Lecture 3; CH 101: Inorganic Chemistry

Dr. Akshai Kumar A. S

Department of Chemistry
&
Centre For Nanotechnology
Indian Institute of Technology Guwahati
Guwahati – 781039, Assam, India

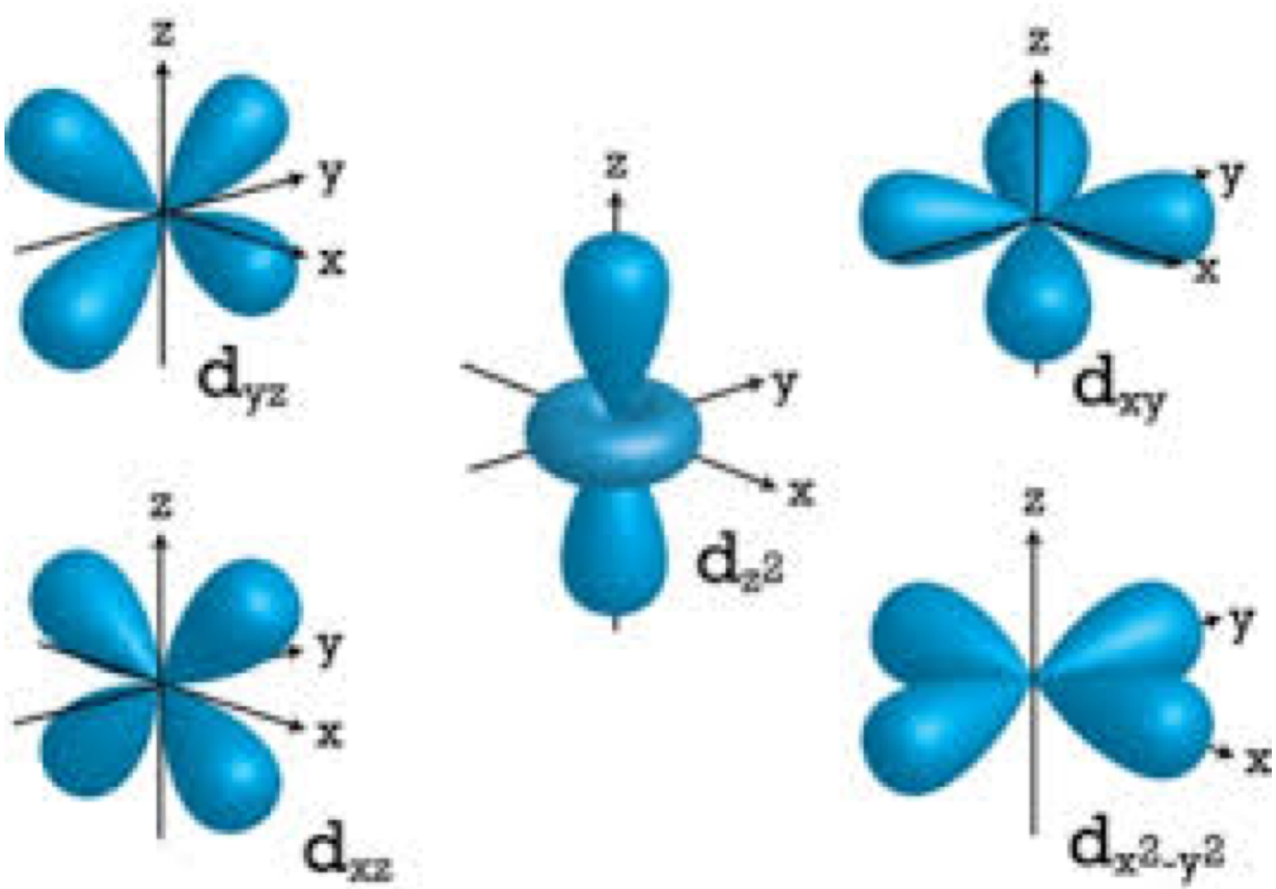
Limitations of Valence Bond Theory

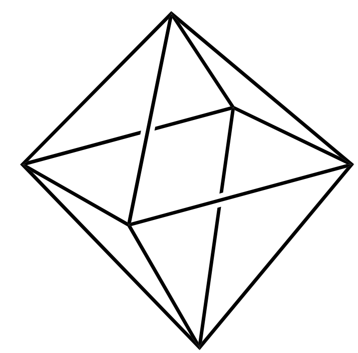
Cannot account for color of complexes

Cannot account for spectrochemical series

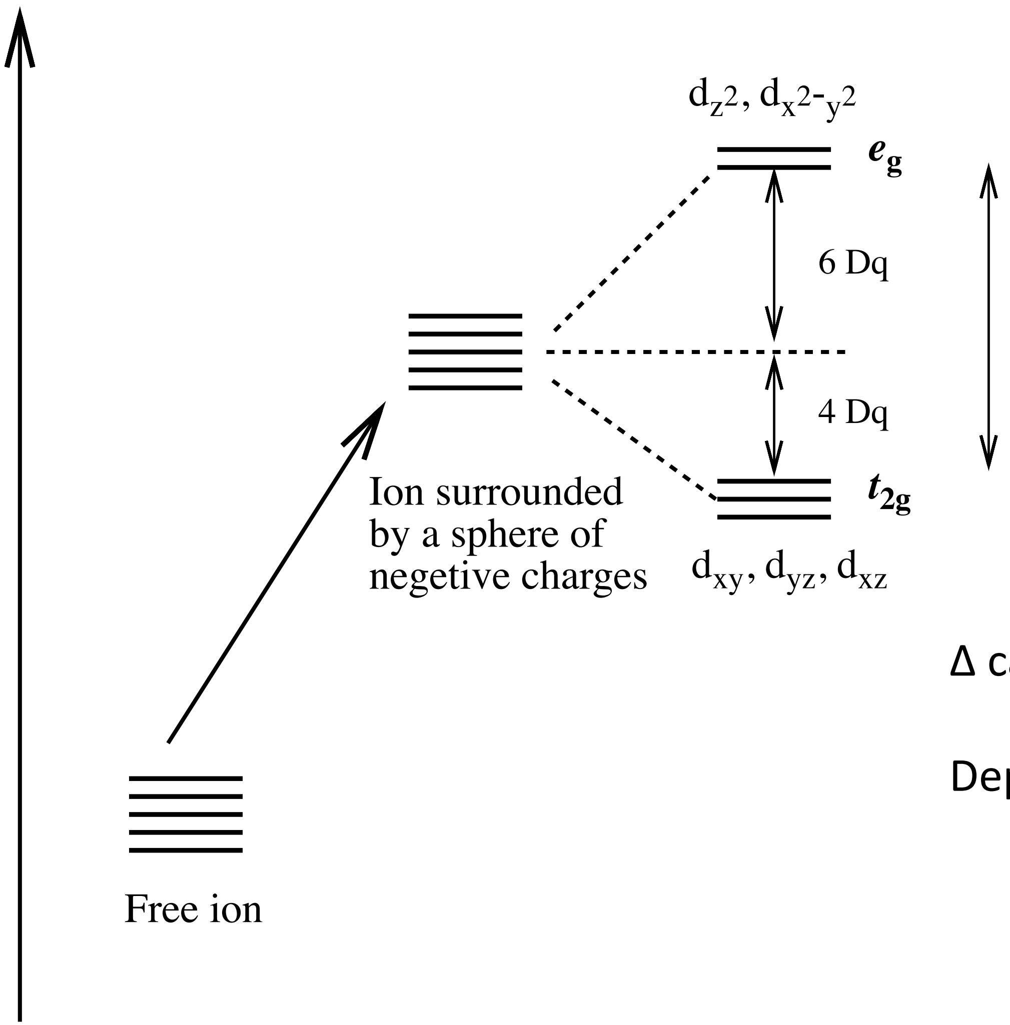
Hybridization actually predicted from magnetization (and not vice-versa)!

In neutral free atom, all d-orbitals have same energy (degenerate)





In an octahedral field

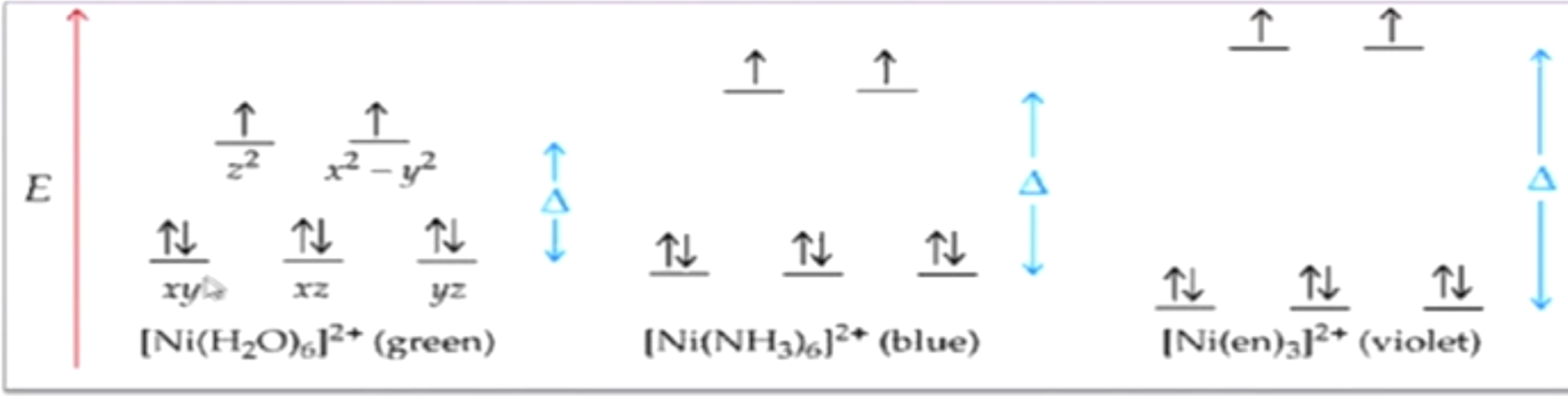


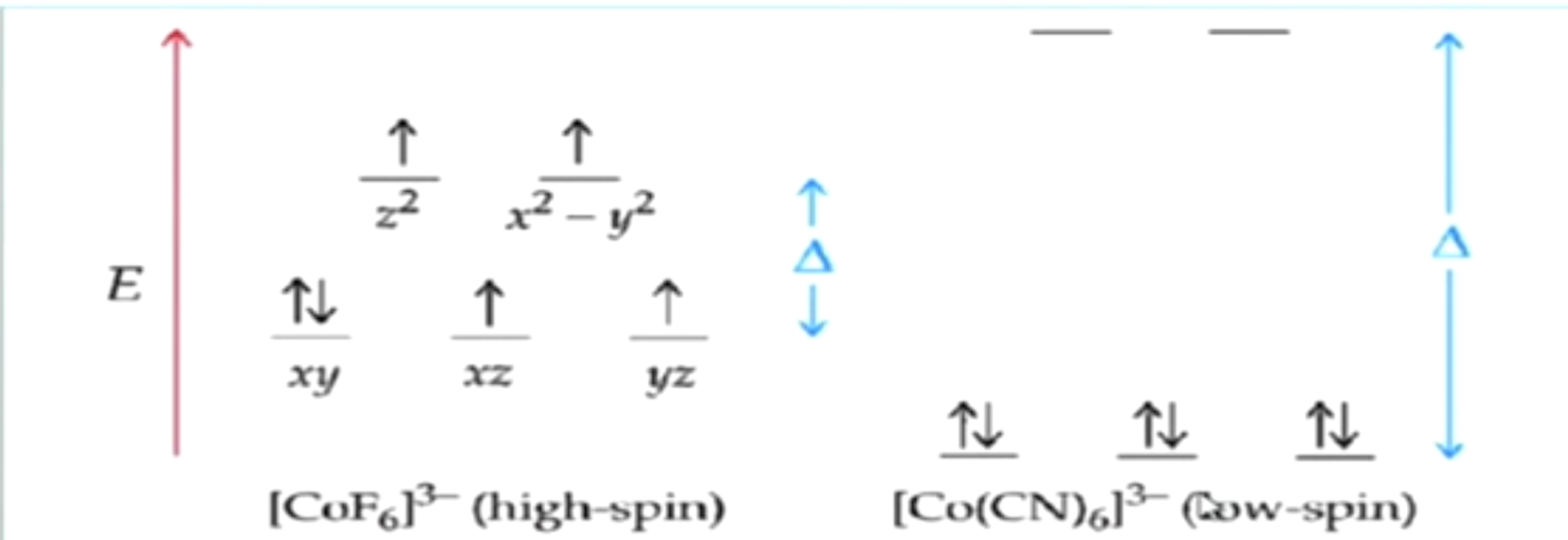
10 Dq = Δ_o

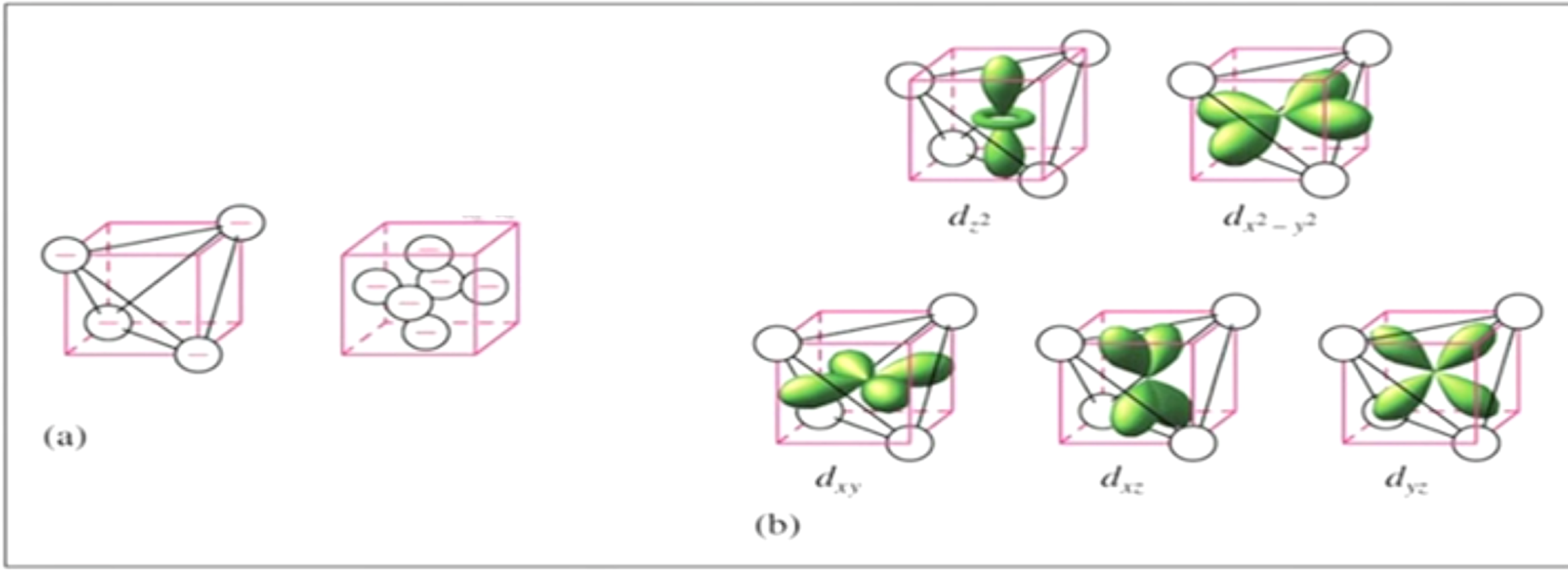
The d-orbitals are no longer degenerate

Δ can be measured; E = hν

Dependent on nature of ligands


E
z^2
x^2-y^2
xy
xz
yz
Δ
$[Ni(H_2O)_6]^{2+}$ (green)
$[Ni(NH_3)_6]^{2+}$ (blue)
$[Ni(en)_3]^{2+}$ (violet)


E
z^2
x^2-y^2
xy
xz
yz
Δ
$[CoF_6]^{3-}$ (high-spin)
$[Co(CN)_6]^{3-}$ (low-spin)

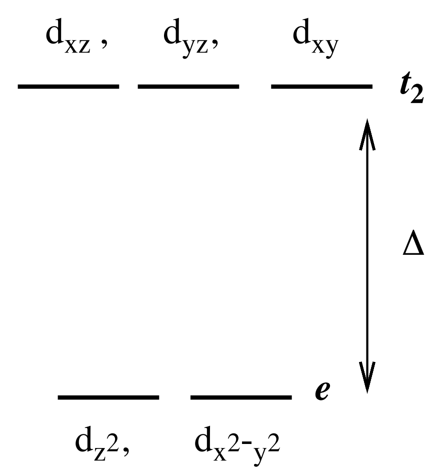


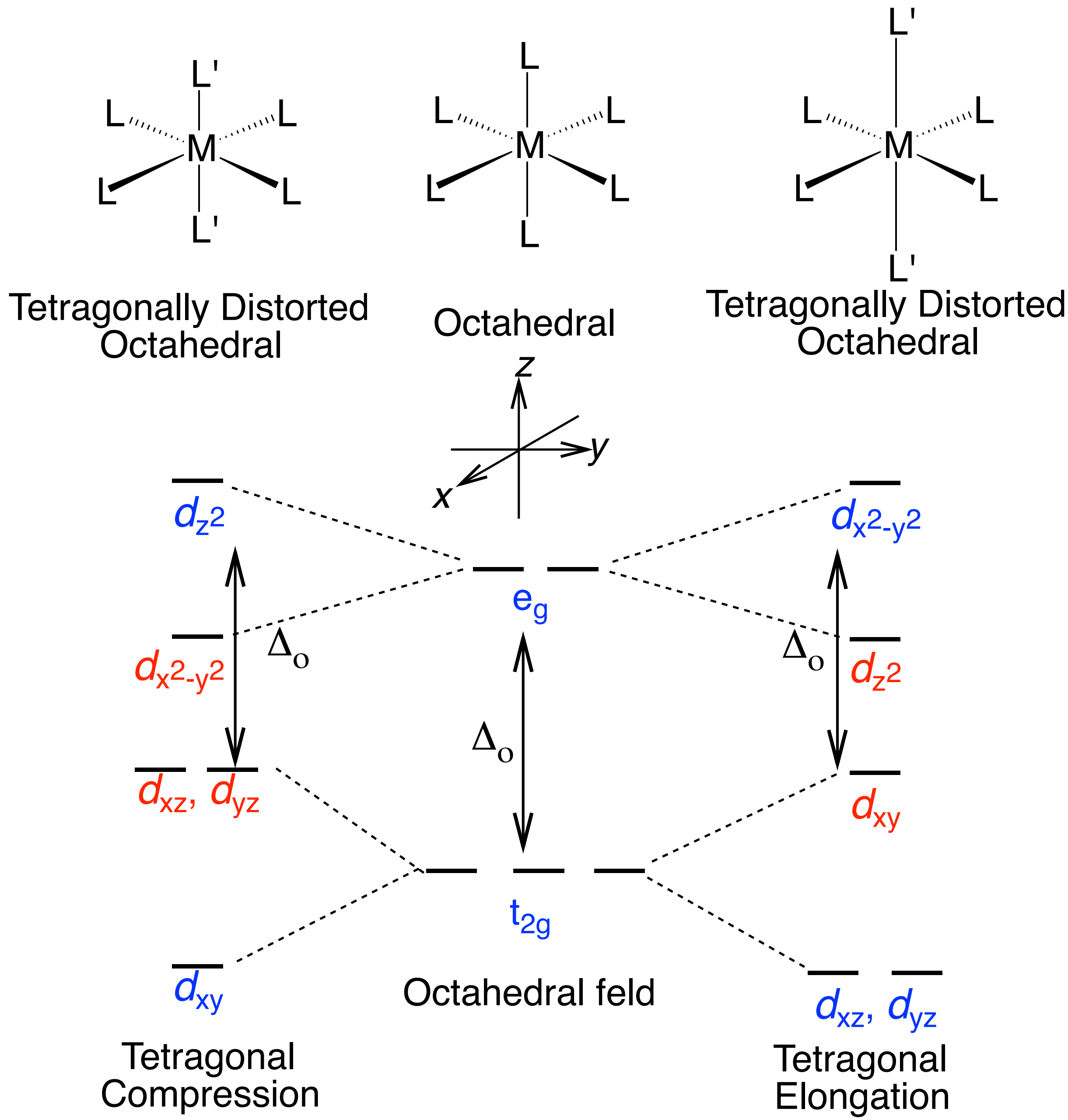
Tetrahedral

Greater chances of High-spin

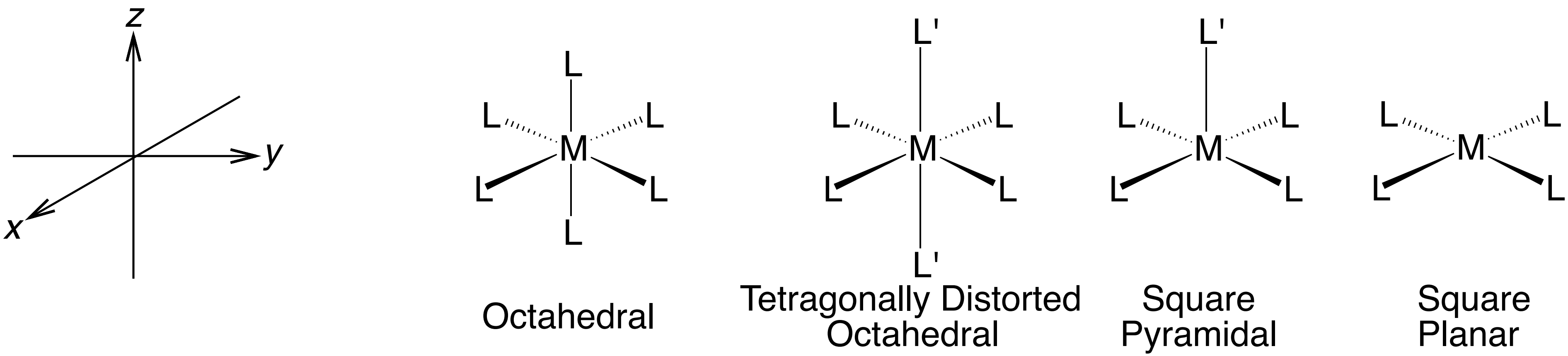
Common Tetrahedral complexes

d^{10} Zn(II), Pt(0), Cu(I)

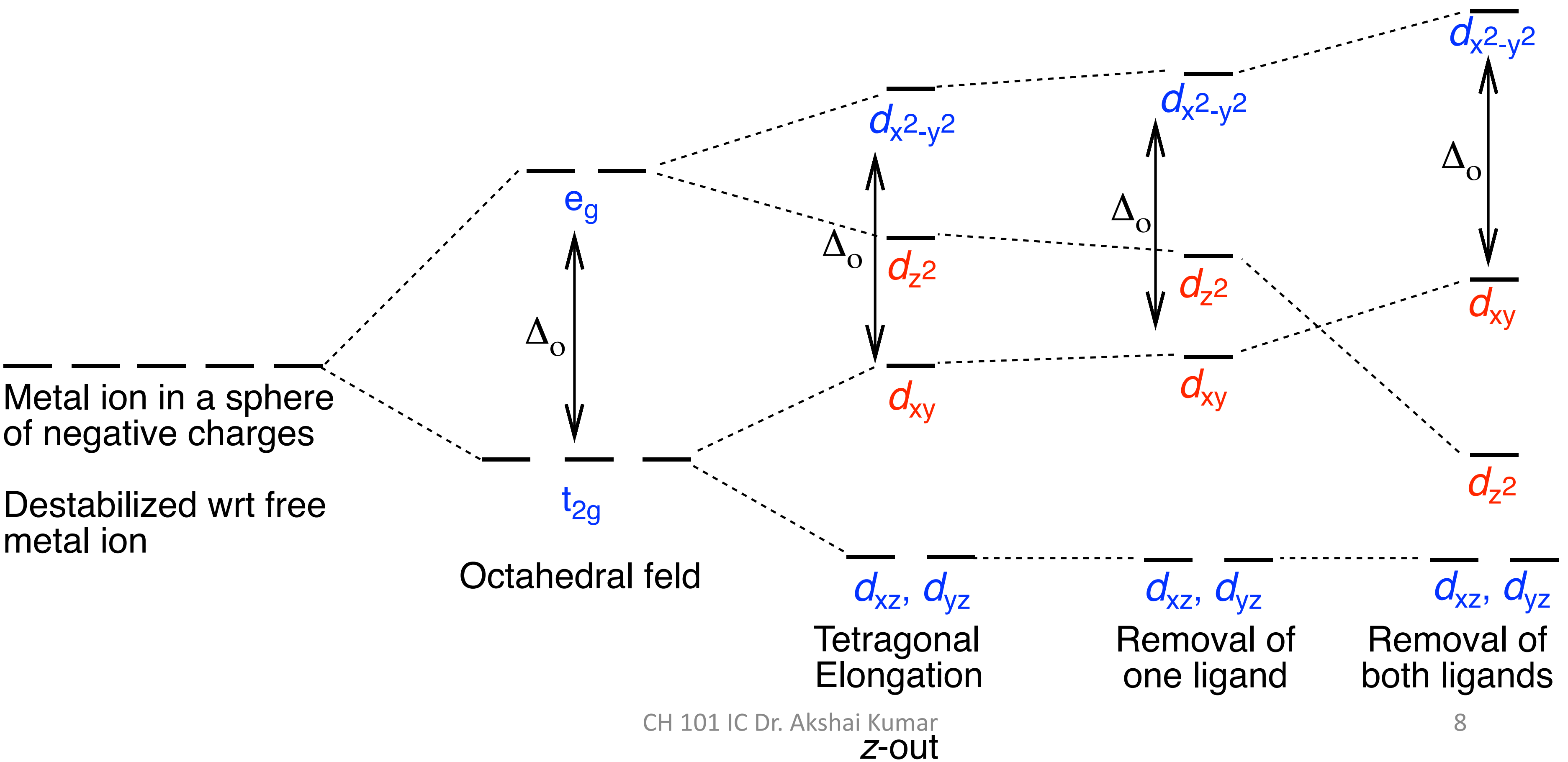



L'
L
M
L'
Tetragonally Distorted Octahedral
Octahedral
Tetragonally Distorted Octahedral
z
y
x
d_{z^2}
$d_{x^2-y^2}$
Δ_o
d_{xz}, d_{yz}
d_{xy}
e_g
t_{2g}
Δ_o
Octahedral feld
$d_{x^2-y^2}$
Δ_o
d_{z^2}
d_{xy}
d_{xz}, d_{yz}
Tetragonal Compression
Tetragonal Elongation

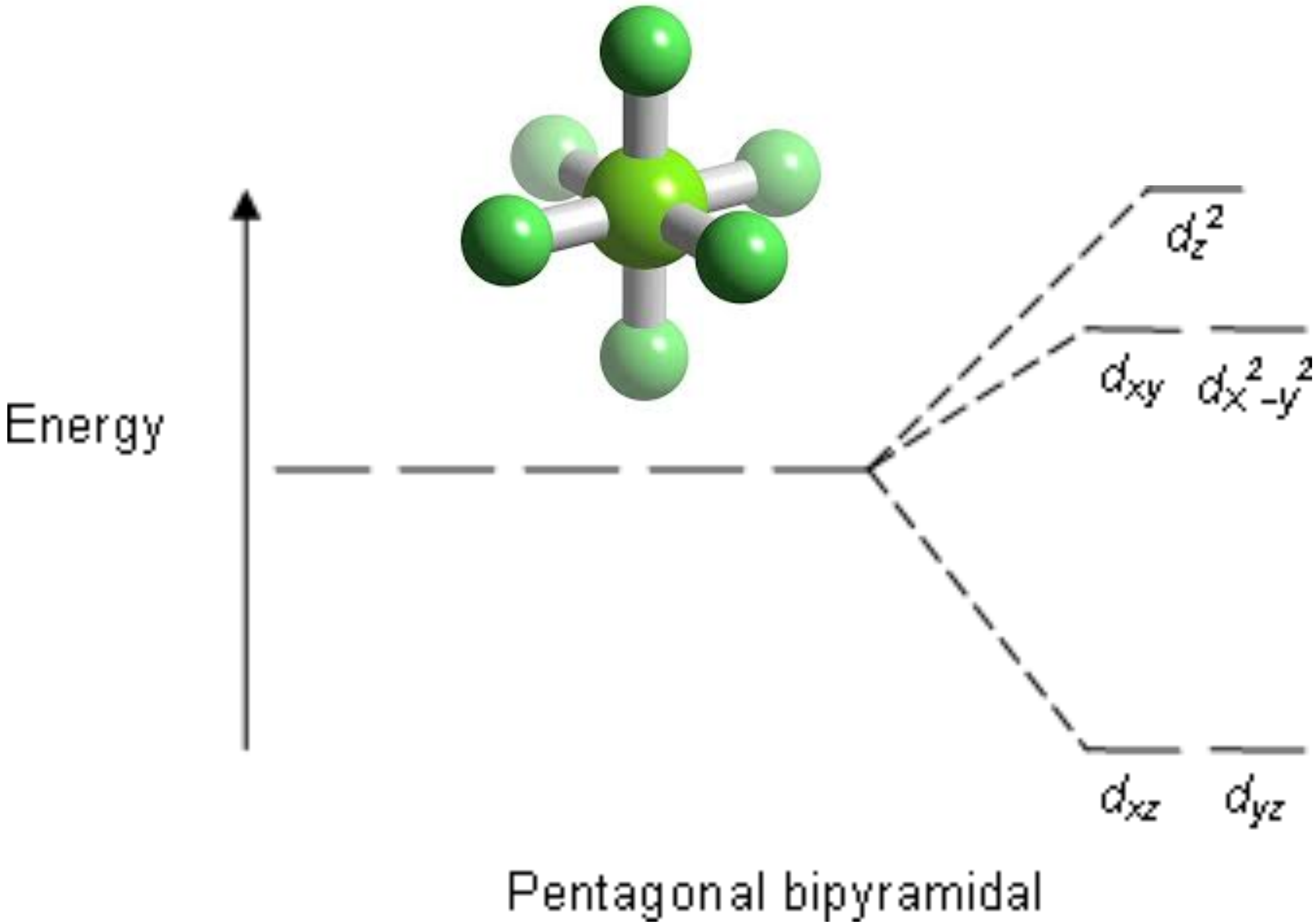
z-in *z*-out

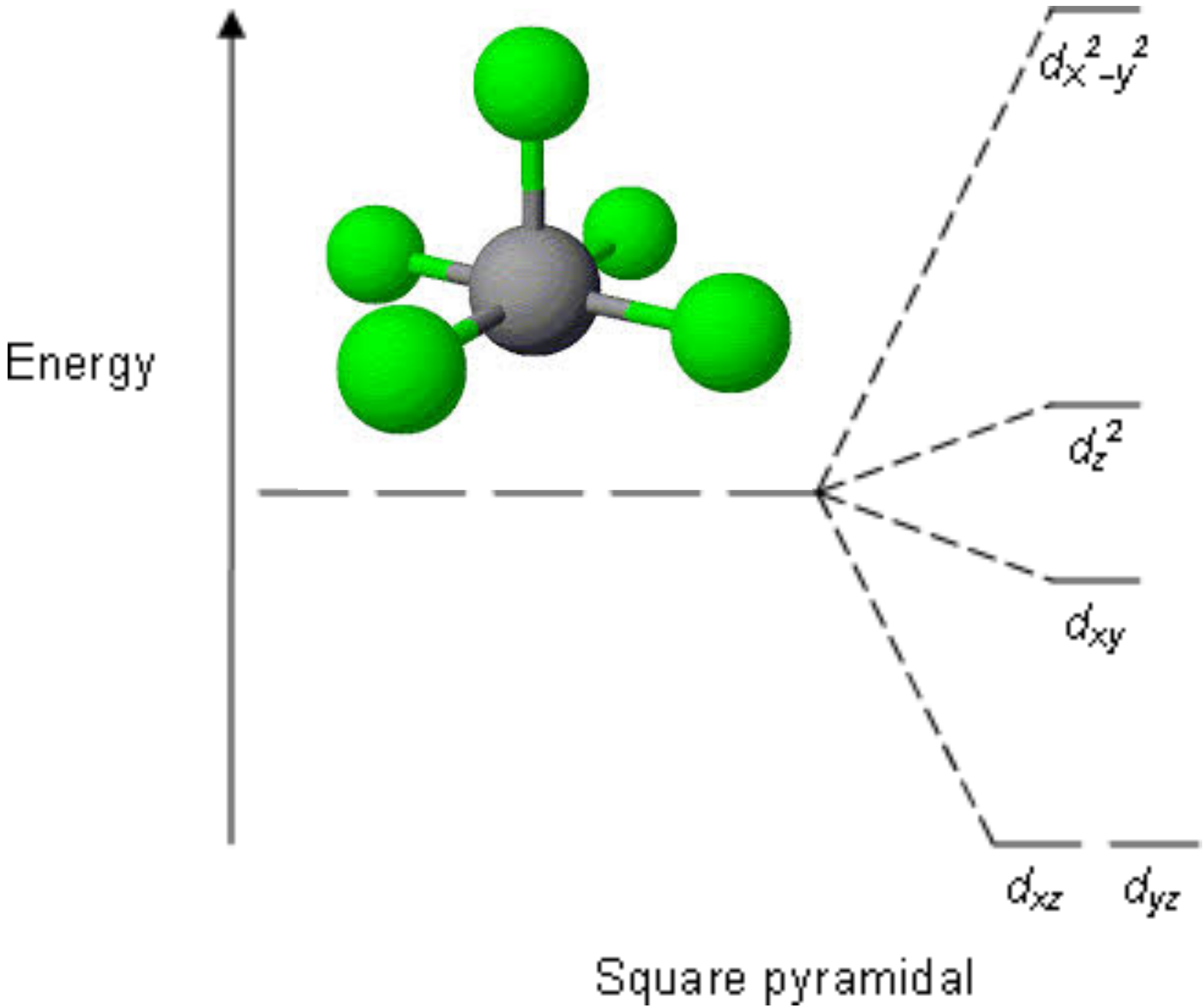


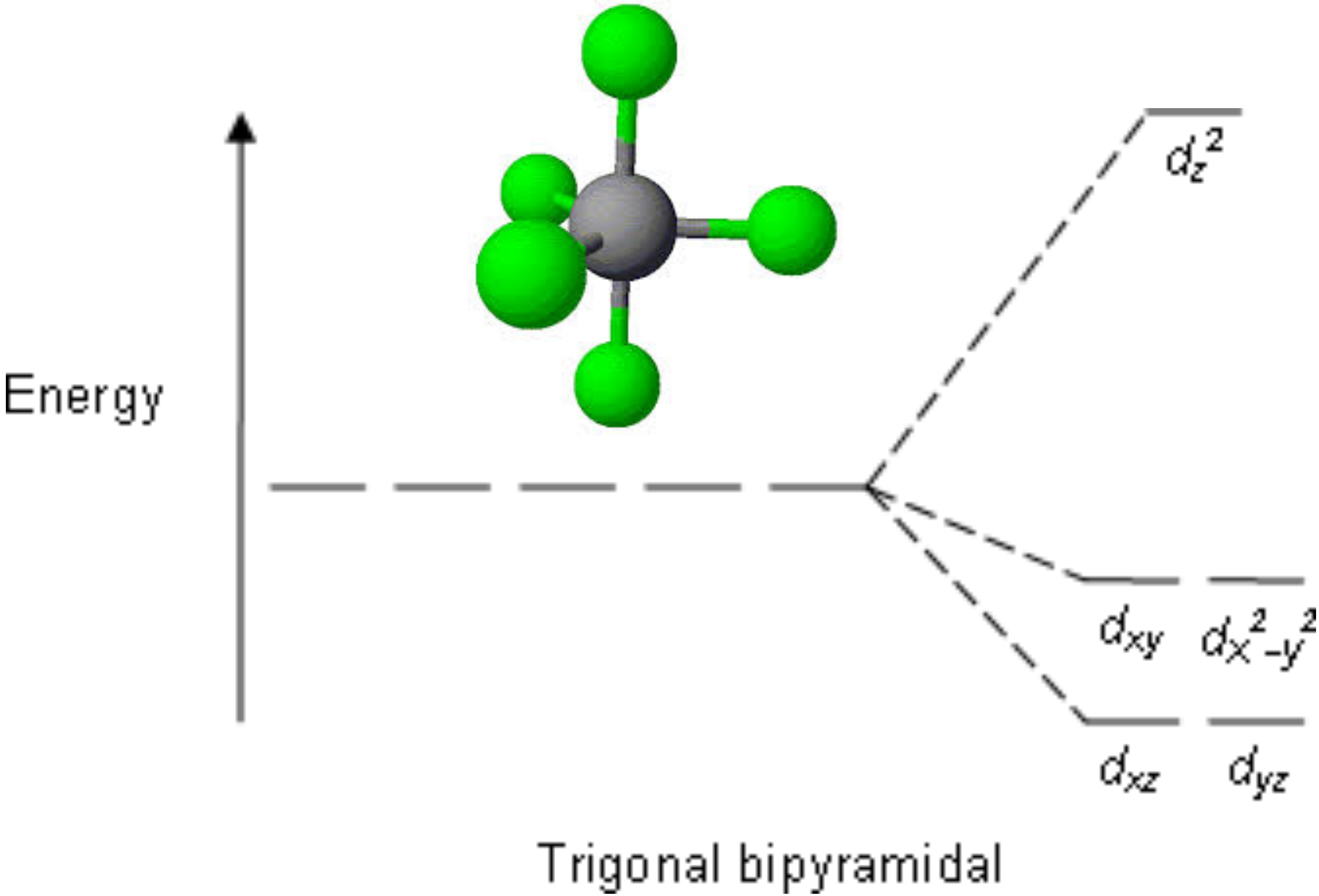
z
y
x
L
L
L
M
L
L
L
Octahedral
L'
L
L
M
L
L
L'
Tetragonally Distorted Octahedral
L'
L
L
M
L
L
Square Pyramidal
L
L
M
L
L
Square Planar



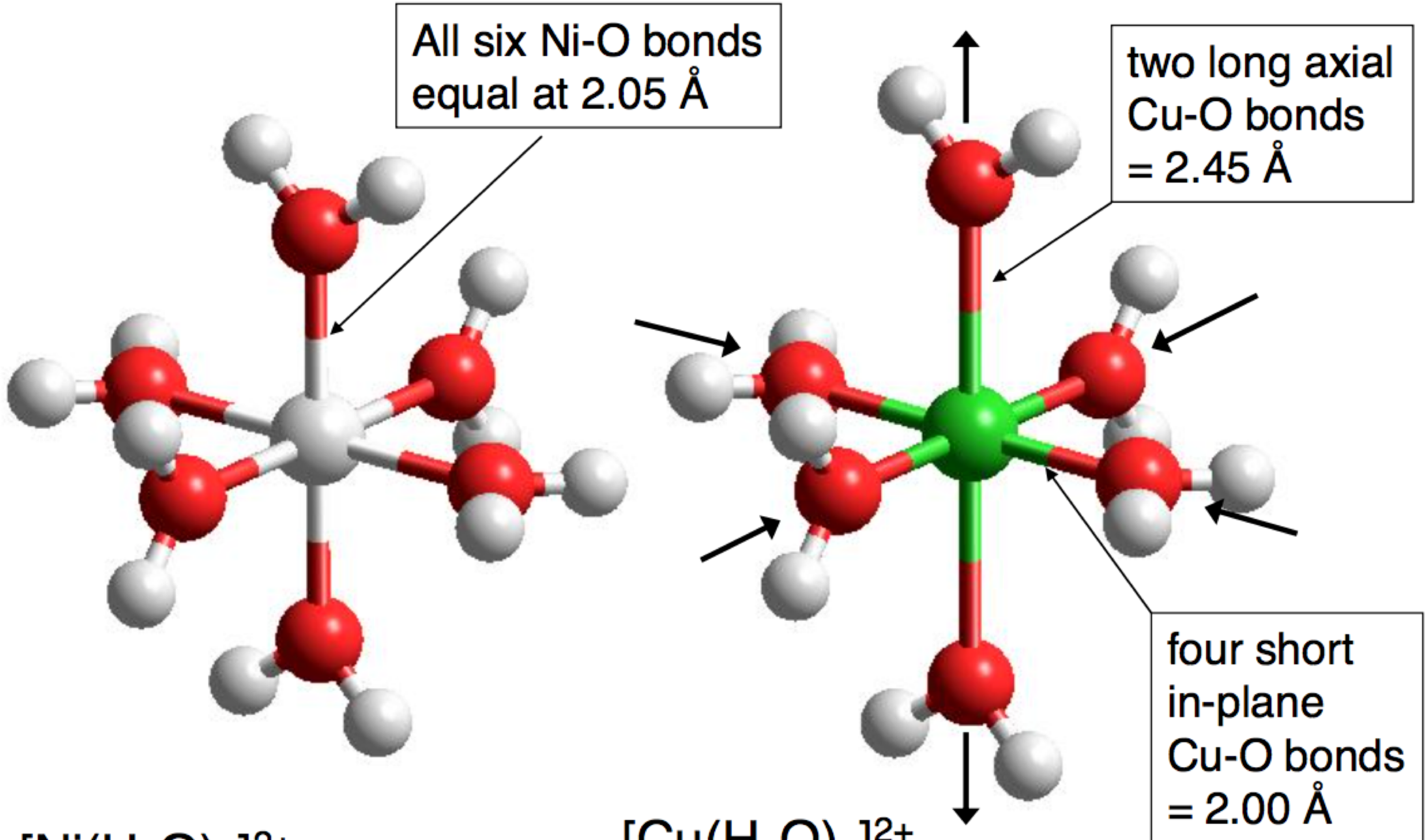
Metal ion in a sphere of negative charges
Destabilized wrt free metal ion
e_g
Δ_o
t_{2g}
Octahedral feld
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz}, d_{yz}
Tetragonal Elongation
z-out
Removal of one ligand
Removal of both ligands


Energy
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Pentagonal bipyramidal


Energy
$d_{x^2-y^2}$
d_{z^2}
d_{xy}
d_{xz}
d_{yz}
Square pyramidal



Energy
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Trigonal bipyramidal



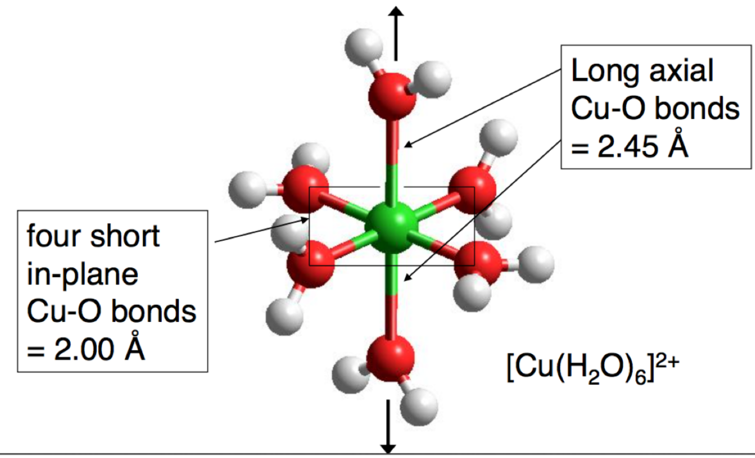
$[Ni(H_2O)_6]^{2+}$
no J-T distortion

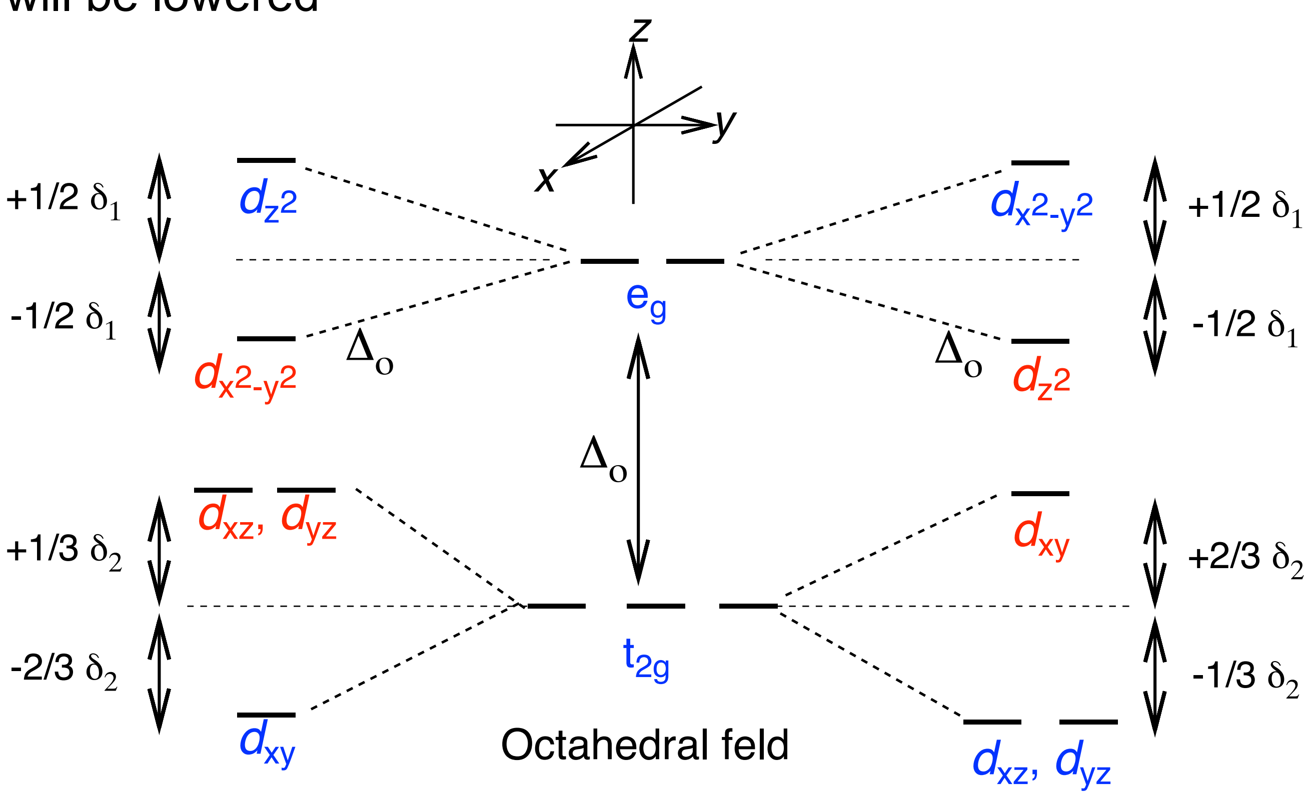
$[Cu(H_2O)_6]^{2+}$
J-T distortion lengthens axial Cu-O's

WHY THE DIFFERENCE ??

Jahn-Teller distortion

Degenerate orbitals of highly symmetric molecules with asymmetry in orbital occupancy are expected to show Jahn-Teller distortions.
Degeneracy will be removed, molecular symmetry will be lowered



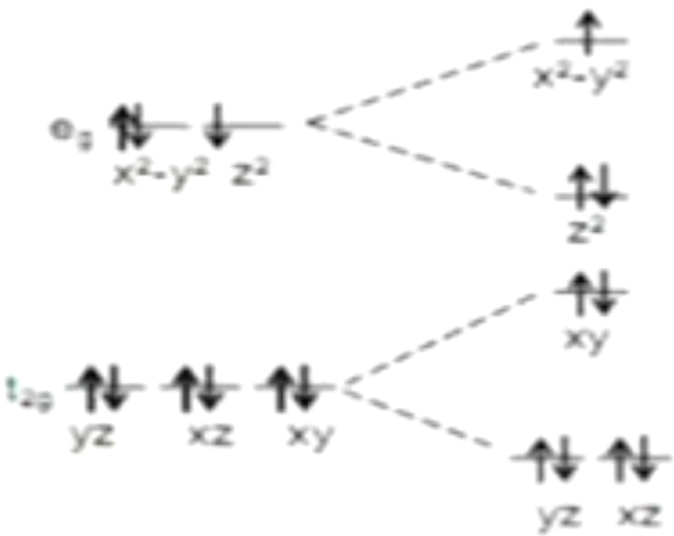


Jahn-Teller distortion
***z*-in**

Jahn-Teller distortion
***z*-out**

Jahn-Teller Theorum

"For a nonlinear molecule in an electronically degenerate state distortion must occur to lower the symmetry, remove the degeneracy and lower the energy"

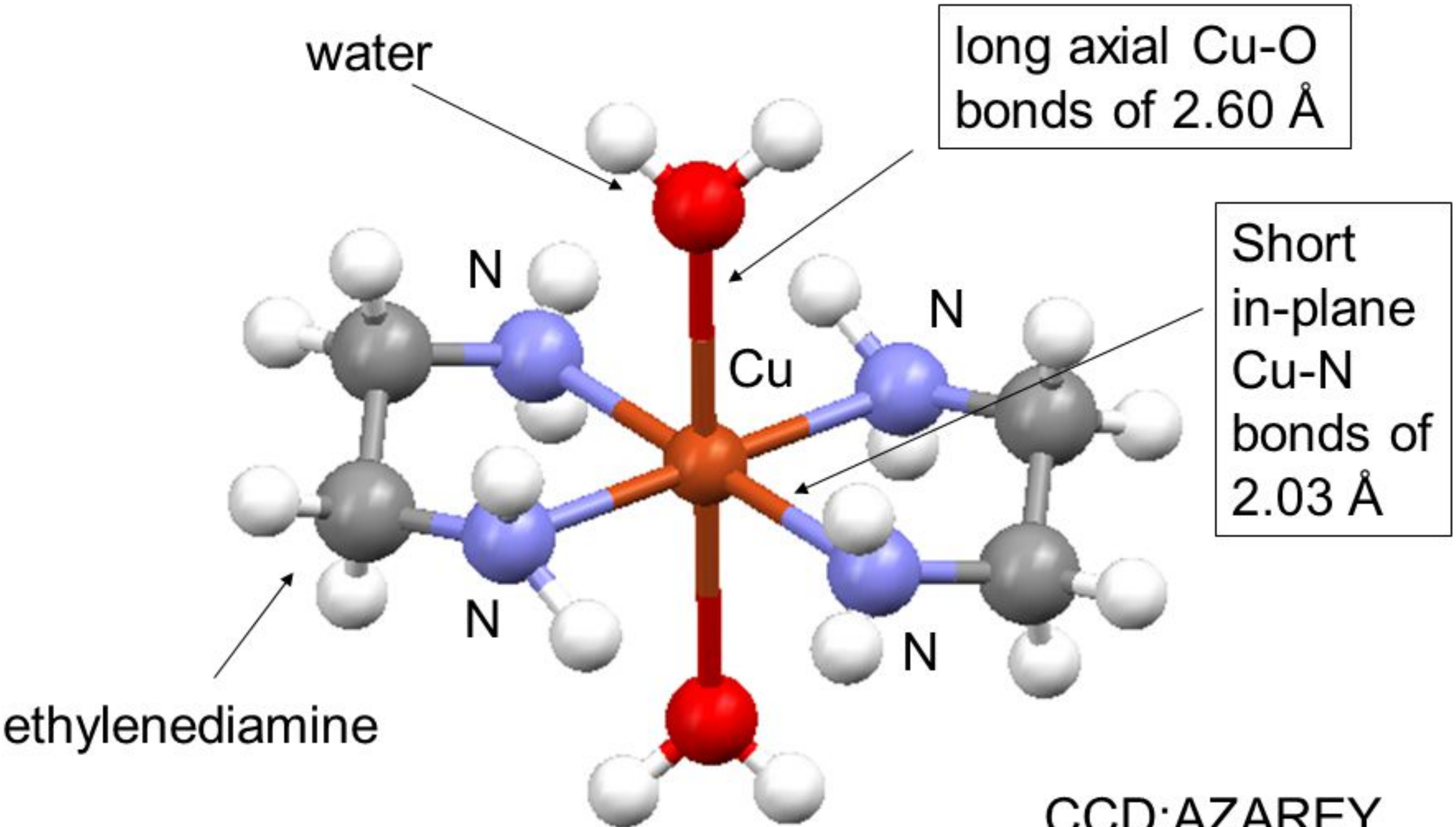


e.g. $[Cu(OH_2)_6]^{2+}$

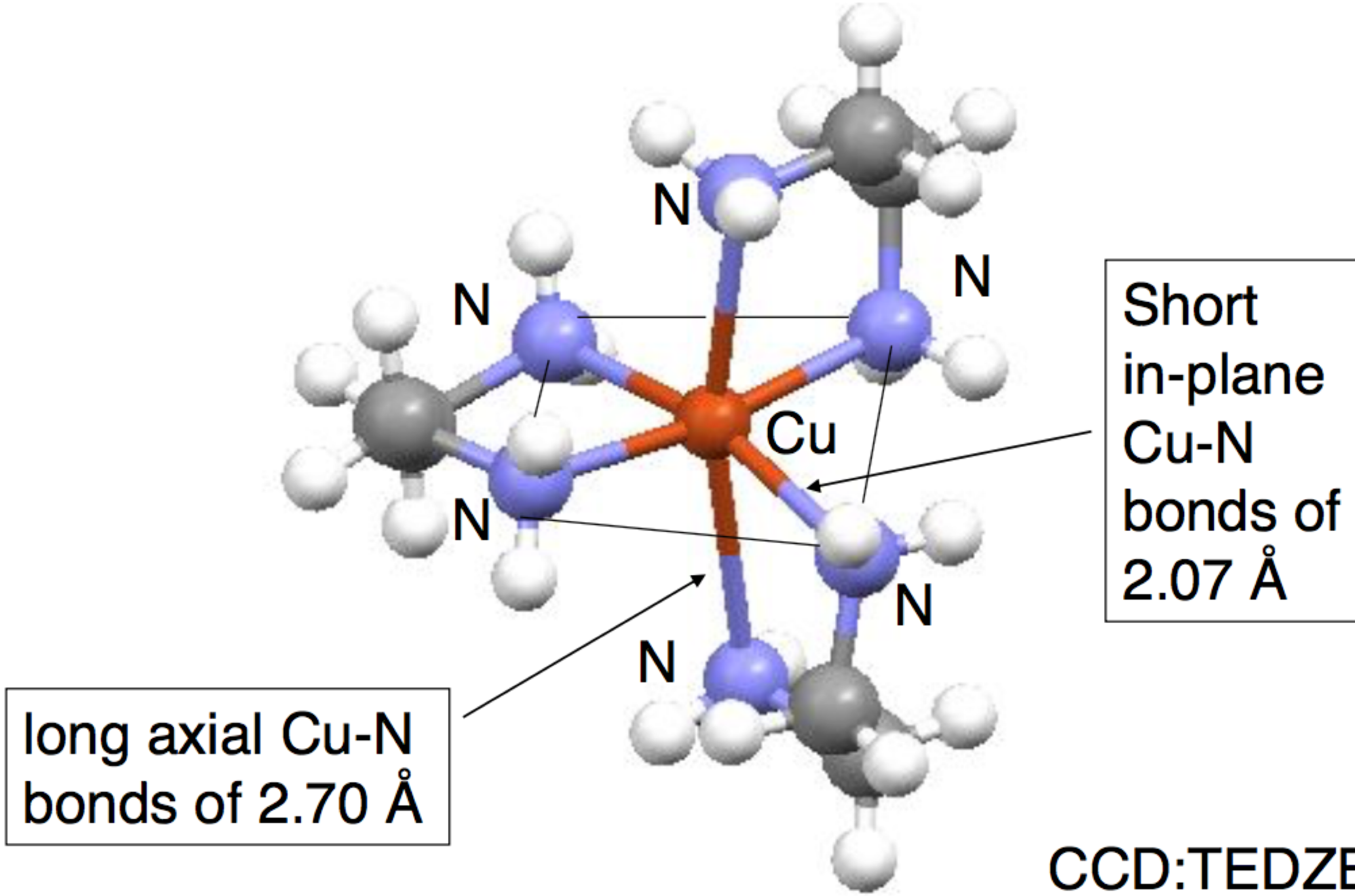
Cu(II) = d^9

z-out

e.g.	$K_2[CuF_4]$	O_h	z-in
	$Na_2[CuF_4]$	O_h	z-out
	Cr_2F_5	O_h	z-out
	Cr(II) = high spin d^4		



water
long axial Cu-O bonds of 2.60 Å
N
Cu
N
Short in-plane Cu-N bonds of 2.03 Å
N
N
ethylenediamine
CCD:AZAREY


N
N
N
Cu
N
N
N
Short in-plane Cu-N bonds of 2.07 Å
long axial Cu-N bonds of 2.70 Å

CCD:TEDZEI

Jahn-Teller distortion

Complexes where e_g orbitals are asymmetrically occupied by electrons show stronger distortions than the corresponding complexes with non-symmetrical orbital occupancy in t_{2g} orbitals.

No. of *d*-electrons	1	2	3	4		5		6		7		8	9	10
High/Low Spin				HS	LS	HS	LS	HS	LS	HS	LS			
Configuration	t_{2g}^1 e_g^0	t_{2g}^2 e_g^0	t_{2g}^3 e_g^0	t_{2g}^3 e_g^1	t_{2g}^4 e_g^0	t_{2g}^3 e_g^2	t_{2g}^5 e_g^0	t_{2g}^4 e_g^2	t_{2g}^6 e_g^0	t_{2g}^5 e_g^2	t_{2g}^6 e_g^1	t_{2g}^6 e_g^2	t_{2g}^6 e_g^3	t_{2g}^6 e_g^4
Strength of Jahn-Teller effect	W	W	N	**S**	W	N	W	W	N	W	**S**	N	**S**	N

W = Weak Jahn-Teller Effect, S = Strong Jahn-Teller Effect and N = No Jahn-Teller Effect