1. Assign each molecule to the proper point group:
   (a) IF$_7$ 
   (b) XeO$_2$F$_2$
   (c) TeCl$_4$
   (d) SF$_4$

2. Under what circumstances, with regard to relative sizes of ions and degree of nonpolar character, are Frenkel and Schottky defects likely?

3. SALC’s can be used to explain bonding situations in systems. Which of the following LCAO’s will result in $\sigma$, $\sigma^*$, $\pi$, or $\pi^*$ bonds in the alignments presented?

   [Diagram with molecular orbitals]

4. Account for the fact that fac-[Mo(PF$_3$)$_3$(CO)$_3$] exhibits C-O stretching frequencies of 2040 and 1991 cm$^{-1}$, whereas fac-[Mo(PMe$_3$)$_3$(CO)$_3$] the corresponding frequencies are found at 1945 and 1851 cm$^{-1}$.

5. How would you design a synthesis of the complex trans-[PtCl$_2$(en)(tu)], {the trans descriptor refers to the fact a pair of identical ligands, Cl in this case, is mutually trans}, given that the trans effect order is tu > Cl > NH$_3$?  [tu=(H$_2$N)$_2$CS]
6. Consider the two complexes $\text{MeTiCl}_3$ and $(\text{CO})_5\text{W(thf)}$. Predict the order of reactivity in each case toward the following sets of ligands: $\text{NMe}_3$, $\text{PMe}_3$, $\text{CO}$.

7. Utilizing standard emf data, calculate $K_p$ for the following reaction which occurs in basic solution.

$$\text{PbO (s)} \rightarrow \text{Pb (s)} + \text{O}_2 (g)$$

Given:

- $\text{PbO}_2 \xrightarrow{0.29^\circ} \text{PbO} \xrightarrow{-0.58^\circ} \text{Pb}$
- $\text{O}_2 \xrightarrow{-0.065^\circ} \text{HO}_2^- \xrightarrow{0.867^\circ} \text{OH}^-$
- $\text{O}_2 \xrightarrow{0.401^\circ} \text{OH}^-$

8. Give the electron counts, formal oxidation states, and $d^*$ configurations of the following:

<table>
<thead>
<tr>
<th>Electron count</th>
<th>Formal ox. st. (metal)</th>
<th>$d^*$ config.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pt(NH}_3)_4]^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[(\text{R}_3\text{P})_3\text{Ru(µ-Cl)}_3\text{Ru(PR}_3)_3]^{-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(\eta^2\text{-C}_5\text{H}_5)_2\text{TiCl}_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CpIrMe}_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{TaMe}_5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

9. Acetone can bind in an $\eta^2$ (via C and O) and an $\eta^1$ fashion (via O). Would you expect the electron count to be the same or different in the two forms? What kind of metal fragments would you expect to most likely bind acetone as (a) an $\eta^1$ and (b) an $\eta^2$ ligand? Would either binding mode be expected to enhance the tendency of the carbonyl carbon to undergo nucleophilic attack?
10. Me₂CHMgBr reacts with IrCl₂ to give IrHL₂. How can this be explained, and what is the organic product formed?

11. Ni(CO)₄ and Co((lin-NO)(CO))₃ are both tetrahedral. Why does the Ni compound undergo dissociative substitution and the Co compound undergo associative substitution? [lin=linear]

12. Given a complex M(CO)₆ undergoing substitution with an entering ligand L*, what isomer(s) of the product would you expect to find in the products if L* were (a) monodentate and a higher-trans-effect ligand than CO, or (b) L* were bidentate and had a lower trans effect than did CO?

13. The products from HCl addition to C and D are unstable, but the addition products to A and B are stable. Explain, and state how C and D will decompose/reductively eliminate given that: A= IrCl(CO)(PPh₃)₂; B=IrCl(CO)(PMe₃)₂; C=IrMe(CO)(PMe₃)₂; D=IrPh(CO)(PMe₃)₂.
14. IrCl(CO)$_2$(PMe$_3$)$_2$ has two solution IR bands in the CO region, for which $I_{\text{sym}}/I_{\text{asym}}$ is 0.33. What is the preferred geometry of this complex in solution? Draw the molecule supporting your assignment of the preferred geometry, indicating which portions of the molecule contribute to the observed symmetrical and asymmetrical stretches.

15. Determine the $\Gamma_{\text{vib}}$ for BCl$_3$, given the following information.

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>2C$_3$</th>
<th>3C$_2$</th>
<th>$\sigma_h$</th>
<th>2S$_3$</th>
<th>3S$_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{\text{sym,d}}$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-2</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_{\text{a.m.a.}}$</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>$\Gamma_{\text{tot}}$</td>
<td>12</td>
<td>0</td>
<td>-2</td>
<td>4</td>
<td>-2</td>
<td>2</td>
</tr>
</tbody>
</table>

$\Gamma_{\text{tot}} = a'_1 + a'_2 + 3a'_3 + 2a''_2 + e''$; $\Gamma_{\text{a.m.a.}} = \Gamma_{\text{unmoved atoms}}$

Correctly assign the vibrations with respect to symmetric or asymmetric stretching, deformation/bending, degenerate, out-of-plane, etc.
16. If the measured absorbance of a transition-metal complex solution has a value of 1.0 what percentage of light is transmitted? What percentage is absorbed?

17. Neither the octet nor the eighteen-electron rule is obeyed for all compounds. How many electrons would one expect to be around the central atom in IF₇?

18. Anation of [Cr(NH₃)₅(H₂O)]³⁺ is thought to proceed by an interchange mechanism. The table below presents rate constants and activation parameters for interchange of the entering and leaving groups in the Cr coordination sphere at 50°C. What do these data suggest about the intimate mechanism of these reactions?

<table>
<thead>
<tr>
<th>Entering ligand</th>
<th>10⁴ k (s⁻¹)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS⁻</td>
<td>6.12</td>
<td>102</td>
<td>12</td>
</tr>
<tr>
<td>HC₅O₄⁻</td>
<td>6.2</td>
<td>112</td>
<td>39</td>
</tr>
<tr>
<td>C₂O₄²⁻</td>
<td>6.2</td>
<td>104</td>
<td>33</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>2.5</td>
<td>103</td>
<td>26</td>
</tr>
<tr>
<td>H₂O (exchange)</td>
<td>13.7</td>
<td>97</td>
<td>0</td>
</tr>
</tbody>
</table>

19. Associative reactions are also possible in octahedral substitutions, but much less common. Propose a mechanism for the following reaction, believed to proceed via the Sₙ,1CB route. Indicate the equilibrium step, the slow step, and the fast step. Write the rate expression.

\[ \text{trans-}[\text{Co(en)}₂(\text{NH₃})\text{Cl}]^{2⁺} + \text{OH}^- \rightarrow \text{trans-}[\text{Co(en)}₂(\text{NH₃})(\text{OH})]^{2⁺} + \text{Cl}^- \]
\[ C = J / V \]
\[ J = N \cdot m \]
\[ N = m \cdot kg \cdot s^{-2} \]
\[ 1 \text{eV} = 1.602 \times 10^{-19} \text{J} = 1.602 \times 10^{-12} \text{erg} \]
\[ 1 \text{J} = 10^7 \text{ergs} \]
\[ R = 109,677 \text{ cm}^{-1} = 13.6 \text{ eV} \]
\[ 1 \text{D} = 3.338 \times 10^{-19} \text{C} \cdot \text{m} \]
\[ \epsilon_0 = 8.854 \times 10^{-12} \text{C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1} \]
\[ \epsilon_0 (\text{H}_2\text{O}) = 78 \]
\[ \epsilon_0 (\text{air}) = 1.00 \]
\[ F = 96,500 \text{ C/mol} \]
\[ C = A \cdot s \]
\[ \mu_B = 9.274 \times 10^{-24} \text{ Joules/Tesla} \]
\[ \mu_{\text{spin}} = 2[(S(S+1))]^{1/2} \]
\[ \# \text{ microstate} = \frac{i!}{j!(i-j)!} \]
\[ I(\text{sym})/I(\text{asym}) = \cot^2 \theta \]
\[ \frac{d}{dx} \sin x = \cos x \]
\[ \frac{d}{dx} \cot x = -\csc^2 x \]
\[ \frac{d}{dx} \tan x = \sec^2 x \]
\[ \int \tan x \, dx = \ln | \sec x | \]
\[ \int \cot x \, dx = \ln | \sin x | \]
\[ E^0 = (0.059/n) \log K_{eq} \]