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The Stereochemistry of Eight-Coordination. The Effect of Bidentate Ligands

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The influence of bidentate ligands on the stereochemistry of eight-coordinate compounds is examined by calculation of the ligand–ligand repulsion energies. The potential energy surfaces are critically dependent upon the "bite" of the bidentate ligand, which is defined as the distance between the two donor atoms of the same bidentate divided by the metal atom–donor atom distance. For ligands having small bites, and for complexes of stoichiometries M(monodentate)$_4$(bidentate)$_2$ or M(bidentate)$_4$, the single minimum which is observed in each case corresponds to the dodecahedron of D_{2d} symmetry, which is also that experimentally observed for such molecules. The calculations for M(bidentate)$_4$ also predict a significant distortion of this D_{2d} dodecahedron due to the creation of a dihedral angle between the two bidentates of the same trapezoid, and this is also in agreement with experiment. As the bite of the bidentate ligand is steadily increased, it is predicted that there is a continuous change from this polyhedron approximating to the D_{2d} dodecahedron to that approximating to the D_2 square antiprism. When the bite of the bidentate ligand becomes similar to the distance between donor atoms observed for complexes containing only monodentate ligands, three stereochemistries appear equally probable, namely, the D_2 square antiprism, the D_4 square antiprism, and the D_2 dodecahedron. Within each stereochemistry, the detailed geometry experimentally observed agrees very well with that predicted (to within about 2°).

The ligand–ligand repulsive energies for eight monodentate ligands, first calculated by Hoard and Silverton[1] and later extended by one of us,[2] have since been independently confirmed by Sahl and Zemann,[3] Parish and Perkins,[4] and King.[5] These results show that the potential energy minima corresponding to the square antiprism and the dodecahedron are very similar and that these stereochemistries are relatively easy to distort. These conclusions are not affected by the fairly arbitrary choice of the assumed repulsive law between the donor atoms.

Extension of these calculations[6] shows, contrary to earlier assumptions,[7,8] that there is no potential energy barrier between dodecahedral and square antiprismatic stereochemistries, so that in the absence of other stereochemically directing forces there may be a continuous movement of ligands about the metal atom creating a fluxional structure.

Experimental data for eight equivalent monodentate ligands is restricted to the octacyano complexes. There is considerably more structural information on eight-coordinate compounds containing bidentate ligands, as incorporation of two donor atoms in the same rigid chelate removes the repulsive term between these atoms allowing the easier attainment of higher coordination numbers.

In this paper, we extend our previous work[6] to compounds of the type M(bidentate)$_4$, which are the most common and which have been studied in some detail, and to compounds of the type M(monodentate)$_4$(bidentate)$_2$ in which we are particularly interested.[9,10]

The calculations are carried out as a function of the bidentate "bite" b, which is defined as the distance between the donor atoms relative to the metal–donor atom distance. This varies from 0.77 for $K_3[Cr(O_2)_4]$[11] to approximately 1.2 corresponding to the distance between donor atoms in M(monodentate)$_8$.[2]

M(monodentate)$_4$(bidentate)$_2$

Method.—It is assumed that the repulsive energy between any two donor atoms i and j is proportional to some inverse power of the distance between them, $u_{ij} \propto d_{ij}^{-n}$. Summing over all such ligand–ligand interactions, where the ligand–ligand distances are expressed in terms of the metal–ligand distance r, yields

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

where X is dependent upon the geometry of the complex.

The dodecahedron and square antiprism are both particular examples of the more general stereochemistry shown in Figure 1. The points on the surface of the sphere are divided into two sets of four as defined by Figure 1. The four points marked A are defined by two independent variables, their "longitude" ϕ_A and "latitude" ψ_A, and the four points marked B are similarly defined by their "longitude" ϕ_B and "latitude" ψ_B. (It should be noted that alternative angular parameters are also commonly used, namely $\theta_A = 90 - \psi_A$ and $\theta_B = 90 - \psi_B$, where θ_A and θ_B are the angles made by the metal–ligand bond to the twofold axis of Figure 1.)

The calculations were carried out as before,[6] starting with the D_{2d} dodecahedron at $\phi_A = \phi_B = 45°$. The two bidentates of bite b span the two A–A edges which are omitted when summing all other ligand–ligand repulsive energies. The variable ψ_A in the previous expressions[6] for ligand–ligand distances is then replaced by $\cos^{-1} b/2$. As ϕ_A is now decreased (or increased), the stereochemistry will change first to a D_2 square antiprism with the bidentates spanning triangular edges of the polyhedron, then to a dodecahedron with the bidentates spanning B–B edges, and finally to a square antiprism with the bidentates spanning the diagonals of the square faces.

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(1) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(2) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

(3) K. Sahl and J. Zemann, *Tschermaks Mineral. Petrogr. Mitt.*, **10**, 7 (1965).

(4) R. V. Parish and P. G. Perkins, *J. Chem. Soc. A*, 345 (1967).

(5) R. B. King, *J. Amer. Chem. Soc.*, **92**, 6455 (1970).

(6) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968).

(7) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967); R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

(8) J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 3177 (1968).

(9) W. P. Crisp, R. L. Deutscher, and D. L. Kepert, *J. Chem. Soc. A*, 2199 (1970), and references therein.

(10) R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, **9**, 2305 (1970), and references therein.

(11) R. Stomberg, *Acta Chem. Scand.*, **17**, 1563 (1963).

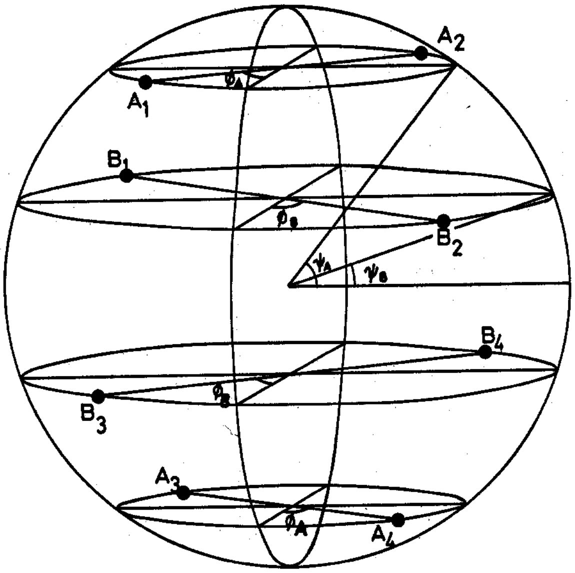

Figure 1.—Generalized eight coordinate stereochemistry. The "A" points have "longitude" ϕ_A and "latitude" ψ_A.

These potential energy valleys were calculated as before.[6] Numerical values for the variables ϕ_A and b were chosen, and ψ_A and ψ_B were allowed to vary freely for each calculation to provide a minimum in the potential energy, with the additional condition that $\psi_A \geqslant \psi_B$.

Results and Discussion.—The ligand–ligand repulsion energy coefficients, X, along the valleys in the five-dimensional potential energy surfaces are shown in Figure 2, together with the results reported earlier[6] for M(monodentate)$_8$ (broken lines). Only two polyhedra can be observed on the potential energy surfaces, the D_{2d} dodecahedron and the D_2 square antiprism. The angular parameters and potential energy coefficients of these stereochemistries are collected in Tables I and II.

For ligands with small bite, b = 0.80, the only minimum on the potential energy surface corresponds to the D_{2d} dodecahedron. This stereochemistry has been observed for $TiCl_4[\textit{o}\text{-}C_6H_4\{As(CH_3)_2\}_2]_2$ for which the angular parameters are in excellent agreement with those predicted ($b = 1.19$, $\psi_A = 53.6°$, $\psi_B = 17.5°$).[12] It may also be noted that the solution spectra due to the d–d transitions in the isomorphous d^1 $NbCl_4[\textit{o}\text{-}C_6H_4\{As(CH_3)_2\}_2]_2$ are very similar to that in the solid state,[10] which is strong evidence that this molecule does not show fluxional behavior in solution. (The value of b would be less than 1.19 because of the larger size of niobium(IV) compared with titanium(IV).)

For bidentate ligands having large bites, b = 1.20, the D_2 square antiprism occurs as a minimum on the potential energy surface. However, the difference in energy between the two stereochemistries is small, being less than that between the dodecahedron and square antiprism for the case of M(monodentate)$_8$.

The only other molecule which is at all similar in stoichiometry and in possessing a twofold axis is $Zr(SO_4)_2 \cdot 4H_2O$.[13] The four B positions are occupied by

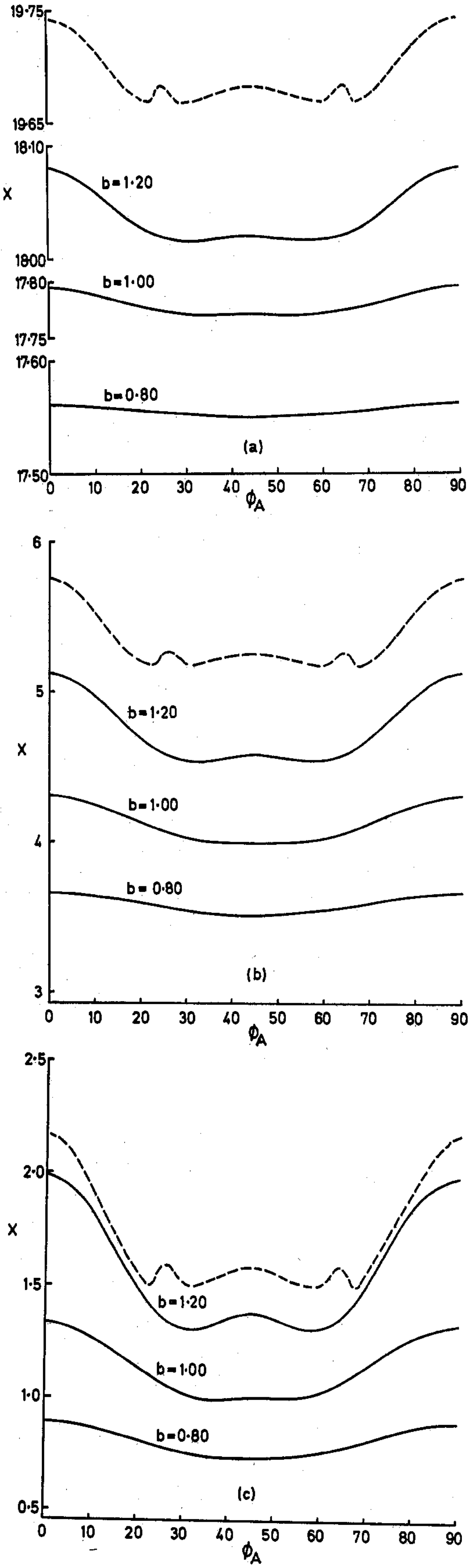

Figure 2.—Ligand–ligand repulsion coefficients for M(monodentate)$_4$(bidentate)$_2$ (solid lines) and M(monodentate)$_8$ (broken lines):[6] (a) $n = 1$, (b) $n = 6$, (c) $n = 12$.

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(12) R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature (London)*, **192**, 222 (1961); R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2460 (1962); P. Pauling and G. B. Robertson, University College, London, personal communication, 1965.

(13) J. Singer and D. T. Cromer, *Acta Crystallogr.*, **12**, 719 (1959).

TABLE I

ANGULAR PARAMETERS AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(MONODENTATE)$_4$(BIDENTATE)$_2$ OF D_{2d} DODECAHEDRAL STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 0.80$	ϕ_A	45.0	45.0	45.0
	ψ_A	66.4	66.4	66.4
	ϕ_B	45.0	45.0	45.0
	ψ_B	7.3	9.3	10.3
	X	17.551	3.500	0.723
$b = 1.00$	ϕ_A	45.0	45.0	45.0
	ψ_A	60.0	60.0	60.0
	ϕ_B	45.0	45.0	45.0
	ψ_B	11.5	13.4	14.3
	X	17.768	3.992	0.994
$b = 1.20$	ϕ_A	45.0	45.0	45.0
	ψ_A	53.1	53.1	53.1
	ϕ_B	45.0	45.0	45.0
	ψ_B	16.8	18.3	19.1
	X	18.017	4.577	1.368

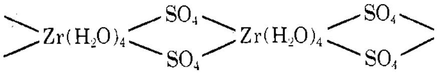
TABLE II

ANGULAR PARAMETERS AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(MONODENTATE)$_4$(BIDENTATE)$_2$ OF D_2 SQUARE ANTIPRISMATIC STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 1.00$	ϕ_A	[a]	[a]	38.0
	ψ_A			60.0
	ϕ_B			49.8
	ψ_B			14.0
	X			0.989
$b = 1.20$	ϕ_A	32.4	32.1	32.5
	ψ_A	53.1	53.1	53.1
	ϕ_B	51.1	53.5	54.8
	ψ_B	16.0	17.3	18.0
	X	18.014	4.535	1.294

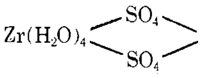
[a] No minimum for $\psi_A \geqslant \psi_B$.

water molecules, and each of the four A positions by an oxygen atom from a sulfate group which bridges two zirconium atoms to form infinite strings of the type



$$>Zr(H_2O)_4<^{SO_4}_{SO_4}>Zr(H_2O)_4<^{SO_4}_{SO_4}>$$

The bite of the



$$Zr(H_2O)_4<^{SO_4}_{SO_4}>$$

bidentate is 1.22, and the stereochemistry about the zirconium atom is that of the D_2 square antiprism.

M(bidentate)$_4$

For a compound of stoichiometry M(bidentate)$_4$, there are three different isomers of square antiprismatic stereochemistry and six different isomers of dodecahedral stereochemistry, depending upon the choice of polyhedral edges spanned by the bidentates.[1,7,14] However, if the condition that all four bidentates span equivalent polyhedral edges is applied, then there remain only the square antiprims of D_2 and D_4 symmetry and the dodecahedra of D_{2d}, D_2, and S_4 symmetry (Figure 3). The S_4 dodecahedron is merely the mesomeric form of the D_2 dodecahedron and will be energetically equivalent to it provided $\phi_A = \phi_B = 45°$. If this equality does not apply (see below), the S_4 dodecahedron will be less stable than the D_2 dodecahedron as again the ligands will not be spanning polyhedral edges of equal length.

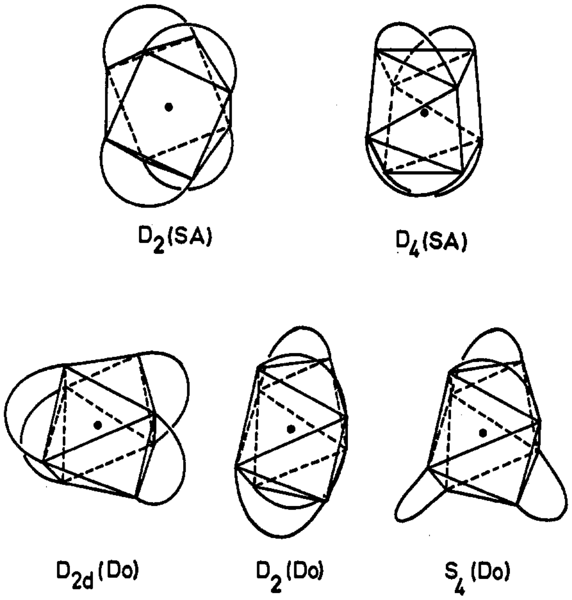


Figure 3.—Isomers for M(bidentate)$_4$.

Method.—Potential energy surfaces incorporating the D_2 square antiprism, the D_4 square antiprism, the D_{2d} dodecahedron, and the D_2 dodecahedron are required. It was found convenient to use two independent but overlapping sets of calculations, both of which were based on that previously used for M(monodentate)$_8$.

In the first case the bidentates were arranged around the central metal atom so that the dodecahedron at $\phi_A = \phi_B = 45°$ was of D_{2d} symmetry, with the chelates spanning the A_1B_3, A_2B_4, A_3B_1, and A_4B_2 edges. The repulsion within each of these pairs is then omitted in the calculation of the total ligand–ligand repulsion energy. One of the four angular variables used in the previous expressions[6] for ligand–ligand distances can now be defined in terms of the other three, plus the bite b. Thus

$$\phi_B = \gamma + \phi_A$$

where γ is defined by

$$\cos \gamma = \frac{2 - b^2 + 2 \sin \psi_A \sin \psi_B}{2 \cos \psi_A \cos \psi_B}$$

By analogy with the case of M(monodentate)$_8$, decreasing ϕ_A from 45° is expected to develop a potential energy valley leading in turn to the D_2 square antiprism, the D_2 dodecahedron, and the D_4 square antiprism.

In the second set of calculations the dodecahedron at $\phi_A = \phi_B = 45°$ was of D_2 symmetry, with the bidentates spanning the A_1B_2, A_2B_1, A_3B_4, and A_4B_3 edges. The ligand–ligand repulsion along these edges is then omitted.

The variable ϕ_B is now defined by

$$\phi_B = \gamma' - \phi_A$$

where

$$\cos \gamma' = \frac{2 - b^2 - 2 \sin \psi_A \sin \psi_B}{2 \cos \psi_A \cos \psi_B}$$

The expected stereochemical changes on decreasing ϕ_A from 45° will now be D_2(dodec) → D_2(sa) → D_{2d}(dodec)

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(14) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

TABLE III

ENERGY COEFFICIENTS X FOR COMPOUNDS OF STOICHIOMETRY M(BIDENTATE)$_4$

		$b = 0.70$	$b = 0.80$	$b = 0.90$	$b = 1.00$	$b = 1.10$	$b = 1.15$	$b = 1.20$	$b = 1.25$	$b = 1.30$
$n = 1$	D_{2d}(dodec)	15.250	15.413	15.597	15.807	16.057	...	...	...	...
	D_2(sa)	...	...	...	...		16.199	16.344	...	...
	D_2(dodec)[a]	...	...	...	...	...	...	(16.349)	(16.484)	...
	D_4(sa)	...	...	...	...	...	...	...	16.478	16.599
$n = 6$	D_{2d}(dodec)	1.888	2.092	2.344	2.688	3.183	...	...	...	...
	D_2(sa)	...	...	...	...		3.498	3.849	...	...
	D_2(dodec)[a]	...	...	...	...	...	...	(3.920)	(4.220)	...
	D_4(sa)	...	...	...	...	...	...	3.905	4.138	4.375
$n = 12$	D_{2d}(dodec)	0.194	0.246	0.322	0.453	0.683	...	...	...	...
	D_2(sa)	...	...	...	...		0.848	1.055	1.310	...
	D_2(dodec)[a]	...	...	...	...	...	...	(1.150)	(1.351)	...
	D_4(sa)	...	...	...	...	...	...	1.093	1.229	1.375

[a] The figures enclosed in parentheses indicate that the D_2 dodecahedron does not occur as a minimum on the potential energy surface, but as a slight saddle between the D_2 square antiprism and the D_4 square antiprism. This energy difference is relatively small (equal to or less than that found in the corresponding M(monodentate)$_8$) for $b = 1.20$ and 1.25 but is much larger for $b = 1.10$, 1.15, and 1.30 (see Table VIII).

TABLE IV

ANGULAR PARAMETERS[a] AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(BIDENTATE)$_4$ OF D_{2d} DODECAHEDRAL STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 0.70$	ϕ_A	43.0	43.5	43.6
	ψ_A	49.0	46.9	45.7
	ϕ_B	45.9	45.8	45.7
	ψ_B	−8.1	−5.9	−4.7
	X	15.250	1.888	0.194
	α^b	7.2	6.1	5.3
$b = 0.80$	ϕ_A	43.0	43.1	43.2
	ψ_A	49.7	47.6	46.7
	ϕ_B	45.7	45.7	45.7
	ψ_B	−2.6	−0.5	0.4
	X	15.413	2.092	0.246
	α^b	5.6	5.4	5.3
$b = 0.90$	ϕ_A	44.0	44.1	44.1
	ψ_A	50.0	48.5	47.9
	ϕ_B	45.3	45.4	45.4
	ψ_B	3.5	5.0	5.6
	X	15.597	2.344	0.322
	α^b	2.3	2.4	2.4
$b = 1.00$	ϕ_A	42.1	42.2	42.9
	ψ_A	50.4	49.8	49.5
	ϕ_B	46.1	46.2	46.8
	ψ_B	9.5	10.1	10.4
	X	15.807	2.688	0.453
	α^b	6.3	6.4	6.6

[a] Angular parameters from the first set of calculations. [b] α is the dihedral angle between the two M–A–B planes within the same trapezoid of the dodecahedron.

→ D_2(sa), and on increasing ϕ_A from 45° will be D_2(dodec) → D_4(sa) → D_2(dodec) → D_2(sa).

These potential energy valleys were calculated as before. As can be seen from the above transformations, each stereochemistry was generated at least twice, which provided a valuable check on the numerical values obtained and was also of considerable assistance in assigning stereochemistries to the minima generated. For ligands having small bites, where the main interest is in the D_{2d} dodecahedron near $\phi_A = 45°$, it is more convenient to quote the results obtained from the first set of calculations but in other cases to quote the results obtained from the more widely applicable second set of calculations.

Results and Discussion.—In spite of, or more correctly because of, the increased number of isomers possible for M(bidentate)$_4$ compared with M(monodentate)$_8$, the results are more simple in the former case, as not all of the idealized stereochemistries occur as minima, or even as saddles, on the five-dimensional potential energy surfaces.

TABLE V

STRUCTURAL PARAMETERS FOR M(BIDENTATE)$_4$ OF D_{2d} DODECAHEDRAL STEREOCHEMISTRY

	b	ψ_A	ψ_B	M–A/ M–B[a]	α^b	Ref
$K_3[Cr(O_2)_4]$	0.77	43.3	0.5	0.95	...	*c*
$[Fe(C_8H_6N_2)_4](ClO_4)_2$	0.96	...	...	1.13	...	*d*
$[Sn(NO_3)_4]$	0.99	38.9	8.3	1.01	5	*e*
$[Ti(NO_3)_4]$	1.03	37.2	9.2	1.01	6	*f*
$Na_4[Zr(C_2O_4)_4]\cdot 3H_2O$	1.17	35.2	16.5	1.03	10	*g*

[a] M–A/M–B is the ratio of the bond lengths between the metal atom and the donor atoms at the A and B sites, respectively. [b] α is the dihedral angle between the two M–A–B planes within the same trapezoid of the dodecahedron. [c] Reference 11. [d] A. Clearfield, P. Singh, and I. Bernal, *Chem. Commun.*, 389 (1970). [e] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc. A*, 1949 (1967). [f] C. D. Garner and S. C. Wallwork, *ibid.*, 1496 (1966). [g] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

The minima which do appear are dependent upon the bidentate bite b. The energy coefficients X of all minima which are observed, and the corresponding stereochemistries, are summarized in Table III.

For bidentate ligands having a small bite, $b = 0.70$–1.00, the single minimum which appears on each potential energy surface corresponds to the D_{2d} dodecahedron. The energy coefficients and angular parameters of these minima are given in Table IV.

This prediction that bidentates with small bites (in particular, peroxide, 1,8-naphthyridine, and nitrate) can only have this D_{2d} dodecahedral stereochemistry is confirmed by those structures which have been determined (Table V). Moreover there is satisfactory agreement (±∼2°) between the observed and calculated angular parameters ψ_A and ψ_B, both in their absolute magnitudes and in their variations with b.

Closer examination of the results from these calculations reveals an additional but less obvious prediction. Table IV shows that the potential energy minima do not occur at $\phi_A = \phi_B = 45°$ but that $\phi_A = 42$–$44°$ and $\phi_B = 45$–$46°$. That is, each of the bidentates is twisted around an axis passing through the bidentate and the central metal atom. The undistorted D_{2d} dodecahedron at $\phi_A = \phi_B = 45°$ may be considered to consist of two interlocking planar trapezoids, BAAB, each formed from two bidentates, but this twist distortion creates a dihedral angle α between the two bidentates of any one trapezoid. These dihedral angles, which are about 5°, are given in Table IV. (These potential energy minima are very flat for dihedral angles in the range 2–7° compared with a steep rise between 2 and 0°, and there are indications of two overlapping minima with dihedral angles of about 3 and about 6°.)

It is very noteworthy that just such a twist distortion is observed for the three molecules whose structures have been determined with precision (Table V).

As the bite of the bidentate ligand is increased to 1.10, a single very broad minimum appears on the potential energy surface which encompasses both the D_{2d} dodecahedron and the distorted D_2 square antiprism, corresponding to dihedral angles of about 5° and about 18°, respectively (Table VI). On increasing b to 1.15, the potential energy minimum corresponds more closely to the D_2 square antiprism (Table VI). That is, as the bite of the bidentate increases, there is a smooth and continuous change from the D_{2d} dodecahedron to the D_2 square antiprism. This intermediate structure has been discussed by Lippard and Russ[15] and appears to occur in the trisacetylacetonato diaquo complexes of yttrium,[15,16] lanthanum,[17] and europium.[18]

TABLE VI

ANGULAR PARAMETERS[a] AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(BIDENTATE)$_4$ OF INTERMEDIATE STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 1.10$	ϕ_A	38–43	37–42	37.4
	ψ_A	50.9–51.2	51.0–51.4	50.9
	ϕ_B	48.5–45.4	49.7–46.8	50.6
	ψ_B	15.2–15.6	14.8–15.2	14.8
	X	16.057–16.058	3.183–3.185	0.683
	α	14.8–3.2	18.3–6.9	19.6
$b = 1.15$	ϕ_A	31.9	33.9	34.4
	ψ_A	50.3	51.2	51.2
	ϕ_B	52.2	52.5	53.7
	ψ_B	17.6	17.1	16.9
	X	16.199	3.498	0.848
	α	(27.6)	(25.8)	(27.3)
	β[b]	57.2, 54.3	58.7, 54.4	58.9, 55.5

[a] Angular parameters from the first set of calculations. [b] β is the angle the eight metal–ligand bonds make with the eightfold inversion axis of the square antiprism.

As the bite of the bidentate is further increased to 1.20 and 1.25, the floor of the valley in the potential energy surface remains fairly flat and similar to that calculated for M(monodentate)$_8$.[6] Separate minima occur for the D_2 square antiprism and the D_4 square antiprism, the energies of which are given in Table III. The D_2 dodecahedron occurs as a saddle between these two antiprisms of only slightly higher energy. The position of this saddle occurs close to, but not exactly at, $\phi_A = 45°$, which means that this stereochemistry is more stable than the S_4 dodecahedron (see above). The values quoted in Table III are those for which $\phi_A = 45°$.

The closely similar energies of these three stereochemistries make it impossible to predict which one is preferred in any one situation, as other energy terms such as crystal field stabilization, covalent σ bonding, π bonding, and crystal packing or solvation forces will become important. Molecules have been observed with D_2 square antiprismatic and D_2 dodecahedral structures. This situation is similar to the octacyanides, where $K_4[Mo^{IV}(CN)_8]\cdot 2H_2O$[8] and $(n\text{-}Bu_4N)_3[Mo(^{V}CN)_8]$[19] have dodecahedral structures, whereas $Na_3[W(CN)_8]$[20] has a square antiprismatic structure. Similarly it can again be postulated that the easy conversion of one stereochemistry into another may lead to stereochemical nonrigidity or fluxional behavior in solution,[6] depending upon the span of the bidentate relative to the radius of the metal atom.

TABLE VII

ANGULAR PARAMETERS[a] AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(BIDENTATE)$_4$ OF D_2 SQUARE ANTIPRISMATIC STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 1.20$	ϕ_A	33.6	32.0	31.6
	ψ_A	51.1	51.3	51.6
	ϕ_B	51.8	54.6	55.9
	ψ_B	17.4	18.3	18.9
	X	16.344	3.849	1.055
	β	58.5, 53.8	58.0, 56.6	58.1, 58.0
$b = 1.25$	ϕ_A	[b]	[b]	36.8
	ψ_A			52.9
	ϕ_B			54.6
	ψ_B			17.2
	X			1.310
	β			61.1, 56.4

[a] Angular parameters from the second set of calculations. [b] No minimum observed.

TABLE VIII

ANGULAR PARAMETERS[a] AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(BIDENTATE)$_4$ OF D_2 DODECAHEDRAL STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 1.10$	ϕ_A	45.0	45.0	45.0
	ψ_A	44.3	49.1	50.7
	ϕ_B	39.7	37.9	37.0
	ψ_B	28.9	25.2	24.0
	X	16.119	3.458	0.860
$b = 1.15$	ϕ_A	45.0	45.0	45.0
	ψ_A	47.8	50.8	51.8
	ϕ_B	41.8	40.6	40.3
	ψ_B	24.3	22.3	21.8
	X	16.233	3.672	0.989
$b = 1.20$	ϕ_A	45.0	45.0	45.0
	ψ_A	50.3	52.2	52.7
	ϕ_B	43.9	43.6	43.9
	ψ_B	20.4	19.7	19.8
	X	16.349	3.920	1.150
$b = 1.25$	ϕ_A	45.0	45.0	45.0
	ψ_A	52.4	53.3	53.5
	ϕ_B	45.7	46.8	47.7
	ψ_B	16.6	17.2	17.8
	X	16.484	4.220	1.351
$b = 1.30$	ϕ_A	45.0	45.0	45.0
	ψ_A	54.2	54.2	54.1
	ϕ_B	47.5	50.0	51.7
	ψ_B	12.8	14.6	15.8
	X	16.631	4.602	1.612

[a] Angular parameters from the second set of calculations.

The angular parameters corresponding to these D_2 square antiprisms are given in Table VII. It is more convenient to specify the shape of a square antiprism by the single variable β, the angle the eight metal–lig-

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(15) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

(16) J. A. Cunningham, D. E. Sands, and W. F. Wagner, *ibid.*, **6**, 499 (1967).

(17) T. Phillips, D. E. Sands, and W. F. Wagner, *ibid.*, **7**, 2295 (1968).

(18) A. L. Il'inskii, L. A. Aslanov, V. I. Ivanov, A. D. Khalilov, and O. M. Petrukhin, *Zh. Strukt. Khim.*, **10**, 285 (1969); *J. Struct. Chem.*, **10**, 263 (1969).

(19) B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970).

(20) L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Acta Crystallogr., Sect. B*, **26**, 684 (1970).

TABLE IX

STRUCTURAL PARAMETERS FOR M(BIDENTATE)$_4$ OF D_2 DODECAHEDRAL STEREOCHEMISTRY

	b	ψ_A	ψ_B	Ref
$Th(S_2CNEt_2)_4$	1.04	46	24	*c*
$(NH_4)[Pr(TTA)_4]H_2O$[a]	1.16	48.6	24.3	*d*
$Cs[Y(HFA)_4]$[b]	1.19	51.4	21.5	*e*

[a] TTA^- is the thenoyltrifluoroacetate ion. [b] HFA^- is the hexafluoroacetylacetonate ion. [c] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc. A*, 423 (1970). [d] R. A. Lalancetto, M. Cefola, W. C. Hamilton, and S. J. La Placa, *Inorg. Chem.*, **6**, 2127 (1967). [e] M. J. Bennett, F. A. Cotton, P. Legzdins, and S. J. Lippard, *ibid.*, **7**, 1770 (1968).

and bonds make with the major eightfold inversion axis, and this is shown in Tables VI and VII. This angle β to the A atoms is not the same as to the B atoms owing to the slight creasing of each of the square faces across a diagonal. This again emphasizes the close relationship and continuous change between real dodecahedra and real square antiprisms, as distinct from the geometrically idealized ones.

It is again found that the predicted value of β of about 57° is close to that experimentally observed in the known molecules with this stereochemistry. These are the tetrakisacetylacetonates of thorium[21] ($b = 1.04$, $\beta = 58.2°$), cerium[22] ($b = 1.17$, $\beta = 58.5°$), and zirconium[23] ($b = 1.22$, $\beta = 57.3°$).

The angular parameters corresponding to the D_2 dodecahedron are given in Table VIII. The agreement between these calculated parameters and those experimentally observed is again within about 2° (Table IX).

TABLE X

ANGULAR PARAMETERS[a] AND LIGAND–LIGAND REPULSION COEFFICIENTS FOR M(BIDENTATE)$_4$ OF D_4 SQUARE ANTIPRISMATIC STEREOCHEMISTRY

		$n = 1$	$n = 6$	$n = 12$
$b = 1.20$	ϕ_A	*b*	55.3	56.0
	ψ_A		49.8	50.8
	ϕ_B		34.8	33.7
	ψ_B		21.6	20.9
	X		3.905	1.093
$b = 1.25$	ϕ_A	57.7	58.5	59.0
	ψ_A	49.0	50.7	51.6
	ϕ_B	20.5	19.3	18.7
	ψ_B	36.5	35.0	34.2
	X	16.478	4.138	1.229
$b = 1.30$	ϕ_A	61.4	62.0	62.4
	ψ_A	50.2	51.5	52.2
	ϕ_B	36.2	35.1	34.5
	ψ_B	17.8	17.0	16.5
	X	16.599	4.375	1.375

[a] Angular parameters from the second set of calculations. [b] No minimum observed.

Finally as the bite of the bidentate is increased to 1.30, the potential energy surface reverts to having only a single minimum (Table III), which in this case corresponds to the D_4 square antiprism. Angular parameters for this stereochemistry are collected in Table X. Bidentates having this large bite, which would force the donor atoms further apart than in M(monodentate)$_8$, are not expected to form discrete M(bidentate)$_4$ complexes with ordinary ligands, as the ligand–ligand repulsion would be lowered if the bidentates bridged different metal atoms forming a polymeric structure. Thus no molecules having this stereochemistry have been experimentally observed.

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(21) D. Grdenic and B. Matkovic, *Nature (London)*, **182**, 465 (1958).

(22) B. Matkovic and D. Grdenic, *Acta Crystallogr.*, **16**, 456 (1963); H. Titze, *Acta Chem. Scand.*, **23**, 399 (1969).

(23) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

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Stereochemistry of Tris(bidentate) Complexes

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Summation of ligand–ligand repulsion energies for complexes of the type $[M(bidentate)_3]^{z+}$ shows that there is expected to be a continuous change from regular octahedral stereochemistry to trigonal prismatic stereochemistry as the "bite" of the bidentate ligand is progressively decreased. This prediction is followed very closely for those compounds whose structures are accurately known (with the exception of the maleonitriledithiolates).

In previous papers[1–3] we have gained new insight into the stereochemistry of complexes of the types $[M(monodentate)_8]^{x\pm}$, $[M(monodentate)_4(bidentate)_2]^{x\pm}$, and $[M(bidentate)_4]^{x\pm}$, by calculation of the sum of the ligand–ligand repulsion energies as a function of geometry.

We now extend this work to the much simpler case of $[M(bidentate)_3]^{x\pm}$, which is nevertheless particularly interesting because of the occurrence of octahedral, trigonal prismatic, and intermediate stereochemistries.

Method

Figure 1 defines the general stereochemistry for M(bidentate)$_3$, viewed down the threefold axis. The bidentate ligands span the AD, BE, and CF edges. The angle of twist between the upper and lower triangular faces defines whether the polyhedron is a regular octahedron ($\theta = 30°$), a trigonal prism ($\theta = 0°$), or an intermediate geometry.

If the metal–donor atom distance is defined as unity and the distance between the two donor atoms of the same chelate is defined as the "bite" of the ligand b, the distances between the other donor atoms are given by

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(1) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

(2) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968).

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