Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Acidopentaminecobalt(III) Complexes with Polyamine Ligands.
VII. The Preparation, Properties and Reactions of some Acido-(1,3-diaminopropane)(diethylenetriamine)cobalt(III) and Acido-(1,3-diaminopropane)(dipropylenetriamine)cobalt(III) Salts

A. R. Gainsford and D. A. House[1]

Received August 10, 1971

Seven solid state forms of $[Co(tmd)(dien)Cl]ZnCl_4$ *and six solid state forms of* $[Co(tmd)(dpt)Cl]ZnCl_4$ *have been isolated by various synthetic routes. However, only four* $Co(tmd)(dien)Cl^{2+}$ *and two* $Co(tmd)(dpt)Cl^{2+}$ *cations are distinguishable in aqueous acidic solution. Several bromo, nitro and azido complexes have been prepared from the chloro isomers and isomeric interconversions have been investigated. Infrared and visible absorption spectra are presented for these complexes and tentative structural assignments are made.*

Introduction

Previous publications[2] in this series have described the preparation,[3,4] properties and structure[2,5,6,7] of some three[4,6] $[Co(en)(dien)Cl]ZnCl_4$ and two [3,6,7] $[Co(en)(dpt)Cl]ZnCl_4$ isomers.[8] In addition, isomerically pure, co-crystallising chloro-nitro mixtures were obtained for certain isomers.[6]

In this paper, we describe the results obtained for similar systems where the bidentate ligand is changed from 1,2-diaminoethane to 1,3-diaminopropane, viz. $Co(tmd)(dien)X^{n+}$ and $Co(tmd)(dpt)X^{n+}$. In these systems, the number of solid state isomers is more than doubled when compared to the 1,2-diaminoethane systems, and an isomerically pure chloro-nitro mixture is again observed.

Experimental Section

The commercial amines were used without further purification. All other chemicals were reagent grade quality. *Trans*-$Co(dien)(NO_2)_3$[9,10] and *trans*-$Co(dpt)Cl_3$[11,12] were prepared by the literature methods. Infrared spectra of the MX_4^{2-} salts (M = Zn, Cd, Cu; X = Cl, Br) were used to determine the isomeric composition of the acido complexes. Each of the infrared distinguishable isomers (or co-crystallising mixtures that do not change composition or recrystallisation) were assigned an alphabetical letter in an arbitary but systematic manner. In several cases the syntheses involving fractional crystallisation have been duplicated with essentially similar results for the isomeric composition of the collected fractions. Analytical data are listed in Tables I and II.

μ-Peroxo-bis[1,3-diaminopropane)(diethylenetriamine)cobalt(III)]Perchlorate Dihydrate. An aqueous solution (200 ml) of 1,3-diaminopropane (7 g) and diethylenetriamine (10.5 g) was added to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (30 g) in 400 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 15 min. three 30 g portions of $NaClO_4 \cdot H_2O$ were added. The solution was stirred for a further 45 min. and then the brown-grey product that deposited was collected, washed with 2-propanol and then ether. The yield was 40.6 g or 84.5%.

A sample for analysis was prepared by dissolving 2 g of the crude product in 125 ml of water at 60° and then adding 20 g $NaClO_4 \cdot H_2O$. The brown crystalline product that deposited was collected, washed and dried as above. A 71% recovery was obtained.

Isomers of Chloro(1,3-diaminopropane)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). Method A: Crude $[Co_2(tmd)_2(dien)_2O_2](ClO_4)_4 . 2H_2O$ (30 g) was added to a solution of 12 *F* HCl (85 ml) in water (170 ml). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (15 min) and then $ZnCl_2$ (50 g) was added. The heating was continued for a further 30 min. during which time a red

---

(1) Author to whom correspondence should be addressed.
(2) Part VI. A.R. Gainsford, D.A. House, and W.T. Robinson, *Inorg. Chim. Acta 5*, 595 (1971)
(3) Part I. A.R. Gainsford and D.A. House, *Inorg. Chim. Acta, 3*, 33 (1969).
(4) Part II. A.R. Gainsford and D.A. House, *Inorg. Chim. Acta, 3*, 367 (1969).
(5) Part. III. P.R. Ireland, D.A. House, and W.T. Robinson, *Inorg. Chim. Acta, 4*, 137 (1970).
(6) Part V. A.R. Gainsford and D.A. House, *Inorg. Chim. Acta, 5*, 544 (1971).
(7) Part IV. D.A. House, P.R. Ireland, I.E. Maxwell, and W.T. Robinson, *Inorg. Chim. Acta, 5*, 397 (1971).
(8) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.
(9) B. Bosnich and F.P. Dwyer, *Australian J. Chem., 19*, 2045 (1966).
(10) Y. Kushi, K. Watanabe, and H. Kuroya, *Bull. Chem. Soc. Japan, 40*, 2985 (1967).
(11) G.G. Schlessinger, *Gannon Coll. Chem. J.*., 2, 14 (1965).
(12) A.R. Gainsford and D.A. House, *J. Inorg. Nucl. Chem., 32*, 688 (1970).

Table I. Analytical Data for $[Co(tmd)(dien)X]Y$.

Complex	Calculated C%	Calculated H%	Calculated N%	Calculated Co%	Calculated X%*	Found C%	Found H%	Found N%	Found Co%	Found X%*
$[Co_2(tmd)_2(dien)_2O_2](ClO_4)_4 . 2H_2O$	17.92	5.37	14.93	12.56	—	18.33	5.21	15.07	12.65	—
$[Co(tmd)(dien)Cl]ZnCl_4$ - *a*	17.56	4.84		12.30	37.02	17.73	4.78		12.25	37.07
- *b*						17.63	4.78		12.41	37.22
- *c*						17.32	4.69		12.82	36.91
- *d*						17.49	4.73		12.36	36.91
- *f*						17.64	4.75		12.45	36.83
- *g***						17.51	4.83		12.25	36.35
$[Co(tmd)(dien)Cl]ZnCl_4 . H_2O$ - *e*	16.92	5.07		11.86	35.68	17.04	4.95		11.92	35.87
- *h*						16.95	4.98		11.89	35.60
$[Co(tmd)(dien)Cl]CdCl_4$ - *a*				11.21	33.71				11.25	33.61
- *d*									11.10	33.75
$[Co(tmd)(dien)Cl]ZnBr_4$ - *b*				8.98	54.07				8.85	53.98
- *d*				8.98	54.07				8.90	54.00
$[Co(tmd)(dien)Cl]CdBr_4$ - *a*	11.95	3.29		8.38	50.46	12.46	3.54		8.35	50.57
- *d*						12.12	3.32		8.42	50.40
$[Co(tmd)(dien)Cl]CuCl_4$ - *d*	17.62	4.86		12.35	37.16	17.46	4.79		12.41	36.82
$[Co(tmd)(dien)Cl]I_2$ - *a*				11.22	55.05				11.20	55.00
- *d*									11.09	54.90
- *h*									11.15	55.08
$[Co(tmd)(dien)Cl]Zn(SCN)_4$ - *d*				10.35	47.04				10.27	47.35
- *d*									10.21	47.23
$[Co(tmd)(dien)Cl](ClO_4)_2$ - *a*	17.86	4.92		12.52	7.53	17.85	5.06		12.42	7.62
- *e*						17.99	5.02		12.35	7.75
$[Co(tmd)(dien)Br]ZnBr_4$ - *a*	11.99	3.31		8.41	56.99	12.35	3.50		8.28	56.51
- *d*						12.42	3.41		8.35	57.15
$[Co(tmd)(dien)Br]CdBr_4$ - *d*	11.24	3.10		7.88	53.41				7.85	53.35
- *h*						11.50	3.17		7.81	53.49
$[Co(tmd)(dien)Br]ZnCl_4$ - *d*				11.26	42.37				11.25	42.15
$[Co(tmd)(dien)Br]Zn(SCN)_4$ - *d*				9.61	50.86				9.52	50.50
$[Co(tmd)(dien)N_3]CdBr_4$ - *d*	11.84	3.26		8.30	45.00	12.10	3.41		8.25	44.65
$[Co(tmd)(dien)NO_2]ZnCl_4$ - *b*	17.18	4.77		12.04	28.97	17.54	4.78		12.05	28.91
- *c*						17.49	4.82		12.12	28.80
- *f*						17.48	4.75		11.96	28.75
- *h*						17.17	4.97		12.05	28.86
$[Co(tmd)(dien)NO_2]CdBr_4$ - *f*				8.25	44.75				8.32	44.62
$[Co(tmd)(dien)NO_2]Zn(SCN)_4$ - *f*	22.97	4.00		10.17	40.05				10.12	40.25

* Total halogen or NCS^- as found by Ag^+ titration. ** Shown to be an approximately 3:1 mixture of *f*-$[Co(tmd)(dien)Cl]ZnCl_4$ and *f*-$[Co(tmd)(dien)NO_2]ZnCl_4$.

crystalline product deposited. This was collected in crops from the cooling solution and was washed with 2-propanol and then ether. Each crop of the crude product was recrystallised by dissolving it in the minimum volume of 0.2 *F* HCl (0.5 g/25 ml) and then adding 12 *F* HCl (10 ml/0.5 g) and $ZnCl_2$ (1.5 g/0.5 g). The purified product that deposited on cooling, was collected in fractions and washed and dried as above.

On further evaporation of the aqueous mother liquor at room temperature, further crops were slowly obtained and these were recrystallised as above but using a corresponding reduction in volumes and weights of the reagents used.

The total yield of chloropentamine product was 15.12 g or 51.6%. Table III lists the isomeric composition of the products.

Method B: Trans-$Co(dien)(NO_2)_3$ (14 g) was suspended in 30 ml of water and 1,3-diaminopropane (4.0 ml, 100%) was added. The mixture was heated on a steam bath for 1 hour during which time the neutral complex dissolved to give a dark brown solution. 15 ml of 12 *F* HCl was added cautiously to the solution and the heating at ca. 80° was continued for a further 1.5 hour in which time a purple-red solution was formed. 10 ml of 12 *F* HCl and 10 g of $ZnCl_2$ were added and the solution was allowed to cool to room temperature. The crude product that deposited, was collected in crops and washed with 2-propanol and then ether.

Each crop of the crude product was recrystallised by dissolving it in 0.1 *F* HCl at 60° (1 g/15 ml) and then adding 12 *F* HCl (5 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling, was collected in fractions and was washed and dried as above.

The total yield of chloropentamine product was 14.21 g or 63.7%. Table IV lists the isomeric composition of the products.

Method C: Method B was repeated on a double scale except that the 80° heating time (after the addition of 12 *F* HCl (30 ml) was reduced to 45 min.

$ZnCl_2$ (15 g) and 12 *F* HCl (5 ml) were then added and the product that deposited on cooling was collected in crops, washed with 2-propanol and then ether. Each crop was recrystallised as in Method B.

On the slow evaporation of the aqueous mother liquor at room temperature, further crops were obtained and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used.

The total yield of chloropentamine product was 25.01 g or 56.2%. Table V lists the isomeric composition of the products.

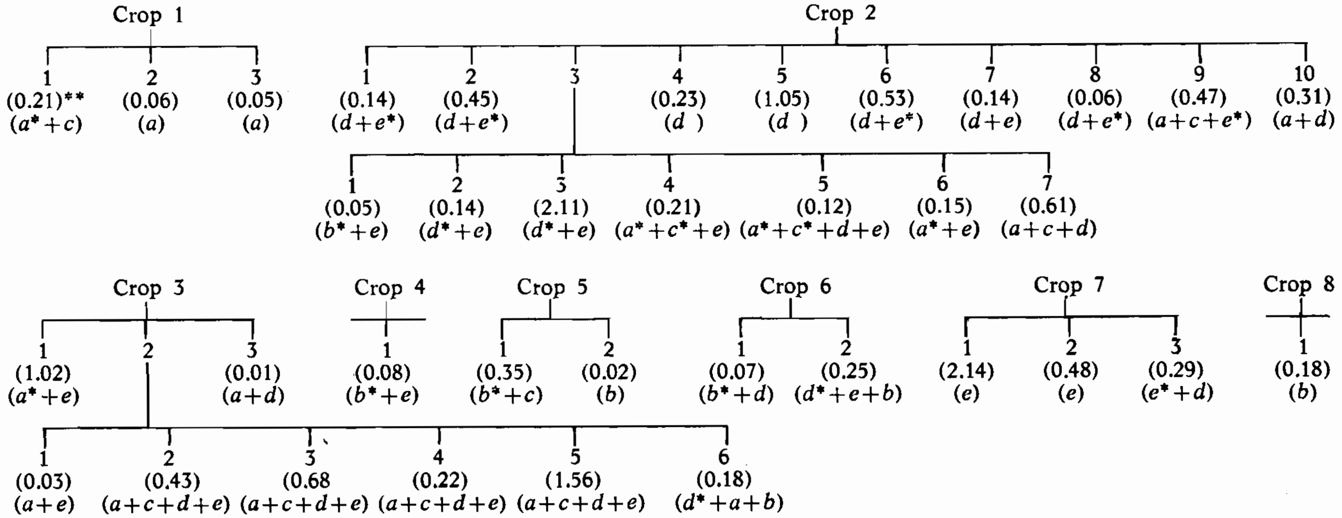
Resolution of d-[Co(tmd)(dien)Cl]ZnCl$_4$. The pure isomer (4 g) was dissolved in water (15 ml) at 50° and glacial acetic acid (0.5 ml) was added. An equal weight of solid ammonium (+)-α-bromo-camphor-π-sulphonate was added slowly with stirring. The precipitate that began to deposit on cooling the solution

Table II. Analytical Data for [Co(tmd)(dpt)X]X.

Complex	Calculated					Found				
	C%	H%	N%	Co%	X%*	C%	H%	N%	Co%	X%*
$[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4 . 3H_2O$	21.35	5.96	13.84	11.65	—	21.25	5.76	13.79	11.73	—
$[Co(tmd)(dpt)Cl]ZnCl_4 . 2H_2O$ - *j*	19.90	5.75	12.87	10.84	32.62	19.64	5.55	12.84	10.88	32.81
- *m*						19.81	5.61	12.82	10.75	32.75
$[Co(tmd)(dpt)Cl]ZnCl_4 . H_2O$ - *n*	20.60	5.56	13.35	11.23	33.81	20.74	5.70	13.24	11.29	33.65
- *l*						20.89	5.58	13.23	11.12	33.92
- *k*						20.55	5.60	13.41	11.12	33.93
$[Co(tmd)(dpt)Cl]ZnCl_4$ - *i*	21.42	5.37	13.84	11.64	35.01	21.36	5.37	13.80	11.71	35.10
$[Co(tmd)(dpt)Cl]CdCl_4$ - *i*				10.64	32.00				10.71	31.92
$[Co(tmd)(dpt)Cl]ZnBr_4$ - *i*				8.61	51.86				8.52	51.41
- *j*									8.55	51.56
- *l*									8.49	51.60
$[Co(tmd)(dpt)Cl]CdBr_4$ - *i*				8.05	48.52				8.12	48.60
- *j*									8.00	48.55
$[Co(tmd)(dpt)Cl](ClO_4)_2$ - *i*	21.68	5.44	14.05	11.82	7.11	21.59	5.60	13.83	11.71	7.05
- *j*						21.85	5.58	13.82	11.67	7.08
- *l*						20.99	5.46	13.30	11.45	6.91
$[Co(tmd)(dpt)Cl]Zn(SCN)_4$ - *i*	26.18	4.56	21.27	9.87	44.98	26.49	5.00	21.76	9.94	44.58
- *j*									9.85	44.95
- *l*									9.93	44.60
$[Co(tmd)(dpt)Br]ZnBr_4$ - *i*	14.82	3.73	9.61	8.08	54.79	15.05	3.85	9.35	7.91	54.61
- *j*						14.71	3.92		7.95	54.47
- *n*						14.74	3.79		7.90	54.50
$[Co(tmd)(dpt)Br]ZnBr_4 . H_2O$ - *k*	14.47	3.91		7.89	53.47	14.57	4.00		7.82	53.69
$[Co(tmd)(dpt)Br](Br_3)_2$ - *i*	13.12	3.30		7.16	67.91	13.65	4.01		7.25	66.50
$[Co(tmd)(dpt)Br]Br_2$ - *i*				11.69	47.57				11.57	47.39
$[Co(tmd)(dpt)Br]ZnCl_4$ - *i*				10.69	40.21				10.41	40.27
$[Co(tmd)(dpt)Br]Zn(SCN)_4$ - *i*				9.18	48.64				9.08	48.29
$[Co(tmd)(dpt)Br](ClO_4)_2$ - *i*				10.85	14.71				10.77	14.61
$[Co(tmd)(dpt)Br]CdBr_4$ - *i*				7.59	51.47				7.62	51.55
$[Co(tmd)(dpt)Br]CdBr_4 . H_2O$ - *k*				7.42	50.30				7.45	50.55
$[Co(tmd)(dpt)OH](ClO_4)_2$ - *i*	22.51	5.88		12.27		22.01	5.65		12.06	
$[Co(tmd)(dpt)N_3]ZnCl_4$ - *i*	21.13	5.28	21.81	11.46	27.61	21.22	5.30	21.95	11.41	27.72
$[Co(tmd)(dpt)N_3]ZnBr_4$ - *i*	15.64	3.94	16.21	8.25	46.24	15.97	3.94	15.95	8.41	45.93
$[Co(tmd)(dpt)N_3]Zn(,SCN)_4$ - *i*				9.76	38.45				9.71	38.18
$[Co(tmd)(dpt)NO_2]ZnCl_4$ - *i*	20.85	5.28	16.23	11.39	27.43	21.03	5.47	16.11	11.45	27.14
- *l*						20.89	5.11		11.40	27.53
$[Co(tmd)(dpt)NO_2](ClO_4)_2$ - *i*	21.23	5.35		11.57		20.78	5.25		11.53	
$[Co(tmd)(dpt)NO_2]Zn(SCN)_4$ - *i*				9.69	38.20				9.51	38.46

* Total halogen or NCS$^-$ as found by Ag$^+$ titration.

Table III. Isomeric Composition of [Co(tmd)(dien)Cl]ZnCl$_4$: Method A.



* Indicates the major component(s) of the fraction. ** Weight in g.

Table IV. Isomeric Composition of [Co(tmd)(dien)Cl]$ZnCl_4$: Method B.

Crop 1

1	2	3	4	5	6	7	8	9
(3.40)**	(1.63)	(2.13)	(0.11)	(0.32)	(0.64)	(0.06)	(0.22)	(0.03)
(f*+e)	(f*+e)	(f+e)	(f+e)	(f+e)	(e*+f+h)	(e*+c+h)	(e*+c+h)	(d*+c+f+h)

Crop 2

1	2	3	4	5	6	7	8	9
(0.07)	(0.19)	(0.45)	(0.39)	(0.12)	(1.63)	(0.53)	(0.19)	(0.39)
(b)	(b*+h)	(h)	(h)	(h)	(h*+c+f)	(h+c+e)	(h+c+e)	(d*+h+f+c)

Crop 3

1	2	3	4
(0.97)	(0.64)	(0.01)	(0.09)
(h*+c*+e)	(h*+c*+f)	(h*+c+d)	(f*+e)

* Indicates the major component(s) of the fraction. ** Weight in g.

Table V. Isomeric Composition of [Co(tmd)(dien)Cl]$ZnCl_4$: Method C.

Crop 1

1	2	3	4	5	6	7	8
(0.12)**	(1.00)	(1.05)	(0.21)	(0.15)	(0.46)	(0.21)	(0.38)
(g)	(g)	(g)	(g)	(g)	(g*+e)	(e*+g)	(b+c+d+g)

Crop 2

1	2	3	4	5	6	7
(0.63)	(1.50)	(0.76)	(0.44)	(1.40)	(0.39)	(1.28)
(e*+g)	(g*+e)	(g+e)	(g+e)	(g+e)	(e*+g)	(e*+c*+g)

Crop 3

1	2	3	4	5	6
(2.49)	(0.91)	(0.20)	(0.79)	(0.23)	(0.51)
(e*+g)	(e*+g)	(e+g)	(e*+g)	(e*+g)	(e+g+a+c)

Crop 4

1	2	3	4	5	6
(0.25)	(0.15)	(0.11)	(0.63)	(0.10)	(0.08)
(b*+e)	(g*+e)	(g*+e)	(g+e)	(b*+c+e+g)	(c*+g*+e)

Crop 5

1	2	3	4
(0.11)	(1.65)	(0.11)	(0.04)
(b*+e)	(e*+d+g)	(a+c+e)	(d*+e*+c)

Crop 6

1	2	3	4	5	6	7	8	9
(0.21)	(0.32)	(0.23)	(0.57)	(0.15)	(1.73)	(0.06)	(0.11)	(0.12)
(f)	(f)	(f+e+h)	(f+e+h)	(f+e+h)	(f+c+h)	(c*+f)	(e*+f+c)	(a*+f)

Crop 7

(1.35)	(0.11)	(0.01)
(c+f)	(e*+h*+f)	(e+h+f)

Crop 8

(0.67)
(f+h+d+e)

Crop 9

(0.03)	(0.13)
(g*+f*+e)	(b)

Crop 10

(0.04)	(0.23)	(0.33)
(b*+f)	(d*+f)	(d*+h)

Crop 11

(0.47)
(d+e)

The « g »-isomer is shown to be a 3:1 f-[Co(tmd)(dien)Cl]$ZnCl_4$/f-[Co(tmd)(dien)NO_2]$ZnCl_4$ mixture.
* Indicates the major component(s) of the fraction. ** Weight in g.

to ca. 30° was collected in fractions (*1-7*). Each fraction was washed with 2-propanol and then ether. The α-bromo-camphor-π-sulphonate salt was converted to the tetrachlorozincate(II) salt by dissolving each fraction separately in 4 *F* HCl (0.5 g/10 ml) and then adding $ZnCl_2$ (1 g/0.5 g). The products that deposited after 24 hr at room temperature were collected and washed and dried as above. The product from fraction *7* was recrystallised giving two crops, *7/1* and *7/2*.

After 2 days at room temperature, the original mother liquor was treated with a solution of 12 *F* HCl (15 ml) containing $ZnCl_2$ (5 g). The product that deposited slowly, was collected in fractions (*8-11*) and washed and dried as above.

The molar rotations $[M]_\lambda$, of the $ZnCl_4^{2-}$ salt fractions, were determined at room temperature in 0.1 *F* $HClO_4$ using a JASCO-ORD-UV5 recording spectropolarimeter. The results were, in the order: *Fraction number,* (weight of $ZnCl_4^{2-}$ salt obtained in g), $[M]_{507}$ [deg.dm^{-1} (moles/100 cm^3)$^{-1}$] *1,* (0.002), +39.8; *2,* (0.187), +40.00; *3,* (0.035), +82.1; *4,* (0.027), +99.2; *5,* (0.051), +1435; *6,* (0.024), +2039; *7/1,* (0.113), +3926; *7/2,* (0.050), +329.7. *8,* (0.405), –211.8; *9,* (0.351), –135.3; *10,* (0.069), –323.6; *11,* (0.275), –2481.

The fraction of $(-)_{589}$-*d*-Co(tmd)(dien)Cl^{2+} with the maximum rotation (crop *7/1*) has the following molar rotations: $[M]_{602} = -1341$, $[M]_{566} = 0$, $[M]_{507} = +3926$, $[M]_{455} = 0$, $[M]_{430} = -943.4$, $[M]_{407} = -739.4$, $[M]_{377} = -1504$, $[M]_{356} = 0^0$.

The fraction of $(+)_{589}$–*d*–Co(tmd) (dien)Cl^{2+} with the maximum rotation (crop *11*) (63.2% optically pure based on the $(-)_{589}$ form) has the following molar rotations: $[M]_{602} = +837.0$, $[M]_{566} = 0$, $[M]_{507} = -2481$, $[M]_{455} = 0$, $[M]_{430} = +588.9$, $[M]_{407} = +416.8$, $[M]_{377} = +866.8$, $[M]_{356} = 0$.

Separation of Isomer h. - A sample containing ca. 30% or greater of the *h* isomer was found to be suitable.

[Co(tmd)(dien)Cl]$ZnCl_4$ (0.2 g) was dissolved in 0.2 *F* CH_3CO_2H (10 ml) at 50° and a solution of NaI (4 g) in water (10 ml) was added. On cooling to room temperature, the product that deposited was collected, washed with acetone and then ether. The crude product was converted to the tetrachlorozincate(II) salt by dissolving it in water (0.1 g/5 ml) and then adding 12 *F* HCl (5 ml) containing $ZnCl_2$ (2.5 g). The purple product (pure *h* isomer) that deposited immediately was collected, washed with acetone, 2–propanol and then ether.

Example of Isomerism with change in Anion. - *e* or *f*–[Co(tmd)(dien)Cl]$ZnCl_4$ (0.5 g) were separately dissolved in room temperature 0.2 *F* CH_3CO_2H (15 ml) and 63% HBr (15 ml) containing $ZnBr_2$ (5 g) was added. The products that deposited on cooling to room temperature were collected in crops, washed with 2–propanol and then ether. The yields of *d*–[Co(tmd)(dien)Cl]$ZnBr_4$ were 75.6% (from *f*) and 74.2% (from *e*), respectively.

Qualitative Isomerisation Reactions. - [Co(tmd)(dien)Cl]$ZnCl_4$. Small quantities of the pure isomers were taken and subjected to the following chemical reactions.

(a) *Reflux in* 6 *F HCl.* The pure isomers of [Co(tmd)(dienCl]$ZnCl_4$ were separately dissolved in 6 *F* HCl (0.25 g/12.5 ml) and the solutions were boiled under reflux for 30 min. 12 *F* HCl (5 ml) containing $ZnCl_2$ (2.5 g) was added and the products that deposited from the ice cooled solutions were collected, washed with 2–propanol and then ether. The results were: *a* → *b* + *d* + *f*, *b* → *b* + *d*, *c* → *c*, *d* → *b* + *d*, *e* → *e* + *d* + *b*, *f* → *b* + *f* + *d*, *"g"* → *b* + *d* + *f*, *h* → *h*.

(b) *Base Hydrolysis* (20-23°). The pure isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in water (0.25 g/5 ml) and ca. 10 ml of 1 *F* NaOH was added until all the $Zn(OH)_2$ had precipitated. The red-orange solutions were allowed to stand at room temperature for 30 min and then 12 *F* HCl (15 ml) and $ZnCl_2$ (4 g) were 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: *a* → *a*; *b* → *a*; *c* → *a*; *d* → *a*; *e* → *a*; *f* → *a*; *"g"* → *a*; *h* → *a*.

(c) *Base Hydrolysis* (80°). The above base hydrolysis reactions were repeated, except that the alkaline solutions were heated at 80° for 20 min. Identical isomeric interconversions were obtained.

(d) *Reaction with Nitrous Acid.* The pure [Co(tmd)(dien)Cl]$ZnCl_4$ isomers were treated with NO_2^-/HCl and [Co(tmd)(dien)NO_2]$ZnCl_4$ salts were obtained (see later). The results were: *a* → *b*, *b* → *b*, *c* → *c*, *d* → *f*, *e* → *f*, *f* → *f*, *"g"* → *f*, *h* → *h*. The pure *a*, *b*, *c*, *f*, and *h*–[Co(tmd)(dien)NO_2]$ZnCl_4$ salts were decomposed by heating (80°) a solution of each in 3 *F* HCl for 1 hr. The $ZnCl_4^{2-}$ salts of the chloro complexes deposited on the addition of $ZnCl_2$. The transformation that resulted were: *a* → *b*; *b* → *b*; *c* → *c*; *f* → *d*; *h* → *h*.

a and d–Chloro(*1,3–propanediamine*)(*diethylenetriamine*)*cobalt*(*III*) *Tetrachlorocadmiumate*(*II*). The *a* and *d* isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ (0.20 g) were separately dissolved in 60° 0.2 *F* CH_3CO_2H (20 ml) and 12 *F* HCl (10 ml) containing $CdCl_2$ (2.5) g) was added. The red and purple-red products that slowly deposited on cooling to room temperature were collected from ice cooled solutions and were washed with 2-propanol and then ether. The yields were: *a*, 55.6%; *d*, 87.9%.

b-Chloro(*1,3-propanediamine*)(*diethylenetriamine*)*cobalt*(*III*) *Tetrabromozincate*(*II*). The *b* isomer of [Co(tmd)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in 40° 0.2 *F* CH_3CO_2H (25 ml) and 63% HBr (15 ml) containing $ZnBr_2$ (2.5 g) was added. The red product (83.8%) that deposited immediately was collected from the ice cooled solution and was washed with 2–propanol and then ether.

a and d-Chloro(*1,3-propanediamine*)(*diethylenetriamine*)*cobalt*(*III*) *Tetrabromocadmiumate*(*II*). The *a* and *d* isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ (0.20 g and 0.25 g respectively) were separately dissolved in

0.2 *F* CH_3CO_2H at 40° (20 ml, 10 ml) and 63% HBr (5 ml, 5ml) containing $CdBr_2 \cdot 4H_2O$ (5 g, 2.5 g) was added. The red and purple-red products deposited immediately. The products were collected from the ice cooled solutions and were washed with 2-propanol and then ether. The yields were: *a*, 77.8%; *d*, 76.8 per cent.

d-Chloro(1,3-propanediamine)(diethylenetriamine)-cobalt(III) Tetrachlorocuprate(II). 0.25 g of *d*-[Co(tmd)(dien)Cl]$ZnCl_4$ was dissolved in 0.2 *F* CH_3CO_2H (10 ml) at room temperature and 12 *F* HCl (10 ml) containing $CuCl_2 \cdot 2H_2O$ (4 g) was added. The orange-red crystals that deposited on cooling in an ice bath were collected and washed with 2-propanol and then ether. The yield was 21.2%.

a and d-Chloro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Di-iodide. The *a* and *d* isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ (0.1 g, 0.1 g respectively) were dissolved in 0.2 *F* CH_3CO_2H (5 ml, 5 ml) and a solution of NaI (2.5 g, 5.0 g) in water (5 ml, 10 ml) was added. The products that slowly deposited on cooling the solutions in an ice bath were collected, washed with 2-propanol, acetone and then ether. The yields were: *a*, 77.2%; *d*, 55.1%.

a and d-Chloro(1,3-diaminopropane)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II). The *a* and *d* isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in 80° 0.2 *F* CH_3CO_2H (0.5 g/60 ml, 0.2 g/30 ml respectively) and a solution of NH_4NCS (1.5 g, 2.5 g) in 5 ml of water was added. The red and purple-red, respectively, tetrathiocyanatozincate(II) salts were deposited slowly on cooling to room temperature. The products were collected from the ice cooled solutions and were washed with 5 ml of ice water. The *a* isomer was washed with 95% ethanol but the *d* isomer forms oils with this reagent and it was washed with 2-propanol. The products were air dried. The yields were: *a*, 78%; *d*, 96.0%.

a and e-Chloro(1,3-diaminopropane)(diethylenetriamine)cobalt(III) Perchlorate. The *a* and *e* isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in 0.2 *F* $HClO_4$ at 60° (0.25 g/15 ml, 0.5 g/15 ml, respectively) and $NaClO_4 . H_2O$ (5 g, 5g) was added. The red perchlorate salts that crystallised on cooling in an ice bath, were collected, washed with 2-propanol and then ether. The yields were: *a*, 60%; *e*, 20.5%.

a and d-Bromo(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromozincate(II). [Co_2(tmd)$_2$(dien)$_2O_2$]$(ClO_4)_4 \cdot 2H_2O$ (4 g) was added to a solution of 10 ml 63% HBr in 20 ml of water. The solution was heated on a steam bath (ca. 80°) for 1 hour during which time there was mild effervescence and some bromine was evolved. $ZnBr_2$ (4 g) was then added and the product that deposited was collected, washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.1 *F* HBr at 60° (total yield in 35 ml) and adding 63% HBr (5 ml) and $ZnBr_2$ (5 g). The product that deposited on cooling was collected in fractions and it was washed and dried as above. The yield was 66.5%. The isomeric composition of the fractions are listed in Table VI.

Table VI. Isomeric Composition of the [Co(tmd)(dien)Br]ZnBr_4 fractions.

Crop	Yield(g)	Isomers(s)
1	0.19	*d*
2	1.05	*d*
3	1.35	*d*
4	0.11	*d**+*a*
5	0.35	*d*
6	0.03	*d**+*a*
7	0.04	*d**+*a*
8	0.08	*d*
9	0.15	*d*
10	0.11	*d**+*a*
11	0.24	*d*
12	0.14	*d*
13	0.24	*d*

* Indicates the major component in the fraction.

d-Bromo(1,3-diaminopropane)(diethylenetriamine)-cobalt(III) Tetrabromocadmiumate(II). Method A: *d*-[Co(tmd)(dien)Br]$ZnBr_4$ (0.25 g) was dissolved in 0.2 *F* CH_3CO_2H (15 ml) at 60° and 63% HBr (5 ml) containing $CdBr_2 \cdot 4H_2O$ (1.5 g) was added. On cooling to room temperature, the purple product was deposted and this was collected from the ice cooled solution and washed with 2-propanol and then ether. The yield was 85.5%.

Method B: *a*-[Co(tmd)(dien)Cl]$ZnCl_4$ (0.25 g) was dissolved in water (60 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux for 20 min. A solution of 40% HBr (15 ml) containing $CdBr_2 . 4H_2O$ (4 g) was then added and on cooling to room temperature the product was deposited. It was collected in two crops and was washed with 2-propanol and then ether. The second crop contained the *a* isomer as a minor component. The yield was 85.6%.

h-Bromo(1,3-propanediamine)(diethylenetriamine)-cobalt(III) Tetrabromocadmiumate(II). *h*-[Co(tmd)(dien)Cl]$ZnCl_4 \cdot H_2O$ (0.1 g) was dissolved in water (12 ml) and 50% HBr (10 ml) was added. The solution was boiled under reflux for 40 min. A solution of 50% HBr (10 ml) containing $CdBr_2 \cdot 4H_2O$ (4 g) was then added. On cooling in an ice bath, the product was slowly deposited and it was collected, washed with 2-propanol and then ether. The yield was 55.8%.

d-Bromo(1,3-propanediamine)(diethylenetriamine)-cobalt(III) Tetrachlorozincate(II). *d*-[Co(tmd)(dien)-Br]$ZnBr_4$ (0.2 g) was dissolved in 0.2 *F* CH_3CO_2H (10 ml) at 40°, and a solution of 12 *F* HCl (5 ml) containing $ZnCl_2$ (2.5 g) was added. After cooling the solution in an ice bath for 24 hr, the purple crystalline product that was slowly deposited was collected, washed with 2-propanol and then ether. The yield was quantitative.

d-Bromo(1,3-propanediamine)(diethylenetriamine)-cobalt(III) Tetrathiocyanatozincate(II). *d*-[Co(tmd)-

(dien)Br]$ZnBr_4$ (0.2 g) was dissolved in 0.2 *F* CH_3CO_2H (40 ml) at 60° and a solution of NH_4SCN (2.5 g) and $Zn(ClO_4)_2$ (2 g) in water (5 ml) was added. On standing at room temperature overnight, the purple-red crystalline product was deposited and it was collected, washed with 2-propanol and air dried. The yield was 83.7%.

d-Azido(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II). *e*-[Co(tmd)(dien)Cl]$ZnCl_4 \cdot H_2O$ (0.65 g) was dissolved in 0.2 *F* CH_3CO_2H (25 ml) and NaN_3 (2.5 g) was added. The solution was boiled under reflux for 30 min. A solution of 50% HBr (20 ml) containing $CdBr_2 \cdot 4H_2O$ (5 g) was then added. After cooling in an ice bath for 30 min. the red-purple product slowly crystallised and it was collected in crops, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 *F* CH_3CO_2H at 40° (0.1 g/10 ml) and then adding 50% HBr (10 ml/0.1 g) and $CdBr_2 \cdot 4H_2O$ (1 g/0.1 g) the product that deposited on cooling was collected from the ice cooled solution and was washed and dried as above. The yield was 23.1%.

b,c,f-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). The *a, b, c, d, e, f*, and «*g*» isomers of [Co(tmd)(dien)Cl]$ZnCl_4$ were separately dissolved in 0.2 *F* HCl (0.5 g/12.5 ml, 0.15 g/10 ml, 0.10 g/5 ml, 0.25 g/10 ml, 0.25 g/10 ml, 0.25 g/10 ml and 1 g/25 ml respectively) and $NaNO_2$ (2 g, 1 g, 0.5 g, 1 g, 1 g, 3 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min. during which time mild effervescence occurred and the colour changed from red to orange-yellow. The hot solutions were poured slowly into 1:1 2-propanol/acetone (50 ml, 20 ml, 12.5 ml, 25 ml, 25 ml, 25 ml, 100 ml) containing $ZnCl_2$ (2.5 g, 1 g, 0.5 g, 1 g, 1 g, 1 g, 2.5 g) and 12 *F* HCl (1 ml, 0.2 ml, 0.2 ml, 0.5 ml, 0.5 ml, 0.5 ml, 0.5 ml). The yellow crystals that deposited on cooling to room temperature were collected, washed with acetone and then ether. The yields were $a \rightarrow b$, 68.4%; $b \rightarrow b$, 65.4%; $c \rightarrow c$, 74.0%; $d \rightarrow f$, 70.1%; $e \rightarrow f$, 60.1%; $f \rightarrow f$, 70.3%; and «*g*»$\rightarrow f$, 84.2%.

h-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). *h*-[Co(tmd)(dien)Cl]$ZnCl_4 \cdot H_2O$ (0.2 g) was dissolved in 0.2 *F* CH_3CO_2H (15 ml) and $NaNO_2$ (1 g) was added. The solution was boiled under reflux for 30 min. during which time the colour changed from purple-red to orange-yellow. The hot solution was slowly poured into 1:1 2-propanol/acetone (25 ml) containing $ZnCl_2$ (1 g) and 12 *F* HCl (0.5 ml). After standing the solution at 0-5° for 3 days, the yellow-orange product that slowly deposited was collected, washed with 2-propanol, acetone and ether. The yield was 45.3%.

f-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrabromocadmiumate(II). *d*-[Co(tmd)(dien)Br]$ZnBr_4$ (0.3 g) was dissolved in 0.2 *F* HBr (8 ml) and $NaNO_2$ (1.5 g) was added. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time a mild effervescence occurred and the colour changed from red-purple to orange-yellow. The hot solution was slowly poured into 1:1 2-propanol/acetone (30 ml) containing $CdBr_2 \cdot 4H_2O$ (2 g) and 63% HBr (1 ml). On cooling to room temperature, the yellow product that slowly deposited was collected, washed with acetone and ether. The yield was 53.6%.

f-Nitro(1,3-propanediamine)(diethylenetriamine)cobalt(III) Tetrathiocyanatozincate(II). *f*-[Co(tmd)(dien)NO_2]$ZnCl_4$ (0.2 g) was dissolved in 0.2 *F* CH_3CO_2H (35 ml) at 80° and NH_4SCN (1.5 g) dissolved in water (5 ml) was added. On cooling to room temperature, the yellow product that slowly deposited was collected, washed with 2-propanol and air dried. The yield was 75.0%.

Crystal Data. *d*-[Co(tmd)(dien)Cl]$ZnCl_4$: The unit cell is monoclinic with $a = 10.23$ Å, $b = 9.64$ Å, $c = 16.67$ Å, $\beta = 96.25°$, $V = 1634$ $(Å)^3$, Dobs = 1.95 (±0.02) g cm^{-3}, $Z = 4$, Dcalc = 1.95 g cm^{-3} for $ZnCoCl_5N_5C_7H_{23}$ with F. Wt. = 478.86, μ(Cu Kα) = 175.09 cm^{-1}. The space group is $P2_1/c$ (No. 14) from systematic absences of reflections. (*h0l* absent for $l = 2n+1$, *0k0* absent for $k = 2n+1$). *e*-[Co(tmd)(dien)Cl]$ZnCl_4 . H_2O$: The unit cell is monoclinic with $a = 9.73$ Å, $b = 11.42$ Å, $c = 28.91$ Å, $\beta = 91.00°$, $V = 3212$ $(Å)^3$, Dobs = 2.04 (±0.02) g cm^{-3}, $Z = 8$, Dcalc = 2.05 g cm^{3-} for $ZnCoCl_5N_5C_7OH_{25}$ with F. Wt. = 496.88, μ(Cu Kα) = 178.94 cm^{-1}. The space group is C2/c (No. 15) from systematic absences of reflections. (*hkl* absent for $h+k = 2n+1$, *0k0* absent for $k = 2n+1$).

μ-Peroxo-bis[(1,3-propanediamine)(dipropylenetriamine)cobalt(III)] Perchlorate Trihydrate. A solution of 1,3-propanediamine (7.4 g) and dipropylenetriamine (13.1 g) in water (200 ml) was added to a stirred solution of $Co(NO_3)_2 \cdot 6H_2O$ (29 g) and $NaClO_4 \cdot H_2O$ (40 g) in 500 ml of water. A rapid stream of O_2 gas was passed through the stirred, room temperature solution and after 2 hr the brown crystals that deposited were collected, washed with 2-propanol, then ether and finally air dried. The yield was 37 g or 74%.

A sample for analysis was prepared by dissolving 2 g of the crude product in the minimum volume (ca. 80 ml) of room temperature water. After filtration, excess $NaClO_4 \cdot H_2O$ was added to the stirred solution and the brown crystalline product that deposited was collected, washed and dried as above. A 60% recovery was obtained.

Isomers of Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II). Method A: *Trans*-Co(dpt)Cl_3 (5 g) was suspended in water (25 ml) and 1,3-propanediamine (2.5 ml, 100%) was added. The purple-red solution was heated at 60° for 10 mins and then 12 *F* HCl (15 ml) was added dropwise. $ZnCl_2$ (5 g) dissolved in water (10 ml) was then added and on cooling to room temperature the crude product slowly deposited. This material was recrystallised by dissolving it in 0.2 *F* HCl at 60° (1 g/40 ml) and then adding 12 *F* HCl (10 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The crystalline product that deposited on cooling was collected in fractions and was washed and dried as above.

Table VII. Isomeric Composition of $[Co(tmd)(dpt)Cl]ZnCl_4$: Method A.

Crop	Fraction	Weight	Composition
Crop 1	1	(1.56)**	(j)
	2	(0.05)	$(j^{*}+i)$
	3	(0.11)	(j)
	4	(0.03)	(j)
Crop.2	1	(0.55)	(t)
Crop 3	1	(0.15)	$(t^{*}+k)$
Crop 4	1	(0.03)	$(l^{*}+k+t)$
Crop 5	1	(0.05)	$(k^{*}+l)$
Crop 6	1	(0.03)	$(k^{*}+l)$
Crop 7	1	(0.06)	$(k^{*}+l)$
Crop 8	1	(0.30)	$(t^{*}+j^{*}+k^{*}+l)$
Crop 9	1	(0.04)	(l)
Crop 10	1	(0.03)	(j)
	2	(0.07)	$(j+l)$

* Denotes the major component(s) of the fraction t=*trans*-$[Co(tmd)_2Cl_2]Cl$. ** Weight in g.

Table VIII. Isomeric Composition of $[Co(tmd)(dpt)Cl]ZnCl_4$: Method B.

Crop	Fraction	Weight	Composition
Crop 1	1	(12.08)**	(m)
	2	(0.77)	$(m+n)$
	3	(0.55)	(n)
	4	(0.49)	$(n+l)$
	5	(0.05)	$(l^{*}+n)$
	6	(0.08)	$(l+n)$
	7	(0.10)	(l)
	8	(0.03)	(l)
Crop 2	1	(2.77)	$(l+n^{*})$
Crop 3	1	(0.01)	(i)

* Indicates the major component(s) of the fractions. ** Weights in g.

The aqueous mother-liquor was reheated to 80° to evaporate it to ca. 40 ml. Further crops were obtained on standing at room temperature, the first of these containing a large percentage of *trans*-$[Co(tmd)_2Cl_2]$-Cl. The crops were recrystallised as above but using a corresponding reduction in volumes and weights of the reagents used.

The total yield of chloropentamine product was 2.21 g or 26.2%. The isomeric composition of the fractions are listed in Table VII.

Method B: Crude $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4 \cdot 3H_2O$ (35 g) was added to a solution of 12 *F* HCl (100 ml) in water (200 ml) containing $ZnCl_2$ (60 g). The solution was heated on a steam bath (ca. 80°) until the effervescence ceased (2.5 hr) during which time a red crystalline material deposited. The solution was cooled to 5° in an ice bath and the crude product was then collected, washed with 2-propanol and then ether.

The crude product was recrystallised by dissolving it in 0.2 *F* HCl at 80° (1 g/25 ml) and then adding 12 *F* HCl (5 ml/1 g) and $ZnCl_2$ (2.5 g/1 g). The purified product that deposited on cooling, was collected in fractions and was washed and dried as above.

On further evaporation of the aqueous mother liquor, further crops were obtained and these were recrystallised as above but using a corresponding reduction in the volumes and weights of the reagents used.

The total yield of chloropentamine product was 16.93 g or 50.9%. The isomeric composition of the fractions are listed in Table VIII.

Qualitative Isomerisation Reactions. $[Co(tmd)$-$(dpt)Cl]ZnCl_4$.

(a) *Reflux in 6 F HCl.* The pure i and j isomers of $[Co(tmd)(dpt)Cl]ZnCl_4$ were separately dissolved in 6 *F* HCl (0.5 g/25 ml) and the solutions were boiled under reflux for 30 min. 12 *F* HCl (5 ml) containing $ZnCl_2$ (5 g) was added and the products that were slowly deposited from the ice cooled solutions were collected in crops and washed with 2-propanol and then ether.

The results were: $i \rightarrow i^{*} + l^{*} + j + k$; $j \rightarrow i^{*} + l^{*} + j + k$. (* denotes the major components of the product).

(b) *Base Hydrolysis (20-25°).* The pure isomers of $[Co(tmd)(dpt)Cl]ZnCl_4$ were separately dissolved in water (0.25 g/8 ml) and ca. 10 ml of 1 *F* NaOH was added until all the $Zn(OH)_2$ had precipitated. The solutions were allowed to stand at room temperature for 20 min and the 12 *F* HCl (10 ml) and $ZnCl_2$ (2.5 g) were added. On standing the solutions at room temperature for 1 day, the product was slowly deposited and it was collected in crops, washed with 2-propanol and then ether.

The results were: $i \rightarrow i$; $j \rightarrow i$; $k \rightarrow i$; $l \rightarrow i$.

(c) *Reaction with Nitrous Acid.* Nitro compounds derived from the pure isomers of $[Co(tmd)(dpt)Cl]$-$ZnCl_4$ were prepared using the method described later in this paper. The nitro products were decomposed by heating (80°) a solution of each in 3 *F* HCl for 1 hr. The $ZnCl_4^{2-}$ salts of the chloro complexes were deposited by the addition of $ZnCl_2$.

The transformations that resulted were: *i*→*i*; *j*→*i*; *k*→*i*; *l*→*i*.

The infrared spectra of the nitro products indicate that these form with the same gross configuration as the parent chloro isomer i.e. *i*, *j*→*i*; *k*, *l*→*l*. It is therefore probable that the isomerisation *l*→*i* occurs in the decomposition procedure above.

i-Chloro(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Tetrachlorocadmiumate(II). *i*-[Co(tmd)-(dpt)Cl]$ZnCl_4$ (0.5 g) was dissolved in 0.2 *F* CH_3CO_2H (15 ml) at 50° and a solution of 4 *F* HCl (25 ml) containing $CdCl_2$ (5 g) was added. The mauve-red product deposited slowly on cooling in an ice bath and it was collected, washed with 2-propanol and then ether. The yield was 87.1%.

i, j, and l-Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II). The *i*, *j*, and *l* isomers of [Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ were separately dissolved 0.2 *F* CH_3CO_2H (1 g/80 ml, 0.25 g/25 ml, 0.25 g/25 ml, respectively) at 50° and a solution of 63% HBr (25 ml, 15 ml, 25 ml) containing $ZnBr_2$ (5 g, 2.5 g, 2 g) was added. The mauve, mauve-red and violet products that were deposited slowly on cooling to room temperature were collected from the ice cooled solutions and were washed with 2-propanol and then ether. The yields were: *i*, 95.0%; *j*, 77.8% and *l*, 65.0%.

i and j-Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrabromocadmiumate(II). The *i* and *j* isomers of [Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ were separately dissolved in 0.2 *F* CH_3CO_2H (0.25 g/15 ml) and a solution of 63% HBr (10 ml) containing $CdBr_2 \cdot 4H_2O$ (2.5 g) was added. On cooling to room temperature, the mauve and purple-red products were deposited and they were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were: *i*, 74.3%; *j*, 82.1%.

i, j, and l-Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Perchlorate. The *i* and *j* and *l* isomers of [Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ were separately dissolved in 0.2 *F* CH_3CO_2H (0.5 g/25 ml, 0.3 g/15 ml, 0.5 g/25 ml respectively) at 40° and $NaClO_4 \cdot H_2O$ (15 g, 10 g, 5 g) was added. The mauve, mauve and violet perchlorate salts were deposited on cooling in an ice bath and they were collected, washed with 2-propanol and then ether. The yields were: *i*, 82.2%; *j*, 81.1% and *l*, 40.6%.

l, j, and l-Chloro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrathiocyanatozincate(II). The *i*, *j*, and *l* isomers of [Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ were separately dissolved in 0.2 *F* CH_3CO_2H (1 g/150 ml, 0.25 g/40 ml, 0.25 g/15 ml respectively) at 50° and a solution of NH_4SCN (3 g, 2.5 g, 2 g) in water (20 ml, 10 ml, 5 ml) was added. The mauve, mauve and violet tetrathiocyanatozincate(II) salts were deposited slowly on cooling in an ice bath and they were collected, washed with 2-propanol and then ether. The yields were: *i*, 72.7%; *j*, 96.2%; *l*, 76.0%.

Isomers of Bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrabromozincate(II). *Method A*: [$Co_2(tmd)_2(dpt)_2O_2$]$(ClO_4)_4 \cdot 3H_2O$ (16 g) was added to a solution of 50 ml 63% HBr in 100 ml of water. The solution was heated on a steam bath (ca. 80°) for 30 min. during which time there was mild effervescence and some bromine was evolved. $ZnBr_2$ (20 g) was then added and the solution was reheated for a further 30 min. The crude product was collected from the hot solution and was washed with 2-propanol and then ether. The crude product was recrystallised by dissolving it in 0.2 *F* CH_3CO_2H (1 g/25 ml) at 80°, filtering to remove the di-tribromide salt (see below), and then adding 63% HBr (5 ml/1 g) and $ZnBr_2$ (2.5 g/1 g). The purified product that deposited was collected in fractions, washed and dried as above.

Further crops were obtained from the aqueous mother liquor on cooling in an ice bath and these were recrystallised as above but using a corresponding reduction in the weights and volumes of the reagents used. The yield was 33.0% (3.8% as the tribromide salt). The isomeric composition of the fractions are listed in Table IX.

Method B: A solution of *i*-[Co(tmd)(dpt)Cl]$ZnCl_4$ (0.5 g) in water (10 ml) containing 63% HBr (2 ml) was boiled under reflux for 20 min. The hot solution was added to a solution of $ZnBr_2$ (2.5 g) in 53% HBr (5 ml) and the product that deposited on cooling to room temperature, was collected in crops, washed with 2-propanol and then ether. The yield was 73.5 per cent. The isomeric composition of the product was, in the order: crop number, isomer composition (* indicates the major isomeric component), (weight in g): 1, *i*, (0.18); 2, k^*+j, 0.11); 3→6, *k*, (0.24).

Table IX. Isomeric Composition of [Co(tmd)(dpt)Br]$ZnBr_4$.

	1	2	3	4
Crop 1	(4.43)** (*i*)	(0.80) (*i*)	(0.30) (i^*+n)	(0.33) ($i+n$)
Crop 2	(0.03) ($i+n$)	(0.23) (*n*)	(0.05) (*k*)	(0.47) (*k*)
Crop 3	(0.35) (*k*)	(0.33) (*k*)		
Crop 4	(0.23) (*n*)	(0.05) (*n*)	(0.02) (*j*)	

Denotes the major component(s) of the fraction. ** Weight in g.

Method C: An analogous reaction to the above using *j*-$[Co(tmd)(dpt)Cl]ZnCl_4 \cdot 2H_2O$. A 67.6% yield was obtained and the isomeric composition of the product was: 1, j^*+k, (0.18); 2, k^*+j, (0.20); 3, k^*+j, (0.03); 4→6, *k*, (0.13).

i-Bromo(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Di-tribromide. $[Co_2(tmd)_2(dpt)_2O_2](ClO_{44})\cdot 3H_2O$ (8 g) was added to 63% HBr (25 ml) in water (50 ml). The solution was heated on a steam bath (ca. 80°) for 10 min during which time mild effervescence occurred and a brown crystalline substance was deposited. The product was collected, washed with 2-propanol and then ether. The yield was 14.6%.

Further heating of the mother liquor and the addition of $ZnBr_2$ (5 g) resulted in the deposition of the *i* and *n* isomers as in the previous synthesis (Method A).

i-Bromo(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Di-bromide. $[Co_2(tmd)_2(dpt)_2O_2](ClO_4)_4 \cdot 3H_2O$ (2 g) was suspended in water (10 ml) and 63% HBr (30 ml) was added. The solution was heated on a steam bath (ca. 80°) for 15 min during which time a purple-violet product was deposited. This product was collected from the ice cooled solution, washed with 2-propanol and then ether. The yield was 17.0%.

i-Bromo(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Tetrachlorozincate(II). *i*-$[Co(tmd)(dpt)Br]ZnBr_4$ (0.5 g) was dissolved in 0.05 *F* HBr (45 ml) at 60° and a solution of 12 *F* (25 ml) containing $ZnCl_2$ (2 g) was added. The violet-purple product deposited immediately and, after cooling the solution in an ice bath, it was collected, washed with 2-propanol and ether. The yield was 96.3%.

i-Bromo(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Tetrathiocyanatozincate(II). *i*–$[Co(tmd)(dpt)Br]ZnCl_4$ (0.25 g) was dissolved in 0.2 *F* CH_3CO_2H (10 ml) and a solution of NH_4NCS (2.5 g) in water (10 ml) was added. The pale purple product deposited immediately and it was collected, washed with 95% ethanol and then air-dried. The yield was 85.0%.

i and k-bromo(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrabromocadmiumate(II). The *i* and *k* isomers of $[Co(tmd)(dpt)Br]ZnBr_4$ (0.5 g, 0.25 g, respectively) were separately dissolved in 0.2 *F* CH_3CO_2H (20 ml, 15 ml) at 50° and a solution of 63% HBr (15 ml, 10 ml) containing $CdBr_2 \cdot 4H_2O$ (5 g, 2.5 g) was added. The purple products were deposited on cooling and they were collected from the ice cooled solutions, washed with 2-propanol and then ether. The yields were *i*, 84.3%; *k*, 63.2%.

i-Hydroxy(1,3-propanediamine)(dipropylenetriamine)cobalt(III) *Perchlorate.* *i*–$[Co(tmd)(dpt)Cl]ZnCl_4$ (2 g) and Ag_2O (2.4 g) were suspended in water (50 ml). The mixture was warmed at 60° for 30 min and then filtered. $NaClO_4 \cdot H_2O$ (5 g) was added to the violet filtrate which was then evaporated to ca. 10 ml at 25° under a slow stream of air. After 4 days, pale violet needle-like crystals were deposited and these were collected, washed with methanol and air dried. The yield was 35%.

i–Azido(1,3–propanediamine)(dipropylenetriamine)-cobalt(III) Tetrachlorozincate(II). *i*–$[Co(tmd)(dpt)Cl]ZnCl_4$ (2 g) was dissolved in 0.2 *F* CH_3CO_2H (40 ml) and NaN_3 (6 g) was added. The solution was heated on a steam (ca. 80°) for 15 min, cooled to ca. 25 in an ice bath and 1:1 2-propanol/methanol (100 ml) containing $ZnCl_2$ (5 g) and 12 *F* HCl (1 ml) was added. On standing at 0–5° for 24 hours the product, that slowly deposited, was collected, washed with 2-propanol and then ether. The yield was 61.2%.

i–Azido(1,3–propanediamine)(dipropylenetriamine)-cobalt(III) Tetrabromozincate(II). *i*–$[Co(tmd)(dpt)N_3]ZnCl_4$ (0.25 g) was dissolved in 0.05 *F* HCl (20 ml) and a solution of 63% HBr (20 ml) containing $ZnBr_2$ (2 g) was added. The red-purple crystalline product deposited on coling the solution in an ice bath. The product was collected, washed with 2-propanol and then ether. The yield was 97.3%.

i-Azido(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Tetrathiocyanatozincate(II). *i*–$[Co(tmd)(dpt)N_3]ZnCl_4$(0.25 g) was dissolved in 0.2 *F* CH_3CO_2H (25 ml) and a solution of NH_4NCS (2 g) in water (5 ml) was added. The red-purple product which deposited on cooling the solution in an ice bath was collected, washed with 95% ethanol and air dried. The yield was 73.2%.

i and l-Nitro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II). The *i* and *l* isomers of $[Co(tmd)(dpt)Cl]ZnCl_4 \cdot xH_2O$ were separately dissolved in 0.2 *F* HCl (2 g/50 ml, 0.25 g/10 ml, respectively) and $NaNO_2$ (6 g, 1 g) was added. The solutions were heated on a steam bath (ca. 80°) for 30 min during which timc mild effervescence occurred and the colour changed rapidly from red to yellow-orange. The hot solutions were slowly poured into 1:1 2-propanol/acetone (200 ml, 50 ml) containing $ZnCl_2$ (5 g, 2.5 g) and 12 *F* HCl (1 ml, 0.5 ml). The orange-yellow products were deposited on cooling to room temperature and they were collected from the ice cooled solutions, washed with acetone and then ether. The yields were: *i*, 90.3%; *l*, 73.8%.

i-Nitro(1,3-propanediamine)(dipropylenetriamine)cobalt(III) Perchlorate. *i*-$[Co(tmd)(dpt)Cl]ZnCl_4$ (2 g) was dissolved in 0.2 *F* HCl (50 ml) and $NaNO_2$ (6 g), was added. The solution was heated on a steam bath (ca. 80°) for 30 min. Mild effervescence occurred and the colour changed from red to orange-yellow. $NaClO_4 \cdot H_2O$ (5 g) was added to the hot solution which was slowly poured into 1:1 2-propanol/acetone containing $NaClO_4 \cdot H_2O$ (5 g) and 4 *F* $HClO_4$ (1 ml). On standing at room temperature for 3 days, the orange crystals that were slowly deposited were collected, washed with 2-propanol and then ether. The yield was 80%.

i-Nitro(1,3-propanediamine)(dipropylenetriamine)-cobalt(III) Tetrathiocyanatozincate(II). *i*-$[Co(tmd)(dien)NO_2]ZnCl_4$ (1 g) was dissolved in 0.2 *F* CH_3CO_2H (60 ml) at 60° and a solution of NH_4NCS (10

g) dissolved in water (15 ml) was added. The orange-yellow product that deposited on cooling to room temperature was collected from the ice cooled solution, washed with 2-propanol and was then air dried. The yield was 95.8%.

Spectral Measurements. The visible absorption spectra were obtained with a Shimadzu MPS-50L recording spectrophotometer using matched 1 cm quartz cells. Spectrophotometric analyses for Co were performed using a Beckman DBG recording spectrophotometer. The infrared spectra were run in both mulls and KBr discs using a Shimadzu IR-27G infrared spectrophotometer.

Chemical Analyses. Co, Cl, Br, I, and NCS were determined as described previously.[3] C, H, and N analyses were performed by Dr. A. D. Campbell of the University of Otago, New Zealand.

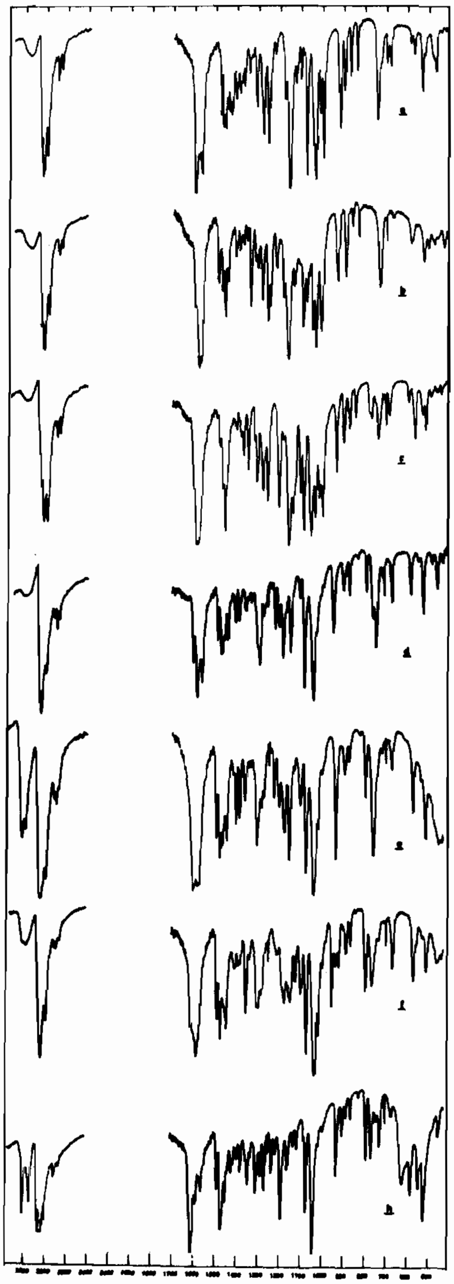


Figure 1. Infrared spectra of *a, b, c, d, e, f, h*-[Co(tmd)(dien)Cl]$ZnCl_4 \cdot xH_2O$ in the 4000-400 cm^{-1} range (KBr disc).

Crystal Data. All unit cell dimensions were calculated from precession photographs using Ni-filtered Cu Kα X-irradiation (λ Cu K$\bar{\alpha}$ = 1.54 Å). Densities were determined by flotation using CCl_4–CH_3I.

Results

Seven infrared distinguishable forms of [Co(tmd)(dien)Cl]$ZnCl_4$ [*a, b, c, d, e* (monohydrate), *f, h* (monohydrate)] and six forms of [Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ [*i* (x = 0), *j* (x = 2), *k* (x = 1), *l* (x = 1), *m* (x = 2), *n* (x = 1)] have been isolated by various synthetic routes and of these, *d*-[Co(tmd)(dien)Cl]$ZnCl_4$ has been separated into its chiral components.

Infrared spectra of these isomers are shown in Figures 1 and 2, and the visible absorption spectra

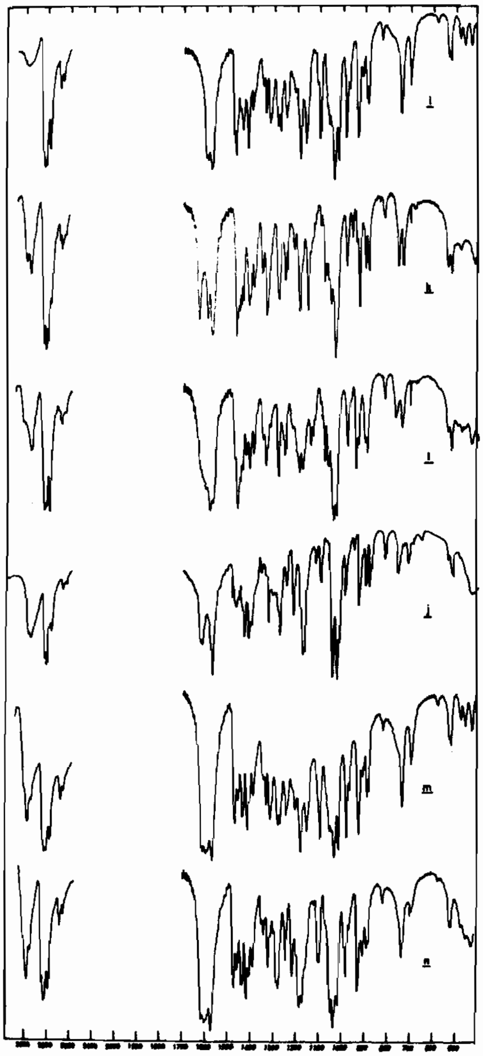


Figure 2. Infrared spectra of *j, m, n, i, k, l*-[Co(tmd)(dpt)Cl]$ZnCl_4 \cdot xH_2O$ in the 4000-400 cm^{-1} range (KBr disc).

are presented in Table X and XI and shown in Figures 3 and 4.

In addition to the separate isomers, a constant composition mixture («*g*»), consisting of *f*-[Co(tmd)(dien)Cl]$ZnCl_4$ and *f*-[Co(tmd)(dien)NO_2]$ZnCl_4$ in about a 3:1 ratio can also be formed.[6]

Other acido salts that have been prepared are listed in Table XII and the chemical and isomeric intercon-

Table X. Visible Absorption Maxima and Minima for the *a, b, c, d, e, f,* « *g* », and *h*-Co(tmd)(dien)X^{2+} and ω, ϰ and π-Co(en)(dien)X^{2+} cations in 0.1 *F* $HClO_4$ at 20-23°.[1]

Complex	λmin	λmax	λmin	λmax	λmin	λmax
a-Co(tmd)(dien)Cl^{2+} [2]	333	372	421	487		540sh [5]
	(44.1)	(78.4)	(31.8)	(84.6)		(62.7)
b-Co(tmd)(dien)Cl^{2+} [2]	335	369	421	487		540sh
	(44.4)	(79.0)	(32.1)	(84.7)		(61.3)
c-Co(tmd)(dien)Cl^{2+} [2]	328	368	417	491		522sh
	(45.2)	(90.9)	(36.6)	(91.9)		(88.6)
d-Co(tmd)(dien)Cl^{2+} [2]	329	369	424	470sh		535
	(39.3)	(97.0)	(26.0)	(55.7)		(75.1)
e-Co(tmd)(dien)Cl^{2+} [2]	329	369	424	475sh		535
	(39.3)	(97.0)	(26.1)	(58.2)		(75.0)
f-Co(tmd)(dien)Cl^{2+} [2]	330	369	424	473sh		535
	(38.8)	(96.8)	(26.0)	(56.9)		(74.8)
« *g* »-Co(tmd)(dien)X^{2+} [2]	317	326	415	468	(59.6)	528
	(354)	(359)	(39.0)	(73.6)	(60.1)	(65.0)
synthetic « *g* » [6]	317	326	415	468	520	528
	(351)	(362)	(39.2)	(73.4)	520	(66.3)
h-Co(tmd)(dien)Cl^{2+} [2]	327	364	424	465sh		546
	(40.7)	(98.5)	(19.0)	(40.0)		(96.6)
ϰ-Co(en)(dien)Cl^{2+} [4]	332	366	416	488sh		515
	(35.2)	(87.9)	(30.3)	(84.0)		(85.6)
π-Co(en)(dien)Cl^{2+} [4]	326	361	412	475sh		525
	(33.6)	(71.0)	(15.0)	(44.0)		(67.0)
ω-Co(en)(dien)Cl^{2+} [4]	323	358	416	480sh		532
	(75.0)	(110.8)	(19.3)	(60.0)		(92.0)
a-Co(tmd)(dien)Br^{2+} [2]		386sh	431	481sh		555
		(102)	(26.3)	(49.7)		(77.0)
d-Co(tmd)(dien)Br^{2+} [2]		390sh	432	483sh		552
		(91.6)	(22.6)	(47.2)		(70.8)
h-Co(tmd)(dien)Br^{2+} [2]		391sh	434	476sh		563
		(77.5)	(12.6)	(28.9)		(124)
ϰ-Co(en)(dien)Br^{2+} [3]			420	476sh		535
			(42.2)	(84.4)		(97.0)
π-Co(en)(dien)Br^{2+} [3]			419	461sh		537
			(20.2)	(35.1)		(69.6)
ω-Co(en)(dien)Br^{2+} [3]			419	462sh		538
			(22.2)	(46.0)		(99.8)
d-Co(tmd)(dien)N_3^{2+} [2]	271	311	438			513
	(3115)	(7495)	(66.8)			(298)
π-Co(en)(dien)N_3^{2+} [3]	262	303	431			506
	(1790)	(8270)	(99.5)			(452)
b-Co(tmd)(dien)NO_2^{2+} [2,7]	297	329	399			462
	(770)	(1400)	(38.2)			(137)
b-Co(tmd)(dien)NO_2^{2+} [2]	296	329	399			462
	(775)	(1410)	(38.3)			(138)
c-Co(tmd)(dien)NO_2^{2+} [2]	293	327	395			454
	(1190)	(2250)	(82.1)			(246)
f-Co(tmd)(dien)NO_2^{2+} [2]	295	327	397			458
	(705)	(1245)	(39.2)			(134)
f-Co(tmd)(dien)NO_2^{2+} [2,8]	295	327	397			459
	(700)	(1250)	(40.1)			(136)
f-Co(tmd)(dien)NO_2^{2+} [2,9]	(295)	327	396			458
	(710)	(1245)	(39.4)			(136)
f-Co(tmd)(dien)NO_2^{2+} [2,10]	295	327	396			458
	(716)	(1240)	(39.6)			(135)
h-Co(tmd)(dien)NO_2^{2+} [2]	294	329	399			457
	(770)	(1685)	(38.4)			(151)
ϰ-Co(en)(dien)NO_2^{2+} [3]	292	326	393			456
	(738)	(1440)	(38.3)			(157)
π-Co(en)(dien)NO_2^{2+} [3]	288	322	387			445
	(659)	(1340)	(29.4)			(109)
ω-Co(en)(dien)NO_2^{2+} [3]	290	325	394			452
	(792)	(1750)	(40.5)			(139)

[1] Everywhere numbers inside parenthesis are the molar absorbancy indices, a_M (extinction coefficients ε) in $M^{-1}cm^{-1}$. Wavelengths are in nanometers. [2] This research; in 0.1 *F* $HClO_4$. [3] A.R. Gainsford, *Thesis*, Univers. of Canterbury, Christchurch, New Zealand (1971). [4] A.R. Gainsford and D.A. House, *Inorg. Chim. Acta*, 3. 367 (1969). [5] sh = shoulder. [6] As calculated from 73% *f*-Co(tmd)(dien)Cl^{2+} + 23% *f*-Co(tmd)(dien)NO_2^{2+}. [7] Derived from *a*-[Co(tmd)(dien)Cl]$ZnCl_4$. [8] Derived from *e*-[Co(tmd)(dien)Cl]$ZnCl_4$. [9] Derived from *d*-[Co(tmd)(dien)Cl]$ZnCl_4$. [10] Derived from « *g* »-[Co(tmd)(dien)X]$ZnCl_4$ (see footnote 6)

Table XI. Visible Absorption Maxima and Minima for the *i, j, k, l, m* and *n*-Co(tmd)(dpt)X^{n+} and α and β-Co(en)(dpt)X^{n+} cations in aqueous solution at 20-23°.[1]

Complex	λmin	λmax	λmin	λmax	λmin	λmax
i-Co(tmd)(dpt)Cl^{2+} [2]	343 (39.3)	377 (73.8)	435 (13.0)	527 (60.4)		555sh [4] (55.2)
j-Co(tmd)(dpt)Cl^{2+} [2]	344 (38.9)	377 (74.0)	434 (12.6)	527 (60.4)		555sh (55.1)
m-Co(tmd)(dpt)Cl^{2+} [2]	344 (39.4)	377 (74.1)	435 (12.8)	528 (60.5)		555sh (55.2)
n-Co(tmd)(dpt)Cl^{2+} [2]	344 (39.5)	377 (74.1)	435 (13.1)	527 (60.4)		555sh (55.4)
k-Co(tmd)(dpt)Cl^{2+} [2]	340 (44.2)	372 (65.3)	432 (12.7)	514 (55.2)		565sh (38.5)
l-Co(tmd)(dpt)Cl^{2+} [2]	340 (44.1)	372 (65.4)	432 (12.8)	514 (55.3)		565sh (38.3)
α-Co(en)(dpt)Cl^{2+} [3]	337 (30.8)	374 (90.1)	431 (13.0)	517sh (60.1)		542 (75.1)
β-Co(en)(dpt)Cl^{2+} [3]	335 (31.5)	375 (83.0)	432 (13.8)	520sh (62.0)		5542 (70.1)
i-Co(tmd)(dpt)Br^{2+} [2]		405sh (66.5)	444 (15.7)	492sh (44.7)		540br [5] (54.8)
n-Co(tmd)(dpt)Br^{2+} [2]		405sh (66.9)	444 (15.8)	493sh (44.9)		541br (54.6)
k-Co(tmd)(dpt)Br^{2+} [2]		386sh (93.4)	437 (20.3)	512sh (60.4)		553 (48.1)
α-Co(en)(dpt)Br^{2+} [3]			447 (20.4)	486sh (42.9)		551 (66.9)
β-Co(en)(dpt)Br^{2+} [3]			437 (10)	532sh (51)		564 (63)
i-Co(tmd)(dpt)N$_3^{2+}$ [2]			457 (66.4)			530 (274)
α-Co(en)(dpt)N$_3^{2+}$ [3]			448 (91.7)			525 (342)
i-Co(tmd)(dpt)NO$_2^{2+}$ [2]	305 (1020)	334 (1590)	410 (26.8)			481 (120)
i-Co(tmd)(dpt)NO$_2^{2+}$ [2,6]	305 (1025)	334 (1580)	410 (26.5)			481 (121)
l-Co(tmd)(dpt)NO$_2^{2+}$ [2]	306 (1560)	336 (1655)	414 (46.4)			480 (188)
α-Co(en)(dpt)NO$_2^{2+}$ [3]			403 (53.8)			462 (143)
β-Co(en)(dpt)NO$_2^{2+}$ [3]			405 (39.5)			368 (133)
i-Co(tmd)(dpt)(OH$_2$)$^{3+}$ [2]		357sh (201)	430 (96.1)			515 (132)
α-Coen)(dpt)(OH$_2$)$^{3+}$ [2]	318 (39.8)	355 (98.6)	412 (20.2)			495 (83.9)
i-Cotmd)(dpt)OH^{2+} [3]	332 (38.3)	367 (65.5)	442 (16.0)	516 (73.1)		550sh (49.4)
α-Co(en)(dpt)OH^{2+} [2]	322 (61.6)	372 (118)	435 (47.4)			510 (112)

[1] Everywhere numbers in parenthesis are the molar absorbancy indices, a_M, (extinction coefficients, ε) in M^{-1} cm^{-1}. [2] This research; in 0.1 *F* HClO$_4$, except 0.1 *F* NaOH for the hydroxo complex. [3] A.R. Gainsford and D.A. House, *Inorg. Chim. Acta*, 3, 33 (1969). [4] sh = shoulder. [5] br = broad. [6] Derived from *j*-[Co(tmd)(dpt)Cl]ZnCl$_4$.

Table XII. Salts formed by the various isomers of [Co(tmd)(ABA)X]Y . xH$_2$OZ (ABA = dien, dpt).

Anion, Y =	$ZnCl_4^{2-}$	$CdCl_4^{2-}$	$CuCl_4^{2-}$	$ZnBr_4^{2-}$	$CdBr_4^{2-}$	$Zn(NCS)_4^{2-}$	$2ClO_4^-$	$2I^-$	$2Br^-$
A. [Co(tmd)(dien)X]Y . xH$_2$O*									
X=Cl	*a,b,c,d,e*(x=1), *f,h*(x=1)	*a,d*	*d*	*b,d*	*a,d*	*a,d*	*a,e*	*a,d,h*	
X=Br	*d*			*a,d*	*d,h*	*d*			
X=N$_3$					*d*				
X=NO$_2$	*b,c,f,h*				*f*	*f*			
B. [Co(tmd)(dpt)X]Y . xH$_2$O*									
X=Cl	*i,j*(x=2),*k*(x=1) *l*(x=1),*m*(x=2) *n*(x=1)	*i*		*i,j.l*	*i,j*	*i,j,l*	*i,j*		
X=Br	*i*			*i,j,n,* *k*(x=1)	*i* *k*(x=1)	*i*	*i*		*i***
X=OH							*i*		
X=NO$_2$	*i,l*					*i*	*i*		
X=N$_3$	*i*			*i*		*i*			

* x = 0 unless otherwise stated. ** Also *i*-[Co(tmd)(dpt)Br](Br$_3$)$_2$.

versions that have been observed are presented in Figures 5 and 6.

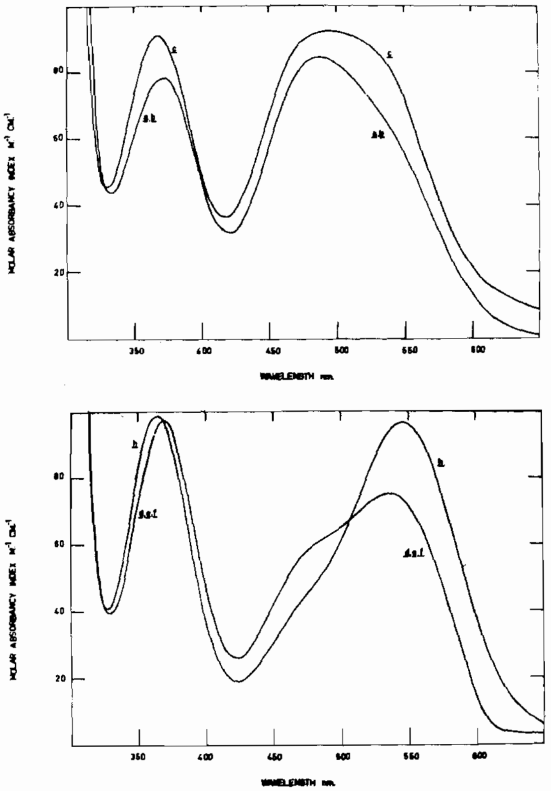


Figure 3. Visible absorption spectra of *d, e, f, h, c* and *a, b*-Co(tmd)(dien)Cl^{2+} in 0.1 *F* $HClO_4$ at 20-25°.

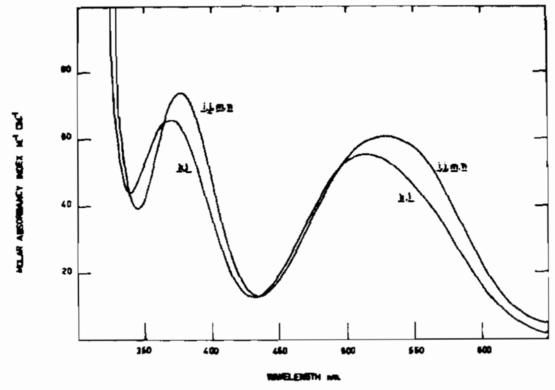


Figure 4. Visible absorption spectra of *i, j, m, n* and *k, l*-Co(tmd)(dpt)Cl^{2+} in 0.1 *F* $HClO_4$ at 20-25°.

Discussion

Chemical Properties. Seven solid state forms of [Co(tmd)(dien)Cl]$ZnCl_4$ have been detected but the visible absorption spectra (Table X) indicate that only four groups viz. *d, e, f; a, b; c* and *h* are distinguishable in aqueous acidic solution.

Although the *e* and *h* forms are monohydrates,, and *e* can be dehydrated to give *d,* they appear to be separate isomers rather than hydrated forms of another isomer. Thus, the *d* form does not yield *e* (but only itself) on recrystallisation from aqueous HCl containing $ZnCl_2$, and a distinct *e*-[Co(tmd)(dien)Cl]$(ClO_4)_2$ can be prepared.

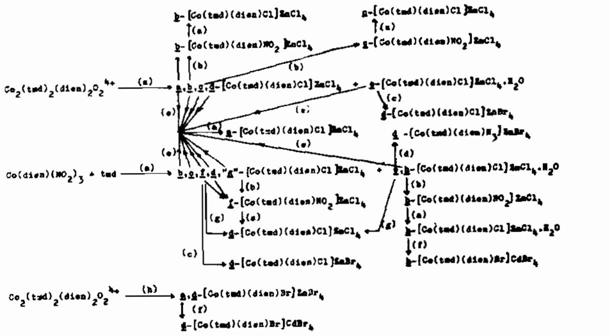


Figure 5. Isomeric and chemical interconversions in the Co(tmd)(dien)X^{n+} system. Reagents: (a) =HCl(6-12*F*)+$ZnCl_2$; (b) = HCl(0.1*F*)+$NaNO_2$; (c) = HBr(6*F*)+$ZnBr_2$ at room temp.; (d) NaN_3 then HBr (6*F*)+$CdBr_2$ at room temp.; (e) NaOH(1*F*); (f) HBr(6*F*)+$CdBr_2$ at 100°; (g) heat at 120° for 12 hr (h) HBr(6*F*)+$ZnBr_2$ at 80-100°.

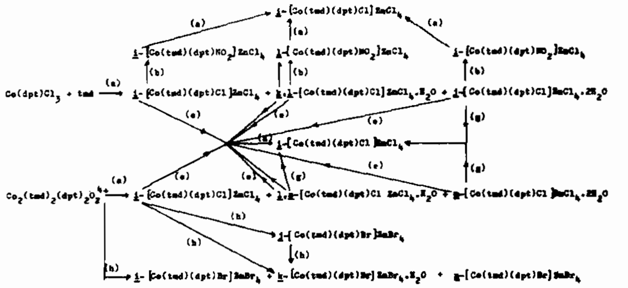


Figure 6. Isomeric and chemical interconversions in the Co(tmd)(dpt)X^{n+} system. Reagents as in Figure 5.

However, heating the *e* and *f* forms at 100° for 12 hr results in complete conversion to the stable *d* isomer.

The *h*-[Co(tmd)(dien)Cl]$ZnCl_4 \cdot H_2O$ isomer also retains its configuration in the anhydrous $CdBr_4^{2-}$ salt and is one of the three forms (the others being *a* and *d*) that form bromo complexes. Heating the *h* (monohydrate) form at 120 for 12 hr results only in dehydration, to give the anhydrous *h* isomer and recrystallisation of this reforms the monohydrate.

Hydrates are more common in the [Co(tmd)(dpt)-Cl]$ZnCl_4 \cdot xH_2O$ system. The *j* (x = 2), *m* (x = 2), and *n* (x = 1) forms are unstable at room temperature, completely and irreversibly converting to the anhydrous *i* isomer after a period of 6 months, 1 day and 3 weeks respectively. Heating these complexes in the solid state at 70° for 12 hr results in the complete conversion to the anhydrous *i* form.

The isomers, *i, j, m,* and *n* all have identical solution spectra (Table XI) and it appears that the *i* isomer is the stable form. The isolation of the unstable forms is apparently facilitated by the relative insolubility of the $ZnCl_4^{2-}$ salts. The order of solubility being $m<i\sim j<n<l\sim k$. The relatively soluble *k* and *l* isomers also have identical solution spectra (Table XI) but both are thermally stable. A similar situation exists for the *a* and *b* isomers of [Co(tmd)-(dien)Cl]$ZnCl_4$.

Interconversions between the two sets of isomers (*i, j, m, n*) and (*k, l*) can be effected via replacement of Cl by Br, when *i*-$[Co(tmd)(dpt)Cl]ZnCl_4$ gives *k*-$[Co(tmd)(dpt)Br]ZnBr_4 \cdot H_2O$ (Figure 6), or by base hydrolysis (where *k* gives *i*). In fact, on reaction with base and acidification and anation with HCl/$ZnCl_2$, all isomeric forms of $[Co(tmd)(dpt)Cl]ZnCl_4 \cdot xH_2O$ give the *i* isomer. Similarly all the isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ are converted to the *a* form on base hydrolysis.

Conversions of the $[Co(tmd)(ABA)Cl]ZnCl_4 \cdot xH_2O$ isomers (ABA = dien, dpt) to $[Co(tmd)(ABA)NO_2]ZnCl_4$ results in extensive isomerism (Figures 5 and 6). Thus, the *d, e,* and *f* chloro complexes give only the *f* nitro, the *a* and *b* isomers give the *b* nitro, while the configurations of the *c* and *h* forms are unchanged in the nitro product. Similarly, the chloro pairs *i, j,* and *k, l* give the *i* and *l* nitro products, respectively. Decomposition of the *f, b, c, h, i,* and *l* nitro isomers with HCl followed by addition of $ZnCl_2$ gives $[Co(tmd)(ABA)Cl]ZnCl_4$ products with retained configuration, except for *f*-$[Co(tmd)(dpt)NO_2]ZnCl_4$ and *l*-$[Co(tmd)(dpt)NO_2]ZnCl_4$, where the *d* and *i* chloro isomers are formed.

Replacement of the coordinated chloride group with iodide or thiocyanate has not been successful in these systems. With iodide there is extensive formation of Co^{II} and I_2 and with thiocyanate, $Co(ABA)(NCS)_3$ is the only identifiable product.

Synthetic Methods. The amount of any particular $[Co(tmd)(ABA)Cl]ZnCl_4 \cdot xH_2O$ isomer produced is markely dependent upon the method of synthesis used. The reaction between *trans*-$Co(ABA)(NO_2)_3$[10,12] and 1,3-diaminopropane (tmd), followed by treatment with HCl/$ZnCl_2$ gives pentamine chloro products only with ABA = dien, in agreement with Schlessinger.[11] All seven $[Co(tmd)(dien)Cl]ZnCl_4$ isomers can be isolated from this reaction, but the *a* form is only detected in small amounts. The isolation of the *e* form is perhaps surprising as the only solid state nitro isomer obtained from this chloro complex has the *f* configuration. The *e* form is assigned to a ring conformational isomer of the stable *d* form (see later) and it is possible that this conformation exists in solution, the isolation as chloro complex being facilitated by the relative insolubility of the $ZnCl_4^{2-}$ salt.

Decomposition of $Co_2(tmd)_2(ABA)_2O_2^{4+}$ in HCl containing $ZnCl_2$ forms the *a, b, c, d,* and *e,* chloro pentamine isomers with ABA = dien and the *i, l, m,* and *n* isomers with ABA = dpt, however, the *i* isomer is only a very minor component.

Reaction of *trans*-$Co(dpt)Cl_3$[12] with tmd in aqueous solutions, followed by addition of HCl/$ZnCl_2$ gives low yields (26% total) of the *i, j, k* and *l*-$[Co(tmd)(dpt)Cl]ZnCl_4$ isomers, the major product being *trans*-$[Co(tmd)_2Cl_2]Cl$. This is again similar to the results reported by Schlessinger[11], but he was unable to dectet any chloro pentamine product.

All the $[Co(tmd)(ABA)Cl]ZnCl_4$ isomers except *c* were obtained as pure (less than 5-10% isomeric contamination) fractions at various stages of the synthetic methods (Tables III, IV, V, VII, and VIII). Careful fractional crystallisation of the $ZnCl_4^{2-}$ salts of mixtures containing high proportions of a particular isomer were also successful in purifyng the major component. For example, fractional crystallisation of the *c* plus *f* mixture from crop 7, Table V gave the pure *c* form. In the case the *h* isomer, excellent separation was achieved via the di-iodide salt. The"*g* isomer" (Table V) although depositing as a constant crystallising phase, is shown to be (Table X) a mixture of *f*–$[Co(tmd)(dien)NO_2]ZnCl_4$ and *f*–$[Co(tmd)(dien)Cl]ZnCl_4$.

In all cases, the isomeric purity of any isolated fraction was monitored using the infrared spectrum. Each pure fraction was recrystallised twice from 2 *F* HCl containing $ZnCl_2$ before recording the characteristic infrared spectrum shown in Figures 1 and 2. The infrared 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 others, provided a constant anion is used.

Spectra. The visible absorption spectra of the $Co(tmd)(ABA)Cl^{2+}$(ABA = dien, dpt) isomeric cations exhibit two well defined maxima at about 370 and 520 nm with prominent shoulders on the 520 nm band (Figures 3 and 4). The intensities of these (Tables X and XI) are less than 100 M^{-1} cm^{-1} and are typical of *d-d* transitions in an octahedral Co^{III} complex with a CoN_5Cl chromophore.

It has been previously mentioned that the seven solid state isomers of $[Co(tmd)(dien)Cl]ZnCl_4$ can be divided into four groups *d, e, f; a, b; h; c* with distinguishable solution spectra. The *i, j, m, n, and k, l*–$[Co(tmd)(dpt)Cl]ZnCl_4 \cdot xH_2O$ isomers are similarly grouped into two systems.

On comparison of the solution spectra in the $Co(AA)(dien)Cl^{2+}$ (AA = en, tmd) systems[2,4], the ω and *h* isomers show the closest similarity both in the position of the maxima and the intensities. There is also a close correspondence with the *d, e, f* group and π–$Co(en)(dien)Cl^{2+}$. From the solution spectra of the $Co(AA)(dpt)Cl^{2+}$ isomers (AA = tmd, en), the *i, j, m, n* group and α[3,7] appear to be similar as these have greater intensities than the *k, l,* and β[3,5] isomers.

Infrared spectra have been the main method of distinguishing between the solid state isomers. This technique appears satisfactory as long as a constant anion is used throughout. Variation in anion, e.g. from $ZnCl_4^{2-}$ to $2I^-$ can cause considerable band shifts (probably due to changes in non-bonded interactions) even though no configurational change occurs.

The characteristic bands used in the discrimination of the $[Co(tmd)(ABA)Cl]ZnCl_4 \cdot xH_2O$ isomers are listed in Table XIII.

Structural Assignments. There are potentially three geometric isomers possible for a $Co(AA)(ABA)X^{n+}$ system (AA = en, tmd; ABA = dien, dpt) (Figure 7, I, II, III), but within these, a variety of conformational isomers can be postulated.

For complexes with a peripherial tridentate ligand (e.g. III, Figure 7), the NH proton on the coordinated secondary amine group can be either adjacent to (IIIa) (as in α-$[Co(en)(dpt)Cl]I_2 \cdot H_2O$[7]) or remote from (IIIb) (as in β-$[Co(en)(dpt)Cl]ZnCl_4$[5] and ϰ-$[Co(en)(dien)Cl]ZnCl_4$[2]) the coordinated acido group. This situation is not possible for diethylenetriamine in the facial configuration (I or II, Figure 7) (as found in π-$[Co(en)(dien)Cl]ZnCl_4$[2] and ω-$[Co(en)(dien)Cl]$-

Table XIII. Characteristic Infrared Frequencies (cm^{-1}) for the [Co(tmd)(ABA)Cl]ZnCl$_4$. xH$_2$O (ABA = dien, tmd) Isomers.

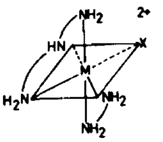
[Co(tmd)(dien)Cl]ZnCl$_4$. xH$_2$O Isomers

a	*b*	*c*	*d*	*e* (x=1)	*f*	*h* (x=1)
1597	1597	1590	1596	1597	1610	1600
1581	1575	1580	1577	1579	1583	1579
1569	1569		1554	1570		1566
					954	
922	930	933	943	936	936	926
913					920	899
893	892	896	893	896	887	882
863	860	870	864	871	866	860
834	832	842				
		778	784	796	796	786
		768				
686		684				
673	667		664	664	670	619

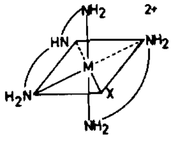
[Co(tmd)(dpt)Cl]ZnCl$_4$. xH$_2$O Isomers

i (x=0)	*j* (x=2)	*k* (x=1)	*l* (x=1)	*m* (x=2)	*n* (x=1)
	1622	1632		1616	1618
1601	1618		1601	1600	1602
1592		1594	1587	1591	1590
1577	1570	1578	1570	1572	1571
				1101	1100
				1060	1108
986	944	981	984	983	982
969	959	964	959	970	970
930	932	942	939	931	933
910	908	931	926	913	910
894	889	901	900	894	892
885	882	892	885	886	887
822	826	814	820	822	825
			813		

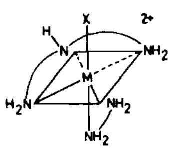
Cl$_2$ · H$_2$O[13] respectively), but with the more flexible dipropylenetriamine ligand, the NH proton can again adopt alternative positions. All structural determinations of complexes containing dpt as a ligand show the triamine in the peripherial configuration and dpt complexes in a facial configuration have not yet been established.[14]



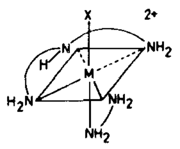
I



II



IIIa



IIIb

Figure 7. Possible geometric isomers of Co(tmd)(ABA)X^{n+} (ABA = dien, dpt). Ring conformations are not distinguished in these diagrams.

In addition to the isomerisation due to NH proton orientation, there exists the possibility of a variety of ring conformations. Such conformational isomerism has been established in the Cr(en)$_3^{3+}$ system[15] and although no ring conformers of Co(tmd)$_3^{3+}$ have been reported (all the tmd rings in [Co(tmd)$_3$]Br$_3$ · H$_2$O adopt the preferred chair conformation[16]), the abnormally rapid ($t_{1/2}$ = 13 sec at 25°[17]) aquation of *trans*-Co(tmd)$_2$Cl$_2^+$ in aqueous acidic solution could be explained by the formation of boat or twist-boat ring conformations in solution. (Both the tmd rings in solid *trans*-[Co(tmd)$_2$Cl$_2$]Cl · HCl · 2H$_2$O adopt the chair conformation[18]).

For the peripherial tridentate dpt ligand, both chair-chair (as in [Ni(dpt)$_2$](ClO$_4$)$_2$[19]) and chair-twist-boat (as in α-[Co(en)(dpt)Cl]I$_2$ · H$_2$O[7] and β-[Co(en)(dpt)Cl]ZnCl$_4$[5]) configurations have been observed, and in the oxalate bridged, trigonal bipyramid [Zn$_2$(dpt)$_2$Ox](ClO$_4$)$_2$ complex,[20] the dpt ligands are not equivalent one being chair-chair and the other chair-twist-boat. However, no isomers due solely to the ring conformations have been reported.

It is probable that in the Co(tmd)(dpt)Cl^{2+} systems, the two groups of solid state isomers that give diffe-

---

(13) J. Johnston, Thesis, Victoria University of Wellington, New Zealand (1969).
(14) M.C. Couldwell and D.A. House, *J. Inorg. Nucl. Chem.*, *33*, 2583 (1971).
(15) K.N. Raymond, P.W.R. Corfield, and J.A. Ibers, *Inorg. Chem.*, *7*, 1362 (1968).
(16) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Japan*, *42*, 1016 (1969).
(17) I.R. Jonasson, R.S. Murray, D.R. Stranks, and J.K. Yandell, *Proc. XII ICCC, Sydney, Australia*, 32 (1969).
(18) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Japan*, *43*, 1903 (1970).
(19) P. Paoletti, S. Biagini, and M. Cannas, *Chem. Commun.*, 513 (1969).
(20) I.R. McCormick, Thesis, University of Auckland, New Zealand, 1970.

rent visible absorpion spectra in solution, namely, *i, j, m, n,* and *k, l* correspond to the α and β-Co(en)(dpt)Cl^{2+} cations (i.e. structures IIIa and IIIb) respectively, and that the thermally unstable solid state isomers are due to different ring conformaions.

If only chair and twist-boat six-membered ring conformations are considered, there are 16 possible configurations for each of the structures IIIa and IIIb. The basic set of 8 configurations[21] is doubled because the tmd ring can lie either above, or below the plane defined by the Co, Cl, and NH(dpt) groups (Figure 8).

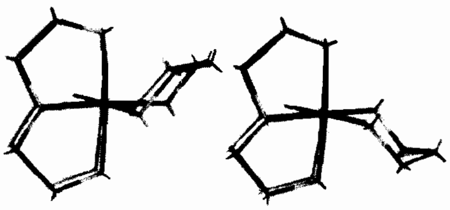


Figure 8. A model of the Co(tmd)(dien)X^{n+} cation with configuration IIIb, showing the two conformations for a chair tmd ring.

By analogy with the α and β-Co(en)(dpt)Cl^{2+} and *trans*-Co(tmd)$_2$Cl$_2$$^+$ cations, the stable *i* and *k, l* forms of Co(tmd)(dpt)Cl^{2+} are believed to have the chair-twist-boat dpt and chair tmd configurations, but the conformations of the thermally unstable *i, m, n* isomers cannot be assigned. The two thermally stable *k* and *l* isomers, with identical visible absorption spectra, are believed to have configuration IIIb with a chair-twist-boat dpt system and a chair tmd ring either above or below the plane of the Co, Cl, and NH(dpt) groups (Figure 8), the exact assignment being unknown.

The assignment of the *i* (and of the *j, m, n* isomers which revert to it) and *k, l* forms to the IIIa and IIIb structures, respectively, is based on a comparison with the visible absorption spectra of α and β-Co(en)(dpt)Cl^{2+} (see Table XI and compare Figure 4 with Figure 2 in reference 3), the α (IIIa) and *i* forms having the greater molar absorptivity coefficients at the maxima. Chemical evidence supports this assignment, as the *k, l* forms isomerise to the *i* form under base hydrolysis and a β to α-Co(en)(dpt)Cl^{2+} isomerisation is similarly effected. Also, the *i*; α and *l*; β-[Co(AA)(dpt)NO$_2$]ZnCl$_4$ (AA = tmd, en respectively) isomer pairs have similar (low and moderate, respectively) solubility in acetone/2-propanol solution.

In the Co(tmd)(dien)Cl^{2+} system, the four solution distinguishable groups (*d, e, f; h; a, b; c*) are believed to correspond to the four configurations I, II, IIIb, and IIIa, respectively, with *d; h; a, b;* and *c* as the thermally stable forms.[22]

The resolution of *d*-[Co(tmd)(dien)Cl]ZnCl$_4$ unambiguously assigns this isomer to structure I (Figure 7) as this is the only geometric form that is potentially optically active.[2,4] The tmd ring probably adopts a chair configuration and models show the conformation adjacent to the coordinated acido ligand to be the least strained. The thermally unstable *e* and *f* forms (also assigned to I) are most likely to have other tmd ring conformations.

The assignments of the *h* and *a, b* isomers to configurations II and IIIb respectively, are based on their similarity with the known ω (II)[13] and $\varkappa$ (IIIb)-[Co(en)(dien)Cl]ZnCl$_4$[2] isomers. The visible absorption (Figure 1) and infrared spectrum (Figure 3) of *h*-[Co(tmd)(dien)Cl]ZnCl$_4\cdot$H$_2$O suggest a facial dien configuration and the chemical reactions (slow chloride replacement by NO$_2^-$ or Br$^-$) parallel[4] those of ω-[Co(en)(dien)Cl]ZnCl$_4$. Similarly, the visible absorption (Figure 3) and infrared spectra (Figure 1) of *a, b* (and *c*)-[Co(tmd)(dien)Cl]ZnCl$_4$ and $\varkappa$-[Co(en)(dien)Cl]ZnCl$_4$ closely correspond. The four bands in the infrared spectrum between 830 and 930 cm^{-1}, and the broad visible absorption maxima at about 500 nm being characteristic of a peripherial dien configuration.[23-25]

The *a, b*-[Co(tmd)(dien)Cl]ZnCl$_4$ pair (assigned to IIIa), have identical solution spectra but are thermally non-interconvertable. Like the *k, l*-[Co(tmd)(dpt)Cl]ZnCl$_4\cdot$H$_2$O pair, they probably correspond to chair tmd ring conformations on either side of the Co, Cl, NH(dien) plane (Figure 8). In these two systems, the tmd configuration in the *b, l,* and *a, k* pairs is probably similar, as both the *a* and *k* chloro isomers are converted to the *b* and *l* nitro forms (Figures 5 and 6).

The *c*-[Co(tmd)(dien)Cl]ZnCl$_4$ isomer (tentatively assigned to structure IIIa, Figure 7) has only been isolated in small amounts. This would correspond to the non-observance of this configuration in the Co(en)(dien)Cl^{2+} system and to the 20% yield of the *cis*-β_2' isomer in the structurally related Co(trien)(NH$_3$)Cl^{2+} system.[26] The unique configuration of structure IIIa would suggest that isomerism from this form would require either proton inversion at the NH(dien) center or simultaneous movement of both tmd and dien terminal NH$_2$ groups. The assignment of the *c* isomer to this configuration is supported by the observation that this form is not isomerised in refluxing 6 *F* HCl (30 min), whereas all other forms in this series (except *h*) undergo at least some stereochemical change. The *c* to *a* isomerisation (i.e. IIIa to IIIb) under basic conditions is possible via NH(dien) proton inversion.

In comparing the Co(AA)(dien)Cl^{2+} (AA = en, tmd) systems, one notable difference is the configuration of the major product resulting from base hydrolysis, acidification and anation with HCl/ZnCl$_2$. All the Co(en)(dien)Cl^{2+} isomers give π-[Co(en)(dien)Cl]ZnCl$_4$, which has configuration I, whereas all the Co(tmd)(dien)Cl^{2+} isomers give *a*-[Co(tmd)(dien)Cl]ZnCl$_4$, which has been assigned to structure IIIb. It

---

[21] If the dpt rings in IIIa or IIIb are labelled R$_1$ and R$_2$ and the tmd ring R$_3$, then the 8 combinations, in the order R$_1$, R$_2$, R$_3$ are: c, c, c,; tb, c, c; c, tb, c; tb, c, tb; c, tb, tb; tb, tb, tb; tb, tb, c; c, c, tb (c = chair, tb = twist-boat).

[22] The first three groups correspond to the π, ω, and $\varkappa$-Co(en)(dien)Cl^{2+} isomers. The fourth Co(en)(dien)Cl^{2+} isomer (IIIa), corresponding to *c*-[Co(tmd)(dien)Cl]ZnCl$_4$, has not yet been isolated.

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

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

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

[26] M. Dwyer, Thesis, Australian National University, Canberra, 1971.

Table XIV. Configurational Assignments that are Proposed or have been Established for the [Co(AA)(ABA)Cl]ZnCl$_4$ Systems (AA = en, tmd; ABA = dien, dpt).

Configuration (Figure 7)	I	II	IIIa	IIIb
Co(en)(dien)Cl^{2+}	π[2]	ω[13]		κ[2]
Co(tmd)(dien)Cl^{2+}	*d, e, f*	*h*	*c*	*a, b*
Co(en)(dpt)Cl^{2+}			α[7]	β[5]
Co(tmd)(dpt)Cl^{2+}			*i, j, m, n*	*k, l*

is probable that under basic conditions, an equilibrium I-IIIb-(IIIa?) mixture is obtained and that the isomers isolated from the work-up of the reaction mixture reflect both the differing positions of the equilibrium for the different systems, and the relative solubility of the chloro tetrachlorozincate(II) salts. In both cases, the π and *a*-[Co(AA)(dien)Cl]ZnCl$_4$ isomers are relatively insoluble, whereas the κ and especially *d*-[Co(AA)(dien)Cl]ZnCl$_4$ salts are more soluble.

The proposed or established configurations for the [Co(AA)(ABA)Cl]ZnCl$_4 \cdot x$H$_2$O isomers (AA = en, tmd; ABA = dien, dpt) are summarised in Table XIV.

Acknowledgments. We acknowledge with thanks, a grant from the New Zealand Universities Grants Committee to purchase the JASCO recording spectropolarimeter.