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Conformational Analysis of Coordination Compounds. IV. Tris(1,2-ethanediamine)- and Tris(2,3-butanediamine)cobalt(III) Complexes *

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A fast convergent energy minimisation programme is used to calculate equilibrium conformations of three series of tris(diamine) coordination complexes with the amines 1,2-ethanediamine and *rac*- and *meso*-2,3-butanediamine. All possible isomers and conformers are treated, their minimum energies are given, and examples of equilibrium conformations are shown in stereo. Ob-lel and axial-equatorial energy differences are derived and compared, and the influence of various non-bonded interactions in determining conformations is analysed. Shapes of chelate rings and of coordination polyhedra MN_6 are discussed in terms of deviations from regular octahedral microsymmetry.

Equilibrium conformations of $M(en)_3$ are compared with summaries of recent crystal structure determinations of $[Co(en)_3]^{3+}$ and $[Cr(en)_3]^{3+}$ salts, which are referenced.

As part of our continuing efforts in developing a consistent force field (CFF)[2] for coordination compounds we have studied the conformations of tris-alkanediamine complexes of cobalt(III) and chromium(III) containing 5-membered metal chelate rings of 1,2-ethanediamine (en) and 2,3-butanediamine (2,3-bn).

In the previous paper[3] we have presented an analysis of the conformations of tris(1,3-propanediamine) and tris(2,4-pentanediamine) Co(III) and Cr(III) systems. The results reported in this paper confirm our assertion that convergent energy minimisation is an expedient method to find equilibrium conformations, and that our present force field, though not ideal, is able to provide some insight into the interactions which determine the shapes of chelate amine coordination compounds.

CHOICE OF THE SYSTEMS

There is no need to emphasise the importance of $M(en)_3$ as a prototype of a family of propeller-like tris(alkanediamine) complexes. On this molecule a number of theoretical models have been developed in parallel with an accumulation of experimental data of a very good quality, comprising X-ray analyses,[4] ORD/CD studies,[5] eleetronic spectra of single crystals at low temperature,[6,7] NMR studies,[8] vibrational spectra[9] and stability constants.[10] $M(en)_3$ therefore represents an indispensable model system for an optimisation of a force field for tris-alkanediamine coordination complexes.

The $M(2,3\text{-bn})_3$ system was chosen because it provides additional sources of isomerism, which will be described in detail below. The possibility for a later comparison of our results with the experimental thermodynamic data on 2,3-bn complexes obtained recently in this laboratory[11] was another incitement for our choice.

ISOMERISM AND NOMENCLATURE

In the present study we have included all theoretically possible isomers and conformers of

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$M(en)_3$ and $M(2,3\text{-bn})_3$ systems. The principal features of their static stereochemistry are those characteristic of three-bladed chiral propeller molecules.[12] Their configurational chirality gives rise to a pair of enantiomers (designated as Λ and Δ according to the IUPAC nomenclature[13]) for each structure.

The $M(en)_3$ system. The source of conformational isomerism in the $M(en)_3$ system is the nonplanarity of the 5-membered metal chelate rings. Considering the two stable chiral (skew) conformations of chelate rings (designated as λ and δ according to the IUPAC nomenclature[13]) four conformationally unique conformers of $M(en)_3$ can be constructed for each absolute configuration:

$$\lambda\lambda\lambda,\ \lambda\lambda\delta,\ \lambda\delta\delta,\ \text{and}\ \delta\delta\delta \qquad (1)$$

As in our previous writings[14] we shall use the chirality invariant nomenclature in which the two possible conformations of an individual ethylenediamine chelate ring in $M(en)_3$ are named *lel* and *ob*, respectively, connoting that the central C–C bond of the ring is (approximately) para*lel* and *ob*lique with respect to the C_3 or pseudo-C_3 symmetry axis. Thus, the four conformers (11) are symbolised as:

$$lel_3,\ lel_2ob,\ ob_2lel\ \text{and}\ ob_3 \qquad (2)$$

and this type of isomerism as lel-ob isomerism. The symbol lel_3, for example, denotes either $\Delta(\lambda\lambda\lambda)$ or $\Lambda(\delta\delta\delta)$, which are energetically identical.

The $M(2,3\text{-bn})_3$ system. Due to the presence of the two chiral centres 2,3-bn exists in optically active (2*R*,3*R*- or 2*S*,3*S*-) and in *meso* (*RS*) form. For convenience, we shall discuss separately $M(2,3\text{-bn})_3$ complexes with optically active (or racemic) forms of 2,3-bn, and with *meso*-2,3-bn.

*Racemic (*rac*) or optically active (*RR- *or* SS-*) 2,3-bn.* By coordination of the *rac*-2,3-bn twenty theoretically possible and conformationally unique forms of $M(2,3\text{-bn})_3$ can be formed (Table 1). They can be systematically enumerated on the basis of the following two principles. Firstly, optically active 2,3-bn forms a chelate ring in which the two methyl groups are either both equatorial (*e.g.*, for λ ring conformation of 2*R*,3*R*-bn) or both axial (*e.g.*, for δ ring conformation of 2*R*,3*R*-bn). Therefore, in the $M(bn)_3$ system with coordinated optically active 2,3-bn, four different species with respect to the methyl group orientation, namely eq_6, eq_4ax_2, eq_2ax_4, and ax_6, are possible. We will refer to this as an eq-ax isomerism. Secondly, the $M(2,3\text{-bn})_3$ system has the same four possibilities for the ring conformations (lel_3, lel_2ob, ob_2lel, and ob_3) as the parent $M(en)_3$ system. By the interplay of lel-ob and eq-ax isomerism, 16 isomers and conformers of $M(2,3\text{-bn})_3$ with racemic amine are generated. However, for conformers whose parent skeletons lack a C_3-axis (lel_2ob and ob_2lel) the degeneracy between otherwise identical rings is lifted, and we get two instead of one representative for eq_4ax_2 and for eq_2ax_4 structures [pairs 6/7, 8/9, 12/13, and 14/15 in Table 1], so that we arrive at a total of 20 isomers and conformers of $M(rac\text{-}2,3\text{-bn})_3$.

Eight of them (two groups of four in each) represent structures containing only one enantiomer of 2,3-bn: either 2*R*,3*R*-bn in structures 4, 9, 13, 17; or 2*S*,3*S*-bn in structures 1, 6, 14, 20; all cases pertaining to Λ configuration. The remaining 12 are "mixed" forms containing both enantiomers of 2,3-bn coordinated to the same metal ion. The former 8 structures are relevant from the point of view of a practicing chemist because they represent all species that are theoretically obtainable from a synthesis with an optically active form of the amine. For example, the coordination of 2*S*,3*S*-bn may produce isomers 1, 6, 14, 20 of Λ configuration, and the enantiomeric forms of 4, 9, 13, and 17 having Δ configuration (Table 1).

In Table 1 the 20 isomers and conformers of $M(2,3\text{-bn})_3$ are given the full IUPAC designation[13] and a shorthand notation which is used in this paper. The chirality invariant shorthand notation emphasizes the conformationally relevant features lel/ob for rings, and eq/ax for methyl groups, and is unambiguous on the condition that the sequence of designators, as written, is consistently adhered to. For example, the (ob lel_2)(eq_4ax_2) designation implies the following sequence of rings: ob ring (eq CH_3 groups), lel ring (eq CH_3 groups), lel ring (ax CH_3 groups), and therefore corresponds to the Λ-[M(2*S*,3*S*-bn)(2*R*,3*R*-bn)(2*S*,3*S*-bn)$\delta\lambda\lambda$] configuration, or to its enantiomer Δ-[M(2*R*,3*R*-bn)-(2*S*,3*S*-bn)(2*R*,3*R*-bn)$\lambda\delta\delta$].

Meso-*2,3-bn.* Coordination of *meso*-2,3-bn gives rise to twelve theoretically possible conformationally unique isomers and conformers of $M(2,3\text{-bn})_3$ (Table 2). In contrast to the optically active form, *meso*-2,3-bn forms chelate rings with one of the methyl groups equatorial and the other axial, both for λ and for δ ring conformation. Therefore, there is no eq-ax isomerism and all tris

Table 1. Twenty isomers and conformers of M(rac-2,3-bn)$_3$. Numbering and nomenclature.

No.	Shorthand notation	Full IUPAC notation for Λ-series
1	(eq$_6$)(lel$_3$)	Λ-[M2*S*,3*S*-bn)$_3\delta\delta\delta$]
2	(eq$_6$)(lel$_2$ob)	Λ-[M(2*S*,3*S*-bn)$_2$(2*R*,3*R*-bn)$\delta\delta\lambda$]
3	(eq$_6$)(lel ob$_2$)	Λ-[M(2*S*,3*S*-bn)(2*R*,3*R*-bn)$_2\delta\lambda\lambda$]
4	(eq$_6$)(ob$_3$)	Λ-[M(2*R*,3*R*-bn)$_2\lambda\lambda\lambda$]
5	(eq$_4$ax$_2$)(lel$_3$)	Λ-[M(2*S*,3*S*-bn)$_2$(2*R*,3*R*-bn)$\delta\delta\delta$]
6	(eq$_4$ax$_2$)(lel$_2$ob)	Λ-[M(2*S*,3*S*-bn)$_3\delta\delta\lambda$]
7	(eq$_4$ax$_2$)(lel ob lel)	Λ-[M(2*S*,3*S*-bn)(2*R*,3*R*-bn)$_2\delta\lambda\delta$]
8	(eq$_4$ax$_2$)(lel ob$_2$)	Λ-[M(2*S*,3*S*-bn)(2*R*,3*R*-bn)(2*S*,3*S*-bn)$\delta\lambda\lambda$]
9	(eq$_4$ax$_2$)(ob$_2$lel)	Λ-[M(2*R*,3*R*-bn)$_3\lambda\lambda\delta$]
10	(eq$_4$ax$_2$)(ob$_3$)	Λ-[M(2*R*,3*R*-bn)$_2$(2*S*,3*S*-bn)$\lambda\lambda\lambda$]
11	(eq$_2$ax$_4$)(lel$_3$)	Λ-[M(2*S*,3*S*-bn)(2*R*,3*R*-bn)$_2\delta\delta\delta$]
12	(eq$_2$ax$_4$)(lel$_2$ob)	Λ-[M2*S*,3*S*-bn)(2*R*,3*R*-bn)(2*S*,3*S*-bn)$\delta\delta\lambda$]
13	(eq$_2$ax$_4$)(ob lel$_2$)	Λ-[M(2*R*,3*R*-bn)$_3\lambda\delta\delta$]
14	(eq$_2$ax$_4$)(lel ob$_2$)	Λ-[M(2*S*,3*S*-bn)$_3\delta\lambda\lambda$]
15	(eq$_2$ax$_4$)(oblel ob)	Λ-[M2*R*,3*R*-bn)$_2$(2*S*,3*S*-bn)$\lambda\delta\lambda$]
16	(eq$_2$ax$_4$)(ob$_3$)	Λ-[M(2*R*,3*R*-bn)(2*S*,3*S*-bn)$_2\lambda\lambda\lambda$]
17	(ax$_6$)(lel$_3$)	Λ-[M(2*R*,3*R*-bn)$_3\delta\delta\delta$]
18	(ax$_6$)(lel$_2$ob)	Λ-[M(2*R*,3*R*-bn)$_2$(2*S*,3*S*-bn)$\delta\delta\lambda$]
19	(ax$_6$)(lel ob$_2$)	Λ-[M(2*R*,3*R*-bn)(2*S*,3*S*-bn)$_2\delta\lambda\lambda$]
20	(ax$_6$)(ob$_3$)	Λ-[M(2*S*,3*S*-bn)$_3\lambda\lambda\lambda$]

Table 2. Twelve isomers and conformers of M(*meso*-2,3-bn)$_3$. Numbering and nomenclature. All are eq$_3$ax$_3$.

No.	Shorthand notation	Full IUPAC notation for Λ-series
1	fac-(lel$_3$)	*fac*-Λ-[M(2*R*,3*S*-bn)$_3\delta\delta\delta$]
2	fac-(lel$_2$ob)	*fac*-Λ-[M(2*R*,3*S*-bn)$_3\delta\delta\lambda$]
3	fac-(lel ob$_2$)	*fac*-Λ-[M(2*R*,3*S*-bn)$_3\delta\lambda\lambda$]
4	fac-(ob$_3$)	*fac*-Λ-[M(2*R*,3*S*-bn)$_3\lambda\lambda\lambda$]
5	mer-(lel$_3$)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\delta\delta\delta$]
6	mer-(lel$_2$ob)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\delta\delta\lambda$]
7	mer-(leloblel)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\delta\lambda\delta$]
8	mer-(oblel$_2$)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\lambda\delta\delta$]
9	mer-(lelob$_2$)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\delta\lambda\lambda$]
10	mer-(oblelob)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\lambda\delta\lambda$]
11	mer-(ob$_2$lel)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\lambda\lambda\delta$]
12	mer-(ob$_3$)	*mer*-Λ-[M(2*R*,3*S*-bn)$_2$(2*S*,3*R*-bn)$\lambda\lambda\lambda$]

complexes of *meso*-2,3-bn are eq$_3$ax$_3$. Another consequence of the difference in chiralities at the C-2 and C-3 atoms is the existence of facial and meridional isomers. Fac-mer isomerism, well-known in the case of tris-bidentate complexes of, *e.g.*, amino acids and β-diketonates, has been recognized in M(*meso*-2,3-bn)$_3$ for a long time,[15] but has only recently been demonstrated.[16]

Since there is no variation in the number of equatorial and axial methyl groups there are only four conformers of the facial isomer of M(*meso*-2,3-bn)$_3$: lel$_3$, lel$_2$ob, ob$_2$lel, and ob$_3$. These have C-atoms of the same chirality adjacent to the ligators spanning an octahedral face. The number of meridional isomers is eight. They have C-atoms of the same chirality adjacent to the ligators spanning an octahedral meridian. They include two sets (lel$_2$ob and ob$_2$lel) of three heteroconformational forms each, arising from the intrinsic non-equivalence of all three rings in meridional structures.

Table 2 illustrates the use of chirality invariant shorthand symbolism for 12 M(*meso*-2,3-bn)$_3$ isomers and conformers along with the full IUPAC specification.

CREATION OF INITIAL STRUCTURES

Initial cartesian atomic coordinates of the four M(en)$_3$ conformers were generated from the standard values of bond lengths and valence angles by our CFF programmes[2] by specifying the appropriate torsional angles.

Thirty-two isomers and conformers of M(2,3-bn)$_3$ were built by adding methyl groups on the conformations of the M(en)$_3$-like skeleton, in turn, in a systematic way, with help of a small (~40 statements) FORTRAN programme written for this purpose, which also labels the conformers as required and stores the sets of coordinates as a member of a partitioned data set compatible with the system of CFF programmes.

Table 3. Force field for coordination compounds. All units are such that energies are given in kJ mol^{-1}; distances are in Å; angles are in rad.

Bond stretching: $E_b = \frac{1}{2}K_b(b-b_0)^2$		
Bond	K_b	b_0
M–N	1052.9	2.00
N–C	3610.0	1.47
C–C	3008.3	1.54
C–H	3008.3	1.093
N–H	3369.3	1.011
Angle bending: $E_t = \frac{1}{2}K_\theta(\theta-\theta_0)^2$		
Angle	K_θ	θ_0
N–M–N	409.13	1.571
M–N–H	120.33	1.911
M–N–C	240.66	1.911
N–C–C	601.66	1.911
N–C–H	311.08	1.911
H–N–H	318.88	1.911
C–N–H	391.08	1.911
H–C–H	312.86	1.911
H–C–C	601.66	1.911
Torsional: $E_p = \frac{1}{2}K_\phi(1+\cos n\phi)$		
	K_ϕ	n
C–C and C–N	12.55	3
M–N	0.0	12
Non-bonded: $E_{nb} = A\exp(-Br) - C/r^6$		
Interaction	$A\times10^{-4}$	B	C
H···H	2.76	4.08	205.9
H···C	13.14	4.20	506.7
H···N	11.76	4.32	415.1
C···N	88.74	4.44	1020.9
C···C	97.16	4.32	1246.0
N···N	77.99	4.55	836.8
M···H	13.14	4.20	506.7
M···C	99.16	4.32	1246.0

CALCULATIONS

Method. A full documentation of the method and programmes for CFF calculations is presented elsewhere.[2]

Force field. Our force field was that used in previous work,[3,14] with slight changes. In the torsional function we used the concept of group torsion rather than bond torsion,[17] whereby only one torsion is counted for each bond rather than nine for an sp^3-sp^3 bond. The change was made because it entailed much fewer internal coordinates, thus easing a vibrational analysis to follow later. The modification caused insignificant differences in computed structures (less than 0.003 Å and 0.02 rad) and in energies (less than 2.0 kJ mol^{-1}).

The potential energy functions and their parameters are shown in Table 3. Bond stretching and angle bending parameters for the hydrocarbon part of our force field were taken over from Wiberg's force field.[17-19] It was supplemented with parameters defining harmonic deformations of bonds and angles involving metal and coordinated nitrogen atoms, which were assumed on the basis of the normal coordinate analyses of Nakagawa and Shimanouchi[20] on ammine complexes of cobalt(III).

Several sets of non-bonding parameters were tried. Our final choice was a set of parameters for the Buckingham-type function developed by Liquori.[21]

Torsional parameters (the same value for both C–C and C–N bonds) were adjusted so that the

force field could reproduce the rotational barrier of about 12.55 kJ mol^{-1} in ethane using the aforementioned non-bonded functions.

The application of this force field for the octahedral trisbidentate metal chelate complexes implied some special considerations: (1) Since the geminal (1,3-) interactions were accounted for in the angle bending terms, they were automatically left out of calculations of non-bonded interactions, wherefore the N···N parameters of Table 3 were actually not in use. (2) Valence angles defined by ligating atoms in *trans* position ($\sim 180°$), as well as those between ligators from different chelate rings were not treated. In this way only three chelate angles were considered at the octahedral metal atom. (3) Exclusion of the so called core field potential (non-bonded interactions involving the central metal atom in our force field M···C and M···H contributions) has practically no significance on the results of force field calculations.[22] This was demonstrated[3] by test computations in which core field terms included with the appropriate parameters for M were set equal to those of C.

Minimisation. A typical minimisation of one molecule using the steepest-descent and modified Newton algorithms required about 150 s on an IBM 370/165. All minimisations were carried through to a gradient norm of less than 10^{-6} kJ mol^{-1} $Å^{-1}$.

RESULTS AND DISCUSSION

Relative energies. All energy contributions and total and relative energy values are listed in Tables 4–6. Energies are in kJ mol^{-1}. The columns headed $\nabla \times 10^9$ give the final gradient norms in kJ mol^{-1} $Å^{-1}$.

All complexes are shown on a common energy scale in Fig. 1. They fall distinctly into six groups according to the presence of axial and equatorial methyl groups. The tables show that from one group to another the various types of energy contributions change in a parallel way. Such regularity was not found for complexes with six-membered rings.[3]

ax-eq Differences. Table 6 shows that the total energy increases in a regular way when two methyl groups are changed from equatorial to axial configuration of the same conformation. An ax-eq energy difference of (15.0 ± 1.0) kJ mol^{-1} reproduces quite well all data for the intermediate groups, including those of Table 5 where all members have the eq_3ax_3 configuration. In earlier work[14b] using

Table 4. Energy contributions for $M(en)_3$ conformers.

Conformer	$\nabla \times 10^9$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
ob_3	192	1.34	8.08	19.44	−16.96	11.91	4.75
$lelob_2$	105	1.39	8.24	19.11	−16.81	11.93	4.77
lel_2ob	92	1.26	8.38	18.21	−18.01	9.84	2.68
lel_3	197	1.11	8.84	16.89	−19.68	7.16	0.00

Table 5. Energy contributions for twelve isomers and conformers of M(*meso*-bn)$_3$.

	Conformer	$\nabla \times 10^9$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
12	mer-(ob_3)	21	4.60	22.79	37.72	−17.32	47.78	8.55
11	mer-(ob_2lel)	430	4.82	23.90	36.28	−15.84	49.16	9.93
10	mer-(oblelob)	100	4.86	24.24	37.08	−15.36	50.83	11.60
9	mer-($lelob_2$)	167	4.47	21.36	35.98	−17.73	44.08	4.85
8	mer-($oblel_2$)	251	4.77	21.97	35.19	−15.79	46.13	6.90
7	mer-(leloblel)	8	4.58	21.96	34.72	−17.30	43.96	4.73
6	mer-(lel_2ob)	96	4.49	21.74	36.32	−17.45	45.10	5.87
5	mer-(lel_3)	42	4.32	19.99	34.06	−19.14	39.23	0.00
4	fac-(ob_3)	13	4.91	24.94	37.08	−16.02	50.91	11.68
3	fac-($lelob_2$)	201	4.84	23.78	36.16	−15.84	48.94	9.71
2	fac-(lel_2ob)	122	4.52	21.76	35.79	−17.55	44.52	5.29
1	fac-(lel_3)	71	3.99	20.37	36.37	−21.26	39.47	0.24

Table 6. Energy contributions for twenty isomers and conformers of M(*rac*-bn)$_3$.

	Conformer	$\nabla \times 10^9$	E_b	E_t	E_p	E_{nb}	E_T	ΔE
20	$(ax_6)(ob_3)$	71	5.81	40.25	59.74	−11.16	94.64	96.72
19	$(ax_6)(lelob_2)$	723	6.03	42.13	55.70	−10.25	93.62	95.70
18	$(ax_6)(lel_2ob)$	1393	5.79	39.41	55.58	− 9.76	91.02	93.10
17	$(ax_6)(lel_3)$	163	5.27	32.78	57.77	− 9.18	86.65	88.73
16	$(eq_2ax_4)(ob_3)$	79	4.55	29.78	48.29	−16.44	66.18	68.26
15	(eq_2ax_4)(oblelob)	1033	4.82	32.01	43.97	−15.48	65.32	67.40
14	$(eq_2ax_4)(lelob_2)$	130	4.69	29.11	45.22	−16.74	62.28	64.36
13	$(eq_2ax_4)(oblel_2)$	42	4.69	30.69	42.72	−15.33	62.77	64.85
12	$(eq_2ax_4)(lel_2ob)$	184	4.46	27.68	42.93	−16.71	58.36	60.44
11	$(eq_2ax_4)(lel_3)$	159	4.14	24.20	43.30	−17.35	54.30	56.38
10	$(eq_4ax_2)(ob_3)$	172	3.42	20.79	34.52	−23.13	35.59	37.67
9	$(eq_4ax_2)(ob_2lel)$	104	3.64	22.28	32.98	−20.04	36.86	38.94
8	$(eq_4ax_2)(lelob_2)$	79	3.54	20.91	31.35	−23.15	32.66	34.74
7	(eq_4ax_2)(leloblel)	134	3.38	19.73	31.54	−23.02	31.63	33.71
6	$(eq_4ax_2)(lel_2ob)$	50	3.29	19.59	27.60	−25.07	25.42	27.50
5	$(eq_4ax_2)(lel_3)$	126	3.10	17.76	39.14	−25.58	24.42	26.50
4	$(eq_6)(ob_3)$	426	2.33	12.77	18.40	−30.68	2.82	4.90
3	$(eq_6)(lelob_2)$	67	2.36	12.93	18.12	−30.41	3.00	5.08
2	$(eq_6)(lel_2ob)$	142	2.24	13.01	17.29	−31.68	0.86	2.94
1	$(eq_6)(lel_3)$	33	2.07	13.53	16.03	−33.72	−2.08	0.00

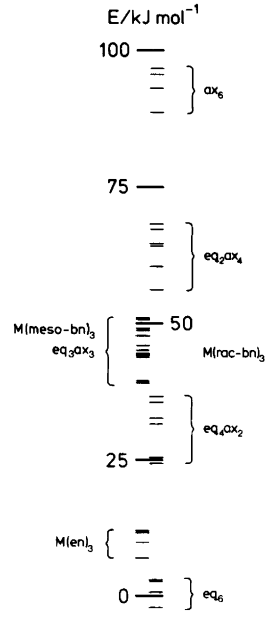

Fig. 1. Relative energies of four conformers of M(en)$_3$ and thirty-two isomers and conformers of M(2,3-bn)$_3$ on a common energy scale.

essentially the same force field but a rather primitive minimisation programme an ax-eq difference of 8.2 kJ mol^{-1} was found. DeHayes and Busch,[23] using a programme essentially the same as ours, and a force field of the same form, though with rather different parameters, also found 8.2 kJ mol^{-1}. The standard value of the ax-eq free enthalpy difference for only one group on a cyclohexane ring is 7.1 kJ mol^{-1}.[24]

When the M(en)$_3$ series is fitted into this picture, we find that the presence of a methyl group in an equatorial position changes the energy by −1.53 kJ mol^{-1}, and in an axial position by 13.52 kJ mol^{-1}. This applies, of course, only to the present force field.

ob-lel Differences. When we examine the energy differences between conformers having the same methyl group disposition but different ring conformations, we find a clear-cut regularity, but no pronounced additivity. Fig. 2 shows that an ob_3 conformation has only slightly higher energy than the corresponding $lelob_2$ conformation whereas the $lelob_2$-lel_2ob and lel_2ob-lel_3 differences are larger, as a rule. We can derive the following average ob-lel energy differences: M(en)$_3$ 1.6±0.9; fac-M(*meso*-bn)$_3$ 3.8±1.1, mer-M(*meso*-bn)$_3$ 2.9±1.8, all M(*meso*-bn)$_3$ 3.3±1.6; M(*rac*-bn)$_3$ eq_6 1.7±1.0, M(*rac*-bn)$_3$ eq_4ax_2 4.9±1.9, M(*rac*-bn)$_3$ eq_2ax_4

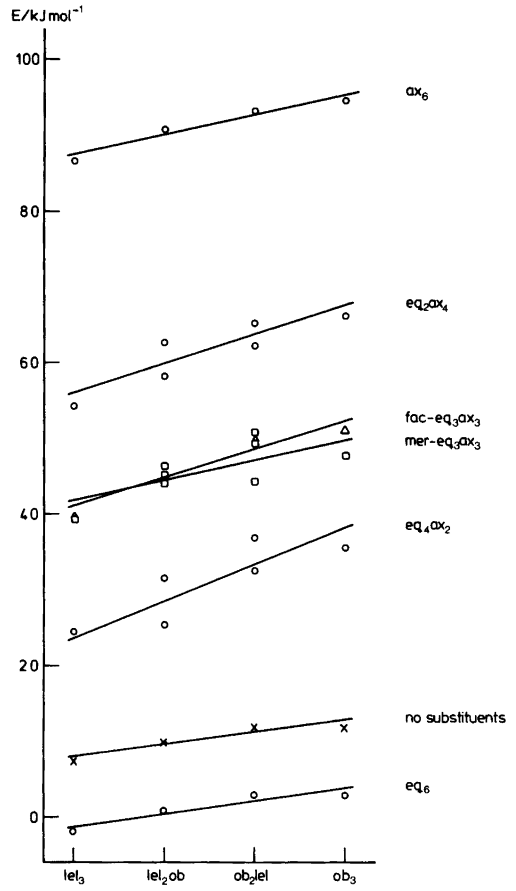

Fig. 2. Relationship between ring conformation (lel/ob), methyl group orientation (eq/ax) and energy of four $M(en)_3$ and thirty-two isomers and conformers of $M(2,3\text{-bn})_3$.

3.9 ± 1.2, $M(rac\text{-bn})_3$ ax_3 2.7 ± 1.1, all $M(rac\text{-bn})_3$ 3.3 ± 1.6; all values in kJ mol^{-1}. These data are illustrated in Fig. 2. The large spread is obvious, as are the deviations from the traditionally accepted value of 0.6 kcal mol^{-1} or 2.5 kJ mol^{-1}. The average value for all our cases is 3.2 kJ mol^{-1}. In the earlier work,[14b] a value of 3.3 kJ mol^{-1} was found.

Non-bonded interactions. A histogram analysis in intervals of 0.2 Å was made for all non-bonded interactions in an attempt to detect clear trends in the relative influence of the various contributions. For each type of interaction we considered only the shorter distances involved, as the interaction energy changes appreciably only at distances shorter than and around the minimum on the potential energy curve.

We found no such clear trends for the $M(en)_3$ and $M(meso\text{-bn})_3$ complexes, but for the $M(rac\text{-bn})_3$ complexes the following observations were made.

H---H. The short-range (2.0 – 2.2 Å), most strongly repulsive, interactions increase in number on going from one group of configurations to the next (eq_6 to eq_4ax_2 *etc*), whereas the number is constant or nearly so within a group. Longer ranges (2.2 – 2.4 and 2.4 – 2.6 Å), weakly repulsive, are almost constant in number.

C---H. Interactions in the shortest range (2.4 – 2.6 Å), strongly repulsive, reveal the same pattern as for H---H, while the range 2.6 – 2.8 Å, weakly repulsive, becomes slightly less populated from one group to the next.

N---H. Interactions in the shortest range (2.4 – 2.6 Å), weakly repulsive, increase in number from one group to the next, and also, within each group, on going from lel to ob conformation. The range (2.6 – 2.8 Å), weakly attractive, shows the reverse trend.

C---C. The shortest interactions found (3.3 – 3.2 Å) include the minimum on the potential energy curve and are thus strongly attractive. Their numbers are constant within a group: 3, 2, 1, and 0, representing the vicinal interactions of methyl carbons within a ring. The next interactions are found much farther out.

C---N. The shortest interactions found (3.0 – 3.6 Å) are all strongly or weakly attractive, and they all increase in frequency from one group to the next. The range (3.2 – 3.4 Å) represents interactions between a methylene carbon in one ring and an amino nitrogen in another and are almost constant through the series. The range (3.0 – 3.2 Å) is interactions between an axial methyl carbon in one ring and an amino nitrogen in another.

The following conclusions may thus be drawn: (1) The vicinal methyl carbon – methyl carbon interactions favour the ax-ax dispositions. (2) This is countered by hydrogen – hydrogen and carbon – hydrogen repulsions between both methyl groups and between a methyl group in one ring and an amino group in another. (3) Nitrogen-hydrogen interactions play a less determining role. (4) Carbon-nitrogen interactions favour the axial disposition of methyl groups. (5) The preference for lel conformation is caused largely by nitrogen-hydrogen interactions.

Shapes of chelate rings. The puckering of a five-

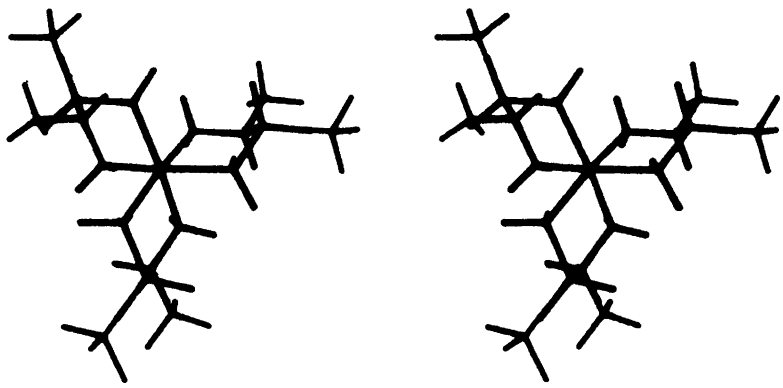

Fig. 3. Stereoscopic pair showing the equilibrium structure of lel$_3$-M(2*S*,3*S*-bn)$_3$ superimposed on the lel$_3$-M(en)$_3$ structure. The rings have practically the same shape. Conformers depicted are those which are expected to predominate in an equilibrium in solution.

membered chelate ring can be conveniently expressed through the torsional angle ϕ = N−C−C−N around the central C−C bond and through the dihedral angle τ defined by lines joining the C−C and N---N atoms.

All 108 chelate rings in the 36 isomers and conformers studied here fall into three distinct groups according to these two ring puckering descriptors. (1) When a ring carries no methyl groups or two equatorial ones (see Fig. 3) it is highly puckered, and both descriptors have a very small range: $\phi=(55.3\pm1.5)°$ and $\tau=(28.5\pm1.0)°$. These values are similar to those found by Duesler and Raymond[25] and Iwata *et al.*[26] in crystal structure determinations, but differ from the older works of Nakatsu *et al.*[27-29] who found less puckered rings. (2) A ring carrying two axial methyl groups is flattened, with a large range for the descriptors: $\phi=(38.5\pm4.5)°$ and $\tau=(20.0\pm2.5)°$. (3) A ring carrying an equatorial and an axial methyl group (all rings of the M(*meso*-bn)$_3$ series) is almost as puckered as the former, and with the same range: $\phi=(49.0\pm2.0)°$ and $\tau=(25.0\pm1.0)°$. These details of ring shape are thus largely determined by the disposition of methyl groups, whether the rings have lel or ob conformation. The ring flattening described above was also found by DeHayes and Busch.[23] The effect of methyl substitution is exemplified in Figs. 3 and 4.

There is a strictly linear relationship between the two ring puckering descriptors for all 108 rings: $\tau=0.51\phi$. This is hardly surprising, as all distances and angles are almost equal, and as all rings have strict or approximate twofold symmetry.

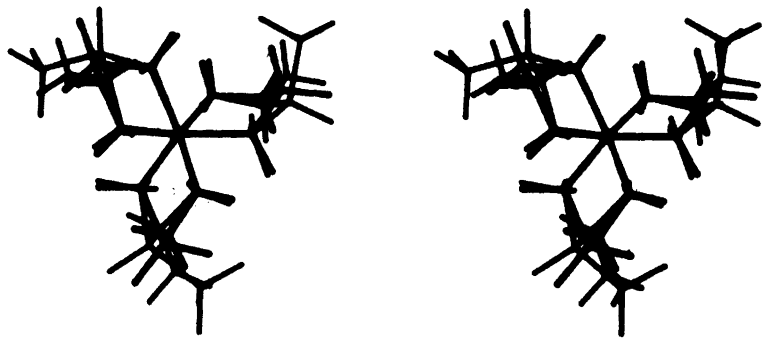

Fig. 4. Stereoscopic pair showing the equilibrium structure of *fac*-lel$_3$-M(*meso*-2,3-bn)$_3$ superimposed on the lel$_3$-M(en)$_3$ structure. The axial methyl groups flatten the rings and remove their twofold symmetry.

Table 7. Average bond lengths and angles in M(en) rings.

	MN	NC	CC	NMN	MNC	NCC
Present work	2.018	1.475	1.541	86.6	106.7	107.7
Early crystal structures, M = Co[27-29]	2.00	1.47	1.54	87.4	107	110
Saito's average ring, M = Co[4]	1.991	1.494	1.567	85.5	108.7	105.4
Recent crystal structures, M = Co[25,26,33-43]	1.973	1.486	1.509	85.3	109.1	107.4
Recent crystal structures, M = Cr[38,39,44-47]	2.067	1.493	1.514	82.9	109.6	107.9

Shapes of coordination octahedra. We use three descriptors for the discussion of departure from octahedral microsymmetry: (1) The twist angle ω,[4] which is zero for a trigonal prismatic and 60° for a regular octahedral arrangement. (2) The tilt angle θ, formerly[4,30] called the polar angle, subtended by a threefold or pseudo-threefold axis and a metal–nitrogen bond; for a regular octahedron $\theta = 54.8°$. It is related to the compression ratio[31] by $s/h = 0.865$ tg θ. (3) The pitch angle ψ[30] defined by a threefold or pseudo-threefold axis and an N---N line. For a regular octahedron $\psi = 35.3°$.

The following observations may be mentioned: (1) ω is about 55° for unsubstituted and hexaequatorially substituted complexes. A similar magnitude and direction of trigonal twisting was observed in a series of crystal structures of lel_3 tris(diamine)cobalt(III) complexes reported by Saito and co-workers.[32] Axial substitution lowers ω and widens its range; the lowest value found is 48° for ax_6ob_3. (2) All complexes are slightly compressed, $\theta = (55.5 \pm 2.0)°$. (3) The pitch angle for all complexes is slightly less than the regular value, $\psi = (33 \pm 4)°$. (4) For all three descriptors, unsubstituted and hexaequatorially substituted complexes show a much smaller range than the rest of the complexes.

Comparison with crystal structures. Crystal structures have been determined for many salts of $[Co(en)_3]^{3+}$[25-29,33-43] and some salts of $[Cr(en)_3]^{3+}$;[38,39,44-47] all four combinations of ring conformers have been found, with no significant differences in bond lengths and angles between lel and ob conformations.

Our calculations give almost identical bond lengths and valence angles for lel and ob conformations of M(en) rings. Average values are shown in Table 7 together with averages evaluated for crystal structure determinations. Our force field was originally developed to reproduce the early crystal structure data. This goal is almost achieved, but comparison with the more recent data is also quite favourable. It is seen that our M–N bond lengths are intermediate between the experimental values for Co–N and Cr–N bonds; our C–N values are a little too short and C–C much too long; the chelate angles and the N–C–C angles are almost correct; and the M–N–C angles are too small. This comparison gives us directions on how to improve our force field at a later stage.

No crystal structure determination of tris-complexes of 2,3-bn with Co(III) or Cr(III) is known to us, but our predicted chelate ring geometries and shapes of coordination octahedra agree well with those found in crystal structures of tris-complexes with other symmetrically substituted 1,2-ethanediamines: 1,2-diphenylethylenediamine,[48] *trans*-cyclopentanediamine,[49] and *trans*-cyclohexanediamine.[50,51]

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