

SECTION A

Inorganic, Physical, and Theoretical Chemistry

Eight-co-ordination. Part III.¹ Ligand-Ligand Repulsions and Crystal Field Stabilisation Energies

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Relative ligand-ligand repulsion energies are calculated for square antiprismatic and dodecahedral configurations, with use of a force-law between point ligands of the type: Force $\propto r^{-n}$ ($n = 1, 2, 6, 7, 10, 12$). The antiprismatic configuration is the more stable but the energies of the two configurations differ by not more than about 1 kcal./mole. The shielding effect of the central metal atom cannot be estimated accurately, but this effect would be appreciable only for Coulombic interactions in a highly polar complex, when the dodecahedral configuration might be stabilised by several kcal./mole. With the possible exception of the latter case, it is therefore unlikely that the configuration adopted by any eight-co-ordinate complex would be determined by inter-ligand repulsion alone.

The d -orbital energies are calculated on a point-charge model. Within the range of observed geometries the crystal-field stabilisation energies of the two configurations are similar.

EIGHT-CO-ORDINATE complexes are becoming increasingly common and it is of interest to determine the factors which govern the shape of the co-ordination polyhedron. For eight-co-ordinate transition-metal complexes two configurations are observed, the square antiprism and the dodecahedron. Hexagonal bi-pyramidal stereochemistry, exhibited in some actinide complexes, has not been reported for transition metals. We now examine the energies of the antiprismatic and dodecahedral configurations on the bases of (a) ligand-ligand repulsion and (b) crystal-field stabilisation. In a later Paper we intend to present relative bond energies, estimated from the relevant overlap integrals.

Ligand-ligand repulsion has been treated previously,^{2,3} Kepert's Paper,² which covers some of the cases reported here, appeared during the course of this work. Since his results for the dodecahedral case disagreed with those of Hoard and Silvertown,³ it was felt worthwhile to continue the calculations, which agree with Kepert's results. We have also attempted to estimate the effect of the shielding produced by the central metal atom. We find that the repulsion energies are very similar, the antiprism being slightly the more stable. The more efficient shielding of the metal atom in a dodecahedral complex might favour this configuration, but only in highly polar complexes.

Crystal-field stabilisation energies do not seem to have been calculated previously, except for the case of the "twisted cube."⁴ We find that the stabilisation energies of the two configurations are very similar and that neither configuration has an optimum shape in the range of geometries observed for transition-metal complexes.

(a) *Ligand-ligand Repulsion*.—The repulsion energy due to interactions between eight ligands is proportional

to the sum Σr_{ij}^{-n} , where the r_{ij} are the twenty-eight ligand-ligand distances. The value of n depends on the type of interaction considered, being unity for Coulombic interaction and 6–12 for Born repulsions between closed electron shells. The sum Σr_{ij}^{-n} was calculated for the antiprismatic and dodecahedral configurations separately, as functions of the characteristic angles, θ , which the metal-ligand bond directions make with

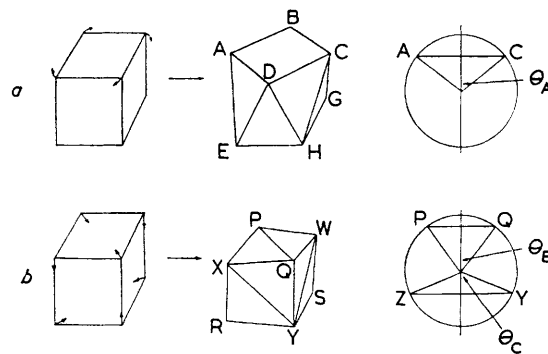


FIGURE 1 Relationship between the cube and (a) the square antiprism, (b) the dodecahedron

the principal axes of the polyhedra. In a square antiprism the eight ligands constitute one equivalent set and the repulsion energy is a function of the metal-ligand distance and the angle θ_A (Figure 1a). In a dodecahedron there are two distinct sets, each containing four equivalent ligands, and the interaction is a function of the two angles θ_B and θ_C and the metal-ligand distance. We have calculated the sum Σr_{ij}^{-n} as a function of the angles, with the limitations that (i) the metal-ligand distance remains constant, and is arbitrarily set to unity, and (ii) the ligands are restricted

¹ Part II, R. V. Parish, *Spectrochim. Acta*, 1966, **22**, 1191.

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

³ J. L. Hoard and J. V. Silvertown, *Inorg. Chem.*, 1963, **2**, 235.

⁴ A. L. Companion and M. A. Komarynsky, *J. Chem. Educ.*, 1964, **41**, 257.

to the appropriate vertical planes, so that strict D_{4d} or D_{2d} symmetry is maintained. (Details of the calculations are given in the Appendix.) The calculated minimum values of Σr_{ij}^{-n} and the corresponding angles are shown in Table I; the values for the cube are included for comparison.

At a metal-ligand distance of 2.2 Å this gives a repulsion energy of 740 kcal./mole. If some positive charge is allowed on the metal atom, and correspondingly greater negative charge on the ligands, this value rises rapidly to about 1000 kcal./mole. However, in this case the difference between the two configurations is only

TABLE I
Optimum repulsion parameters

	n	1	2	6	7	10	12
Antiprism	Σr_{ij}^{-n}	19.6753	14.3368	5.1864	4.1681	2.2415	1.5034
	θ_A	55.9	56.2	57.1	57.3	57.7	57.9
	p^*	100.00	100.00	100.00	100.00	100.00	100.00
Dodecahedron	Σr_{ij}^{-n}	19.6816	14.3520	5.2453	4.2387	2.3292	1.5916
	θ_B	38.30	38.05	37.35	37.25	37.10	37.05
	θ_C	71.95	71.80	71.40	71.30	71.00	70.85
	p^*	100.03	100.06	101.13	101.69	103.91	105.86
Cube	Σr_{ij}^{-n}	19.7408	14.5000	5.7578	4.8030	2.9406	2.1701
	$\theta_B = \theta_C = 54.7^\circ$						
	p^*	100.33	101.14	112.95	115.2	131.2	144.3
<i>With shielding.</i> Antiprism (0.8) †	Σr_{ij}^{-n}	18.8317	13.8919	5.1500	4.1497	2.2388	1.5026
	θ_A	56.0	56.3	57.1	57.3	57.7	57.9
	p	95.71	96.90	99.30	99.56	99.88	99.95
	(0.7)	Σr_{ij}^{-n}	18.4099	13.6692	5.1326	4.1406	2.2374
		θ_A	56.1	56.3	57.1	57.3	57.7
		p	93.57	95.34	98.96	99.34	99.82
	(0.5)	Σr_{ij}^{-n}	17.5662	13.2239	5.0980	4.1222	2.2347
		θ_A	56.2	56.35	57.1	57.3	57.7
		p	89.28	92.23	98.29	98.90	99.70
	Dodecahedron (1.0, 0.2)	Σr_{ij}^{-n}	17.9832	13.4674	5.1797	4.2045	2.3244
		θ_B	33.5	35.5	37.2	37.2	37.0
		θ_C	78.5	75.0	71.6	71.4	71.1
		p	91.39	93.94	99.99	100.87	103.70
	(1.0, 0.1)	Σr_{ij}^{-n}	17.7667	13.3545	5.1715	4.2002	2.3238
		θ_B	33.5	35.5	37.2	37.2	37.0
		θ_C	78.5	75.0	71.6	71.4	71.1
		p	90.30	93.15	99.97	100.77	103.68
	(0.9, 0.4)	Σr_{ij}^{-n}	18.3106	13.6361	5.1918	4.2107	2.3253
		θ_B	35.0	36.5	37.2	37.2	37.0
		θ_C	76.0	73.5	71.5	71.3	71.1
		p	93.06	95.11	100.10	101.02	103.74
	(0.9, 0.2)	Σr_{ij}^{-n}	17.8811	13.4130	5.1754	4.2022	2.3241
		θ_B	33.5	36.0	37.2	37.2	37.0
		θ_C	78.0	74.5	71.5	71.3	71.1
		p	90.88	93.56	99.98	100.82	103.68
	(0.9, 0.1)	Σr_{ij}^{-n}	17.6646	13.3009	5.1672	4.1979	2.3235
		θ_B	33.5	35.5	37.2	37.2	37.0
		θ_C	78.5	75.0	71.5	71.4	71.1
		p	89.79	92.78	99.98	100.71	103.66
Cube	(0)	Σr_{ij}^{-n}	17.708	13.5000	5.6953	4.7718	2.9067
		p	90.16	96.16	110.03	114.5	129.7

* p gives the value of Σr_{ij}^{-n} relative to the corresponding value for the unshielded antiprism as 100. † Figures in parentheses are the values of the shielding parameters.

It is apparent that in all cases the antiprism is more stable than the dodecahedron and the cube is the least stable, although for small n -values the differences are very small. Hoard and Silverton³ have estimated that, for $n = 7$ and a metal-ligand distance of 2.2 Å, the repulsion energy amounts to about 56 kcal./mole. This is a significant contribution to the total energy of the complex but the difference between the antiprismatic and dodecahedral energies is only 1.7%, about 1 kcal./mole. For the Coulombic case ($n = 1$) we assume that the charge of a complex ion is distributed equally among the ligands. Thus, in a complex of the type ML_8^{4-} , each ligand would have a charge of -0.5 .

0.03%, or 0.1–0.5 kcal./mole. For neutral complexes the energy difference will be even smaller. On this basis, then, it seems unlikely that repulsion effects alone will determine the type of co-ordination polyhedron adopted by any given eight-co-ordinate complex.

Even the characteristic angles, θ , may not be determined by the forces of repulsion for either configuration. In both cases the minima are ill-defined, being particularly shallow for $n = 1$. (Diagrams of the energy surfaces are given by Kepert.²) As n increases the minima become better defined, but even for $n = 12$ a deviation of 1° from the optimum angles produces only a 2% increase in repulsion energy for the antiprism and

1–3% for the dodecahedron. For 2° deviations the figures are 5 and 3–13%, respectively. (The energy minima are elongated and the energy surfaces have their steepest slopes in the directions in which θ_B and θ_C both increase or both decrease. The directions of minimum slope, along which distortion is most likely, are those in which one angle increases while the other decreases.) In the crystal, variations of 2–3° occur between corresponding angles of the same molecule, presumably owing to the exigencies of crystal packing. For example, in ReF_8^{2-5} the average value of θ_A is 57.7°, the same as the calculated value for $n = 10$,

distances, *i.e.*, those of the type AH for the antiprism (eight distances) and PY (four) and ZY (two) for the dodecahedron. We have calculated the repulsion energies for several cases in which the contributions of terms involving these distances have been reduced. For the cube it is assumed that the shielding over the four diagonal interactions is complete. The resulting energies are listed in Table 1.

As would be expected, for high n values ($n \geq 6$) the effects of shielding are very small. For the Coulombic case, however, the effect is quite marked and it seems likely that the dodecahedron could become significantly

TABLE 2

Crystal-field functions

$$\begin{aligned} D_{00} &= \alpha_0^i \\ D_{20} &= \alpha_2^i (3 \cos^2 \theta_i - 1) \\ D_{40} &= \alpha_4^i \left(\frac{35}{3} \cos^4 \theta_i - 10 \cos^2 \theta_i + 1 \right) \\ D_{44} &= \alpha_4^i \sin^4 \theta_i (= 0 \text{ for antiprism}) \end{aligned}$$

Antiprism

$$\begin{aligned} \left. \begin{aligned} H_{11} \\ H_{55} \end{aligned} \right\} &= 8\alpha_0 - \frac{8\alpha_2}{7} (3 \cos^2 \theta_A - 1) + \frac{\alpha_4}{7} \left(\frac{35}{3} \cos^4 \theta_A - 10 \cos^2 \theta_A + 1 \right) \\ \left. \begin{aligned} H_{22} \\ H_{44} \end{aligned} \right\} &= 8\alpha_0 + \frac{4\alpha_2}{7} (3 \cos^2 \theta_A - 1) - \frac{4\alpha_4}{7} \left(\frac{35}{3} \cos^4 \theta_A - 10 \cos^2 \theta_A + 1 \right) \\ H_{33} &= 8\alpha_0 + \frac{8\alpha_2}{7} (3 \cos^2 \theta_A - 1) + \frac{6\alpha_4}{7} \left(\frac{35}{7} \cos^4 \theta_A - 10 \cos^2 \theta_A + 1 \right) \end{aligned}$$

Dodecahedron

$$\begin{aligned} H_{11} &= 8\alpha_0 - \frac{4\alpha_2}{7} (3 \cos^2 \theta_B + 3 \cos^2 \theta_C - 2) + \frac{\alpha_4}{14} \left[\frac{35}{3} (\cos^4 \theta_B + \cos^4 \theta_C) - 10 (\cos^2 \theta_B + \cos^2 \theta_C) + 2 \right] + \frac{5\alpha_4}{6} (\sin^4 \theta_B + \sin^4 \theta_C) \\ \left. \begin{aligned} H_{22} \\ H_{44} \end{aligned} \right\} &= 8\alpha_0 + \frac{4\alpha_2}{7} (3 \cos^2 \theta_B + 3 \cos^2 \theta_C - 2) - \frac{2\alpha_4}{7} \left[\frac{35}{3} (\cos^4 \theta_B + \cos^4 \theta_C) - 10 (\cos^2 \theta_B + \cos^2 \theta_C) + 2 \right] \\ H_{33} &= 8\alpha_0 + \frac{4\alpha_2}{7} (3 \cos^2 \theta_B + 3 \cos^2 \theta_C - 2) + \frac{3\alpha_4}{7} \left[\frac{35}{3} (\cos^4 \theta_B + \cos^4 \theta_C) - 10 (\cos^2 \theta_B + \cos^2 \theta_C) + 2 \right] \\ H_{55} &= 8\alpha_0 - \frac{4\alpha_2}{7} (3 \cos^2 \theta_B + 3 \cos^2 \theta_C - 2) + \frac{\alpha_4}{14} \left[\frac{35}{3} (\cos^4 \theta_B + \cos^4 \theta_C) - 10 (\cos^2 \theta_B + \cos^2 \theta_C) + 2 \right] - \frac{5\alpha_4}{6} (\sin^4 \theta_B + \sin^4 \theta_C) \\ H_{11} &= \text{energy of } d_{x^2-y^2}; H_{22} = \text{energy of } d_{xx}; H_{33} = \text{energy of } d_{z^2}; H_{44} = \text{energy of } d_{yz}; H_{55} = \text{energy of } d_{xy} \end{aligned}$$

but the individual angles (estimated as $\frac{1}{2}\text{F}_A\text{ReF}_C$, etc.) are 58.5° (2) and 56.9° (2). Similarly for $\text{Mo}(\text{CN})_8^{4-}$ (using the original figures;⁶ more accurate values have not yet been published³), $\theta_B = 33.1$ and 35.2° and $\theta_C = 72.0$ and 76.1° .

The above calculations take no account of the shielding produced by the central metal atom. A rigorous treatment of this shielding would be extremely involved, but qualitatively it is obvious that the shielding should increase in the order antiprism < dodecahedron < cube. Using the above model, we can estimate the effects of shielding by reducing the contribution of the interactions between those ligands which are separated by the metal atom. Unfortunately, it is not possible to select weighting factors on an absolute basis and any arbitrary selection necessarily prejudices the result. The interactions which are affected are those over the longer

more stable than the antiprism (even by several kcal./mole). The cube is stabilised to an even greater extent and becomes comparable in energy to the dodecahedron.

In summary, it appears that the repulsive forces, both Coulombic and Born type, will not by themselves determine the type of co-ordination polyhedron adopted by an eight-co-ordinate complex. The only possible exception is that in highly polar complexes the dodecahedral (or cubic) configuration might be considerably stabilised relative to the antiprism by Coulombic effects. It is interesting that the stereochemistry of the octacyano-complexes of molybdenum and tungsten appears to follow this pattern. Recent electron spin resonance (e.s.r.) results^{7,8} suggest that the complexes of the quinquivalent metals, $\text{M}(\text{CN})_8^{3-}$, have an antiprismatic configuration. The derivatives of the quadrivalent metals, $\text{M}(\text{CN})_8^{4-}$, in which the negative charge is greater and which are therefore more polar, are dodeca-

⁵ P. A. Kozmin, *J. Struct. Chem.*, 1964, **5**, 60.

⁶ J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

⁷ B. R. McGarvey, *Inorg. Chem.*, 1966, **5**, 476.

⁸ R. G. Hayes, *J. Phys. Chem.*, 1966, **44**, 2210.

hedra^{1,6,9} While other effects (*e.g.*, π -bonding) are no doubt operative, ligand-ligand repulsion may well play a significant part in determining the stereochemistry of these complexes.

(b) *Crystal Field Stabilisation*.—The eight-co-ordinate transition-metal complexes obtained so far have d^0 , d^1 , or (spin-paired) d^2 electronic configurations.¹⁰ It is therefore of interest to examine the influence which crystal-field stabilisation might have on the stereochemistry. We have calculated the energies of the d orbitals in fields of the appropriate geometry by the method of Companion and Komarynsky.⁴ All the ligand-position functions, D_{lm} and G_{lm} , are zero except D_{00} , D_{20} , D_{40} , and D_{44} , although the latter is also zero for the antiprism. These functions have the forms shown in Table 2, where α_0 , α_2 , and α_4 are radial integrals and θ_i is the θ -co-ordinate of the i th ligand. The energies of the d orbitals are then given exactly by the integrals H_{11} – H_{55} , since the off-diagonal elements are all zero. The appropriate

Both Figures have been drawn using the assumption that $\alpha_2 = 3\alpha_4$. Use of $\alpha_2 = 4\alpha_4$ makes no significant changes in the arguments below.

Provided that the metal-ligand distances are the same, the results for the antiprism and the dodecahedron are directly comparable, since the radial integrals α_2 and α_4 will have the same values in each case. For d^2 systems the two energies are also directly comparable as the configurations $(d_{z^2})^2$ and $(d_{x^2-y^2})^2$ have the same interelectronic repulsion energies. In neither case is there a minimum in the energy of the lowest orbital, in the region scanned, and the energies are similar, being in the range $-0.8\alpha_4$ to $-1.5\alpha_4$ (for $\alpha_2 = 3\alpha_4$). It is thus not possible to predict the more stable configuration for the molecule on this basis. The treatment does show, however, that a dodecahedral complex would tend to distort in the direction of decreasing θ_B and θ_C , although distortions of the type permitted by the repulsive interactions (one angle increasing, the other decreasing)

TABLE 3
Contributions to the sum Σr_{ij}^{-n}

Antiprism		Dodecahedron	
Type	Term	Type	Term
AB	$8[\sqrt{2} \sin \theta_A]^{-n}$	PQ	$2[2 \sin \theta_C]^{-n}$
AC	$4[2 \sin \theta_A]^{-n}$	YZ	$2C[2 \sin \theta_B]^{-n}$
AE	$8[4 - (2 + \sqrt{2}) \sin^2 \theta_A]^{-n/2}$	PZ	$4[4 - 4 \sin^2 \frac{1}{2}(\theta_B + \theta_C)]^{-n/2}$
AH	$8B[4 - (2 - \sqrt{2}) \sin^2 \theta_A]^{-n/2}$	PX	$8[2 - 2 \cos \theta_B \cos \theta_C]^{-n/2}$
		PY	$4D[4 - 4 \sin^2 \frac{1}{2}(\theta_B - \theta_C)]^{-n/2}$
		PR	$4[4 - 2 \sin^2 \theta_B]^{-n/2}$
		YZ	$4[4 - 2 \sin^2 \theta_C]^{-n/2}$

forms are given in Table 2, where θ_A , θ_B , and θ_C retain their previous significance. The energies of the orbitals can thus be calculated as a function of these angles and

could occur with very little change in crystal field stabilisation. The effect of crystal-field stabilisation on an antiprismatic complex would be to favour an increase in θ_A .

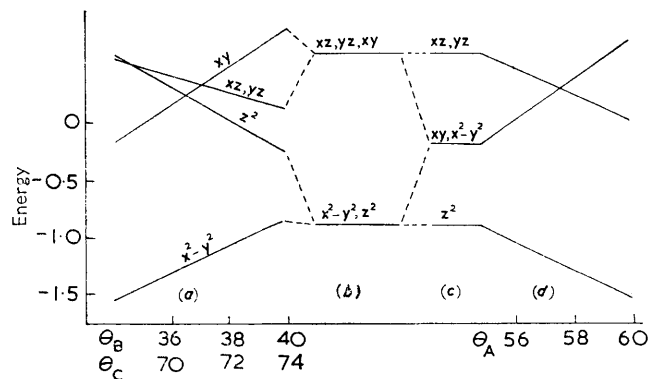


FIGURE 2 Crystal-field energy levels of the d orbitals for (a) dodecahedron, (b) cube, (c) twisted cube, and (d) square antiprism (energies in units of α_4 , relative to $\alpha_0 = 0$).

the results are shown in Figures 2(a)–(d). Figure 2(a) is a cross-section across the orbital energy surfaces for the dodecahedron, in the direction of maximum slope.

⁹ S. F. A. Kettle and R. V. Parish, *Spectrochim. Acta*, 1965, **21**, 1087.

¹⁰ R. V. Parish, *Co-ordination Chem. Revs.*, in the press.

APPENDIX

The geometry of the models leads to the expressions listed in Table 3, the sum of which gives Σr_{ij}^{-n} . B , C , and D are the shielding parameters, all unity for the case of no shielding and zero for complete shielding. Inspection shows that significant shielding would occur in interactions of the type AH (antiprism) and PY and YZ (dodecahedron), and that they would lie in the order $YZ < AH < PY$. The shielding constants were therefore given the following sets of values: B : 0.8, 0.7, 0.5; C : 1.0, 0.9; D : 0.4, 0.2, 0.1.

For the antiprism the minimum values were found by calculating Σr_{ij}^{-n} over a range of θ_A values in the neighbourhood of the suspected minimum, using 0.1° increments. For the dodecahedron the minima were located by scanning a grid alternately in the θ_B and θ_C directions, using steps of 0.1° in all cases except for $n = 1$ or 2 when shielding was being considered, when the steps were 0.5° . All calculations were performed on the Atlas computer in the University of Manchester.

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