Chem 450 Exam 1. In-Class Portion

Name _____ Key _____
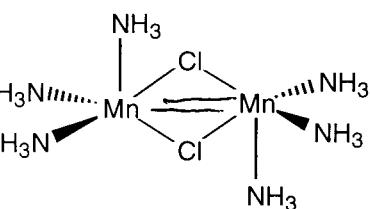
(1)(15 points) List all of the symmetry elements and give the point group for the following molecules

(a)

E, C_3, σ_h

C_{3h}

(b)   (this object is planar)

$E, 2\sigma_v, C_2,$

C_{2v}
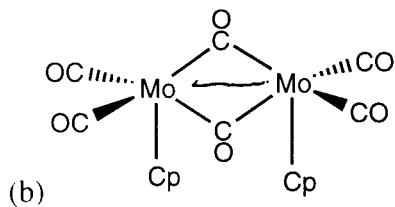
(8)(30 points) How many metal-metal bonds do each of the following molecules have?

(a)
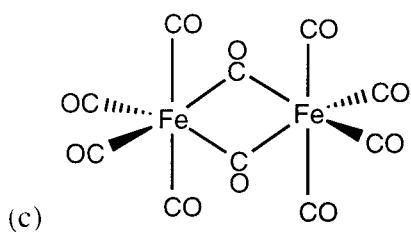
$2 Mn \quad 14 e^-$
$2 Cl \quad 6 e^- \leftarrow bridge$
$6 NH_3 + 12 e^-$
_____
$32 e^-$

need
18
$\dfrac{2}{3} 6 e^-$
$\therefore 2 M-M \; bonds$

(b)
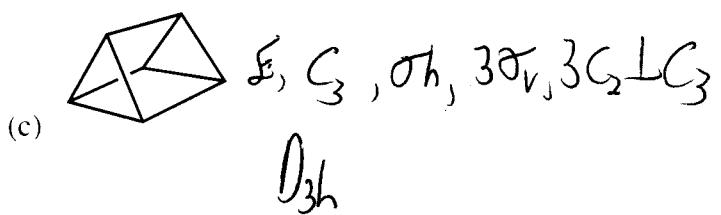
$2 Mo \quad 12 e^-$
$2 Cp \quad 10 e^-$
$6 CO \quad 12 e^-$
_____
$34 e^-$

$\therefore 2 e^- \; needed$
$1 M-M \; bond$

(c)
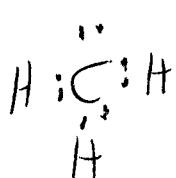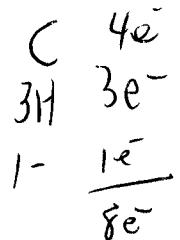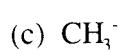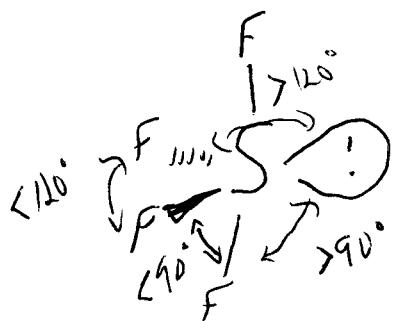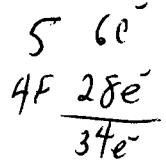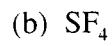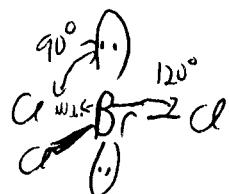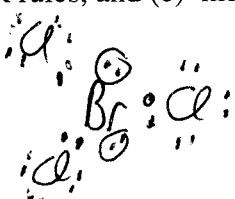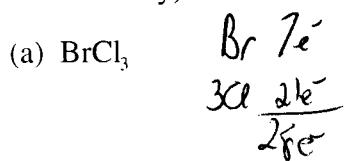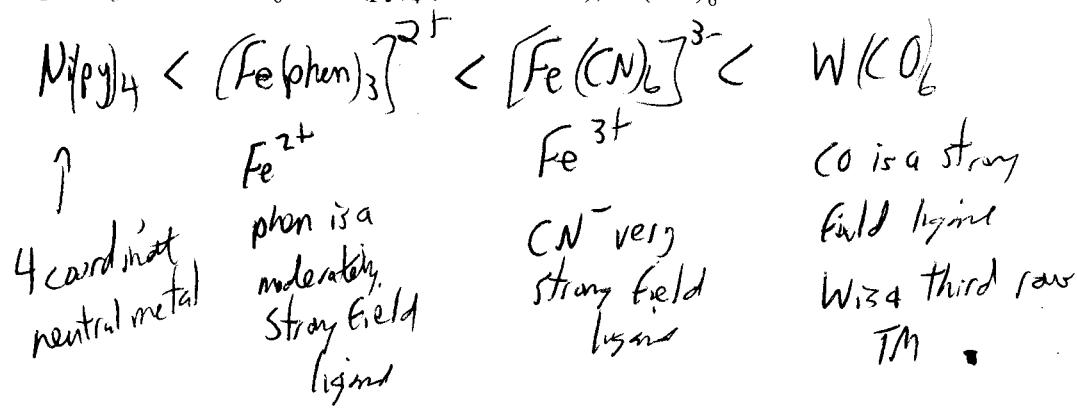
$2 Fe \quad 16 e^-$
$10 CO \quad 20 e^-$
_____
$36 e^-$

No $M-M \; bonds$

(c) $E, C_3, \sigma_h, 3\sigma_v, 3C_2 \perp C_3$

D_{3h}

(2)(15 points) For the following molecules (a) draw the correct Lewis Dot Structure, (b) draw the proper structure following VSEPR rules, and (c) indicate the bond angles (ideal or deviations from ideality).

(a) $BrCl_3$

$Br \; 7e^-$
$3Cl \; \underline{21e^-}$
$\overline{28e^-}$

$90°$ ... $120°$
$Cl \cdots Br - Cl$
Cl

(b) SF_4

$S \; 6e^-$
$4F \; \underline{28e^-}$
$\overline{34e^-}$

F
$> 120°$
$< 120°$
$< 90°$
$> 90°$
F

(c) CH_3^-

$C \; 4e^-$
$3H \; 3e^-$
$1^- \; \underline{1e^-}$
$\overline{8e^-}$

$H : C : H$
H

$> 105°$
$H \cdots C \nearrow H$
H
$< 105°$
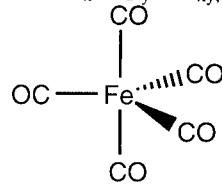
(3)(20 points) Put the following in order of increasing $10 D_q$ and explain your reasoning.
$[Fe(phen)_3]^{2+}$, $[Fe(CN)_6]^{3-}$, $Ni(py)_4$ (Tetrahedral), $W(CO)_6$

$$Ni(py)_4 < (Fe(phen)_3)^{2+} < [Fe(CN)_6]^{3-} < W(CO)_6$$

↑

Fe^{2+} Fe^{3+} CO is a strong
                                        field ligand

4 coord inate   phen is a CN^- very   With a third row
neutral metal   moderately   strong field   TM
                 strong field   ligand
   ligand

(4)(15 points) Using the character tables provided, list the irreducible representations of the following orbitals on the central atom of the molecule below. List the point group.
$4s$, $4p_x$, $4p_y$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$
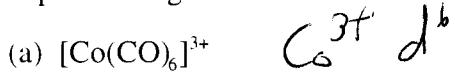
```
        CO
        |
OC —— Fe....ιιιιCO
        |  ◥CO
        CO
```

$E,\ C_3\ ,\ 3C_2\ ,\ \sigma_h,\ 3\sigma_V$

D_{3h}
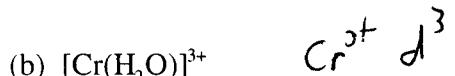
(5) (10 points) Determine the crystal field stabilization energy (in terms of Dq and SPE) and expected magnetic moments for the following compounds.

(a) $[Co(CO)_6]^{3+}$ $\quad Co^{3+} \; d^6$

$\sim \; - \; e_g \quad CFSE = 6(4Dq) + 3SPE$

$\text{-}\!\!\!\uparrow\!\downarrow \; \uparrow\!\downarrow \; \uparrow\!\downarrow \; t_{2g} \qquad = 24Dq - 3SPE$

$\mu_\beta = 0$

(b) $[Cr(H_2O)]^{3+}$ $\quad Cr^{3+} \; d^3$

$- \; - \; e_g \qquad CFSE = 12Dq$

$\uparrow \; \uparrow \; \uparrow \; t_{2g} \qquad \mu_\beta = \sqrt{3(3+2)} = \sqrt{15}$

(c) $[Cu(H_2O)_6]^{2+}$ $\quad Cu^{2+} \; d^9$

$\uparrow\!\downarrow \; \uparrow \; e_g$
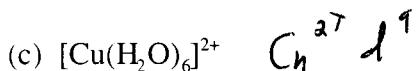
$\uparrow\!\downarrow \; \uparrow\!\downarrow \; \uparrow\!\downarrow \; t_{2g} \qquad CFSE = 6(4Dq) - 3(6Dq) + 4SPE$

$\boxed{= 6Dq - 4SPE}$
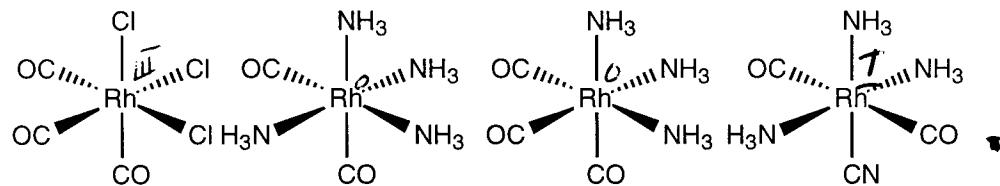
$\mu_\beta = \sqrt{1(1+2)} = \sqrt{3}$

Chem 450 Exam 1. Take-Home Portion
Name_____Key_____
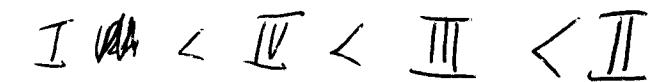
You may use your notes and your textbook for this portion of the exam, but you may not discuss it with anyone but the instructor.
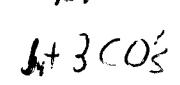
(6)(30 points) Place the following in order of increasing CO bond length. Then place them in order of increasing M-C distance. Explain your orderings.

I   II   ,   III   ,   IV

C O bond length

$\longrightarrow$)

$$\underline{I} \; \text{(M)} < \underline{IV} < \underline{III} < \underline{II}$$

Rh^{III}

$2CO$

$1CN$

Rh^{I}

Rh^0

$Rh + 3CO$

$2CO$

$4NH_3$ Rh^0, more
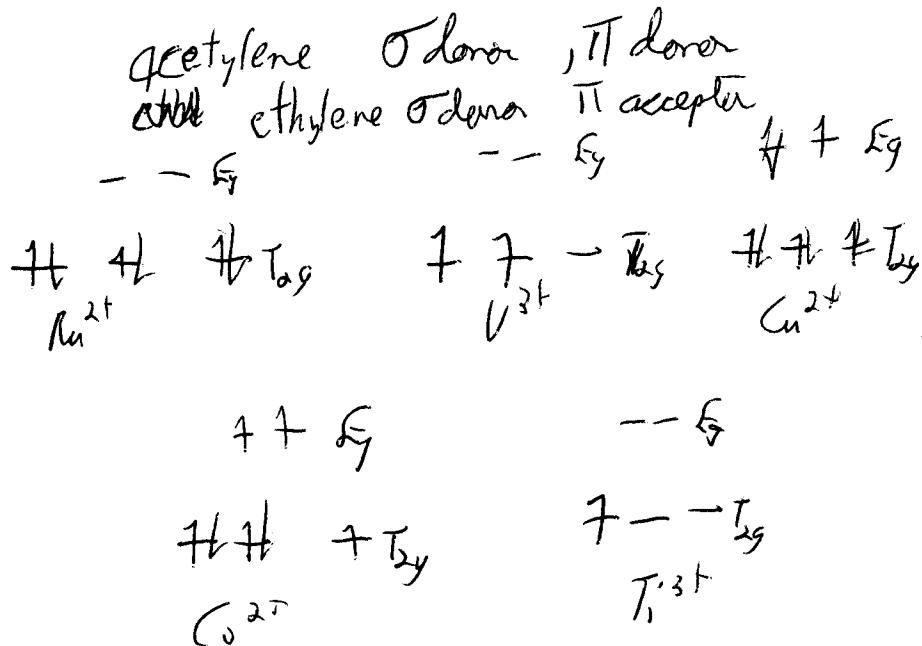
e^- density

$\longleftarrow$

M-C distance

Weaker C≡O bond because more π donation from Rh. More π donation from Rh results in a stronger M-C bond.

(7)(20 points) Place the metals in order of increasing bond strength with acetylene and then in order of increasing bond strength with ethylene. Explain the reasoning behind your orderings. Ru^{2+}, V^{3+}, Cu^{2+}, Co^{2+}, Ti^{3+}

acetylene σ donor , π donor

and ethylene σ donor π acceptor

$$-\ -\ e_g \qquad\qquad -\ -\ e_g \qquad \uparrow\uparrow\ \uparrow\ e_g$$

$$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ t_{2g} \qquad \uparrow\ \uparrow\ -\ t_{2g} \qquad \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ t_{2g}$$
$$Ru^{2+} \qquad\qquad V^{3+} \qquad\qquad Cu^{2+}$$

$$\uparrow\ \uparrow\ e_g \qquad\qquad -\ -\ e_g$$

$$\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ t_{2g} \qquad \uparrow\ -\ -\ t_{2g}$$
$$Co^{2+} \qquad\qquad Ti^{3+}$$

acetylene wants to see no t_{2g} or e_g e's.

$$Cu^{2+} < Co^{2+} < Ru^{2+} < V^{3+} < Ti^{3+}$$

ethylene wants t_{2g} electrons, not e_g electrons

$$Ti^{3+} < V^{3+} < Co^{2+} < Cu^{2+} < Ru^{2+}$$
$$\uparrow$$
$$no\ e_g\ electrons$$