Ligand Field Splitting of d-Orbitals in Eight Coordinated Complexes of Square Antiprism Structure

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The splitting of d-orbitals in the ligand field of a square anti-prism structure is given. Fivefold degenerate level splits into $A_1 + E_2 + E_3$. The energy order of d orbitals is obtained from known order of d orbitals in a cube considering the effect of distortion of a cube into an antiprism on each of d orbitals. It follows that d_{z^2} orbital is substantially more stable than others.

The UV spectra and magnetic properties of transition metal complexes may be interpreted by the splitting of the d orbitals in the electrostatic field of the ligands. Bethe[1] has described the splitting of different degenerate orbitals under the influence of the outer electrostatic fields in crystals. Following this work Ilse and Hartmann[2] successfully explained the observed absorption spectra of a few metal ions, assuming that the absorption is due to a promotion of an electron from a lower to a higher level of the originally degenerate set of levels. Several authors have later studied a large number of complexes of different symmetry and structure and most of the important cases have now been examined. However, the ligand field splittings for complexes of the Archimedean square antiprism geometry have not yet been reported. This problem is of interest since the antiprism as a coordination polyhedron is found[3] in the methyl acetylacetonates of Zr, Ce, Th and U.

The splitting of the degenerate levels depends on the symmetry properties of the perturbation potential field only. This is determined by the symmetry of the coordination polyhedron and can be obtained by the methods of group theory. The square antiprism belongs to the symmetry point group D_{4d} and for this group the fivefold degenerate d orbitals split into one single and two double degenerate levels (see Appendix). The order of these levels depends generally on the geometry of the structure considered and can be calculated by perturbation theory (for an example see ref. 4). The calculation of the perturbation matrix elements is very lengthy since the corresponding integrals involve the factor $1/r_{12}$. However, in the case of the antiprism, the order of d orbitals can be obtained by a comparison of the known order of the splitting of d orbitals in a tetrahedron and a cube.

A cube and a tetrahedron are simply related: alternate corners of a cube make a tetrahedron. Therefore the splitting for a cube is twice as large as

the one for a coresponding tetrahedron (see Fig. 1). The order of the d electron orbital levels in this case is well known:

$$d_{xy} \; d_{yz} \; d_{zx} \qquad \text{belong to } T_{2g} \text{ level}$$
$$d_{x^2-y^2} \; d_{z^2} \qquad \text{belong to } E_g \text{ level}$$

the T_{2g} levels having the higher energy. The Archimedean antiprism can be obtained from a cube by a relative rotation of two opposite bases through 45°. The axis of rotation is one of the three fourfold axes of the cube. The energy behaviour of each of the five d orbitals during the distortion of the cube into the antiprism is as follows:

d_{z^2}	is axially symmetrical and is therefore unaffected by the relative twist of the two bases of the cube.
d_{xy} and $d_{x^2-y^2}$	which belong to different levels (T_{2g} and E_g respectively) in the cube become equivalent (degenerate) in the antiprism. The energies of these orbitals are expected to meet halfway between the d_{z^2} orbital and the d_{xz} and d_{yz} orbitals, since in the antiprism four ligands contribute towards stability of the orbital, and the other four increase the energy of the two d orbitals concerned.
d_{xz} and d_{yz}	are not stabilized on passing from a cube to an antiprism. In the cube these orbitals avoid ligands situated at the corners, but after the distortion each of them is directed towards two ligands.

From these considerations we conclude that the d_{z^2} orbitals is substantially more stable than others. The orbital energies are shown in Fig. 1. It is interesting to note that the d_{z^2} orbital is not used in d^4sp^3 hybridization for square antiprism structures[5]. This orbital, on account of its symmetry properties, makes no contribution to bonds directed to the corners of the square antiprism and therefore is expected to be the most stable.
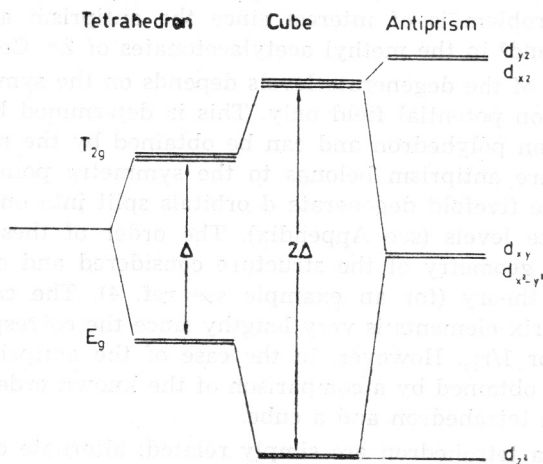

Fig. 1: Splitting of d-orbitals in tetrahedron, cube and square antiprism. The order of levels is indicated on the right of the energy diagram.

APPENDIX

Characters for $(2l + 1)$ dimensional representation can be obtained using

$\chi(I) = 2l + 1$

$\chi(C_2) = (-)^l$

$\chi(C_4) = (-)^{l/2}$

$\chi(\sigma) = 1$

$$\chi(S_4) = \sum_{-l}^{+l} (-)^{l + |m|} e^{im\frac{\pi}{2}}$$

These relations are derived from representation matrices of symmetry elements, and are described at some length for example by Kelen[6], where the explanation of the symbols used and the origin of the formulae can be found.

The characters of the n dimensional representations of the square antiprism are given in Table I. This table can be compared with the character table for the point group D_{4d} (see for example Herzberg[7]).

TABLE I

Characters of the n *dimensional representations of the rotation group restricted by the symmetry properties of square antiprism.*

l	I	S_8	C_4	$S_8{}^3$	C_2''	C_2	σ_d
0	1	1	1	1	1	1	1
1	3	$1+\sqrt{2}$	1	$1-\sqrt{2}$	-1	1	1
2	5	$1+\sqrt{2}$	-1	$1-\sqrt{2}$	-1	1	1
3	7	1	-1	1	-1	1	1

TABLE II

Symmetry types and characters for the point group D_{4d}

D_{4d}	I	S_8	C_4	$S_8{}^3$	C_2''	C_2	σ_d
A_1	1	1	1	1	1	1	1
A_2	1	1	1	1	1	-1	-1
B_1	1	-1	1	-1	1	1	-1
B_2	1	-1	1	-1	1	-1	1
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0
E_2	2	0	-2	0	2	0	0
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0

The point group D_{4d} has four one-dimensional and three two-dimensional irreducible representations Table II. Therefore every term of free atom of a higher degree of degeneracy than two will split in the crystal field of an antiprism. By a comparison of the two tables of characters one obtains:

$l = 0 \quad s \quad A_1$

$l = 1 \quad p \quad A_1 + E_3$

$l = 2 \quad d \quad A_1 + E_2 + E_3$

$l = 3 \quad f \quad A_1 + E_1 + E_2 + E_3$

i. e., Table I can be obtained from Table II by performing the above indicated additions of the corresponding rows. We see that the three p orbitals and the five d orbitals are no longer equivalent. The five d orbitals are split into three terms A_1, E_2 and E_3. That is, the orbitals are not all equally efficient in avoiding negative charges situated at the corners of the antiprism. Knowing the forms of these orbitals, these results are to be expected.

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IZVOD

Cijepanje d orbitala kompleksa koordinacije osam u ligandnom polju strukture kvadratične antiprizme

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Opisano je cijepanje degeneriranoga terma d elektrona u elektrostatskom polju kompleksa geometrije kvadratične antiprizme. Peterostruko degenerirani term se cijepa u tri nivoa: $A_1 + E_2 + E_3$. Energetski redoslijed novih nivoa dobiven je iz poznatoga redoslijeda d orbitala u kocki razmatrajući efekt deformacije kocke u antiprizmu na pojedine d orbitale. Rezultat je znatna stabilizacija d_{z^2} orbitale u odnosu na ostale d orbitale.

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