

Conformational Analysis of Coordination Compounds. V. Tris(2-methyl-1,2-propanediamine)- and (2,3-Butanediamine)bis-(1,2-ethanediamine)cobalt(III) Complexes

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For all members of the $[\text{Co}(\text{ibn})_3]$ series and those members of the $[\text{Co}(\text{rac-bn})\text{en}_2]$ series containing equatorial methyl groups, equilibrium conformations are found by convergent energy minimization in a force field developed for tris(diamine) complexes of cobalt(III). Ob-lel and axial-equatorial energy differences are compared with earlier results, and shapes of chelate rings and coordination polyhedra are discussed in terms of deviations from regular octahedral microsymmetry. The energetics of the tris-(ibn) series closely follows that of the tris(*m*-bn) series studied previously; the ring distortions are shown in stereo. The energetics of the (rac-bn) en_2 series fits those of the tris(en) and tris-(rac-bn) series; the geometries are less regular.

Recently, some insight in the energetics and structures of tris(diamine) chelate complexes of cobalt was gained from convergent conformational energy minimization using the Consistent Force Field System,¹ particular concerning the shapes of the chelate rings.^{2,3} Both works reported studies on symmetrically substituted diamines, and we thought it might be interesting to include in this series a study of a system with a non-symmetrical diamine, 2-methyl-1,2-propanediamine (=“isobutylenediamine”=ibn). In a tris(ibn) complex each ring will have one methyl group in each of the configurations traditionally termed axial and equatorial, as in tris(*meso*-2,3-butanediamine) complexes. In contrast to these tris(*m*-bn) complexes, the methyl groups in tris(ibn) complexes are situated two at one carbon atom in each ring, and

it might be expected that the regularity of *m*-bn chelate rings is distorted.

In addition to tris-(ibn) complexes, we included in this work a study of the conformers of a mixed complex, $[\text{Co}(\text{rac-2,3-bn})(\text{en})_2]$ (en=ethylenediamine=1,2-ethanediamine) in order to see to which extent the ob-lel conformational differences of the Coen ring³ are modified by the presence of the methyl group, and to see whether there is any difference in the geometry of a Co(rac-2,3-bn) ring between this series and the Co(rac-2,3-bn)₃ series. We have found no references to earlier studies of these series, neither from a computational nor from a structural point of view.

ISOMERISM AND NOMENCLATURE

Analogously to the tris-(*meso*-2,3-bn) complexes,³ the tris(ibn) series has 12 conformationally distinct members within the overall Λ (or Δ) configuration, 4 having facial (*fac*) and 8 having meridional (*mer*) configuration. Their numbering in the series and their notation will be completely analogous to the tris(*meso*-2,3-bn) series (Ref. 3, Table 2) and shall not be repeated here.

In the Co(rac-2,3-bn)(en)₂ series we only deal with equatorial disposition of the methyl groups. Considering only the Λ absolute configuration, the two ligands 2*S*,3*S*-bn and 2*R*,3*R*-bn will then have the conformations lel and ob. The two en rings of each molecule can each take the conformations lel and ob. Altogether we get 6 isomers and conformers, which are listed in Table 1.

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Table 1. Six conformers of $M(\text{rac-2,3-bn})(\text{en})_2$. Both methyl groups are equatorial, and the overall configuration is Λ .

No.	Shorthand notation	Full notation for Λ -series
1	lellel ₂	$[M(2S,3S\text{-bn})(\text{en})_2\delta\delta\delta]$
2	lellelob	$[M(2S,3S\text{-bn})(\text{en})_2\delta\delta\lambda]$
3	lelob ₂	$[M(2S,3S\text{-bn})(\text{en})_2\delta\lambda\lambda]$
4	oblel ₂	$[M(2R,3R\text{-bn})(\text{en})_2\lambda\delta\delta]$
5	oblelob	$[M(2R,3R\text{-bn})(\text{en})_2\lambda\delta\lambda]$
6	obob ₂	$[M(2R,3R\text{-bn})(\text{en})_2\lambda\lambda\lambda]$

CALCULATIONS

Method. A full documentation of the methods and programmes for Consistent Force Field calculations is available.¹

Force Field. Exactly the same force field as in the previous work³ was used.

Initial structures. Starting conformations of the tris-(ibn) series were constructed with a modification of a small programme used for the tris(*m*-bn) series;² for the (rac-2,3-bn)(en)₂ series they were

taken from the minimized conformations of the tris(rac-2,3-bn) series² by substituting hydrogen atoms for four methyl groups of Nos. 1, 6, 14, 13, 9, and 4 of the previous work (Ref. 3, Table 1).

Minimization. The steepest-descent and modified Newton algorithms were used. The resources required per molecule were on average as in the previous study.³

RESULTS AND DISCUSSION

Relative energies. All energy contributions and total and relative energy values are listed in Tables 2 and 3. Energies are in kJ mol^{-1} . The columns headed $\nabla \times 10^9$ give the final gradient norms in $\text{kJ mol}^{-1} \text{ \AA}^{-1}$, which is a good measure of the success of the minimization.

When the absolute energies are plotted on a common energy scale, pictures exactly like Figs. 1 and 2 of the previous study³ result. The tris-(ibn) system lies 10.5 kJ mol^{-1} below the tris-(*m*-bn) system, with the same spread of 12 kJ mol^{-1} , and with the same relative positions, to within 0.5 kJ mol^{-1} , for corresponding conformations. The (rac-

Table 2. Energy contributions for twelve iso- and conformers of $M(\text{ibn})_3$. E in kJ mol^{-1} , ∇ in $\text{kJ mol}^{-1} \text{ \AA}^{-1}$.

Conformer	$\nabla \times 10^9$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
12 mer(ob ₃)	3	4.48	16.30	36.75	-20.84	36.70	8.12
11 mer(ob ₂ lel)	21	4.74	16.89	36.01	-18.86	38.78	10.20
10 mer(oblelob)	67	4.78	17.21	36.67	-18.13	40.54	11.96
9 mer(lelob ₂)	25	4.33	14.64	35.54	-21.81	32.69	4.11
8 mer(oblel ₂)	29	4.66	14.82	34.80	-19.20	35.08	6.50
7 mer(leloblel)	29	4.62	15.13	34.10	-19.59	34.25	5.67
6 mer(lel ₂ ob)	13	4.43	14.69	36.34	-20.91	34.54	5.96
5 mer(lel ₃)	398	4.32	13.14	33.36	-22.24	28.58	0.00
4 fac(ob ₃)	13	4.86	18.39	35.94	-18.62	40.58	12.00
3 fac(lelob ₂)	42	4.76	16.84	35.60	-18.67	38.54	9.96
2 fac(lel ₂ ob)	88	4.46	14.87	35.48	-20.88	33.94	5.46
1 fac(lel ₃)	38	4.04	13.61	36.07	-24.65	29.07	0.49

Table 3. Energy contributions for six conformers of $M(\text{rac-bn})(\text{en})_2$. E in kJ mol^{-1} , ∇ in $\text{kJ mol}^{-1} \text{ \AA}^{-1}$.

Conformer	$\nabla \times 10^9$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
6 obob ₂	38	1.68	9.65	19.09	-21.45	8.97	4.79
5 oblelob	25	1.71	9.83	18.79	-21.29	9.04	4.86
4 oblel ₂	209	1.58	10.03	17.85	-22.52	6.94	2.76
3 lelob ₂	42	1.73	9.75	18.81	-21.18	9.10	4.92
2 lellelob	25	1.61	9.86	17.98	-22.45	6.99	2.81
1 lellel ₂	96	1.43	10.42	16.60	-24.28	4.18	0.00

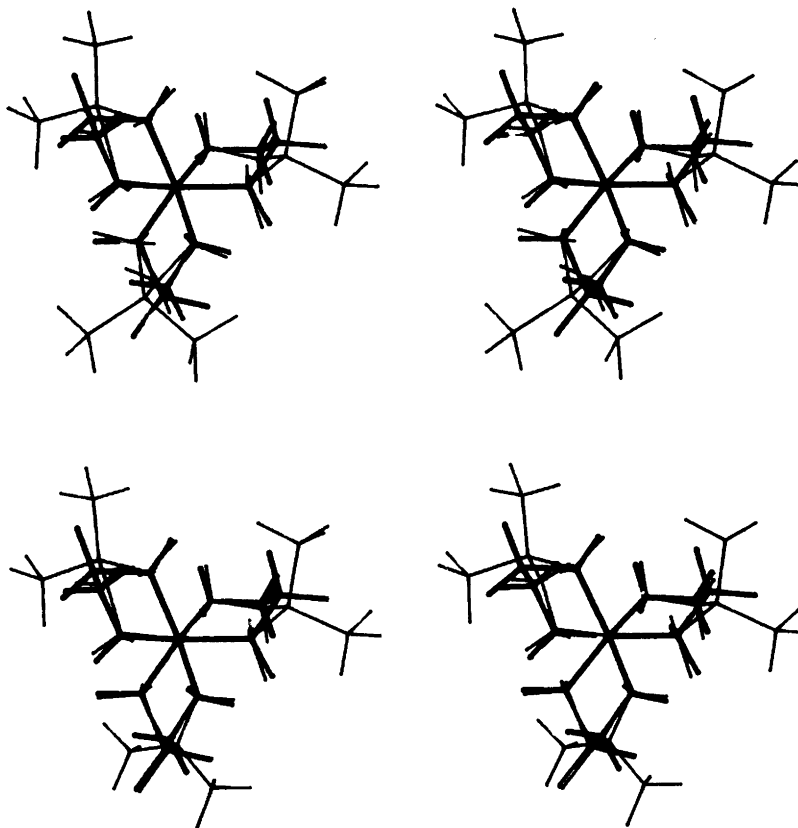


Fig. 1. Stereo drawings of (upper) Λ -*fac*-[Co(ibn)₃, $\delta\delta\delta$] and (lower) Λ -*mer*-[Co(ibn)₃, $\delta\delta\delta$], the *lel*₃ conformations.

bn(en)₂ system conforms strikingly to a linear combination of the tris(en) and the tris(*rac*-bn) eq₆ systems.

ob-lel Differences. For the energy differences between chelate rings having *ob* and *lel* conformations, we find much the same results as for the series studied previously:³ *fac*-M(ibn)₃ 3.9 ± 0.9, *mer*-M(ibn)₃ 2.7 ± 2.2, all M(ibn)₃ 3.3 ± 1.8; M(*rac*-bn)(en)₂ 1.6 ± 0.9 kJ mol⁻¹.

ax-eq Differences. Previously,³ an equatorially placed methyl group was found to change the energy by -1.53 kJ mol⁻¹, whereas an axial methyl group would add 13.52 kJ mol⁻¹ to the energy. The (*rac*-bn)(en)₂ series conforms singularly well to this picture, giving an average of -1.46 kJ mol⁻¹ per equatorial methyl group. The tris(ibn) series, as pointed out above, is displaced 10.5 kJ mol⁻¹ down the energy scale from the correspond-

ing tris(*m*-bn) series, which also has the eq₃ax₃ configuration. This is hardly surprising, as the chelate ring would be expected to deform when an "axial" and an "equatorial" methyl group are placed on the same carbon atom. Fig. 1 shows this deformation, tending to give both methyl groups on a ring axial as well as equatorial character.

Non-bonded interactions. A histogram analysis of all non-bonded interactions revealed no clear trends as to the importance of any particular type of interaction for either set of molecules. This is analogous to what was found for the tris(en) and tris(*m*-bn) series.³

Shapes of chelate rings. The introduction of two methyl groups on one carbon atom induces slight changes in the calculated values of bond lengths, valence angles and torsional angles connected with that atom. Table 4 shows that, with two methyl

Table 4. Structures of the twelve isomers and conformers of $M(\text{ibn})_3$, with methyl groups on C1, compared with $M(\text{en})_3$. The average values and ranges found in the calculations are shown.

Bonds/Å	$M(\text{ibn})_3$	$M(\text{en})_3$
M-N1	2.026 ± 0.003	2.018 ± 0.002
M-N2	2.018 ± 0.006	
C1-N1	1.483 ± 0.003	1.475 ± 0.001
C2-N2	1.474 ± 0.002	
C1-C2	1.548 ± 0.001	1.540 ± 0.001
Angles/°		
N-M-N	84.9 ± 0.6	86.7 ± 0.3
M-N1-C1	111.2 ± 0.8	106.5 ± 0.6
M-N2-C2	107.0 ± 1.2	
N1-C1-C2	108.4 ± 0.5	107.8 ± 0.1
N2-C2-C1	108.8 ± 0.8	
Torsions/°		
N2-M-N1-C1	3.7 ± 3.7	15.6 ± 1.3
C2-N2-M-N1	23.8 ± 4.5	
M-N1-C1-C2	24.8 ± 3.7	40.2 ± 1.2
C1-C2-N2-M	44.3 ± 3.0	
N1-C1-C2-N2	44.6 ± 3.3	55.5 ± 1.2

groups on C1, the bonds M-N1, N1-C1 and C1-C2 increase slightly, while the M-N1-C1 angle opens and the N1-M-N2 closes; torsions around M-N1, N1-C1 and C1-C2 are most affected. C1 is found almost in the (M,N1,N2) plane. The valence and torsional angle changes, in particular, are seen in stereo in Fig. 1. There are no significant differences between rings in *fac* and *mer* isomers of the tris(ibn) series.

Table 5 shows, together with Table 4, that bonds, angles and torsions are very alike for the two systems $M(\text{en})_3$ and $M(\text{rac-bn})\text{en}_2$. From the previous study we see that also the $M(\text{rac-bn})_3$ system is very close hereto.

The ring puckering descriptors, the N-C-C-N torsional angle ϕ and the dihedral angle τ defined by lines joining the C-C and N-N atoms, are, for the tris(ibn) series, almost like those found³ in the tris(*rac-bn*) eq₆ and tris(en) series: $\phi = 44.6 \pm 3.3$ and $\tau = 23.5 \pm 1.3$, with the ratio $\tau:\phi = 0.53$. For the (*rac-bn*)(en)₂ series the correspondence is even closer: $\phi = 55.2 \pm 1.2$ and $\tau = 28.1 \pm 1.3$, and their ratio is 0.51 as found in the earlier work.³

Shapes of coordination octahedra. As before,³ we use three angles to describe deviations of the MN₆ octahedron from a regular one: the twist ω (regular: 60°), the tilt θ (regular: 54.8°) and the pitch ψ

Table 5. Structures of the six conformers of $M(\text{rac-bn})\text{en}_2$. The average values and ranges found in the calculations are shown.

Bonds/Å	<i>rac-bn</i>	en
M-N	2.015 ± 0.001	2.019 ± 0.002
C-N	1.476 ± 0.001	1.474 ± 0.001
C-C	1.547 ± 0.001	1.540 ± 0.001
Angles/°		
N-M-N	86.5 ± 0.3	86.4 ± 0.6
M-N-C	107.0 ± 0.6	106.5 ± 0.5
N-C-C	107.5 ± 0.2	107.8 ± 0.2
Torsions/°		
N-M-N-C	15.0 ± 1.6	15.0 ± 2.0
M-N-C-C	40.6 ± 0.6	50.7 ± 1.6
N-C-C-N	55.2 ± 1.2	55.5 ± 1.2

(regular: 35.3°). All ω values range from 50 to 58°, showing that the octahedron is twisted towards a trigonal prism ($\omega = 0^\circ$) as befits tris-chelates with five-membered rings. All θ values are approximately regular, 51–58°; all ibn rings are slightly compressed along the threefold or pseudo-threefold axis; the (*rac-bn*)(en)₂ series shows a larger variation, with cases of elongation, though with no apparent regularity. The degree of helicity, as measured by ψ , ranges from 31 to 35° for the tris(ibn) series and from 25 to 44° for the (*rac-bn*)(en)₂ series.

Acknowledgement. Computations were done on an IBM 370/165 at the Technical University Computer Centre NEUCC and were paid for with a grant from the Danish Natural Science Research Council, which is gratefully acknowledged. Stereo drawings were produced from the coordinates of the equilibrium conformers with a programme MONSTER written by Mr. Per Jacobi of The Royal Danish Academy of Fine Arts, Laboratory of Datalogy.

REFERENCES

1. Niketić, S. R. and Rasmussen, K. *The Consistent Force Field: A Documentation*. Lecture Notes in Chemistry, Vol. 3, Springer, Berlin-Heidelberg-New York 1977.
2. Niketić, S. R., Rasmussen, K., Woldbye, F. and Lifson, S. *Acta Chem. Scand. A* 30 (1976) 485.
3. Niketić, S. R. and Rasmussen, K. *Acta Chem. Scand. A* 32 (1978) 391.

Received April 5, 1978.