(6) **Coordination Number Nine.** The only nine-coordinate polyhedron found in molecular complexes is the 4,4,4-tricapped trigonal prism (Υ = 19.253), which is also the minimum-EDEC-repulsivity polyhedron. The α values of 45.8 and 47.8° for the two crystallographically independent ReH_9^{2-} ions in the unit cell of K_2ReH_9[18] are relatively close to the calculated ψ value of 45° 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[1]

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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[3] 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[1] 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[4] 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[5] satisfying the following relationships.

(1) **Euler's relationship:**[6] $e + 2 = v + f$.

(2) **Lower limit of e and f for a given v:** $e \leq 2f$. This relationship arises from the previously used[3] 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[3] $2v - 4 \geq f \geq v/2 + 2$ 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[3] 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[3] 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.

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[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.

Table I. Generation of Polyhedra from Parallel Planes of Points

Stack	Coord no.	Polyhedra[a]
13	4	4,6,4-T_d (tetrahedron)
14	5	5,8,5-C_{4v} (square pyramid)
22	4	4,6,4-T_d (tetrahedron)
24	6	6,11,7-C_{2v}
33	6	6,12,8-O_h (octahedron); 6,9,5-D_{3h} (trigonal prism)
44	8	8,16,10-D_{4d} (square antiprism); 8,12,6-O_h (cube)
131	5	5,9,6-D_{3h} (trigonal bipyramid)
133	7	7,15,10-C_{3v} (capped octahedron); 7,12,7-C_{3v} (3 capped trigonal prism)
141	6	6,12,8-O_h (octahedron)
142	7	7,13,8-C_{2v} (4-capped trigonal prism)
144	9	9,20,13-C_{4v}; 9,16,9-C_{4v}
151	7	7,15,10-D_{5h} (pentagonal bipyramid)
161	8	8,18,12-D_{6h} (hexagonal bipyramid)
162	9	9,19,12-C_{2v}; 9,17,10-C_{2v}
163	10	10,21,13-C_{3v}
164	11	11,24,15-C_{2v}; 11,22,13-C_{2v}
222	6	6,10,6-C_2
224	8	8,17,11-C_{2v} (4,4-bicapped trigonal prism)
242	8	8,14,8-D_{2h}
244	10	10,21,13-C_{2v}; 10,17,9-C_{2v}
252	9	9,21,14-C_{2v}; 9,19,12-C_{2v}; 9,17,10-C_{2v}; 9,15,8-C_{2v}
262	10	10,20,12-D_{2h}; 10,16,8-D_{2h}
264	12	12,23,13-C_{2v}
272	11	11,23,14-C_{2v}
282	12	12,26,16-D_{2h}
284	14	14,33,21-C_{2v}; 14,29,17-C_{2v}
313	7	7,13,8-C_{2v} (4-capped trigonal prism)
323	8	8,17,11-C_{2v} (4,4-bicapped trigonal prism)
333	9	9,21,14-D_{3h}; 9,18,11-C_{3v}; 9,15,8-D_{3h}
343	10	10,24,16-C_{2v}; 10,18,10-C_{2v}
353	11	11,27,18-C_{2v}; 11,23,14-C_{2v}; 11,19,10-C_{2v}
363	12	12,30,20-I_h; 12,24,14-O_h
373	13	13,29,18-C_{2v}; 13,27,16-C_{2v}; 13,25,14-C_{2v}
383	14	14,34,22-C_{2v}; 14,30,18-C_{2v}
414	9	9,16,9-C_{4v}
424	10	10,20,12-D_{4h}
434	11	11,19,10-C_{2v}
444	12	12,28,18-D_{4h}; 12,24,14-O_h; 12,20,10-D_{4h}
454	13	13,29,18-C_{2v}; 13,25,14-C_{2v}; 13,23,12-C_{2v}
464	14	14,34,22-D_{2h}; 14,26,14-D_{2h}
474	15	15,37,24-C_{2v}; 15,35,22-C_{2v}; 15,33,20-C_{2v}; 15,31,18-C_{2v}; 15,29,16-C_{2v}
484	16	16,32,18-D_{4h}
1331	8	8,18,12-D_{3d} (bicapped octahedron); 8,15,9-D_{3h} (3,3-bicapped trigonal prism)
1333	10	10,24,16-C_{3v}; 10,21,13-C_{3v}; 10,18,10-C_{3v}
1361	11	11,24,15-C_{3v}
1363	13	13,33,22-C_{3v}; 13,30,19-C_{3v}
1422	9	9,21,14-D_{3h}
1441	10	10,24,16-D_{4d}; 10,20,12-D_{4h}
1442	11	11,25,16-C_{2v}; 11,21,12-C_{2v}
1444	13	13,32,21-C_{4v}; 13,28,17-C_{4v}; 13,24,13-C_{4v}
1461	12	12,26,16-C_{2v}
1462	13	13,30,19-C_{2v}; 13,26,15-C_{2v}
1464	15	15,38,25-C_{2v}; 15,30,17-C_{2v}
1482	15	15,37,24-C_{2v}; 15,33,20-C_{2v}
1551	12	12,30,20-I_h (icosahedron); 12,25,15-D_{5h}
1661	14	14,36,24-D_{6d}(6,6-bicapped hexagonal antiprism); 14,30,18-D_{6h}
1622	11	11,27,18-C_{2v}; 11,25,16-C_{2v}
2222	8	8,18,12-D_{2d} ("dodecahedron")
2224	10	10,23,15-C_{2v}; 10,19,11-C_{2v}
2242	10	10,22,14-C_{2v}
2244	12	12,29,19-C_{2v}; 12,25,15-C_{2v}
2262	12	12,28,18-C_{2v}; 12,26,16-C_{2v}; 12,24,14-C_{2v}; 12,22,12-C_{2v}
2264	14	14,33,21-C_{2v}; 14,31,19-C_{2v}; 14,29,17-C_{2v}; 14,27,15-C_{2v}
2282	14	14,34,22-C_{3v}
2284	16	16,37,23-C_{2v}
2424	12	12,25,15-C_{2v}
2442	12	12,22,12-D_{2h}
2444	14	14,33,21-C_{2v}; 14,29,17-C_{2v}; 14,25,13-C_{2v}
2462	14	14,28,16-C_{2v}
2464	16	16,39,25-C_{2v}
2482	16	16,34,20-C_{2v}
2552	14	14,31,19-C_{2v}; 14,29,17-C_{2v}; 14,27,15-C_{2v}; 14,25,13-C_{2v}
2624	14	14,33,21-C_{2v}; 14,31,19-C_{2v}
2644	16	16,37,23-C_{2v}; 16,35,21-C_{2v}; 16,33,19-C_{2v}; 16,31,17-C_{2v}; 16,29,15-C_{2v}
2662	16	16,32,18-D_{2h}; 16,28,14-D_{2h}
3223	10	10,19,11-C_{2v}
3333	12	12,30,20-I_h (icosahedron); 12,27,17-D_{3h}; 12,24,14-O_h (cuboctahedron); 12,21,11-D_{3h}
3443	14	14,32,20-C_{2v}; 14,26,14-C_{2v}
3553	16	16,37,23-C_{2v}; 16,35,21-C_{2v}; 16,33,19-C_{2v}; 16,31,17-C_{2v}; 16,29,15-C_{2v}
4224	12	12,28,18-D_{2d}
4444	16	16,40,26-D_{4d}; 16,36,22-D_{4h}; 16,32,18-D_{4d}; 16,28,14-D_{4h}
13131	9	9,19,12-C_{2v}
13231	10	10,23,15-C_{2v}
13331	11	11,27,18-D_{3h}, 11,24,15-C_{3v}; 11,21,12-D_{3h}
13333	13	13,33,22-C_{3v}; 13,30,19-C_{3v}; 13,27,16-C_{3v}; 13,24,13-C_{3v}
13431	12	12,30,20-C_{2v}; 12,24,14-C_{2v}
13531	13	13,31,20-C_{2v}; 13,29,18-C_{2v}; 13,27,16-C_{2v}; 13,25,14-C_{2v}
13631	14	14,30,18-D_{2h}
13633	16	16,36,22-C_{2v}; 16,33,19-C_{3v}
13731	15	15,39,26-C_{3v}; 15,35,22-C_{2v}; 15,31,18-C_{2v}
13831	16	16,40,26-C_{2v}; 16,36,22-C_{2v}
13361	14	14,33,21-C_{3v}; 14,30,18-C_{3v}
14141	11	11,24,15-C_{2v}
14241	12	12,28,18-D_{4h}
14222	11	11,27,18-D_{3h}
14341	13	13,33,22-C_{2v}; 13,27,16-C_{2v}
14441	14	14,36,24-D_{4h}; 14,32,20-D_{4h}; 14,28,16-D_{4h}
14442	15	15,37,24-C_{2v}; 15,33,20-C_{2v}; 15,29,16-C_{2v}
14541	15	15,37,24-C_{2v}; 15,35,22-C_{2v}; 15,33,20-C_{2v}; 15,31,18-C_{2v}
14641	16	16,42,28-D_{2h}; 16,38,24-D_{2h}; 16,34,20-D_{2h}
14461	16	16,42,28-C_{2v}; 16,28,24-C_{2v}; 16,34,20-C_{2v}
15151	13	13,29,18-C_{2v}
15251	14	14,33,21-C_{2v}
15351	15	15,37,24-C_{2v}
15451	16	16,41,27-C_{2v}
16161	15	15,34,21-C_{2v}
16222	13	13,33,22-C_{2v}
16261	16	16,38,24-D_{2h}
22222	10	10,20,12-D_{4h}
22422	12	12,30,20-D_{2h}
24222	12	12,28,18-C_{2v}
22522	13	13,31,20-C_{2v}
22622	14	14,36,24-D_{2h}; 14,32,20-C_{2v}
26222	14	14,32,20-C_{2v}
22722	15	15,37,24-C_{2v}; 15,33,20-C_{2v}
22822	16	16,34,20-D_{2h}
28222	16	16,38,24-C_{2v}
22442	14	14,30,18-C_{2v}
22244	14	14,31,19-C_{2v}
24242	14	14,30,18-D_{2h}
22424	14	14,33,21-C_{2v}
24224	14	14,33,21-C_{2v}
22462	16	16,36,22-C_{2v}
22642	16	16,36,22-C_{2v}
33333	15	15,39,26-D_{3h}; 15,36,23-C_{2v}; 15,33,20-D_{3h}; 15,30,17-C_{3v}; 15,27,14-D_{3h}
33433	16	16,42,28-C_{2v}; 16,36,22-C_{2v}; 16,30,16-C_{2v}
42224	14	14,32,20-D_2
42324	15	15,31,18-C_{2v}
42424	16	16,36,22-D_{2h}

[a] In general, each polyhedron is identified by its v, e, and f values and its point group: R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969). Common names of polyhedra are given in parentheses.

Table II. Possible Polyhedra for Coordination Numbers 10–16, Inclusive

Polyhedron	No. of elements[a]			Face type		Types of vertices[a]				Point group	s	x_d	x_f
	v	e	f	t	q	j_3	j_4	j_5	j_6				
(A) Coordination number 10													
Dualized square antiprism	10	16	8	0	8	8	2	0	0	D_{4d}	16	1	1
244 stack	10	17	9	2	7	6	4	0	0	C_{2v}	4	0	2
1333 stack	10	18	10	4	6	4	6	0	0	C_{3v}	6	1	2
2224 stack	10	19	11	6	5	4	4	2	0	C_{2v}	4	0	4
Bicapped cube	10	20	12	8	4	0	12	0	0	D_{4h}	16	0	1
Staggered 1333 stack	10	21	13	10	3	1	6	3	0	C_{3v}	6	1	2
2242 stack	10	22	14	12	2	2	2	6	0	C_{2v}	4	1	2
3,3,4,4-Tetracapped trigonal prism	10	23	15	14	1	2	2	4	2	C_{2v}	4	1	2
4,4-Bicapped square antiprism	10	24	16	16	0	0	2	8	0	D_{4d}	16	1	1
(B) Coordination number 11													
b	11	18	9	0	9	8	3	0	0	C_{2v}	4	1	4
434 stack	11	19	10	2	8	8	2	0	1	C_{2v}	4	1	2
Distorted 11,18,9 polyhedron	11	20	11	4	7	4	7	0	0	C_{2v}	4	1	4
13331 stack	11	21	12	6	6	2	9	0	0	D_{3h}	12	1	1
164 stack	11	22	13	8	5	2	8	0	1	C_{2v}	4	1	4
272 stack	11	23	14	10	4	0	9	2	0	C_{2v}	4	0	2
Staggered 13331 stack	11	24	15	12	3	2	3	6	0	C_{3v}	6	1	1
1442 stack	11	25	16	14	2	2	1	8	0	C_{2v}	4	1	4
Staggered 164 stack	11	26	17	16	1	0	4	6	1	C_{2v}	4	1	4
Pentacapped trigonal prism	11	27	18	18	0	2	3	0	6	D_{3h}	12	1	1
(C) Coordination number 12													
444 stack	12	20	10	0	10	8	4	0	0	D_{4h}	16	0	0
3333 stack	12	21	11	2	9	6	6	0	0	D_{3h}	12	1	1
2442 stack	12	22	12	4	8	4	8	0	0	D_{2h}	8	0	0
264 stack	12	23	13	6	7	6	2	4	0	C_{2v}	4	1	2
Cuboctahedron	12	24	14	8	6	0	12	0	0	O_h	48	1	1
5,5-Bicapped pentagonal prism	12	25	15	10	5	0	10	2	0	D_{5h}	20	1	1
282 stack	12	26	16	12	4	0	8	4	0	D_{2h}	8	0	0
Bistaggered 3333 stack	12	27	17	14	3	0	6	6	0	D_{3h}	12	1	1
Tetracapped cube	12	28	18	16	2	0	4	8	0	D_{4h}	16	1	2
Staggered 2244 stack	12	29	19	18	1	1	6	2	4	C_{2v}	4	1	8
Icosahedron	12	30	20	20	0	0	0	12	0	I_h	120	1	1
(D) Coordination number 13													
454 stack	13	22	11	0	11	8	5	0	0	C_{2v}	4	1	4
454 stack	13	23	12	2	10	6	7	0	0	C_{2v}	4	1	4
1444 stack	13	24	13	4	9	4	9	0	0	C_{4v}	8	0	0
33133 stack	13	25	14	6	8	6	3	4	0	C_{2v}	4	1	2
24142 stack	13	26	15	8	7	4	5	4	0	C_{2v}	4	1	2
3-Capped cuboctahedron	13	27	16	10	6	1	9	3	0	C_{3v}	6	1	2
4-Capped cuboctahedron	13	28	17	12	5	0	9	4	0	C_{4v}	8	1	2
4,5,5-Tricapped pentagonal prism	13	29	18	14	4	1	7	6	0	C_{2v}	4	1	2
Bistaggered 13333 stack	13	30	19	16	3	1	3	9	0	C_{3v}	6	1	2
Staggered 454 stack	13	31	20	18	2	0	7	2	4	C_{2v}	4	1	4
Bistaggered 1444 stack	13	32	21	20	1	0	5	4	4	C_{4v}	8	1	2
Capped icosahedron	13	33	22	22	0	1	0	9	3	C_{3v}	6	1	2
(E) Coordination number 14													
Dualized cuboctahedron	14	24	12	0	12	8	6	0	0	O_h	48	1	0
2444 stack	14	25	13	2	11	8	4	2	0	C_{2v}	4	1	0
464 stack	14	26	14	4	10	8	2	4	0	D_{2h}	8	1	0
133331 stack	14	27	15	6	9	2	12	0	0	D_{3h}	12	1	0
14441 stack	14	28	16	8	8	0	14	0	0	D_{4h}	16	0	0
2444 stack	14	29	17	10	7	2	8	4	0	C_{2v}	4	1	4
3,3-Bicapped cuboctahedron	14	30	18	12	6	2	6	6	0	D_{3h}	12	1	0
2264 stack	14	31	19	14	5	2	6	4	2	C_{2v}	4	1	0
4,4-Bicapped cuboctahedron	14	32	20	16	4	0	6	8	0	D_{4h}	16	1	0
Bistaggered 133331 stack	14	33	21	18	3	2	0	12	0	D_{3h}	12	1	0
Staggered 464 stack	14	34	22	20	2	0	6	4	4	D_{2h}	8	1	0
Bistaggered 33233 stack	14	35	23	22	1	$(2j_7)$	8	0	4	C_{2v}	4	1	4
6,6-Bicapped hexagonal antiprism	14	36	24	24	0	0	0	12	2	D_{6d}	24	1	0
(F) Coordination number 15													
474 stack	15	26	13	0	13	8	7	0	0	C_{2v}	4	1	0
33333 stack	15	27	14	2	12	6	9	0	0	D_{3h}	12	1	1
4-Capped dualized cuboctahedron	15	28	15	4	11	6	7	2	0	C_{2v}	4	1	0
14442 stack	15	29	16	6	10	8	1	6	0	C_{2v}	4	1	0
Staggered 33333 stack	15	20	17	8	9	3	9	3	0	C_{3v}	6	1	1
25152 stack	15	31	18	10	8	2	9	4	0	C_{2v}	4	1	0
474 stack	15	32	19	12	7	2	9	2	2	C_{2v}	4	1	0
Bistaggered 33333 stack	15	33	20	14	6	0	9	6	0	D_{3h}	12	1	1
16161 stack	15	34	21	16	5	0	9	4	2	C_{2v}	4	1	0
474 stack	15	35	22	18	4	0	8	4	3	C_{2v}	4	1	0
Tristaggered 33333 stack	15	36	23	20	3	0	6	6	3	C_{3v}	6	1	1
Bistaggered 1331331 stack	15	37	24	22	2	2	1	8	4	C_{2v}	4	1	0
Bistaggered 1464 stack	15	38	25	24	1	0	5	4	6	C_{2v}	4	1	0
Omnistaggered 33333 stack	15	39	26	26	0	0	6	0	9	D_{3h}	12	1	1

Table II (*Continued*)

Polyhedron	No. of elements[a] v	e	f	Face type t	q	Types of vertices[a] j_3	j_4	j_5	j_6	Point group	s	x_d	x_f
(G) Coordination number 16													
4444 stack	16	28	14	0	14	8	8	0	0	D_{4h}	16	0	0
3553 stack	16	29	15	2	13	6	10	0	0	C_{2v}	4	1	0
24442 stack	16	30	16	4	12	4	12	0	0	D_{2h}	8	1	0
3553 stack	16	31	17	6	11	4	10	2	0	C_{2v}	4	1	0
Staggered 4444 stack	16	32	18	8	10	8	0	8	0	D_{4d}	16	1	1
13633 stack	16	33	19	10	9	4	6	6	0	C_{3v}	6	1	0
24442 stack	16	34	20	12	8	4	4	8	0	D_{2h}	8	1	0
1332331 stack	16	36	21	14	7	2	8	4	2	C_{2v}	4	1	0
Bistaggered 4444 stack	16	36	22	16	6	0	8	8	0	D_{4h}	16	1	0
3553 stack	16	37	23	18	5	0	6	10	0	C_{2v}	4	1	0
16261 stack	16	38	24	20	4	0	6	8	2	D_{2h}	8	1	0
	16	39	25	22	3								
Omnistaggered 4444 stack	16	40	26	24	2	0	8	0	8	D_{4d}	16	1	1
15451 stack	16	41	27	26	1	0	4	6	6	C_{2v}	4	1	0
Omnistaggered 14641 stack	16	42	28	28	0	0	4	4	8	D_{2h}	8	1	0

[a] The terminology used in this table is the same as in R. B. King, *J. Amer. Chem. Soc.*, **91,** 7211 (1969). [b] A map of this 11,18,9 polyhedron is given by H. S. M. Coxeter, "Regular Polytopes," 2nd ed, Macmillan, New York, N. Y., 1963, p 8, Figure 1.5A.

In the parallel plane method each coordination polyhedron may be considered as a stack of parallel planes such that the donor atoms of each ligand are in one of the parallel planes. A set of numbers may be assigned to each coordination polyhedron designating the number of ligands in each of the parallel planes starting from the top plane and proceeding in sequence to the bottom plane. In this manner, the octahedron can be considered as a 141 stack, the pentagonal bipyramid as a 151 stack, the 8,14,8 polyhedron as a 242 stack, etc.

In order to use the parallel plane method for generating coordination polyhedra, series of integers are generated which can correspond to the number of ligands in each parallel plane of a coordination polyhedron as described above. In order to restrict the possibilities to a manageable number, only sequences of numbers generating polyhedra of C_{2v} or higher symmetry are considered. The following desired attributes of the coordination polyhedra restrict the allowed sequences of integers as follows.

(1) **Only triangular and quadrilateral faces:** the integers at both ends of the sequence cannot be greater than four.

(2) **An order of all vertices of at least three:** the pairs 12 and 23 are not allowed at either end of the sequence since they would give rise to a vertex with an order of only two.

(3) **Avoidance of excessive interligand repulsion:** no more than eight ligands can be in one plane.

(4) **Generation of polyhedra of C_{2v} or greater symmetry:** in order to generate polyhedra of at least C_{2v} symmetry, one of the two following conditions must be satisfied. (a) The lowest common multiple of the nonterminal integers must be greater than one. In general, the order of any rotation axis greater than two will be reflected in the lowest common multiple of the nonterminal integers of the sequence defining the polyhedron. (b) The sequence must remain unchanged when reversed. This generates a C_2 axis.

Table I lists sequences of five or fewer integers defining stacks of parallel planes which generate possible coordination polyhedra of C_{2v} or greater symmetry. All of the polyhedra discussed in the first paper of the series[3] show up somewhere in Table I. Furthermore, Table I contains polyhedra corresponding to almost all of the possible v, e, f triads for polyhedra for coordination numbers 10–16, inclusive.

Table II lists the coordination polyhedra for coordination numbers 10–16, inclusive, according to their v, e, and f values in a manner very similar to the listing in Table I of the first paper of this series[3] for coordination numbers 4–9, inclusive.

A detailed inspection of Table I indicates that sequences with three or more ligands in two successive planes can correspond to more than one coordination polyhedron depending upon the relative rotation of the sets of ligands in the successive planes. The "normal" arrangement is considered to be that in which the relative rotation of the ligands in the successive planes maximizes the number of quadrilateral faces between the two planes. In cases where the numbers of ligands in the two successive planes are the same, the "normal" arrangement is that in which the corresponding ligands are directly on "top" of each other, *i.e.*, have the same geodesic ϕ coordinates.[1,7] Staggered arrangements of the ligands in two parallel planes are those with more triangular faces between the two planes than the "normal" arrangement. In cases of two successive parallel planes with the same number of ligands the staggered arrangements have only triangular faces between the two planes in question and maximize the minimum difference between the geodesic ϕ coordinates[1,7] of any ligand in one plane and any ligand in the other plane. In the case of the relatively simple 44 stack the normal arrangement corresponds to the 8,12,6 cube and the staggered arrangement to the 8,16,10 square antiprism. In cases where more than one pair of adjacent parallel planes, each with three or more ligands, exist, the terms "staggered," "bistaggered," "tristaggered," . . . , "omnistaggered" are used to differentiate between polyhedra corresponding to the same stack but differing in the occurrence of staggering between adjacent planes. Thus, in a bistaggered stack the relative rotations of the ligands in *two pairs* of parallel planes each correspond to the staggered arrangement as defined above.

The following are additional characteristics of the parallel plane method for generating polyhedra. (1)

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(7) In this discussion the geodesic coordinate system is oriented to give all of the ligands in the same plane the same geodesic η coordinates.

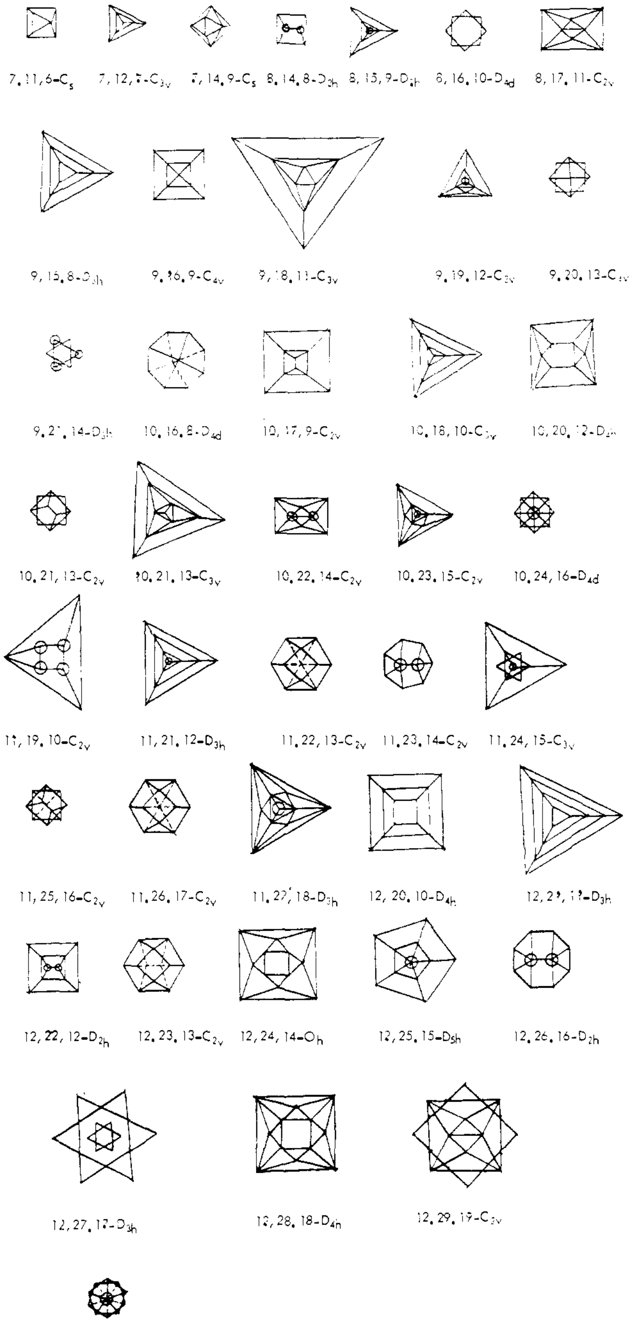

Figure 1. Two-dimensional representations of some coordination polyhedra.

Polyhedra of high symmetry, particularly those belonging to the O_h and I_h point groups, may be represented by more than one sequence of numbers depending upon which rotation axis is normal to the set of parallel planes of ligands. Thus the octahedron corresponds either to the 141 stack or the staggered 33 stack. (2) Pairs of different polyhedra can be found with the same triad of v, e, and f values but belonging to two different point groups, neither of which is a subgroup of the other. The simplest such pair is the 7,15,10-D_{5h} pentagonal bipyramid (151 stack) and the 7,15,10-C_{3v} capped octahedron (staggered 133 stack). In Table II only the polyhedron of such a pair with the largest number of symmetry elements is listed.

The parallel plane method generated some polyhedra for coordination numbers below ten that were not discussed in the first paper of this series.[3] The C_{3v} 9,18,11 polyhedron (staggered 333 stack; unit flexibility and permutivity[3]) was found, which is of higher symmetry than the C_s 9,18,11 polyhedron listed in the first paper. The D_{3d} 8,18,12 bicapped octahedron (staggered 1331 stack) is of higher symmetry than the D_{2d} 8,18,12 dodecahedron. The zero permutivity of the bicapped octahedron as contrasted with the unit permutivity of the less symmetrical D_{2d} dodecahedron accounts for the fact that the D_{2d} dodecahedron rather than the more symmetrical D_{3d} bicapped octahedron is the triangulated eight-coordinate polyhedron found in actual complexes, except possibly for certain uranyl derivatives.

Many of the polyhedra encountered in this work were very difficult to visualize and draw in two dimensions. In order to facilitate working with these polyhedra Schlegel diagrams[8] and/or two-dimensional projections looking along the highest rotational axis were used. The Schlegel diagrams had the advantage of depicting individually each edge and vertex, whereas the projections made clearer some of the symmetry elements. Two-dimensional representations combining some of the features of both actual projections and Schlegel diagrams were most useful in this work; some of these two-dimensional representations for the more important polyhedra encountered in this work are given in Figure 1. In this figure an apparently single vertex corresponding to two overlapping vertices from a projection is circled. Several of these polyhedra have been depicted in a recent review.[9]

Discussion

In the cases of polyhedra for coordination numbers nine or less, the flexibility[3] was used as a crude indicator of the relative tendencies for different polyhedra to occur in coordination complexes. In this context flexibility was defined as the number of different sp^3d^n hybrids corresponding to a fixed spatial orientation of the polyhedron.

Analogous concepts can be used for the evaluation of polyhedra for coordination numbers ten or greater. The f-flexibility (x_f) may be defined as the number of $sp^3d^5f^n$ hybrids corresponding to a fixed orientation of such a polyhedron in space. The d-flexibility (x_d) is defined analogous to the flexibility[3] (x) of polyhedra of coordination numbers nine or less: it thus refers to the number of sp^3d^5 combinations in the hybrid corresponding to a fixed spatial orientation of a polyhedron of coordination number ten or greater. Since only one sp^3d^5 combination is possible, the value for the d-flexibility can only be zero or one. A zero d-flexibility for polyhedra for coordination number ten or greater means that all five d orbitals cannot be included along with the s and three p orbitals in the hybrid for the polyhedron. Similarly, a unit d-flexibility for such a polyhedron means that all five d orbitals as well as the s and three p orbitals can be included in the hybrid for the polyhedron. A zero f-flexibility for a polyhedron means that the polyhedron cannot be formed by a $sp^3d^5f^n$ hybrid (or by a $sp^3d^yf^z$ hybrid, where y, the

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(8) Reference 6, pp 42–46.
(9) Reference 4, pp 179–180.

maximum number of d orbitals in the hybrid, is less than five in cases of polyhedra of zero d-flexibility).

Presently known chemistry suggests that the higher the nodality of atomic orbitals the less likely they are to participate in forming hybrid orbitals. Thus, with the exception of the dsp^2 square-planar hybrid, the binodal d orbitals are only involved in forming hybrid orbitals after all three mononodal p orbitals and the anodal s orbital are utilized. In a similar manner the trinodal f orbitals are much less likely to be involved in the coordination hybrid than even the binodal d orbitals; presently available chemistry[3,4,10] supports this assumption except for certain complexes of the lighter actinides such as uranium.[11] Tetranodal g orbitals are completely unavailable for bonding in currently available chemical elements.

These definitions and assumptions permit applications of the d-flexibility and f-flexibility criteria as follows. (1) Polyhedra requiring g orbitals ($x_f = 0$) are impossible since g orbitals are not available at all. (2) Polyhedra using f orbitals but not all of the d orbitals ($x_d = 0$, $x_f \neq 0$) are very unfavorable (except possibly for complexes of the lighter actinides) since d orbitals are more readily involved in bonding than f orbitals. (3) In the cases of polyhedra with nonzero d-flexibilities and f-flexibilities, the polyhedron with the minimum f-flexibility will probably be the most favored for reasons similar to the favoring of minimum nonzero flexibility polyhedra for coordination numbers nine or below.[3]

The d-flexibility and f-flexibility values for the various coordination polyhedra listed in Table II were obtained by conventional group theoretical methods[12] using Table I of Kettle and Smith[13] for the transformation properties of the various f orbitals[14] under the operations of the various point groups. In view of the relative lack of empirical data on complexes of coordination number ten or greater[4] as well as the complexity of the problem, no attempt was made to look specifically at the 128 possible $sp^3d^5f^n$ combinations as was done in the first paper of this series[3] for the 32 possible sp^3d^n combinations.

The preceding paper of this series[1] demonstrates the value of relative Coulombic repulsion energies (repulsivities) in an EDEC (point charges on a sphere) model for determining which coordination polyhedra are favored. Similar repulsivity calculations are difficult for many of the polyhedra for coordination numbers ten or greater owing to the presence of several variables in their geodesic coordinates.[1] A few repulsivity calculations (Table III) were made for some of the more symmetrical polyhedra of coordination numbers 10 and 12. Fortunately, the relatively tractable cases covered in Table III include the observed polyhedra for almost all known 10- and 12-coordinate complexes.[4]

With these general considerations in mind, the predictions for coordination numbers greater than nine can be compared with relevant empirical observations.

Table III. Repulsivity and ψ Values of Various Polyhedra for Coordination Numbers 10 and 12

Polyhedron[a]	No. of elements[a] v	e	f	Υ^b	ψ,[b] deg
Coordination number 10					
Bicapped cube (D_{4h})	10	20	12	25.738	29
3,3,4,4-Tetracapped trigonal prism (C_{2v})	10	23	15	26.214	31
4,4-Bicapped square antiprism (D_{4d})	10	24	16	25.042	25
Coordination number 12					
444 stack (D_{4h})	12	20	10	41.459	50
Cuboctahedron (O_h)	12	24	14	39.500	45
5,5-Bicapped pentagonal prism (D_{5h})	12	25	15	39.382	28
282 stack (D_{2h})	12	26	16	42.513	63
Icosahedron (I_h)	12	30	20	39.005	27

[a] The terminology in these columns of this table is the same as given in R. B. King, *J. Amer. Chem. Soc.*, **91**, 7211 (1969). [b] The terminology in these columns of this table is the same as given in R. B. King, *J. Amer. Chem. Soc.*, **92**, 6455 (1970).

(1) Coordination Number 10. The triangulated 10-coordinate polyhedron of maximum symmetry is the 10,24,16-D_{4d} 4,4-bicapped square antiprism similar to that formed by the ten boron atoms in $B_{10}H_{10}^{2-}$. This polyhedron has the favored d-flexibility and f-flexibility values of unity as well as the minimum repulsivity value for the three 10-coordinate polyhedra investigated (Table III). This polyhedron is found in polymeric uranium(IV) acetate.[15] The staggered 244-stack 10,-21,13 polyhedron ($x_d = 1$, $x_f = 2$) is found in lanthanum ethylenediaminetetracetate tetrahydrate[16] and in ytterbium diantimonide;[17] it is a lower symmetry 10,21,13 polyhedron than the C_{3v} staggered 1333 stack listed in Table II.

(2) Coordination Number 11. The triangulated 11-coordinate polyhedron of maximum symmetry is the D_{3h} 11,27,18 pentacapped trigonal prism which also has favored d-flexibility and f-flexibility values of unity but which has the possibly unfavorable feature of six vertices of order six. The C_{2v} 11,26,17 staggered 164 stack has all but one triangular faces and has only one vertex of order six; a somewhat distorted version of this polyhedron was recently[18] found in the thorium complex $Th(NO_3)_4 \cdot 5H_2O$. No other 11-coordinate complexes appear to have been characterized.

(3) Coordination Number 12. The regular icosahedron is an unusually favorable coordination polyhedron since it has the maximum possible symmetry, unit d-flexibility and f-flexibility, minimum repulsivity of the 12-coordinate polyhedra investigated (Table III), and no vertices with order higher than five. It therefore is not at all surprising that all molecular 12-coordinate complexes utilize the icosahedron.[4]

(4) Coordination Numbers Greater than 12. No unambiguous examples of coordination numbers greater than 12 are known except for closely packed metallic structures where the definition of coordination number is a semantic one when factors not considered in this series of papers are involved in bonding.[4] This is con-

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(10) For evidence of the very minor involvement of the f orbitals in the bonding of metal carbonyls, see R. B. King, *Inorg. Nucl. Chem. Lett.*, 5, 905 (1969).

(11) R. E. Connick and Z. Z. Hugus, Jr., *J. Amer. Chem. Soc.*, 74, 6012 (1952).

(12) For a summary of these techniques, see F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963.

(13) S. F. A. Kettle and A. J. Smith, *J. Chem. Soc. A*, 688 (1967).

(14) (a) H. G. Friedman, G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, 41, 354 (1964); (b) C. Becker, *ibid.*, 41, 358 (1964).

(15) I. Jelenic, D. Grdenić, and A. Bezjak, *Acta Crystallogr.*, 17, 758 (1964).

(16) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 87, 1611 (1965).

(17) R. Wang, R. Bodnar, and H. Steinfink, *Inorg. Chem.*, 5, 1468 (1966).

(18) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, 20, 836 (1966); J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *ibid.*, 20, 842 (1966).

sistent with the fact that the 12-coordinate icosahedron is such a favorable coordination polyhedron that it is likely to be nearly impossible to add further ligands to a 12-coordinate system. Even though 12 may be the maximum coordination number for any complex other than a close-packed metallic structure, the following observations based on the information presented in Table II are given below.

a. Coordination Number 13. None of the polyhedra have very high symmetries and all except one have nonzero d- and f-flexibilities.

b. Coordination Number 14. Although several relatively symmetrical polyhedra are found, surprisingly few polyhedra have nonzero f-flexibilities. Furthermore, the only polyhedra with nonzero f-flexibilities have only C_{2v} symmetry.

c. Coordination Number 15. The only polyhedra with nonzero f-flexibilities all have five parallel planes with three ligands each and a threefold rotational axis.

d. Coordination Number 16. Few polyhedra with nonzero f-flexibilities occur. Conspicuous among these few polyhedra are the two D_{4d} polyhedra with at least one staggered pair of four-ligand planes, *i.e.*, a "built-up" version of the square antiprism which is a favorable polyhedron for coordination number eight.

In view of the uncertainty whether molecular complexes with coordination numbers greater than 12 will ever be prepared, it appears inappropriate to attempt to derive any chemical conclusions or predictions at the present time from the above observations concerning possible polyhedra for these very high coordination numbers.

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Kinetic Studies of the Racemization of Optically Active (Amino acidato)triethylenetetraminecobalt(III) Complexes. *cis*-β_2-*l*-(Phenylalaninato)(triethylenetetramine)cobalt Iodide and *cis*-β_2-*d*- and -*l*-(L-Prolinato)(triethylenetetramine)cobalt Iodides in Aqueous Solutions

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Abstract: Some optically active (L-amino acidato)triethylenetetraminecobalt iodides (abbreviated *cis*-β_2-[Co(trien)-(L-AA)]I_2) have been prepared, and the loss of optical rotation of aqueous solutions containing these compounds has been studied. Possible structural changes which occur in the overall racemization may include (a) change in relative configuration of the triethylenetetramine ligand about the cobalt atom with respect to the amino acid ligand, (b) racemization of the asymmetric secondary planar amino in the trien group, (c) displacement of various ligands about the Co by water or hydroxyl ions, and (d) racemization of the asymmetric carbon atom in the amino acid. The kinetics of the racemization have been studied by measuring the optical rotation, ellipticity (CD), and absorption spectra as a function of time and by studying the influence on these racemization *vs.* time curves of pH, charcoal, and the variation of the type of amino acid in the initial reactant. From these measurements a mechanism for racemization is proposed and the relative rates of the various steps in the mechanism are deduced for the various conditions.

The optically active compounds *cis*-β_2-*l*-[Co(trien)-(L-phala)]I_2, *cis*-β_2-*l*-[Co(trien)(L-prol)]I_2, and *cis*-β_2-*d*-[Co(trien)(L-prol)]I_2 have been prepared, and the loss of optical rotation and of ellipticity of aqueous solutions containing these compounds has been studied.[2] One of the features of these complexes is that they have three centers of optical activity, the first due to the arrangement of the quadridentate trien ligand with respect to the other two ligand positions about the cobalt, the second due to the asymmetric carbon of the amino acid, and the third due to the asymmetric secondary planar amine of the trien group. Hence they can go through several types of molecular changes in the process of racemization. In this work we try to delineate the various changes occurring during racemization as well as the relative rates of these changes. Besides yielding information relating structure and chemical activity of these rather complex systems it is hoped that these metal complexes may serve as chemical and optical models for even more complicated enzymatic systems which are potentiated by metal ions.[3]

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[2] The following abbreviations will be used: trien = triethylenetetramine = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, phala = phenylalaninato = $(C_6H_5)CH_2CH(NH_2)COO^-$, prol = prolinato = $\underline{NHCH_2CH_2CH_2CH}COO^-$, ala = alinato = $CH_3CH(NH_2)COO^-$.

[3] (a) J. P. Collman and D. A. Buckingham, *J. Amer. Chem. Soc.*,