isomerizes completely to the cis.[22] The cis disposition of coordinated dien would thus appear to be considerably stabilized only by coordinated water. This might be attributed to more favorable hydrogen bonding between the aquo ligands all cis, as this factor may be used to rationalize the greater stability of β-[Co(trien)(H_2O)-(OH)]^{2+} compared with the α configuration.[24] The identity of the complex species purported to be *cis*-

(24) A. M. Sargeson and G. H. Searle, to be submitted for publication.

[Co(dien)(H_2O)_3]^{3+} remains in some doubt however since it has been obtained only in solution.

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Conformational Analysis of Coordination Compounds. V. Six-Membered Diamine Chelate Rings

BY J. R. GOLLOGLY AND C. J. HAWKINS*

The conformational preferences for the chelate ring formed by 1,3-diaminopropane in its octahedral mono, bis, and tris complexes have been studied by *a priori* calculations of conformational energies. The chair conformation was found to be the most stable for each of the compounds studied. The minimum energy geometries were found to agree well with the solid state structures determined by X-ray crystallography. The lowest energy pathway for converting one chair conformation into the other possible chair conformation was similarly studied, and the barrier of activation was calculated to be of the order of 7 kcal mol^{-1}.

The six-membered carbocyclic ring system has been extensively studied by conformational analysis. In contrast, the analogous diamine chelate ring formed by 1,3-diaminopropane (tn) has attracted little attention since the early comments of Corey and Bailar.[1]

As found for the cyclohexane ring, there are two basic types of conformations available to the six-membered diamine chelate ring: (i) a chair form in which the metal atom and the central carbon atom lie on different sides of a plane containing the other four atoms of the ring, and (ii) a flexible boat which corresponds to a wide range of conformations that contains two special symmetrical forms, (a) the symmetrical boat in which the metal and central carbon atoms lie on the same side of a plane containing the remaining four atoms, and (b) the symmetrical skew boat in which the central carbon, the metal, and the two nitrogen atoms are coplanar, with the remaining carbon atoms lying, respectively, above and below this plane (see Figure 1).

In this paper, the methods of analysis developed by the present authors for the five-membered diamine systems[2-4] have been applied to the systems M(tn)b_2, M(tn)a_2b_2, *trans*-M(tn)_2a_2, and M(tn)_3 with a M–N bond length of 2.0 Å. Both the ground-state conformations and the activated complexes for conformational interconversion have been studied in order to determine the preferred geometries of the conformations, the energy differences between the stable conformations, and the energy barrier that exists in the chair-to-chair interconversion.

Geometrical Model

The chelate ring is initially placed in a right-hand Cartesian coordinate system as shown in Figure 2 with the coordinate bonds in the xy plane equidistant from the x and y axes. The conformations have been specified by a constant set of bond lengths and by a set of internal coordinates, z_1, z_2, z_3, α, γ, and γ' where z_1, z_2, and z_3 are the z coordinates of the ring carbon atoms C(1), C(2), and C(3) and the angles are as specified in Figure 2.

The positions of the unidentate ligands have been determined and varied in the manner outlined previously.[2] The apical ligands, a, have been permitted to bend back away from the z axis in order to relieve unfavorable interactions where necessary, and also have been allowed to rotate freely to minimize the interactions.

For the bis and tris complexes, the rings have been first constructed in the position shown in Figure 2, and then transformed to their correct position in the octahedron. Reorientation of the rings and groups has been carried out in the way described previously for M(en)_3.[4]

Energy Calculations

The set of empirical van der Waals energy equations derived from free energy data for the cobalt(III)–(R)-propylenediamine–(S)propylenediamine system has been applied to the present system.[4,5] The methods for calculating the torsional and angle-bending energies have also been described previously.[2]

Conformational energy calculations for six-membered rings are potentially much more laborious than those for

(1) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).
(2) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).
(3) J. R. Gollogly and C. J. Hawkins, *ibid.*, **9**, 576 (1970).
(4) J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *ibid.*, **10**, 317 (1971).
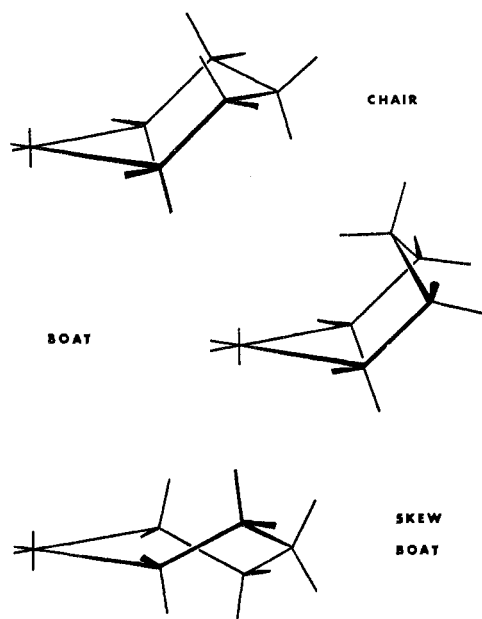(5) J. R. Gollogly, Ph.D. Thesis, University of Queensland, 1970.

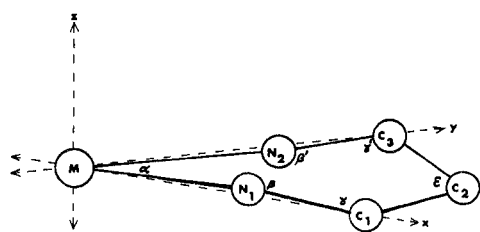Figure 1.—Conformations of a six-membered diamine chelate ring.

Figure 2.—Metal–1,3-diaminopropane chelate ring oriented in the xy plane of a right-handed Cartesian coordinate system.

the five-membered ring systems because they require a minimum of six parameter variables and the rings may exist in a much wider range of conformations. For example, scanning the six-dimensional energy surface for at least ten increments of each variable would require the evaluation of 10^6 structures. However, the calculation can be reduced to an acceptable size while maintaining reasonable accuracy, by dividing the parameter variables into two distinct groups according to their effect on the conformational energy surface. The total energy was found to be more sensitive to z_1, z_2, and z_3 than to the remaining three internal parameters. On this basis, α, γ, γ' were held constant while scanning the conformational energy surface as a function of (z_1, z_2, z_3) in the range 0.0 to 2.0 Å, with increments of 0.2 Å. The minima so determined were refined with respect to $(\alpha, \gamma, \gamma')$ and (z_1, z_2, z_3) alternatively, until their increments were 2.5° and 0.5 Å, respectively. The transition states were similarly determined from the energy surface and were refined with respect to $(\alpha, \gamma, \gamma')$.

The ring-strain energy term, $E_\theta + E_\omega$, was the crucial term in defining the preferred ring geometries for the isolated ring. This has also been found for the ethylenediamine chelate[2] and cyclohexane.[6] In an octahedral complex the properties determined for the isolated chelate ring are modified by the interactions of the ring with groups external to it.

(6) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961).

An entropy contribution to the conformational free energy resulting from the statistical freedom of the chelate ring in a particular conformation has been determined by the method discussed in detail in the previous paper in this series.[4]

Results

M(tn)b₂.—In a square-planar complex $M(tn)b_2$ interactions external to the chelate ring are unimportant and the chelate ring can be considered as if it is isolated. Geometrical details for the minimum energy conformations for this system are given in Table I.

TABLE I
MINIMUM-ENERGY CONFORMATIONS AND APPROXIMATE
TRANSITION-STATE CONFORMATIONS FOR $M(tn)b_2$
WITH M–N = 2.0 Å[a]

	Chair	Skew boat	Boat	Transition state b	Transition state d
z_1	1.10	0.80	1.15	0.00	0.80
z_2	0.95	0.00	1.80	0.00	0.00
z_3	1.10	−0.80	1.15	0.80	0.00
α	92.5	92.5	87.5	95.0	95.0
β	111.9	107.1	109.3	125.7	110.7
β'	111.9	107.1	109.3	110.7	125.7
γ	112.0	112.0	109.5	119.5	109.5
γ'	112.0	112.0	109.5	109.5	119.5
ϵ	112.9	108.3	112.8	111.6	111.6
ΔH	0.75	2.45	4.05	. . .	. . .
$-T\Delta S$	0.00	−0.10	0.05	. . .	. . .
ΔG	0.75	2.35	4.10	7.8	7.8

[a] z_1, z_2, z_3 in Å, angles in degrees, and ΔH, $T\Delta S$, and ΔG in kcal mol⁻¹.

The conformation of lowest energy is a symmetrical chair. In this conformation, the bonds of the rings are well staggered and the torsional contribution to its energy is only 0.25 kcal mol⁻¹. The ring angles undergo small distortions in order to accommodate this staggering.

The second energy minimum corresponds to a symmetrical skew boat. The two chiralities of this conformation have identical energies and structures. Each bond of the ring is partly eclipsed and the energy difference (1.70 kcal mol⁻¹) between this conformation and the symmetrical chair conformation derives mainly from torsional strain.

In the symmetrical boat conformation, the ring suffers almost complete eclipsing about the N–C bonds and its energy is about 3.3 kcal mol⁻¹ higher than the favored chair conformation.

In the symmetrical chair conformation, the NCCCN fragment may bend away from the NMN plane (see Figure 3) with a moderate increase in energy. This flexibility derives from the ease of distortion of $\angle$ MNC and the absence of a torsional barrier about the M–N bond. The NCCCN fragment in this conformation does not flatten readily because of the torsional preferences of the N–C and C–C bonds, and the larger force constants for the $\angle$ NCC and $\angle$ CCC angles. As the favored mode of distortion of the chair proceeds, z_1 ($z_1 = z_3$) and z_2 decrease together; the difference $z_1 - z_2$ remains fairly constant in order to maintain the puckering of NCCCN.

In the symmetrical skew boat conformation, the ring may distort unsymmetrically (see Figure 3) while maintaining the puckering of the conformation. The flexibility of the skew boat conformation arises because the changes in the torsional energy associated with the
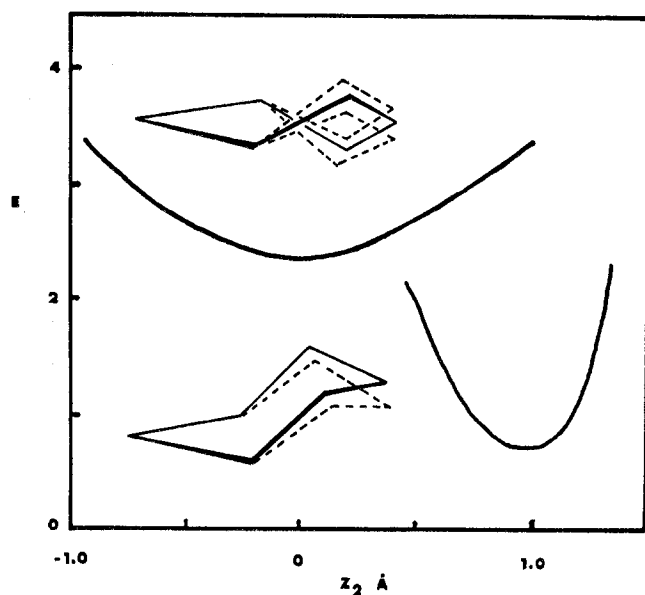
Figure 3.—Changes in geometry and ring strain energy (in kcal mol^{-1}) during the favored modes of distortion of the symmetrical chair and skew-boat conformations.
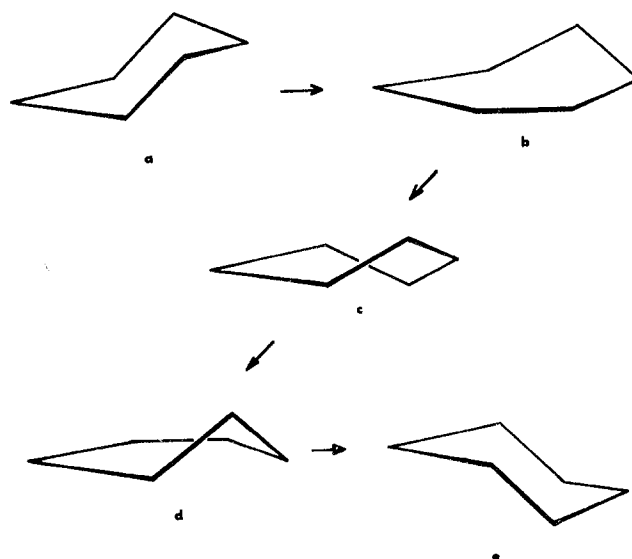

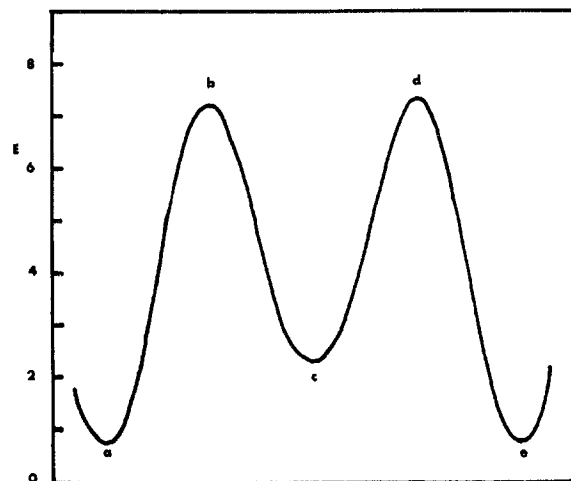Figure 4.—Lowest-energy pathway for chair-to-chair interconversion.

Figure 5.—Change in ring strain energy (kcal mol^{-1}) during chair-to-chair interconversion for $M(tn)b_2$. The letters refer to the structures in Figure 4.

$C(1)-C(2)$ and $C(2)-C(3)$ bonds compensate for each other, provided that z_1, z_2, and z_3 vary by approximately the same amount. Although the skew boat conformation possesses considerable intrinsic torsional strain (~2 kcal mol^{-1}), the complementary variation of the torsional energy terms in this mode of distortion makes the skew boat more flexible than the chair conformation. The favored modes of distortion are represented in Figure 3, where the changes in geometry are characterized by the variation of z_2, and the conformational energy is simultaneously minimized with respect to all the other parameters. The vibrational entropy term, calculated with respect to z_2, favors the skew boat form by 0.10 kcal mol^{-1}.

Within a range of 0.2 kcal mol^{-1} of their minimum energies, these conformations may undergo bond angle distortions of $\pm2.5°$ from the angles shown in Table I. For z_1, z_2, and z_3 the range is ±0.2 Å for the symmetrical chair and ±0.4 Å for the skew boat conformation.

The minimum energy pathway for chair-to-chair interconversion is shown in Figure 4 and the energy profile in Figure 5. This proceeds *via* a skew boat intermediate and involves twisting the ring atoms about the $N(1)-C(2)$ axis. During this transition the torsional angles about the $N(1)-C(1)$ and $C(1)-C(2)$ bonds pass through zero and the ring angles suffer large distortions, leading to large torsional and angle-bending contributions to the energy of the activated complex. The geometrical details and energy of the activated complex are given in Table I.

$M(tn)a_2b_2$.—The minimum-energy geometries calculated for $M(tn)b_2$ were used as initial trial structures in the minimization for the octahedral complex. Each apical unidentate group was defined in the normal way by a set of bond lengths and bond angles and was oriented using the angles θ_x, θ_y, θ_z, defined in the previous paper,[4] and Ω, the dihedral angle between one X–H bond (X is N for NH$_3$, and O for H$_2$O and OH$^-$) and the x axis when viewed down the M–X axis. The increments used for the variation of θ and Ω were 2.5°

and 10°, respectively. The results of the minimization are given in Table II.

TABLE II

GEOMETRICAL AND FREE-ENERGY DATA FOR $M(tn)a_2b_2$ WITH M–N = 2.0 Å[a]

	a = NH$_3$		a = OH$^-$	a = Cl$^-$
	Sym chair	Skew boat	Sym chair	Sym chair
z_1	0.75	0.75	1.05	0.80
z_2	0.30	0.00	0.75	0.35
z_3	0.75	−0.75	1.05	0.80
α	92.5	90.0	90.0	95.0
β,β'	119.5	114.5	114.5	117.0
γ,γ'	109.5	109.5	109.5	109.5
ϵ	112.0	112.0	112.0	112.0
Ω_a	45	−30	45	. . .
θ_x	5.0	5.0	5.0	5.0
θ_y	−5.0	−2.5	−5.0	−5.0
θ_z	0.0	0.0	0.0	0.0
ΔH	2.65	4.30	1.54	2.95
$-T\Delta S$	0.0	−0.05	0.0	0.0
ΔG	2.65	4.25	1.54	2.95

[a] z_1, z_2, z_3 in Å, angles in degrees, and ΔH, $T\Delta S$, and ΔG in kcal mol^{-1}.

The general properties and conformational preferences of the 1,3-diaminopropane chelate ring in the

square-planar complex are preserved in the octahedral complex, the geometry and energy of the ring being modified by interactions with the apical unidentate ligands. In the chair conformation the ring interacts strongly with one of the apical groups (see Figure 6a).
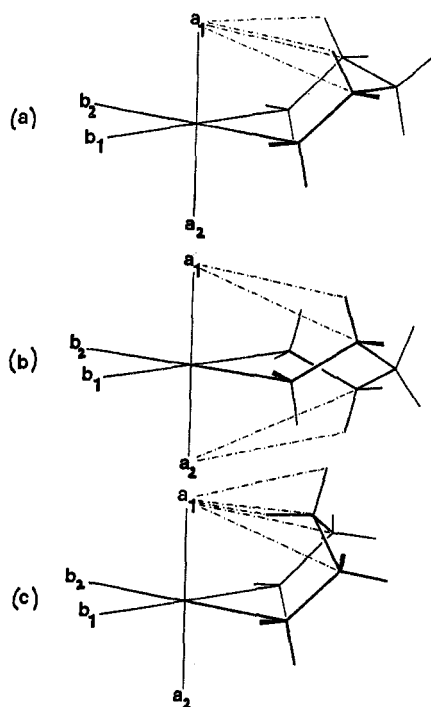

Figure 6.—Major interactions in (a) chair, (b) skew-boat, and (c) boat conformations of the metal–1,3-diaminopropane chelate ring in $M(tn)a_2b_2$.

These interactions involve mainly the carbon atoms C(1) and C(3) and their substituents and are relieved by a symmetrical flattening of the ring and by symmetrical distortion of a_1 in the $(-x, -y)$ direction. In the symmetrical skew-boat conformation, the carbon atoms C(1) and C(3) and their substituents interact with different apical ligands (see Figure 6b). To relieve these interactions, the ring flattens symmetrically and the apical group distorts away from C(1) and C(3) while maintaining the C_2 symmetry of the complex. Finally, in the symmetrical boat conformation, there are very severe interactions (>10 kcal mol^{-1}) between an apical ligand and the C(1)C(2)C(3) fragment of the ring (see Figure 6c). These interactions can only be relieved by prohibitively large distortions of the bond angles.

Consequently, in the simple monooctahedral complex, the 1,3-diaminopropane chelate ring will exist as a symmetrical chair, this conformation being preferred over the skew boat by more than 2 kcal mol^{-1}.

The lowest energy pathway for chair-to-chair interconversion is again as shown in Figure 4. The interaction system for the activated complex is similar to that of the symmetrical skew-boat conformation and its interactions will be of the same order of magnitude. Because of this, the activation energy for conformational inversion in the monooctahedral complex is only slightly higher than for $M(tn)b_2$ and is of the order of 8 kcal mol^{-1}.

trans-$M(tn)_2a_2$.—The interaction system of each

ring in a trans-bis complex is almost identical with that of the corresponding mono complex. Thus, their conformational properties can be inferred directly from the calculations previously carried out for the mono complexes (see Table II). For example, it follows that in the trans-bis complexes both chelate rings will prefer to exist in symmetrical chair conformations.

There are two possible configurations containing two chair conformations: the carbon atoms of the two chelate rings may be on the same side of the plane of the coordinate bonds (Figure 7a), or on opposite sides of
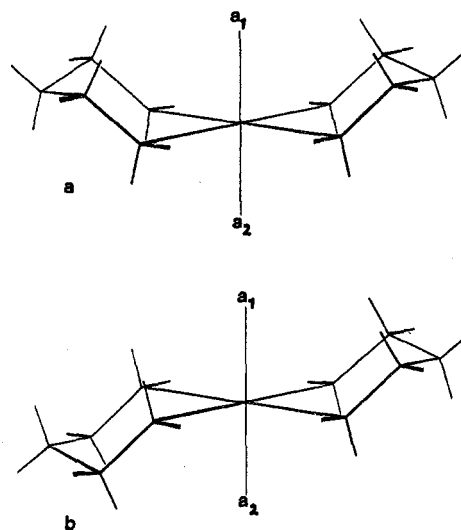

Figure 7.—Configurations of *trans*-$M(tn)_2a_2$.

this plane (Figure 7b). Small direct interactions between the amine groups of the trans rings favor configuration b. However, indirect interactions between the rings *via* one of the unidentate ligands are far more significant in determining the conformational preferences. As noted above, chair conformations interact strongly with one of the unidentate ligands forcing it to adopt the orientations and positions defined in Table II. In the structure shown in Figure 7a, therefore, there are strong indirect interactions between the two chair conformations because of the mutually unfavorable position of the unidentate ligand a_1. No comparable interactions occur in the configuration shown in Figure 7b and, as a result, this configuration is favored energetically by at least 0.5 kcal mol^{-1}. As the two ring conformations of this structure are effectively independent, their calculated geometries are found to correspond closely to those listed in Table II.

$M(tn)_3$.—When considering the tris complex it is obvious from an inspection of Dreiding stereomodels that only two configurational types need to be considered: the tris chair and the tris skew boat. Of the two possible tris-chair configurations, one that lacks an axis of symmetry is intrinsically unstable because of the crowding of two adjacent rings. The other that possesses a threefold axis of symmetry is strongly favored. When each ring is in a skew-boat conformation, there are four possible configurations; for a D complex, these may be represented as $D(\delta\delta\delta)$, $D(\delta\delta\lambda)$, $D(\delta\lambda\lambda)$, and $D(\lambda\lambda\lambda)$. The properties of the interaction system in $M(tn)_3$ are completely characterized, at

least in a qualitative sense, by those described previously for M(en)₃.[4] For example, the free energy terms arising from interactions, ring strain, and the flexibility of the rings increase in the order $D(\delta\delta\delta)$, $D(\delta\delta\lambda)$, $D(\delta\lambda\lambda)$, and $D(\lambda\lambda\lambda)$. However, interactions between the skew-boat conformations in M(tn)₃ are much stronger than the corresponding interactions in M(en)₃ and the enthalpy differences between these configurations far outweigh the statistical entropy terms which favor the "mixed" $D(\delta\delta\lambda)$ and $D(\delta\lambda\lambda)$ configurations. Thus the $D(\delta\delta\delta)$ form is the most preferred tris-skew-boat configuration.

The energies of the most favored tris-chair and tris-skew-boat configurations were minimized with respect to each of the ring parameters using the preferred ring geometries of M(tn)(NH₃)₄ as initial structures. Because the geometries of both configurations are controlled by a threefold axis, it was only necessary to define one ring in each structure; the coordinates of the other rings were generated simply by rotation about the threefold axis. The interaction systems for each cis pair of rings are illustrated in Figure 8 and the
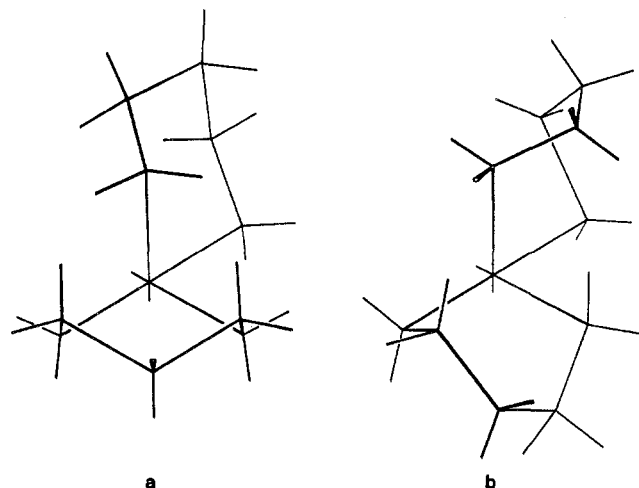

a   **b**

Figure 8.—Cis-bis interaction systems in M(tn)₃ for tris configurations containing (a) chair and (b) skew boat conformations.

minimum energy geometries of the rings are listed in Table III.

TABLE III
MINIMUM-ENERGY CONFORMATIONS FOR M(tn)₃
WITH M–N = 2.0 Å

(a) Ring parameters[a]

	z_1	z_2	z_3	α	β,β'	γ,γ'	ϵ
Chair	0.65	0.10	0.65	95	119.5	112.0	109.5
Skew-boat	0.70	0.00	−0.70	87.5	114.5	114.5	108.9

(b) Energies[b]

	ΔH	$T \Delta S$	ΔG
Chair	11.55	0.0	11.55
Skew-boat	12.15	−0.3	12.45

[a] z_1, z_2, z_3 in Å, and the angles in degrees. [b] In kcal mol⁻¹ with $T = 300°K$.

The energy barrier for conformational interconversion has been estimated by comparison with the barriers calculated for the mono complex. The preferred transition-state conformation (Figure 4) experiences large interactions with the rest of the molecule. However, these are of the same order of magnitude as the

interactions of a ring in a tris-chair or tris-skew-boat configuration (about 1–2 kcal mol⁻¹). Consequently, the energy barrier for each ring is about 7 kcal mol⁻¹ and the interchange between configurations will involve only one ring at a time.

Discussion

Although the above calculated geometries refer to complexes isolated from all external interactions, it is of interest to compare these structures with those found in the crystalline state and in solution. Unfortunately, experimental evidence regarding the preferred geometries in solution is presently lacking although the published nmr spectra of some substituted 1,3-diaminopropane complexes are consistent with a preferrd chair conformation.[7] In the crystalline state, all the 1,3-diaminopropane complexes studied by X-ray have had chair conformations (see Table IV).

The four trans bis complexes listed in Table IV have the two chair conformations on opposite sides of the plane of the metal–amine coordinate bonds, consistent with the present calculations. The geometries calculated and experimentally found for the trans dichlorocobalt(III) complex are in agreement except for the angle γ which is 5° larger in the crystalline state than that calculated here. No calculations were carried out for the trans dinitrato complex. However, the observed angle for α of 87.7° is somewhat surprising and probably results from some favorable interaction between the ring atoms and the nitrato group.

The complex M(tn)₃ provides an interesting test of the calculative model since the interactions and the ring-strain energy surface for each ring are dramatically different from those of the Co(en)₃³⁺ system, from which the model was derived.[4] The calculations carried out for M(tn)₃ suggest that this complex will exist in a threefold chair configuration, which is favored over the lowest energy tris-skew-boat configuration by about 0.9 kcal mol⁻¹. The preference for the tris-chair configuration has been confirmed by the X-ray structural studies of Saito;[8] the ring parameters predicted by these calculations (Table III) correspond closely to the experimentally determined values (Table IV).

In 1967, Woldbye had predicted that the tris-skew-boat configuration would be preferred.[9] Woldbye's calculations were based on a model in which all the ring angles were assumed to maintain constant values: $\angle NMN = 90°$, $\angle MNC = 109.5°$, $\angle NCC = 109.5°$, and $\angle CCC = 110.9°$; the $H \cdots H$ interaction equations of Simmons and Williams[10] were used to calculate the ring–ring interaction energies. The apparent failure of this model illustrates the necessity to permit these rings to minimize their interactions by geometrical distortions. In their undistorted geometries, ring–ring interactions intrinsically favor the tris-skew-boat form because of the more efficient "packing" of the methylene groups in this configuration. In the tris-chair form, the major interactions involve two methylene groups of each ring and one apical amine group of an adjacent ring (see Figure 8); these interactions may be markedly

(7) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1807 (1970).
(8) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).
(9) F. Woldbye, *Proc. Roy. Soc., Ser. A*, **297**, 79 (1967).
(10) H. E. Simmons and J. K. Williams, *J. Amer. Chem. Soc.*, **86**, 3222 (1964).

TABLE IV
RING PARAMETERS FROM X-RAY STRUCTURAL STUDIES[a]

Complex	M–N	α	β	γ	ε	z_1	z_2	z_3	Ref
trans-[Co(tn)$_2$(NO$_3$)$_2$](NO$_3$)$_2$	1.99	87.7	117.9	108.8	113.3	+1.06[b]	+0.81[b]	+0.99[b]	f
			120.1	111.0					
trans-[Co(tn)$_2$Cl$_2$]Cl·HCl·2H$_2$O	2.00	95.4	119.1	114.6	111.3	c	c	c	g
[Cu(tn)$_2$](NO$_3$)$_2$	2.06	94.9	119.4	109.6	112.0	+0.61[b]	−0.04[b]	+0.51[b]	h
			119.7	112.1					
trans-[Ni(tn)$_2$(H$_2$O)$_2$](NO$_3$)$_2$	2.09	92.9	121.3	110.1	115.1	0.55[b]	0.00[b]	0.55[b]	i
			121.3	110.1					
[Co(tn)$_3$]Br$_3$·H$_2$O[e]	2.00	94.3	117.0	113.7	114.0	d	d	d	
			118.0	111.0					

[a] z_1, z_2, z_3 and M–N in Å, angles in degrees.   [b] Calculated from published atomic parameters.   [c] Atomic parameters not published.   [d] Unable to reproduce published ring parameters from published atomic parameters.   [e] Averaged values.   [f] E. Yasaki, I. Oonishi, H. Kawaguchi, and Y. Komiyama, *Bull. Chem. Soc. Jap.*, **43**, 1354 (1970).   [g] K. Matsumoto, S. Ooi, and H. Kuroya, *ibid.*, **43**, 1903 (1970).   [h] A. Pajunen, *Suom. Kemistilehti, B*, **42**, 15 (1969).   [i] A. Pajunen, *ibid., B*, **41**, 232 (1968).   [j] T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jap.*, **42**, 1016 (1969).

reduced at the expense of minor increases in ring-strain energy if the NCCCN fragment distorts away from the amine group. As mentioned above, this is the most favored mode of distortion of the chair conformation.

Although the interactions of each skew-boat ring are smaller, the ability of this conformation to reduce the interactions is limited by the nature of the interaction system. The methylene groups of this conformation interact with both apical amine groups. In the D($\delta\delta\delta$) configuration each skew-boat conformation retains its intrinsic twofold symmetry. Consequently, each ring can only relieve its interactions by modes of distortion which preserve this symmetry, resulting in the rings flattening symmetrically. This is a highly unfavorable mode of distortion since it requires large angular and torsional strain.

Clearly, the configurational preferences predicted for M(tn)$_3$ are heavily dependent on the relative magnitudes of the nonbonded interaction and ring-strain energy terms used in the calculations. If the bond angles and torsional angles are rigid, as is implicit in Woldbye's model, the preference for the tris-chair configuration can only be accounted for by unreasonably weak interaction equations, such that the natural preference of each ring for the chair conformation predominates. By treating the interactions and geometrical distortions in a more realistic manner, the present calculative model is able to account for the observed configuration as well as the rather large angular distortions present in the X-ray structure.

Experimental information concerning the pathway for ring inversion and the energy of activation is not available. However, the nmr spectra of 1,3-diaminopropane complexes are consistent with rapid conformational interconversion at room temperature,[7] which would be expected from the calculated value of about 7 kcal mol^{-1}. Low-temperature nmr studies are presently in progress in this laboratory in an attempt to determine the experimental value of the energy of activation for the chair-to-chair interconversion.

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The Crystal and Molecular Structure of
trans-Bis(triphenyl phosphite)tetracarbonylchromium(0)[1]

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The crystal and molecular structure of *trans*-bis(triphenyl phosphite)tetracarbonylchromium(0) has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic with $a = 7.977$ (2) Å, $b = 11.779$ (3) Å, $c = 20.667$ (9) Å, $\beta = 108.08$ (1)°, $V = 1846.02$ Å^3; density 1.42 g/cm^3 (by flotation), 1.417 g/cm^3 (calcd for $Z = 2$). The intensity data were collected with an automated General Electric XRD-6 diffractometer with Nb-filtered Mo Kα radiation. Final refinement of the structure resulted in a residual of 0.056 and a weighted residual of 0.048. The chromium lies on a center of symmetry, and surrounding it, in an approximately octahedral configuration, are four chemically equivalent carbonyl carbons [Cr–C = 1.88 (1) Å] and two phosphorus atoms [Cr–P = 2.252 (1) Å].

Introduction

There have been several recent reports of X-ray structural determinations of phosphorus ligand deriva-

tives of chromium hexacarbonyl.[2-6] The main interest

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