$[TiBr_3(Me_3N)_2]$,[14] $[VCl_3(Me_3N)_2]$,[15] and $[CrCl_3(Me_3N)_2]$.[16] The second type is found in $[Cu(PhOCH_2COO)_2(H_2O)_3]$,[17] the dimethylimidazole derivative $[CuCl_2(C_5H_8N_2)_3]$,[18] $[RuCl_2(Ph_3P)_3]$,[19] $[CoBr_2(Ph_2PH)_3]$, and $[NiI_2(Ph_2PH)_3]$,[20] four tertiary phosphine derivatives of the type $[Ni(CN)_2(phosphine)_3]$,[21] and the anion of $[SnMe_2Cl(terpy)][SnMe_2Cl_3]$.[22] The angular parameters corresponding to the individual stereochemistries lie in the trough between the trigonal bipyramid at $\phi_A < \phi_B$ and the saddle at $\phi_A = \phi_B$ corresponding to the square pyramid in a similar manner to that observed for complexes with five equivalent ligands. Again a more detailed comparison is not justified.

The stereochemistry of the d^8 complex $[PdBr_2(C_{14}H_{13}P)_3]$[23] is best considered as a square plane with one additional long bond normal to the plane and, like d^8 square-planar complexes themselves, cannot be rationalized on the basis of ligand-ligand repulsion energies.

Energy factors for five-coordination other than ligand-ligand repulsion energies have been discussed in detail elsewhere.[24]

Acknowledgments. This work was carried out while on leave at the University Chemical Laboratories, University of Cambridge, and thanks are due to Professor J. Lewis and his colleagues for their hospitality.

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Stereochemistry of Five-Coordination. II. Compounds of Stoichiometry M(bidentate)$_2$(monodentate)

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Received October 31, 1972

Minimization of the total ligand-ligand repulsion energies has shown that the introduction of bidentate ligands into six-[1] and eight-coordinate[2] compounds significantly affects the relative stability of the different isomeric forms and also the activation energy for intramolecular isomerization. At least for the cases when all ligands are equivalent, the detailed stereochemistry can also be successfully predicted.

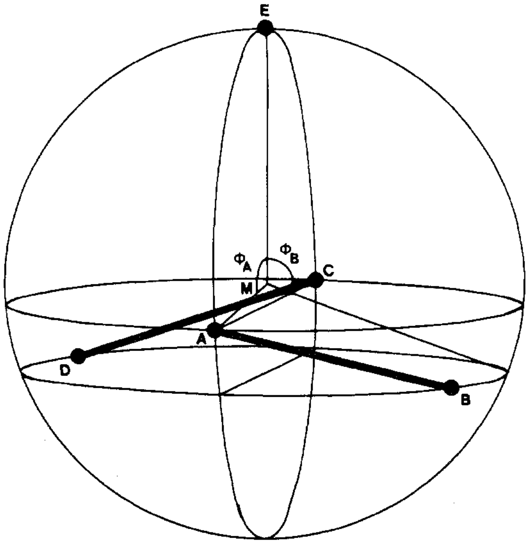

Figure 1. General stereochemistry for M(bidentate)$_2$(monodentate).

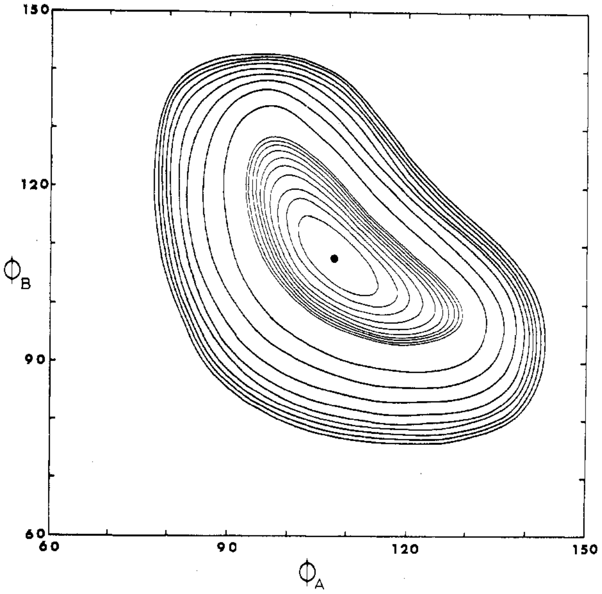

Figure 2. Potential energy surface for M(bidentate)$_2$(monodentate) ($n = 6$). Normalized ligand bite, $b = 1.1$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

At present this simple model is the only way such predictions can be successfully made.

The effect of the introduction of two bidentate ligands into the five-coordinate structures[3] is examined in this paper.

Method

Figure 1 defines the general stereochemistry for M(bidentate)$_2$(monodentate), the bidentate ligands spanning the AB and CD edges. The angles between the twofold axis incorporating the metal-monodentate ligand bond and the two ends of each bidentate are denoted by ϕ_A and ϕ_B, respectively.

The regular trigonal-bipyramidal and regular square-pyramidal stereochemistries observed as the limiting cases in M(monodentate)$_5$ are necessarily distorted by the introduction of the bidentate ligands. The analogous stereochemistries for M(bidentate)$_2$(monodentate) will, for the sake of

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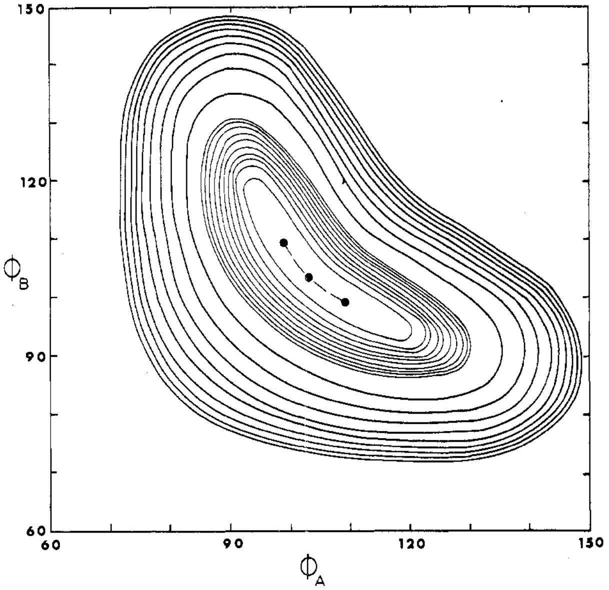

Figure 3. Potential energy surface for M(bidentate)$_2$(monodentate) ($n = 6$). Normalized ligand bite, $b = 1.3$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

convenience, be referred to as the irregular trigonal bipyramid ($\phi_A \neq \phi_B$) and the rectangular pyramid ($\phi_A = \phi_B$), respectively.

All metal atom-donor atom distances are defined as r, and the distance between the two donor atoms of the same bidentate divided by the metal-ligand bond length is defined as the "normalized bite" of the chelate, b

$$b = (\text{A-B})/r = (\text{C-D})/r$$

The distances between the other donor atoms are given by

$$\text{AC} = (2 \sin \phi_A)r$$

$$\text{AD} = \text{BC} = (4 - b^2 - 4 \cos \phi_A \cos \phi_B)^{1/2}r$$

$$\text{AE} = \text{CE} = (2 - 2 \cos \phi_A)^{1/2}r$$

$$\text{BD} = (2 \sin \phi_B)r$$

$$\text{BE} = \text{DE} = (2 - 2 \cos \phi_B)^{1/2}r$$

It is assumed that each bonded bidentate is sufficiently rigid that the interaction between its donor atoms can be considered to be constant and can therefore be neglected. The repulsion energy u_{ij} between any other pair of donor atoms i and j is again assumed to be inversely proportional to the nth power of the distance between them. The total repulsive energy U is obtained by summing over all such pairs of donor atoms and is expressed in the form

$$U = \sum_{ij} u_{ij} = aXr^{-n}$$

where a is a constant and the coefficient X is dependent upon the value of n and the geometry and is a direct measure of the ligand-ligand repulsion energy.

Results and Discussion

Three representative potential energy surfaces for $n = 6$ are shown in Figures 2-4. The repulsion energy coefficients in these figures have again been normalized so that the minimum value of X is equated to unity. They should be compared with the rather shallower potential energy surface obtained for the case of five monodentate ligands, shown in Figure 3 of the preceding paper.[3]

For small values of the ligand bite ($b = 1.1$, Figure 2), a single minimum on the potential energy surface occurs at $\phi_A = \phi_B$ corresponding to the rectangular pyramid. This minimum becomes deeper as the normalized bite is further decreased. It is clearly predicted that bidentates of very small bite (for example, peroxide or nitrate) will form complexes with this rectangular-pyramidal stereochemistry.

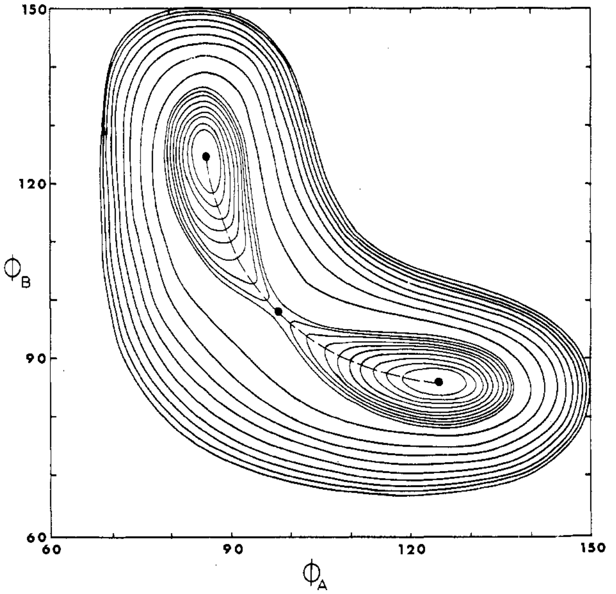

Figure 4. Potential energy surface for M(bidentate)$_2$(monodentate) ($n = 6$). Normalized ligand bite, $b = 1.5$. The faint contour lines are for 1% energy increases, and the dark contour lines for 10% energy increases, above the bottom of the potential energy surface.

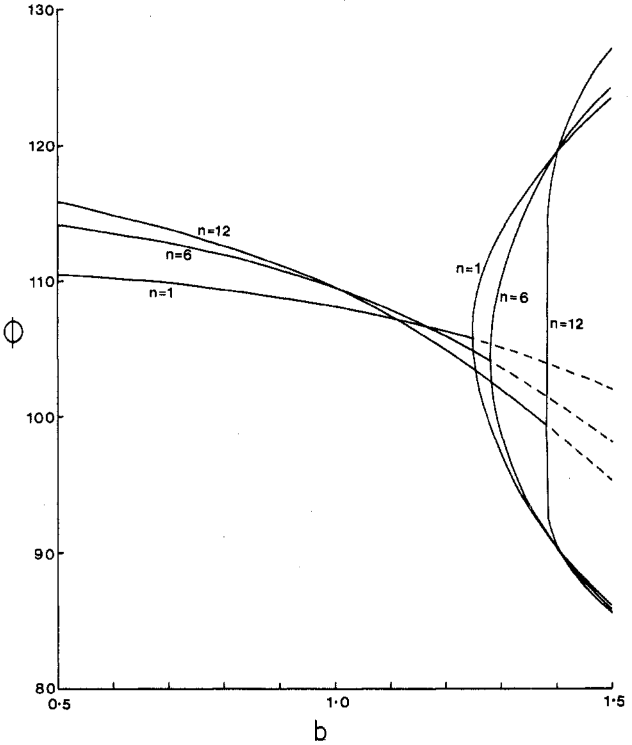

Figure 5. Angular parameters for the most stable M(bidentate)$_2$-(monodentate) stereochemistries as a function of normalized bidentate bite, b.

As the normalized bite is progressively increased ($b = 1.3$, Figure 3), the minimum becomes shallower and boomerang-shaped and then symmetrically splits into two minima corresponding to the two equivalent irregular trigonal bipyramids. For these intermediate cases where the potential energy surfaces are fairly flat, the precise locations of the

Table I. Angular Parameters and Ligand–Ligand Repulsion Coefficients for M(bidentate)$_2$(monodentate)

		Irregular trigonal bipyramid			Rectangular pyramid		
		$n = 1$	$n = 6$	$n = 12$	$n = 1$	$n = 6$	$n = 12$
$b = 1.0$	ϕ_A[b]	*a*	*a*	*a*	108.0	109.4	109.5
	ϕ_B				108.0	109.5	109.5
	X				4.7597	0.3753	0.0193
$b = 1.1$	ϕ_A	*a*	*a*	*a*	107.2	107.8	107.4
	ϕ_B				107.2	107.8	107.4
	X				4.8119	0.4083	0.0235
$b = 1.2$	ϕ_A	*a*	*a*	*a*	106.2	105.8	104.9
	ϕ_B				106.2	105.9	104.9
	X				4.8761	0.4546	0.0302
$b = 1.3$	ϕ_A	97.5	99.0	*a*	105.0	103.6	102.0
	ϕ_B	113.4	109.2		105.0	103.6	102.0
	X	4.9549	0.5217		4.9558	0.5219	0.0418
$b = 1.4$	ϕ_A	90.8	90.8	90.9	103.7	101.0	98.8
	ϕ_B	119.3	119.1	117.6	103.7	101.0	98.8
	X	5.0464	0.6119	0.0632	5.0568	0.6252	0.0640
$b = 1.5$	ϕ_A	85.7	85.9	86.1	102.0	98.0	95.3
	ϕ_B	123.6	124.6	127.1	102.0	98.0	95.3
	X	5.1517	0.7292	0.0941	5.1884	0.7988	0.1157

[a] Does not occur as a minimum on the potential energy surface. [b] ϕ values in degrees.

Table II. Structural Parameters for M(bidentate)$_2$(monodentate)[a]

	b	ϕ_A, deg	ϕ_B, deg	Ref
$[As^{III}(S_2CNEt_2)_2(Ph)]$	1.12	93.9	94.4	*b*
$[Zn^{II}(S_2CNMe_2)_2(C_5H_5N)]\cdot 0.5C_6H_6$	1.19	94.9	116.5	*c*
$[Fe(S_2CNMe_2)_2(NO)]$	1.23	105.7	105.9	*d*
$[Fe^{III}(S_2CNEt_2)_2I]$	1.23	101.3	108.8	*e*
$[Fe^{III}(S_2CNEt_2)_2Cl]$	1.24	105.5	105.9	*f*
$[Co(S_2CNMe_2)_2(NO)]$	1.24	102.9	103.6	*g*
$[Cu^{II}(bipy)_2(NH_3)](BF_4)_2$	1.28	92.2	125.9	*h*
$[Cu^{II}(MeCHOHCOO)_2(H_2O)]\cdot 0.5C_6H_6$	1.31	92.7	95.9	*i*
$[Cu^{II}(bipy)_2I]I$	1.31	90.5	123.0	*j*
$Na(Et_4N)[V^{IV}O(Ph_2COCOO)_2]\cdot 2PrOH$	1.31	104.2	113.6	*k*
$[V^{IV}O(MeCOCHCOMe)_2]$	1.38	105.2	107.3	*l, m*
$[V^{IV}O(PhCOCHCOMe)_2]$	1.38	105.0	106.6	*m, n*
$[Zn^{II}(MeCOCHCOMe)_2(H_2O)]$	1.39	98.9	104.9	*o*
$[Zn^{II}(PhCOCHCOMe)_2(EtOH)]$	1.41	97.2	101.5	*p*
$[Cu^{II}(MeCOC_6H_4O)_2(MeC_5H_4N)]$	1.43	94.4	101.1	*q*
$[Cu^{II}(PhN{=}CC_6H_4O)_2(C_5H_5N)]$	1.43	95.3	96.9	*r*

[a] Restricted to compounds which have at least an approximate twofold axis. [b] R. Bally, *Acta Crystallogr.*, **23**, 295 (1967). [c] K. A. Fraser and M. M. Harding, *ibid.*, **22**, 75 (1967). [d] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourne, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970). [e] P. C. Healy, A. H. White, and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1369 (1972). [f] B. F. Hoskins and A. H. White, *J. Chem. Soc. A*, 1668 (1970). [g] J. H. Enemark and R. D. Feltham, *J. Chem. Soc., Dalton Trans.*, 718 (1972). [h] F. S. Stephens, *ibid.*, 1350 (1972). [i] C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust, and F. J. C. Rossotti, *J. Chem. Soc. A*, 2791 (1968). [j] G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 5691 (1963). [k] N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **8**, 408 (1969). [l] R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961). [m] P.-K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, **43**, 3111 (1965). [n] P.-K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, **43**, 1323 (1965). [o] H. Montgomery and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 748 (1963). [p] R. L. Belford, N. D. Chasteen, M. A. Hitchman, P.-K. Hon, C. E. Pfluger, and I. C. Paul, *Inorg. Chem.*, **8**, 1312 (1969). [q] V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 2245 (1969). [r] D. Hall, S. V. Sheat-Rumball, and T. N. Waters, *J. Chem. Soc. A*, 2721 (1968).

shallow minima are very dependent upon the value of *n*. These minima progressively deepen and move further apart as the normalized bite is further increased ($b = 1.5$, Figure 4).

Detailed angular parameters for these minima for *n* values of 1, 6, and 12 and over a larger range of normalized bite are illustrated in Figure 5 and, including the ligand–ligand repulsion coefficients, in Table I. Removal of the restrictions imposed by the assumed C_2 axis showed that each of these minima were true minima. Although the single minimum at small bites corresponding to the rectangular pyramid is replaced by the two minima at large bites due to the irregular trigonal bipyramids, the rectangular pyramid can still be located as the saddle separating these minima. This extension is shown by the broken lines in Figure 5. The curves for different values of *n* cross at $b = 2^{1/2} = 1.414$ and $\phi = 90.0$ and 120.0° corresponding to the *regular* trigonal bipyramid.

Those compounds which have been structurally characterized (Table II) have normalized bites below 1.4 where the potential energy surfaces are at least as flat as those observed for M(monodentate)$_5$.[3] As expected the observed stereochemistry again ranges from trigonal bipyramidal to rectangular pyramidal. The apparent concentration of structures near the rectangular pyramid is partly due to the stabilization of this structure relative to the irregular trigonal bipyramid, but is also at least partly due to the inclusion of vanadyl complexes and copper complexes in Table II. In VO^{2+} complexes the single, short vanadium–oxygen bond stabilizes the pyramidal structure with relatively high values of ϕ_A and ϕ_B. Some of the copper(II) complexes can alternatively be regarded as being square planar with one additional weak bond normal to the plane and have relatively low values of ϕ_A and ϕ_B. The poor agreement between calculated and observed stereochemistry for $[As^{III}(S_2CNEt_2)_2(Ph)]$ can be attributed to the very asymmetric chelate rings (As-S bond lengths of 2.33 and 2.87 Å to each chelate) and/or to the steric effect of the lone pair on the arsenic(III).

Acknowledgments. This work was carried out while on leave at the University Chemical Laboratories, University of Cambridge, and thanks are due to Professor J. Lewis and his colleagues for their hospitality.

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Stereochemistry of Six-Coordinate M(bidentate)$_2$(monodentate)$_2$

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Received October 31, 1972

The relative stability of different isomers and also their detailed stereochemistry resulting from the introduction of bidentate ligands into the coordination sphere can be determined with remarkable accuracy and simplicity by calculating the total ligand–ligand repulsion energy. The previous investigations into five-,[1] six-,[2] and eight-coordinate[3] complexes of the types M(bidentate)$_2$(monodentate), M(bidentate)$_3$, M(bidentate)$_2$(monodentate)$_4$, and M(bidentate)$_4$ is now extended to the six-coordinate M(bidentate)$_2$(monodentate)$_2$.

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(3) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 11, 1556 (1972).