1. What does the following table tell you about the likely mechanism for anation (replacement of water by the anions listed) for the following Cr³⁺ complexes?

<table>
<thead>
<tr>
<th>Entering Ligand L</th>
<th>( \text{Cr(H}_2\text{O)}_6^{3+} )</th>
<th>( k )</th>
<th>( \text{Cr(NH}_3)_5(\text{H}_2\text{O})^{3+} )</th>
<th>( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS⁻</td>
<td>( 1.8 \times 10^{-6} )</td>
<td>( k )</td>
<td>( 4.2 \times 10^{-4} ) M⁻¹ s⁻¹</td>
<td>( k )</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>( 7.2 \times 10^{-7} )</td>
<td>( k )</td>
<td>( 4.0 \times 10^{-4} )</td>
<td>( k )</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>( 2.9 \times 10^{-8} )</td>
<td>( k )</td>
<td>( 0.7 \times 10^{-4} )</td>
<td>( k )</td>
</tr>
<tr>
<td>Br⁻</td>
<td>( 1.0 \times 10^{-8} )</td>
<td>( k )</td>
<td>( 3.7 \times 10^{-4} )</td>
<td>( k )</td>
</tr>
<tr>
<td>I⁻</td>
<td>( 8.0 \times 10^{-10} )</td>
<td>( k )</td>
<td>( 2.8 \times 10^{-4} )</td>
<td>( k )</td>
</tr>
</tbody>
</table>

The observation of a strong entering ligand effect on reaction rate suggests an associative (or associative interchange) mechanism. In this example, there is a very strong dependence on entering ligand identity for \( \text{[Cr(H}_2\text{O)}_6^{3+} \) but NOT for \( \text{[Cr(NH}_3)_5(\text{H}_2\text{O})^{3+} \) suggesting the former proceeds by an associative pathway and the latter by a dissociative pathway.

2. Suggest a reason why the Cr³⁺ ion in Q1 shows such remarkable differences in the two complexes given.

Normally, first row, octahedral transition metal ions undergo dissociative exchange (\( I_d \) mechanism) but this is strongly disfavoured electronically for \( d^3 \) ions due to the large loss in CFSE. This makes an associative pathway competitive so that simply changing the identity of the ancillary ligands is enough to alter the mechanism. The switch is can be understood by noting that the better donor (NH₃) favours the dissociative mechanism because it is better able to compensate for the lower electron density at the metal in the 5 coordinate transition state.

3. Account for the observation that there are two very different \( k_w \) (water exchange rate constants) for \( \text{Cu(H}_2\text{O)}_6^{2+} \) in aqueous solution.

This is a Jahn-Teller ion (\( d^9 \)) and as such, the two axial waters are more weakly bonded to \( \text{Cu}^{2+} \) compared to the four equatorial waters. This is reflected in different exchange rates for the axial and equatorial waters.
4. Explain why the entropy of activation is not always a reliable indicator of mechanism in a highly polar solvent like water.

*Normally we would expect a dissociative mechanism to show a positive entropy and an associative mechanism a negative entropy of activation. However, polar solvents like water strongly solvate the complex and transition state (or intermediate). If there is a large difference in solvation for the ground state and transition state then this may be more significant that any changes associated with complex association or dissociation. For example, if there is much less solvation in the transition state for an associative mechanism then the increase in ‘free waters’ at the transition state may offset the normally negative entropy of activation. This is certainly possible because there are more particles in the ground state than in the transition state for such a mechanism and therefore more bound waters in the ground state.*

5. When the two isomers of \( \text{Pt(NH}_3\text{)}_2\text{Cl}_2 \) are reacted with thiourea \((\text{S}=\text{C(NH}_2\text{)_2})\) the products are have the formula \([\text{Pt(tu)}_4]^{2+}\) and \([\text{Pt((NH}_3\text{)}_2\text{tu)}_2]^{2+}\). Identify which isomer gives which product and explain why this occurs.

*Thiourea bonds to \( \text{Pt}^{2+} \) (a relatively soft metal) through the S atom and is a good sigma donor (a moderately strong trans effect ligand). Of the three ligands involved in this question, the trans effect order, which governs the products formed, is \( \text{tu}>\text{Cl}>\text{NH}_3 \). In order to see the possible sequence of events, we consider what occurs at each step where the bond trans to the strongest trans labilizing ligand is the one replaced:*
Since only the trans isomer ever goes through a complex of formula \([\text{Pt(NH}_3\text{)}_2\text{(tu)}_2]^{2+}\), we assume it stops at this stage. The cis isomer on the other hand, never forms this stoichiometry product and is must continue on to the completely substituted product.

6. Give the products of the following reactions (equimolar mixtures):
   a) \([\text{Pt(CO)}\text{Cl}_3]^− + \text{NH}_3 \rightarrow \text{trans-[Pt(CO)(NH}_3\text{)Cl}_2]\]
   b) \([\text{Pt(NH}_3\text{)}\text{Br}_3]^− + \text{NH}_3 \rightarrow \text{cis-[Pt(NH}_3\text{)Br}_2]\]
   c) \([\text{Pt(η}^2\text{-C}_2\text{H}_4)\text{Cl}_3]^− + \text{NH}_3 \rightarrow \text{trans-[Pt(η}^2\text{-C}_2\text{H}_4)(NH}_3\text{)Cl}_2]\]
   d) Cis-[\text{Rh(CO)}_2\text{I}_4]^− + \text{CO} \rightarrow \text{mer-Rh(CO)}_2\text{I}_3

7. Cyclopropane reacts with \(\text{Pt(PR}_3\text{)}_3\) (\(R = \text{large alkyl like cyclohexyl}\)) complexes upon heating but the reaction does not occur if free \(\text{PR}_3\) is present in the mixture. No reaction is observed under any conditions with \(\text{n-propane}\) as substrate. Identify the product of the cyclopropane reaction and explain the observations that \(\text{n-propane}\) is inert and \(\text{PR}_3\) suppresses the reaction.

   \(\text{If PR}_3\) suppresses the reaction this suggests that the first step is \(\text{PR}_3\) dissociation to form \(\text{Pt(PR}_3\text{)}_2\) as a highly reactive intermediate. Oxidative addition of a C-C bond is possible in cyclopropane because of the ring strain energy. This results in formation of a metallacyclobutane as shown below. \(\text{n-Propane}\) has no strained C-C bonds and so will not add to \(\text{Pt(0)}\).