Application of the Duality Principle to Chiral Icosahedral Metal Complexes

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Symmetry lowering from I_h to T symmetry in mononuclear complexes was the subject of a recent communication by Hegetschweiler and co-workers[1] and of a corrigendum[2] quoting two other complexes of this type previously obtained by Prinzbach and co-workers.[3] These complexes are made up of a central ion surrounded by twelve atoms in an idealized icosahedral I_h symmetry. Because of the presence of four tripodal ligands in a tetrahedral arrangement, the (idealized) symmetry group of the complex is lowered to T.

I would like to draw attention to the occurrence of the same symmetry lowering in a dodecahedrane derivative $C_{20}H_{16}F_4$ reported by Schulman and Disch,[4] and to the fact that their example is exactly related to the more recent cases by application of the "duality principle" to the ligands of these polyhedral molecules. In three dimensions, the duality principle[5] expresses the fact that, with appropriate changes, similar properties are obtained upon interchanging points and planes. In the case of polyhedra, this corresponds to an exchange of vertices and faces. The dual or reciprocal of a polyhedron[5d,6] is thus the new polyhedron obtained by connecting the centers of the adjacent faces of the first one: the numbers of faces and of vertices are interchanged, and the number of edges remains the same. The permutation representation of the vertices of one member of the pair is identical with that of the faces of the other and the permutation representation of the edges is the same for both members. For instance, as is well known for the platonic solids,[5d,6] the cube and the dodecahedron are duals of the octahedron and the icosahedron, respectively, and the tetrahedron is its own dual. Table 1 presents the relationships between the vertices, edges, and faces of these solids, and Figure 1 shows how a regular octahedron is obtained by connecting the centers of the faces of a cube.

Theoretical consequences of the relationships between dual polyhedra have been explored in the theoretical chemistry of fullerenes,[7] boron hydrides,[8] and transition-metal–silicon clusters.[9] Experimentally, dual polyhedral backbones of molecular assemblies have been found in intermetallic crystals,[10] and dual infinite networks have also been reported.[11]

Apparently, the duality principle has not been extended to ligands. A monovalent substituent on a polyhedral molecule can be considered as a label attached to a vertex, producing a labeled face in the dual. It thus seems legitimate to consider that the dual of a monovalent substituent on a trivalent vertex of a polyhedral molecule is a tridentate ligand connected to the atoms of a triangular face of the dual, the symmetry of the labeled dual being maintained when the tridentate ligand is C_3-symmetric. Precisely this situation exists in the molecules described in references [1,3], in which tripodal ligands are connected to triangular faces of the

Table 1: Relationship between the numbers v of n-coordinated vertices, f of m-sided faces and e of edges in the platonic polyhedra. These numbers obey Euler's formula $v-e+f=2$

Polyhedron	Symmetry group	v	n	f	m	e
Tetrahedron	T_d	4	3	4	3	6
Octahedron	O_h	6	4	8	3	12
Cube	O_h	8	3	6	4	12
Icosahedron	I_h	12	5	20	3	30
Dodecahedron	I_h	20	3	12	5	30

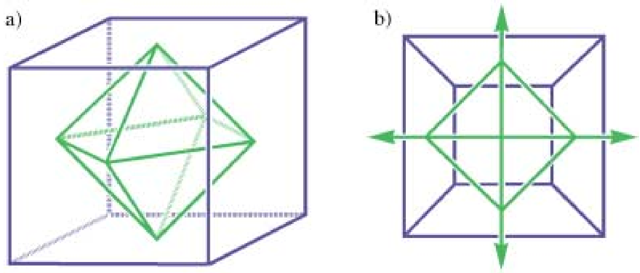

Figure 1. By connecting the centers of the faces of a cube, the dual octahedron is obtained; the dual of a three-coordinated vertex is a triangular face and the dual of a square face is a four-coordinated vertex. a) Perspective view. b) Corresponding Schlegel diagram; the four arrows represent a single vertex at infinity.

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coordination polyhedron. The symmetry characteristics of these molecules may be represented by a regular icosahedron with faces labeled in such a way that the total object has *T* symmetry (Figure 2 d). The dual of this schematic figure is a dodecahedron with labeled vertices at the symmetrical tetrahedral positions (Figure 2 a).[12]

As mentioned above, a molecule of this type, $C_{20}H_{16}F_4$ (Figure 2), was studied more than twenty years ago,[4] so that the experimental examples of references [1,3] are dual transpositions of this symmetry lowering from I_h to T.

A transposed version of this vertex/face duality exists (Figure 3): in *para*-dicarbaclosododecaborane (Figure 3 a), the I_h symmetry of $(B_{12}H_{12})^{2-}$ is lowered to D_{5d} by vertex labeling, whereas the dodecahedrapentaene of Schleyer and co-workers[13] (Figure 3 b) represents a dual molecule in which the symmetry of the smallest fullerene has been lowered by labeling the upper and lower faces with ten hydrogen atoms. Other D_{5d} dodecahedral molecules such as (the unknown) $C_{20}H_{10}F_{10}$, with its ten fluorine substituents either on the upper and lower rings or on the "equatorial" ring, are similarly related to *para*-dicarbaclosododecaborane.

Application of the duality principle is not restricted to labeled vertices and faces of dual polyhedra: examples of symmetry lowering by labeling corresponding edges in a pair of dual polyhedra can also be envisaged. I would like to suggest that this principle, a useful heuristic tool in geometry,[5] could play a similar role in structural chemistry.

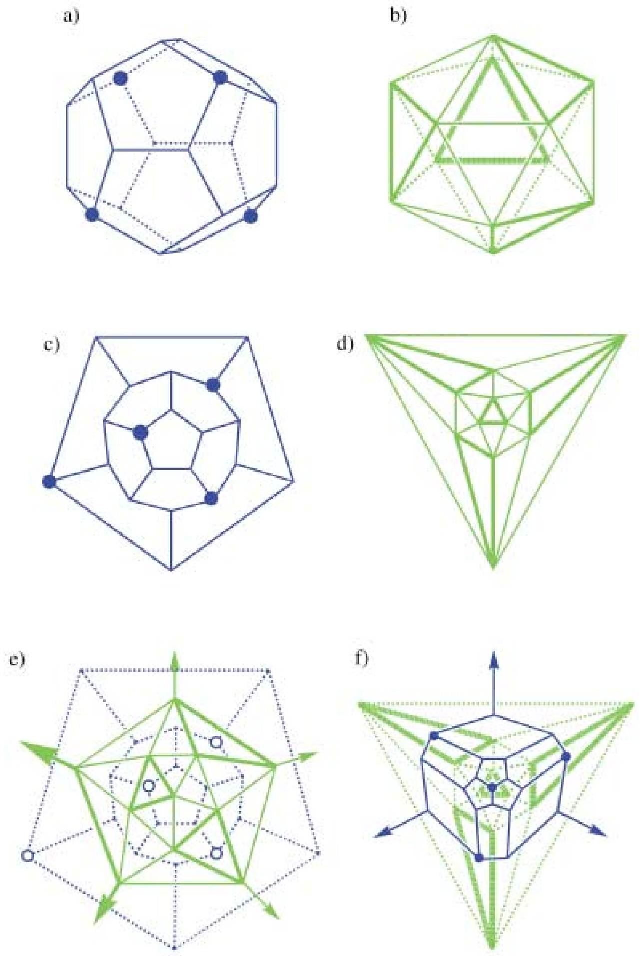

Figure 2. a) Perspective view of a labeled dodecahedron: symmetry is lowered from I_h to T by labeling four vertices (dots) in a regular tetrahedral arrangement. When dots and unlabeled vertices are taken as CF and CH respectively, the figure represents $C_{20}H_{16}F_4$. b) Schlegel diagram corresponding to a). c) Schlegel diagram of the dual icosahedron (in green) superimposed on b): the dual is obtained from b) by connecting the centers of the adjacent faces and labeling the faces corresponding to the four labeled vertices with thick lines. The five arrows represent a single pentavalent vertex at infinity. d) Perspective view of a labeled icosahedron: symmetry is lowered from I_h to T by labeling four faces (thick lines) in a regular tetrahedral arrangement, as in Figure 1 b of reference [1]. e) Schlegel diagram corresponding to d). f) Schlegel diagram of the dual dodecahedron (in blue) superimposed on e): the dual is obtained from e) by connecting the centers of the adjacent faces and labeling the vertices corresponding to the four labeled faces with dots. The three arrows represent a single trivalent vertex at infinity.

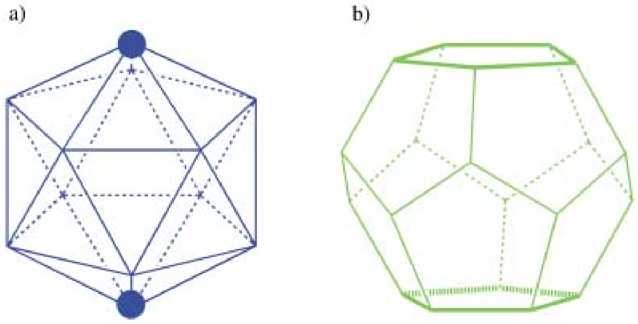

Figure 3. Symmetry lowering from I_h to D_{5d} by labeling a) two vertices (dots) in an icosahedron, and b) the dual faces (thick lines) in a dodecahedron. In a), when labeled and unlabeled vertices represent CH and BH, respectively, the figure represents $p\text{-}B_{10}C_2H_{12}$. In b), when vertices on the labeled faces are taken as CH, and the unlabeled faces as C, the figure represents the aromatic $C_{20}H_{10}$ of reference [13].

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