12 F HCl was added. The product that deposited was collected in fractions and recrystallised as above (Crops 5-7). The total yield was 12.4 g ,63%). The 1st, 2nd and 3rd crops were the pure ω isomer (6.5 g), the 4th crop an ε-ω mixture, the 5th and 6th crops a π–κ mixture and the 7th crop consisted of the κ isomer contaminated with hexamine impurities.

Method D. $CoCl_2 . 6H_2O$ (7 g), NH_4Cl (25 g) and NH_4I (0.5 g) were added to 40 ml of water and I_2 (3.7 g) dissolved in 80 ml of ethanol was added to the stirred aqueous suspension. This was followed by the addition of ethlylenediamine (2.1 ml) and diethylenetriamine (3.4 ml) in 20 ml of water. The mixture was stirred at room temperature for 3 hr, during which time a deep red color developed. The solution was allowed to stand overnight when red needles along with some NH_4Cl were deposited. The crude product was converted to the $ZnCl_4^{2-}$ salt as in Method C. Two further crops were obtained by addition of acetone and methanol (150 ml of a 1:1 mixture) after filtration of the precipitated ammonium salts and these were converted to the $ZnCl_4^{2-}$ salt. A total yield of 0.8 g of the pure ω isomer was obtained. Finally, the mother liquor (450 ml) was evaporated on a steam bath to 250 ml and 15 g of $ZnCl_2$ in 50 ml of 12 F HCl was added. The red product that deposited from the ice cold solution was collected in 1-2 g fractions. These were washed with 2-propanol and ether and recrystallised as above. The three crops that were collected consisted of a π–κ mixture and the third crop also contained some ω isomer. The total yield was 6 g or 45%.

Method E. Freshly prepared $Na_3[Co(CO_3)_3] . 3H_2O$[8] (10 g) was suspended in 30 ml of water and a mixture of ethylenediamine (2.15 ml) and diethylenetriamine (4.95 ml) was added. After heating at 80° for 15 min, 12 F HCl (20 ml) and $ZnCl_2$ (10 g) were cautiously added to the now red solution. Successive crystal crops were collected over a period of several days and were recrystallised as in Method A. Crops one and two (0.5 g each) consisted of the π isomer and the third crop was a π-ω-κ mixture (0.6 g). Subsequent crops were contaminated with hexamine salts. The yield of the chloropentamine complex was only 9%.

Analysis. Analytical data for the pure isomers (infrared spectra) are: Calcd. for $[Co(en)(dien)Cl]ZnCl_4$: C, 15.5; H, 4.55; N, 15.0; Co, 12.7; Cl, 38.2%. Found: ω isomer C, 15.9 H, 4.56 N, 14.9 Co, 12.6 Cl, 37.8: κ isomer C, 15.7 H, 4.59 N, 14.9 Co, 12.6 Cl, 38.1: π isomer C, 15.8 H, 4.64 N, 15.1 Co, 12.6 Cl, 38.1: ε isomer C, 15.8 H, 4.48 N, 15.4 Co, 12.5 Cl, 37.9%.

Separation of a π-κ Mixture. Method 1. The mixture of the π-κ isomers (generated by Method A, ca. 35% κ was dissolved in 0.2 F $HClO_4$ (15 g, 150 ml) and twice the weight of solid $NaClO_4 . H_2O$ was stirred in. Pure κ–$[Co(en)(dien)Cl](ClO_4)_2$ (5 g) was deposited immediately and this was collected, washed with 2-propanol and the ether. $ZnCl_2$ (20 g) in 12 F HCl (50 ml) was added to the mother liquor and the pure or partly purified π–$[Co(en)(dien)Cl]ZnCl_4$ was precipitated. This was recrystallised as described previously in Method A. κ–$[Co(en)(dien)Cl]$-$ZnCl_4$ was made from the perchlorate salt by dissolving the latter in water (5 g, 50 ml) and adding 12 F HCl (25 ml) and $ZnCl_2$ (10 g). The precipitated product was collected, washed and dried as above. Losses in this procedure were mechanical.

Method 2. The π-κ isomeric mixture (20 g) generated by Method A, was dissolved in water (150 ml) and a solution of KOH (20 g) in water (50 ml) was added. The solution was heated at 60° for 20 min, filtered, cooled in ice, and ice cold 12 F HCl (350 ml) containing $ZnCl_2$ (20 g) was added dropwise. The orange colored solution was set aside at room temperature and after 2 days, the first crystal crop

(3 g pure π–[Co(en)(dien)Cl]$\mathrm{ZnCl_4}$) was collected, washed with 2-propanol then ether and air dried. Subsequent crops were again π-κ mixtures (14 g).

Qualitative Isomerisation Reactions. Small quantities of the pure isomers were taken and subjected to the following chemical reactions. The isomeric composition of the chloro $\mathrm{ZnCl_4^{2-}}$ product was determined by examination of the infrared spectrum.

(*a*) *Base Hydrolysis.* The π, ε, ω and κ isomers of [Co(en)(dien)Cl]$\mathrm{ZnCl_4}$ were separately dissolved in water (0.25 g, 15 ml, 0.25g, 15 ml, 0.1 g, 15 ml and 0.25 g, 15 ml respectively) and ca. 10 ml of 1 F NaOH was added until all the $\mathrm{Zn(OH)_2}$ had precipitated. The solutions were heated at 70° for 20 min and then 4 g of $\mathrm{ZnCl_2}$ in 10 ml of 12 F HCl was added. The solutions were left to stand at room temperature overnight and the product was collected, washed with 2-propanol and then ether. The results were: ω→π+κ; ε→π; κ→π+κ; π→π.

(*b*) *Reflux in 6 F HCl.* The pure isomers of [Co(en)(dien)Cl]$\mathrm{ZnCl_4}$ were separately dissolved in 6 F HCl (0.2 g/25 ml) and the solutions were boiled under reflux for 1 hr. Concentrated HCl (15 ml, 12 F) containing $\mathrm{ZnCl_2}$ (5 g) was added and the products that deposited from the ice cooled solutions were collected. The results were: κ→κ; π→π; ω→ω; ε→π.

(*c*) *Refluxed in 0.05 F HCl.* Similar amounts and conditions were used as in (b) except that the 6 F HCl was replaced by 0.05 F HCl. The results were: ε→π+κ+ε; κ→κ+π; π→π+κ; ω→ω.

(*d*) *Reaction with Nitrous Acid.* Nitro compounds derived from the π, κ, ε and ω–[Co(en)(dien)Cl]$\mathrm{ZnCl_4}$ isomers were prepared using a method to be described in a later publication. These were decomposed by heating (80°) a solution of each in 3 F HCl for one hr. The $\mathrm{ZnCl_4^{2-}}$ salts of the chloro isomers generated in this manner were deposited by the addition of $\mathrm{ZnCl_2}$. The transformations that resulted were: π→ε; κ→κ; ε→ε; ω→ω.

Perchlorate Salts. One half gramme of the isomerically pure [Co(en)(dien)Cl]$\mathrm{ZnCl_4}$ salts were dissolved in the minimum volume of 80° 3 F $\mathrm{HClO_4}$ (25-30 ml) and excess $\mathrm{NaClO_4 \cdot H_2O}$ (*ca.* 5 g) was added. The products that crystallised from the ice cooled solutions were collected, washed with 2-propanol, then ether and air dried. The ε and π isomers crystallised as the diperchlorate monohydrates, the κ isomer as the diperchlorate and the ω isomer as the chloride-perchlorate salt. The yields were: ε, 49%; π, 55%; κ, 53% and ω, 53%.

Anal. Calcd. for [Co(en)(dien)Cl]$\mathrm{(ClO_4)_2 \cdot H_2O}$: C, 15.18; H, 4.88; N, 14.75; Co, 12.41; Cl (non-perchlorate) 7.47. Found: ε isomer; C, 15.39; H, 4.99; N, 15.08; Co, 11.99; Cl, 7.51: π isomer; C, 15.09; H, 4.96; Co, 12.44; Cl, 7.85. Calcd. for [Co(en)(dien)Cl]$\mathrm{(ClO_4)_2}$: C, 15.78; H, 4.64; N, 15.34; Co, 12.91; Cl (non-perchlorate), 7.77. Found: κ isomer; C, 15.75; H, 4.72; N, 14.96; Co, 12.85; Cl, 7.71. Calcd. for [Co(en)(dien)Cl]$\mathrm{(ClO_4)Cl}$: C, 18.35; H, 5.39; N, 17.84; Co, 15.01; Cl (non-perchlorate), 18.06. Found: ω isomer; C, 18.46; H, 5.51; N, 17.61; Co, 15.50; Cl, 18.25.

Anal. Co and Cl were determined as described previously.[1] C, H and N analyses were performed by Dr A. D. Campbell of the University of Otago, New Zealand.

Spectral Measurements. The visible absorption spectra were obtained with a Cary 14 recording spectrophotometer using matched 1 cm quartz cells. Spectrophotometric analyses for Co were performed using a Beckman DBG recording spectrophotometer. The infrared spectra were determined in both mulls and KBr discs using a Perkin Elmer 337 or a Shimadzu IR-27 G infrared spectrophotometer.

Results

The four isomers (ω, ε, π and κ) of [Co(en)(dien)Cl]$\mathrm{ZnCl_4}$ have been prepared and structural assignments made according to Figure 1. The infrared spectra of these salts (1700-400 $\mathrm{cm^{-1}}$ range) (KBr discs) are shown in Figure 2 and the visible absorption spectra (0.1 F $\mathrm{HClO_4}$) of the isomeric cations are shown in Figure 3. Spectral parameters for the $\mathrm{Co(en)(dien)Cl^{2+}}$ and $\mathrm{Co(en)(dien)OH_2^{3+}}$ ions are listed in Table I, together with similar data for α and β–$\mathrm{Co(tetren)Cl^{2+}}$ and α–$\mathrm{Co(tetren)OH_2^{3+}}$.[10-12] The a_M values for the various $\mathrm{Co(en)(dien)Cl^{2+}}$ isomers were within 3% for different preparations of the $\mathrm{ZnCl_4^{2-}}$ salts with similar infrared spectra characteristic of that particular isomer.

The isomeric aquo cations were generated in solution from the chloro analogs by addition of $\mathrm{Hg^{2+}}$ (as the acetate salt) in 0.1 F $\mathrm{HClO_4}$. The rates of color change (red → orange) at room temperature were in the order $\varepsilon > \pi > \kappa \sim \omega$ and the $\mathrm{Hg^{2+}}$ catalysed hydrolysis was complete for all isomers after 18 hr as evidenced by constant and reproducible spectral parameters. Identical aquo cations were also generated from the chloro isomers by addition of base (0.1 F NaOH) and acidification with 0.3 F $\mathrm{HClO_4}$ after 5 min at room temperature.

Discussion

Synthetic Methods. The amount of any particular $\mathrm{Co(en)(dien)Cl^{2+}}$ isomer is markedly dependent upon the method of synthesis. The reaction between *trans*-$\mathrm{Co(dien)(NO_2)_3}$[13] gives, presumably, a mixture of the $\mathrm{Co(en)(dien)NO_2^{2+}}$ isomers which form nitro complexes (ω, κ and ε), as the corresponding chloro isomers are isolated as the $\mathrm{ZnCl_4^{2-}}$ salts by treating the solution with HCl/$\mathrm{ZnCl_2}$. The π chloro isomer cannot be formed directly in this synthesis as treatment of π-$\mathrm{Co(en)(dien)Cl^{2+}}$ with $\mathrm{HNO_2}$ produces ε-$\mathrm{Co(en)(dien)NO_2^{2+}}$. The formation of the π chloro isomer in small

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[10] D. A. House and C. S. Garner, *Inorg. Chem.*, 5, 2097 (1966).
[11] D. A. House and C. S. Garner, *Inorg. Chem.*, 6, 272 (1967).
[12] T. L. Ni and C. S. Garner, *Inorg. Chem.*, 6, 1071 (1967).
[13] Y. Kushi, K. Watanabe, and H. Kuroya, *Bull. Chem. Soc., Japan*, 40, 2985 (1967).

Table I. Visible Absorption Maxima and Minima for ω, ε, π and ϰ—Co(en)(dien)Cl^{2+}; ω, ε, π and ϰ—Co(en)(dien)OH$_2^{3+}$; α and β—Co(tetren)Cl^{2+} and α—Co(tetren)OH$_2^{3+}$ in 0.1 F HClO$_4$ at 20-25° [a] [b]

Complex	min	max	min	max	min	max
ω—Co(en)(dien)Cl^{2+}	323	358	416	480 sh		532
	(75.0)	(100.8)	(19.3)	(60)		(92.0)
ε—Co(en)(dien)Cl^{2+}		314 sh	405	463	485	522
		(346)	(29.8)	(55.9)	(50.7)	(53.9)
π—Co(en)(dien)Cl^{2+}	326	361	412	475 sh		525
	(33.6)	(71.0)	(15.0)	(44)		(67.0)
ϰ—Co(en)(dien)Cl^{2+}	332	366	416	488 sh		515
	(35.2)	(87.9)	(30.3)	(84)		(85.6)
α—Co(tetren)Cl^{2+}	328	362	417	480 sh		522
	(43.6)	(103)	(37.5)	(105)		(109)
β—Co(tetren)Cl^{2+}	332	360	415	480	508	525
	(64.5)	(107)	(37.2)	(101)	(97.3)	(98.6)
ω—Co(en)(dien)OH$_2^{3+}$	300	342	398	487		
	(30.3)	(86.2)	(17.0)	(72.1)		
ε—Co(en)(dien)OH$_2^{3+}$		324	384	436		
		(332)	(24.4)	(79.5)		
π—Co(en)(dien)OH$_2^{3+}$	303	346	397	476		
	(20.5)	(71.0)	(21.0)	(78.5)		
ϰ—Co(en)(dien)OH$_2^{3+}$	304	361	402	473		
	(22.2)	(80.2)	(27.4)	(99.5)		
α—Co(tetren)OH$_2^{3+}$		350	405	472		
		(85.3)	(33.0)	(122)		

[a] Everywhere, numbers inside parenthesis are the molar absorbancy indeces, a_M (extinction coefficients, ε) in M^{-1} cm^{-1}. Wavelengths are in nanometers (millimicrons). [b] Data for the Co(tetren)X^{n+} cations are from references 10-12.

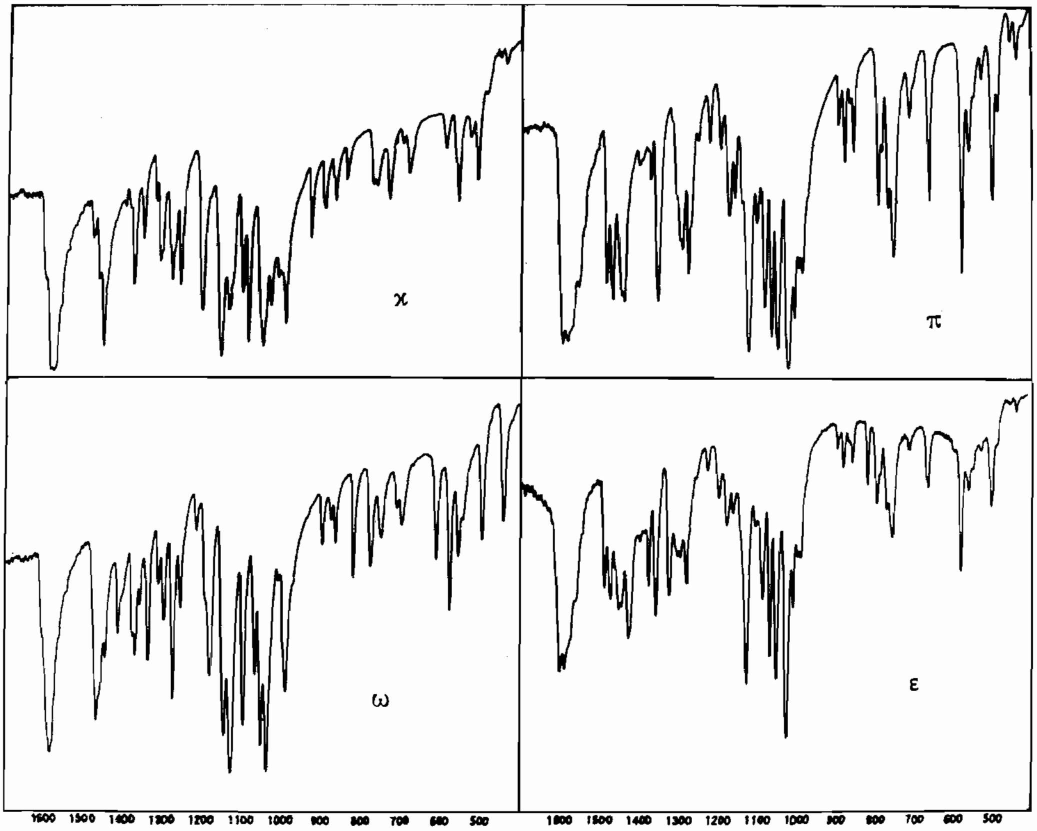

Figure 2. Infrared spectra of ω, ε, π and ϰ—[Co(en)(dien)Cl]ZnCl$_4$ in the 1700-400 cm^{-1} range (KBr disc).

amounts, presumably arises via isomeric conversion of the ε chloro isomer, which has been shown to transform to the π chloro form in refluxing 6 F HCl. The above method of synthesis was originally used by Bosnich and Dwyer[5] who isolated the ω chloro chloride as the major product from the nitro intermediates after treatment with 12 F HCl. They tentatively assigned this form to either configurations **III** or **IV** (Figure 1), but from evidence presented later, we suggest that the ω isomer has configuration **I**. A minor component was also isolated and from the visible absorption spectrum, this appears to be the chloro chloride of our ϰ isomer. The chloride salts of the ε and π isomers are apparently too soluble to be isolated by this method. The use of the larger tetrachlorozincate(II) ion, does however. allow their isolation using this route.

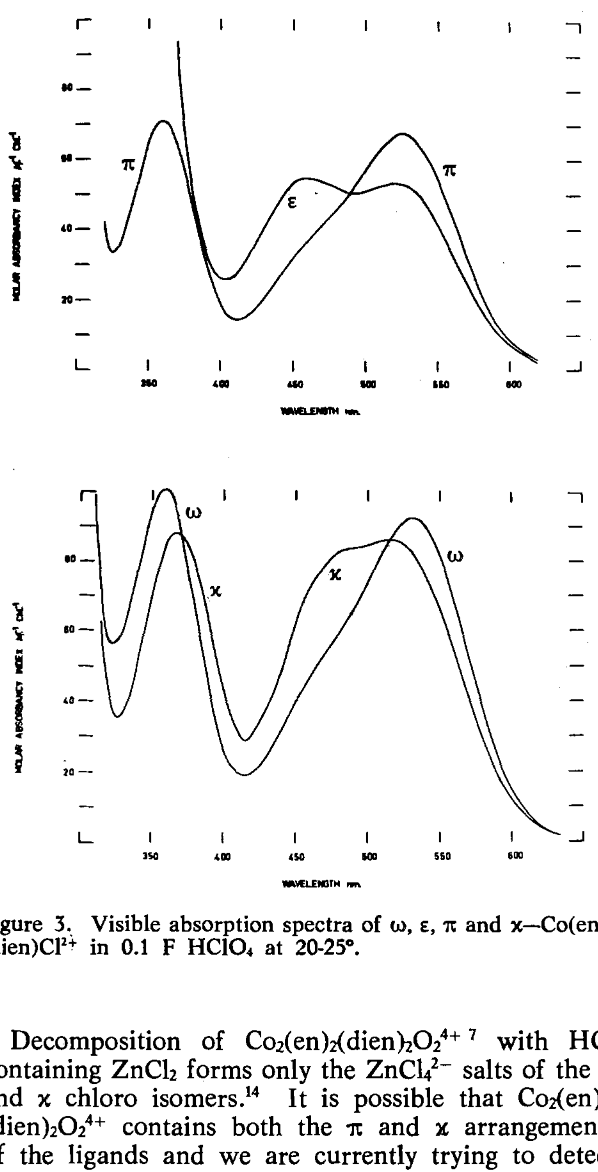

Figure 3. Visible absorption spectra of ω, ε, π and ϰ—Co(en-)(dien)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°.

Decomposition of $Co_2(en)_2(dien)_2O_2^{4+}$ [7] with HCl containing $ZnCl_2$ forms only the $ZnCl_4^{2-}$ salts of the π and ϰ chloro isomers.[14] It is possible that $Co_2(en)_2(dien)_2O_2^{4+}$ contains both the π and ϰ arrangements of the ligands and we are currently trying to detect isomeric mixture in μ peroxo polyamine complexes of this type.[7] A more likely explanation is that the μ peroxo complex contains only one polyamine configuration and that the aquo intermediate originally produced in the decomposition, forms a π–ϰ equilibrium mixture. Support for this latter hypothesis comes from the fact that refluxing ϰ–[Co(en)(dien)Cl]$ZnCl_4$ in 0.05 F HCl for one hr and adding 12 F HCl results in about 30% conversion to the π chloro isomer.

$Na_3Co(CO_3)_3 \cdot 3H_2O$[8] reacts with an en/dien mixture forming mixtures of the π–ϰ chloro isomers on acidification with HCl/$ZnCl_2$, but the yields are low and considerable amounts of hexamine products are produced. An attempt was made to prepare [Co(en)(dien)I]Cl_2 using the method of Yalman[15] for the formation of the ammine analog. However, ω–[Co(en)(dien)Cl]Cl_2 was deposited, and when the solution was acidified with HCl/$ZnCl_2$, mixtures of the π and ϰ chloro isomers were isolated.

Several methods were found to interconvert the isomers and these were investigated qualitativly. Treatment of the pure ω, ε and ϰ chloro isomers with excess hot NaOH solution and reacidification with HCl to form the chloro $ZnCl_4^{2-}$ salts resulted in conversion to a mixture of the π and ϰ forms. It is probable that the π and ϰ hydroxo (or aquo) ions form an equilibrium mixture which gives the chloro mixture on anation. Mention has already been made of the π→ε isomerisation via the nitro complex and the ε→π rearrangement in refluxing 6 F HCl.

It is difficult to generalise from these data, but it appears probable that the π and ϰ isomer result from the formation of Co^{II} or Co^{III} hydroxo complexes and that the ω, ε and ϰ isomers can form when the synthetic route does not involve these intermediates.

Spectra. The most noticeable difference between the four isomers of [Co(en)(dien)Cl]$ZnCl_4$ is in the infrared spectrum (Figure 2). Even here, however, there are often only one or two significant bands that allow isomer differentiation. In particular, the bands that serve to distinguish the ϰ, ε and ω isomeres, respectively, from each other and from π are ϰ, 930; ε, 820, 661 and ω, 820, 610 cm^{-1}. The infrared spectrum have also been used as an index of purity for any particular isomer. The spectra of synthetic mixtures of the pure isomers show that it is possible to detect 5-10% of one isomer in the presence of the other. Nevertheless, care must be taken in the interpretation of the infrared spectrum, as fractional crystallisation does not always lead to isomer separation especially with π and ϰ–[Co(en)(dien)Cl]$ZnCl_4$ mixtures. The separation of this particular mixture is best effected by fractional crystallisation as the perchlorate salts, when ϰ–[Co(en)(dien)Cl]$(ClO_4)_2$ crystallises first, followed by the $ZnCl_4^{2-}$ salt of the π isomer.

The visible absorption spectra of the π, ϰ and ω chloro isomers are quite similar (Figure 3) showing two well defined maxima at about 360 and 520 nm. The 520 nm bands are broad and exhibit a shoulder on the low wavelength side which becomes more pronounced in the order $\omega < \pi < \varkappa$. The ε chloro isomer exhibits only the 520 nm maxima of comparable intensity but here the band is split into two well resolved maxima. In addition there is a high intensity ($a_M = 346$) shoulder at 314 nm (not shown in Figure 3) on the high wavelength side of the charge transfer bands in the ultraviolet.

Thus the spectra of these Co(en)(dien)Cl^{2+} isomers are similar to those of the Co(en)(dpt)Cl^{2+} [1] and Co(tetren)Cl^{2+} [10-12] isomers. Such similarity is expected as these systems all contain the CoN_5Cl^{2+} chromophore.

All four aquo isomers exhibit two bands in the 300-700 nm region, however, the maxima for the ε aquo isomer are shifted about 10 nm to lower wavelengths and the low wavelength maxima is of much greater intensity than for the comparable band in the other forms.

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[14] A. R. Gainsford and D. A. House, *Inorg. Nucl. Chem. Letters*, *4*, 621 (1968).

[15] R. G. Yalman, *J. Am. Chem. Soc.*, *77*, 3219 (1955).

Structural Assignments. Consideration of the structures **I-IV** (Figure 1) suggest that the configurations **II-IV** should form an interconvertable system via edgewise displacement of the dien or en ligands. Such displacements in structures **I** cannot take place because of the position of the NH proton. This implies that the isomer corresponding to **I** should not rearrange under conditions where the NH proton remains intact. Rearrangement is possible, however, if the NH proton were removed such as in an S_N 1CB base hydrolysis mechanism.[16]

We are currently investigating this and related systems to see if such rearrangements can provide evidence to support the S_N1CB mechanism.

Structures **I** and **II** can be regarded as *cis* and *trans* NH forms and similarly related configurations have been postulated in the *trans*—(O-X)-Co(dien)(gly)X^+ (X = CN) system[17] where two distinct forms were detected in solution by nuclear magnetic resonance.

Of the structures **I-IV**, only **III** is potentially optically active. Unfortunately we have not been able to resolve any of the chloro isomers described here and the property of optical activity cannot, at present, be used for structural assignments.

The structural pairs **I-II** and **III-IV** contain the dien ligand in the peripherial (*trans*) and facial (*cis*) configurations, respectively. Previous workers[18-20] have used infrared spectral data to assign the configuration of the dien ligand in monodiethylenetriamine complexes. Of particular significance are the bands in the 800-950 cm^{-1} region where the *cis* and *trans* monodiethylenetriamine complexes have 3 and 4 bands respectively. Using this criterion for the assignment of the dien ligand, the infrared spectra of the [Co(en)(dien)Cl]$ZnCl_4$ isomers (Figure 2) suggest that the ω and κ forms have the *trans* arrangement and the π and ε isomers the *cis* form, assuming the en ligand has little influence on the spectra in the 800-950 cm^{-1} region. In the infrared spectrum of monoethylenediamine complexes such as $Co(en)(NH_3)(NO_2)_3$ and $[Co(en)(NH_3)(OH_2)Cl_2]Cl$, there are two weak bands at 880 and 900 cm^{-1} due to the en and these probably appear as low intensity shoulders on the dien bands of the [Co(en)(dien)Cl]$ZnCl_4$ isomers.

Of the four chloro isomers isolated, only the π chloro form has been found to give two different isomers by chemical conversion. Thus, treatment with HNO_2 yields the ε nitro isomer and on refluxing with 0.05 F HCl, followed by the addition of 12 F HCl, there is partial conversion to the κ chloro. This suggests that the π chloro has the configuration **III**, as it is this form which would be expected to give rise to two different products via displacement of the dien (configuration **II**) or the en (configuration **IV**). If this is the case, the behaviour of the π chloro isomer is slightly different from the analogous α–Co(en)(dpt)Cl^{2+} [1] with configuration **III**, which gives a mixture of two nitro complexes, corresponding to configurations **II** and **IV**, on treatment with HNO_2.

The similarity of the infrared spectrum of the π chloro isomer with that of the ε chloro form suggests that the ε form corresponds to **IV**, with the acido ligand now *trans* to the coordinated secondary amine group and the dien remaining in the 1, 2, 3 configuration. The assignment of configuration **IV** to the analogous γ–Co(en)(dpt)Cl^{+2} [1] was based on similar evidence. In addition, the visible absorption spectra of the ε–Co(en)(dien)Cl^{2+} and γ–Co(en)dpt)Cl^{2+} [1] ions are very similar, and different from the other isomers in their respective series, again suggesting similar geometries for these forms.

Acido ligands *trans* to coordinated secondary amine groups are known to aquate more rapidly than those *trans* to primary amine groups.[21] This provides further support for the assignment of the ε chloro isomer to configuration **IV**, as it is this form which exhibits the greatest rate of reaction with Hg^{2+} in $HClO_4$. The uncatalysed aquation rates for these chloro isomers are now under investigation.

The assignment of the κ chloro isomer to configuration **II** is based on the observation that this form is converted to the π chloro isomer under both acid alkaline conditions (*i.e.* via both the aquo and hydroxo intermediates). The ω chloro form is converted to the π chloro isomer only via base hydrolysis and is particularly stable in all other respects to isomer interconversion. Hence the ω isomer is assigned to configuration **I**.

The magnitude of the rate constants for the base hydrolyses of the three chloro isomers that have been measured[22] are in the order $\pi > \kappa > \omega$ with a rate ratio of 10^4: 5: 1 respectively. Similar variations in the magnitude of the rates of base hydrolysis have also been observed in the four Co(tetren)Cl^{2+} isomers.[23]

Bosnich and Dwyer[6] have measured the hydrolysis rates of the two Co(en)(dien)Cl^{2+} isomers they isolated (apparently our ω and κ) in 0.01 F $HClO_4$. Their results show that the κ chloro isomer hydrolyses approximately 2.3 times faster than the ω isomer at this acidity. Such a rate difference would be expected as the released halide is *trans* to a primary group in both complexes, if they have configurations **II** and **I** respectively, as we propose.

Acknowledgments. We thank Professor A. G. McLellan of the Department of Physics, University of Canterbury, for the use of the Cary 14 Spectrophotometer.

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[16] F. Basolo and R. G. Pearson « *Mechanisms of Inorganic Reactions* », 2nd Ed. John Wiley, N. Y., 1967 p. 177.

[17] K. OhKawa, S. Yano, and J. Fujita, *Bull. Chem. Soc. Japan*, *41*, 2224 (1968).

[18] D. A. House, *Inorg. Nucl. Chem. Letters*, *3*, 67 (1967).

[19] S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, *31*, 811 (1969).

[20] H. H. Schmidtke and D. Garthoff, *Inorg. Chim. Acta*, *2*, 357 (1968).

[21] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, *6*, 2172 (1967).

[22] R. W. Hay, Victoria University of Wellington, New Zealand, personal communication.

[23] P. A. Marzilli, Pater presented at the 40th ANZAAS Conference, Jan. 1968, Cristchurch, New Zealand.