Question 1 Multiple choice and short answer. Complete all questions directly on the examination paper. (2 points each, 24 total)

Questions (i)-(iii) refer to the molecular orbital of ClO. Below is the empty MO diagram for ClO. Fill in the appropriate number of electrons and answer the following questions.

(i) What is the bond order of ClO?

(d) 1.5

(ii) Which of the following will have the strongest bond?

(a) ClO^+

(iii) If ClO is a radical, will the unpaired electron be mainly associated with the Cl, the O, or shared equally between them? Explain.

The unpaired electron is in a π* level, which is closer in energy to the O 2*p* orbital, therefore it will spend most of its time closer to the O than the Cl. Therefore, it can be considered an O-centred radical.

Questions (iv) to (vi) deal with the Xe-F scissor vibration of the molecule $XeOF_4$, shown below. It has point group C_{4v}, which is given along with the axis directions used for the point group. Answer the following questions about this system.

(iv) The vibration has what symmetry?

(e) B_2

(v) Therefore, the vibration is

(c) active in Raman only

(vi) If the O atom was removed to leave XeF_4, what would be the point group?

(c) D_{4h}

Questions (vii) to (ix) refer to the following inorganic ring system:

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Questions (x) to (xii) refer to the potential redox reaction between technicium (a medical imaging agent) and iodine (a vital mineral required to prevent the disease goiter). The redox predominance diagrams for the two species are shown.

(x) I^- is the biologically safe form of iodine, while I_2 and IO_3^- are poisonous. In what form(s) would technicium be safe (*i.e.* not react with I^- to generate I_2 or IO_3^-)?

(a) both Tc and TcO_2

(xi) What is the standard reduction potential for the overall reaction

$$IO_3^-(aq) + 6\,e^- \rightarrow I^-(aq)$$

(d) 1.08 V

(xii) Give the voltage generated from the following (unbalanced) reaction (assume standard conditions).

$$IO_3^-(aq) + TcO_2(s) \rightarrow I_2(s) + TcO_4^-(aq)$$

$\Delta E^o = 1.19 - 0.74 = 0.45V$

Question 2 Do 5 of the following 6. (3 points each, 15 total)

(a) Imine ligands have the structure R=NH (the lone pair on the nitrogen donates to the metal). You can make bidentate imine ligands by attaching two imine functionalities to a carbon backbone to make a "carbodiimine" chelate. The ligands HN=CH-CH=NH (2 carbon bridge) and HN=CH-CH_2-CH=NH (3 carbon bridge) bind to metals strongly, while HN=CH-CH_2-CH_2-CH=NH (4 carbon bridge) does not. Explain.

Bidentate chelates form the strongest bonds when they can create a 5- or 6-membered ring, due to the fact that these ring sizes give the least amount of strain in the C and N bond angles. The 2-carbon bridge (4 atoms in chain) will form a 5-membered ring when chelated. Smilarly, the 3-carbon bridge will form a 6-membered ring, while the longest example would form an unfavorable 7-membered ring.

(b) The compound ion $[Cr(PMe_3)_6]^{2+}$ was found to have a magnetic moment of 2.82 μ_B. How many unpaired electrons are in the complex? Is it high spin or low spin?

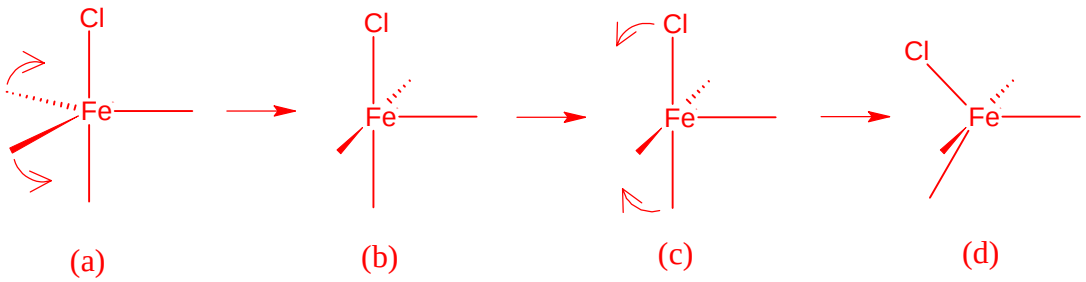
Using $\mu = (N(N+2))^{1/2}$, then $2.82^2 = N^2 + 2N$ or $N^2 + 2N - 2.822 = 0$
solving for N gives 1.99 (or 2 unpaired electrons)
Knowing that the Cr in this complex is d^4 (Cr^{2+} has 4 e^-), in an octahedral field the high-spin would have 4 unpaired electrons, the low spin would have 2 (therefore it's low spin)

(c) Explain why ligands with strong σ-donor ability give a large value of Δ_O.

Recall that the e_g level (the d_{z^2} and the $d_{x^2-y^2}$ orbitals) are slightly σ* (and the t_{2g} level is π-bonding). Thus, the stronger the bond, the more the s bonding levels in the molecular orbital picture will be stabilised, and (more importantly for this question), the more the σ* levels will be destabilized (rise in energy). Thus, the stronger the σ-bond, the higher in energy the e_g level (and the larger the Δ_O)

(d) The trigonal bipyramidal compound $Fe(CH_3)_4Cl$ has only one signal for the methyl groups in the ^1H NMR, implying that the following equilibrium is occurring: Suggest how this could occur without breaking any bonds in the complex.

This compound is undergoing a pseudorotation isomerization mechanism. (a) the two equatorial methyls come back (a) to make a square planar structure (b). The other two (former axial methyls) then bend down (c) to become new equatorial substituents (d). This can happen multiple times and mix the methyls into every potential position.



(a) (b) (c) (d)

(e) The rule of mutual exclusion states: "In a centrosymmetric complex (one that contains an inversion centre), a vibration cannot be both IR and Raman active." Given the point groups attached to this exam (and for C_{4v} given in Question 1), show that this is the case. Also show that the rule does not apply for non-centrosymmetric groups.

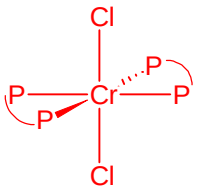
The exam had a number of point groups included. If you look at any point group that contains the *i* symmetry element, you'll see that no irreducible representation has both a linear (*x*, *y*, or *z*) and a square (*xy*, x^2, etc.) element. Therefore IR activity and Raman activity are exclusive of each other. Similarly, those point groups without an *i* can have both (*e.g.* for C_{4v}, A_1 and *E* are both IR and Raman active).

(f) Predict the structure of BH_2F (*i.e.* is it a monomer or a dimer). For your structure, justify your choice by explaining how the B atom satisfies its octet rule.

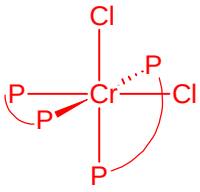
I think the easiest (and best) solution would be to point out that the B can satisfy its octet by drawing a double bond between B and F. There is no reason to invoke a dimer.

Question 3 Answer both questions. (4 points each, 8 points total).

(a) Draw all the isomers of $Cr(dppe)_2Cl_2$. Comment on which isomers (if any) are chiral. Assign the absolute configuration to any chiral molecule you draw. Note: dppe is1,2-bis(diphenylphosphino)ethane, $R_2P\text{-}CH_2\text{-}CH_2\text{-}PR_2$, which binds through the P atoms. You can abbreviate it with P⌒P if you prefer.



trans



cis

chiral - this is the Δ isomer

(c) Explain how a d^9 octahedral complex might distort and justify the energetic reason for it doing so.

A d^9 octahedral complex is likely to distort by elongation of its two "axial" ligands along the *z*-axis (similarly, the 4 equatorial bonds compress). When that occurs (assuming the absence of π-bonds), the d_{z^2} orbital goes down in energy (longer bond = weaker bond = smaller σ* energy change). Similarly the $d_{x^2-y^2}$ goes up in energy an equal amount. These two orbitals have 3 total electrons, so 2 go down in energy while 1 goes up in energy, for a net lowering of energy.

Question 4 Do 4 of the following 5. (2 points each, 8 total)

(a) The boiling point of H_2O is anomalously high (by comparison, CH_4 boils at -161°C and H_2S boils at -60°C). Explain why.

The H-O bond is very polar due to the high electronegativity of O (it has the 2nd-highest electronegativity on the periodic table). Therefore, there is a slight positive charge on the H and a slight negative on the O. The interaction between these δ^+ and δ^- charges are "hydrogen bonds", and these bonds must be broken (more energy must be added = higher temperature) before water can vaporize. By contrast, CH_4 is non-polar (due to its symmetry) and the bond polarity of H_2S is much lower.

(b) When the ligand $S\text{-}C{\equiv}N^-$ reacts with Fe^{3+}, it binds through the nitrogen. However, when binding with Pb^{2+}, it binds through the sulfur. Explain.

Fe^{3+} is both a smaller ion and a higher charge than Pb^{2+}. Therefore, Fe^{3+} is a "harder" acid in the HSAB (hard-soft acid-base) classification than is Pb^{2+}. By the same token, the larger S is softer than the smaller N. Because hard acids like hard bases (to form more purely ionic bonds), the Fe^{3+} will bind through N, while the soft acid Pb^{2+} will want to form a partially covalent bond with the soft base S.

(c) The compound $N(GeH_3)_3$ is trigonal planar (D_{3h}) because of π-bonding between the N and the Ge. Does this observation contradict the general rule that π bonds cannot be formed between 2*p* and 4*p* orbitals? Explain.

The p-bond in this species is most likely between that of a 2*p* on the nitrogen and a *d*-orbital (not a *p*) on the Ge. Because the *d*-orbital "leans" towards the N atom, this interaction is stronger (and the 2*p*-4*p* rule is not contradicted).

(d) V^{4+} complexes are highly coloured. If the visible absorption spectrum for $(Cp^*)_2VCl_2$ has a λ_{MAX} of 585 nm, what is the value of Δ_O? Answer in units of kJ/mol.

$\Delta E = \Delta_O = h\nu = hc/\lambda = 3x10^8$ m/s) $(6.63x10^{-34}$ Js) / $585x10^{-9}$ m = 3.40 x 10^{-19} J
Converting to kJ/mol (multiplying by Avagadro's number) gives 205 kJ/mol.

(e) A tetrahedral complex is always high-spin. Explain why, comparing two hypothetical complexes with identical ligands MX_4 (T_d) and MX_6 (O_h).

The value of Δ_O is often close to the pairing energy, so a small change in bond strength might switch octahedral complexes between high spin and low spin. However, Δ_t is only 4/9 Δ_O! Therefore, the energy difference between the *e* and the t_2 orbitals never gets big enough to overcome the pairing energy, and tetrahedral complexes are always high spin.