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Coordination Polyhedra with Nine and Ten Atoms¹

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An irregular nine-coordinate polyhedron may be characterized by comparing it to two polytopal nine-coordinate polyhedra, the D_{3h} tricapped trigonal prism and the C_{4v} monocapped square antiprism. An irregular ten-coordinate polyhedron may be characterized by comparing it to two polytopal ten-coordinate polyhedra, the D_{4d} bicapped square antiprism and a C_{2v} decatetrahedron which is closely related to the Hoard dodecahedron. A sensitive indication of polyhedral type is provided by the set of dihedral angles formed by the two faces meeting at each edge of the polyhedron (the δ parameters introduced by Porai-Koshits and Aslanov). The set of δ angles for the aforementioned polytopes have been calculated and they show that the transition from the tricapped trigonal prism to the monocapped square antiprism is characterized by a change in the δ at one edge of the former from ca. 26.4 to 0° in the latter. The transition from the bicapped square antiprism to the decatetrahedron is characterized by a change in the δ at two edges in the former from ca. 30.9 to 0° in the latter.

Introduction

To a first order of approximation, the average quantity of discussion of a coordination polyhedron appears to be inversely proportional to the number of atoms in the coordination sphere. There exist several plausible explanations for this phenomenon, some of which follow.

Polyhedra with higher coordination number often contain chelating ligands which are themselves asymmetric and which pack to form low-symmetry space groups. The point groups of some large symmetric coordination polyhedra, such as the icosahedron and derivatives thereof, are not consistent with the demands of translational symmetry, and therefore must become distorted in order to be tessellated. Therefore, in the solid state, such polyhedra often show either low point symmetry or none at all.

In the event that the coordination polyhedron does not approximate to one with a nontrivial point symmetry operation, it is generally assumed that there is little to be gained from detailed consideration of its geometry. Coordination polyhedra of larger coordination number are often identified by investigators solely by inspection. It would therefore seem relevant to add the somewhat trivial remark that such polyhedra are not easily visualized.

Those authors of crystallographic reports who consider the distortions of a polyhedron from the appropriate reference polyhedra (polytopes) have used several related approaches. Day and Hoard² discussed the distorted monocapped square antiprismatic coordination polyhedron in $\text{ThT}_4(\text{CH}_3)_2\text{NCHO}$ (where T is the tropolonato ligand $\text{C}_7\text{H}_5\text{O}_2$) in terms of the less symmetric stereoisomers allowed by the bidentate tropolonato ligands. Many authors have adopted a criterion first suggested by Porai-Koshits and Aslanov³ which allows for a quantitative assessment of polyhedral type. This criterion makes use of the set of dihedral angles, δ , formed by the pairs

of faces that meet at each edge of the polyhedron. Porai-Koshits and Aslanov, in their original discussion, presented reference data only for eight-coordinate polyhedra. Muettterties and Guggenberger⁴ have extended the analysis to lower coordination polyhedra. At that time they also indicated their intention to pursue the analysis of nine-coordinate polyhedra. We recently found ourselves in need for some basis for the discussion of a nine-coordinate polyhedron and therefore undertook the analysis of both nine- and ten-coordinate polyhedra. Since then the results of Guggenberger and Muettterties have appeared in print.⁵ However, the approach we have taken here is a somewhat different one than that of the latter authors.

Identification of Polyhedra

The most straightforward basis for the comparison or identification of polyhedra is the number of faces meeting at each vertex (the order of the vertices) and the positions of the vertices of given order in the polyhedron with respect to each other. In practice, this technique has at least two shortcomings if no other parameters are considered: (i) it does not give any estimation of the degree of distortion from the idealized polyhedron which is approximated, and (ii) in order to properly count the faces meeting at a vertex it is first necessary to decide if four or more vertices are sufficiently near to the least-squares plane through them that they should be considered as forming a nontriangular face. It is not possible to give an a priori lower limit for these out-of-plane distances which will be universally applicable.

In order to obtain further information as to the best description of a polyhedron and, in addition, information concerning the nature of the distortions from ideal geometry, one may also consider the relative lengths of the edges of the polyhedron and the angles subtended at the central cation. However, edge lengths tend to be insensitive to changes in

Table I. Principal Reference Polyhedra

No.	
4	T_d regular tetrahedron, D_{4h} square
5	D_{3h} trigonal bipyramid, C_{4v} tetragonal pyramid
6	O_h regular octahedron, D_{3h} trigonal prism
7	C_{3v} monocapped octahedron, C_{2v} monocapped prism, D_{5h} pentagonal bipyramid
8	D_{4d} square antiprism, ^a D_{2d} Hoard dodecahedron, ^b C_{2v} bicapped trigonal prism
9	D_{3h} tricapped trigonal prism, C_{4v} monocapped square antiprism
10	D_{4d} bicapped square antiprism, C_{2v} decatetrahedron ^c
11	C_{5v} monocapped pentagonal antiprism
12	I_h regular icosahedron, O_h cuboctahedron, T_d truncated tetrahedron

^a Also known as the Archimedean antiprism. ^b Also known as the bisdisphenoid and the triangular dodecahedron. ^c Discussed in text.

polyhedral shape. The criterion of Porai-Koshits and Aslanov was mentioned earlier as a useful test of polyhedral type. Usually one or two of the δ angles (the δ' angles) undergo large changes as the polyhedron is altered continuously from one polytope to another. Furthermore, when four vertices approach the formation of a rectangular face, the δ' angle at one of the diagonals of the face approaches zero which enables such faces to be quickly identified and which also provides a quantitative estimate of the deviation from planarity if the four vertices are not exactly coplanar.

Reference Idealized Polyhedra

Assuming that identification is a valuable prerequisite to the rationalization of a polyhedron in terms of factors influencing the positions of the atoms in it, we shall attempt to elucidate the important polytopal polyhedra with nine and ten vertices and present data which will enable the identification of a polyhedron with nine or ten atoms which has been found by crystallographic investigation, when such identification is possible and meaningful.

Hoard and Silverton⁶ have listed the contributions to the energy of discrete eight-coordinate polyhedra as (1) direct interaction of the central atom with its ligands, (2) mutual repulsions between the ligands, (3) the effect of nonbonding electrons in the valence shell of the central atom, and (4) constraints associated with the geometry of multidentate ligands.

For each coordination number several highly symmetric polyhedra exist and each may be treated as a polytope for that coordination number. Many are highly improbable from the aforementioned considerations and would only be expected to be found in cases of unusual packing or directionality of the orbitals of the central atom. In order to form a basis for a discussion of the stereochemistry of higher coordination molecular complexes, we will focus our attention therefore only on those polyhedra which will appear favorable from the simple energy considerations embodied in the first two items listed by Hoard and Silverton.⁶

Day and Hoard² have chosen as a more quantitative criterion for judging the relative merits of polyhedra the ratio of the cation bond lengths to the minimum ligand-ligand separations, with lower values of the ratio being more favorable. Muetterties and Guggenberger⁴ have added the observation that the energetically most favorable polyhedra tend to have faces which are triangular. Both points of view acknowledge the importance of the three regular polyhedra with equilateral triangular faces, namely the tetrahedron, octahedron, and icosahedron. A list of the more important reference polyhedra and their point symmetries is given for coordination numbers four to twelve in Table I.

By definition, regular polyhedra contain only one set of symmetry related vertices, edges, and faces. Highly symmetric

Table II. Edge Lengths (Å) of Nine-Coordinate Polyhedra

Edge	TTP ^a			MSAP ^b		
	$n = 1$	$n = 6$	$n = \infty$	$n = 1$	$n = 6$	$n = \infty$
<i>a</i>	1.407	1.422	1.491	1.583	1.598	1.624
<i>b</i>	1.407	1.422	1.491	1.318	1.319	1.329
<i>c</i>	1.136	1.139	1.155	1.119	1.130	1.148
<i>d</i>	1.231	1.218	1.155	1.318	1.319	1.329
<i>e</i>	1.136	1.139	1.155	1.129	1.131	1.148
<i>f</i>	1.136	1.139	1.155	1.183	1.175	1.148
<i>g</i>	1.231	1.218	1.155	1.183	1.175	1.148

^a Edges are defined in Figure 1. ^b Edges are defined in Figure 2.

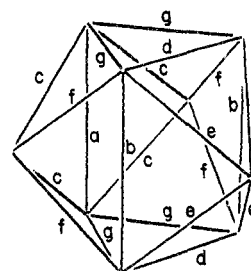


Figure 1. Edges of the tricapped trigonal prism. Equivalent edges are related by the C_{2v} symmetry of the polyhedron intermediate between the TTP and the MSAP.

but nonregular polyhedra contain more than one set of symmetry related edges. In the process of designing the polytopes it is necessary to establish the relative lengths of the edges belonging to each symmetrically equivalent set of edges. In the event that the vertices are also not all equivalent, the relative lengths of the radius vectors to each of the sets of symmetrically equivalent vertices must also be established. We may avoid the necessity for choosing some criterion for establishing the relative lengths of the radius vectors by working only with *points on a sphere* polyhedra; i.e., all radii will be set to unity. In order to remove the effects of unequal bond lengths on the δ angles, the sample polyhedra will also be reduced to *points on a sphere* polyhedra by moving each vertex along the radius vector to the surface of a sphere. This procedure has recently been used by Kouba and Wreford⁷ with favorable results. It will also allow an analysis of the more distorted polyhedra such as those arising in the case of chelation, lattice structures, or the presence of more than one atomic species among the coordinating atoms.

Muetterties and Guggenberger⁴ have used an energy minimization technique based on R_{ij}^{-n} repulsion potentials (where R_{ij} is the separation of atoms i and j) in order to establish the coordinates of their reference polytopes, and thus the relative edge lengths. This procedure has been discussed in detail by Claxton and Benson.⁸ In the case of eight-coordinate Porai-Koshits and Aslanov³ fixed the maximum possible number of sets of equivalent edges at the same minimum length and then allowed the remainder to be adjusted accordingly. This corresponds to the aforementioned energy minimization procedure in the limit as n becomes infinite. For the sake of brevity, we shall refer in the future to the latter as the $n = \infty$ case.

Nine-Coordination

Based on considerations discussed in the previous section, there are two important nine-coordinate polyhedra which are the tricapped trigonal prism (TTP) with D_{3h} symmetry and the monocapped square antiprism (MSAP) with C_{4v} symmetry. The geometries of both polyhedra were determined with repulsive potentials R_{ij}^{-n} for several values of n . Table II lists the edge lengths for $n = 1, 6$, and ∞ . The edges are labeled in Figures 1 and 2. The algorithm of Claxton and Benson⁸

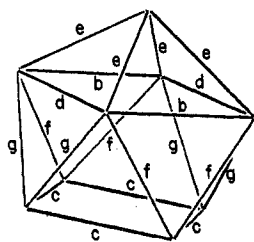


Figure 2. Edges of the monocapped square antiprism.

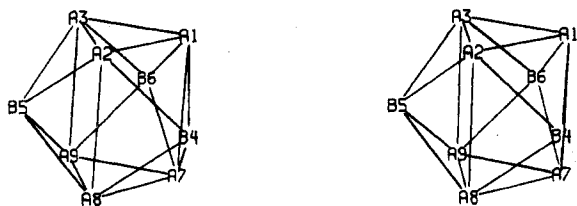


Figure 3. Stereoscopic representation of the tricapped trigonal prism (TTP).

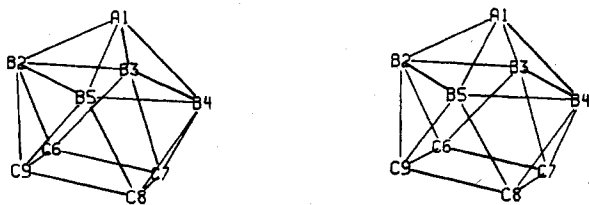


Figure 4. Stereoscopic representation of the monocapped square antiprism (MSAP).

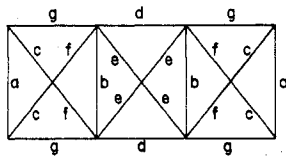


Figure 5. Schematic representation of the general nine-coordinate polyhedron with three capped rectangular faces.

were used⁹ except in the case of $n = \infty$ where for the TTP the c , d , e , f , and g edges were set equal and for the MSAP the c , e , f , and g edges were set equal. The coordinates were then determined using analytical geometry and spherical trigonometry. Details of these calculations are available.⁹

Figures 3 and 4 show stereographic projections of the TTP and MSAP, respectively.¹⁰ Equivalent vertices are labeled with the same letter. The sequential numbering of the vertices follows the rules suggested by Muetterties and Wright.¹¹ In the case of the TTP the a and b edges are symmetrically equivalent, as are the d and g edges and the e , f , and c edges. In the case of the MSAP, the f and g edges and the d and b edges are symmetrically equivalent.

The lower square of the MSAP is formed from the c edges of the TTP. The upper square is formed from the b and d edges. The correspondence between edges and the C_{2v} symmetry of the polyhedron intermediate between the two polytopes is illustrated in Figure 5. The face of the TTP capped with e edges becomes the single capped face of the MSAP.

The calculated edge lengths, including those given in Table II, change monotonically with the index n , as n varies from 1 to ∞ . The changes are small and of a similar order of magnitude as the changes which characterize the change from the TTP to the MSAP.

The δ angles were also calculated for the same six polyhedra and are listed in Table III. These are clearly more sensitive to small changes in the geometry of the polyhedron, partic-

Table III. δ (deg) for Nine-Coordinate Polyhedra

Edges	TTP			MSAP		
	$n = 1$	$n = 6$	$n = \infty$	$n = 1$	$n = 6$	$n = \infty$
a	27.3	26.4	21.8	0.0	0.0	0.0
b	27.3	26.4	21.8	38.2	37.6	36.2
c	59.4	59.6	60.8	69.1	69.1	68.4
d	47.5	47.6	48.2	38.2	37.6	36.2
e	59.4	59.6	60.8	58.9	59.0	59.7
f	59.4	59.6	60.8	52.7	53.0	53.7
g	47.5	47.6	48.2	52.7	53.0	53.7

ularly those changes associated with the conversion from a TTP to an MSAP. The δ associated with the a edge goes to zero for the MSAP and in the case of a distorted TTP, the smallest δ may usually be assigned to the a edge. It is therefore the most convenient single parameter with which to identify the polyhedron, i.e., the δ' .

Table III gives the δ angles for a number of nine-coordinate polyhedra selected from the literature. All of the bond lengths to the central atom have been set to unity before calculating the δ angles.

Guggenberger and Muetterties⁵ list a number of structures which contain nine-coordinate polyhedra with full D_{3h} symmetry or which approximate closely to full D_{3h} symmetry. Their δ angles differ slightly from those presented here because they have not reduced their polyhedra to *points on a sphere* polyhedra as we have done. For these polyhedra, however, the variations in bond length are not large and the differences in the δ angles as obtained by the two approaches are therefore not large.

An average of the δ_a and δ_b (vicinal parallel to the threefold axis, using the terminology of Guggenberger and Muetterties) for six of their coordination polyhedra with an approximate threefold axis gives 25.6° , remarkably close to the value of 26.4° for the $n = 6$ TTP as given in Table III. In polyhedra which form a part of a lattice structure, however, the variations from the average may be large, as exemplified by the polyhedron around Th(1) in $\text{RbTh}_3\text{F}_{13}$ ¹² and the polyhedron surrounding the site fully occupied by Nd in NaNdF_4 .¹³ A more extreme example, still showing D_{3h} symmetry, is the polyhedron in the structure of $\beta_1\text{-K}_2\text{UF}_6$, which has been redetermined by Brunton.¹⁴

These variations in the δ angles correspond to changes in the length of the a and b edges in relation to the length of the g and d edges which form the end faces of the TTP. In general, as the two atoms joined by an edge of the polyhedron are moved apart, two atoms on opposite sides of the edge find space to move toward each other, thus decreasing the δ at that edge. Therefore, an approximate reciprocal relation exists between a δ and the length of the corresponding edge, or, the angle subtended by that edge at the central atom. The large variations in the δ angles in the case of lattice structures would warn against the temptation to infer the nature to repulsive potentials from the δ angles in such cases.

As we move to structures that do not approach closely to threefold symmetry, the principal distortions may be toward the parameters of the MSAP as in $\text{NH}_4\text{Y}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ¹⁵ and $\text{Nd}_2(\text{C}_4\text{H}_7\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$.¹⁶ However, another important distortion may also be present as manifested in the structures of $\text{Nd}(\text{OCOCH}_2\text{NHCH}_2\text{OCO})\text{Cl} \cdot 3\text{H}_2\text{O}$ ¹⁷ and $\text{Pr}_2(\text{H}_2\text{O})_4(\text{C}_4\text{H}_6\text{NO}_4)_2(\text{C}_4\text{H}_5\text{NO}_4)\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ¹⁸ by the unequal δ_b . The δ_b for the MSAP are equal and therefore this distortion in low-symmetry nine-coordinate polyhedra is not a distortion toward the geometry of the MSAP. We note that these structures involve some degree of chelation.

In more physical terms, the two ends of the TTP tilt from being coplanar in the TTP in order to form the MSAP. This tilt has been proposed by Guggenberger and Muetterties⁵ as an important measure of polyhedral type. In the case of lower

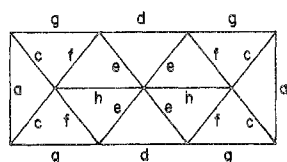


Figure 6. Schematic representation of the highly distorted polyhedron in NdOHCO_3 .

symmetry or intermediate polyhedra, another tilt, about an axis at right angles to the first, seems to be common and may be easily confused with the first tilt.

Discreet coordination polyhedra with the full symmetry C_{4v} of the MSAP are not known but the structural type represented by LaOCl^{19} contains an MSAP surrounding the lanthanide ion which is part of a continuous lattice and which has C_{4v} symmetry. The δ angles are in reasonable agreement with those in Table III for the MSAP.

The polyhedron in $\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_4\text{S})\text{Cl}\cdot 4\text{H}_2\text{O}^{20}$ has only C_2 symmetry. Three of the coordinating atoms belong to one ligand, and one of these is a sulfur atom. Nevertheless, it approximates remarkably close to the idealized MSAP. Table IV contains three examples of distorted MSAP where the major distortion brings the polyhedron toward the parameters of the TTP. These are $\text{Gd}(\text{HOCH}_2\text{COO})_3$,²¹ $\text{Th}(\text{C}_7\text{H}_5\text{O}_2)_4((\text{CH}_3)_2\text{NCHO})_2$,² and $\text{Nd}_2(\text{C}_3\text{H}_2\text{O}_4)_3\cdot 8\text{H}_2\text{O}$.²² All involve some degree of chelation.

Other polyhedra which are labeled as distorted MSAP in Table IV show a principal distortion which is not along a reaction path to the parameters defining the TTP. In $\text{ThF}_8(\text{NH}_4)_4$,²³ KU_2F_9 ,²⁴ and the second polyhedron of $\text{RbTh}_3\text{F}_{13}$,¹² the δ_b differ by 16° or more. This is then the analogous distortion to that which occurs in the TTP and which also results in unequal δ_b . Chelation is not present in these latter cases and it would therefore appear that both packing and chelation may give rise to this category of distortion. In the polyhedron surrounding $\text{Nd}(1)$ in NdOHCO_3 ²⁵ and in $\text{CsU}_6\text{F}_{25}$ ²⁶ a third category of distortion is evident and arises from the capping atom being displaced toward one of the edges of the upper square of the MSAP and away from the opposite edge.

Two polyhedra in Table IV, from the structure of NdOHCO_3 ,²⁵ possess such distortions that it seems hardly constructive to label them as being related to either of the two polytopes for nine-coordination. However, the number of such highly distorted polyhedra which occur in the literature, even in the presence of unusual chelation or packing, is surprisingly small. Furthermore, the arrangement of the positions of the vertices in one of them is the same as in that of the polyhedra intermediate between the reference polyhedra as shown in Figure 5, i.e., three vertices of fourth order separated by three pairs of vertices of fifth order with the six fifth-order faces joining into two groups of three each. The remarkable consistency of the connectivity of the polyhedra with nine vertices as found in nature would support the credibility of the analysis proposed here.

The connectivity of the polyhedron surrounding $\text{Nd}(3)$ in NdOHCO_3 ²⁵ is the exception to the foregoing generalization. Nevertheless, the distortions may still be understood in terms of the intermediate polyhedron. Figure 6 shows the edge labeling for this polyhedron. Two of the capping atoms of the TTP are sufficiently removed from the centers of the rectangular faces which they occupy in the TTP toward the third capping atom (forming the e edges in Figure 6) that they form the new edges h and the b edges disappear or must be assigned a negative δ .

The radius to edge length ratio is only meaningful when $n = \infty$, where for the TTP and the MSAP it is 0.866 and 0.871, respectively. Also the MSAP has one nontriangular face



Figure 7. Stereoscopic view of the bicapped square antiprism (BSAP).



Figure 8. Stereoscopic view of the Hoard dodecahedron.

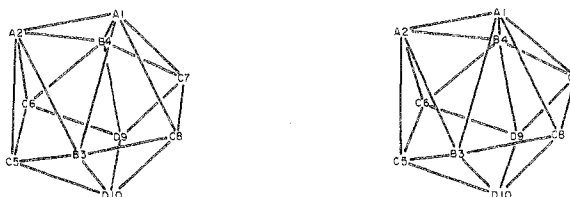


Figure 9. Stereoscopic view of the decatetrahedron (DTH) oriented similarly to the Hoard dodecahedron.

whereas the TTP has none. When a repulsive potential energy function is used to fix the geometry, the TTP is also favored although only marginally. For $n = 6$ the TTP has 0.15% less energy of repulsion than the MSAP.

We might then expect some preferences in nature for polyhedra which approximate the TTP over those which approximate the MSAP. In their survey of nine-coordinate polyhedra, Guggenberger and Muettterties⁵ have included mostly polyhedra which approximate to the full symmetry of the TTP or MSAP. They conclude that in such cases the TTP indeed occurs more often than the MSAP. The sample of the polyhedra contained in Table IV is not intended to be representative of all known nine-coordinate polyhedra. Nevertheless, from the cursory survey of polyhedra which was made in order to construct Table IV, we would suggest that when polyhedra with large distortions are included in the sample, polyhedra which resemble the MSAP are encountered roughly with the same frequency as those which resemble the TTP.

Ten-Coordination

Previous discussions of ten-coordination^{2,11} have concentrated on the D_{4d} bicapped square antiprism (BSAP) shown in Figure 7. Muettterties and Wright¹¹ suggested as an alternative for ten-coordination a bicapped Hoard dodecahedron. Such a polyhedron would seem unlikely because it would, of necessity, have two vertices which enter into the formation of only three faces, a situation which would be unlikely to occur in a high-coordination polyhedron. No such polyhedron has been reported to date.

Another important ten-coordinate polyhedron does indeed exist. Shinn and Eick²⁷ have discussed the relationship of this polyhedron to the Hoard dodecahedron (Figure 8) which was described by Hoard and Silverton.⁶ The Hoard dodecahedron may conveniently be described as the figure formed from two interpenetrating trapezoids, the short edge of each trapezoid joining A-type vertices and the long edges joining B-type vertices. The new ten-coordinate polyhedron is created by splitting two B-type vertices belonging to the same trapezoid to form the four vertices labeled C in Figure 9. This creates two new equilateral faces and the faces now formed between

Table IV. Nine-Coordinate Polyhedra

Compd	Dihedral angles (δ), deg	Point symmetry	Chelation	Type	Ref
RbTh ₃ F ₁₃ polyhedron around Th(1)	$a = 32.1; b = 30.1; c = 50.5, 59.9; d = 42.6, 59.8; e = 59.8, 63.1; f = 59.2, 60.0; g = 40.9, 52.1$	C_8	None	TTP	12
NaNdF ₄	$a = 18.9; b = 18.9; c = 60.8, 62.4; d = 48.5; e = 60.8, 62.4; f = 60.8, 62.4; g = 48.5$	C_{3h}	None	TTP	13
β_1 -K ₂ UF ₆	$a = 14.6; b = 14.6; c = 62.9; d = 48.7; e = 62.9; f = 62.9; g = 48.7$	D_{3h}	None	TTP	14
NH ₄ Y(C ₂ O ₄) ₂ ·2H ₂ O	$a = 15.4; b = 27.4; c = 61.7, 62.5; d = 44.7; e = 60.8, 61.1; f = 55.3, 61.1; g = 46.8, 52.5$	C_2	None	TTP, distorted toward MSAP	15
Nd ₂ (C ₃ H ₂ O ₄) ₃ ·6H ₂ O	$a = 19.6; b = 28.8, 34.4; c = 50.6, 58.6, 61.9, 65.6; d = 37.6, 54.6; e = 53.8, 60.7, 62.4, 69.8; f = 46.5, 58.4, 60.9, 63.4; g = 43.0, 43.9, 51.8, 54.5$	Near C_8	Two bidentate	TTP, distorted toward MSAP	16
Nd(OCOCH ₂ NHCH ₂ OCO)Cl·3H ₂ O	$a = 18.5; b = 29.6, 43.4; c = 60.5, 64.4, 67.6, 70.3; d = 35.0, 53.9; e = 48.5, 53.9, 55.5, 66.1; f = 53.1, 54.8, 55.0, 57.6; g = 40.8, 46.4, 51.2, 55.3$	Near C_8	One tridentate, one bidentate	Distorted TTP ^a	17
Pr ₂ (H ₂ O) ₄ (C ₄ H ₆ NO ₄) ₂ ·(C ₄ H ₇ NO ₄)Cl ₂ ·3H ₂ O	$a = 17.3; b = 23.5, 44.0; c = 56.2, 58.2, 58.8, 68.4; d = 43.8, 43.9; e = 52.0, 59.2, 65.2, 69.2; f = 48.9, 50.1, 58.7, 67.3; g = 39.8, 49.2, 50.8, 57.2$	Near C_8	One bidentate	Distorted TTP	18
LaOCl	$a = 0.0; b = 34.1; c = 72.6; d = 34.1; e = 56.3; f = 54.4; g = 54.4$	C_{4v}	None	MSAP	19
Nd ₂ (C ₄ H ₄ O ₄ S)Cl ₂ ·4H ₂ O	$a = 2.1; b = 38.0, 38.5; c = 70.9, 78.7; d = 36.9; e = 54.8, 56.1; f = 51.4, 53.9; g = 52.6, 52.8$	C_8	One tridentate	MSAP	20
Gd(HOCH ₂ COO) ₃	$a = 8.6; b = 36.9, 38.9; c = 63.4, 65.6, 68.4, 70.0; d = 36.8, 45.6; e = 56.6, 57.1, 58.0, 61.5; f = 49.6, 53.3, 53.5, 57.5; g = 47.0, 50.6, 54.5$	Near C_2	Three bidentate	MSAP, distorted toward TTP	21
Th(C ₇ H ₅ O ₂) ₄ ((CH ₃) ₂ NCHO)	$a = 6.3; b = 30.2, 38.2; c = 62.6, 62.8, 69.3, 73.0; d = 33.8, 45.4; e = 52.6, 55.3, 58.4, 71.9; f = 49.4, 53.0, 56.1, 61.1; g = 45.0, 51.9, 52.4, 58.7$	Near C_8	Four bidentate	MSAP, distorted toward TTP	1
Nd ₂ (C ₃ H ₂ O ₄) ₃ ·8H ₂ O	$a = 8.9; b = 31.7, 41.8; c = 66.2, 66.9, 74.1, 77.0; d = 36.0, 46.3; e = 47.6, 48.4, 55.6, 65.8; f = 51.5, 52.9, 54.9, 56.2; g = 42.8, 45.0, 56.6, 58.2$	C_1	Two bidentate	MSAP, distorted toward TTP	22
ThF ₈ (NH ₄) ₄	$a = 5.2; b = 25.2, 45.7; c = 64.0, 66.1, 66.3, 72.8; d = 36.3, 45.6; e = 54.0, 54.8, 59.5, 68.5; f = 50.9, 51.5, 55.1, 58.9; g = 43.8, 51.3, 54.6, 56.2$	Near C_8	None	Distorted MSAP	23
KU ₂ F ₉	$a = 9.5; b = 26.5, 46.5; c = 62.0, 62.2, 66.6, 66.7; d = 39.9, 45.1; e = 55.1, 56.4, 62.4, 66.3; f = 51.5, 52.8, 55.9, 56.0; g = 48.1, 48.2, 52.4, 52.8$	Near C_8	None	Distorted MSAP	24
RbTh ₃ F ₁₃ polyhedron around Th(2)	$a = 9.6; b = 21.0, 47.4; c = 60.4, 63.1, 66.0, 75.2; d = 32.7, 48.7; e = 53.4, 55.7, 58.3, 69.2; f = 48.2, 53.1, 55.2, 64.1; g = 39.1, 51.5, 56.3, 58.7$	C_1	None	Distorted MSAP	12
NdOHCO ₃ polyhedron around Nd(1)	$a = 2.6; b = 32.3, 48.7; c = 63.8, 63.8, 71.6, 74.0; d = 12.9, 46.1; e = 49.3, 52.3, 71.1, 72.7; f = 39.2, 45.4, 61.1, 62.9; g = 48.6, 51.9, 61.0, 61.1$	C_1^c	One bidentate	Distorted MSAP	25
CsU ₆ F ₂₅	$a = 7.6; b = 42.0; c = 67.3, 75.0; d = 18.4, 59.1; e = 43.4, 67.1; f = 52.5, 53.3; g = 45.3, 55.6$	C_8	None	Distorted MSAP	26
NdOHCO ₃ polyhedron around Nd(2)	$a = 1.1; b = 31.6, 54.4; c = 64.7, 65.3, 74.2, 75.0; d = 1.1, 43.4; e = 49.5, 51.2, 70.9, 80.4; f = 29.2, 46.6, 59.6, 69.4; g = 48.8, 54.2, 59.2, 70.8$	C_1^c	Two bidentate	Neither	25
NdOHCO ₃ polyhedron around Nd(3)	$a = 45.7; h = 2.5, 11.0; b^c = 43.1, 52.3, 69.1, 78.5; d = 64.0, 68.6; e = 52.0, 59.1, 72.4, 79.3; f = 64.1, 69.1, 78.5, 78.6; g = 21.6, 29.6, 51.5, 58.6$	C_1	Two bidentate	Neither	25

^a Two of the three capping atoms were identified differently in the original description. ^b See Figure 6 and the text. ^c Partial occupancy by cations.

the C-C edges and the D-D edge are four sided.

Although this polyhedron was known at least by 1961 it has received little attention. Recently, Bandurkin and Dzhurinskii²⁸ have compiled a list of structures which contain this polyhedron although they did not specify which criteria they used in order to differentiate between it and the other polyhedra. Also they claimed that the polyhedron had been named the bicapped dodecahedron by some authors. This statement does not seem to be consistent with the structural papers reporting on ten-coordinate polyhedra or with the original discussion of the bicapped dodecahedron by Muetterties and Wright.¹¹ The new polyhedron is derived from the Hoard dodecahedron and has 14 faces. An appropriate appellation from the classical Greek is then *decatetrahedron* (DTH).

The geometries of the BSAP and the DTH were determined using the algorithm of Claxton and Benson^{8,9} for several values of n . Also the geometry of both polyhedra were determined

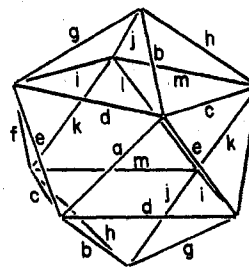


Figure 10. Edges of the bicapped square antiprism.

using rigid spheres in place of atoms at the vertices, i.e., the $n = \infty$ case. The edge lengths and δ angles for $n = 1, 6$, and ∞ are given in Tables V and VI, respectively. The edges are labeled in Figures 10 and 11. For the DTH, with $n = \infty$, the a edge, the f and g edges, the h edge, the i edge, the j and k edges, and the l edge were all made equal. For the BSAP,

Table V. Edge Lengths of Ten-Coordinate Polyhedra

Edge	BSAP ^a			DTH ^b		
	$n = 1$	$n = 6$	$n = \infty$	$n = 1$	$n = 6$	$n = \infty$
<i>a</i>	1.082	1.098	1.082	1.133	1.137	1.000
<i>b</i>	1.074	1.071	1.082	1.171	1.154	1.297
<i>c</i>	1.282	1.279	1.287	1.171	1.154	1.297
<i>d</i>	1.282	1.279	1.287	1.154	1.147	1.414
<i>e</i>	1.082	1.098	1.082	1.154	1.147	1.414
<i>f</i>	1.082	1.098	1.082	1.089	1.084	1.000
<i>g</i>	1.074	1.071	1.082	1.089	1.084	1.000
<i>h</i>	1.074	1.071	1.082	1.056	1.060	1.000
<i>i</i>	1.282	1.279	1.287	1.311	1.311	1.000
<i>j</i>	1.074	1.071	1.082	1.059	1.070	1.000
<i>k</i>	1.082	1.098	1.082	1.059	1.070	1.000
<i>l</i>	1.082	1.098	1.082	1.058	1.080	1.000
<i>m</i>	1.282	1.279	1.287	1.497	1.513	1.414

^a Edges are defined in Figure 10. ^b Edges are defined in Figure 11.

Table VI. δ (deg) for Ten-Coordinate Polyhedra

Edge	BSAP			DTH		
	$n = 1$	$n = 6$	$n = \infty$	$n = 1$	$n = 6$	$n = \infty$
<i>a</i>	56.4	56.2	56.8	49.2	48.2	81.8
<i>b</i>	56.5	56.3	56.8	43.2	43.3	47.5
<i>c</i>	30.6	30.9	29.8	43.2	43.3	47.5
<i>d</i>	30.6	30.9	29.8	46.2	45.8	38.0
<i>e</i>	56.4	56.2	56.8	46.2	45.8	38.0
<i>f</i>	56.4	56.2	56.8	54.9	54.6	57.7
<i>g</i>	56.5	56.3	56.8	54.9	54.6	57.7
<i>h</i>	56.5	56.3	56.8	65.9	65.8	70.1
<i>i</i>	30.6	30.9	29.8	26.5	27.0	38.9
<i>j</i>	56.5	56.3	56.8	68.5	68.9	54.7
<i>k</i>	56.4	56.2	56.8	68.5	68.9	54.7
<i>l</i>	56.4	56.2	56.8	77.2	78.1	70.5
<i>m</i>	30.6	30.9	29.8	0.0	0.0	0.0

the *b*, *g*, *h*, and *j* edge and the *a*, *e*, *f*, and *k* edges were all made equal. For the BSAP both the edge lengths and δ angles are not monotonic in n but change very little over the entire range $1 \leq n \leq \infty$. For the DTH, however, the variations are much larger. This seems to be related to the low point symmetry (C_{2v}) of the DTH. Also for the $n = \infty$ case, several choices are possible for sets of symmetry-related edges that will be forced to be equal and each choice leads to quite different polyhedra. The sets which were used give the results closest to those from the repulsive potential method.

Both polytopes and the polyhedron intermediate between them are conveniently represented as in Figure 12. The symmetry of the intermediate polyhedron is C_2 with the twofold rotation axis passing through the centers of the *a* and *l* edges. The new edges formed in the generation of the DTH from the DDH (the *h* edges), the *a* edge and the edges which formed the remaining trapezoid of the DDH used to generate

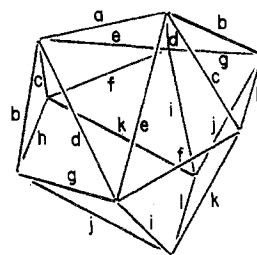


Figure 11. Edges of the decatetrahedron.

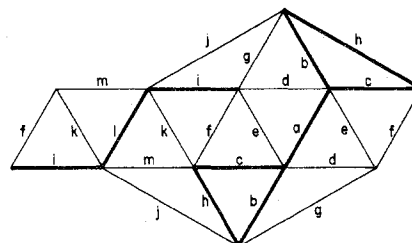


Figure 12. Schematic representation of general ten-coordinate polyhedron with two capped square faces.

the DTH, are emphasized in Figure 12.

In going from the BSAP to the DTH, the *m* edges, which are a member of the set joining the upper and lower squares of the BSAP, become diagonals of the four-sided faces in the DTH. Hence, δ_m goes to zero for the latter polyhedron and is therefore an appropriate choice as a δ' angle. We shall also include δ_l because it is shared by two faces which become parts of four-sided faces in the DTH, and for the more realistic values of n , it is the δ angle which shows the second largest change, after δ_m between the BSAP and the DTH.

It is perhaps instructive to observe that if the *a* edge of the DTH is rotated $\pi/2$ about a line through its center and the center of the polyhedron, we have, after a small movement of the *h* edges, a bicapped square prism.

Table VII gives a short list of ten-coordinate polyhedra selected from the literature. Two polyhedra, that in $U(\text{OCOCH}_3)_4$ ²⁹ and the polyhedron around the La(1) atom in the structure of $\text{La}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$,²⁷ based on the δ_l and δ_m values, are clearly better described as BSAP. The general degree of correspondence, however, between all the δ angles of the sample polyhedra and the reference BSAP, for any value of n , is not good. Two other polyhedra in Table VII, that in $\text{NaTh}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ ³⁰ and the polyhedron around the La(2) atom in $\text{La}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$,²⁷ are from their δ_l and δ_m values, clearly best described as DTH. Again, the overall agreement with the data for the reference DTH in Table VI is not good.

The polyhedron in $\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ has a new edge which replaces one of the *m* edges. Of the two possible di-

Table VII. Ten-Coordinate Polyhedra

Compd	Dihedral angles (δ), deg	Point symmetry	Chelation	Type	Ref
$U(\text{OCOCH}_3)_4$	$a = 46; b = 48; c = 33; d = 46; e = 58; f = 47; g = 44; h = 66; i = 40; j = 63; k = 62; l = 51; m = 18$	C_2	Two bidentate	BSAP	29
$\text{La}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$ polyhedron around La(1)	$a = 62; b = 47; c = 37; d = 32; e = 56; f = 44; g = 59; h = 67; i = 44; j = 47; k = 59; l = 60; m = 21$	C_2	Two bidentate	BSAP	27
$\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$	$a = 69.4; b = 40.4, 44.8; c = 44.4, 45.9; d = 27.9, 31.5; e = 39.9, 43.0; f = 49.3, 65.2; g = 63.4, 64.8; h = 63.4, 72.9; i = 36.3, 39.4; j = 53.9, 55.3; k = 57.0, 60.6; l = 83.5; m = 3.9; n = 8.8^a$	C_1	Five bidentate	DTH	30
$\text{La}_2(\text{CO}_3)_3 \cdot \text{H}_2\text{O}$ polyhedron around La(2)	$a = 66; b = 38; c = 43; d = 39; e = 38; f = 49; g = 57; h = 77; i = 48; j = 56; k = 65; l = 78; m = 0$	C_2	Three bidentate	DTH	27
$\text{Ce}(\text{CO}_3)_5(\text{C}(\text{NH}_2)_3)_6 \cdot 4\text{H}_2\text{O}$	$a = 72.0; b = 45.3; c = 39.8, 41.9; d = 26.8, 30.9; e = 44.1, 45.5; f = 50.7, 65.7; g = 60.7, 62.2; h = 65.8, 66.7; i = 35.1, 43.2; l = 75.8; m = 6.3, 20.9$	C_1	Five bidentate	Neither	31

^a See text and Figure 13.

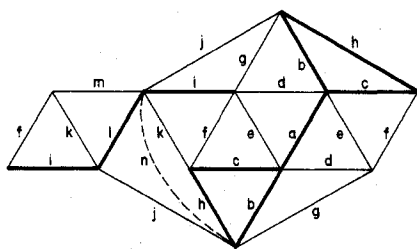


Figure 13. Schematic representation of the polyhedron in $\text{Na}_6\text{-Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$.

agons which can arise in the four-sided faces of the DTH, the one that appears in this case is not the one that could become an edge of a BSAP. This situation is entirely analogous to the creation of the h edges in the third polyhedron of NdOHCO_3 ²⁵ in the discussion of nine-coordination. Therefore, as illustrated in Figure 13, the m edge disappears or must be assigned a negative δ .

The remaining ten-coordinate polyhedron in Table VII, from $\text{Ce}(\text{CO}_3)_5(\text{C}(\text{NH}_2)_3)_6 \cdot 4\text{H}_2\text{O}$,³¹ has one δ_m nearer the value for the DTH and one nearer to the value for the BSAP. It is perhaps best then not to attempt to assign any label to it.

As was the case with nine-coordinate polyhedra, the pattern of the vertices of the ten-coordinate polyhedra found in nature seems to be the same as that of the polyhedron intermediate between the two important reference polyhedra, i.e., two vertices of fourth order separated by two rings of four vertices each, with all of the eight vertices in the two rings being of fifth order. The exception discussed above in $\text{Na}_6\text{-Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ ³⁰ may still be understood in terms of its deviation from the geometry of the polyhedron intermediate between the BSAP and the DTH.

The bond length to the edge length ratio for the somewhat artificial DTH with $n = \infty$ is 1.000. For the equivalent BSAP, it is considerably less at 0.924. Furthermore, the DTH has two nontriangular faces while the BSAP has none. The difference in energy between the two polyhedra is small but slightly greater than that between the two nine-coordinate polytopes. The BSAP is favored by 0.2%. We might then expect that the BSAP should be found more often in nature than the DTH. There does not exist to date adequate information with which to test this assumption.

Conclusion

The descriptions given in the original publications for the polyhedra which appear in Tables IV and VII were quite often different from that which we have arrived at by the method outlined in the preceding sections. Kouba and Wreford⁷ encountered a similar phenomenon in their analysis of seven-coordinate polyhedra. In order to determine if the reduction of the original polyhedra to *points on a sphere* polyhedra led to significantly different results than that which would be obtained using the unmodified original coordinates, the δ angles were recalculated for all of the polyhedra using the unmodified coordinates. In general, polyhedra characterized in this manner were not as easily identified with the appropriate polytope and two polyhedra developed a pattern of vertices as in Figure 6, in addition to the third polyhedron in NdOHCO_3 .²⁵ However, none of the polyhedra were changed to agree with the description given in the original publication, where that description differed from ours.

Descriptions of large coordination number polyhedra based only on the inspection of coordinates, stereograms, or ball and stick models often lead either to errors or, at least, to an inconsistent terminology and would therefore seem unwise. The δ criterion of Porai-Koshits and Aslanov³ is a sensitive and useful device for the identification of polyhedra and its use can avoid these problems.

It was stated earlier, however, that all polyhedra would not necessarily fit into a classification scheme based on their similarity to a limited number of polytopes. We are now in a position to comment further. Minerals often contain relatively small ions, in particular alkali ions, which balance the charge of other more highly charged ions. It is the ions carrying the greater charge which largely determine the packing of these structures. Then the singly charged ions often show high coordination, including nine- and ten-coordination, but the geometry of the coordinating atoms is not strongly influenced by interactions between themselves and the singly charged central atom. In such cases, as would be expected, the analysis discussed here yields results which may have little value.

Another area of crystallographic investigation which involves large coordination polyhedra and which has not been considered here is that of intermetallic structures. Indeed in such structures nine and ten might be considered lower coordination numbers. The polyhedra which occur in such structures are governed very much by the demands of three-dimensional tessellation as well as the interactions which we have been considering. We might therefore expect that a larger number of polytopes would be required to form the basis of a discussion of such polyhedra.

We have restricted ourselves to polyhedra in which the central atom and the coordinating atoms bring a strong influence to bear on the choice of polyhedral geometry, i.e., the polyhedra found around the lanthanides and actinides. In such cases most but not all nine- and ten-coordinate polyhedra can be labeled as being related to one of the four polyhedra discussed in the preceding sections even when the distortions from such polyhedra are large. For both nine- and ten-coordinate polyhedra, the pattern of the vertices of fourth and fifth order is usually consistent with the pattern in the polyhedron intermediate between the important polytopes. Nevertheless, large distortions also occur which cannot be associated with an interconversion between the polytopes.

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Supplementary Material Available: (A) Calculation of the geometry of the tricapped trigonal prism, the monocapped square antiprism, the bicapped square antiprism, and the decatetrahedron as formed from solid spheres; (B) Cartesian and spherical polar coordinates for the polyhedra listed under (A); (C) listing of a general purpose program for the minimization of the repulsive energy of a polyhedron; and (D) listing of a general purpose program for the calculation of dihedral angles between faces of a polyhedron (18 pages). Ordering information is given on any current masthead page.

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Mechanism of the Complex Formation between Aluminum and Sulfosalicylate Ions. Role of the Hydrolyzed Metal Ion

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The kinetics of the reaction between Al(III) and the ions of 5-sulfosalicylic acid, H_3L , were investigated in the pH range between 1.3 and 4.1 at 25 °C and at an ionic strength of 0.1 M. The results were interpreted in terms of three reaction paths; some evidence for an additional path, namely, that between Al^{3+} and H_2L^- , was also obtained, and an upper limit of $0.02 M^{-1} s^{-1}$ was estimated for the rate constant. The pathway via $AlOH^{2+}$ and HL^{2-} has the much higher rate constant of $2.5 \times 10^3 M^{-1} s^{-1}$, confirming the enhanced reactivity of the hydrolyzed cation. Two other pathways, involving $AlOH^{2+} + H_2L^-$ and $Al^{3+} + HL^{2-}$, respectively, have exactly the same pH dependence. If the rate constant of the former path is assumed to be calculable from the rate of similar reactions, then that of the latter becomes $\sim 1.5 M^{-1} s^{-1}$, higher than normal for the charge type in question but not significantly so. This result is discussed in terms of "internal hydrolysis". No retarding influence of the internal hydrogen bond was observed, nor was there any sign of rate-determining ring closure. The results were obtained by the stopped-flow technique or by following the reaction spectrophotometrically with the aid of a recorder.

Introduction

The mechanism of the formation of labile complexes is by now well established. According to the Eigen mechanism¹ the observed rate constant equals $K_{os}k^*$, where K_{os} is an outer-sphere association constant and k^* the first-order constant for the rate at which the ligand present in the outer sphere changes places with a water molecule in the inner coordination sphere of the metal ion.

For some labile metal ions which undergo strong hydrolysis the mechanism is complicated by the labilizing effect of OH^- on the remaining water molecules in the inner coordination sphere² and by the possibility of "internal hydrolysis" when the metal reacts with the anion of a weak acid.² Whereas these problems have been investigated and discussed in detail for Fe(III),³ comparatively few data⁴⁻⁹ are available for Al(III) which has the drawback of forming much weaker complexes and of exhibiting no absorbance in an accessible wavelength range.

Additional data on systems involving Al(III) seemed desirable in order to get some insight into the role of the hydrolyzed species.

Using pH indicators to monitor the reaction, we have not been able to detect the formation, to a significant extent, of a complex between Al(III) and acetic acid, in a range of pH and concentration where the complications arising from polymerization and further hydrolysis can be neglected.

For the present investigation, we therefore chose the chelating ligand 5-sulfosalicylic acid which we shall abbreviate as H_3L . The reaction can be monitored spectrophotometrically, owing to the difference in absorbance between the complex and the free ligand. The ion H_2L^- is the anion of a

strong acid, and the ion HL^{2-} that of a moderately strong acid ($pK = 2.4$).

Experimental Section

Materials. An acidified stock solution of $Al(ClO_4)_3 \cdot 8H_2O$ was prepared from Fluka "purum" salt and perchloric acid (Merck). The metal ion concentration was determined by direct titration with EDTA in the presence of Cu^{2+} using PAN as an indicator.¹⁰

Stock solutions of the 5-sulfosalicylic and perchloric acids were prepared and were titrated with CO_2 -free sodium hydroxide solution.

The ionic strength was 0.1 M, regulated by the addition of sodium perchlorate (Fluka puriss.).

Instruments. The pH of the solutions was measured with a digital pH meter (Radiometer PHM52) having an accuracy of ± 0.005 unit of pH. All spectrophotometric measurements were carried out with a Hilger-Gilford spectrophotometer.

Kinetic measurements in the higher pH range were carried out by the stopped-flow technique, using an Aminco-Morrow apparatus. Oscilloscope traces were analyzed by transferring the data to punched cards by means of a magnifying manual trace-follower coupled to an analog to digital converter and processing the cards in a CDC computer.

In the lower pH range the reactions were so slow that they could be followed with the aid of our spectrophotometer. Its output measures directly the optical density and was recorded on a Honeywell recorder.

At $pH \geq 2.0$ formation rates were measured by mixing suitable solutions of Al(III) and ligand. At lower pH the degree of complexation is very low; therefore, decomposition rates were measured by mixing the complex with perchloric acid solution. At pH 2.0 both methods were employed and yielded identical results.

The concentration of aluminum, a , was varied between 1.0×10^{-3} and 5.8×10^{-3} M and was always much higher than that of the ligand, b , which was 10^{-4} to 2×10^{-4} M. The formation of complexes in which the ratio of ligand to metal ion is higher than unity can therefore be