Lecture 8; CH 101: Inorganic Chemistry

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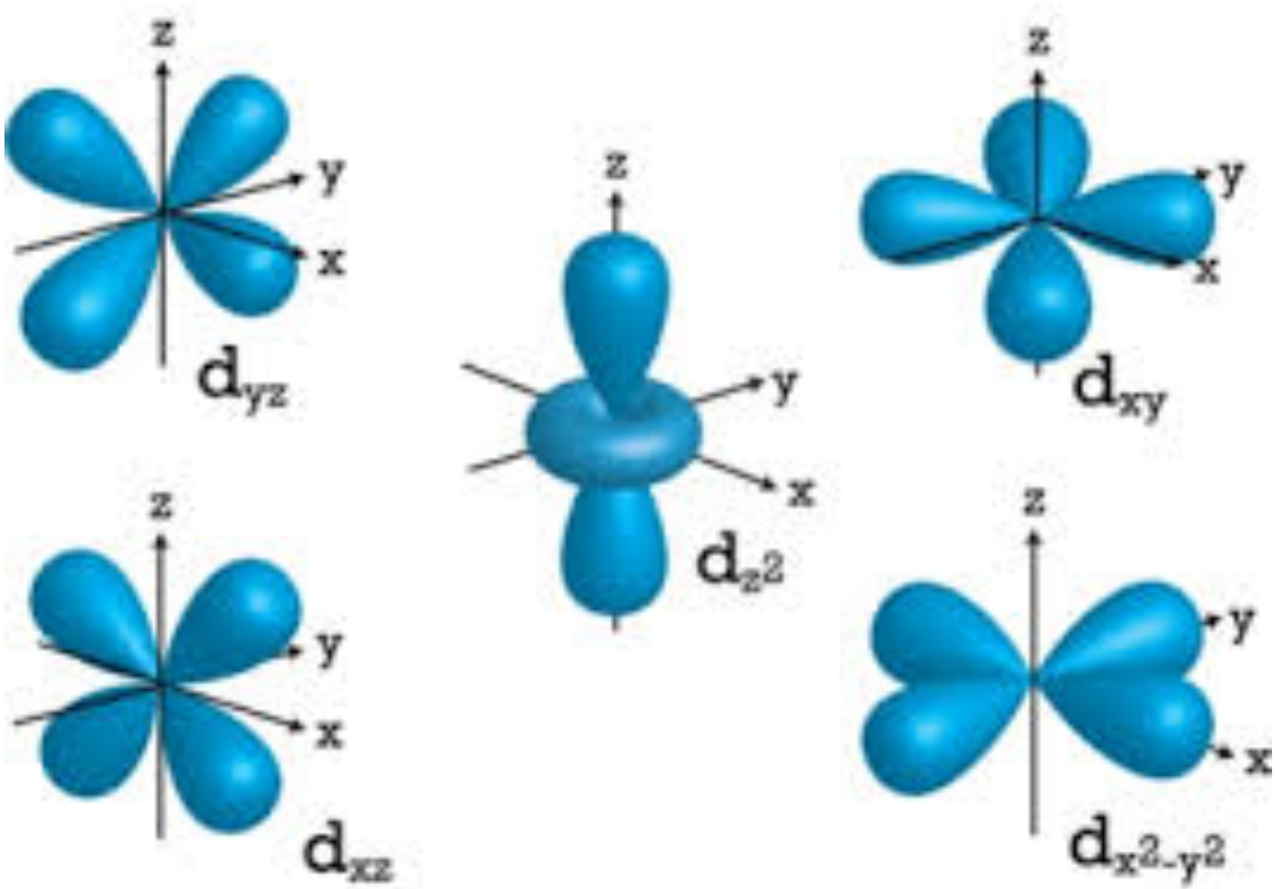
Limitations of Valence Bond Theory

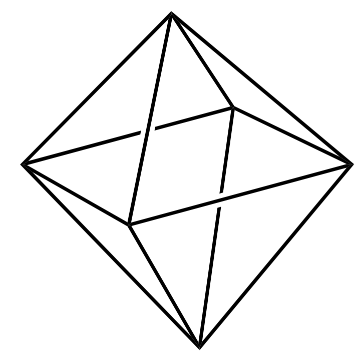
Cannot account for color of complexes

Cannot account for spectrochemical series

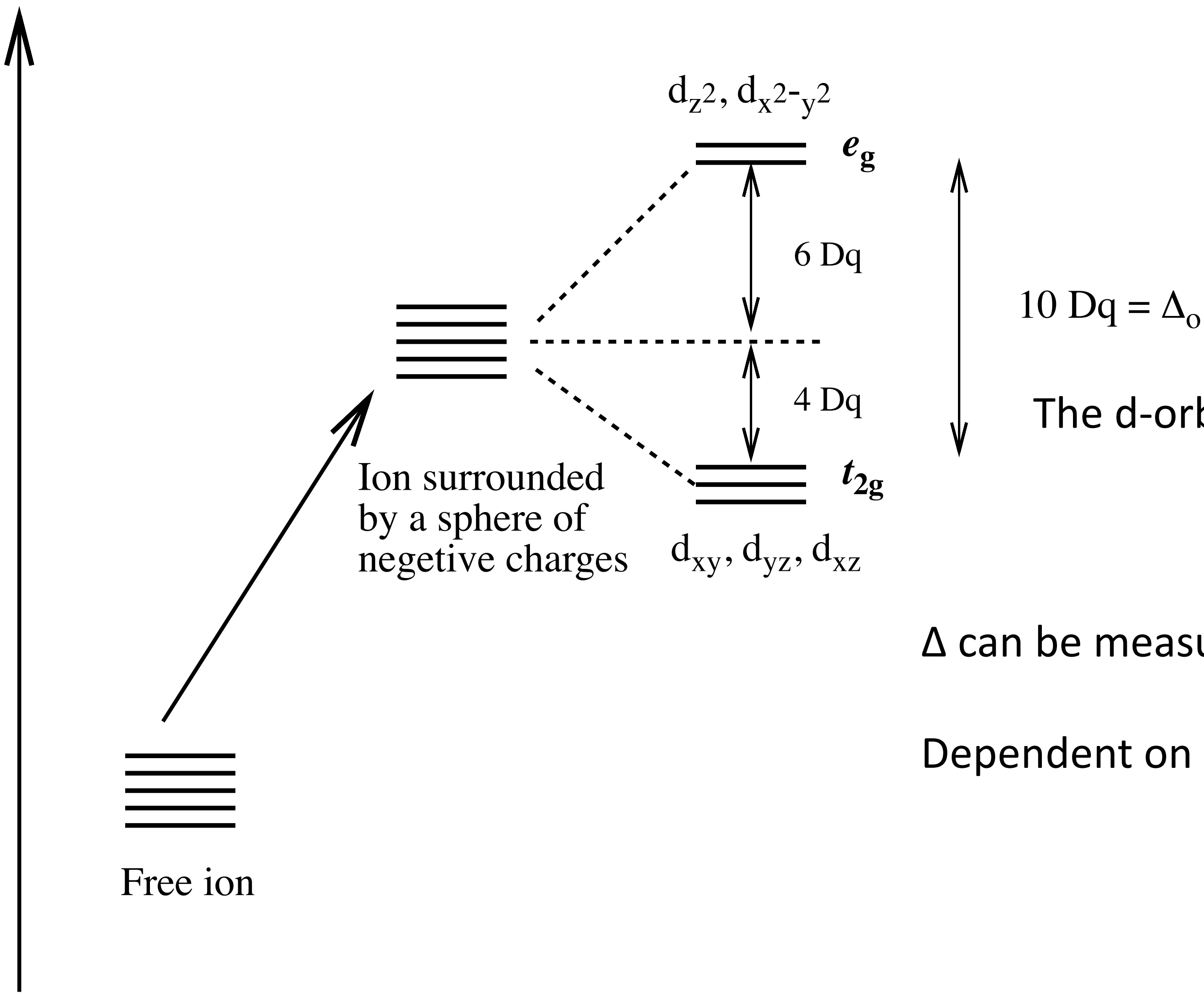
Hybridization actually predicted from magnetization (and not vice-versa)!

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





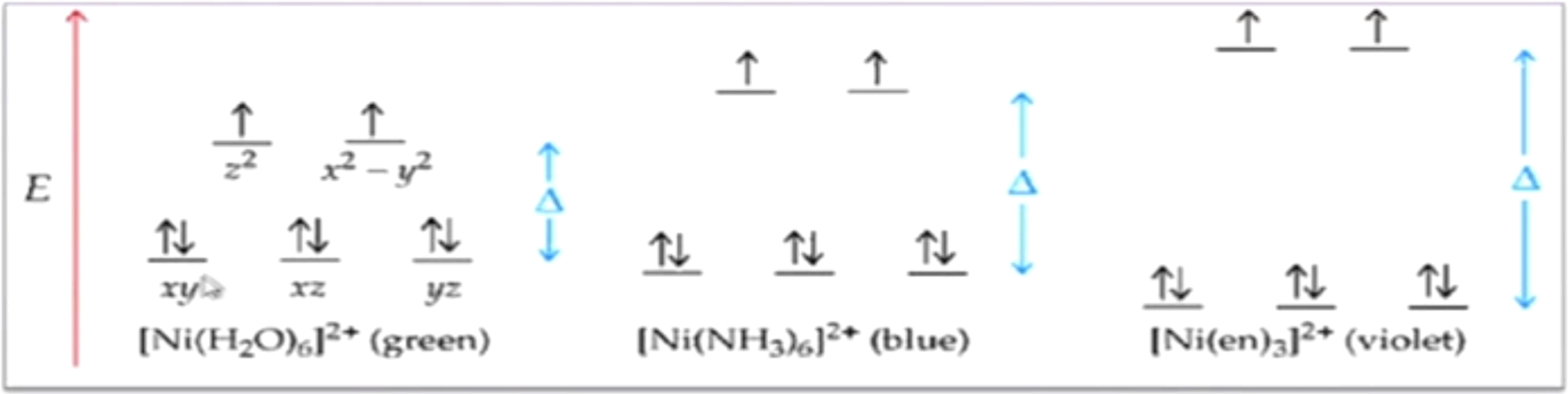
In an octahedral field

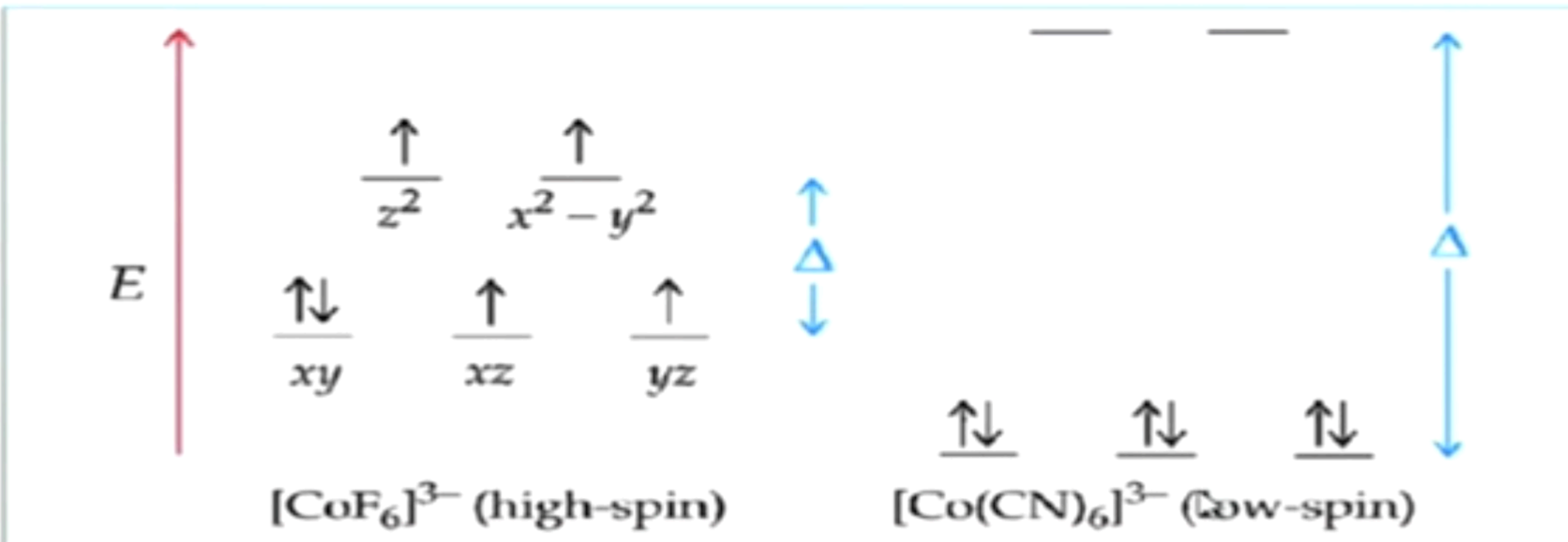


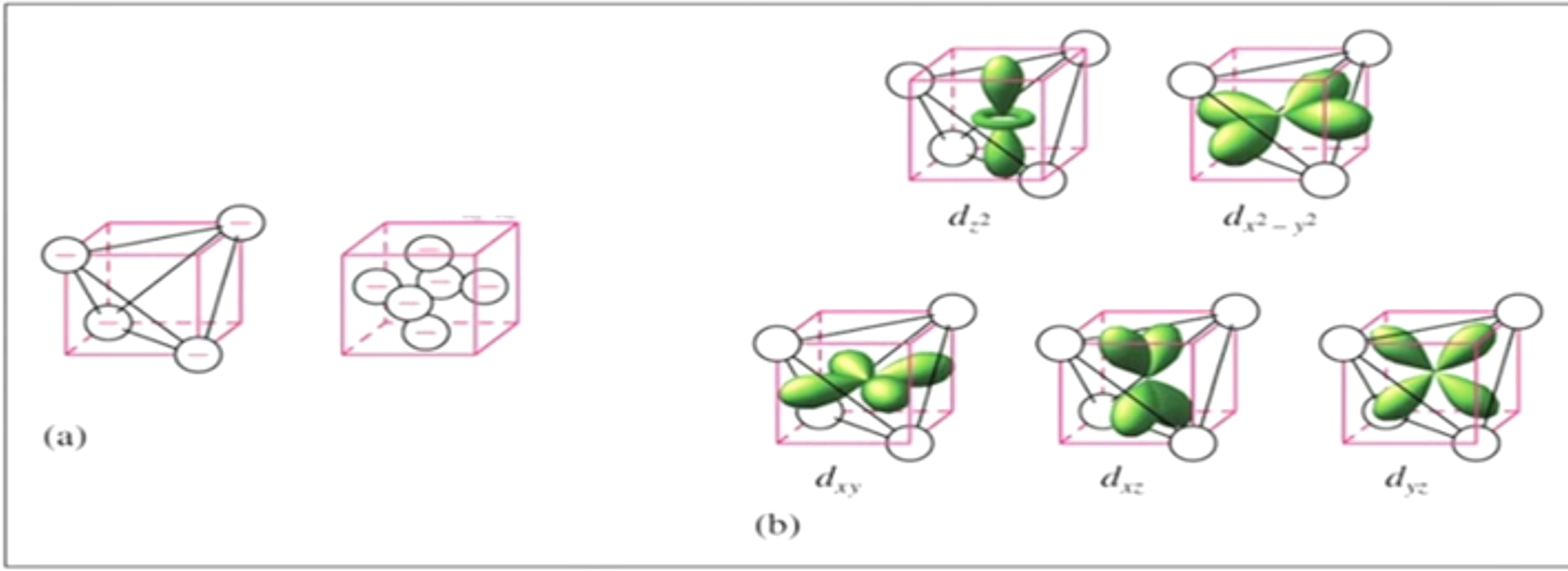
The d-orbitals are no longer degenerate

Δ can be measured; $E = h\nu$

Dependent on nature of ligands


E
↑ ↑
z^2 x^2-y^2
↑↓ ↑↓ ↑↓
xy xz yz
Δ
[Ni(H2O)6]2+ (green)
[Ni(NH3)6]2+ (blue)
[Ni(en)3]2+ (violet)


E
z^2 x^2-y^2
xy xz yz
Δ
[CoF6]3− (high-spin)
[Co(CN)6]3− (low-spin)

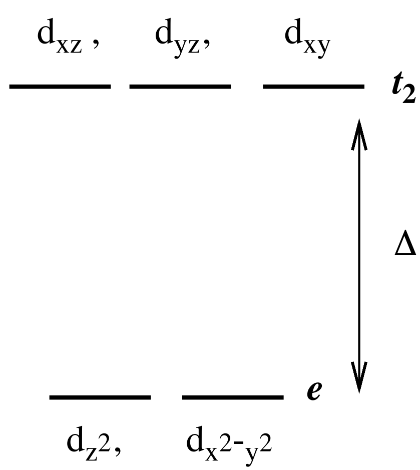


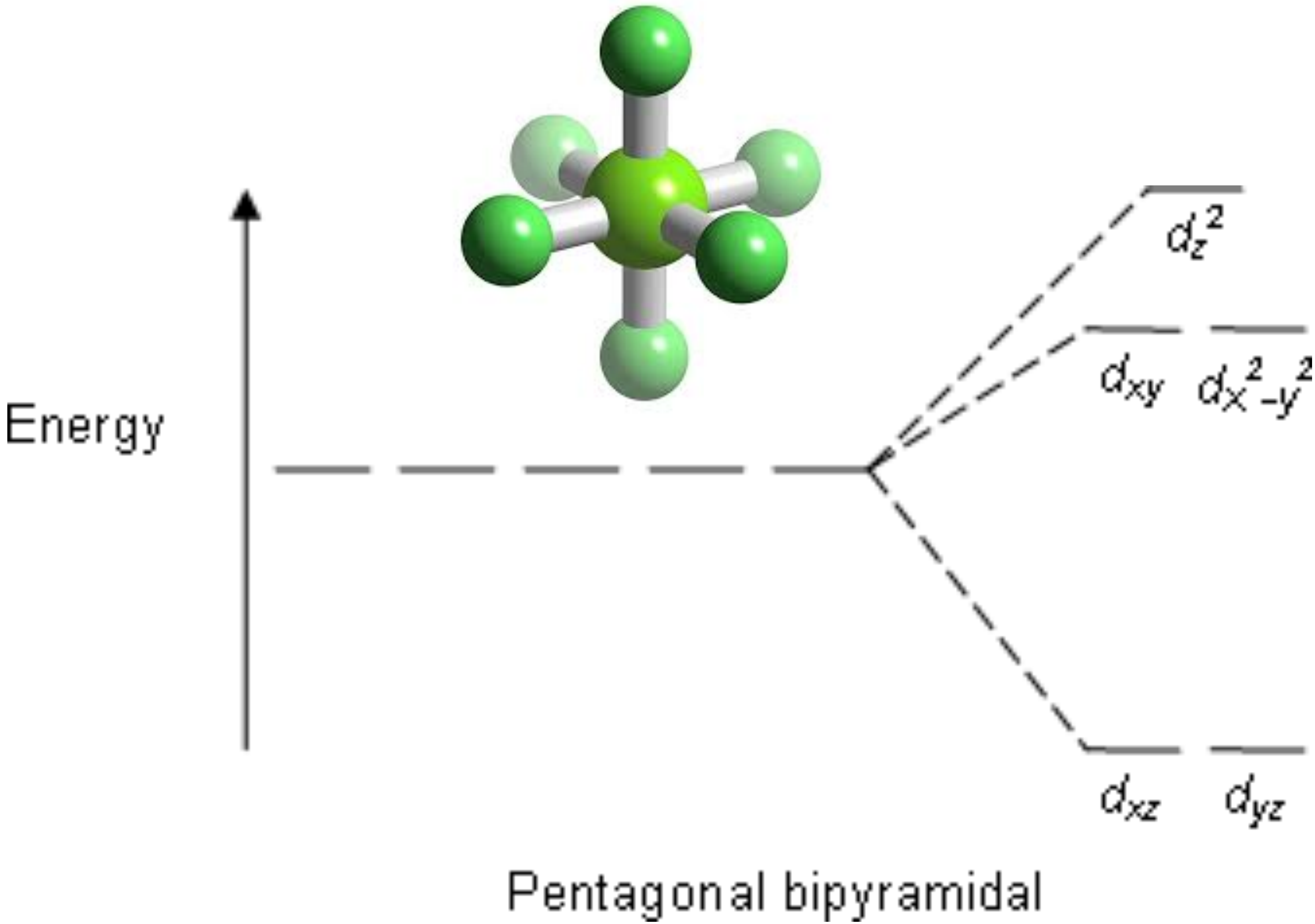
Tetrahedral

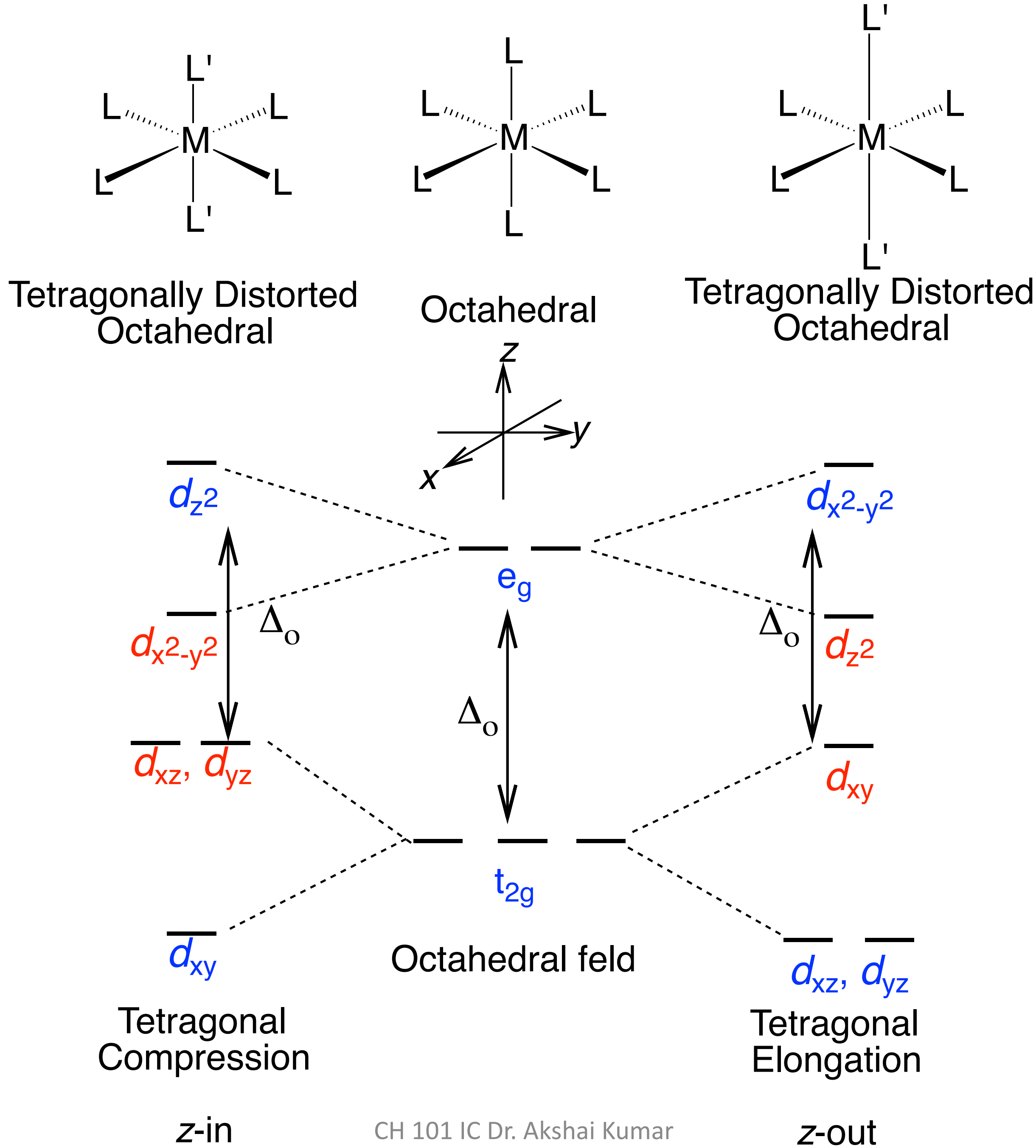
Greater chances of High-spin

Common Tetrahedral complexes

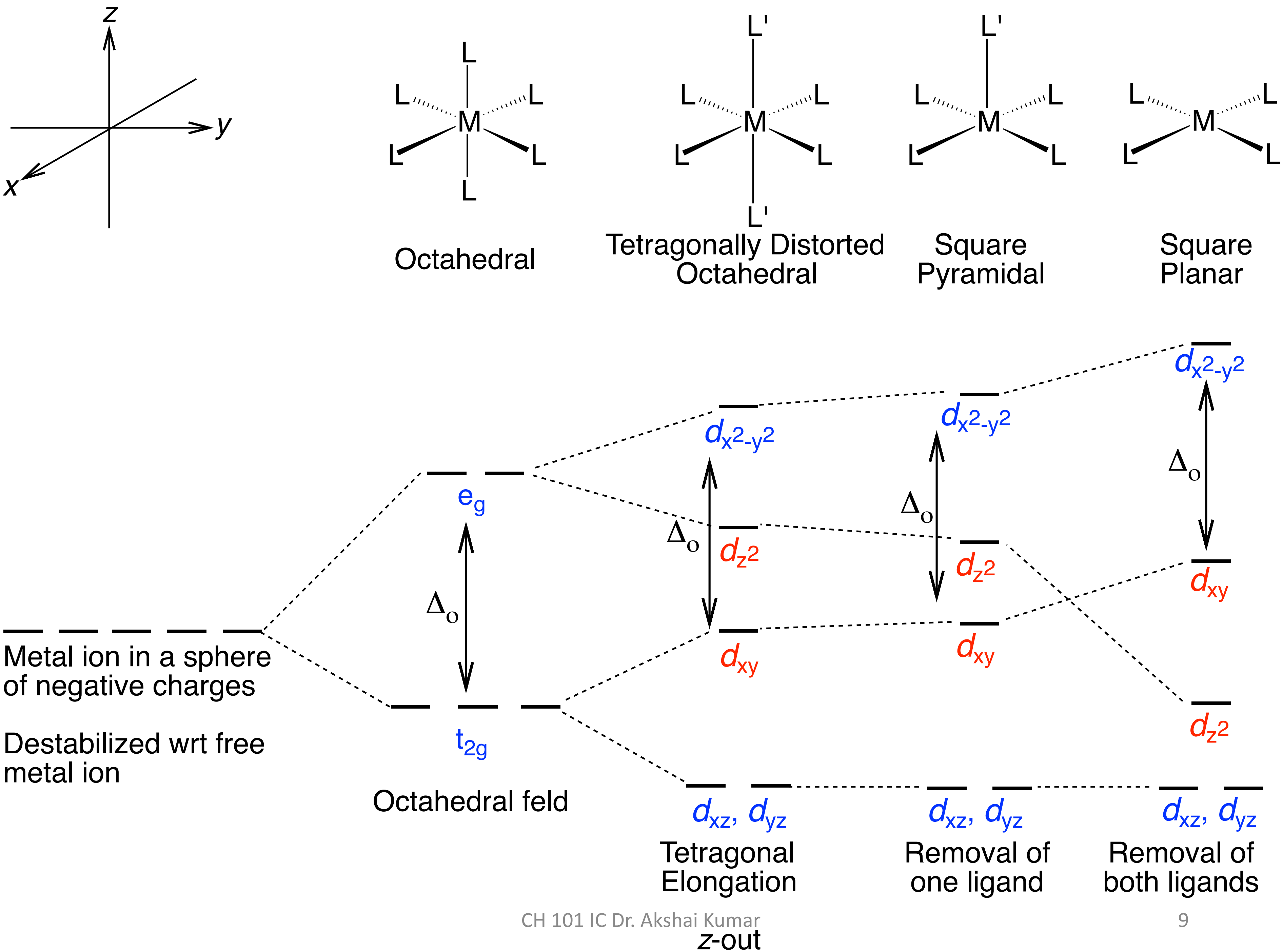
d^{10} Zn(II), Pt(0), Cu(I)

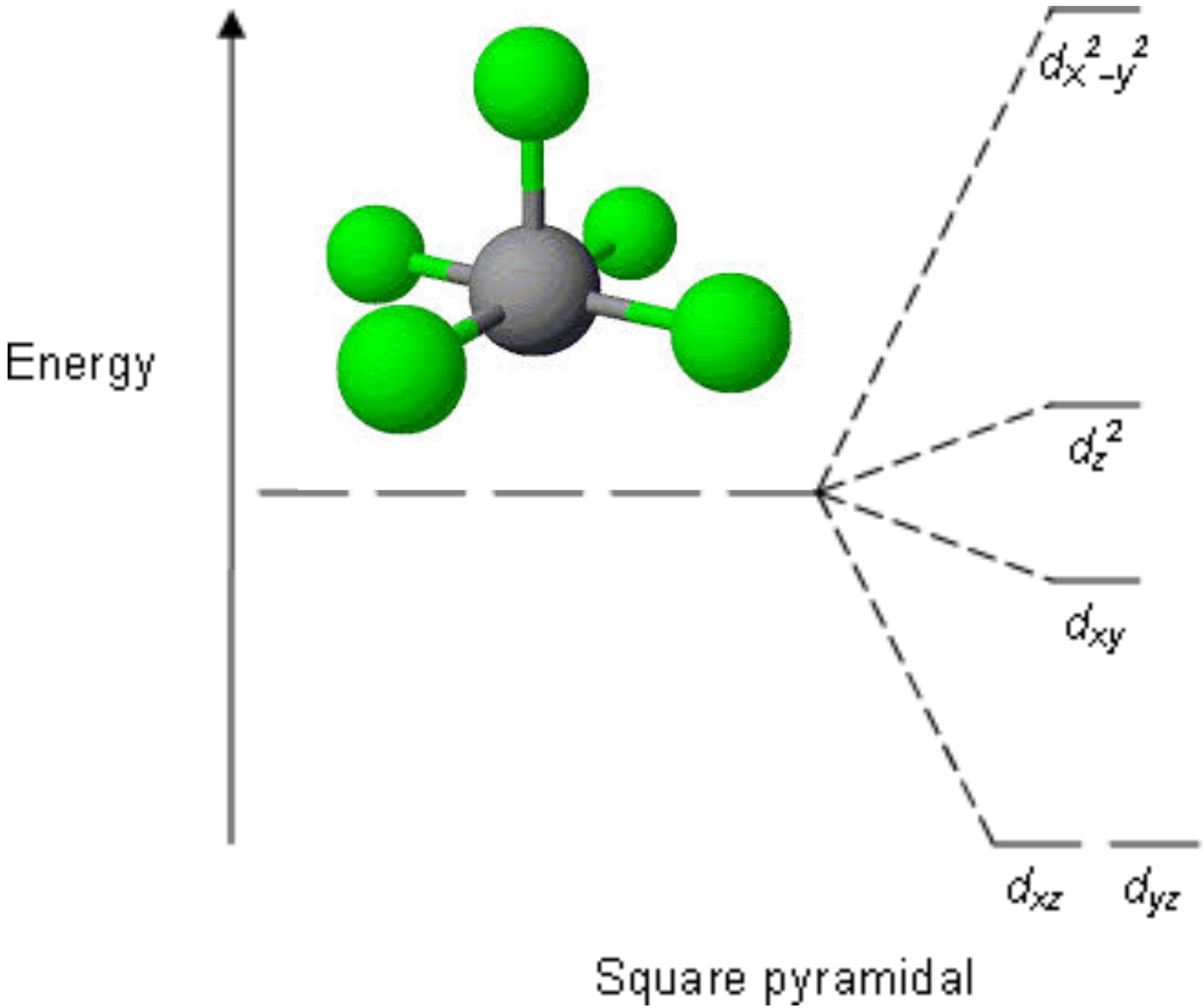



Energy
d_{z^2}
d_{xy} $d_{x^2-y^2}$
d_{xz} d_{yz}
Pentagonal bipyramidal

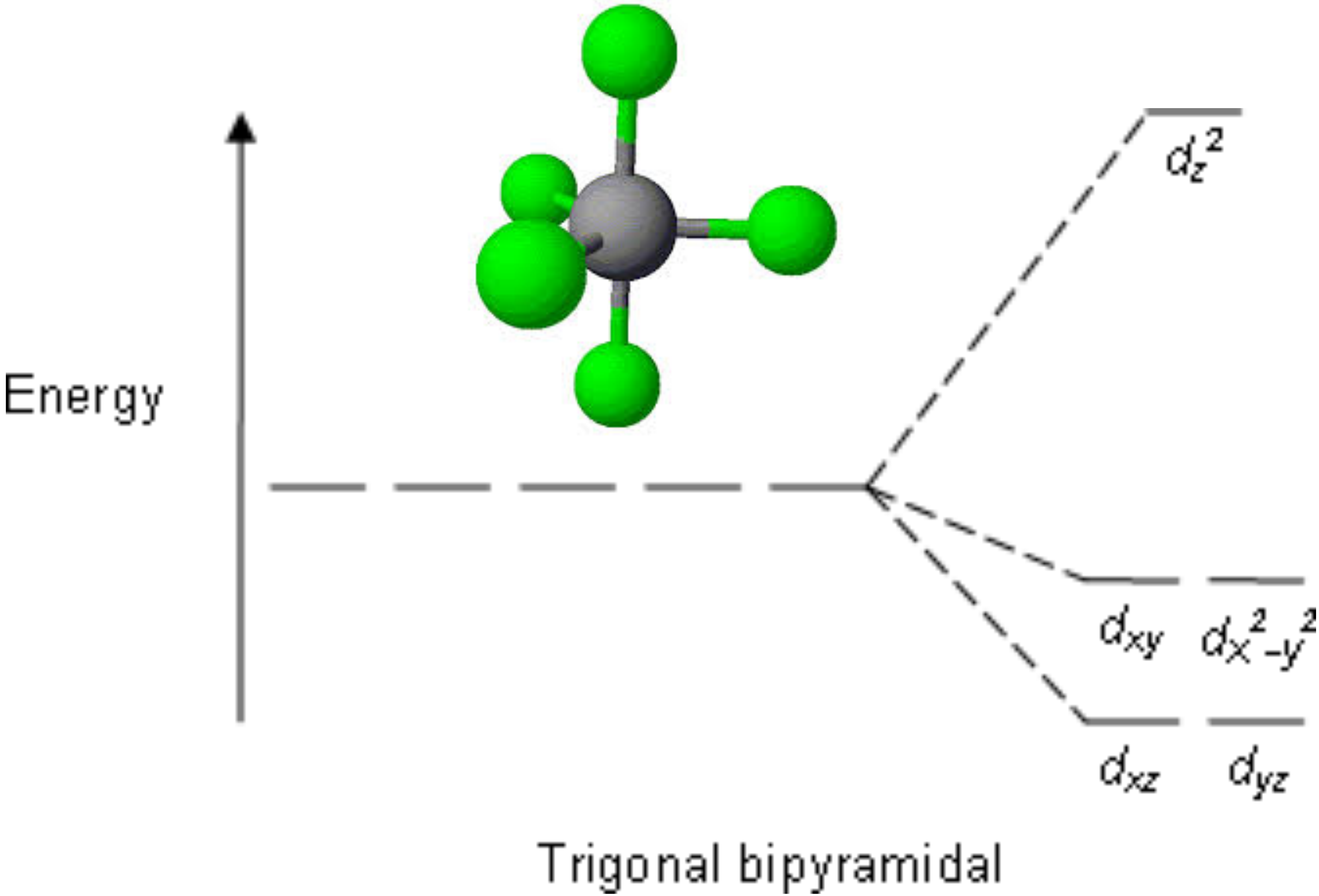


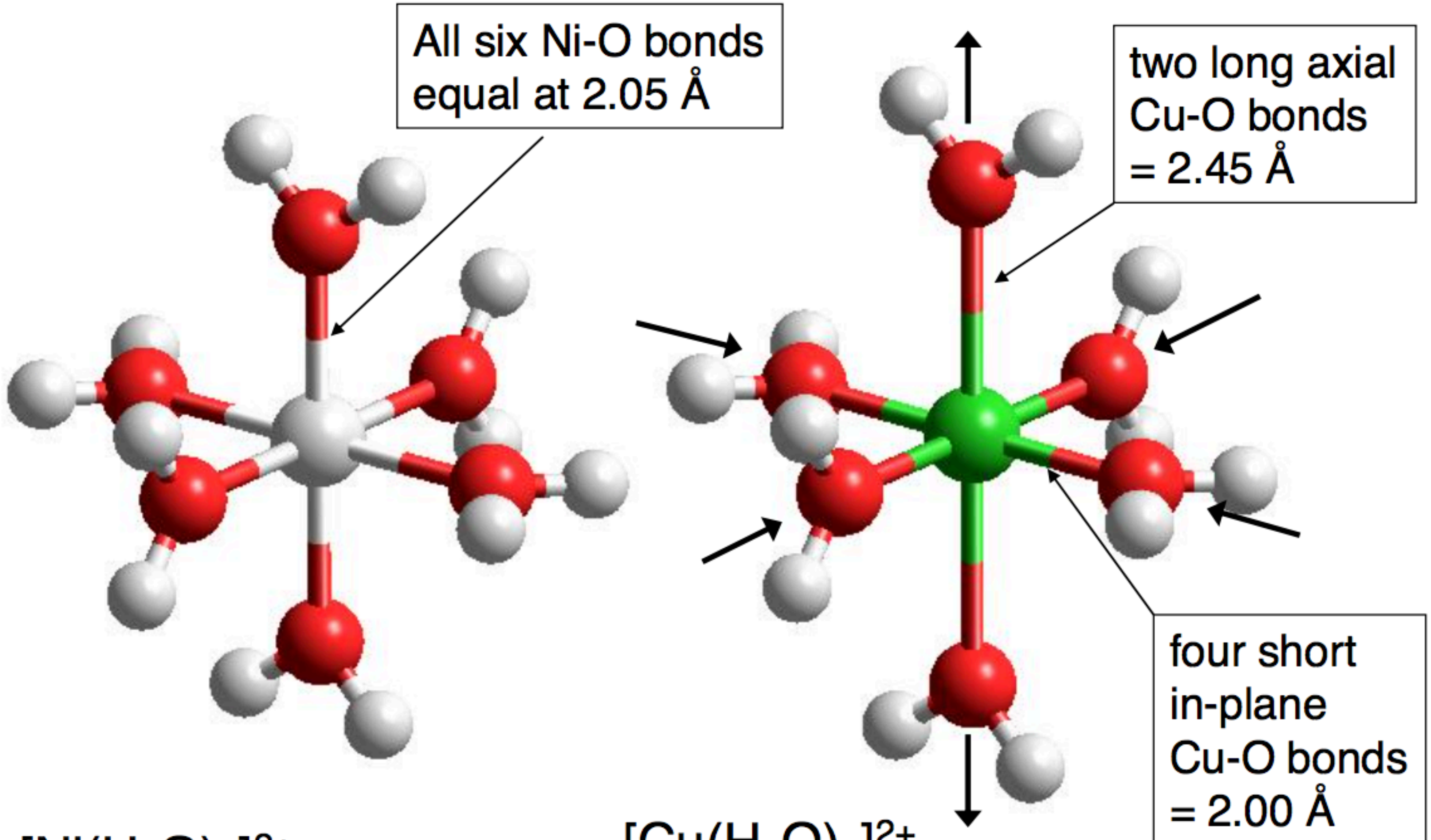
L'
L
M
L'
Tetragonally Distorted Octahedral
Octahedral
Tetragonally Distorted Octahedral
z
y
x
d_{z^2}
$d_{x^2-y^2}$
e_g
Δ_o
$d_{x^2-y^2}$
d_{z^2}
d_{xz}, d_{yz}
d_{xy}
t_{2g}
d_{xy}
Octahedral feld
d_{xz}, d_{yz}
Tetragonal Compression
Tetragonal Elongation
z-in
z-out


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



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



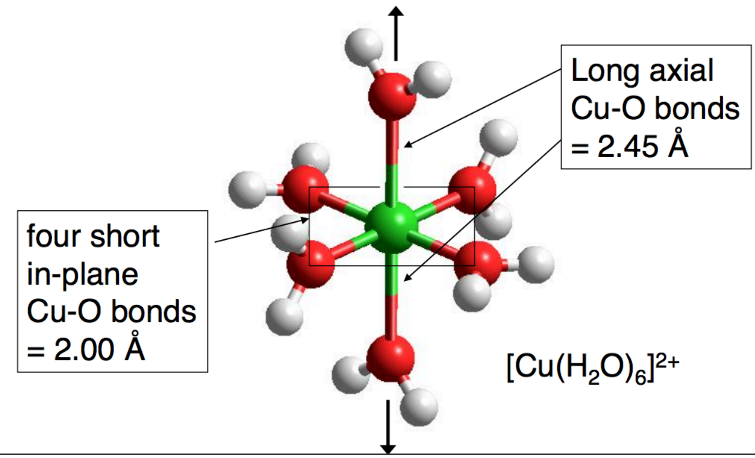
$[Ni(H_2O)_6]^{2+}$
no J-T distortion

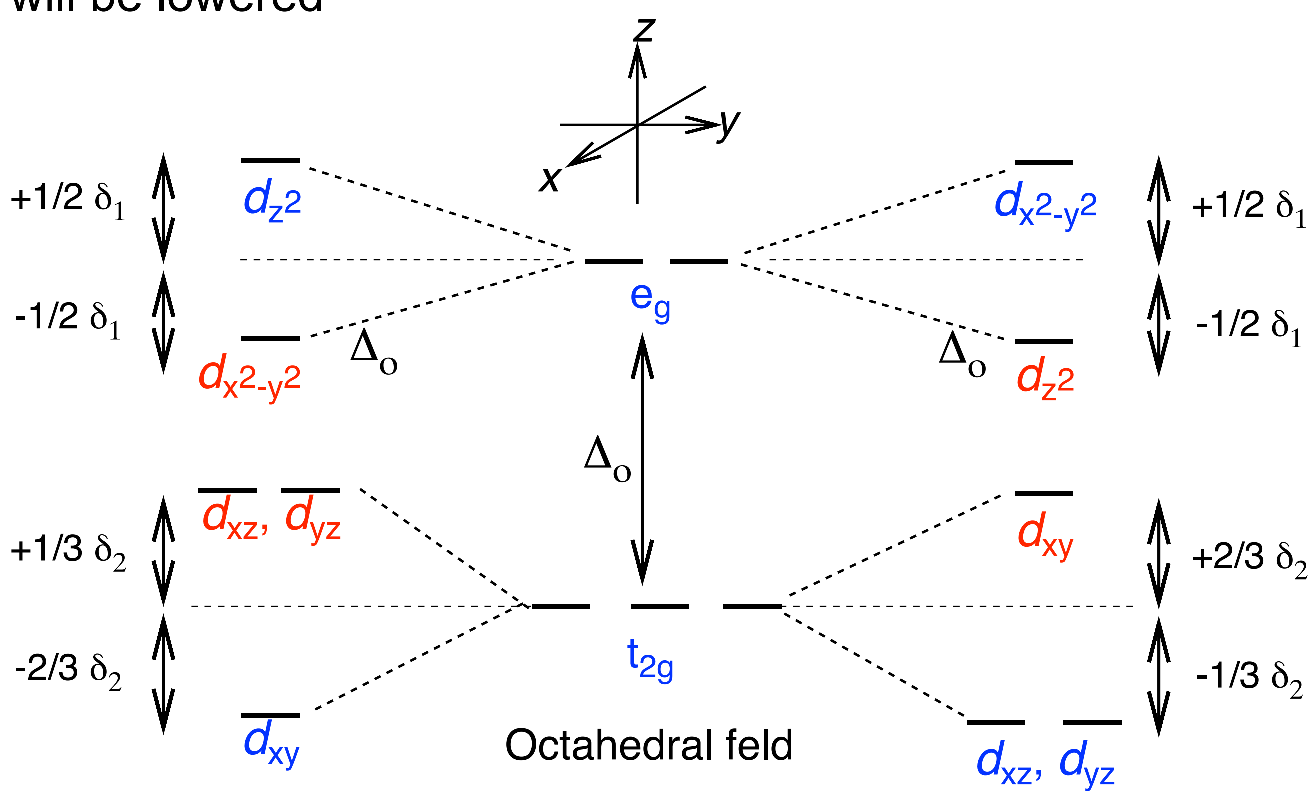
$[Cu(H_2O)_6]^{2+}$
J-T distortion lengthens axial Cu-O's

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



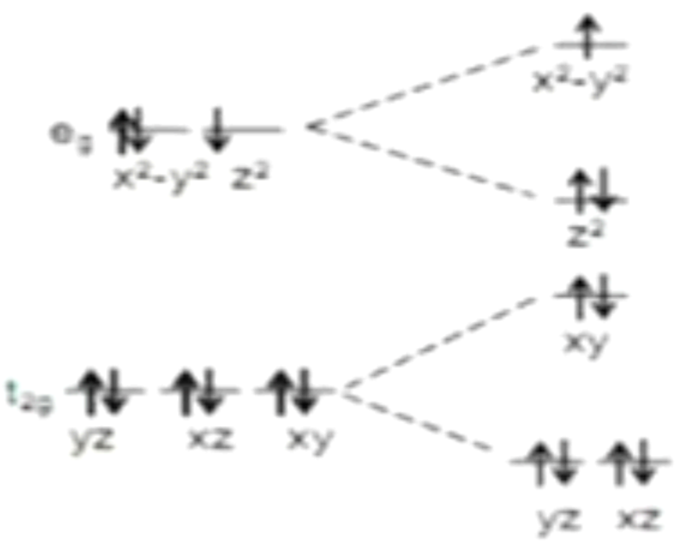


Jahn-Teller distortion *z*-in

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"

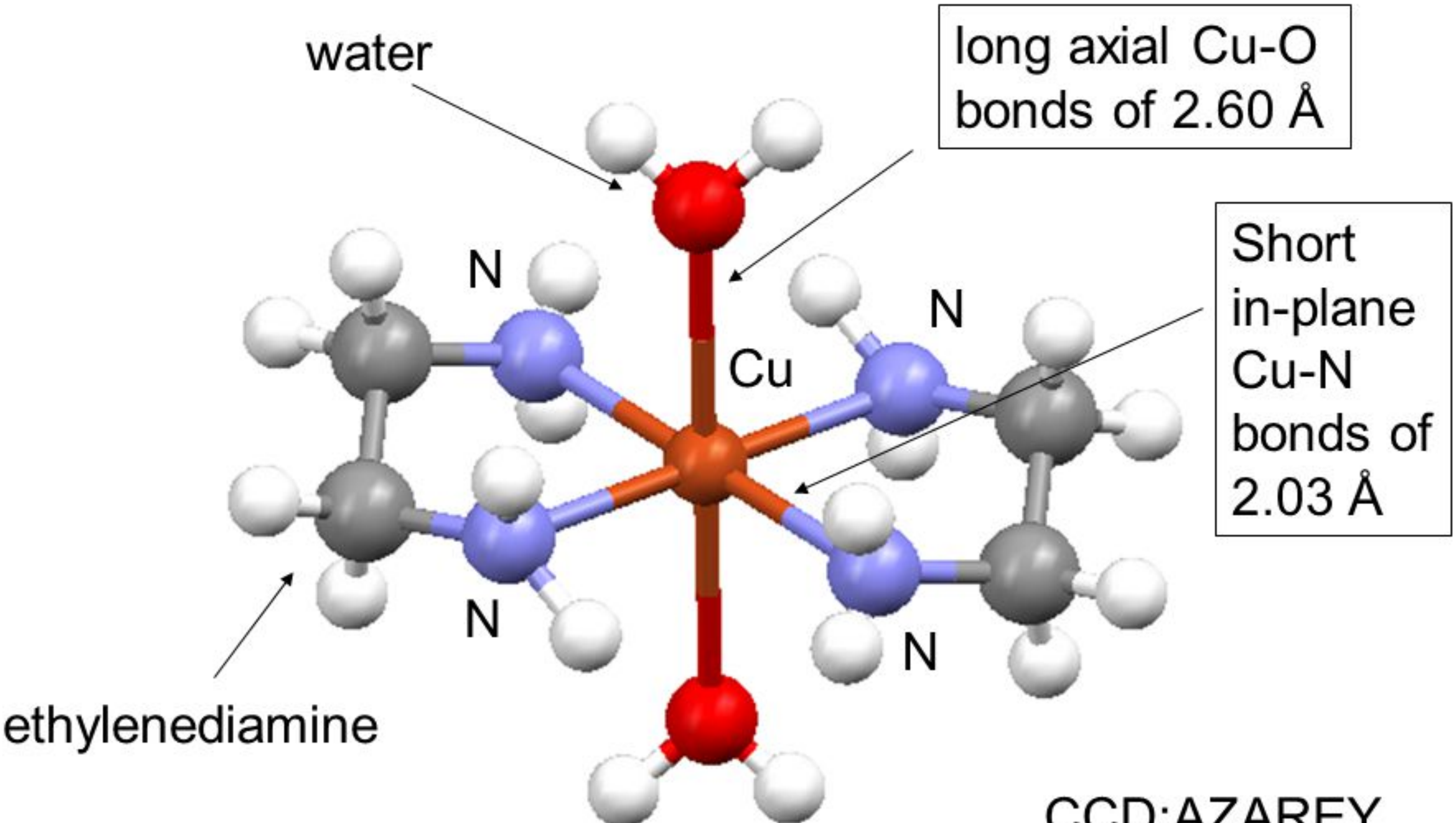


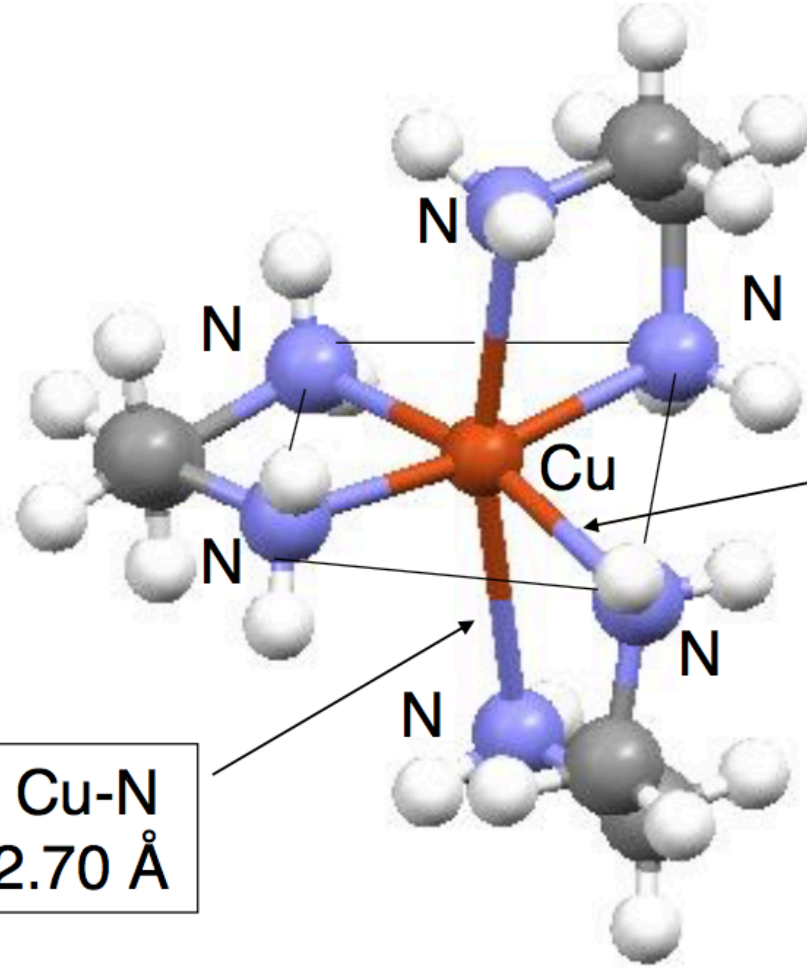
e.g. $[Cu(OH_2)_6]^{2+}$

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
Short in-plane Cu-N bonds of 2.03 Å
N
N
N
N
Cu
ethylenediamine
CCD:AZAREY



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