

Conformational Analysis of Coordination Compounds IX. Structures of the (1,2-Ethanediamine)(1,3-propanediamine)(1,4-butanediamine)cobalt(III) Complex

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Strain-energy minimization for 16 conformations of the title complex, $[\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+}$ was achieved. The conformation of lowest energy is $\text{en}(\text{le}l)$, $\text{tn}(\text{chair}(p,\text{tmd}))$, $\text{tmd}(\text{le}l)$. The $\text{le}l_3$ conformer, which was observed in crystals of $[\text{Co}(\text{en})(\text{tn})(\text{tmd})][\text{Co}(\text{CN})_6]\cdot\text{H}_2\text{O}$, has the second lowest strain energy by a difference of only 2.2 kJ mol^{-1} . The total strain energy was divided into intra- and inter-chelate ring components to see the key points which determine the stability of the conformers. A partition analysis of the strain energy was also carried out for $[\text{Co}(\text{en})_x(\text{tn})_{3-x}]^{3+}$ complexes with $x = 0, 1, 2$ and 3 . The intra-chelate ring strain energy for en and tn chelate rings indicate that the steric interactions between the chelate rings increase in the following order: $[\text{Co}(\text{en})_3]^{3+} < [\text{Co}(\text{en})_2(\text{tn})]^{3+} < [\text{Co}(\text{en})(\text{tn})_2]^{3+} < [\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+} < [\text{Co}(\text{tn})_3]^{3+}$.

The conformation of the title complex ion is of fundamental interest in terms of the steric interactions in mixed chelate ring systems. However, there is a structural disorder in the crystals of $[\text{Co}(\text{en})(\text{tn})(\text{tmd})][\text{Co}(\text{CN})_6]\cdot\text{H}_2\text{O}$.¹ In order to examine the X-ray structural model from an energetical point of view, a molecular mechanics calculation has been carried out. Conformational analyses for $[\text{Co}(\text{en})_3]^{3+}$,² $[\text{Co}(\text{tn})_3]^{3+}$,³ $[\text{Co}(\text{en})_2(\text{tn})]^{3+}$ and $[\text{Co}(\text{en})(\text{tn})_2]^{3+}$,⁴ and for other tris(diamine)cobalt(III) complexes with methyl substituents were reported in a series of papers from this laboratory. Very recently, the conformations of $[\text{Co}(\text{tn})_2(\text{tmd})]^{3+}$ and $[\text{Co}(\text{tn})(\text{tmd})_2]^{3+}$ complexes have also been investigated.⁵

Nomenclature

We use the same nomenclature as in previous papers to describe the relative orientations of the chelate rings. The seven-membered tmd ring as well as the *skew-boat* tn ring can be noted *lel* or *ob* when the line which can be drawn between the two carbon atoms bonded to N is approximately parallel (*lel*) or oblique (*ob*) to the pseudo-three-

fold axis of the complex. The two possible orientations of the *chair* form of the tn ring are written as *chair(p,en)* or *chair(p,tmd)*, when the carbon atoms of the tn ring lie near the one side of en or tmd chelate rings, indicating that the chair is effectively proximal (*p*) to the ring.⁴ The opposite term is distal (*d*). These notations for chair orientation are invariant and may be more convenient than those proposed by Jurnak and Raymond,⁶ because their notations parallel (*p*) and antiparallel (*a*), the orientation of the C–C–C plane with respect to the chirality around the metal atom, interconverts when the direction of the perspective view is reversed, as is also stated in their paper.

Calculations

The conformational strain energy was calculated as the sum over all individual interactions of bond stretching deformation (E_b), valence-angle deformation (E_ϕ), torsional strain (E_ψ) and non-bonded interaction (E_{nb}) energies. Electrostatic interactions were not introduced. Strain-energy minimization for 16 conformations was achieved using the program CFF using the force field parameter set NIKIPAR6.^{7,8}

The strain energies were classified into intra- and inter-chelate ring interactions. The effective strain energy for each atom was also calculated to see the stress distribution in the complex. Each contribution to E_b and E_{nb} was

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Table 1. Conformers of Co(en)(tn)(tmd), their energies (in kJ mol⁻¹), free enthalpies (in kJ mol⁻¹) and populations.

No.	Conformer			E_b	E_\ominus	E_ϕ	E_{nb}	E_T	ΔE_T	G	ΔG	n
	en	tn	tmd									
1	lel	chair(p,tmd)	lel	5.52	38.18	29.78	-6.53	66.95	0.00	1175.26	0.00	0.430
2	lel	lel	lel	5.33	27.40	41.23	-4.84	69.13	2.18	1177.03	1.77	0.210
3	lel	chair(p,en)	lel	6.35	33.35	32.56	-1.61	70.66	3.71	1178.37	3.11	0.123
4	lel	chair(p,tmd)	ob	5.73	36.85	33.25	-4.75	71.08	4.13	1178.50	3.24	0.116
5	ob	chair(p,tmd)	lel	5.87	40.94	29.17	-4.60	71.39	4.44	1180.72	5.46	0.048
6	ob	chair(p,tmd)	ob	6.14	39.46	32.24	-3.58	74.26	7.31	1181.73	6.47	0.032
7	ob	chair(p,en)	lel	6.50	44.39	29.43	-4.19	76.14	9.19	1184.17	8.91	0.012
8	ob	chair(p,en)	ob	6.81	44.44	27.98	-2.84	76.40	9.45	1185.48	10.22	0.007
9	lel	chair(p,en)	ob	7.10	34.70	32.79	3.89	78.47	11.52	1187.35	12.09	0.003
10	lel	ob	lel	5.78	35.42	38.58	-0.90	78.88	11.93	1186.02	10.76	0.006
11	lel	lel	ob	5.98	29.94	43.62	0.87	80.41	13.46	1186.63	11.37	0.004
12	ob	lel	lel	6.19	34.94	39.82	-0.23	80.71	13.76	1185.40	10.14	0.007
13	ob	ob	lel	6.56	38.84	36.80	0.45	82.64	15.69	1191.12	15.86	0.001
14	ob	ob	ob	6.48	38.25	39.40	-0.45	83.68	16.73	1191.47	16.21	0.001
15	ob	lel	ob	5.69	33.26	45.17	-0.23	83.90	16.95	1191.36	16.10	0.001
16	lel	ob	ob	6.93	31.56	42.87	2.55	83.91	16.96	1191.78	16.52	0.001

divided into half for each atom, and the contributions to E_\ominus and E_ϕ were assigned half their values to each of the two terminal atoms. Using this analysis, those H atoms which cause strong H···H repulsions can easily be found.

The equilibrium distribution of conformers of

[Co(en)(tn)(tmd)]³⁺ in aqueous solution at room temperature was estimated, assuming Boltzmann distribution based on the calculated free enthalpies for all conformers. In the calculation of free enthalpy both internal (vibrational) and external (rotational and translational) degrees of freedom were considered.^{9,10}

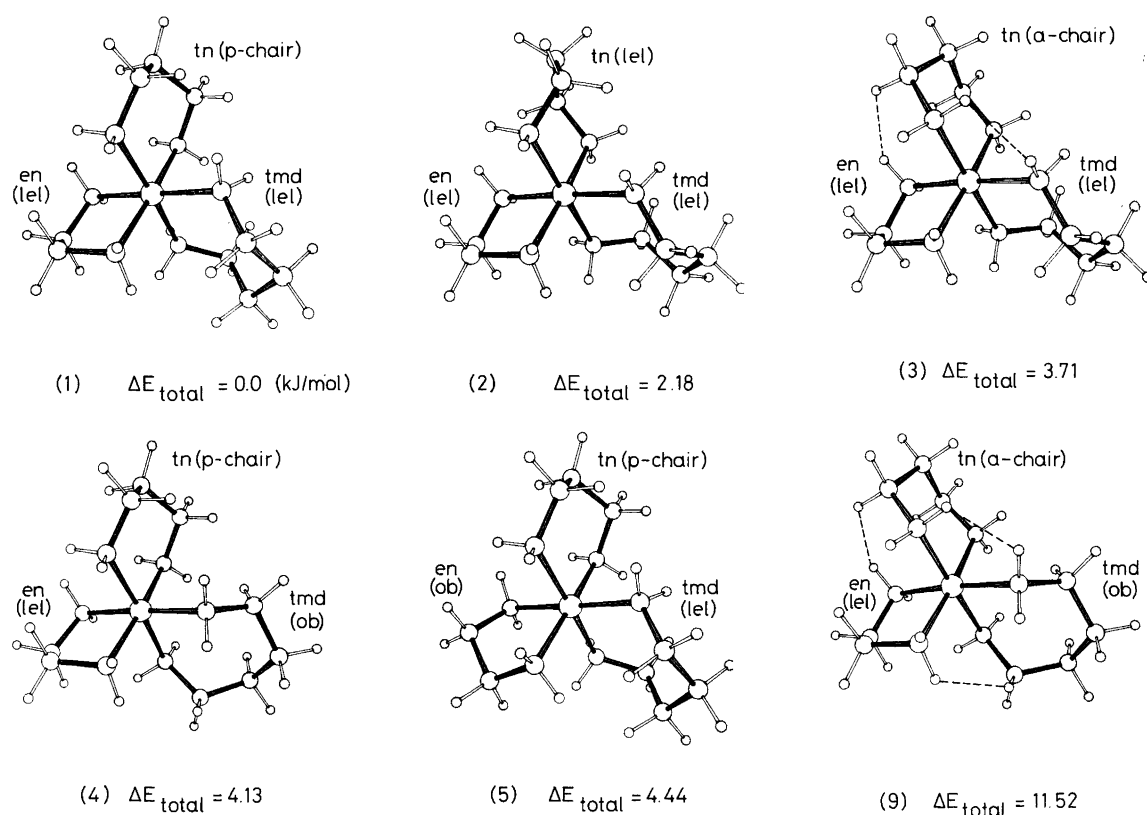


Fig. 1. Molecular structures of the five conformers of lowest strain energy and ninth conformer of [Co(en)(tn)(tmd)]³⁺. Difference in total strain energy, ΔE_T , is also shown. Strong H···H repulsions in the third and ninth conformers are indicated by the broken lines. *p-chair* is short for *chair(p,tmd)* and *a-chair* for *chair(p,en)*.

Results and discussion

Conformers of [Co(en)(tn)(tmd)]³⁺. Energy contributions, total strain energy E_T , free enthalpy G , and conformer population n from the Boltzmann distribution for [Co(en)(tn)(tmd)]³⁺ are listed in Table 1. The molecular structures for the five conformers of lowest strain energy are shown in Fig. 1. The key point of the strain energy is in the six-membered chelate ring which can take *skew-boat* (*lel* or *ob*) and *chair* (*p,en*) or (*p,tmd*) forms. The nine conformers of lowest E_T have the tn ring in the *chair* form, except for the *lel*₃ conformer. It is thus confirmed that the *lel*₃ conformation observed in the crystals of [Co(en)(tn)(tmd)][Co(CN)₆].H₂O¹ is reasonable from an energetic point of view. The *skew-boat* tn ring is less stable than the *chair* tn ring because of larger torsional strain. However, the *lel*₃ conformer has the second lowest strain energy owing to the small strain in bond angle and in non-bonded interactions. The *lel*₃ conformer has relatively small strain energy also in the series of mixed complexes [Co(en)_x(tn)_{3-x}]³⁺, $x = 0, 1, 2$ and 3 , as listed in Table 2.

In crystals of [Co(en)(tn)(tmd)][Co(CN)₆].H₂O the positions of the carbon atoms of tn and tmd are disordered. The disorder was attributed¹ to orientational disorder, in which the complex cation takes two possible orientations around the approximate twofold axis through the Co atom and the center of the C-C bond of en, the six- and seven-membered rings interchanging around the pseudo-twofold axis. There was no indication of the *chair* conformation of the tn chelate ring in the X-ray analysis.¹ The present conformational study indeed supports the explanation of the disorder in the crystal. Because the first three conformers listed in Table 1 are expected to cover 76% of the structures in solution, only the tn ring would be disordered if the disorder were to be found in the form of the chelate rings. In crystals of [Co(tn)(tmd)₂]Cl₃, the skew tn and tmd rings again interchange their positions owing to the orientational disorder of the complex cation.⁵

Correlation between non-bonded interactions and total strain energy. A rough correlation between ΔE_{nb} and ΔE_T was found for [Co(en)(tn)(tmd)]³⁺, as seen in Fig. 2, except for conformers nos. 3 and 9 with *chair* (*p,en*) rings.

Table 2. Global minimum and difference in strain energy (in kJ mol⁻¹) with respect to the *lel*₃ conformer.

Complex	Global minimum	Information about <i>lel</i> ₃ conformer	
		n th/all	ΔE_T
Co(en) ₃	<i>lel</i> ₃	1/4	0.00
Co(en) ₂ (tn)	<i>lel</i> ₂ , <i>chair</i>	4/10	4.62
Co(en)(tn) ₂	<i>lel</i> , <i>chair</i> ₂ (C ₁)	6/20	4.42
Co(en)(tn)(tmd)	<i>lel</i> , <i>chair</i> (<i>p,tmd</i>), <i>lel</i>	2/16	2.18
Co(tn) ₃	(C ₃)- <i>chair</i> ₃	2/16	5.63

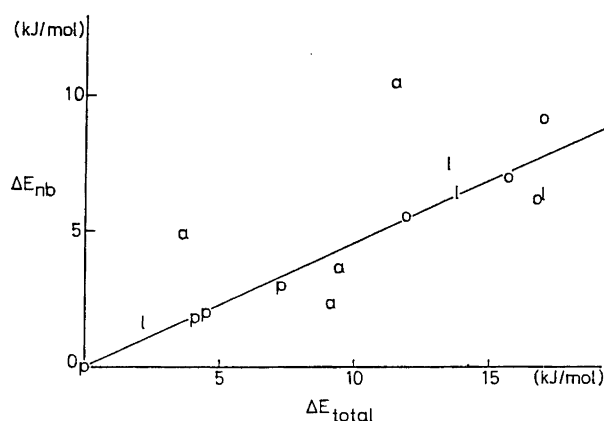


Fig. 2. The difference in non-bonded strain energy, ΔE_{nb} , plotted against the difference in total strain energy for [Co(en)(tn)(tmd)]³⁺. The type of the molecular conformation is represented by the form and orientation of the six-membered tn chelate ring being *p-chair* (*p*), *a-chair* (*a*), *lel* (*l*) or *ob* (*o*). The *p*- and *a*-chairs shown in Fig. 1 correspond to the *chair*(*p,tmd*) and *chair*(*p,en*), respectively. The solid line shows the least-squares line calculated excluding conformers nos. 3 and 9 with symbol a.

In order to find the reason for the exceptions, E_{nb} was classified into intra- and inter-chelate interactions. As shown in Fig. 3, the intra-chelate ring part of E_{nb} for the nine conformers of lowest E_T is almost constant within

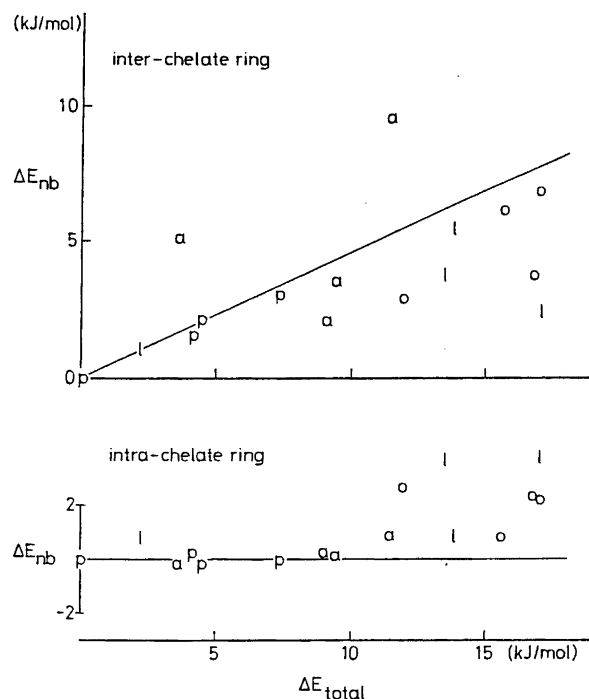


Fig. 3. Plots of the difference in inter- and intra-chelate ring non-bonded strain energy against ΔE_T for the [Co(en)(tn)(tmd)]³⁺ conformers. For inter-chelate ring interactions, the least-squares line shown in Fig. 2 is also presented for comparison.

$\pm 0.5 \text{ kJ mol}^{-1}$, and the inter-chelate ring E_{nb} contributes predominantly to ΔE_{nb} .

For conformer no. 3, strong $\text{H}\cdots\text{H}$ repulsions are indicated in Fig. 1 by broken lines. Each interaction has an energy of 4.3 kJ mol^{-1} , with the $\text{H}\cdots\text{H}$ distance of 2.02 \AA . The ninth conformer, which is the other one with the *en(lep)* and *chair-tn(p,en)* combination, has strong $\text{H}\cdots\text{H}$ non-bonded repulsions between each pair of the chelate rings, with energies of $4.2\text{--}5.1 \text{ kJ mol}^{-1}$. There are also many attractive long-range non-bonded interactions and, as a total, inter-chelate ring non-bonded interaction energies of *en* \cdots *tn*, *tn* \cdots *tmd* and *en* \cdots *tmd* for these conformers are -3.14 , 1.02 and $-2.70 \text{ kJ mol}^{-1}$ for conformer no. 3; and -0.57 , 1.82 and $-1.63 \text{ kJ mol}^{-1}$ for conformer no. 9.

For the *lel*₂*chair* conformer of the $[\text{Co}(\text{en})_2(\text{tn})]^{3+}$ complex, the non-bonded interactions between the *en* and *tn* rings with (*p,lep*) and (*d,lep*) combinations are -3.72 and 4.89 kJ mol^{-1} , respectively, indicating that the *en(lep)-tn(chair(p,en))* arrangement is not unfavourable in the less crowded complex. In the crowded $[\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+}$ system, the relaxation of the *tn-tmd* steric repulsion is prevented by the short $\text{H}\cdots\text{H}$ contact between the rigid *en* and *chair-tn* chelate rings.

As seen from Fig. 4, ΔE_T for $[\text{Co}(\text{en})_3]^{3+}$ is proportional to ΔE_{nb} . The same trend is observed for $[\text{Co}(\text{en})_2(\text{tn})]^{3+}$ conformers with a *chair* *tn* ring. The intra-chelate ring component of ΔE_{nb} is almost constant. Therefore, the total strain energy increases by the inter-chelate ring non-bonded interactions. The proportionality constant k (and the standard deviation) of the equation $\Delta E_{nb} = k\Delta E_T$ is 0.60 (0.02), 0.60 (0.12) and 0.45 (0.12) for $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{en})_2(\text{chair-tn})]^{3+}$ and $[\text{Co}(\text{en})(\text{tn})(\text{tmd})]^{3+}$ (except for conformers nos. 3 and 9). The fact that the coefficients are smaller than unity suggests that the steric interactions are somewhat relaxed by deformation of the chelate rings and of the CoN_6 coordination octahedron.

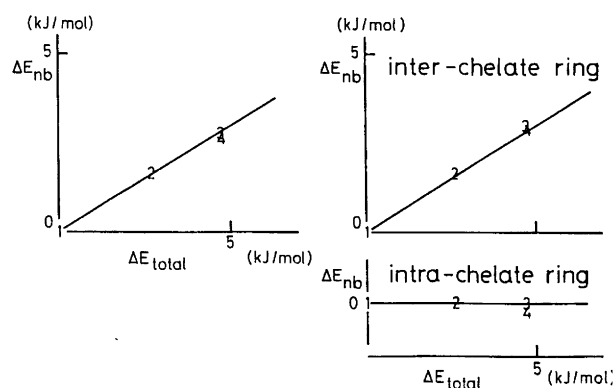


Fig. 4. Plots of the difference in non-bonded strain energy against ΔE_T for the $[\text{Co}(\text{en})_3]^{3+}$ conformers. The numbers are the order of the total strain energy: (1) *lel*₃, (2) *lel*₂*ob*, (3) *lelob*₂ and (4) *ob*₃ conformers. The plots for (3) and (4) are superposed.

A linear correlation between ΔE_T and ΔE_{nb} is not found for $[\text{Co}(\text{en})_2(\text{skew-boat-tn})]^{3+}$, $[\text{Co}(\text{en})(\text{tn})_2]^{3+}$, and $[\text{Co}(\text{tn})_3]^{3+}$. This suggests that the inter-chelate ring non-bonded interactions in these systems are largely relaxed by deformation of the chelate rings.

Intra-chelate ring strain energies. The individual intra-chelate ring strain energies, E_{en} , E_{tn} , and E_{tmd} are calculated. The ranges of the variation among all of the conformers of several tris(diamine)cobalt(III) complexes are listed in Table 3. It is seen that the *skew-boat* *tn* ring has a larger strain than the *chair* form by $6\text{--}10 \text{ kJ mol}^{-1}$ based on the energy parameter set NIKIPAR6. This accounts for the observed preference of the *chair* form in the less-crowded complexes, *trans*- $[\text{Co}(\text{tn})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$,¹¹ *trans*-

Table 3. Effective strain energy (in kJ mol^{-1}) in the chelate ring and CoN_6 moiety.

Complex	Distribution	<i>n</i>	Average	E.s.d. ^a
(1) $\text{Co}(\text{en})$ ring				
$\text{Co}(\text{en})_3$	9.24–9.84	12	9.585	0.22
$\text{Co}(\text{en})_2(\text{tn})$	9.91–11.25	20	10.589	0.41
$\text{Co}(\text{en})(\text{tn})_2$	10.56–12.78	20	11.460	0.57
$\text{Co}(\text{en})(\text{tn})(\text{tmd})$	10.85–13.78	16	12.068	0.79
(2) $\text{Co}(\text{tn})$ ring with <i>chair</i> form				
$\text{Co}(\text{en})_2(\text{tn})$	11.44–12.42	4	11.933	0.47
$\text{Co}(\text{en})(\text{tn})_2$	12.71–17.86	20	15.731	1.36
$\text{Co}(\text{en})(\text{tn})(\text{tmd})$	14.53–20.72	8	17.393	1.89
$\text{Co}(\text{tn})_3$	14.87–24.02	22	18.779	2.19
(3) $\text{Co}(\text{tn})$ ring with <i>skew-boat</i> form				
$\text{Co}(\text{en})_2(\text{tn})$	18.30–28.21	6	22.348	3.05
$\text{Co}(\text{en})(\text{tn})_2$	19.41–30.60	20	24.139	3.72
$\text{Co}(\text{en})(\text{tn})(\text{tmd})$	20.12–29.50	8	24.253	2.61
$\text{Co}(\text{tn})_3$	20.35–31.97	26	24.726	4.04
(4) $\text{Co}(\text{tmd})$ ring				
$\text{Co}(\text{en})(\text{tn})(\text{tmd})$	45.52–50.55	16	47.965	1.34
(5) $\text{Co}(2,4\text{-ptn})$ ring in $\text{Co}(2,4\text{-ptn})_3$				
<i>chair</i> (<i>eq</i>) ₂	17.11–19.01	7	17.951	0.53
<i>skew-boat</i> (<i>eq</i>) ₂	18.73–23.33	10	20.819	1.74
<i>chair</i> (<i>eq</i>)(<i>ax</i>)	31.28–37.88	5	33.236	2.36
<i>skew-boat</i> (<i>eq</i>)(<i>ax</i>)	36.68–46.55	8	42.873	3.40
(6) CoN_6 moiety				
$\text{Co}(\text{en})_3$	3.50–4.64	4	4.083	0.48
$\text{Co}(\text{en})_2(\text{tn})$	4.85–7.52	10	6.078	0.78
$\text{Co}(\text{en})(\text{tn})_2$	5.78–9.58	20	7.619	1.15
$\text{Co}(\text{en})(\text{tn})(\text{tmd})$	6.81–10.68	16	8.988	1.19
$\text{Co}(\text{tn})_3$	5.40–17.56	16	9.931	2.93
$\text{Co}(2,4\text{-ptn})_3$	7.34–22.64	10	11.476	4.10

^a Estimated standard deviation was calculated by the following equation:

$$\sigma(E) = \left[\sum_i (E_i - \bar{E})^2 / n(n-1) \right]^{1/2},$$

where E_i is an individual value, \bar{E} is the mean, and n is the number of samples.

Table 4. Energy contributions (in kJ mol⁻¹) in intra-chelate ring strain energy for Co(2,4-ptn)₃.^a

Energy	<i>chair</i>		<i>skew-boat</i>	
	(eq) ₂	(eq)(ax)	(eq) ₂	(eq)(ax)
E _b	2.40	2.70	2.58	3.21
E _⊖	13.22	24.20	5.51	19.82
E _φ	3.38	5.26	11.29	14.78
E _{nb}	-1.89	-0.87	-0.64	-1.13
E _T	17.11	31.28	18.73	36.68

^aThe Co(2,4-ptn) ring with smallest strain energy among the same type was selected. For the chair form with (eq)₂, (eq)(ax), and the skew-boat form with (eq)₂, (eq)(ax), ring 3 of the chair₃(eq)₅(ax) conformer of Co(meso-2,4-ptn)₂(2*R*,4*R*-ptn), ring 1 of chair₃(eq)₅(ax) of Co(meso-2,4-ptn)₂(2*S*,4*S*-ptn), rings of (D₃)-*lel*₃(eq)₆, and ring 1 of *lel*₃(eq)₅(ax), respectively.³

[Co(tn)₂(NO₃)₂]NO₃,¹² *trans*-[Cr(tn)₂F₂]ClO₄¹³ and *trans*-[Co(tn)₂(CN)₂]Cl·3H₂O.¹⁴ In *trans*-[Co(tn)₂(CN)₂]Cl·H₂O, one ring has the chair form, the other the skew-boat form.¹⁴ This may be due to hydrogen bonding or to other non-bonded interactions in the crystal. The average values of E_{en} and E_{tn} listed in Table 3 suggest that the steric interactions between the chelate rings increase in the following order: [Co(en)₃]³⁺ < [Co(en)₂(tn)]³⁺ < [Co(en)(tn)₂]³⁺ < [Co(en)(tn)(tmd)]³⁺ < [Co(tn)₃]³⁺.

This order agrees with that of the strain energy in the CoN₆ moiety of the complexes (Table 3).

The usefulness of the partition of the strain energy is further illustrated in the application to the [Co(2,4-ptn)₃]³⁺ complex (2,4-ptn = 2,4-pentanediamine).³ As seen from Table 3, the Co(2,4-ptn) ring with an (eq)(ax) methyl configuration has larger strain energy by 15–22 kJ mol⁻¹ than that with an (eq)₂ configuration. The difference is mostly in the valence-angle distortion, as shown in Table 4. This is due to the flattening of the segments of chelate rings with axial methyl groups, which is reflected in the opening of the valence angles.³

Accuracy of energies. It is very difficult to estimate the reliability of calculated energies and energy differences. With the same potential-energy function, satisfactory results in energy and free enthalpy differences were obtained, as has been discussed earlier for slightly simpler coordination compounds.^{9,10} As an example, the equilibrium distributions of four conformers of [Co(en)₃]³⁺ measured by a chromatographic method are well reproduced.⁹

An estimate of the precision of the calculated barrier to inversion in a five-membered chelate ring was made¹⁵ for [Co(en)₃]³⁺, and is about 8 kJ mol⁻¹.

Unsymmetrical forms of chelate rings. The skew-boat tn ring shows larger variation of the intra-chelate ring strain energy E_{tn} than that of the chair form (Table 3). The unsymmetric skew-boat form has a larger strain energy. For example, in the [Co(tn)₃]³⁺ system, the strain energy lies

in the range 30 ≤ E_{tn} ≤ 32 kJ mol⁻¹ for the skew-boat form with two imbalanced N–M–N–C torsion angles, 5–16 and 46–50°. The symmetric one with 28 < |N–M–N–C| < 39° has strain energy from 20 to 27 kJ mol⁻¹. The deformation of the skew-boat tn ring increases the intra-chelate ring partial energies E_⊖, E_φ and E_{nb} by 4.4, 2.2 and 2.5 kJ mol⁻¹ on average.

On the other hand, the tmd ring can be deformed without altering the strain energy. Ten conformers of the [Co(en)(tn)(tmd)]³⁺ system have an unsymmetric tmd ring with N–Co–N–C torsion angles of 5–27 and 53–68° (see conformers nos. 1, 4 and 5 in Fig. 1). The unsymmetric tmd ring has a larger bond-angle strain by 5.5 kJ mol⁻¹, but a smaller torsional strain by 4.9 kJ mol⁻¹ on an average than the symmetric one with 34° < |N–M–N–C| < 48°. There are no significant differences in E_b and E_{nb}. These results may well depend on the potential energy parameter set.

Flattening of chelate rings. The flattening of the chair tn ring caused by the pronounced interannular interactions

Table 5. Components of strain energy and selected structural data for Co(en), Co(tn), and Co(tmd) chelate rings before and after the energy minimization independently.^a

Energy or structure	tn			
	en	<i>chair</i>	<i>skew-boat</i>	tmd
E _T	11.190	16.975	20.116	46.409
	8.553	5.157	15.475	37.223
	8.493	2.496	14.595	30.930
E _b	1.108	2.58	1.903	2.352
	0.124	0.461	0.632	1.140
	0.089	0.369	0.380	0.667
E _e	2.948	11.943	6.462	21.021
	2.645	5.121	4.127	17.083
	2.760	2.381	3.391	9.518
E _φ	6.274	2.792	10.754	20.716
	5.439	1.033	10.186	17.962
	5.345	1.415	9.945	19.575
E _{nb}	0.861	0.182	0.998	2.321
	0.345	-1.458	0.530	1.039
	0.299	-1.669	0.880	1.171
Co–N	2.031	2.041	2.038	2.041
	2.005	2.013	2.016	2.022
	2.002	1.995	2.006	2.003
N–Co–N	85.8	92.4	89.4	93.8
	87.9	91.2	91.8	95.6
	87.7	90.3	93.2	95.1
Co–N–C	107.1	119.8	113.9	121.6
	105.4	115.2	111.7	119.0
	105.5	110.8	109.8	112.9

^aFirst row: initial geometry. As the initial geometry, the en(*lel*), tn(*chair*(*p*,*tmd*)), tmd(*lel*) conformer was used. The skew-boat form of the tn ring was taken from the *lel*₃ conformer. Second row: final geometry for Co(diamine)N₄. Third row: final geometry for Co(diamine).

has been discussed based on the dihedral angles of the *chair* chelate rings in Co(III) and Cr(III) complexes.³

In order to obtain further information about the perturbation of the ring form by the steric interactions between the chelate rings, a strain-energy minimization for the non-molecular entities, Co(diamine)N₄ and Co(diamine), was carried out. As seen from Table 5, the strain in the Co–N–C bond angles was relaxed for *tn(chair)* and *tmd* rings because the flattened rings can stretch after removing the inter-chelate ring non-bonded interactions.

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References

1. Takazawa, H., Ohba, S., Saito, Y., Ichida, H. and Rasmussen, K. *Acta Crystallogr., Sect. C46* (1990) 2354.
2. Niketić, S. R. and Rasmussen, K. *Acta Chem. Scand., Ser. A32* (1978) 391.
3. Niketić, S. R., Rasmussen, K., Woldbye, F. and Lifson, S. *Acta Chem. Scand., Ser. A30* (1976) 485.
4. Niketić, S. R. and Rasmussen, K. *Acta Chem. Scand., Ser. A35* (1981) 623.
5. Kurachi, S. and Ohba, S. *Bull. Chem. Soc. Jpn.* 65 (1992) 3033.
6. Jurnak, F. A. and Raymond, K. N. *Inorg. Chem.* 11 (1972) 3149.
7. Niketić, S. R. and Rasmussen, K. *The Consistent Force Field: A Documentation*, Lecture Notes in Chemistry, Vol. 3, Springer-Verlag, Berlin 1977.
8. Rasmussen, K. *Potential Energy Functions in Conformational Analysis*, Lecture Notes in Chemistry, Vol. 37, Springer-Verlag, Berlin 1985.
9. Hald, N. C. P. and Rasmussen, K. *Acta Chem. Scand., Ser. A32* (1978) 879.
10. Rasmussen, K. and Woldbye, F. In: Banerjee, D., Ed., *Coordination Chemistry 20*, Pergamon, Oxford 1980, p. 219.
11. Matsumoto, K., Ooi, S. and Kuroya, H. *Bull. Chem. Soc. Jpn.* 43 (1970) 1903.
12. Yasaki, E., Oonishi, I., Kawaguchi, H., Kawaguchi, S. and Komiyama, Y. *Bull. Chem. Soc. Jpn.* 43 (1970) 1354.
13. Vaughn, J. W. and Rogers, R. D. J. *Crystallogr. Spectrosc. Res.* 15 (1985) 281.
14. Kupka, H., Degen, J., Urushiyama, A., Angermund, K. and Krüger, C. *Inorg. Chem.* 25 (1986) 3294.
15. Niketić, S. R. and Rasmussen, K. *Acta Chem. Scand., Ser. A35* (1981) 213.

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