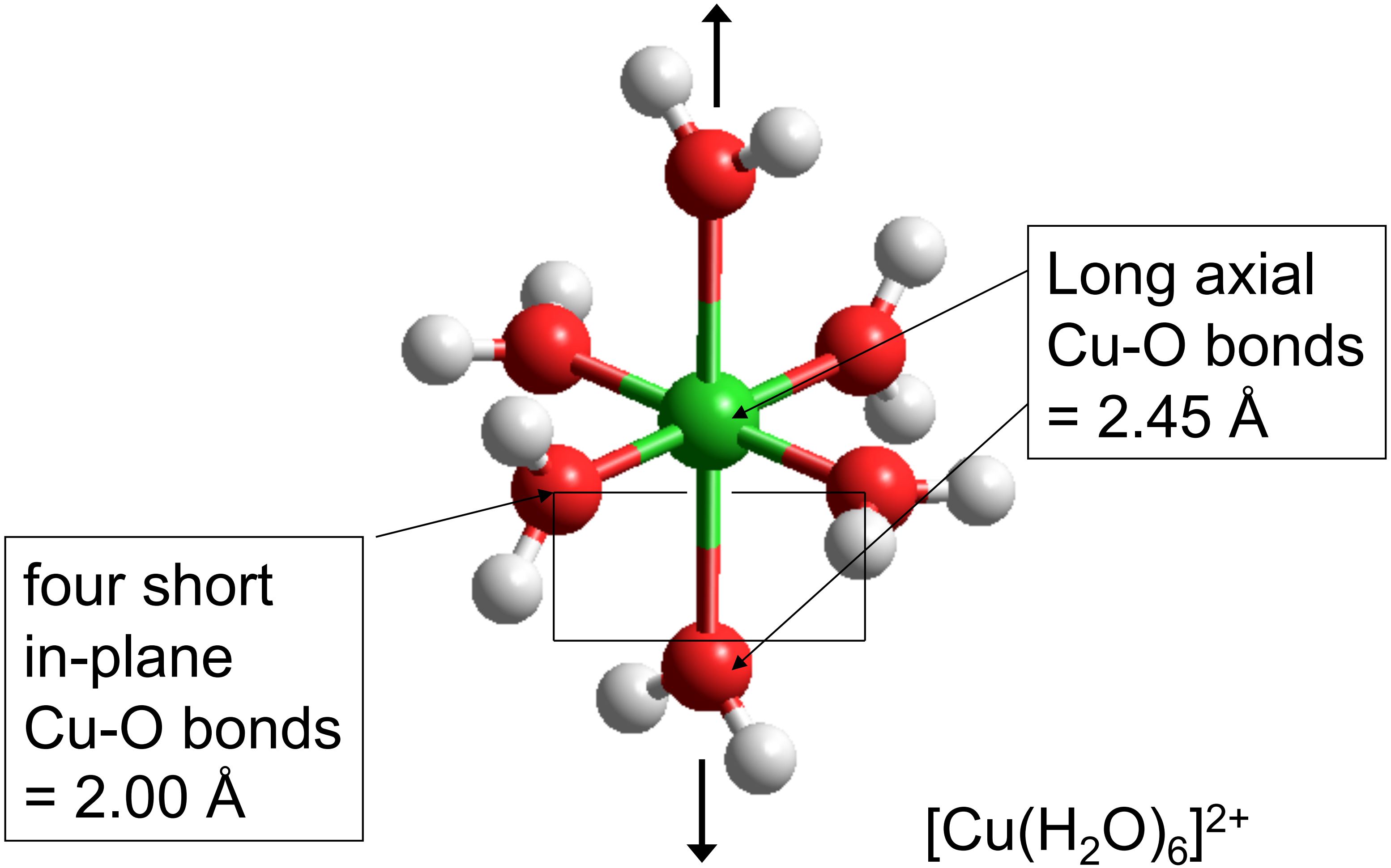
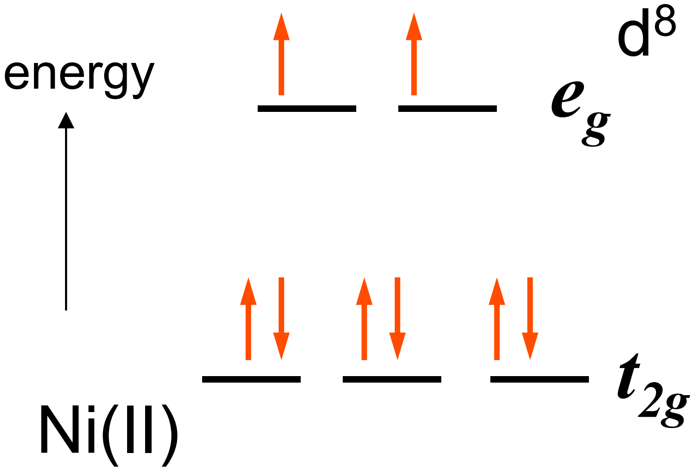
Jahn-Teller distortion and coordination number four



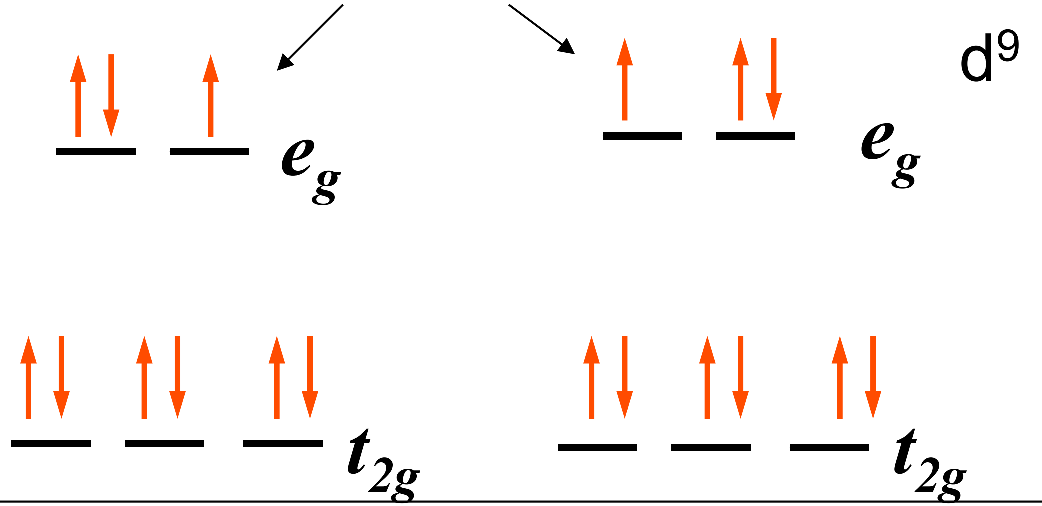
The Jahn-Teller Theorem

The Jahn-Teller (J-T) theorem states that in molecules/ ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy. This is a fancy way of saying that when orbitals in the same level are occupied by different numbers of electrons, this will lead to distortion of the molecule. For us, what is important is that if the two orbitals of the e_g level have different numbers of electrons, this will lead to J-T distortion. Cu(II) with its d^9 configuration is degenerate and has J-T distortion:

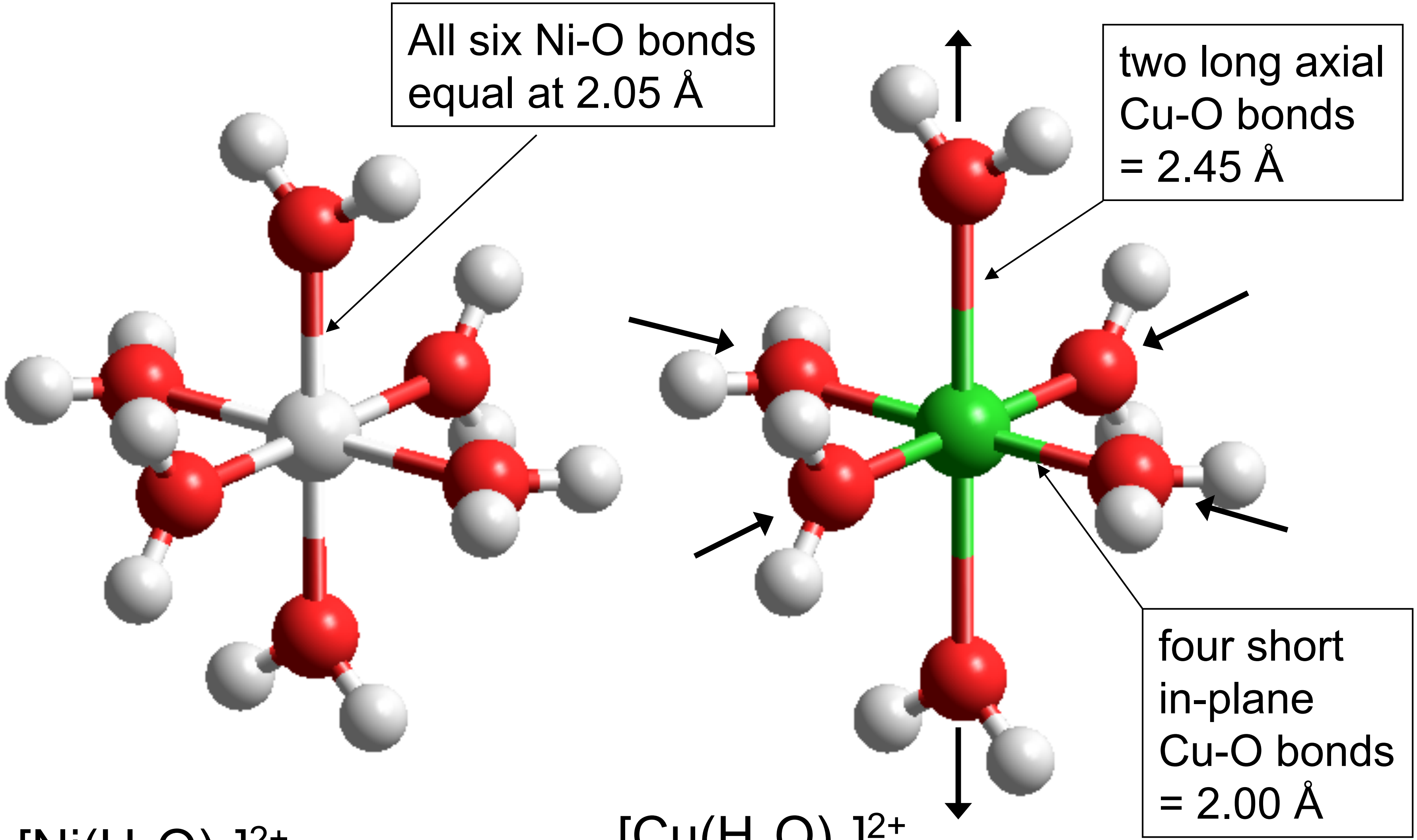
High-spin Ni(II) – only one way of filling the e_g level – not degenerate, no J-T distortion



Cu(II) – two ways of filling e_g level – it is degenerate, and has J-T distortion



Structural effects of Jahn-Teller distortion

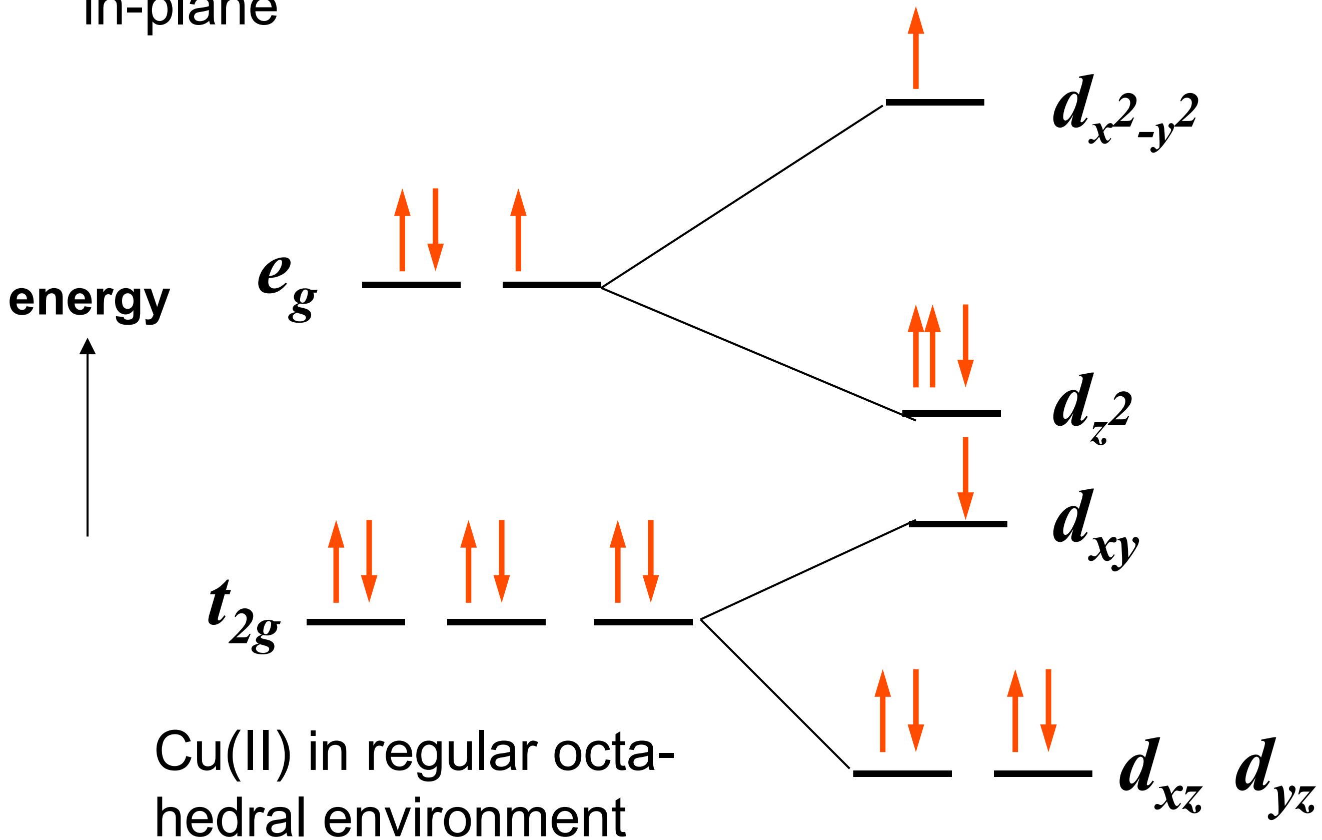


$[Ni(H_2O)_6]^{2+}$
no J-T distortion

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

Splitting of the d-subshell by Jahn-Teller distortion

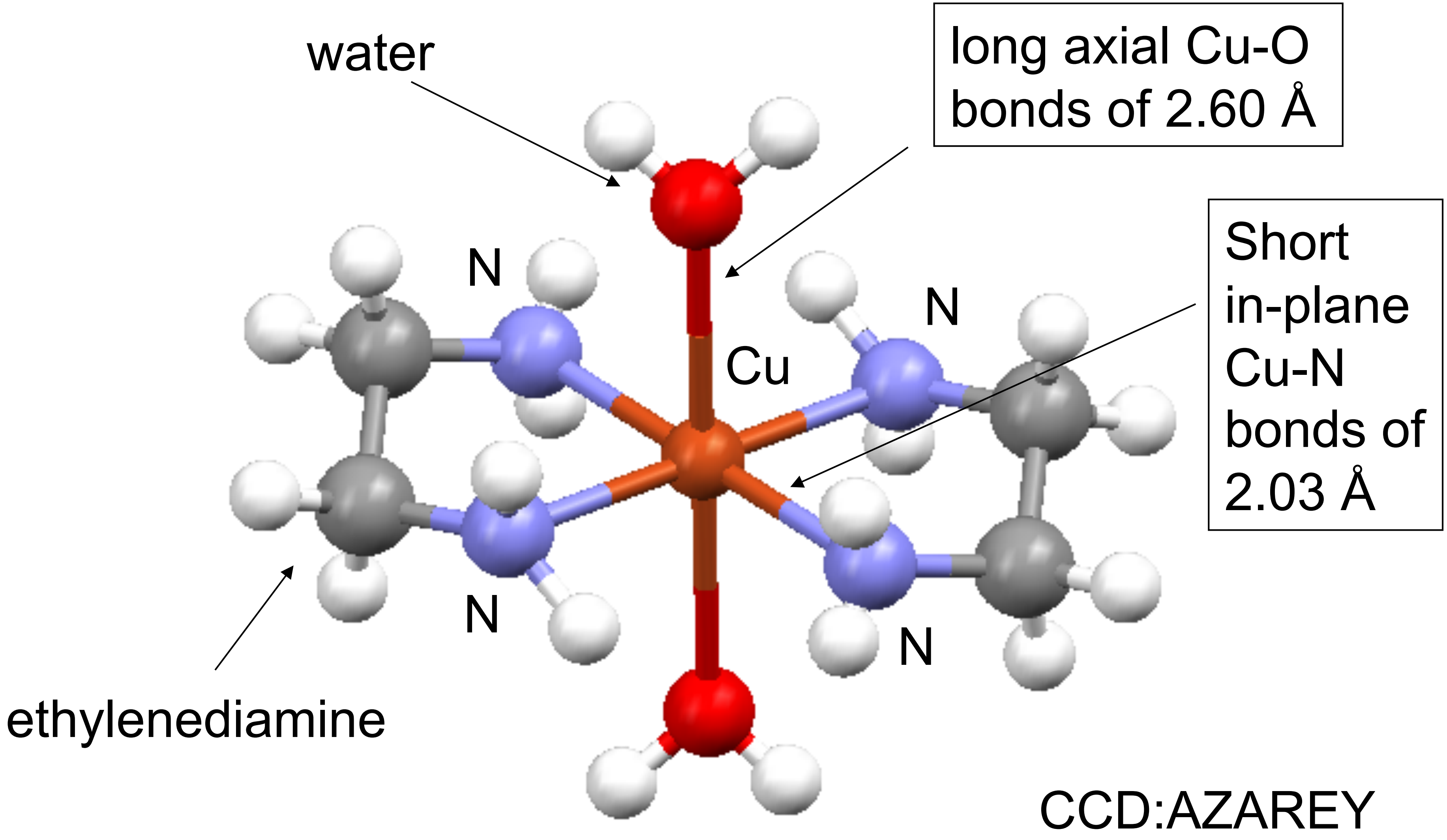
The CF view of the splitting of the d-orbitals is that those aligned with the two more distant donor atoms along the z-coordinate experience less repulsion and so drop in energy (d_{xz}, d_{yz}, and d_{z^2}), while those closer to the in-plane donor atoms (d_{xy}, $d_{x^2-y^2}$) rise in energy. An MO view of the splitting is that the $d_{x^2-y^2}$ in particular overlaps more strongly with the ligand donor orbitals, and so is raised in energy. Note that all d-orbitals with a 'z' in the subscript drop in energy.



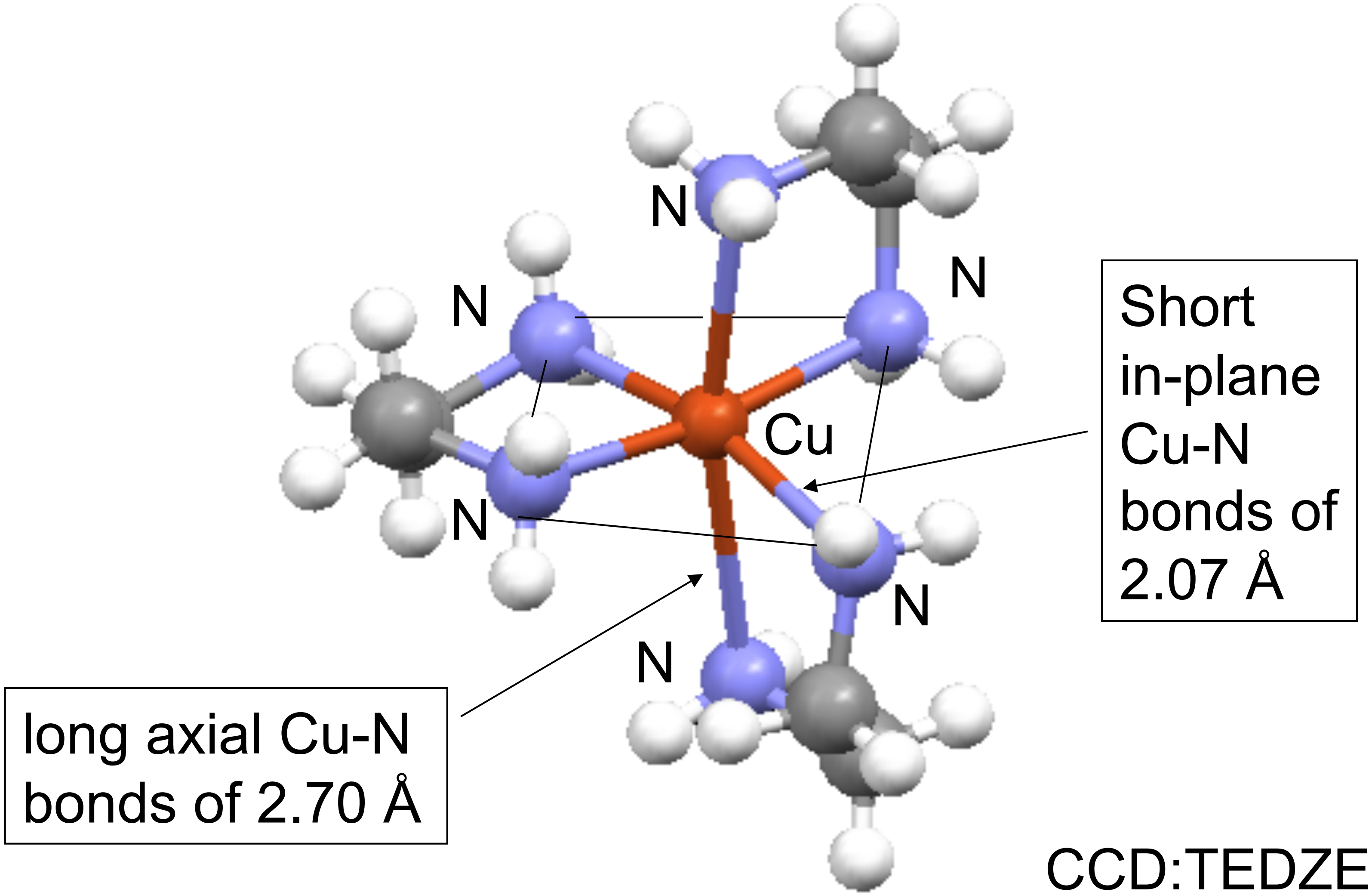
Cu(II) in regular octa-hedral environment

Cu(II) after J-T distortion

Structural effects of Jahn-Teller distortion on $[Cu(en)_2(H_2O)_2]^{2+}$

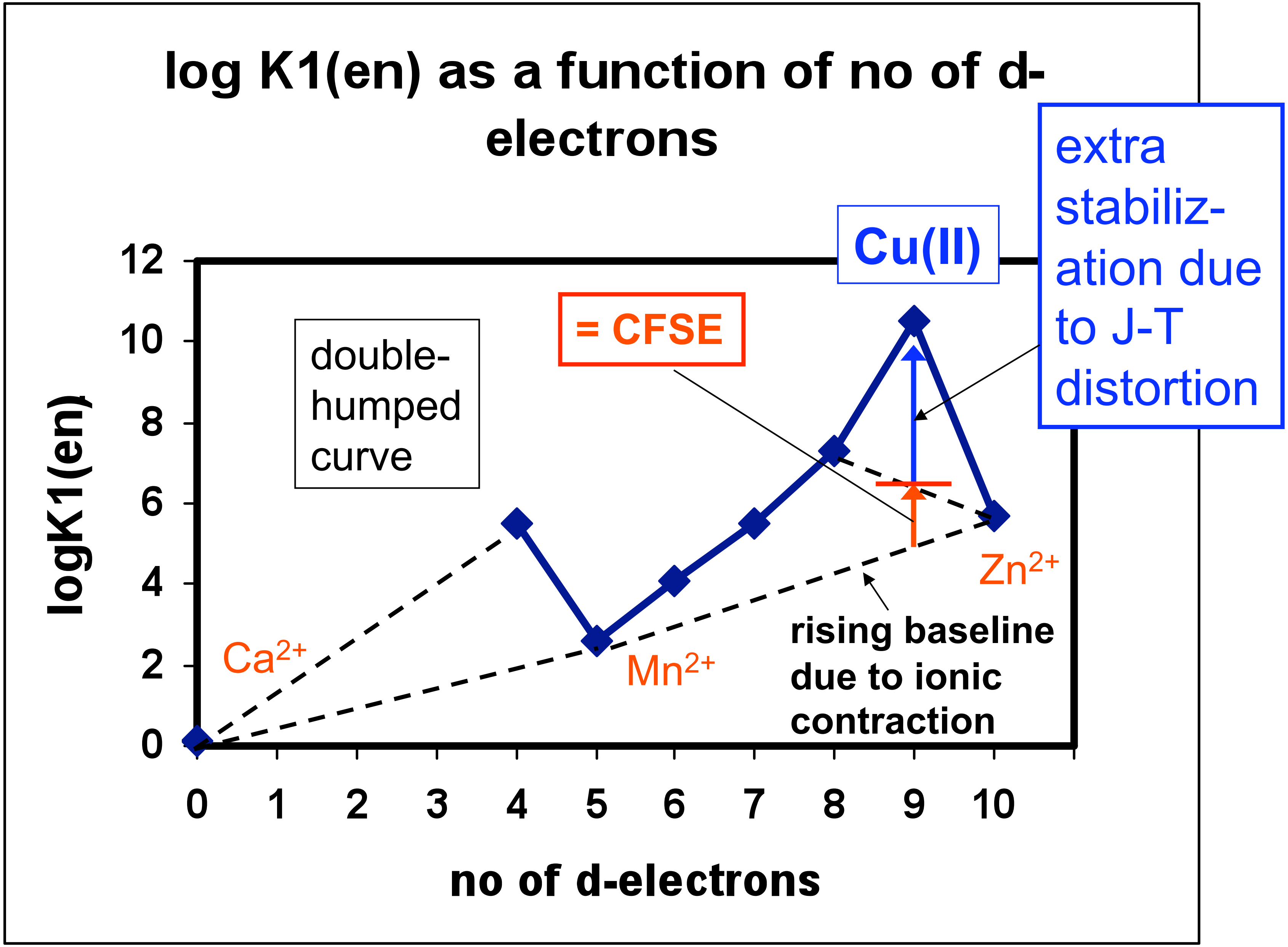


Structural effects of Jahn-Teller distortion on $[Cu(en)_3]^{2+}$

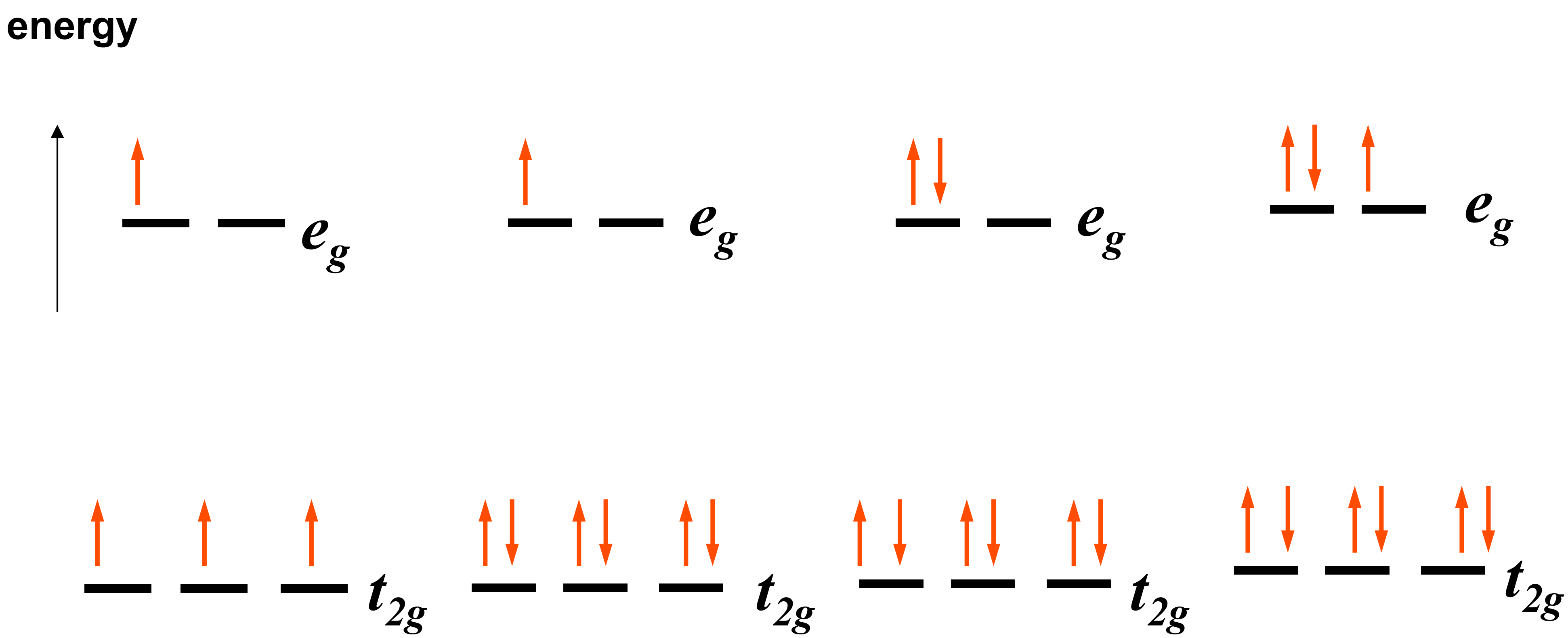


CCD:TEDZEI

Thermodynamic effects of Jahn-Teller distortion:



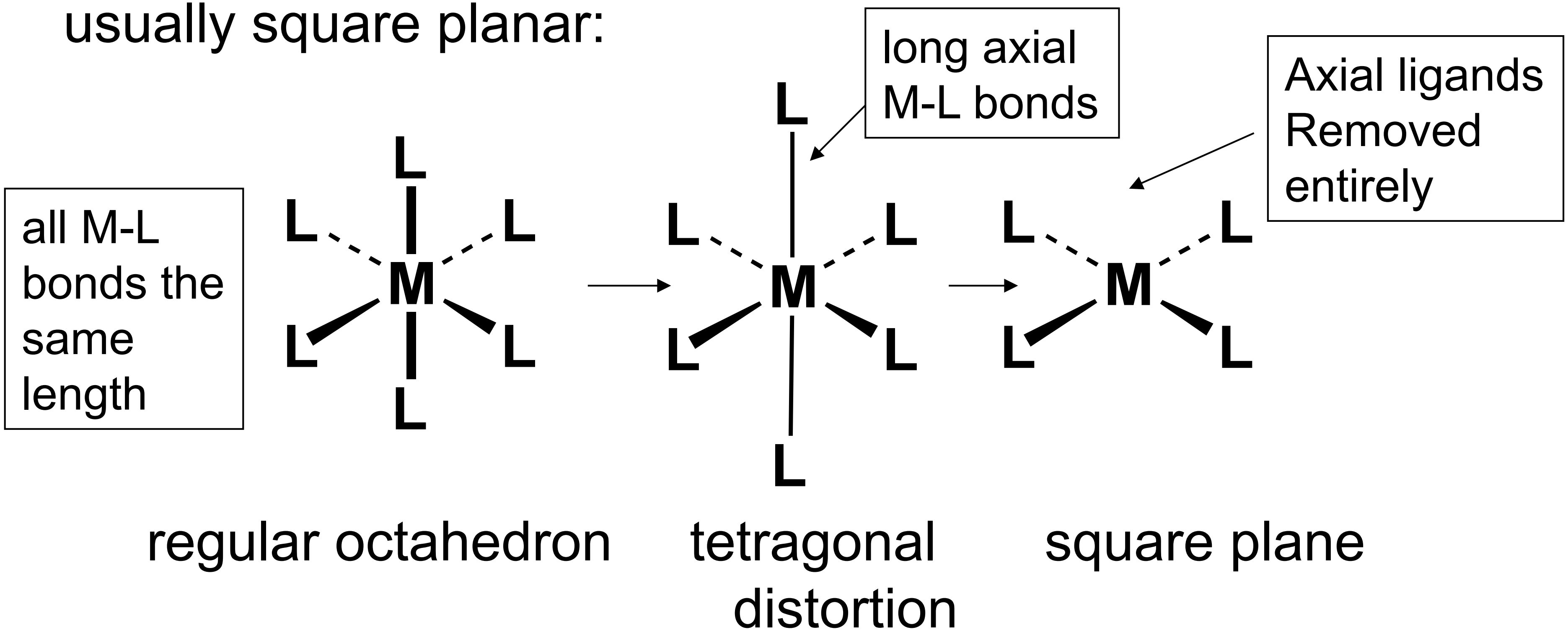
d-electron configurations that lead to Jahn-Teller distortion:



d^4 high-spin	d^7 low-spin	d^8 low-spin	d^9
Cr(II) Mn(III)	Co(II) Ni(III)	Co(I), Ni(II), Pd(II) Rh(I),Pt(II), Au(III)	Cu(II) Ag(II)

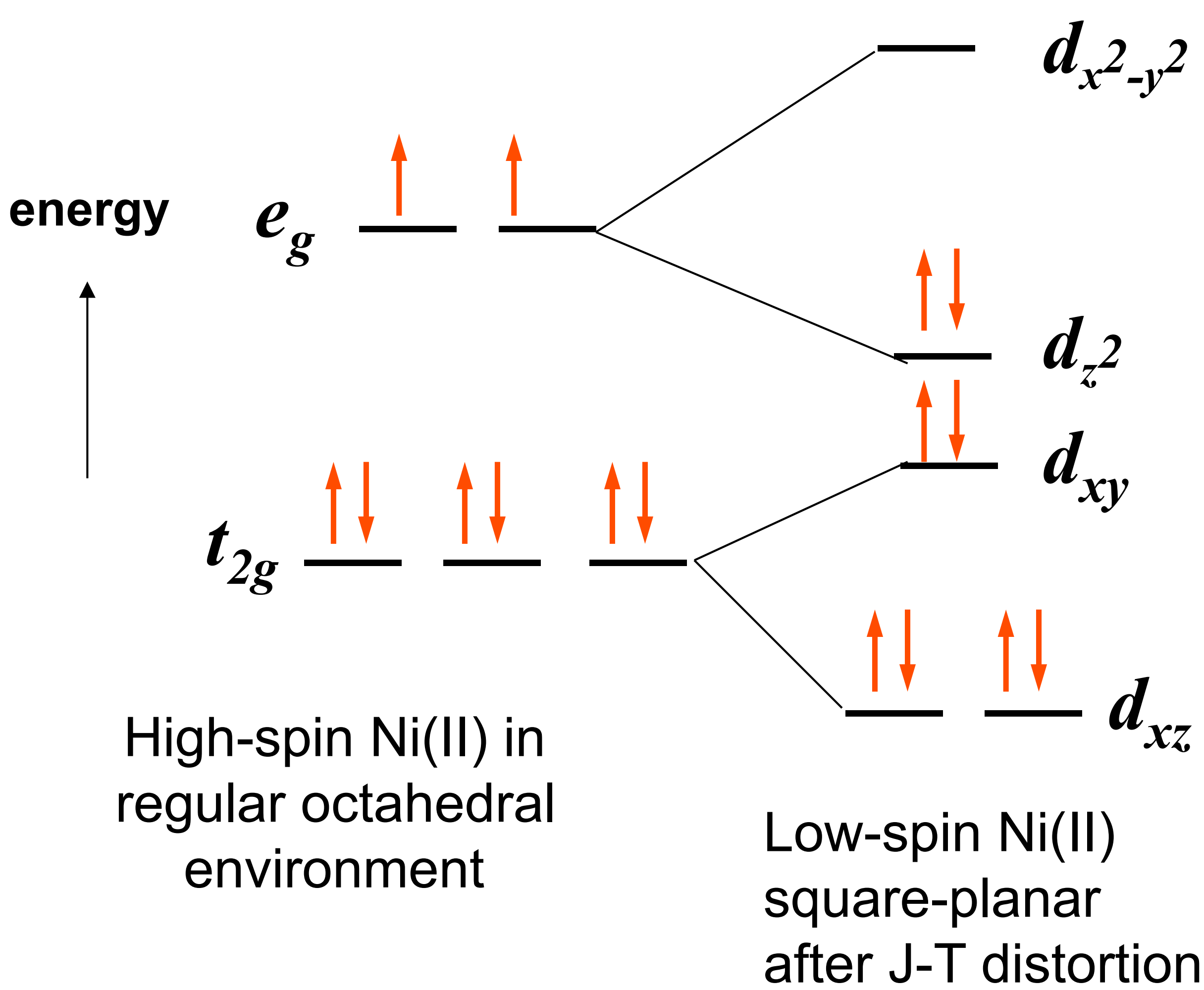
Square planar complexes

Jahn-Teller distortion leads to tetragonal distortion of the octahedron, with the extreme of tetragonal distortion being the complete loss of axial ligands, and formation of a square-planar complex. Tetragonal distortion is the stretching of the axial M-L bonds, and shortening of the in-plane bonds. Cu(II) is usually tetragonally distorted, while low-spin Ni(II) is usually square planar:



Square planar complexes – the low-spin d^8 metal ions

All high-spin d^8 metal ions are octahedral (or tetrahedral), but the low-spin d^8 metal ions are all square planar.

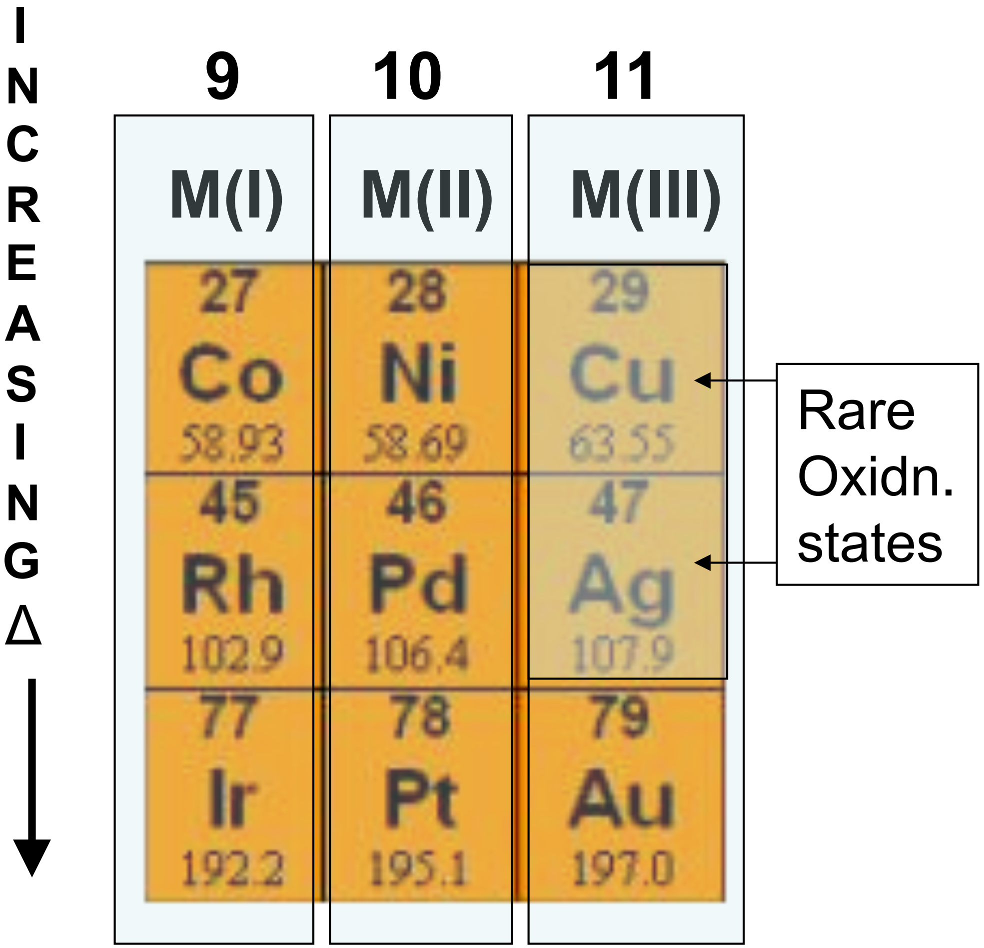


Important examples of square-planar low-spin d^8 metal Ions are Ni(II), Pd(II), Pt(II), Au(III), Co(I), Rh(I), and Ir(I). At left is seen the splitting of the d sub-shell in Ni(II) low-spin square-planar complexes.

Occurrence of Square planar complexes in low-spin d^8 metal ions

d^8 metal ions:

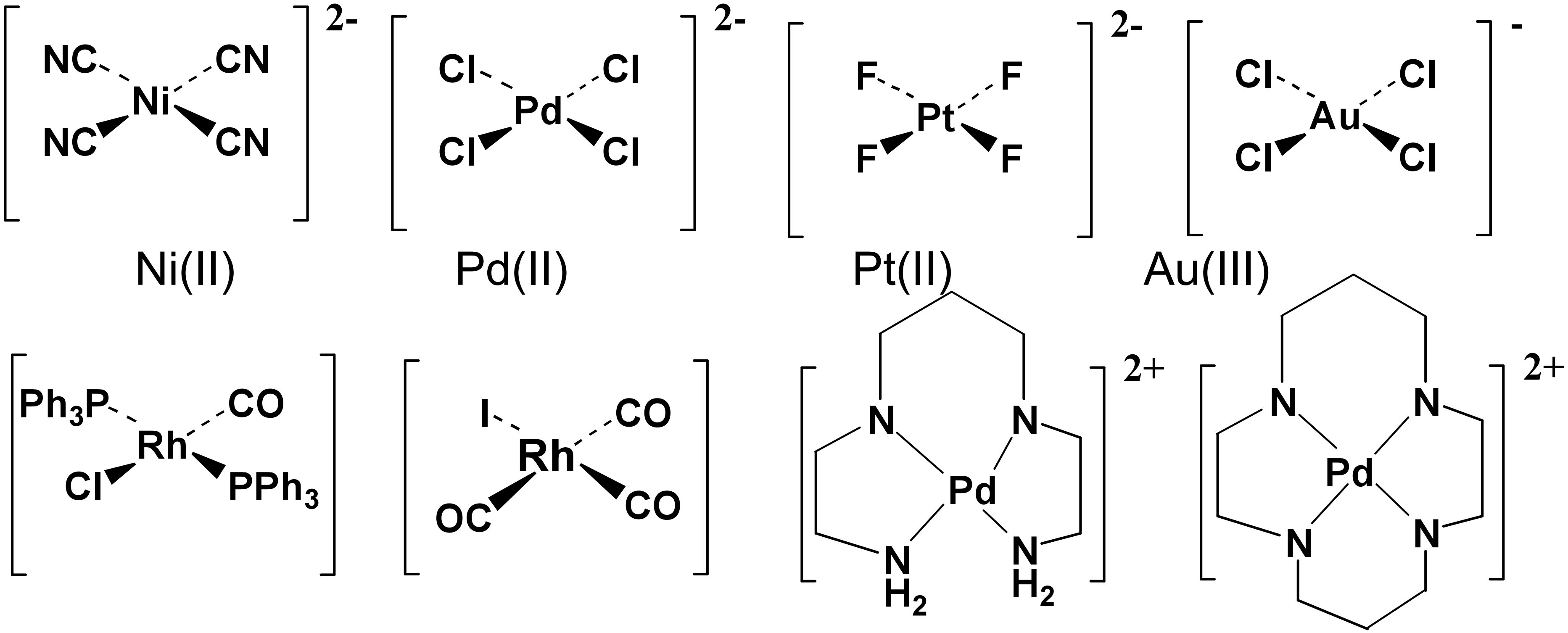
Group:



Obviously the group 9 M(I) ions, the group 10 M(II) ions, and the group 11 M(III) ions are d^8 metal ions. d^8 metal ions must be low-spin to become square planar. Since Δ increases down groups in the periodic table, it is larger for the heavier members of each group. Thus, all Pt(II) complexes are low-spin and square-planar, while for Ni(II) most are high-spin octahedral except for ligands high in the spectrochemical series, so that $[Ni(CN)_4]^{2-}$ is square planar.

Occurrence of Square planar complexes in low-spin d^8 metal ions

Because of increasing Δ down groups, most Ni(II) complexes are high-spin octahedral, whereas virtually all Pt(II) complexes are low-spin square planar. For Pd(II), the only high-spin complex is $[PdF_6]^{4-}$ (and PdF_2, which has Pd in an octahedron of bridging F^- groups), while all others are low-spin square planar. Some examples are:

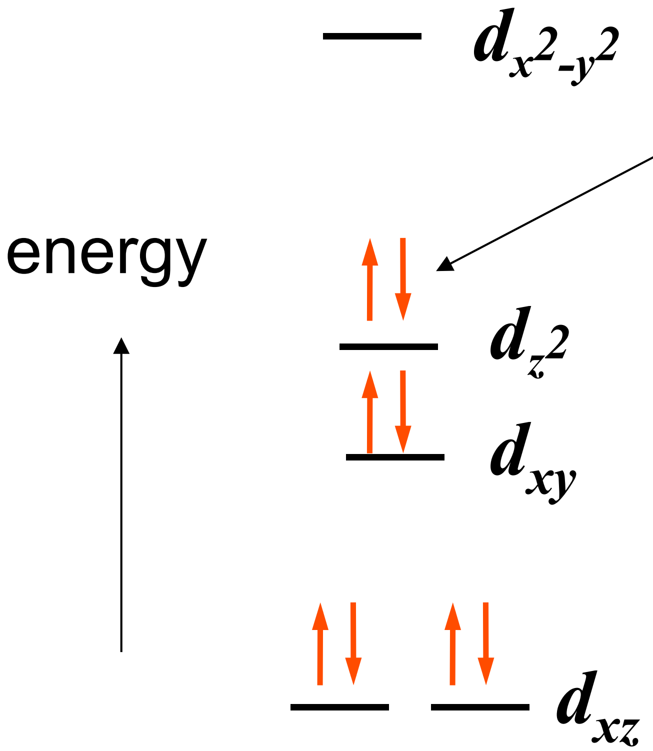


Ni(II) Pd(II) Pt(II) Au(III)

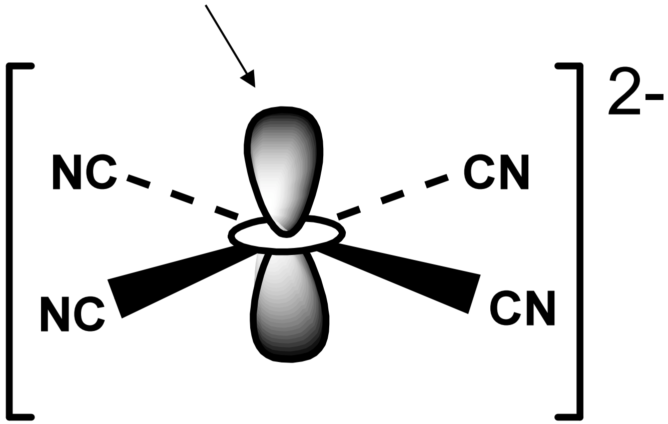
Rh(I) Rh(I) Pd(II) Pd(II)

VSEPR view of d^8 square planar complexes

The filled d_{z^2} orbital occupies two coordination sites in the VSEPR view, and so the four donor atoms occupy the plane:



low-spin d^8 ion,
e.g. Ni(II), Pd(II)



$[Ni(CN)_4]^{2-}$

The structure of $[Ni(CN)_4]^{2-}$ can be compared to that of square planar $[IF_4]^-$, where from VSEPR two lone pairs occupy the axial sites.

Tetrahedral complexes:

Tetrahedral complexes are favored with metal ions that have a low CFSE, which is particularly true for d^{10} Zn(II), which has CFSE = zero. Ligands that are very low in the spectrochemical series also tend to produce tetrahedral complexes, such as Cl, Br^-, and I^-. Thus, Ni(II) that has high CFSE = 1.2 Δ is very reluctant to form tetrahedral complexes, but it forms tetrahedral complexes such as $[NiCl_4]^{2-}$ and $[NiI_4]^{2-}$. If we look at the spectrochemical series in relation to the geometry of complexes of Ni(II), we have:

I^- < Br^- < Cl^- <	F^- < H_2O < NH_3	< CN^-
tetrahedral	octahedral	square planar

low CFSE ← → high CFSE

Splitting of the d-orbitals in tetrahedral complexes

The donor atoms in tetrahedral coordination do not overlap well with the metal d-orbitals, so that Δ_{tet} is much smaller than Δ_{oct} in octahedral complexes with the same ligands, e.g. $[Co(NH_3)_4]^{2+}$ versus $[Co(NH_3)_6]^{2+}$. Calculation suggests $\Delta_{tet} \approx 4/9\ \Delta_{oct}$ in that situation. Note the lack of a g in the subscripts (t_2, e) because T_d complexes do not have a center of symmetry.