

Cristal Field Theory

Giuseppe Marco Randazzo

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Sommario

Questo testo riguardante la teoria del Cristal field è riferito verso coloro che hanno avuto difficoltà di comprensione su tale argomento, il quale è stato discusso durante le lezioni di Chimica Inorganica 3 tenute dal Prof. Enrico Rizzarelli. Si tratta semplicemente di una rielaborazione degli appunti. Buona lettura. Se incontrate errori concettuali e/o errori di scrittura (molto probabile a causa del mio pessimo inglese) non esitate a notificarlo. Grazie!

[<zeld@freaknet.org>](mailto:zeld@freaknet.org)

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Indice

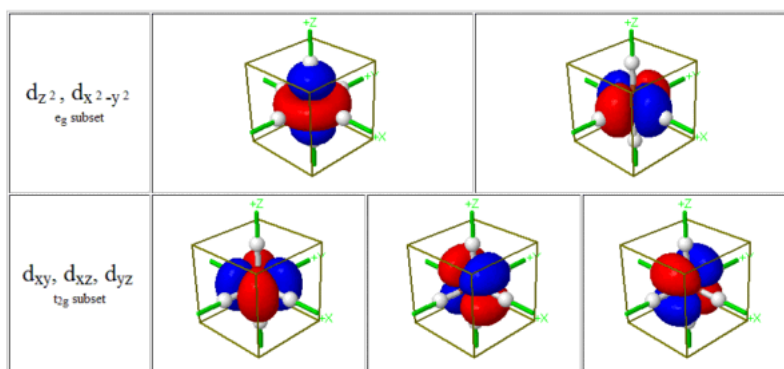
1	The Theory and an application of this to d block of periodic table	3
2	Cristal Field Stabilization Energy: paramagnetic and diamagnetic system	5
3	Characterization of complex	6
4	The failure of cristal field theory	6
5	Spectro-chemical series	6

1 The Theory and an application of this to d block of periodic table

The crystal field theory was developed after the failure of valence bond theory in explaining compound with high spin or low spin. In the ionic CFT, it is assumed that the ions are simple point charges. When applied to alkali metal ions containing a symmetric sphere of charge, calculations of energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

$$\text{Electrostatic Potential is proportional to } \frac{q_1 q_2}{r}$$

where q_1 and q_2 are the charges of the interacting ions and r is the distance separating them. This leads to the correct prediction that large cations of low charge, such as K^+ and Na^+ , should form few coordination compounds. For transition metal cations that contain varying numbers of d electrons in orbitals that are NOT spherically symmetric, however, the situation is quite different. The shape and occupation of these d-orbitals then becomes important in an accurate description of the bond energy and properties of the transition metal compound. To be able to understand and use CFT then, it is essential to have a clear picture of the shapes (angular dependence functions) of the d-orbitals.

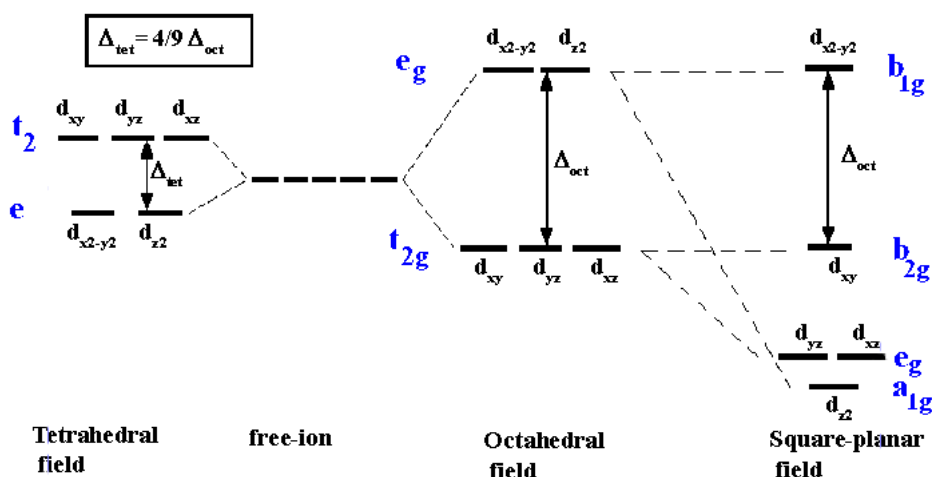


The d orbitals are 5, and can accommodate 10 electrons. The d_{z^2} and $d_{x^2-y^2}$ are oriented respectively on the z-axis and x-y axis, the other 3 orbitals are named d_{x-y} , d_{x-z} and d_{y-z} and are oriented respectively on the angle bisector x-y, angle bisector x-z and angle bisector y-z. This type of orbital is purely directional and it has an orbital angular component. This symmetry is derived from the resolution of the Schrödinger equation, in particular from the spherical harmonics component of Ψ . If these orbitals interact with a ligand that is considered also a charge, in a particular geometrical position, it interacts with the directional orbital of the metal, and from this interaction generates a splitting of the interacting orbitals with the non-interacting orbitals. For example, consider the $[Ti(Cl)_6]^{3-}$ complex in which six chloride ions octahedrally surround the Ti^{3+} cation. On Ti^{3+} there is only one d-electron to be allocated to one of the five d-orbitals because $Ti(0)$ is a d_2 with electron configuration $4s^2 3d^2$, and if we forget 3 electrons it becomes

Ti^{3+} with electron configuration $3d^0 4s^1$ (this is an ion and the d orbitals are the first of the s orbitals) In an octahedral complex, the ligands approach along the z, x and y axes with a coordination number of 6. In the z axis is the d_z^2 , and in the x-y axis there is the $d_{x^2-y^2}$, and the ligands interact with these orbitals bringing them to high energy in front of d_{x-y} , d_{x-z} and d_{y-z} and it generates an energy gap named splitting. In particular for octahedral symmetry is named octahedral splitting and the symbol is Δ_{oct} (See the image on octahedral field).

This diagram describes the crystal field d-orbital splitting for common stereochemistries

Crystal field d orbital splitting diagrams for common stereochemistries.



Generally the d_{x-y} , d_{x-z} and d_{y-z} are named t_{2g} and the d_{z^2} , $d_{x^2-y^2}$ e_g . t is referred to triple degenerate orbitals and e for doubly degenerate orbitals, g indicates the orbital symmetry (gerade, ungerade) and is used where the system has a symmetric center and 2 is referred to other symmetry information. In a tetrahedral system it can't use gerade, ungerade because it doesn't have a symmetric center and the orbitals are named t_2 and e .

The CFT approach can be easily extended to other geometries and the next most important case is the tetrahedron. To predict the splitting pattern of the d-orbitals under a tetrahedral crystal field you may once again find it convenient to consider how the ligands approach into a metal to give a tetrahedron. For tetrahedral complexes, the d-orbitals that interact with ligand orbitals (field) are the d_{x-y} , d_{x-z} and d_{y-z} because in the angle bisectors of x, y and z you can give a tetrahedron. These orbitals are split in front of d_{z^2} and $d_{x^2-y^2}$ with an energy gap named Δ_{tet} .

The same considerations are for square-planar geometry and the other.

2 Cristal Field Stabilization Energy: paramagnetic and diamagnetic system

With the different CFT energy splitting and with spectrophotometric measures you can identify the geometry of sistem. In fact generally the Δ_{tet} is 4/9 of Δ_{oct} (1/2). In over, all the tetrahedral system are at high spin because it have a low energy splitting and the electron can dispose following pauli principle one electron every orbitals on hand. This type of disposition generates an high spin system, and thi type of system is paramagnetic, and in the presence of a magnetic field this system polarize it in the same direction of the applied field. The octaedral system generally stretch to do diamagnetic compoun because the Δ_{oct} is high, and the energy gap is very high for dispose one electron in every orbitals on hand, and for give a total low energy, the system coupling the electron always following pauli principle two electron for one orbital with $m_s +1/2; -1/2$. This type of system have all the electron coupled and in presence of a magnetic field they polarize it in the opposite direction of field. This type of measurement can be realized by magnetic susceptibility measurement.

Generally the CFSE is function of d electron on system. Analyze the cases in an octaedral field for all the d electron from 1 to 8:

for t_{2g} Δ_{oct} misurated in front of 5 d degenerate orbitals is $-0,4 \Delta_{oct}$ and for e_g the Δ_{oct} misurated in front of 5 d degenerate orbitals is $-0,6 \Delta_{oct}$.

d^1 : electronic configuration t_{2g}^1 with a CFSE= $1 * (-0,4 \Delta_{oct}) = -0,4 \Delta_{oct}$

d^2 : electronic configuration t_{2g}^2 with a CFSE= $2 * (-0,4 \Delta_{oct}) = -0,8 \Delta_{oct}$

d^3 : electronic configuration t_{2g}^3 with a CFSE= $3 * (-0,4 \Delta_{oct}) = -1,2 \Delta_{oct}$

d^4 : i've two electronic possible disposition:

1) electronic configuration t_{2g}^4

2) electronic configuration $t_{2g}^3 e_g^1$ with a CFSE= $3 * (-0,4 \Delta_{oct}) + (1 * 0,6 \Delta_{oct}) = -0,6 \Delta_{oct}$

d^5 : electronic configuration $t_{2g}^3 e_g^2$ with a CFSE= $3 * (-0,4 \Delta_{oct}) + (2 * 0,6 \Delta_{oct}) = 0$

d^6 : electronic configuration $t_{2g}^4 e_g^2$ with a CFSE= $4 * (-0,4 \Delta_{oct}) + (2 * 0,6 \Delta_{oct}) = -0,4 \Delta_{oct}$

d^7 : electronic configuration $t_{2g}^5 e_g^2$ with a CFSE= $5 * (-0,4 \Delta_{oct}) + (2 * 0,6 \Delta_{oct}) = -0,8 \Delta_{oct}$

d^8 : electronic configuration $t_{2g}^6 e_g^2$ with a CFSE= $6 * (-0,4 \Delta_{oct}) + (2 * 0,6 \Delta_{oct}) = -1,2 \Delta_{oct}$

Now analyze the d^4 electronic configuration 1:

In this case the coupling of two electron generate a coupling energy named P and the CFSE is:

CFSE= $4 * (-0,4 \Delta_{oct}) + P$

This P if is:

$p+$ and Na^+ , should form few coordination compounds. For transition metal cations th $\Delta_{oct} < P$: i give high spin complex

$\Delta_{oct} > P$: i give low spin complex

3 Characterization of complex

There are three types of experimental measurement possible:

- * Light-matter interaction
- * Magnetic susceptibility
- * Thermodynamics measurement

With the light-matter interaction, one can measure the splitting Δ . For example, if one considers a d^1 ion like $[Ti(H_2O)]^{3+}$, it gives only one absorption band, and the energy value of this band is Δ_{oct} . For the light-matter interaction, it is important to consider the selection rules, and the most important are: $\Delta l = \pm 1$ and $\Delta S = 0$ where S is the spin multiplicity.

4 The failure of crystal field theory

Now analyze the case where you change the ligand and measure the Δ_{oct} .

1) $[Fe(CN)_6]^{3-}$ and 2) $[Fe(oxalate)_3]^{3-}$

The Δ_{oct1} is Δ_{oct2} and crystal field theory cannot explain this difference... From this data, we learn of the insufficiency of the theory, and this limit is derived from the consideration of ligand and metal center like charge.

5 Spectrochemical series

A prediction of λ_{max} of absorption can be previewed by using the spectrochemical series that is oriented from a low field to a high field for ligands independently of metal ion and metal ion independently of ligand:

$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < [oxalate]^{2-} < H_2O < NCS^- < NH_3 < bpy < phen < CN^- < CO$
the field increasing \rightarrow

$Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pd(IV)$
the field increasing \rightarrow