Inorganica Chimica Acta, 86 (1984) 33–36

Idealized Eleven-Coordinate Geometries

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Received October 7, 1983

The method of points on a sphere is employed to determine three types of eleven-coordinated polyhedra. These are: a pentacapped trigonal prism (D3h), a monocapped pentagonal antiprism (C5v), and a skewed trigonal prism with an interpenetrating pentagon (C2v). Associated relative repulsive energies for various particle potentials and polar coordinates are reported.

Introduction

In the past two decades increased research related to lanthanide and actinide compounds has generated unusual coordination geometries, especially those with high coordination numbers. The majority of the compounds of the lanthanoid series favors eight or nine ligands in the coordination shell. With increasing lanthanide cation size and small hard ligands, higher coordination systems are expected. Several systems, other than alloys, having a coordination number (CN) of eleven have been reported. Thorium nitrate pentahydrate [1, 2] has eight oxygen atoms from four bidentate nitrate groups and three other oxygen atoms from water molecules. Another eleven-coordinated thorium complex has been reported by Johansson [3]. Further, uranium trifluoride [4] can also be described as having a CN of eleven as well as CeF_3 [5] and LaF_3 [5, 6]. The lack of idealized eleven-coordinate geometries to serve as models has often produced inadvertent misassignment of bonding arrangements. This paper reports three idealized model systems for a CN of eleven.

Method and Results

The method of points on a sphere involving interparticle repulsions was employed in the determination of the model systems. Claxton and Benson [7] have outlined an algorithm which allows ready convergence (zero tangential force) of test systems with varing particle potentials which are in the form of a Born exponent.

The coordinate of each ligand, of a set of m identical ligands, can be represented by a vector $\vec{R}_i$ (for the i th particle). The 'points on the sphere' method requires that the distances of the ligands to the central atom are equal. Therefore this vector $\vec{R}_i$ can be normalized.

$$\frac{\vec{R}_i}{|\vec{R}_i|} = \hat{R}_i \quad \text{where } \hat{R}_i \text{ is a unit vector} \qquad (1)$$

The repulsive energy between each ligand can be expressed as

$$E = \sum_{i=1}^{m-1} \sum_{i=i+1}^{m} |\hat{R}_i - \hat{R}_j|^{-n} \quad \text{where n is the Born exponent.} \qquad (2)$$

The repulsive force acting on the i th ligand is:

$$\vec{F}_i = -\nabla E = n \sum_{\substack{j-1 \\ j \neq i}}^{m} (\hat{R}_i - \hat{R}_j)|\hat{R}_i - \hat{R}_j|^{-(n+2)}. \qquad (3)$$

∇ is the divergence along the direction of $\hat{R}_i - \hat{R}_j$. The new position of $\hat{R}_i$ is obtained by allowing the i th ligand to move in the direction of the resultant force acting on it. Usually, this results in the departure of the point representing the ligand from the surface of the coordination sphere. Thus a renormalization of the ligand–central atom distance is required. The new position of the i th ligand is

$$\hat{R}_i\,(\text{new}) = (\hat{R}_i + \gamma\vec{F}_i)/|\hat{R}_i + \gamma\vec{F}_i| \qquad (4)$$

where γ is a scalar which determines the extent of displacement. γ equals (K/F_{max}) where F_{max} is the maximum value of $|\vec{F}_i|$ and i = 1 to m and K is between 0.1 and 0.2.

This 'points on a sphere' method seeks a balance of repulsive force between the ligands rather than an energy minima. This balance requires that the tangential force on each ligand is zero. This tangential force can be shown by using the dot product of $\hat{R}_i$ and $\vec{F}_i$. Zero tangential force means that $\vec{F}_i$ is normal to the tangential plane on the sphere at point $\hat{R}_i$.

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0020-1693/84/$3.00

$$\vec{F}_i \cdot \hat{R}_i = |\vec{F}_i| \cdot |\hat{R}_i| \cos \theta \qquad (5)$$

where θ is the angle between the force $\vec{F}_i$ and $\hat{R}_i$. Since $|\hat{R}_i| = 1$ from eqn. (1), eqn. (5) becomes

$$\vec{F}_i \cdot \hat{R}_i = |\vec{F}_i| \cos \theta . \qquad (6)$$

$\vec{F}_i$ and $\hat{R}_i$ are in the same direction only if θ approaches zero and $\cos \theta = 1$. In an interative procedure, the convergence criteria is met if

$$|\vec{F}_i \cdot \hat{R}_i - |\vec{F}_i|| < \epsilon \qquad (7)$$

where ϵ is a small number arbitrarily chosen to define convergency.

Three idealized geometries described in Cartesian terms are found at ligand repulsion energy minima. Table I gives the repulsive energies at the zero tangential force condition for varing values of the Born exponent. The three determined 11-coordinate geometries are the pentacapped trigonal prism (D3h), the monocapped pentagonal antiprism (C5v), and a skewed trigonal prism with an interpenetrating pentagon (C2v). The polar coordinates of the eleven ligands for these three cases are listed in Table II.

TABLE I. Repulsive Energies (arbitrary units) at Zero Tangential Force.

n	D3h	C5v	C2v
1	40.6221	40.6152	40.5968
2	31.9123	31.8789	31.8348
3	26.4922	26.4017	26.3366
4	23.0092	22.8232	22.7530
5	20.6856	20.3631	20.3107
6	19.0684	18.5710	18.5616
7	17.8911	17.1862	17.2428
8	16.9942	16.0565	16.1978
9	16.2813	15.0926	15.3322

Discussion

Table I shows that for the eleven particles on a sphere the C2v distribution is the most stable (lowest repulsive force) for $1 < n < 6$. For higher values of n (the Born exponent), the monocapped pentagonal antiprism arrangement should be favored. It should be emphasized that this applies to systems with equivalent ligands; non-equivalent or bidentate ligands can approximate these arrangements but may not necessarily adhere to them.

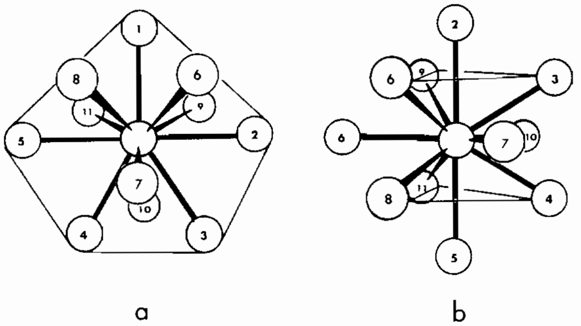

Fig. 1. The pentacapped trigonal prism (D3h). Note the five member plane in a. The C_3 rotational axis is along L2–C–L5.

The pentacapped trigonal prism is illustrated in Fig. 1a and 1b. This type of 11-coordinated polyhedron is the most symmetrical of the three presented geometries but has the highest repulsive force (see Table I). The general arrangement resembles the classical nine-coordinated tricapped trigonal prism except the prism is shorter and has two additional caps located above and below the trigonal apical planes. The two apical capping ligands and the central atom lie on a three-fold axis of rotation. This particular form also contains three five-member planes intersecting the central atom.

TABLE II. Spherical Angular Coordinates (°) for D3h, C5v, C2v Configurations.

D3h		C5v		C2v	
PHI	CHI	PHI	CHI	PHI	CHI
0.00	0.00	0.00	0.00	0.00	0.00
0.00	59.06	0.00	66.08	0.00	59.65
120.00	59.06	72.00	66.08	0.72	122.73
240.00	59.06	144.00	66.08	180.06	122.73
60.00	90.00	216.00	66.08	180.77	59.65
180.00	90.00	288.00	66.08	59.96	82.25
300.00	90.00	36.00	122.86	90.39	144.21
0.00	120.94	108.00	122.86	120.81	82.25
120.00	120.94	180.00	122.86	300.69	83.13
240.00	120.94	252.00	122.86	270.39	145.25
0.00	180.00	324.00	122.86	240.08	83.13

TABLE III. Angles and Distances (sphere radius = 1.00, n = 6).

D3h		C5v		C2v	
L1–C–L2	90.00	L1–C–L2	66.08	L1–C–L2	59.70
L1–C–L5	90.00	L1–C–L7	122.86	L1–C–L5	59.70
L2–C–L3	59.06	L2–C–L3	72.00	L2–C–L3	63.10
L2–C–L5	180.00	L7–C–L8	72.00	L4–C–L5	63.10
L6–L3–L9	60.00			L3–C–L4	114.50
L10–L7–L1	60.00			L8–L7–L6	54.00
L8–L11–L4	60.00			L11–L10–L9	54.00
				L8–L6–L7	63.00
				L11–L9–L10	63.00
				L1–L7–L10	72.60
				L1–L10–L7	72.10
				L7–L1–L10	35.30
L2–L5	2.00	L1–L2	1.09	L1–L2	0.99
L2–L3	0.99	L2–L3	1.07	L2–L3	1.05
L2–L10	1.41	L2–L7	1.09	L3–L4	1.68
L3–L9	1.49			L6–L8	1.00
L3–L10	1.07			L6–L7	1.10
L4–L10	1.07			L8–L11	1.71
L4–L5	0.99			L6–L9	1.71
				L7–L10	1.16

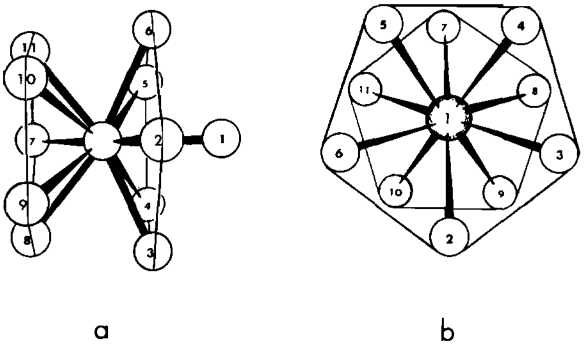

Fig. 2. Two views of the monocapped pentagonal antiprism (C5v). The monocap is directly over the center in b. A C_5 rotational axis exists along L1–C.

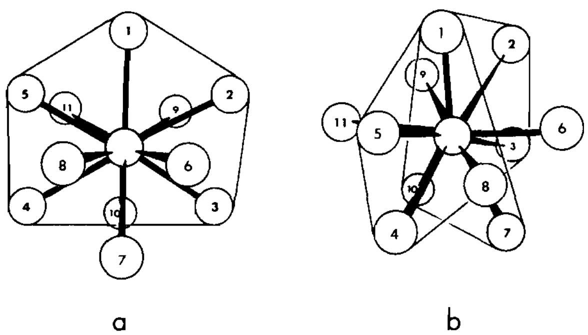

Fig. 3. The skewed trigonal prism with an interpenetrating pentagon (C2v). The five member plane can be seen in a. The C_2 rotational axis is along L1–C.

The monocapped pentagonal antiprism (C5v) is presented in Fig. 2a and 2b. The presented arrangement is expected for this type of geometry. The ligands on each pentagonal plane are separated by an angle (72°) defined by the two involved ligands and a central point on the plane. The L–L distance in this arrangement is greater for the capped plane. The lower pentagonal plane is rotated 36° with respect to the capped plane.

The geometry of the C2v case (shown in Fig. 3a and 3b) exhibits a five-member horizontal plane which is orthogonally bisected by the L(1)–L(7)–L(10) plane. The four remaining ligands are symmetrically located, two on each side of this vertical mirror plane. The C2 rotational axis is observed along the bond formed by the central atom (C) and L1. This polyhedron resembles the D3h case. The primary difference between the two types (D3h and C2v) is related to the bond angles on the five member planes. Note that angles L1–C–L2 and L1–C–L5 in cases D3h and C2v are 90.00° and 59.70°, respectively. Important bond angles and distances are given in Table III.

Most reported eleven CN systems appear to fit C2v geometry. A text example is the monodentate trifloride, CeF_3 [5], which fits very well. LaF_3 [5, 6] is similar to CeF_3 [5]. These two systems favor the C2v over the D3h case because distortion is found about the D3h required equatorial plane. This bisecting plane is not parallel to the apical trigonal planes of the prism. Bidentates, such as the thorium compounds [1–3], approach this C2v arrangement but have some distortions about the five member interpenetrating plane. UF_3 [4] can also be described by C2v geometry; there is only a slight shift out of plane by one of its ligands. A search for other 11-coordinate compounds is ongoing.

Acknowledgements

The authors wish to thank The Robert A. Welch Foundation (grant No. AA-668) and Baylor University for financial support of this work.

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