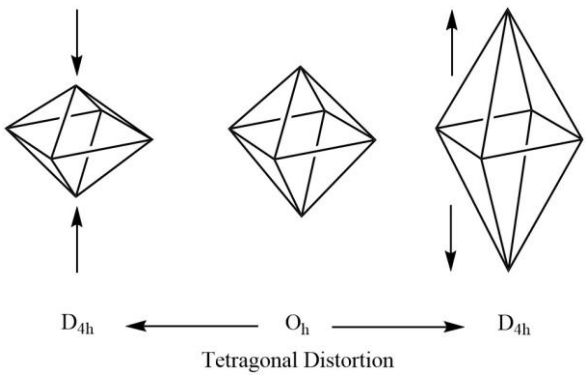
❖ Effect of Distortion on the *d*-Orbital Energy Levels

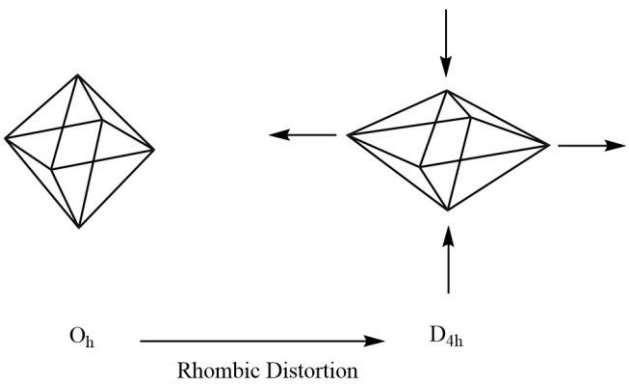
The splitting pattern of five *d*-orbitals for different geometries is also different; and therefore, this also induces an evident effect upon the *d-d* transitions in a metal ion complex. The UV-visible spectrum arising from these transitions provide information about the structure of these complexes. Hence, the effect of structural distortion upon the energies of the various free ion terms must be studied in detail.

➢ *Distortion in Six-Coordinated Complexes*

The hexa-coordination of ligands in different metal complexes can be categorized as octahedral, tetragonal, rhombic and trigonal anti-prismatic. If six ligands are supposed to approach the metal center along *x*, *y*, and *z*-axis (each passing through the two faces of a cube) then the octahedral, tetragonal and rhombic geometries can be represented by the bond length correlation of $x = y = z$, $x = y \neq z$ and $x \neq y \neq z$, respectively. The tetragonal distortions from perfect octahedron occur as the elongation or compression along only one four-fold axis while the rhombic distortions occur as the unequal amount of elongation or compression along two four-fold axes of rotation. Moreover, the trigonal distortions occur as the elongation or compression along one of the four three-fold symmetry axis.

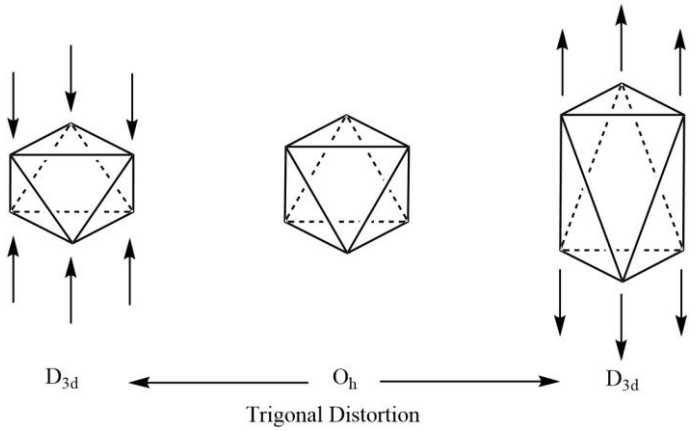


(a)



(b)

Figure 43. Continued on the next page…



(c)

Figure 43. The (a) tetragonal (b) rhombic and (c) trigonal distortion in octahedral metal complexes.

1. Tetragonal distortion: As there is no inter-electronic repulsion in the d^1-complexes, the electronic energy states can be correlated with the splitting pattern of d-orbital set. Hence, in the case of z-out tetragonal distortion, the repulsion between metal electrons and ligand electrons will be less for the states comprising of electron density concentrated in orbitals directed toward z-axis. However, the tetragonal compression along z-axis will destabilize the electronic states having electron density distribution along or near z-axis. The effect of tetragonal distortion upon free ion terms of and d^1 and d^4-metal complexes can be shown as:

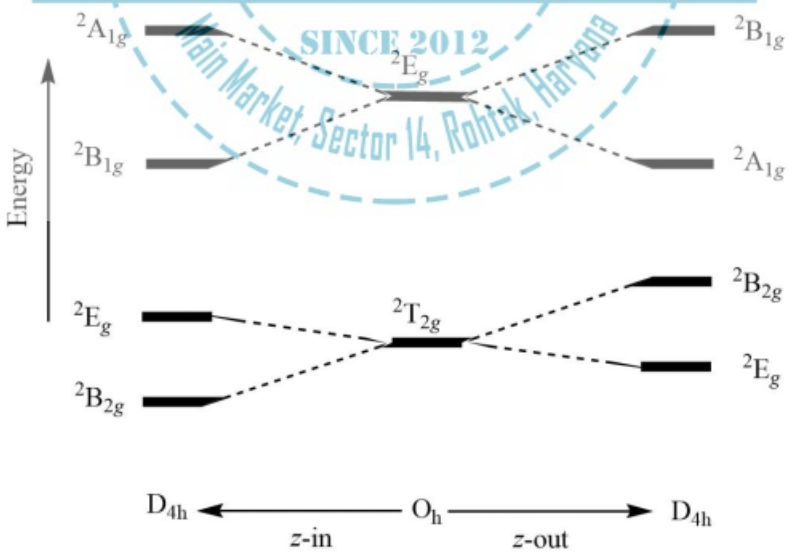


Figure 44. The splitting pattern of d-orbital energy levels of d^1-metal complexes undergoing tetragonal distortion.

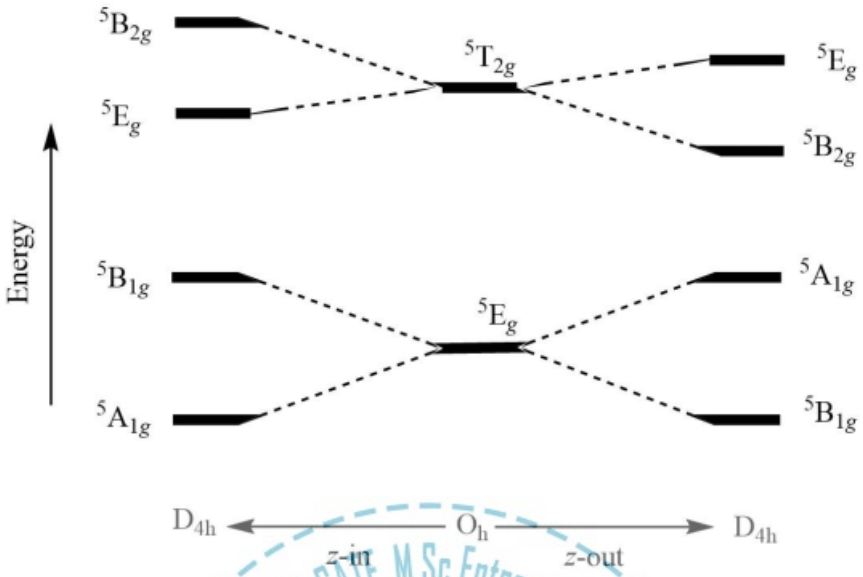


Figure 45. The splitting pattern of *d*-orbital energy levels of d^4-metal complexes undergoing tetragonal distortion.

It is worthy to mention that the homoleptic complexes of d^1-configuration prefer to undergo tetragonal compression due to Jahn-Teller distortion rather than the elongation. However, the heteroleptic complexes do show a splitting profile shown in the left side of Figure 44, like trans-$[TiA_4B_2]^{3+}$, if A-type ligands occupy a higher position in the spectrochemical series than B-type.

Apart from the Jahn-Teller distortions, the degeneracy of electronic states of octahedral complexes is also lifted when all the six ligands are not the same. This lowering of symmetry creates additional energy levels. For instance, Cr^{3+} is a d^3 system and does not show conventional Jahn-Teller distortion but the complexes like trans-$[CrA_4B_2]^{3+}$ show quite complex UV-visible spectrum which can only be explained in terms of energy levels of D_{4h} symmetry. Furthermore, chelate metal complexes like $[Cr(ox)_3]^{3-}$ and $[Cr(en)_3]^{3+}$ are no longer ideal octahedral geometries as their symmetry is lowered down to D_3 point group. However, the UV-visible spectrum of these complexes can successfully be rationalized as if they are arising from a perfectly octahedral complex like $[CrA_6]^{3+}$. This is obviously due to the fact that the extent of perturbation in these chelate complexes is quite small. Nevertheless, if we replace one ethylenediamine with two F^- ligands to form trans-$[Cr(en)_3]^{3+}$, the perturbation produced by the differentiation of the ligands is no more intolerable limit for ideal octahedral coordination.

The energy levels for a d^3 system in an octahedral complex and their splitting during tetragonal distortion is shown below.

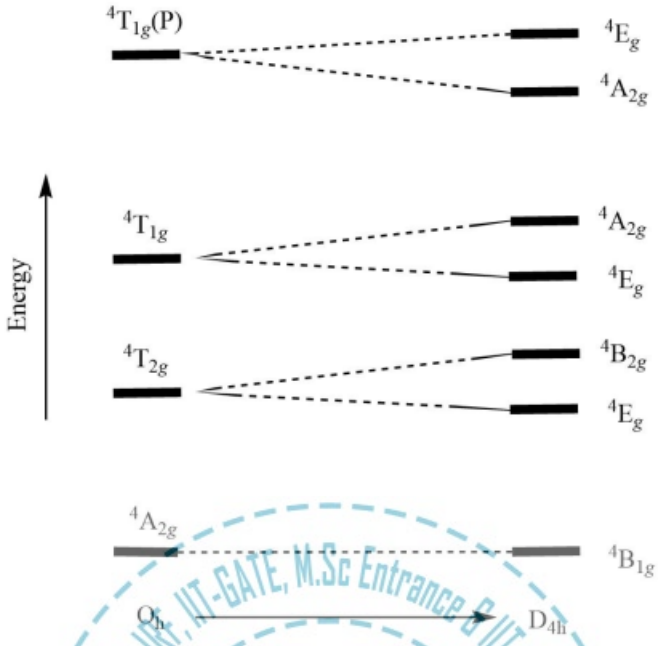


Figure 46. The splitting pattern of *d*-orbital energy levels of d^3-metal complexes in tetragonal distortion.

2. Rhombic distortion: The unequal amount of elongation or compression along two four-fold axes of rotation in octahedral complexes produces rhombic distortions. The common examples of rhombic distortion are high-spin Mn(III) and spin-paired Co(III) complex. Owing to more than one *d*-electron, we must consider ourselves with electronic states and not simply orbitals. The splitting pattern that occurs in a rhombic field is also shown below.

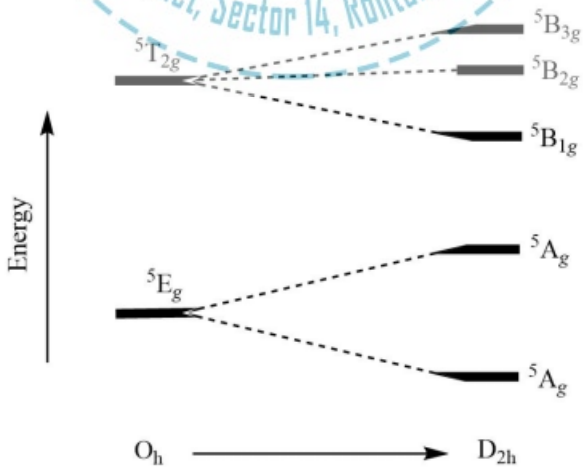


Figure 47. The splitting pattern of *d*-orbital energy levels of d^4-metal complexes in tetragonal distortion.

3. Trigonal distortion: The trigonal distortions occur as the elongation or compression along one of the four three-fold symmetry axis. The splitting pattern that occurs in a rhombic field is also shown below.

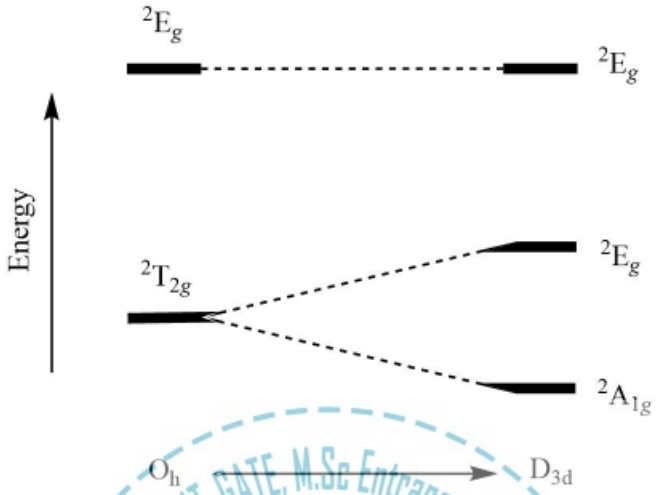
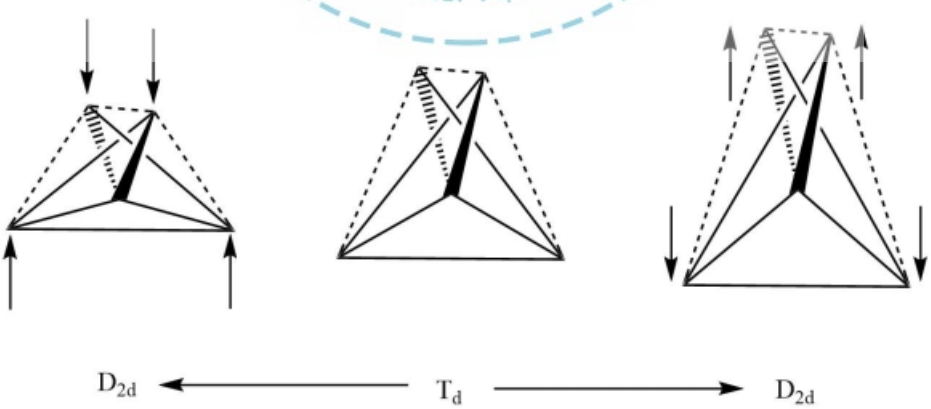


Figure 48. The splitting pattern of *d*-orbital energy levels of d^1-metal complexes in trigonal distortion.

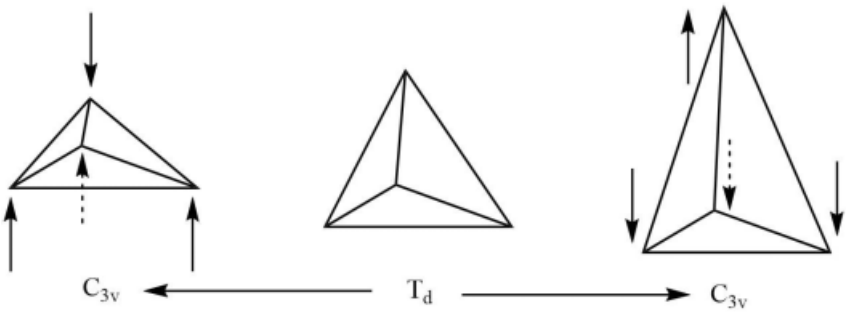
➢ ***Distortion in Four-Coordinated Complexes***

The tetra-coordination of ligands in different metal complexes can be categorized mainly as the tetrahedral and square planer. The tetrahedral geometry can be distorted in various ways to produce other four-coordinated structures. For instance, a perfect tetrahedral geometry can be compressed or elongated along two-fold and three-fold axis of symmetry to produces structures having D_{2d} and C_{3v} symmetry profiles, respectively. Moreover, the extreme case of compression along one two-fold axis is bound to yield a perfectly flat square-planar structure with D_{4h} point group.



(a)

Figure 49. Continued on the next page…



(b)

(c)

Figure 49. The (a) two-fold (b) three-fold and (c) square-planar distortion in tetrahedral metal complexes.

1. Two-fold distortion: The two-fold distortions occur as the elongation or compression along one of the six two-fold symmetry axis. The splitting pattern that occurs in a D_{2d} crystal field is also shown below.

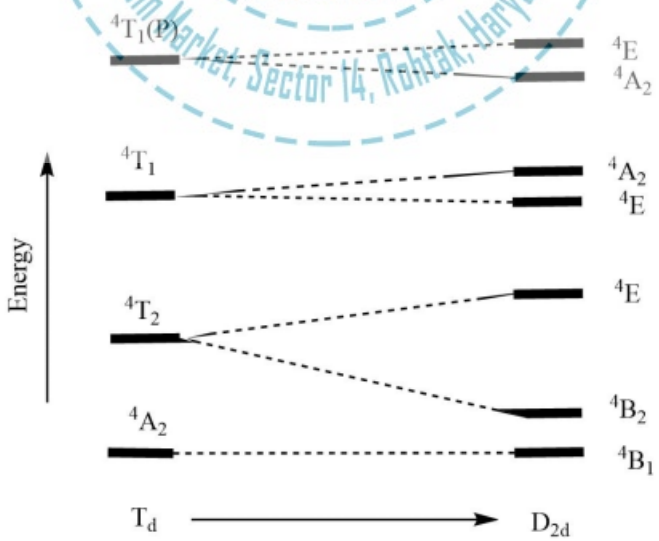


Figure 50. The splitting pattern of *d*-orbital energy levels of d^7-metal complexes in two-fold distortion.

2. Three-fold distortion: The three-fold distortions occur as the elongation or compression along one of the four three-fold symmetry axis. The splitting pattern that occurs in a C_{3v} crystal field is also shown below.

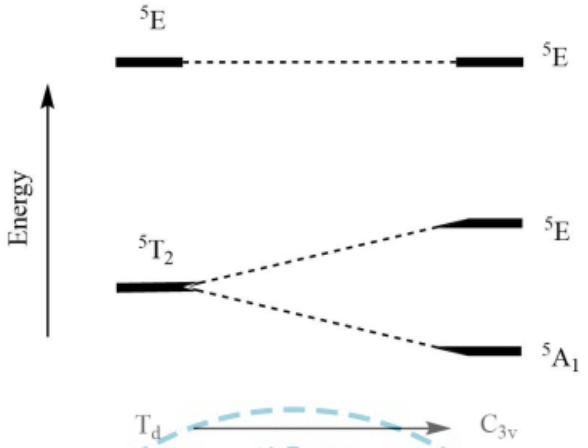


Figure 51. The splitting pattern of *d*-orbital energy levels of d^4-metal complexes in three-fold distortion.

3. Square-planer distortion: The square-planar distortions occur as the extreme compression along one of the six two-fold symmetry axis. The splitting pattern that occurs in a D_{4h} crystal field is shown below.

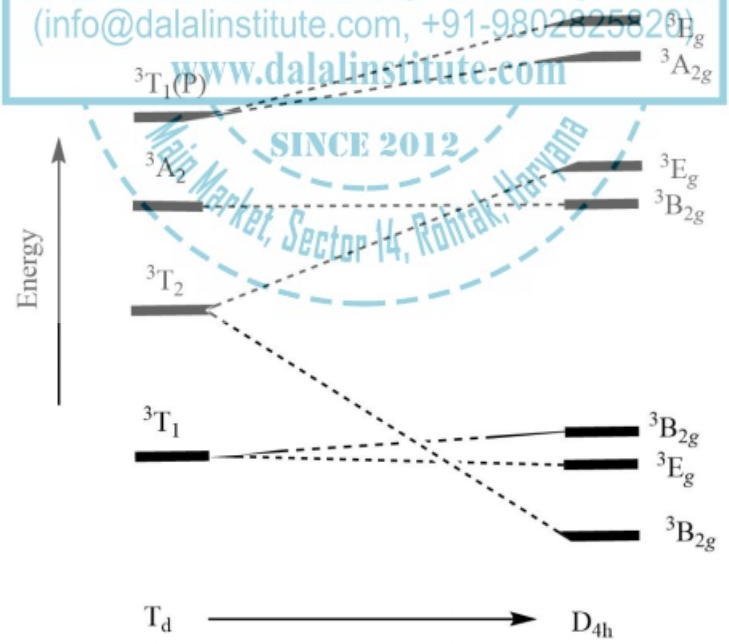


Figure 52. The splitting pattern of *d*-orbital energy levels of d^8-metal complexes in square-planer distortion.

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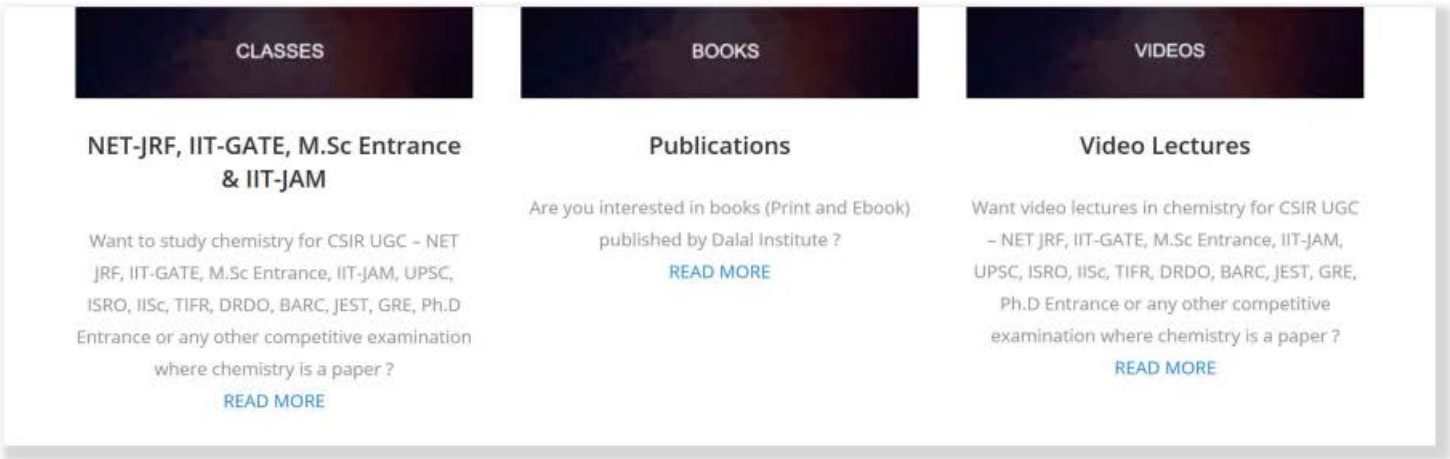

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