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).

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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).

$$AB = BC = CA = DE = EF = FD = (3 - {}^3/_4b^2)^{1/2}/\cos\theta$$

$$AE = BF = CD = [4\cos^2\theta - (4 - b^2)\cos^2(60 - \theta)]^{1/2}/\cos\theta$$

$$AF = BD = CE = [4\cos^2\theta - (4 - b^2)\cos^2(60 + \theta)]^{1/2}/\cos\theta$$

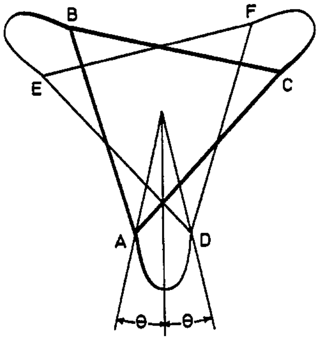

Figure 1.—General stereochemistry for M(bidentate)$_3$.

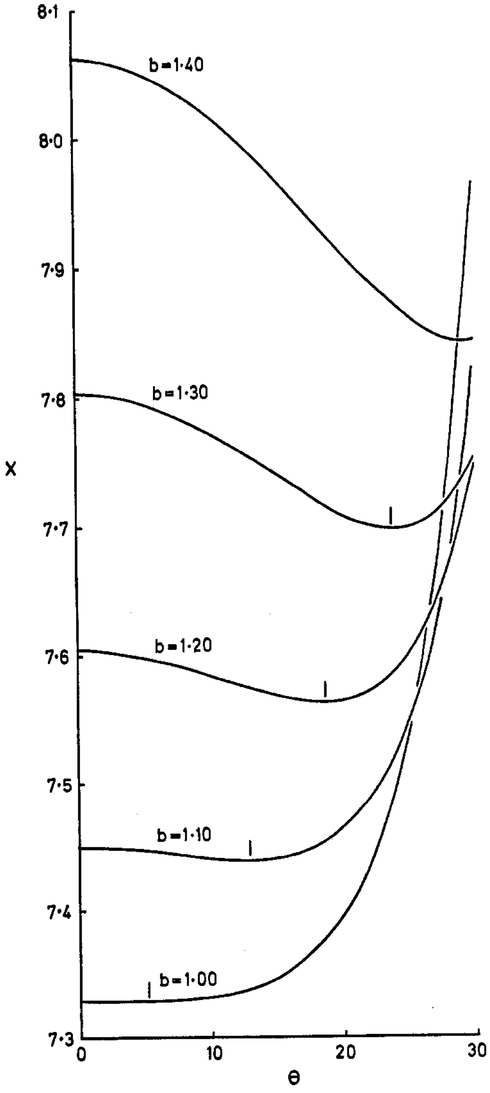

Figure 2.—Ligand–ligand repulsion coefficients for M(bidentate)$_3$ (n = 1).

TABLE I

STRUCTURAL PARAMETERS FOR M(BIDENTATE)$_3$[a]

	b	*θ*	Ref
Mn(acac)$_3$	1.50	33.8	*b*
Cr(acac)$_3$	1.43	30.8	*c*
Fe(acac)$_3$	1.38	26.8	*d*
$(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$	1.44	30.3	*e*
$[Cu(OMPP)_3](ClO_4)_2$	1.39	29.0	*f*
$[Co(OMPP)_3](ClO_4)_2$	1.39	28.8	*f*
$[Mg(OMPP)_3](ClO_4)_2$	1.37	27.7	*f*
$[Co(en)_3]Br_3\cdot H_2O$	1.39	28.5	*g*
$[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$	1.32	25.5	*h*
	1.31	25.8	*h*
$[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$	1.31	25.2	*i*
$[Ni(en)_3](SO_4)$	1.31	25.2	*j*
$[Cu(en)_3](SO_4)$	1.30	24.5	*k*
$Co(S_2CNEt_2)_3$	1.23	21.8	*l*
$Co(S_2COEt)_3$	1.23	21.6	*m*
$Fe(S_2COEt)_3$	1.22	20.5	*n*
$Fe(S_2CNMePh)_3$	1.22	20.2	*o*
$Fe(S_2CN(CH_2)_4)_3$	1.21	19.3	*o*
$Fe(S_2CNBu_2)_3$	1.19	16.8	*p*
$Fe(O_2N_2Ph)_3$	1.22	16.1	*q*
$V(S_2P(OEt)_2)_3$	1.31	20.7	*r*
$(Me_4N)_2[V(S_2C_2(CN)_2)_3]$	1.33	17.0	*s*
$Mo(S_2C_2H_2)_3$	1.33	0	*t*
$V(S_2C_2Ph_2)_3$	1.31	0	*u*
$Re(S_2C_2Ph_2)_3$	1.30	0	*v*

[a] Ligand abbreviations: acac, acetylacetonate; OMPP, octamethylpyrophosphoramide; en, ethylenediamine. [b] B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17,** 705 (1964). [c] B. Morosin, *ibid.*, **19,** 131 (1965). [d] J. Iball and C. H. Morgan, *ibid.*, **23,** 239 (1967). [e] P. E. Jones and L. Katz, *Acta Crystallogr., Sect. B*, **25,** 745 (1969). [f] M. D. Joesten, M. S. Hussain, and P. G. Lenhert, *Inorg. Chem.*, **9,** 151 (1970). [g] K. Nakatsu, *Bull. Chem. Soc. Jap.*, **35,** 832 (1962). [h] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.* **7,** 1362 (1968). [i] K. N. Raymond and J. A. Ibers, *ibid.*, **7,** 2333 (1968). [j] Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *ibid.*, **9,** 2421 (1970). [k] D. L. Cullen and E. C. Lingafetter, *ibid.*, **9,** 1858 (1970). [l] S. Merlino, *Acta Crystallogr., Sect. B*, **24,** 1441 (1968); T. Brennan and I. Bernal, *J. Phys. Chem.*, **73,** 443 (1969). [m] S. Merlino, *Acta Crystallogr., Sect. B*, **25,** 2270 (1969). [n] B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970). [o] P. C. Healy and A. H. White, private communication, University of Western Australia, 1971. [p] B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968). [q] D. Van der Helm, L. L. Merritt, and R. Degeilh, *Acta Crystallogr.*, **18,** 355 (1965). [r] C. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc. A*, 2929 (1970). [s] E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, **89,** 3353 (1967). [t] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87,** 5798 (1965). [u] R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6,** 1844 (1967). [v] R. Eisenberg and J. A. Ibers, *ibid.*, **5,** 411 (1966).

The repulsion between each pair of donor atoms is again assumed to be inversely proportional to the nth power of the distance between them. The total repulsion energy U is the sum over all donor atoms and is expressed in the form $U = Xr^{-n}$, where X is dependent upon the geometry of the complex. It is assumed that the interaction between the two ends of each coordinated bidentate is constant and can therefore be neglected.

Results and Discussion

The repulsion energy coefficient X has been calculated as a function of θ for each value of the bidentate bite b. A selection of these results is shown in Figure 2, for the particular case of n = 1.

For bidentate bites of $b = 2^{1/2} = 1.414$, the minimum energy corresponding to the most stable stereochemistry occurs for the regular octahedron at θ = 30°. The energy difference between this minimum and the

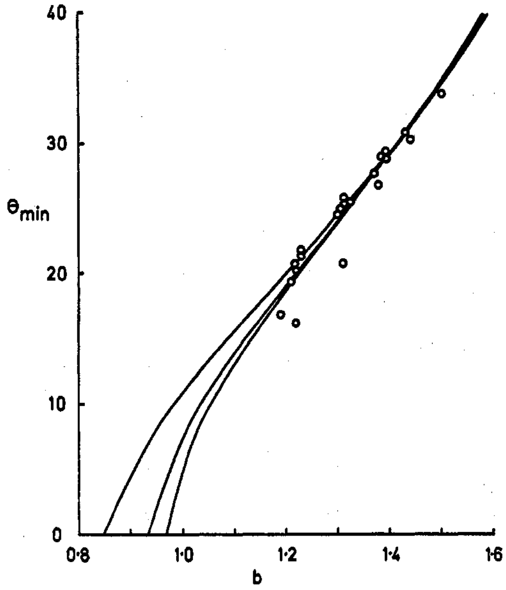

Figure 3.—Values of θ_{min} for the most favorable polyhedron as a function of bidentate bite b. The points shown correspond to the compounds in Table I: bottom curve, $n = 1$; middle curve, $n = 2$; top curve, $n = 6$.

maximum at $\theta = 0°$ is the activation energy for racemization of these optically active compounds by a twist mechanism.

As the bite of the bidentate ligands is decreased to 1.3 and 1.2, the upper triangular face is brought into a more eclipsed configuration relative to the lower triangular face, and the minimum energy moves to lower values of θ (Figure 2).

The location of this minimum, θ_{min}, is plotted as a function of bidentate bite in Figure 3. Also shown are the minimum values assuming $n = 2$ and 6, again confirming that the locations of these minima are not critically dependent upon the assumed repulsive law. The three theoretical curves cross at $b = 1.414$ and $\theta = 30°$.

Figure 3 also shows the experimental values for all molecules whose crystal structures have been described with sufficient detail to enable θ to be calculated (Table I). (The parameter θ used in this work has not usually been quoted in the reports of these structures. The values in Table I have been calculated from the ligand–metal–ligand angles in those cases where all 12 such angles have been quoted, or directly from the atom coordinates.)

The agreement between theory and experiment shown in Figure 3 is very good, in most cases being better than to ±1°. This clearly demonstrates that regular octahedral stereochemistry is not generally expected for tris(chelate) complexes and that the stereochemistry depends mainly upon the bite of the bidentate. This conclusion is of some importance to many of the studies on complexes of this type.

The only compounds which do not adapt the stereochemistries defined by Figure 3 are maleonitriledithiolates, $[M(S_2C_2R_2)_3]^{z\pm}$ (Table I). In contrast, the structures intermediate between a regular octahedron and a trigonal prism observed for the xanthate and dithiocarbamate complexes, which also contain three bidentate sulfur-donor ligands, can be attributed solely to the small bite of these bidentates.

As the bite of the bidentate ligand is further decreased, a trigonal prism is formed. The predictions in the range $b = 0.8$–1.1 are somewhat less quantitative because of the very shallow minima in the range $\theta = 0$–$15°$ (Figure 2) and because the positions of the minima are more dependent upon the assumed repulsive law (Figure 3). Preparative and structural work in this area is in progress.

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