tained from the same starting material under the neutral or basic conditions which permit the inversion of the configuration at the secondary N centers.

Registry No. Chloroacetyl chloride, 79-04-9; butane-2,3-diamine, 563-86-0; *N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-35-2; *meso-N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-36-3; (±)-*N,N'*-bis(chloroacetyl)butane-2,3-diamine, 39721-37-4; *meso-N,N'*-bis(glycyl)butane-2,3-diamine·2HCl, 39721-38-5; *meso*-5,6-dmtrien·4HCl, 39721-39-6; carbobenzoxy-(*S*)-alanyl azide, 17350-66-2; *meso*-butane-2,3-diamine, 20759-15-3; *N,N'*-bis[carbobenzoxy-(*S*)-alanyl]-*meso*-butane-2,3-diamine, 39721-42-1; (2*S*,5*R*,6*S*,9*S*)-tmtrien·4HCl, 39721-43-2; *cis*-β-[Co(*meso*-5,6-dmtrien)-$(NO_2)_2$]Cl, 22850-35-7; *cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]I, 39721-45-4; [(+)-*cis*-β-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$] α-bromo-*d*-camphor-π-sulfonate, 39836-74-3; (−)-*cis*-β-[Co-(*meso*-5,6-dmtrien$(NO_2)_2$]ClO_4, 39721-14-7; *cis*-β-[Co(*meso*-5,6-dmtrien)Cl_2]Cl, 39721-15-8; *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, 39721-16-9; *trans*-(*RR,SS*)-[Co(*meso*-5,6-dmtrien)Cl_2]ClO_4, 39721-17-0; *trans*-(*RS*)-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4, 39721-18-1; *trans*-(*RR,SS*)-[Co(*meso*-5,6-dmtrien)$(NO_2)_2$]ClO_4, 39900-58-8; Δ-*cis*-β-(*RS*)-[Co-(tmtrien)$(NO_2)_2$]ClO_4, 39721-19-2; Δ-*cis*-β-(*RS*)-[Co(tmtrien)-Cl_2]ClO_4, 39721-20-5; *trans*-(*SS*)-[Co(tmtrien)Cl_2]ClO_4, 39721-21-6.

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Conformational Studies of Metal Chelates. I. Intra-ring Strain in Five- and Six-Membered Chelate Rings

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Strain energies are calculated for a series of bidentate chelate species which may be formulated as $M(L)a_4$, where a is chloride and L is ethylenediamine (en), trimethylenediamine (tn), and various *N*- and *C*-methyl-substituted derivatives. Minimum energy conformations are deduced and their conformational enthalpies and free energies are calculated using the Newton–Raphson minimization scheme developed by Boyd. For unsubstituted en, the principal nonbonded repulsions are those between N–H and C–H equatorial-axial pairs. In the pn complex, equatorial orientation of the methyl group leads to a decrease in strain energy as compared to the en complex, because (1) one C–H· · ·N–H repulsion is removed and (2) most of the CH_3 interactions are attractive. An axial CH_3 is destabilized by increases in the torsional bond angle distortion and nonbonded repulsions; the chelate ring is severely flattened; the Co–N and N–C bonds elongated and the Cl–Co–Cl and N–Co–Cl angles distorted. Axial and equatorial *N*-CH_3's are not so strongly distinguished and both produce increased Co–N and N–C bonds. Equatorial *N*-CH_3 increases five-membered ring puckering while axial *N*-CH_3 decreases it. The minimum energy conformations for six-membered rings have larger bond angles and longer bonds. Chair rings are more stable than twist because of torsional distortions in the latter. The distinction between axial and equatorial methyls is greater for six-membered rings. For a twist ring, an axial orientation is favored for *N*-CH_3. Multiple substitution is considered.

Introduction

In the years subsequent to the pioneering work of Corey and Bailar[1] a number of studies have appeared utilizing computational schemes to predict and rationalize the conformational behavior of chelates in metal complexes. The most general of these studies were those of Gollogly and Hawkins on mono-, bis-, and tris-chelate complexes of ethylenediamine, propylenediamine, *N*-methylethylenediamine, and trimethylenediamine.[2]

The approach that they used in their calculations was based on the fact that for a chelate ring there are $3N - 6$ independent variables which specify the exact conformation of the ring. In their calculations they held all bond lengths constant and then systematically varied the other parameters over a given range. At each interval they would calculate an energy for that particular conformation. These energies could then be plotted as a function of the different variables and energy minima located.

There are a number of difficulties with this approach. First, although the variables they chose may be independent of each other, the energy is not an independent function of each individual variable. Second, they have only considered the atoms in the chelate ring skeleton as having the freedom to distort. Hydrogens bound to the chelate ring are not allowed to move independently. An additional criticism is that their energy values cannot be related to experimental energies since they have neglected entropies and, at best, their values are enthalpies not free energies. Despite these criticisms, their work was valuable in that it gave us some feel for the flexibility and range of conformations which are accessible to a chelate.

A second and more rigorous approach to the computation of conformational energies and geometries utilized a Newton-Raphson minimization scheme developed by Boyd[3] and was applied to metal chelates by Snow, *et al.*[4] It is this second approach which we also have chosen to use, with the notable addition of an entropy calculation which allows us to calculate not just conformational enthalpies but relative conformational free energies.

Our aim in using these techniques of conformational analysis in the study of transition metal chelate complexes was (1) to identify those structural features which lead to "preferred" structures and (2) to calculate the relative free energy differences which accompany changes in these particular structural features.

With this dual aim in mind, we undertook a systematic

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study of chelate complexes commencing with a determination of those features within a single chelate ring which lead to a definite conformation.

II. Calculational Scheme

Calculation of the relative conformational free energies of the possible conformers in this work was undertaken using the classical model of the strained molecule.[5-8] The calculations are then a measure of the structural deformation (strain) or instability of the conformer. The conformational or strain energy is defined as

$$U = U_R + U_\theta + U_\phi + U_{\mathrm{NB}}$$

where U_R is the energy associated with bond stretching, U_θ is the energy resulting from bond angle deformation, U_ϕ is the energy involving bond torsions, and U_{NB} is the energy arising from the nonbonded or van der Waals interactions in the molecule.

Using this approach, the differences in the calculated conformational energies of two molecules or of a series of conformers may be approximated to a relative conformational enthalpy difference. This, in turn, can be related to a relative conformational free energy upon consideration of an appropriate entropy contribution.

For calculation of U_R and U_θ we have used the commonly accepted Hooke's law functions[8]

$$U_R = \Sigma \frac{1}{2} k_R (R - R_0)^2$$

$$U_\theta = \Sigma \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

where R_0 and θ_0 are the strain-free values for the bond lengths and angles as listed in Table I. The force field contains one such term for each bond and bond angle in the molecule.

For the bond between two tetrahedral atoms, the torsional potential can be described as[8]

$$U_\phi = \Sigma_i \frac{1}{2} k_{\phi_i} (1 + \cos 3\phi_i) \qquad i = 1, 9$$

where k_{ϕ_i} is the barrier height and ϕ_i is the dihedral angle. Values of k_{ϕ_i} are tabulated in Table I. The 12-fold barriers about metal-ammine bonds have been shown to be effectively zero.[9] The calculations will then include nine of the above torsional terms for each C-C and C-N bond.

The nonbonded interactions were calculated using a Buckingham-type function[8]

$$U_{\mathrm{NB}} = a \exp(-br) - c/r^6$$

where the r^{-6} term represents the attractive forces and the exponential term approximates the repulsive forces. The set of nonbonded interactions $[(N!/2!(N-2)!)$ – number of bonding interactions, where N is the number of atoms in the molecule] has been modified as suggested by Allinger[10] to eliminate all 1,3 interactions, since it can be considered that these interactions have been implicitly included in the bending (k_θ) and bonding (k_R) constants. The rationale for this approximation is that the 1,3 interactions have large

Table I. Parameters for Calculations of Conformational Enthalpies

Bond Stretching Constants

Bond type	k_R, mdyn/Å	R_0, Å	Ref
Co-N	1.47	2.00	1, 2
Co-Cl	1.68	2.30	2
N-C	3.89	1.47	1, 2
N-H	4.92	1.00	*a*
C-C	4.50	1.54	*a*
C-H	4.55	1.09	*a*

Angle Bending Constants

Angle type	k_θ, mdyn/Å	θ_0, radians	Ref
N-Co-N	0.400	1.571	2, 4
Co-N-C	0.278	1.911	2, 4
Co-N-H	0.278	1.911	2, 4
Cl-Co-Cl	0.278	1.511	2, 4
Cl-Co-N	0.278	1.511	2, 4
C-C-C	0.694	1.911	2, 4, *a*
C-C-H	0.485	1.911	2, 4, *a*
C-N-H	0.278	1.911	2, 4, *a*
C-N-C	0.694	1.911	2, 4, *a*
N-C-C	0.694	1.911	2, 4, *a*
N-C-H	0.485	1.911	2, 4, *a*
H-C-H	0.555	1.911	2, 4, *a*
H-N-H	0.417	1.911	2, 4, *a*

Torsional Parameters[b]

Torsion	$10^3 k_\phi$[c]	Torsion	$10^3 k_\phi$[c]
HCCH	1.51	CoNCC	0.76
HCNH	1.00	CNCC	0.76
HCNCo	1.51	NCoNC	0.00
HCCC	2.27	NCCN	1.14
HCNC	1.51	NCCC	1.14
HNCC	1.51	CCCC	1.14
HCCN	2.27		

Nonbonded Interaction Parameters

Atoms	$10^{11} a$, ergs molecule^{-1}	b, Å^{-1}	$10^{11} c$, Å molecule^{-1}	Ref
H···H	375.0	4.685	0.6041	*d*
H···C	363.7	4.384	0.8771	*e, f*
H···N	481.1	4.544	0.9342	*e, f*
H···Cl	883.3	4.038	3.485	*e, f*
C···C	229.9	4.117	0.8070	*e, f*
C···N	304.3	4.259	0.8713	*e, f*
C···Cl	558.7	3.811	3.117	*e, f*
N···N	402.5	4.411	0.9337	*e, f*
N···Cl	739.0	3.933	3.416	*e, f*
Cl···Cl	1357.0	3.548	11.64	*e, f*

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Table II. Minimized Geometries of the Five-Membered Mono Chelates

	Bond lengths (R), Å					Bond angles (θ), deg					Torsional angles (ϕ), deg				
Conformer	Co-N	N-C	C-C	C-N	N-Co	N-Co-N	Co-N-C	N-C-C	C-C-N	C-N-Co	Co-N	N-C	C-C	C-N	N-Co
en	2.02	1.48	1.55	1.48	2.02	87.2	106.1	107.9	107.9	106.1	14.9	40.7	55.7	40.7	14.9
pn (eq)	2.02	1.48	1.55	1.48	2.02	87.2	106.2	107.8	108.0	106.1	14.8	40.6	55.6	40.8	14.9
pn (ax)	2.03	1.49	1.55	1.48	2.02	86.2	110.0	108.2	109.7	106.5	4.8	28.8	47.9	42.6	21.1
rac-bn (eq, eq)	2.02	1.48	1.55	1.48	2.02	86.7	106.7	107.4	107.4	106.7	15.0	40.9	55.5	40.9	15.0
meso-bn (eq, ax)	2.02	1.49	1.56	1.49	2.02	86.1	106.8	109.7	107.4	110.1	19.9	42.2	48.8	30.7	6.8
rac-bn (ax, ax)	2.02	1.49	1.55	1.49	2.02	84.9	111.2	109.2	109.2	111.2	11.8	32.0	41.6	32.0	11.8
N-Meen (eq)	2.05	1.49	1.55	1.48	2.03	87.4	104.5	108.4	107.9	106.3	16.7	42.6	56.8	39.6	13.1
N-Meen (ax)	2.04	1.49	1.55	1.48	2.02	87.8	105.1	109.2	108.2	106.0	13.3	38.9	54.9	40.5	15.6
N,N'-DMeen (eq, eq)	2.05	1.48	1.55	1.48	2.05	87.7	104.6	108.5	108.5	104.6	15.0	41.5	58.1	41.6	15.0
N,N'-DMeen (eq, ax)	2.04	1.49	1.55	1.48	2.05	88.0	105.1	109.2	108.7	104.5	12.4	38.6	56.2	41.9	16.7
N,N'-DMeen (ax, ax)	2.04	1.49	1.55	1.49	2.04	88.4	105.0	109.4	109.4	105.0	14.1	39.0	54.4	39.0	14.1
N_1-Mepn (eq, eq)	2.05	1.49	1.55	1.48	2.02	87.4	105.0	108.2	108.3	105.9	13.5	39.5	56.2	42.0	16.2
N_1-Mepn ($\mathrm{C_{ax}}$, $\mathrm{N_{eq}}$)	2.05	1.50	1.55	1.48	2.02	86.1	108.7	107.6	109.5	106.5	7.3	32.2	51.2	43.7	20.2
N_1-Mepn ($\mathrm{N_{ax}}$, $\mathrm{C_{eq}}$)	2.04	1.49	1.55	1.48	2.02	87.9	104.5	109.0	108.1	106.1	14.8	40.5	55.8	40.1	14.5
N_1-Mepn (ax, ax)	2.05	1.50	1.55	1.48	2.02	86.6	108.5	108.6	109.8	106.3	5.4	29.7	49.4	43.1	21.0
N_2-Mepn (eq, eq)	2.04	1.49	1.55	1.48	2.03	87.3	104.6	108.5	107.8	106.5	16.7	42.6	56.7	39.5	13.1
N_2-Mepn ($\mathrm{C_{ax}}$, $\mathrm{N_{eq}}$)	2.04	1.49	1.55	1.49	2.03	86.5	104.7	110.3	108.4	110.0	23.4	44.6	48.5	26.6	2.2
N_2-Mepn ($\mathrm{N_{ax}}$, $\mathrm{C_{eq}}$)	2.04	1.49	1.55	1.48	2.02	87.8	105.1	109.3	108.0	106.2	13.2	38.9	54.8	40.6	15.7
N_2-Mepn (ax, ax)	2.03	1.49	1.56	1.49	2.03	87.5	106.4	112.5	109.1	110.0	15.4	35.2	42.7	27.7	7.3

Table III. Minimized Energies of the Five-Membered Mono Chelates (kcal/mol)

Conformer	R	NB	θ	ϕ	H	TS^a	G
en	0.25	−1.51	1.25	0.60	0.58	32.42	−31.84
pn (eq)	0.29	−2.59	1.34	0.58	−0.38	34.74	−35.12
pn (ax)	0.41	−1.85	1.95	1.30	1.81	34.48	−32.67
rac-bn (eq, eq)	0.37	−3.53	1.66	0.76	−0.75	36.14	−36.89
meso-bn (eq, ax)	0.53	−2.71	2.54	1.31	1.68	36.17	−35.64
rac-bn (ax, ax)	0.63	−2.17	3.20	2.11	3.77	35.85	−32.08
N-Meen (eq)	0.56	−1.08	2.50	0.50	2.49	34.70	−32.21
N-Meen (ax)	0.55	−1.06	2.22	0.93	2.63	34.35	−31.72
N,N'-DMeen (eq, eq)	0.95	−0.58	3.87	0.39	4.63	36.18	−31.55
N,N'-DMeen (eq, ax)	0.90	−0.59	3.56	0.80	4.66	36.17	−31.51
N,N'-DMeen (ax, ax)	0.87	−0.53	3.25	1.27	4.87	35.39	−30.52
N_1-Mepn (eq, eq)	0.76	−1.77	2.94	0.58	2.52	36.61	−34.09
N_1-Mepn ($\mathrm{C_{ax}}$, $\mathrm{N_{eq}}$)	0.86	−1.19	4.08	0.97	4.72	35.78	−31.06
N_1-Mepn ($\mathrm{N_{ax}}$, $\mathrm{C_{eq}}$)	0.71	−1.88	3.01	0.91	2.74	35.79	−31.05
N_1-Mepn (ax, ax)	0.81	−1.37	3.02	1.45	3.91	35.93	−32.03
N_2-Mepn (eq, eq)	0.61	−2.17	2.59	0.48	1.51	36.62	−35.11
N_2-Mepn ($\mathrm{C_{ax}}$, $\mathrm{N_{eq}}$)	0.70	−1.44	3.02	1.33	3.61	36.19	−32.58
N_2-Mepn ($\mathrm{N_{ax}}$, $\mathrm{C_{eq}}$)	0.59	−2.13	2.30	0.91	1.68	36.26	−34.58
N_2-Mepn (ax, ax)	0.77	−0.78	3.64	2.37	6.01	36.08	−30.07

[a] $T = 298.15°\mathrm{K}$.

values (strongly repulsive) which tend to dominate the total value of U_{NB}. This domination would require that the constants which are used to calculate U_{NB} be very well known and such is not the case. We have therefore chosen explicitly not to include these interactions. All other nonbonded interactions have been included in the force field.

Starting cartesian coordinates for the skeletal atoms were derived from an idealized set of bond lengths and bond angles (Table I) using the relationships presented by Hendrickson.[11] Coordinates for the hydrogens and methyl substituents were calculated using simple vector methods. Any unreasonable values for bond lengths or angles which this procedure produced and which we felt might jeopardize minimization could be improved by attempting minimization in two stages: (1) using a modified force field containing no nonbonded terms and then (2) using the coordinates from this previous step with the full force field.

Energy minimization was accomplished utilizing a modified Newton-Raphson approach due to Boyd.[3] An advantage of this approach is that the same matrix which yields the minimized coordinates can be used to calculate a set of vibrational energy levels for the molecule.[3,12] These vibrational energy levels can then be used to calculate the vibrational contribution to the entropy[13]

$$\bar{S}_{\mathrm{vib}} = R \sum_{i=1}^{3N-6} \frac{h\nu_i/kT}{\exp\left(\frac{h\nu_i}{kT} - 1\right)} - \ln\left(1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right)$$

The molar entropy (cal deg^{-1}) for the molecule can then be obtained by adding the translational entropy[14]

$$\bar{S}_T = R\left\{\frac{3}{2}\ln \mathrm{MW} + \frac{5}{2}\ln T - \ln P - 3.664 + \frac{5}{2}\right\}$$

where MW is the molecular weight, T is the temperature in degrees Kelvin, and P is the pressure in atmospheres. The rotational entropy[13] is

$$\bar{S}_{\mathrm{rot}} = R \ln\left(\frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}\right) + \frac{3}{2}R$$

where ABC is the product of the moments of inertia and σ is the rotational symmetry number, corresponding to the number of identical spatial orientations the molecule can achieve through simple rotations. To this classical entropy is then added any statistical entropy terms which may apply to a

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Table IV. Nonbonded Interactions for the $[Co(en)Cl_4]^-$ Complex Depicted in Figure 1

Atoms	Nonbonded strain energy, kcal/mol	Atoms	Nonbonded strain energy, kcal/mol	Atoms	Nonbonded strain energy, kcal/mol
2-6	−0.07	4-12	−0.05	9-11	−0.01
8	−0.03	13	−0.04	10-12	0.03
9	−0.05	14	−0.07	13	0.37
10	−0.04	15	−0.06	14	−0.03
11	−0.04	16	0.00	15	−0.02
12	−0.01	17	−0.11	16	−0.01
13	−0.03	5-8	−0.12	17	−0.02
14	−0.04	9	−0.09	11-12	0.36
15	−0.02	10	0.00	13	−0.08
16	−0.03	11	−0.11	14	−0.03
17	−0.18	12	−0.06	15	−0.03
3-7	−0.07	13	−0.07	16	−0.02
8	−0.05	14	−0.04	17	−0.02
9	−0.03	15	−0.05	12-14	0.10
10	−0.03	16	−0.12	15	0.05
11	−0.18	17	0.23	16	−0.02
12	−0.02	6-14	−0.02	17	−0.03
13	−0.04	15	−0.07	13-14	−0.07
14	−0.03	16	−0.06	15	0.10
15	−0.01	17	−0.08	16	−0.03
16	−0.04	7-10	−0.06	17	−0.03
17	−0.04	11	−0.08	14-16	0.37
4-5	−0.16	12	−0.07	17	−0.08
8	−0.09	13	−0.02	15-16	0.03
9	−0.12	8-16	−0.07	17	0.36
10	−0.12	17	−0.01		
11	0.23	9-10	−0.07		

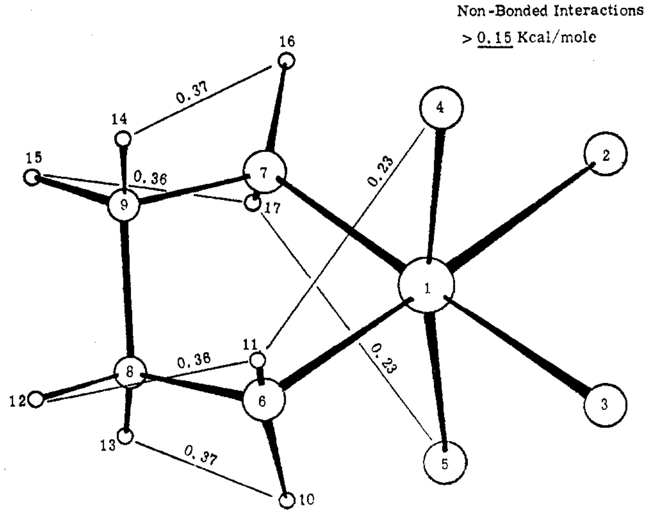

Figure 1. The $[Co(en)Cl_4]^+$ complex.

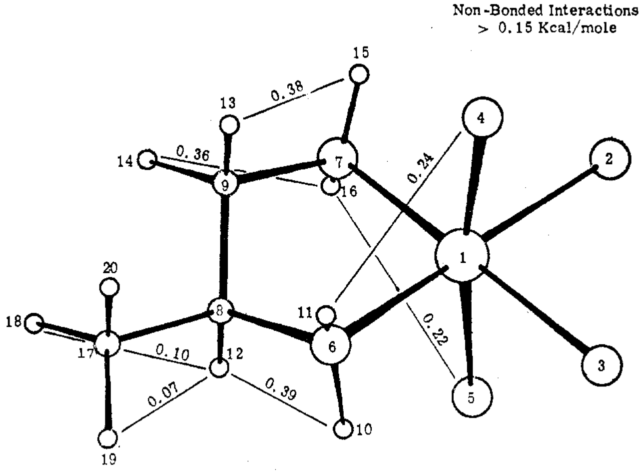

Figure 2. The $[Co(S\text{-}pn)_\delta Cl_4]^-$ complex.

particular conformer. These are of the form[15]

$$\bar{S}_{\text{stat}} = -R \ln \sigma'$$

where σ' is the number of ways in which a given conformer can be formed.

The final entropy term ($-TS$) is then added to the calculated conformational enthalpy (strain energy) to obtain a relative conformational free energy for each molecule or conformer

$$G = \Sigma U_R + \Sigma U_\theta + \Sigma U_\phi + \Sigma U_{\text{NB}} - TS$$

A summary of the force constants and parameters used in our calculations is presented in Table I.

III. Results and Discussion

Systems of the type $M(L)a_4$ where L is a bidentate ligand should be ideal for locating the principal sources of strain *within* the individual chelate rings. The ligands which we incorporated into the complexes were a series of methyl-substituted chelates based on ethylenediamine and trimethylenediamine. We chose these because they form five- and six-membered chelate rings upon complexation and therefore are representative of the vast majority of known complexes containing amine donors.

Five-Membered Chelate Systems. The ethylenediamine chelate is shown in Figure 1 as the complex $[Co(en)Cl_4]^-$. An examination of Table II, which contains the "minimized geometry" (geometry corresponding to the minimum strain energy) for the complex, shows that the chief sources of strain within the ethylenediamine chelate arise from small deviations of the bond angles from the "ideal" tetrahedral value of 109.5° and of the torsional angles about the C-N bonds. The strain-free values for the latter angles should be ~60°, a value which the C-C bond approaches in this example. A substantial source of strain which is not readily apparent in Table II arises from nonbonded repulsions between the axial C-H's and the equatorial N-H's, as well as the equatorial C-H's and the axial N-H's. These eight inter-

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[15] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 56.

actions are shown in Figure 1 and represent about 0.36 kcal/mol of strain energy each. Also within the complex and again depicted in Figure 1, we find nonbonded repulsions between the axial N-H's and the axial Cl's amounting to 0.23 kcal/mol per interaction. All of the terms contributing to the total strain energy are summarized in Table III, while Table IV contains *all* of the nonbonded interactions for this molecule. It should be noted in Table IV that the majority of the nonbonded interactions are small and attractive (negative). This observation is true for all of the molecules we have examined. Thus even though the sum of the principal nonbonded interactions shown in the figures is repulsive (positive), the sum of *all* the nonbonded interactions in the molecule, designated as "NB" in the tables, often is a negative number due to the large number of these attractive terms.

If we now replace one of the equatorial C-H's on the ethylenediamine ring with a methyl group, we can see from Table II that there is no significant change in the geometry of the complex. The chelate is now propylenediamine and is depicted in Figure 2. Examination of the strain energies in Table III, however, shows us that there is now a marked decrease in the nonbonded interaction term. We can account for some of this increased stability if we recall that what we have effectively done is to remove one of the C-H· · ·N-H interactions from the chelate. The remaining difference results from the fact that with the exception of the interactions noted in Figure 2 most of the nonbonded interactions with the methyl group are small and attractive as shown in Table V. If we compare the calculated free energies (Table III) of the ethylenediamine and propylenediamine complexes, we see that we would predict the propylenediamine complex to be more stable.

Suppose, however, that we had replaced the axial C-H instead of the equatorial C-H with the methyl group. This complex is depicted in Figure 3. From Table II we can see that significant changes occur in the geometry as a result of the axial methyl group. We can see a slight elongation of the Co-N and N-C bonds, as well as a severe flattening of the chelate ring as reflected in the torsional angles. This flattening is probably the mode by which the chelate ring alleviates the strong repulsion between the axial Cl^- and the axial methyl. In the starting trial geometry, this ring also had a symmetrical conformation derived from that of the ethylenediamine chelate, and the axial CH_3-Cl^- repulsion represented a strain of 65.25 kcal/mol. After the ring has flattened, this interaction represents a strain energy of only 0.25 kcal/mol. In addition to this flattening, some of the nonbonded strain is relieved by distortions in the Cl-Co-Cl and N-Co-Cl bond angles. The strain energy associated with these angles is 0.29 kcal/mol greater in the complex with the axial methyl than in the complex with an equatorial methyl. These changes in the minimized geometry are reflected in the strain energy terms contained in Table III. We note especially the increase in the nonbonded strain energy (a few significant contributions to this energy are shown in Figure 3) relative to the propylenediamine chelate with an equatorial methyl and the marked increase in the torsional term resulting from the ring flattening. The calculated free energy barrier for the conversion of the methyl group from an equatorial to an axial site is 2.45 kcal/mol and corresponds (using $\Delta G = -RT \ln K$) to a distribution of 98% equatorial, 2% axial at 25°.

Analogous results are obtained for the complex in which two methyl groups are placed on the ethylenediamine chelate. These 2,3-diaminobutane complexes display an in-

Table V. Nonbonded Interactions with the Methyl Group of the Complex $[Co(pn)Cl_4]^-$ Depicted in Figure 2

Atoms	Nonbonded strain energy, kcal/mol	Atoms	Nonbonded strain energy, kcal/mol
17-2	−0.01	19-4	−0.02
3	−0.01	5	−0.03
4	−0.03	6	−0.05
5	−0.03	7	−0.01
7	−0.04	9	−0.06
10	−0.04	10	−0.05
11	0.16	11	−0.08
13	0.00	12	0.07
14	−0.02	13	−0.03
15	−0.01	14	−0.03
16	−0.02	15	0.00
18-2	0.00	16	−0.01
3	−0.01	20-2	−0.01
4	−0.01	3	−0.01
5	−0.02	4	−0.05
6	−0.07	5	−0.02
7	−0.03	6	−0.07
9	−0.02	7	−0.03
10	−0.03	9	−0.01
11	−0.04	10	−0.06
12	0.10	11	0.10
13	−0.07	12	−0.07
14	−0.02	13	0.03
15	−0.01	14	−0.07
16	−0.01	15	−0.01
19-2	0.00	16	−0.01
3	−0.02		

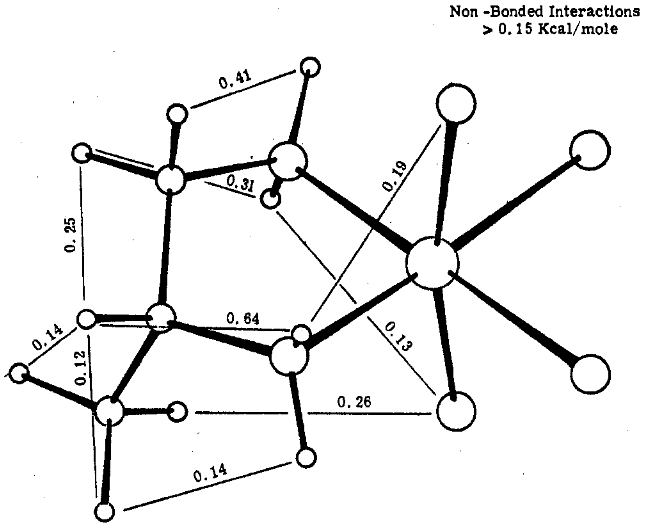

Figure 3. The $[Co(R\text{-pn})_\delta Cl_4]^-$ complex.

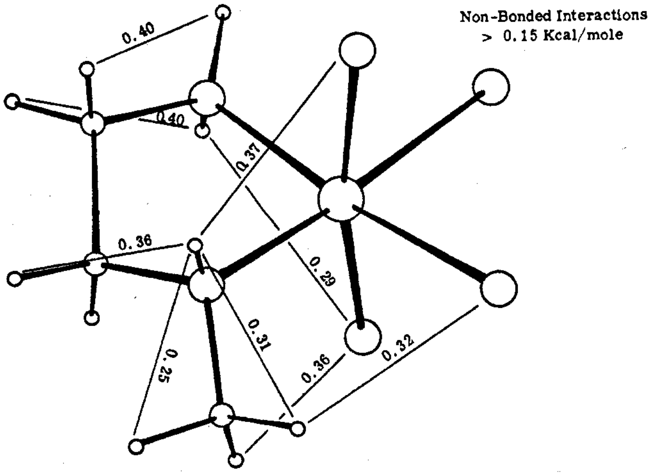

Figure 4. The R-$[Co(N\text{-Meen})_\delta Cl_4]^-$ complex.

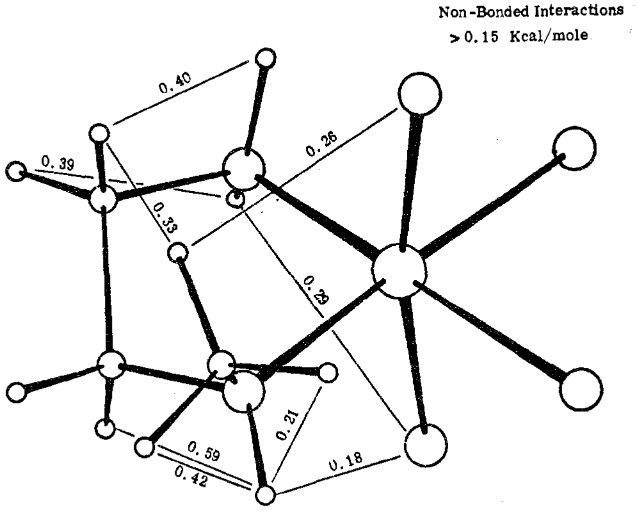

Figure 5. The *S*-[Co(*N*-Meen)$_\delta$Cl$_4$]$^-$ complex.

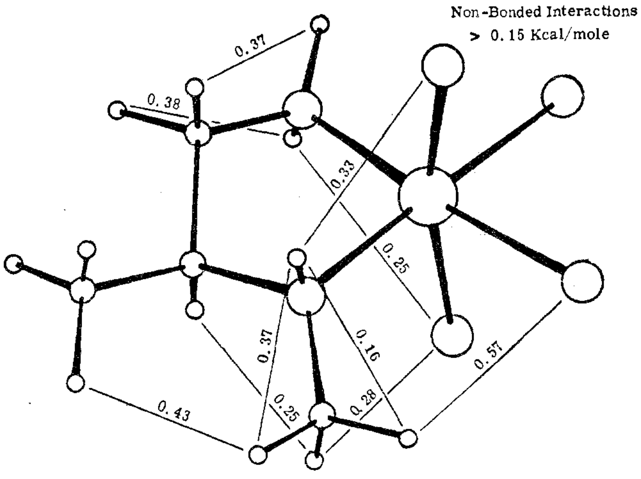

Figure 6. The *R*-[Co(*N*$_1$-Me-*S*-pn)$_\delta$Cl$_4$]$^-$ complex.

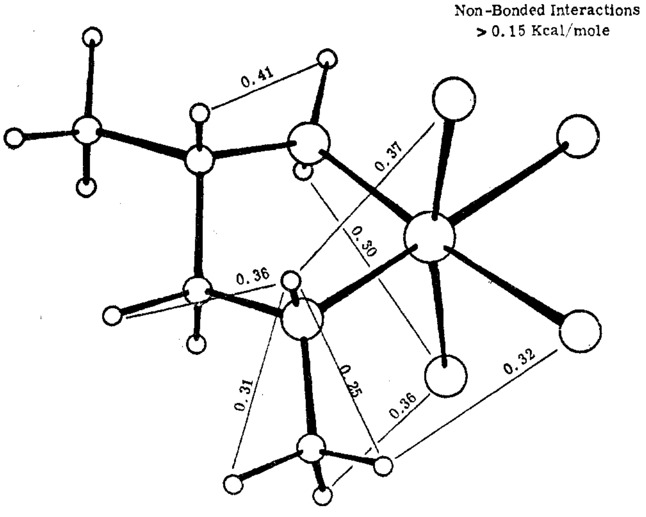

Figure 7. The *R*-[Co(*N*$_2$-Me-*S*-pn)$_\delta$Cl$_4$]$^-$ complex.

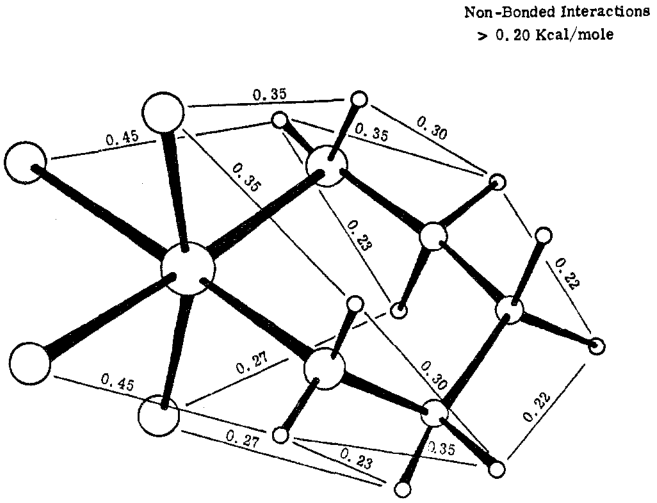

Figure 8. The [Co(tn)$_\gamma$Cl$_4$]$^-$ complex.

creased flattening of the chelate ring as we go from a complex with two equatorial methyls to a complex with one equatorial and one axial methyl to the complex with two axial methyls (Table II). In Table III we can follow the increase in the nonbonded and torsional strain energies as we make the same substitutions. We can also note that the terms appear to be almost additive; *i.e.*, the complex with two axial methyls has a ΔH of 4.5 kcal/mol relative to the complex with two equatorial methyls, while the difference for the propylenediamine case was ΔH = 2.2 kcal/mol. The deviation from exact linearity can be attributed to the strain in the angle between the methyl carbons and the methine hydrogens. Since there are two axial substituents in the 2,3-butanediamine complex the chelate ring cannot flatten as much as in the propylenediamine example. In order to reduce further the axial Cl-CH$_3$ repulsions these two angles close down to 106°.

Initially we could have placed our methyl substituent on a nitrogen instead of a carbon atom. Such an *N*-methylethylenediamine complex is shown in Figure 4 with the methyl group equatorial and in Figure 5 with the methyl substituent axial. Table II shows two effects on the chelate ring geometry of the *N*-methyl substituent. First, we note that for both the axial and equatorial orientations there is an increase in the Co-N and N-C bond lengths relative to the unsubstituted ethylenediamine ring. For the equatorial orientation this is a result of interactions between the Cl$^-$ ligand which lies in the plane of the chelate ring and the *N*-methyl group. This interaction as shown in Figure 4 contributes 0.32 kcal/mol to the nonbonded strain energy in the minimized structure. Such steric interactions could account for the decrease in Pt-amine bond strengths in chelates of this type which Erickson has reported accompanies *N*-methyl substituents.[16] For the axial methyl orientation there are a number of significant nonbonded repulsions among which those between the axial Cl$^-$, an axial C-H, and the axial methyl are prominent. In the minimized structure these interactions make contributions of 0.26 and 0.33 kcal/mol to the strain energy, respectively. These interactions also account for the second effect we can see in the geometry of these complexes. For the equatorial substituent we can see from the torsional angles that there is an increase in the puckering of the chelate ring relative to the ethylenediamine chelate, while for the axial substituent we note that there is a slight flattening of the ring as was the case with the axial *C*-methyl substituents. The increase in puckering corresponds to a movement of the equatorial methyl away from the in-plane Cl$^-$ and results in a further lowering of the strain energy associated with this nonbonded interaction. Related interactions and changes in geometry can be seen in the three conformers of the *N,N'*-dimethylethylenediamine complexes. Table III shows one outstanding difference between the *C*-methyl and *N*-methyl complexes, and this is in the relative

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(16) L. E. Erickson, *J. Amer. Chem. Soc.*, 91, 6284 (1969).

Table VI. Minimized Geometries of the Six Membered Mono Chelates

	Bond length (R), Å						Bond angles (θ), deg						Torsional angles (ϕ), deg					
Conformer	Co-N	N-C	C-C	C-C	C-N	N-Co	N-Co-N	Co-N-C	N-C-C	C-C-C	C-C-N	C-N-Co	Co-N	N-C	C-C	C-C	C-N	N-Co
tn (γ)[a]	2.04	1.49	1.55	1.55	1.49	2.04	91.1	117.2	112.0	111.9	112.0	117.2	45.1	61.4	67.8	67.8	61.4	45.1
tn (δ)[b]	2.00	1.49	1.55	1.55	1.49	2.04	90.4	113.7	112.6	112.7	112.5	113.1	33.4	73.8	37.9	31.7	73.1	33.7
1,3-bn (γ eq)	2.04	1.49	1.55	1.55	1.49	2.04	91.0	117.8	111.4	112.2	112.1	117.0	45.2	61.0	67.3	68.2	61.6	45.0
1,3-bn (γ ax)	2.05	1.49	1.55	1.55	1.48	2.03	97.2	122.9	112.1	113.8	111.6	117.2	16.5	36.1	65.4	77.5	54.3	24.7
1,3-bn (δ eq)	2.06	1.49	1.55	1.55	1.49	2.04	89.5	114.6	112.9	112.4	111.9	116.7	50.1	64.2	66.3	64.8	63.7	50.8
1,3-bn (δ ax)	2.06	1.50	1.55	1.55	1.49	2.04	91.6	115.4	114.0	112.0	111.9	117.0	44.3	60.0	66.8	66.9	62.6	46.7
N-Metn (γ eq)	2.04	1.49	1.55	1.55	1.49	2.04	90.0	113.0	112.7	113.1	112.1	113.5	33.6	73.7	37.7	37.8	73.7	33.8
N-Metn (γ ax)	2.04	1.50	1.56	1.55	1.49	2.03	89.4	121.4	113.4	114.5	113.4	112.8	29.0	59.0	20.6	47.7	76.5	34.1
N-Metn (δ eq)	2.06	1.49	1.55	1.55	1.48	2.04	90.7	110.0	113.0	113.0	112.1	113.7	35.8	75.5	38.9	38.7	72.6	31.2
N-Metn (δ ax)	2.00	1.49	1.55	1.55	1.48	2.04	92.2	112.5	114.3	113.6	112.6	113.5	26.9	71.2	44.3	29.8	70.2	37.8

[a] γ designates a chair conformation. [b] δ (or λ) designates the twist conformation.

Table VII. Minimized Energies of the Six-Membered Mono Chelates (kcal/mol)

Conformer	R	NB	θ	ϕ	H	TS[a]	G
tn (γ)	0.54	−0.21	3.07	0.14	3.55	34.47	−30.92
tn (δ)	0.41	−0.28	2.90	1.70	4.73	33.95	−29.22
1,3-bn (γ eq)	0.62	−1.14	3.17	0.15	2.80	36.38	−33.58
1,3-bn (γ ax)	0.81	−0.14	5.08	1.28	7.03	36.30	−29.27
1,3-bn (δ eq)	0.61	−1.43	2.89	1.70	3.77	36.19	−32.42
1,3-bn (δ ax)	0.82	−0.30	5.50	2.65	8.67	35.88	−27.21
N-Metn (γ eq)	0.96	0.16	4.62	0.17	5.90	35.94	−30.04
N-Metn (γ ax)	0.97	0.26	4.88	0.27	6.39	35.80	−29.41
N-Metn (δ eq)	1.04	0.32	4.14	1.76	7.26	35.57	−28.31
N-Metn (δ ax)	0.65	0.05	4.73	1.67	7.09	35.53	−28.44

[a] $T = 298.15$°K.

free energy difference between the axial and equatorial methyl orientations.

An nmr study by Haake and Turley[17] has shown that for the conversion of the *rac*-$[Pt(NH_3)_2DMeen]^{2+}$ complex to the meso isomer, $K_{eq} \approx 1$. The calculations (Table III) on the analogous isomers *rac*-$[Co(Cl)_4DMeen]^-$ and *meso*-$[Co(Cl)_4DMeen]^-$ show a free energy difference of 0.04 kcal/mol, corresponding to a K_{eq} of ~1.07. The *N*-methyl complexes, therefore, do not show as great a preference for the equatorial orientation as do the *C*-methyl complexes, the implication being that there is not much difference between the axial and equatorial sites for substituents on the coordinated amines in five-membered rings. For the *N*-methyl complexes this difference is 0.49 kcal/mol which corresponds to a 70% equatorial, 30% axial equilibrium distribution. For the *N,N'*-dimethyl complexes the differences correspond to a 48:44:8 distribution. Both of these distributions are significantly less extreme than those predicted for the corresponding *C*-methyl complexes.

Reilley and coworkers have attempted to measure the energy differences between conformers in the mono-chelate systems $[Ni(H_2O)_4L]^{2+}$, where L is a diamine, using contact shift nmr.[18,19] The two chelates they have examined which are relevant to our study are *R*-pn and *N,N'*-DMeen. For these two systems they report ΔG values at 305°K of 1.1 and 0.86 kcal/mol, respectively, as compared to our calculated values of 2.45 and 1.03 kcal/mol. By studying the temperature dependence of the free energy they attempted to separate the ΔH and ΔS contributions to ΔG for the *N,N'*-DMeen complex. Their reported values for these contributions in this system are $\Delta H = 0.71$ kcal/mol and $T\Delta S = -0.15$ kcal/mol. There are some difficulties in comparing their data with the results of the calculations on these two systems. The first difficulty is that the calculations use complexes incorporating Cl^- ligands while their experiment uses H_2O for ligands. Gollogly and Hawkins[2] have shown that, at least for unsubstituted diamines, replacement of the H_2O ligands by Cl^- increases the calculated energy differences for the system. Even allowing for this there are discrepancies between the two sets of "data." Especially disconcerting is the disparity between the $T\Delta S$ estimates. Experimentally most of Reilley's $T\Delta S$ terms are in the order of 0.1–0.2 kcal/mol, which are just slightly lower than the 0.2–0.4 kcal/mol we calculate for the singly substituted rings. The chelates with more than one methyl group, however, show much higher calculated values for $T\Delta S$, usually on the order of 0.6–0.8 kcal/mol. In view of these difficulties and the fact that the experimental results are based on assumed values for the intrinsic chemical shifts of the axial and equatorial protons while the calculations actually assume gaseous complexes, one might consider the values obtained to be surprisingly close.

Tables II and III also contain data on mixed *N*- and *C*-methyl complexes. Figures 6 and 7 exemplify the conformers of the *N*-methylpropylenediamine complexes. The mixed complexes all show the same trends as the simpler monosubstituted complexes, in particular, elongation of the Co–N bonds on *N*-methyl substitution and the severe flattening of the rings with an axial *C*-methyl substituent.

Six-Membered Chelate Systems. We have carried out an analogous study for complexes containing six-membered chelate rings, and the results of these calculations are presented in Tables VI and VII. The three basic conformations for the six-membered chelate ring are the chair, skew boat (twist), and boat. Previous studies have shown[2] the boat conformer to be considerably more strained than either the chain or twist conformers. As a result of the high strain energy of the boat conformation, we have only further investigated the chair and twist conformers. The geometries of both these conformers, depicted in Figures 8 and 9, are significantly different from those of the five-membered ethylenediamine chelate rings. The metal–nitrogen bond lengths

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(17) P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, **90**, 2293 (1968).

(18) F. F. L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969); **42**, 600 (1970).

(19) L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970).

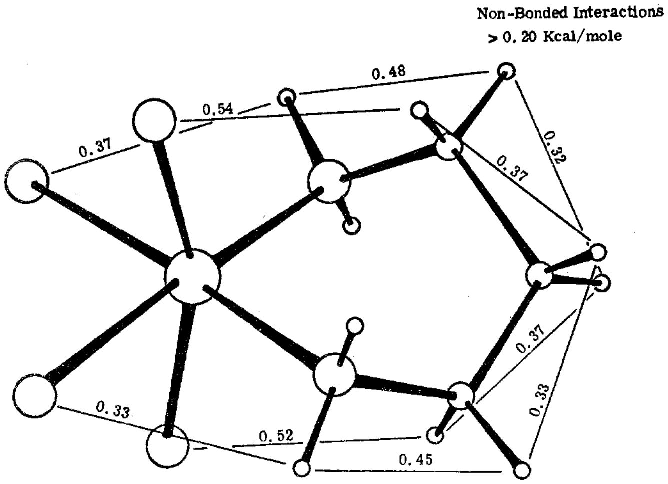

Figure 9. The $[\mathrm{Co(tn)}_{\lambda}\mathrm{Cl}_4]^-$ complex.

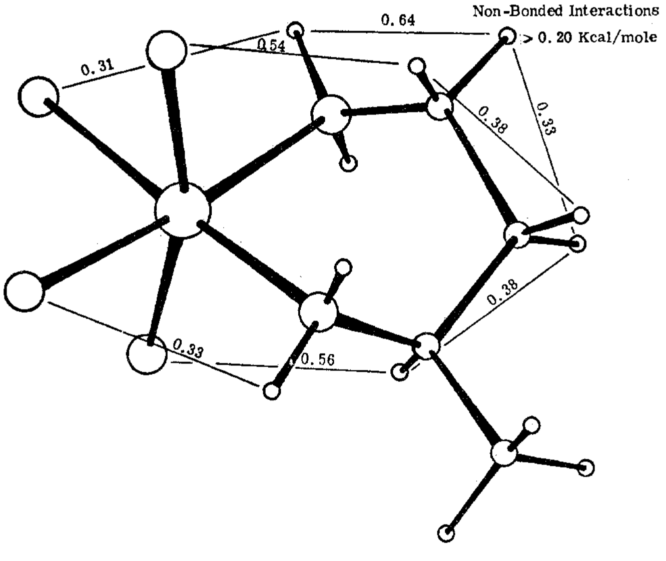

Figure 10. The $[\mathrm{Co}(R\text{-}1,3\text{-bn})_{\lambda}\mathrm{Cl}_4]^-$ complex.

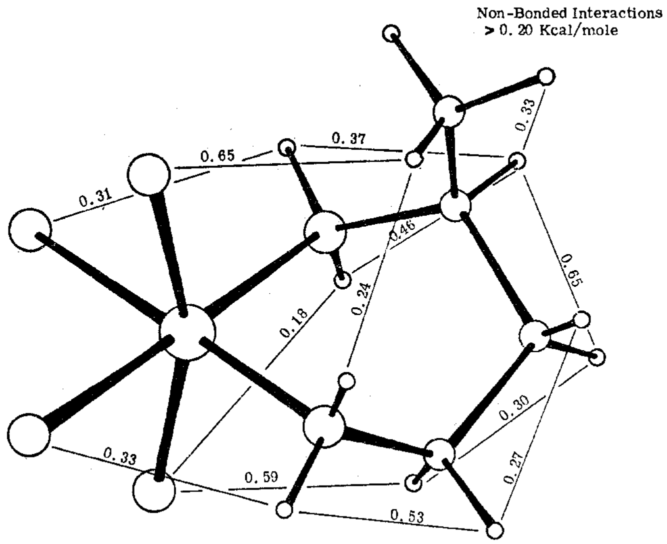

Figure 11. The $[\mathrm{Co}(S\text{-}1,3\text{-bn})_{\lambda}\mathrm{Cl}_4]^-$ complex.

are longer and most of the angles are significantly larger in the case of six-membered rings. We note, especially, the large Co-N-C angles as well as the fact that the N-Co-N angle for the six-membered chelates is greater than 90°.

A comparison of the two six-membered chelate conformers can best be made by examining Table VII. From the data in this table we can see that the chair and twist conformers have approximately the same strain energies associated with their bond length, bond angle, and nonbonded terms. The torsional term, however, differs by 1.56 kcal/mol and results mainly from the flattening of the ring in the twist conformation. In Table VI we can, for example, compare the torsional angles about the C-C bonds in the two conformers. In the chair conformer these angles are within 8° of the "ideal" 60° value usually associated with cyclohexane, while in the twist conformer they are 38°, a deviation of 22° from this minimum. The relative stabilities of the chelates would therefore be en $>$ tn (γ) $\gg$ tn (twist).

It is of interest to compare the effects of methyl substitution on the six-membered chelates with what we have previously learned about the influence of methyl groups on five-membered chelate ring strain energies. For the 1,3-butanediamine chelate with the methyl in the equatorial orientation and the chelate ring in the chair conformation, Table VI shows that there is little change in the geometry from the unsubstituted ring. When the methyl group is in an axial orientation, we note the same kinds of effects as in the five-membered chelates, namely, elongation of the Co-N and C-N bonds and severe flattening of the ring as reflected in the torsional angles. Figures 10 and 11 depict the 1,3-butanediamine chelate with the methyl in equatorial and axial orientations and the chelate ring in the twist conformation. Again we can see the same trends in the geometry and the energy terms. We also note that for this case there is also an increase in the bond angle strain energy of 2.6 kcal/mol on going from an equatorial to an axial methyl. This follows from the opening of the Co-N-C angle to 121°. This opening is a direct result of the flattening of the ring which causes the chelate bite to increase.

Recent studies by Appleton and Hall[20] implied that for complexes of racemic 2,4-pentanediamine, the preferred conformation is a chair with one methyl group axial and one methyl group equatorial. Other workers have postulated that the *rac*-2,4-pentanediamine chelate assumes a twist conformation with both methyl groups equatorial in its cobalt(III) complexes. This conclusion was based on similarities in the nmr spectra of the cobalt(III) complexes of the diamine and the cobalt(III) complex of the *rac*-2,4-pentanediaminetetraacetato ligand, as well as a study of the circular dichroism spectra of the diamine complexes.[21] Insofar as solid-state data for the tris complexes are applicable, we might conclude from the recent X-ray study[22] of the Λ-$\lambda\lambda\lambda$-$[\mathrm{Co}(R,R\text{-}2,4\text{-ptn})_3]^{3+}$ cation and the 1,3-butanediamine data in Table VII that the preferred conformation would be a twist ring with both methyls equatorial.

With the six-membered chelates we do not see an increase in the Co-N bond length with *N*-methyl substitution. This is probably because the bond lengths are already elongated in the unsubstituted trimethylenediamine chelates relative to the ethylenediamine chelates (2.04 *vs.* 2.02 Å). As a result of this, our calculations predict that for the twist conformation the axial *N*-methyl is favored over the equatorial *N*-methyl by 0.13 kcal/mol. All of the other methyl-substituted six-membered chelates show the "expected" preference for the equatorial orientation. Data from nmr studies of the racemic and meso platinum complexes of

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(20) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 10, 1717 (1971).

(21) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, 44, 3051 (1971).

(22) A. Kobayashi, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, 7, 777 (1971).

N,N'-dimethyltrimethylenediamine[23] would seem to imply that the energy difference between an equatorial and axial *N*-methyl substituent on a six-membered chelate ring in the chair conformation is about 0.618 kcal/mol ($K = 2.8$ at 30°). This value, even considering the difference in the systems, compares quite well with the calculated value of 0.62 kcal/mol (Table VII).

The several systems studied here indicate that the principal source of strain *within* the chelate ring comes from the nonbonded repulsions between the CH_2 and the NH_2 hydrogens and that the stabilities of the individual chelate rings are related to the degree of methyl substitution for this reason. In addition we have seen that in these simple systems there are interactions between the chelate ring and the other atoms in the complex. These interactions bring about changes in the geometry of the chelate ring skeleton which tend to minimize the strain associated with these interactions. The main changes we have seen in the complexes are the result of interactions between the axial methyl substituents and the axial ligands on the metal ion. In order to relieve this interaction, we have noted that the ring usually flattens, the bond lengths generally increase slightly, and the axial ligands tend to bend away from the chelate ring. In general we also saw that for the *N*-methyl substituents, even the equatorial methyl substituents were involved in nonbonded repulsions with the other ligands. This resulted in an increase in both the bond lengths and the degree of puckering in the rings for these complexes.

The published calculations which have appeared on mono-chelate complexes to date cannot be used to generate a relative list of stabilities, since they represent only enthalpy values. The three systems of interest which have appeared contain the chelates (*R*)-propylenediamine, *N*-methylethylenediamine, and trimethylenediamine. Our results agree qualitatively with those of earlier workers; *i.e.*, they predict that the methyl group prefers an equatorial site for both the *N*-methyl and *C*-methyl derivatives and that for six-membered chelates the chair conformation is preferred over the twist or skew-boat conformation. Quantitatively as shown in Table VIII we can see that our calculations give larger values of ΔG for these three systems than the previously published studies.

It might also be of interest to compare the experimental stabilities for the series of mono-chelated complexes with the relative stabilities based on the calculated conformational free energies. In comparing equilibrium data for the same metal ion and different ligands we are, of course, ignoring solvation effects in general and variations in the solvational behavior of the ligands and their resultant complexes in particular. Clearly such comparisons are tenuous at best; however, such comparisons may eventually reveal whether the conformational energies of the complexes are more or less important than these competing effects. With the full realization that the apparent correlations that emerge may ultimately prove to be fortuitous, we still feel it useful to offer the correlations demonstrated in Table IX, if only to stimulate their challenge and further testing.[24] We note that there are discrepancies in the relative ordering of stabilities between the calculated and observed values, but there are also variations in the relative ordering between the observed values for the Cu^{2+} and Ni^{2+} complexes. Basically the calculations agree very well with the observed order of stabilities relative to the ethylenediamine chelate and reflect the conclusions made previously that five-membered chelate complexes are more stable than six-membered chelate complexes and that *C*-methyl substitution increases the stability of a complex.

Table VIII. Comparison of the Calculated Energy Differences for the $[Co(diamine)Cl_4]^-$ Complex

Diamine	ΔG (this work), kcal/mol	ΔE,[2] eV
R-pn (eq–ax)	2.45	0.3[a]
N-Meen (eq–ax)	0.49	0.2[a]
tn (γ, twist)	1.70	2.7[b]

[a] Using Hill's nonbonded potentials. [b] Potentials not cited.

Table IX. Comparison of the Calculated[a] and Observed Stabilities[b] for the Mono-Chelate Complexes[c]

Obsd for Cu^{2+}		Calcd	Obsd for Ni^{2+}	
rac-bn[d]	*rac*-bn[e]	*rac*-bn	*rac*-bn[d]	*rac*-bn[e]
pn	pn	*meso*-bn		
meso-bn	*meso*-bn	pn *N*-Meen	pn *N*-Meen	
en	en	en	en	en
N,N'-DMeen	*N*-Meen	*N,N'*-DMeen	*N,N'*-DMeen	pn *N*-Meen
N-Meen	*N,N'*-DMeen		*meso*-bn	*N,N'*-DMeen *meso*-bn
tn	tn	tn	tn	tn

[a] Based on the *G* values in Tables III and VIII. [b] Based on the log K_1 values in *Chem. Soc., Spec. Publ.*, No. 17 (1964). [c] All compounds are listed in order of decreasing stability. [d] At 0° in 0.5 *M* KNO_3. [e] At 25° in 0.5 *M* KNO_3.

Registry No. $[Co(en)Cl_4]^-$, 39732-88-2; $[Co(S\text{-pn})_\delta Cl_4]^-$, 39732-89-3; $[Co(R\text{-pn})_\delta Cl_4]^-$, 39732-90-6; *R*-$[Co(N\text{-Meen})_\delta Cl_4]^-$, 39732-91-7; *S*-$[Co(N\text{-Meen})_\delta Cl_4]^-$, 39836-67-4; *R*-$[Co(N_1\text{-Me-}S\text{-pn})_\delta Cl_4]^-$, 39836-68-5; *R*-$[Co(N_2\text{-Me-}S\text{-pn})_\delta Cl_4]^-$, 39836-69-6; $[Co(tn)_\gamma Cl_4]^-$, 39732-92-8; $[Co(R\text{-}1,3bn)_\lambda Cl_4]^-$, 39732-93-9; $[Co(S\text{-}1,3bn)_\lambda Cl_4]^-$, 39732-94-0.

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(23) T. G. Appleton and J. R. Hall, *Inorg. Chem.*, 11, 124 (1972).

(24) Ignoring solvational and metal ion differences, the correct procedure for a comparison of the type we propose (as pointed out by a reviewer) would involve a comparison of the differences in the ΔG's of the complexes (ML_{aq}) and of the ligands (L_{aq}).