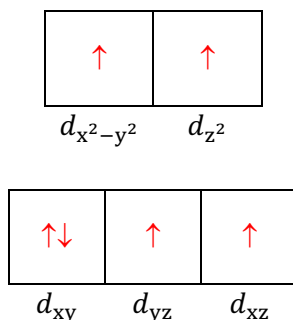


1. Complete the following table.

Chemical Formula	Metal Ox. State	Systematic Name
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	+3	Hexaaquairon(III)
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	+3	Pentaamminechlorocobalt(III)
$\text{Na}_2[\text{NiCl}_4]$	+2	Sodium tetrachloronickelate(II)
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	+2	Tetraammineplatinum(II)
$[\text{Fe}(\text{CN})_6]^{3-}$	+3	Hexacyanoferrate(III)
$[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Cl}$	+2	Triamminebromoplatinum(II) chloride

2. Fill in the  $d$ -orbital splitting diagram for a  $d^6$  octahedral complex that is paramagnetic.

Is this a high-spin or a low-spin complex?



The complex would need to be high-spin in order for it to have unpaired electrons. If the complex were low-spin, all 6  $d$ -electrons would be paired and occupy the bottom 3 orbitals only.

3. Consider the following complex ions and their associated/observed colors.

(i)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  (green)

(ii)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  (blue)

(iii)  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$  (yellow)

A) Order the complex ions in order of smallest to largest crystal field splitting energy ( $\Delta_o$ ).

Consider the complementary colors: (i) absorbs red; (ii) absorbs orange; (iii) absorbs violet.

The  $\lambda_{\text{absorbed}}$  is a measure of the  $\Delta_o$  via  $E = hc/\lambda$ ; therefore, the ordering of  $\Delta_o$  is: i < ii < iii.

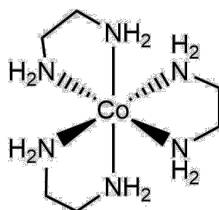
B) Why might some coordination complexes be colorless?

The energy required to excite an electron would be outside of the visible spectrum. This is typically the case for high-spin  $d^5$  and for the completely filled  $d^{10}$  configurations.

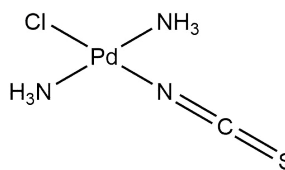
C) Would you expect a colorless coordination complex to require more or less energy to excite an electron from its ground state than a colored coordination complex?

More energy because an excitation would excite a  $d$  electron to the next available orbital ( $p$ ), which is much higher in energy.

4. Determine the relationship between each pair of complexes as cis-trans isomers, linkage isomers, or enantiomers.



Enantiomers



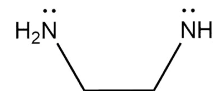
Linkage isomers

5. The chelate effect describes the phenomenon wherein polydentate ligand coordination is significantly more favorable than monodentate ligand coordination, which is proposed to be primarily an effect driven by entropy.

Consider the following two aqueous reactions:

- i.  $[\text{Co}(\text{H}_2\text{O})]^{3+} + 6 \text{NH}_3 \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+} + 6 \text{H}_2\text{O}$
- ii.  $[\text{Co}(\text{H}_2\text{O})]^{3+} + 3 \text{en} \rightleftharpoons [\text{Co}(\text{en})_3]^{3+} + 6 \text{H}_2\text{O}$

Hint:  $\text{NH}_3$  is a monodentate ligand. The “en” ligand is an abbreviation for ethylenediamine, a bidentate ligand with the following structure:



Using the information above and given that the  $\Delta H$  for both reactions are approximately equal, circle the correct relationship between each of the following thermodynamic properties.

- A)  $K_{f(i)}$  is (larger than/smaller than/about equal to)  $K_{f(ii)}$ .
- B)  $\Delta S_{(i)}$  is (more positive than/more negative than/about equal to) than  $\Delta S_{(ii)}$ .
- C)  $\Delta G_{(i)}$  is (more positive than/more negative than/about equal to) than  $\Delta G_{(ii)}$ .

Reaction (ii) is entropically favored because we are converting 4 moles of reactants into 7 moles of products; hence, there is greater change in disorder and  $\Delta S_{(ii)} > \Delta S_{(i)}$ .

Recall that  $\Delta G = \Delta H - T\Delta S$ . Since  $\Delta H_{(i)} \approx \Delta H_{(ii)}$ , we need only consider the effect of the  $\Delta S$  term for both reactions. Because reaction (ii) is more entropically favored than reaction (i), the value of  $\Delta G_{(ii)} < \Delta G_{(i)}$ . In other words, reaction (ii) is more spontaneous/favorable. As such, the equilibrium constant of formation for reaction (ii) favors the products more than it would in reaction (i):  $K_{f(ii)} > K_{f(i)}$ .