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Acidopentaminecobalt(III) Complexes with Polyamine Ligands. VI. The Crystal Structures of the π(Racemic)- and ϰ-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II) Salts

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The crystal structures of the π(racemic)- and ϰ-chloro-(ethylenediamine)(diethylenetriamine)cobalt(III) tetrachlorozincate(II) salts, π and ϰ–[Co(en)(dien)Cl]Zn-Cl_4, have been determined from three-dimensional X-ray data collected by counter methods at 23°.

The crystals of the π isomer are monoclinic: space group C_{2h}^5–$P2_1/n$ with four molecules in a cell of dimensions a = *13.745(3),* b = *8.202(2),* c = *15.117 (6) Å, β 98.56(1)°. Observed and calculated densities are 1.85 (±0.01) and 1.85 g. cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R-factor (on F) of 0.061 for the 2098 reflections having $F^2 \geqslant \sigma(F^2)$. The structure consists of an equimolar mixture of two enantiomorphic cations and discrete tetrachlorozincate(II) anions.*

The crystals of the ϰ isomer are monoclinic: space group C_s^4–Cc, with four molecules in a unit cell of dimensions a = *9.676(1),* b = *12.790(2),* c = *13.888 (3) Å, β = 93.63(1)°. Observed and calculated densities are 1.83 (±0.01) and 1.83 g. cm^{-3}. A final value of the conventional R-factor (on F) of 0.057 was obtained from the 1353 reflections having $F^2 \geqslant 3\sigma(F^2)$. This structure consists of the complex cation and discrete tetrachlorozincate(II) anions.*

In both isomers, the complex cations contain the cobalt atom surrounded by one chlorine atom and five nitrogen atoms in an approximately octahedral configuration.

For the π isomer, the three nitrogen atoms of the diethylenetriamine ligand are in a facial configuration and the chlorine atom occupies one of the two equivalent cis *positions relative to the coordinated secondary amine group of the diethylenetriamine. The ethylenediamine ligand occupies the remaining two coordination positions.*

For the ϰ isomer, the three nitrogen atoms of the diethylenetriamine ligand are in a plane with one nitrogen atom of the ethylenediamine ligand, while the second ethylenediamine nitrogen atom is trans *to the chlorine atom. The orientation about the secondary nitrogen group of the diethylenetriamine ligand is such that the NH proton is remote from the coordinated chlorine atom.*

In both salts, the tetrachlorozincate(II) anions have slightly distorted tetrahedral configurations.

Introduction

In an earlier paper of this series,[1] the preparation and characterisation of the π, ϰ, ω, and ε isomers[2] of the Co(en)(dien)Cl^{2+} cation (en = ethylenediamine = $NH_2(CH_2)_2NH_2$, dien = diethylenetriamine = $NH_2(CH_2)_2NH(CH_2)_2NH_2$) were reported. There are potentially three distinct geometric configurations for these isomeric cations (Figure 1). In addition, there exists the possibility of conformational isomerism for isomer I. This arises from the different configurations of the chemically inert proton (in acid solution) on the secondary nitrogen of the peripheral dien ligand. This type of conformational isomerism is now well established for cobalt(III) polyamine complexes.[3-10]

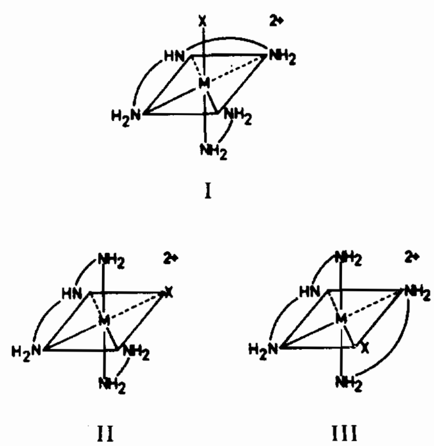

Figure 1. The three possible geometric forms of the Co(en)-(dien)Cl^{2+} cation. Conformational isomers are not distinguished in these diagrams.

(1) Part II, Gainsford A.R. and House D.A., *Inorg. Chim. Acta*, 3, 367 (1969).
(2) Part V, Gainsford A.R. and House D.A., *Inorg. Chim. Acta*, 5, 544 (1971).
(3) Buckingham D.A., Marzilli P.A., and Sargeson A.M., *Inorg. Chem.*, 6, 1032 (1967).
(4) Buckingham D.A. Marzilli P.A., and Sargeson A.M., *Inorg. Chem.*, 7, 915 (1968).
(5) Snow M.R. Buckingham D.A., Marzilli P.A., and Sargeson A.M., *Chem. Commun.*, 891 (1969); Snow M.A., *Proc. XII ICCC.*, Sydney, Australia, 92 (1969).
(6) Part III, Ireland P.R., House D.A., and Robinson W.T., *Inorg. Chim. Acta*, 4, 137 (1970).
(7) Part IV, House D.A., Ireland Peter R., Maxwell Ian E., and Robinson Ward T., *Inorg. Chim. Acta*, 5, 379 (1971).

Clearly, for isomers II and III (Figure 1) which have a *cis* or facial arrangement of the dien ligand, the configuration at the secondary nitrogen centre is fixed and this type of conformational isomerism cannot occur.

From a single crystal X-ray analysis,[11] the ω isomer (as the dichloride hemihydrate salt) has been shown to have the geometrical configuration III. Furthermore, we have recently shown that the ε isomer is in fact a mixture of the π-nitro and π-chloro isomeric complexes.[2]

This paper reports the single crystal X-ray structure analyses of the π and χ–[Co(en)(dien)Cl]$ZnCl_4$ isomers.

Experimental Section

(Racemic) π-Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II). Racemic π–[Co(en)(dien)Cl]$ZnCl_4$ (prepared as described previously[1]) forms purple-red crystals which are stable to both air and X-rays. Precession photography, using Mo Kα and Cu Kα radiation on several samples revealed that the salt crystallises in the monoclinic system. Unit cell dimensions were obtained at 23°C by the least-squares precedure described below. A density of 1.85 (±0.01) g. cm^{-3} was obtained by flotation in methyl iodide-carbon tetrachloride solution.

Crystal Data.[12] $ZnCoCl_5N_5C_6H_{21}$, formula weight 464.9; monoclinic with $a = 13.745(3)$, $b = 8.202(2)$, $c = 15.117(6)$ Å, $\beta = 98.56(1)°$; $V = 1686.0$ (Å)^3; $D_{obs} = 1.85$ (±0.01) g. cm^{-3}; $Z = 4$; $D_{calc} = 1.85$ g. cm^{-3}; μ(Mo Kα) = 32.8 cm^{-1}. The space group is $P2_1/n$ (an alternate setting of $P2_1/c$, No. 14) for which conditions limiting possible reflections are $k0l$, $h+l=2n$; $0k0$, $k = 2n$. In this setting the general equivalent positions are xyz; $\bar{x}\bar{y}\bar{z}$; 1/2–x, 1/2+y, 1/2–z; 1/2+x, 1/2–y, 1/2+z.

X-ray Data Collection and Reduction. Diffraction data were collected from a well-formed crystal of centrosymmetric habit and of average diameter 0.15 mm; the ten boundary faces were ($\bar{1}$ 0 2), (1 0 $\bar{2}$), (0 0 $\bar{1}$), (0 0 1), (1 0 $\bar{1}$), ($\bar{1}$ 0 1), ($\bar{1}$ 0 0), (1 0 0), (0 $\bar{1}$ 0) and (0 1 0) and their distances from an arbitrary origin within the crystal were measured to facilitate later corrections for absorption.

The crystal was mounted in a random orientation on a Hilger and Watts computor controlled four-circle diffractometer. Twelve reflections from this crystal were accurately centred in a 3.5 mm diameter circular receiving aperture. The setting angles of these reflections were data used for a least-squares refinement[13] of cell parameters and crystal orientation, in which the wavelength of the Mo Kα radiation was taken as 0.71070 Å.

The mosaicity of the crystal was examined by means of open-counter ω-scans at a take-off angle of 3°. The width at half-height for a typical strong, low-angle reflection was 0.14°.

The intensity data were collected with Zr filtered Mo Kα radiation at the same take-off angle. The circular receiving aperture, positioned 23 cm from the crystal, was of diameter 5 mm. Data were collected by the θ-2θ scan technique. A symmetric scan range of 1.20° in 2θ, centred on the calculated peak position for Mo Kα radiation, was composed of 60 steps of 1 second duration. Stationary-crystal, stationary-counter background counts of 15 sec were measured at each end of the scan range. Attenuation was required as the intensity of the diffracted beam exceeded 6000 counts per second for several reflections.

Attenuation factors for the thin nickel foils used were determined from 120 ten second stationary-crystal stationary-counter measurements covering a complete range of diffracted X-ray intensity. Altogether, 2834 $hk+l$ reflections were recorded with $0 \leqslant 2\theta \leqslant 48°$. The intensities of three reflections, monitored at regular intervals showed only deviations from the mean predicted by counting statistics. After averaging 62 reflections which had been measured more than once, the data consisted of 2772 reflections of which 2089 had $F^2 \geqslant \sigma(F^2)$.

Background scattering was considered to be linear throughout the scan range, so that $I = C-0.5(t_c/t_b)(B_1+B_2)$, where C is the scan count, B_1 and B_2 are the first and second background counts and t_c and t_b are the scan and background counting times. The error in the intensity, I, was computed as $\sigma(I) = [C+0.25(t_c/t_b)(B_1+B_2)+(pI)^2]^{1/2}$ where p is a factor introduced[14] to avoid overweighting strong reflections. Initially, the p–factor was taken as 0.05, and this was not required to be changed in the subsequent refinement.

An absorption correction was applied[15] using Gaussian Integration (4^3 grid points) and the transmission factors ranged from 0.62 to 0.75.

Solution and Refinement of Crystal Structure. Initial positions for the zinc and cobalt atoms were obtained from a three-dimensional Patterson synthesis. Full matrix least-squares refinement was begun using those data for which $F^2 \geqslant \sigma(F^2)$. Refinement was based on F and the function $\Sigma w(|F_o|-|F_c|)^2$ was minimised. The weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$; $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for hydrogen were taken from Stewart, Davidson, and Simpson[16] and those for all other atoms and ions from the usual tabulation.[17] The effects of anomalous dispersion were included in F_c;[18] values of $\Delta f'$ and $\Delta f''$ for Zn^{2+}, Co^{3+}, and Cl^- were taken from the International Tables.[17]

(8) Keene F.R., Searle G.H., Yoshikawa Y., Imai A., and Yamasaki K., *Chem. Commun.*, 784 (1970).
(9) Keene F.R., Searle G.H., and Mason S.F., *Chem. Commun.*, 893 (1970).
(10) Ohkawa K., Yano S., and Fujita J., *Bull. Chem. Soc. Japan*, *41*, 2224 (1968).
(11) Johnston J., Thesis M.Sc., Victoria University of Wellington, New Zeland, 1969: *Z. Krist*, *131*, 155 (1970).
(12) Here, and throughout this paper, the uncertainties given in parentheses are estimated standard deviations (e.s.d. = σ) in the least significant digits quoted.
(13) Busing W.R. Paper 12, International Summer School on Crystallographic Computing, Ottawa, Canad, 1969; W.R. Busing and H.A. Levy, ORN-4054, Oak Ridge National Laboratory, Tennessee.
(14) Grant, D.F., Killean, R.C.G., and Lawrence, J.L., *Acta Cryst.*, *B25*, 374 (1969).
(15) Programs for the IBM 360/44 used in the crystal structure analyses include local modifications of Busing and Levy's ORFFE function and error program, Zalkin's FORDAP fourier program, Johnson's ORTEP thermal ellipsoid plotting diagram and Copper's DATAPH absorption program.
(16) Stewart R.F., Davidson E.R., and Simpson W.T., *J. Chem. Phys.*, *42*, 3175 (1965).

Table I. Positional and Thermal Parameters for (Racemic) π–[Co(en)(dien)Cl]$ZnCl_4$.

Atom	x	y	z	β_{11} [a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	.25780(7)	.1714(1)	−.04905(7)	.00375(6)	.0125(2)	.00266(5)	−.00083(9)	.00095(4)	.00014(8)
Co	.02122(8)	.2407(1)	.22607(7)	.00271(6)	.0087(2)	.00243(5)	.0001(1)	.00091(4)	.00000(9)
Cl_1	.0981(2)	.2279(3)	−.1035(2)	.0040(1)	.0135(5)	.0043(1)	−.0009(2)	−.0001(1)	.0003(2)
Cl_2	.2532(2)	.0731(3)	.0892(2)	.0059(2)	.0175(5)	.0032(1)	.0034(2)	.0019(1)	.0022(2)
Cl_3	.3565(2)	.3894(3)	−.0474(2)	.0049(2)	.0150(5)	.0043(1)	−.0031(2)	.0019(1)	−.0018(2)
Cl_4	.3139(2)	−.0145(4)	−.1414(2)	.0073(2)	.0150(5)	.0047(1)	−.0020(3)	.0034(1)	−.0021(2)
Cl_5	.1199(2)	.4361(3)	.1845(2)	.0038(1)	.0121(4)	.0039(1)	−.0019(2)	.0010(1)	.0005(2)

Atom	x	y	z	B($Å^2$)	Atom	x	y	z	B($Å^2$)
N_1	.0072(5)	.1551(9)	.1038(4)	2.5(1)	C_2	.3601(8)	.174(1)	.5944(7)	4.5(2)
N_2	.4059(5)	.1231(9)	.6823(5)	2.9(1)	C_3	.1072(7)	.230(1)	.4127(6)	3.1(2)
N_3	.5374(5)	.1623(9)	.8447(4)	2.6(1)	C_4	.1821(6)	.163(1)	.3592(6)	2.7(2)
N_4	.1363(5)	.1031(9)	.2695(4)	2.5(1)	C_5	.8976(7)	.076(1)	.7308(6)	3.4(2)
N_5	.9377(5)	.0627(9)	.2639(5)	2.8(1)	C_6	.0002(6)	.080(1)	.6927(6)	2.9(2)
C_1	.4322(8	.238(1)	.5421(7)	4.6(2)					

[a] The expression used for the atomic temperature factor was, exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table II. *Root-mean-square Amplitudes of Vibration* (Å) for π–[Co(en)(dien)Cl]$ZnCl_4$.

Atom	Minimum	Itermediate	Maximum
Zn	.160(2)	.190(2)	.212(2)
Co	.141(2)	.172(2)	.177(2)
Cl_1	.182(4)	.211(4)	.236(3)
Cl_2	.163(4)	.195(4)	.286(4)
Cl_3	.172(4)	.198(4)	.272(3)
Cl_4	.169(4)	.213(4)	.302(4)
Cl_5	.156(4)	.214(3)	.223(4)

The initial least-squares refinement, in which all atoms were assigned variable isotropic vibrational parameters, gave agreement factors $R_1 = 0.473$ and $R_2 = 0.543$, where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and R_2 (the weighted R–factor) $= [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Subsequent difference Fourier syntheses and least-squares refinements revealed the positions of all Cl, N, and C atoms of the cation as well as the Cl atoms of the anion. The second map also showed regions of high electron density (up to 2.8e $Å^{-3}$) around the Zn, Co, and Cl atoms. Accordingly, in the next least-squares refinement, the Zn, Co, and Cl were included with anisotropic vibrational parameters while the remaining eleven atoms were included with isotropic vibrational parameters. This refinement, using 2098 data which had $F^2 \geqslant \sigma(F^2)$, converged to give agreement factors $R_1 = 0.063$ and $R_2 = 0.068$.

A further difference Fourier synthesis showed peaks of height up to 1.2e $Å^{-3}$ close to calculated hydrogen atom positions. In the next cycles of refinement, the twenty-one hydrogen atoms of the cation were included in their calculated positions (d(N–H) = 0.995 Å, d(C–H) = 1.073 Å;[17] B = 6.0 $Å^2$); no parameters were varied for these atoms. This calculation converged with $R_1 = 0.062$ and $R_2 = 0.067$. Following recalculation of the hydrogen atom positions and the application of an absorption correction, two cycles of least-squares refinement, in which a single scale factor and 107 positional and vibrational parameters were varied, produced final agreement factors of $R_1 = 0.061$ and $R_2 = 0.066$.

Apart from twelve low angle reflections average values of the minimised function obtained after the last cycle of refinement show little dependance on $|F_o|$ or on $\lambda^{-1}\sin\theta$ which indicated that the weighting scheme is reasonable. The error in an observation of unit weight is 1.08 electrons. A final difference Fourier synthesis still shows peaks of height up to 0.8e $Å^{-3}$ around the Co and Zn atoms although the electron density does not rise above 0.6e $Å^{-3}$ elsewhere or one-tenth the height of the last carbon atom located by this technique. Structure factor calculations for the 674 reflections having $F_o^2 < \sigma(F_o^2)$ show that none have $|F_o^2|-F_c^2| > \sigma(F_o)^2$. The positional and vibrational parameters and their e.s.d.'s obtained from the final cycle of least-squares refinement are listed in Table I. In Table II are presented the root-mean-square amplitudes of vibration of the zinc, cobalt, and chlorine atoms. Table III contains final values of $|F_c|$ and $|F_o|$ for the 2098 reflections which were used in the refinement. No corrections were made for secondary extinction.

$\varkappa$-Chloro(ethylenediamine)(diethylenetriamine)Cobalt (III) Tetrachlorozincate(II). Orange-red crystals of $\varkappa$–[Co(en)(dien)Cl]$ZnCl_4$ (prepared as described previously[1]) are stable to both air and X-rays. Precession photography, using Cu Kα and Mo Kα radiation on several samples revealed that the salt crystallises in the monoclinic system. Unit cell dimensions were obtained at 23°C by a least-squares procedure.[13] A density of 1.83 g. cm^{-3} was obtained by flotation in methyl iodide-carbon tetrachloride solution.

Crystal Data. $ZnCoCl_5N_5C_6H_{21}$, formula weight 464.9; monoclinic with a = 9.676(1), b = 12.790 (2), c = 13.888(3) Å, β = 93.63(1)°, V = 1715.2 $(Å)^3$; D_{obs} = 1.83 ($\pm$0.01) g. cm^{-3}; Z = 4; D_{calc} = 1.83 g. cm^{-1}; μ(Mo Kα) = 32.8 cm^{-1}. Two space groups (Cc acentric and C2/c centrosymmetric) were consistent with the observed conditions limiting possible reflections (hkl, $h+k = 2n$; $00l$, $l = 2n$). Exact crystallographic symmetry could not be imposed on conceivable cationic structures so that the acentric possibility had to be correct.

X-Ray Data Collection and Reduction. Diffraction

(17) « International Tables of X-ray Crystallography », Vo. 3, The Kynoch Press, Birmingham, England.
(18) Ibers J.A. and Hamilton W.C., *Acta Cryst.*, *17*, 781 (1964).

Table III. Observed and Calculated Structure Amplitudes for π–[Co(en)(dien)Cl]ZnCl$_4$.

H	L	FOBS	CALC
[illegible]	[illegible]	[illegible]	[illegible]

data were collected from a well-formed crystal of non-centrosymmetric habit and average diameter 0.3 mm; the ten boundary faces were $(\bar{1}\,\bar{1}\,\bar{1})$, $(\bar{1}\,1\,\bar{1})$, $(\bar{1}\,1\,1)$, $(\bar{1}\,\bar{1}\,1)$, $(1\,1\,1)$, $(1\,1\,0)$, $(1\,1\,\bar{1})$, $(1\,\bar{1}\,\bar{1})$, $(1\,\bar{1}\,0)$, and $(1\,\bar{1}\,1)$ and the necessary measurements were made to enable accurate absorption corrections to be applied.

The crystal was mounted, and a data set collected using the same techniques as those described for the π isomer, except that the mosaicity for a typical strong, low angle reflection was 0.09°.

The intensities of 1708 unique reflections, with $\theta \leqslant 50°$, were recorded and processed. The 1507 intensities $\geqslant 3\sigma$ were then collected again in the strictly equivalent form using a symmetric scan range of 1.60° in 2θ with 80 one-second steps.

The intensities of three reflections which were monitored at regular intervals showed only the deviations from the mean predicted by counting statistics.

Solution and Refinement of the Crystal Strucure. The structure has been successfully solved and refined in space group Cc. Positions for the zinc and cobalt atoms were obtained from a three-dimensional Patterson synthesis. The cobalt atom was initially assigned (0, y, 0) to fix the origin of the unit cell. The initial least-squares refinement, in which these atoms were assigned variable isotropic vibrational parameters, gave agreement factors $R_1 = 0.375$ and $R_2 = 0.443$.

Two subsequent difference Fourier syntheses revealed the positions of all Cl, N, and C atoms for the cation, as well as the Cl atoms of the anion. This map did not show regions of high electron density around the Zn and Co atoms and isotropic temperature factors were used for all atoms throughout the analysis. This refinement converged to give agreement factors $R_1 = 0.067$ and $R_2 = 0.084$. For convenience, the coordinates of all of the atoms were transformed so that those of the Zn atom were (0, y, 0). In all subsequent least-squares refinements, the effects of anomalous dispersion were included in F_c.[17,18] These calculations were used to determine the polarity of the space group, using the coordinates obtained above, and coordinates obtained by inverting the structure through the origin. The same scale factor and isotropic vibrational parameters were used in each calculation. The resulting agreement factors were $R_1 = 0.072$ and $R_2 = 0.091$ for one structure, and $R_1 = 0.069$ and $R_2 = 0.088$ for the other. The coordinates xyz (Table IV) define the polarity of the space group and were used in the final refinements.

In the next cycles of refinement, the twenty-one hydrogen atoms of the cation were included in their calculated positions (d(H–H) = 0.995 Å, d(C–H) = 1.073 Å, H–X–H = 109.5°;[17] B = 8.0 Å^2); no parameters were varied for these atoms. This calculation converged with $R_1 = 0.062$ and $R_2 = 0.078$. An absorption correction was applied using Gaussian integration (4^3 grid points) with transmission factors ranging from 0.44 to 0.57 and, after averaging the equivalent forms, the data set consisted of 1592 reflections of which 1355 had intensities of $\geqslant 3\sigma$.

Following recalculation of the hydrogen positions, two cycles of least-squares refinement, in which a single scale factor and 70 positional and vibrational parameters were varied, produced final agreement factors of $R_1 = 0.057$ and $R_2 = 0.071$.

Average values of the minimised function obtained after the final cycle of refinement show very little dependence on $|F_o|$ or on $\lambda^{-1}\sin\theta$, which indicates that the relative weighting scheme (using p = 0.05) is reasonable. A final difference Fourier map still contained peaks of height up to 3.95e Å^{-3} around the Zn, Co, and Cl atoms although the electron density did not rise above 1.0e Å^{-3}, or 0.15 of the last carbon atom located by this technique. Structure factor calculations for the 239 reflections having $F_o^2 < 3\sigma(F_o^2)$ show that none have $|F_o^2 - F_c^2| > 3\sigma(F_o)^2$.

The positional and vibrational parameters and their e.s.d.'s obtained from the final cycle of least-squares refinement are listed in Table IV. Table V contains the final values of $|F_o|$ and $|F_c|$ for the 1353 reflections which were used in the refinement. There was no evidence for secondary extinction and no corrections were made.

Anisotropic thermal parameters were not refined since such expensive calculations were not expected to reveal any further points of chemical interest.[19]

Table IV. Positional and Thermal Parameters for x–[Co(en)(dien)Cl]$ZnCl_4$.

Atom	x	y	z	B(Å^2)
Zn	1.00000	1.0149(1)	1.00000	2.55(3)
Co	1.4400(3)	0.8323(1)	1.2700(2)	1.69(3)
Cl_1	1.1684(5)	1.1156(3)	1.0764(3)	2.73(6)
Cl_2	1.0373(5)	1.0083(3)	0.8402(3)	3.67(8)
Cl_3	0.7949(5)	1.0919(3)	1.0229(3)	3.35(7)
Cl_4	1.0074(5)	0.8482(3)	1.0580(3)	3.22(7)
Cl_5	1.4844(5)	0.9966(3)	1.3251(3)	3.14(7)
N_1	1.379(1)	0.6915(9)	1.2306(8)	2.2(2)
N_2	1.296(1)	0.824(1)	1.3626(9)	2.5(2)
N_3	1.589(1)	0.781(1)	1.3630(1)	2.9(2)
N_4	1.581(1)	0.8346(9)	1.1774(9)	2.4(2)
N_5	1.320(1)	0.894(1)	1.1651(9)	2.7(2)
C_1	1.239(2)	0.675(1)	1.265(1)	4.0(3)
C_2	1.231(2)	0.718(1)	1.361(1)	4.1(3)
C_3	1.716(2)	0.761(1)	1.311(1)	3.4(3)
C_4	1.721(2)	0.839(1)	1.228(1)	3.6(3)
C_5	1.546(2)	0.911(1)	1.103(1)	4.0(3)
C_6	1.393(2)	0.895(1)	1.075(1)	3.8(3)

Description of the Crystal Structures

The structure analysis has revealed that for the π isomer, the crystals contain an equimolar mixture of two enantiomorphic cations, together with tetrachlorozincate(II) anions, linked by electrostatic and Van der Waals forces. Similar results have been obtained for the x isomer, except that the cation is optically inactive. Perspective views of the complex cations are presented in Figures 2-4, while the $ZnCl_4^{2-}$ anion, as it occurs in the π isomer, is shown in Figure 5. Figure 6 shows the arrangement of ions with respect to the unit cell for the π isomer and Figure 7 is a similar diagram for the x isomer.

Description of the Co(en)(dien)Cl^{2+} Cations. Figures 2, 3, and 4 present perspective views of the π and

(19) Hamilton W.C., *Science*, *169*, 133 (1970).

Table V. Observed and Calculated Structure Amplitudes for $\varkappa$–[Co(en)(dien)Cl]$ZnCl_4$.

K	L	OBS	CALC
[illegible]	[illegible]	[illegible]	[illegible]

$\varkappa$–Co(en)(dien)Cl^{2+} cations and indicate the atom numbering systems. As expected, for both cations, the dien ligand is coordinated tridentate, the en ligand bidentate and the coordinated chloride completes the coordination sphere. For the π isomer, the geometry of the complex is of type II (Figure 1), with the

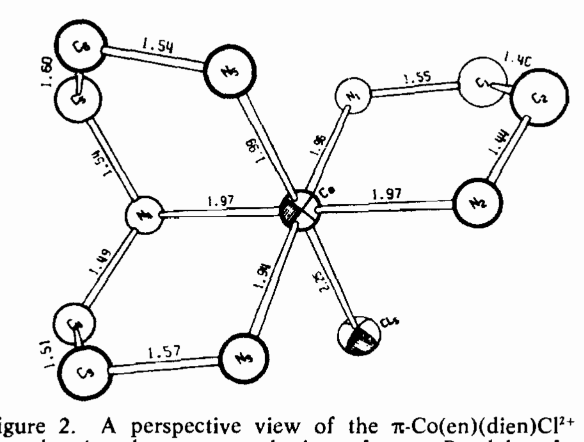

Figure 2. A perspective view of the π-Co(en)(dien)Cl^{2+} cation showing the atom numbering scheme. Bond lengths are in Å (1 Å $= 10^{-10}$ m).

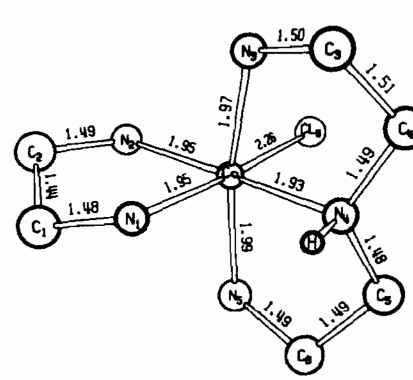

Figure 3. A general view of the $\varkappa$-Co(en)(dien)Cl^{2+} cation showing the atom numbering scheme. Bond lengths are in Å.

nitrogen atoms of the dien ligand in a facial configuration. For the ϰ isomer, the geometry is of type I, with the hydrogen atom bonded to the secondary amine of the peripherial dien ligand being remote from the chloride ligand (a similar arrangement occurs in the β–Co(en)(dpt)Cl^{2+} cation[6]).

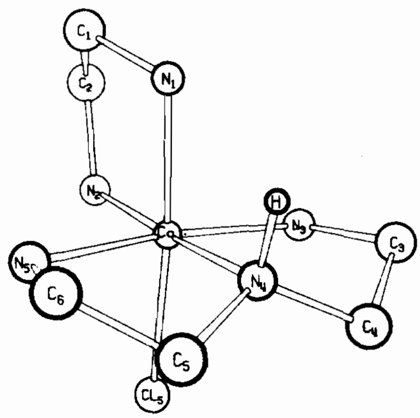

Figure 4. A perspective view of the ϰ-Co(en)(dien)Cl^{2+} cation.

Intramolecular bond distances and angles within the complex cations are presented in Tables VI (π isomer) and VII (ϰ isomer). The mean Co^{III}–N bond distance for the π isomer is 1.97(4) Å, and comparable distances for related complexes[20] are 1.955(5) Å in racemic α–[Co(trien)(NH_3)Cl]$(NO_3)_2$,[21] 1.955 Å in Λ–β_2–(*SSS*)–[Co(trien)(*S*–pro)]$ZnCl_4$,[22] 1.967(6) Å in αα–[Co(tetren)Cl]Cl · ClO_4,[26] 1.99(2) Å in β–[Co(en)(dpt)Cl]$ZnCl_4$,[6] and 1.95(5) Å in α–[Co(en)-(dpt)Cl]I_2 · H_2O.[7]

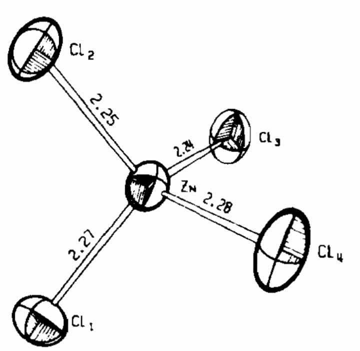

Figure 5. A perspective view of the $ZnCl_4^{2-}$ anion in π-[Co-(en)(dien)Cl]$ZnCl_4$ showing the atom numbering scheme. A similar nurmbering system is used for the $ZnCl_4^{2-}$ anion in the ϰ isomer. Bond lengths are in Å.

For the ϰ isomer, the mean Co^{III}–N(primary) bond distance is 1.97(2) Å and this is comparable with the values in the complexes quoted above. However, the Co^{III}–N(secondary) bond distance (1.93(1) Å) is significantly shorter than the mean Co^{III}–N(primary) bond length. Also the N(3)–Co–N(5) bond angle is 169.6(5)°, a significant deviation form 180°. Even greater Cu–N(secondary) bond length deviations and N–Cu–N angular distortions are found for some pe-

Table VI. Intramolecular bond distances and angles for the π-Co(en)(dien)Cl^{2+} Cation

Intramolecular Bond Distances

Atoms	Distance, Å.	Atoms	Distance, Å.
Co-Cl_5	2.249(3)	C_2-N_2	1.44(1)
Co-N_1	1.960(7)	N_3-C_3	1.57(1)
Co-N_2	1.971(7)	C_3-C_4	1.51(1)
Co-N_3	1.944(7)	C_4-N_4	1.49(1)
Co-N_4	1.974(7)	N_4-C_5	1.54(1)
Co-N_5	1.993(7)	C_5-C_6	1.60(1)
N_1-C_1	1.55(1)	C_6-N_5	1.54(1)
C_1-C_2	1.46(1)		

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_5-Co-N_1	88.3(2)	Co-N_1-C_1	109.1(6)
Cl_5-Co-N_2	89.5(2)	N_1-C_1-C_2	108.9(8)
Cl_5-Co-N_3	88.6(2)	C_1-C_2-N_2	111.4(9)
Cl_5-Co-N_4	90.8(2)	C_2-N_2-Co	111.4(6)
Cl_5-Co-N_5	178.1(2)	Co-N_3-C_3	110.4(5)
N_1-Co-N_2	85.7(3)	N_3-C_3-C_4	104.8(7)
N_1-Co-N_3	176.7(3)	C_3-C_4-N_4	112.2(7)
N_1-Co-N_4	94.0(3)	C_4-N_4-Co	109.0(5)
N_1-Co-N_5	91.6(3)	Co-N_4-C_5	108.6(5)
N_2-Co-N_3	93.1(3)	C_4-N_4-C_5	113.6(7)
N_2-Co-N_4	179.6(3)	N_4-C_5-C_6	107.3(7)
N_2-Co-N_5	92.4(3)	C_5-C_6-N_5	107.2(7)
N_3-Co-N_4	87.2(3)	C_6-N_5-Co	111.9(5)
N_3-Co-N_5	91.5(3)		
N_4-Co-N_5	87.3(3)		

Table VII. Intramolecular bond distances and angles for the ϰ–Co(en)(dien)Cl^{2+} Cation.

Intramolecular Bond Distances

Atoms	Distance, Å.	Atoms	Distance, Å.
Co-Cl_5	2.268(4)	C_2-N_2	1.49(2)
Co-N_1	1.96(1)	N_3-C_3	1.49(2)
Co-N_2	1.95(1)	C_3-C_4	1.53(2)
Co-N_3	1.98(1)	C_4-N_4	1.49(2)
Co-N_4	1.93(1)	N_4-C_5	1.45(2)
Co-N_5	1.97(1)	C_5-C_6	1.51(3)
N_1-C_1	1.48(2)	C_6-N_5	1.47(2)
C_1-C_2	1.44(3)		

Intramolecular Bond Angles

Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_5-Co-N_1	172.5(4)	Co-N_1-C_1	108.1(9)
Cl_5-Co-N_2	87.7(4)	N_1-C_1-C_2	109(1)
Cl_5-Co-N_3	88.4(4)	C_1-C_2-N_2	108(1)
Cl_5-Co-N_4	94.8(4)	C_2-N_2-Co	111(1)
Cl_5-Co-N_5	88.2(4)	Co-N_3-C_3	109.6(9)
N_1-Co-N_2	85.1(5)	N_3-C_3-C_4	108(1)
N_1-Co-N_3	94.1(5)	C_3-C_4-N_4	105(1)
N_1-Co-N_4	92.4(5)	C_4-N_4-Co	110.4(9)
N_1-Co-N_5	90.5(5)	Co-N_4-C_5	110(1)
N_2-Co-N_3	94.3(5)	C_4-N_4-C_5	118(1)
N_2-Co-N_4	177.5(5)	N_4-C_5-C_6	105(1)
N_2-Co-N_5	95.4(5)	C_5-C_6-N_5	107(1)
N_3-Co-N_4	85.6(6)	C_6-N_5-Co	109(1)
N_3-Co-N_5	169.6(5)		
N_4-Co-N_5	84.9(5)		

(20) Abbreviations used are: trien = triethylenetetramine, *S*-pro = *S*-proline, dpt = dipropylenetriamine, tetren = tetraethylenepentamine.
(21) Dwyer M.M. and Maxwell I.E., *Inorg. Chem.*, 9, 1459 (1970).
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(26) Snow M.R. *J. Am. Chem. Soc.*, 92, 3610 (1970).

ripherial Cu^{II} dien complexes.[27-29]

An increase in the N(3)–Co–N(5) angle to 180° would result in a decrease in the Co–N(secondary) bond distance and the observed values are probably a balance between these two effects. These distorsions are not found in the peripherial Co(en)(dpt) Cl^{2+} isomers,[6,7] presumably because the strain is relievied by the larger size of the six-membered chelate rings.

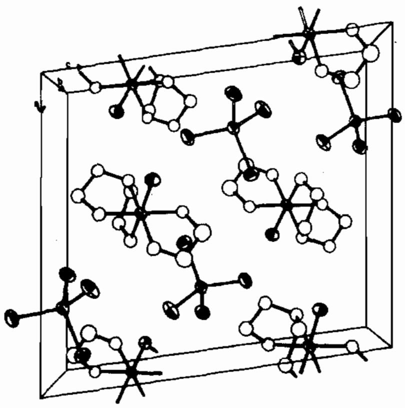

Figure 6. The packing of the ions in π-[Co(en)(dien)Cl]$ZnCl_4$ as viewed down the *b* axis.

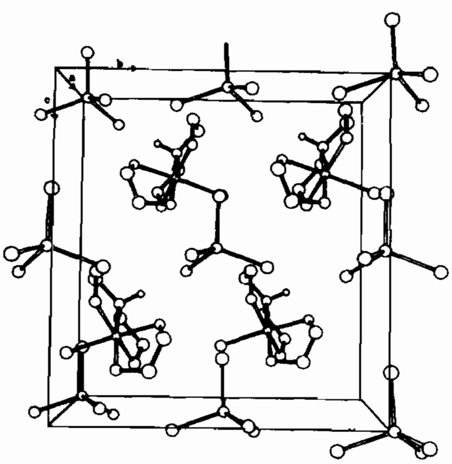

Figure 7. The packing of the ions in ϰ-[Co(en)(dien)Cl]$ZnCl_4$ as viewed down the *a* axis.

The Co-Cl(5) bond distances are 2.249(3)Å (π isomer) and 2.268(4)Å (ϰ isomer). Comparable distances for related complexes are 2.271(2) Å in α–[Co-(trien)NH_3Cl]$(NO_3)_2$,[21] 2.286(2) Å in [Co$(NH_3)_5$Cl]-Cl_2,[23] 2.237(4) Å in β–[Co(trien)(OH_2)Cl]$(ClO_4)_2$,[24] 2.259(9) Å in β–[Co(en)(dpt)Cl]$ZnCl_4$,[6] 2.263(3) Å in αα–[Co(tetren)Cl]Cl · ClO_4,[26] and 2.21(2) Å α–[Co(en)(dpt)Cl]I_2 · H_2O.[7]

For the π isomer, the angles subtended at the cobalt atom by the two dien chelate rings (87.2(3) and 87.3 (3)°) are equal within probable limits of error. However, the angle subtended by the en chelate ring is very significantly contracted (85.7(3)°) from the angles subtended by each of the other rings. Nevertheless, all of these angles are within the range of values found in other Co^{III}–C_2 bridged polyamine complexes.[6,7,21,22,24] These chelate angles combine to produce significant distortions from regular octahedral coordination about the central cobalt atom (Table VI).

In the ϰ isomer, the angles subtended at the cobalt atom by the two dien chelate rings (85.6(6) and 84.9 (5)°) are equal but they are significantly contracted from the values obtained for the π isomer. Comparable values are 78.8(6), 82.0(4) and 81.9(4), 81.8(5)° in [Cu$(dien)_2$]Br_2 · H_2O,[28] and 85.2(3), 85.0(3)° in Cu(dien)C_2O_4 · $4H_2O$.[29]

The range of C–N and C–C bond distances is similar to that found in other Co^{III}–en complexes.[6,7,30] For the π isomer, the C(5)–C(6) bond distance (1.60(1) Å) is expanded significantly from the C(3)–C(4) bond distance (1.51(1) Å) showing the effects of chelate ring distortion in the facial configuration of the dien ligand and of non-bonded interactions with the anion (see later). A similar, though less marked effect is observed in facial Cr(dien)Cl_3.[25]

In the ϰ isomer, the C(3)–C(4) and C(5)–C(6) bond distances (1.53(2) and 1.51(3) Å respectively) are not significantly different. This is expected as the dien chelate ring is coordinated in a near symmetrical orientation with respect to the en chelate ring.

Significant angular distortions occur at the secondary nitrogen atom in the dien ligand: C(4)–N(4)–C (5), 113.6(7)° (π); 118(1)° (ϰ). The angle in the facial π isomer can be compared with similar angular distortions where «bends» occur in the chain of a coordinated polyamine ligand eg. αα–Co(tetren)Cl^{2+} (113.7(9), 114.0(10), 112.5(9)°)[26] and α–Co(trien)NH_3-Cl^{2+} (113.1(6), 114.0(6)°).[21] Comparative angles for the peripherial ϰ isomer can be found in [Cu$(dien)_2$]-$(NO_3)_2$ (115.3(11), 115.1(13)°),[27] [Cu$(dien)_2$]Br_2 · H_2O (117.4(26), 111.3(22)°),[28] Cu(dien)C_2O_4 · $4H_2O$ (112.6 (8)°),[29] and β–[Co(trien)(gly)]I_2 · $0.5H_2O$ (117.8(7)°, Δ–β_1–*RS*–isomer).[31]

As is evident from Figures 2 and 5, the chelate rings are considerably puckered, the effect being more marked in the ϰ isomer. For this isomer, torsion angles[32] about the C–C bonds of the five-membered rings are C(1)–C(2) (en), –45(2)°; C(3)–C(4) (dien), 48(2)°; C(5)–C(6) (dien), –49(2)°. Observed torsion angles in other –NH$(CH_2)_2$NH– chelate rings are 65 (5)° and 60(9)° in the isomeric Co(en)(dpt)Cl^{2+} cations,[6,7] and 46.5, 37.2, 44.9° and 49.2, 41.6, 38.7, 50.6° in the α–trien[21] and αβ*S*–tetren[5] chelate rings, respectively. Thus, the observed degree of ring puckering is typical for five-membered Co^{III} polyamine complexes and indicates that the anion is symmetrically placed with respect to the tridentate plane so as to have little non-bonded effect (Table VIII). Non-

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(29) Stephens F.S., *J. Chem. Soc. (A)*, 2493 (1969).

(30) Jensen K.G., Soling H., and Thorup N., *Acta Chem. Scand.*, *24*, 908 (1970).
(31) Dellaca R.J., personal communication.
(32) The torsion angles (also known as dihedral angles) are defined as follows.[23] Travelling around the ligand chain from A to D, the torsion angle formed by the atoms A, B, C, and D is the angle which the ABC plane is rotated from the BCD plane. The angle is positive when the AB bond must be rotated clockwise to lie on the BCD plane: Klyne W. and Prelog V., *Experientia*, *16*, 521 (1960); Allen F.H. and Rodgers D., *Acta Cryst.*, *B25*, 1362 (1969). The theoretical value for an unperturbed torsion angle in a chelated –NH$(CH_2)_2$NH– residue is ± 48.8°.
(33) These data were calculated from data presented in Table I, reference 25.

bonded interactions with the hydrogen atoms on the polyamine ligands appear to be of minor importance when the amine is in the peripherial configuration.

However, the torsion angles[32] about the C–C bonds of the five-membered rings in the π isomer are C(1)–C(2) (en), 14.3(8)°; C(3)–C(4) (dien), 15.3(6)°; C(5)–C(6) (dien), –2.6(1)°. These are very much smaller than those observed for other systems (eg. the corresponding dien torsion angles in facial $Cr(dien)Cl_3$[25] are 47.6 and –44.3°),[33] indicating that the degree of ring pucekring is small. Table VIII presents the close interionic contact distances in the π–[Co(en)(dien)-Cl]$ZnCl_4$ crystal. There are thirteen vectors between anion and cation atoms that are less than 3.5 Å and these all involve the tetrachlorozincate(II) chlorine atoms. Their combined effect is to distort the chelate rings and to produce the small torsion angles observed. A low torsion angle is also observed in the αβ*R*–tetren–chelate ring, and is attributed to close contact of the perchlorate anion.[5] Non-bonded interactions with the hydrogen atoms on the ligands are also thought to be important, especially as the dien ligand is in the facial configuration. Indeed, models indicate that the configuration having the least non-bonded interactions (en protons with dien protons) has the Co–N(4)–C(5)–C(6)–N(5) ring nearly planar.

Table IX. Intramolecular bond distances and angles for the Tetrachlorozincate(II) Anion.

Atoms	Distance, Å	Atoms	Distance, Å
π-Isomer			
Intramolecular Bond Distances			
Zn-Cl_1	2.274(3)	Zn-Cl_3	2.242(3)
Zn-Cl_2	2.250(3)	Zn-Cl_4	2.278(3)
Intramolecular Bond Angles			
Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_1-Zn-Cl_2	104.5(1)	Cl_2-Zn-Cl_3	112.1(1)
Cl-Zn-Cl_3	113.0(1)	Cl_3-Zn-Cl_4	112.9(1)
Cl_1-Zn-Cl_4	108.1(1)	Cl_3-Zn-Cl_4	106.3(1)
x-Isomer			
Intracolecular Bond Distances			
Atoms	Distance, Å	Atoms	Distance, Å
Zn-Cl_1	2.284(4)	Zn-Cl_3	2.256(5)
Zn-Cl_2	2.272(5)	Zn-Cl_4	2.279(4)
Intramolecular Bond Angles			
Atoms	Angle, deg.	Atoms	Angle, deg.
Cl_1-Zn-Cl_2	108.8(2)	Cl_2-Zn-Cl_3	110.5(2)
Cl_1-Zn-Cl_3	107.3(2)	Cl_2-Zn-Cl_4	107.8(2)
Cl_1-Zn-Cl_4	111.0(2)	Cl_3-Zn-Cl_4	111.5(2)

Table VIII. Close Contacts in the π and x–[Co(en)(dien)-Cl]$ZnCl_4$. Crystals.

Atoms X...Y	d(X...Y),Å	Atoms X...Y	d(X...Y),Å
x Isomer			
$Cl_1 \ldots N_4$	3.27(1)	$Cl_2 \ldots N_2$	3.30(1)
$Cl_1 \ldots N_2$	3.39(1)	$Cl_2 \ldots N_1$	3.30(1)
$Cl_1 \ldots N_5$	3.39(1)		
$Cl_3 \ldots N_1$	3.21(1)	$Cl_4 \ldots N_3$	3.32(1)
$Cl_3 \ldots N_3$	3.32(1)	$Cl_4 \ldots N_5$	3.34(1)
π Isomer			
$Cl_1 \ldots N_5$	3.384(8)	$Cl_2 \ldots N_4$	3.373(7)
$Cl_1 \ldots C_6$	3.398(9)	$Cl_2 \ldots C_3$	3.41(1)
$Cl_1 \ldots C_1$	3.41(1)	$Cl_2 \ldots N_1$	3.486(7)
$Cl_1 \ldots N_2$	3.452(8)	$Cl_2 \ldots N_3$	3.487(7)
$Cl_1 \ldots N_1$	3.458(8)		
$Cl_3 \ldots N_5$	3.238(7)	$Cl_4 \ldots N_2$	3.314(8)
$Cl_3 \ldots C_3$	3.45(1)	$Cl_4 \ldots N_3$	3.432(7)

The Tetrachlorozincate(II) Anion. A perspective view of the tetrachlorozincate(II) anion (as it occurs in the π isomer) is presented in Figure 5. In both isomers, a slightly distorted tetrahedral arrangement of chlorine atoms about the central zinc atom is observed (Table IX), with mean Zn–Cl bond distances of 2.26(3) Å (π) and 2.27(1) Å (x). Comparable values in related compounds are 2.264(17) Å in β–[Co(en)(dpt)Cl]$ZnCl_4$,[6] 2.26 Å in $Na_2ZnCl_4 \cdot 3H_2O$,[34] and 2.287(15) Å in $[N(CH_3)_4]_2[ZnCl_4]$.[35]

Chemical Implications. The structure of π and x–[Co(en)(dien)Cl]$ZnCl_4$ are as predicted by Gainsford and House.[1] However, for the ω isomer[11] (Figure 1, type III) the previous structural assignment[1] is in error. The occurrence of both optical isomers in the same crystal of π–[Co(en)(dien)Cl]$ZnCl_4$ was expected, but attempts to resolve the complex have so far been unsuccessful. The remaining Co(en)-(dien)Cl^{2+} isomer of type I with the NH proton adjacent to the coordinated chloride (similar to α–Co(en)-(dpt)Cl^{2+7}) has not yet been isolated as it has previously been shown that the so called ε isomer[1] is in fact a 73:27 mixture of the π–[Co(en)(dien)Cl]$ZnCl_4$ and π–[Co(en)(dien)NO_2]$ZnCl_4$ salts.[2]

The π and x isomers are isolated as an approximately 65:35 mixture from the HCl decomposition of $[Co_2(en)_2(dien)_2O_2](ClO_4)_4$[1,36-38] at 80° followed by the addition of $ZnCl_2$. This suggests that the parent μ–peroxo could be a symmetrical isomeric mixture or contain unsymmetrical pentamine residues, one with the π and one with the x configurations. In a study of the aquation rates of the Co(en)(dien)Cl^{2+} isomers, at present under investigation, we have found that x–Co(en)(dien)OH_2^{3+} isomerises quantitatively to the π isomer ($t_{1/2}$ = 76 min at 75° in 1.0 *F* $HClO_4$). Thus if the μ–peroxo contains the polyamine ligands in the x configuration, then at least some of this form would be isomerised to the π form in the course of the decomposition.

No trace of the ω isomer has been detected in the products from the decomposition of the μ–peroxo and our aquation studies show that ω–Co(en)(dien)Cl^{2+} is not isomerised to, or generated from either of the other forms.

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(35) Wierner P.R., Srivastava R.C., Lennard C.H.L., DiVaira M., and Lingafelter E.C., *Acta Crist.*, *23*, 565 (1967).
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The reaction of peripherial–Co(dien)$(NO_2)_3$[39] with ethylenediamine and the subsequent decomposition of the resulting pentamine nitro isomers with $HCl/ZnCl_2$ (Method C, reference 1) yields mainly the ω and π isomers with small amounts of ϰ form. Thus, this reaction sequence involves extensive isomerisation of the diethylenetriamine ligand, as both the π and ω isomers have facial configurations.

It is perhaps surprising that the fourth Co(en)(dien)Cl^{2+} isomer has not been detected. In both the Co(en)(dpt)Cl^{2+} and Co(tetren)Cl^{2+} systems, inversion from the configuration where the NH proton is remote from the coordinate chloride to the alternate configuration can be achieved quantitatively by base hydrolysis, acidification and subsequent chloride anation of the resulting aquo product. However, the only chloro products so far isolated from the work up of base hydrolysed ϰ–Co(en)(dien)Cl^{2+} are the parent or the π isomer. This latter almost certainly results from isomerisation of the ϰ aquo to the π aquo and its subsequent anation.

The stereochemistry of several isomeric chloropentaminepolyamine cobalt(III) cations has now been established by X-ray or other studies and reaction rates for these species are being investigated. From the limited amount of published data, it appears that aquation rates (replacement of Cl by H_2O in acid solution) are rather insensitive to stereochemistry. Thus, α(or α β *R*) and β(or α β *S*)-Co(tetren)Cl^{2+} (related to each other by proton inversion at a secondary nitrogen in a peripherial configuration[5]) aquate with rate constants of 2.2 and 1.3×10^{-5} sec^{-1} in 1 *F* $HClO_4$ at 70°.

Under similar conditions the three Co(en)(dien)Cl^{2+} isomers aquate with rate constants of 8.7 (π), 4.3 (ϰ) and 3.7(ω) $\times$ 10^{-5} $sec.^{-1}$.[41]

These data are consistent with the hypothesis[42] that increasing chelation beyond a certain point has little influence on the aquation rate.

Base hydrolysis rates (replacement of Cl by OH in basic solution), however, appear to be much more sensitive to stereochemistry. For the three Co(en)(dien)Cl^{2+} isomers, the relative rates for base hydrolysis[43] are 1 (ω): 5 (π): 10^4 (ϰ) and the three Co(tetren)Cl^{2+} isomers also have base hydrolysis rates varying over several orders of magnitude.[44] It is also reported[21] that α–Co(trien)$(NH_3)Cl^{2+}$ is the isomer in this system with the slowest rate of base hydrolysis.

Thus it appears that chloropentaminepolyaminecobalt(III) systems with part of the chain in the peripherial configuration have base hydrolysis rate constants several orders of magnitude greater than those complexes where such configurations are absent. This is supported by the observation that *trans* and *cis*–Co$(en)_2NH_3Cl^{2+}$ and β and α–Co(en)(dpt)Cl^{2+} (peripherial dpt, related by proton inversion) have relative base hydrolysis rate ratios of 1:2.5[45] and 1:3.9[43], although the magnitudes of the rate constants are about 10^6 times greater in the Co(en)(dpt)Cl^{2+} systems.

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(44) Marzilli P.A., Abstracts 40th A.N.Z.A.A.S. Congress, Section B, Christchurch, New Zealand, 50 (1968).
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