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Acidopentaminecobalt(III) Complexes with Polyamine Ligands. I. Geometric Isomers of Some Acido(ethylenediamine)-(dipropylenetriamine)cobalt(III) Complexes

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Received August 17, 1968

The three geometric isomers (α, β and γ) of Co(en)(dpt)Cl^{2+} have been isolated as the $ZnCl_4^{2-}$, $ZnBr_4^{2-}$, $Zn(NCS)_4^{2-}$ and ClO_4^- salts. The α and β forms are prepared by the decomposition of $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ in HCl. α–[Co(en)(dpt)Cl]$ZnCl_4$ forms two (β and γ) Co(en)(dpt)NO_2^{2+} isomers, and from these the β and γ–[Co(en)(dpt)Cl]$ZnCl_4$ isomers respectively, can be obtained. Bromo, iodo, azido, isothiocyanato and aquo complexes have also been prepared. The configurations of these isomers are discussed in terms of chemical reactions and infrared and visible spectral considerations.

Introduction

Recent interest in the properties of geometric isomers of Co^{III} complexes formed by different conformations of polyamine ligands[1] *e.g.* tetren[2-6] or trien[7] has prompted us to study several acidopentaminecobalt(III) systems formed with mixed triamine-diamine ligands.

There are potentially three geometric configurations generated by edgewise displacements in a M(AA)(ABA)X^{2+} system (AA = bidentate linear polyamine, ABA = tridentate linear polyamine) (Figure 1; I, II, and III). In adition, each of these modifications can exist in two conformations, depending whether the hydrogen associated with the coordinated secondary amine of the tridentate polyamine is *cis* or *trans* to the diamine (Figure 1).

Complexes of the acido diamine-triamine type that have previously been reported[2,8-10] are Co(en)(dien)X^{2+} (2 isomers[9,10]) Co(pn)(dien)X^{2+} (1 isomer[8]) and Co(tmd)(dien)$^{2+}$ (1 isomer[8]) .These were all prepared by reacting a trinitrotriaminecobalt(III) complex with another polyamine.[2,8-10]

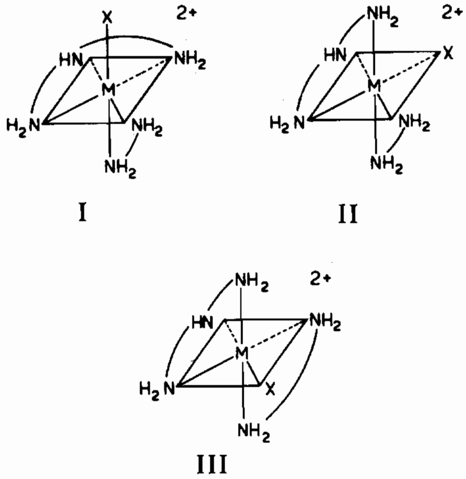

Figure 1. Possible geometric isomers of M(AA)(ABA)X^{2+} (AA = bidentate linear polyamine, ABA = tridentate linear polyamine).

Using a different synthetic method for mixed polyamine systems,[11] we have isolated Co(en)(dien)X^{2+} (4 isomers), Co(pn)(dien)X^{2+} (3 isomers), Co(ibn)(dien)X^{2+} (1 isomer), Co(tmd)(dien)X^{2+} (2 isomers), Co(en)(dpt)X^{2+} (3 isomers), Co(pn)(dpt)X^{2+} (2 isomers) and Co(tmd)(dpt)$^{2+}$ (3 isomers).

We describe here the preparation, properties, reactions and geometric configurations of the three isomers isolated for the Co(en)(dpt)X^{n+} system.

Two (α and β) (probably configurations II and I respectively) of the three chloro isomers are isolated as the tetrachlorozincate(II) salts when $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ is reacted with HCl containing $ZnCl_2$ and the third chloro isomer (γ) (probably configuration III) is generated by the HCl/$ZnCl_2$ decomposition of a nitro complex derived from the α isomer. The isomers have been distinguished on the basis of infrared and visible absorption spectra and by their X-ray powder diffraction patterns. These methods are not, however, expected to differentiate between the different conformations due to the NH proton.

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(1) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ and tetren=$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$

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Table I. Analitical data

Complex	Calculated					Found				
	C%	H%	N%	Co%	X% [a]	C%	H%	N%	Co%	X% [a]
$[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 2H_2O$	19.88	5.61	14.50	12.20	—	19.99	5.83	13.88	12.22	—
$[Co(en)(dpt)Cl]ZnCl_4$—α	19.49	5.11	14.29	11.96	35.96	19.56	5.20	14.19	11.86	35.81
—β						19.51	5.10	14.08	12.11	36.02
—γ						19.50	5.06	14.43	12.05	36.01
$[Co(en)(dpt)Cl](ClO_4)_2$—α	19.83	5.21	14.43	12.17	7.36	20.27	5.50	13.97	12.11	7.45
—β						20.17	5.55	13.93	12.07	7.41
—γ						19.86	5.33	14.68	12.05	7.45
$[Co(en)(dpt)Cl]Zn(NCS)_4$—α	24.71	4.32	21.61	10.10	45.89	24.76	4.87	21.37	10.20	45.82
—β						24.37	4.89	21.67	10.22	45.37
—γ						23.78	4.68	20.32	10.05	45.49
$[Co(en)(dpt)Cl]ZnBr_4$—α	14.32	3.76	10.44	8.79	52.95	15.08	3.95	10.73	8.75	52.91
—β						14.77	3.94	10.27	8.62	52.69
—γ						14.50	3.91	10.85	8.67	52.61
$[Co(en)(dpt)Cl]ZnI_4$—α				6.86	62.34				6.77	63.11
$[Co(en)(dpt)Br]ZnBr_4$—α	13.27	3.48	9.68	8.13	55.12	13.59	3.54	9.62	8.11	55.34
—β						13.77	3.68	9.48	8.07	55.27
—γ						13.64	3.58	9.39	8.17	55.19
$[Co(en)(dpt)Br](ClO_4)_2$—α	17.63	4.26	12.85	10.81	14.66	18.98	5.18	13.10	10.83	14.59
—γ									10.81	14.63
$[Co(en)(dpt)Br]Br_2$—α	19.61	5.14	14.29	12.03	48.93	19.00	5.29	14.07	11.98	48.87
$[Co(en)(dpt)Br]ZnCl_4$—α	17.88	4.69	13.03	10.79	41.28	18.55	4.97	12.84	10.89	41.28
—γ									10.81	41.16
$[Co(en)(dpt)Br]Zn(NCS)_4$—α	22.98	4.01	20.07	9.38	49.71	23.39	4.22	20.26	9.24	49.38
—γ									9.38	49.54
$[Co(en)(dpt)I]I_2$—α				9.34	60.34				9.24	60.31
—β									9.25	60.27
—γ									9.27	60.45
$[Co(en)(dpt)I](ClO_4)_2$—α	16.68	4.37		10.23	22.03	16.61	4.28		10.11	21.97
$[Co(en)(dpt)I]ZnCl_4$—α				10.08	45.99				10.05	45.89
$[Co(en)(dpt)I]Zn(NCS)_4$—α				8.73	53.19				8.68	53.36
$[Co(en)(dpt)I]ZnBr_4$—α				7.73	58.59				7.70	58.53
$[Co(en)(dpt)NO_2]ZnCl_4$—β	19.08	5.00	16.69	11.70	28.16	19.02	5.04	16.43	11.54	28.28
—γ						19.05	4.99	16.22	11.73	28.21
$[Co(en)(dpt)NO_2](ClO_4)_2$—β	19.40	5.08	16.98	11.88	—	19.11	5.21	17.31	11.72	—
—γ						19.47	5.15	17.78	11.92	—
$[Co(en)(dpt)NO_2]Zn(NCS)_4$—γ	24.10	4.21	23.43	9.86	38.85	25.05	4.68		9.91	38.78
$[Co(en)(dpt)NO_2]ZnBr_4$—γ				8.65	46.92				8.55	46.99
$[Co(en)(dpt)(NCS)]Zn(NCS)_4$—β	25.75	4.16	23.11	9.72	47.89	26.50	4.89	22.57	9.65	48.04
—γ									9.65	47.80
$[Co(en)(dpt)(NCS)]ZnCl_4$—β				12.04	40.83				12.01	40.74
$[Co(en)(dpt)N_3]ZnCl_4$—α				11.80	28.39				11.72	28.56
$[Co(en)(dpt)N_3](ClO_4)_2$—α				11.62	—				11.51	—
$[Co(en)(dpt)N_3]ZnBr_4$—α				8.70	47.20				8.69	47.23
$[Co(en)(dpt)N_3]Zn(NCS)_4$—α				9.99	39.38				9.82	39.29
$[Co(en)(dpt)(OH_2)](ClO_4)_3$—α				10.40	—				10.22	—

[a] Total halogen or NCS^- as found by Ag^+ titration.

Experimental Section

The commercial amines were used without further purification. All other chemicals were reagent grade. Analytical data are listed in Table I.

μ-Peroxobis(ethylenediamine)bis(dipropylenetriamine)dicobalt(III) Perchlorate Dihydrate: An aqueuos solution (200 ml) of ethylenediamine (6 g) and dipropylenetriamine (13.1 g) was added to a stirred solution of $Co(NO_3)_2 . 6H_2O$ (29 g) and $NaClO_4 . H_2O$ (30 g) in 500 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after two hr the brown crystals that deposited were collected, washed with 2-propanol ,then ether and finally air dried . The yield was 37 g or 45%.

A sample for analysis was prepared by dissolving 2 g of the crude material in the minimum volume (75 ml) of room temperature water. Excess solid $NaClO_4 . H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as above. An 82% recovery was obtained.

α and β-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): The crude $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ prepared above (30 g) was added to a solution of 85 ml of 12 F HCl and 170 ml of water containing 50 g of $ZnCl_2$. The mixture was heated on a steam bath (ca. 80°) until the effervescence ceased (*ca.* 45 min). During this time the mauve-pink crude α isomer deposited. The cooled solution was filtered through sintered glass and the product (14 g, 75%) was washed with 2-propanol and then ether.

The aqueous mother liquor was evaporated to about 200 ml on a steam bath and then allowed to stand at room temperature for two days. About 2 g (10% yeild) of violet crystals (β isomer) were obtained.

The impure α isomer was recrystallised by dissolving it in the minimum volume (ca. 250 ml) of 80° 0.2 F HCl and adding 50 ml of 6 F HCl together with

25 g of $ZnCl_2$. The pure α isomer commenced to crystallise from the hot solution and after cooling to room temperature in an ice bath, was collected and washed as above. Recrystallisation of the β isomer was effected similarly but with a corresponding reduction in volumes and weights of reagents. Losses on recrystallisation were mechanical.

The effect of the HCl concentration on the yield was determined by adding 2 g of $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ to solutions of HCl (16.6 ml) containing 3.3 g of $ZnCl_2$ and heating at 80° for 30 min.

The product was filtered from the cooled solution, washed and dried as above and weighed. Results are presented in the order, acid strength (F), (weigth of α-$[Co(en)(dpt)Cl]ZnCl_4$ obtained): 7.2 (0.53 g), 6.0 (0.57 g), 4.8 (0.57 g), 3.6 (1.01 g), 2.4 (0.75 g), 1.2 (0.33 g). There was incomplete reaction with 1.2 F HCl and with 7.2 F HCl, much $CoCl_4^{2-}$ was formed.

γ-Nitro(ethyenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): Two grams of α-$[Co(en)(dpt)Cl]ZnCl_4$ was dissolved in 50 ml of 0.2 F HCl and 6 g of $NaNO_2$ added. The solution was heated at 80° for 30 min. Mild effervescence occurred and the color changed from red to orange-yellow. The hot solution was slowly poured into a hot solution of 5 g of $ZnCl_2$ in 200 ml. of 50/50 acetone/2-propanol solution. The yellow crystals that deposited on cooling were collected on sintered glass and washed with acetone and ether: yield 60%.

The mother liquor from this synthesis slowly deposited orange-red crystals of β-$[Co(en)(dpt)NO_2]ZnCl_4$ (see below) as the acetone evaporated.

The crude γ-nitro (1.2 g) was recrystallised by dissolving it in the minimum volume of 0.2 F HCl and adding this to 100 ml of acetone. Yellow crystal spangles (75% recovery) were slowly deposited and were collected and washed as above.

β-Nitro (ethylenediamine) (dipropylenetriamine) cobalt(III) Tetrachlorozincate(II): Similar reaction conditions were used as for the synthesis of the γ-nitro isomer except that β-$[Co(en)(dpt)Cl]ZnCl_4$ was used. The orange crystals that deposited from the aqueous acetone/2-propanol solution, after two days, were washed with 2-propanol and then ether; yield 75%.

This isomer is soluble in acetone and was recrystallised as for the γ form but using 2- propanol.

γ-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One gram of γ-$[Co(en)(dpt)NO_2]ZnCl_4$ was dissolved in 10 ml of hot water and 20 ml of 12 F HCl added. The solution was heated at 80° until a wine red color (about 30 min) and then 5 g of $ZnCl_2$ was added. The heating was continued and the product commenced to crystallise from the hot solution. After cooling, the crystals were collected on sintered glass, washed with 2-propanol and then ether. The yield was 0.6 g or 55%.

α, β and γ-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: The α, β and γ isomers of $[Co(en)(dpt)Cl]ZnCl_4$ were separately dissolved in the minimum volume of 60° 3 F $HClO_4$ and ten times the weight of $NaClO_4 . H_2O$ added. The mauve-red, pale purple and pale red, respectively, perchlorate salts that crystallised on cooling in an ice bath, were washed with 2-propanol, ether and air dried. The yields were α 85%, β 45% and γ 60%.

α, β and γ - Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): The α, β and γ isomers of $[Co(en)(dpt)Cl]ZnCl_4$ were separately dissolved in 80° 0.2 F acetic acid (1 g/ 150 ml, 1 g/ 50 ml and 1 g/ 40 ml respectively) and a solution of 3 g of NH_4NCS in 10 ml of water was added. The mauve, purple and red, respectively, tetrathiocyanatozincate(II) salts crystallised immediately. The products were filtered from the well cooled solutions and washed with 5 ml of ice water. The α isomer was also washed with 95% ethanol but the β and γ isomers form oils with this reagent. The yields were α 92%, β 60% and γ 73%.

α, β and γ - Chloro(ethylenediamine)(dipropylenetriamine)Cobalt(III) Tetrabromozincate(II): The α, β and γ isomers of $[Co(en)(dpt)Cl]ZnCl_4$ (2 g, 0.5 g and 0.5 g respectively) were separately dissolved in 80° HCl (50 ml 0.2 F, 15 ml 0.05 F and 15 ml 0.05 F) and 63% HBr (25 ml, 15 ml, and 15 ml) containing $ZnBr_2$ (5 g, 3 g and 3 g) was added. Mauve, purple and red products crystallised immediately. The products were filtered from the well cooled solutions and washed with 2-propanol and ether. The yields were α 97%, β 82% and γ92%.

α-Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetraiodozincate(II): One half gram of α-$[Co(en)(dpt)Cl]ZnCl_4$ was dissolved in 50 ml of 80° 0.2 F CH_3CO_2H and 1 g of $Zn(ClO_4)_2$ and 5 g of NaI were added. The violet needles that deposited from the ice cooled solution were washed with 2-propanol and recrystallised from 50 ml of 0.2 F CH_3CO_2H by addition of NaI (5 g); yield 60%.

α, β, and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II): *α-Isomer.* $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ (6 g) was added to a solution of 16.6 ml of 48% HBr in 33.3 ml of water containing 10 g of $ZnBr_2$. Effervescence occurred and some bromine was evolved. The mixture was heated on a steam bath at 80°, until the effervescence ceased (about 30 min), during which time the purple crystalline product deposited. This was collected on sintered glass and washed sucessively with 50/50 2-propanol/water, 2-propanol and ether; yield 91%.

β-Isomer: One gram of β-$[Co(en)(dpt)Cl]ZnCl_4$ was dissolved in 25 ml of water and 1.2 g of Ag_2O added. The mixture was warmed to 60° for 15 min. and then filtered. A solution of 5 g of $ZnBr_2$ in 10 ml of 48% HBr was added to the hot solution and the crystalline product deposited on cooling; yield 40%

γ-Isomer: One half gram of γ-$[Co(en)(dpt)NO_2]ZnCl_4$ was dissolved in 10 ml of water and 15 ml of 63% HBr added. The solution was heated at 80° for 2 hr and then $ZnBr_2$ (3 g) was added. Shining purple crystals (0.31 g, 65%)were deposited when the solution was cooled in an ice bath.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: One half gram of α or γ-

$[Co(en)(dpt)Br]ZnBr_4$ were separately dissolved in 80° 3 F $HClO_4$ (20 ml) and $NaClO_4 . H_2O$ (5 g) was added. The purple-red perchlorate salts that crystallised on cooling were collected and recrystallised from 3 F $HClO_4$ by the addition of excess $NaClO_4 . H_2O$; yields, α 95%; γ 90%.

α-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Bromide: Six grams of $[Co_2(en)_2(O_2)](ClO_4)_4 . 2H_2O$ was added to 25 ml of 63% HBr in 25 ml of water. The brown tribromide salt (75%) precipitated, after evolution of oxygen and bromine. This material is unstable in air and decomposes to the purple bromide salt. The pure bromide salt (17%) crystallised slowly from the mother liquor and, after filtration, was washed with acetone.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): Two grams of α-$[Co(en)(dpt)Br]ZnBr_4$ was dissolved in 80 ml of 0.1 F HBr and a solution of $ZnCl_2$ (10 g) in 8 F HCl (40 ml) was added. The microcrystalline purple product crystallised immediately and, after filtration, was washed with 2-propanol and ether; yield 88%.

The γ tetrachlorozincate salt was similarly prepared from γ-$[Co(en)(dpt)Br]ZnBr_4$ in an 85% yield.

α and γ-Bromo(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One gram of α-$[Co(en)(dpt)Br]ZnBr_4$ was dissolved in 100 ml of 0.2 F CH_3COOH at room temperature and a solution of 3 g of NH_4SCN in 10 ml of water was added. The pale purple product deposited immediately and after filtration from the ice cooled solution, was washed with 5 ml of ice water and air dried; yield 85%.

The γ tetrathiocyanatozincate salt was prepared similarly from γ-$[Co(en)(dpt)Br]ZnBr_4$ in a 95% yield. These compounds form oils with 95% ethanol and ether and turn brown on standing in air.

α, β and γ-Iodo(ethylenediamine)(dipropylenetriaminei cobalt(III) Iodide: Solutions of 2 g of the isomerically pure chloro perchlorate salts in 30 ml of water containing 4 g of NaI were reluxed for 30 min. The olive green iodo iodide salts slowly deposited from the cooled solutions (yellow) on addition of 10 g of NaI. These were collected, washed with 50% aqueous ethanol and then acetone. The yields were: α 75%, β 30%, and γ 25%.

α-Iodo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate, Tetrachlorozincate(II), Tetrabromozincate(II) and Tetrathiocyanatozincate(II): These salts were prepared by dissolving α-$[Co(en)(dpt)I]I_2$ in water and adding an excess of the appropriate anion. Data are presented in the order: weight of α-$[Co(en)(dpt)I]I_2$, volume of water, weight or volume of precipitating agent, yield. 1 g, 50 ml, 10 g $NaClO_4$, 65%. 0.2 g, 40 ml, 2 g $ZnCl_2$ in 20 ml 12 F HCl, 65%. 0.2 g, 30 ml, 2 g $ZnBr_2$ in 10 ml 63% HBr, 60%. 0.25 g, 50 ml, 1.5 g NH_4SCN and 0.5 g $Zn(ClO_4)_2$ in 10 ml water, 50%.

The green salts that were deposited were washed with 2-propanol and ether and air dried.

α-Azido(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One gram of α-$[Co(en)(dpt)Cl]ZnCl_4$ was dissolved in 0.2 F CH_3COOH (20 ml) containing NaN_3 (3 g.). As the solution was heated at 80° for 15-20 min the color changed to dark red. The solution was cooled to room tempreature and 100 ml of 1:1 2-propanol-methanol containing 5 of $ZnCl_2$ was added. The red crystalline product that deposited was collected after 24 hr. More product was obtained from the mother liquor on the addition of 20 ml of 2-propanol containing 2 g of $ZnCl_2$. The total yield was 50%.

If $ZnCl_2$ is not added in the above synthesis, a green, water insoluble product (probably $Co(dpt)(N_3)_3$) is slowly deposited.

α-Azido(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate, Tetrabromozincate(II) and Tetrabromozincate(II) and Tetrathiocyanatozincate(II); These salts were prepared by dissolving α-$[Co(en)(dpt)N_3]ZnCl_4$ in dilute acid and adding an excess of the precipitating anion. Data are presented in the order: weight of α-$[Co(en)(dpt)N_3]ZnCl_4$, volume of acid, weight or volume of the appropriate anion, yield. 0.5 g, 10 ml 0.2 F $HClO_4$, 5 g $NaClO_4$, 30%. 0.25 g, 20 ml 0.2 F CH_3CO_2H, 2.5 g $ZnBr_2$ in 10 ml 63% HBr, 75%. 0.25 g, 20 ml 0.2 F CH_3CO_2H, 2.5 g NH_4SCN in 5 ml water, 65%.

The deep purple salts that deposited (slowly in the case of the perchlorate) were washed with 2-propanol and ether and air dried. The $Zn(NCS)_4^{2-}$ salt was washed with ice water only as this forms oils in organic solvents.

β-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One and a half grams of α-$[Co(en)(dpt)Cl]ZnCl_4$ was dissolved in 180 ml of water and 20 ml of 2 F NaOH was added. The solution was warmed at 80° for 10 min to hydrolyse the chloro ligand completely and was then made acid (pH 5) by the dropwise addition of glacial acetic acid. A solution of 5 g of NH_4SCN in 20 ml of water was then added and the reaction mixture was allowed to stand to anate. Sparingly water soluble deep red-violet crystal clusters separated after 2 weeks. The product was washed with 3×10 ml portions of ice water and then with 2-propanol, and then air dried; yield 55%.

The product was found to be an isomeric mixture of the α and β forms. Recrystallisation from boiling water produced the isomerically pure β form with a 75% recovery.

β-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II): One half gram of β-$[Co(en)(dpt)NCS]Zn(NCS)_4$ was dissolved in 20 ml of 0.1 F HCl at 80° and the hot solution poured into 100 ml of 2-propanol containing 2.5 g $ZnCl_2$. The red crystals that deposited after two days at room temperature were collected, washed with 2-propanol and air dried; yield 25%.

γ-Isothiocyanato(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): A suspension of 0.25 g γ-$[Co(en)(dpt)NO_2]ZnCl_4$, 1 g $Zn(ClO_4)_2$ and 3 g NH_4SCN in 30 ml of 1.5 F $HClO_4$ was heated at 80° for 1 hr to form a clear orange solution. The yellow-orange product that deposited on cooling was recrystallised from hot water and washed with 2-propanol; yield 55%.

β-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: One gram of β-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 20 ml of 0.2 F $HClO_4$ and 3 g of $NaNO_2$ added. The solution was heated at 80° for 15 min and the color changed from red to orange-red. The hot solution was slowly poured into 50 ml of 50/50 2-propanol/acetone containing 10 g of $NaClO_4 . H_2O$. The orange crystals that deposited after five days were collected and washed with ether; yield 55%. No γ-isomer was detected in this synthesis.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: Two grams of α-[Co(en)(dpt)Cl]$ZnCl_4$ was dissolved in 50 ml of 0.2 F HCl, 6 g of $NaNO_2$ was added and the solution heated at 80° for 30 min. Five grams of $NaClO_4 . H_2O$ was added to the hot orange-yellow solution and heating was continued for a further 30 min. The solution was then poured into 200 ml of 1:1 2-propanol/acetone containing 1 ml 70% $HClO_4$, but evaporation to 50 ml was required before orange plates deposited. The product was filtered on sintered glass and washed with acetone and ether; yield 60%.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II): One quarter gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 10 ml. 0.2 F CH_3CO_2H and a solution of 2 g of $ZnBr_2$ in 5 ml of 63% HBr was added. The pale yellow product slowly deposited from the ice cooled solution and was washed with acetone and ether; yield 90%.

γ-Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II): One half gram of γ-[Co(en)(dpt)NO_2]$ZnCl_4$ was dissolved in 50 ml of 80° 0.2 F CH_3COOH and a solution of NH_4SCN (4 g) in 5 ml of water was added. Crystallisation was effected by adding $Zn(ClO_4)_2$ (2 g) and NH_4SCN (4 g) in 10 ml of water to the cooled solution. Yellow spangles were slowly deposited on further cooling in an ice bath. The product was filtered and washed with ether; yield 65%.

α-Aquo(ethylenediamine)(dipropylenetriamine)cobalt(III) Perchlorate: Two grams of α-[Co(en)(dpt)Cl]$ZnCl_4$ and 2.4 g of Ag_2O were suspended in 50 ml of water and the mixture heated at 60° for 15 min. Sodium perchlorate (8 g) was added to the cooled, filtered solution and this was made acid (pH 2) by dropwise addition of 3 F $HClO_4$. The orange-red solution was evaporated at room temperature with an air stream to about 10 ml and after five days orange crystals were deposited. These were collected, washed with methanol and air dried; yield 25%.

Spectral Measurements: The visible absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. Data for the molar absorbancy indices were obtained in 0.1 F $HClO_4$ at 20-25° using matched 1 cm quartz cell with 0.1 F $HClO_4$ in the reference path. 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 infrared spectrophotometer. The X-ray powder diffraction patterns were obtained using a Phillips Model PW 1050/25 wide range goniometer connected to a Phillips (PR 2500) one line recorder.

Chemical Analyses: Co was determined by decomposing the complexes with ammonium peroxodisulfate and estimating the Co(II) spectrophotometrically at 620 mμ as the thiocyanate complex in aqueous acetone. Halogen and thiocyanate were determined by potentiometric titration with standard $AgNO_3$ using a Radiometer pH meter. The complexes were decomposed with ammonium peroxodisulfate and acidified with HNO_3 prior to titration. C, H and N analyses were performed by Dr A. D. Campbell of the University of Otago, New Zealand.

Results

Forty-five new [Co(en)(dpt)X]Z_n complexes have been synthesised and of these, the chloro, bromo and iodo salts have been isolated in three isomeric forms (α, β and γ), the isothiocyanato and nitro salts in two forms (β and γ), and the azido and aquo salts in one (α) form. The different isomers are thought to result from different geometric arrangements of the polyamines about the central cobalt(III) atom (Figure 1).

These complexes exhibit colors typical of cobalt(III) pentamine complexes *viz.* the chloro and bromo isomers have various shades of mauve to violet, the iodo isomers are green, the isothiocyanato and nitro isomers are yellow or orange, the aquo complex is orange and the azido salts are dark violet. Maxima and minima in the visible absorption spectra of the Co(en)(dpt)X^{n+} cations in solution are given in Table II, together with those reported earlier for the related $Co(NH_3)_5X^{n+}$ and Co(tetren)X^{n+} cations. Molar absorbancy index vs. wavelength plots for the α, β and γ chloro complexes are presented in Figure 2.

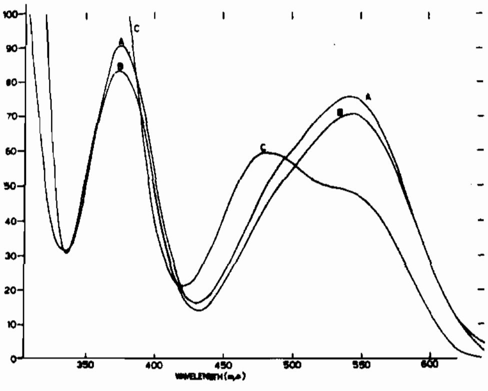

Figure 2. Visible absorption spectra of α, β and γ-Co(en)(dpt)Cl^{2+} in 0.1 F $HClO_4$ at 20-25°. Ordinate is molar absorbancy index, $M^{-1} cm^{-1}$. A = α isomer, B = β isomer, C = γ isomer.

There are some differences in the visible absorption spectra of the three isomeric Co(en)(dpt)X^{2+} (X = Cl, Br) cations (Table II, Figure 2) and this has been one

Table II. Visible Absorption Maxima and Minima of α, β and γ-Co(en)(dpt)X^{n+}, α and β-Co(tetren)X^{n+} and Co(NH$_3$)$_5$X^{n+} in Aqueous Solution at 20-25° [a].

Complex	λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	λ_{min}
α-Co(en)(dpt)Cl^{2+} [b]	542(75.1)		517(60.1) sh	431(13.0)	374(90.1)	337(30.8)
β-Co(en)(dpt)Cl^{2+} [b]	542(70.1)		520(62.0) sh [d]	432(13.8)	375(83.0)	335(31.5)
γ-Co(en)(dpt)Cl^{2+} [b]	543(47.9)sh		484(59.4)	422(21.1)		
α-Co(tetren)Cl^{2+} [c]	522(109)		480(105) sh	417(37.5)	362(103)	328(43.6)
β-Co(tetren)Cl^{2+} [c]	525(98.6)	508(97.3)	480(101)	415(37.2)	360(107)	332(64.5)
Co(NH$_3$)$_5$Cl^{2+} [e]	534(50.1)		467(11.0) sh		364(46.8)	
α-Co(en)(dpt)Br^{2+} [b]	551(66.9)		486(42.9) sh	447(20.4)		
β-Co(en)(dpt)Br^{2+} [b]	564(63)		532(51) sh	437(10)		
γ-Co(en)(dpt)Br^{2+} [b]	548(65.7)	512(53.8)	485(55.5)	429(31.6)		
α-Co(tetren)Br^{2+} [c]	548(132)		480(100) sh	423(48.1)		
β-Co(tetren)Br^{2+} [c]	550(121)	495(97.8)	480(98.0)	422(46.5)		
Co(NH$_3$)$_5$Br^{2+} [e]	552(57.6)		470(11.5) sh		310(831) sh	
α-Co(en)(dpt)I^{2+} [b]	613(84.6)		593(80.2) sh	536(59.6)		
β-Co(en)(dpt)I^{2+} [b]	606(96.7)			540(68.8)		
Co(NH$_3$)$_5$I^{2+} [f]	581(79.5)			527(56)	383(269)	
β-Co(en)(dpt)(NCS)$^{2+}$ [b]	506(237)			427(69.7)	312(1634)	
γ-Co(en)(dpt)(NCS)$^{2+}$ [b]	478(171)			417(94.1)		
α-Co(tetren)(NCS)$^{2+}$ [c]	490(219)			415(50.8)		
β-Co(tetren)(NCS)$^{2+}$ [c]	487(318)			412(71.7)		
Co(NH$_3$)$_5$(NCS)$^{2+}$ [e]	497(186)			430(35.5)	357(39.8) sh	
α-Co(en)(dpt)N$_3$$^{2+}$ [b]	525(342)			448(91.7)		
α-Co(tetren)N$_3$$^{2+}$ [c]	508(490)			432(117)		
Co(NH$_3$)$_5$N$_3$$^{2+}$ [e]	519(257)					
β-Co(en)(dpt)(NO$_2$)$^{2+}$ [b]	468(133)			405(39.5)		
γ-Co(en)(dpt)(NO$_2$)$^{2+}$ [b]	462(143)			403(53.8)		
β-Co(tetren)(NO$_2$)$^{2+}$ [c]	460(207)			397(51.6)		
Co(NH$_3$)$_5$(NO$_2$)$^{2+}$ [e]	458(100)				325(1660)	
α-Co(en)(dpt)(OH$_2$)$^{3+}$ [b]	495(83.9)			412(20.2)	355(98.6)	318(39.8)
α-Co(tetren)(OH$_2$)$^{3+}$ [c]	472(122)			405(33.0)	350(85.3	
Co(NH$_3$)$_5$(OH$_2$)$^{3+}$ [e]	485(48)				340	
α-Co(en)(dpt)(OH)$^{2+}$ [b]	510(112)			435(47.4)	372(118)	322(61.6)
α-Co(tetren)(OH)$^{2+}$ [c]	490(149)			417(51)	348(147)	
Co(NH$_3$)$_5$OH^{2+} [e]	503(62.5)			425(20)	370(70.8)	360(69)

[a] Everywhere numbers inside parenthesis are the molar absorbancy indeces, a_M (extinction coefficients ε) in M^{-1} cm^{-1}. Wavelengths are in milimicrons. [b] This research; in 0.1 F HClO$_4$, except in 0.1 F NaOH for the hydroxo complex. [c] D. A. House and C. S. Garner, *Inorg. Chem.* 6, 272 (1967), [d] sh = shoulder, [e] For references see Table II in D. A. House and C. S. Garner., *Inorg. Chem.* 6, 272 (1967), [f] M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, *266*, 49 (1951).

means of establishing isomeric purity, but the main method of isomer characterisation has been through the infrared spectra.

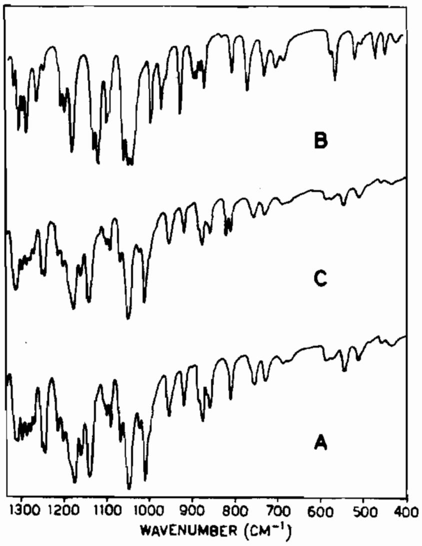

Figure 3. Infrared spectra of α, β and γ-[Co(en)(dpt)Cl]·ZnCl$_4$ in the 1300-400 cm^{-1} range (KBr disc.) A = α isomer, B = β isomer, C = γ isomer.

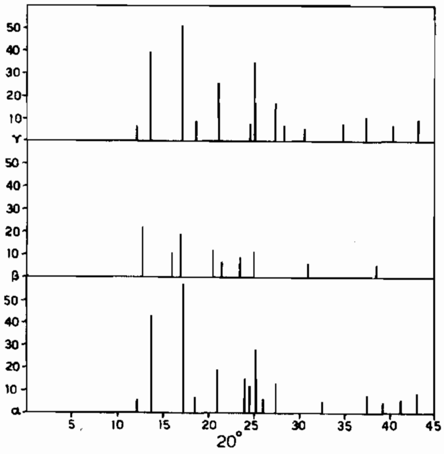

Figure 4. X-ray powder diffraction patterns of α, β and γ-[Co(en)(dpt)Cl]ZnCl$_4$ (2Θ = 4-45°). Vertical lines represent the positions and intensities (arbitary units) of the major peaks.

Figure 3 shows the infrared spectra of the α, β and γ chloro isomers, as the tetrachlorozincate(II) salts, in the 1300-400 cm^{-1} region. The infrared spectra of the other acido isomers show similar differences.

The α, β and γ-$[Co(en)(dpt)Cl]ZnCl_4$ salts also exhibit different X-ray powder diffraction patterns and Figure 4 schematically presents this data. The other acido isomers with a common anion show similar differences.

Discussion

Chemical Reactions: The α and β-chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) tetrachlorozincate complexes described here are derived from the μ-peroxodicobalt(III) complex $[Co_2(en)_2(dpt)_2O_2](ClO_4)_4 . 2H_2O$ [12] by decomposition of this in 30% HCl solution (3.6 F) containing zinc chloride.

The tetrachlorozincate anion has proved most useful, for these complexes, as the salts have satisfactory solubility properties, and this anion, unlike the perchlorate ion, is not infrared active in the 3500-400 cm^{-1} region. It does, however, have the disadvantage that for kinetic hydrolysis studies based on halide halide titration measurements, of providing a high halide background, and perchlorate salts are more useful for this purpose.

The α chloro complex yields two isomeric nitro complexes (β and γ) on treatment with nitrous acid and these generate the β and γ chloro isomers with 12 F HCl. The β and γ chloro complexes generate only the β and γ nitro complexes respectively with nitrous acid. These reactions are summarised in Figure 5.

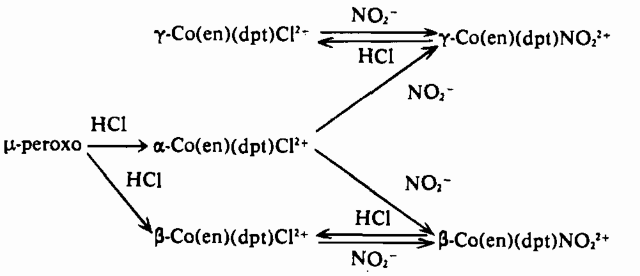

Figure 5. Isomeric interconversions for the α, β and γ chloro and nitro complexes.

Other acido complexes are prepared from the chloro isomers by conventional techniques.

Spectra: The most noticeable difference in the visible absorption spectra of the α, β and γ-$Co(en)(dpt)Cl^{2+}$ cations (Table II, Figure 2) is that the α and β isomers have two bands in the 700-320 mμ region with a shoulder on the high wavelength band, while the γ isomer shows only the assymetric high wavelength band before the onset of charge transfer bands in the near ultraviolet region. This difference is ascribed to the different environment of the halide ligand in these complexes (Figure 1). The intensities at the band maxima of the acido(ethylenediamine)(dipropylenetriamine) complexes are intermediate between those of the corresponding acido pentammine and acidotetraethylenepentamine complexes, suggesting that the number of chelate rings may be influencing this parameter. In other respects, the spectra of the analogs in these three classes of complex are similar, as would be expected from the fact that in each class the chromophore is CoN_5X.

The infrared spectra of α, β and γ-$[Co(en)(dpt)Cl]ZnCl_4$ in the 1300-400 cm^{-1} region (KBr disc) are shown in Figure 3. The α and γ forms have very similar spectra in this region apart from the characteristic γ doublet at about 820 cm^{-1}, while the spectrum of the β isomer shows many differences from the spectra of the γ and α forms. In addition, the α and γ-$[Co(en)(dpt)Cl]ZnCl_4$ isomers show two broad bands at about 3200 cm^{-1} (due to NH_2 stretch) and a singlet band at about 1580 cm^{-1} (NH_2 bend). In the β form, the 3200 cm^{-1} bands are resolved into four and the 1580 cm^{-1} band is split into a triplet. These splittings in the infrared spectra are characteristic of all the acido β salts isolated and together with the 820 cm^{-1} γ doublet served to detect the presence of isomeric mixtures in any 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 differences in the infrared spectra are ascribed to the different geometric arangements of the polyamine ligands about the central metal ion (Figure 1) causing different ring vibrations and hydrogen bond effects. Similar differences in the infrared spectra of $Co(tetren)X^{n+}$ [3,4] and $M(trien)X_2^{n+}$ [13,14] isomers have also been observed.

The infrared spectra of the bromo and iodo tetrachlorozincate salts are very similar to their chloro analogs but those of the nitro, isothiocyanato and azido tetrachlorozincate salts show bands characteristic of the acido ligand and these sometimes obscured the bands used for isomeric assignment. If such were the case, these acido complexes were converted to the chloro isomers and the infrared spectra of the tetrachlorozincate salts used for isomer identification.

The positions of the $-NO_2$ bands in the β and γ-$[Co(en)(dpt)NO_2]X_2$ salts showed that these were nitro rather than the isomeric nitrito complexes.

Geometric Configurations: Assuming that these isomers are related by the successive edgewise displacement of amine groups in the order I, II and III in Figure 1, the only configuration that could produce two different isomeric forms in a single displacement process would be II. That is, displacement of $-NH_2$ in ethylenediamine to give III or displacement of $-NH_2$ in dipropylenetriamine to give I. On this basis we assign the α chloro isomer to configuration II, as this form gives a mixture of the β and γ nitro isomers. We can rule out a series of successive displacements *e.g.* I→II→III or III→II→I as, if this were the case, some reversibility in the system between II and III (or II and I) would be expected. This has not been observed and the β and γ chloro

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(12) The properties of this and other brown diamagnetic μ-peroxo and green paramagnetic μ-superoxo polyaminecobalt (III) complexes will be described subsequently.

(13) D. A. Buckingham and D. Jones, *Inorg. Chem.*, *4*, 1387 (1965).

(14) D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, *88*, 2156 (1966).

isomers give *only* the β and γ nitro isomers respectively. (Figure 5).

In addition, configuration II is the only potentially optically active system of the three configurations. Unfortunately we have not been able to resolve the α-[Co(en)(dpt)Cl]$ZnCl_4$ salt using potassium *d*-antimony(III) oxytartrate but this in no way indicates that this compound is optically inactive, and other resolving agents are being tried.

We further suggest that the γ and β isomers correspond to configurations III and I (Figure 1) respectively. The variations in the infrared spectra of these isomeric forms are believed to be primarily due to the various arrangements of the polyamine ligands about the central metal ion. The spectra of the α and γ forms are very similar (Figure 3) and as the polyamine arrangement in configurations II and III are also very similar (Figure 1), the γ form is assigned to configuration III. On the other hand, the variations in the visible absorption spectra are believed to be due to the different environments of the halide ligand in the complex ion. The absorption spectra of the α and β forms are similar (Figure 2), in contrast to that of the γ isomer, and as the position of the halide ligand in configurations I and II are also similar (*trans* to a primary amine group in each case) we believe configuration I to correspond to the β form.

Up till now we have made mention of conformational isomers that could arise due to the *cis* or *trans* position of the coordinated secondary amine hydrogen atom. The techniques we have used here would not be expected to detect such isomerism, and optical activity, used to detect similar isomerism in N-methylethylenediamine[15] and triethylenetetramine[7] cobalt(III) complexes cannot be used as the coordinated secondary amine in the dipropylenetriamine ligand is not assymetric.

Preliminary data on the rate of base hydrolysis[16] of the α, β and γ-Co(en)(dpt)Cl^{2+} cations, does however, suggest that conformational isomers are present in these systems.

The rate data can be resolved into two components for each isomer and the rate ratios k_{fast}/k_{slow} are almost constant for the three isomeric systems.

The different rate detectable components could arise from either twinned crystals, crystal mixtures, or a rapidly established equilibrium mixture when the conformationally pure isomer is dissolved. Work is in progress to understand this problem more fully.

Acknowledgements: We thank Professor A. G. McLellan of the Department of Physics, University of Canterbury, for the use of the Cary 14 spectrophotometer and Dr W. Oldershaw of the Department of Geology, University of Canterbury for the use of the X-ray poyder diffraction apparatus. We also thank Dr D. A. Buckingham and Mr M. Dwyer of the Australian National University, Canberra, for optical rotatory dispersion measurements.

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(15) D. A. Buckingham, L. G. Marzilli and A. M. Sargeson, *Inorg. Chem.*, 7, 915 (1968) and the references cited therein.
(16) R. W. Hay and coworkers, Victoria University of Wellington, New Zealand, personal communication.