

**Inorganic Chemistry with Doc M.
Fall Semester, 2011
Day 18. Transition Metals Complexes III:
Ligand Field Theory (MO Theory)**

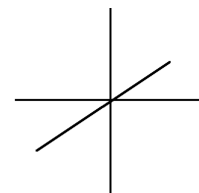
Name(s):	Element:
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Topics:

1. Molecular orbital theory and the octahedron
2. The MO energy diagram and Δ_o
3. The three scenarios
4. Scenario 3: π -back bonding

1. Octahedral transition metal complexes utilize s, p and d-orbitals in their bonding. For a first row transition metal, these are the 3d, 4s and 4p orbitals (the valence orbitals). Here we will create a molecular orbital diagram that could be used for most octahedral first row complexes. (By simply switching the principle quantum numbers, the diagram will work for second and third row complexes as well. You will need the O_h character table. We will use the 10-step approach, as guided below, to create a molecular orbital diagram for $ML_6^{+/-n}$.

Step 1. (3 pts) Sketch the ligand group orbitals needed for s-bonding on a Cartesian coordinate system. Label each circle with a number. Each circle represents the lone pair being donated by the ligand. (Eventually, we will encounter situations where the metal and ligand each donate one to make true covalent bonds, as opposed to coordinate covalent bonds, but the approach is exactly the same.) These six circles will form the SALC sets.



Step 2. Determine the point group symmetry of the set of orbitals drawn and look up its character table. Answer: O_h

Step 3. (4 pts) Determine the *reducible representation*, G. Note: it is not necessary to do each and every symmetry operation in order to go on. If any are ambiguous, skip them for now.

O_h	E	8C ₃	6C ₂	6C ₄	3C ₂	i	6S ₄	8S ₆	3 σ_h	6 σ_d
Γ										

Step 4. (5 pts) Determine the irreducible representations. This can be determined from the following formula, used to determine the number of each irreducible representation:

$$n_{\text{irreducible representation}} = \frac{1}{\text{order}} \sum(\Gamma)(\text{coef})(X)$$

where “order” is the sum of the coefficients from along the top of the character table (1 + 8 + 6 + 6 + 3 + 1 + 6 + 8 + 3 + 6 = 48 for the O_h character table below), Γ is the familiar reducible contribution and X is the character for each irreducible component.

O_h	E	8C ₃	6C ₂	6C ₄	3C ₂	i	6S ₄	8S ₆	3σ _h	6σ _d

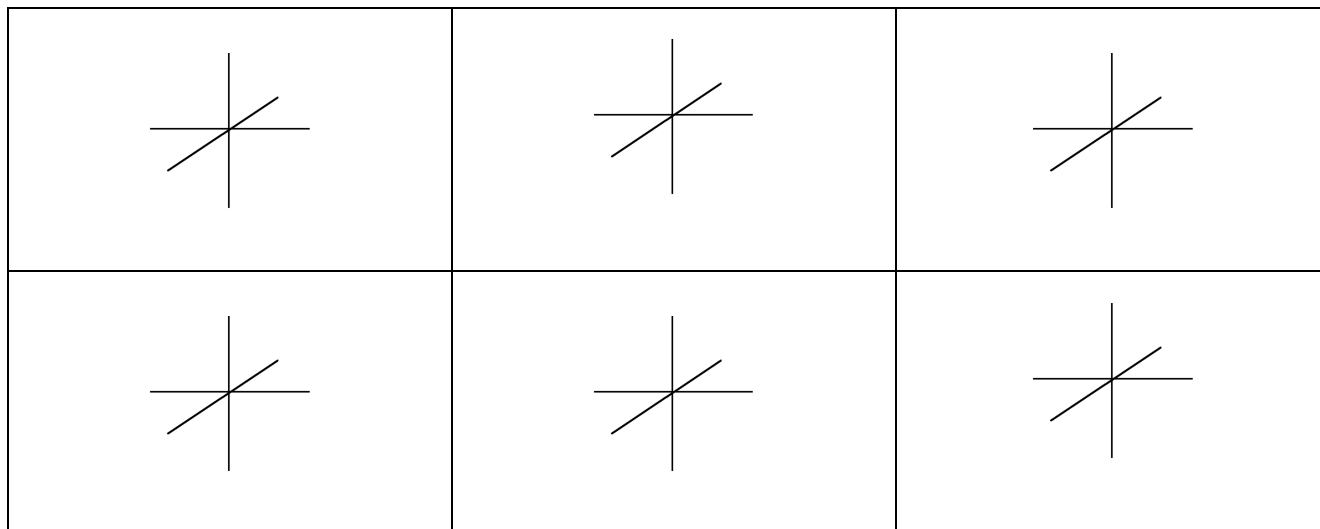
You do not need to use this formula (because of the tricks we’ve learned), but if you did use it because the columns that list how orbitals transform was missing, for example, the calculation would look like this for the first irreducible representation for O_h , namely a_{1g} :

$$n_{a_{1g}} = [(6)(1)(1) + (0)(8)(1) + (0)(6)(1) + (2)(6)(1) + (2)(3)(1) + (0)(1)(1) + (0)(6)(1) + (0)(8)(1) + (4)(3)(1) + (2)(6)(1)]/48 = 1$$

$$n_{a_{2g}} = [(6)(1)(1) + (0)(8)(1) + (0)(6)(-1) + (2)(6)(-1) + (2)(3)(1) + (0)(1)(1) + (0)(6)(-1) + (0)(8)(1) + (4)(3)(1) + (2)(6)(-1)]/48 = 0$$

Continuing on, determine how many e_g irreducible representations are present, and so on. Using the formula or making educated guesses, finish determining what the irreducible components are for the SALC orbitals in an octahedral arrangement.

Step 5. (6 pts) Sketch each of the 6 SALCs (no orbitals from the metal!) with appropriate symmetry labels. Shade in the appropriate lobes of the SALC sets. Complete the table on the next page summarizing how the atomic orbitals are deployed to form the SALCs.



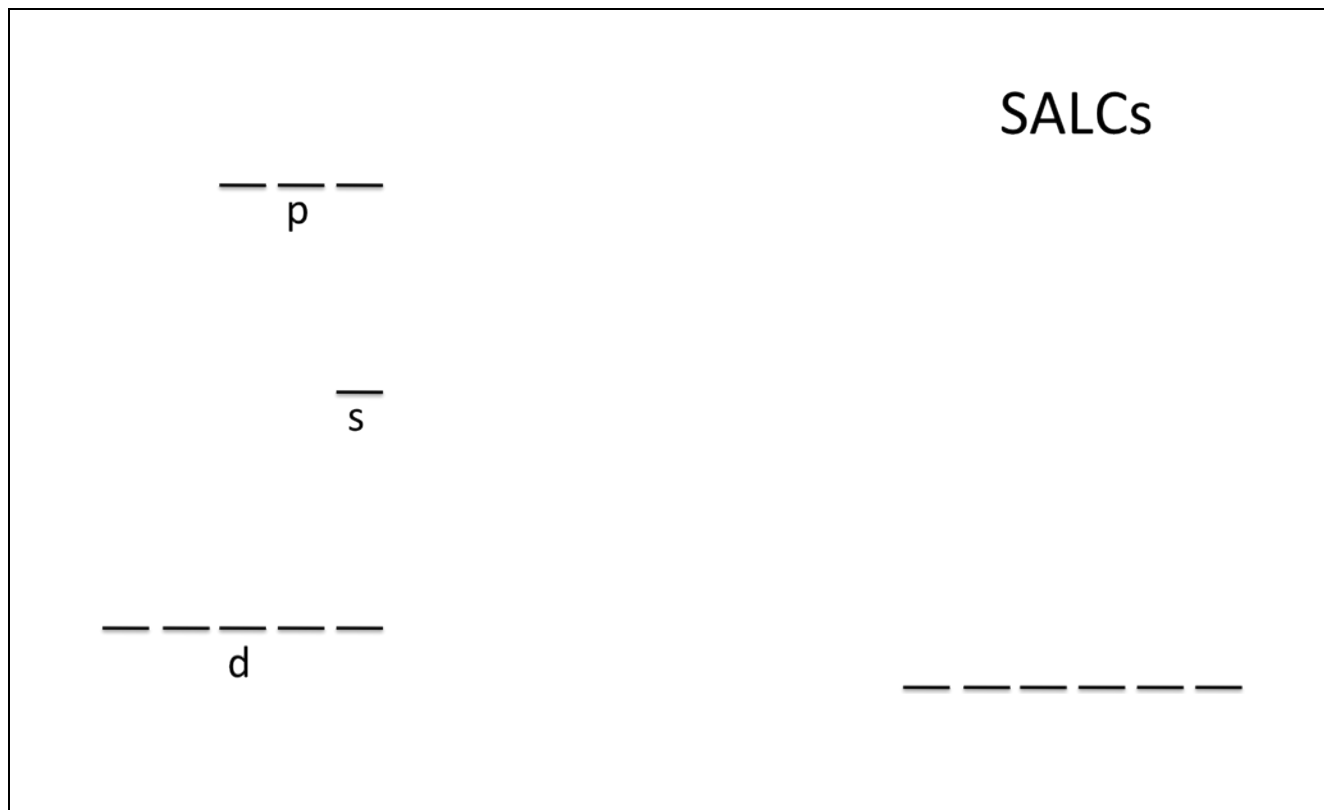
(symmetry)	AO #1	AO #2	AO #3	AO #4	AO #5	AO #6	Total:
SALC ()							=1
SALC ()							=1
SALC ()							=1
SALC ()							=1
SALC ()							=1
SALC ()							=1
Total:	=1	=1	=1	=1	=1	=1	

Step 6. (3 pts) List all the metal atom's valence orbitals (there are 9: the 4s, the three 4ps and the five 3ds) and assign each one a symmetry label. The first one is done for you.

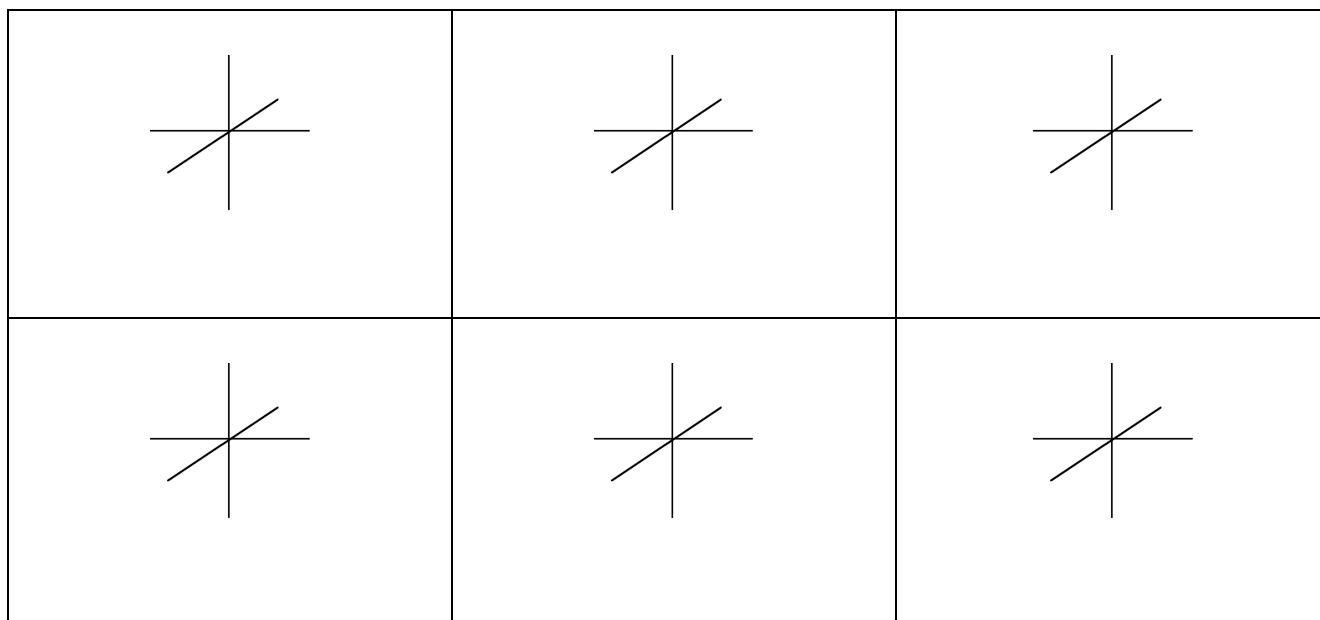
4s (a_{1g})		

Step 7. (8 pts) Create a MO energy diagram. Start with the correct relative energies! For the metal (sketch AOs on the left side of diagram), the 3d orbitals are lowest in energy providing the metal is a cation, which is almost always the case. The 4s orbital is next lowest in energy and the 4p orbitals are the highest. The ligands have electron pairs and are usually quite content with or without a metal — evidence that the energy of the donating electron pair isn't too high. As a "general" rule, you can sketch the energies of the six SALCs somewhere near

in energy to the lowest of the metal's valence orbitals. I will be checking for labels and for how you connect the atomic and SALC orbitals with lines.



Step 8. (6 pts) Sketch molecular orbital line drawings from overlapping SALCs from Step 5 with the symmetry appropriate AOs from Step 6. Just sketch the bonding interactions — skip the antibonding. You can do it here or, if you prefer, add them to the MO energy diagram above.



Step 9. (3 pts) Double check to see if you have conserved orbitals.

B. Using the MO energy diagram. Populate the MO diagram (sketched in Step 7, above) for the complex $\text{Cr}(\text{NH}_3)_6^{+3}$.

i. To do so, you should first determine how many electrons are coming from the Cr^{+3} and how many are coming from the six ammonia ligands. Do your math here:

ii. Write the electron configuration here using the notation $(a_{1g})^2 (e_g)^4$ etc.

iii. Write electron configurations for these complexes:

$\text{Co}(\text{H}_2\text{O})_6^{+2}$

VCl_6^{-4}

$\text{Fe}(\text{py})_6^{+3}$

iv. Draw a box around the HOMO and LUMO orbitals in the energy diagram (page 3) — that represent the crystal field orbital energy splitting pattern. Remember this connection! Label Δ_o .

C. The three scenarios for the MO energy diagram.

Scenario #1. Weak field ligands. When Δ_o is small as is the case with weak field ligands (see the Spectrochemical Series from the previous worksheet.), the e_g orbitals are not out of reach from energy considerations. Since the ligands are “good for” $6 \times 2 = 12$ electrons, and the metal cation can have between zero and ten valence electrons, the MO diagram can have between 12 and 22 electrons populating it. Complete the chart. In the third row, list at least two common examples of metals.

d^0	d^1								
12 e^-	13 e^-								
Sc^{+3}									
Ti^{+4}									

Scenario #2. Strong field ligands. When Δ_o is larger as is the case with _____ field ligands, the e_g orbitals are generally too high in energy (too antibonding). Populating them is not done very often, although examples exist. As usual, the ligands deliver 12 electrons. This limits the metal cation. It can donate between _____ and _____ electrons. Thus, the range in total electrons in the molecular orbital diagram is between _____

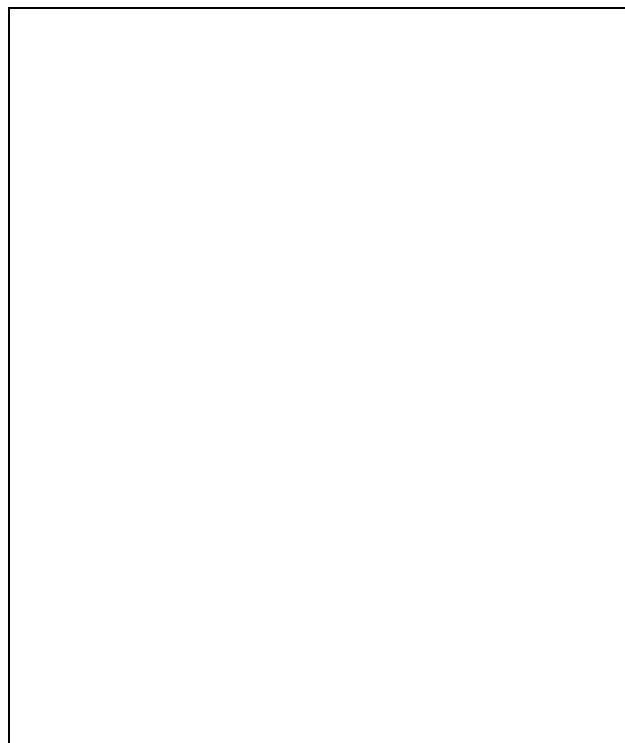
_____ and _____ electrons. Draw a dark vertical line through the table above marking this “cut-off.” Metal ions with more than this number of electrons will have some bonding issues — such as they are easily oxidized.

Scenario 3. π -back bonding. Certain ligands, specifically those with π -bonding, are capable of a new interaction with transition metal d-orbitals. Let’s discover how this works.

Recall the molecular orbital diagram’s we created for diatomics back on Day 6 – 8. Sketch such a diagram for cyanide and populate it.

Label the HOMO and LUMO.

Next, sketch the Lewis dot structure for cyanide and assign formal charges to each atom. From the standpoint of formal charges, does cyanide coordinate to the metal via the carbon or nitrogen atom?



The lone pair on carbon corresponds to an sp -orbital from the standpoint of Lewis dot and valence bond theory (the theory that brought us hybridization.) It also corresponds to the HOMO in terms of molecular orbital theory. In either case, the electron pair is the Lewis base pair that is donated to the Lewis acid metal. The bond is a coordinate-covalent bond (both electrons from the same donor) and this sort of interaction is called **σ -donation** by the ligand. When we drew the molecular orbital structure for the octahedral metal complex above, the SALC set consisted of six of these σ -donation orbitals. In terms of hybridization, for ammonia the SALCs would be the sp^3 orbitals. What hybrid orbitals would be used for σ -bonding from cyanide to the metal?



Oxygen is transported through the blood by an octahedral Fe^{+2} in hemoglobin. What orbital would be used for σ -donation by a coordinated O_2 ligand?



Back to cyanide. The LUMO orbital is the π^* orbital. Sketch it here.

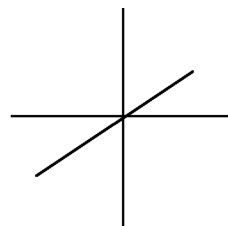


This empty orbital has the right symmetry to overlap with a t_{2g} orbital on the metal. Add this $\pi^* - t_{2g}$ interaction to your π^* sketch in the box above.

Prior to this, the t_{2g} orbitals were non-bonding, but for ligands with π -bonding and thus π^* orbitals, this new interaction is possible. Copy your MO diagram sketched above here, but do not populate it and leave off the t_{2g} non-bonding orbitals.

To start, Let's consider the relative energies of the SALC set of σ -donors and the empty π^* orbitals on the ligands. The answer is simple: they are exactly the same as they were in your MO diagram for cyanide above! Relative to the metal's d-orbitals, the π^* orbitals are at about the same energy level as the empty s- and p-orbitals on the metal.

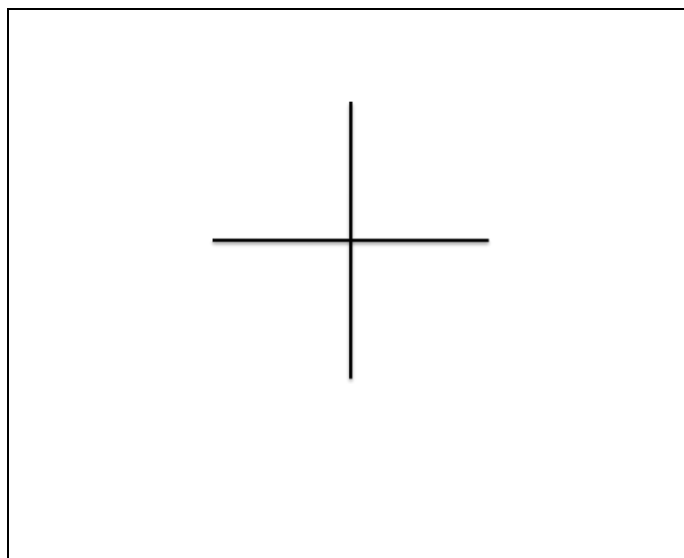
For cyanide and carbon monoxide, there is a triple bond: two p-bonds and two π -antibonds. (For ligands with only a double bond, there is only one p and p^* bond.) Thus, for a SALC set for cyanide, there are $6 \times 2 = 12 \pi^*$ orbitals, Sketch an octahedron, and to the best of your ability, sketch the 12 π^* orbitals that would be used to form the SALC orbitals.



We could go through the usual drill where we perform the octahedral symmetry operations on the 12 π^* orbitals and then use that to produce the irreducible representations, however, it takes a long time and you wouldn't learn anything that you don't already know in terms of procedure. What does come out of this workup, however is a triply degenerate irreducible representation with the same symmetry as the metal's t_{2g} orbitals — and a bunch of other sets that are all non-bonding with s, p and d-orbitals (no additional symmetry-allowed sets.)

The next step, as you recall, was to sketch the MOs and to place them in the energy diagram. Sketch just one of the three equivalent MO drawings (all in one plane) — the result of one of the metals t_{2g} d-orbitals overlapping with four π^* orbitals, all within the same plane. Sketch the MO here.

Is the bonding interaction that you sketched between metal and SALC best described as σ or π in nature?



Suppose the one you sketched featured the d_{yz} orbital and your MO bonding sketch was in the yz -plane (the plane of this paper.) There are two equivalent MO bonding schemes in the d_{xz} and d_{yz} planes. Considering the first one again — the one you sketched, what fraction of each π^* orbital from each ligand participates in each MO? In other words, if we looked at this one t_{2g} SALC set (in the yz plane) and recalling that the contributing atomic orbitals must sum to 1, what fraction of each ligand π^* would you use from each ligand to make the SALC set to overlap with the d_{yz} ?

All together, how many “orbital equivalents” out of the twelve SALCs that we started with are involved in this sort of bonding? The rest of these are non-bonding orbitals.

Finish the MO energy diagram now and populate it for $\text{Fe}(\text{CN})_6^{-4}$.

The π -bonding interaction that we have just explored features electrons from the filled t_{2g} orbitals being distributed out to the ligand's π^* orbitals. Just as we used s-donation to describe the ligand donating electrons to the metal, this π interaction of metal's electrons back to the ligand's π^* orbitals is called **π -back bonding**.

Phosphine and ethane are both capable of π -back bonding. Phosphine uses its empty 3d orbitals. Sketch the interaction between a filled d_{xy} orbital from the metal and phosphine's empty $3d_{xy}$ orbital in an octahedral complex.

The π -back bonding is more important if the ligand has electron withdrawing groups such as fluorine atoms.

Thus, PF_3 is better at p-back bonding than is $\text{P}(\text{CH}_3)_3$. So, comparing CN^- and CO , why do you suppose that CO is much better at π -back bonding than cyanide?

In an upcoming worksheet we will learn that if the metal is in a low oxidation state, π -back bonding is more significant. Why is this so?

Review for ACS Final Exam

- The molecular orbitals for octahedral metal complexes are constructed by a linear combination of ligand group orbitals and which atomic orbitals of the metal?
 - $ns + np_x + np_y + np_z + (n-1)d_{x^2-y^2} + (n-1)d_{z^2}$
 - $nd_{xy} + nd_{xz} + nd_{yz} + nd_{x^2-y^2} + nd_{z^2}$
 - $ns + np_x + np_y + np_z$
 - $ns + np_x + np_y + np_z + (n-1)d_{xy} + (n-1)d_{xz} + (n-1)d_{yz}$
 - $np_x + np_y + np_z + nd_{xy} + nd_{xz} + nd_{yz}$
- Rank the d-orbitals from lowest to highest energy for the trigonal prism.
 - $d_{xy} < d_{xz} < d_{yz} < d_{x^2-y^2} < d_{z^2}$
 - $(d_{xy}, d_{x^2-y^2}) < d_{z^2} < (d_{xz}, d_{yz})$
 - $d_{z^2} < (d_{xz}, d_{xy}) < (d_{yz}, d_{x^2-y^2})$
 - $d_{xy} < d_{x^2-y^2} < d_{z^2} < d_{xz} < d_{yz}$
 - $(d_{xy}, d_{xz}, d_{yz}) < (d_{x^2-y^2}, d_{z^2})$
- What ligand is a p-acceptor and what is the consequence?
 - F^- ; Δ decreases
 - F^- ; Δ increases
 - NH_3 ; Δ decreases
 - NH_3 ; Δ increases
 - CO ; Δ increases
- Which of the following is a characteristic of p-acceptor ligands?
 - Δ decreases
 - Unusually high oxidation states are stabilized
 - The coordination number is always 6
 - The ligands have HOMO orbitals with symmetry allowed overlap with empty d-orbitals.
 - π -acceptor ligands are also σ -donors.

Answers: A, B, E, E