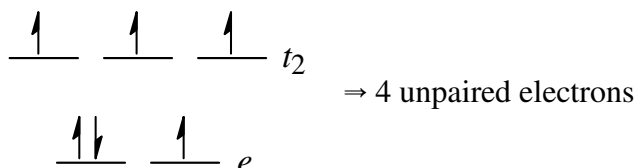
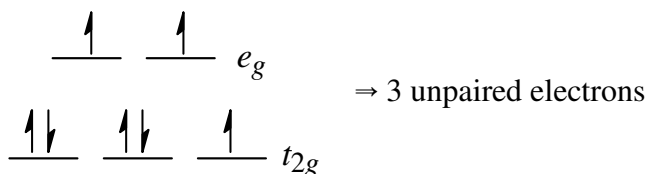


Chem 370 - Spring, 2019
Assignment 8 - Solutions

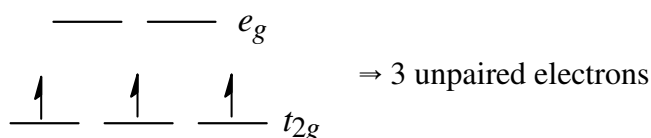
- 10.1 a. All tetrahedral complexes are high spin. For $T_d d^6$ the configuration is $e^3 t_2^3$:



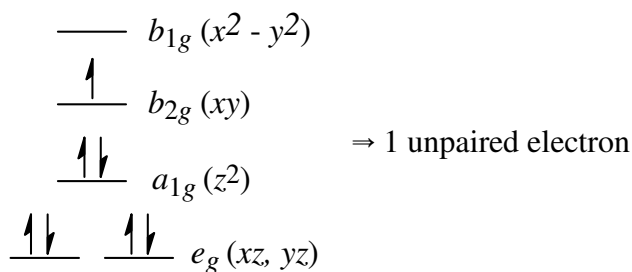
- b. $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is d^7 high-spin O_h because H_2O is a weak-field ligand. (Do not confuse Co^{2+} with Co^{3+} , which tends to be low-spin, even with H_2O .)



- c. $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ is d^3 O_h .



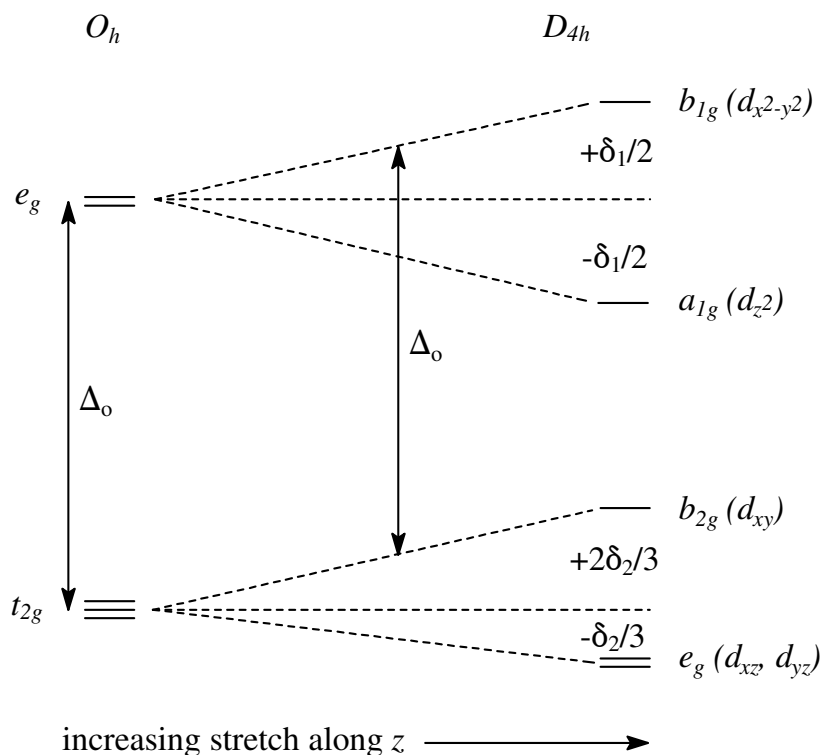
- d. Square planar complexes have the following splitting scheme, filled in a low-spin manner. (The middle two levels may be reversed in some cases, but that does not generally affect the overall configuration or number of unpaired electrons.)



- e. $\mu = \sqrt{n(n+2)} = 5.1 \Rightarrow n = 4.2 \approx 4$

- 10.2 a. To have M^{3+} with $3d^1$, the neutral atom would need to be $3d^2 4s^2$, which is Ti.
 b. The most unpaired electrons is d^5 . $[\text{MBr}_4]^-$ has a M^{3+} ion. These two facts make it Fe.
 c. Diamagnetic $[\text{M}(\text{CN})_6]^{3-}$ would be a low-spin d^6 , because CN^- is a high-field ligand. The M^{3+} ion with a $3d^6$ configuration is Co.
 d. If $\text{CFSE} = -0.6\Delta_o$ with no pairing terms, there are no paired electrons. The high-spin configuration $t_{2g}^3 e_g^1$ would have a $\text{CFSE} = (-0.4)(3)\Delta_o + (0.6)(1)\Delta_o = -0.6\Delta_o$. This would be the configuration for Cr^{2+} . If pairing energy is ignored, the configuration $d^9 = t_{2g}^6 e_g^3$ would also fit this description, but with pairing energy $\text{CFSE} = (-0.4)(6)\Delta_o + (0.6)(3)\Delta_o + 4P = -0.6 + 4P$. This would be the configuration for Cu^{2+} .

- 10.7 This is $\{[\text{Fe}(\text{H}_2\text{O})_6]^{2+}\}_2\{[\text{Fe}(\text{CN})_6]^{4-}\}$. The cation is high-spin d^6 with $\mu = 4.89$ B.M., and the anion is low-spin d^6 with $\mu = 0$. Thus, $\mu = (2/3)(4.89 \text{ B.M.}) = 3.27$. For 2.67 electrons, $\mu = \sqrt{n(n+2)} = \sqrt{(2.67)(4.67)} = 3.53$, which is close to the expected average of two paramagnetic cations and one diamagnetic anion.
- 10.8 Co^{2+} is d^7 . Tetrahedral would be 3 unpaired electrons with $\mu = 3.87$ B.M. Octahedral high-spin would also be 3 unpaired electrons with $\mu = 3.87$ B.M. Square planar would be 1 unpaired electron with $\mu = 1.73$ B.M. A d^7 low-spin octahedral complex would also be 1 unpaired electron with $\mu = 1.73$ B.M.
- 10.21 a. When compression occurs on the z axis, those orbitals with a z component (d_{xz} , d_{yz} , d_{z^2}) are destabilized, and those with an xy component (d_{xy} , $d_{x^2-y^2}$) are stabilized. The degeneracies of O_h are split on descent to D_{4h} . The effect is the opposite of stretching along z (see below).
- b. Stretching along z destabilizes those orbitals with an xy component (d_{xy} , $d_{x^2-y^2}$) and stabilizes those orbitals with a z component (d_{xz} , d_{yz} , d_{z^2}). The splitting of the octahedral t_{2g} and e_g levels is shown below.



- 10.23 a. The answers below also include the pairing energy (P) contributions, which the authors ignore in their answers (as do many other sources). Each electron in a t_{2g} orbital contributes $-0.4\Delta_o$ to CFSE, and each electron in an e_g orbital contributes $+0.6$ to CFSE.

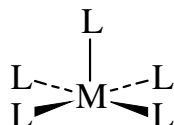
Complex	Config.	n	μ (B.M.)	CFSE
$[\text{Co}(\text{CO})_4]^-$	d^{10}	0	0	0
$[\text{Cr}(\text{CN})_6]^{4-}$	t_{2g}^4	2	2.83	$-1.6\Delta_o + P$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$t_{2g}^3 e_g^2$	5	5.92	0
$[\text{Co}(\text{NO}_2)_6]^{4-}$ *	$t_{2g}^6 e_g^1$	1	1.73	$-1.8\Delta_o + 3P$
$[\text{Co}(\text{NH}_3)_6]^{3+}$	t_{2g}^6	0	0	$-2.4\Delta_o + 3P$
MnO_4^-	d^0	0	0	0
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	$t_{2g}^6 e_g^3$	1	1.73	$-0.6\Delta_o + 4P$

- * The authors' answer book has $[\text{Co}(\text{NO}_2)_6]^{4-}$ as a high-spin d^7 case, but from the position of NO_2^- in the spectrochemical series you would predict this to be low-spin with 1 unpaired electron, as shown here.
- b. Both $[\text{Co}(\text{CO})_4]^-$ and MnO_4^- have no CFSE. The octahedral ions (except $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$) have CFSE values that favor octahedral coordination. The tetrahedral ions are stabilized by π bonding, with CO as an acceptor and O^{2-} as a donor. Fe^{3+} would have no CFSE, either as an octahedral or tetrahedral complex.
- c. Compare the CFSE values (ignoring pairing). Recall that $\Delta_t = (4/9)\Delta_o$.

Ion	Spin State	O_h CFSE	T_d CFSE
Co(II)	d^7 high spin	$-0.8\Delta_o$	$-1.2\Delta_t = (4/9)(-1.2)\Delta_o = -0.53\Delta_o$
Ni(II)	d^8	$-1.2\Delta_o$	$-0.8\Delta_t = (4/9)(-0.8)\Delta_o = -0.36\Delta_o$

As these results show, for Co(II) O_h CFSE is better than T_d CFSE by only $0.27\Delta_o$. For Ni(II), O_h CFSE is better by $0.84\Delta_o$. The smaller octahedral advantage with Co(II) makes it more likely that tetrahedral complexes may be stable, whereas with Ni(II) the octahedral advantage is so great that tetrahedral complexes are less likely.

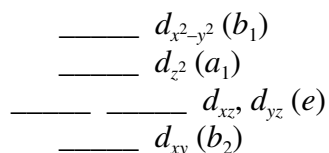
10.26 a. A square pyramid is C_{4v} .



From the direct product transformation properties listed in the C_{4v} character table, we can determine that the five-fold degeneracy among d orbitals in the free ion is lifted as follows:

$$d_{z^2} = a_1 \quad d_{x^2-y^2} = b_1 \quad d_{xy} = b_2 \quad (d_{xz}, d_{yz}) = e$$

The d_{xy} orbital is lowest, because its lobes lie between ligands, which are actually in a plane below. The degenerate (d_{xz}, d_{yz}) orbitals with their lobes oriented between all ligands are next in order. The d_{z^2} orbital is next higher in energy, because it points directly at the axial ligand and its annular part is in the xy plane. The $d_{x^2-y^2}$ orbital is the highest in energy, because its lobes point directly at the four basal ligands. The following CFT splitting scheme results:

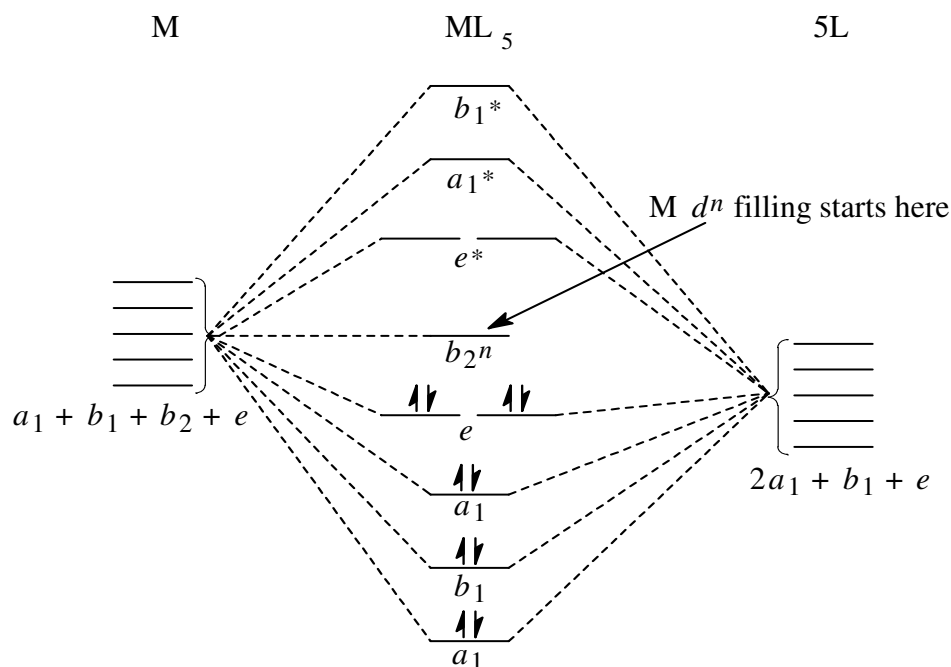


With the preceding CFT results, we can construct an MO scheme, using five σ -SALCs from the ligands to interact with the d orbitals, whose symmetries we have already determined.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
Γ_σ	5	1	1	3	1	Σ	$\Sigma/8$
A_1	5	2	1	6	2	16	2
A_2	5	2	1	-6	-2	0	0
B_1	5	-2	1	6	-2	8	1
B_2	5	-2	1	-6	2	0	0
E	10	0	-2	0	0	8	1

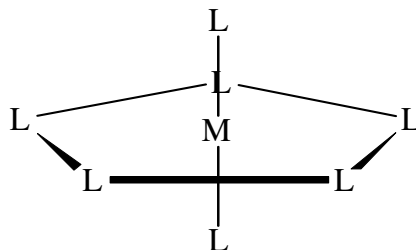
$$\Gamma_\sigma = 2 A_1 + B_1 + E$$

All SALCs have same-symmetry matches with d orbital symmetries and will form bonding and antibonding MOs. There are two A_1 SALCs and only one A_1 AO (d_{z^2}), so we can form only three MOs of this symmetry. For simplicity, the scheme below assumes two bonding and one mixed antibonding MO. We do not have a B_2 symmetry SALC, so the d_{xy} AO on the metal will be nonbonding. Electron pairs from the five ligands will fill the bonding MOs. Electrons from the metal will result in partial filling of the nonbonding b_2 MO, then the antibonding e MO, the antibonding a_1 MO, and finally the antibonding b_1 MO, depending on the metal ion's d^n configuration. There is no simple way of predicting the order of the bonding MOs, so the order shown below is just a reasonable guess. However, as seen with octahedral and tetrahedral cases, the ordering of MOs filled from metal electrons is the same as predicted by CFT considerations.



Note that the pattern of electron filling in MOs beyond the five pairs from the ligands is the same as the order we deduced for the CFT d -orbital splitting (above). In the MO model, however, the lowest of these is a nonbonding level and the others are antibonding levels.

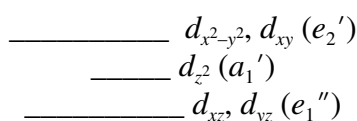
b. A pentagonal bipyramid is D_{5h} .



From the direct product transformation properties listed in the D_{5h} character table, we can determine that the five-fold degeneracy among d orbitals in the free ion is lifted as follows:

$$d_{z^2} = a_1' \quad (d_{x^2-y^2}, d_{xy}) = e_2' \quad (d_{xz}, d_{yz}) = e_1''$$

The lobes of the degenerate d_{xz} and d_{yz} orbitals (e_1'') have no density in the xy plane (a nodal plane) and lie between the two axial positions. This makes them the most favorable (lowest energy) level in a CFT scheme. Conversely, the least favored (highest energy) pair would be the degenerate $d_{x^2-y^2}$ and d_{xy} orbitals, which lie in the xy plane and interact with the five equatorial ligands. The d_{z^2} orbital energy will lie in the middle, because its interaction is primarily with the two axial ligands, with a more minor interaction between the annular part and the five equatorial ligands. The following CFT splitting scheme results:



MOs can be formed between the seven σ -SALCs from the ligands and the d orbitals from the metal, whose symmetries we have already determined. The following Γ_{SALC} can be generated:

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$
Γ_{SALC}	7	2	2	1	5	0	0	3

Systematic reduction gives $\Gamma_{\text{SALC}} = 2A_1' + E_1' + E_2' + A_2''$. [Note that in carrying out the systematic reduction, $2 \cos 72^\circ = 0.6180$ and $2 \cos 144^\circ = -1.6180$, so the arithmetic is much cleaner than one might anticipate.] One of the two A_1' SALCs (with all positive wave function signs) could interact to make bonding and anti-bonding MOs with the ns orbital on the central metal, and the other (with all positive signs in the equatorial positions and negative signs in the two axial positions) will form bonding and antibonding combinations with the d_{z^2} orbital on the metal. The E_1' SALC pair has no match in d orbitals and must be strictly nonbonding, as is the case for the A_2'' SALC. The E_2' pair of SALCs forms bonding and antibonding MOs with the $d_{x^2-y^2}$, d_{xy} degenerate pair of orbitals, which have the same symmetry. The d_{xz} , d_{yz} (e_1'') pair on the metal have no symmetry match with SALCs and must remain nonbonding. As we have seen previously, seven pairs of electrons from the ligands would fill the lowest bonding and nonbonding levels [$2\sigma(a_1')$, $\sigma''(e_1')$, $\sigma(e_2')$, $\sigma''(a_2'')$, not necessarily in that order]. Adding electrons from the metal would begin filling at the e_1'' level, a pair of nonbonding MOs, followed by successive filling of the a_1' and e_2' levels, which are antibonding MOs. Once again, the symmetries, energy order, and electron filling of the MOs above those accounting for ligand electron contributions are the same as predicted by the CFT approach. Only their identities as nonbonding and antibonding MOs are different.