Tetragonal Distortion from Octahedral Geometry (Jahn-Teller Theorem / Distortion) :→

This theorem states that "Any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove degeneracy".

In simple terms, molecules or complexes which have an unequally filled set of orbitals either (e_g or t_{2g}) will be distorted. In Octahedral complexes distortion from t_{2g} levels are too small to detect. However distortions resulting from e_g orbitals are very important.

The shapes of transition metal complexes are effected by whether the d-orbitals are symmetrically or asymmetrically filled. If d-orbitals are symmetrically arranged they will repel all six ligands equally. Thus the structure will be regular octahedron. The structural arrangement of d-electrons are shown below:

Elec. Config.	t_{2g}	e_g	Example	Nature of ligand field
d^0	☐☐☐	☐☐	Ti^{4+}	Strong or weak
d^3	↑↑↑	☐☐	Cr^{3+}	Strong / weak
d^5	↑↑↑	↑↑	Mn^{2+}	Weak
d^6	↑↓ ↑↓ ↑↓	☐☐	Co^{3+}	Strong
d^8	↑↓ ↑↓ ↑↓	↑ ↑	Ni^{2+}	Weak
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	Zn^{2+}	Strong / weak

All other arrangements have an asymmetrical arrangement of d-es.

If d electrons are asymmetrically filled, they will repel some ligand in the complex more than the other. Thus the structure is distorted. The eg orbitals point directly at the ligand. Thus asymmetric filling of eg orbitals results in some ligands being repelled more than others. This causes significant distortion of octahedral shape. In contrast t_{2g} orbitals donot point directly at ligands but in between the ligands. Thus asymmetric filling of t_{2g} orbitals has a very small effect on the geometry.

The two eg orbitals i.e. dz^2 and $d(x^2-y^2)$ are normally degenerate. If the dz^2 orbital contains one more electron than $d(x^2-y^2)$ orbital then the ligand approaching along Z-axis will encounter greater repulsion than the other four ligands. The repulsion & distortion results in elongation of octahedron along Z axis. This is called tetragonal elongation. This form of distortion is commonly observed in:

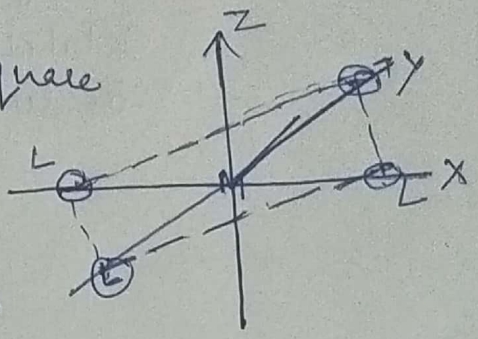
E.C.	t_{2g}	eg	Nature of ligand field	Examples
d^4	↑ ↑ ↑	↑	Weak field	Cr^{2+}, Mn^{3+}
d^7	↑↓ ↑↓ ↑↓	↑	Strong field	Co^{2+}
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑ (dz^2 dx^2-y^2)	Stronger / Weak	Cu^{2+}

If dx^2-y^2 contain an extra electron, then elongation will occur along X & Y axes. Thus there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along Z-axis and this is known as tetragonal compression. Tetragonal elongation is more common.

Square planar coordination:

The square planar arrangement of complexes may be considered to be derived from octahedral geometry by removing two trans ligands located on Z-axis. In this process, the e_g & t_{2g} orbitals will no longer remain degenerate.

The four ligands in square planar complex along coordinate axis around central metal ion is shown in figure →



As such ligands approaches towards central metal ion through coordinate axes, they have greater influence on $d(x^2-y^2)$ orbital so that energy of that orbital is very high. The dxy orbital lying in the same plane but between the ligands will also have greater energy but the effect is less than that in dx^2-y^2 orbitals. On the other hand, due to the absence of ligand on Z-axis, the dz^2 orbital becomes stable and has lower energy than dxy. Similarly the dxz and dyz orbitals becomes more stable having even lower energy than dz^2. The energy level diagram showing square planar coordination is given below: