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Study of relationships between ligand binding in a metal complex a

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The Crystal Field Theory (CFT) is a model for the bonding interaction between transition metals and ligands. It describes the effect of the attraction between the positive charge of the metal cation and negative charge on the non-bonding electrons of the ligand. When the ligands approach the central metal ion, the degeneracy of electronic orbital states, usually d or f orbitals, are broken due to the static electric field produced by a surrounding charge distribution. CFT successfully accounts for some magnetic properties, colors, and hydration energies of transition metal complexes, but it does not attempt to describe bonding.

Bonding in Transition Metal Complexes

Many approaches have been put forth to explain the nature of bonding in complexes.

Important ones are:

1. Valence Bond Approach (VBA)
2. Crystal Field Approach (CFA).
3. Ligand Field Approach (LFA)
4. Molecular Orbital Approach (MOA)

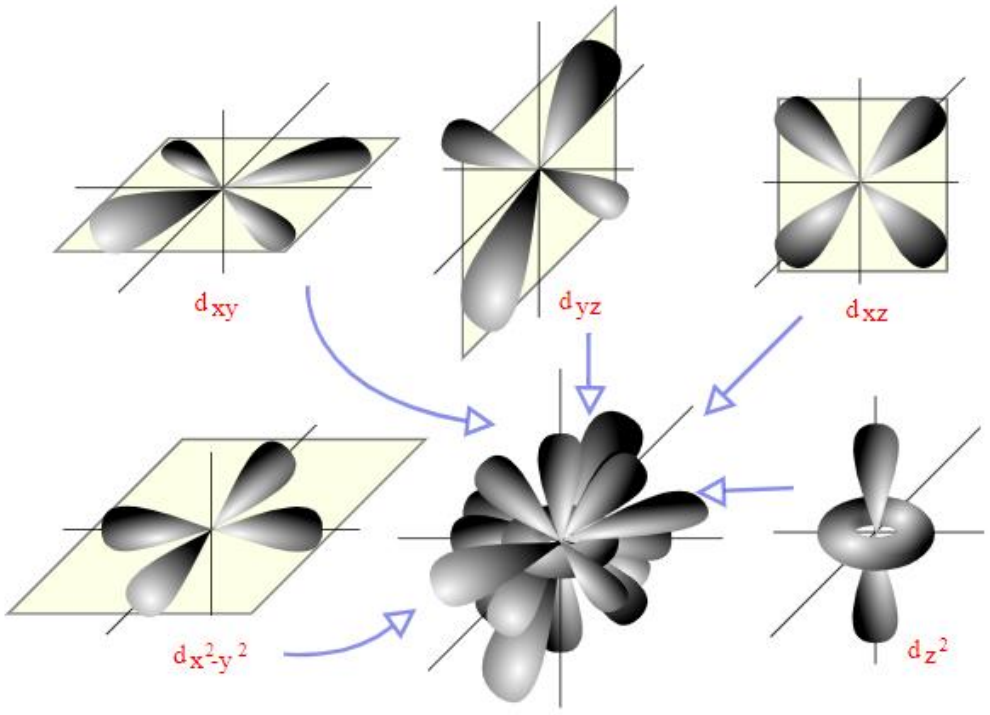
The crystal field approach (CFA) is an electrostatic model which considers the metal – ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. The transition metal(central metal atom) is regarded as a positive ion and is surrounded by negative or neutral ligands which have a lone pair of electrons. If the ligand is neutral like NH3, the negative end of the dipole in the molecule is directed towards the metal atom. The electrons on the central metal atom are under repulsive forces from the ligands, hence they occupy the d orbital furthest from the direction of the ligands.

The electrons in the d orbitals of the central metal ion and those in the ligand repel each other due to repulsion between like charges. Therefore, the d electrons closer to the ligands will have

a higher energy than those further away, which results in the d orbitals splitting in energy. This splitting is affected by:

- The nature of the metal ion
- The metal's oxidation state (a higher oxidation state leads to a larger splitting)
- The arrangement of the ligands around the metal ion
- The nature of the ligands surrounding the metal ion

All of the d orbitals have four lobes of electron density, except for the dz2 orbital, which has two opposing lobes and a doughnut of electron density around the middle. The d orbitals can also be divided into two smaller sets. The dx2–y2 and dz2 all point directly along the x, y, and z axes. They form an eg set. On the other hand, the lobes of the dxy, dxz, and dyz all line up in the quadrants, with no electron density on the axes. These three orbitals form the t2g set. In most cases, the d orbitals are degenerate, but sometimes they can split, with the eg and t2g subsets having different energy. The CFT accounts for this.



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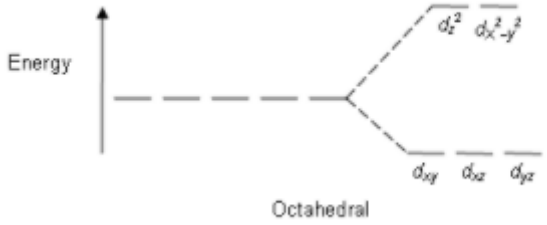
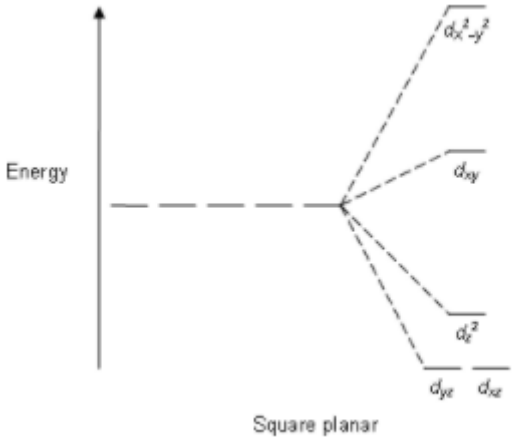
The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the d orbitals are split in a ligand field, some of them become lower in energy than before. For example, in the case of an octahedron, the t2g set becomes lower in energy. As a result, if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field by the amount known as the CFSE. Conversely, the eg orbitals are higher in energy. So, putting electrons in them reduces the amount of CFSE.



Octahedral

Crystal field stabilization is applicable to the transition-metal complexes of all geometries. The reason that many d8 complexes are square-planar is the very large amount of crystal field stabilization that this geometry produces with this number of electrons.



Square planar

The most common type of complex is octahedral, in which six ligands form the vertices of an octahedron around the metal ion. In octahedral symmetry the d-orbitals split into two sets with

an energy difference, Δoct (the crystal-field splitting parameter, also commonly denoted by 10Dq for ten times the "differential of quanta"[3][4]) where the dxy, dxz and dyz orbitals will be lower in energy than the dz2 and dx2-y2, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experiences less repulsion. The three lower-energy orbitals are collectively referred to as t2g, and the two higher-energy orbitals as eg. These labels are based on the theory of molecular symmetry: they are the names of irreducible representations of the octahedral point group, Oh.(see the Oh character table) Typical orbital energy diagrams are given below in the section High-spin and low-spin.

Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal ion. In a tetrahedral crystal field splitting, the d-orbitals again split into two groups, with an energy difference of Δtet. The lower energy orbitals will be dz2 and dx2-y2, and the higher energy orbitals will be dxy, dxz and dyz - opposite to the octahedral case. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d-orbitals, the energy splitting will be lower than in the octahedral case. Square planar and other complex geometries can also be described by CFT.

The size of the gap Δ between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of Δ, while others always give a large splitting. The reasons behind this can be explained by ligand field theory. The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce.

References :

- Bethe, H. (1929). "Termaufspaltung in Kristallen". Annalen der Physik (in German). 395 (2): 133–208
- Van Vleck, J. (1932). "Theory of the Variations in Paramagnetic Anisotropy Among Different Salts of the Iron Group". Physical Review. 41 (2): 208–215.
- Penney, William G.; Schlapp, Robert (1932). "The Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. I. The Rare Earths, Especially Pr and Nd". Physical Review. 41 (2): 194–207.

- Schlapp, Robert; Penney, William G. (1932). "Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. II. The Iron Group, Especially Ni, Cr and Co". Physical Review. 42 (5): 666–686.
- G. L. Miessler and D. A. Tarr “Inorganic Chemistry” 2nd Ed. (Prentice Hall 1999), p.379