EXAM II
Chemistry 4610/5560, Dr. Mohammad Omary
Inorganic Chemistry, Fall, 2003
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(1) a) Construct molecular orbital schemes to describe the bonding in the following diatomic species. Fill the electrons in the appropriate molecular orbitals and label the HOMO and LUMO.
O_2 NaCl NO^+ $[Ni^{2+}]_2$

b) For each of the molecules in part a, determine the bond order and spin multiplicity for the molecule in the following forms:
(i) As written. (ii) Upon 1-e oxidation.
(iii) Upon 1-e reduction. (iv) Upon photoexcitation while preserving the spin state.

Molecule (form)	O_2 (i)	(ii)	(iii)	(iv)	NaCl (i)	(ii)	(iii)	(iv)	NO^+ (i)	(ii)	(iii)	(iv)	$[Ni^{2+}]_2$ (i)	(ii)	(iii)	(iv)
bond order																
spin multiplicity																

(2) Construct a reasonable molecular orbital scheme to describe the σ-bonding scheme in the polyatomic ion $[BF_4]^-$. Fill the electrons in the appropriate molecular orbitals and label the HOMO and LUMO.

(3) Determine the relative solubility of $PbCl_2$, $PbBr_2$, and PbI_2. Explain your answer.

(4) Aqueous solutions of the following oxides lead to the formation of hydroxide species (M-O-H). The resulting B_2O_3 solutions are acidic, Sc_2O_3 solutions are basic, while Al_2O_3 solutions are amphoteric (i.e., have both acidic and basic properties). Explain.

(5) Naphthalene solutions emits UV light. When silver ions are added (e.g., $AgClO_4$), a white precipitate formed that has a green emission. NMR and IR data suggest that the naphthalene units are intact with no loss of aromaticity or hydrogen or carbon atoms. Explain the kind of interaction might have taken place between naphthalene and silver perchlorate.

(6) Answer the following questions about the complex $Cr(CO)_2(CN)_2(NH_3)_2$:

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 $\nu_{C\text{-}O}$ bands and one $\nu_{C\text{-}N}$ band, identify the actual structure amongst the isomers you have drawn above. Explain.

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

(8) 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.

a. Predict the splitting of *d*-orbitals in both tetrahedral and octahedral environments.

Free ion *Octahedral* *Tetrahedral*

$\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$ $\overline{d_{z2}}$ $\overline{d_{x2-y2}}$

b. 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.

c. 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:

(9) Answer the following questions for all complexes below:

a. Name each complex.
b. Sketch the electronic distribution of the d electrons in the crystal field orbitals for the appropriate geometry of each.
c. Calculate the spin multiplicity for each.
d. Calculate the spin-only magnetic moment for each.

$[Cr(H_2O)_6]^{2+}$

a.

b.

c.

d.

$[Cr(H_2O)_6]^{3+}$

a.

b.

c.

d.

$[FeCl_4]^-$

a.

b.

c.

d.

$[Co(CO)_4]^-$

a.

b.

c.

d.

(10) Predict whether the following 4-coordinate complexes are likely to be square planar or octahedral:

a. $[NiCl_4]^{2-}$
b. $[PtBr_4]^{2-}$
c. $[Ni(CN)_4]^{2-}$
d. $[Ni(CO)_4]$

-GOOD LUCK-