

Semester IV

CHE-HC-4014: INORGANIC
CHEMISTRY-III

Topic: Coordination Chemistry

Jahn Teller (JT) Distortion

Jahn-Teller Theorem

- ❑ The theorem states that for a non-linear molecule in electronically degenerate state which are unsymmetrically filled undergoes distortion to lower the symmetry, remove the degeneracy and lower the energy.
- ❑ In octahedral complexes, distortion occurred in such a way that two trans ligands (say along the z-axis) are moved either towards the metal (**z-in**) or away from the metal center (**z-out**).
- ❑ The resulting complex is thus said to be **tetragonally distorted**.

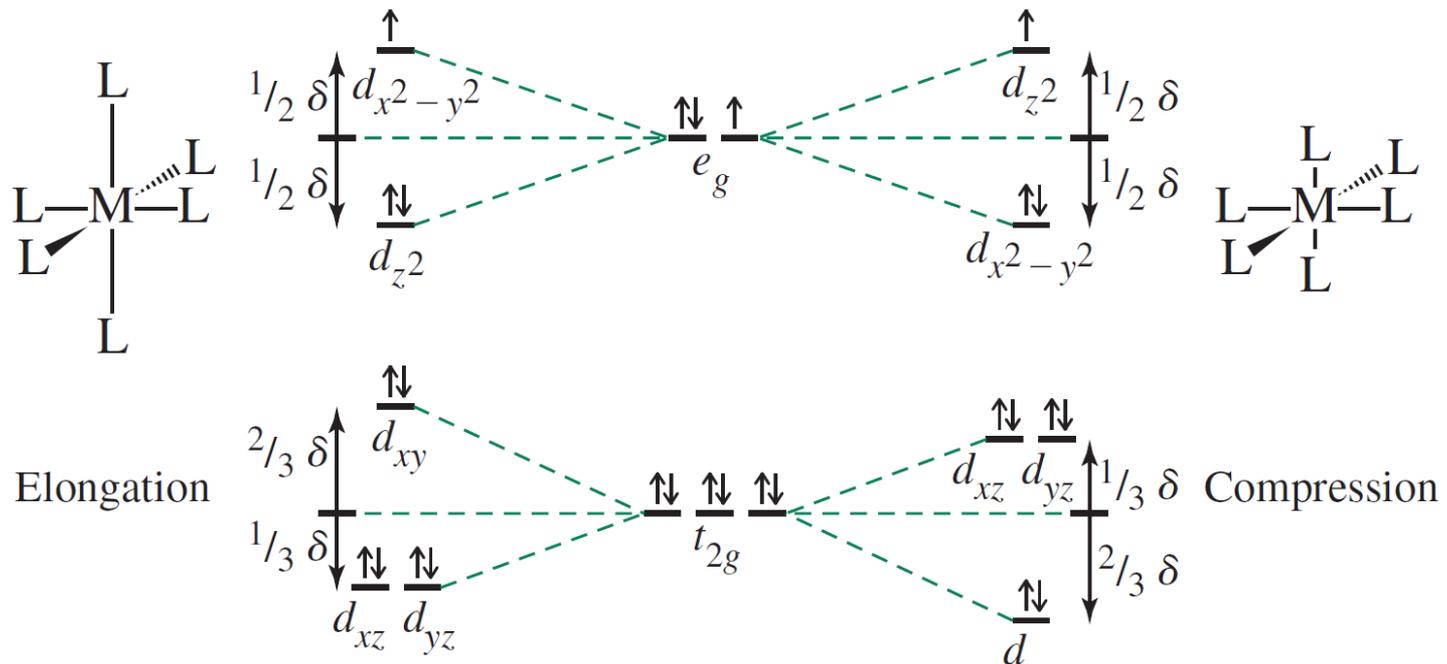


Fig: JT effect in an octahedral Cu(II) complex

Jahn-Teller Theorem

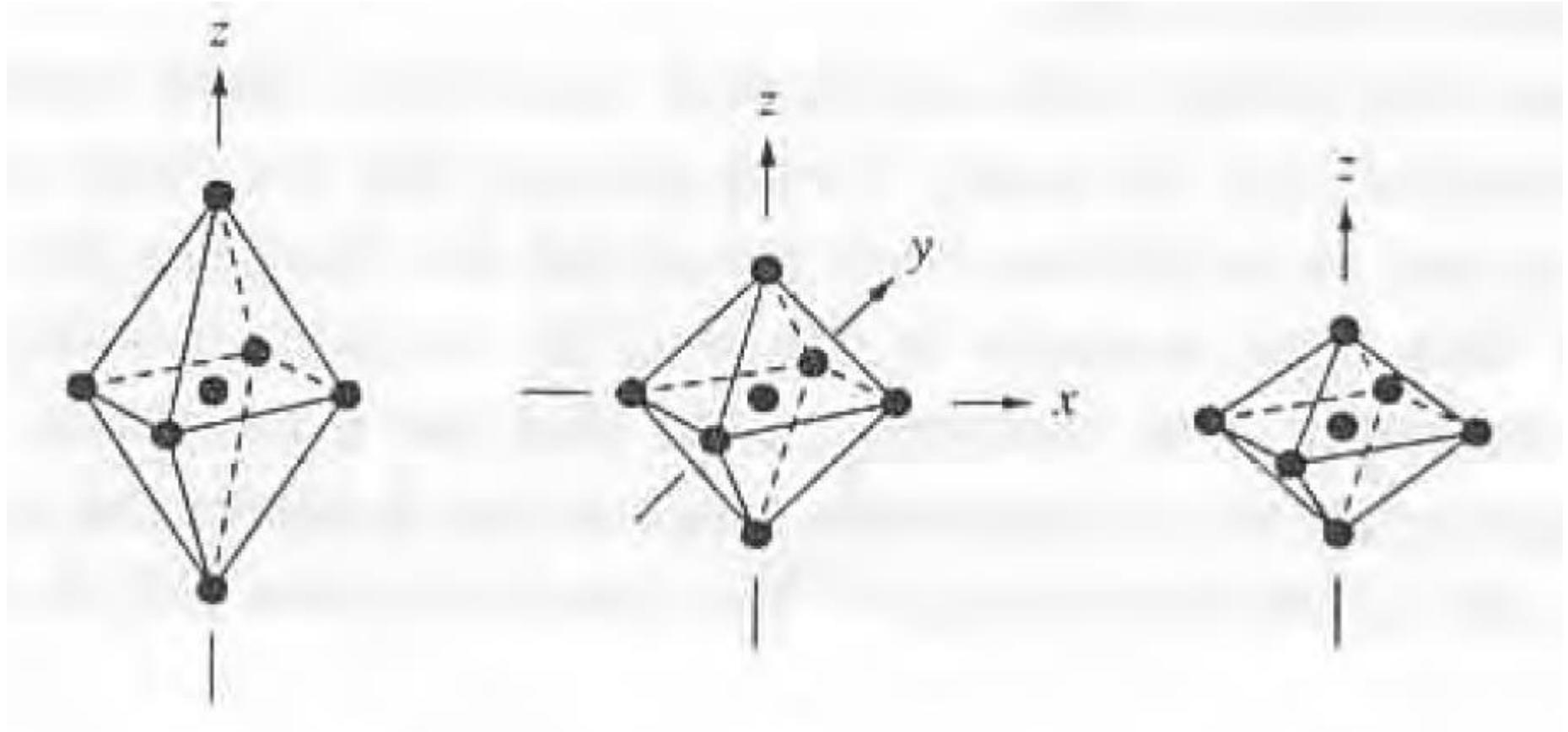


Figure: Tetragonal distortion from octahedral geometry

Configurations for which Jahn-Teller distortion are expected in octahedral ML_6 complexes

Configuration	Ground-state term	Jahn-Teller distortion?
d^1	${}^2T_{2g}$	Yes
d^2	${}^3T_{1g}$	Yes
d^3	${}^4A_{2g}$	No
d^4	5E_g (high spin)	Yes
	${}^3T_{1g}$ (low spin)	Yes
d^5	${}^6A_{1g}$ (high spin)	No
	${}^2T_{2g}$ (low spin)	Yes
d^6	${}^5T_{2g}$ (high spin)	Yes
	${}^1A_{1g}$ (low spin)	No
d^7	${}^4T_{1g}$ (high spin)	Yes
	2E_g (low spin)	Yes
d^8	${}^3A_{2g}$	No
d^9	2E_g	Yes

Jahn-Teller Theorem

Square planar complexes

- ✓ We can determine which octahedral complexes will be subject to Jahn Teller distortions.

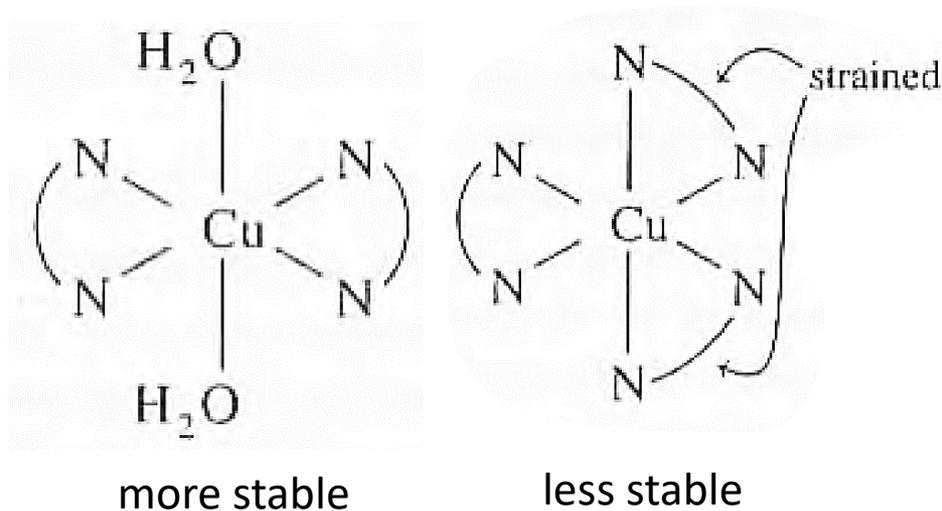
Number of Electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn–Teller	w	w		s		w	w		s	
Low-spin Jahn–Teller	w	w		w	w		s		s	

- ✓ *More significant Jahn–Teller distortions occur when e_g^* orbitals would be unequally occupied within an octahedral geometry.*
- ✓ The JT theorem does not predict which type of distortion will take place except the center of symmetry will remain.
- ✓ Complexes having measurable bond-length distances that can confirm the presence of JT distortion are examples of **static JT distortion**. For example, in CrF_2 , four Cr-F bonds are at 200 Å while two Cu-F bonds are at 234 Å.
- ✓ Complexes where distortion cannot be detected at room temperature crystal structures, but other evidences show JT distortion are examples of **dynamic JT distortion**. For e.g, $\text{K}_2\text{Pb}[\text{Cu}(\text{NO}_2)_6]$ show undistorted octahedral structure.

Jahn-Teller Theorem

Consequences

- We know that chelate complexes are stable due to the chelate effect. But the Cu(II) complex, $[\text{Cu}(\text{en})_3]^{2+}$ is unstable compared to the $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ due to JT distortion. The distortion causes strain into *en* molecule attached along z-axis.



- The Irving-William series represents the relative stability of dipositive metal ions for a given ligand: $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$
The extra stability of Cu(II) complexes in this series is due to JT distortion which results in strong binding of four of the ligands in the plane of the tetragonally distorted Cu(II) complex.

Square Planar Crystal Field

Square planar complexes

- ❑ If we consider the **z-out distortion**, it is to be noted that complete removal of the trans ligands in the z-direction results in square planar crystal field.
- ❑ Metal cations with d^8 configuration form square planar complex with strong ligands such as CN^- . E.g. $[\text{Ni}(\text{CN})_4]^{2-}$
- ❑ Heavier 4d and 5d transition (d^8) metals such as Pd(II), Pt(II), and Au(III) forms low-spin square planar complexes irrespective of the nature of ligands. E.g., $[\text{PtCl}_4]^{2-}$, $[\text{AuCl}_4]^-$, etc.
- ❑ Spectroscopic studies revealed

$$\Delta_{sp} = 1.3 \Delta_o \quad (\text{i.e., } \Delta_{sp} > \Delta_o)$$

