

Stereochemistry of Five-co-ordination. Part IV.¹ Compounds of Stoichiometry (Bidentate ligand)tris(unidentate ligand)metal

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Repulsion-energy calculations show that for compounds of the type $[M(\text{bidentate})(\text{unidentate})_3]^{*±}$ a long trough exists on the potential-energy surface which includes a distorted square pyramid, with the bidentate ligand spanning one of the square edges, and a trigonal bipyramid with the bidentate ligand spanning one of the non-equatorial edges. Intramolecular rearrangements along this trough can be considered as free rotation of the bidentate ligand about the metal–bidentate ligand axis, above the triangular arrangement of the three unidentate ligands. The effects of varying the bidentate ligand bite, and the metal–ligand bond lengths, are discussed.

THE consequences of introducing chelate groups into the co-ordination sphere of a five-co-ordinate metal atom² on the stereochemistry and the intramolecular-rearrangement reactions have previously been examined for $[M(\text{bidentate})_2(\text{unidentate})]_3$ and $[M(\text{tridentate})(\text{unidentate})_2]$.¹ This study is now extended to five-co-ordinate complexes containing a single bidentate chelate group.

METHOD

The stereochemical arrangement of a number of ligand donor atoms surrounding a central metal atom may be calculated by minimisation of the total repulsion energy U , obtained by summing over all individual donor atom–donor atom repulsions (or alternatively the equivalent valence-shell electron-pair repulsions). It is assumed that the repulsive energy U_{ij} between any two donor atoms i and j

(or alternatively, between any two electron pairs i and j) 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_n is the

$$U = \sum_{ij} U_{ij} = \sum_{ij} a_n d_{ij}^{-n} = a_n X r^{-n} \quad (j > i) \quad (1)$$

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, the best fit with experiment being obtained for values in the range 6–12. Fortunately the conclusions obtained are usually not very dependent on

¹ Part III, D. L. Kepert, *J.C.S. Dalton*, 1974, 612.

² D. L. Kepert, *Inorg. Chem.*, 1973, **12**, 1938.

³ D. L. Kepert, *Inorg. Chem.*, 1973, **12**, 1942.

the assumed value of n . In this work the previous custom of using values of 1 (for a purely Coulombic interaction), 6, and 12 is continued.

It is assumed that each bonded 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 bidentate ligand AB and the three unidentate ligands C, D, and E lie on the surface of a sphere of unit radius about the metal atom M, the ligand locations being given by the spherical co-ordinates ϕ_i and θ_i (Figure 1).

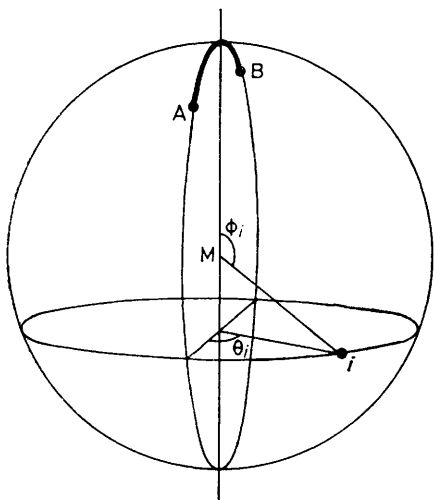


FIGURE 1 General stereochemistry of $[M(\text{bidentate})(\text{unidentate})_3]^{n\pm}$

The axes are defined by placing the bidentate AB symmetrically across the 'North Pole' at $\phi = 0$, with the 'longitudes' given by $\theta_A = 0$ and $\theta_B = 180^\circ$. The angle ϕ_i is defined as the angle between the M- i bond and the axis passing through the metal atom and the midpoint of AB. The 'longitude' θ_i is defined as the angle between the MAB plane and the plane incorporating M, i , and the midpoint of AB. The distance d_{ij} between any two such ligand sites i and j is given by (2). The 'normalised bite' of the

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

bidentate ligand is defined by $b = AB/MA = AB/MB$ and $b = 2 \sin \phi_A = 2 \sin \phi_B$. The total repulsion energy was calculated as a function of $\phi_C, \theta_C, \phi_D, \theta_D, \phi_E,$ and θ_E , and the location of each energy minimum determined to the nearest 0.1° in each of these angular co-ordinates.

Potential-energy surfaces are shown for convenience projected onto the θ_C - θ_D plane, which most clearly separates and illustrates the relation between the different stereochemistries. To prevent the overlap of several minima on these projections, due merely to an interchange of labels on the donor atoms, it is also convenient to impose the conditions $\phi_E \geq \phi_C, \phi_E \geq \phi_D,$ and $\theta_D \leq \theta_E \leq (360 + \theta_C)$.

RESULTS

For values of the normalised bite b in the range 0.5–1.3, a single minimum occurred on each potential-energy surface, a typical example being shown in Figure 2 ($b = 0.9, n = 6$). Each minimum consisted of an extraordinarily long and level valley encompassing stereochemistries (I) and (II),

both of which have $\phi_C \sim \phi_D \sim \phi_E \sim 120^\circ$ (Figures 3 and 4). Stereochemistry (I) contains a mirror plane through the metal atom and ligand C, and bisecting the bidentate ligand AB, so that $\theta_C = 90^\circ, \theta_E = 180^\circ - \theta_D,$ and $\phi_E = \phi_D$. The

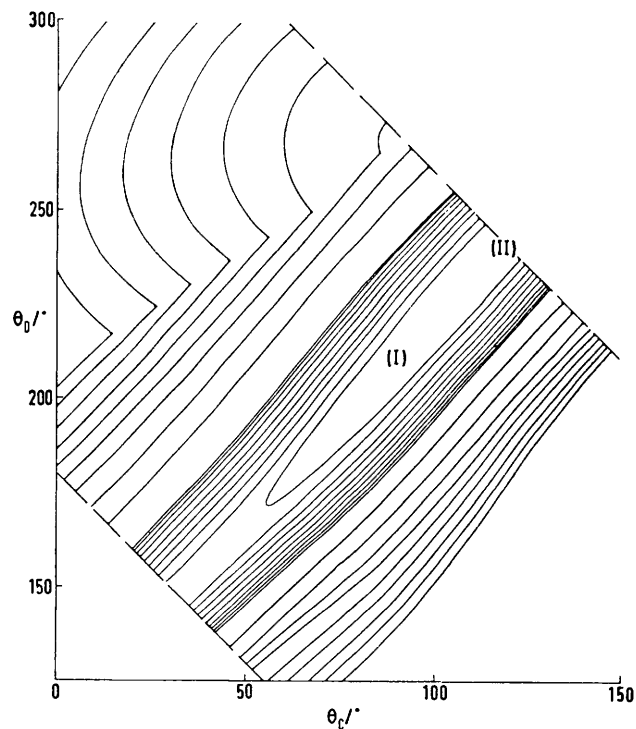


FIGURE 2 Potential-energy surface for $[M(\text{bidentate})(\text{unidentate})_3]$ ($n = 6$). Normalised ligand bite, $b = 0.9$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential-energy surface. The locations of stereochemistries (I) and (II) are shown

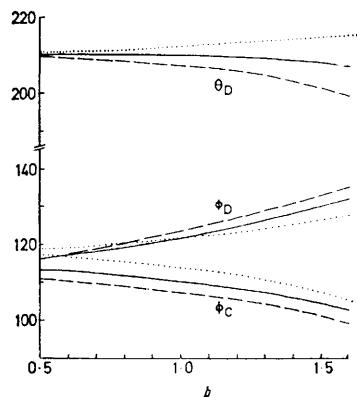


FIGURE 3 Angular parameters ($^\circ$) for stereochemistry (I) of $[M(\text{bidentate})(\text{unidentate})_3]$ as a function of normalised ligand bite, b : (\cdots), $n = 1$; (—), $n = 6$; (---), $n = 12$. $\theta_C = 90^\circ, \theta_E = 180^\circ - \theta_D,$ and $\phi_E = \phi_D$

bidentate ligand AB is therefore parallel to the edge DE, and this stereochemistry may alternatively be pictured as a distorted square pyramid with the bidentate ligand spanning one of the sides of the distorted square (Figure 5). Stereochemistry (II) contains a mirror plane through the metal atom, ligand E, and the bidentate ligand AB, so that $\theta_D = -\theta_C, \theta_E = 0^\circ,$ and $\phi_D = \phi_C$. The projection of the bi-

dentate ligand AB is therefore normal to the edge CD, and this stereochemistry may be pictured as an irregular trigonal bipyramid (Figure 5). At $b = 2^{\frac{1}{2}} = 1.414$, the stereochemistry becomes a regular trigonal bipyramid with $\phi_C = 180 - \arccos(8^{-\frac{1}{2}}) = 110.7$, $\theta_C = 180 - \arccos(7^{-\frac{1}{2}}) = 112.2$, and $\phi_E = 135.0^\circ$.

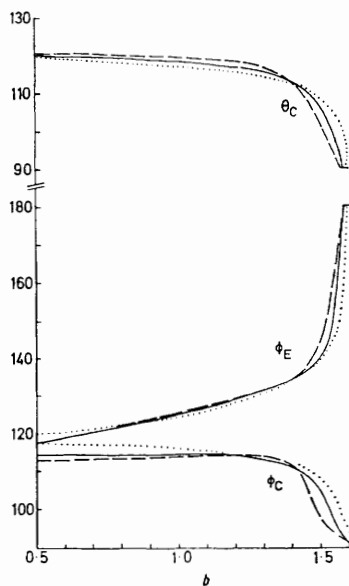


FIGURE 4 Angular parameters ($^\circ$) for stereochemistries (II) and (III) of $[M(\text{bidentate})(\text{unidentate})_3]$ as a function of normalised ligand bite, b : (\cdots), $n = 1$; (—), $n = 6$; (— — —), $n = 12$. $\theta_D = -\theta_C$, $\theta_E = 0$, and $\phi_D = \phi_C$

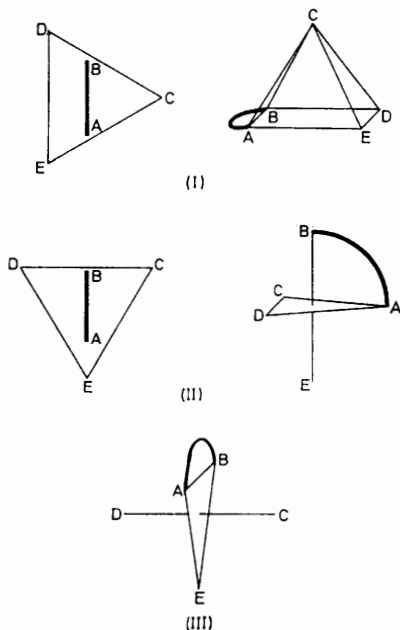


FIGURE 5 Stereochemistries (I)—(III)

As the normalised bite was further increased, stereochemistry (II) became increasingly stable with respect to (I), a typical potential-energy surface being shown in Figure 6 ($b = 1.5$, $n = 6$). Stereochemistry (II) simultaneously and progressively changed by decreasing ϕ_C and θ_C and increasing ϕ_E (Figure 4) to approach (III). Stereochemistry

(III) occurred as the minimum on the potential-energy surface at high values of the normalised bite ($b \geq 1.59$ for

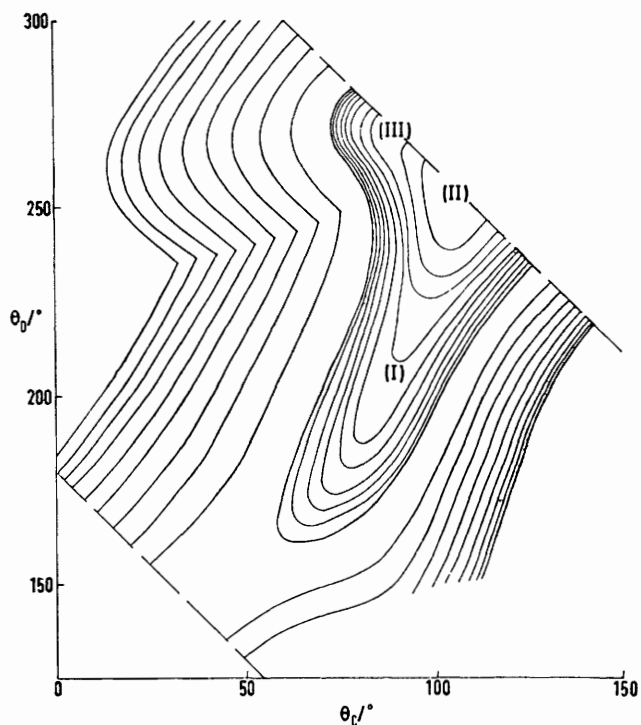


FIGURE 6 Potential-energy surface for $[M(\text{bidentate})(\text{unidentate})_3]$ ($n = 6$). Normalised ligand bite, $b = 1.5$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential-energy surface. The location of stereochemistries (I)—(III) are shown

$n = 1$, $b \geq 1.58$ for $n = 6$ and $n = 12$), and contains two mirror planes, one through M, AB, and E, the other through C, D, E, and the midpoint of AB, so that $\theta_C = 90$, $\theta_D = 270$, and $\phi_D = \phi_C$, $\phi_E = 180^\circ$. This corresponds to a trigonal

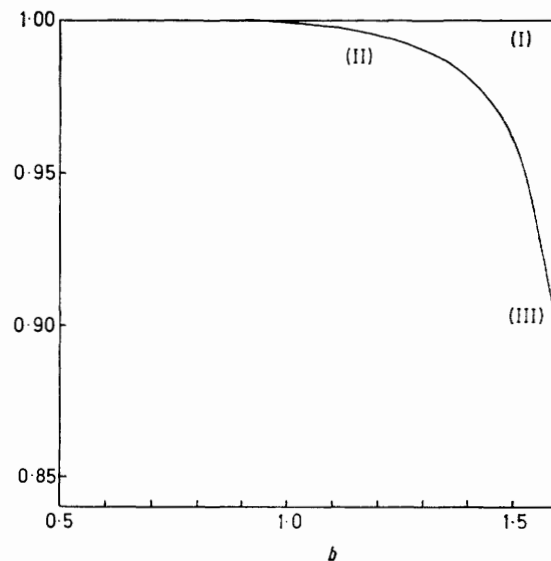


FIGURE 7 Ligand-ligand repulsion-energy coefficients of stereochemistries (II) and (III) normalised to those of (I), as a function of normalised ligand bite b

bipyramid with the bidentate ligand spanning one of the equatorial edges (Figure 5). For a regular trigonal bipyramid, $b = 3^{\frac{1}{2}} = 1.732$ and $\phi_C = 90.0^\circ$.

The relative repulsion-energy coefficients for these stereochemistries, normalised to those for stereochemistry (I), are shown in Figure 7 for $n = 6$. Similar curves were obtained for $n = 1$ and 12.

DISCUSSION

For values of the normalised bite less than 1.3, the difference in energy between stereochemistries (I) and (II)

(unidentate)],³ which is consistent with the non-rigid nature of these molecules.⁶⁻⁸ [The intramolecular rearrangement, stereochemistry (II) \leftrightarrow (III), does not lead to all unidentate ligands becoming identical.]

Stereochemistry (III) is at present unknown for $[M(\text{bidentate})(\text{unidentate})_3]$, but is observed for $[\text{Te}\{(\text{C}_6\text{H}_4)_2\text{O}\}(\text{O}_2\text{CCF}_3)_2]$ ⁹ if it is assumed that a lone pair of electrons occupies the least-crowded equatorial site E (Table). This stabilisation of stereochemistry (III) can be simulated by repeating the above calculations with one

Structural parameters for compounds $[M(\text{bidentate})(\text{unidentate})_3]^{z\pm}$

Compound	b	Stereochemistry	Angle/ $^\circ$						Ref.
			ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	
$[\text{Ni}\{(\text{Me}_2\text{As}\cdot\text{C}_6\text{H}_4)_2\text{Fe}\}\text{I}_2(\text{CO})]$	1.46	(II)	115	112	112	246	139	3	<i>a</i>
$[\text{Te}\{(\text{C}_6\text{H}_4)_2\text{O}\}(\text{O}_2\text{CCF}_3)_2(\text{lone pair})]$	1.43	(III)	84	86	83	266	(180)		<i>c</i>
$[\text{Fe}\{(\text{Me}_2\text{As})_2\text{C}_6\text{H}_4\}(\text{CO})_3]$	1.34	(II)	108	113	108	247	134	0	<i>d</i>
$[\text{Fe}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}(\text{CO})_3]$	1.20	(I)–(II)	108	98	116	230	128	344	<i>e</i>
$[\text{Sn}\{\text{OC}(\text{Ph})\text{N}(\text{Ph})\text{O}\}\text{Ph}_3]$	1.16	(II)?							<i>f</i>
$[\text{P}(\text{C}_{14}\text{H}_{16}\text{O}_2)(\text{OPr})_3]$		(I)?							<i>g</i>

^a C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 828. ^c Ref. 9. ^d D. S. Brown and G. W. Bushnell, *Acta Cryst.*, 1967, **22**, 296. ^e Ref. 6. ^f No details available; T. J. King and P. G. Harrison, *J.C.S. Chem. Comm.*, 1972, 815. ^g No details available; W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Amer. Chem. Soc.*, 1965, **87**, 127.

is probably not chemically significant, and it can only be predicted that the observed stereochemistry will lie somewhere in the valley between these extremes. Known structures for monomeric molecules of the type $[M(\text{bidentate})(\text{unidentate})_3]^{z\pm}$ are restricted to those listed in the Table. The agreement is satisfactory. Platinum(II) d^8 complexes with alkenes and alkynes such as $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ and $[\text{PtCl}_3(\text{RC}\equiv\text{CR})]^-$ are best considered as four-co-ordinate square-planar species, rather than as five-co-ordinate complexes containing a bidentate alkene or alkyne with normalised bites of ~ 0.65 ⁴ or ~ 0.55 ⁵ respectively.

Progression along this valley floor from stereochemistry (I) to (II), corresponding to free rotation of the bidentate ligand about the metal–bidentate ligand axis, causes all the unidentate ligands to become equivalent and also both ends of the bidentate ligand become equivalent. This spinning of the bidentate ligand is closely related to the mechanism described by Cotton *et al.*⁶ for the fluxional molecule $[\text{Fe}\{(\text{Ph}_2\text{P})_2\text{CH}_2\}(\text{CO})_3]$. This barrier to intramolecular isomerisation is much less than that calculated for $[M(\text{unidentate})_5]$ ² or $[M(\text{bidentate})_2-$

of the metal–unidentate ligand bonds being much shorter than the other two (Figure 8).

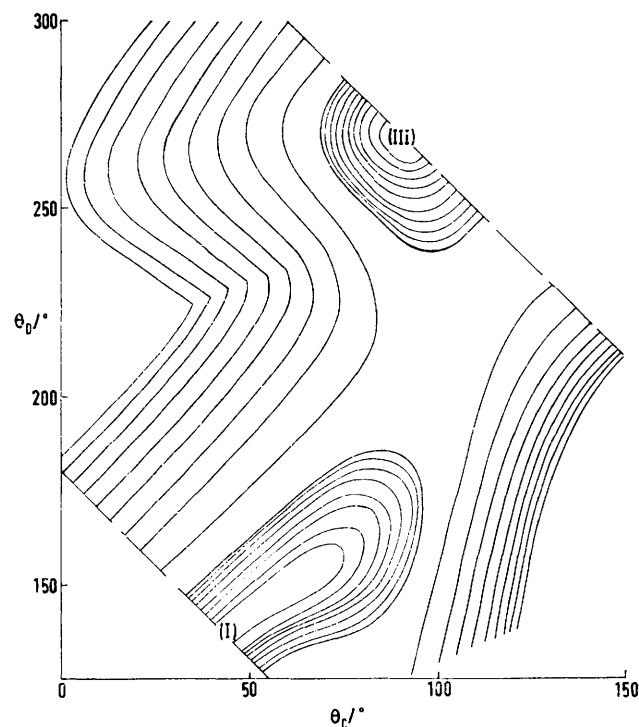


FIGURE 8 Potential-energy surface for $[M(\text{bidentate})(\text{unidentate})_2(\text{unidentate}')]$ ($n = 6$). Normalised ligand bite, $b = 1.5$, $\text{MA} = \text{MB} = \text{MC} = \text{MD} = r$, $\text{ME} = r/2$. The faint contour lines are for 1% energy increases, above the bottom of the potential-energy surface. The dark contour lines for 10% energy increases, above the bottom of the potential-energy surface. The location of stereochemistries (I) and (III) are shown

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