

SOME ASPECTS OF THE STEREOCHEMISTRY  
OF EIGHT-COORDINATE COMPLEXES

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A study was made of the basic characteristics of eight-coordinate polyhedra in the dodecahedral class: the Hoard dodecahedron, the tetragonal antiprism, and the trigonal prism with two additional vertices over the centers of two of the rectangular faces. A criterion, based on the dihedral angles  $\delta$  between pairs of faces intersecting along the b-edges of a dodecahedron, is proposed for determining the polyhedral shape. An additional criterion is based on the nonplanarity of the body-diagonal trapezoids of the dodecahedron. The nonplanarity is characterized by the dihedral angle  $\varphi$  between two planes: the first passes through the short base of the trapezoid and the midpoint of the long base, while the second includes the long base of the trapezoid and passes through the midpoint of the short base. Problems in the stereoisomerism of eight-coordinate complexes with chelating ligands were examined.

I. INTRODUCTION. EIGHT-COORDINATE POLYHEDRA

There is presently no generally accepted nomenclature for the description of high-coordinate polyhedra. There is not even agreement as to which polyhedra are of the same type (differing only by the degree of distortion of one or the other form) and which ones are basically different in structure. For example, [1] enumerates 23 different polyhedra, with coordination numbers from six to 12, which are found in rare earth compounds. Included are five different ten-coordinate polyhedra, six eight-coordinate polyhedra, and four six-coordinate polyhedra. However, the hexagonal bipyramid is not listed among the eight-coordinate polyhedra. In all probability this is due to the stereochemical characteristics of the rare earths, which are different from those of the actinides.

Generally speaking, in any convex eight-coordinate polyhedron a quadrangle (nonplanar in the general case) can be chosen such that four of the vertices lie at the corners of the quadrangle and the remaining four are distributed two on each side of the quadrangle. When projections of various polyhedra onto the average plane of the quadrangle are examined, four limiting cases can be distinguished for the relative positioning of the polyhedral vertices (Fig. 1). When these polyhedra are idealized (by choosing the lengths of the sides and the values of the angles), each gives one of the known highly symmetrical distributions met in crystal structures (Fig. 2).

The  $\delta_A$  polyhedron, formed by two trigonal prisms laid crosswise on the common square face, is comparatively unusual. This polyhedron is found for the potassium ion in the structure of  $K_2OsO_2(OH)_4$  [2]. The remaining three polyhedra are the  $\delta_B$  hexagonal bipyramid, the  $\delta_C$  cube, and the  $\delta_D$  Hoard dodecahedron. They are familiar enough not to require illustrative examples.

It is well known that polyhedra made up mainly or completely of triangular faces are the rule in island structures (those structures in which the complexes are not linked into chains, layers, or three-dimensional lattices). Without touching on the question of the requirements imposed on the symmetry of the polyhedron by the atomic orbitals which take part in forming the valence molecular orbitals, we can explain this phenomenon simply by the demands of interligand interactions. Crudely speaking, the repulsion forces force the ligands as far apart as possible subject to the maintenance of a constant distance from the central atom. In polyhedra inscribed in a sphere, the average edge length increases as the number of sides of the defining polygons decreases. This may explain the absence of type  $\delta_C$  and  $\delta_A$  discrete complexes for the rare earth (these geometries are the cubic and crossed-prismatic ones), although these polyhedra are theoretically possible if the  $f$ -orbitals of the central atom can take part in the molecular orbitals.

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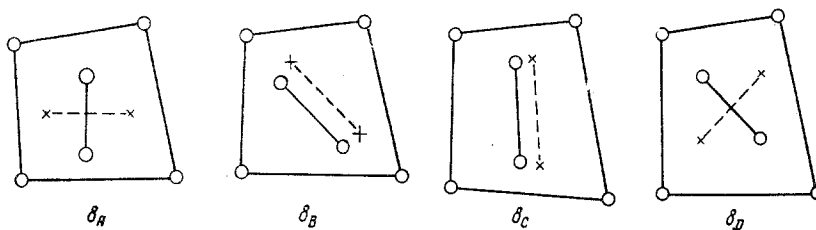


Fig. 1. The four types of convex eight-coordinate polyhedra.

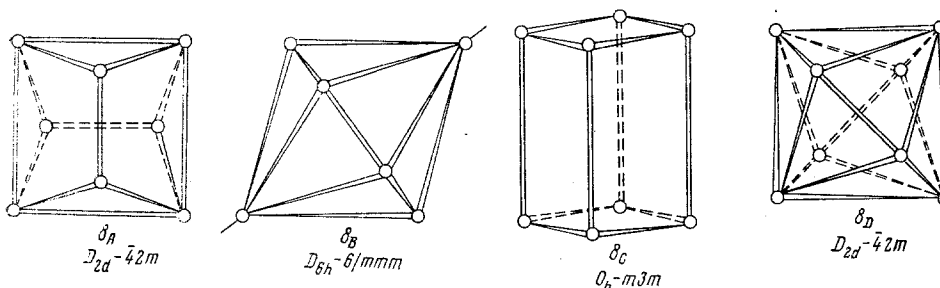


Fig. 2. Idealized shapes of the four eight-coordinate polyhedra.

The hexagonal bipyramid generally is found much less frequently than the dodecahedron and related polyhedra. The obvious reason for this is the inevitable chemical nonequivalence of the atoms at the vertices and those in the equatorial plane of the hexagonal bipyramid, coupled with the differences in the interligand distances along the equatorial perimeter and along the pyramidal edges. This polyhedron is found mainly in uranyl compounds with bidentate ligands in the equatorial plane, where four-membered chelate rings are formed and the ligand bites are short.

The present work examines the basic characteristic of eight-coordinate polyhedra in the dodecahedral class. All three of the most typical eight-coordinate polyhedra belong to this class: the Hoard dodecahedron,  $\delta_d$ , the tetragonal antiprism,  $\delta_{an}$ , and the trigonal prism with two additional vertices above two of the rectangular faces,  $\delta_{ct}$ . The name of the last polyhedron is a cumbersome one, making it difficult to talk about this polyhedron in the paper. We therefore use the English name for this polyhedron, the bicapped trigonal prism. The  $\delta_{an}$  and  $\delta_{ct}$  polyhedra can be obtained by appropriate deformations of the  $\delta_d$  dodecahedron. The transition  $\delta_d \rightarrow \delta_{ct}$  can be brought about by deformations of the planar rectangle: one of the sides ( $b_1$  in Fig. 3) is shifted to form a planar rectangle, while another side,  $b_2$ , is rotated slightly about the two-fold axis. In order to accomplish the transition  $\delta_d \rightarrow \delta_{an}$ , one more transformation must be added to the previous set: shifting of the  $b_2$  side to form a second planar rectangle. In this sense the bicapped trigonal prism is a polyhedron intermediate between the dodecahedron and antiprism.

Finally, the choice of which of the polyhedra is characteristic is fairly arbitrary. The symmetries are different, and conversion of one to another leaves only one two-fold symmetry axis fixed. However, in the analysis of complexes with different ligands, the symmetries of the polyhedra play a secondary role. It was just such cases as these that we had in mind in the present work.

## II. CRITERIA FOR DETERMINING THE SHAPES OF THE POLYHEDRA IN THE DODECAHEDRAL CLASS

Hoard and Silverton [3] introduced the concept of the ideal dodecahedron and ideal antiprism inscribed in a sphere. By analogy we can introduce the concept of a bicapped trigonal prism inscribed in a sphere. The three polyhedra are characterized by the following parameters. For the dodecahedron,  $a = m = g = 1.199r$ ,  $b = 1.250r$ ,  $a = 1.499r$ . For the bicapped trigonal prism,  $t = p = 1.156r$ ,  $h = 1.290r$ ,  $t = 1.492r$ . For the antiprism,  $s = l = 1.215r$ . Here  $r$  is the radius of the sphere, and the meaning of the other symbols is apparent from Fig. 4.

Differences in the ligands of necessity result in distortion of the polyhedra. It is thus fairly important to establish certain criteria for distinguishing the polyhedra. These criteria should also be capable of defining the extent of distortion, and of showing whether it is allowable (or artificial) to describe a polyhedron as intermediate between two ideal forms.

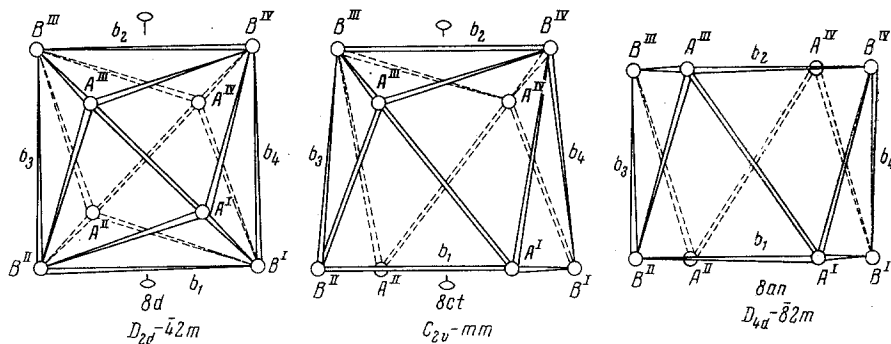


Fig. 3. Relationships between the dodecahedron, bicapped trigonal prism, and antiprism.

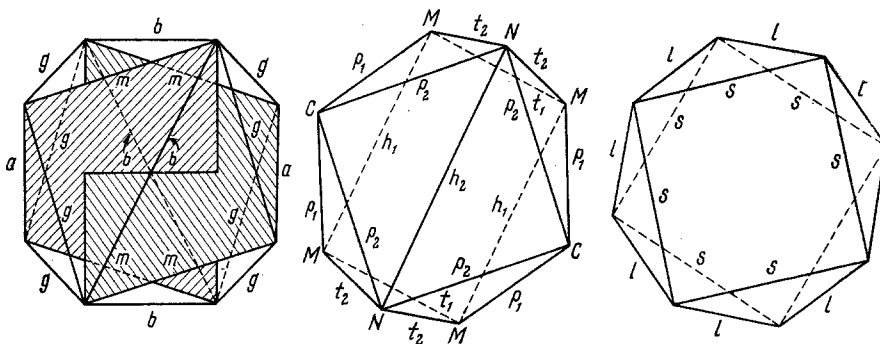


Fig. 4. Designation of the edges of the dodecahedron, bicapped trigonal prism, and antiprism.

One such criterion was proposed by Lippard and Russ [4]. The basic parameter chosen was the angle  $\omega$  between the body-diagonal trapezoids of the dodecahedron,  $B^I A^I A^{III} B^{III}$  and  $B^{II} A^{II} A^{IV} B^{IV}$  (Fig. 3). In the ideal dodecahedron this angle is  $90^\circ$ , while in the ideal antiprism it is  $79.3^\circ$ . The bicapped trigonal prism was not examined.

The Lippard-Russ criterion seems to us to be a poor choice, for several reasons. First, distortions of each of the polyhedra are possible such that, although  $\omega$  can change and approximate the value characteristic for the other polyhedron, the polyhedron itself retains its characteristic external shape. For example, the dodecahedron can be elongated along the two-fold axis (by lengthening the  $b_3$  and  $b_4$  edges in Fig. 3). Any desired decrease in  $\omega$  can be obtained in this way, but the polyhedron will not resemble an antiprism. Similarly, in the antiprism the angle  $\omega$  can be made equal to  $90^\circ$  just by changing the  $s/l$  ratio.

Second, before the angle  $\omega$  can be determined, it is necessary to define the trapezoids of interest, i.e., to determine the type b edges in the dodecahedron or to find the planar or nearly planar rectangular bases in the antiprism. The choice of the trapezoids can predetermine the results, as is obvious from the first criticism above.

Third, the body-diagonal trapezoids in the antiprism (and in the bicapped trigonal prism) are not planar, and the best mean square plates through them must be determined in order to calculate  $\omega$ . Their positions will naturally be very sensitive to random distortions in the polyhedron.

Clearly, a more natural and simple criterion would be based on the same parameters by which we visually characterize the shape of a polyhedron. The set of angles,  $\delta$ , between pairs of faces intersecting along the type b edges (of a dodecahedron) can serve as such a criterion. The first step of the analysis thus consists of choosing these edges. Generally speaking, when a model of the polyhedron is available the type b edges are easily located from the differences in the number of edges intersecting at the various vertices. In a dodecahedron there are four edges joined at the type A vertices and five edges joined at the type B vertices. The b edges are the ones which link the four type B vertices. However, if a model is not available it is not immediately clear how the vertices should be joined so that the polyhedron remains convex. Therefore, the choice of the b edges should be based on measuring the dihedral angles between all possible triangular faces which intersect each other, and to choose from this set the ones which are

TABLE 1. The Angles  $\delta$ ,  $\delta'$ ,  $\varphi$ , and  $\omega$  for Some Eight-Coordinate Polyhedra in Rare Earth Compounds

Compound	Dihedral angles $\delta$ at type b edges	Dihedral angles $\delta'$ , at remaining edges	Angle $\varphi$ in trapezoids	Angle $\omega$ bet. the mean sq. planes of trap.	Polyhedron and isomer type	Ref.
	degrees					
La(AA) <sub>3</sub> ·2H <sub>2</sub> O	4,5 26,1 37,6 и 43,8	46,8—56,9—57,4— —57,4—58,3—61,4	7,6 15,6	86,1	Bicapped trigonal prism, $t_1t_1P_2 + P_2$	[5]
Nd(AA) <sub>3</sub> ·2H <sub>2</sub> O	3,1 24,9 37,9 и 43,2	46,9—53,7—56,9 57,1—60,6—66,5	8,8 16,2	85,7	Bicapped trigonal prism, $t_1t_1P_2 + P_2$	[6]
Eu(AA) <sub>3</sub> ·3H <sub>2</sub> O	5,4 25,1 41,6 и 49,4	46,8—51,7—55,7— —57,0—62,3—66,7	7,9 14,6	86,4	Bicapped trigonal prism, $t_1t_1P_2 + P_2$	[7]
Ho(AA) <sub>3</sub> ·4H <sub>2</sub> O	23,7, 25,3 34,3 и 37,7	51,6—52,0—54,6— —57,1—63,1—63,6	4,5 5,0	85,8	Dodecahedron, mmm + m	[8]
HPipEu(BA) <sub>4</sub>	0, 1, 3 52,2 и 54,1	55,0—51,9—50,7 51,5—49,0—49,6	20,7 26,3	83,0	Antiprism, ssss	[9]
HGd(BA) <sub>4</sub> ·Pip	10,0 10,0 44,7, 44,7	50,5, 53,4, 57,2	13,0 19,7	86,7	Antiprism, ssss	[10]
HEu(BA) <sub>4</sub> ·DE A	7,0, 7,0 45,7, 45,7	56,2, 56,3, 51,0 51,8	13,2 21,4	85,8	Antiprism, ssss	[9]
Cs[Y(HFA) <sub>4</sub> ]	21,1, 21,1 31,8, 31,8	—	4,6 5,3	88,3	Dodecahedron, ggg'g'	[11]
EuCl <sub>3</sub> ·6H <sub>2</sub> O	14,4, 14,4 41,8, 56,9	50,1, 50,9, 56,6	27,9 30,6	82,3	Antiprism	[12]

convex. After this is done the choice of the type b edges is not a difficult problem. In general, the  $\delta$ -criterion rests on two assumptions:

1) The edges must belong to a single closed quadrangle, the "body-diagonal" of the polyhedron, and generate the  $8_D$  type of polyhedron (Fig. 1);

2) of all such possible quadrangles, the one must be chosen which contains the edges supporting the largest (but convex!) dihedral angle in the polyhedron (the smallest angle between normals to the faces).

In essence, the criterion is based on evaluating just those angles which are readily visible in the polyhedron and which are easily measured on models and calculated from the coordinates of the atoms at the vertices of the polyhedron.

The  $\delta$ -criterion permits the distinction not only between the dodecahedron and the antiprism, but also between these two polyhedra and the bicapped trigonal prism. In the ideal dodecahedron, all four  $\delta$  angles are equal to  $29.5^\circ$ ; in the bicapped trigonal prism,  $\delta_1 = 0$ ,  $\delta_2 = 21.7^\circ$  (trans to  $\delta_1$ ),  $\delta_3 = \delta_4 = 48.2^\circ$ ; and in the antiprism  $\delta_1 = \delta_2 = 0$ ,  $\delta_3 = \delta_4 = 52.5^\circ$ .

An additional criterion is the degree of nonplanarity of the diagonal trapezoids. This quantity is conveniently characterized by the angle  $\varphi$  between two planes: the first contains the short base of the trapezoid and passes through the midpoint of the long base, while the second contains the long base of the trapezoid and passes through the midpoint of the short base. It is not difficult to calculate this angle. In the ideal dodecahedron the angle  $\varphi = 0$ , in the ideal bicapped trigonal prism it is  $16.1^\circ$ , and in the antiprism it is  $24.5^\circ$ .

Table 1 gives the values of the angles  $\delta$ ,  $\varphi$ ,  $\omega$  for most of the rare earth tris- and tetrakis- $\beta$ -diketonates whose structures are known.\* According to the criterion of Lippard and Russ, all of the tris- and tetrakis- $\beta$ -diketonates would be classified as dodecahedral (the  $\omega$  angles are all close to  $90^\circ$ ; the range is  $85.2$  to  $88.3^\circ$ ). This classification in no way agrees with the external shapes of the models of these compounds. The  $\delta$  and  $\varphi$  criteria can be

\*The dihedral angles  $\delta'$  are also given, where  $\delta'$  is the angle between faces intersecting along the other edges, which join the vertices of the two more nearly planar quadrangles to form the polyhedron.

used to give a more definite description to the polyhedra, one that corresponds to their external shapes. The polyhedra of all of the tris acetylacetonates except the holmium compound can best be described as bicapped trigonal prisms. The holmium compound,  $[\text{Ho}(\text{AA})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , contains a dodecahedral polyhedron. All of the tetrakis benzoylacetonates have an antiprismatic shape, but  $[\text{Pr}(\text{TFA})_4]^-$  and  $[\text{Ln}(\text{HFA})_4]^-$ , where  $\text{Ln} = \text{Eu}$  and  $\text{Y}$ , are dodecahedral. The application of the proposed criteria to the coordination polyhedron of europium in  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  shows that the polyhedron can be described as a trigonal antiprism. However, the quadrangular bases of the antiprism are the faces containing the ligands  $\text{H}_2\text{O}_I - \text{H}_2\text{O}_{II} - \text{H}_2\text{O}_{III} - \text{Cl}_{II}$  (two faces related by a two-fold axis) and not  $\text{H}_2\text{O}_{II} - \text{H}_2\text{O}_{II}' - \text{H}_2\text{O}_{III} - \text{H}_2\text{O}_{III}'$  and  $\text{H}_2\text{O}_I - \text{H}_2\text{O}_I' - \text{Cl}_{II} - \text{Cl}_{II}'$  [12].

### III. STEREOISOMERS OF EIGHT-COORDINATE COMPLEXES WITH CHELATING LIGANDS

Hoard and Silverton [3], in their fundamental work on the stereochemistry of dodecahedral and tetragonal antiprismatic complexes, examined, among other things, the problems of stereoisomerism of such complexes in the presence of four identical chelating ligands. Possible stereoisomers of the dodecahedron and antiprism are given in Table 2, in the notation of Hoard and Silverton. There also are indicated the stereoisomers for the bicapped trigonal prism (see Fig. 4 for the meaning of the symbols). It is clear from the table that there are six possible isomers for the dodecahedron, six for the bicapped trigonal prism, and three for the antiprism.

If the complex contains only three identical chelating ligands, the number of possible isomers increases significantly. Simply replacing the fourth ligand with a different chelating ligand gives 11 dodecahedral isomers, 17 trigonal prismatic isomers, and four antiprismatic isomers. If there are two monodentate ligands and three identical chelating ligands, then new isomers are possible since the monodentate ligands do not have to span a given edge. The corresponding numbers of new isomers are now eight, eleven, and four (not counting mirror images). The possibilities are listed in Table 3.

When examining the relationship between antiprismatic and dodecahedral complexes with four identical chelating ligands, Hoard and Silverton considered the identical way of linking the vertices as well as analogies in the symmetries of the complexes (agreement of the symmetry groups with possible loss of some of the symmetry operations). A priori, it is not clear if the second factor is ever important in real cases. Since the two donor atoms of the ligand are not equivalent (e.g., in benzoylacetonates) because of factors due to steric effects, and since the molecular packing affects the coordination sphere, the symmetry will always be perturbed, and the shape of the complex may be an intermediate one. Thus it is highly important to establish the relationships between the isomers of the three polyhedra. This can be done on the basis of the deformational transitions, discussed previously with respect to Fig. 3, of the polyhedra. No reference to symmetry is necessary.

As an illustration, Fig. 5 shows two ways to deform a  $ggg'g'$  dodecahedron ( $D_2$ ), and Fig. 6 indicates three possible ways to deform an  $ssss$  antiprism. A complete scheme for the mutual deformational transitions of the three polyhedra (dodecahedron, bicapped trigonal prism, and antiprism) is shown below for complexes with four identical chelating ligands:

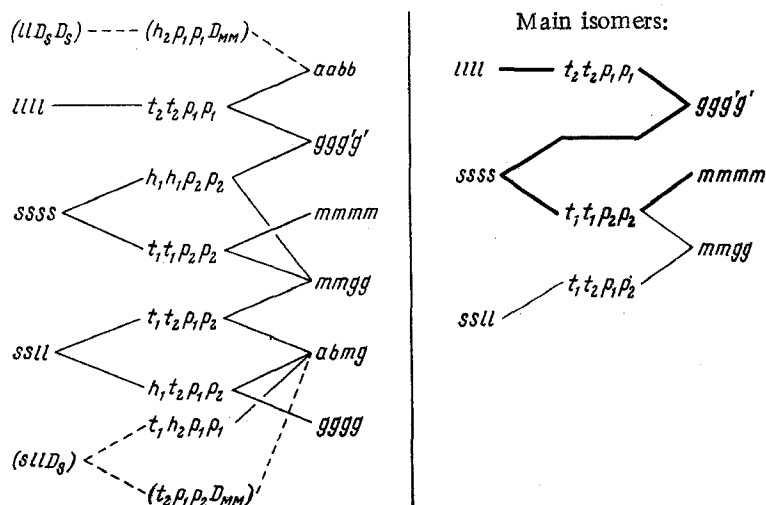
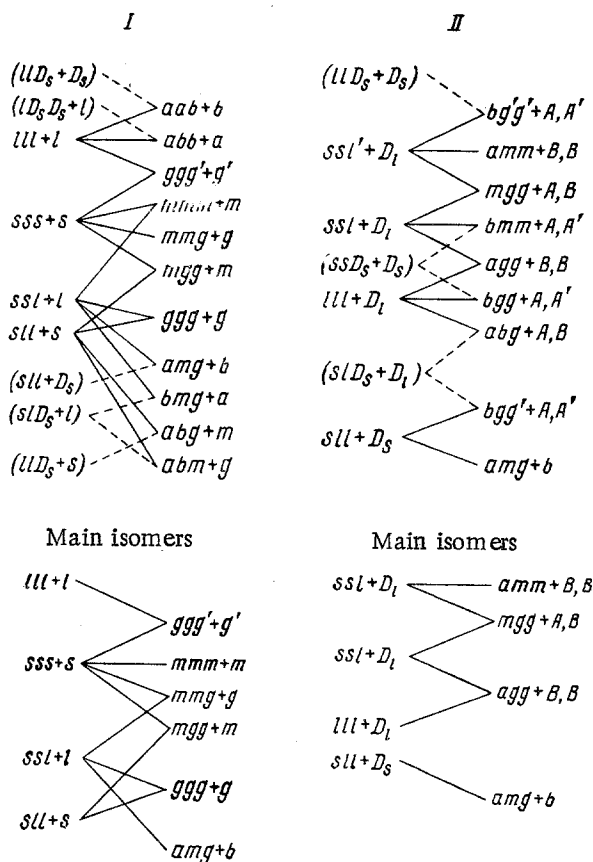


TABLE 2. Stereoisomers of Eight-Coordinate Complexes with Four Identical Chelating Ligands

Dodecahedron	Bicapped trigonal prism	Antiprism
$mmmm$ $D_{2d} - \bar{4}2m$	$t_1t_1p_2p_2 C_2 - 2$	$ssss D_2 - 222$
$gggg S_4 - \bar{4}$ $ggg'g' D_2 - 222$	$h_1h_1p p_2 C_2 - 2$ $t_2t_2p_1p_1 C_2 - 2$	$lll D_4 - 422$ $ssll C_2 - 2$
$mmgg C_2 - 2$ $aabb D_2 - 222$	$t_1h_2p_1p_1 S - m$ $t_1t_2p_1p_2 C_1 - 1$	
$abmg C_1 - 1$	$h_1t_2p_1p_2 C_1 - 1$	

Use of the preceding scheme makes it easy to establish the relationships between stereoisomers of the dodecahedron, bicapped trigonal prism, and antiprism when there are three identical chelating ligands and one chelating ligand which is different (or two identical monodentate ligands located in a given edge of the polyhedron). The corresponding scheme for dodecahedral-antiprismatic conversions is:\*



In each of the symbols, the fourth letter (the one with the plus sign) refers to the edge which is occupied by the pair of monodentate ligands. Some deformations of the dodecahedron lead to antiprism stereoisomers where the bidentate ligands spanning pairs of vertices are not located on the edges of the polyhedron (such pairs are designated by  $D_5$  if they belong to one of the rectangular faces of the antiprism, and by  $D_1$  if they do not). The cases where such pairs occur are given in parentheses.

The right-hand part of the scheme shows the deformations between the dodecahedron and antiprism when the monodentate ligands do not lie on the same polyhedron edge. The vertices of the dodecahedron occupied by these

\* See note in Table 3.

TABLE 3. Stereoisomers of Eight-Coordinate Complexes with Three Identical Chelating Ligands\*

Dodecahedron		Bicapped trigonal prism		Antiprism	
I	II	I	II	I	II
$mmm + m$ $ggg + g$ $ggg' + g'$	$\{ amm + B, B$ $agg + B, B$	$\{ t_1 t_1 p_2 + p_2$ $t_1 p_2 p_2 + t_1$	$\{ h_1 h_1 h_2 + C, C$ $t_1 t_1 h_2 + C, C$ $t_2 t_2 h_1 + C, C$	$sss + s$ $lll + l$	$sll + D_s$
$\{ mmg + g$ $mgg + m$	$\{ bmm + A, A'$ $bgg + A, A'$ $bgg' + A, A'$ $bg'g + A, A'$	$\{ h_1 h_1 p_2 + p_2$ $h_1 p_2 p_2 + h_1$		$\{ ssl + l$ $sll + s$	$\{ lll + D_l$ $ssl + D_l$ $ssl' + D_l$
$\{ aab + b$ $abb + a$		$\{ t_2 t_2 p_1 + p_1$ $t_2 p_1 p_1 + t_2$	$\{ h_2 p_1 p_1 + M, M$ $t_2 p_1 p_2 + M, M$		
$\{ abm + g$ $abg + m$ $amg + b$ $bmg + a$	$\{ abg + A, B$ $mgg + A, B$	$\{ t_1 h_2 p_1 + p_1$ $t_1 p_1 p_1 + h_2$ $h_2 p_1 p_1 + t_1$	$\{ t_2 p_1 p_1 + M, N$ $h_1 p_1 p_2 + M, N$		
		$\{ t_1 t_2 p_1 + p_2$ $t_1 t_2 p_2 + p_1$ $t_1 p_1 p_2 + t_2$ $t_2 p_1 p_2 + t_1$	$\{ t_2 t_2 p_1 + M, C$ $t_1 t_2 p_2 + M, C$ $t_2 h_1 p_2 + M, C$ $h_1 h_2 p_1 + M, C$		
		$h_1 t_2 p_1 + p_2$ $h_1 t_2 p_2 + p_1$ $h_1 p_1 p_2 + t_2$ $t_2 p_1 p_2 + h_1$			

\*Column I is for complexes with four chelating ligands, one of which differs from the other three; column II is for complexes with two monodentate ligands in addition to the three chelating ligands.

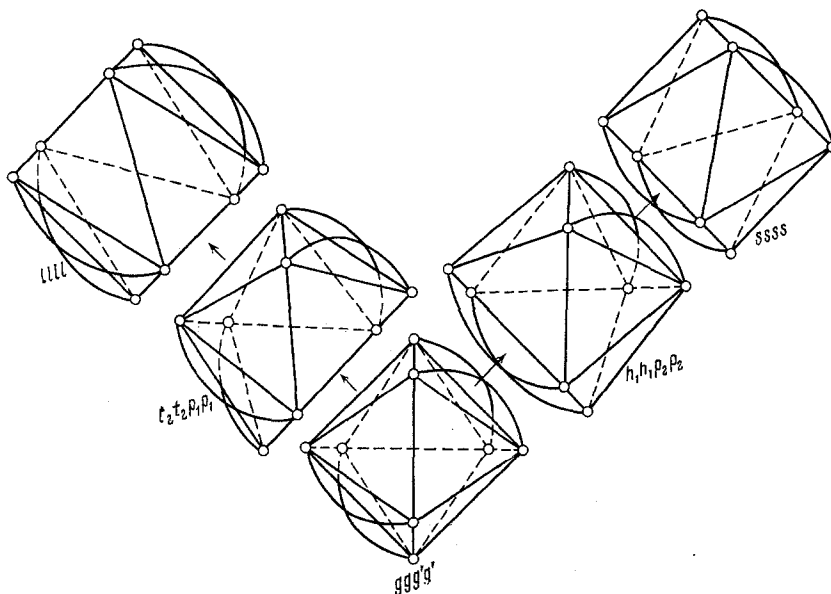


Fig. 5. Deformation of the  $ggg'g'$  dodecahedron to form bicapped trigonal prisms and antiprisms.

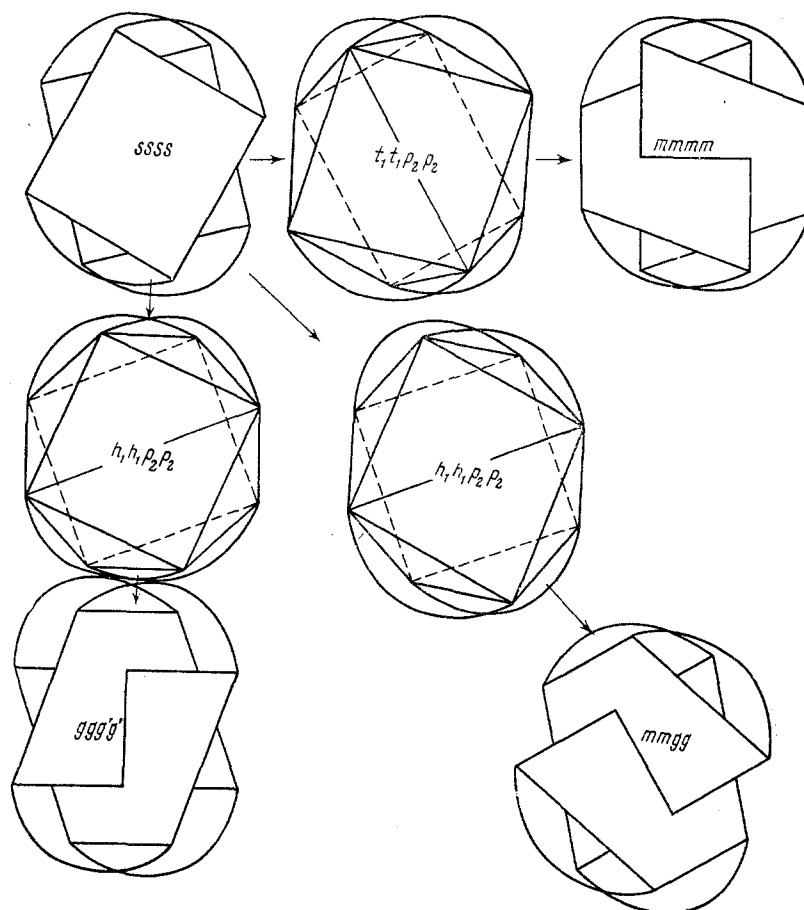


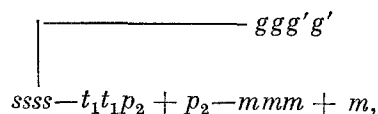
Fig. 6. Deformation of the *ssss* antiprism to form bicapped trigonal prisms and dodecahedra.

ligands are designated by the letters A and B: the combinations A, B and B, B refer to nonadjacent vertices on the same trapezoid, while the combination AA' refers to different trapezoids.

The probabilities of getting the various isomers are different. Some consideration was given to the reasons for this in [3]. For example, it is not likely that identical bidentate ligands would span edges whose lengths are essentially different. This excludes from consideration all of the dodecahedra in which a type b edge is involved, the bicapped trigonal prisms with type  $h_1$  and  $h_2$  edges, and the antiprism where the ligands would span the diagonals, D. In view of these considerations, the isomers which are actually possible and the associated transitions between them are listed separately under the heading, "Main isomers."

It is clear that isomers involving like edges are more probable than the isomers involving unlike edges. Also, according to [3], electronic repulsions between the ligands make the lengths of the *s* and *l* edges of the antiprism nonequivalent, and the *a*, *m*, and *g* edges of the dodecahedron nonequivalent ( $a = m \neq g$ ). Thus, combinations using *s* and *l*, *a* and *g*, or *m* and *g* simultaneously are less probable. The most favorable isomers — the ones which remain after these considerations are applied — are shown in the schemes in bold type.

In the last column of Table 1 are shown the isomer types found in rare earth  $\beta$ -diketonates whose structures have been determined. In all cases, they fall into the group of the most probable isomers: the antiprismatic complexes are *ssss* isomers, the dodecahedral complexes are *mmm* + *m* (holmium tris acetylacetonate) or *ggg'g'* isomers (thenoyltrifluoroacetate and hexafluoroacetylacetonate), and the bicapped trigonal prismatic complexes are  $t_1t_1p_2 + p_2$  isomers. They all form a common link in the deformation chain:



that is, they can be regarded as various distortions of a single shape.



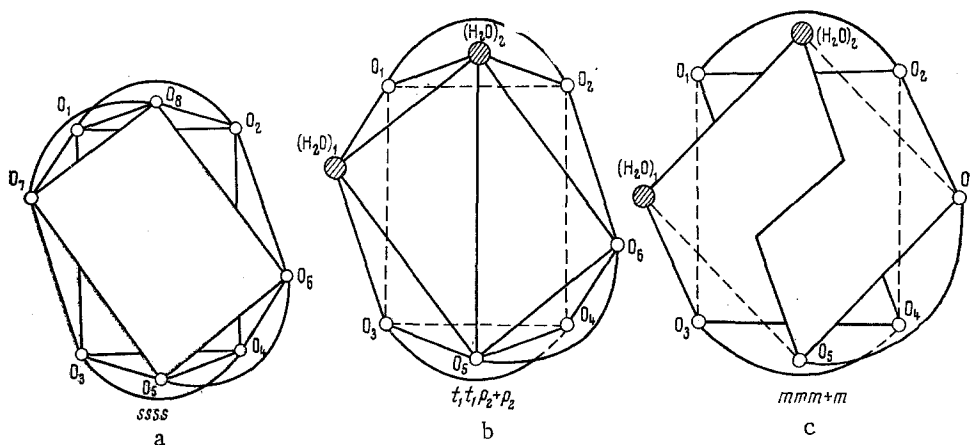


Fig. 7. Coordination polyhedra of rare earth  $\beta$ -diketonates. a) Eu and Gd tetrakis-benzoylacetates; b) La, Nd, and Eu diaquo-tris-acetylacetonates; c) Ho diaquo-tris-acetylacetonate.

The transition, antiprism  $\rightarrow$  bicapped trigonal prism  $\rightarrow$  dodecahedron in the series  $[\text{Ln}(\text{BA})_4]^- \rightarrow [\text{Ln}(\text{AA})_3(\text{H}_2\text{O})_2] \rightarrow [\text{Ho}(\text{AA})_3(\text{H}_2\text{O})_2]$ , can be briefly explained in the following way. In accordance with Hoard and Silverton, the most suitable isomers for acetylacetonate complexes will be the mmmm dodecahedron or the ssss antiprism when the metal-ligand distance is greater than  $2.30 \text{ \AA}$ . The advantage of the latter isomer is that it can be easily deformed to match the requirements of the chelate rings without significantly increasing the interligand repulsions: the square faces of the antiprism can readily be converted into rectangular ones with the edges linked pairwise by the ligands, while the distances between the vertices on the various faces are kept unchanged. Evidently when the metal-ligand distance is close to  $2.30 \text{ \AA}$ , the mmmm dodecahedron is more suitable. The ssss antiprism is more probable when the metal-ligand distance greatly exceeds  $2.30 \text{ \AA}$ . Thus, for most rare earth tetrakis- $\beta$ -diketonates, the ssss antiprism should be characteristic. These conclusions apply especially to the benzoylacetates (Fig. 7a).

The same configuration is found for  $[\text{Ln}(\text{AA})_3(\text{H}_2\text{O})_2]$  molecules (Fig. 7b). However, the rectangular shape of the lower quadrangular face of the antiprism (the one which contains two chelating ligands) allows two of the atoms on the upper face to be closer to the plane of the lower base than the other two. The atoms which are closer are the  $\text{O}_6$  atom and the water molecule,  $(\text{H}_2\text{O})_1$ ; these occupy vertices opposed to the long edges of the lower rectangle. The result is that the upper face is folded about the  $\text{O}_5 \dots (\text{H}_2\text{O})_2$  line, and the polyhedron becomes a  $t_1t_1p_2 + p_2$  isomer of the bicapped trigonal prism.

Further distortions of the polyhedron upon going to  $[\text{Ho}(\text{AA})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  may be due to the decreased radius of the metal atom as the rare earth series is traversed. Decreasing the radius of the metal would lead to an overall shrinkage of the complex. As a consequence of this, steric problems would be increased for contacts involving chelating ligands on the two bases of the polyhedron. The  $\text{O}_4$  and  $\text{O}_5$  vertices would tend to move apart, and there would be folding about the  $\text{O}_1 \dots \text{O}_4$  line (Fig. 7c). The polyhedron takes on the characteristics of an  $\text{mmm} + \text{m}$  dodecahedron.

All of these interpretations are conditional, because the distances between the vertices of the two bases (type 1 edges) differ quite significantly from each other in all of the complexes examined to date.

#### LITERATURE CITED

1. G. A. Bandurkin, Candidate's Dissertation [in Russian], IONKh AN SSSR, Moscow (1967).
2. L. O. Atovmyan, V. G. Andrianov, and M. A. Porai-Koshits, Zh. Strukt. Khim., 3, 685 (1962).
3. J. L. Hoard and J. V. Silverton, Inorgan. Chem., 2, 235 (1963).
4. S. J. Lippard and B. J. Russ, Inorgan. Chem., 7, 1686 (1968).
5. T. Phillips, D. E. Sands, and W. F. Wagner, Inorgan. Chem., 7, 2295 (1968).
6. L. A. Aslanov, M. A. Porai-Koshits, and M. O. Dekaprilevich, Zh. Strukt. Khim., 12, 470 (1971).
7. A. L. Il'inskii, L. A. Aslanov, et al., Zh. Strukt. Khim., 10, 285 (1969).
8. L. A. Aslanov, E. F. Korymyi, and M. A. Porai-Koshits, Zh. Strukt. Khim., 12, 661 (1971).
9. A. L. Il'inskii, M. A. Porai-Koshits, et al., Zh. Strukt. Khim., 13, 277 (1972).

10. L. A. Butman, M. A. Porai-Koshits, and L. A. Aslanov, *Zh. Strukt. Khim.*, 11, 46 (1970).
11. M. J. Bennett, F. A. Cotton, et al., *Inorgan. Chem.*, 7, 1770 (1968).
12. V. K. Bel'skii and Yu. T. Struchkov, *Kristallografiya*, 10, 23 (1965).