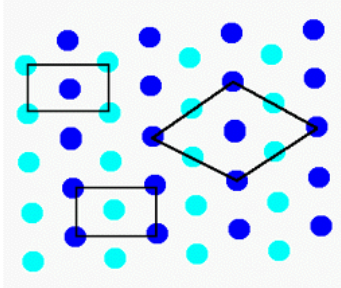


Chapter 2: Molecular structure and bonding

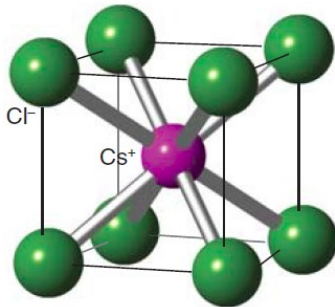
- Draw the MO diagram for O_2 . Draw the shape of each molecular orbital and label the MOs with the appropriate symmetry (σ/π and g/u).
- Give a brief definition of the term 'paramagnetic'. Use your MO diagram of O_2 to explain whether or not the O_2 molecule (in its electronic ground state) is paramagnetic.
- Give the bond order for the following molecules/ions, and rank them by increasing bond length: O_2 , O_2^+ , O_2^- , O_2^{2-} .
- Explain the occurrence of σ -, π - and δ -bonding with d-orbitals. Illustrate your answer with 3 drawings that show how a $d_{x^2-y^2}$ atomic orbital can interact with a second orbital of your choice to form σ -, π - and δ -bonds. (3 pts)

Chapter 4: Structure of simple solids

a. Consider the 2D lattice shown below: which of the three choices indicated represent(s) a proper unit cell for this lattice? Justify your answer.



b. What is the lattice type for the unit cell shown below, and what is the ratio between the cations and anions in the unit cell?



c. Calculate the packing efficiency in the CsCl unit cell (shown under b), assuming that Cs and Cl have identical radii. Show how you arrive at your answer.

Chapter 5: Lewis acids and bases

a. Consider the following reaction: $\text{BF}_3 + \text{Et}_2\text{O} \rightarrow \text{F}_3\text{B-OEt}_2$

Draw (complete) Lewis electron structures for starting materials and product. Identify the Lewis acid and base in this reaction.

b. Describe formation of the B-O bond in the product (see 4a) in terms of a simplified MO diagram.

c. Add the following molecules/ions to the table below, classifying them in the appropriate category (soft/hard, acid/base)

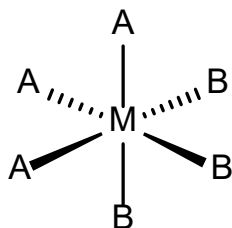
H^+ , H^- , HS^- , Mg^{2+} , PMe_3 , Pt^{2+} , CN^- , Co^{3+}

<i>Hard</i>	<i>Soft</i>
Acids	
Bases	

d. Compounds that contain iron are known to exist in a variety of oxidation states: Fe(0), Fe(II) and Fe(III) are all relatively common. Which of these will bind CO most strongly? Briefly explain your choice by making use of hard/soft preferences.

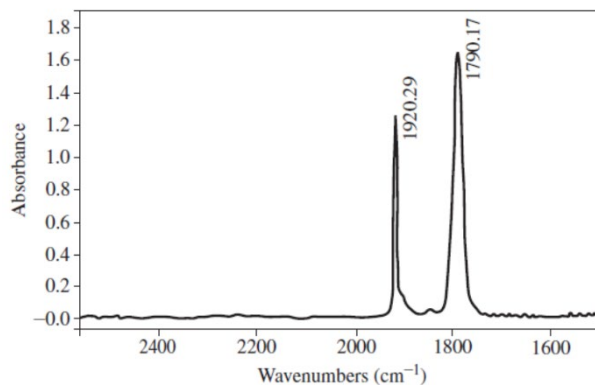
Chapter 3: Symmetry

a. Consider the generic complex MA_3B_3 shown below. The point group of this molecule is C_{3v} ; indicate all rotation axes and mirror planes in the structure. (if you find these difficult to draw in the structure, you may use words to describe what you mean).



b. Draw the structure of the other possible geometric isomer for MA_3B_3 : to which point group does this isomer belong?

c. Reaction of Mo(CO)_6 with PMe_3 leads to a product with the formula $\text{Mo(CO)}_3(\text{PMe}_3)_3$. The IR spectrum for the product shows 2 CO stretching bands. Use a symmetry analysis to demonstrate that this is consistent with the C_{3v} symmetric structure shown in 5a.



d. i) Use the appropriate character table to determine to which symmetry species (irreducible representations) the metal d-orbitals belong in complexes with this structure.

ii) Is the d_{z^2} orbital involved in bonding with the CO ligands? Briefly explain your reasoning.

Chapter 7: Coordination compounds

a. Draw all possible geometric isomers for the following complexes. (4 pts)

i) tris(ethylenediamine)iron(3+) nitrate

ii) diamminetetra(κ N-thiocyanato)chromate(1-)

b. Are any of the complexes in 6a chiral? Draw the enantiomers for the chiral complexes, and identify the plane of symmetry in the ones that are not chiral. (4 pts)

c. The stepwise formation constants for reaction of NH_3 with $[\text{Cu}(\text{OH}_2)_6]^{2+}$ in aqueous solution are $\log K_{f1} = 4.15$, $\log K_{f2} = 3.50$, $\log K_{f3} = 2.89$, $\log K_{f4} = 2.13$, and $\log K_{f5} = -0.52$. Show the chemical equilibria that are associated with these formation constants and suggest a reason why K_{f5} is so different when compared to the others. (3 pts)

Chapter 20: electronic structure of d-metal complexes

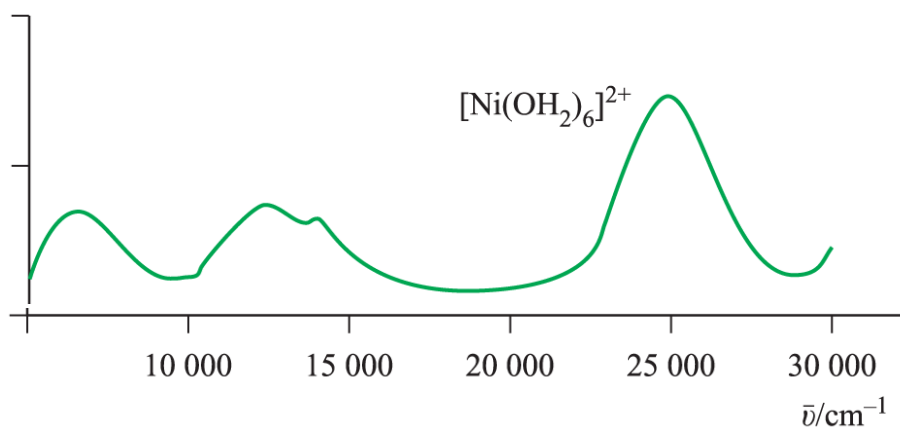
a. The compound $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has a square planar structure. Use d-orbital splitting diagrams to show why this complex has an electronic preference for the square planar coordination environment.

b. Give the ligand-field stabilization energies (LFSE, expressed in terms of Δ and P) for the following complexes. If both high- and low-spin states are possible, give the LFSE for all possibilities, but also indicate which you think will be most stable (explain!).

i) $[\text{Fe}(\text{CN})_6]^{3-}$

ii) $[\text{CoCl}_4]^{2-}$

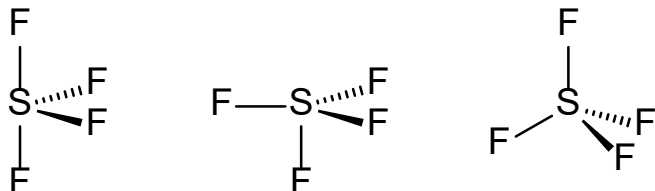
c. The electronic absorption spectrum of $[\text{Ni}(\text{OH}_2)_6]^{2+}$ shows three medium-intensity bands as shown below (please note the x-axis (energy) is in cm^{-1} *not* nm). Assign the electronic transitions (ground state and excited state) that are responsible for each band.



d. Upon addition of potassium cyanide to an aqueous solution of $[\text{Ni}(\text{OH}_2)_6]^{2+}$, the absorption spectrum only shows bands at energies higher than 25,000 cm^{-1} , which suggests that CN^- is a much stronger-field ligand than H_2O . Explain this using Ligand-Field Theory; use an MO diagram in your answer.

Other exercises:

1. Let's consider the molecule SF_4 . Which of the following Lewis structure do you think is most likely? Explain your answer.



2. Define what is meant with the term 'covalent radius'. Illustrate what you mean by taking the molecule SF_4 as an example

3. The S-F single bonds in SF_4 are determined to be ca. 1.6 \AA ($= 1.6 \times 10^{-10} \text{ m}$). Do you expect a S-O single bond to be longer or shorter? And a S-Cl bond? Explain your answer.

4. The bonds in the sulfate anion (SO_4^{2-}) are determined to be ca. 1.5 \AA . Is this in line with your reasoning above? If not, how can you rationalize this?

5. Determine the point group for all three structures given in question 1.

6. How many vibrational degrees of freedom does SF_4 have?

7. The IR spectrum of SF_4 shows a total of 8 absorption bands (to be precise: 7 are observed experimentally because 2 of those are very close in energy and not resolved under most conditions). Use a symmetry analysis to show that this is **not** consistent with a tetrahedral structure.

NB: this is about *all* modes of motion in the molecule

8. The correct structure of SF_4 is the one shown on the left in question 1. Determine the symmetries of the S-F stretching vibrations and indicate how many stretching vibrations are observed in the Raman spectrum.