Structures of Monoadducts of Tris(β-diketonato) Lanthanoid Shift Reagents

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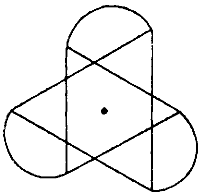
Ligand–ligand repulsion energies have been calculated for [M(bidentate)$_3$(unidentate)]$^{x\pm}$ complexes using a normalised bite ' of 1·22, which is the appropriate value for bidentate β-diketonate ligands attached to a lanthanoid element. (' Normalised bite ' is defined as the distance between the two donor atoms of the same bidentate ligand divided by the metal atom–donor atom distance.) Three minima of closely similar energies appear on the potential-energy surfaces. The first two correspond to a capped octahedron (C_{3v} symmetry) and an irregular polyhedron (C_1 symmetry), and are the structures observed for compounds whose structures have been determined, and where the unidentate ligand is water or a carbonyl compound. The third minima (C_s symmetry) corresponds to a stereochemistry intermediate between a pentagonal bipyramid and a capped trigonal prism, and it is predicted that it will be formed only with unidentate ligands which form particularly stable ligand ⟶ lanthanoid bonds.

CURRENT interest in tris(β-diketonato) complexes of the lanthanoid elements centres on the very large shifts in ^{1}H n.m.r. spectra of molecules which form adducts with them in solution. Crucial to an understanding of this process are the symmetries and structures of the seven-co-ordinate adducts formed.[1]

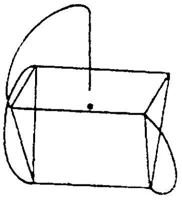
The stereochemistry of seven-co-ordination is very complex.[2] Minimisation of the total-repulsion energy between seven metal–ligand bonds leads to a number of minima on the potential-energy surfaces, each corresponding to a different stereochemistry.[3] These stereochemistries include the capped octahedron (C_{3v} symmetry), pentagonal bipyramid (D_{5h} symmetry), and capped trigonal prism (C_{2v} symmetry). Depending on assumptions used in these calculations the last two minima may exist only as very shallow troughs, requiring negligible energy to significantly pucker the pentagonal plane of the pentagonal bipyramid and the capped rectangular plane of the capped trigonal prism.

Introduction of three bidentate ligands spanning three non-joining polyhedral edges increases considerably the number of possible isomers. Three planar pentagonal bipyramids, seven capped octahedra, and nine unpuckered capped trigonal prisms may be envisaged. Allowing the central planes of the pentagonal bipyramid and the capped trigonal prism to pucker increases the total possible isomer count to 67. Only one of these, the capped octahedron of C_{3v} symmetry, has all three bidentate ligands equivalent, nine have two equivalent, while the majority have all non-equivalent. Of these 67 isomers, 58 will be optically active and may be present in both isomeric forms.

Crystal-structure determinations on solids obtained from solution confirm that more than one isomer is possible. Only in the complex [Ho(PhCOCHCOPh)$_3$(H$_2$O)] does the space group uniquely define the symmetry properties of the molecule.[4] In the other cases the idealised polyhedron chosen to describe the stereochemistry is to a certain extent rather arbitrary. The capped octahedron, (I), is observed in the complexes [Ho(PhCOCHCOPh)$_3$(H$_2$O)] [4] and [Y(PhCOCHCOMe)$_3$(H$_2$O)],[5] although in the latter case the three-fold axis of the molecule is destroyed by the arrangement of phenyl and methyl groups. The capped trigonal prism, (II), has been used to describe the structure of the complexes [Yb(MeCOCHCOMe)$_3${MeCOCHC(NH$_2$)Me}],[6] [Dy(BuCOCHCOBu)$_3$(H$_2$O)],[7] [Lu(BuCOCHCOBu)$_3$(MeC$_5$H$_4$N)],[8] and [Lu(C$_3$F$_7$COCHCOBu)$_3$(H$_2$O)] (two independent molecules in the unit cell),[9] while the capped trigonal prism, (III), has been used to describe the structures of [Yb(MeCOCHCOMe)$_3$(H$_2$O)] (two independent molecules in the unit cell),[10] and [Yb(MeCOCHCOMe)$_3$(H$_2$O)],$\frac{1}{2}$C$_6$H$_6$.[11]



(I)



(II)

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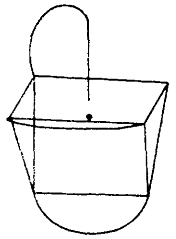
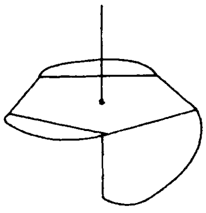
Although not yet observed for [Ln(β-diketonate)$_3$(unidentate)] complexes, the closely analogous [ZrCl(MeCOCHCOMe)$_3$],[12] [SnCl($C_7H_5O_2$)$_3$] and [Sn(OH)($C_7H_5O_2$)$_3$] ($C_7H_5O_2^-$ = tropolonate),[13] [NbO(C_2O_4)$_3$]$^{3-}$,[14] [NbO(S_2CNEt_2)$_3$] and [VO(S_2CNEt_2)$_3$],[15] [Mo(NO)(S_2CNBu_2)$_3$],[16] [TePh(S_2CNEt_2)$_3$],[17] [Pb(lone pair)(S_2COEt)$_3$]$^-$,[18] and [Sb(lone pair)(C_2O_4)$_3$]$^{3-}$,[19] have been described as puckered pentagonal-bipyramidal stereochemistries with the unidentate ligand (or non-bonding pair of electrons in the last examples) occupying one of the axial sites, (IV), or as stereochemistries intermediate between (IV) and the capped trigonal prism, (V).


(III)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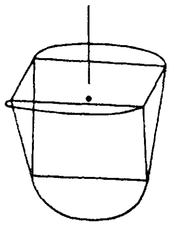
(V)

This proliferation of structural types makes it seemingly impossible to predict even the general stereochemistries which might be expected in solution. However we have shown for the cases of five-co-ordinate [M(bidentate)$_2$(unidentate)]$^{x\pm}$,[20] six-co-ordinate [M(bidentate)$_2$(unidentate)$_2$]$^{x\pm}$ [21] and [M(bidentate)$_3$]$^{x\pm}$,[22] and the eight-co-ordinate [M(bidentate)$_2$(unidentate)$_4$]$^{x\pm}$ and [M(bidentate)$_4$]$^{x\pm}$ [23] complexes that the constants of the bidentate ligands markedly stabilise only one (or very few) of the isomers compared with all other possible isomers. Moreover it is possible to predict the detailed stereochemistry of each isomer, at least in those cases where all donor atoms are approximately equivalent. The calculated stereochemistries are not necessarily the same as those found with only unidentate ligands.

METHOD

The stereochemical arrangement of a number of ligand donor atoms surrounding a central metal atom may be calculated by minimisation of the total ' ligand–ligand repulsion energy,' U, obtained by summing over all individual donor atom–donor atom repulsions (or alternatively, the equivalent bond–bond repulsions). It is assumed that the repulsive energy u_{ij} between any two donor atoms i and j (or alternatively, between the bonds joining the central atom and i and j respectively), is proportional to some inverse power n of the distance d_{ij} between them. If all bond lengths are equal, that is all donor atoms lie on the surface of a sphere of radius r, then the results can be expressed in the form (1), where a is the

$$U = \sum_{ij} u_{ij} = \sum_{ij} a d_{ij}^{-n} = aXr^{-n} \qquad (1)$$

proportionality constant and X the repulsive-energy coefficient which is a function of n and the geometry of the co-ordination polyhedron. The most appropriate value of n cannot be known exactly, but certainly lies between the limits of 1 (for a purely Coulombic interaction) and 12. Fortunately conclusions from this work are not very dependent on the assumed value of n.

It is assumed that each bonded β-diketonate bidentate ligand is sufficiently rigid that interaction between its donor atoms can be considered to be constant, and can therefore be neglected when comparing otherwise different stereochemistries. The success of previous work [20-23] shows that this assumption is justified.

The location of the unidentate ligand A and of each donor atom of the bidentate ligands BC, DE, and FG on the surface of the sphere is defined by its polar co-ordinates ϕ_i and θ_i, the axes being defined by placing the unidentate A at the ' North Pole ' with $\phi_A = 0$, and the donor atom B at ' zero longitude,' $\theta_B = 0$. The co-ordinates of the i atom are ϕ_i, which is defined as the angle between the metal–ligand M–i bond and the axis incorporating the metal–ligand bond M–A. The ' longitude ' θ_i is defined as the angle between the vertical plane incorporating MAB and the vertical plane incorporating MAi.

The distance d_{ij} between any two ligand sites i and j is given by (2). One of the four variables ϕ_P, θ_P, ϕ_Q, and θ_Q

$$d_{ij} = [2 - 2\cos\phi_i\cos\phi_j - 2\sin\phi_i\sin\phi_j\cos(\theta_i - \theta_j)]^{\frac{1}{2}}r \qquad (2)$$

for any general bidentate ligand PQ can therefore be calculated from the other three and the ' normalised bite '

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of the chelate b, which is defined as the distance between the two donor atoms of the chelate divided by the metal–ligand bond length [equation (3)].

$$b = d_{PQ}/r \qquad (3)$$

The normalised bidentate bite b for the above [Ln(β-diketonate)$_3$(unidentate)] complexes ranges from 1·20 {for [Dy($C_4H_9COCHCOC_4H_9$)$_3$(H_2O)]} to 1·24 {for one of the crystallographic independent molecules in [Yb(MeCOCH-COMe)$_3$(H_2O)]}. The average for all structures is 1·22, and this value is used in this work. The results obtained are not dependent on small variations in b. The total ligand–ligand repulsion energy was calculated as a function of ϕ_B and θ_C, ϕ_D, θ_D, and θ_E, and ϕ_F, θ_F, and θ_G. The location of each minimum on the appropriate nine-dimensional potential-energy surface was determined to the nearest 0·1° in each of the angular co-ordinates.

RESULTS

Each potential-energy surface contained three approximately equally deep minima corresponding to three different geometrical isomers. Angular co-ordinates and repulsive-energy coefficients X corresponding to each of these minima are given in Table 1 for n values of 1, 6, and 12. The optical isomer and the labels on the atoms were chosen purely to facilitate comparisons between the different structures. The arrangement of bidentate ligands on the surface of the globe is shown as the usual geographical Mercator's projections in Figures 1—3.

TABLE 1

Angular co-ordinates (°) and repulsive-energy coefficients X for the three isomers of complexes [Ln(β-diketonate)$_3$-(unidentate)]

	$n = 1$		$n = 6$		$n = 12$	
	ϕ	θ	ϕ	θ	ϕ	θ
			Isomer (A)			
A	0		0		0	
B	128·0	0	129·5	0	130·7	0
C	74·2	56·1	75·6	56·4	76·7	56·6
D	128·0	120·0	129·5	120·0	130·7	120·0
E	74·2	176·1	75·6	176·4	76·7	176·6
F	128·0	240·0	129·5	240·0	130·7	240·0
G	74·2	296·1	75·6	296·4	76·7	296·6
X	12·0050		2·3499		0·5032	
			Isomer (B)			
A	0		0		0	
B	130·5	0	128·7	0	129·8	0
C	81·6	62·2	80·8	62·5	79·7	60·7
D	152·8	154·6	154·3	160·5	153·0	168·6
E	77·7	149·2	80·1	144·6	80·8	141·3
F	94·5	234·9	89·1	227·4	84·2	223·1
G	75·4	308·3	77·3	302·4	78·6	299·1
X	12·0003		2·3340		0·4942	
			Isomer (C)			
A	0		0		0	
B	89·7	0	86·9	0	83·4	0
C	79·8	75·0	79·6	75·5	79·3	76·1
D	171·7	321·5	165·2	320·8	158·4	319·9
E	113·1	141·5	119·6	140·8	126·4	139·9
F	79·8	208·0	79·6	206·1	79·3	203·7
G	89·7	283·0	86·9	281·6	83·4	279·8
X	11·9983		2·3277		0·4924	

Isomer (A) (Figure 1) contains a three-fold axis, and is the usual capped octahedron, (I). Isomer (B) is obtained by rotating two of the three equivalent bidentate ligands of the capped octahedron in opposite directions, for example by rotating DE and FG of Figure 1 anticlockwise and clockwise respectively (Figure 2). Isomer (C) may be formed by moving the ligand DE by increasing ϕ_D and ϕ_E so that D moves through the 'South Pole' at $\phi = 180°$. This stereochemistry is not optically active, the ligand atoms ADE and the metal atom lying on a mirror plane.

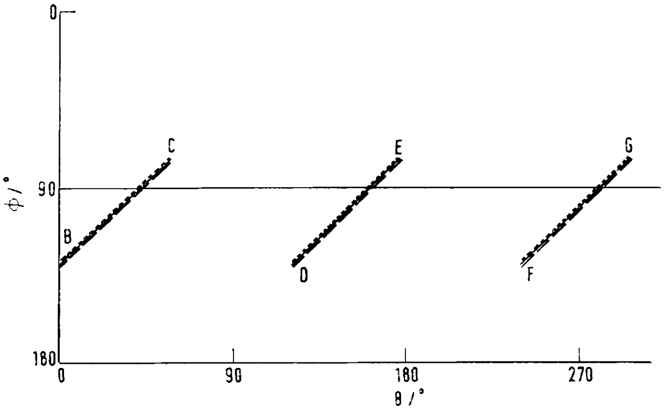


FIGURE 1 Isomer (A) of the complexes [Ln(β-diketonate)$_3$(unidentate)] showing the arrangement of the three bidentate ligands. The unidentate ligand is at $\phi_A = 0$: (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

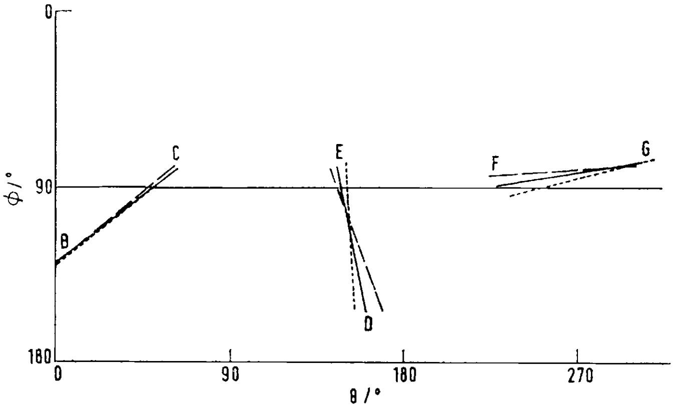


FIGURE 2 Isomer (B) of the complexes [Ln(β-diketonate)$_3$(unidentate)] showing the arrangement of the three bidentate ligands. For key see Figure 1

Isomer (C) is intermediate between the pentagonal bipyramid, with the atoms BCEF and G comprising the pentagonal plane with atoms A and D forming the two vertices, and the capped trigonal prism, where the A atom is above the BCFG rectangular face, the prism being completed by the bidentate ligand DE which is parallel to the other two ligands BC and FG. Calculations show that as the normalised bite b is progressively increased the minimum on the potential-energy surface moves away from the pentagonal bipyramid (IV), towards the capped trigonal prism, (V).

Extensive searches to locate other minima on the potential energy surfaces were based on the following approaches. (*a*) Commencing with the three bidentate ligands arranged along various edges of the polyhedra corresponding to minima for $[\mathrm{M(unidentate)_7}]^{x\pm}$ complexes, and then allowing the stereochemistry to refine to the nearest minimum. (*b*) Calculation of complete potential-energy surfaces for stereochemistries which had first of all been simplified by incorporation of some symmetry elements. Whether or not these minima were true minima was then determined by removal of the applied symmetry restrictions, and then allowing the stereochemistry to refine to the nearest minimum. It was found, for example, that the pentagonal bipyramid, (VI), and the capped trigonal prism, (VII), occurred as minima when a two-fold axis and mirror plane respectively were introduced, but these stereochemistries refined to isomers (C) and (B) respectively on removal of these restrictions. (*c*) The above three minima can be loosely classified as $3(\phi_P \gg \phi_Q)$ [isomer (A)], $2(\phi_P \gg \phi_Q) + 1(\phi_P \sim \phi_Q)$ [isomer (B)], and $1(\phi_P \gg \phi_Q) + 2(\phi_P \sim \phi_Q)$ [isomer (C)]. The third general possibility, $3(\phi_P \sim \phi_Q)$, was examined and the capped trigonal prism, (VIII) [isomer (D)], was found as a small dimple minimum at relatively high energies on a saddle between other minima for the particular case of $n = 12$ ($\phi_B = \phi_C = \phi_F = \phi_G =$ 75·3°, $\phi_D = \phi_E =$ 142·4°, $\theta_C =$ 78·2°, $\theta_F =$ 180°, $\theta_G = \theta_C + \theta_F$, $\theta_E = \theta_C/2$, $\theta_D = \theta_E +$ 180°, $X =$ 0·7528). For $n = 1$ and $n = 6$ where the donor atoms can more readily move past one another, this particular stereochemistry occurs only as a saddle ($X =$ 12·1636 and 2·7859 respectively) between other minima.

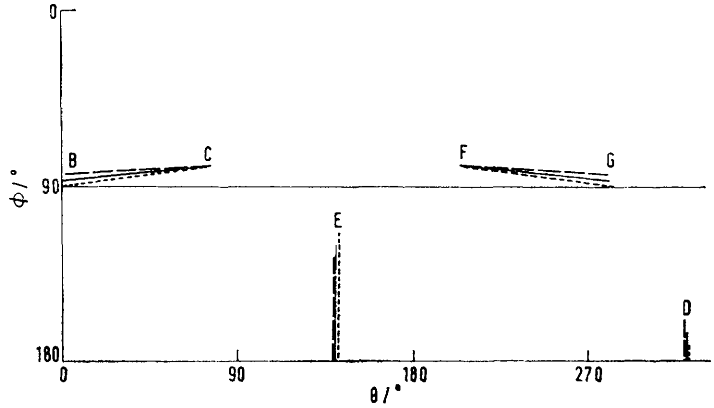
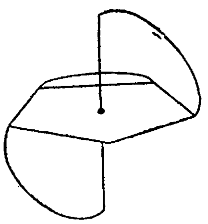


FIGURE 3 Isomer (C) of the complexes $[\mathrm{Ln(\beta\text{-}diketonate)_3(unidentate)}]$ showing the arrangement of the three bidentate ligands. For key see Figure 1



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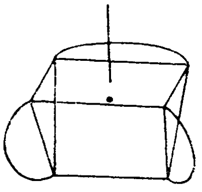

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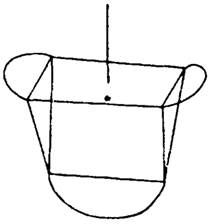

(VIII)

DISCUSSION

Four different stereochemistries occur as separate minima on the potential-energy surfaces. Three of these have virtually identical values for the repulsion-energy coefficient X (Table 2). The fourth only occurs as a minimum for $n = 12$, and is much more unstable than the other three. (Experience suggests that differences in the ratios of X of less than about 0·001 for $n = 1$, 0·01 for $n = 6$, and 0·1 : 1 for $n = 12$, are not sufficiently important to favour one stereochemistry over another.[21,23-25])

TABLE 2

Ligand–ligand repulsion-energy coefficients normalised to those of the capped octahedron

	Isomer (A)	Isomer (B)	Isomer (C)	Isomer (D)
$n = 1$	1·0000	0·9996	0·9994	(1·0132)
$n = 6$	1·0000	0·9932	0·9906	(1·1856)
$n = 12$	1·0000	0·9823	0·9786	1·4962

Isomer (A), the capped octahedron (I), is the stereochemistry found for the complexes $[\mathrm{Ho(PhCOCHCOPh)_3(H_2O)}]$ [4] and $[\mathrm{Y(PhCOCHCOMe)_3(H_2O)}]$.[5] The detailed

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[24] D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, 1968, **11**, 51.

[25] D. L. Kepert, *Inorg. Chem.*, 1973, **12**, 1938.

stereochemistry is not significantly different to the analogous capped octahedral complexes $[\mathrm{M(unidentate)}_7]^{x\pm}$.[3] It may be predicted that this stereochemistry will become progressively more stable relative to the other stereochemistries as the metal–unidentate ligand bond becomes progressively longer relative to the metal–bidentate ligand bonds, that is as it approaches the C_3 octahedron (necessarily distorted about the three-fold axis).[22] The other isomers will approach more distorted six-co-ordinate polyhedra.

The second stereochemistry, isomer (B), has no elements of symmetry, and the solid figure chosen to describe the conventional co-ordination polyhedron is somewhat arbitrary. The ligand atoms ACDF describe a very good plane, which with the BG edge form a trigonal prism, while E completes the capped trigonal prism, (II). The angles that selected metal–ligand bonds and the BG polyhedral edge make with the least-squares ACDF plane are shown in Table 3. This polyhedron has been used to describe the stereochemistry of the complexes $[\mathrm{Yb(MeCOCHCOMe)_3\{MeCOCHC(NH_2)Me\}}]$,[6] $[\mathrm{Dy(BuCOCHCOBu)_3(H_2O)}]$,[7] $[\mathrm{Lu(BuCOCHCOBu)_3(MeC_5H_4N)}]$,[8] and $[\mathrm{Lu(C_3F_7COCHCOBu)_3(H_2O)}]$.[9] The alternative set of atoms AEDG also form a very good plane, and the somewhat distorted capped trigonal prism, (III), is completed by the edge BC and the capping atom F (Table 3). It is this alternative which has been used to describe the stereochemistry of the complex $[\mathrm{Yb(MeCOCHCOMe)_3(H_2O)}]$.[10,11]

Table 3

Deviations from least-squares planes in isomer (B)

ACDF Plane	M–A	M–C	M–D	M–F	B–G	M–E
$n = 1$	4·8°	−4·7°	4·7°	−4·8°	1·0°	88·4°
$n = 6$	2·1	−1·9	1·9	−2·1	2·9	87·2
$n = 12$	1·0	−0·9	0·9	−1·0	5·1	87·0

AEDG Plane	M–A	M–E	M–D	M–G	B–C	M–F
$n = 1$	−4·1°	4·1°	−2·9°	2·8°	19·4°	79·6°
$n = 6$	−3·3	3·4	−2·5	2·4	13·3	83·5
$n = 12$	−2·1	2·1	−1·6	1·6	9·7	85·9

The third stereochemistry [isomer (C)] contains a mirror plane, and is intermediate between the pentagonal bipyramid, (IV), and the capped trigonal prism, (V). This isomer is not yet known for the complexes [Ln(β-diketonate)$_3$(unidentate)], but has been observed for transition-metal and post-transition-metal complexes listed in the Introduction section. This difference in behaviour can be readily understood if the repulsion felt by the unidentate ligand alone is considered for each of the isomers (Table 4). It can be seen that the unidentate ligand in isomer (C) is subjected to a very much lesser repulsion than are the unidentate ligands in isomers (A) and (B), in spite of the total ligand–ligand repulsion energies being equal. [It can also be seen that the unidentate ligand is subjected to a significantly higher repulsion energy (*ca.* 20% of the total) than are the individual bidentate ligand donor atoms.] It is therefore predicted that unidentate ligands which form unusually short and/or strong bonds with the metal concerned, will favour isomer (C) rather than isomers (A) or (B). Thus isomer (C) is found for the above metal complexes which contain oxo- or other charged unidentate ligands, but not in lanthanoid complexes where the unidentate ligand is water or uncharged organic ligand. It is therefore further predicted that unidentate ligands which form unusually strong ligand–lanthanoid bonds may form isomer (C). It may also be noted that this difference in isomer stability is comparable to, for example, the difference between the five-co-ordinate stereochemistries, where the introduction of one short metal–ligand bond enforces the square-pyramidal rather than the trigonal-bipyramidal structure.[25]

Table 4

Contribution of the unidentate ligand to the total ligand–ligand repulsion-energy coefficient

	Isomer (A)	Isomer (B)	Isomer (C)
$n = 1$	2·0778	2·0629	2·0387
$n = 6$	0·4849	0·4363	0·4018
$n = 12$	0·1136	0·0924	0·0867

It is of interest that racemisation of the optically active isomer (A) may occur through rotation of two bidentate ligands in opposite directions to overcome one potential-energy barrier to form isomer (B), followed by movement of one of these bidentate ligands to overcome a second potential-energy barrier to form the inactive isomer (C), which may then revert to the mirror image of (A) by passing across the same two potential-energy barriers. This is in contrast to racemisation of isomer (A) by simultaneously rotating all three bidentate ligands in the same anticlockwise direction to form the intermediate trigonal prism with the unidentate ligand capping a triangular face. This process involves a single large potential-energy barrier, and is the seven-co-ordinate analogue of the six-co-ordinate Bailar-twist mechanism. Thus although a Bailar-twist mechanism may be appropriate for racemisation of the complexes $[\mathrm{M(bidentate)}_3]^{x\pm}$ in non-complexing solvents, the solvent-assisted mechanism isomer (A)* $\longrightarrow$ isomer (B)* $\longrightarrow$ isomer (C) $\longrightarrow$ isomer (B) $\longrightarrow$ isomer (A) may be appropriate for complexes and for solvents which may form a seven-co-ordinate or quasi-seven-co-ordinate intermediate.

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