1 (a) \([\text{Cr}(\text{NH}_3)_6]^{3+}\) must be recrystallized in acidic solution because a base would deprotonate an ammonia ligand, promoting substitution to give \([\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}\) or \([\text{Cr}(\text{NH}_3)_5(\text{OH})]^{2+}\).

(b) \([\text{M}(\text{H}_2\text{O})_6]^{2+}\) is colorless for \(\text{M} = \text{Mn}\) or \(\text{Zn}\) (other examples are possible for other charges). Such compounds have no spin-allowed d-d transitions and hence no absorptions in the visible spectrum.

(c) Rh acetate contains Rh(II) which is \(d^7\). For 2 rhodiums this gives 14 electrons. Plugging them into the MO scheme for the Cr-Cr bond gives \((\sigma)^2(\pi)^4(\delta)^2\) \((\pi^*)^4(\delta)^2\), which predicts a Rh-Rh bond order of 1 and no magnetic moment for this complex: Note that the relative order of the antibonding \(\pi\) and \(\delta\) MO's doesn't matter in this case.

2 (a) This is an associative-type substitution, so expect the activation entropy and volume to both be negative (more order in the transition state than in the reactants, and smaller volume occupied by the transition state than the reactants). The activation enthalpy is positive as always.

(b) Here are syntheses of the 3 isomers:

(c) (1) the en complex has \(D_3\) symmetry so d-d transitions are not Laporte forbidden as they are in the \(O_h\) NH3 complex; hence the NH3 one is less intense.

(2) The trans complex has a center of symmetry so its transitions are again Laporte forbidden and less intense than the cis one.

(3) The octahedral one will be less intense than the tetrahedral one (again \(O_h\) has Laporte forbidden transitions but \(T_d\) does not since it
lacks the i symmetry element).

(d) The energy of 2 does not depend on $\Delta_0$ so it goes with $Y$, while the energy of 1 does depend on the $t_{2g}$-$e_g$ splitting, so it goes with $X$.

(e) These are Ti(III) $d^1$ so there is only one transition, whose energy should be $\Delta_0$. The larger $\Delta_0$ should go with the cyanide complex, as expected from the spectrochemical series.

3 (a) The Cr(II) high spin $d^4$ and Cu(II) $d^9$ ions undergo tetragonal Jahn-Teller distortions which elongate and weaken the axial M-OH$_2$ bonds, thus speeding up the dissociative water ligand substitutions.

(b) The acid hydrolysis is dissociative-type, so breaking the Ru-X bond affects the rate. The Ru(NH$_3$)$_5^{2+}$ fragment is soft so it forms stronger bonds to the soft I$^-$, which gives slower rates than with the hard F$^-$.

(c) The rate dependence on the entering group suggests an associative mechanism whose relative rates can be rationalized by considering the nucleophilicity of the entering group (negatively charged ones attack with faster rates).

(d) Acid hydrolysis in the more hindered system is accelerated since loss of chloride ion is favored by destabilizing steric interactions in the ground state.

(e) Base hydrolysis in the same system has the opposite rates, because the base can deprotonate the en ligand, leading to the rapid $S_N1$-CB mechanism for substitution, but the permethylated en ligand cannot undergo substitution by this pathway.

(f) At pH 10, the Co complex is deprotonated and exists as the hydroxide [Co(NH$_3$)$_5$(OH)]$^{2+}$; the hydroxide ligand can bridge Co and the labile high spin Cr(II) $d^4$ center to enable fast inner sphere electron transfer; at pH 6 slower outer sphere electron transfer occurs. Inert low spin Ru(II) $d^6$, however, cannot undergo inner sphere e-transfer so the slow outer sphere rate is observed over the pH range.

(g) These are outer-sphere electron transfers. In the Os case, we have low spin Os(II) $d^6$ and Os(III) ($d^5$) so rapid $t_{2g}$-$t_{2g}$ electron transfer can occur without much reorganization required. However the Co case involves e transfer between high spin Co(II) $d^7$ and low spin Co(III) $d^6$ which requires extensive reorganization--hence the slower rate.

Question 4
(a) These compounds are low spin Co(III) d^6, which is consistent with the Tanabe-Sugano diagram, which predicts 2 low-energy spin-allowed d-d transitions from the 1A_1 ground state to the 1T_1 and 1T_2 excited states. These can be assigned to the bands centered at about 18,000 and 25,000 cm^{-1}, respectively. [Note that the high-spin case would predict only 1 spin-allowed transition]. The energies of these bands change as expected from the spectrochemical series.

The much more intense bands at the right of the spectrum are charge transfer bands, presumably LMCT since the halides are π-donor ligands. Since these transitions are affected by the nature of the halide more directly than the d-d ones (which also must take into account the effect of the ammonia ligands on Δ_0), their energies change a lot more with X, in order expected with ease of oxidation: Br^{-} > Cl^{-} > F^{-} (highest energy).

(b) [Co(CO)₄]⁻ is Co(-1) d¹⁰ and therefore has no d-d transitions. Its electronic spectrum will be featureless (see sketch) and it will be colorless.

(c) Lowering T will decrease both intensity and bandwidth of a spectral band. There will be less molecular vibrations capable of distorting the complex to lose the inversion center i, thus satisfying the Laporte selection rule and leading to increased intensity. The smaller number and decreased energy of vibrations will also lead to a narrower envelope of transition energies and thus sharper bandwidths.

**Question 5**  
(a-b) Sketches are on next page
Backbonding refers to the synergistic interaction between a metal and CO in which electron density (donated to the metal from the CO HOMO) is delocalized from the metal into the C-O LUMO, a $\pi^*$ C-O MO, resulting in decreased C-O bond strength and IR stretching frequency.

(c) The silver complex is quite unusual. The C-O stretch in the free molecule is at 2143 cm$^{-1}$, and in most transition metal complexes it is greatly decreased, for the reasons discussed above. The strange observation of an increased C-O stretching frequency in the Ag complex suggests that donation from the C-O HOMO to Ag is occurring, thus strengthening the C-O bond by removing electron density from this C-O sigma-antibonding MO. However, backbonding by donation from a filled M orbital into the CO LUMO does not seem to be an important effect. This is probably because the high effective nuclear charge on silver holds the d electrons close to the nucleus and makes them less available for this interaction.