Inorganic Cumulative Exam
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1. For the $[PtCl_4]^{2-}$ ion, which has D_{4h} symmetry, the four Pt-Cl stretching combinations have the symmetry labels $A_{1g} + B_{1g} + E_u$. Which of these Pt-Cl vibrations are detectable by IR spectroscopy? Which of them are detectable by Raman spectroscopy?

Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

2. The molecule $POCl_3$ is a member of the C_{3v} point group.
   a. Draw the 3-dimensional structure using dashes and wedges according to VSEPR.
   b. How many vibrational degrees of freedom does $POCl_3$ have? How many are P-Cl stretching modes?
   c. How many IR-active P-Cl stretching modes are there?
   d. Does $POCl_3$ have a P-O multiple bond? If so, how is this possible considering that the phosphorous center must obey the octet rule? Provide a qualitative discussion to explain your view on this topic.

Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)

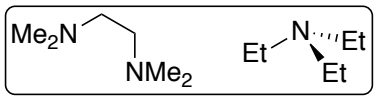
3. Do you expect a fluorine atom to have a larger or smaller radius than a nitrogen atom? Why?

4. Do you expect Fe^{3+} to have a larger or smaller radius than Fe^{2+}? Why?

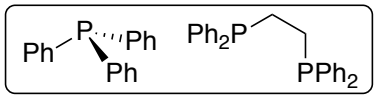
5. Provide S-S bond orders for S_2, S_2^-, and S_2^{2-}. Use qualitative MO analysis to justify your answers.

6. In the diagrams below, Group A shows two nitrogen ligands and Group B shows two phosphorus ligands. One group tends to bind Fe(III) tightly, while the other group tends to bind Pd(II) tightly. (a) Indicate which group corresponds to which of these metal ions. (b) Within each group, indicate the ligand that will bind to its metal the most strongly.

Group A:

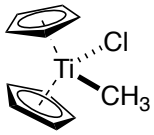


Group B:



7. Predict the number of unpaired electrons for any 4 of the following complexes: $[FeCl_6]^{3-}$, $[Mn(OH_2)_6]^{3+}$, $[NiBr_4]^{2-}$, $[PdCl_4]^{2-}$, $ZnCl_2(OH_2)_2$, $[IrCl_6]^{4-}$, $[Fe(CN)_6]^{4-}$.

8. Give the (a) metal oxidation state, (b) d-electron count, and (c) total valence electron count for the following:



9. According to MO analysis, what is the total bond order for XeF_4?

10. Name any two d-block metals that are particularly abundant in the human body, and describe their biological functions.

11. For each complex below, predict whether it would undergo associative or dissociative ligand substitution when exposed to a strong nucleophile. Explain the logic used to determine each answer.