

# Chemical Applications of Topology and Group Theory. III. Relative Interligand Repulsions of Coordination Polyhedra<sup>1</sup>

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**Abstract:** The relative Coulombic repulsions (repulsivities) are calculated for possible polyhedra for coordination numbers four through nine, inclusive, assuming equal charges and bond distances for all metal–ligand bonds (EDEC model). Comparison with the coordination polyhedra found in actual complexes indicates that polyhedra with low repulsivity values are favored. In medium-symmetry coordination polyhedra one or two bond angles can be varied, keeping the same metal–ligand bond lengths and the same symmetry elements. In these cases the bond angles giving the minimum EDEC repulsivity are close to those found in actual complexes by X-ray crystallography except in cases where other factors such as  $\pi$  bonding or special steric requirements of chelating ligands are clearly involved.

The first paper of this series<sup>3</sup> generated possible polyhedra for coordination numbers four through nine, inclusive, by considering maximum-symmetry polyhedra satisfying the relationships  $e + 2 = v + f$  (Euler's relationship),  $2e \geq 3f$ , and  $3v \leq 2e$ . The property of flexibility was next defined as the number of the 32 possible  $sp^3d^n$  combinations which can form the polyhedron in a fixed spatial orientation. It was shown that polyhedra with minimum flexibilities, maximum symmetries, and maximum numbers of faces are favored in actual complexes.

This paper examines the total interligand repulsions of the coordination polyhedra generated in the first paper of this series<sup>3</sup> in an attempt to develop a more quantitative basis for determining which coordination polyhedra are favored in various complexes. This work represents an extension and expansion of a treatment initiated by Gillespie<sup>4</sup> and further developed by others<sup>5,6</sup> for the particularly difficult case of seven coordination.

## Method

Consider a complex as a central metal atom surrounded by point charges corresponding to the centers of charge of the various metal–ligand bonds. These point charges are located at the vertices of the coordination polyhedron. In order to make the calculations as general as possible, assume that the distances of all point charges from the central metal atom are equal and that all of the charges have equal magnitudes; this idealized model may be called the equal-distances–equal-charges (EDEC) model. Assume further that the repulsion between the point charges corresponding to the ligands follows an inverse square law (Coulomb's law). The repulsion between ligands  $i$  and  $j$ ,  $f_{ij}$ , can thus be represented by

$$f_{ij} = \frac{ke_i e_j}{d_{ij}^2} \quad (1)$$

where  $e_i$  and  $e_j$  are the point charges corresponding

to the center of charge of the bonds of the central metal atom to ligands  $i$  and  $j$ , respectively,  $d_{ij}$  is the distance between the two point charges  $i$  and  $j$ , and  $k$  is a constant. However, the EDEC model requires that  $e_i = e_j = e$  for all  $i$  and  $j$ , which means that a new constant  $w = ke^2$  can be defined. Using the constant  $w$  eq 1 becomes

$$f_{ij} = \frac{w}{d_{ij}^2} \quad (2)$$

The locations of the point charges can be expressed by the coordinates  $r$ ,  $\eta$ ,  $\phi$  corresponding to the Cartesian coordinates as follows

$$x = r \cos \eta \cos \phi \quad (3a)$$

$$y = r \cos \eta \sin \phi \quad (3b)$$

$$z = r \sin \eta \quad (3c)$$

The coordinates  $r$  and  $\phi$  are identical with these coordinates in conventional spherical polar coordinates<sup>7</sup> and the new coordinate  $\eta$  is related to the  $\theta$  of spherical polar coordinates by the simple relationship  $\eta = \theta - 90^\circ$ . Since  $\eta$  and  $\phi$  correspond to the latitude and longitude of the earth represented by these coordinates, the coordinate system  $r$ ,  $\eta$ ,  $\phi$  will be called the *geodesic* coordinate system. The angular geodesic coordinates  $\eta$  and  $\phi$  for the coordination polyhedra examined in this study are listed in Table I. (Since the EDEC model requires  $r$  to be constant for all vertices, values for  $r$  are not given in Table I).

The distance between the point charges  $i$  and  $j$  in Cartesian coordinates is

$$d_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2} \quad (4)$$

Upon transformation into geodesic coordinates, eq 4 can be separated into a radial term and an angular term. Since the EDEC model requires  $r$  to remain constant the following equation is obtained

$$d_{ij} = r\sqrt{A_{ij}} \quad (5)$$

In eq 5 the angular term  $A_{ij}$  depends solely upon the angular geodesic coordinates  $\eta$  and  $\phi$ . Substituting eq

(7) Y. R. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience, New York, N. Y., 1950, p 12.

(1) For Part II of this series, see R. B. King, *J. Amer. Chem. Soc.*, **91**, 7217 (1969).

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969).

(4) R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960).

(5) D. Britton, *ibid.*, **41**, 1632 (1963).

(6) T. A. Claxton and G. C. Benson, *ibid.*, **44**, 157 (1966).

Table I. Angular Geodesic Coordinates for Coordination Polyhedra<sup>a</sup>

Polyhedron <sup>b</sup>	Angular geodesic coordinates of vertices <sup>a</sup>																			
	$\eta$									$\phi$										
	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9		
(A) Coordination number four																				
Planar square ( $D_{4h}$ )	0	0	0	0								0	90	180	270					
Tetrahedron ( $T_d$ )	90	-19	-19	-19								0	0	120	240					
(B) Coordination number five																				
Square pyramid ( $C_{4v}$ )	90	$\alpha$	$\alpha$	$\alpha$	$\alpha$							0	0	90	180	270				
Trigonal bipyramid ( $D_{3h}$ )	90	0	0	0	-90							0	0	120	240	0				
(C) Coordination number six																				
Trigonal prism ( $D_{3h}$ )	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$						0	120	240	0	120	240			
Irregular hexahedron ( $C_2$ )	0	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	0						0	$\beta$	$\beta + 180$	$\gamma$	$\gamma + 180$	180			
Diagonally deficient cube ( $C_{2v}$ )	$\beta$	$\beta$	$\beta$	$\beta$	$\alpha$	$\alpha$						0	90	180	270	0	180			
Octahedron ( $O_h$ )	0	0	0	0	90	-90						0	90	180	270	0	0			
(D) Coordinating number seven																				
7,11,6 polyhedron ( $C_2$ )	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\beta$					0	90	180	270	$\gamma$	$\gamma + 120$	$\gamma + 240$		
3-Capped trigonal prism ( $C_{3v}$ )	90	$\beta$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\alpha$					0	0	120	240	0	120	240		
4-Capped trigonal prism ( $C_{2v}$ )	0	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$					0	60	180	300	60	180	300		
7,14,9 polyhedron ( $C_2$ )	Same as 7,11,6 polyhedron <sup>c</sup>																			
Capped octahedron ( $C_{3v}$ )	90	$\beta$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\alpha$					0	0	120	240	60	180	300		
Pentagonal bipyramid ( $D_{5h}$ )	90	0	0	0	0	0	-90					0	0	72	144	216	288	0		
(E) Coordination number eight																				
Cube ( $O_h$ )	45	45	45	45	-45	-45	-45	-45				0	90	180	270	0	90	180	270	
8,13,7 polyhedron ( $C_{2v}$ )	45	$-\alpha$	45	$+\alpha$	45	$-\alpha$	45	$+\alpha$	-45	-45	-45	-45								
8,14,8-polyhedron ( $D_{2h}$ )	$\alpha$	$\alpha$	0	0	0	0	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$								
3,3-Bicapped trigonal prism ( $D_{3h}$ )	90	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	0	0	120	240	0	120	240	0	
Square antiprism ( $D_{4h}$ )	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	0	90	180	270	45	135	225	315	
4,4-Bicapped trigonal prism ( $C_{2v}$ )	0	0	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	60	300	0	120	240	0	120	240	
Bicapped octahedron ( $D_{3d}$ )	90	$\alpha$	$\alpha$	$\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	0	0	120	240	60	180	300	0	
"Dodecahedron" ( $D_{3d}$ )	$\alpha$	$\alpha$	$\beta$	$\beta$	$-\beta$	$-\beta$	$-\alpha$	$-\alpha$				0	180	90	270	0	180	90	270	
(F) Coordination number nine																				
Doubled trigonal prism ( $D_{3h}$ )	$\alpha$	$\alpha$	$\alpha$	0	0	0	$-\alpha$	$-\alpha$	$-\alpha$			0	120	240	0	120	240	0	120	240
Capped cube ( $C_{4v}$ )	90	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$		0	0	90	180	270	0	90	180	270
9,17,10 polyhedron ( $C_{2v}$ )	-90	$\alpha$	$\alpha$	$\alpha$	$\alpha$	45	$-\beta$	45	$+\beta$	45	$-\beta$	45	$+\beta$							
3,4,3-Tricapped trigonal prism ( $C_{2v}$ )	90	$\alpha$	$\alpha$	$\alpha$	0	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$		0	60	180	300	0	60	180	300	0
4-Capped square antiprism ( $C_{4v}$ )	90	$\alpha$	$\alpha$	$\alpha$	$\alpha$	$\beta$	$\beta$	$\beta$	$\beta$	$\beta$		0	0	90	180	170	45	135	225	315
4,4,4-Tricapped trigonal prism ( $C_{3h}$ )	$\alpha$	$\alpha$	$\alpha$	0	0	0	$-\alpha$	$-\alpha$	$-\alpha$	$-\alpha$		0	120	240	60	180	300	0	120	240

<sup>a</sup> See text for definitions of the geodesic coordinates. The geodesic coordinate  $r$  is always a constant. <sup>b</sup> The nomenclature of the polyhedra is similar to that used in R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969). <sup>c</sup> The 7,11,6 and 7,14,9 polyhedra have geodesic coordinates differing only in the values of  $\gamma$  relative to  $\alpha$  and  $\beta$ .

5 into eq 2 gives the following equation

$$f_{ij} = \frac{w}{r^2 A_{ij}} \quad (6)$$

However, since the EDEC model requires  $r$  to be constant for all  $i$  and  $j$ , it is possible to define a new constant  $K$  such that  $K = w/r^2$ . This gives the following equation

$$f_{ij} = \frac{K}{A_{ij}} \quad (7)$$

The total interligand repulsion in a metal complex,  $F$ , is the sum of the individual repulsions  $f_{ij}$  over all possible interactions, *i.e.*

$$F = \sum_{i=1}^v \sum_{j=i+1}^v f_{ij} \quad (8)$$

where  $v$  is the number of vertices in the coordination polyhedron under consideration. Substituting eq 7 into eq 8 and moving the constant  $K$  outside the summation signs gives

$$F = K \sum_{i=1}^v \sum_{j=i+1}^v \frac{1}{A_{ij}} \quad (9)$$

The repulsivity,  $\Upsilon$ , may then be defined according to the following equation:

$$\Upsilon = \sum_{i=1}^v \sum_{j=i+1}^v \frac{1}{A_{ij}} \quad (10)$$

The total interligand repulsion is thus directly proportional to the repulsivity, *i.e.*, (11). Calculation of the

$$F = K\Upsilon \quad (11)$$

repulsivity for various coordination polyhedra will give a direct indication of the relative favorability of various coordination polyhedra with minimum-repulsivity polyhedra being most favored.

In order to calculate the repulsivity for various coordination polyhedra it is necessary to evaluate the angular terms  $A_{ij}$ . Substituting the definitions of the geodesic coordinates (eq 3) into eq 4 and removing the radial terms as in eq 5 gives the following relationship after expansion and simplification by utilizing twice the relationship  $\sin^2 x + \cos^2 x = 1$

$$A_{ij} = 2 - 2 \cos \eta_j \cos \phi_j \cos \eta_i \cos \phi_i - 2 \cos \eta_j \sin \phi_j \cos \eta_i \sin \phi_i - 2 \sin \eta_j \sin \eta_i \quad (12)$$

This equation may also be expressed in the following form in order to minimize computer time by minimizing the use of the trigonometric functions

$$A_{ij} = 2 - [\cos(\eta_j - \eta_i) + \cos(\eta_j + \eta_i)][\cos(\phi_j + \phi_i)] - [\cos(\eta_j - \eta_i) - \cos(\eta_j + \eta_i)]$$

The requirement of the EDEC model that all metal-ligand distances are equal is equivalent to regarding the ligands as point charges on the surface of a sphere as done by previous workers.<sup>4-6</sup> In the cases of polyhedra of highest symmetry (tetrahedron, planar square, trigonal bipyramid, octahedron, pentagonal bipyramid, and cube), this requirement combined with the symmetry restrictions unambiguously defines a unique position of all ligands. However, in the case of polyhedra of intermediate symmetry (square pyramid,

trigonal prism, 4-capped trigonal prism, all eight-coordinate polyhedra *except* the cube and  $D_{2d}$  dodecahedron, the doubled trigonal prism, and the 3,4,3- and 4,4,4-tricapped trigonal prisms), even the combination of symmetry requirements and the location on the surface of a sphere is insufficient to define a unique position of all ligands. Instead, the angular geodesic coordinates (Table I) of these polyhedra can be expressed as a function of a single variable designated as  $\alpha$ . The repulsivity values for these polyhedra are defined as minimum repulsivities as  $\alpha$  is varied through the total possible range (generally  $0^\circ < \alpha < 90^\circ$ ). The complexity of the function relating repulsivity to  $\alpha$  made it unfeasible to determine the minimum repulsivity by analytical methods such as setting an appropriate derivative equal to zero and solving the resulting equation. Instead, repulsivity values were calculated as  $\alpha$  was varied in  $1^\circ$  increments throughout the range and the minimum value taken. The value of  $\alpha$  giving the minimum EDEC repulsivity value is designated as  $\psi$ .

Some still less symmetrical polyhedra presented even more severe problems, since even after imposing the requirements of their point group and of location on a spherical surface their coordinates required a function of two ( $\alpha, \beta$ ) or sometimes even three variables ( $\alpha, \beta, \gamma$ ). It was not feasible to calculate minimum repulsivity values by analytical minimization or by systematic variation of the two or more variables in sufficiently small increments; therefore, in most cases a relationship between the variables was assumed consistent with observed geometry and with a relatively large minimum interligand distance, thereby eliminating all of the variables except one in the geodesic coordinates of the polyhedron under consideration. Only in the case of the particularly important  $D_{2d}$  8,18,12 dodecahedron was the minimization carried out by alternate variation of both variables in  $1^\circ$  increments until a minimum repulsivity value was obtained; here the values of  $\alpha$  and  $\beta$  leading to the minimum repulsivity are designated as  $\psi_1$  and  $\psi_2$ , respectively.

The calculations of repulsivity and  $\psi$  values were carried out on the University of Georgia IBM 360/65 computer.

## Discussion

The repulsivity and  $\psi$  calculations summarized in Table II relate to the following two categories of empirical observations.

**I. The Favored Coordination Polyhedron for a Given Coordination Number.** If the EDEC model were strictly followed, the minimum-repulsivity polyhedron for a given coordination number would always be found. Deviations from the EDEC assumptions can change the repulsivities of different polyhedra for a given coordination number enough to change the minimum repulsivity polyhedron for a given type of complex. However, polyhedra with EDEC repulsivity values close to the minimum EDEC repulsivity value for a given coordination number are much more likely to become the minimum-repulsivity polyhedron by deviations from the EDEC assumptions than polyhedra with EDEC repulsivity values far above the minimum EDEC repulsivity value. Thus the ordering of EDEC repulsivity values gives an indication of the probability

Table II. EDEC Repulsivity and  $\psi$  Values for Various Coordination Polyhedra

Polyhedron <sup>a</sup>	$\Upsilon$	$\psi$ , deg	Assumptions
Coordination number four			
Planar square (D <sub>4h</sub> )	2.500		
Tetrahedron (T <sub>d</sub> )	2.250		
Coordination number five			
Square pyramid (C <sub>4v</sub> )	4.266	-14	
Trigonal bipyramid (D <sub>3h</sub> )	4.250		
Coordination number six			
Trigonal prism (D <sub>3h</sub> )	6.972	39	
Irregular hexahedron (C <sub>2</sub> )	7.185	47	$\beta = 60^\circ, \gamma = 120^\circ$
Diagonally deficient cube (C <sub>2v</sub> )	7.623	35	$\beta = -\alpha$
Octahedron (O <sub>h</sub> )	6.750		
Coordination number seven			
7,11,6 polyhedron (C <sub>s</sub> )	10.446	35	$\beta = -\alpha, \gamma = 45^\circ$
3-Capped trigonal prism (C <sub>3v</sub> )	10.793	46	$\beta = -\alpha/2$
3-Capped trigonal prism (C <sub>3v</sub> )	10.969	43	$\alpha = 29^\circ, \beta$ varied
4-Capped trigonal prism (C <sub>2v</sub> )	10.785	41	
7,14,6 polyhedron (C <sub>s</sub> )	10.446	35	$\beta = -\alpha, \gamma = 0$
Capped octahedron (C <sub>3v</sub> )	10.276	38	$\beta = -\alpha/2$
Pentagonal bipyramid (D <sub>5h</sub> )	10.250		
Coordination number eight			
Cube (O <sub>h</sub> )	15.667		
8,13,7 polyhedron (C <sub>2v</sub> )	15.658	7	
8,14,8 polyhedron (D <sub>2h</sub> )	14.783	58	
3,3-Bicapped trigonal prism (D <sub>3h</sub> )	15.754	29	
Square antiprism (D <sub>4d</sub> )	14.337	34	
4,4-Bicapped trigonal prism (C <sub>2v</sub> )	14.878	43	
Bicapped octahedron (D <sub>3d</sub> )	14.501	19	
"Dodecahedron" (D <sub>2d</sub> )	14.390	47	$\beta = \alpha/2$
"Dodecahedron" (D <sub>2d</sub> )	14.354	$\psi_1 = 51, \psi_2 = 19^\circ$	
Coordination number nine			
Doubled trigonal prism (D <sub>3h</sub> )	21.492	54	
Capped cube (C <sub>4v</sub> )	20.181	31	$\beta = -\alpha$
9,17,10 polyhedron (C <sub>2v</sub> )	23.664	5	$\alpha = 45^\circ, \beta$ varied
9,18,11 polyhedron (C <sub>3v</sub> )	20.560	51	$\beta = -\alpha$
3,4,3-Tricapped trigonal prism (C <sub>2v</sub> )	20.826	30	
4-Capped square antiprism (C <sub>4v</sub> )	19.780	28	$\beta = -\alpha$
4,4,4-Tricapped trigonal prism (D <sub>3h</sub> )	19.253	45	

<sup>a</sup> The terminology used in this table is similar to that used in R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969).

of finding a particular polyhedron for a given coordination number, with a lower repulsivity indicating a higher probability.

**II. The Relative Dimensions of Medium-Symmetry Coordination Polyhedra.** If the EDEC model were strictly followed, the coordinates of the medium-symmetry polyhedra actually found in complexes would correspond to the  $\psi$  values of the minimum-repulsivity polyhedra. Comparisons of corresponding angles found by X-ray crystallography in complexes with medium-symmetry coordination polyhedra with the calculated EDEC minimum-repulsivity  $\psi$  values provide indications as to how closely actual systems are approximated by the EDEC model.

With these general considerations in mind, the various coordination numbers can now be treated individually. A more detailed summary of the empirical data is given in the first paper of this series.<sup>3</sup>

**(1) Coordination Number Four.** The tetrahedron is the minimum-repulsivity polyhedron ( $\Upsilon = 2.250$ ) and is found in the majority of four-coordinate complexes. Deviations from the EDEC model can cause the higher EDEC repulsivity planar square ( $\Upsilon = 2.500$ ) to be the favored polyhedron in 16-electron four-coordinate complexes (d<sup>8</sup> transition metal derivatives).

**(2) Coordination Number Five.** The trigonal bipyramid is the minimum-repulsivity polyhedron ( $\Upsilon = 4.250$ ) and is found in the majority of five-coordinate complexes.<sup>8</sup> The square pyramid ( $\Upsilon = 4.266$ ) has

a repulsivity only slightly higher than that of the trigonal bipyramid and is also found in a significant number of five-coordinate derivatives.

Table III lists the  $\alpha$  values for a variety of square-pyramidal five-coordinate complexes. In general these complexes have widely different types of ligands as well as different metal-ligand distances; they thus deviate considerably from EDEC conditions. As might be expected, a rather large range of  $\alpha$  values is found for these complexes. The average  $\alpha$  values found for all of the square-pyramidal complexes except the vanadyl  $\beta$ -diketonates are somewhat less negative than the calculated  $\psi$  of  $-14^\circ$  for the square pyramid. This discrepancy may arise from  $\pi$  bonding between the metal atom and the four basal ligand atoms of the square pyramid, which places the metal atom closer to the plane of these four ligand atoms.

**(3) Coordination Number Six.** The octahedron is the minimum-repulsivity six-coordinate polyhedron ( $\Upsilon = 6.750$ ) and is found in all six-coordinate derivatives except for certain ethylenedithiolate complexes of the early and middle transition metals. These ethylenedithiolate complexes use the trigonal prism ( $\Upsilon = 6.972$ )<sup>9,10</sup> or, in one case, the 6,10,6 polyhedron

(8) E. L. Muetterties and R. A. Schuim, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

(9) R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 3776 (1965).

(10) E. I. Stiefel and H. B. Gray, *ibid.*, **87**, 4012 (1965).

Table III.  $\alpha$  Values for Some Square-Pyramidal Complexes<sup>a</sup>

Complex	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	Mean $\alpha^t$	Ref
(C <sub>14</sub> H <sub>13</sub> P) <sub>3</sub> PdBr <sub>2</sub>	-2	-1	-15	+6	-3	a
Re <sub>2</sub> Cl <sub>6</sub> <sup>2-</sup>	-4	-4	-4	-4	-4	b
Cu(salicyl-pn)(H <sub>2</sub> O)	+1	-9	-12	-3	-6	c
(triams)NiBr <sub>2</sub>	-2	-5	-3	-21	-8	d
[Cu(S <sub>2</sub> CNPr <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>	-8	-13	-6	-12	-10	e
Ni[CIC <sub>6</sub> H <sub>5</sub> (O)CH=NC <sub>2</sub> H <sub>4</sub> NEt <sub>2</sub> ] <sub>2</sub>	-15	-15	-10	-2	-10	f
[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P] <sub>3</sub> RuCl <sub>2</sub>	-3	-11	-11	-20	-11	g
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> Sb	-11	-14	-19	-5	-12	h
(CH <sub>3</sub> COCHCOCH <sub>3</sub> ) <sub>2</sub> VO	-16	-16	-16	-16	-16	i
(C <sub>6</sub> H <sub>5</sub> COCHCOCH <sub>3</sub> ) <sub>2</sub> VO	-17	-16	-14	-17	-16	j

<sup>a</sup> J. W. Collier, F. G. Mann, D. G. Watson, and H. R. Watson, *J. Chem. Soc.*, 1803 (1964). <sup>b</sup> F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965). <sup>c</sup> F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 2639 (1960). <sup>d</sup> G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc., London*, 415 (1960). <sup>e</sup> A. Pignedoli and G. Peyronel, *Gazz. Chim. Ital.*, **92**, 745 (1962). <sup>f</sup> L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Amer. Chem. Soc.*, **87**, 2059 (1965). <sup>g</sup> S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965). <sup>h</sup> P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964). <sup>i</sup> R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961). <sup>j</sup> P. K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, **43**, 1323 (1965). <sup>k</sup>  $\alpha$  values are given in degrees. <sup>t</sup> For comparison, the calculated EDEC  $\psi$  value for the square pyramid is  $-14^\circ$ .

( $\Upsilon = 7.185$ ).<sup>11</sup> The much higher repulsivity 6,11,7 polyhedron ( $\Upsilon = 7.623$ ) has not yet been found in six-coordinate complexes.

The observed<sup>9</sup>  $\alpha$  value of  $40.7^\circ$  for the trigonal prism in [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C<sub>2</sub>S<sub>2</sub>]<sub>3</sub>Re is relatively close to the EDEC  $\Upsilon$  value of  $39^\circ$  for this polyhedron.

**(4) Coordination Number Seven.** The coordination number seven has been the most difficult to treat by this method, as was found to be the case with previous methods.<sup>3,5,6</sup> In this work the difficulty arises from the relatively low symmetry of some of the seven-coordinate polyhedra, which leads to two or three independent variables among the angular geodesic coordinates. Thus for the 7,11,6 and 7,14,9 polyhedra the latitude of the four-ligand "belt" ( $\alpha$ ), the latitude of the three-ligand "belt" ( $\beta$ ), and the relative rotations of the ligands in the three- and four-ligand belts ( $\gamma$ ) are all independent variables. Since it was not feasible to vary two or three independent variables in sufficiently narrow steps over a sufficiently broad range, the minimum repulsivities were found with arbitrarily imposed relationships (see Table II) which eliminated all independent variables but one, which then could be varied over a sufficiently broad range in sufficiently narrow steps to seek minima. Thus the minimum repulsivities for these polyhedra given in Table II may not be the ultimate minima, as all combinations of  $\alpha$ ,  $\beta$ , and  $\gamma$  (where applicable) could not be systematically checked.

The minimum-repulsivity seven-coordinate polyhedron is the pentagonal bipyramid ( $\Upsilon = 10.250$ ) which is found in many actual seven-coordinate complexes.<sup>12</sup> The next lowest repulsivity seven-coordinate polyhedron is the C<sub>3v</sub> capped octahedron ( $\Upsilon = 10.276$ ) which is found in a few seven-coordinate complexes (e.g., NbOF<sub>6</sub><sup>13-</sup>).<sup>12</sup> The two tetragonal-base-trigonal-base polyhedra (7,14,9 and 7,11,6 polyhedra) have the next lowest repulsivities ( $\Upsilon = 10.446$ ); the 7,14,9 polyhedron is found in the monoclinic forms of ZrO<sub>2</sub> and HfO<sub>2</sub>.<sup>13</sup> Next on the repulsivity scale is the 4-capped trigonal prism ( $\Upsilon = 10.785$ ); a few complexes with this polyhedron are known.<sup>12</sup> Among the basic seven-coordinate polyhedra the 3-capped trigonal prism

(11) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3353 (1967).

(12) E. L. Muettterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(13) J. D. McCullough and K. N. Trueblood, *Acta Crystallogr.*, **12**, 507 (1959); D. K. Smith and H. W. Newkirk, *ibid.*, **18**, 983 (1965); J. Adam and M. D. Rogers, *ibid.*, **12**, 951 (1959).

(7,12,7 polyhedron) has the highest repulsivity ( $\Upsilon = 10.793$ ); no complexes with this polyhedron are known.<sup>12</sup>

**(5) Coordination Number Eight.** The two lowest repulsivity eight-coordinate polyhedra are the square antiprism ( $\Upsilon = 14.337$ ) and the D<sub>2d</sub> dodecahedron ( $\Upsilon = 14.354$ ). These two polyhedra are the ones almost always found in eight-coordinate complexes.<sup>12,14</sup> The next lowest repulsivity eight-coordinate polyhedra are the D<sub>3d</sub> bicapped octahedron ( $\Upsilon = 14.501$ ) and the D<sub>2h</sub> 8,14,8 polyhedron ( $\Upsilon = 14.783$ ), but these polyhedra cannot be formed by hybrids using only s, p, and d orbitals (zero permutivities).<sup>3</sup> Next on the repulsivity scale is the 4,4-bicapped trigonal prism ( $\Upsilon = 14.878$ ); this polyhedron is found in some lanthanide trihalides.<sup>15</sup>

The calculated EDEC  $\psi$  for the square antiprism is  $34^\circ$ . This compares favorably with observed  $\alpha$  values such as  $32.7^\circ$  for zirconium tetrakis(acetylacetonate)<sup>16</sup> and  $34.4^\circ$  for barium hydroxide octahydrate.<sup>17</sup> Similarly, Table IV compares the calculated EDEC  $\psi_1$  and

Table IV.  $\alpha$  and  $\beta$  Values for Some D<sub>2d</sub> Dodecahedral Complexes<sup>a</sup>

Complex	$\alpha$	$\beta$
(diars) <sub>2</sub> TiCl <sub>4</sub>	54	17
Na <sub>4</sub> Zr(C <sub>2</sub> O <sub>4</sub> ) <sub>4</sub> ·3H <sub>2</sub> O	55	17
K <sub>4</sub> Mo(CN) <sub>8</sub>	54	18
ThCl <sub>4</sub>	54	15
Minimum-repulsivity D <sub>2d</sub> dodecahedron	51	19

<sup>a</sup> These  $\alpha$  and  $\beta$  values were calculated from data presented in Table 3 of E. L. Muettterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 143 (1967). Complexes of bidentate ligands with abnormally small "bites" (e.g., O<sub>2</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup>) were omitted from consideration.

$\psi_2$  values of 51 and  $19^\circ$  of the D<sub>2d</sub> dodecahedron with the corresponding angles found in eight-coordinate complexes of this geometry; again, agreement is relatively good. In addition, the calculated EDEC  $\psi$  for the 4,4-bicapped trigonal prism is  $43^\circ$ , which is relatively close to the observed  $\alpha$  value of  $44.8^\circ$  for terbium trichloride, which utilizes this coordination polyhedron.<sup>15</sup>

(14) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

(15) J. D. Forrester, A. Zalkin, D. H. Templeton, and J. C. Wallman, *Inorg. Chem.*, **3**, 185 (1964).

(16) J. V. Silverton and J. L. Hoard, *ibid.*, **2**, 243 (1963).

(17) H. Manohar and S. Ramaseshan, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **119**, 357 (1964).

(6) **Coordination Number Nine.** The only nine-coordinate polyhedron found in molecular complexes is the 4,4,4-tricapped trigonal prism ( $T = 19.253$ ), which is also the minimum-EDEC-repulsivity polyhedron. The  $\alpha$  values of  $45.8$  and  $47.8^\circ$  for the two crystallographically independent  $\text{ReH}_9^{2-}$  ions in the unit cell of  $\text{K}_2\text{ReH}_9^{18}$  are relatively close to the calculated  $\psi$  value of  $45^\circ$  for this polyhedron.

(18) K. Knox and A. P. Ginsberg, *Inorg. Chem.*, **3**, 555 (1964); S. C. Abrahams, A. P. Ginsberg, and K. Knox, *ibid.*, **3**, 559 (1964).

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## Chemical Applications of Topology and Group Theory. IV. Polyhedra for Coordination Numbers 10–16<sup>1</sup>

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**Abstract:** A given polyhedron may be considered as a stack of parallel planes containing all of its vertices. Possible polyhedra of at least  $C_{2v}$  symmetry for coordination numbers up to 16 are generated by considering all possible combinations of parallel planes containing different numbers of vertices. An  $f$ -flexibility value for each possible polyhedron for coordination numbers 10–16, inclusive, is derived by considering the number of different  $sp^3d^5f^n$  hybrids which can form this polyhedron. Calculation of the relative Coulombic repulsions (repulsivities) for the more symmetrical polyhedra of coordination numbers 10 and 12 indicate the 4,4-bicapped square antiprism and regular icosahedron to be the minimum-repulsivity polyhedra for these coordination numbers.

The first paper of this series<sup>3</sup> generated possible polyhedra for coordination numbers four through nine, inclusive, by considering maximum-symmetry polyhedra with numbers of vertices ( $v$ ), edges ( $e$ ), and faces ( $f$ ) satisfying the relationships  $e + 2 = v + f$  (Euler's relationship),  $2e \geq 3f$ , and  $3v \leq 2e$ . Next the number of  $sp^3d^n$  hybrids which can form each polyhedron was considered in order to predict the relative tendencies for various polyhedra to be found in actual complexes. In an earlier paper of this series<sup>1</sup> the relative Coulombic repulsion energies were examined using a model with equal metal–ligand distances and equal ligand charges (EDEC model).

The purpose of this paper is the examination of possible polyhedra for coordination numbers 10–16. Some of these coordination numbers sometimes occur in lanthanide and actinide chemistry<sup>4</sup> and necessarily involve  $sp^3d^5f^n$  hybrids.

### Generation of Possible Polyhedra

The first step in the generation of possible polyhedra for coordination numbers 10–16 is the listing of all possible triads of  $v$ ,  $e$ , and  $f$  values<sup>5</sup> satisfying the following relationships.

(1) **Euler's relationship:**<sup>6</sup>  $e + 2 = v + f$ .

(1) For Part III of this series, see R. B. King, *J. Amer. Chem. Soc.*, **92**, 6455 (1970).

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969).

(4) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(5) The terminology and symbols in this paper are the same as those used in the first paper of this series (ref 3).

(6) B. Grünbaum, "Convex Polytopes," Interscience, New York, N. Y., 1967, pp 130–138.

(2) **Lower limit of  $e$  and  $f$  for a given  $v$ :**  $e \leq 2f$ . This relationship arises from the previously used<sup>3</sup> limitation of coordination polyhedra to those with triangular and quadrilateral faces and is more restrictive than the previously used relationship  $3v \leq 2e$ , which arises from the fact that in three-dimensional polyhedra each vertex must have an order of at least three. Combination with Euler's relationship gives the inequalities  $2v - 4 \geq f \geq v - 2$  and  $3v - 6 \geq e \geq 2v - 4$ , which are more restrictive than the previously used<sup>3</sup>  $2v - 4 \geq f \geq v/2 + 2$  and  $3v - 6 \geq e \geq 3v/2$ . Incidentally, it appears that even this more restrictive relationship  $e \leq 2f$  is not sufficient to exclude all polyhedra with faces with five or more sides (pentagonal, hexagonal, etc.) or divalent vertices, since it appears impossible to form the 9,14,7 polyhedron without at least one pentagonal face or divalent vertex.

(3) **Upper limit of  $e$  and  $f$  for a given  $v$ :**  $2e \geq 3f$ . This relationship is the same as that used in the earlier paper<sup>3</sup> and is based on the fact that each face must have at least three sides. It may be reasonable to introduce a limitation of a maximum order of five for a vertex. This would then define the upper limit more restrictively by the relationship  $2e \leq 5v$  and would exclude all triangulated polyhedra<sup>3</sup> for coordination numbers 13 and greater.

Using these relationships, triads of possible  $v$ ,  $e$ , and  $f$  values with  $10 \leq v \leq 16$  can be generated relatively easily. However, in many cases it is difficult to find actual polyhedra corresponding to a given triad of  $v$ ,  $e$ , and  $f$  values. In order to facilitate greatly the search for actual polyhedra the "parallel plane" method was used.