

Conformational Analysis of Coordination Compounds Tris-diamine Cobalt(III) Complexes with Three Six-membered Chelate Rings*

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The method for strain energy minimization due to Wiberg has been elaborated and applied to the conformational analysis of transition metal octahedral complex ions: Tris(1,3-diaminopropane)cobalt(III), Co tn_3 , and tris(*R,R*-2,4-diaminopentane)cobalt(III), Co ptn_3 . Energy contributions from bond length and angle deformations, non-bonded interactions and torsional strain have been considered, the required force constants being taken from the available literature data. Equilibrium geometry parameters and relative conformational energies for three symmetrical conformations (chair_3 , 1el_3 , and ob_3) and ten "mixed" conformations of Co tn_3 , and two conformations (1el_3 and ob_3) of Co ptn_3 were calculated and the stereochemistry of these systems was described in detail. The order of conformational energies and the comparison between calculated and X-ray conformations are presented.

The first general scheme for strain energy minimization was developed by Wiberg¹ who wrote a computer program capable of searching the minimum energy conformation by the method of steepest descent. This method has been successfully applied to the conformational analysis of cyclooctane, cyclodecane and cyclododecane,¹ some oxygen substituted carbocyclic molecules,² and cyclic carbonium ions.³ The method was further developed by Allinger and co-workers⁴ who have used it for a wide range of conformational calculations.

In the present study Wiberg's program has been elaborated, modified and applied to the conformational analysis of tris(chelate) octahedral coordination

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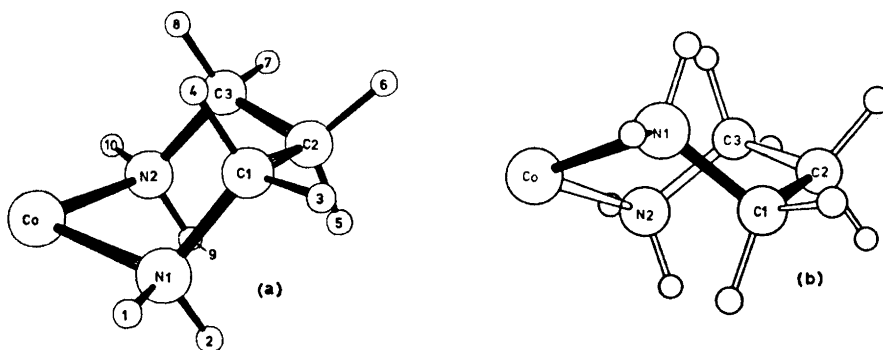
compounds. Here we report our results from a study of the tris(trimethylenediamine)cobalt(III) and tris(*R,R*-2,4-diaminopentane)cobalt(III) complexes.*

We have chosen to carry out the detailed conformational analysis of the Co tn_3 system** because it represents a prototype of a tris(bidentate)₃ complex with three saturated six-membered chelate rings. The detailed stereochemistry of this system is of particular importance in connection with the interpretation of its CD spectra⁵ and the relation of the N–Co–N angle to the sign of Cotton effect in T_{1g} region.⁵ This is revealed by considerable recent interest in the stereochemistry of trimethylenediamine complexes and particularly Co tn_3 and by appearance of several papers^{5d-f} on this issue during the progress of our work.

STEREOCHEMISTRY

One single metal-trimethylenediamine chelate ring has basically the same conformational possibilities as the cyclohexane ring. Three of the conformations of the Co–tn ring are characterized by their energy minima: one rigid chair form with C_3 symmetry (Fig. 1(a)), and two enantiomeric twist-boat forms with C_2 symmetry (Fig. 1(b) and (c)) belonging to the family of flexible boat forms. For each of the twist-boat conformations of the Co–tn ring two skew lines could be defined: one connecting N-atoms and the other connecting terminal C-atoms (Fig. 1(d) and (e)). According to the helicity associated with these lines⁷ the twist forms are labelled as λ and δ .

When entering a tris(chelate) a Co–tn ring in its chair conformation may adopt one of two orientations which give rise to two conformers if – and only if – the two other rings are not connected by a C_2 operation (Fig. 1(f) and (g)). Now to calculate the total number of theoretically possible conformations of Co tn_3 , combinations of all four forms of chelate rings (λ , δ , and chair



* We have also analyzed the series of tris-diamine metal complexes with ethylenediamine, propylenediamine, and 2,3-diaminobutane. These results will be described elsewhere.⁶

** Abbreviations: tn = trimethylenediamine, ptn = 2,4-diaminopentane. Ionic charges are omitted.

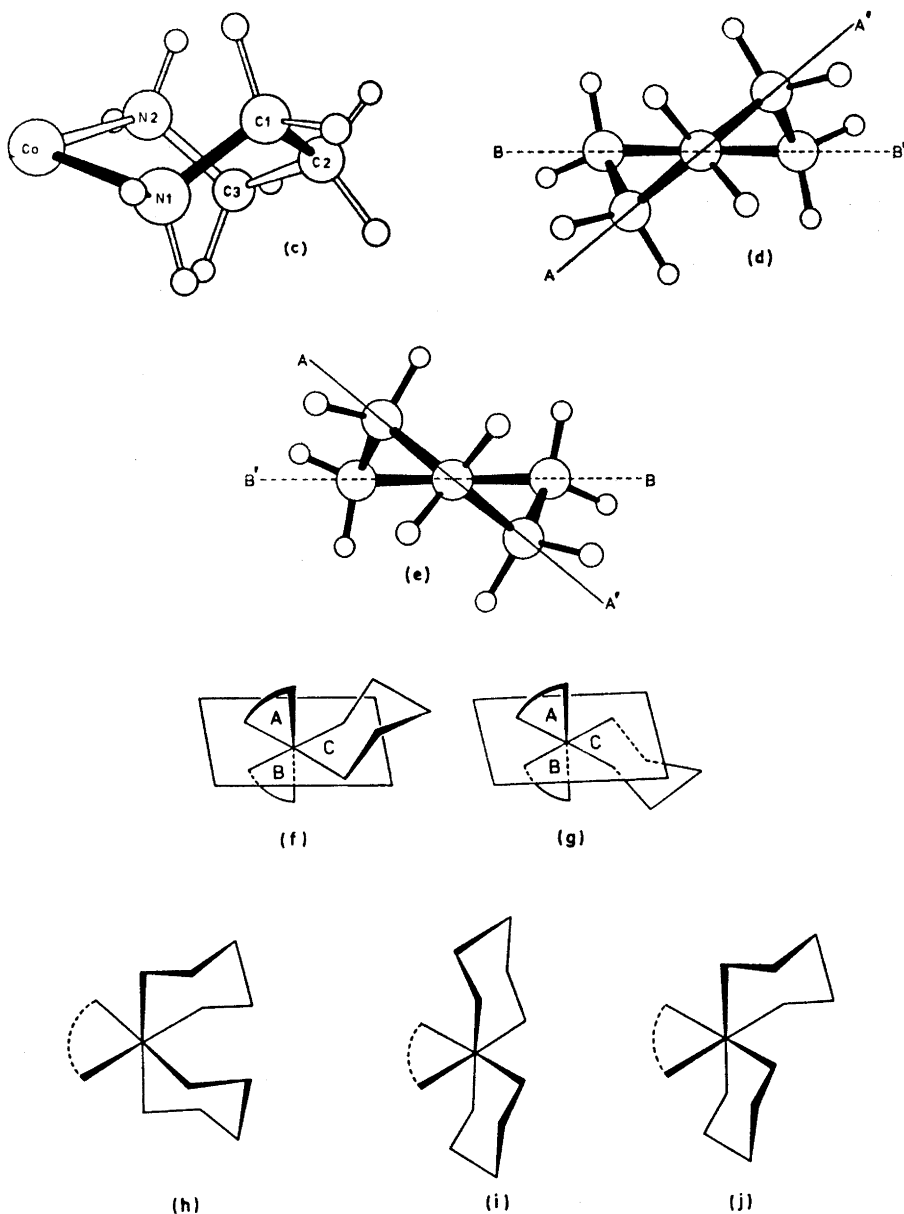


Fig. 1. Stereochemistry of a single Co-tn chelate ring. Chair conformation (a); two enantiomeric twist-boat conformations (b) and (c); skew lines AA' and BB' defining left-handed helix of λ -twist-boat (d) or right-handed helix of δ -twist-boat (e) conformation; provided the two rings A and B are not C_2 -symmetry connected the two different orientations of a chair, C, give rise to two conformers, $cis_{(A,C)} \equiv trans_{(B,C)}$ (f), and $cis_{(B,C)} \equiv trans_{(A,C)}$ (g); *syn*-, *anti*-, and (C_1)-constellation of a pair of chairs (h), (i), and (j).

in two orientations) have to be considered. This leads to a total of 16 different conformations (Table 1)* for each of the absolute configurations, Δ , and Λ .

The *lel-ob* nomenclature lends itself for a convenient designation of the conformers but because of the above mentioned possibility for the chair to adopt two orientations – in some cases leading to different conformers – there is need for an additional nomenclature.** In conformers with only one chair the plane defined by the central atom and the two nitrogen atoms of that chair could form a basis for a *cis-trans* nomenclature (*vide* Fig. 1(f) and (g)). In conformers with two chairs these can adopt two conformations designated *syn* and *anti* in Fig. 1(h) and (i) in which they are connected by a C_2 operation and one conformation of symmetry C_1 . In Table 1 *syn*, *anti*, and C_1 are used to distinguish conformers with two chairs. With three chairs Co tn_3 may adopt two conformations, one of symmetry C_3 and one of symmetry C_1 . Three “symmetrical” conformations: (C_3)-*chair*₃, *lel*₃, and *ob*₃, together with 10 of the “mixed” conformations were subjected to the minimization procedure. Conformers 9, 11, and 14 from Table 1, all having a pair of *syn-chair*₂ rings, were not analysed since they appear to be sterically impossible on molecular models.

The molecular structure of $[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$ as determined by the X-ray diffraction method⁹ shows that Co tn_3 has *chair*₃ conformation in the crystalline state. Preliminary results of the X-ray analysis of $[\text{Co}(R,R\text{-}2,4\text{-ptn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ show¹⁰ that the crystalline state conformation of this complex ion is *ob*₃ with all the methyl groups in equatorial positions.

The chair conformation of *tn* rings was also found in crystal structures of $[\text{Co en}_2\text{tn}]\text{Br}_3$,¹¹ *trans*- $[\text{Co}(\text{NO}_3)_2\text{tn}_2]\text{NO}_3$,^{12a} *trans*- $[\text{Co Cl}_2\text{tn}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$,^{12b} and *cis*- $[\text{Co}(\text{NCS})_2\text{tn}_2][\text{Sb tart}] \cdot 2\text{H}_2\text{O}$,^{12c} as well as in some bis(chelate) copper(II) and nickel(II) complexes of *tn*.¹³

METHOD

The conformational calculations described in the present study were carried out with a single computer program *** which represents an extended and modified version of Wiberg's energy minimization program.^{1,2}

* Total number of conformers was calculated using the formula: $\binom{n+i-1}{i} + \binom{n}{i}$ for the combinations with repetition of *i*-th order with *n* elements augmented by a number of sequential isomers (equal to the number of combinations without repetition). In general, for the cyclic systems of three rings with four possible ring conformations $n=4$ and $i=3$, and the total number of conformations is 24. However, due to the above-mentioned fact that among the Co tn_3 conformers containing chairs some (actually 16 of the conformers counted by this formula) are pairwise identical, as shown in the last column of Table 1, we are left with a total of 16 different conformers.

** *Note added in proof*: An ambiguity in the nomenclature used in the first version of our paper was kindly drawn to our attention by Professor K. N. Raymond whom we thank for making his results available to us prior to publication. Jurnak and Raymond⁹ in an X-ray investigation of $[\text{Cr tn}_3][\text{Ni}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ have found that the conformation of the $[\text{Cr tn}_3]^{3+}$ ion corresponds to our *anti-chair*₂*lel* (No. 9 in Table 1), the conformer predicted by our calculations (using FF-2) to have the lowest energy (*vide* Fig. 8).

*** The program that treats 64 atoms (currently) and about 2240 interactions requires 104 K of storage on an IBM 360/75. One cycle of minimization including calculation of derivatives and energy contributions takes approx. 36 sec on an IBM 360/75.

Table 1. Conformations of Mtn_3 system.^a

No.	Conformation	Symmetry	Ring conformations (exemplified for A absolute configuration using Journak & Raymond's ³² nomen- clature ^b)
1	(C_3) -chair ₃	C_3	ppp \equiv aaa
2	lel ₃	D_3	$\delta\delta\delta$
3	ob ₃	D_3	$\lambda\lambda\lambda$
4	lel ₂ ob	C_2	$\delta\delta\lambda$
5	ob ₂ lel	C_2	$\lambda\lambda\delta$
6	(C_1) -chair ₂ ob	C_1	pp $\lambda\equiv$ aa λ
7	(C_1) -chair ₂ lel	C_1	pp $\delta\equiv$ aa δ
8	<i>anti</i> -chair ₂ lel	C_2	ap δ
9	<i>syn</i> -chair ₂ lel	C_2	pa δ
10	<i>anti</i> -chair ₂ ob	C_2	ap λ
11	<i>syn</i> -chair ₂ ob	C_2	pa λ
12	lel ₂ chair	C_1	$\delta\delta p\equiv\delta\delta a$
13	ob ₂ chair	C_1	$\lambda\lambda p\equiv\lambda\lambda a$
14	(C_1) -chair ₃	C_1	ppa \equiv aap
15	<i>cis</i> _(lel,chair) -lel ob chair	C_1	$\delta\lambda p\equiv\lambda\delta a$
16	<i>trans</i> _(lel,chair) -lel ob chair	C_1	$\delta\lambda a\equiv\lambda\delta p$

^a ob and lel refer to diastereoisomerism between *e.g.* $A(\lambda\lambda\lambda)$ and $A(\delta\delta\delta)$; $A(\lambda\lambda\lambda)$ [and $A(\delta\delta\delta)$] being lel, in analogy to the tris(ethylenediamine) complexes.⁶

^b Added in proof after the appearance of Ref. 32.

The search for a minimum of strain energy is performed by the method of steepest descent which is described in detail elsewhere.¹⁴ It consists of the calculation of the gradient (that is, direction of steepest descent) on an energy surface of a N -atomic molecule in $3N + 1$ dimensional space.

The basic ideas and the advantages of the steepest descent minimization procedure have been discussed already by Wiberg¹ and others.^{3,4,15} Therefore, we shall describe only briefly some of our modifications and refinements.

The subprograms of Wiberg's conformational program could be divided into four main groups. The first group consists of a series of subroutines which build the geometry of a molecule and effects various transformations of coordinates. These routines were modified in order to account for the sexaligacy and for the symmetry operations in D_3 . Routines were added to generate methyl groups on the specified positions of the molecular framework. In addition, the program automatically places the hydrogens on primary, secondary, or tertiary carbon and nitrogen atoms maintaining tetrahedral angles. In order to decrease the computational time attached hydrogens were moved together with nonhydrogen atoms in the initial stages of minimization. This was done by recalculating the positions of hydrogens each time any one of the nonhydrogen atoms is moved, that is, both in the gradient calculation and in movement along the gradient. In this way both rotation and translation of tetrahedra were achieved. The second group of subroutines calculates the internal coordinates from the Cartesian atomic coordinates (supplied as

input or generated by the program itself) which are then used in the calculation of energy contributions. Here also the necessary changes for sexaligacy were made. The third group of subroutines calculates the various energy contributions and their sum for the conformation under consideration. These routines were rewritten in order to allow the use of individual expressions for each type of interaction (*e.g.*, in the present study five different bond-stretching types, 10 different angle-bending types, and six different non-bonded interaction types). Different subroutines were used for the characterization of different force fields (*vide infra*). The fourth group of subroutines computes the gradient.

In our program it was possible to select the size of increments to be used in the calculation of partial derivatives. The choice of increments has already been discussed by Allinger and co-workers.⁴ Our program starts with increments of 0.01 Å, but it switches to smaller increments (down to 0.002 Å) when desired, either after a predetermined number of iterations or when the energy fails to decrease. In practice we have used the following simple convergence criterion:

$$|E_i - E_{i+1}| \leq \delta_i$$

where i = iteration number, and δ_i = accuracy which was numerically equal to the current increment. When this condition is satisfied the program changes to smaller increments or, if the increments are already 0.002 Å, it terminates the search. The resulting root-mean-square deviation of atomic coordinates in the final cycle of iterations proved less than 10^{-4} Å.

CALCULATIONS

Initial coordinates for Co tn₃ and Co ptn₃. The conformational program starts with an assumed initial geometry of a molecule expressed in terms of Cartesian atomic coordinates.

Initial coordinates for the tris(trimethylenediamine)cobalt(III) ion were derived in two ways. The idealized initial conformations were obtained from two sets of Cartesian coordinates calculated by the vector method¹⁶ for two principal forms (*chair* and *twist-boat*) of a single Co-tn chelate ring.¹⁷ Given the Cartesians for one Co-tn ring placed with its two Co-N bonds along the +X and +Y axes, the program calculates the atomic coordinates for the remaining two chelate rings and defines the new coordinate system in which the C₃ or quasi C₃ molecular axis is coincident with the Z-axis. In this way the entire molecule is generated with the minimum of input data (for example: coordinates of five chelate ring atoms for the Co tn₃ system). By specifying the absolute configuration and the sequence of conformations of individual chelate rings the idealized forms of the tris(*chair*) and the tris(*twist-boat*) forms were built (Table 1).

Secondly, the Cartesians for the crystalline state conformation of Co tn₃ were calculated from the available fractional crystal coordinates^{9,*} using a

* The z-coordinate of Co (in Table 2 of Ref. 9) should read 4393(5), also the y-coordinate of Br(2) (*ibid.*) should read -0730(6); (Personal communication from Professor Y. Saito, 1971).

computer program which also effects the reorientation of the molecule in the same way as for the idealized initial conformations.

Coordinates for the Co ptn₃ were obtained by the generation of methyl groups on terminal carbon atoms in a Co-tn ring creating either *R* or *S* absolute configurations.

Minimization. In general minimizations have been carried out under the following conditions:

(a) All the geminal nonbonded interactions (1,3-interactions) were excluded but were accounted for in the corresponding angle-bending terms. In this way all the non-bonded interactions between ligating atoms (N...N) were omitted.

(b) Non-bonded interactions involving the cobalt atom were excluded from the present calculations.

(c) Only three chelate angles (N-Co-N) were included. These were the angles between ligating atoms belonging to a common chelate ring. The equilibrium value of 90° was assigned to these angles.

(d) All of the six possible bond angles on each tetrahedral atom were included in the calculation of angle-bending strain.

(e) All of the nine possible torsional angles formed by a pair of tetrahedra were included in the calculation of torsional strain, whereas the rotational barriers along the coordinate bonds (Co-N) were neglected (*vide infra* "Torsional Strain").

Furthermore, a series of calculations was carried out in which the chelate angle-bending terms were omitted but with the inclusion of all the 12 non-bonded interactions between nitrogen atoms.

All the calculations on idealized "symmetrical" forms (chair₃, 1el₃, and ob₃) were carried out in two ways: with and without the C₃-symmetry constraint.

The effects of different minimization conditions will be discussed in the section "Conformational Results".

POTENTIAL FUNCTIONS

Bond-stretching and angle-bending strain. Potential energy due to the bond stretching and angle bending is described by simple harmonic functions:

$$E_{ij}^l = \frac{1}{2} K_{ij}^l (l_{ij} - l_{ij}^0)^2$$

$$E_{ijk}^\theta = \frac{1}{2} K_{ijk}^\theta (\theta_{ijk} - \theta_{ijk}^0)^2$$

Standard values¹⁸ were used as equilibrium values for bond lengths. Equilibrium bond lengths and angles with the corresponding stretching and bending force constants are given in Table 2.

Bending force constants for different angles at carbon atoms (*i.e.*, X-C-Y, where X, Y = H, N, and C) were taken from the computer program of Wiberg and Harris.^{1,2} Force constants for H-N-H and H-N-C angles were set equal to the constants for H-C-H and H-C-C angles, respectively.

Table 2. Equilibrium bond lengths and stretching force constants.

Bond	l^0 (Å)	K^l (kcal mol ⁻¹ Å ⁻²)	Ref.
Co-N	2.00	288	19
N-C	1.47	864	1
C-C	1.54	720	1
C-H	1.093	720	1
N-H	1.011	812	19

Equilibrium bond angles and bending force constants

Angle	θ^0 (deg)	K^θ (kcal mol ⁻¹ deg ⁻²)	Ref.
N-Co-N	90.0	47.3	20
Co-N-H	109.5	13.9	20
Co-N-C	109.5	27.8	20
N-C-C	109.5	77.5	1, 2
N-C-H	109.5	45.6	1, 2
H-N-H	109.5	38.3	"
C-N-H	109.5	45.6	"
H-C-H	109.5	38.3	1, 2
H-C-C	109.5	45.6	1, 2
C-C-C	109.5	77.5	1, 2

^a Estimate (see text).

Angle-bending terms involving the cobalt(III) atom were calculated with the force constants of Snow.^{20,*}

Torsional strain. Torsional strain is represented by the simple cosine function:²¹

$$E^\phi = \frac{1}{2}V^\phi (1 + \cos 3\phi)$$

Following Wiberg's concept^{1,3a} of "bond torsional energy" (contrary to "group torsional energy") we took all nine possible torsional interactions for a pair of tetrahedral atoms into account by adding their contributions as follows:

$$E^\phi = \sum_{i=1}^9 \frac{1}{2} \times 0.330 \times (1 + \cos 3\phi_i)$$

where 0.330 represents 1/9 of the rotational barrier in ethane. The torsional barrier around the C-N bonds was assumed to be the same as the barrier around the C-C bonds. This is supported by the fact that the rotational barrier is (to a first approximation) independent of the nature of the atoms

* While our work was still in progress Dr. M. R. Snow published²⁰ his results on the conformational analysis of the α,α -chlorotetraethylenepentaminecobalt(III) ion. We have adopted some of the values for bending force constants chosen by Dr. Snow for his "second set" of parameters in preference to the various estimates which we used before.

involved.^{3a} Torsional contributions from rotations about coordinate bonds (Co-N) were omitted assuming that they should be negligibly small,^{3a,22} owing to the 12-fold symmetry of the rotational barrier in this case.

Non-bonded interactions. Strain energy contributions due to the non-bonded interactions were calculated using a modified Buckingham-type potential function:

$$E_{ij} = A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij}/r_{ij}^6$$

where i , and $j = \text{N, C, and H atoms}$.

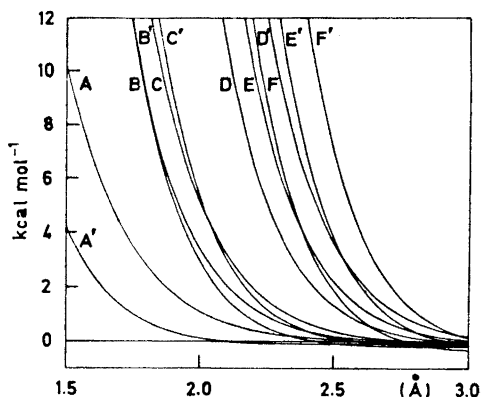


Fig. 2. Potential functions for non-bonded interactions. First set: H...H (A), H...C (B), H...N (C), C...C (D), C...N (E), N...N (F). Second set: H...H (A'), H...C (B'), H...N (C'), C...C (D'), C...N (E'), and N...N (F').

Two sets of coefficients were used in the present study (Fig. 2 and Table 3). The first set given by Liquori and co-workers²³ is derived from the experimental data of De Coen and co-workers.²⁴ The function for H...H non-bonded interactions in this set is of "medium" type and is similar to Bartell's H...H function.²⁵ The second set given by Ramachandran and co-workers²⁶ yields a rather "soft" H...H function comparable to Hill's function.²⁷ However, the functions for non-bonded interactions between non-hydrogen atoms are "harder" than in the first set.

Table 3. Parameters for non-bonded potential functions (in kcal/atom pair).

Interaction	First set ²³			Second set ²⁶		
	$A_{ij} \times 10^{-4}$	B_{ij}	C_{ij}	$A_{ij} \times 10^{-4}$	B_{ij}	C_{ij}
H...H	0.66	4.08	49.2	0.829	4.6	46.8
H...C	3.14	4.32	99.2	7.79	4.6	165.8
H...N	2.81	4.20	121.1	5.34	4.6	156.0
C...C	21.21	4.32	244.0	92.4	4.6	599.9
C...N	23.70	4.44	297.8	60.5	4.6	571.2
N...N	18.64	4.55	200.0	40.4	4.6	546.9

CONFORMATIONAL RESULTS

In the following discussion FF-1 and FF-2 refer to the sets of functions with Liquori's and Ramachandran's non-bonded parameters, respectively. The FF-3 force field was the same as FF-1 with regard to the coefficients used for the different strain energy functions, except that the N-Co-N angle bending terms were omitted and the N...N non-bonded interactions included instead.

The single Co-tn chelate ring

The hypothetical system of one Co-tn chelate ring was first examined. Two principal conformations were minimized: symmetrical *chair* form and symmetrical *twist-boat* form for which the initial Cartesian atomic coordinates have been calculated by the vector method.^{28,29} Table 4 summarizes the final minimized geometry of the single Co-tn ring. The main energy differences between initial chair and initial twist-boat conformations were found in the torsional and non-bonded terms. Minimization of the single ring conformations with FF-1 gave equilibrium conformations with the energy difference

Table 4.^{a,b} Minimized geometry of the hypothetical single Co-tn ring system.

Bond lengths (in Å)	FF-1		FF-2		FF-3	
	C	TB	C	TB	C	TB
Co-N(1)	2.000	2.060	2.001	2.008	2.000	2.005
N(1)-C(1)	1.475	1.476	1.477	1.476	1.471	1.473
C(1)-C(2)	1.548	1.548	1.549	1.549	1.540	1.546
C(2)-C(3)	1.548	1.548	1.549	1.549	1.540	1.546
C(3)-N(2)	1.475	1.476	1.477	1.476	1.471	1.473
N(2)-Co	2.000	2.060	2.001	2.008	2.000	2.005
Bond angles (in deg.)						
N(2)-Co-N(1)	91.23	92.18	91.40	92.72	90.35	91.74
Co-N(1)-C(1)	110.37	109.80	110.10	109.50	110.20	109.50
N(1)-C(1)-C(2)	111.24	111.30	111.20	111.70	110.60	110.80
C(1)-C(2)-C(3)	111.64	111.90	111.30	111.96	111.10	111.60
C(2)-C(3)-N(2)	111.24	111.30	111.20	111.70	110.60	110.80
C(3)-N(2)-Co	110.37	109.80	110.10	109.50	110.20	109.50
Dihedral angles (in deg.)						
Co-N(1)-C(1)-C(2)	67.98	76.38	68.20	75.93	69.22	77.42
N(1)-C(1)-C(2)-C(3)	67.71	40.20	68.17	40.28	69.10	40.65
C(1)-C(2)-C(3)-N(2)	67.71	40.20	68.17	40.28	69.10	40.65
C(2)-C(3)-N(2)-Co	67.98	76.38	68.20	75.93	69.22	77.42

^a C= chair conformation, TB= twist-boat conformation.

^b Numbering scheme for the atoms is given in Fig. 1.

of 2.9 kcal/mol in favour of the chair form. The twist-boat was destabilized over the chair due almost entirely to the torsional strain. Similar calculations using FF-2 and FF-3 yielded energy differences of 2.6 and 2.9 kcal/mol, respectively, in favour of the chair conformation. Comparison of energy differences and geometry parameters obtained with all three force fields (Table 4) indicates that the final equilibrium conformation of a single Co-tn ring is relatively independent of the force field. Torsional angles were evenly distributed in the minimized chair form of the chelate ring, all being $68^\circ \pm 1$. In the minimized twist-boat form dihedral angles of N-C-C-C and Co-N-C-C type were $40^\circ \pm 1$ and $76^\circ \pm 1$, respectively. The torsional strain, therefore, remained much higher in the latter. In addition to the torsional strain, which contributes mostly to the energy difference between chair and twist-boat conformations, the H...H non-bonded and other 1,4 non-bonded interactions although relieved to approximately the same extent in both conformations are slightly more pronounced in the twist-boat form. The chelate angle (N-Co-N) is increased by $1-2^\circ$ in both chair and twist-boat minimized conformations, which does not necessarily mean that similar widening should be expected in Co-tn₃. Although in the treatment of the single Co-tn ring ligands other than the two nitrogens were ignored it is to be expected that the chair conformation of the ring should be preferred over the twist-boat conformation in complexes of the type [Co(tn)(X₄)] at least for relatively small ligands, X. Minimization was carried out without any symmetry constraint. Nevertheless the initial symmetries of the chelate rings (*C*₂ for twist-boat and *C*_s for chair) were preserved whereas the endocyclic bonds were slightly stretched and the endocyclic angles were widened (Table 4).

Tris-chair conformations of Co-tn₃

Next we have examined the idealized and the X-ray conformations of Co-tn₃. The chair₃ form was of special interest since it was the conformation found by X-ray diffraction studies.⁹ The strain energy of the initial idealized chair₃ form was extremely high due to the inter-annular non-bonded H...H repulsions between amino-groups and terminal methylene groups, *i.e.*, three distances of 1.109 Å between H(8)...H(19), H(18)...H(29), and H(28)...H(9), and three distances of 1.417 Å between H(3)...H(20), H(13)...H(30), and H(23)...H(10). By minimization these distances were increased to 2.071 Å and 2.022 Å, respectively. These interactions involve only the hydrogen atoms from amino groups occupying one of the octahedral faces perpendicular to the *C*₃ axis, whereas inter-annular non-bonded H...H interactions involving the other three amino groups are of the same order of magnitude as the intra-annular (axial-axial) interactions. The inequality of the two sets of NH₂ groups in chair₃ is a corollary of its lower symmetry (*C*₃) as compared to the symmetry of the twist-boat₃ (*D*₃).

During the minimization of the idealized chair₃ either with inclusion of the N-Co-N bending terms (FF-1), or with inclusion of the non-bonded terms for N...N interactions instead (FF-3), it was observed that the chelate angles contract considerably in order to relieve the non-bonded inter-annular H...H

interactions. However, carrying out the minimization with the X-ray structure as the initial conformation we arrived at a conformation with a considerably lower energy in which the three chelate angles remained larger than or equal to 90° . We therefore suspected that the minimized idealized chair₃ had been trapped in a local minimum far from the extreme minimum for that system. In order to overcome this situation we chose a different route for the minimization, *i.e.*, starting with the idealized chair₃ we carried out the usual minimization under the constraint that the nitrogens remain fixed at their initial positions at the apices of the octahedron. The conformation thus produced served subsequently as the starting point for the complete minimization. In this way we arrived at a lower minimum with a much better correlation between the geometry parameters in the minimized chair₃ and X-ray chair₃ conformation (Figs. 3(a), 4, and 5).

Minimization of the X-ray chair₃ conformation causes the structure to approach slowly the C_3 symmetry and the chelate angles to decrease. Although the minimization of the X-ray structure does not lead to a conformation which is identical to that obtained from the idealized chair₃ when terminated ac-

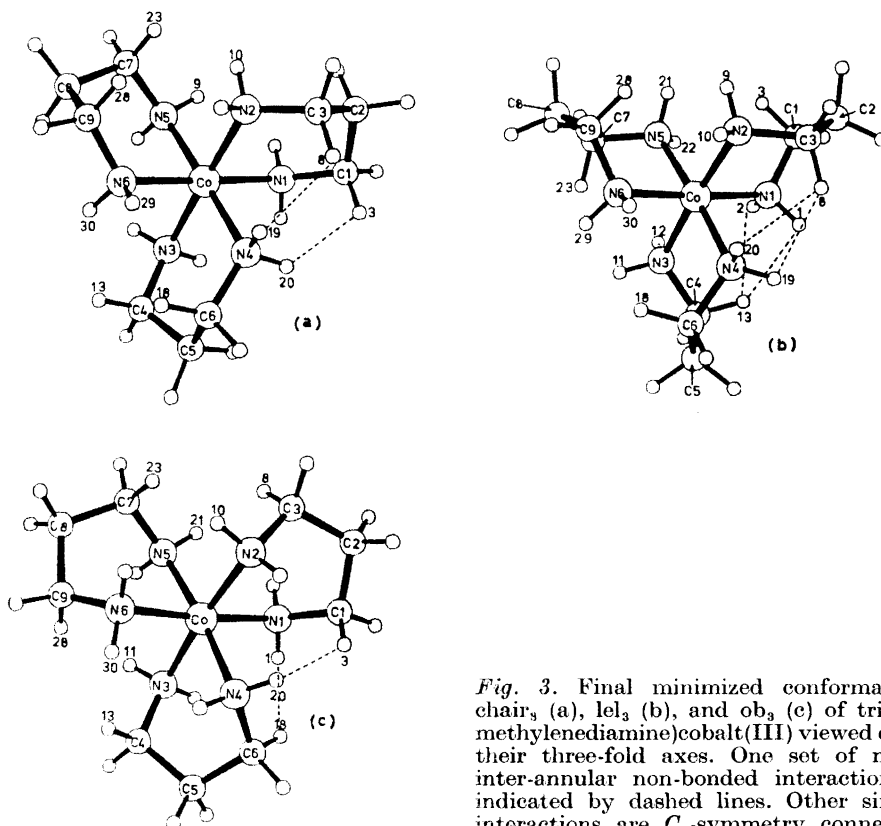


Fig. 3. Final minimized conformations chair₃ (a), 1el₃ (b), and ob₃ (c) of tris(trimethylenediamine)cobalt(III) viewed down their three-fold axes. One set of major inter-annular non-bonded interactions is indicated by dashed lines. Other similar interactions are C_3 -symmetry connected.

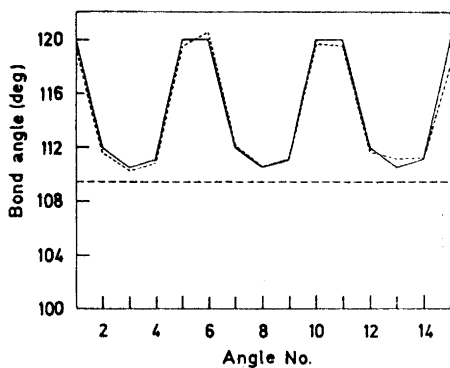


Fig. 4. Endocyclic bond angles in minimized idealized chair₃ (—), and in minimized X-ray chair₃ (- - -) conformations of Co tn₃. Angle numbers: 1. Co-N(1)-C(1), 2. N(1)-C(1)-C(2), 3. C(1)-C(2)-C(3), 4. C(2)-C(3)-N(2), 5. C(3)-N(2)-Co, 6. Co-N(3)-C(4), 7. N(3)-C(4)-C(5), 8. C(4)-C(5)-C(6), 9. C(5)-C(6)-N(4), 10. C(6)-N(4)-Co, 11. Co-N(5)-C(7), 12. N(5)-C(7)-C(8), 13. C(7)-C(8)-C(9), 14. C(8)-C(9)-N(6), and 15. C(9)-N(6)-Co (cf. Fig. 3 (a)).

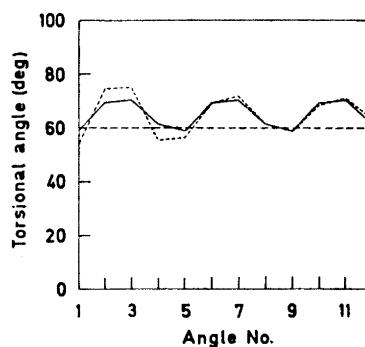


Fig. 5. Torsional angles in minimized idealized chair₃ (—), and in minimized X-ray chair₃ (- - -) conformations of Co tn₃. Angle numbers: 1. Co-N(1)-C(1)-C(2), 2. N(1)-C(1)-C(2)-C(3), 3. C(1)-C(2)-C(3)-N(2), 4. C(2)-C(3)-N(2)-Co, 5. Co-N(3)-C(4)-C(5), 6. N(3)-C(4)-C(5)-C(6), 7. C(4)-C(5)-C(6)-N(4), 8. C(5)-C(6)-N(4)-Co, 9. Co-N(5)-C(7)-C(8), 10. N(5)-C(7)-C(8)-C(9), 11. C(7)-C(8)-C(9)-N(6), and 12. C(8)-C(9)-N(6)-Co (cf. Fig. 3 (a)).

According to the above-mentioned criterion ($\delta_E \leq 0.002$ kcal mol⁻¹) it is reasonable to suppose that they represent points in the same shallow minimum of the potential energy surface. In order to check — if not prove — this assumption we have constructed an “average conformation” from the two minimized conformations, *i.e.* one in which the Cartesian atomic coordinates for each atom were taken as the mean values of the corresponding coordinates in the minimized conformations. As expected, the energy of this average conformation was intermediate between the two minimized energies and it remained unchanged when the conformation was subjected to the minimization procedure. In particular this minimum or “valley” seems to be flat with respect to the variations of the N-Co-N angles in either direction from the “zero-strain” value of 90°. If so, the differences between X-ray and minimized chair₃ conformations may be attributed to specific crystal forces. In fact the chelate angle in the Co-tn ring is known to vary considerably in varying environment, *e.g.*, \angle N-Co-N = 87.7° in Co tn₂(NO₃)₂,^{12a} 95.4° in Co tn₂Cl₂,^{12b} 90.2° in Co en₂tn.¹¹

Bond lengths were slightly stretched in the minimized idealized chair₃ (Table 5) but are still within the ranges of the values found by the X-ray diffraction study.⁹ Endocyclic bond angles were opened out from their assumed tetrahedral “zero-strain” values (Fig. 4 and Table 5). The N-C-C and C-C-C angles were in the range 119.5 to 120.5°, and 110.0 to 111.5°, respectively. Similar widening was also observed in the X-ray structure.⁹ Dihedral angles of the type Co-N-C-C are lower than those of the type

Table 5.^{a,b} Minimized conformations of tris(trimethylenediamine)-cobalt(III).

Bond lengths (in Å)	chair ₃		1el ₃		ob ₃	
	FF-1	FF-2	FF-1	FF-2	FF-1	FF-2
Co-N(1)	2.060	2.035	2.035	2.015	2.054	2.025
N(1)-C(1)	1.480	1.475	1.474	1.470	1.476	1.472
C(1)-C(2)	1.542	1.538	1.547	1.544	1.549	1.545
C(2)-C(3)	1.542	1.538	1.547	1.544	1.548	1.546
C(3)-N(2)	1.477	1.473	1.474	1.469	1.476	1.472
N(2)-Co	2.049	2.030	2.035	2.012	2.053	2.025
Bond angles (in deg.)						
N(2)-Co-N(1)	89.35	89.79	89.14	90.98	88.02	90.14
Co-N(1)-C(1)	120.03	119.36	113.78	111.79	113.85	111.77
N(1)-C(1)-C(2)	111.98	111.60	112.08	111.61	111.83	111.40
C(1)-C(2)-C(3)	110.49	109.95	113.28	113.01	112.71	112.71
C(2)-C(3)-N(2)	111.11	110.94	112.06	111.73	111.96	111.33
C(3)-N(2)-Co	120.08	118.68	113.80	111.76	113.72	111.86
Dihedral angles (in deg.)						
Co-N(1)-C(1)-C(2)	58.73	60.02	73.86	74.70	75.06	75.70
N(1)-C(1)-C(2)-C(3)	69.52	69.73	37.58	38.84	37.76	38.77
C(1)-C(2)-C(3)-N(2)	70.48	71.26	37.65	38.80	38.39	39.42
C(2)-C(3)-N(2)-Co	61.20	62.90	73.87	74.74	75.16	75.60

^a Numbering scheme for the atoms is given in Fig. 3.

^b Corresponding geometry parameters for the other two chelate rings are C_3 -symmetry connected and therefore identical to the values presented in the table.

N-C-C-C in the minimized idealized chair ($59 \pm 2^\circ$ against $70 \pm 2^\circ$) as well as in the crystal structure (56.7° against 67.1° *). This indicates a similar mode of puckering of the chelate rings which are flattened out in the "inner" moiety (*i.e.*, C-N-Co-N-C fragment) and puckered in the outer one (*i.e.*, N-C-C-C-N fragment).

Symmetrical twist-boat₃ conformations of Co tn₃

Next we have examined two symmetrical twist-boat₃ conformations: 1el₃ and ob₃. As the bond lengths and angles of the initial idealized forms are at their equilibrium values the only sources of steric energy are non-bonded interactions and torsional strain.

However, the diastereoisomeric conformations 1el₃ and ob₃ differed only in the non-bonded interactions. Dominant non-bonded repulsions in 1el₃ conformation arise from interactions within the following six symmetry con-

* Mean value for all three rings.

nected pairs: H(8)...H(19), H(18)...H(29), H(28)...H(9), H(2)...H(13), H(12)...H(23), and H(22)...H(3), in which the initial interatomic distance of 1.98 Å increased to 2.28 Å during the minimization. There were six more contacts of 2.08 Å (increased to 2.23 Å) between H(8)...H(20), H(18)...H(30), H(28)...H(10), H(1)...H(13), H(11)...H(23), and H(21)...H(3). Corresponding dominant inter-annular H...H distances in the ob_3 conformation were: H(1)...H(18), H(11)...H(28), H(21)...H(8), H(3)...H(20), H(13)...H(30), and H(23)...H(10), all of 1.64 Å, which were increased to 2.14 Å in the minimized conformations. Other H...H non-bonded distances were of the same order of magnitude as intra-annular non-bonded distances. Calculated geometry parameters for lel_3 and ob_3 conformations obtained with different force fields are presented in Table 5. There is a slight difference between the equilibrium geometry parameters calculated using the two force fields FF-1 and FF-2. The distortions of the initial idealized structures were smaller when the minimization was carried out with FF-2 in lel_3 as well as in ob_3 conformation. This is due to the nature of the potential function for non-bonded H...H interactions chosen for FF-2 which is of the "soft" type. On the other hand differences in final geometry parameters between lel_3 and ob_3 might be regarded as a consequence of inter-annular non-bonded interactions which were more pronounced in the ob_3 conformation. With FF-1 (and FF-3) the chelate angles in lel_3 and ob_3 minimized conformations were $\sim 89.1^\circ$ and $\sim 88.0^\circ$, respectively. However, with the FF-2 ("soft" H...H non-bonded potential function) the final equilibrium angles were 90.98° for lel_3 and 90.14° for the ob_3 form (recall the widening of N-Co-N angles in the minimized single Co-tn chelate rings). The range of torsional angles were: 73.2° to 75.5° for Co-N-C-C type, and 37.4° to 39.4° for N-C-C-C type, both in lel_3 and ob_3 conformations of Co tn_3 . The difference between the two types of dihedral angles indicates a considerably twisted shape of chelate rings in these conformations. Final minimized geometries are shown in Figs. 3(b) and (c).

Mixed conformations of Co tn_3

Next we have examined the ten sterically possible mixed conformations of Co tn_3 (see Table 1). It was found that whenever both lel and ob rings are present as in lel_2ob and ob_2lel there exist strong inter-annular H...H repulsions between, *e.g.*, H(1)...H(18) and H(7)...H(19), where the distances are 1.64 and 1.44 Å, respectively (Fig. 6). Furthermore, it was found that $E_{lel_2ob} < E_{ob_2lel}$. Because of the strong inter-annular repulsions the energies of these two conformers exceed those of the pure lel_3 and ob_3 and of any of the remaining eight mixed conformers. This is contrary to the order of conformational energies in the Co en_3 species.^{6,30}

Three mixed forms consisting of chair and ob ring conformations: ob_2chair , (C_1) - $chair_2ob$, and *anti*- $chair_2ob$, were found to have nearly the same energies slightly below that of the pure ob_3 form. Similarly, three mixed forms consisting of chair and lel ring conformations: (C_1) - $chair_2lel$, lel_2chair , and *anti*- $chair_2lel$, were lower in energy than (or comparable to) the pure (C_3) - $chair_3$ form.

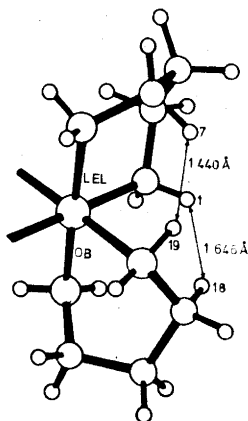


Fig. 6. The lel-ob interactions in "mixed" conformations of Co tn_3 .

Finally there were two mixed forms with three different ring conformations: *cis*_(lel, chair)-lel ob chair, and *trans*_(lel, chair)-lel ob chair. The high energy of these conformations was due to the lel-ob inter-annular interactions.

Tris(*R,R*-2,4-diaminopentane)cobalt(III)

The most favourable conformation of a single $\text{Co}(R,R\text{-}2,4\text{-ptn})$ ring is undoubtedly the λ -twist-boat which permits both of the methyl groups to become equatorial. (The chair and the δ -twist-boat have one and two axial substituents, respectively.) Furthermore, molecular models show very convincingly that the presence of chair and δ -twist-boat rings in a tris complex may be excluded, whereas the tris (λ -twist-boat) appears very favourable. Therefore, $\text{Co}(R,R\text{-}2,4\text{-ptn})_3$ complex ion is expected to have lel₃ conformation for Δ absolute configuration, and ob₃ conformation for Λ absolute configuration. This was indeed found by the X-ray diffraction study¹⁰ of $(+)_546\text{-}[\text{Co}(R,R\text{-}2,4\text{-ptn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ for which the Δ absolute configuration and ob₃ chelate ring conformation were established. A preliminary examination of Δ -lel₃ and Λ -ob₃ conformations of $\text{Co}(R,R\text{-}2,4\text{-ptn})_3$ was carried out. Minimized geometries are summarized in Table 6 and Fig. 7.

Table 6.^{a,b} Minimized conformations of tris(*R,R*-2,4-diaminopentane)cobalt(III).

Bond lengths (in Å)	ob ₃	lel ₃
Co - N(1)	2.07	2.04
Co - N(2)	2.07	2.04
N(1) - C(1)	1.48	1.48
N(2) - C(3)	1.48	1.48
C(1) - C(2)	1.55	1.55
C(2) - C(3)	1.55	1.55
C(1) - C(4)	1.55	1.55
C(3) - C(5)	1.55	1.55

Table 6. Continued.

Bond angles (in deg.)		
N(1)–Co–N(2)	87.36	89.14 ₅
Co–N(1)–C(1)	112.41	113.50
Co–N(2)–C(3)	112.48	113.42
N(1)–C(1)–C(2)	110.63	111.51
N(2)–C(3)–C(2)	110.69	111.47
N(1)–C(1)–C(4)	110.57 ₅	109.89
N(2)–C(3)–C(5)	110.69	109.89
C(1)–C(2)–C(3)	112.36	113.39
C(4)–C(1)–C(2)	109.45	109.96
C(5)–C(3)–C(2)	109.52	109.95
Dihedral angles (in deg.)		
Co–N(1)–C(1)–C(2)	77.81	74.42
Co–N(1)–C(1)–C(4)	160.76	163.39
N(1)–C(1)–C(2)–C(3)	39.62	37.72
C(4)–C(1)–C(2)–C(3)	161.71	159.87
C(1)–C(2)–C(3)–N(2)	39.37	38.13
C(1)–C(2)–C(3)–C(5)	161.69	160.24
Co–N(2)–C(3)–C(2)	77.62	74.60
Co–N(2)–C(3)–C(5)	160.75 ₅	163.26

^a Numbering scheme for the atoms is given in Fig. 7.

^b Corresponding geometry parameters for the other two chelate rings are C_3 -symmetry connected and therefore identical to the values presented in the table.

Short of fractional crystal coordinates we were unable to compare the calculated and observed¹⁰ structures except for the value of chelate angles. Observed¹⁰ N–Co–N angles are all less than 90°, the average being $87.9 \pm 1.3^\circ$, which is in very good agreement with the calculated value of 87.36° for ob_3 conformer. Calculated chelate angles in the $1el_3$ form are also less than 90° (Table 6). The contraction of the N–Co–N angles may be considered as a consequence of inter-annular non-bonded repulsions which are relieved in the similar way as in the Co tn_3 .

CONCLUDING REMARKS

Relative minimized energies of Co tn_3 conformations are given in Fig. 8 together with earlier results of similar calculations by Gollogly and Hawkins³¹ and by Geue and Snow.^{5†} The energy terms for “pure” tris conformations of Co tn_3 are specified in Table 7 and the energy terms for two twist-boat₃ conformations of Co ptn_3 in Table 8.*

* Numerical values for the energies of conformations not included in Table 7 and Cartesian atomic coordinates of conformations studied in this work may be obtained from the authors upon request.

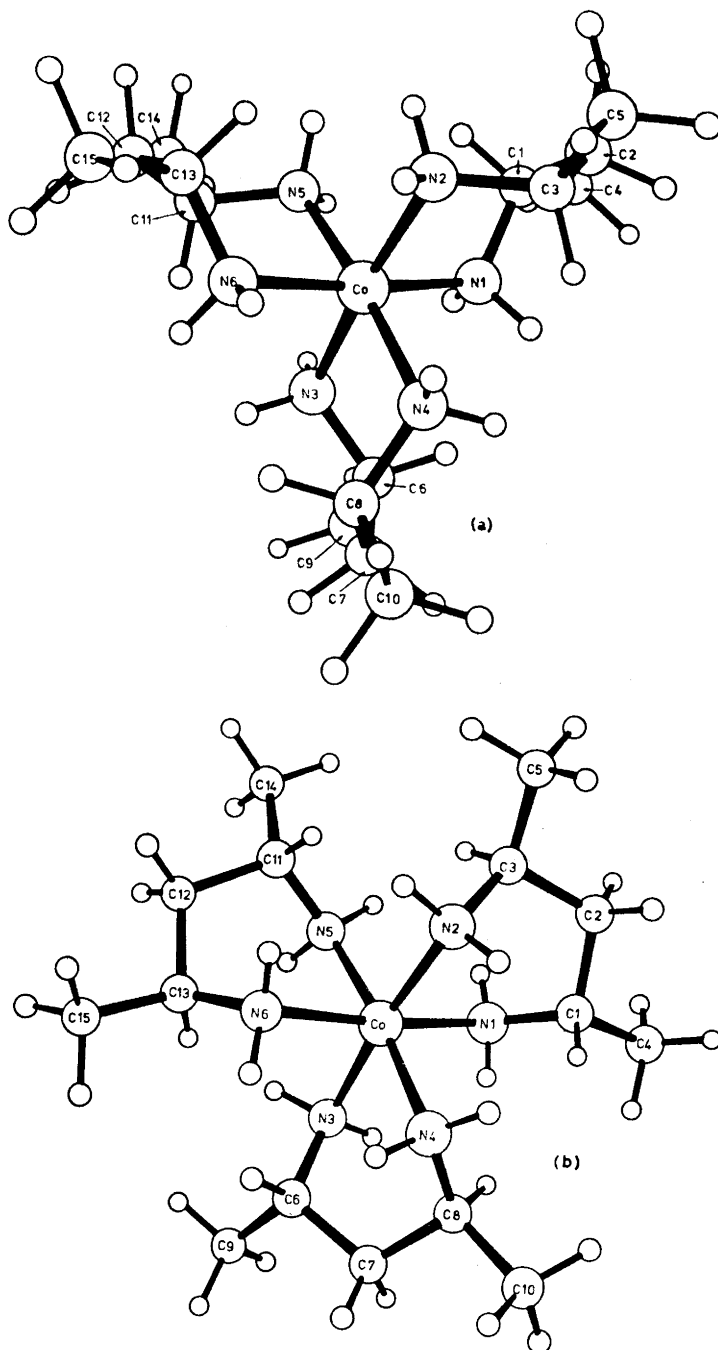


Fig. 7. Final minimized lel_3 (a) and ob_3 (b) conformations of tris(2,4-diaminopentane)-cobalt(III).

Table 7. Energy contributions for the "pure" tris conformations of Co tn_3 (kcal mol⁻¹).

FF-1	1el ₃	minimized X-ray	chair ₃	ob ₃	X-ray
Bond stretching	1.11	2.84	2.57	2.55	0.63
H...H non-bonded	7.47	9.45	10.13	10.38	16.80
Other non-bonded	-6.13	-7.47	-7.38	-6.67	-5.91
N-Co-N bending	0.03	0.18	0.02	0.17	1.03
Endocyclic bend.	2.77	5.85	6.49	2.40	5.71
Exocyclic bend.	0.88	2.16	2.38	1.62	4.84
Torsional	7.36	1.62	0.94	7.72	0.98
Total energy	13.49	14.63	15.15	18.19	24.08
Conformational energy	0.00	1.14	1.66	4.70	10.59
FF-2					
Bond stretching	0.19	0.80	0.93	0.63	0.51
H...H non-bonded	-9.38	-6.17	-7.03	-7.21	-5.14
Other non-bonded	-20.99	-23.07	-23.15	-22.36	-23.10
N-Co-N bending	0.04	0.39	0.00	0.00	1.03
Endocyclic bend.	1.70	3.30	5.20	1.42	5.71
Exocyclic bend.	0.35	1.25	1.42	0.54	1.92
Torsional	7.25	1.66	1.07	7.46	0.88
Total energy	-20.84	-21.84	-21.56	-19.52	-18.19
Conformational energy	1.00	0.00	0.28	2.32	3.65

Table 8. Energy contributions for the Co(*R,R*-2,4-ptn)₃ conformations (kcal mol⁻¹).

FF-1	Δ -ob ₃ (C ₃)	Δ -1el ₃ (C ₃)
Bond stretching	4.78	2.06
H...H non-bonded	10.95	5.89
Other non-bonded	-6.55	-6.27
N-Co-N bending	0.31	0.03
Endocyclic bending	1.34	2.38
Exocyclic bending	0.56	0.83
Torsional	8.04	7.70
Total energy	19.44	12.63
Conformational energy	6.81	0.00

One of the questions originally raised in this context was whether the most stable conformation could be predicted with some degree of certainty by conformational analysis. In the first primitive calculations,^{5b,17,29} in which only

“pure” tris conformations were considered, the $1e_3$ was found to be lowest in energy. Calculations by Gollogly and Hawkins,³¹ already at a considerably higher level of sophistication in which they attempt a partial mapping of the energy surface for “pure” tris conformations, led to the result that the $chair_3$ is the most stable conformation. Snow’s calculations^{5f} which involve a complete minimization procedure, not very different from ours, and which are based on a force field very similar to our FF-1 again place $1e_3$ below $chair_3$. We have extended the calculations to include “mixed” conformations, as well as the unsymmetrical “pure” tris conformations (*e.g.* the X-ray conformation), and we have studied the effect of replacing a force field with relatively “hard” non-bonded H...H interactions and “soft” skeleton interactions (FF-1) by one with relatively “hard” skeleton but “soft” H...H non-bonded interactions (FF-2). The results are evident from Fig. 8.

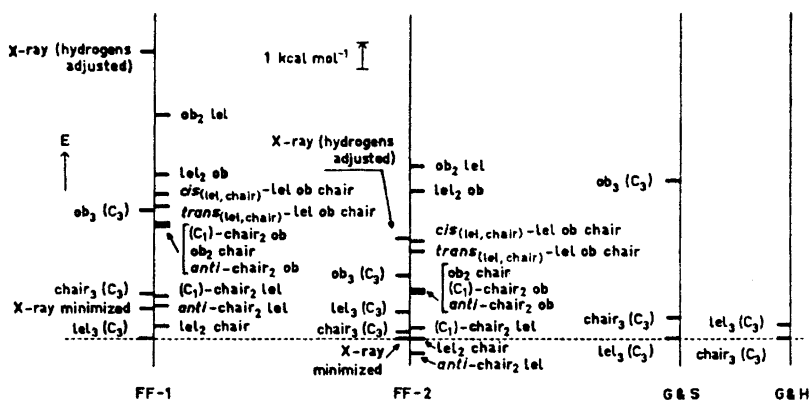


Fig. 8. Comparison of minimized energies of $Co\ tn_3$ conformations. Symbols are explained in Table 1. G & S = results by Geue and Snow,^{5f} G & H = results by Gollogly and Hawkins.³¹ X-ray (hydrogens adjusted) indicates the energy of a conformation obtained by supplementing the skeleton obtained from the X-ray structure⁹ with hydrogens, and minimizing with respect to the positions of the hydrogens but keeping the non-hydrogen atoms fixed. (Subsequent minimization of this conformation with respect to all the atoms led to the same result as a minimization carried directly on the supplemented X-ray conformation.)

We conclude that at the present state of the art one can not by conformational analysis definitively identify the most stable conformation — not even of the gaseous ion, let alone the ion in solution. However, we think it is a safe conclusion that in solution at room temperature a conformational equilibrium involving significant amounts of two or more conformers — probably including “mixed” forms — prevails. This is in good agreement with considerations by Mason and co-workers^{5e} although they did not take “mixed” conformations into account.

A further point should be kept in mind when one considers results as those given in Fig. 8. As indicated in our discussion of the minimization of the tris-chair conformation the potential energy surface of the system is complicated

enough to make the minimum actually reached by the program dependent not only on the starting conformation but also on the initial route of minimization. Therefore there is reason to believe that by further exploration of the energy surface conformations of even lower energy than those indicated in Fig. 8 may be found. *E.g.*, it seems likely that the removal of the C_3 symmetry constraint from a minimized conformation generally will make a further small but significant minimization possible. Although by further investigation lower conformational energy minima than those indicated in Fig. 8 may be located, we have at present no indication that the above conclusions or the general features of the conformational distribution as presented in Fig. 8 will be invalidated.

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