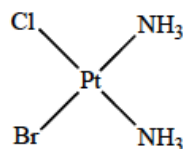


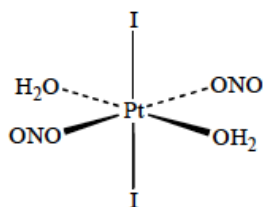
CHEM-457 PS5 Solutions

1.
MF&T #9.9

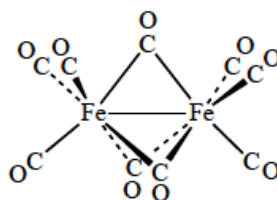
a. *cis*-diamminebromochloroplatinum(II)



b. diaquadiiododinitritopalladium(IV)

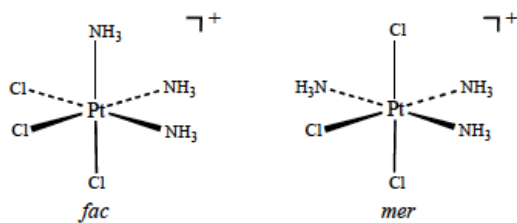


c. tri- μ -carbonylbis(tricarbonyliron(0))

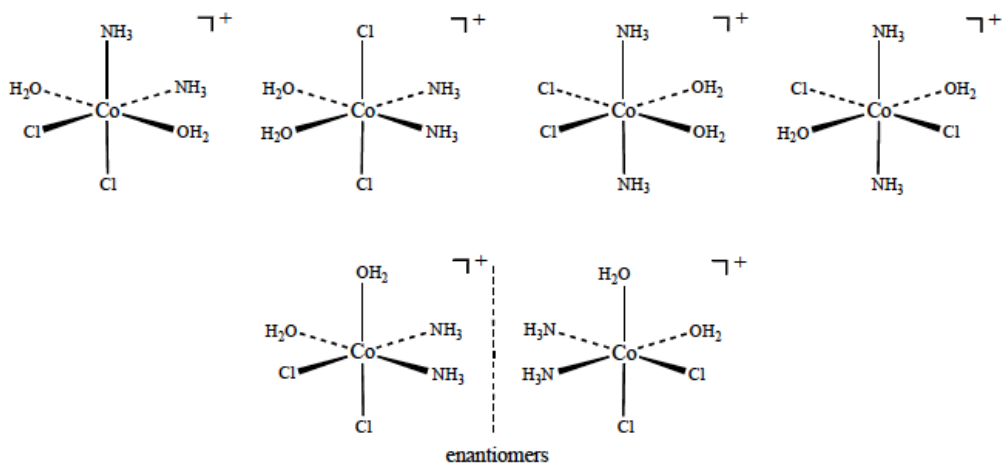


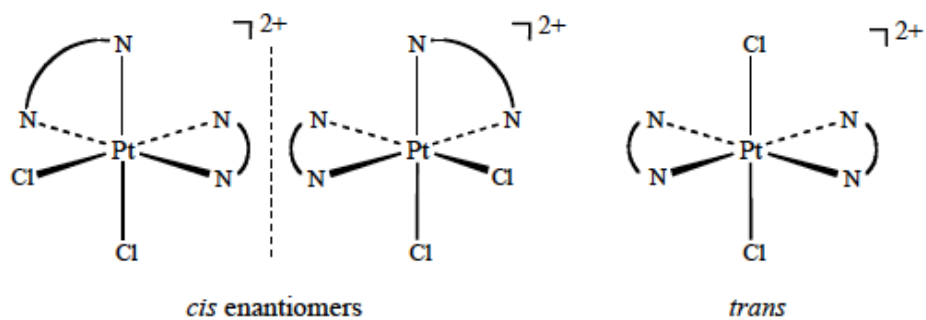
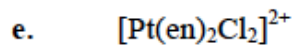
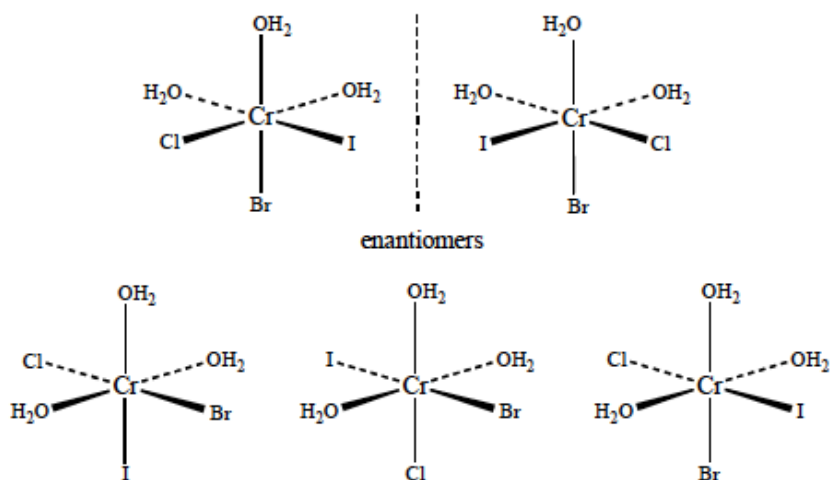
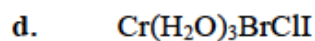
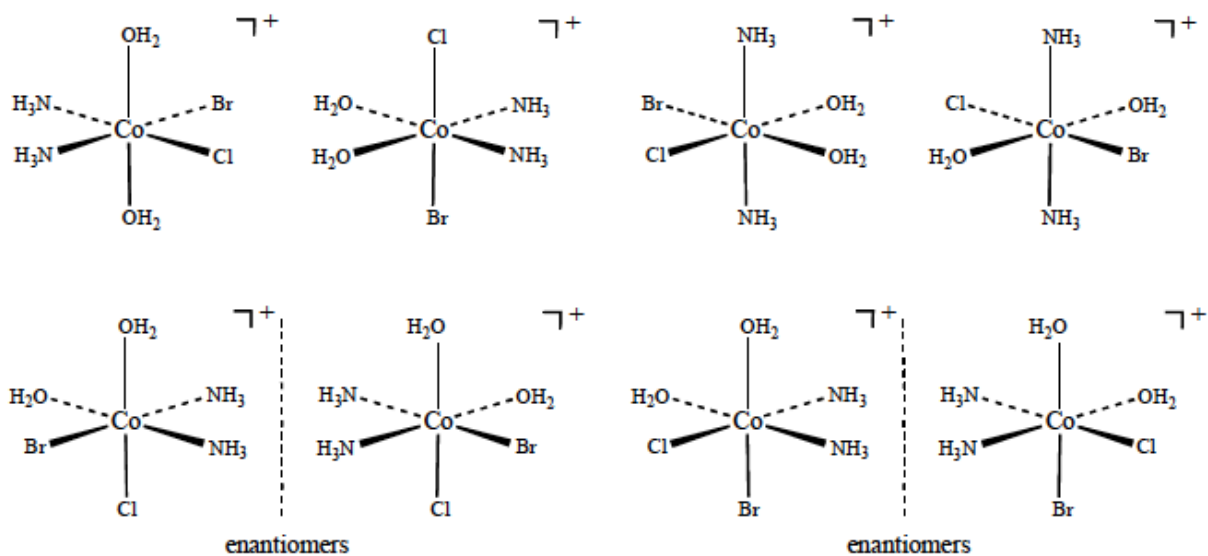
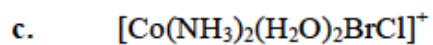
MF&T #9.12

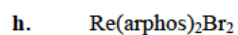
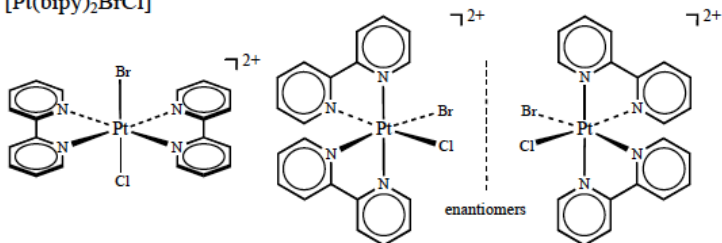
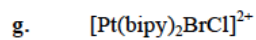
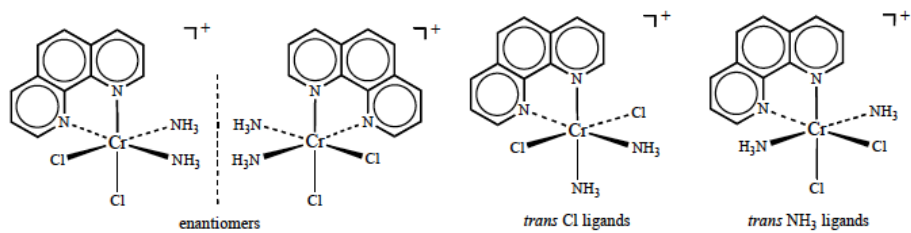
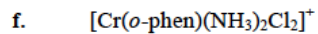
a. $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$



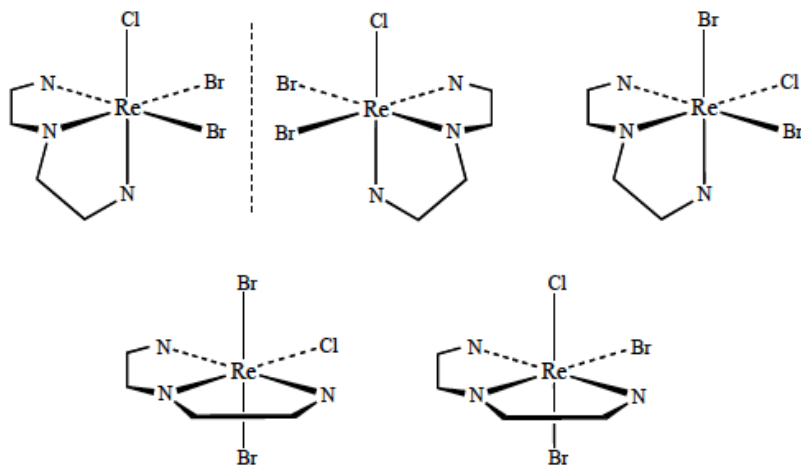
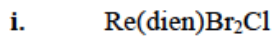
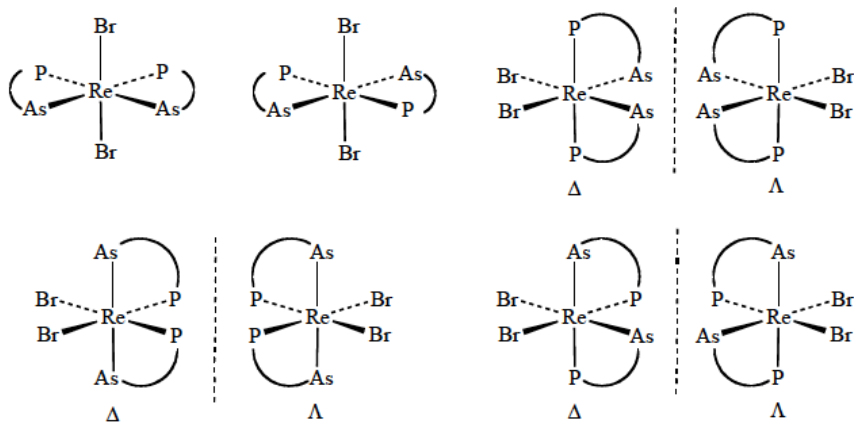
b. $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$







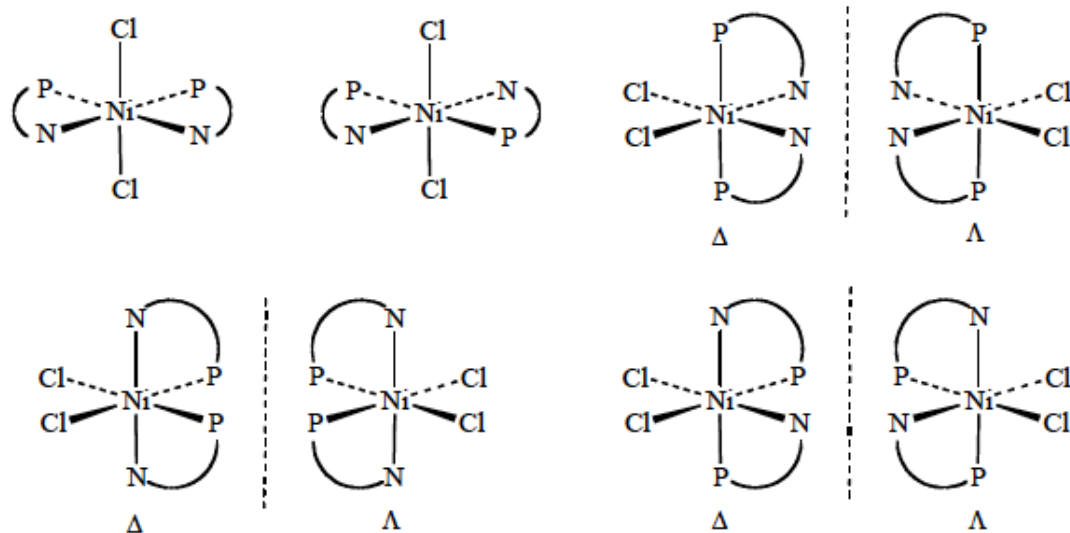
Abbreviating the bidentate ligands As P:



MF&T #9.15

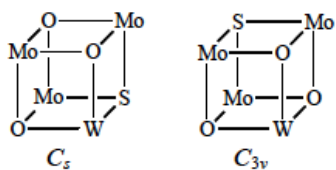
a. The “softer” phosphorus atom bonds preferentially to the soft metal Pd (see Section 6.6.1).

b, c. Abbreviating the bidentate ligands $\overset{\curvearrowright}{\text{N}} \text{P}$:

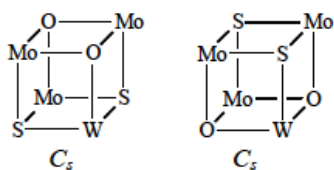


MF&T #9.22

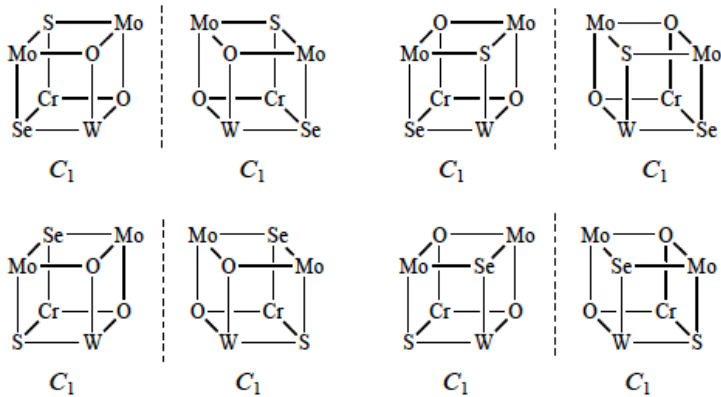
a, b. 1.

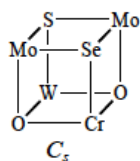
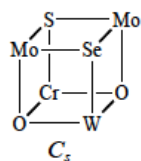


2.



3.





- c. Yes, provided the structure has no symmetry or only C_n axes. Examples are the structures with C_1 symmetry in part a.

MF&T #10.6

- a. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ $n = 4$ $\mu = \sqrt{1(3)} = 1.7 \mu_B$
 $\mu = \sqrt{4(6)} = 4.9 \mu_B$
- b. $[\text{Cr}(\text{CN})_6]^{4-}$ $n = 2$ $\mu = \sqrt{2(4)} = 2.8 \mu_B$
- c. $[\text{FeCl}_4]^-$ $n = 5$ $\mu = \sqrt{5(7)} = 5.9 \mu_B$
- d. $[\text{Fe}(\text{CN})_6]^{3-}$ $n = 1$
- e. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ $n = 2$ $\mu = \sqrt{2(4)} = 2.8 \mu_B$
- f. $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ $n = 1$ $\mu = \sqrt{1(3)} = 1.7 \mu_B$

MF&T #10.18

The ammine Co(III) complex is considerably more stable and is less easily reduced, with the difference primarily in the 3+ species. In addition, the metal in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is surrounded by ammonia molecules, which are more difficult to oxidize than water. This makes transfer of electrons through the ligand more difficult for the ammine complexes.

		LFSE	Δ_o	LFSE	Difference
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	d^6 (1s)	$-2.4\Delta_o$	16,750	-40,200	33,480
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	d^7 (hs)	$-0.8\Delta_o$	8,400	-6,720	
$[\text{Co}(\text{NH}_3)_6]^{3+}$	d^6 (1s)	$-2.4\Delta_o$	24,000	-57,600	49,440
$[\text{Co}(\text{NH}_3)_6]^{2+}$	d^7 (hs)	$-0.8\Delta_o$	10,200	-8,160	

MF&T #10.19

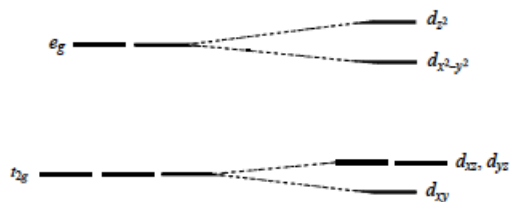
Cl^- has the lowest Δ_o value and fairly good π donor properties that reduce Δ_o . F^- is next, with less π donor ability. Water has very small π donor ability (only one lone pair not involved in σ bonding), and ammonia and en have nearly insignificant π donor nor acceptor ability (no lone pairs, antibonding orbitals with the wrong shapes and energies for π bonding). CN^- has good π acceptor properties, making Δ_o largest for this ligand.

MF&T #10.20

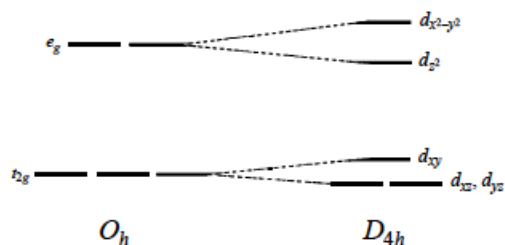
Ammonia is a stronger field ligand than water. It is a stronger Lewis base (σ donor) than water. Water also has a lone pair that can act as a π donor (which leads to a reduction in the ligand field splitting). These factors result in the less electronegative nitrogen on ammonia being a better donor atom than the oxygen atom of water. In the halide ions, all have the same valence electronic structure, so the electronegativity is the determining factor in ligand field strength. Fluoride is also a stronger Brønsted base than the other halides.

MF&T #10.21

- a. Compression moves d_{z^2} up in energy and lowers the ligand energies of positions 1 and 6.



- b. Stretching reverses the changes. In the limit of a square planar structure, d_{z^2} is affected only through interactions with the ring in the xy plane.



MF&T #10.22

Cr^{3+} has three singly occupied t_{2g} orbitals and two empty e_g orbitals. As a result, its complexes exhibit no Jahn-Teller distortion. Mn^{3+} has one electron in the e_g orbitals; its complexes show Jahn-Teller distortion.

MF&T #10.23

a.

	n	μ	LFSE (in Δ_o)
$[\text{Co}(\text{CO})_4]^-$	0	0	0
$[\text{Cr}(\text{CN})_6]^{4-}$	2	2.8	-1.6
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	5	5.9	0
$[\text{Co}(\text{NO}_2)_6]^{4-}$	3	3.9	-0.8
$[\text{Co}(\text{NH}_3)_6]^{3+}$	0	0	-2.4
$[\text{MnO}_4]^-$	0	0	0
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	1	1.7	-0.6

b. The two tetrahedral ions ($[\text{Co}(\text{CO})_4]^-$ and $[\text{MnO}_4]^-$) have zero LFSE (10 or 0 d electrons, respectively) and have ligand equipped to participate in significant π bonding, with CO as an acceptor and O^{2-} as donor. With the exception of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, the others have LFSE values that favor octahedral structures. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has LFSE = 0 for either octahedral or tetrahedral shapes, but water is a slight π donor and Fe(III) is only a moderately good π acceptor. As a result, electrostatics favors six ligands.

c. The difference in the LFSEs can be used to assess the relative stabilities of these geometries for Co(II) and Ni(II):

For Co^{2+} : High-spin octahedral d^7 has LFSE = $-0.8\Delta_o$
 Tetrahedral d^7 has LFSE = $-1.2\Delta_t = -0.53\Delta_o$

For Ni^{2+} : High-spin octahedral d^8 has LFSE = $-1.2\Delta_o$
 Tetrahedral d^8 has LFSE = $-0.6\Delta_t = -0.27\Delta_o$

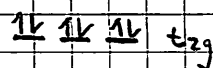
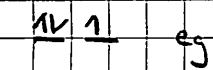
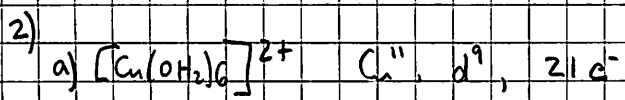
Co(II) (d^7) has only $-0.27\Delta_o$ favoring the octahedral shape, while Ni(II) (d^8) has $-0.93\Delta_o$. Therefore, Co(II) compounds are more likely to be tetrahedral than are Ni(II) compounds.

MF&T #10.29

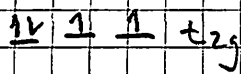
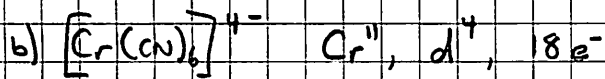
a. When these compounds are oxidized, in the positively charged products there is less π acceptance by the CO ligands than in the neutral compounds. Because CO is acting less as a π acceptor in the products, the products have less donation into their π^* orbitals, which are antibonding with respect to the C–O bonds. This means that the oxidation products have stronger and shorter C–O bonds than the reactants. In the reference cited, the C–O bonds are calculated to be shortened by 0.014 to 0.018 Å in the PH_3 complex and by 0.015 to 0.020 Å in the NH_3 complex.

- b.** In the phosphine compound, oxidation reduces the π acceptance by the phosphine (as it reduces the π acceptance by the carbonyls), and there is weaker Cr–P bonding. Therefore, the Cr–P bond is longer in the product (by 0.094 Å).

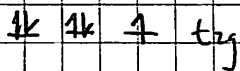
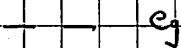
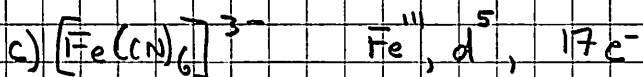
In the ammine compound, the NH_3 is not a π acceptor; it is a σ donor only. Because oxidation increases the positive charge on the metal, there is stronger attraction between the metal and the sigma-donating NH_3 , shortening the Cr–N bond (by 0.050 Å).



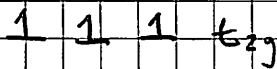
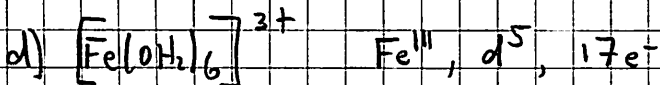
$$\text{LFSE} = 6(0.4 \Delta_o) - 3(0.6 \Delta_o) = 0.6 \Delta_o$$



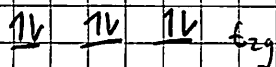
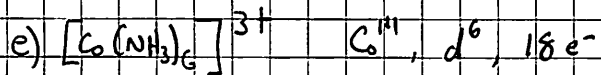
$$\text{LFSE} = 4(0.4) \Delta_o - P = 1.6 \Delta_o - P$$



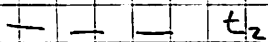
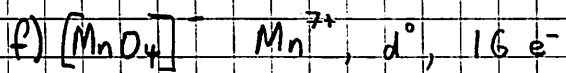
$$\text{LFSE} = 5(0.4 \Delta_o) - 2P = 2.0 \Delta_o - 2P$$



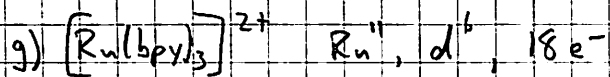
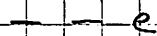
$$\text{LFSE} = 3(0.4 \Delta_o) - 2(0.6 \Delta_o) = 0$$



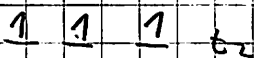
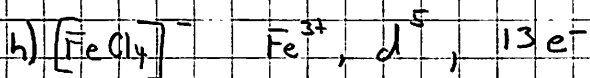
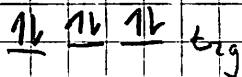
$$\text{LFSE} = 6(0.4 \Delta_o) - 3P = 2.4 \Delta_o - 3P$$



LFSE = 0



LFSE = $6(0.4 \Delta_0) - 3P = 2.4 \Delta_0 - 3P$



LFSE = 0

