880. The Stereochemistry of Eight-co-ordination

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Calculation of the total ligand–ligand repulsion energies for different eight-co-ordinate stereochemistries, show that for each stereochemistry a more stable structure can be obtained by a significant distortion from the structure based on a hard-sphere model. These distortions are invariably observed in those molecules whose structure is known. However the energy differences between different stereochemistries are small, and it is suggested that the stoicheiometry is important in determining the stereochemistry.

ONE possible method of viewing the stereochemistry of simple molecules is to assume that it is determined by the ligand–ligand repulsion energy, or for molecules possessing non-bonding electron pairs, by the repulsion of all electron pairs. This concept has been extensively discussed by Gillespie and Nyholm,[1] particularly for co-ordination numbers from two to six. For the case of co-ordination numbers greater than six, it is shown in this Paper that not only does the most stable stereochemistry depend upon the assumed repulsive law, but also the detailed geometry of each stereochemistry. The calculations can be tedious unless by computer, owing to the inclusion of a number of parameters which must be systematically varied to obtain the most stable configuration. This Paper extends the work of Hoard and Silverton [2] who reported some results of this type, in particular for the square antiprism which involves only a single variable parameter, and for complexes containing four bidentate ligands. They also showed that the ligand–ligand repulsive energy is significant in comparison with the bonding energy; for example, a value of about 56 kcal.mole^{-1} was reported for the eight co-ordinate zirconium tetrakis-acetylacetone complex. We have reviewed eight-co-ordination elsewhere,[3] and these Papers should be consulted for other aspects.

It is assumed that the repulsive energy u_{ij} between any two donor atoms, i and j, can be given [4] by: $u_{ij} = u_C + u_B$. u_C is the energy due to Coulombic repulsion and is given by $Z_iZ_je^2/d_{ij}$, where $Z_iZ_je^2$ is the product of the charges and d_{ij} the distance between them. u_B is a term due to Born and arises from the repulsion of the outer electrons of the atoms, and will be taken to be equal to $b_{ij}e^2/d_{ij}^n$, where b_{ij} is a constant and n is some positive number (an exponential form of the Born term has also been used, and leads to similar results). The value of n must lie between two extremes, from $n = 1$ corresponding to the Coulombic model, to $n = \infty$ corresponding to the interaction between incompressible spheres. Experimental determination of the isothermal compressibilities allows n to be calculated, and for purely ionic lattices it is found to lie between 6 (for the light elements) and 12 (for the heavy elements). For polarisable ions, a third term involving the dispersion energy should be included in the above equation, but the effect of this term will not be discussed separately, as it is of the same form as the Born term for $n = 6$.

If it is specified at this stage that all metal–ligand distances are equal to r, the individual d_{ij} can be calculated, and the total repulsive energy U for identical unidentate ligands can be expressed in the form:

$$U = \sum_{ij} u_{ij} \equiv X\frac{Z^2e^2}{r} + Y\frac{be^2}{r^n}$$

If intermolecular forces are neglected, the numerical coefficients X and Y will be a direct measure of the relative stability of the different stereochemistries.

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[1] R. J. Gillespie and R. S. Nyholm, *Quart. Revs.*, 1957, **11**, 339; R. J. Gillespie, *Canad. J. Chem.*, 1960, **38**, 818.

[2] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[3] R. J. H. Clark, D. L. Kepert, R. S. Nyholm, and J. Lewis, *Nature*, 1963, **199**, 559.

[4] L. Pauling, "The Nature of the Chemical Bond," O.U.P., 1960; E. A. Moelwyn-Hughes, "Treatise on Physical Chemistry," Pergamon, Oxford, 1961.

Square Antiprism (*Symmetry D_{4d}*).—It will be considered that the shape of this polyhedron can be specified by θ, the angle that the metal–ligand bond makes with the eightfold inversion axis (Figure 1). For all metal–ligand distances to be equal to r:

$$\mathrm{AB} = \sqrt{2}r\sin\theta$$
$$\mathrm{AE} = (2r^2 - \sqrt{2}r^2\sin^2\theta + 2r^2\cos^2\theta)^{\frac{1}{2}}$$

For a hard-sphere model, AB = AE = 1·2155 r, θ = 59·26°, and the radius ratio of cation to anion is 0·6453. The other ligand–ligand distances are given by:

$$\mathrm{AC} = 2r\sin\theta$$
$$\mathrm{AF} = (2r^2 + \sqrt{2}r^2\sin^2\theta + 2r^2\cos^2\theta)^{\frac{1}{2}}$$

The total ligand–ligand repulsion energy is then:

$$U = \sum_{\mathrm{ij}} u_{\mathrm{ij}} = 8u_{\mathrm{AB}} + 8u_{\mathrm{AE}} + 4u_{\mathrm{AC}} + 8u_{\mathrm{AF}}$$
$$\equiv \mathrm{X}\frac{Z^2e^2}{r} + \mathrm{Y}\frac{be^2}{r^n}$$

The coefficients X and Y have been calculated as a function of θ. Table 1 shows the minimum values of X and Y and the values of θ where they occur corresponding to the most favourable polyhedron for the particular energy term, together with the values for the hard-sphere model. The variation of U with θ is shown in Figure 2, where the energies have been normalised so that the energies of the most favourable polyhedra are unity.

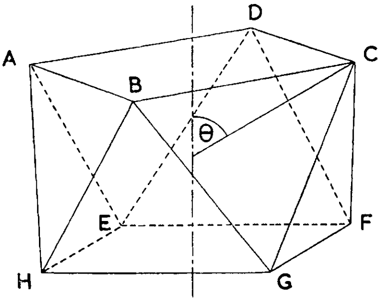

FIGURE 1. Square antiprism

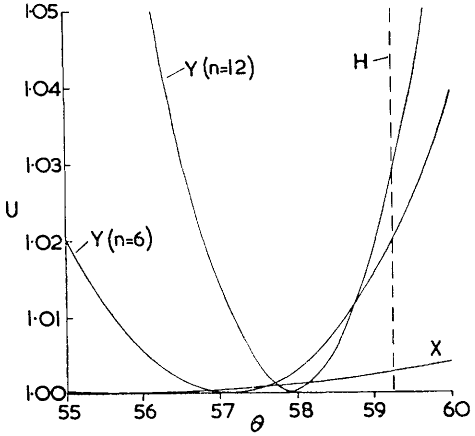

FIGURE 2. Normalised ligand–ligand repulsion-energy coefficients as function of θ for square antiprism. H = Hard-sphere model

TABLE 1

X, Y, and θ for the most favourable polyhedra (M.F.P.) of the square antiprism compared with the hard-sphere model (H.S.M.) of the square antiprism.

		H.S.M.	M.F.P.	$\frac{\text{M.F.P.}}{\text{H.S.M.}}$
Coulombic term	X	19·727	19·675	0·9975
	θ	59·26°	55·91°	
Born term (n = 6)	Y	5·295	5·185	0·9800
	θ	59·26°	57·13°	
Born term (n = 12)	Y	1·549	1·503	0·9717
	θ	59·26°	57·93°	

It can be seen that the ligand–ligand repulsion energy falls to a minimum if θ is lowered by 2—3° from the value of the hard-sphere model. That is, it is qualitatively predicted that the square antiprism will be distorted by stretching along the eight-fold inversion axis. Table 2 shows that this distortion is always observed.

TABLE 2

Parameters of square antiprismatic molecules

	θ (average)	Ref.		θ (average)	Ref.
Hard Sphere model	59·26°		$Ce(IO_3)_4,H_2O$ (layer)	58°	*f*
d^5p^3 Hybrid orbitals	60·9	*a*	$Zr(IO_3)_4$ (layer)	58	*g*
d^4sp^3 Hybrid orbitals	57·6	*a*	ThI_4 (layer)	58	*h*
$Zr(AcAc)_4$ (monomeric)	57·3	*b*	$Zr(SO_4)_2,4H_2O$ (chain)	57	*i*
α-$Th(AcAc)_4$ (monomeric)	58·2	*c*	ZrF_4 (lattice)	57	*j*
$Ce(AcAc)_4$ (monomeric)	58·5	*d*	$Th(OH)_2SO_4$ (chain)	54	*k*
Na_3TaF_8 (monomeric)	59·0	*e*			

[a] G. H. Duffey, *J. Chem. Phys.*, 1950, **18**, 746. [b] J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 1963, **2**, 243. [c] D. Grdenic and B. Matkovic, *Acta Cryst.*, 1959, **12**, 817; *Nature*, 1958, **182**, 465. [d] B. Matkovic and D. Grdenic, *Acta Cryst.*, 1963, **16**, 456. [e] J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *J. Amer. Chem. Soc.*, 1954, **76**, 3820. [f] J. A. Ibers, *Acta Cryst.*, 1956, **9**, 225. [g] A. C. Larsen and D. T. Cromer, *Acta Cryst.*, 1961, **14**, 128. [h] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, 1964, **3**, 639. [i] J. Singer and D. T. Cromer, *Acta Cryst.*, 1956, **12**, 929. [j] R. D. Burbank and F. N. Bensey, *U.S. At. Energy Comm. K*-1280, 1956. [k] G. Lundgren, *Arkiv. Kemi*, 1950, **2**, 535.

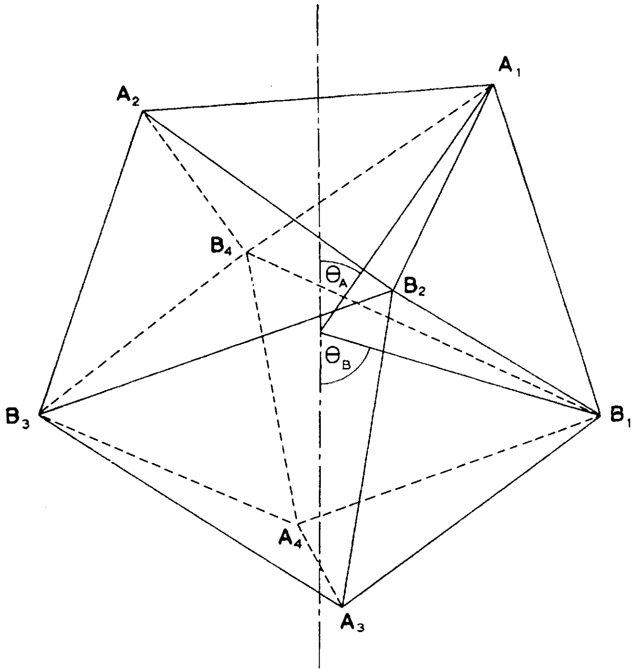

FIGURE 3. Dodecahedron

Another eight-co-ordinate stereochemistry related to the square antiprism is the hendecahedron, formed from a triangular prism with an additional ligand outside two of the rectangular faces. Although in this case other parameters are also changed, the angle θ which the metal–ligand bond makes with the principal axis is again lowered, for example; Th_7S_{12}, θ = 54°;[5] $PuBr_3$, θ = 53°.[6]

Dodecahedron (*Symmetry* D_{2d}).—All ligand positions of a dodecahedron are not identical

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[5] W. H. Zachariasen, *Acta Cryst.*, 1949, **2**, 288.
[6] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 265.

(Figure 3). There are four "A" atoms, such that there are two A–A edges at right angles to each other, and also normal to the principle four-fold inversion axis. The four " B " atoms form a flattened tetrahedron between the two A–A edges. At this stage, it will be considered that all metal–ligand distances are equal to r, and that the shape of the dodecahedron is specified by two parameters, θ_A and θ_B, the angles which the metal–ligand bond M–A and M–B make with the four-fold inversion axis respectively. The ligand–ligand distances are then given by:

$$\begin{aligned} A_1\text{–}A_2 &= 2r \sin \theta_A \\ A_1\text{–}B_1 &= (2r^2 + 2r^2 \cos (\theta_A + \theta_B))^{\frac{1}{2}} \\ A_1\text{–}B_2 &= (2r^2 - 2r^2 \cos \theta_A \cos \theta_B)^{\frac{1}{2}} \end{aligned}$$

For a hard-sphere model, $A_1\text{–}A_2 = A_1\text{–}B_1 = A_1\text{–}B_2 = 1{\cdot}1993r$, $\theta_A = 36{\cdot}85°$, $\theta_B = 69{\cdot}46°$, and the radius ratio of cation to anion is 0·6676. The other ligand–ligand distances are given by:

$$B_1\text{–}B_2 = (2r^2 + 2r^2 \cos^2\theta_B)^{\frac{1}{2}} = 1{\cdot}4986r = 1{\cdot}2496A_1\text{–}A_2$$

for a hard-sphere model,

$$\begin{aligned} A_1\text{–}A_3 &= (2r^2 + 2r^2 \cos^2\theta_A)^{\frac{1}{2}} \\ A_1\text{–}B_3 &= (2r^2 + 2r^2 \cos \theta_A \cos \theta_B + 2r^2 \sin \theta_A \sin \theta_B)^{\frac{1}{2}} \\ B_1\text{–}B_3 &= 2r \sin \theta_B \end{aligned}$$

The total ligand–ligand repulsion energy is then:

$$\begin{aligned} U = \sum_{ij} u_{ij} &= 2u_{A_1A_2} + 4u_{A_1B_1} + 8u_{A_1B_2} + 4u_{B_1B_2} + 4u_{A_1A_3} + 4u_{A_1B_3} + 2u_{B_1B_3} \\ &= X\frac{Z^2e^2}{r} + Y\frac{be^2}{r^n} \end{aligned}$$

The coefficients X and Y have been calculated as a function of θ_A and θ_B; the minimum values of X and Y corresponding to the most favourable polyhedra, and the values of θ_A and θ_B where these occur are shown in Table 3, together with the values for the hard-sphere model. The relative decreases in ligand–ligand repulsion energies of the most favourable polyhedra compared with the hard-sphere model are shown in the last column, and also in Figures 4—6, which show the ligand–ligand repulsion energy as a function of θ_A and θ_B, where the energy terms have been normalised so that the energies of the most favourable polyhedra are unity.

TABLE 3

X, Y, θ_A, and θ_B for the most favourable polyhedra (M.F.P.) of the dodecahedron compared to the hard-sphere model (H.S.M.) of the dodecahedron

		H.S.M.	M.F.P.	$\frac{\text{M.F.P.}}{\text{H.S.M.}}$
Coulombic term	X	19·704	19·681	0·9988
	θ_A	36·85°	38·5°	
	θ_B	69·46°	71·7°	
Born term ($n = 6$)	Y	5·318	5·245	0·9863
	θ_A	36·85°	37·3°	
	θ_B	69·46°	71·4°	
Born term ($n = 12$)	Y	1·618	1·591	0·9834
	θ_A	36·85°	37·1°	
	θ_B	69·46°	70·8°	

The results show that distortion from the hard-sphere model again leads to a more stable structure, an energetically more favourable polyhedron being obtained by increasing θ_B by about 2°, that is, by a further flattening of the " B " atoms into a plane. It is again found that this distortion which is qualitatively predicted is always observed in real dodecahedral

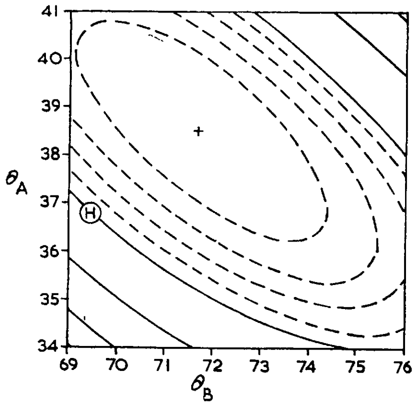

FIGURE 4. Potential-energy diagram for the Coulombic term applied to the dodecahedron. Full contour lines are for 0·1% energy increases, and broken contour lines 0·02% energy increases above the bottom of the well, which is marked by +. H = Hard-sphere model

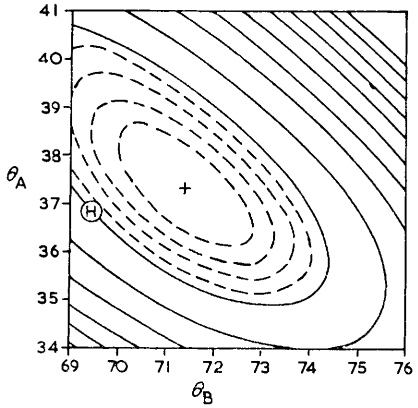

FIGURE 5. Potential-energy diagram for the Born term (n = 6) applied to the dodecahedron. Full contour lines are for 1% energy increases, and broken contour lines 0·2% energy increases above the bottom of the well, which is marked by +. H = Hard-sphere model

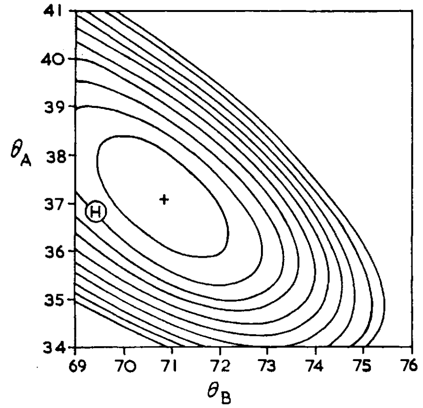

FIGURE 6. Potential-energy diagram for the Born term (n = 12) applied to the dodecahedron. Contour lines are for 1% energy increases above the bottom of the well, which is marked by +. H = Hard-sphere model

molecules (Table 4). The peroxychromate ion $Cr(O_2)_4^{3-}$ is [7] obviously exceptional [θ_A = 43·4°, θ_B = 86·8°, (M–A)/(M–B) = 0·95], owing to the large distortion caused by the short O–O distance.

TABLE 4

Parameters of dodecahedral molecules

	θ_A (average)	θ_B (average)	$\frac{\text{M–A}}{\text{M–B}}$	Ref.
Hard Sphere model	36·85°	69·46°	1·00	
$TiCl_4$,2Diarsine (monomeric)	36·4	72·5		*a*
$Zr(C_2O_4)_4^{4-}$ (monomeric)	35·2	73·5	1·03	*b*
$Mo(CN)_8^{4-}$	36·0	71·8	1·00	*c*
ZrF_6^{2-} (chain)	35·3	74·6	1·02	*d*
$ThCl_4$ (lattice)	36	75	1·26	*e*

[a] R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature*, 1961, **192**, 222; R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J.*, 1962, 2460; P. Pauling and G. B. Robertson, unpublished results. [b] J. L. Hoard, G. L. Glen, and J. V. Silverton, *J. Amer. Chem. Soc.*, 1961, **83**, 4293; *Inorg. Chem.*, 1963, **2**, 250. [c] J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853; ref. 2. [d] H. Bode and G. Teufer, *Acta Cryst.*, 1956, **9**, 929. [e] R. C. L. Mooney, *Acta Cryst.*, 1949, **2**, 189.

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[7] R. Stomberg and C. Brossett, *Acta Chem. Scand.*, 1960, **14**, 441.

Although the broad conclusions are found to agree with experiment, closer examination of the experimental results show that there is an unexpected decrease in θ_A, and also that θ_B is increased more than expected. If, in view of the assumptions made in the above calculations, and the crystallographic errors, it is decided that these differences are significant, they may be attributed to one of two effects, which are not necessarily independent.

(*a*) It has been assumed that all bond lengths are equal, but experimental evidence suggests that this may not necessarily be true (Table 4). The calculations of the most favourable polyhedra have therefore been repeated, with the additional variable parameter (M–A)/(M–B). As this ratio is increased, the positions of the minima in the potential/energy wells are shifted to lower values of θ_A and higher values of θ_B, in better agreement with experiment (Figure 7).

(*b*) A purely ionic model has been assumed, but a decrease in θ_A will increase the overlap between the donor electrons and a set of d^4sp^3 hybrid orbitals ($\theta_A = 34{\cdot}6°$, $\theta_B = 72{\cdot}8°$).[8]

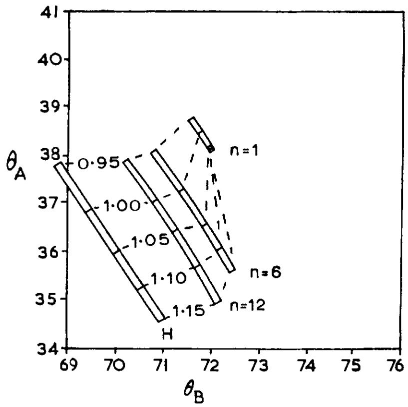

FIGURE 7. Most favourable polyhedra for dodecahedra having different bond lengths [(M–A)/(M–B) = 0·95, 1·00, 1·05, 1·10 and 1·15 respectively]. $n = 1$: most favourable polyhedra for Coulombic term; $n = 6$, 12: most favourable polyhedra for Born term. *H* = Hard-sphere models

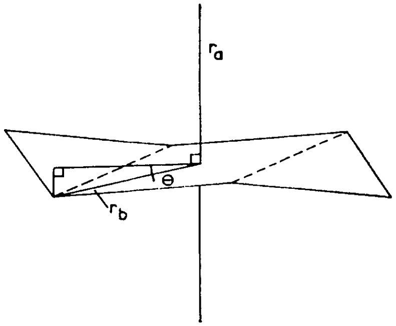

FIGURE 8. Puckered hexagonal bipyramid

It must be remembered that in the absence of a defined symmetry, the parameters θ_A and θ_B do not by themselves define a dodecahedron. For example, if we consider the angles the metal–ligand bonds make with one of the minor two-fold axes of a square antiprism, it is found that for the hard sphere model there are four at 37·43° and four at 70·80°, which are very close to those for the dodecahedron.

Puckered Hexagonal Bipyramid (*Symmetry* D_{3d}).—The hexagonal plane is normally puckered by an angle θ (Figure 8). As θ approaches 19·53°, the structure approaches a cube, which in turn can be considered as a dodecahedron for which $\theta_A = \theta_B = 54{\cdot}74°$. The puckered hexagonal bipyramid can also be considered to be derived from an octahedron by adding ligands outside opposite triangular faces, that is, 1 : 3 : 3 : 1 co-ordination.

It is qualitatively found that as the axial bond lengths r_a are shortened, the radial bonds are forced more into a plane (Table 5). The ligand–ligand repulsion energy coefficients have been calculated as before, but a reasonable agreement with the experimentally found dependence of θ on the ratio of the bond lengths r_a/r_b, can only be obtained if it is assumed

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[8] G. Racah, *J. Chem. Phys.*, 1943, **11**, 214.

that the axial–planar repulsion is of a different type to the axial–axial repulsion. The results for $r_a/r_b = 1$ are shown in Table 6.

TABLE 5

Parameters of puckered hexagonal bipyramid molecules. Cubic stereochemistry is commonly found in compounds having the cæsium chloride or fluorite (CaF_2) structures, which have been listed elsewhere.[3]

	r_a/r_b	θ	Ref.
Cube (lattice)	1·00	19·5°	
α-UO_3 (layer)	0·87	16·6	*a*
$CaUO_4$ (layer)	0·83	12·4	*a*
UO_2F_2 (layer)	0·76	14·1	*b*
$[UO_2(NO_3)_2(H_2O)_2],4H_2O$ (monomeric)	0·72	0·3	*c*
$NaUO_2(OAc)_3$ (monomeric)	0·69	0·9	*d*
$UO_2(NO_3)_2,2(EtO)_3PO$ (monomeric)	0·68	2·7	*e*
UO_2CO_3 (layer)	0·67	0	*f*
$RbUO_2(NO_3)_2$ (monomeric)	—	0	*g*

[a] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 281. [b] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 277. [c] J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1416. [d] W. H. Zachariasen and H. A. Plettinger, *Acta Cryst.*, 1959, **12**, 526. [e] H. Lynton and J. E. Fleming, *Chem. and Ind.*, 1959, 1409. C. L. Christ, J. R. Clark, and H. T. Evans, *Science*, 1955, **121**, 472; D. T. Cromer and P. E. Harper, *Acta Cryst.*, 1955, **8**, 847. [g] J. L. Hoard and J. D. Stroupe, Natl. Nuclear Energy Series, Div. III, vol. 2, 1949, ch. 2, p. 15.

TABLE 6

X and Y for the hexagonal bipyramid ($r_a = r_b$)

	Cube (θ = 19·53°)	Planar hexagonal bipyramid (θ = 0°)
Coulombic term X	19·741	19·949
Born term ($n = 6$) Y	5·768	7·785
Born term ($n = 12$) Y	2·170	6·197

TABLE 7

Relative ligand–ligand repulsion energy coefficients X and Y for eight-co-ordinate stereochemistries

	Square antiprism (M.F.P.)	Dodecahedron (M.F.P.)	Cube	Planar hexagonal bipyramid
Coulombic term X	1·000	1·000$_3$	1·003	1·014
Born term ($n = 6$) Y	1·000	1·012	1·112	1·502
Born term ($n = 12$) Y	1·000	1·058	1·444	4·122

Relative Stabilities of Eight-co-ordinate Stereochemistries.—The relative ligand–ligand repulsion energy coefficients for the eight-co-ordinate stereochemistries are shown in Table 7, but provide a measure of the relative stabilities only if it is further assumed that the attractive forces holding the molecules together are the same. It can be seen that the difference between the square antiprism and dodecahedron is negligible (although the former may be preferred for high values of *n*, that is, for non-polarisable ligands), but that both are more stable than the other stereochemistries.

In the case of the dodecahedron, there appears to be some experimental evidence which suggests that an increase in the M–A bond length relative to the M–B bond length lowers the energy of the molecule as a whole. This is expected to be particularly important for compounds of the type MX_4Y_4 where all ligands are not identical, as the sorting of the ligands into the appropriate A and B sites will take advantage of this further stabilisation. As expected, the ligands which form the longer bonds (for example, the less electronegative arsenic as compared with halogen in the MX_4,2Diarsine compounds) favour the A sites. Similarly for the case of the puckered hexagonal bipyramid, although the calculations show it is not favoured if there are eight equivalent ligands, the introduction of two short metal–ligand bonds stabilises this structure, and it is found for all known MX_2Y_6 compounds.

That is, we can summarise by saying that in these cases we have *stoicheiometrically controlled stereochemistry.*

Seven-co-ordination.—Similar calculations to those above have also been carried out for some seven-co-ordinate stereochemistries, which have been independently published by Britton.[9] It is again found that qualitative distortion of about 2—3° from the hard-sphere models stabilise each particular stereochemistry, but in these cases it is unfortunate that the predictions cannot be verified as there are insufficient seven-co-ordinate molecules whose structures are accurately known.

The energy differences between different stereochemistries are again small, but examination of the known structures strongly indicate that we again have stoicheiometrically controlled stereochemistry. For example: pentagonal bipyramid for $UO_2F_5^{3-}$;[10] octahedral monopyramid[11] or " 1 : 4 : 2 " co-ordination for the $Mn(Y)H_2O$ unit in $Mn_3(HY)_2,10H_2O$ (where H_4Y is ethylenediaminetetra-acetic acid); decahedral or " 1 : 3 : 3 " coordination[12] for $NbOF_6^{3-}$; enneahedral or " 4 : 3 " co-ordination for $(Me_4C_4,NiCl_2)_2$,[13] $Ph_4C_4,Fe(CO)_3$,[14] and $(CO)_6Fe_2Se_2,Fe(CO)_3$.[15]

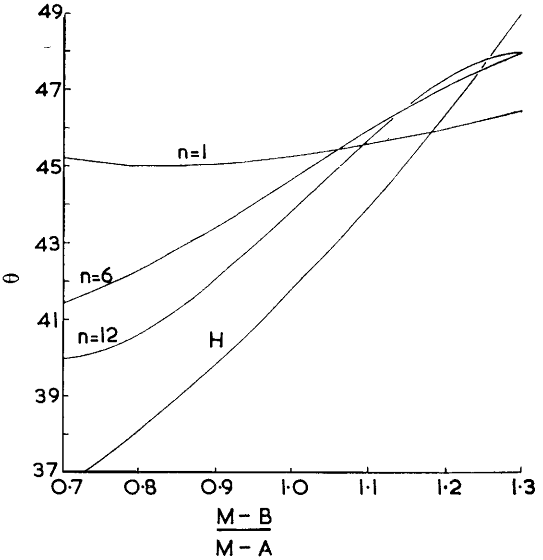

FIGURE 9. Most favourable polyhedra for 3 : 3 : 3 co-ordination with bond-length ratio (M–B)/(M–A). $n = 1$: most favourable polyhedra for Coulombic term; $n = 6$, 12: most favourable polyhedra for Born term. H = Hard-sphere models

Nine-co-ordination (*Symmetry D_{3h}*).—Similar calculations to those described above have also been carried out for the " 3 : 3 : 3 " stereochemistry of nine-co-ordination, which can be considered as a trigonal prism with additional ligands outside each of the rectangular faces. This appears to be the only stereochemistry known for co-ordination number nine. The polyhedron is defined by θ, the angle made by the six " prismatic " metal–ligand (A) bonds to the three-fold axis, and (M–B/(M–A), the ratio of the " equatorial " bond lengths to the " prismatic " bond lengths. Evaluation of the ligand–ligand repulsion energy coefficients X and Y as a function of these parameters shows that, provided $(M-B)/(M-A) < 1{\cdot}1$, a more stable structure is obtained by qualitatively increasing θ by about 3° (Figure 9). However, as was also found for seven-co-ordination, the structures have not been determined with sufficient accuracy to enable this prediction to be tested.

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[9] D. Britton, *Canad. J. Chem.*, 1963, **41**, 1632.
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Experimental.—The equations were analysed by direct numerical analysis on the University of London's Atlas and Mercury Computers using the $CHLF_3$ facilities for the trigonometrical functions.

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