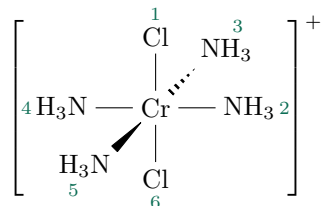


3/5: I) Do the following problems from Chapter 10: 13, 14, 27, 30, 33.

10.13 Use the angular overlap method to calculate the energies of both ligand and metal orbitals for *trans*-[Cr(NH₃)₄Cl₂]⁺, taking into account that ammonia is a stronger σ -donor ligand than chloride, but chloride is a stronger π donor. Use the 1 and 6 positions for the chloride ions.

Answer.



We have from the question that NH₃ is a pure σ donor whereas Cl⁻ is a σ and π donor. Thus, we can add up

$\sigma(\text{NH}_3)$	z^2	$x^2 - y^2$	xy	xz	yz
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
3	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
4	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
5	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
Sum:	1	3	0	0	0

$\sigma(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
6	1	0	0	0	0
Sum:	2	0	0	0	0

$\pi(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
6	0	0	0	1	1
Sum:	0	0	0	2	2

Adding up the sums for each d orbital reveals that the metal orbitals are destabilized by^[1]:

$$\begin{aligned}
 E(d_{z^2}) &= 1e_{\sigma}(\text{NH}_3) + 2e_{\sigma}(\text{Cl}) \\
 E(d_{x^2-y^2}) &= 3e_{\sigma}(\text{NH}_3) \\
 E(d_{xy}) &= 0 \\
 E(d_{xz}) &= 2e_{\pi}(\text{Cl}) \\
 E(d_{yz}) &= 2e_{\pi}(\text{Cl})
 \end{aligned}$$

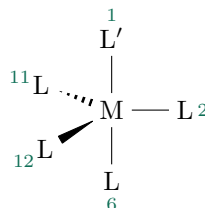
If we now add up the values in the sum rows and divide by the corresponding number of orbitals, we'll get the stabilization energy contribution of each table to its orbitals. For example, the sum in the $\sigma(\text{NH}_3)$ table is 4, and there are 4 NH₃(σ) orbitals; thus, each NH₃ ligand orbital is stabilized, at least in part, by $\frac{4}{4} = 1e_{\sigma}(\text{NH}_3)$. If we continue in this fashion for the other two, we'll eventually end up with four ligand orbitals stabilized by $1e_{\sigma}(\text{NH}_3)$ and two ligand orbitals stabilized by $1e_{\sigma}(\text{Cl}) + 2e_{\pi}(\text{Cl})$. \square

¹Note that by $e_{\sigma}(\text{NH}_3)$, for example, we mean the angular overlap parameter for a σ bond formed in an MA₂B₄-type complex containing amine groups as the B ligands.

10.14 Consider a transition metal complex of formula ML_4L' . Using the angular overlap model and assuming trigonal-bipyramidal geometry, determine the energies of the d orbitals...

a. considering sigma interactions only (assume L and L' are similar in donor ability);

Answer.



Although L' is pictured as axial above, it does not matter where it is because we're considering it to be equivalent to L in σ -donor ability. Having established that, we can add up

σ	z^2	$x^2 - y^2$	xy	xz	yz
1	1	0	0	0	0
2	$\frac{1}{4}$	$\frac{3}{4}$	0	0	0
6	1	0	0	0	0
11	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
12	$\frac{1}{4}$	$\frac{3}{16}$	$\frac{9}{16}$	0	0
Sum:	$\frac{11}{4}$	$\frac{9}{8}$	$\frac{9}{8}$	0	0

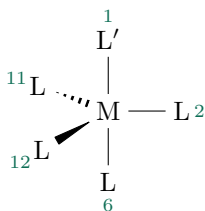
With the sums for each d orbital, we can determine that the metal orbitals are destabilized by^[2]:

$$\begin{aligned}
 E(d_{z^2}) &= \frac{11}{4}e_\sigma \\
 E(d_{x^2-y^2}) &= \frac{9}{8}e_\sigma \\
 E(d_{xy}) &= \frac{9}{8}e_\sigma \\
 E(d_{xz}) &= 0 \\
 E(d_{yz}) &= 0
 \end{aligned}$$

□

b. and considering L' as a π acceptor as well. Consider L' in both
(1) an axial position;

Answer.



The σ contributions to the metal orbitals will be identical to the above. However, we now have to account for the π -acceptor contribution of the axial L' ligand. Since the rows in the table for positions 1 and 6 are equal, arbitrarily consider row 1:

$\pi(L')$	z^2	$x^2 - y^2$	xy	xz	yz
1	0	0	0	1	1
Sum:	0	0	0	1	1

²We don't distinguish between $e_\sigma(L)$ and $e_\sigma(L')$ here because we are told that both ligands have comparable σ -donating abilities.

With the sums for each d orbital, we can determine that three of the metal orbitals are destabilized by:

$$\begin{aligned} E(d_{z^2}) &= \frac{11}{4}e_\sigma \\ E(d_{x^2-y^2}) &= \frac{9}{8}e_\sigma \\ E(d_{xy}) &= \frac{9}{8}e_\sigma \end{aligned}$$

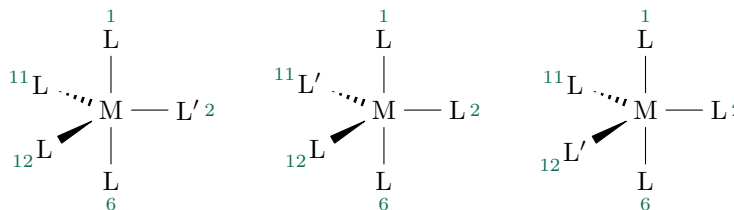
and the other two are stabilized by

$$\begin{aligned} E(d_{xz}) &= e_\pi(L') \\ E(d_{yz}) &= e_\pi(L') \end{aligned}$$

□

(2) and an equatorial position.

Answer.



The σ contributions to the metal orbitals will be identical to the above. However, we now have to account for the π -acceptor contribution of the equatorial L' ligand. Since the rows in the table for positions 2, 11, and 12 vary, we will average the three:

$\pi(L')$	z^2	$x^2 - y^2$	xy	xz	yz
2	0	0	1	1	0
11	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
12	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
Avg:	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

With the average contribution for each d orbital, we can determine that the metal orbitals are destabilized by:

$$\begin{aligned} E(d_{z^2}) &= \frac{11}{4}e_\sigma \\ E(d_{x^2-y^2}) &= \frac{9}{8}e_\sigma - \frac{1}{2}e_\pi(L') \\ E(d_{xy}) &= \frac{9}{8}e_\sigma - \frac{1}{2}e_\pi(L') \\ E(d_{xz}) &= -\frac{1}{2}e_\pi(L') \\ E(d_{yz}) &= -\frac{1}{2}e_\pi(L') \end{aligned}$$

Note that we subtract the $e_\pi(L')$ contributions because for π -acceptor ligands, these contributions are stabilizing. Thus, they reduce the destabilization energy (they don't increase it). □

- c. Based on the preceding answers, would you expect π -acceptor ligands to preferentially occupy axial or equatorial positions in five-coordinate complexes? What other factors should be considered in addition to angular overlap?

Answer. We can construct orbital diagrams for both the axial L' case and the equatorial L' case.

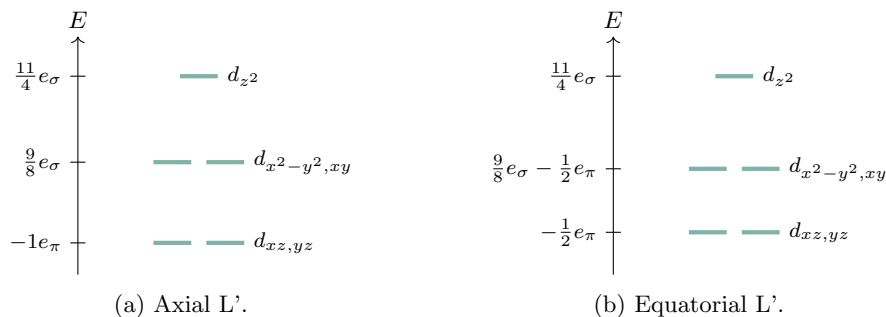


Figure 1: Axial and equatorial ML_4L' d -orbital digrams.

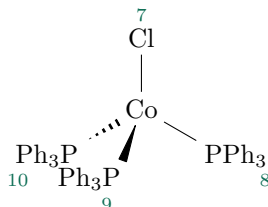
The important factor to be considered in addition to angular overlap is electron configuration — for d^1 to d^7 configurations, the axial complex is preferred; however, for d^8 to d^{10} configurations, neither is preferred. We can determine this by calculating the energies of each configuration from Figure 1. In the following equations, the axial energy is on the left and the equatorial on the right.

$$\begin{aligned}
 -1e_\pi &< -\frac{1}{2}e_\pi & (d^1) \\
 -2e_\pi &< -1e_\pi & (d^2) \\
 -3e_\pi &< -\frac{3}{2}e_\pi & (d^3) \\
 -4e_\pi &< -2e_\pi & (d^4) \\
 \frac{9}{8}e_\sigma - 4e_\pi &< \frac{9}{8}e_\sigma - \frac{5}{2}e_\pi & (d^5) \\
 \frac{9}{4}e_\sigma - 4e_\pi &< \frac{9}{4}e_\sigma - 3e_\pi & (d^6) \\
 \frac{27}{8}e_\sigma - 4e_\pi &< \frac{27}{8}e_\sigma - \frac{7}{2}e_\pi & (d^7) \\
 \frac{9}{2}e_\sigma - 4e_\pi &= \frac{9}{2}e_\sigma - 4e_\pi & (d^8) \\
 \frac{29}{4}e_\sigma - 4e_\pi &= \frac{29}{4}e_\sigma - 4e_\pi & (d^9) \\
 10e_\sigma - 4e_\pi &= 10e_\sigma - 4e_\pi & (d^{10})
 \end{aligned}$$

□

10.27 Cobalt(I) complexes are relatively rare compared to Co(II) and Co(0), but the complexes $\text{CoX}(\text{PPh}_3)_3$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ are known with approximate tetrahedral coordination geometry about the high spin d^8 metal center. The angular overlap model was used to analyze the electronic structure of $\text{CoCl}(\text{PPh}_3)_3$, where three independent molecules (with very similar yet statistically different bond lengths and angles) were observed in the unit cell (Krzystek et al., 2012). Using the angular overlap parameters for molecule 1 in Table 3 of this reference, generate an energy-level diagram for $\text{CoCl}(\text{PPh}_3)_3$. Does the electronic structure predicted by this method surprise you? Explain. On the basis of Table 3, the chloride ligands are better π donors, and the triphenylphosphine ligands better σ donors in $\text{NiCl}_2(\text{PPh}_3)_2$ relative to $\text{CoCl}(\text{PPh}_3)_3$. What is probably the most important factor that causes these differences?

Answer.



From Krzystek et al. (2012), we know that

$$\varepsilon_\sigma(\text{Cl}) = 5430 \text{ cm}^{-1} \quad \varepsilon_\pi(\text{Cl}) = +1380 \text{ cm}^{-1} \quad \varepsilon_\sigma(\text{P}) = 3340 \text{ cm}^{-1} \quad \varepsilon_\pi(\text{P}) = -310 \text{ cm}^{-1}$$

We now add up

$\sigma(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
7	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
Sum:	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

$\sigma(\text{P})$	z^2	$x^2 - y^2$	xy	xz	yz
8	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
9	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
10	0	0	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
Sum:	0	0	1	1	1

$\pi(\text{Cl})$	z^2	$x^2 - y^2$	xy	xz	yz
7	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
Sum:	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$

$\pi(\text{P})$	z^2	$x^2 - y^2$	xy	xz	yz
8	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
9	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
10	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{9}$	$\frac{2}{9}$	$\frac{2}{9}$
Sum:	2	2	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$

Adding up the sums for each d orbital (and accounting for the fact that Cl^- is a π donor whereas PPh_3 is a π acceptor) reveals that the metal orbitals are destabilized by

$$E(d_{z^2}) = \frac{2}{3}\varepsilon_\pi(\text{Cl}) + 2\varepsilon_\pi(\text{P}) = 300 \text{ cm}^{-1}$$

$$E(d_{x^2-y^2}) = \frac{2}{3}\varepsilon_\pi(\text{Cl}) + 2\varepsilon_\pi(\text{P}) = 300 \text{ cm}^{-1}$$

$$E(d_{xy}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{P}) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}e_{\pi}(\text{P}) = 5250 \text{ cm}^{-1}$$

$$E(d_{xz}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{P}) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}e_{\pi}(\text{P}) = 5250 \text{ cm}^{-1}$$

$$E(d_{yz}) = \frac{1}{3}\varepsilon_{\sigma}(\text{Cl}) + 1\varepsilon_{\sigma}(\text{P}) + \frac{2}{9}\varepsilon_{\pi}(\text{Cl}) + \frac{2}{3}e_{\pi}(\text{P}) = 5250 \text{ cm}^{-1}$$

As to the ligand pairs, we must add up the values in the sum rows and divide by the corresponding number of orbitals (note that L_n corresponds to the ligand numbered n), as follows. For the chloride ligand, there is a simple stabilization of the combined σ, π -ligand orbital corresponding to a destabilization of every metal d orbital. For the triphenylphosphine ligands, there is a stabilization of the σ -ligand orbitals corresponding to a destabilization of the metal $d_{xy, xz, yz}$ orbitals, and there is a destabilization of the π -ligand orbitals corresponding to a stabilization of the metal $d_{xy, xz, yz}$ orbitals.

$$E(L_7) = 1\varepsilon_{\sigma}(\text{Cl}) + 2\varepsilon_{\pi}(\text{Cl}) = 8190 \text{ cm}^{-1}$$

$$E(L_{8\sigma}) = 1\varepsilon_{\sigma}(\text{P}) = 3340 \text{ cm}^{-1}$$

$$E(L_{9\sigma}) = 1\varepsilon_{\sigma}(\text{P}) = 3340 \text{ cm}^{-1}$$

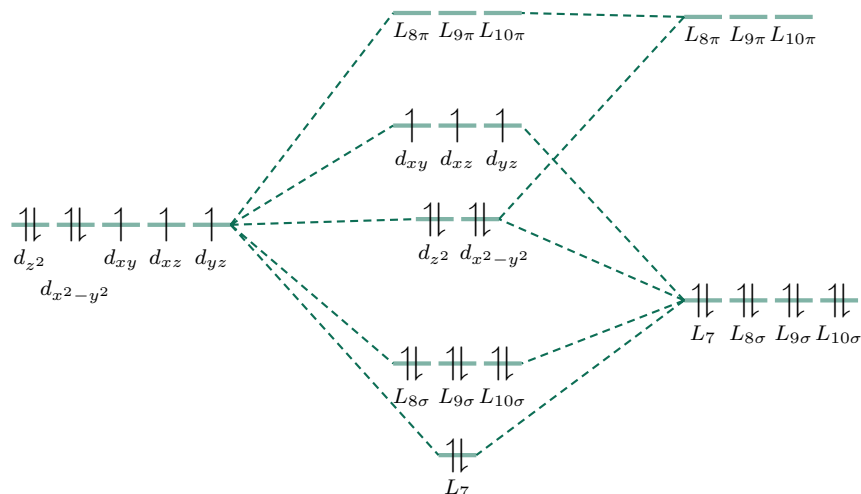
$$E(L_{10\sigma}) = 1\varepsilon_{\sigma}(\text{P}) = 3340 \text{ cm}^{-1}$$

$$E(L_{8\pi}) = \frac{2}{3}\varepsilon_{\pi}(\text{P}) = 207 \text{ cm}^{-1}$$

$$E(L_{9\pi}) = \frac{2}{3}\varepsilon_{\pi}(\text{P}) = 207 \text{ cm}^{-1}$$

$$E(L_{10\pi}) = \frac{2}{3}\varepsilon_{\pi}(\text{P}) = 207 \text{ cm}^{-1}$$

Putting it all together, we have:

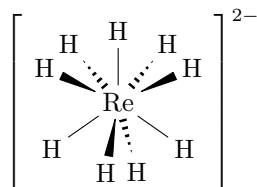


What's surprising: In the angular overlap model, chloride is clearly a stabilizing ligand overall. However, in ligand field theory, π -donor ligands are destabilizing.

Chloride is probably a better π donor in $\text{NiCl}_2(\text{PPh}_3)_2$ than $\text{CoCl}(\text{PPh}_3)_3$ because the increased oxidation state of Ni(II) means it has a greater tendency to attract electrons. On the other hand, triphenylphosphine is likely a better σ donor in $\text{NiCl}_2(\text{PPh}_3)_2$ than $\text{CoCl}(\text{PPh}_3)_3$ because the reduction in steric bulk allows for better head-on overlap with the orbitals of the metal center. \square

- 10.30** One of the more striking hydride complexes is enneahydridorhenate ($[\text{ReH}_9]^{2-}$), which has tricapped trigonal-pyramidal geometry. What is the point group of this ion? Construct a representation using the hydrogen orbitals as a basis. Reduce this to its component irreducible representations, and determine which orbitals of Re are of suitable symmetry to interact with the hydrogen group orbitals.

Answer.



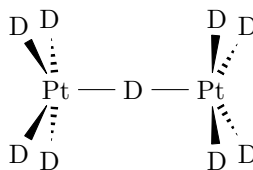
Point group: D_{3h} .

Construct a reducible representation and reduce it to its component irreducible representations:

$$\Gamma_{\text{H}} = (9, 0, 1, 3, 0, 3) = 2A'_1 + 2E' + A''_2 + E''$$

Rhenium's $6s$ orbital interacts with the A'_1 hydrogen group orbitals, its $5p$ orbitals interact with the E' ($p_{x,y}$) and A''_2 (p_z) hydrogen group orbitals, and its $5d$ orbitals interact with the A'_1 (d_{z^2}), E' ($d_{x^2-y^2, xy}$), and E'' ($d_{xz, yz}$) hydrogen group orbitals. \square

10.33 The ion $[\text{Pt}_2\text{D}_9]^{5-}$, shown below, has eclipsed geometry.



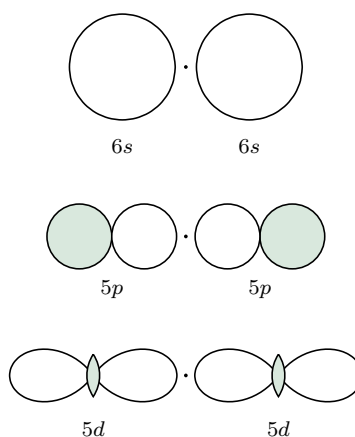
- a. What is point group of this ion?

Answer. D_{4h} . □

- b. Assume that the platinum atoms can potentially use s , p , and d orbitals to interact with the central deuterium. If the z -axis is chosen to be collinear with the principal axis of rotation:

1. Sketch the group orbitals of the platinum atoms that potentially could interact with the central D. Be sure to label all orbitals.

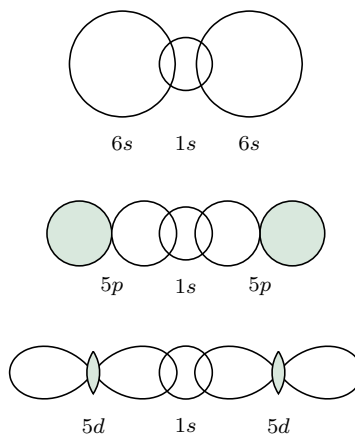
Answer.



□

2. Show how the group orbitals and the central atom would interact.

Answer.



□

3. Which interaction would you expect to be the strongest, and why?

Answer. The d_{z^2} interaction should be the strongest. In the MO energy diagram for MH_6 bonding, the hydrogen orbitals are closest in energy to the metal d orbitals. It stands to reason that it would be similar for square pyramidal bonding and deuterium. □

- II) We derived in class the MO diagram for $\text{Re}_2\text{Cl}_8^{2-}$, a complex with a Re–Re quadruple bond. Two chloride ligands on each Re can be replaced with two (neutral) PMe_2Ph ligands to give the cationic complex $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^{2+}$, which has a similar $\sigma^2\pi^4\delta^2$ electronic configuration and a Re–Re quadruple bond of 2.215 Å in length. The 1-electron and 2-electron reduced species $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^+$ and $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4$ can be prepared, and their structures show Re–Re bond lengths of 2.218 Å and 2.241 Å, respectively. Give the electronic configurations for the 1- and 2-electron reduced species (as given above for the unreduced species), and suggest how this could account for the different Re–Re bond lengths in the three compounds.

Answer. From the MO diagram discussed in lecture, we know that adding more electrons to a complex isoelectronic to $\text{Re}_2\text{Cl}_8^{2-}$ will begin to occupy the δ^* molecular orbitals. Thus, the electronic configuration of $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4^+$ is $\sigma^2\pi^4\delta^2\delta^{*1}$, and the electronic configuration of $\text{Re}_2(\text{PMe}_2\text{Ph})_4\text{Cl}_4$ is $\sigma^2\pi^4\delta^2\delta^{*2}$.

Because the increasingly reduced species have increasing antibonding character, it stands to reason that the bond will weaken and lengthen. \square