

Conformational Analysis of Coordination Compounds

II. Dimethyl-substituted Five- and Six-membered Metal Chelate Rings

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Steepest descent energy minimization technique has been applied to the conformational analysis of tris(chelate)metal complexes containing dimethyl substituted metal-diamine rings. Eight conformers of tris(2,3-diaminobutane) and five conformers of tris(2,4-diaminopentane) complexes were submitted to energy minimization, including complexes containing the ligands in their chiral as well as their *meso* forms.

Conformational energies are presented and partly interpreted in terms of energy differences between *lel* and *ob* rings, and between equatorial and axial methyl substituents.

The general problem of "local minima" inherent in the method is clearly exemplified.

As in our previous paper¹ the basic goal of this research was to explore the capabilities of a steepest descent energy minimization program for the conformational analysis of the tris-diamine metal complexes.

Here we report our analysis of the conformations of various forms of $M(2,3\text{-bn})_3$ and $M(2,4\text{-ptn})_3$ ** and compare their strain energies and geometries. The computational model was that of full relaxation of internal coordinates. Minimization was performed over the sum of energy terms due to bond stretching, angle bending, torsional and non-bonded contributions. Energy functions and parameters were the same as those used previously¹ for the analysis of the $Co\text{tn}_3$ system and labeled FF-1.

As illustrated in the following, conformational analysis of 2,3-bn and 2,4-ptn complexes is considerably more complicated than that of unsubstituted complexes (of, *e.g.*, en and tn) due to the presence of methyl groups

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** Abbreviations: M=central metal ion. M-N bond lengths are chosen to correspond to M=Co(III); 2,3-bn=2,3-diaminobutane; 2,4-ptn=2,4-diaminopentane; tn=1,3-diaminopropane; en=ethylenediamine. Ionic charges are omitted for simplicity.

whose internal rotation makes the potential energy surface particularly intricate.

The metal-2,3-bn chelate ring

First we have analyzed the conformations of a single isolated M-2,3-bn ring. This system may correspond to a square planar $M(2,3\text{-bn})X_2$ complex in which the interactions between ligands X and chelate ring as well as non-bonded interactions involving M are neglected.*

The ring assumes the puckered form in which methyl groups could be equatorial (eq) or axial (ax). The resulting stereochemistry of the single M-2,3-bn chelate ring is indicated in Fig. 1.

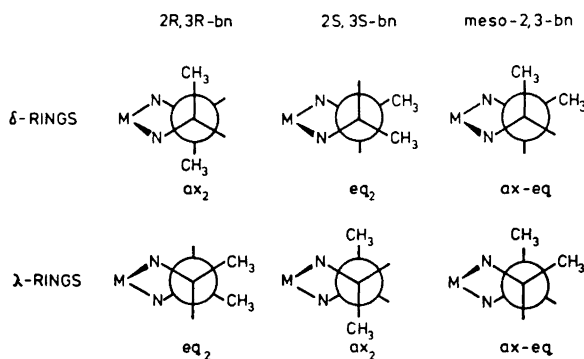


Fig. 1. The stereochemistry of a single metal-2,3-bn chelate ring.

As starting conformations for minimization we constructed two planar M-2,3-bn chelate rings having *meso* and optically active configurations of 2,3-bn. During the minimization, the ring containing the ligand in its chiral form converged rapidly towards the puckered eq_2 form characterised by endocyclic and exocyclic torsional angles about the C-C bond of 41.2° and 77.7° , respectively.

In contrast, the M-*meso*-2,3-bn ring remained planar on minimization retaining an unrealistically high strain energy in comparison to the ring with the chiral ligand. Even when the ring atoms of the initial conformation were slightly off-set alternately up and down with respect to the plane of the ring, the structure remained essentially planar on minimization. This may be due to the intrinsic property of the steepest descent minimization technique to tend to retain the initial symmetry (C_2 of chiral and C_s of *meso*-2,3-bn) of the chelate rings.

In order to approach the minimum of the puckered form of the M-*meso*-2,3-bn ring we have inverted the position of one of the methyl groups of

* The latter type of interaction is not considered quantitatively negligible; it was omitted for the lack of adequate potential functions.

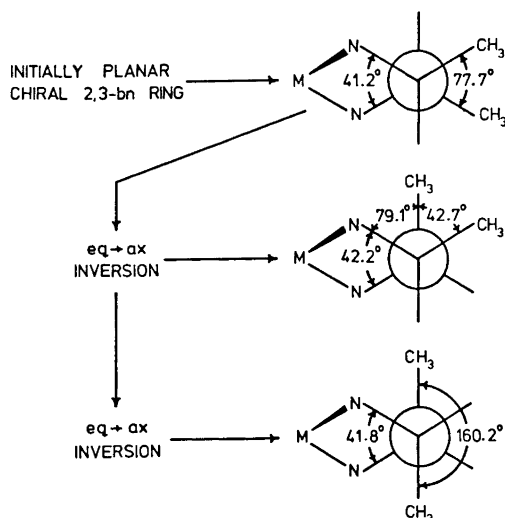


Fig. 2. Summary of the minimization of a single metal-2,3-bn chelate ring.

the minimized eq_2 ring into the ax position. This new starting conformation proved to be very close to the minimum both in energy and in conformational space, and upon minimization indeed converged rapidly. For comparison, we have constructed an ax_2 conformer by inverting both of the methyl groups of the minimized eq_2 ring containing chiral ligand. Minimization of this conformer did not lead back to the eq_2 conformation; the structure remained in its own local minimum indicating the existence of a barrier to ring inversion.

Results of the minimization of a single M-2,3-bn ring are summarized in Fig. 2.

Tris(2,3-bn) chelate complexes

With either one of the optically active forms of the ligand $M(2,3-bn)_3$ may exist as 2 stereoisomers (Δ and Λ) each of which may adopt 4 conformations (combinations of δ and λ) yielding a total of 8 energetically unique structures. The complex containing the ligand in its *meso* form may be expected to exist in a total of 24 pairwise enantiomeric forms yielding 12 energetically unique structures, namely 2 stereoisomers (*fac* and *mer*), in 4 and 8 conformations, respectively.

In order to see if conformational energy differences between such structures could be interpreted in terms of energy differences between *lel* and *ob* chelate rings, between equatorial and axial methyl groups, and between *fac* and *mer* configurations, we have selected 8 of the above mentioned 20 energetically unique structures for minimization (Fig. 3).

Initial conformations were constructed by placing methyl groups on the

appropriate positions of the frameworks of three conformations of $M en_3$: lel_3 , lel_2ob , and ob_2lel , for which the coordinates of chain atoms were taken from the X-ray diffraction data² on Cr(III) complexes.

Geometry parameters of the final minimized conformations* show that the variations in bond lengths are not very important in the discussion of the resulting structures. Slight irregularities in bond angles and steady contraction of chelate angles in all cases is a result of the interannular non-bonded interactions which are most easily alleviated *via* the angle deformations.¹ The order of conformational energies of the final minimized forms with chiral 2,3-bn is presented in Fig. 3. Differences in strain energies among the isomers of $M(2,3-bn)_3$ arise primarily from non-bonded interactions. Other energy terms (particularly bond-stretching and N-M-N angle bending contributions) follow the increase in non-bonded terms in an approximately regular way.

The energy differences between the conformations containing the chiral form of the ligand (Fig. 3) may, in fact, be interpreted by assigning ≈ 2.2 kcal/mol CH_3 to the equatorial preference of methyl groups and ≈ 0.8 kcal/mol ring to the preference of *lel* ring conformation. In addition, eq/ax differences appeared to be slightly greater in *ob* than in *lel* rings.

The *mer* and *fac* isomers with *meso*-2,3-bn (eq_3ax_3 conformations), although constructed from the same $M en_3$ framework, remained on minimization at higher energies than ax_6 conformation of optically active 2,3-bn. This was considered to be a physically unrealistic situation so we sought other starting points which might lead to lower points on the energy surface of $M(meso-2,3-bn)_3$. Indeed, when we restarted the minimization from the points artificially generated by eq \rightarrow ax inversion of the appropriate three methyl groups in the eq_6 conformer, or by a similar ax \rightarrow eq inversion in the ax_6 conformer (both of which have previously been minimized) we obtained structures that were lower in energy than the ax_6 conformer containing chiral ligands. An estimate of the energy could be made by applying the energy values for the eq/ax preference of the methyl groups in the complex containing the *chiral* form of the ligand to the complex containing its *meso* form. This estimate (6.8 kcal/mol, *i.e.*, the average value of the lel_3eq_6 and lel_3ax_6 conformations), however, is about 4 kcal/mol lower than the values found by minimization (*vide* Fig. 3). The difficulties in the minimization of *mer* and *fac* isomers probably originate in the particularly intricate form of the energy surface of these systems.

It is interesting to note that the energy contributions corresponding to the interannular non-bonded interactions were approximately the same in *mer* and *fac* isomers of $M(meso-2,3-bn)_3$.

Tris(2,4-ptn) chelate complexes

In the $M(2,4-ptn)_3$ system conformations with axial methyl groups are sterically too strained to be appreciably populated. Therefore, the discussion of the stereochemistry of this system reduces itself to the following three

* Which may be obtained from the authors upon request.

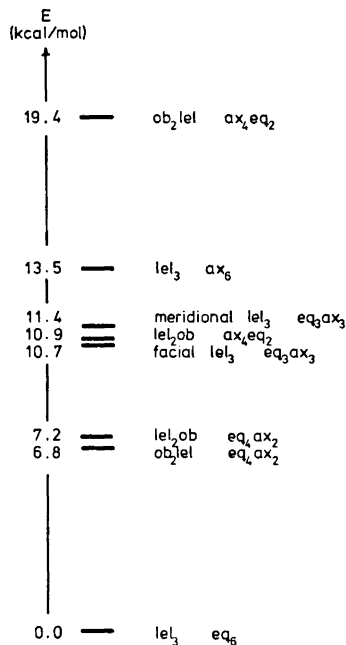


Fig. 3. Comparison of minimized energies of $M(2,3\text{-bn})_3$ conformations.

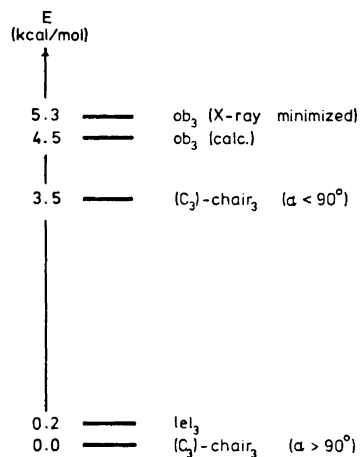


Fig. 4. Comparison of minimized energies of $M(2,4\text{-ptn})_3$ conformations.

energetically unique structures all being eq₆: (C_3)-chair₃, δ_3 , and λ_3 formed on coordination of 2*R*,4*S*-ptn (*meso* form), 2*S*,4*S*- and 2*R*,4*R*-ptn, respectively. The latter two forms containing optically active 2,4-ptn appear, for example, as *lel*₃ and *ob*₃ conformations in the complexes of Λ absolute configuration.

Four starting conformations for energy minimization were obtained by substitution of methyl groups on eq(2) and eq(4) positions on the frameworks of four of the conformations of Co tn_3 described in Ref. 1, namely on (C_3)-chair₃ (with N-Co-N angle $> 90^\circ$ and $< 90^\circ$), *lel*₃, and *ob*₃.

The two chair forms with acute and obtuse chelate angles which were shown¹ to represent two points belonging to the same overall minimum on the energy surface of the Co tn_3 led to two quite different local-minimum conformations of $M(\text{meso-}2,4\text{-ptn})_3$ system. The conformer with obtuse chelate angles proved to be stabilized over the other by ≈ 3.5 kcal/mol. The *lel*₃ conformation containing chiral 2,4-ptn rings was found to be very close to the (C_3)-chair₃ in conformational energy. The other structure containing chiral 2,4-ptn, *ob*₃ conformation, was about 4.5 kcal/mol above the *lel*₃ form indicating the conformational preference for *lel* rings of ≈ 1.5 kcal/mol ring in $M(2,4\text{-ptn})_3$ system (Fig. 4).

For comparison we have also minimized the *ob*₃ conformation corresponding to the structure of $\Lambda\text{-[Co}(2*R*,4*R*\text{-ptn})_3]$ ion as known from the X-ray diffrac-

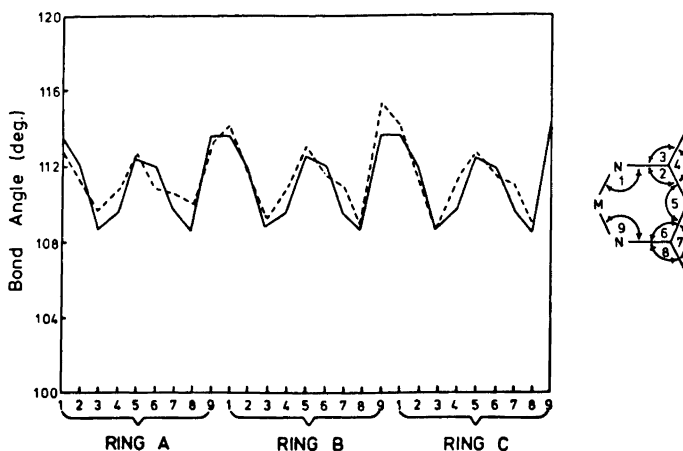


Fig. 5. Comparison of bond angles in minimized generated ob_3 (—), and in minimized X-ray ob_3 (- - -) conformations of $Co(2,4-ptn)_3$. The values of chelate angles (not shown in figure) are 88.1° , 87.9° , and 88.0° for the minimized generated ob_3 , and 87.8° , 86.9° , and 87.3° for the minimized X-ray ob_3 conformation.

tion study.³ The final minimized conformation obtained in this way was very close to the minimized ob_3 conformation described above. Bond lengths and torsional angles were almost identical in both of the structures; differences between the structures — although marginal — were found only in the bond angles (*vide* Fig. 5).

As already concluded in our previous paper¹ the conformational analyses of systems of the type studied here have not yet shown a reliability or general validity comparable to those obtained by applying similar methods to certain classes of hydrocarbons. The capricious behaviour of the $M(meso-2,3-bn)_3$ system, for example, may appear somewhat discouraging. Nevertheless, we find these results and their agreement with experimental energy values in the admittedly few cases (*e.g.* the eq/ax preferences) where comparisons could be ventured, promising enough to warrant the efforts involved in improving our approach by developing more versatile, refined and powerful computational methods. The development of such methods based on the original work by Lifson and Warshel⁴ is currently in progress in our laboratory.

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