KEY

Answer all questions on this paper. There are 12 pts total.

1. For the substitution of Cl by NH$_3$ in cis-[Cr(Cl)$_4$(H$_2$O)$_2$]$^{2-}$:
   
a) Do you expect substitution to be fast ($k > 10^2$ s$^{-1}$) or slow? Explain your answer. [1 pts]

   In a dissociative substitution it is the identity of the metal not the incoming ligand that matters. Since this is Cr$^{2+}$ it is a d$^4$ Jahn-Teller ion and these ions substitute very fast as the ligand-metal bond is already elongated.

b) How can you tell if this is an A (or I$_a$) versus D (or I$_d$) mechanism without changing the ligands or complex involved or the pressure? [1 pts]

   The easiest option is to change the incoming ligand concentration because the rate of an associative process depends on both [complex] and [incoming ligand]. The rate of a dissociative substitution will be unaffected by changes in the incoming ligand concentration. Entropy of activation is also an acceptable answer as it would be negative for an associative process and positive for a dissociative one. However, the entropy is not an infallible guide as the error is large and other factors such as solvent reorganization can alter the value from these expectations. Volume of activation is a good answer but the question said you cannot alter the pressure so that is not an option here.

c) Would you expect the rate to increase or decrease if you replaced the ancillary (spectator) water ligands by CH$_3$OCH$_3$ (dimethyl ether)? Explain your answer. [1 pts]

   Generally speaking, more crowding ligands and better donors should increase the rate of a dissociative process because they favour a lower coordination environment and provide adequate electron density to compensate for fewer donors. Dimethyl ether is larger than water and possibly a better donor.
2. Distinguish between the trans influence and the trans effect. Give at least two examples showing how you can detect the presence of the trans influence in a complex. (3 pts)

The trans influence is a ground state effect where strong sigma donors weaken the bond trans to themselves. Since this is a ground state effect, it can be directly observed in changes in bond lengths, coupling constants and stretching frequencies.

The (true) trans effect is an excited state effect whereby strong pi acceptors stabilize the transition state by withdrawing electron density from the equatorial plane of the five coordinate trigonal bipyramidal geometry.

3. Give the products of ligand substitution for the following reactions [2 pt each]:

a) $[\text{Rh(Cl)}_3(\text{CO})]^2-$ with one equivalent of $\text{PPh}_3$

$$\text{trans-}[\text{Rh(Cl)}_2(\text{CO})(\text{PPh}_3)]^- + \text{Cl}^-$$

Substitution occurs trans to the strongest trans effect ligand $\text{CO} > \text{Cl}^-.$

b) $[\text{AuI}_4]^- \text{ with first one equivalent of }\text{PPh}_3 \text{ followed by one equivalent of }\text{py}.$

$$\text{trans-}[\text{Au(I)}_2(\text{py})(\text{PPh}_3)]^+ + 2\text{I}^-$$

The first substitution occurs can only give $[\text{Au(I)}_3(\text{PPh}_3)]$ and the second substitutes trans to the stronger trans effect ligand, $\text{PPh}_3 > \text{I}^-.$

4. For which d counts is substitution in octahedral complexes the most unfavourable for electronic reasons? [2 pts]

This will occur where there is the greatest loss of CFSE: that is, when the $t_{2g}$ set is either full with nothing in $e_g$ ($d^3$ or low spin $d^6$) OR when the complex is $d^8$ (same CFSE as $d^3$).