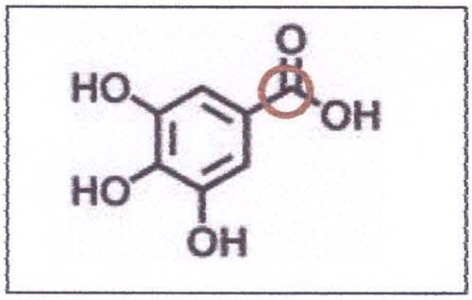
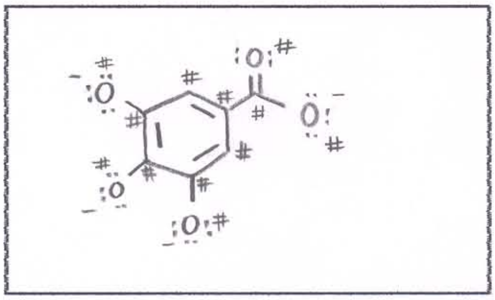
I. **Hybridization:** (25 points)

American Chemical Society Molecule of the Week (June 11, 2007) "Gallic Acid, or 3,4,5-trihydroxybenzoic acid, is produced by plants such as sumac, tea leaves, oak bark, and witch hazel; it provides the astringent property and anti-hemorrhoid activity of witch hazel. Derivatives are used in the production of azo dyes and photographic developers. It gets its name from gallnuts, which are the swelling of plant tissue in response to parasitic infection."





Assume that hydrogens are removed from all four OH groups of gallic acid. Redraw the molecule in the space provided above and use it to answer the following questions. (Don't forget to include implicit hydrogens and lone pairs of electrons!)

a) Mark sp^3 hybridized atoms with a * sign, sp^2 hybridized atoms with a # sign and sp hybridized atoms with a @ sign. (2.5 points)

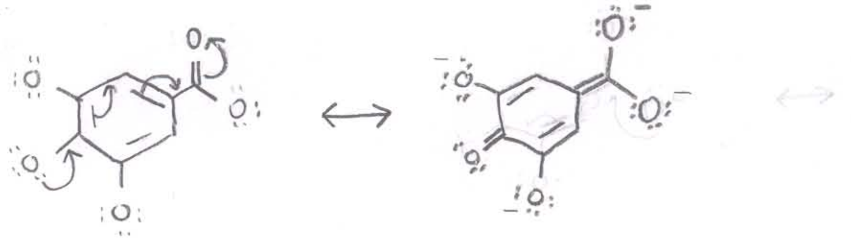
b) There are __7__ sp^2 hybridized atoms for which the geometry is

___trigonal planar_____ and the bond angles are ___120____. (5 points)

c) Consider the dipole moments of all bonds in this molecule. Circle the most electropositive carbon atom in the molecule in the original gallic acid structure. (2.5 points)

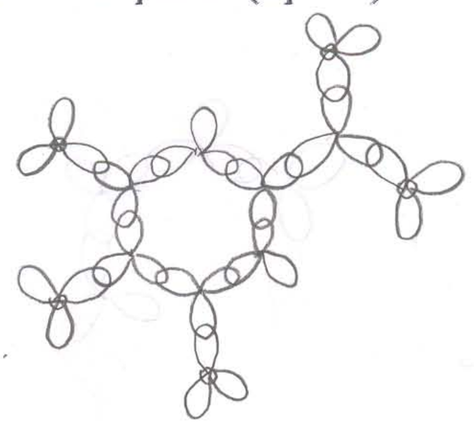
d) Do you think this molecule has resonance structures? If yes, draw one possible structure. (5 points)

Yes.



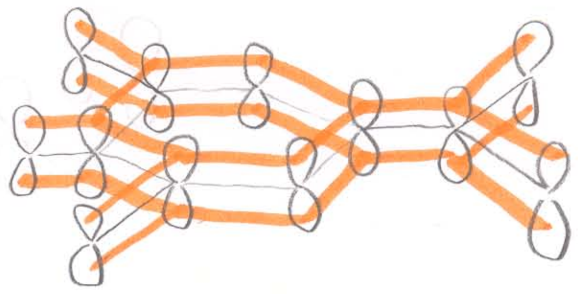
e) Draw all of the sp^2 hybridized orbitals in the molecule and their overlap to show the σ bonds. Is this molecule planar? (5 points)

Yes.



f) Draw all unhybridized p_z orbitals of the molecule to show where the electrons would be delocalized. Would this delocalization have an effect on the bond lengths of the two C-O bonds on the upper right? (5 points)

Both C-O bonds should be equal in length due to resonance.



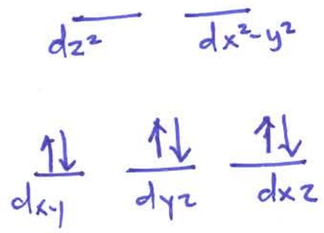
III. **Transition Metal Chemistry** (15 points)

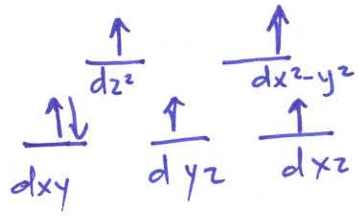
Spectrochemical Series:

Large splitting: $CN^- > NO_2^- >$ en $> NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$ Small splitting

1. Draw the crystal field splitting of the d orbitals for **each** of the complex ions below and insert electrons. Only one of the complexes is paramagnetic. (6 points)

$[Fe(CN)_6]^{-4}$ $[Fe(H_2O)_6]^{+2}$

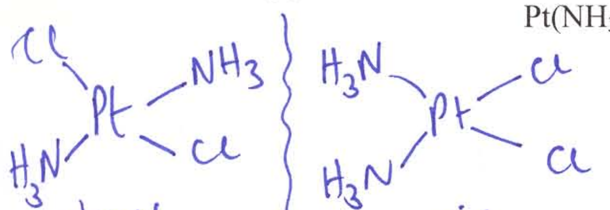




2. How does the splitting of the d orbitals affect the color of each of the complex ions above? (3 points)

Large splitting → large ΔE → small λ absorbed → large λ emitted → Red color
Small splitting → small ΔE → large λ absorbed → small λ emitted → blue/violet

3. Suggest a method that would help you to distinguish between cis-$Pt(NH_3)_2Cl_2$ and trans-$Pt(NH_3)_2Cl_2$. (3 points)



The cis- isomer is more polarised. It will be more soluble in a polar solvent

4. Explain why Nb and Ta have approximately the same atomic radius DESPITE the fact that Nb is in the 5th period and Ta is in the 6th period. (3 points)

The atomic radius of Ta is expected to be much larger than that of Nb. However, the presence of 4f orbitals in the inner electronic structure of Ta (the Lanthanides) do not give effective shielding of the valence d-orbital of Ta. So the increase in number of orbitals is not associated with an increase in atomic radius.

IV. Concentration and Mass Spectroscopy (25 pts)

Substance	MCLG	Highest Level	90% Value*	Action Level
Lead	0 ppb	290 ppb	2.9 ppb	15 ppb
Copper	1.3 ppm	0.29 ppm	.097 ppm	1.3 ppm

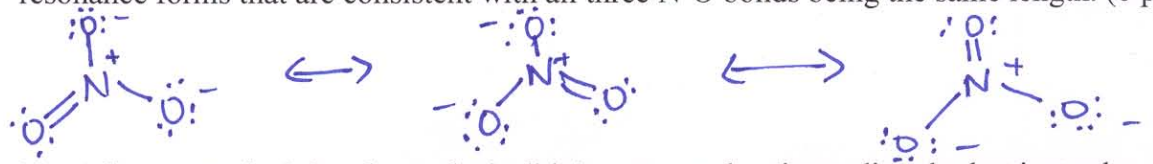
1. Shown above are levels of lead and copper in the Town of Amherst Drinking Water. The second column reports the MCLG, or maximum contaminant level goal and the third column reports the highest level measured over the year. Convert the contaminant level reported in the third column from ppb or ppm to molarity (moles per liter). (5 points)

$$290\,ppb\ Pb = \frac{290\,g\ Pb}{10^9\,g\ H_2O} = \frac{290\,g / 207.2\,g/mol\ Pb}{10^6\ L\ H_2O} = 1.399 \times 10^{-6}\ M\ Pb$$

$$0.29\,ppm\ Cu = \frac{0.29\,g\ Cu}{10^6\,g\ H_2O} = \frac{0.29\,g / 63.546\,g/mol\ Cu}{10^3\ L\ H_2O} = 4.563 \times 10^{-6}\ M\ Cu$$

2. The Town of Amherst reported that drinking water in Amherst in 2006 contains nitrate ions, $[NO_3]^{-1}$, which contaminate drinking water from fertilizer run-off.

a) Draw the Lewis structure for the nitrate ion, including formal charge on the atoms and draw resonance forms that are consistent with all three N-O bonds being the same length. (6 point)



b) Next, the report cited that the analysis didn't measure the nitrate directly, but instead measured the nitrogen in the nitrate, and that was reported as 2.5 ppm and cited as being within the safe limits. Calculate the weight percent of nitrogen in nitrate, and from this number, the ppm of nitrate itself in the drinking water. (8 points)

Mwt of NO_3^- $\Rightarrow 14.007 + 3(15.999) = 62.004$

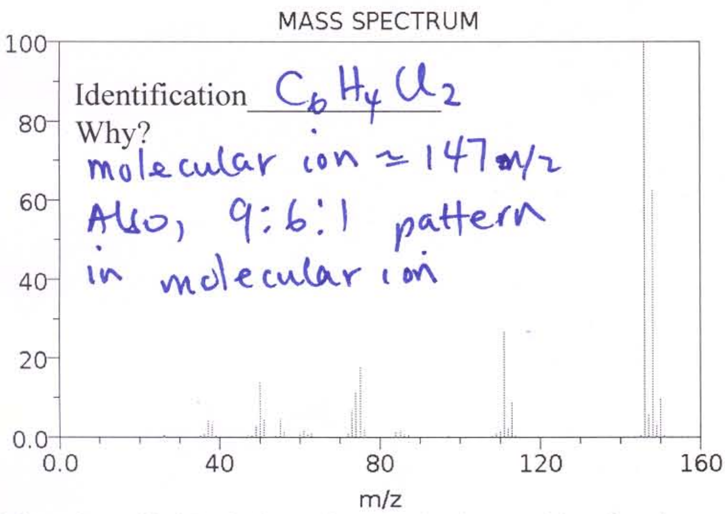
Weight % of N in NO_3^- $= \frac{14.007}{62.004} = 22.59\%$

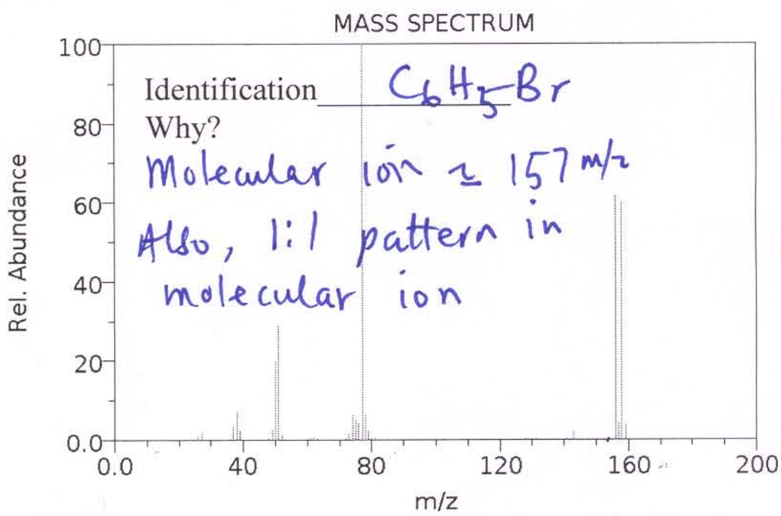
Now $22.59\% \equiv 2.5$ ppm

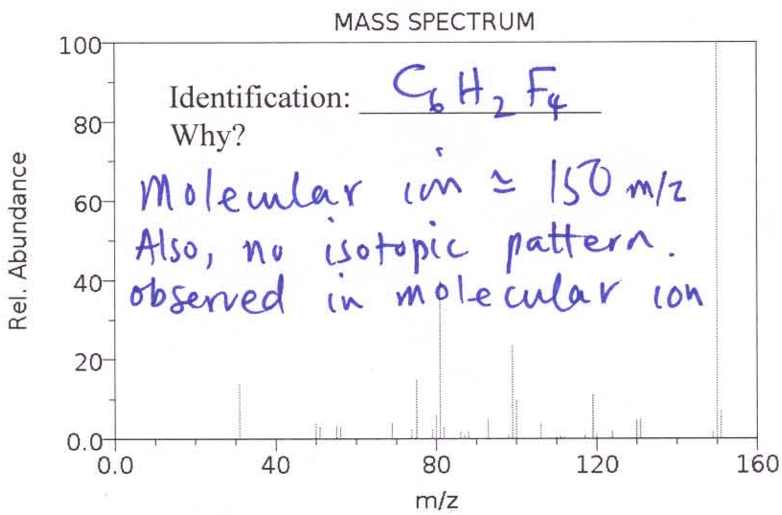
$\therefore$ $100\% \longrightarrow \frac{100 \times 2.5}{22.59}$ ppm $= 11.07$ ppm

3. The town drinking water report also included the levels of chlorinated, fluorinated and brominated hydrocarbons, those nasty substances left over from pesticides and cleaning solvents. Below are the mass spec for three of the hydrocarbons: Identify which mass spec belongs with which substance using the knowledge that F has only one predominant isotope, Cl exists as two isotopes, ^{35}Cl and ^{37}Cl with natural abundances of 0.75 and 0.25 and the Br exists as two isotopes, ^{79}Br and ^{81}Br with roughly equal natural abundances. (6 points)

Difluorobenzene	$C_6H_2F_4$	150.07 g/mole
Dichlorobenzene	$C_6H_4Cl_2$	147.00 g/mole
Bromobenzene	C_6H_5Br	157.01 g/mole





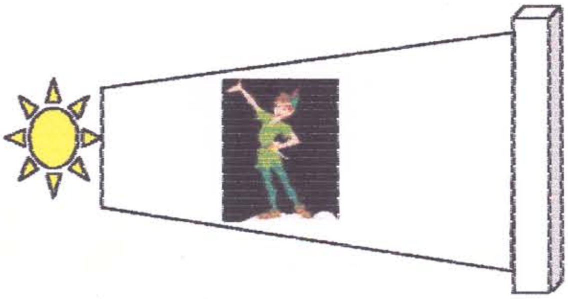


V. Classical and Quantum Mechanics (25 points)

Pan's Shadow
Photo credit to KL

A classic children's story is about a fictional character, a young boy named Peter Pan, who can fly and has found out how to stay young forever. He lives in a land with other lost boys called Never Never land and he likes to spy on human families. He has a friend who is a fairy, whose name is Tinker Bell. Once when spying on a human family, he had to escape quickly and in so doing, he lost his shadow. How terrible is that? This question asks you to use quantum mechanics to understand Peter Pan's shadow and how Peter Pan might be able to fly.

1. In the box below, sketch the physical set-up by which shadows are cast by large objects like people. Locate the light source, the object (Peter, assume he is 1 m tall and 0.5 m wide), and the screen on which you would see the shadow. Why does Peter Pan's shadow (or your own shadow) not show diffraction? (4 pts)



Peter Pan is too large. His size is much larger than the wavelength of light.

2. Another fictional character in this story is a fairy named Tinkerbell. She is extremely small, let's imagine she is 6.6×10^{-7} m in diameter. What happens to her shadow when she becomes the object imaged (instead of Peter Pan) in your sketch above? (4 pts)

Tinkerbell has a diameter in the order of the wavelength of light, so she will cause the light to diffract.

3. It is necessary in this story for Peter Pan to "fly" home. DeBroglie argues that P. Pan might be able to fly home if his wave length, □, = distance to Peter's home = 2.4 km. The boy has a mass of 22.0 kg, and flies with a velocity of 1.00 x 10^2 m/s. Calculate □ and see if DeBroglie can get P. Pan home. (6 points)

$\lambda = h/mv$

λ = (6.626x10^{-34} J.s) / (22.0 kg x 1.00 x 10^2 m/s) = 3.02 x 10^{-37} m

Will this get P. Pan home? Comment. No. His wavelength is much smaller than the distance to be traveled (2.4km).

4. Heisenberg believes that P. Pan can get to his home 2.4 km away if the uncertainty in his position, Δx, = distance home. He says P.Pan's velocity (1.00 x 10^2 m/s) has an uncertainty of 0.01%. Calculate Δx and see if Heisenberg can get P. Pan home. (6 points)

$\Delta x = h / 4\pi . m\Delta v$

Δx = (6.626x10^{-34} J.s) / (4 x 3.14259 x 22.0 kg x 1.00 x 10^2 m/s x 0.01/100) = 2.40 x 10^{-34} m

Will this get P.Pan home? Comment. Still no. The uncertainity is much smaller than than the distance to be traveled (2.4km).

5. Maybe Tinkerbell can get Peter back home. Given the values above for velocity (1.00 x 10^2 m/s), the uncertainty in velocity of 0.01%), and uncertainty in the distance of 2.4 km, calculate the mass Tinkerbell would have to be in order to make Heisenberg correct. (5 points)

$m \geq h / (4\pi \Delta x\, m\Delta v)$

m = (6.626x10^{-34} J.s) / (4 x 3.14259 x 2400 m x 1.00 x 10^2 m/s x 0.01/100) = 2.20 x 10^{-36} kg

Comment on the magnitude of this mass. Tinkerbell needs to weigh very little, even smaller than an electron.

VII. **Lab Questions (15 points)**:

a) Write the complete electron configuration of an atom (not an ion) of cobalt. (1 point)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$

b) What is the oxidation number of Co within $CoCl_2.6H_2O$? (1 point)

+2

c) What is the complete electron configuration of a Co ion in the oxidation state described in (b)? (1 point)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$

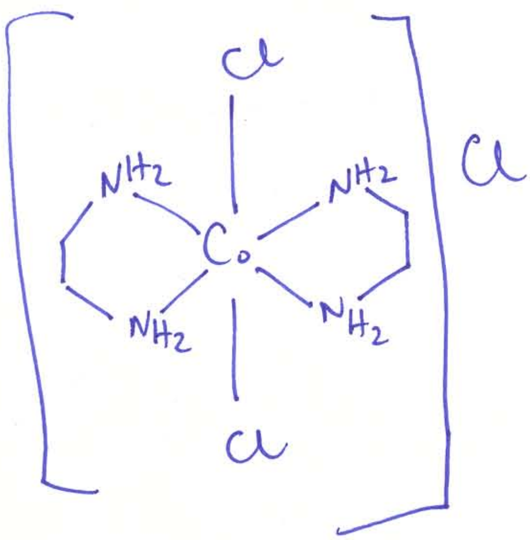
d) Describe what happens in words when one mole of $[Co(en)_2Cl_2]Cl$ is treated with excess silver nitrate. (2 points)

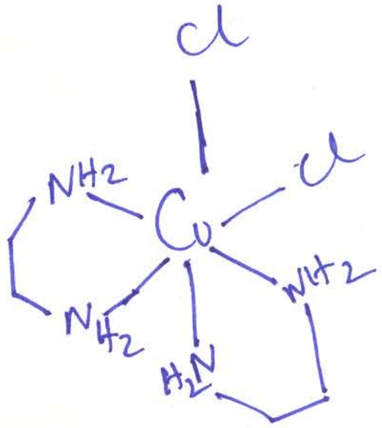
The $AgNO_3$ reacts with the Cl^- outside the complex, to form AgCl solid.

e) Balance the equation: (3 points)

2 $CoCl_2.6H_2O$ + 2 HCl + ____ H_2O_2 + 4 en → 2 *trans*-$[Co(en)_2Cl_2]Cl$ + 14 H_2O

f) Draw the trans- and the cis-isomers of $[Co(en)_2Cl_2]Cl$. (you are expected to know the chemical formula of en, if you don't, then perhaps knowing that it is ethylene diamine will help.) (6 points)





g) The terms cis- and trans refer to what kind of isomerism? (1 points)

Geometric