Structure and Conformational Analysis of Co-ordination Complexes. Part III.† A Diastereoisomeric Pair of αβ-Chloro(tetraethylenepentamine)-cobalt(III) Cations

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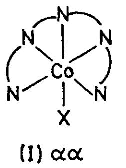
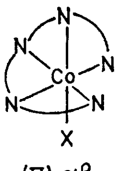
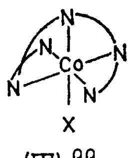
The crystal structures of the αβ*R*- and αβ*S*-chlorotetraencobalt(III) diperchlorates (tetraen = 1,4,7,10,13-penta-azatridecane) have been determined from photographic data. Both unit cells are orthorhombic with $Z = 4$ and space group $P2_12_12_1$; αβ*S*: $a = 17{\cdot}37(1)$, $b = 12{\cdot}44(1)$, and $c = 8{\cdot}43(1)$; R 0·135 (1601 reflections) and for αβR $a = 17{\cdot}26(2)$, $b = 12{\cdot}03(1)$, and $c = 8{\cdot}72(3)$, R 0·129 (1529 reflections). The absolute configurations of both isomers were determined by the anomalous scattering technique. In both cations the ligand chain is bound by nitrogen co-ordination successively to the cobalt octahedral sites. The cations only differ by an inversion at the secondary nitrogen atom. Quantitative conformational analysis, using energy minimization, has been applied to the isomers and their molecular geometry was well reproduced in the absence of packing distortions. The calculations confirm the experimental result that the αβ*S* isomer is more stable than αβ*R* by *ca.* 2 kcal mol^{-1}.



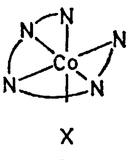
(I) αα



(II) αβ



(III) ββ



(IV) β*trans*

Of the modes of co-ordination of 1,4,7,10,13-penta-azatridecane [(I)—(IV); tetraethylenepenta-amine = tetraen],‡ αα has a plane of symmetry if the conformations of the chelate rings are ignored, and αβ, ββ, and β*trans* will always be asymmetric. In addition to the stereochemistry generated by the topology of the co-ordinated ligand, there is the possibility of the existence of diastereoisomeric forms arising from alternative configurations about the secondary nitrogen atoms which fuse chelate rings in the same plane. This leads to two diastereoisomeric forms for the αβ structure and four such forms for the β*trans* structure. The two orientations of the central NH proton in the ββ structure lead

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† Part II, R. J. Geue and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 2981.

‡ The trivial αβ nomenclature is extended from that used for trien complexes in ref. 1. The tetraen ligand viewed from the two ends has either α, β, or *trans* characteristics. *R* and *S* refer to the configuration about the N atom fusing the chelate rings in the same plane and conforms to the IUPAC rules.

[1] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 1965, **4**, 45.

to identical structures since they are equivalent by rotation around the vertical N,Co,X axis.

Several isomers of cobalt(III) complexes [Co(tetraen)-Cl]$^{2+}$ have been isolated [2,3] and their crystal structures were undertaken to assign their structures and absolute configurations. The structure of the αα isomer has been reported [4] and submitted to a full and quantitative energy minimization procedure to determine whether the conformation found in the crystal corresponded to the calculated 'gas state' geometry.[5] This isomer was found to be distorted by the crystal lattice in contrast to two cobalt(III) triethylenetetramine-*S*-prolinato-complexes where the crystal and calculated 'gas state' geometries agreed within experimental error.[6] This procedure has also been applied to the structures of the two diastereoisomeric αβ isomers described below to determine the influence of crystal forces on their conformations and to estimate the strain-energy difference between these interconvertible isomers. Preliminary accounts of this work have been published.[4,7]

EXPERIMENTAL

Crystals of the two isomers were shown after structure analysis to be $(+)_{540}\alpha\beta S$- and $(+)_{540}\alpha\beta R$-chloro(tetraen)-cobalt(III) diperchlorate. The unit-cell dimensions were obtained from zero-level precession photographs corrected for film shrinkage [λ(Cu-K_α) = 1·542 Å]. Both crystals were subject to radiation damage and specimens typically started to develop powder rings in their precession photographs after 100 h exposure to *X*-rays. Since the absolute configurations of the complexes were required it was thought desirable to collect the entire data set from one crystal. Larger crystals than usual were therefore chosen and absorption corrections applied to the intensity data collected with nickel-filtered Cu-K_α radiation.

Crystal Data for the αβS Isomer.—$C_8H_{23}Cl_3Co_5O_8$, M = 482·535, red orthorhombic plates, a = 17·37(1), b = 12·44(1), c = 8·43(1) Å, U = 1821·6 Å^3, D_m not obtained, Z = 4, D_c = 1·759, $F(000)$ = 992, μ(Cu-K_α) = 114·0 cm^{-1}. Space group $P2_12_12_1$ from systematic absences.

A crystal of dimensions 0·05 × 0·25 × 0·1 mm along the *a*, *b*, and *c* directions respectively was mounted along *c* and the levels *hk*0—5 were recorded by the multiple-film, equi-inclinational, Weissenberg technique. The same crystal was remounted along *b* and the levels *h*0—3*l* were similarly recorded. The data were estimated visually and corrected for Lorentz and polarization effects, $\alpha_1\alpha_2$ resolution,[8] and absorption.[9] Inter-film and -layer scale factors were determined by a least-squares procedure described by Rae,[10] developed by Paul,[11] and modified locally to allow for the estimation of standard deviations from the agreement between the multiple observation during interfilm scaling. In all 1601 reflections in the unique octant were obtained which corresponds to 77% of those in the sphere of reflection for Cu-K_α radiation. These include 203 reflections whose intensities were below the observational limit.

*Crystal Data for αβR Isomer.**—$C_8H_{23}Cl_3CoN_5O_8$, M = 482·538, red orthorhombic needles, a = 17·26(2), b = 12·03(1), c = 8·72(3) Å, D_m not obtained, Z = 4, D_c = 1·770, $F(000)$ = 992, μ(Cu-K_α) = 114·0 cm^{-1}, μ(Mo-K_α) = 14·3 cm^{-1}. Space group $P2_12_12_1$ from systematic absences.

A crystal of dimensions 0·3 × 0·2 × 0·5 mm corresponding to the *a*, *b*, and *c* directions was rotated about *c* and integrated, multiple-film Weissenberg levels *hk*0—6 were collected with Cu-K_α radiation. The unintegrated levels 0*kl* and *h*0*l* were collected with a precession camera using zirconium-filtered Mo-K_α (λ = 0·7107 Å) radiation and a second crystal of similar dimensions to the first. The reflections were measured with a non-scanning type Nonius II densitometer. Both octants hkl and $\bar{h}kl$ were measured for the Cu-K_α data for use in the β-anomalous synthesis [12] and in the determination of the absolute configuration of the complex. The data were processed in the same way as for the αβ*S* crystal data, but absorption corrections were not applied to the Mo-K_α data. It was appreciated that the merging of the Cu-K_α and Mo-K_α reflection data would result in errors through differences in the real part of the wavelength dependent component of the cobalt scattering factor [$\Delta f'$(Mo-K_α) 0·37, $\Delta f'$(Cu-K_α) −2·51). This effect was not considered important in view of crystal decomposition and the only moderate precision of the unintegrated precession data. A total of 1529 reflections were gathered including 503 Friedel pairs and 247 reflections below the observable limit. There were 1026 reflections of index $|h||k||l|$ which corresponds to 49% of those in the sphere of reflection for Cu-K_α radiation.

Solution and Refinement of the Structures.†—Three-dimensional Patterson functions were computed and used to obtain sites for cobalt and chloride (αβ*S* crystal) and cobalt only (αβ*R* crystal). In both functions and in the sharpened Patterson functions, self-consistent peaks for the two perchlorate anions could not be found. Sites for the perchlorate anions were indicated for the αβ*S* crystal by a Fourier synthesis using phases calculated from the cobalt and chloride positions. A β-synthesis [12] using coefficients $W(|F_o|^2/|F_c|)\exp(i\alpha_c)$ (where W is a probability weight appropriate for noncentrosymmetric crystals,[14] and α_c is

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* The racemate of this active isomer as the diperchlorate was found to be monoclinic, space group $P2_1/c$ from systematic absences and Laue symmetry with a = 14·93 (2), b = 14·93 (2), c = 13·51 (2) Å, β = 90·0° (2).

† Calculations were carried out on the University of Adelaide CDC 6400 computer with programs described in ref. 13.

[2] D. A. House and C. S. Garner, *Inorg. Chem.*, 1966, **5**, 2097.

[3] P. A. Marzilli, Ph.D. Thesis, Australian National University, 1969.

[4] M. R. Snow, Proc. XII Internat. Conf. on Co-ordination Chemistry, Communication *W*4 33, 92, Sydney, 1969.

[5] M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3610.

[6] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3617; D. A. Buckingham, H. C. Freeman, L. G. Marzilli, I. E. Maxwell, and A. M. Sargeson, ref. 4, Communication *W*4 55, 157, Sydney, 1969.

[7] M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Comm.*, 1969, 891.

[8] E. G. Boonstra, *Acta Cryst.*, 1966, **21**, 834.

[9] Local version of C. W. Burnhams absorption program, *Am. Mineral.*, 1966, **51**, 159.

[10] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

[11] G. L. Paul, SUFFAC, A FORTRAN IV program for the least-squares determination of film factors, School of Chemistry, University of Sydney, 1966.

[12] G. N. Ramachandran, in 'Advanced Methods of Crystallography,' Academic Press, London, 1964.

[13] PREPFLS and FOURIER; local modifications of the data packing and Fourier programs of F. R. Ahmed, Division of Pure Physics, National Research Council, Ottawa; FOURFLS modification of ORFLS (least-squares) by M. R. Taylor, Flinders University of South Australia; BLANDA and PLANET geometry routines by J. F. Blount, University of Sydney, ORTEP plot routine by C. K. Johnson, Oak Ridge National Laboratory, Tennessee.

[14] G. A. Sim, *Acta Cryst.*, 1960, **13**, 511.

the phase angle for the known cobalt and chloride contributions to the structure) was calculated and revealed the chlorine atoms of the perchlorates with twice the peak height of a previous heavy-atom synthesis based on the cobalt and chloride positions. Many peaks appropriate to the light atom positions also appeared and the remainder of the non-hydrogen atom positions were located in a second β-synthesis based on four heavy-atom positions.

Refinement by full-matrix least-squares was commenced with these trial positions and the complete set of observed reflections. [Scattering factors for Co^{2+} and Cl^- were taken from ref. 15(*a*), and for oxygen, nitrogen, and carbon from ref. 15(*b*); the effects of real and imaginary scattering for Cu-K_α by Co radiation were included according to ref. 15(*c*) ($\Delta f'$ −2·51, $\Delta f''$ 3·95), and only the real part by Cl ($\Delta f' = 0\cdot33$).] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, the weights w, were initially unity and later changed to $1/\sigma|F_o|^2$) where σF_o was derived during data reduction.[5] After one cycle of refinement of the atomic positional and isotropic temperature factors R was 0·296 and R' 0·360 [$R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. Three further cycles reduced these values to 0·238 and 0·261 after which it became apparent from the high temperature-factor of the perchlorate oxygen O(3) that it was mispositioned. This was corrected and in addition the heavy atoms (Co and 3Cl) were allowed to refine anisotropically in the next 6 cycles. These and subsequent cycles were carried out in pairs setting up the normal equation matrix in the first cycle and using it unchanged for the second cycle. R and R' converged to 0·175 and 0·219 respectively. Some data processing errors were corrected and 23 low-angle reflections which had high absorption corrections (chiefly *b* axis reflections with indices *h*0*l*) were omitted from the refinement and a separate scale factor for *h*0*l* data was subsequently refined. The refinement converged again after 6 cycles with R 0·139 and R' 0·180. The hydrogen atom positions were calculated by a modification of PLANET (ref. 13). [The hydrogen atoms were placed at the expected electron-density maxima appropriate to the scattering curve of Stewart *et al.*; C–H 1·02, N–H 0·95, H–C–H and H–N–H 109° 28′, for secondary N–H the X–N–H angles were made equal and obtuse.] The contributions from these 23 hydrogen atoms were included in the next pair of cycles with fixed positional and thermal parameters when R was 0·136 and R' 0·173. Application of Hamilton's R' significance test [16] shows that the inclusion of the hydrogen atoms is significant at the 0·005 level ($R_{92,1620,0\cdot005}$ 1·035). A final pair of least-squares cycles after the hydrogen positions were recalculated resulted in a final R of 0·135 (R' 0·172). The error in an observation of unit weight, $\sqrt{\Sigma w(|F_o| - |F_c|)^2/(n - m)}$, was 1·31, where $n - m$ is the excess of reflections over refined parameters. For the reflections used in the refinement the quantity $\Sigma w(|F_o| - |F_c|)^2/k$, computed in ranges of k reflections as a function of $\sin\theta/\lambda$ and of F_o, is constant at 1·5 ± 0·5 for both plots. These results show that the weighting scheme based on the data reduction processing was satisfactory for the refinement. The list of observed and calculated structure factors * includes at the end values for selected $\bar{h},k,l$ reflections. Comparison of these with the corresponding *hkl* reflections in the body of the Table shows that the correct absolute configuration has been refined. Tables 1 and 3—6 contain the final fractional atomic co-ordinates and thermal parameters and the important molecular geometry.

TABLE 1

Final least-squares parameters [a] for αβ*S*-[Co(tetraen)Cl]$(ClO_4)_2$

Atom	*X*	*Y*	*Z*	*B*/Å²
Co	0·0617(2)	0·2381(2)	0·2055(5)	
Cl(1)	−0·0045(3)	0·0835(3)	0·2483(8)	
Cl(2)	0·1783(3)	0·0633(4)	0·7205(9)	
Cl(3)	0·3974(3)	0·4416(4)	0·2859(9)	
N(1)	0·1531(10)	0·1477(15)	0·1557(27)	3·39(36)
N(2)	0·0267(9)	0·2352(13)	−0·0159(23)	2·90(30)
N(3)	0·0837(11)	0·2485(15)	0·4324(27)	3·67(36)
N(4)	−0·0288(8)	0·3255(12)	0·2480(23)	2·14(25)
N(5)	0·1347(7)	0·3607(11)	0·1719(22)	1·92(25)
O(1)	0·1544(11)	0·1667(16)	0·7631(25)	5·20(45)
O(2)	0·2597(11)	0·0586(15)	0·7135(29)	6·50(46)
O(3)	0·3529(21)	0·0109(28)	0·3201(47)	11·33(96)
O(4)	0·1480(11)	0·0412(15)	0·5662(28)	5·25(41)
O(5)	0·3585(18)	0·3469(25)	0·3345(42)	10·66(86)
O(6)	0·4784(17)	0·4137(22)	0·3198(42)	9·57(73)
O(7)	0·3701(20)	0·4451(24)	0·1252(42)	10·39(91)
O(8)	0·3912(19)	0·5462(25)	0·3184(41)	10·04(89)
C(1)	−0·0415(12)	0·3132(18)	−0·0321(31)	3·14(41)
C(2)	−0·0867(11)	0·3099(17)	0·1117(31)	3·02(38)
C(5)	0·1595(11)	0·4003(16)	0·3335(30)	2·92(36)
C(6)	0·1557(14)	0·3129(21)	0·4556(36)	4·12(49)
C(3)	−0·0547(13)	0·3091(20)	0·4082(33)	3·76(44)
C(4)	0·0186(16)	0·3049(23)	0·5070(38)	5·04(61)
C(7)	0·1972(14)	0·3161(20)	0·0702(38)	4·21(48)
C(8)	0·2230(15)	0·2076(21)	0·1323(39)	4·77(56)
H(1)N(1) [b]	0·1433	0·1082	0·0625	4·0
H(2)N(1)	0·1612	0·0990	0·2422	4·0
H(1)N(2)	0·0672	0·2571	−0·0839	4·0
H(2)N(2)	0·0108	0·1645	−0·0431	4·0
H(2)N(3)	0·0889	0·1833	0·4753	4·0
H(2)N(4)	−0·0135	0·3931	0·2415	4·0
H(2)N(5)	0·1109	0·4134	0·1200	4·0
H(1)C(1)	−0·0773	0·2897	−0·1318	5·0
H(2)C(1)	−0·0207	0·3942	−0·0503	5·0
H(1)C(2)	−0·1293	0·3729	0·1123	5·0
H(2)C(2)	−0·1153	0·2322	0·1224	5·0
H(1)C(3)	−0·0866	0·2351	0·4187	5·0
H(2)C(3)	−0·0910	0·3761	0·4450	5·0
H(1)C(4)	0·0368	0·3874	0·5315	5·0
H(2)C(4)	0·0055	0·2656	0·6187	5·0
H(1)C(6)	0·2049	0·2598	0·4402	5·0
H(2)C(6)	0·1561	0·3469	0·5724	5·0
H(1)C(5)	0·2183	0·4296	0·3274	5·0
H(2)C(5)	0·1219	0·4653	0·3707	5·0
H(1)C(7)	0·1770	0·3084	−0·0496	5·0
H(2)C(7)	0·2460	0·3717	0·0734	5·0
H(1)C(8)	0·2598	0·1663	0·0480	5·0
H(2)C(8)	0·2540	0·2149	0·2449	5·0

Anisotropic thermal parameters (× 10^5) [c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	169(7)	234(16)	933(73)	5(10)	− 36(19)	−70(25)
Cl(1)	382(18)	156(24)	1625(162)	−93(17)	−143(40)	86(42)
Cl(2)	272(16)	531(34)	1219(143)	62(21)	−139(38)	−93(56)
Cl(3)	238(16)	568(36)	1340(151)	−94(19)	−1(36)	54(60)

[a] The estimated standard deviations are given in parentheses in this and succeeding Tables. [b] The hydrogen atomic positions were recalculated after the last least-squares cycle. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

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[15] (*a*) P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, *A*, **24**, 390; (*b*) ' International Tables for *X*-Ray Crystallography, vol. III, Kynoch Press, Birmingham, 1962, p. 202; H. R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175; (*c*) D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[16] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

TABLE 2 [a]

Final least-squares parameters for αβ*R*-[Co(tetraen)Cl](ClO_4)$_2$

Atom	*X*	*Y*	*Z*	*B*/Å^2
Co	0·1863(2)	0·1787(4)	0·1881(4)	
Cl(1)	0·2407(4)	0·0751(7)	0·0078(8)	
Cl(2)	0·3339(5)	0·3186(9)	0·6868(14)	
Cl(3)	0·0022(5)	−0·0139(7)	0·8507(9)	
N(1)	0·1387(22)	0·0492(31)	0·2598(34)	7·64(92)
N(2)	0·2808(10)	0·1742(22)	0·3096(21)	3·02(89)
N(3)	0·0990(16)	0·2148(23)	0·0478(29)	4·70(67)
N(4)	0·2329(16)	0·3035(21)	0·1007(23)	3·96(54)
N(5)	0·1293(14)	0·2382(23)	0·3437(26)	4·26(57)
O(1)	0·2699(16)	0·3450(35)	0·6127(34)	10·6(11)
O(2)	0·3937(10)	0·3623(17)	0·6019(19)	3·90(46)
O(3)	0·3431(21)	0·2053(25)	0·7180(37)	11·3(11)
O(4)	0·3305(14)	0·3755(47)	0·8040(44)	15·0(12)
O(5)	0·0683(20)	0·4416(28)	0·6258(32)	11·2(10)
O(6)	0·5008(19)	0·4080(27)	0·1822(30)	8·31(84)
O(7)	0·4640(20)	0·0751(36)	0·2311(37)	10·9(10)
O(8)	0·4526(16)	0·0259(27)	0·4626(30)	9·26(77)
C(1)	0·3360(15)	0·2582(27)	0·2501(26)	3·19(54)
C(2)	0·2952(17)	0·3496(30)	0·2020(34)	5·18(71)
C(3)	0·1835(25)	0·3757(38)	0·0043(40)	7·8(10)
C(4)	0·1224(28)	0·3194(45)	−0·0310(46)	8·1(11)
C(5)	0·0566(14)	0·3014(27)	0·2842(25)	3·14(57)
C(6)	0·0284(23)	0·2483(42)	0·1699(42)	6·8(10)
C(7)	0·1095(14)	0·1705(25)	0·4744(26)	3·01(52)
C(8)	0·0812(14)	0·0586(26)	0·3928(27)	2·89(52)
H(1)N(1)	0·1116	0·0173	0·1759	5·0
H(2)N(1)	0·1787	0·0003	0·2917	5·0
H(1)N(2)	0·3033	0·1023	0·3027	5·0
H(2)N(2)	0·2690	0·1901	0·4137	5·0
H(2)N(3)	0·0867	0·1598	−0·0160	5·0
H(2)N(4)	0·2617	0·2712	0·0287	5·0
H(2)N(5)	0·1595	0·2913	0·3820	5·0
H(1)C(1)	0·3682	0·2236	0·1546	5·0
H(2)C(1)	0·3760	0·2821	0·3401	5·0
H(1)C(2)	0·3322	0·4057	0·1385	5·0
H(2)C(2)	0·2701	0·3931	0·2990	5·0
H(1)C(3)	0·2144	0·3995	−0·0988	5·0
H(2)C(3)	0·1672	0·4997	0·0676	5·0
H(1)C(4)	0·1289	0·2979	−0·1511	5·0
H(2)C(4)	0·0741	0·3760	−0·0176	5·0
H(1)C(5)	0·0729	0·3845	0·2486	5·0
H(2)C(5)	0·0137	0·3066	0·3747	5·0
H(1)C(6)	−0·0138	0·3001	0·1118	5·0
H(2)C(6)	0·0004	0·1732	0·2103	5·0
H(1)C(7)	0·0636	0·2079	0·5415	5·0
H(2)C(7)	0·1594	0·1559	0·5471	5·0
H(1)C(8)	0·0222	0·0660	0·3518	5·0
H(2)C(8)	0·0855	−0·0120	0·4695	5·0

Anisotropic thermal parameters (× 10^5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	74(12)	311(29)	228(39)	22(27)	93(24)	124(39)
Cl(1)	274(32)	704(75)	2012(118)	1(58)	314(55)	−530(106)
Cl(2)	143(30)	694(81)	1746(161)	36(60)	65(68)	148(132)
Cl(3)	181(25)	410(64)	1059(90)	−99(54)	−151(48)	176(90)

[a] See footnotes to preceding Table.

For the αβ*R* structure a β-anomalous synthesis [12] with coefficients $[1/2(F_h^2 - F_{\bar{h}}^2)/F_c'' \exp i(\alpha_c' + \pi/2)]$ was calculated using 384 observed Friedel pairs $F_h, F_{\bar{h}}$. Here F_c'' is the calculated amplitude of the imaginary ($\Delta f''$) component of scattering by cobalt and α_c' is the phase angle for the real ($f_o + \Delta f'$) component of scattering by cobalt. The chloride and chlorines of the two perchlorates were located in this synthesis in their correct absolute configuration. These atoms were refined by least-squares when *R* and *R′* were reduced from 0·425 and 0·492 to 0·254 and 0·298 after 2 cycles. A β-synthesis of the type employed with the αβ*S* structure yielded the positions of the remaining non-hydrogen atoms. Four refinement cycles using an averaged data set $[|F_o| = (|F_h| + |F_{\bar{h}}|)/2]$ and isotropic temperature factors lowered *R* and *R′* to 0·207 and 0·241. Two further cycles with unaveraged data and including anomalous dispersion effects converged with *R* 0·167 and *R′* 0·159. Calculation of bond lengths at this stage showed that atom C(6) was involved in a very short and a very long bond. A difference-Fourier map suggested that it might be shifted to partly equalize these bonds. The shifted C(6) atom, however, returned to its former position upon resumption of the refinement. Introduction of anisotropic thermal parameters for the chlorine and cobalt atoms reduced *R* and *R′* to 0·133 and 0·133 after 4 cycles. Inclusion of the hydrogen atom which were not refined reduced *R* and *R′* to 0·129 and 0·129. Application of Hamilton's test [16] again shows a significant improvement in the model at the 0·005 level ($R_{92,1460,0{\cdot}005}$ 1·035). In both structures the inclusion of the hydrogen atoms had the effect of contracting the apparent carbon–carbon and carbon–nitrogen by up to 0·05 Å in cases where they were longer than the accepted values (1·50 and 1·49 Å). Four cycles of refinement were performed refining anisotropic thermal parameters for the perchlorate oxygens, but *R* remained constant and *R′* increased slightly. The large range of the bond lengths in the perchlorate groups and of the isotropic temperature factors of the oxygens indicate disorder in these groups, but this cannot be modelled

TABLE 3

Positional co-ordinates (Å) of [Co(tetraen)Cl]$^{2+}$ isomers from energy minimization

	αβ*S*			αβ*R*		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Co	1·070	2·963	1·735	3·213	2·153	1·633
Cl	−0·048	1·037	2·119	4·253	0·908	0·066
N(1)	2·720	1·905	1·537	2·370	0·494	2·287
N(5)	2·196	4·557	1·473	2·111	3·084	3·007
N(3)	1·239	3·198	3·680	1·796	2·606	0·337
N(2)	0·646	2·817	−0·193	4·751	1·966	2·877
N(4)	−0·543	4·048	1·891	4·154	3·730	0·970
C(8)	3·910	2·787	1·327	1·459	0·753	3·446
C(7)	3·462	4·120	0·794	1·810	2·072	4·075
C(5)	2·445	5·153	2·830	0·838	3·580	2·377
C(6)	2·426	4·084	3·893	0·538	2·809	1·120
C(1)	−0·553	3·669	−0·478	5·747	3·056	2·612
C(2)	−1·431	3·697	0·744	5·028	4·256	2·057
C(3)	−1·135	3·770	3·233	3·152	4·685	0·427
C(4)	−0·012	3·833	4·236	2·198	3·858	−0·400
H(1)N(2)	1·429	3·120	−0·787	5·200	1·052	2·716
H(2)N(2)	0·432	1·837	−0·431	4·479	2·009	3·866
H(1)N(1)	2·611	1·273	0·730	1·838	0·058	1·519
H(2)N(1)	2·861	1·331	2·381	3·113	−0·160	2·576
H(2)N(4)	−0·312	5·052	1·837	4·767	3·451	0·189
H(2)N(3)	1·403	2·289	4·139	1·656	1·836	−0·336
H(2)N(5)	1·719	5·247	0·872	2·609	3·876	3·436
H(1)C(1)	−1·111	3·260	−1·324	6·490	2·710	1·891
H(2)C(1)	−0·237	4·684	−0·726	6·260	3·330	3·536
H(1)C(2)	−2·212	4·451	0·628	5·748	4·968	1·648
H(2)C(2)	−1·896	2·722	0·890	4·448	4·749	2·835
H(1)C(3)	−1·618	2·794	3·264	3·649	5·419	−0·209
H(2)C(3)	−1·883	4·530	3·468	2·643	5·215	1·228
H(1)C(4)	0·159	4·877	4·503	2·691	3·579	−1·333
H(2)C(4)	−0·314	3·304	5·143	1·324	4·461	−0·653
H(1)C(6)	3·340	3·496	3·868	−0·194	3·357	0·525
H(2)C(6)	2·374	4·551	4·879	0·094	1·844	1·359
H(1)C(5)	3·408	5·666	2·853	0·905	4·644	2·153
H(2)C(5)	1·674	5·894	3·046	−0·002	3·463	3·064
H(1)C(7)	3·302	4·045	−0·282	0·977	2·410	4·695
H(2)C(7)	4·251	4·858	0·953	2·660	1·946	4·743
H(1)C(8)	4·578	2·322	0·598	0·414	0·748	3·134
H(2)C(8)	4·477	2·914	2·248	1·582	−0·039	4·188

TABLE 4

Comparison of important crystal bond distances (Å) in [Co(tetraen)Cl]$(ClO_4)_2$ isomers

	αβ*S*	αβ*R*
Co–N(2)	1·96(2)	1·95(2)
Co–N(4)	1·95(2)	1·87(3)
Co–N(3)	1·95(2)	1·99(3)
Co–N(5)	2·00(2)	1·82(3)
Co–N(1)	1·99(2)	1·87(4)
Mean [a]	1·97(1)	1·90(3)
Co–Cl(1)	2·271(5)	2·215(9)
N(1)–C(8)	1·44(3)	1·53(4)
N(2)–C(1)	1·54(3)	1·48(4)
N(4)–C(2)	1·54(3)	1·50(4)
N(4)–C(3)	1·44(3)	1·48(5)
N(3)–C(4)	1·47(4)	1·49(5)
N(3)–C(6)	1·50(4)	1·67(5)
N(5)–C(5)	1·51(3)	1·56(4)
N(5)–C(7)	1·49(4)	1·44(4)
Mean [a]	1·49(1)	1·52(2)
C(1)–C(2)	1·45(3)	1·37(4)
C(3)–C(4)	1·52(4)	1·29(7)
C(5)–C(6)	1·50(4)	1·28(5)
C(7)–C(8)	1·52(4)	1·60(4)
Mean [a]	1·50(2)	1·39(8)
Cl(2)–O(1)	1·40(2)	1·32(4)
Cl(2)–O(2)	1·42(2)	1·37(2)
Cl(2)–O(3)	1·36(4)	1·40(3)
Cl(2)–O(4)	1·43(2)	1·23(5)
Cl(3)–O(5)	1·42(3)	1·35(3)
Cl(3)–O(6)	1·48(3)	1·31(3)
Cl(3)–O(7)	1·44(3)	1·40(4)
Cl(3)–O(8)	1·34(3)	1·26(3)
Mean [a]	1·41(2)	1·33(2)

[a] Mean for each bond type with standard derivation of the mean calculated from internal agreement.

TABLE 5

Comparison of bond angles (deg.) in chloro(tetraethylenepentamine)cobalt(III) isomers

	αβ*S*		αβ*R*	
	Minimization [a]	Crystal	Minimization [a]	Crystal
N(2)–C(1)–C(2)	108·8	109·1(1·8)	109·1	108·9(2·4)
C(1)–C(2)–N(4)	106·4	105·5(1·8)	105·5	104·6(2·5)
N(4)–C(3)–C(4)	107·2	104·9(2·0)	105·9	107·3(3·5)
C(3)–C(4)–N(3)	110·7	115·1(2·2)	110·8	123·8(3·8)
N(5)–C(5)–C(6)	110·7	111·8(1·9)	110·4	108·8(2·2)
C(5)–C(6)–N(3)	109·2	109·6(2·1)	109·8	109·9(3·3)
N(5)–C(7)–C(8)	110·5	110·4(2·2)	109·9	101·3(2·4)
N(1)–C(8)–C(7)	109·5	105·1(2·2)	109·5	101·6(2·4)
Co–N(2)–C(1)	108·4	108·2(1·4)	109·6	109·2(1·7)
C(2)–N(4)–Co	107·4	108·7(1·4)	108·7	111·5(1·3)
C(2)–N(4)–C(3)	114·3	118·6(1·6)	115·7	122·1(2·6)
C(3)–N(4)–Co	107·2	110·3(1·6)	108·5	117·1(2·2)
C(4)–N(3)–C(6)	110·9	109·3(2·0)	111·5	106·8(3·1)
C(4)–N(3)–Co	110·1	107·5(1·6)	108·7	105·2(2·5)
C(6)–N(3)–Co	106·2	109·0(1·5)	106·9	102·3(2·2)
C(5)–N(5)–C(7)	112·6	115·6(1·6)	110·5	110·4(2·1)
C(5)–N(5)–Co	107·2	107·5(1·4)	109·5	112·3(1·7)
C(7)–N(5)–Co	107·8	105·0(1·6)	106·6	119·7(1·8)
C(8)–N(1)–Co	111·3	114·2(1·6)	111·8	118·5(2·2)
N(2)–Co–N(4)	92·9	86·3(0·8)	85·1	83·3(1·0)
N(4)–Co–N(3)	85·7	86·6(0·8)	86·4	88·3(1·1)
N(3)–Co–N(5)	89·2	88·0(0·8)	87·1	87·9(1·1)
N(5)–Co–N(1)	86·7	84·0(0·8)	85·9	80·8(1·3)
N(1)–Co–Cl(1)	88·5	87·7(0·6)	87·9	87·4(1·1)
N(2)–Co–Cl(1)	89·8	88·8(0·6)	91·5	90·9(0·7)
N(3)–Co–Cl(1)	88·6	89·9(0·6)	90·1	90·4(0·8)
N(4)–Co–Cl(1)	92·9	92·0(0·6)	89·3	88·9(0·7)
N(5)–Co–Cl(1)		171·2(0·6)		168·0(0·8)

[a] Obtained using set 2 of parameters in ref. 5.

TABLE 6

Comparison of the torsion angles (deg.) in the ligand skeletons

Torsion angles *I* *J* *K* L [a]	αβ*S* Crystal	Minimization [b]	αβ*R* Crystal	Minimization
Co–N(2)–C(1)–C(2)	−35·6(19)	−31·1	+53·2(25)	+28·1
N(2)–C(1)–C(2)–N(4)	+50·6(22)	+50·4	−50·2(28)	−48·4
C(1)–C(2)–N(4)–C(3)	−170·3(28)	−164·3	+169·7(37)	+169·2
C(2)–N(4)–C(3)–C(4)	+167·2(30)	+165·5	−160·7(43)	−167·1
N(4)–C(3)–C(4)–N(3)	−38·7(25)	−39·8	+15·0(39)	+45·5
C(3)–C(4)–N(3)–C(6)	+135·7(31)	+132·0	+101·3(45)	+92·6
C(4)–N(3)–C(6)–C(5)	−81·7(26)	−80·6	−73·0(39)	−77·1
N(3)–C(6)–C(5)–N(5)	−41·6(23)	−46·2	−47·3(33)	−41·9
C(6)–C(5)–N(5)–C(7)	−89·8(26)	−89·1	−98·5(32)	−95·7
C(5)–N(5)–C(7)–C(8)	+72·4(28)	+79·9	+86·8(30)	+76·7
N(5)–C(7)–C(8)–N(1)	+49·2(26)	+39·6	+38·6(28)	+40·9
C(7)–C(8)–N(1)–Co	−28·7(23)	−22·3	−24·5(28)	−19·9

[a] The dihedral angle about the bond *J–K* is the angle the bond *K–L* is rotated from the *IJK* plane. It is positive when on looking from *IJ* to *KL* the rotation is clockwise. [b] Obtained using set (2) of parameters in ref. 5.

effectively through the use of anisotropic thermal parameters for oxygen and only the isotropic parameters are given in Table 2. The final difference-Fourier synthesis was essentially featureless and suggested no better model for the disorder. The final value of an observation of unit weight was 1·0 and this, considered with the constancy of the quantity $\Sigma w(|F_o| - |F_c|)^2/k$ (0·7 ± 0·3) with sin θ/λ and F_o shows that the weighting scheme was satisfactory. Comparison of Friedel pair reflections in the list of observed and calculated structure factors* confirms that the correct absolute configuration was refined. Tables 2 and 4—6 contain the final least-squares parameters and the important molecular geometry.

DISCUSSION

Description of the Structures.—The crystal structures of the isomers are shown in Figures 1 and 2. They are both anhydrous and in spite of their very similar unit cells and common space group the similarly shaped cations pack quite differently. The αβ*S* isomer has alternate sheets of cations and anions packed perpendicular to *b*, while the αβ*R* structure has no simple description. The crystals are held together primarily by electrostatic forces while weaker and more directed forces must be responsible for their structural differences. Table 7 shows there are numbers of chloride to amino and perchlorate oxygen to amino close contacts which could be assigned as weak hydrogen bonds though few of these are equal to or less than the accepted distances for significant interaction (Cl · · · N–N 3·3, O · · · H–N 2·9 Å). The correct absolute configurations of the diastereoisomers are shown in Figure 3 which also shows the atom numbering system used.

Conformation Analysis and Discussion.—The equilibrium molecular geometry and strain energy of these complexes have been studied by an energy minimization technique.[5,6] The strain energy, *U*, of the molecule is considered to be a summation over the relevant internal co-ordinates with four energy types: $U = \Sigma(E_r + E_\theta +$

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* Supplementary Publication No. SUP 20375, see earlier footnote.

$E_\phi + E_{\mathrm{nb}}$). These represent bond-length distortion strain, bond-angle distortion strain, torsional energy of rotation about bonds, and nonbonded interaction, respectively. U is minimized by an iterative procedure in which $3N - 6$ independent Cartesian co-ordinates are allowed to vary (N atoms less six degrees of freedom to prevent rotation and translation of the molecule). The functional forms used for the energy types were (i) $E(c) = \frac{1}{2}2A(c - B)$; $c = r$ or θ where A is a Urey–Bradley force constant, and B is the value of c in the absence of the force field, *i.e.*, a strain-free value; (ii) $E\phi = \frac{1}{2}A(1 + \cos 3\phi)$ where ϕ is the torsion angle about a bond of the ligand skeleton and A is that part of the experimental barrier height not accounted for in E_{nb} terms; (iii) $E_{\mathrm{nb}} = A\exp(-Bd) - C/d^6$ where d is the nonbonded distance between two atoms and A, B, and C are parameters for the Buckingham function.

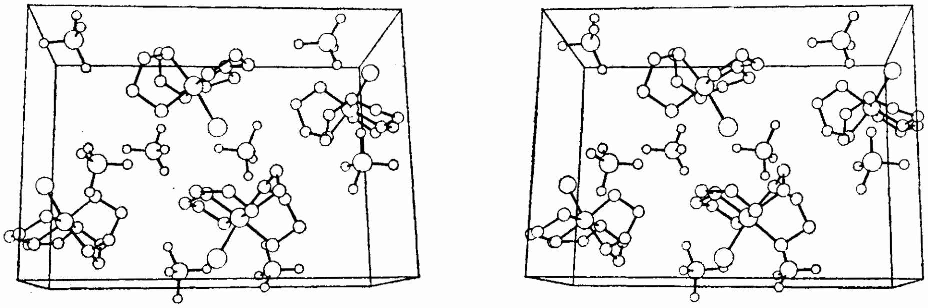

FIGURE 1 Stereoscopic view of the αβ*S*-[Co(tetraen)Cl](ClO_4)$_2$ structure in the [001] direction

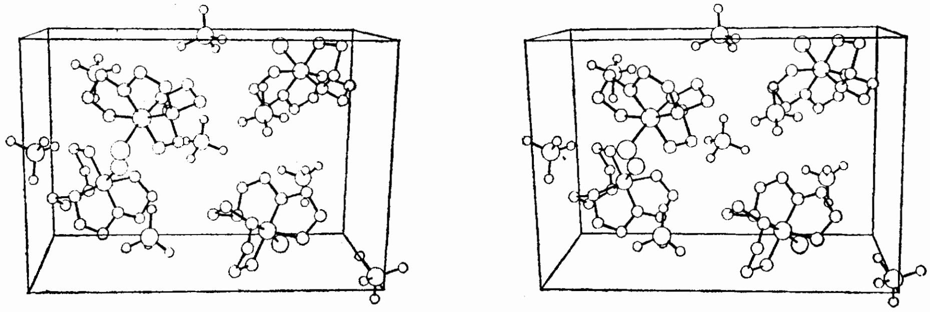

FIGURE 2 Stereoscopic view of the αβ*R*-[Co(tetraen)Cl](ClO_4)$_2$ structure in the [001] direction

TABLE 7

Important intermolecular distances (<3·5 Å)

(*a*) αβ*R*			
Cl(1) ··· N(1^{I})	3·35	O(4) ··· N(4^{V})	3·21
Cl(1) ··· N(2^{I})	3·48	O(4) ··· C(3^{V})	3·08
Cl(1) ··· O(3^{II})	3·46	O(5) ··· C(4^{V})	3·46
O(2) ··· C(8^{III})	3·37	O(6) ··· N(3^{VI})	3·01
O(2) ··· C(6^{III})	3·34	O(7) ··· C(8^{I})	3·45
O(3) ··· C(6^{III})	3·39	O(7) ··· C(4^{VI})	3·48
O(3) ··· N(1^{IV})	3·10		
(*b*) αβ*S*			
Cl(1) ··· N(4^{VII})	3·04	O(5) ··· C(3^{III})	3·28
Cl(1) ··· N(4^{I})	3·26	O(6) ··· N(3^{III})	3·43
O(1) ··· N(1^{V})	3·32	O(6) ··· C(4^{III})	3·17
O(1) ··· N(2^{V})	3·02	O(6) ··· N(2^{VI})	3·27
O(1) ··· C(7^{V})	3·27	O(7) ··· C(5^{XI})	3·16
O(1) ··· C(8^{V})	3·37	O(7) ··· C(6^{XI})	3·36
O(2) ··· C(2^{III})	3·46	O(8) ··· N(2^{X})	3·37
O(3) ··· N(1^{IV})	3·45	O(8) ··· N(5^{X})	3·23
O(4) ··· C(1^{VIII})	3·40	O(8) ··· C(1^{X})	3·39
O(4) ··· C(2^{VIII})	3·42	O(8) ··· C(7^{X})	3·13

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I	$\frac{1}{2} - x, -y, -\frac{1}{2} + z$	VI	$\frac{1}{2} + x, \frac{1}{2} - y, -z$
II	$x, y, -1 + z$	VII	$-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
III	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	VIII	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
IV	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	IX	$\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
V	$x, y, 1 + z$	X	$\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$

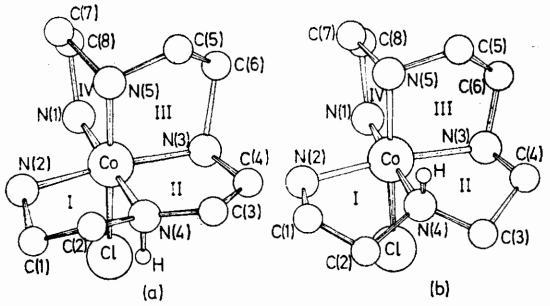

FIGURE 3 Absolute configurations of (a) αβ*R*- and (b) αβ*S*-chloro(tetraethylenepentamine)cobalt(III) cations showing atom and chelate ring labels

The parameters chosen for this study were those employed in previous work on polyamine cobalt complexes.[5]

Using the atomic co-ordinates found from the crystal structure analysis the energy minimization procedure converged in less than 8 cycles; the root-mean-square shift of the atomic co-ordinates in the final cycles was <0·005 Å. Approximately 280 interactions of the previously defined types were included in each set of calculations. In these isomers there was little difference in the lengths of chemically similar bonds. The Co–N bonds show the greatest variation especially in the αβ*R* isomer where Co–N(4) (1·953 Å) is much shorter than Co–N(5) (1·992 Å). The bond distances found in the crystals (Table 4) show no correlation with these, those for the αβ*R* crystal are especially unsatisfactory and must result from a data set inadequate for precision results coupled with perchlorate ion disorder and crystal decomposition. The αβ*S* bond lengths are within the expected range and their means over chemical similar bonds are in good agreement with other cobalt amine structures.[5,6]

For the αβ*S* isomer the crystal and energy-minimized torsion angles in the ligand chain (Table 6) compare well except in the values associated with ring IV. The root-mean-square difference between the crystal and energy-minimized values is 4·9° for all 12 values in Table 6, but only 3·3° if the values for ring IV are excluded. This is close to the values of standard deviations of the torsion angles in the crystal. The closest approach of a perchlorate oxygen to carbon is O(8) · · · C(7^{X}) (3·13 Å), C(7) is in ring IV and this approach could readily account for the difference from the energy minimized values. For the αβ*R* isomer the crystal and energy-minimized torsion angles agree to within 2σ with the exceptions of the Co–N(1)–C(1)–C(2) and N(4)–C(3)–C(4)–N(3) values. No explanation of the difference can be offered in the former case, but the considerable lowering of the angle in the crystal for the latter angle may be ascribed to packing forces. The closest perchlorate oxygen to carbon contact in this crystal is O(4) · · · C(3^{V}) (3·08 Å) in a direction seen from a model to be consistent with constraining this torsion angle to a low value. Since this interaction is across a cell wall it cannot be seen in Figure 2.

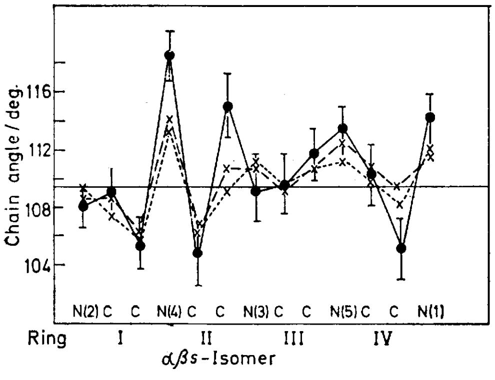

FIGURE 4 Plot of the bond angles in the ligand chain of the αβ*S*-[Co(tetraen)Cl]$^{2+}$ ion at the indicated atoms: full line, in the crystal; short dashes, calculated for the vapour phase with force set (1); and long dashes, force set (2) of ref. 5

Figures 4 and 5 compare the bond angles of the ligand chain found in the crystals with those obtained by energy minimization. The same patterns are found for the angles in the case of the αβ*S* isomer; the poorer correlation for the αβ*R* isomer can mainly be attributed to the inadequate crystal-structure analysis. Thus the angles at carbon atoms in rings II and IV of the αβ*R* structure are unreasonable and this is well high-lighted by comparison with the corresponding energy-minimized angles. The flattening of ring II in this crystal structure noted above could well give rise to N–C–C angles of the order of 113° as was found for the αα isomer,[5] but this is far from the angle of 124° found at the C(4) atom of this ring. The energy-minimized bond angles for both isomers show a closely similar pattern and confirm the major departures from tetrahedral angles in the vicinity of the N(4) atoms. The energy-minimized angles do not differ by more than *ca.* 1° for the two sets of calculations plotted. The energy terms used in these calculations differ mainly in the values chosen for the bond-angle bending terms. Larger *A* values in the expression $E(\theta) = \frac{1}{2}A(\theta - B)$, where chosen for all bond angles in set (2) force constants. This has the effect of stiffening the bond angle to distortion, but Figures 4 and 5 show that this does not move all the equilibrium bond angles closer to 109·5°.

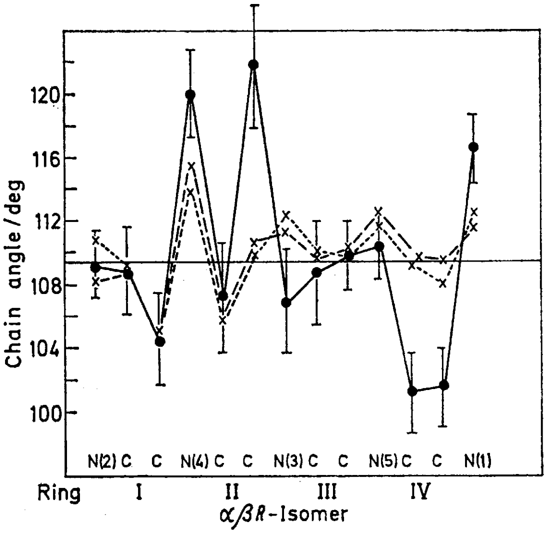

FIGURE 5 Plot of the bond angles in the ligand chain of the αβ*R*-[Co(tetraen)Cl]$^{2+}$ ion at the indicated atoms: full line, in the crystal; short dashes, calculated for the vapour phase with force set (1); and long dashes, force set (2) of ref. 5

The energy-minimization calculations show that αβ*S* is the least strained isomer. The αβ*R* is either 2·6 [set (2)] or 1·5 [set (1)] kcal mol^{-1} higher in strain energy depending on which force field is chosen. The source of the stability differences are distributed over the whole molecules and few strong interactions remain in the minimized molecules. There are only two interactions exceeding 1 kcal mol^{-1}: the torsion terms Co–N(1)–C(8)–C(7) (1·1) and C(3)–C(4)–N(3)–C(6) (1·4 kcal mol^{-1}) in the αβ*S* isomer and Co–N(1)–C(8)–C(7) (1·2) and the non-bonded interaction H(2)N(2) · · · H(2)C(7) (1·01 kcal mol^{-1}) in the αβ*R* isomer. The greatest difference in conformation between the two isomers is in their C(3)–C(4)–N(3)–C(6) torsion angles (Table 6; αβ*S* +132°, αβ*R* +93°) which arises from the different absolute configurations of the chelate rings. With reference to the ring numbering of Figure 3 the rings in sequence I—IV have the configurations δλλδ for αβ*S* and λδλδ for the αβ*R* isomer in terms of the proposed IUPAC nomenclature. The fusion of the λλ rings in the αβ*S* isomer is energetically less favourable in terms of the torsion energy, though not in overall energy since larger nonbonded and angle-bending terms result in the αβ*R* isomer from interactions between rings II (δ) and III (λ).

The free-energy difference between the isomers in solution is unknown. In basic solution the complexes hydrolyse rapidly and the *D*αβ*R* isomer is converted substantially into the *D*αβ*S*-hydroxo-complex. Under these conditions proton exchange is rapid at the N(4) centre and the results require the *D*αβ*S* hydroxo-complex to be *ca.* 1·5 kcal mol^{-1} more stable than the *D*αβ*R* hydroxo-form.[3] This result is in accord with the order of strain energies of the chloro complexes. This may be fortuitous since it is not possible that the reliability of the strain-energy differences could be better than ±1 or 2 kcal mol^{-1}. In this connection, the energy-minimization calculations for a particular molecule do not appear transferable to other systems. Thus these isomers could be considered models for facial and meridional co-ordination of $(NH_2{-}CH_2{-}CH_2)_2NH$(dien) by separate evaluation of the interactions in rings I and II and rings III and IV of the isomers. Restriction of attention to torsion and angle-bending terms shows that dien would favour meridional co-ordination by *ca.* 1 kcal mol^{-1} per ligand based on the αβ*S* data, but the two co-ordination modes would be closely equal in energy based on the αβ*R* data. Equilibrium mixtures of $[Co(dien)_2]Br_3$ do in fact contain a predominance of the bis-meridional form,[17] but these transferred results cannot be regarded as predictive and work is in progress to compute the relative energies of these systems.[18]

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