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# Acidopentaminecobalt(III) Complexes with Polyamine Ligands. IV.[1a] The Crystal Stucture of α-Chloro-(ethylenediamine)(dipropylenetriamine)cobalt(III) Iodide Monohydrate and Strain Energy Minimisation Calculations for the α- and β- Isomeric Cations

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*The crystal structure of α–chloro(ethylenediamine) (dipropylenetriamine)cobalt(III) iodide monohydrate α–[Co(en)(dpt)Cl]$I_2$ . $H_2O$ has been determined by three-dimensional X-ray diffraction techniques using 468 reflections collected at ambient temperature by multiple film methods.*

*Full-matrix least-squares refinement led to a conventional R factor of 0.066. The salt crystallises in space group* Pna2*₁ of the orthorhombic system with 4 formula units in a cell of dimensions* a*=14.49,* b*= 9.123,* c*=13.27 Å. The observed and calculated densities are 2.09 and 2.11 g/cm$^3$ respectively. The cobalt atom is surrounded by one chlorine and five nitrogen atoms in an approximately octahedral configuration. The three nitrogen atoms of the dipropylenetriamine ligand ($NH_2(CH_2)_3NH(CH_2)_3NH_2$) are in a plane with one nitrogen atom of the ethylenediamine while the second nitrogen atom is* trans *to the chlorine atom. The orientation about the co-ordinated secondary amine nitrogen of the dipropylenetriamine, is such that the NH proton is adjacent to the chlorine atom.*

*This is in contrast with the β-isomer, where the NH proton is remote from the chlorine atom.*

*In both isomers, the fused six-membered ring systems adopt a 'chair-boat' conformation. Strain energy minimisation calculations have been performed on the α and the β–Co(en)(dpt)Cl$^{2+}$ isomers for 'chair-chair', 'chair-boat', and 'chair-boat' (inverted (λ) en ring) conformations of the dpt ligand. The energy difference between the most stable conformers (chair-boat, δ en as determined by crystal structure analysis) is small, with the α-isomer being 0.4 kcal/mole more stable.*

## Introduction

In an earlier paper in this series,[1c] the preparation and characterisation of salts of the α, β, and γ isomers of the Co(en)(dpt)Cl$^{2+}$ cation (en=ethylenediamine, dpt=dipropylenetriamine=$NH_2(CH_2)_3NH(CH_2)_3NH_2$) were reported. There are potentially three distinct geometrical configurations for these three isomeric cations (Figure 1). In addition, there exists the possibility of conformation isomerism for isomer I. This arises from the different configurations of the kinetically inert proton (in acid solution) on the secondary nitrogen of the dpt ligand. This type of conformational isomerism is now well established for cobalt(III) polyamine complexes.[2-4] Clearly, for isomers II and III (Figure 1), which have a *cis* or facial arrangement of the dpt ligand, the configuration at the secondary nitrogen center is fixed and this type of conformational isomerism cannot occur.

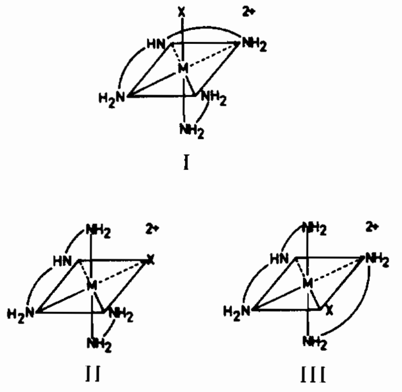

Figure 1. The three possible geometric forms of the Co(en)-(dpt)Cl$^{2+}$ cation. Conformational isomers are not distinguished in these diagrams.

From a single crystal X-ray analysis, the β-isomer (as the $ZnCl_4^{2-}$ salt) was shown to have the geome-

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(1a) Part III, P. R. Ireland, D. A. House, and W T. Robinson, *Inorg. Chim. Acta, 4,* 137 (1970): (1b) All correspondence should be addressed to D.A. House, Department of Chemistry, University of Canterbury, Christchurch, New Zealand: (1c) Part I, A.R. Gainsford and D. A. House, *Inorg. Chim. Acta, 3,* 33 (1969).

(2) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.,* 6, 1032 (1967).

(3) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.,* 7, 915 (1968).

(4) M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Commun.,* 891 (1969).

trical configuration I.[5] The conformation of the dpt chelate rings is such that the proton on the secondary nitrogen, N(4) (Figure 2), is directed away from the co-ordinated chlorine atom.

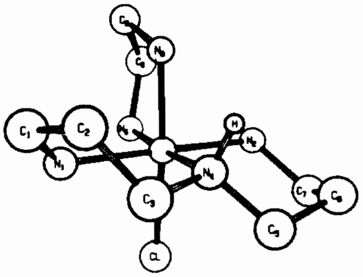

Figure 2. A perspective view of the β—Co(en)(dpt)Cl$^{2+}$ cation.

This paper reports the results of a single crystal X-ray analysis of the α-Co(en)(dpt)Cl$^{2+}$ cation (as the di-iodide monohydrate salt). In addition we have performed strain energy minimisation calculations on the isomeric α and β—Co(en)(dpt)Cl$^{2+}$ cations. These calculations were carried out to examine the distribution of molecular strain within these complexes and to determine the most stable conformations of the chelate rings. Further, the calculations provide a measure of the stability difference between the α and β forms.

## Experimental Section

*Crystal Data.* α—[Co(en)(dpt)Cl]$I_2$ . $H_2O$ forms violet-mauve crystals which are stable to both air and X-rays.[6] The unit cell is orthorhombic with $a = 14.49$ (1) Å, $b = 9.123(6)$ Å, $c = 13.27(1)$ Å, $V = 1754$ Å$^3$, $D_m = 2.09(2)$ g.cm$^{-3}$ (by gradient tube method), Z = 4, $D_X = 2.11$ g.cm$^{-3}$ for $C_8H_{27}N_5OClI_2Co$ with F.W. = 557.6 and μ(Co Kα) = 445.0 cm$^{-1}$. The space group is $Pna2_1$ (No. 33) or $Pnam$ (equivalent to $Pnma$, No. 62) from systematic absences of reflections ($h0l$ absent for $h = 2n+l, 0kl$ absent for $k+l = 2n+l$). This space group ambiguity could be resolved since the compound was known to contain dissymmetric molecules which cannot have the required point group symmetry ($C_s$ or $C_i$) in the centric space group. The subsequent solution and refinement of the structure confirmed the space group as $Pna2_1$. The unit cell dimensions were calculated by a least-squares procedure from values of θ measured from Polaroid precession photographs using Cu Kα radiation. [λ(Cu K$\alpha_1$) = 1.5405 Å, λ(Cu K$\alpha_2$) = 1.5443 Å]. Throughout this paper, numbers in parentheses are estimated standard deviations in the least significant digits quoted.

*X-Ray data Collection and Reduction.* A well formed crystal of dimensions 0.40×0.10×0.06 mm parallel to the *a*, *b*, and *c* axes respectively, was mounted about its *a* axis for data collection. The crystal was rotated about its longest morphological axis to minimise absorption effects. Intensity data were collected by the multiple film method on a Nonius integrating Weissenberg camera with Fe-filtered Co Kα radiation. Data were collected for the reciprocal lattice levels $hkl$ ($0 \leqslant h \leqslant 8$). In addition, a set of Bijvoet related reflections were collected for the $0kl$ zone. Measurements of the integrated reflection data were made using a single beam microdensitometer equipped with a photoelectric cell and a galvanometer calibrated to read intensities directly. Lorentz polarization and absorption corrections were applied, the latter by the method of Coppens, Leiserowitz, and Rabinovich[7] using a total of 512 integration points. Transmission factors ranged from 0.086 to 0.135. The data were initially scaled according to exposure times and a total of 686 independent reflections were obtained of which 218 were weak and treated as unobserved. Although long film exposure times were used (142-234 hr) only a relatively low number of observed reflection data were obtained.

*Solution and Refinement of the Structure.* The structure was solved by the use of a Patterson synthesis and standard Fourier methods. A difference map in the final stages of the solution indicated the presence of one lattice water molecule. Full-matrix least-squares refinements were carried out by minimising the function $\Sigma w(|F_o| - s|F_c|)^2$ where $w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$ and $s$ is the scale factor associated with each reciprocal lattice level.

The weighting parameters, $A$, $B$, $C$, and $D$ were derived so that $\Sigma w\Delta^2$ was independent of $|F_o|$ and sin $\theta/\lambda[\Delta = ||F_o| - s|F_c||]$.

The weighting parameters were modified throughout the least-squares refinement, the final values being, $A = 101.9$, $B = -1.91$, $C = 0.066$, and $D = 0$.

The least-squares refinement with coordinates and isotropic temperature factors as variable parameters converged with residuals, $R_1 = \Sigma\Delta/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ of 0.066 and 0.081 respectively. Anisotropic refinement was not carried out since there was no evidence of such thermal motion from Fourier calculations and additional least-squares parameters were not justified with the relatively small data set. The highest peak on a final difference Fourier had a density of 1.3 e$^-$/Å$^3$ and was in the vicinity of an iodine atom.

The determination of the correct space group polarity was important in view of the significant contributions from anomalous scattering (Δf″(Co Kα) = 8.3, for iodine). Cruickshank and McDonald[8] have shown that serious coordinate errors arise from the anomalous dispersion effect if the space group polarity is incorrect.

Least-squares refinement of the inverse structure resulted in a significantly higher residual $R_1 = 0.083$, showing that the original choice was correct. Intensity differences between Bijvoet related reflections of the type $0kl$, $0\bar{k}\bar{l}$ confirmed this choice (see Table I). Atomic scattering factors for Co, Cl, C, N, and O

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[5] Part III, P. R. Ireland, D. A. House, and W. T. Robinson, *Inorg. Chim. Acta*, *4*, 137 (1970).

[6] We thank Mr A. R. Gainsford for the preparation of this salt in a suitable form for structural analysis.

[7] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta. Cryst.*, *18*, 1035 (1965).

[8] D. W. J. Cruickshank and W. S. McDonald, *Acta Cryst.*, *23*, 9 (1967).

[9] « International Tables for X-ray Crystallography », Vol. 3, The Kynoch Press, Birmingham, England, 1962.

**Table I.** Observed and calculated structure amplitudes for $\alpha$–[Co(en)(dpt)Cl]$I_2$ . $H_2O$.

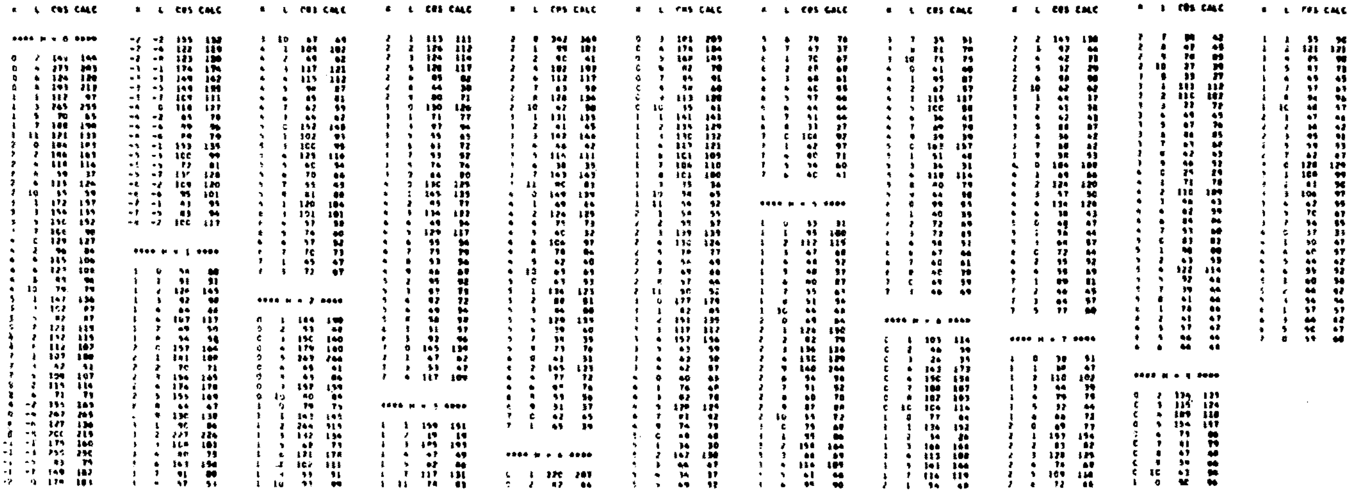

**Table II.** Fractional atomic positional parameters and isotropic temperature factors $\alpha$–[Co(en)(dpt)Cl]$I_2$ . $H_2O$[a]

| Atom | x | y | z | B(Å²) |
|---|---|---|---|---|
| I(1) | 0.0954(3) | 0.1794(4) | 0.5 | 3.75(8) |
| I(2) | 0.0729(3) | 0.6198(5) | 0.2747(5) | 3.81(9) |
| Co | 0.3283(7) | 0.2262(9) | 0.2417(7) | 1.9(0.2) |
| Cl | 0.229(1) | 0.287(2) | 0.123(1) | 2.7(0.3) |
| N(1) | 0.262(4) | 0.369(6) | 0.326(4) | 3.9(1.2) |
| N(2) | 0.383(4) | 0.085(6) | 0.151(4) | 4.7(1.5) |
| N(4) | 0.411(3) | 0.379(4) | 0.194(3) | 1.7(0.9) |
| N(5) | 0.247(3) | 0.076(4) | 0.293(3) | 1.3(0.9) |
| N(0) | 0.407(4) | 0.158(5) | 0.352(3) | 2.3(1.0) |
| C(1) | 0.305(5) | 0.476(7) | 0.389(4) | 3.4(1.5) |
| C(2) | 0.365(5) | 0.574(6) | 0.316(4) | 2.7(1.5) |
| C(3) | 0.450(5) | 0.499(6) | 0.274(5) | 4.0(1.5) |
| C(5) | 0.501(4) | 0.323(5) | 0.157(4) | 1.5(1.2) |
| C(6) | 0.491(4) | 0.243(7) | 0.054(4) | 3.2(1.3) |
| C(7) | 0.427(6) | 0.111(7) | 0.060(6) | 5.2(1.6) |
| C(8) | 0.309(5) | —0.010(7) | 0.371(5) | 4.3(1.7) |
| C(9) | 0.360(5) | 0.083(7) | 0.427(5) | 3.6(1.6) |
| O(1) | 0.223(3) | 0.845(5) | 0.137(4) | 4.4(1.0) |

[a] Numbers in parentheses are estimated standard deviations right adjusted to the least significant digit of the preceding number.

atoms were those tabulated by Ibers.[9] Anomalous dispersion terms Δf′ and Δf″ for I, Co, and Cl were from values listed by Cromer.[10] An examination of the data showed no evidence of secondary extinction effects.

The observed and calculated structure factor amplitudes are compared in Table I. Final atomic positional and thermal parameters with estimated standard deviations are presented in Table II.

*Strain Energy Minimisation Calculations.* The strain energy minimisation method has been described in some detail in a previous publication[11] and only the important features will be reiterated.

The total molecular strain, U is assumed to be represented by four terms, *i.e.*

$$U=\sum_{(ij)}U(r_{ij})_{nb}+\sum_{(ijk)}U(\theta_{ijk})+\sum_{(ijkl)}U(\varphi_{ijkl})+\sum_{(ij)}U(r_{ij})_b.$$

$U(r_{ij})_{nb}$ is a non-bonded interaction term for atoms i and j and is normally of the Buckingham form *i.e.*

$$U(r_{ij})_{nb}=a_{ij}\exp(-b_{ij}r_{ij})-c_{ij}/r_{ij}^6$$

where $a_{ij}$, $b_{ij}$, and $c_{ij}$ are constants for a particular type of atom-atom interaction. $U(\theta_{ijk})$ and $U(r_{ij})_b$ are terms for bond angle and bond length deformation respectively. These functions are assumed to be harmonic, *i.e.*

$$U(\theta_{ijk})=\tfrac{1}{2}k^{\theta}_{ijk}(\theta^{o}_{ijk}-\theta_{ijk})^2$$

where $V^{\theta}_{\underline{ijk}}$ is the force constant for the bond angle $\theta_{ijk}$ and $\theta_{ijk}^{o}$ is the strain free value. Similarly,

$$U(r_{ij})_b=\tfrac{1}{2}k_{ij}^{r}\ (r_{ij}^{o}-r_{ij})^2$$

where $k_{ij}^{r}$ is the force constant for the bond $r_{ij}$, and $r_{ij}^{o}$ is the strain free value. $U(\theta_{ijkl})$ is the torsional potential term to account for restricted rotation about single bonds and has the usual form;

$$U(\varphi_{ijkl})=\tfrac{1}{2}V^{\varphi}_{ijkl}\ (1-\cos3\varphi_{ijkl})$$

where $V^{\varphi}_{ijk}$ is the potential energy barrier to rotation about the bond jk as defined by atoms i, j, k, and l, with the non-bonded atom contributions removed. Parameters in all these various terms are the same as those used in previous papers unless otherwise stated.[11,12] The minimisation method used is a modified Newton-Raphson technique which was developed by Boyd.[14] This method has the particular advantage that the atom coordinate shifts which lead to a minimum energy configuration are calculated directly and the rate of convergence is generally quite rapid.

## Description of the Structure

The crystal lattice consits of discrete cations, anions and water molecules linked by hydrogen bonding,

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(10) D. T. Cromer, *Acta Cryst.*, *18*, 17 (1965).

(11) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, *92*, 3617 (1970).

(12) M. R. Snow, *J. Amer. Chem. Soc.*, *92*, 3610 (1970).

(13) R. H. Boyd, *J. Chem. Phys.*, *49*, 2574 (1968).

(14) L. Pauling, « The Nature of the Chemical Bond », Cornell University Press, Ithaca, New York, 1960.

electrostatic and Van der Waals forces (see Figure 3). Each water molecule makes one short and one long hydrogen bond to the NH groups of the same complex cation. The closest interionic approaches are summarized in Table III. An important feature of the crystal packing is the relatively close approach between neighbouring cations. Hydrogen atoms placed at calculated positions (assuming $C_{2v}$ symetry at the carbon atoms and a C–H bond distance of 1.0 Å) on carbon atoms C(7) of the dpt ligand, and C(9) of the en ligand of the neighbouring cation are 2.18 Å apart. This distance is significantly shorter than the expected Van der Waals contact distance of 2.40 Å[14] and has considerable bearing on the later discussion on the effect of intermolecular forces on chelate ring conformations.

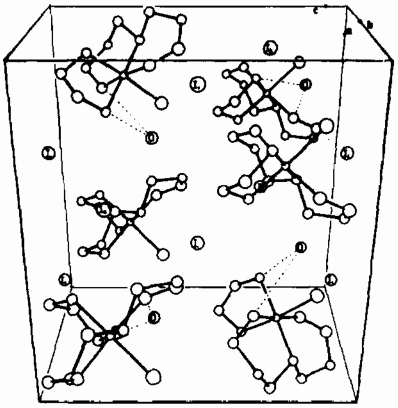

Figure 3. The packing of the ions in α–[Co(en)(dpt)Cl]$I_2$.-$H_2O$, as viewed down the b-axis.

**Table III.** Interionic approaches in the α–[Co(en)(dpt)Cl]-$I_2$ . $H_2O$ crystal

| Atoms | d(N-X),Å | d(H-X) [a],Å | angle(N-H-X) |
|---|---|---|---|
| I(1) ··· N(5) | 3.64 | 2.74 | 150° |
| I(1) ··· N(1) | 3.76 | 2.77 | 172° |
| I(2) ··· N(6) | 3.64 | 2.65 | 169° |
| I(2) ··· N(2) | 3.71 | 2.72 | 170° |
| O(1) ··· N(5) | 2.98 | 2.02 | 161° |
| O(1) ··· N(2) | 3.20 | 2.22 | 166° |

| Atoms | d(O-X),Å |
|---|---|
| O(1)··I(1) | 3.54 |
| O(1)··I(2) | 3.50 |

[a] Hydrogen atoms were placed at calculated positions assuming $C_{2v}$ symmetry about the N atom and an N-H bond distance of 1.0Å.

*Description of the α–Co(en)(dpt)$Cl^{2+}$ Cation.* Figure 4 shows a perspective view of the α–Co(en)(dpt)-$Cl^{2+}$ cation and indicates the atom numbering system. As expected, the dpt ligand is coordinated tridentate, the en ligand bidentate and the coordinated chloride ion completes the octahedral coordination sphere. Clearly, the geometry of the complex is of type I (Figure 1) with the nitrogen atoms of the dpt ligand in the same coordination plane. The configuration at the secondary nitrogen atom, N(4) is such that the proton is directed towards the coordinated chlorine atom. Thus α and β–Co(en)(dpt)$Cl^{2+}$ are conformational isomers related by inversion at the secondary nitrogen center of the dpt ligand and not geometric isomers of the II-I type as suggested by Gainsford and House.[1c]

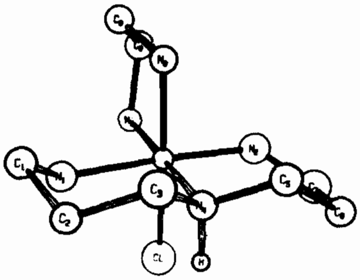

Figure 4. A perspective view of the α–Co(en)(dpt)$Cl^{2+}$ cation.

As is evident in Figure 4, the dpt six-membered chelate rings adopt 'chair' and 'boat' conformations, like the β-isomer (Figure 2), but in the reverse order. Chelate ring conformations will be discussed in more detail in a later section of this paper.

Intramolecular bond distances and angles within the complex cation are presented in Table IV. The $Co^{III}$–N bond lengths do not differ by more than one standard deviation from the mean value, 1.95(5) Å. This value is smaller than for the β–Co(en)(dpt)$Cl^{2+}$ cation (mean $Co^{III}$–N, 1.99(2) Å),[5] but this difference is not significant. Angular strain is evident at the

**Table IV.** Intramolecular bond distances and angles for α–Co(en)(dpt)$Cl^{2+}$ cation [a]

Intramolecular Bond Distances

| Atoms | Distance,Å | Atoms | Distance,Å |
|---|---|---|---|
| Co-Cl | 2.21(2) | C(3)-N(4) | 1.62(7) |
| Co-N(1) | 1.97(6) | N(4)-C(5) | 1.49(6) |
| Co-N(2) | 1.94(6) | C(5)-C(6) | 1.56(7) |
| Co-N(4) | 1.94(4) | C(6)-C(7) | 1.53(9) |
| Co-N(5) | 1.93(4) | C(7)-N(2) | 1.38(8) |
| Co-N(6) | 1.95(5) | N(5)-C(8) | 1.58(8) |
| N(1)-C(1) | 1.44(8) | C(8)-C(9) | 1.35(9) |
| C(1)-C(2) | 1.57(8) | C(9)-N(6) | 1.39(7) |
| C(2)-C(3) | 1.52(8) | | |

Intramolecular Bond Angles

| Atoms | Angle, deg. | Atoms | Angle,deg. |
|---|---|---|---|
| Cl-Co-N(1) | 85(2) | Co-N(1)-C(1) | 125(5) |
| Cl-Co-N(2) | 89(2) | N(1)-C(1)-C(2) | 105(5) |
| Cl-Co-N(4) | 89(1) | C(1)-C(2)-C(3) | 115(5) |
| Cl-Co-N(5) | 92(1) | C(2)-C(3)-N(4) | 105(5) |
| Cl-Co-N(6) | 174(2) | C(3)-N(4)-Co | 119(3) |
| N(1)-Co-N(2) | 175(2) | C(5)-N(4)-Co | 114(3) |
| N(1)-Co-N(4) | 91(2) | C(3)-N(4)-C(5) | 98(4) |
| N(1)-Co-N(5) | 88(2) | N(4)-C(5)-C(6) | 111(4) |
| N(1)-Co-N(6) | 94(2) | C(5)-C(6)-C(7) | 113(5) |
| N(2)-Co-N(4) | 91(2) | C(6)-C(7)-N(2) | 117(6) |
| N(2)-Co-N(5) | 90(2) | C(7)-N(2)-Co | 128(5) |
| N(2)-Co-N(6) | 91(2) | Co-N(5)-C(8) | 103(3) |
| N(4)-Co-N(5) | 178(2) | N(5)-C(8)-C(9) | 112(5) |
| N(4)-Co-N(6) | 97(2) | C(8)-C(9)-N(6) | 100(6) |
| N(5)-Co-N(6) | 82(2) | C(9)-N(6)-Co | 115(4) |

[a] Figures in parentheses are estimated standard deviations right-adjusted to the least significant digit of the preceding number.

Co—N—C bond angles of the dpt ligand. The angles at the primary nitrogen atoms are more strained (Co—N(1)—C(1), 125(5)°; Co—N(2)—C(7), 128(5)°) than those at the secondary nitrogen center (Co—N(4)—C(3), 119(3)°; Co—N(4)—C(5), 114(3)°). A similar effect was observed in the β-form, and a detailed comparison, along with the strain energy minimisation results will be presented in the next section.

*Strain Energy Minimisation Calculations on Co(en)(dpt)$Cl^{2+}$ Isomers.* Strain energy minimisation calculations have been carried out on α and β—Co(en)(dpt)$Cl^{2+}$ isomers in an attempt to reproduce the crystal structure molecular geometries, to examine alternative chelate ring conformations and to calculate the expected relative stabilities between various isomeric forms. By this method it was hoped to gain a better understanding of the degree and distribution of molecular strain, and the most stable chelate ring conformations for polyamine metal complexes of this type.

Initially trial coordinates for the minimisation of α and β forms of the Co(en)(dpt)$Cl^{2+}$ cations were obtained from the crystal structure analysis results. Hydrogen atoms were placed at calculated positions assuming $C_{2v}$ symmetry at each carbon or nitrogen center. Trial coordinates for different conformations of the chelate rings were obtained by carrying out symmetry operations on the appropriate atoms. These cordinates were all transformed to a common internal coordinate system before commencing minimisation. The internal Cartesian coordinate system of axes, **X**, **Y**, and **Z**, were defined as follows:

$$\mathbf{X}=\mathbf{U}$$
$$\mathbf{Y}=(\mathbf{U}\times\mathbf{V})\times\mathbf{U}$$
$$\mathbf{Z}=\mathbf{U}\times\mathbf{V}$$

were **U** = Co→N(1), **V** = Co→N(4) with the origin at Co.

Minimisation of each isomer was carried out simultaneously varying a total of 114 coordinates and including approximately 280 interactions in each calculation. Convergence was generally quite rapid and was assumed to be complete when the root mean square deviation of the coordinate shifts was less than 0.005 Å.

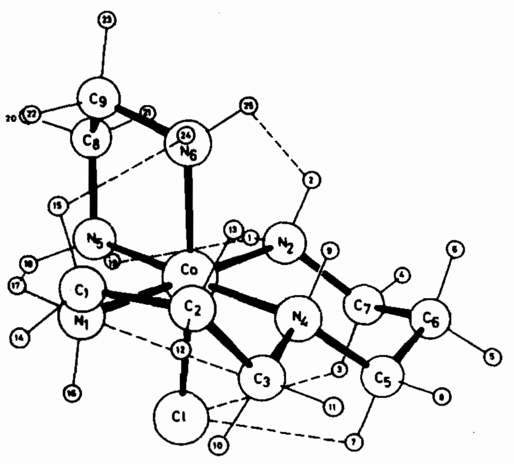

Figure 5. A perspective view of the strain energy minimised β—Co(en)(dpt)$Cl^{2+}$ cation with the 'chair-boat' dpt and δ en conformations.

*Comparison Between Oberved and Calculated Molecular Geometries. β—Co(en)(dpt)$Cl^{2+}$ Cation.* Strain energy minimisation calculations were carried out on three conformational isomers of the β—Co(en)(dpt)$Cl^{2+}$ cation. These included the conformer found in the crystal lattice[5] which had a 'chair-boat' conformation of the dpt chelate rings. In addition calculations were carried out on a conformer with the en chelate ring inverted and finally on a conformer with a 'chair-chair' conformation of the dpt chelate rings. Perspective views of these complex cations are shown in Figures 5, 6, and 7, where dashed lines indicate the major non-bonded interactions. These diagrams were drawn accurately under computer control from the minimised coordinates.[15]

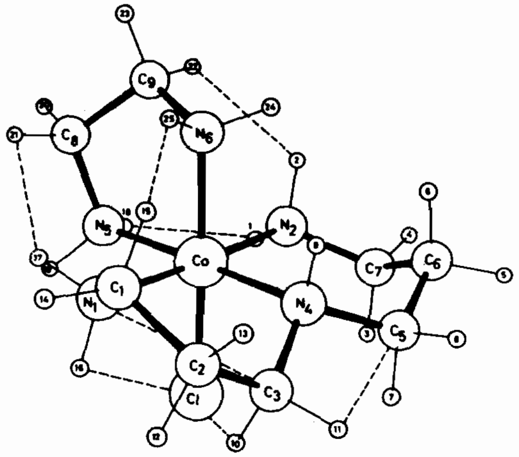

Figure 6. A perspective view of the strain energy minimised β—Co(en)(dpt)$Cl^{2+}$ cation with the 'chair-boat' dpt and λ en conformations.

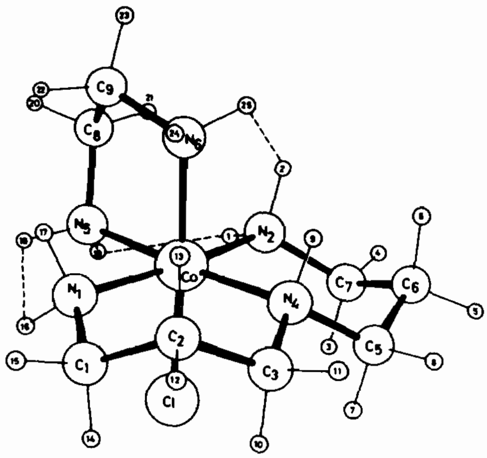

Figure 7. A perspective view of the strain energy minimised β—Co(en)(dpt)$Cl^{2+}$ cation with the 'chair-chair' and δ en conformations.

*'Chair-Boat' Conformer.* Considerable steric strain exists within this conformer and the major non-bonded interactions are as follows: H(2) ... H(25), 2.03 Å, 1.0 kcal/mole; H(1) ... H(19), 2.10 Å, 0.7 kcal/mole;

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(15) Final minimised coordinates for all the conformational isomers examined (three β and four α forms), can be obtained on request from the authors.[1b]

H(15) ... H(24), 2.17 Å, 0.5 kcal/mole; H(17) ... H(18), 2.03 Å, 1.0 kcal/mole; Cl ... H(3), 2.65 Å, 0.5 kcal/mole; Cl ... H(7), 2.66 Å, 0.5 kcal/mole; Cl ... H(16), 2.59 Å, 0.7 kcal/mole; N(1) ... C(3), 2.73 Å, 0.6 kcal/mole; (see Figure 5). Further molecular strain is evidenced by significant bond angle and bond length distortions from strain free values. Bond angle bending is most pronounced at the dpt nitrogen centres where the strain free angles are 109° *i.e.* Co–N(1)–C(1), 120.8°, [120(2)°], 1.1 kcal/mole; Co–N(4)–C(5), 117.4° [118(2)°], 0.5 kcal/mole; Co–N(2)–C(7), 119.1° [117(2)°], 0.8 kcal/mole; Co–N(4)–C(3), 113.8° [114(2)°], 0.2 kcal/mole (Figures in square brackets are the comparable values found by X-ray analysis[5] with standard deviations in rounded brackets). Bond length distortions are also most pronounced at the dpt nitrogen centres *i.e.* Co–N(2), 1.987 Å, 0.5 kcal/mole; Co–N(4), 1.989 Å, 0.5 kcal/mole; Co–N(1), 1.987 Å, 0.5 kcal/mole.

Comparable distances for the en ligand are: Co–N(5), 1.970 Å, 0.3 kcal/mole; Co–N(6), 1.969 Å, 0.3 kcal/mole. This result is consistent with the crystal structure where Co–N(dpt) (mean 2.00(1) Å) bond distances were longer than the Co–N(en) distances (mean 1.97(1) Å).[5] Observed and calculated torsion angles about the carbon-carbon and carbon-nitrogen bonds for dpt and en ligands are compared in Figure 8. Clearly, considerable torsion strain is associated with the dpt chelate ring in the 'boat' conformation. The smallest torsion angle and hence the most strained, is the angle about the C(1)–C(2) bond which is nearly eclipsed (see Figure 8). In general there is good agreement between the calculated and observed molecular geometries.

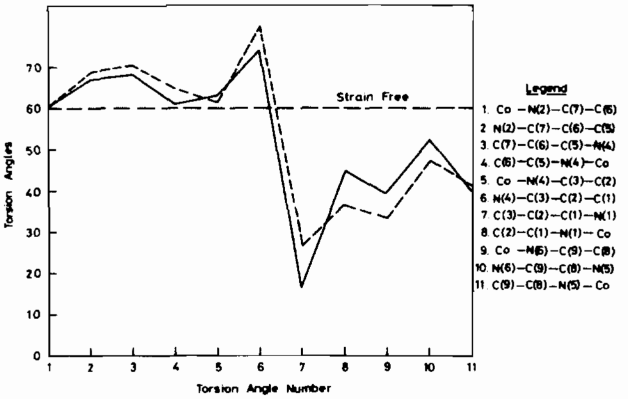

Figure 8. Observed (- - -) and calculated (——) torsion angles for the β–Co(en)(dpt)$Cl^{2+}$ cation. For atom numbering see Figure 2.

The most significant differences between calculation and observation occur for torsion angles. This result is perhaps not unexpected since six-membered chelate rings are rather flexible and are therefore likely to be easily distorted by intermolecular force in the crystal lattice.

*Inverted en Ring Conformer.* Calculations were carried out on this conformer primarily to determine the most stable conformation for the five membered en chelate ring. An increase in steric strain results with major interactions; H(2) ... H(22), 2.13 Å, 0.6 kcal/mole; H(1) ... H(18), 2.05 Å, 0.9 kcal/mole; H(15) ... H(25), 1.96 Å, 1.3 kcal/mole; H(17) ... H(21), 2.19 Å, 0.4 kcal/mole; C(5) ... H(11), 2.44 Å, 0.6 kcal/mole; Cl ... H(10), 2.59 Å, 0.7 kcal/mole; Cl ... H(16), 2.67 Å, 0.4 kcal/mole; N(1) ... C(3), 2.76 Å, 0.5 kcal/mole (see Figure 6). Similar angular and bond length distortions occur in the dpt chelate rings for this conformer; Co–N(1)–C(1), 117.2°, 0.5 kcal/mole; Co–N(4)–C(5), 118.7°, 0.7 kcal/mole; Co–N(2)–C(7), 120.0°, 1.0 kcal/mole; N(2)–Co–N(4), 95.5°, 0.5 kcal/mole; N(4)–C(3)–C(2), 113.9°, 0.4 kcal/mole and Co–N(2), 1.986 Å, 0.5 kcal/mole; Co–N(4), 2.010 Å, 0.9 kcal/mole; Co–N(1), 1.987 Å, 0.5 kcal/mole. An examination of the torsion angles in the dpt chelate rings (see Figure 6) shows that 'boat' conformation is significantly twisted. The twisted 'boat' conformation reduces torsional strain in the chelate ring but only at the expense of increased bond angle strain.

*'Chair-Chair Conformer.* Strain energy calculations on the 'chair-chair' conformer are of particular interest since prior to the α and β–Co(en)(dpt)$Cl^{2+}$ structure analyses this conformation was thought to be the most stable. Non-bonded interactions are considerably reduced for this conformer, the major repulsions are: H(16) ... H(18), 2.04 Å, 0.9 kcal/mole; H(1) .. H(19), 2.09 Å, 0.7 kcal/mole; H(2) ... H(25), 2.09 Å, 0 7 kcal/mole (see Figure 7). However this reduction in non-bonded strain is only at the expense of increased bond angle and bond length strain. Angular distortions are centred at the dpt nitrogen atoms and particularly the two primary nitrogen centres, N(1) and N(2); Co–N(1)–C(1), 121.7°, 1.3 kcal/mole; Co–N(2)–C(7), 120.4°, 1.1 kcal/mole; Co–N(4)–C(3), 118.5°, 0.7 kcal/mole; Co–N(4)–C(5), 116.8°, 0.5 kcal/mole; N(4)–Co–N(1), 96.1°, 0.5 kcal/mole; C(3)–N(4)–C(5), 105.2°, 0.4 kcal/mole. Bond stretching appears to be concentrated at the central secondary nitrogen atom, N(4) of the dpt chelate ring; Co–N(4), 2.018 Å, 1.1 kcal/mole; Co–N(2), 1.989 Å, 0.5 kcal/mole; Co–N(1), 1.985 Å, 0.5 kcal/mole. As expected for a 'chair-chair' geometry there is a reduction

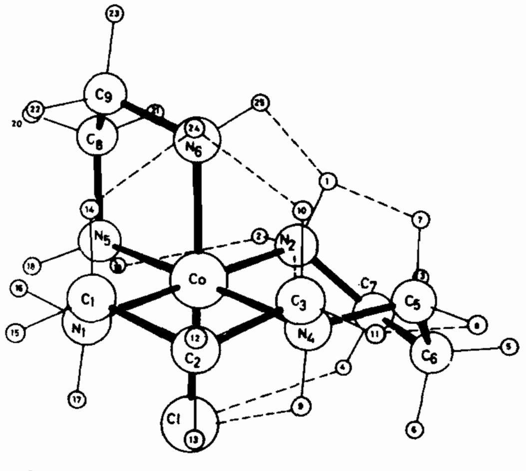

Figure 9. A perspective view of the strain energy minimised α–Co(en)(dpt)$Cl^{2+}$ cation with the 'chair-boat' dpt and δ en conformations.

in torsional strain but this is offset by the increases in bond angle and bond length strain. The relative energy terms for all the β–Co(en)(dpt)Cl$^{2+}$ conformers are discussed in a later section.

*α–Co(en)(dpt)Cl$^{2+}$ Cation.* Four conformers of α–Co(en)(dpt)Cl$^{2+}$ were examined: these included 'chair-boat', 'chair-twist boat' and 'chair-chair' conformations of the dpt chelate rings and an inverted conformation of the en chelate ring. For the 'chair-boat' conformer the crystal structure reported in a previous section of this paper provides a comparison between calculated and observed molecular geometries. Molecular drawings of the minimised conformers are shown in Figures 9, 10, 11, and 12.

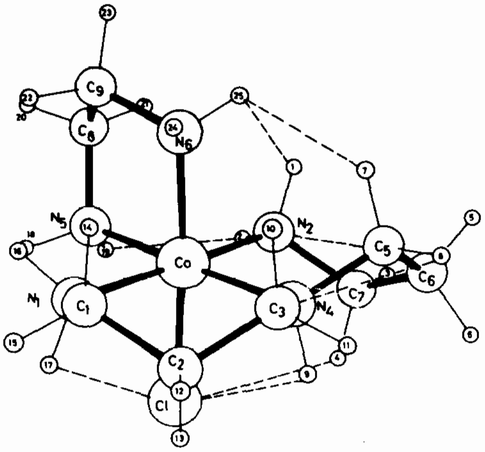

Figure 10. A perspective view of the strain energy minimised α–Co(en)(dpt)Cl$^{2+}$ cation with the 'chair-twist boat' dpt and δ en conformations.

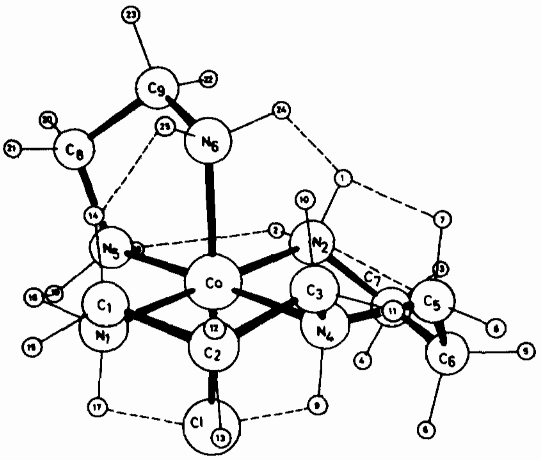

Figure 11. A perspective view of the strain energy minimised α–Co(en)(dpt)Cl$^{2+}$ cation with the 'chair-boat' dpt and λ en conformations.

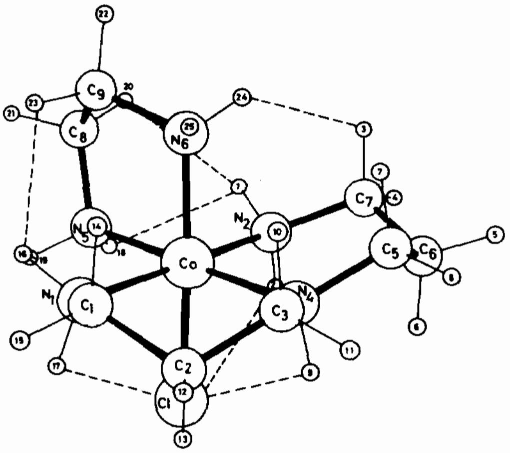

Figure 12. A perspective view of the strain energy minimised α–Co(en)(dpt)Cl$^{2+}$ cation with the 'chair-chair' dpt and δ en conformations.

*'Chair-Boat' Conformer.* Complete minimisation to a strictly 'chair-boat' conformation could not be achieved as this appears to be unstable relative to the 'chair-twist boat' conformer. Partial minimisation of the 'chair-boat' conformation was obtained to a root mean square deviation in the coordinate shifts of 0.02 Å. Further minimisation cycles resulted in the conversion to a more stable 'chair-twist boat' conformation. However it is useful to examine the almost completely minimised conformer and compare this geometry with that of the crystal structure. Major non-bonded interactions are: N(2) ... C(3), 2.72 Å, 0.6 kcal/mole; Cl ... H(4), 2.66 Å, 0.5 kcal/mole; Cl ... H(9), 2.60 Å, 0.7 kcal/mole; Cl ... H(17), 2.57 Å, 0.8 kcal/mole; H(1) ... H(7), 2.20 Å, 0.4 kcal/mole; H(1) ... H(25), 2.05 Å, 0.9 kcal/mole; H(2) ... H(19), 2.10 Å, 0.7 kcal/mole; H(8) ... H(11), 2.20 Å, 0.4 kcal/mole; H(10) ... H(24), 2.09 Å, 0.7 kcal/mole; H(14) ... H(24), 2.07 Å, 0.8 kcal/mole; H(16) ... H(18), 2.05 Å, 0.9 kcal/mole (see Figure 9). These interactions are indicative of the considerable steric crowding associated with this conformation. Important angular and bond length distortions are: Co–N(2)–C(7), 118.9° [128(5)°], 0.8 kcal/mole; Co–N(4)–C(3), 118.0° [119(3)°], 0.6 kcal/mole; Co–N(1)–C(1), 120.4° [125(5)°], 1.1 kcal/mole; N(2)–C(7)–C(6), 113.8° [117(6)°], 0.4 kcal/mole; and Co–N(1), 1.985 Å [1.97(6) Å], 0.5 kcal/mole; Co–N(4), 1.990 Å [1.94(4) Å], 0.5 kcal/mole; Co–N(2), 1.990 Å [1.94(6) Å], 0.5 kcal/mole (Figures in square brackets are the comparable values from the α–Co(en)(dpt)Cl$^{2+}$ crystal structure with standard devia-

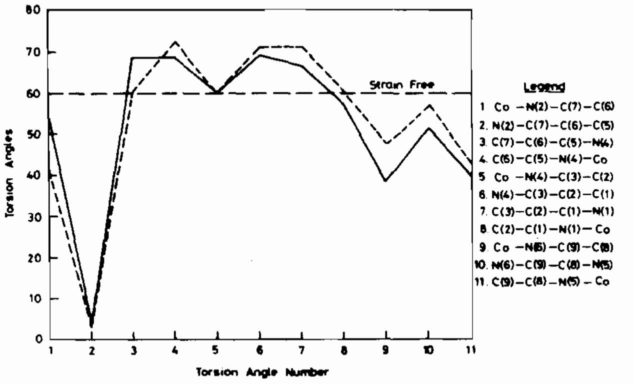

Figure 13. Observed (- - - -) and calculated (——) torsion angles for the α–Co(en)(dpt)Cl$^{2+}$ cation. For atom numbering see Figure 4.

tions in round brackets, see Table IV). Although the agreement between observed and calculated geometries is not very good the major distortions are reproduced. The minimised geometry is almost certainly affected by the incomplete refinement. However, the agreement between calculated and observed chelate ring conformations as demonstrated by torsion angles (Figure 13) is remarkably good.

*'Chair-Twist Boat' Conformer.* As previously discussed minimisation of this conformer was achieved from the less stable 'chair-boat' form. This result is indicative of a relatively small energy barrier between these two conformations. Major non-bonded interactions are: N(2) ... C(5), 2.78 Å, 0.4 kcal/mole; Cl ... H(4), 2.57 Å, 0.8 kcal/mole; Cl ... H(9), 2.63 Å, 0.6 kcal/mole; Cl ... H(17), 2.56 Å, 0.9 kcal/mole; C(3) ... H(8), 2.46 Å, 0.5 kcal/mole; H(1) ... H(25), 2.13 Å, 0.6 kcal/mole; H(2) ... H(19), 2.11 Å, 0.7 kcal/mole; H(7) ... H(25), 2.09 Å, 0.7 kcal/mole; H(16) ... H(18), 2.12 Å, 0.6 kcal/mole (see Figure 10). Angular and bond length distortions are also evident; Co–N(4)–C(3), 118.1°, 0.7 kcal/mole; Co–N(1)–C(1), 121.1°, 1.2 kcal/mole; N(1)–Co–N(4), 95.3°, 0.4 kcal/mole and Co–N(1), 1.986 Å, 0.5 kcal/mole; Co–N(4), 2.006 Å, 0.8 kcal/mole; Co–N(2), 1.985 Å, 0.5 kcal/mole.

*Inverted en ring Conformer.* As for the β-isomer, calculations were carried out on the conformer with the en chelate ring inverted to determine the most stable conformation. Major non-bonded interaction include: N(2) ... C(5), 2.73 Å, 0.6 kcal/mole; Cl ... H(9), 2.63 Å, 0.6 kcal/mole; Cl ... H(17), 2.59 Å, 0.7 kcal/mole; H(1) ... H(7), 2.20 Å, 0.4 kcal/mole; H(1) ... H(24), 2.18 Å, 0.5 kcal/mole; H(2) ... H(18), 2.04 Å, 0.9 kcal/mole; H(14) ... H(25), 2.02 Å, 1.0 kcal/mole; H(16) ... H(19), 2.17 Å, 0.5 kcal/mole (see Figure 11). Angular and bond length distortions occur for the dpt chelate rings; Co–N(2)–C(7), 119.5°, 0.9 kcal/mole; Co–N(1)–C(1), 121.1°, 1.2 kcal/mole and Co–N(1), 1.987 Å, 0.5 kcal/mole; Co–N(4), 1.982 Å, 0.4 kcal/mole; Co–N(2), 1.985 Å, 0.5 kcal/mole. For the inverted en chelate ring conformation (λ) the most stable conformation for the dpt chelate rings appears to be 'chair-boat' with only a minor distortion of the 'boat' conformation.

*'Chair-Chair' Conformer.* As for the β-isomer, calculations were carried out on this conformer to examine the relative stability between 'chair-chair' and 'chair-boat' conformations of the dpt chelate rings. Major non-bonded interactions include H(1) ... H(20), 2.20 Å, 0.4 kcal/mole; H(1) ... H(18), 2.20 Å, 0.4 kcal/mole; H(3) ... H(24), 2.17 Å, 0.5 kcal/mole; H(16) ... H(23), 2.14 Å, 0.6 kcal/mole; H(16) ... H(19), 2.11 Å, 0.6 kcal/mole; Cl ... H(2), 2.55 Å, 0.9 kcal/mole; Cl ... H(9), 2.58 Å, 0.7 kcal/mole; Cl ... H(17), 2.55 Å, 0.9 kcal/mole (see Figure 12). Angle and bond-length distortions are similar to those for previously discussed conformers; Co–(1)–C(1), 121.1°, 1.2 kcal/mole; Co–N(4)–C(3), 118.5°, 0.7 kcal/mole; Co–N(2)–C(7), 122.2°, 1.4 kcal/mole, and Co–N(2), 1.993 Å, 0.6 kcal/mole; Co–N(4), 2.015 Å, 1.0 kcal/mole; Co–N(1), 1.989 Å, 0.5/mole. The calculated relative stabilities between the various conformational isomers of the α–Co(en)(dpt)Cl$^{2+}$ cation will be discussed in the next section.

*Relative Stabilities of Co(en)(dpt)Cl$^{2+}$ Isomers. β–Co(en)(dpt)Cl$^{2+}$ Conformers.* Final energy terms for the three β–Co(en)(dpt)Cl$^{2+}$ conformers studied are presented in Table V. The calculated energy difference between conformers differing in the conformation of the en chelate ring (δ, Figure 5 and λ, Figure 6) is 1.2 kcal/mole in favour of the δ conformation. Thus the calculations show that the en chelate ring conformation as found by X-ray analysis (Figure 2) is the most stable. For the less stable λ conformation of the en chelate ring a 'chair-twist boat' conformation of the dpt chelate rings was found to be favoured (Figure 6). However, as shown in Table V, although the torsional strain is reduced for the dpt chelate ring 1 by adopting a 'twisted boat' conformation, there is an associated increase in torsional strain for the 'chair' conformation of ring 2, (ring 1, N(1)-C(1)-C(2)-C(3)-N(4); ring 2, N(4)-C(5)-C(6)-C(7)-N(2); Figure 6). For this reason the total torsional strain within the dpt chelate rings for 'chair-boat' and 'chair-twist boat' conformations are almost equal at 2.8 kcal/mole and 2.9 kcal/mole respectively. The 'chair-twist boat' conformation of the dpt chelate rings for this isomer almost certainly results from unfavourable non-bonded interactions for the undistorted 'boat' conformation.

Calculations on the 'chair-chair' conformation for the dpt chelate rings are of particular interest, since from a consideration of torsional strain alone this conformer might be expected to be the most stable. The present calculations indicate that the 'boat-chair'

**Table V.** Final energy terms for Co(en)(dpt)Cl$^{2+}$ Isomers

| | β-Co(en)(dpt)Cl$^{2+}$ | | | α-Co(en)(dpt)Cl$^{2+}$ | | | |
|---|---|---|---|---|---|---|---|
| | 'chair-boat' | 'chair-boat' (inverted en ring) | 'chair-chair' | 'chair-boat' | 'chair-twist boat' | 'chair-boat' (inverted en ring) | 'chair-chair' |
| $\Sigma r_{ijb}$ | 2.4 | 2.8 | 2.8 | 2.5 | 2.5 | 2.2 | 2.8 |
| $\Sigma_{ijnb}$ | 9.2 | 9.5 | 8.1 | 9.7 | 8.8 | 9.2 | 8.5 |
| $\Sigma\theta_{ijk}$ | 6.8 | 7.1 | 8.6 | 7.1 | 6.6 | 7.0 | 8.5 |
| $\Sigma\varphi_{ijkl}$ | 3.8 | 4.1 | 2.8 | 3.8 | 3.8 | 3.8 | 2.9 |
| $\Sigma U$ | 22.2 | 23.4 | 22.3 | 23.1 | 21.8 | 22.2 | 22.7 |
| Σφ en ring | 1.0 | 1.2 | 1.1 | 1.0 | 1.0 | 1.0 | 1.4 |
| Σφ dpt ring 1[a] | 2.6 | 2.0 | 0.5 | 2.6 | 1.9 | 2.5 | 0.8 |
| Σφ dpt ring 2[a] | 0.2 | 0.9 | 1.2 | 0.2 | 0.8 | 0.2 | 0.7 |

[a] Ring 1, N(1)-C(1)-C(2)-C(3)-N(4); ring 2, N(4)-C(5)-C(6)-C(7)-N(2) in Figure 6.

and 'chair-chair' conformations are of comparable stability with a calculated strain energy difference of 0.1 kcal/mole in favour of the 'boat-chair' conformer. As indicated in Table V, the reduced torsional and non-bonded strain for the 'chair-chair' conformer is offset by a large increase in bond angle strain and a smaller but significant increase in bond stretching energy. However, the calculations indicate that the strain energy difference between these two conformers is sufficiently small for a significant proportion of the 'chair-chair' conformer to exist in solution. By comparison with cyclohexane conformational studies it would seem likely that interconversion between 'chair-boat' and 'chair-chair' conformers in solution at room temperature would be very rapid.

*α–Co(en)(dpt)$Cl^{2+}$ Conformers.* Final energy terms for the four α–Co(en)(dpt)$Cl^{2+}$ conformers are presented in Table V. The results indicate that the conformer with the 'chair-twist boat' dpt conformation and the δ en chelate ring conformation is the most stable. This suggests that the less sable 'chair-boat' conformation as found by X-ray analysis might result from intermolecular interactions in the crystal. In fact as previously discussed there is a short intermolecular distance of 2.18 Å in the crystal between the hydrogen atoms (placed at calculated positions) on carbon atoms C(7) of the dpt ligand and C(9) of the en ligand of a neighbouring cation. Hence there is convincing evidence that the dpt chelate ring conformations as found in the crystal lattice are distorted by intermolecular forces. Inversion of the en chelate ring to the λ conformation results in an increase of 0.4 kcal/mole of strain energy. For this en chelate ring conformation an undistorted 'chair-boat' conformation for the dpt chelate rings is more favourable.

In contrast to the β-isomer, the 'chair-chair' conformation of the dpt chelate rings for the α–Co(en)(dpt)$Cl^{2+}$ conformers is significantly less stable (0.9 kcal/mole) than a 'chair-twist boat' conformation. Although similar to the β–isomer, the gain in torsion energy for the 'chair-chair' conformation of the dpt chelate rings is offset by a considerable increase in bond angle strain. This increased angle strain is concentrated at the primary and secondary nitrogen centres, N(1), N(2), and N(4) of the dpt ligand.

## Conclusions

The minimisation calculations indicate that the energy difference between the most stable conformers of α and β isomers is quite small (0.4 kcal/mole) and in favour of the α–isomer. Experimental measurements of the relative stability between α and β isomers may be possible. Previous work[2] has shown that mutarotation of coordinated secondary nitrogen centres can occur in mildly basic solution. However, for the present complexes mutarotation studies are not possible as the coordinated secondary N atom is not asymmetric.

Measurements of relative stabilities between conformers (*e.g.* 'chair-boat' and 'chair-chair') would be more difficult. As previously discussed the energy barriers would be expected to be sufficiently small for interconversion to be rapid at room temperature. Thus experiments would need to be carried out in solution at very low temperatures where solubility in suitable solvents is a major problem.

In general, minimisation calculations have reproduced the molecular geometries for both α and β–Co(en)(dpt)$Cl^{2+}$ isomers where structural data is available for comparison. These results have provided some understanding of relative stabilities for various possible chelate ring conformations and distortions from ideal geometrics.