

Problems Bank for Chapters 9-11
Chemistry 4610/5560, Dr. Mohammad Omary
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Department of Chemistry, University of North Texas

Chapter 9 Material:

(1) Answer the following questions about the complex $\text{Cr}(\text{CO})_2(\text{CN})_2(\text{NH}_3)_2$:

a. Name the complex.

b. Draw all possible geometric isomers and indicate which isomers are chiral (*for chiral isomers, do NOT draw their mirror images; just indicate that they are chiral*).

c. If the infrared spectrum of a compound with the above formula shows two $\nu_{\text{C-O}}$ bands and one $\nu_{\text{C-N}}$ band, identify the actual structure amongst the isomers you have drawn above. Explain.

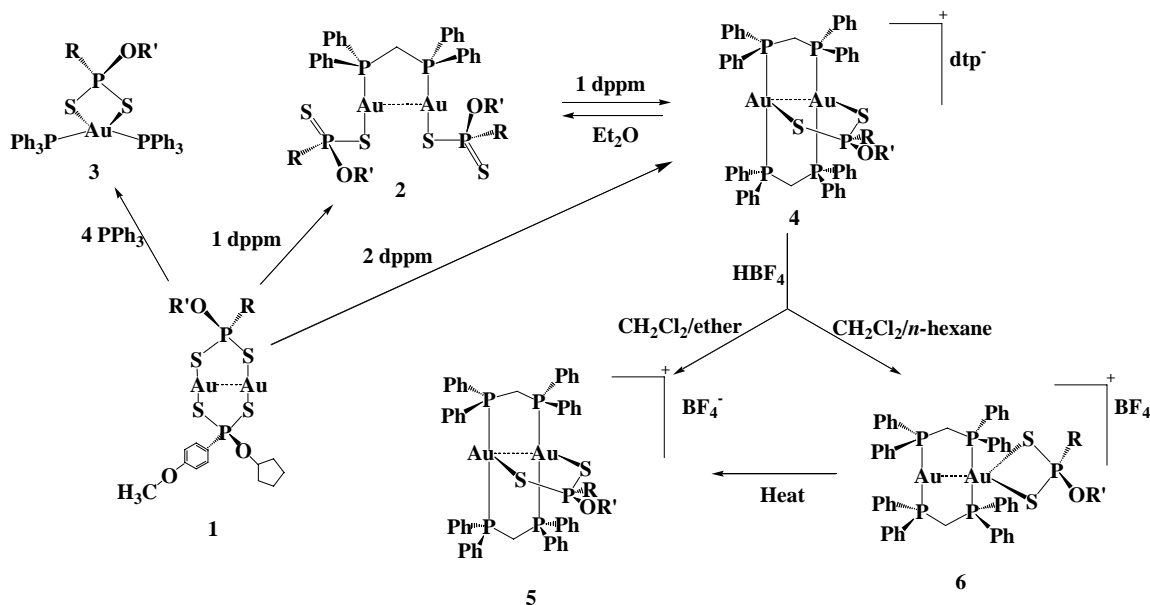
(2) a. Name the compounds $[\text{Re}(\text{CO})_3(\text{en})\text{Br}]$, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$, $[\text{Co}(\text{en})_3]\text{Cl}_2$, and $[\text{Ru}(\text{SCN})_2(\text{bipy})_2](\text{NO}_3)_2$

b. Draw ALL possible stereoisomers for the complex in each compound and indicate which are chiral (*for chiral isomers, do NOT draw their mirror images; just indicate that they are chiral*).

(you may use $\text{N} \text{---} \text{N}$ to represent "en" and "bipy"):

(3) Draw the structure of di- μ -carbonylbis(tricarbonylcobalt)(0).

(4) The same dithiophosphonate (dtp) ligand below exists in different modes in different coordination compound, as seen in the following scheme from a recent paper for Dr. Omary (*Inorg. Chem.* **2003**, *42*, 5311-5319). Determine the mode(s) of the dtp ligand in each of compounds **1-6** in this scheme (i.e., monodentated, bridging bidentate, chelating bidentate, counter ion, etc.).



Compound 1:

Compound 2:

Compound 3:

Compound 4:

Compound 5:

Compound 6:

Chapter 10 Material:

PART I. Multiple-choice:

- Which statement most correctly describes crystal field theory for a d block complex of unspecified geometry?
 - The theory considers covalent interactions between a metal centre and the surrounding ligands.
 - The theory considers electrostatic interactions between a metal ion and the surrounding ligands which are taken to be point charges.
 - The theory rationalizes the non-degeneracy of the metal d orbitals by considering the electrostatic repulsions between point charge ligands and electrons in the metal d orbitals.
 - The theory rationalizes why the metal d orbitals are split into two levels.
- Which of the following correctly places the ligands in their order in the spectrochemical series?
 - $\text{Br}^- < \text{Cl}^- < \text{NH}_3 < \text{H}_2\text{O}$
 - $\text{I}^- < \text{Br}^- < \text{H}_2\text{O} < [\text{OH}]^-$
 - $\text{F}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$
 - $\text{I}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{en}$

3. Which of the following correctly places the metal centers in order of increasing field strength?
- Mn(II) < Fe(III) < Rh(III)
 - Co(III) < Co(II) < Rh(III)
 - Pt(IV) < Pd(II) < Ni(II)
 - Pd(II) < Ni(II) < Pt(IV)
4. Which of the following complex ions is tetrahedral?
- [PdCl₄]²⁻
 - [PtCl₄]²⁻
 - [NiCl₄]²⁻
 - [AuCl₄]²⁻
5. Match up the correct formula and magnetic property. Which pair is correct?
- [Zn(H₂O)₆]²⁺; paramagnetic
 - [Co(NH₃)₆]³⁺; diamagnetic
 - [CoF₆]³⁻; diamagnetic
 - [V(H₂O)₆]²⁺; diamagnetic

PART II. Problems

1. According to the crystal field theory, the five *d* orbitals, which are degenerate in a free ion, become no longer degenerate when a transition metal ion is placed in a ligand field environment. Predict the splitting of *d*-orbitals in both *Oh* and *Td* environments (σ -only scheme when there are only σ -donor ligands).

Free ion

Oh

Td

$\overline{d_{xy}} \quad \overline{d_{xz}} \quad \overline{d_{yz}} \quad \overline{d_{z^2}} \quad \overline{d_{x^2-y^2}}$

2. Predict the splitting of *d*-orbitals in octahedral environments when the ligands are σ -donor/ π -acceptor and σ -donor/ π -donor.

Free ion

Oh (σ -donor/ π -acceptor)

Oh (σ -donor/ π -donor)

$\overline{d_{xy}} \quad \overline{d_{xz}} \quad \overline{d_{yz}} \quad \overline{d_{z^2}} \quad \overline{d_{x^2-y^2}}$

3. Compare the largest crystal field splitting in octahedral (Δ_o) vs. tetrahedral (Δ_t) complexes; and in tetrahedral (Δ_t) vs. square planar (Δ_1) complexes.

4. Use the concepts of crystal field theory to predict the *highest-energy* orbital or group of orbitals among the five d orbitals when a transition metal ion is placed in the following types of ligand field environments (assuming conventional axes definition is used):

a. Square planar:

b. Trigonal bipyramidal:

c. Linear:

d. Trigonal planar:

e. Square pyramidal:

f. T-shape:

5. Predict the correct hybridization for the metal ion in the following complexes, based on the concepts of the valence bond theory.

a. a diamagnetic d^6 octahedral complex.

b. a paramagnetic d^6 octahedral complex.

c. a diamagnetic d^8 square planar complex.

d. a paramagnetic d^5 tetrahedral complex.

e. a linear 2-coordinate d^{10} complex.

6. Sketch the electronic distribution of the d electrons in the crystal field orbitals for the appropriate geometry of each complex and then calculate the spin-only magnetic moment ($\mu_{\text{spin-only}}$) for the complex. If there is a possibility for high-spin or low-spin configuration, explain your selection.

<u>Complex:</u>	<u>crystal-field electronic configuration</u>	<u>$\mu_{\text{spin-only}}$</u>
i. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$		
ii. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$		
iii. $[\text{FeCl}_4]^-$		
iv. $[\text{Fe}(\text{CN})_6]^{3-}$		
v. $[\text{Ni}(\text{SCN})_4]^{2-}$		
vi. $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$		
vii. $[\text{CoF}_6]^{3-}$		
viii. $[\text{IrF}_6]^{3-}$		
ix. $[\text{Co}(\text{en})_3]^{2+}$		
x. $[\text{Rh}(\text{en})_3]^{2+}$		
xi. $[\text{Co}(\text{bpy})_3]^{3+}$		
xii. $[\text{Co}(\text{CO})_4]^-$		

7. Make up a spectrochemical series from the following ligands (i.e., arrange their relative field strength): Cl^- , NH_3 , CO , $-\text{SCN}^-$, $-\text{NCS}^-$, H_2O , en , CN^- .

8. Predict whether the following 4-coordinate complexes are likely to be square planar or tetrahedral:

- $[\text{NiCl}_4]^{2-}$
- $[\text{PtBr}_4]^{2-}$
- $[\text{Ni}(\text{CN})_4]^{2-}$
- $[\text{Ni}(\text{CO})_4]$

Chapter 11 Material:

(1) Fill the following table for **octahedral** complexes. Refer to your class notes and the Tanabe-Sugano diagrams (Figure 11-7).

d^n	Ground state term symbol for free ion	Ground state term symbol for complex	Excited state term symbols for allowed transitions (see note* below)
2			
3			
4 (HS)			
4 (LS)			
5 (HS)			
5 (LS)			
6 (HS)			
6 (LS)			
7 (HS)			
7 (LS)			
8			

* If there is more than one allowed transition, list them in order of increasing energy.

2) Fill the above table but now for **tetrahedral** complexes.

d^n	Ground state term symbol for free ion	Ground state term symbol for complex	Excited state term symbols for allowed transitions (see note* below)
2			
3			
4			
5			
6			
7			
8			

* If there is more than one allowed transition, list them in order of increasing energy.

3) Practice making and filling tables similar to the above tables but instead of generic d^n in the first column use real octahedral and tetrahedral complexes from among those given in Problem 6 above about Chapter 10.