(confirmed by metastable transition[4]) in which a stable molecule is formed. From reaction 1, $\Delta H_f^\circ(H_2SiCH_3^+) = 9.35 \pm 0.02$ eV (215.6 ± 0.5 kcal mol^{-1}) is obtained.

From heats of formation,[13,14] the Si^+ ion threshold value is 21.17 eV. This onset is too high to be obtained by direct measurements with the present apparatus. Using the calculated value in connection with heats of formation and the molecular ionization threshold, the following total bond energies (in kcal mol^{-1}) are obtained: $D((CH_3)_4\text{–}Si) = 298.85$ and $D((CH_3)_4\text{–}Si^+) = 260.82$. These results suggest that ionization occurs by the loss of one of the bonding electrons between the central atom and the methyl groups.

The measurements have been performed by using the apparatus described by Dibeler, *et al.*,[17,18] with an optical resolution of about 1 Å and an ionization efficiency uncertainty of the order of 3%.

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CONTRIBUTION FROM THE RESEARCH SCHOOL OF CHEMISTRY,
AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA 2600, AUSTRALIA,
AND THE SCHOOL OF CHEMISTRY, UNIVERSITY OF SYDNEY 2006,
SYDNEY, AUSTRALIA

The Chelate Ring Conformations of the β-Triethylenetetramine Configuration in Cobalt(III) Complexes

BY D. A. BUCKINGHAM,[1a] I. E. MAXWELL,[1a] A. M. SARGESON,[1a] AND H. C. FREEMAN[1b]

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Recently X-ray crystal structure analyses have been carried out on a number of cobalt(III) complexes containing trien coordinated in the β configuration (Figure 1), namely, $[Co(trien)Cl(OH_2)](ClO_4)_2$,[2a] Δ-$\beta_2$-(*RRS*)-[Co(trien)((*S*)-Pro)]$I_2 \cdot 2H_2O$,[2b] and Λ-β_2-(*SSS*)-[Co(trien)((*S*)-Pro)]$ZnCl_4$[2b] (trien = triethylenetetramine). In addition, in the complex *sym*-[Co(trenen)N_3]$(NO_3)_2 \cdot H_2O$[3] (trenen = 4-(2-aminoethyl)-1,4,7,10-tetraazadecane) trenen can be considered as β-trien substituted at the "angular" nitrogen atom by an aminoethyl group. These four structures provide independent determinations of the geometry of the β-trien configuration in different crystal lattices. Prior to these structural analyses only the gross features of the geometry of the β-trien configuration could be inferred from Dreiding stereomodels. However, the models did indicate which were likely to be the more important conformational features. In particular, it was decided that conformational inversion was possible for the apical chelate ring, but at the time it was difficult to decide which was the preferred conformation. Angular strain was also evident, particularly at the "planar" secondary nitrogen atom, but it was difficult to determine how this strain was distributed. With these problems in mind the conformations of the chelate rings in coordinated trien are now compared using three different criteria. In this way any correlations are not biased to one particular set of results. Also the comparison is made between molecular conformations which are found in different crystal lattices where the molecules are subject to different types of intermolecular forces (*e.g.*, H-bonding, electrostatic, and nonbonded forces). Such a comparison should give some indication of the relative importance of intermolecular and intramolecular forces in determining conformation; for example, large conformational differences have been observed for the $Cr(en)_3^{3+}$ ion in different lattices.[4]

Comparison of β-trien Geometries

Bond Angles and Bond Lengths.—A comparison of the Co–N bond distances involving trien for the β-Co(trien)$Cl(OH_2)^{2+}$,[2a] Δ-β_2-(*RRS*)-Co(trien)((*S*)-Pro)$^{2+}$,[2b] and Λ-β_2-(*SSS*)-Co(trien)((*S*)-Pro)$^{2+}$ [2b] structures showed that in each case the bond to the "planar" nitrogen was the shortest. The Co–N(2) bond lengths averaged to 1.921 (7) Å, whereas the mean value for the other Co–N distances was 1.953 (4) Å (the standard deviations of the means, σ_{av}, were calculated using the relationship $\sigma_{av}^2 = 1/\Sigma_i 1/\sigma_i^2$). Another geometrical feature of the "planar" secondary N atom common to all three structures was the expansion of the C(2)–N(2)–C(3) bond angle (mean 114.0 (7)°). The Co–N(2) bond length is reduced relative to the other Co–N bond distances in order to reduce angular strain at this center. By comparison there is no significant distortion in the C(4)–N(3)–C(5) bond angle (110.7 (7)°) or any other angle about the "angular" secondary N atom. Likewise there are no other significant intraligand angular distortions in the polyamine skeleton.

The angles subtended by the chelate rings at the metal ion are similar. For the three complexes the mean N–Co–N angle is 85.8 (2)°. This angle compares with an N–Co–N angle of 86° found in cobalt(III)–ethylenediamine complexes[5,6] where the chelate rings are not fused. Mean C–C and C–N bond lengths for the trien ligand are 1.509 (8) and 1.499 (3) Å, respectively. For the present structures these bond lengths were sensitive to the inclusion of hydrogen atoms at calculated positions during least-squares refinement. When hydrogen atom contributions were not included,

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(1) (a) Australian National University. (b) University of Sydney.

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the bond lengths obtained were significantly longer, particularly for the C–C bonds (∼0.02 Å).

Conformations of the Chelate Rings.—The relative chiralities of the trien chelate rings are the same for the three structures containing the β-trien configuration and for the relevant part of *sym*-Co(trenen)N_3^{2+}.[3]

For the Δ configuration about the metal ion the chiralities of the chelate rings are as follows: N(1)–C(1)–C(2)–N(2), λ; N(2)–C(3)–C(4)–N(3), δ; N(3)–C(5)–C(6)–N(4), δ (Figure 1). For convenience these chelate rings will be referred to as rings 1, 2, and 3, respectively. In the following discussion concerning the stabilities of conformations, for the enantiomeric configuration about the metal ion the chelate ring chiralities are inverted but the relative stabilities are the same.

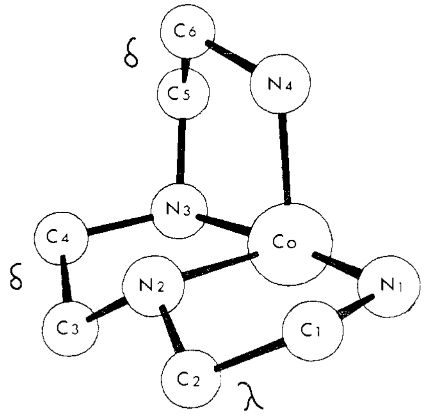

Figure 1.—Conformations of chelate rings for the Δ configuration of β-trien.

The conformations are primarily determined by the configuration at the two asymmetric secondary N atoms which link chelate rings. Clearly, the chiralities of the rings joined by the "planar" secondary N atom, N(2), must be enantiomeric and these chelate rings cannot invert without synchronous inversion at the secondary N center. However, models indicate that inversion of conformation at ring 3 could occur with retention of configuration at the "angular" secondary N atom, N(3). The reason that this inverted conformation is not observed is attributed to increased conformational strain for this form. An inverted conformation of ring 3 (λ for the Δ configuration about the metal) would involve smaller torsion angles about the C–C and C–N bonds, resulting in an increase in torsional and nonbonded strain energy.

The conformations of the chelate rings are compared quantitatively in three different ways. First, the deviations of chelate ring carbon atoms from their N–Co–N planes are compared in Table I and Figure 2. Second, the torsion angles about the C–N and C–C bonds are compared in Table II and Figure 3. The torsion angles were defined as follows: for atoms A, B, C, and D bonded in a chain, the torsion angle about the bond BC was taken as positive if the bond AB was required to be rotated clockwise to lie in the BCD plane. This system follows the suggestions of Klyne and Prelog[7] and more recently Allen and Rogers.[8] Moreover, for the N–C–C–N chains of the chelate rings the method would assign a positive sign to the torsion angle about the C–C bond where the conformation is δ and a negative sign for the λ conformation.

TABLE I

COMPARISON OF DEVIATIONS OF CHELATE RING CARBON ATOMS FROM N–Co–N PLANES FOR β-trien COMPLEXES

	Deviations (in Å)			
Atom	β-[Co(trien)ClOH$_2$]$^{2+}$	Δ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	Λ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	sym-[Co(trenen)N$_3$]$^{2+}$ [c]
C(1)	0.11	0.01	0.11	0.11
C(2)	-0.54	-0.66	-0.48	-0.51
C(3)	-0.73	-0.77	-0.82	-0.64
C(4)	-0.23	-0.15	-0.31	-0.13
C(5)	-0.48	-0.47	-0.44	-0.56
C(6)	0.20	0.20	0.22	0.07

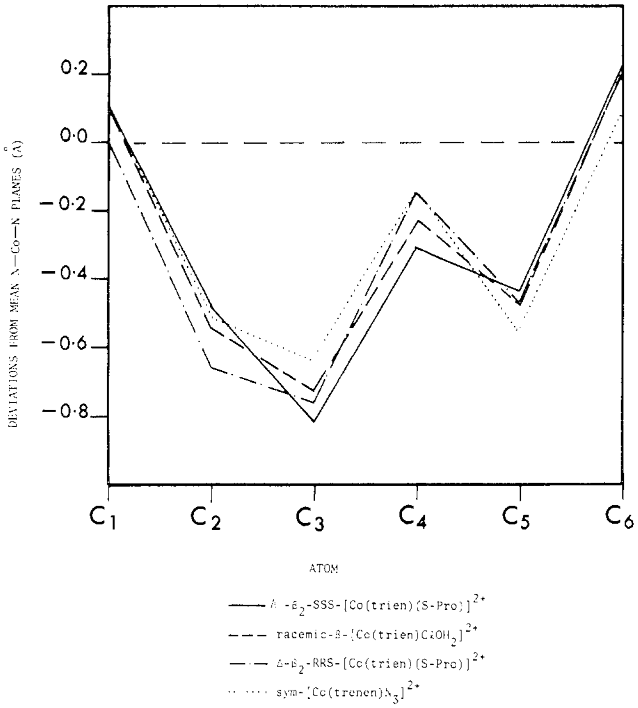

Figure 2.—Comparison of deviations of carbon atoms from their respective N–Co–N planes for β-trien chelate rings.

TABLE II

COMPARISON OF TORSION ANGLES FOR β-trien COMPLEXES

Plane 1	Plane 2	β-[Co(trien)ClOH$_2$]$^{2+}$	Δ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	Λ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	sym-[Co(trenen)N$_3$]$^{2+}$ [3]
Co, N(1), C(1)	N(1), C(1), C(2)	30.1	27.6	-33.4	28.6
N(1), C(1), C(2)	C(1), C(2), N(2)	-47.1	-38.2	48.9	45.4
C(1), C(2), N(2)	C(2), N(2), Co	43.5	48.6	-42.5	31.6
Co, N(2), C(3)	N(2), C(3), C(4)	-11.5	-52.2	44.6	33.9
N(2), C(3), C(4)	C(3), C(4), N(3)	37.0	46.5	-39.7	58.5
C(3), C(4), N(3)	C(4), N(3), Co	-11.6	-20.6	12.0	-10.8
Co, N(3), C(5)	N(3), C(5), C(6)	-45.9	-42.2	41.2	-43.0
N(3), C(5), C(6)	C(5), C(6), N(4)	51.8	49.0	52.7	17.3
C(5), C(6), N(4)	C(6), N(4), Co	-35.2	-33.6	32.5	-27.7

Finally, the conformations of the chelate rings have been compared by calculating the dihedral angles between planes containing atoms of the type Co, N, C and Co, C, C (*e.g.*, the angle between the Co, N(1), C(1) plane and the Co, C(1), C(2) plane.[9] The sequence of

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TABLE III

COMPARISON OF DIHEDRAL ANGLES FOR β-trien COMPLEXES[a]

		Dihedral Angles (in deg.)			
Plane 1	Plane 2	β-[Co(trien)ClOH$_2$]$^{2+}$	Λ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	Δ-β$_2$-[Co(trien)(S-Pro)]$^{2+}$	sym-[Co(trenen)N$_3$]$^{2+}$
Co, N(1), C(1)	Co, C(1), C(2)	33.2	27.7	33.2	28.3
Co, C(1), C(2)	Co, C(2), N(2)	43.2	48.0	42.0	40.9
Co, C(2), N(2)	Co, N(2), C(3)	53.2	59.1	54.0	50.4
Co, N(2), C(3)	Co, C(3), C(4)	43.9	51.3	45.0	41.1
Co, C(3), C(4)	Co, C(4), N(3)	14.2	21.0	11.9	16.5
Co, C(4), N(3)	Co, N(3), C(5)	57.5	61.0	57.5	59.9
Co, N(3), C(5)	Co, C(5), C(6)	43.5	41.7	40.7	42.7
Co, C(5), C(6)	Co, C(6), N(4)	35.2	33.5	34.1	27.8

[a] For convenience in comparison, obtuse dihedral angles have been subtracted from 180°.

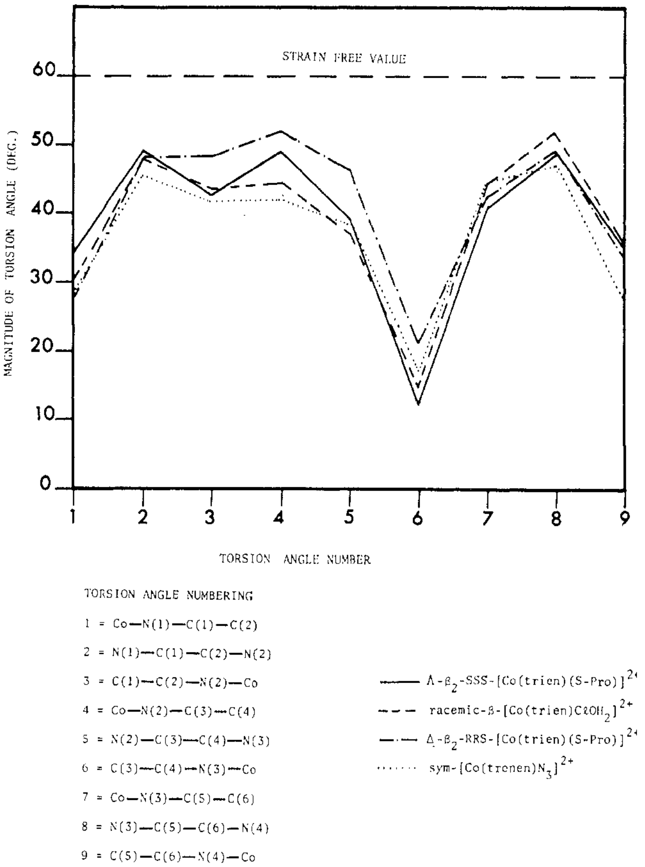

Figure 3.—Comparison of torsion angles for β-trien chelate rings.

dihedral angles progressing around the chelate rings gives a measure of the folding of the ligand. These dihedral angles for the various complexes are compared in Table III and Figure 4.

Each method of comparison shows that the conformations of the β-trien configuration in each structure are remarkably similar. The result is surprising in view of the markedly different lattice forces associated with each complex ion. These forces arise from different H bonding to the complex ion, the presence or absence of water of crystallization, different charges on the anions, and different closest nonbonded contacts.[2,3] It would appear, therefore, that the β-trien configuration is comparatively rigid and is not easily distorted by external interactions. Moreover, it seems likely that the conformations of the β-trien complexes in solution are close

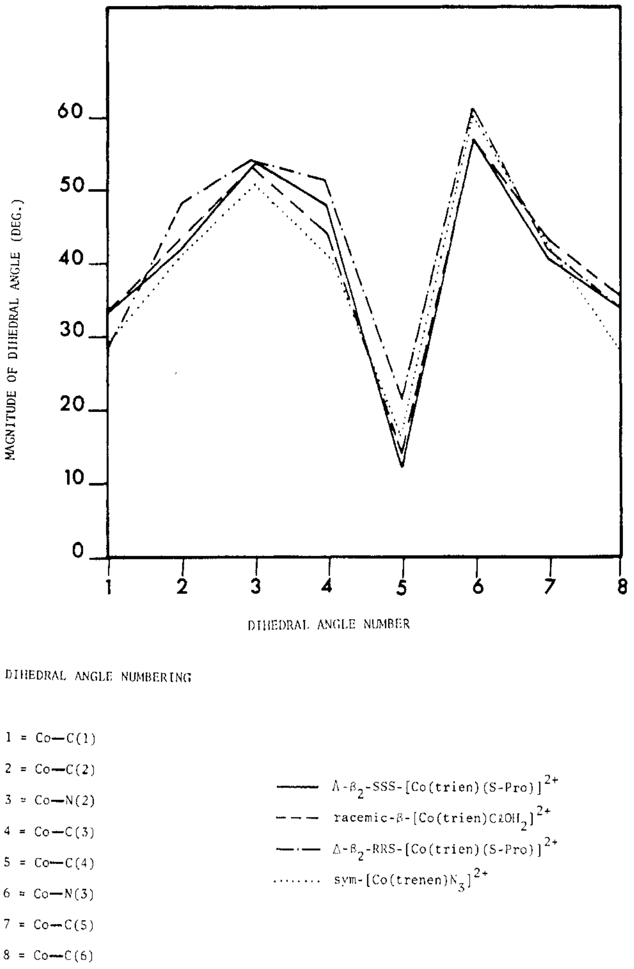

Figure 4.—Comparison of dihedral angles for β-trien chelate rings.

to those found in the solid state. In general proton magnetic resonance studies of β-trien–cobalt(III) complexes show sharp superimposed multiplets for the methylene region of the spectrum.[10,11] Further, the geometry of the proline complex ions[2b] was accurately reproduced using strain energy minimization calculations.[12] The force field included nonbonding, angular deformations, bond stretching, and torsional terms and the trien conformations given above were reproduced in close detail. The minimization procedure essentially calculates the geometry of the isolated ion free of intermolecular interactions. All these results provide evidence for the restricted mobility and thermodynamic stability of the chelate ring conformations in solution.

In view of the consistent formation of hydrogen bonds by anions and water molecules to the primary and secondary nitrogen atoms of trien in the solid phase, it seems likely that these N–H centers would also participate in hydrogen bonding to solvent and anions in solution.

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