

Conformational Analysis of Coordination Compounds. III.

Tris-diamine Cobalt(III) and Chromium(III) Complexes with Six-membered Chelate Rings

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A fast convergent minimization programme is applied to calculate equilibrium conformations of coordination compounds.

Energy equations containing harmonic bond stretching and angle bending functions, Pitzer-type torsional functions, and Buckingham-type functions for non-bonded interactions (with parameters chosen previously) were used to calculate equilibrium geometries and energies of all possible conformers of the tris(1,3-propanediamine)cobalt(III) system and of ten species of the tris(2,4-pentanediamine)cobalt(III) system.

These calculations demonstrate that various previously suggested conformations of the same type converge to a common equilibrium conformation having the highest possible symmetry. The (C_3)-chair₃ conformer represents the global minimum in the force field chosen. Distribution of equilibrium conformations on an energy scale is governed by a delicate balance of all energy contributions. It is suggested that the effect of long range non-bonded interactions is not negligible.

The shapes of chair and twist-boat chelate rings are discussed in detail, and comparison with X-ray structures is made in terms of the deviations from idealized ring geometries.

In previous papers¹ two of us investigated the capability of a steepest-descent energy minimization based on Wiberg's programme² for the conformational analysis of tris-diamine metal complexes.

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The conclusions of the earlier work were that (1) several energetically almost equivalent conformations should exist in equilibrium in solution; (2) with the steepest-descent method one cannot definitively identify the most stable conformation; (3) different initial conformations of the same gross conformational type did not coalesce during minimization. The main deficiency of the approach is due to the intrinsic limitation of the steepest-descent algorithm, namely the extremely slow convergence when a system is close to its minimum. Therefore the termination criterion adopted was the attainment of identical rates of convergence for different conformations rather than true convergence.

In the present work a more refined energy minimization was employed, leading to true convergence. A programme was developed,³ based on the Consistent Force Field (CFF) approach of Lifson and Warshel,⁴ with a very flexible structure and a minimum of input requirements. The work reported here was undertaken with a twofold aim: (1) to evaluate the performance of the energy minimization part of our version of the CFF system; and (2) to further refine the results of the former calculations,¹ using the same force field. We confined our investigations to complexes with six-membered metal-chelate rings represented by $M(tn)_3$ and $M(2,4-ptn)_3$, where $tn =$ trimethylenediamine = 1,3-propanediamine and $2,4-ptn =$ 2,4-pentanediamine. Comparisons with

experimental structures were done for M = Co(III) and, in two cases, Cr(III). The results were also compared with other relevant calculations of a similar nature.

THE PROGRAMME

It is our intention to present elsewhere a full documentation of the version ³ of the CFF system ^{4,5} developed at Chemistry Department A of the Technical University of Denmark. Therefore we shall give here only a short account of the main features.

The types of potential energy functions (the "force field") are chosen automatically by the programme from two control parameters. Harmonic, anharmonic and Morse functions are possible choices for bond stretching; harmonic or Urey-Bradley for angle bending; Pitzer-type for torsions; and Lennard-Jones or Buckingham, plus Coulomb terms, for non-bonded interactions.

The programme reads a molecular formula written in a line notation very close to the usual chemical one, and constructs the topology of the molecule as lists of all types of interactions according to the force field chosen. Chirality symbols *R* and *S* are used for dissymmetric carbon or other atoms; for metal atoms *R* and *S* are interpreted as Δ and Λ .

Molecular geometry in cartesian coordinates is either calculated from a built-in library of standard bond lengths and valence angles, according to the topology, or is taken from a previous calculation or from a crystal structure determination. Transformation from fractional coordinates and unit cell parameters is performed with a separate utility programme.

Conformational energy and analytical first and second derivatives are calculated according to the force field chosen and the type of calculation specified. This part of the programme is usually called an appreciable number of times during a minimization run.

A hierarchy of three gradient algorithms was developed for energy minimization. (1) After investigating various steepest-descent algorithms,^{3,6,7} we abandoned all as they either were too slow, became oscillatory or required frequent changes in the programme to optimize their functioning on different types of molecules. We therefore developed an algorithm of our

own, which was reasonably fast and would automatically work well on all problems tackled so far. (2) Our next choice was a variable metric method, the Davidon-Fletcher-Powell algorithm.⁸ We introduced a few minor changes in a routine, which was a standard one at The Weizmann Institute of Science in 1970. (3) As the most powerful method in terms of convergence rate we used a modified Newton, second-order gradient algorithm (MNA) developed by Gill, Murray, and Picken.⁹ It is based on the Cholesky factorisation of the Hessian matrix of second derivatives, and it is both stable and relatively fast. The original ALGOL procedure was completely rewritten to conform with our addressing of the Hessian matrix and with our FORTRAN library.

It may happen that convergence is slow, even with the Newton method. In such cases a separate utility programme is used to scramble the conformation by adding randomly generated increments to all cartesian coordinates of the conformer. Subsequent minimization has not yet failed to converge properly.

Convergence to a true minimum was considered adequate when all partial derivatives of potential energy with respect to cartesian coordinates were reduced to $<10^{-6}$ kcal mol⁻¹ Å⁻¹. A typical minimization of a previously¹ minimized complex molecule of 46–64 atoms, using 20–50 steepest-descent and 5–8 Newton iterations, required 2–3 min on an IBM 370/165 and 380K without overlay structure.

CALCULATIONS

Stereochemistry. All structures studied in this work contain three six-membered metal chelate rings in an octahedral environment. Their stereochemistry and nomenclature proposals were previously described in detail.¹⁴

There are 16 theoretically possible conformers of the M(tn)₃ system¹⁴ for each of the absolute octahedral configurations Δ and Λ , in which the individual chelate rings adopt any of the three stable conformations: *chair*, δ -*twist-boat*, and λ -*twist-boat*. Three of these: *chair*, le_3 [= $\Lambda(\lambda\lambda\lambda)$ or $\Lambda(\delta\delta\delta)$], and ob_3 [= $\Delta(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$] of idealized symmetries *C*₃, *D*₃ and *D*₃, respectively, will be termed *homoconformational*. The other 13 forms containing two or three rings of different conformations, or

different orientations of chair conformations,^{1a} are termed *heteroconformational*.

Among the numerous theoretically possible isomers of the $M(2,4\text{-ptn})_3$ system three species — each of which containing three identical stereoisomers of coordinated diamine (*i.e.*, either $2R,4R$ -, or $2S,4S$ -, or *meso*- $2,4\text{-ptn}$) — are of chemical interest. Equatorial preference of all methyl groups limits the number of conformers to one for each stereoisomer of $2,4\text{-ptn}$ as shown in Table 1. (See also Fig. 7 of Ref. 1a.) Two other sets of theoretically possible homoconformational forms of $M(2,4\text{-ptn})_3$ comprise four $(\text{eq})_3(\text{ax})_3$ conformers having C_3 symmetry (also shown in Table 1), and three hexa-axial conformers (not shown in Table 1). All other conformers having a distribution of methyl groups different from $(\text{eq})_3$, $C_2\text{-}(\text{eq})_2(\text{ax})_2$, or $(\text{ax})_6$ are heteroconformational. They are derived either from heteroconformational forms of the basic $M(\text{tn})_3$ skeleton, or from species containing different stereoisomers of coordinated $2,4\text{-ptn}$. A set of four conformers of the latter type is exemplified in Table 1. They were investigated in an attempt to study the effect of one methyl group in an axial position.

Initial coordinates. The starting conformations were taken as the "final minimized conformations" obtained from our former calculations.^{1a} All distinct forms resulting from various minimizations of the same conformer were subjected to the refinement procedure.

In addition, calculations were carried out on $M(\text{tn})_3$ conformations corresponding to those found by X-ray diffraction studies on $(-)_D\text{-}[\text{Co}(\text{tn})_3]\text{Br}_3 \cdot \text{H}_2\text{O}$;¹⁰ $(-)_D\text{-}[\text{Co}(\text{tn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$;¹¹ $[\text{Cr}(\text{tn})_3][\text{Ni}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$;¹² as well as on $M(2,4\text{-ptn})_3$ conformations found in $(+)_\text{546}\text{-}[\text{Co}(2R,4R\text{-ptn})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ ^{13a} and $(-)_\text{546}\text{-}[\text{Co}(2R,4R\text{-ptn})_3]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$.^{13a}

Force field. In the previous work^{1a} two force fields were used, FF-1 and FF-2. In the present work, we have used only FF-1. In a series of calculations on $\text{Co}(\text{tn})_3$ conformations FF-1 was supplemented with $\text{Co}\cdots\text{C}$ and $\text{Co}\cdots\text{H}$ non-bonded interactions with parameter values similar to those used for $\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{H}$ interactions, respectively. These modifications produced only insignificant changes in the final results and were not studied further.

RESULTS

Tris(trimethylenediamine) conformations. The initial conformations, on which the present minimizations were carried out, were 41 distinct conformations of the $M(\text{tn})_3$ system, part of which were minimized previously.^{1a} They comprised three idealized* homoconformational forms (chair_3 , 1el_3 , and ob_3) minimized in FF-1; the same three forms minimized in FF-2;

* The term idealized means that the conformation in question was generated from standard bond lengths and valence angles, with torsional angles chosen to fit the desired conformation.

Table 1. Some of the theoretically possible conformations of $M(2,4\text{-ptn})_3$ exemplified for the overall Δ absolute configuration.^a

Isomer	Methyl groups		
	$(\text{eq})_6$	$(\text{eq})_2(\text{ax})_4$	$(\text{eq})_3(\text{ax})_3$
Homoconformational			
$M(2R,4R\text{-ptn})_3$	$\text{1el}_3 (D_3)$	—	$\text{chair}_3 (C_3)$
$M(2S,4S\text{-ptn})_3$	$\text{ob}_3 (D_3)$	—	$\text{chair}_3 (C_3)$
$M(\text{meso-}2,4\text{-ptn})_3$	$\text{chair}_3 (C_3)$	—	$\text{1el}_3, \text{ob}_3 (C_3)$
Heteroconformational			
$M(\text{meso-}2,4\text{-ptn})_2(2R,4R\text{-ptn})$	—	$\text{chair}_3 (C_1)$	—
$M(\text{meso-}2,4\text{-ptn})_2(2S,4S\text{-ptn})$	—	$\text{chair}_3 (C_1)$	—
$M(2R,4R\text{-ptn})_2(\text{meso-}2,4\text{-ptn})$	—	$\text{1el}_3 (C_1)$	—
$M(2S,4S\text{-ptn})_2(\text{meso-}2,4\text{-ptn})$	—	$\text{ob}_3 (C_1)$	—

^a Molecular symmetries are given in parentheses.

two chair₃ conformations corresponding to X-ray structures of the Co(tn)₃ ion; 10 idealized heteroconformational forms^{1a} minimized in FF-1 and FF-2; idealized and X-ray *syn*-chair₂lel conformations; *syn*-chair₂ob and (C₁)₁-chair₃ conformations; and eight (C₃)₁-chair₃ forms of M(tn)₃ artificially generated from various ring conformations of complexes containing trimethylenediamine of known X-ray structures; and an average (C₃)₁-chair₃ conformation obtained from minimized idealized and minimized X-ray conformations of Co(tn)₃.

Previously^{1a} we omitted three of the heteroconformational forms having a pair of *syn*-chair₂ rings partly because molecular models indicated that in their *idealized* forms they would be highly unstable. Meanwhile, the *syn*-chair₂lel conformation has been found in crystalline [Cr(tn)₃] [Ni(CN)₆]. 2H₂O.^{1a,b} Consequently, we have included in our calculations two *syn*-chair₂lel conformations: the one found by Jurnak and Raymond^{1a} and the idealized form which required a modified treatment^{1c} in order to be minimized successfully; and the *syn*-chair₂ob and (C₁)₁-chair₃ conformers.

All *prima facie* distinct forms of the same gross conformation converged to the unique conformation. The minimization procedure, therefore, led to 16 unique local-minimum conformations of the M(tn)₃ system.

Energy contributions for 16 M(tn)₃ conformations are given in Table 2, and distributions of bond lengths and valence angles are given in Table 3. Six examples of individual conformations are shown in Fig. 1.

One of the most remarkable results obtained here was that the same minimum-energy chair₃ conformation of M(tn)₃ was reached from all 13 distinct initial chair₃ conformations showing (a) the superiority of the present method, and (b) a proof of our assumption that various chair₃ conformations found before^{1a} belong to the same energy minimum on the potential energy surface of M(tn)₃. Furthermore, the (C₃)₁-chair₃ conformer was found to represent the global minimum of the M(tn)₃ system in FF-1 (see Table 2).

Another striking result of the minimizations was that each conformer showed a strong tendency to attain its highest possible symmetry (for the notation, see Table 1 in Ref. 1a) irrespective of the structure of its initial conformation. Thus, all chair₃ forms, including the X-ray structures, converged to the chair₃ conformation having rigorous C₃ symmetry; all lel₃ and ob₃ approached rigorous D₃ symmetry, *etc.*

The next lowest conformation minimized in FF-1 was lel₃ (< 1 kcal mol⁻¹ above the global minimum). The ob₃ and the remaining hetero-

Table 2. Energy contributions for M(tn)₃ conformations.^a

Conformer of M(tn) ₃	E _b	E _t	E _p	E _{nb}	E _T	ΔE
(C ₃) ₁ -chair ₃	1.61	9.39	2.80	-1.80	11.99	0.00
lel ₃	1.56	4.50	7.14	-0.41	12.79	0.80
lel ₂ chair	1.75	6.75	5.03	0.32	13.86	1.87
(C ₁) ₁ -chair ₃	2.08	9.89	2.63	-0.22	14.39	2.40
<i>syn</i> -chair ₂ lel	2.08	8.53	3.32	0.66	14.59	2.60
(C ₁) ₁ -chair ₂ lel	2.06	8.60	2.91	1.06	14.60	2.61
(C ₁) ₁ -chair ₂ ob	1.60	9.23	4.86	-0.90	14.79	2.80
<i>anti</i> -chair ₂ lel	1.93	9.28	2.74	1.04	15.00	3.01
<i>trans</i> _(chair, lel) -chair lel ob	1.65	8.04	6.05	0.09	15.82	3.83
<i>anti</i> -chair ₂ ob	2.39	8.58	3.48	1.56	16.01	4.02
ob ₂ chair	1.76	7.98	6.17	0.35	16.26	4.27
<i>syn</i> -chair ₂ ob	2.36	9.21	3.23	2.02	16.82	4.83
lel ₂ ob	1.48	6.67	8.58	0.59	17.32	5.33
<i>cis</i> _(chair, lel) -chair lel ob	2.23	8.04	5.38	2.40	18.05	6.06
ob ₃	2.32	6.11	7.60	2.22	18.26	6.27
ob ₂ lel	1.60	7.76	8.54	0.83	18.73	6.74

^a All energies are given in kcal mol⁻¹; E_b, E_t, E_p, E_{nb}, E_T, and ΔE are bond stretching, angle bending, torsional and non-bonded contributions, total energy, and energy relative to (C₃)₁-chair₃, respectively.

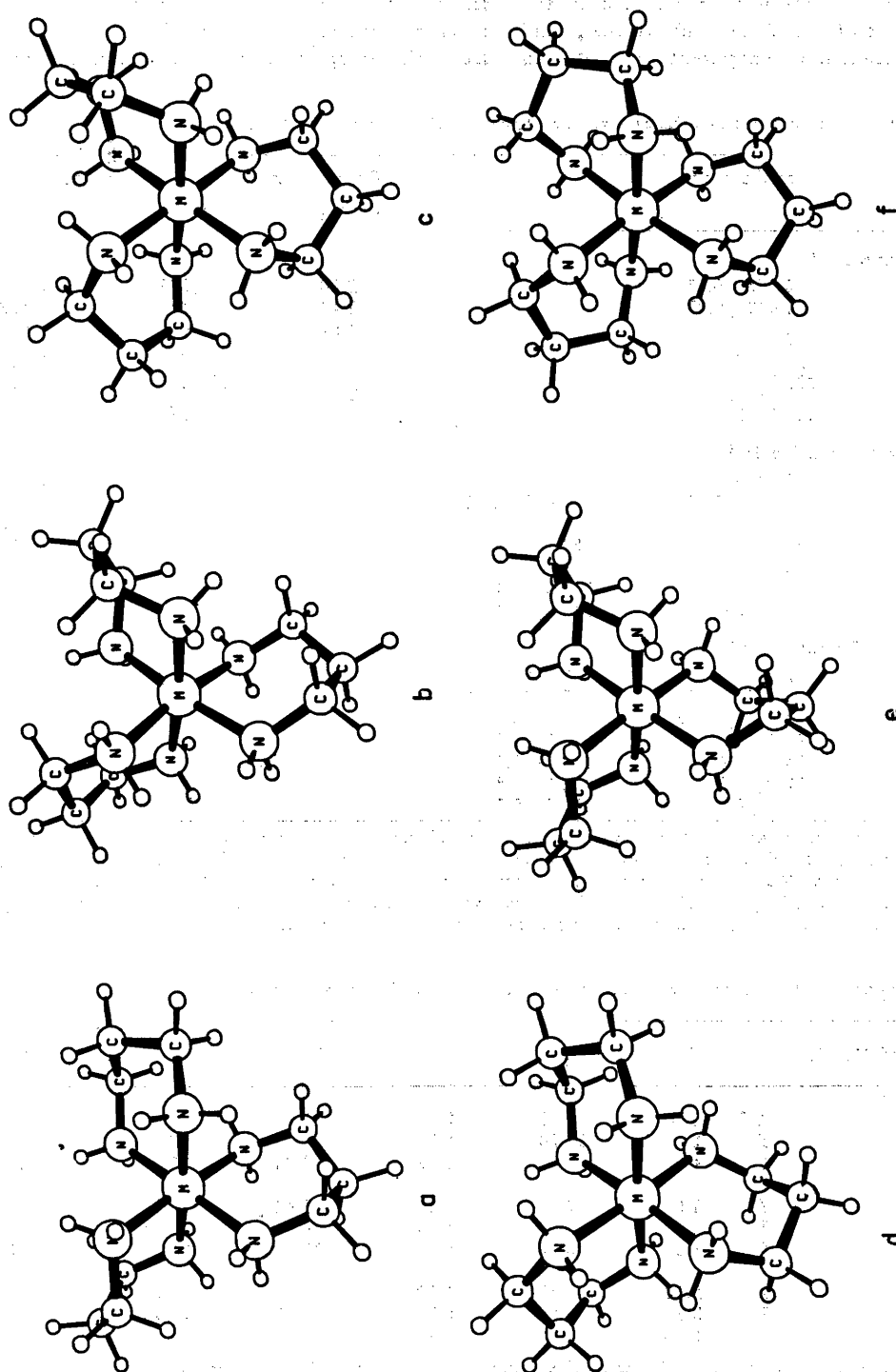


Fig. 1. The three homoconformational and selected heteroconformational forms of the $\text{Co}(\text{tn})_3$ system. a, *syn*-chair₃lel; b, *anti*-chair₃lel; c, ob₃lel; d, chair₃; e, lel₃; f, ob₃. The drawings were produced by ORTEP.

Table 5. Energy contributions for $M(2,4\text{-ptn})_3$ conformations.^a

Conformer of $M(2,4\text{-ptn})_3$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
chair ₃ (eq) ₆	1.82	9.45	3.00	-4.56	9.71	0.00
lel ₃ (eq) ₆	1.87	4.64	7.05	-3.49	10.07	0.32
chair ₃ (eq) ₃ (ax) ^b	1.91	12.31	3.45	-4.22	13.47	3.74
chair ₃ (eq) ₃ (ax) ^c	1.94	11.79	4.11	-4.11	13.73	4.02
ob ₃ (eq) ₆	2.75	6.02	7.51	-0.91	15.37	5.66
lel ₃ (eq) ₃ (ax)	2.08	8.16	8.39	-2.58	16.04	6.33
chair ₃ (eq) ₃ (ax) ₃	2.13	18.53	3.99	-3.18	21.47	11.76
ob ₃ (eq) ₃ (ax)	2.99	10.46	8.88	-0.18	22.15	12.44
lel ₃ (eq) ₃ (ax) ₃	2.28	15.92	11.51	-1.01	28.70	18.99
ob ₃ (eq) ₃ (ax) ₃	4.12	20.18	11.01	1.79	37.11	27.40

^a See footnote in Table 2. ^b $M(\text{meso-2,4-ptn})_2(2S,4S\text{-ptn})$ species. ^c $M(\text{meso-2,4-ptn})_2(2R,4R\text{-ptn})$ species.

forms. This is not surprising, as there are subtle but important differences in the minimized geometries of a particular gross ring conformer in the various conformational forms. Without exception, the heteroconformational forms have higher energies than what can be found from interpolation; this shows that different ring conformers in the same complex distort each other away from the symmetrical low-energy geometries.

The global minimum found here is different from that found by Geue and Snow,¹⁴ who found the lel₃ conformer to be 0.77 kcal mol⁻¹ lower in energy than the chair₃ conformer. This prompted us to minimize the three homoconformational forms using their force field.¹⁵ The result was that the chair₃ conformer is still the global minimum, but that the lel₃ conformer lies only 0.38 kcal mol⁻¹ above the chair₃ conformer. A comparison of these results and those of Geue and Snow is given in Table 4. There are substantial differences, particularly for the bond and non-bonded contributions. The geometries of the three forms as given by Geue and Snow¹⁵ (their Table 8) are very close to those found here, the deviations being for torsional angles 0.3 (av.) and 2.0° (max), and for valence angles 0.4 (av.) and 1.4° (max).

The reason for the discrepancy is most probably that Geue and Snow omit the longer non-bonded interactions.¹⁵ As far as we can check it, this means that, e.g., H...H interactions are omitted for distances longer than 2.78 Å, or more than 300 individual H...H interactions or more than 80%. Some of the

interactions omitted correspond to situations where the two atoms do actually "see" each other directly, and not through other atoms or through bonding regions. The significance of including also the longer non-bonded interactions will be discussed below.

Due to the proximity of lel₃ and some of the low-energy heteroconformational forms of $M(\text{tn})_3$ to the global minimum (Fig. 1) the definitive prediction of the most stable conformation requires the choice of a more refined force field, and calculation of conformational entropy contributions to the free energies. These supplementary calculations require a complete consistent force field study of $M(\text{tn})_3$, which will be undertaken after an extension of our programme.

Tris(2,4-pentanediamine) conformations. Initially we considered only the three hexaequatorial conformers (cf. Table 1), since the non-existence of conformations of $M(2,4\text{-ptn})_3$ with axial methyl groups, in aqueous solutions, at room temperature, for $M=\text{Co(III)}$, was assumed by Mizukami *et al.*¹⁶ on the basis of NMR studies. Starting with six distinct (eq)₆ conformations of $M(2,4\text{-ptn})_3$ systems: two idealized (C_3)-chair₃ conformations with acute and obtuse NMN angles; X-ray and idealized lel₃; and X-ray and idealized ob₃ conformations, the minimization led to three minimum-energy conformations (Table 5). The lowest energy conformations were (C_3)-chair₃ and (D_3)-lel₃. (D_3)-ob₃ was found 5.6 kcal mol⁻¹ above the global minimum of the system (Table 5).

In order to investigate the accessibility of conformers with axial methyl groups, we included in our calculations two additional series of $M(2,4\text{-ptn})_3$ conformers. One consisted of four $(eq)_3(ax)$ conformations (Table 1) generated from homoconformational $(eq)_6$ forms by changing the position of one of six equivalent equatorial methyl groups on $1el_3$ and ob_3 , or any of methyl groups from two non-equivalent sets on $(eq)_6\text{-chair}_3$. The other series consisted of three * $(eq)_3(ax)_3$ conformations (Table 1) generated from $chair_3$, $1el_3$, and ob_3 homoconformational forms by changing positions of three equatorial methyl groups while preserving the C_3 molecular symmetry.

The conformational distribution of hexa-equatorial $M(2,4\text{-ptn})_3$ forms (Table 5) is similar to that of homoconformational forms of $M(tn)_3$ (Table 2). The presence of equatorial methyl groups does not cause any significant deviation of bond lengths, valence angles, and torsional angles from the values in the corresponding $M(tn)_3$ structures. However, deformations due to the presence of axial methyl groups are

* Only one of two possible $(eq)_3(ax)_3\text{-chair}_3$ conformers (cf. Table 1) was chosen in order to reduce the amount of computational work, since the preliminary calculations and the results of minimization of two $(eq)_3(ax)\text{-chair}_3$ conformers indicated only slight differences between two $(eq)_3(ax)_3\text{-chair}_3$ forms.

appreciable, but almost entirely localized on the ring atom(s) carrying axial substituent(s). Axial methyl groups in $M(2,4\text{-ptn})_3$ conformations increase the conformational energies by about 4, 6, and 7 kcal mol⁻¹ per $ax\text{-CH}_3$ group (for $chair_3$, $1el_3$, and ob_3 forms, respectively) relative to the energies for the corresponding hexa-equatorial forms. It is, therefore, very unlikely to find $1el_3$ and ob_3 conformations in $M(2,4\text{-ptn})_3$ complexes with *meso*-diamine, or to find $chair_3$ conformations in complexes with optically active diamine. Energy contributions are given in Table 5, and average bond lengths and valence angles in Table 6. The four conformations of lowest energy are shown in Fig. 2.

ANALYSIS OF ENERGY CONTRIBUTIONS

Co(tn)₃ complexes. Analysis of the various contributions from bond, angle and torsional deformations and non-bonded interactions revealed absolutely no correlations between these contributions and the number of rings having $chair$, $1el$ and ob conformations.

A separate programme was written to allow for histogram analysis of non-bonded distances of all types, $H\cdots H$, $H\cdots N$, $H\cdots C$ etc. Neither in this way could any correlation be found, e.g. between the position on either the total or the non-bonded energy scale and the number

Table 6. Average bond lengths and valence angles in $M(2,4\text{-ptn})_3$ conformations.^a

Type ^b	$chair_3$ ^c	$1el_3$ Calc.	Obs. ^d	ob_3 Calc.	Obs. ^e
M-N	2.043	2.043	1.985	2.054	1.988
C-N	1.477	1.479	1.489	1.478	1.50
C-C	1.544	1.549	1.516	1.550	1.53
C-C _{Me}	1.549	1.548	1.530	1.549	1.50
N-M-N	93.85	88.10	89.1	87.80	87.9
M-N-C	120.13 (124.7)	114.10 (124.4)	118.0	114.62 (124.5)	115.7
N-C-C	110.68 (112.2)	111.83 (114.0)	112.0	111.96 (114.6)	109.0
C-C-C	110.21	112.64	117.3	113.24	116.7
N-C-C _{Me}	109.38 (112.8)	110.26 (113.5)	109.4	110.24 (113.6)	112.2
C-C-C _{Me}	109.53 (112.6)	109.38 (110.5)	111.0	109.26 (110.2)	105.7

^a Average values are given for hexa-equatorial conformations. Valence angles involving carbon atoms bearing axial methyl groups are given for comparison in parentheses. For further details see text. ^b M = Co(III); C_{Me} = methyl carbon. ^c Averaged assuming C_3 symmetry of chelate rings. ^d In (-)-[Co(2R,4R-ptn)₃]Cl₃·2H₂O (Kobayashi, Marumo and Saito^{13b}); averaged assuming D_3 symmetry. ^e In (+)-[Co(2R,4R-ptn)₃]Cl₃·H₂O (Kobayashi, Marumo and Saito^{13a}); averaged assuming D_3 symmetry.

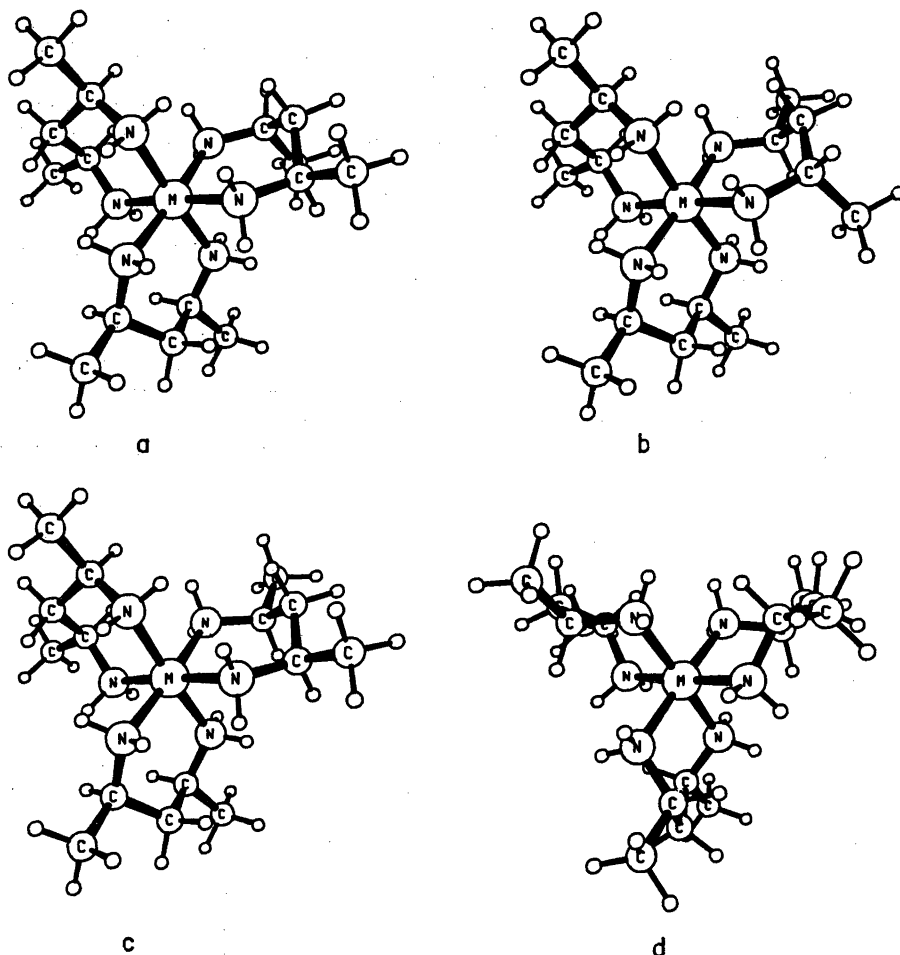


Fig. 2. The four lowest-energy conformations of the $\text{Co}(2,4\text{-ptn})_3$ system. a, chair₃(eq)₃(ax)₃ (2*R*,4*R*); b, chair₃(eq)₃(ax)₃ (2*S*,4*S*); c, chair₃(eq)₃; d, 1el₃(eq)₃. The drawings were produced by ORTEP.

of short non-bonded distances. Three conformers had H...H distances shorter than 2 Å, the 1el₂chair, the *syn*-chair₂ob and the *cis*-chair 1el ob.

It must be concluded that the minima are reached by very delicate balancing of all energy contributions through adjustment of practically all internal variables in these flexible molecules.

Co(ptn)₃ complexes. Similar analyses of energy contributions revealed the following trends. Chair conformations have relatively high angle deformation and low torsional energies. Ob conformations have relatively high bonded and non-bonded energies. There

is, rather unexpectedly, no correlation between the number of equatorial (or axial) methyl groups and either the total energy or the individual contributions.

There is, however, a pronounced additivity in the total energy. An axial methyl group increases the energy of a TB ring by (6.50 ± 0.75) kcal mol⁻¹ and that of a chair ring by (3.90 ± 0.15) kcal mol⁻¹.

The histogram analysis gave the same result as for the $\text{Co}(\text{tn})_3$ complexes. No contact distances were shorter than 2.00 Å.

For both series the longer non-bonded interactions contributed markedly to the stabilization. As a typical example we may mention

the global minimum conformation of $M(\text{tn})_3$, where non-bonded contributions shorter than 3 Å contribute with 10.074, and the longer ones with -11.880 kcal mol⁻¹. See also the column headed E_{nb} in Table 4, and compare numbers from B and C.

SHAPES OF CHELATE RINGS

We shall here summarize our results on some of the structural features of six-membered chelate rings formed by the coordination of alkanediamines, and compare them with relevant experimental studies.

Chair conformations. Most of the examined 21 individual chair rings in minimum-energy conformations of the $M(\text{tn})_3$ system (Table 2) differ slightly from each other so that they constitute a range of conformations "bracketed" by the following two extreme forms:

(i) chair rings found in the (C_3) -chair₃ conformer characterized by obtuse chelate angles ($N-M-N=93.91^\circ$) and

(ii) chair rings found in the *anti*-chair₂lel conformer characterized by acute chelate angles ($N-M-N=85.52^\circ$).

The sequence of endocyclic torsional angles along the chain bonds (starting from Co-N) is 26.6, 49.0, 71.6, 76.7, 57.2, and 30.3° for chair rings in the (C_3) -chair₃ conformer, and 57.2, 66.0, 64.9, 63.9, 65.7, and 52.0° for chair rings in the *anti*-chair₂lel conformer. With respect to their structural features all other distinct chair rings are intermediate between these two extremes.

Comparison of dihedral angles between the NMN, least-square NCCN and CCC planes (as defined by Geue and Snow¹⁴) reveal (Table 7) interesting conformational features of the chair conformations studied in the present

Table 7. Dihedral angles ^a in chair conformers of Co(III) and Cr(III) tn complexes.

Structure ^b	Source	D_1 (°)	D_2 (°)
(C_3) -chair ₃ -Co(tn) ₃	highly strained idealized conformation	125	125
<i>anti</i> -chair ₂ lel-Co(tn) ₃	minimum-energy conformation	136	121
<i>trans</i> -[Co(tn) ₂ (NO ₂) ₂]NO ₃	X-ray ¹⁷	139	121
(C_1) -chair ₂ -[Co(tn) ₂ (CO ₃) ₂]ClO ₄	X-ray ¹⁴ Ring A Ring B	147 136	119 122
chair-[Co(en) ₂ (tn)]Br ₃	X-ray ¹⁸	148	122
(C_3) -chair ₃ -[Co(tn) ₃]Br ₃ ·H ₂ O	X-ray ¹⁰ Ring A Ring B Ring C	149 142 146	122 122 119
<i>anti</i> -chair ₂ -[Co(tn) ₂ (acac)] ²⁺	X-ray ¹⁹ Ring A Ring B	145 156	119 113
<i>syn</i> -chair ₂ lel-[Cr(tn) ₃] ³⁺	X-ray ^{13b} Ring A Ring B	151 152	119 119
<i>trans</i> -[Co(tn)(β-ala)(NO ₂) ₂]	X-ray ²⁰	153	121
<i>cis</i> -[Co(tn)(β-ala)(NO ₂) ₂]	X-ray ²¹	158	119
<i>syn</i> -chair ₂ lel(C_2) Co(tn) ₃	minimum-energy conformation	151	118
(C_3) -chair ₃ Co(tn) ₃	minimum-energy conformation	155	113

^a D_1 = dihedral angle between NMN and NCCN planes. D_2 = dihedral angle between NCCN and CCC planes. ^b Structures studied by conformational analysis are shown without ionic charges. Symmetry symbols indicate approximate and rigorous symmetries for X-ray structures and minimum-energy structures, respectively.

work and in most of the known X-ray conformations of the chair rings in Co(III) and Cr(III) complexes of trimethylenediamine. The unique strain relieving mechanism for chair rings appears to be flattening of the inner fragment (C-N-M-N-C) and slight puckering of the outer one (N-C-C-C-N), accompanied by opening of the N-M-N angle and closing of the C-C-C angle. The puckering of chair rings in *anti*-chair₂lel is similar to that of idealized chair conformations (see top entries in Table 7) indicating weak interannular interactions. Conversely, pronounced interannular interactions produce flattening of the chairs in *syn*-chair₂lel and (C₃)-chair₂ (see bottom entries in Table 7) to such extent that the central carbon atom of trimethylenediamine is brought almost to the NMN plane.

The extent of puckering of chair rings in other heteroconformational forms of M(tn)₃ (not shown in Table 7) is intermediate between that of *anti*-chair₂lel and (C₃)-chair₂. In hexa-equatorial (C₃)-chair₂ Co(*meso*-2,4-ptn)₃ the angles D₁ and D₂ are 155.5° and 115.0°, respectively, implying the same mode of flattening of chair rings as in the (C₃)-chair₂ Co(tn)₃ conformation.

A summary of geometries of tn rings as found by X-ray diffraction has been tabulated by Jurnak and Raymond^{12b} (their Table XIX).

When we compare our results (Table 3) with those for M(tn)₃ complexes, we find that the experimental geometries are reproduced fairly well by our calculations. The largest deviations (experimental data falling outside the ranges of calculated ones) are found for M-N, C-C (partly), C-C-C (partly), and torsional angles, where the calculated values are too large. The remaining conformational quantities are well reproduced, including dihedral angles.

Twist-boat conformations. Twist-boat (TB) conformations of chelate rings found in minimum-energy lel₂, ob₂ and all heteroconformational forms studied (see Fig. 1) also constitute a range of conformations, but contrarily to the distribution of chair ring conformations, they are clustered around two distinct structural types:

(i) rings with essentially C₂ symmetry, not very different from idealized TB rings, found in lel₂, ob₂, and a few low-energy heteroconformational forms containing lel rings (Fig. 1) including the *syn*-chair₂lel conformer found in the X-ray structure of Cr(tn)₃ ion (Jurnak and Raymond^{12b}).

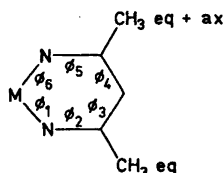
(ii) distorted TB conformations found both in lel and in ob rings of high-energy heteroconformational forms (*e.g.*, ob₂lel, lel₂ob).

The distribution of bond lengths and valence angles in TB rings is shown in Table 3 for

Table 8. Comparison of endocyclic torsional angles in chelate rings of M(2,4-ptn)₃ with equatorial and axial methyl groups

Torsional ^a angle	chair		lel		ob	
	(eq) ₂	(eq) (ax)	(eq) ₂	(eq) (ax)	(eq) ₂	(eq) (ax)
φ ₁	26.34	22.09	-34.42	-35.41	34.25	41.45
φ ₂	-48.69	-50.09	75.03	79.46	-74.29	-78.84
φ ₃	71.60	73.27	-37.80	-51.82	37.44	41.96
φ ₄	-76.82	-67.46	-37.80	-14.25	37.44	22.97
φ ₅	57.18	40.80	75.03	55.56	-74.29	-55.11
φ ₆	-30.20	-17.81	-34.42	-28.21	34.25	21.38

^a The endocyclic torsional angles are labeled as follows:



rings of approximate C_2 symmetry (left column) and distorted rings (right column). Chelate angles in both types of TB rings are invariably less than 90° . Also in minimum-energy lel_3 and ob_3 conformations of eq_6 -M(2,4-ptn)₃, chelate angles are acute and in very good agreement with X-ray data (see Table 6).

NMNC torsional angles in (C_2)-TB rings of lel_3 and ob_3 conformers of M(tn)₃ are $34 \pm 1^\circ$. However, in TB rings of approximate C_2 symmetry they vary in the range 30 to 37° .

In distorted TB conformations NMNC torsional angles are found to be in the ranges 5–15 and $45-50^\circ$, indicating the close resemblance of these structures and idealized boat conformations.

Comparing with the experimental geometry of the only TB ring found^{12b} so far, we find that our calculated ranges (Table 3) do not bracket M–N, C–C, N–C–C, and C–C–C; calculated values of MN and NC torsions are too large. The remaining quantities are well reproduced, including the dihedral angles.

Rings with axial substituents. In (eq)₃(ax) and (eq)₃(ax)₃ conformations of M(2,4-ptn)₃, appreciable flattening of the segments of chelate rings carrying axial methyl groups is observed both in chair and in twist-boat rings. This is reflected both in opening of the valence angles (see Table 7), and in decrease of the values of the corresponding torsional angles (as shown in Table 8).

A comparison between (1) the conclusions on shapes of six-membered chelate rings drawn by Jurnak and Raymond^{12b} on the basis of X-ray structures and (2) conclusions drawn from empirical force field calculations will have to await the development of an optimized force field.

CONCLUSION

Our work corroborates the conclusions of others^{14,15,22} that energy minimization is successful in predicting detailed geometries of coordination compounds.

It has been clearly demonstrated here that truly convergent minimization methods are imperative for meaningful results.

The scope of this work was not to obtain very accurate geometries. For such purpose we shall need a force field which is optimized

on geometries of model compounds, and this means that the full potentiality of the CFF approach^{4,5} must be utilized. Revised methods for simultaneous optimization on experimental conformations and vibrational spectra are now being worked out for our new version of the CFF system.

Final cartesian atomic coordinates and corresponding internal coordinates of sixteen M(tn)₃ and ten M(ptn)₃ conformers may be obtained from the authors upon request. ORTEP drawings of all minimum conformations are also available.

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