CHAPTER 21

TRANSITION METALS AND COORDINATION CHEMISTRY

## Questions

5. $Fe_2O_3(s) + 6\ H_2C_2O_4(aq) \rightarrow 2\ Fe(C_2O_4)_3^{3-}(aq) + 3\ H_2O(l) + 6\ H^+(aq)$; the oxalate anion forms a soluble complex ion with iron in rust (Fe_2O_3), which allows rust stains to be removed.

6.   Only the Cr^{3+} ion can form four different compounds with H_2O ligands and Cl^- ions. The Cr^{2+} ion could form only three different compounds, while the Cr^{4+} ion could form five different compounds.
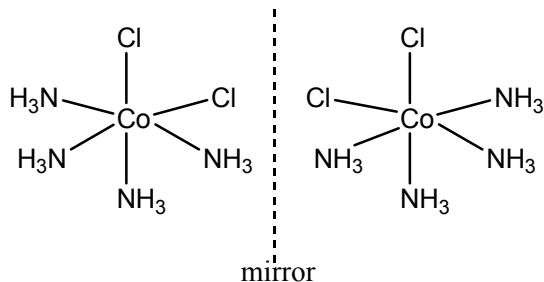
The Cl^- ions that form precipitates with Ag^+ are the counter ions, not the ligands in the complex ion. The four compounds and mol AgCl precipitate that would form with 1 mol of compound are:

Compound	Mol AgCl(s)
$[Cr(H_2O)_6]Cl_3$	3 mol
$[Cr(H_2O)_5Cl]Cl_2$	2 mol
$[Cr(H_2O)_4Cl_2]Cl$	1 mol
$[Cr(H_2O)_3Cl_3]$	0 mol

7.
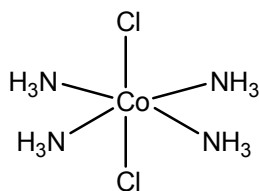

|		
trans	cis	
(mirror image is superimposable)		The mirror image of the cis isomer is also superimposable.

No; both the trans and the cis forms of $Co(NH_3)_4Cl_2^+$ have mirror images that are superimposable. For the cis form, the mirror image only needs a $90°$ rotation to produce the original structure. Hence neither the trans nor cis form is optically active.

8.   The transition metal ion must form octahedral complex ions; only with the octahedral geometry are two different arrangements of d electrons possible in the split d orbitals. These two arrangements depend on whether a weak field or strong field is present. For four

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unpaired electrons, the two possible weak field cases are for transition metal ions with $3d^4$ or $3d^6$ electron configurations:


small Δ   small Δ

d^4 d^6
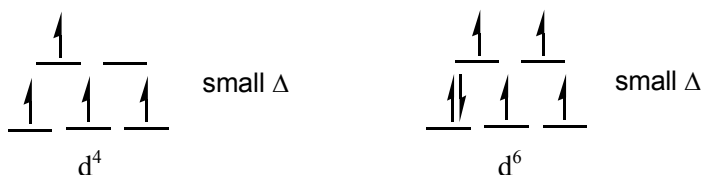
Of these two, only d^6 ions have no unpaired electron in the strong field case.

large Δ
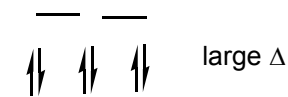
Therefore, the transition metal ion has a $3d^6$ arrangement of electrons. Two possible metal ions that are $3d^6$ are Fe^{2+} and Co^{3+}. Thus one of these ions is present in the four coordination compounds, and each of these complex ions has a coordination number of 6.

The colors of the compounds are related to the magnitude of Δ (the d-orbital splitting value). The weak-field compounds will have the smallest Δ, so the λ of light absorbed will be longest. Using Table 21.16, the green solution (absorbs 650-nm light) and the blue solution (absorbs 600-nm light) absorb the longest-wavelength light; these solutions contain the complex ions that are the weak-field cases with four unpaired electrons. The red solution (absorbs 490-nm light) and yellow solution (absorbs 450-nm light) contain the two strong-field case complex ions because they absorb the shortest-wavelength (highest-energy) light. These complex ions are diamagnetic.

9.   a. $CoCl_4^{2-}$; Co^{2+}: $4s^03d^7$; all tetrahedral complexes are a weak field (high spin).
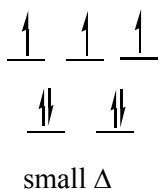
$CoCl_4^{2-}$ is an example of a weak-field case having three unpaired electrons.

small Δ

   b. $Co(CN)_6^{3-}$: Co^{3+} : $4s^03d^6$;   because CN^- is a strong-field ligand, $Co(CN)_6^{3-}$ will be a strong-field case (low-spin case).
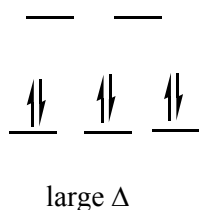
CN^- is a strong-field ligand, so $Co(CN)_6^{3-}$ will be a low-spin case having zero unpaired electrons.

large Δ

10.   a.   The coordination compound has the formula $[Co(H_2O)_6]Cl_2$. The complex ion is $Co(H_2O)_6^{2+}$, and the counter ions are the Cl^- ions. The geometry would be octahedral, and the electron configuration of Co^{2+} is $[Ar]3d^7$.

       b.   The coordination compound is $Na_3[Ag(S_2O_3)_2]$.The compound consists of Na^+ counter-ions and the $Ag(S_2O_3)_2^{3-}$ complex ion. The complex ion is linear, and the electron configuration of Ag^+ is $[Kr]4d^{10}$.

       c.   The reactant coordination compound is $[Cu(NH_3)_4]Cl_2$. The complex ion is $Cu(NH_3)_4^{2+}$, and the counter ions are Cl^- ions. The complex ion is tetrahedral (given in the question), and the electron configuration of Cu^{2+} is $[Ar]3d^9$. The product coordination compound is $[Cu(NH_3)_4]Cl$. The complex ion is $Cu(NH_3)_4^+$ with Cl^- counter ions. The complex ion is tetrahedral, and the electron configuration of Cu^+ is $[Ar]3d^{10}$.

11.   From Table 21.16, the red octahedral $Co(H_2O)_6^{2+}$ complex ion absorbs blue-green light ($\lambda \approx$ 490 nm), whereas the blue tetrahedral $CoCl_4^{2-}$ complex ion absorbs orange light ($\lambda \approx 600$ nm). Because tetrahedral complexes have a d-orbital splitting much less than octahedral complexes, one would expect the tetrahedral complex to have a smaller energy difference between split d orbitals. This translates into longer-wavelength light absorbed ($E = hc/\lambda$) for tetrahedral complex ions compared to octahedral complex ions. Information from Table 21.16 confirms this.

12. Co^{2+}: $[Ar]3d^7$; the corresponding d-orbital splitting diagram for tetrahedral Co^{2+} complexes is:

$$\underline{\uparrow} \qquad \underline{\uparrow} \qquad \underline{\uparrow}$$

$$\underline{\uparrow\downarrow} \qquad \underline{\uparrow\downarrow}$$
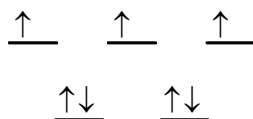
       All tetrahedral complexes are high spin since the d-orbital splitting is small. Ions with two or seven d electrons should give the most stable tetrahedral complexes because they have the greatest number of electrons in the lower-energy orbitals as compared with the number of electrons in the higher-energy orbitals.

13.   Linkage isomers differ in the way that the ligand bonds to the metal. SCN^- can bond through the sulfur or through the nitrogen atom. NO_2^- can bond through the nitrogen or through the oxygen atom. OCN^- can bond through the oxygen or through the nitrogen atom. N_3^-, $NH_2CH_2CH_2NH_2$, and I^- are not capable of linkage isomerism.

14. Cu^{2+}: $[Ar]3d^9$; Cu^+: $[Ar]3d^{10}$; Cu(II) is d^9 and Cu(I) is d^{10}. Color is a result of the electron transfer between split d orbitals. This cannot occur for the filled d orbitals in Cu(I). Cd^{2+}, like Cu^+, is also d^{10}. We would not expect $Cd(NH_3)_4Cl_2$ to be colored since the d orbitals are filled in this Cd^{2+} complex.

15. Sc^{3+} has no electrons in d orbitals. Ti^{3+} and V^{3+} have d electrons present. The color of transition metal complexes results from electron transfer between split d orbitals. If no d electrons are present, no electron transfer can occur, and the compounds are not colored.

16.   Metals are easily oxidized by oxygen and other substances to form the metal cations. Because of this, metals are found in nature combined with nonmetals such as oxygen, sulfur, and the halogens. These compounds are called ores. To recover and use the metals, we must separate them from their ores and reduce the metal ions. Then, because most metals are unsuitable for use in the pure state, we must form alloys with the metals in order to form materials having desirable properties.

Exercises

Transition Metals and Coordination Compounds

17.   a.   Ni: $[Ar]4s^2 3d^8$ b.   Cd: $[Kr]5s^2 4d^{10}$

        c.   Zr: $[Kr]5s^2 4d^2$ d.   Os: $[Xe]6s^2 4f^{14} 5d^6$

18.   Transition metal ions lose the s electrons before the d electrons.

        a. Ni^{2+}: $[Ar]3d^8$ b. Cd^{2+}: $[Kr]4d^{10}$

        c. Zr^{3+}: $[Kr]4d^1$; Zr^{4+}: $[Kr]$ d. Os^{2+}: $[Xe]4f^{14}5d^6$; Os^{3+}: $[Xe]4f^{14}5d^5$

19.   Transition metal ions lose the s electrons before the d electrons.

        a.   Ti: $[Ar]4s^2 3d^2$ b.   Re: $[Xe]6s^2 4f^{14} 5d^5$ c.   Ir: $[Xe]6s^2 4f^{14} 5d^7$

             Ti^{2+}: $[Ar]3d^2$ Re^{2+}: $[Xe]4f^{14} 5d^5$ Ir^{2+}: $[Xe]4f^{14} 5d^7$

             Ti^{4+}: $[Ar]$ or $[Ne]3s^2 3p^6$ Re^{3+}: $[Xe]4f^{14} 5d^4$ Ir^{3+}: $[Xe]4f^{14} 5d^6$

20.   Cr and Cu are exceptions to the normal filling order of electrons.

        a.   Cr: $[Ar]4s^1 3d^5$ b.   Cu: $[Ar]4s^1 3d^{10}$ c.   V: $[Ar]4s^2 3d^3$

             Cr^{2+}: $[Ar]3d^4$ Cu^+: $[Ar]3d^{10}$ V^{2+}: $[Ar]3d^3$

             Cr^{3+}: $[Ar]3d^3$ Cu^{2+}: $[Ar]3d^9$ V^{3+}: $[Ar]3d^2$

21.   a.   With K^+ and CN^- ions present, iron has a 3+ charge. Fe^{3+}: $[Ar]3d^5$

        b.   With a Cl^- ion and neutral NH_3 molecules present, silver has a 1+ charge. Ag^+: $[Kr]4d^{10}$

        c.   With Br^- ions and neutral H_2O molecules present, nickel has a 2+ charge. Ni^{2+}: $[Ar]3d^8$

        d.   With NO_2^- ions, an I^- ion, and neutral H_2O molecules present, chromium has a 3+ charge. Cr^{3+}: $[Ar]3d^3$

22.   a.   With NH_4^+ ions, Cl^- ions, and neutral H_2O molecules present, iron has a 2+ charge.
          Fe^{2+}: $[Ar]3d^6$

      b.   With I^- ions and neutral NH_3 and $NH_2CH_2CH_2NH_2$ molecules present, cobalt has a 2+
          charge. Co^{2+}: $[Ar]3d^7$

      c.   With Na^+ and F^- ions present, tantalum has a 5+ charge. Ta^{5+}: $[Xe]4f^{14}$ (expected)

      d.   Each platinum complex ion must have an overall charge if the two complex ions are
          counter ions to each. Knowing that platinum forms 2+ and 4+ charged ions, we can
          deduce that the six coordinate complex ion has a 4+ charged platinum ion and the four
          coordinate complex ion has a 2+ charged ion. With I^- ions and neutral NH_3 molecules
          present, the two complex ions are $[Pt(NH_3)_4I_2]^{2+}$ and $[PtI_4]^{2-}$.

          Pt^{2+}: $[Xe]4f^{14}5d^8$; Pt^{4+}: $[Xe]4f^{14}5d^6$
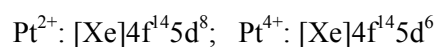
23.   a.   molybdenum(IV) sulfide; molybdenum(VI) oxide

      b. MoS_2, +4; MoO_3, +6; $(NH_4)_2Mo_2O_7$, +6; $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, +6

24.   a.   4 O atoms on faces $\times$ 1/2 O/face = 2 O atoms, 2 O atoms inside body; total: 4 O atoms

          8 Ti atoms on corners $\times$ 1/8 Ti/corner + 1 Ti atom/body center = 2 Ti atoms

          Formula of the unit cell is Ti_2O_4. The empirical formula is TiO_2.

          $\quad$ +4 –2 $\quad\quad$ 0 $\quad\quad$ 0 $\quad\quad\quad$ +4 –1 $\quad$ +4 –2 $\quad\quad$ +2 –2
      b.   2 TiO_2 + 3 C + 4 Cl_2 $\rightarrow$ 2 $TiCl_4$ + CO_2 + 2 CO; Cl is reduced, and C is oxidized.
          Cl_2 is the oxidizing agent, and C is the reducing agent.

          $\quad$ +4 –1 $\quad\quad$ 0 $\quad\quad$ +4 –2 $\quad\quad$ 0
          $TiCl_4$ + O_2 $\rightarrow$ TiO_2 + 2 Cl_2; O is reduced, and Cl is oxidized. O_2 is the oxidizing
          agent, and $TiCl_4$ is the reducing agent.

25.   The lanthanide elements are located just before the 5d transition metals. The lanthanide
      contraction is the steady decrease in the atomic radii of the lanthanide elements when going
      from left to right across the periodic table. As a result of the lanthanide contraction, the sizes
      of the 4d and 5d elements are very similar (see the following exercise). This leads to a
      greater similarity in the chemistry of the 4d and 5d elements in a given vertical group.

26.   Size also decreases going across a period. Sc and Ti and Y and Zr are adjacent elements.
      There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.

27. $CoCl_2(s)$ + 6 $H_2O(g)$ $\rightleftharpoons$ $CoCl_2\cdot6H_2O(s)$; if rain were imminent, there would be a lot of water
      vapor in the air causing the reaction to shift to the right.   The indicator would take on the
      color of $CoCl_2\cdot6H_2O$, pink.

28. H^+ + OH^- $\rightarrow$ H_2O; sodium hydroxide (NaOH) will react with the H^+ on the product side of
      the reaction. This effectively removes H^+ from the equilibrium, which will shift the reaction

to the right to produce more H^+ and CrO_4^{2-}. As more CrO_4^{2-} is produced, the solution turns yellow.

29.   Test tube 1: Added Cl^- reacts with Ag^+ to form a silver chloride precipitate. The net ionic equation is $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Test tube 2: Added NH_3 reacts with Ag^+ ions to form the soluble complex ion $Ag(NH_3)_2^+$. As this complex ion forms, Ag^+ is removed from solution, which causes the $AgCl(s)$ to dissolve. When enough NH_3 is added, all the silver chloride precipitate will dissolve. The equation is $AgCl(s) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$. Test tube 3: Added H^+ reacts with the weak base NH_3 to form NH_4^+. As NH_3 is removed from the $Ag(NH_3)_2^+$ complex ion equilibrium, Ag^+ ions are released to the solution that can then react with Cl^- to re-form $AgCl(s)$.   The equations are $Ag(NH_3)_2^+(aq) + 2\ H^+(aq) \rightarrow Ag^+(aq) + 2\ NH_4^+(aq)$ and $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$.

30. CN^- is a weak base, so OH^- ions are present that lead to precipitation of $Ni(OH)_2(s)$. As excess CN^- is added, the $Ni(CN)_4^{2-}$ complex ion forms. The two reactions are:

$Ni^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ni(OH)_2(s)$; the precipitate is $Ni(OH)_2(s)$.

$Ni(OH)_2(s) + 4\ CN^-(aq) \rightarrow Ni(CN)_4^{2-}(aq) + 2\ OH^-(aq)$; $Ni(CN)_4^{2-}$ is a soluble species.
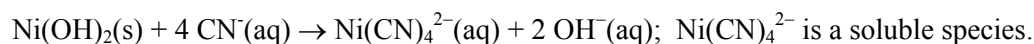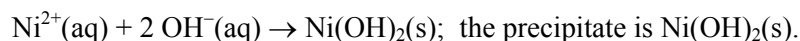
31.   Because each compound contains an octahedral complex ion, the formulas for the compounds are $[Co(NH_3)_6]I_3$, $[Pt(NH_3)_4I_2]I_2$, $Na_2[PtI_6]$, and $[Cr(NH_3)_4I_2]I$. Note that in some cases the I^- ions are ligands bound to the transition metal ion as required for a coordination number of 6, while in other cases the I^- ions are counter ions required to balance the charge of the complex ion. The $AgNO_3$ solution will only precipitate the I^- counter ions and will not precipitate the I^- ligands.   Therefore, 3 moles of AgI will precipitate per mole of $[Co(NH_3)_6]I_3$, 2 moles of AgI will precipitate per mole of $[Pt(NH_3)_4I_2]I_2$, 0 moles of AgI will precipitate per mole of $Na_2[PtI_6]$, and l mole of AgI will precipitate per mole of $[Cr(NH_3)_4I_2]I$.

32. $BaCl_2$ gives no precipitate, so SO_4^{2-} must be in the coordination sphere ($BaSO_4$ is insoluble). A precipitate with $AgNO_3$ means the Cl^- is not in the coordination sphere. Because there are only four ammonia molecules in the coordination sphere, SO_4^{2-} must be acting as a bidentate ligand. The structure is:
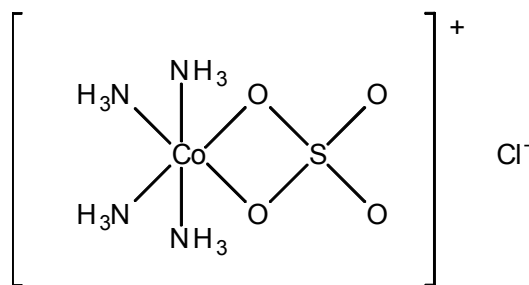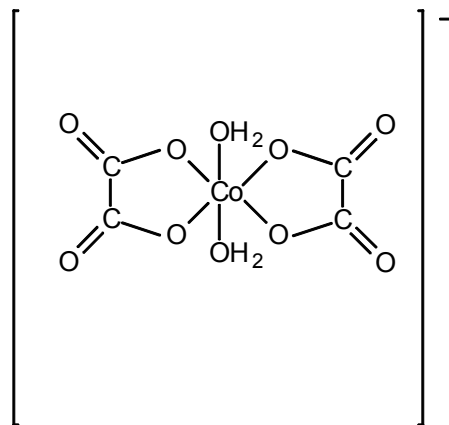

33.   To determine the oxidation state of the metal, you must know the charges of the various common ligands (see Table 21.13 of the text).

    a.   pentaamminechlororuthenium(III) ion   b.   hexacyanoferrate(II) ion

    c.   tris(ethylenediamine)manganese(II) ion   d.   pentaamminenitrocobalt(III) ion

34.   a.   tetracyanonicklate(II) ion   b.   tetraamminedichlorochromium(III) ion

      c.   tris(oxalato)ferrate(III) ion   d.   tetraaquadithiocyanatocobalt(III) ion

35.   a.   hexaamminecobalt(II) chloride   b.   hexaaquacobalt(III) iodide

      c.   potassium tetrachloroplatinate(II)   d.   potassium hexachloroplatinate(II)

      e.   pentaamminechlorocobalt(III) chloride   f.   triamminetrinitrocobalt(III)

36.   a.   pentaaquabromochromium(III) bromide   b.   sodium hexacyanocobaltate(III)

      c.   bis(ethylenediamine)dinitroiron(III) chloride   d.   tetraamminediiodoplatinum(IV) tetraiodoplatinate(II)

37.   a. $K_2[CoCl_4]$ b. $[Pt(H_2O)(CO)_3]Br_2$

      c. $Na_3[Fe(CN)_2(C_2O_4)_2]$ d. $[Cr(NH_3)_3Cl(H_2NCH_2CH_2NH_2)]I_2$

38.   a. $FeCl_4^-$ b. $[Ru(NH_3)_5H_2O]^{3+}$

      c. $[Cr(CO)_4(OH)_2]^+$ d. $[Pt(NH_3)Cl_3]^-$

39.   a.
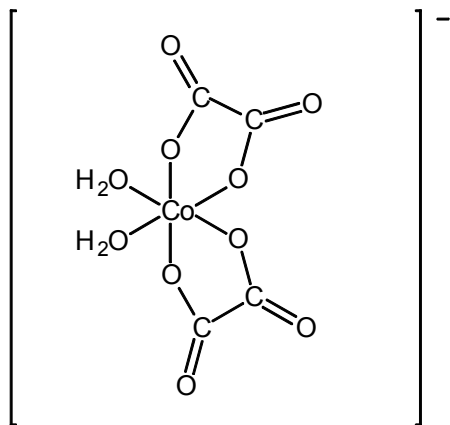
cis   trans

Note: $C_2O_4^{2-}$ is a bidentate ligand. Bidentate ligands bond to the metal at two positions that are 90° apart from each other in octahedral complexes. Bidentate ligands do not bond to the metal at positions 180° apart.

b.

cis   trans

c.

d.
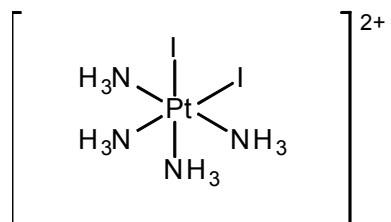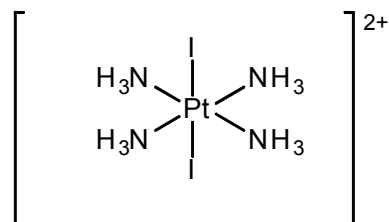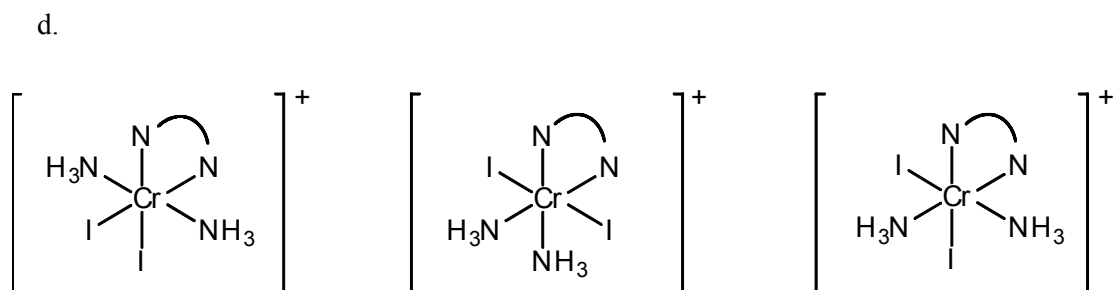
Note: en = N⌢N are abbreviations for the bidentate ligand ethylenediamine ($H_2NCH_2CH_2NH_2$).
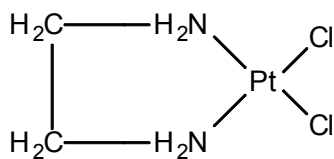
40.   a.   b.
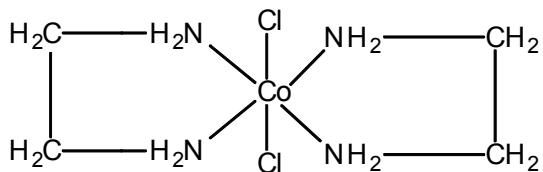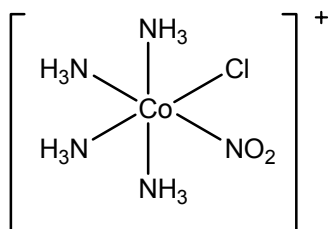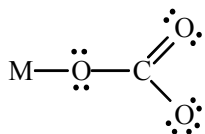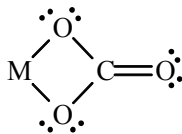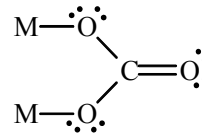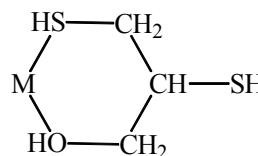

c.   d.
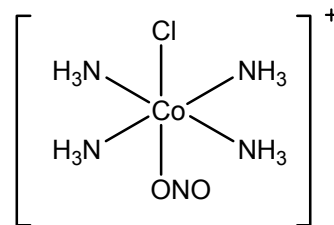
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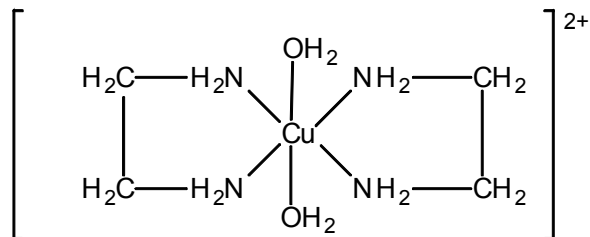
41.

monodentate	bidentate	bridging

42.   M = transition metal ion
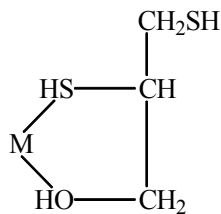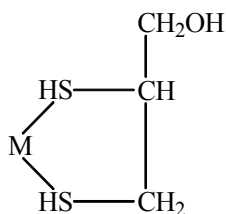
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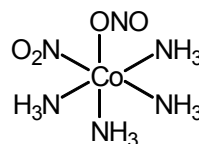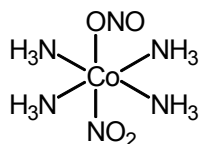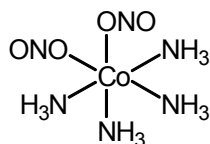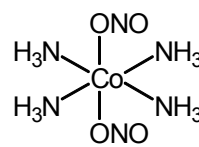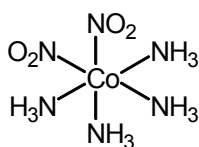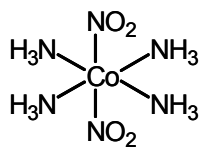
44.
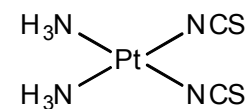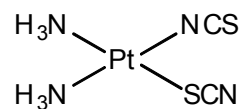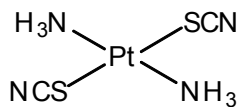
45.   Similar to the molecules discussed in Figures 21.16 and 21.17 of the text, $Cr(acac)_3$ and cis-$Cr(acac)_2(H_2O)_2$ are optically active.   The mirror images of these two complexes are nonsuperimposable. There is a plane of symmetry in trans-$Cr(acac)_2(H_2O)_2$, so it is not optically active. A molecule with a plane of symmetry is never optically active because the mirror images are always superimposable. A plane of symmetry is a plane through a molecule where one side reflects the other side of the molecule.

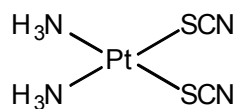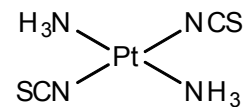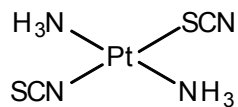46.   There are five geometrical isomers (labeled i-v). Only isomer v, where the CN^-, Br^-, and H_2O ligands are cis to each other, is optically active. The nonsuperimposable mirror image is shown for isomer v.
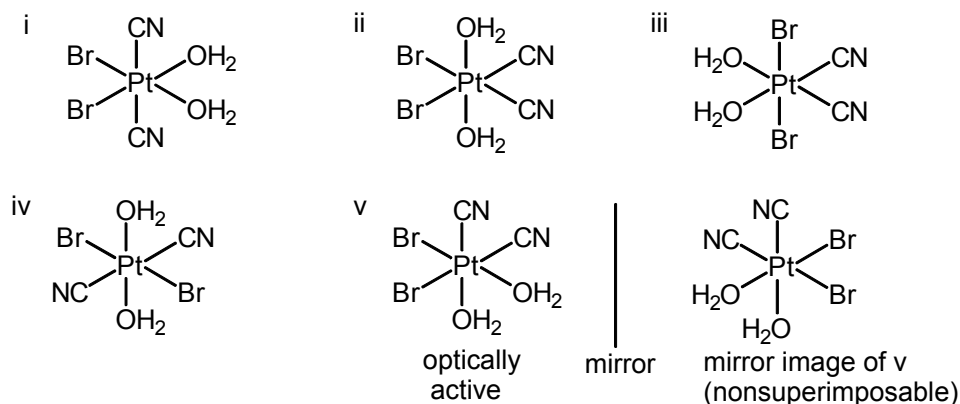
Bonding, Color, and Magnetism in Coordination Compounds

47.   a. Fe^{2+}: $[Ar]3d^6$
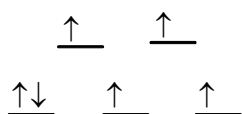
          High spin, small Δ Low spin, large Δ

        b. Fe^{3+}: $[Ar]3d^5$ c. Ni^{2+}: $[Ar]3d^8$
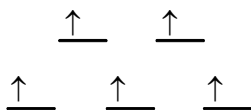
          High spin, small Δ
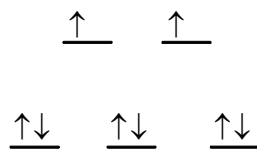
48.   a. Zn^{2+}: $[Ar]3d^{10}$

   ↑↓   ↑↓

   ↑↓   ↑↓   ↑↓

   b. Co^{2+}: $[Ar]3d^7$

                                                          ↑   __

   ↑   ↑

   ↑↓   ↑↓   ↑   ↑↓   ↑↓   ↑↓

   High spin, small Δ Low spin, large Δ
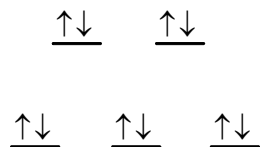
   c. Ti^{3+}: $[Ar]3d^1$

   __   __

   ↑   __   __

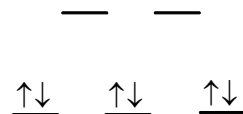49.   Because fluorine has a –1 charge as a ligand, chromium has a +2 oxidation state in CrF_6^{4-}. The electron configuration of Cr^{2+} is $[Ar]3d^4$. For four unpaired electrons, this must be a weak-field (high-spin) case where the splitting of the d-orbitals is small and the number of unpaired electrons is maximized. The crystal field diagram for this ion is:

   ↑   __

   ↑   ↑   ↑   small Δ
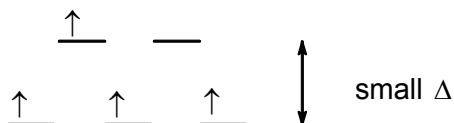
50. NH_3 and H_2O are neutral ligands, so the oxidation states of the metals are Co^{3+} and Fe^{2+}. Both have six d electrons ($[Ar]3d^6$). To explain the magnetic properties, we must have a strong-field for $Co(NH_3)_6^{3+}$ and a weak-field for $Fe(H_2O)_6^{2+}$.

   Co^{3+}: $[Ar]3d^6$ Fe^{2+}: $[Ar]3d^6$

   __   __   ↑   ↑

   ↑↓   ↑↓   ↑↓   large Δ ↑↓   ↑   ↑   small Δ
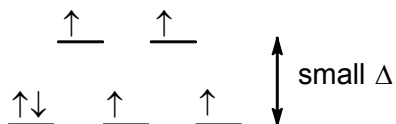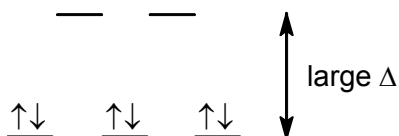
Only this splitting of d-orbitals gives a diamagnetic $Co(NH_3)_6^{3+}$ (no unpaired electrons) and a paramagnetic $Fe(H_2O)_6^{2+}$ (unpaired electrons present).

51.   To determine the crystal field diagrams, you need to determine the oxidation state of the transition metal, which can only be determined if you know the charges of the ligands (see Table 21.13). The electron configurations and the crystal field diagrams follow.

a. Ru^{2+}: $[Kr]4d^6$, no unpaired e⁻

     ___ ___

     ↑↓   ↑↓   ↑↓
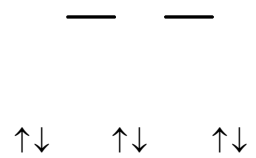
     Low spin, large Δ

b. Ni^{2+}: $[Ar]3d^8$, 2 unpaired e⁻

     ↑   ↑

     ↑↓   ↑↓   ↑↓
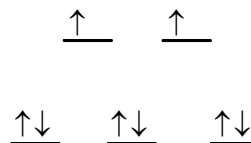
c. V^{3+}: $[Ar]3d^2$, 2 unpaired e⁻

     ___ ___

     ↑   ↑   ___
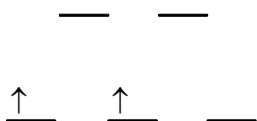
Note: Ni^{2+} must have 2 unpaired electrons, whether high-spin or low-spin, and V^{3+} must have 2 unpaired electrons, whether high-spin or low-spin.

52.   In both compounds, iron is in the +3 oxidation state with an electron configuration of $[Ar]3d^5$. Fe^{3+} complexes have one unpaired electron when a strong-field case and five unpaired electrons when a weak-field case. $Fe(CN)_6^{2-}$ is a strong-field case, and $Fe(SCN)_6^{3-}$ is a weak-field case. Therefore, cyanide (CN⁻) is a stronger-field ligand than thiocyanate (SCN⁻).

53.   All have octahedral Co^{3+} ions, so the difference in d orbital splitting and the wavelength of light absorbed only depends on the ligands. From the spectrochemical series, the order of the ligands from strongest to weakest field is CN⁻ > en > H_2O > I⁻. The strongest-field ligand produces the greatest d-orbital splitting (Δ) and will absorb light having the smallest wavelength. The weakest-field ligand produces the smallest Δ and absorbs light having the longest wavelength. The order is

     $Co(CN)_6^{3-}$ < $Co(en)_3^{3+}$ < $Co(H_2O)_6^{3+}$ < CoI_6^{3-}
     shortest λ   longest λ
     absorbed   absorbed
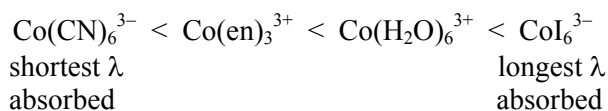
54.   Replacement of water ligands by ammonia ligands resulted in shorter wavelengths of light being absorbed. Energy and wavelength are inversely related, so the presence of the NH_3 ligands resulted in a larger d-orbital splitting (larger Δ). Therefore, NH_3 is a stronger-field ligand than H_2O.

55.   From Table 21.16 of the text, the violet complex ion absorbs yellow-green light ($\lambda \approx 570$ nm), the yellow complex ion absorbs blue light ($\lambda \approx 450$ nm), and the green complex ion absorbs red light ($\lambda \approx 650$ nm). The spectrochemical series shows that NH_3 is a stronger-field ligand than H_2O, which is a stronger-field ligand than Cl^-. Therefore, $Cr(NH_3)_6^{3+}$ will have the largest d-orbital splitting and will absorb the lowest-wavelength electromagnetic radiation ($\lambda \approx 450$ nm) since energy and wavelength are inversely related ($\lambda = hc/E$). Thus the yellow solution contains the $Cr(NH_3)_6^{3+}$ complex ion. Similarly, we would expect the $Cr(H_2O)_4Cl_2^+$ complex ion to have the smallest d-orbital splitting since it contains the weakest-field ligands. The green solution with the longest wavelength of absorbed light contains the $Cr(H_2O)_4Cl_2^+$ complex ion. This leaves the violet solution, which contains the $Cr(H_2O)_6^{3+}$ complex ion. This makes sense because we would expect $Cr(H_2O)_6^{3+}$ to absorb light of a wavelength between that of $Cr(NH_3)_6^{3+}$ and $Cr(H_2O)_4Cl_2^+$.

56.   All these complex ions contain Co^{3+} bound to different ligands, so the difference in d-orbital splitting for each complex ion is due to the difference in ligands. The spectrochemical series indicates that CN^- is a stronger-field ligand than NH_3 which is a stronger-field ligand than F^-. Therefore, $Co(CN)_6^{3-}$ will have the largest d-orbital splitting and will absorb the lowest-wavelength electromagnetic radiation ($\lambda = 290$ nm) since energy and wavelength are inversely related ($\lambda = hc/E$). $Co(NH_3)_6^{3+}$ will absorb 440-nm electromagnetic radiation, while CoF_6^{3-} will absorb the longest-wavelength electromagnetic radiation ($\lambda = 770$ nm) since F^- is the weakest-field ligand present.

57. $CoBr_6^{4-}$ has an octahedral structure, and $CoBr_4^{2-}$ has a tetrahedral structure (as do most Co^{2+} complexes with four ligands). Coordination complexes absorb electromagnetic radiation (EMR) of energy equal to the energy difference between the split d-orbitals. Because the tetrahedral d-orbital splitting is less than one-half the octahedral d-orbital splitting, tetrahedral complexes will absorb lower energy EMR, which corresponds to longer-wavelength EMR ($E = hc/\lambda$). Therefore, $CoBr_6^{2-}$ will absorb EMR having a wavelength shorter than 3.4×10^{-6} m.

58.   In both complexes, nickel is in the +2 oxidation state: Ni^{2+}: $[Ar]3d^8$. The differences in unpaired electrons must be due to differences in molecular structure. $NiCl_4^{2-}$ is a tetrahedral complex, and $Ni(CN)_4^{2-}$ is a square planar complex. The corresponding d-orbital splitting diagrams are:
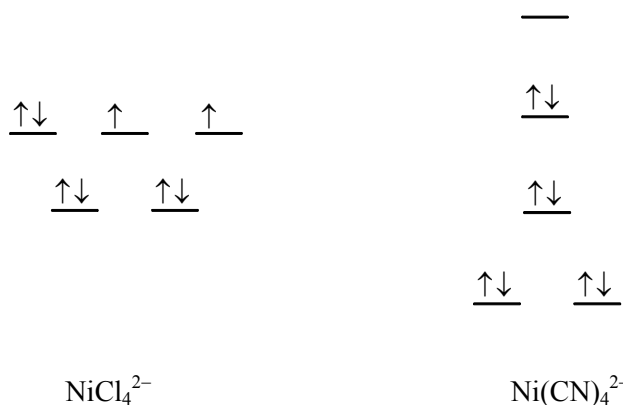
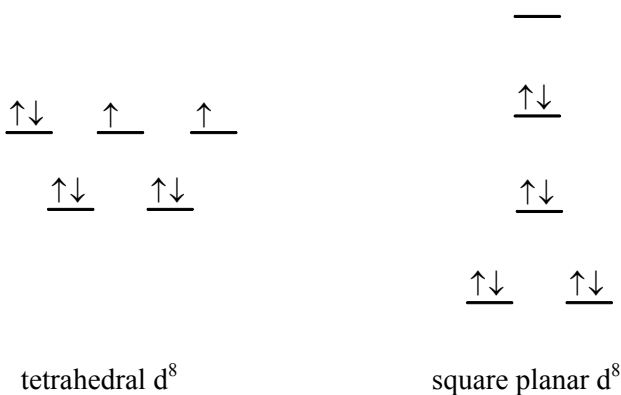59.   Because the ligands are Cl^-, iron is in the +3 oxidation state. Fe^{3+}: $[Ar]3d^5$

$\underline{\uparrow} \quad \underline{\uparrow} \quad \underline{\uparrow}$

$\underline{\uparrow} \quad \underline{\uparrow}$
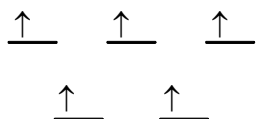
Because all tetrahedral complexes are high spin, there are 5 unpaired electrons in $FeCl_4^-$.

60.   Pd is in the +2 oxidation state in $PdCl_4^{2-}$; Pd^{2+}: $[Kr]4d^8$. If $PdCl_4^{2-}$ were a tetrahedral complex, then it would have 2 unpaired electrons and would be paramagnetic (see diagram below). Instead, $PdCl_4^{2-}$ has a square planar molecular structure with the d-orbital splitting diagram also shown below. Note that all electrons are paired in the square planar diagram; this explains the diamagnetic properties of $PdCl_4^{2-}$.

$\underline{}$

$\underline{\uparrow\downarrow} \quad \underline{\uparrow} \quad \underline{\uparrow}$ $\underline{\uparrow\downarrow}$

$\underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$

$\underline{\uparrow\downarrow} \quad \underline{\uparrow\downarrow}$

tetrahedral d^8 square planar d^8

Metallurgy

61.   a.   To avoid fractions, let's first calculate ΔH for the reaction:

6 FeO(s) + 6 CO(g) → 6 Fe(s) + 6 CO$_2$(g)

6 FeO + 2 CO$_2$ → 2 Fe$_3$O$_4$ + 2 CO	$\Delta H° = -2(18 \text{ kJ})$
2 Fe$_3$O$_4$ + CO$_2$ → 3 Fe$_2$O$_3$ + CO	$\Delta H° = -(-39 \text{ kJ})$
3 Fe$_2$O$_3$ + 9 CO → 6 Fe + 9 CO$_2$	$\Delta H° = 3(-23 \text{ kJ})$

6 FeO(s) + 6 CO(g) → 6 Fe(s) + 6 CO$_2$(g) $\Delta H° = -66$ kJ
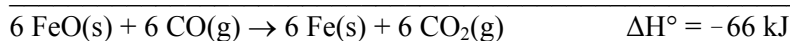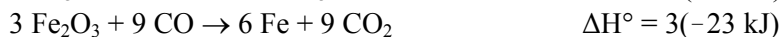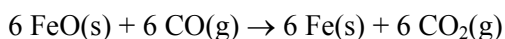
So for: FeO(s) + CO(g) → Fe(s) + CO$_2$(g) $\Delta H° = \dfrac{-66\,\text{kJ}}{6} = -11$ kJ

b. $\Delta H° = 2(-110.5 \text{ kJ}) - (-393.5 \text{ kJ} + 0) = 172.5$ kJ

$\Delta S° = 2(198 \text{ J/K}) - (214 \text{ J/K} + 6 \text{ J/K}) = 176$ J/K

$\Delta G° = \Delta H° - T\Delta S°$, $\Delta G° = 0$ when $T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{172.5\,\text{kJ}}{0.176\,\text{kJ}/\text{K}} = 980.$ K

Due to the favorable $\Delta S°$ term, this reaction is spontaneous at T > 980. K. From Figure 21.36 of the text, this reaction takes place in the blast furnace at temperatures greater than 980. K, as required by thermodynamics.

62.   a. $\Delta H° = 2(-1117) + (-393.5) - [3(-826) + (-110.5)] = -39$ kJ

$\Delta S° = 2(146) + 214 - [3(90.) + 198] = 38$ J/K

b. $\Delta G° = \Delta H° - T\Delta S°$;   T = 800. + 273 = 1073 K

$\Delta G° = -39$ kJ $- 1073$ K$(0.038$ kJ/K$) = -39$ kJ $- 41$ kJ $= -80.$ kJ

63. Fe_2O_3: iron has a +3 oxidation state; Fe_3O_4: iron has a +8/3 oxidation state. The three iron ions in Fe_3O_4 must have a total charge of +8. The only combination that works is to have two Fe^{3+} ions and one Fe^{2+} ion per formula unit. This makes sense from the other formula for magnetite, $FeO \cdot Fe_2O_3$. FeO has an Fe^{2+} ion, and Fe_2O_3 has two Fe^{3+} ions.

64. $3\ Fe + C \rightarrow Fe_3C$; $\Delta H° = 21 - [3(0) + 0] = 21$ kJ; $\Delta S° = 108 - [3(27) + 6] = 21$ J/K

$\Delta G° = \Delta H° - T\Delta S°$; when $\Delta H°$ and $\Delta S°$ are both positive, the reaction is spontaneous at high temperatures, where the favorable $\Delta S°$ term becomes dominant. Thus, to incorporate carbon into steel, high temperatures are needed for thermodynamic reasons but will also be beneficial for kinetic reasons (as the temperature increases, the rate of the reaction will increase). The relative amount of Fe_3C (cementite) that remains in the steel depends on the cooling process. If the steel is cooled slowly, there is time for the equilibrium to shift back to the left; small crystals of carbon form, giving a relatively ductile steel. If cooling is rapid, there is not enough time for the equilibrium to shift back to the left; Fe_3C is still present in the steel, and the steel is more brittle. Which cooling process occurs depends on the desired properties of the steel. The process of tempering fine-tunes the steel to the desired properties by repeated heating and cooling.

65.   Review Section 18.1 for balancing reactions in basic solution by the half-reaction method.

$$(2\ CN^- + Ag \rightarrow Ag(CN)^{2-} + e^-) \times 4$$
$$4\ e^- + O_2 + 4\ H^+ \rightarrow 2\ H_2O$$

$$\overline{8\ CN^- + 4\ Ag + O_2 + 4\ H^+ \rightarrow 4\ Ag(CN)_2^- + 2\ H_2O}$$
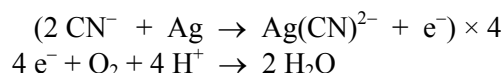
Adding 4 OH^- to both sides and crossing off 2 H_2O on both sides of the equation gives the balanced equation:

$$8\ CN^-(aq) + 4\ Ag(s) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ Ag(CN)_2^-(aq) + 4\ OH^-(aq)$$

66. $Mn + HNO_3 \rightarrow Mn^{2+} + NO_2$

$$Mn \rightarrow Mn^{2+} + 2\ e^- \qquad\qquad HNO_3 \rightarrow NO_2$$
$$HNO_3 \rightarrow NO_2 + H_2O$$
$$(e^- + H^+ + HNO_3 \rightarrow NO_2 + H_2O) \times 2$$

$$Mn \rightarrow Mn^{2+} + 2\ e^-$$
$$2\ e^- + 2\ H^+ + 2\ HNO_3 \rightarrow 2\ NO_2 + 2\ H_2O$$

$$2\ H^+(aq) + Mn(s) + 2\ HNO_3(aq) \rightarrow Mn^{2+}(aq) + 2\ NO_2(g) + 2\ H_2O(l)$$

$$Mn^{2+} + IO_4^- \rightarrow MnO_4^- + IO_3^-$$

$$(4\ H_2O + Mn^{2+} \rightarrow MnO_4^- + 8\ H^+ + 5\ e^-) \times 2 \qquad\qquad (2\ e^- + 2\ H^+ + IO_4^- \rightarrow IO_3^- + H_2O) \times 5$$

$$8\ H_2O + 2\ Mn^{2+} \rightarrow 2\ MnO_4^- + 16\ H^+ + 10\ e^-$$
$$10\ e^- + 10\ H^+ + 5\ IO_4^- \rightarrow 5\ IO_3^- + 5\ H_2O$$

$$3\ H_2O(l) + 2\ Mn^{2+}(aq) + 5\ IO_4^-(aq) \rightarrow 2\ MnO_4^-(aq) + 5\ IO_3^-(aq) + 6\ H^+(aq)$$
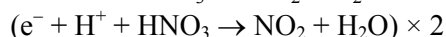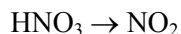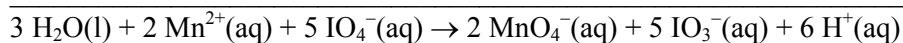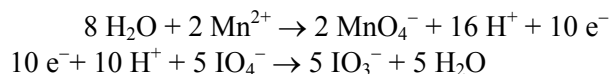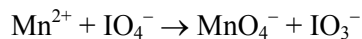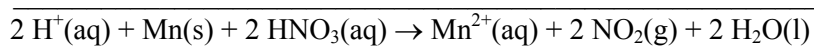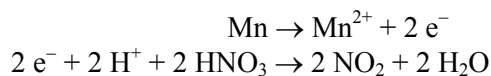
Connecting to Biochemistry

67.   The complex ion is $PtCl_4^{2-}$, which is composed of Pt^{2+} and four Cl^- ligands. Pt^{2+}:
       $[Xe]4f^{14}5d^8$. With square planar geometry, geometric isomerism is possible. Cisplatin is the
       cis isomer of the compound and has the following structural formula.
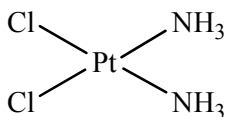
68.
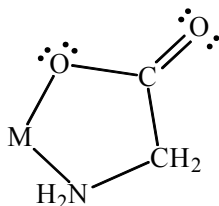
M = transition metal ion
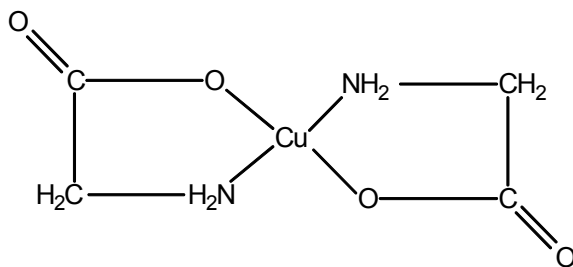
and
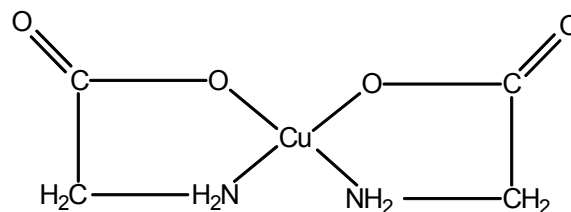
69.   a. 2; forms bonds through the lone pairs on the two oxygen atoms.

       b. 3; forms bonds through the lone pairs on the three nitrogen atoms.

c. 4; forms bonds through the two nitrogen atoms and the two oxygen atoms.

d. 4; forms bonds through the four nitrogen atoms.

70. a. $Ru(phen)_3^{2+}$ exhibits optical isomerism [similar to $Co(en)_3^{3+}$ in Figure 21.16 of the text].

b. Ru^{2+}: $[Kr]4d^6$; because there are no unpaired electrons, Ru^{2+} is a strong-field (low-spin) case.

large Δ
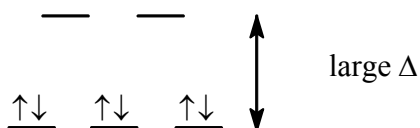
71. a. In the lungs, there is a lot of O_2, and the equilibrium favors $Hb(O_2)_4$. In the cells, there is a deficiency of O_2, and the equilibrium favors HbH_4^{4+}.

b. $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$; H_2CO_3 is a weak acid, $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$. Removing CO_2 essentially decreases H^+. $Hb(O_2)_4$ is then favored, and O_2 is not released by hemoglobin in the cells. Breathing into a paper bag increases $[CO_2]$ in the blood, thus increasing $[H^+]$, which shifts the reaction left.

c. As CO_2 builds up in the blood, and it becomes too acidic, driving the equilibrium to the left. Hemoglobin can't bind O_2 as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.

72. CN^- and CO form much stronger complexes with Fe^{2+} than O_2. Thus O_2 cannot be transported by hemoglobin in the presence of CN^- or CO because the binding sites prefer the toxic CN^- and CO ligands.
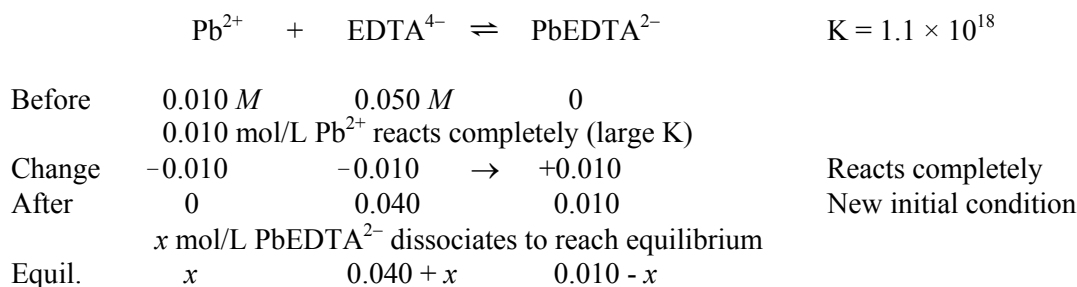
73. At high altitudes, the oxygen content of air is lower, so less oxyhemoglobin is formed, which diminishes the transport of oxygen in the blood. A serious illness called high-altitude sickness can result from the decrease of O_2 in the blood. High-altitude acclimatization is the phenomenon that occurs in the human body in response to the lower amounts of oxyhemoglobin in the blood. This response is to produce more hemoglobin and hence, increase the oxyhemoglobin in the blood. High-altitude acclimatization takes several weeks to take hold for people moving from lower altitudes to higher altitudes.

74. We need to calculate the Pb^{2+} concentration in equilibrium with $EDTA^{4-}$. Because K is large for the formation of $PbEDTA^{2-}$, let the reaction go to completion; then solve an equilibrium problem to get the Pb^{2+} concentration.

$$Pb^{2+} \quad + \quad EDTA^{4-} \rightleftharpoons PbEDTA^{2-} \qquad\qquad K = 1.1 \times 10^{18}$$

	Pb^{2+}	$EDTA^{4-}$	$PbEDTA^{2-}$	
Before	0.010 M	0.050 M	0	
	0.010 mol/L Pb^{2+} reacts completely (large K)			
Change	-0.010	$-0.010 \rightarrow$	$+0.010$	Reacts completely
After	0	0.040	0.010	New initial condition
	x mol/L $PbEDTA^{2-}$ dissociates to reach equilibrium			
Equil.	x	$0.040 + x$	$0.010 - x$	

$$1.1 \times 10^{18} = \frac{(0.010 - x)}{(x)(0.040 + x)} \approx \frac{(0.010)}{x(0.040)}, \quad x = [Pb^{2+}] = 2.3 \times 10^{-19} \, M; \quad \text{assumptions good.}$$

Now calculate the solubility quotient for $Pb(OH)_2$ to see if precipitation occurs. The concentration of OH^- is 0.10 M because we have a solution buffered at pH = 13.00.

$$Q = [Pb^{2+}]_0[OH^-]_0^{\,2} = (2.3 \times 10^{-19})(0.10)^2 = 2.3 \times 10^{-21} < K_{sp} \, (1.2 \times 10^{-15})$$

$Pb(OH)_2(s)$ will not form because Q is less than K_{sp}.

Additional Exercises

75. $0.112 \text{ g Eu}_2\text{O}_3 \times \dfrac{304.0 \text{ g Eu}}{352.0 \text{ g Eu}_2\text{O}_3} = 0.0967 \text{ g Eu}; \quad \text{mass \% Eu} = \dfrac{0.0967 \text{ g}}{0.286 \text{ g}} \times 100 = 33.8\% \text{ Eu}$

Mass % O = $100.00 - (33.8 + 40.1 + 4.71) = 21.4\%$ O

Assuming 100.00 g of compound:

$33.8 \text{ g Eu} \times \dfrac{1 \text{ mol}}{152.0 \text{ g}} = 0.222 \text{ mol Eu}; \quad 40.1 \text{ g C} \times \dfrac{1 \text{ mol}}{12.01 \text{ g}} = 3.34 \text{ mol C}$

$4.71 \text{ g H} \times \dfrac{1 \text{ mol}}{1.008 \text{ g}} = 4.67 \text{ mol H}; \quad 21.4 \text{ g O} \times \dfrac{1 \text{ mol}}{16.00 \text{ g}} = 1.34 \text{ mol O}$

$\dfrac{3.34}{0.222} = 15.0, \quad \dfrac{4.67}{0.222} = 21.0, \quad \dfrac{1.34}{0.222} = 6.04$

The molecular formula is $EuC_{15}H_{21}O_6$. Because each $acac^-$ ligand has a formula of $C_5H_7O_2^-$, an abbreviated molecular formula is $Eu(acac)_3$.

76. $0.308 \text{ g AgCl} \times \dfrac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} = 0.0761 \text{ g Cl}; \quad \% \text{ Cl} = \dfrac{0.0761 \text{ g}}{0.256 \text{ g}} \times 100 = 29.7\% \text{ Cl}$

Cobalt(III) oxide, Co_2O_3: $2(58.93) + 3(16.00) = 165.86$ g/mol

$0.145 \text{ g Co}_2\text{O}_3 \times \dfrac{117.86 \text{ g Co}}{165.86 \text{ g Co}_2\text{O}_3} = 0.103 \text{ g Co}; \quad \% \text{ Co} = \dfrac{0.103 \text{ g}}{0.416 \text{ g}} \times 100 = 24.8\% \text{ Co}$
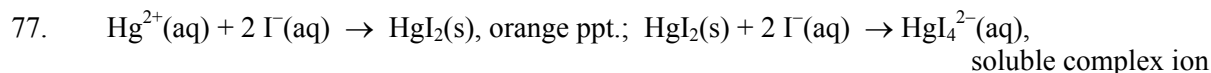
The remainder, $100.0 - (29.7 + 24.8) = 45.5\%$, is water.
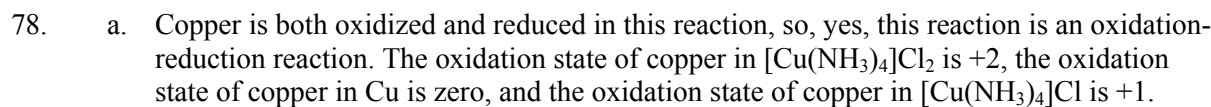
Out of 100.0 g of compound, there are:

$24.8 \text{ g Co} \times \dfrac{1 \text{ mol Co}}{58.93 \text{ g Co}} = 0.421 \text{ mol Co}; \quad 29.7 \text{ g Cl} \times \dfrac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.838 \text{ mol Cl}$

$$45.5 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g H}_2\text{O}} = 2.52 \text{ mol H}_2\text{O}$$

Dividing all results by 0.421, we get $CoCl_2 \bullet 6H_2O$ for the formula. The oxidation state of cobalt is +2 because the chloride counter ions have a 1– charge. Because the waters are the ligands, the formula of the compound is $[Co(H_2O)_6]Cl_2$.

77. $Hg^{2+}(aq) + 2 \text{ I}^-(aq) \rightarrow HgI_2(s)$, orange ppt.; $HgI_2(s) + 2 \text{ I}^-(aq) \rightarrow HgI_4^{2-}(aq)$,

<div align="right">soluble complex ion</div>

Hg^{2+} is a d^{10} ion. Color is the result of electron transfer between split d orbitals. Electron transfer cannot occur for the filled d orbitals in Hg^{2+}. Therefore, we would not expect Hg^{2+} complex ions to form colored solutions.

78.   a.   Copper is both oxidized and reduced in this reaction, so, yes, this reaction is an oxidation-reduction reaction. The oxidation state of copper in $[Cu(NH_3)_4]Cl_2$ is +2, the oxidation state of copper in Cu is zero, and the oxidation state of copper in $[Cu(NH_3)_4]Cl$ is +1.
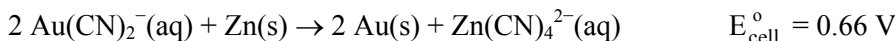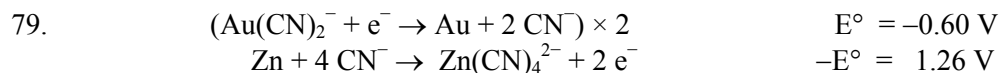
        b.   Total mass of copper used:

$$10,000 \text{ boards} \times \frac{(8.0 \text{ cm} \times 16.0 \text{ cm} \times 0.060 \text{ cm})}{\text{board}} \times \frac{8.96 \text{ g}}{\text{cm}^3} = 6.9 \times 10^5 \text{ g Cu}$$

Amount of Cu to be recovered = $0.80 \times 6.9 \times 10^5 \text{ g} = 5.5 \times 10^5 \text{ g Cu}$

$$5.5 \times 10^5 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{1 \text{ mol } [Cu(NH_3)_4]Cl_2}{\text{mol Cu}} \times \frac{202.59 \text{ g } [Cu(NH_3)_4]Cl_2}{\text{mol } [Cu(NH_3)_4]Cl_2}$$

$$= 1.8 \times 10^6 \text{ g } [Cu(NH_3)_4]Cl_2$$

$$5.5 \times 10^5 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{4 \text{ mol NH}_3}{\text{mol Cu}} \times \frac{17.03 \text{ g NH}_3}{\text{mol NH}_3} = 5.9 \times 10^5 \text{ g NH}_3$$

79.

$(Au(CN)_2^- + e^- \rightarrow Au + 2 \text{ CN}^-) \times 2$	$E° = -0.60 \text{ V}$
$Zn + 4 \text{ CN}^- \rightarrow Zn(CN)_4^{2-} + 2 \text{ e}^-$	$-E° = 1.26 \text{ V}$

<hr>

$2 \text{ Au(CN)}_2^-(aq) + Zn(s) \rightarrow 2 \text{ Au}(s) + Zn(CN)_4^{2-}(aq)$	$E°_{cell} = 0.66 \text{ V}$

$$\Delta G° = -nFE°_{cell} = -(2 \text{ mol e}^-)(96,485 \text{ C/mol e}^-)(0.66 \text{ J/C}) = -1.3 \times 10^5 \text{ J} = -130 \text{ kJ}$$

$$E° = \frac{0.0591}{n} \log K, \quad \log K = \frac{nE°}{0.0591} = \frac{2(0.66)}{0.0591} = 22.34, \quad K = 10^{22.34} = 2.2 \times 10^{22}$$

Note: We carried extra significant figures to determine K.

80.   a.   In the following structures, we omitted the 4 NH_3 ligands coordinated to the outside cobalt atoms.

mirror
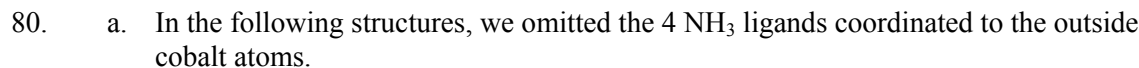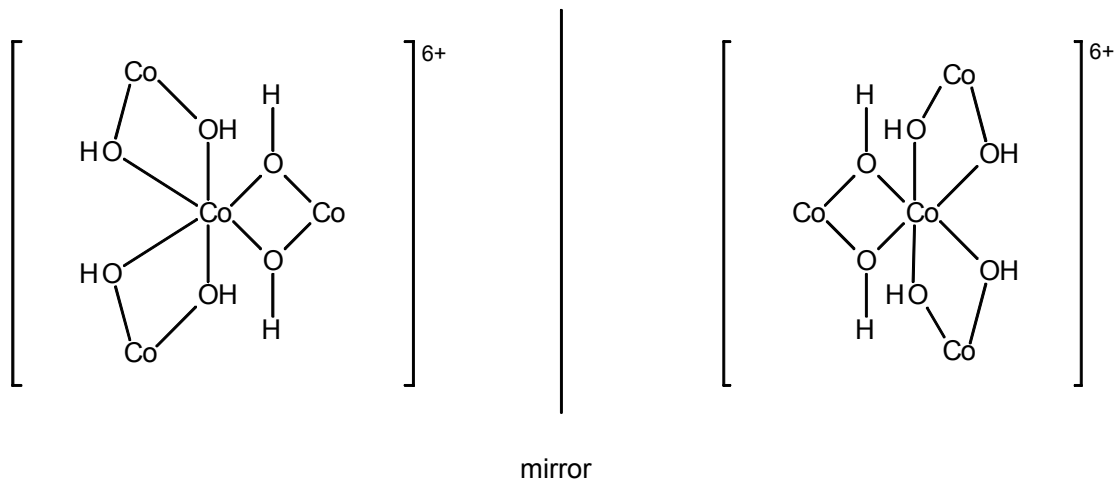
b. All are Co(III). The three "ligands" each contain 2 OH^- and 4 NH_3 groups. If each cobalt is in the +3 oxidation state, then each ligand has a +1 overall charge. The 3+ charge from the three ligands, along with the 3+ charge of the central cobalt atom, gives the overall complex a +6 charge. This is balanced by the 6– charge of the six Cl^- ions.

c. Co^{3+}: $[Ar]3d^6$; there are zero unpaired electrons if a low-spin (strong-field) case.
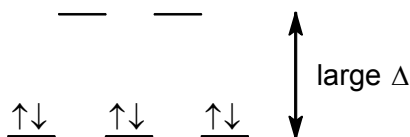
81.   There are four geometrical isomers (labeled i-iv). Isomers iii and iv are optically active, and the nonsuperimposable mirror images are shown.

iii.

optically active   mirror   mirror image of iii
(nonsuperimposable)

iv.

optically active   mirror   mirror image of iv
(nonsuperimposable)
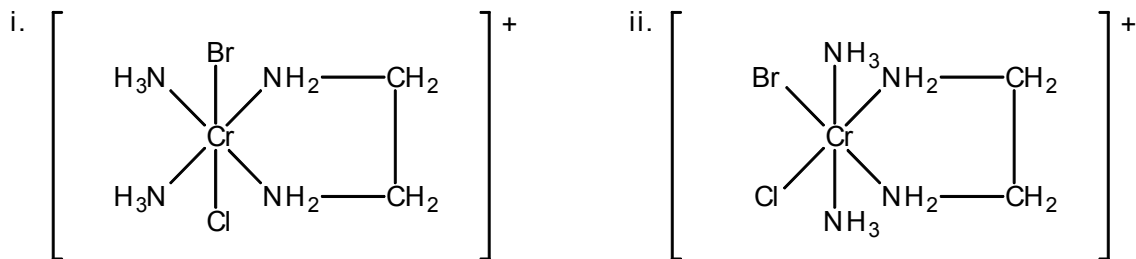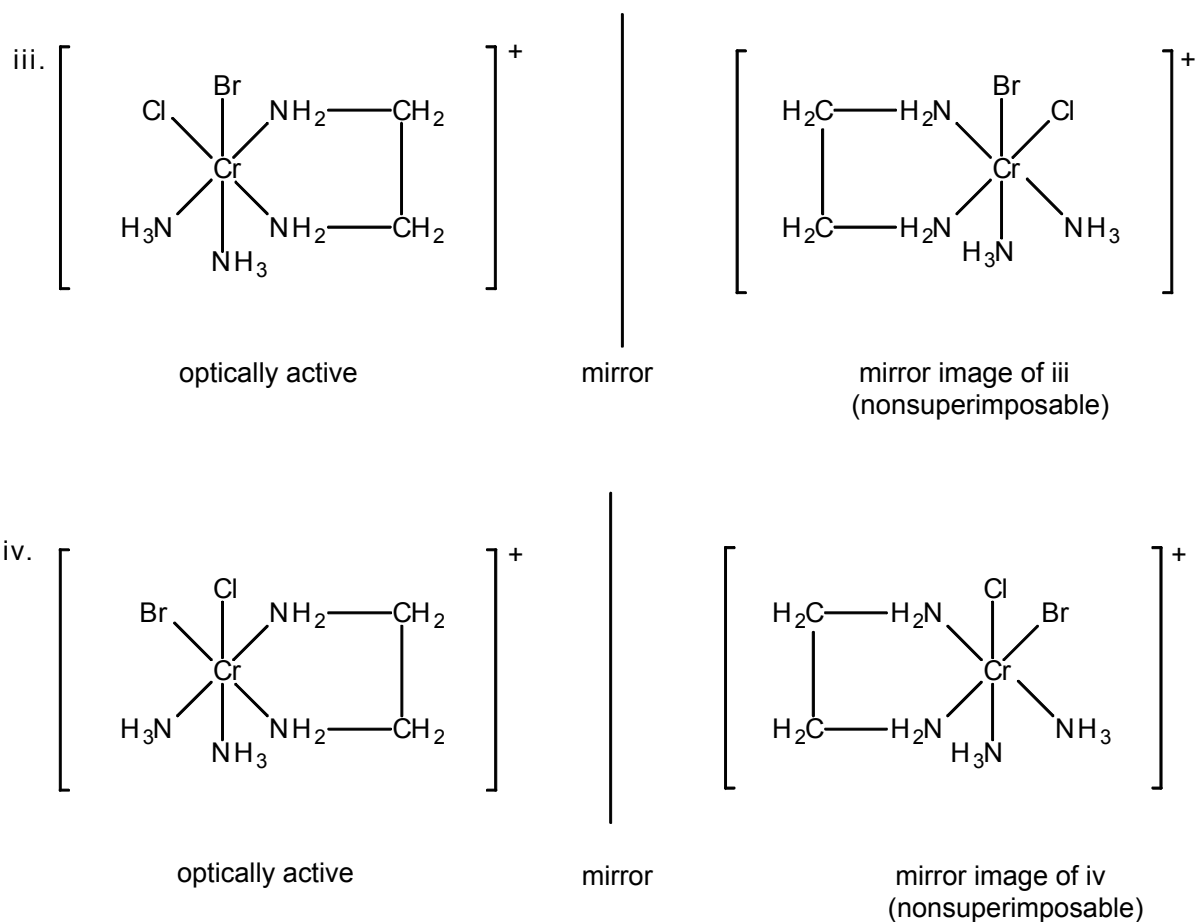
82.   a.   Be(tfa)$_2$ exhibits optical isomerism. A representation for the tetrahedral optical isomers is:

mirror
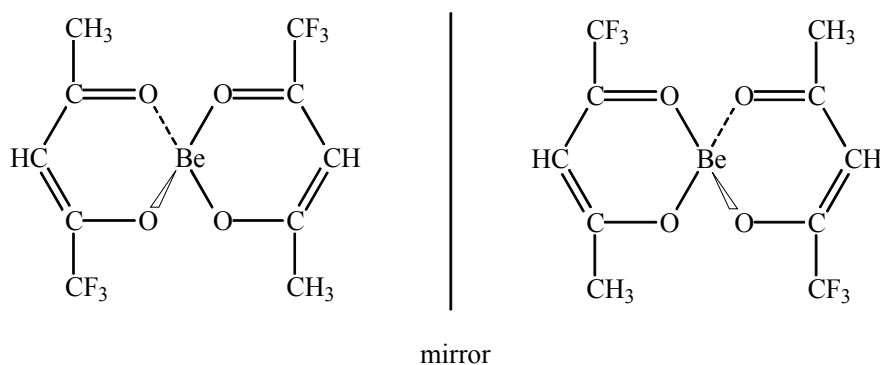
Note: The dotted line indicates a bond pointing into the plane of the paper, and the wedge indicates a bond pointing out of the plane of the paper.

b.   Square planar Cu(tfa)$_2$ molecules exhibit geometric isomerism. In one geometric isomer, the CF$_3$ groups are cis to each other, and in the other isomer, the CF$_3$ groups are trans.
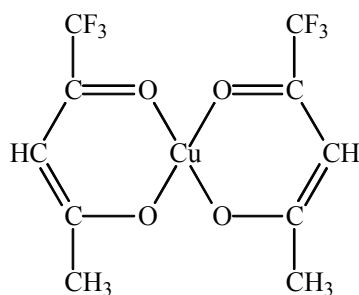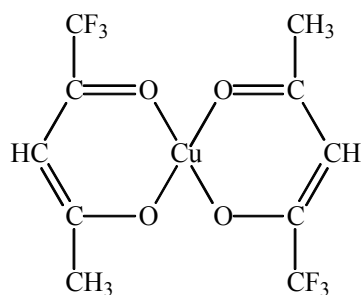
            cis   trans

83.   Octahedral Cr^{2+} complexes should be used. Cr^{2+}: $[Ar]3d^4$; high-spin (weak-field) Cr^{2+} com-
      plexes have 4 unpaired electrons, and low-spin (strong-field) Cr^{2+} complexes have 2 unpaired
      electrons. Ni^{2+}: $[Ar]3d^8$; octahedral Ni^{2+} complexes will always have 2 unpaired electrons,
      whether high or low spin. Therefore, Ni^{2+} complexes cannot be used to distinguish weak-
      from strong-field ligands by examining magnetic properties. Alternatively, the ligand field
      strengths can be measured using visible spectra. Either Cr^{2+} or Ni^{2+} complexes can be used
      for this method.

84.   a.   sodium tris(oxalato)nickelate(II)   b. potassium tetrachlorocobaltate(II)

      c.   tetraamminecopper(II) sulfate

      d.   chlorobis(ethylenediamine)thiocyanatocobalt(III) chloride

85.   a. $[Co(C_5H_5N)_6]Cl_3$ b. $[Cr(NH_3)_5I]I_2$ c. $[Ni(NH_2CH_2CH_2NH_2)_3]Br_2$

      d. $K_2[Ni(CN)_4]$ e. $[Pt(NH_3)_4Cl_2][PtCl_4]$

86.   a. $Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$

      Initial   0.10 M   0   ~0
      Equil.   0.10 − x   x   x

      $$K_a = \frac{[Fe(H_2O)_5(OH)^{2+}][H_3O^+]}{[Fe(H_2O)_6^{3+}]} = 6.0 \times 10^{-3} = \frac{x^2}{0.10-x} \approx \frac{x^2}{0.10}$$
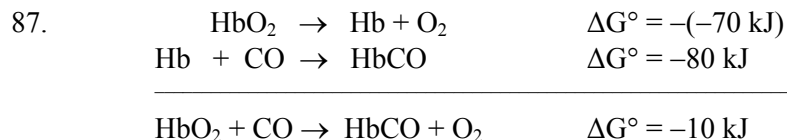
      $x = 2.4 \times 10^{-2}$; assumption is poor (x is 24% of 0.10). Using successive approximations:

 $$\frac{x^2}{0.10 - 0.024} = 6.0 \times 10^{-3}, \ x = 0.021$$

      $$\frac{x^2}{0.10 - 0.021} = 6.0 \times 10^{-3}, \ x = 0.022; \quad \frac{x^2}{0.10 - 0.022} = 6.0 \times 10^{-3}, \ x = 0.022$$

      $x = [H^+] = 0.022 \ M$; pH = 1.66

b. Because of the lower charge, $Fe^{2+}(aq)$ will not be as strong an acid as $Fe^{3+}(aq)$. A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate.

87.

$$HbO_2 \rightarrow Hb + O_2 \qquad \Delta G° = -(-70 \text{ kJ})$$
$$Hb + CO \rightarrow HbCO \qquad \Delta G° = -80 \text{ kJ}$$

$$HbO_2 + CO \rightarrow HbCO + O_2 \qquad \Delta G° = -10 \text{ kJ}$$

$$\Delta G° = -RT \ln K, \quad K = \left(\frac{-\Delta G°}{RT}\right) = \exp\left[\frac{-(-10 \times 10^3 \text{ J})}{(8.3145 \text{ J/K} \bullet \text{mol})(298 \text{ kJ})}\right] = 60$$

88.
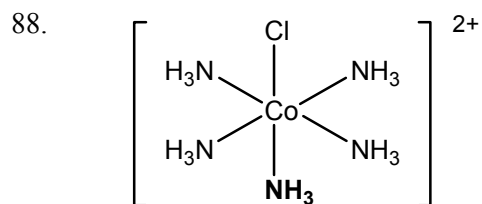
To form the trans isomer, Cl^- would replace the NH_3 ligand that is bold in the structure above. If any of the other four NH_3 molecules are replaced by Cl^-, the cis isomer results. Therefore, the expected ratio of the cis:trans isomer in the product is 4 : 1.

Challenge Problems

89. $Ni^{2+} = d^8$; if ligands A and B produced very similar crystal fields, the trans-$[NiA_2B_4]^{2+}$ complex ion would give the following octahedral crystal field diagram for a d^8 ion:
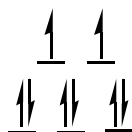
This is paramagnetic.

Because it is given that the complex ion is diamagnetic, the A and B ligands must produce different crystal fields, giving a unique d-orbital splitting diagram that would result in a diamagnetic species.

90.   a. $\Delta S°$ will be negative because there is a decrease in the number of moles of gas.

b. Because $\Delta S°$ is negative, $\Delta H°$ must be negative for the reaction to be spontaneous at some temperatures. Therefore, ΔS_{surr} is positive.

c. $Ni(s) + 4 CO(g) \rightleftharpoons Ni(CO)_4(g)$
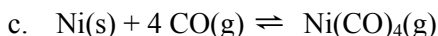
$\Delta H° = -607 - [4(-110.5)] = -165 \text{ kJ}; \ \Delta S° = 417 - [4(198) + (30.)] = -405 \text{ J/K}$

d. $\Delta G° = 0 = \Delta H° - T\Delta S°, \ T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{-165 \times 10^3 \text{ J}}{-405 \text{ J/K}} = 407 \text{ K or } 134°C$

e. $T = 50.°C + 273 = 323$ K

$$\Delta G^\circ_{323} = -165 \text{ kJ} - (323 \text{ K})(-0.405 \text{ kJ/K}) = -34 \text{ kJ}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-34{,}000 \text{ J})}{(8.3145 \text{ J/K} \bullet \text{mol})(323 \text{ K})} = 12.66, \ \ K = e^{12.66} = 3.1 \times 10^5$$
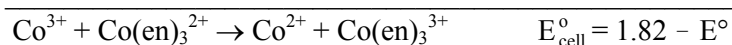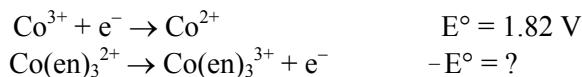
f. $T = 227°C + 273 = 500.$ K

$$\Delta G^\circ_{500} = -165 \text{ kJ} - (500. \text{ K})(-0.405 \text{ kJ/K}) = 38 \text{ kJ}$$
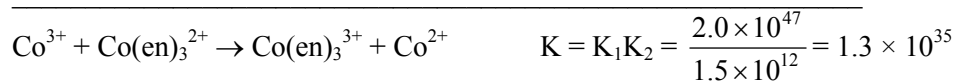
$$\ln K = \frac{-38{,}000 \text{ J}}{(8.145)(500.)} = -9.14, \ \ K = e^{-9.14} = 1.1 \times 10^{-4}$$

g.   The temperature change causes the value of the equilibrium constant to change from a large value favoring formation of $Ni(CO)_4$ to a small value favoring the decomposition of $Ni(CO)_4$ into pure Ni and CO. This is exactly what is wanted in order to purify a nickel sample.

91.   a.   Consider the following electrochemical cell:

$$\begin{array}{ll} Co^{3+} + e^- \rightarrow Co^{2+} & E^\circ = 1.82 \text{ V} \\ Co(en)_3{}^{2+} \rightarrow Co(en)_3{}^{3+} + e^- & -E^\circ = ? \\ \hline Co^{3+} + Co(en)_3{}^{2+} \rightarrow Co^{2+} + Co(en)_3{}^{3+} & E^\circ_{cell} = 1.82 - E^\circ \end{array}$$

The equilibrium constant for this overall reaction is:

$$\begin{array}{ll} Co^{3+} + 3 \text{ en} \rightarrow Co(en)_3{}^{3+} & K_1 = 2.0 \times 10^{47} \\ Co(en)_3{}^{2+} \rightarrow Co^{2+} + 3 \text{ en} & K_2 = 1/1.5 \times 10^{12} \\ \hline Co^{3+} + Co(en)_3{}^{2+} \rightarrow Co(en)_3{}^{3+} + Co^{2+} & K = K_1 K_2 = \dfrac{2.0 \times 10^{47}}{1.5 \times 10^{12}} = 1.3 \times 10^{35} \end{array}$$

From the Nernst equation for the overall reaction:

$$E^\circ_{cell} = \frac{0.0591}{n} \log K = \frac{0.0591}{1} \log(1.3 \times 10^{35}), \ \log(1.3 \times 10^{35}), \ E^\circ_{cell} = 2.08 \text{ V}$$

$$E^\circ_{cell} = 1.82 - E^\circ = 2.08 \text{ V}, \ E^\circ = 1.82 \text{ V} - 2.08 \text{ V} = -0.26 \text{ V}$$

b.   The stronger oxidizing agent will be the more easily reduced species and will have the more positive standard reduction potential. From the reduction potentials, Co^{3+} ($E^\circ = 1.82$ V) is a much stronger oxidizing agent than $Co(en)_3{}^{3+}$ ($E^\circ = -0.26$ V).

c. In aqueous solution, Co^{3+} forms the hydrated transition metal complex $Co(H_2O)_6^{3+}$. In both complexes, $Co(H_2O)_6^{3+}$ and $Co(en)_3^{3+}$, cobalt exists as Co^{3+}, which has 6 d electrons. Assuming a strong-field case for each complex ion, the d-orbital splitting diagram for each is:

$$\underline{\quad}\quad\underline{\quad}\qquad\qquad e_g$$

$$\underline{\uparrow\downarrow}\quad\underline{\uparrow\downarrow}\quad\underline{\uparrow\downarrow}\qquad t_{2g}$$
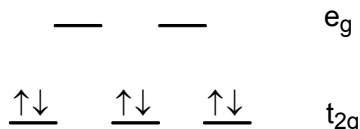
When each complex gains an electron, the electron enters a higher energy e_g orbital. Since en is a stronger-field ligand than H_2O, the d-orbital splitting is larger for $Co(en)_3^{3+}$, and it takes more energy to add an electron to $Co(en)_3^{3+}$ than to $Co(H_2O)_6^{3+}$. Therefore, it is more favorable for $Co(H_2O)_6^{3+}$ to gain an electron than for $Co(en)_3^{3+}$ to gain an electron.

$$\qquad\quad\ \ \text{II}\qquad\text{III}\qquad\qquad\qquad\ \text{III}\qquad\text{II}$$
92. $(H_2O)_5Cr–Cl–Co(NH_3)_5 \rightarrow (H_2O)_5Cr–Cl–Co(NH_3)_5 \rightarrow Cr(H_2O)_5Cl^{2+} + Co(II)$ complex

Yes; after the oxidation, the ligands on Cr(III) won't exchange. Since Cl^- is in the coordination sphere, it must have formed a bond to Cr(II) before the electron transfer occurred (as proposed through the formation of the intermediate).

93.   No; in all three cases, six bonds are formed between Ni^{2+} and nitrogen, so ΔH values should be similar. $\Delta S°$ for formation of the complex ion is most negative for 6 NH_3 molecules reacting with a metal ion (7 independent species become 1). For penten reacting with a metal ion, 2 independent species become 1, so $\Delta S°$ is least negative of all three of the reactions. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the less unfavorable $\Delta S°$ becomes for the formation of the complex ion, and the larger the formation constant.

94.
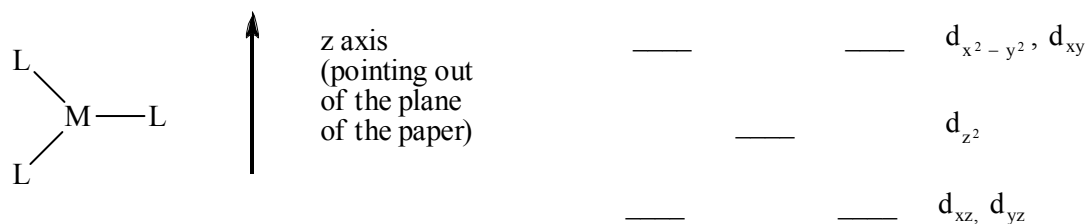
The $d_{x^2-y^2}$ and d_{xy} orbitals are in the plane of the three ligands and should be destabilized the most. The amount of destabilization should be about equal when all the possible interactions are considered. The d_{z^2} orbital has some electron density in the xy plane (the doughnut) and should be destabilized a lesser amount than the $d_{x^2-y^2}$ and d_{xy} orbitals. The d_{xz} and d_{yz} orbitals have no electron density in the plane and should be lowest in energy.

95.
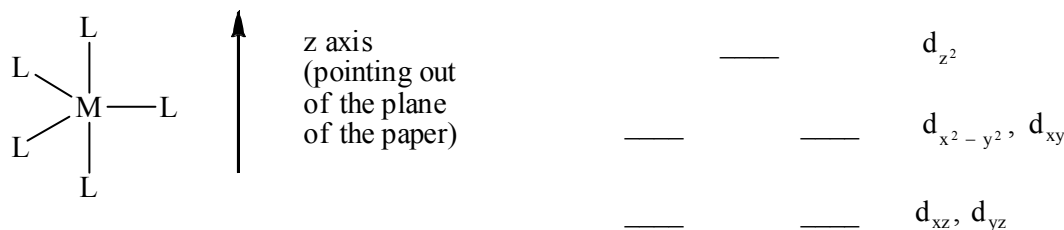
The d_{z^2} orbital will be destabilized much more than in the trigonal planar case (see Exercise 94). The d_{z^2} orbital has 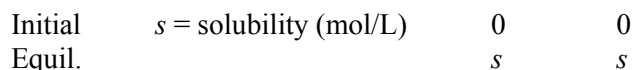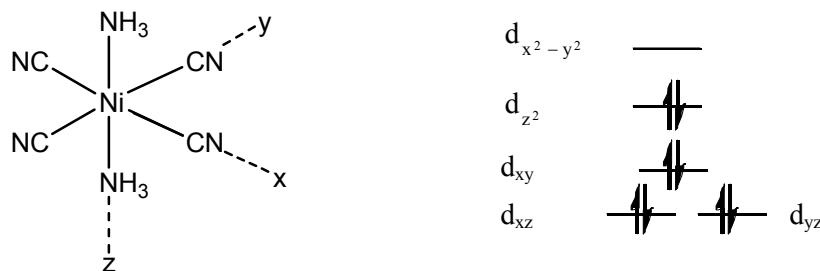electron density on the z axis directed at the two axial ligands. The $d_{x^2-y^2}$ and d_{xy} orbitals are in the plane of the three trigonal planar ligands and should be destabilized a lesser amount than the d_{z^2} orbital; only a portion of the electron density in the $d_{x^2-y^2}$ and d_{xy} orbitals is directed at the ligands. The d_{xz} and d_{yz} orbitals will be destabilized the least since the electron density is directed between the ligands.

96.   For a linear complex ion with ligands on the x axis, the $d_{x^2-y^2}$ orbital will be destabilized the most, with the lobes pointing directly at the ligands. The d_{yz} orbital has the fewest interactions with x-axis ligands, so it is destabilized the least. The d_{xy} and d_{xz} orbitals will have similar destabi-lization but will have more interactions with x-axis ligands than the d_{yz} orbital. Finally, the d_{z^2} orbital with the doughnut of electron density in the xy plane will probably be destabilized more than the d_{xy} and d_{xz} orbitals but will have nowhere near the amount of destabilization that occurs with the $d_{x^2-y^2}$ orbital. The only difference that would occur in the diagram if the ligands were on the y axis is the relative positions of the d_{xy}, d_{xz}, and d_{yz} orbitals. The d_{xz} will have the smallest destabilization of all these orbitals, whereas the d_{xy} and d_{yz} orbitals will be degenerate since we expect both to be destabilized equivalently from y-axis ligands. The d-orbital splitting diagrams are:

a.

b.

linear x-axis ligands

linear y-axis ligands
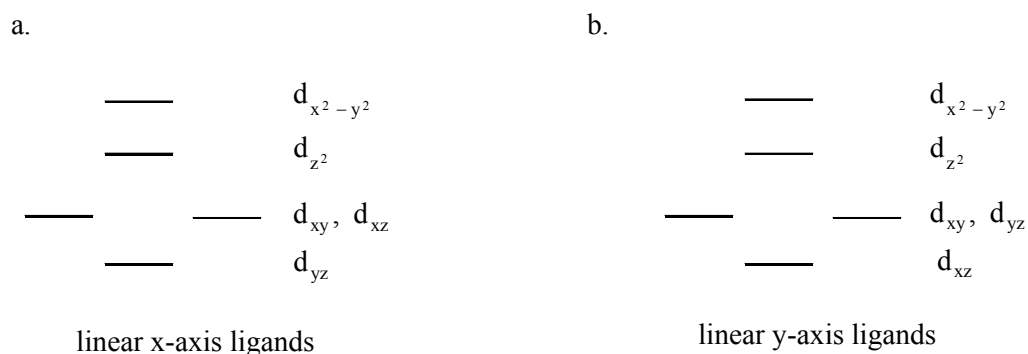
97. Ni^{2+}: $[Ar]3d^8$; the coordinate system for trans-$[Ni(NH_3)_2(CN)_4]^{2-}$ is shown below. Because CN^- produces a much stronger crystal field, it will dominate the d-orbital splitting. From the coordinate system, the CN^- ligands are in a square planar arrangement. Therefore, the diagram will most resemble the square planar diagram given in Figure 21.28. Note that the relative position of d_{z^2} orbital is hard to predict. With the NH_3 ligands on the z axis, we will

assume the $d_z{}^2$ orbital is destabilized more than the d_{xy} orbital. However, this is only an assumption. It could be that the d_{xy} orbital is destabilized more.

98.   a.   AgBr(s) $\rightleftharpoons$ Ag^+ + Br^- $K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$

Initial   s = solubility (mol/L)   0   0
Equil.   s   s

$K_{sp} = 5.0 \times 10^{-13} = s^2$, $s = 7.1 \times 10^{-7}$ mol/L

b.   AgBr(s) $\rightleftharpoons$ Ag^+ + Br^- $K_{sp} = 5.0 \times 10^{-13}$
                    Ag^+ + 2 NH_3 $\rightleftharpoons$ $Ag(NH_3)_2{}^+$ K_f = 1.7×10^7

AgBr(s) + 2 NH_3(aq) $\rightleftharpoons$ $Ag(NH_3)_2{}^+$(aq) + Br^-(aq) K = $K_{sp} \times K_f = 8.5 \times 10^{-6}$

AgBr(s)   +   2 NH_3 $\rightleftharpoons$ $Ag(NH_3)_2{}^+$ + Br^-

Initial   3.0 M 0   0
            s mol/L of AgBr(s) dissolves to reach equilibrium = molar solubility
Equil.   3.0 − 2s   s   s
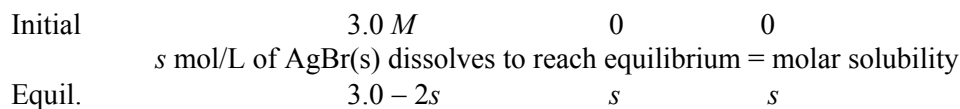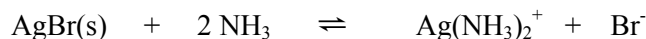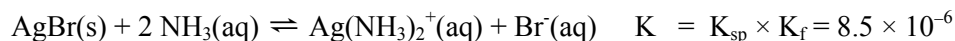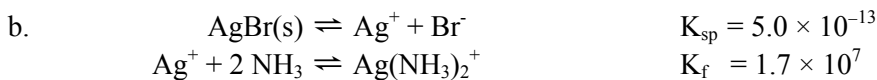
$K = \dfrac{[Ag(NH_3)_2{}^+][Br^-]}{[NH_3]^2} = \dfrac{s^2}{(3.0 - 2s)^2}$, $8.5 \times 10^{-6} \approx \dfrac{s^2}{(3.0)^2}$, $s = 8.7 \times 10^{-3}$ mol/L;
assumption good.

c. The presence of NH_3 increases the solubility of AgBr. Added NH_3 removes Ag^+ from solution by forming the complex ion $Ag(NH_3)_2{}^+$. As Ag^+ is removed, more AgBr(s) will dissolve to replenish the Ag^+ concentration.

d. Mass AgBr = 0.2500 L $\times$ $\dfrac{8.7 \times 10^{-3} \text{ mol AgBr}}{L}$ $\times$ $\dfrac{187.8 \text{ g AgBr}}{\text{mol AgBr}}$ = 0.41 g AgBr

e. Added HNO_3 will have no effect on the AgBr(s) solubility in pure water. Neither H^+ nor $NO_3{}^-$ reacts with Ag^+ or Br^- ions. Br^- is the conjugate base of the strong acid HBr, so it is a terrible base. Added H^+ will not react with Br^- to any great extent. However, added HNO_3 will reduce the solubility of AgBr(s) in the ammonia solution. NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$). Added H^+ will react with NH_3 to form $NH_4{}^+$. As NH_3 is removed, a smaller amount of the $Ag(NH_3)_2{}^+$ complex ion will form, resulting in a smaller amount of AgBr(s) that will dissolve.

Integrative Problems

99.   a.   Because O is in the -2 oxidation state, iron must be in the $+6$ oxidation state. Fe^{6+}: $[Ar]3d^2$.

       b.   Using the half-reaction method of balancing redox reactions, the balanced equation is:

$$10\ H^+(aq) + 2\ FeO_4^{2-}(aq) + 2\ NH_3(aq)\ \rightarrow\ 2\ Fe^{3+}(aq) + N_2(g) + 8\ H_2O(l)$$
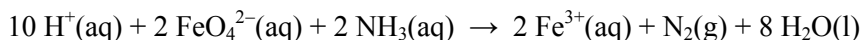
$$0.0250\ L \times \frac{0.243\ mol}{L} = 6.08 \times 10^{-3}\ mol\ FeO_4^{2-}$$

$$0.0550\ L \times \frac{1.45\ mol}{L} = 7.98 \times 10^{-2}\ mol\ NH_3$$

$$\frac{Mol\ NH_3}{Mol\ FeO_4^{2-}} = \frac{7.98 \times 10^{-2}\ mol}{6.08 \times 10^{-3}\ mol} = 13.1$$

The actual mole ratio is larger than the theoretical ratio of $1:1$, so FeO_4^{2-} is limiting.

$$V_{N_2} = \frac{nRT}{P} = \frac{6.08 \times 10^{-3}\ mol\ FeO_4^{2-} \times \dfrac{1\ mol\ N_2}{2\ mol\ FeO_4^{2-}} \times \dfrac{0.08206\ L\ atm}{K\ mol} \times 298\ K}{1.50\ atm}$$

$$V_{N_2} = 0.0496\ L = 49.6\ mL\ N_2$$

100.   a. $\lambda = \dfrac{hc}{E} = \dfrac{6.626 \times 10^{-34}\ J\ s\ \times 2.998 \times 10^8\ m/s}{1.75 \times 10^4\ cm^{-1} \times \dfrac{1.986 \times 10^{-23}\ J}{cm^{-1}}} = 5.72 \times 10^{-7}\ m = 572\ nm$

       b.   There are three resonance structures for NCS^-. From a formal charge standpoint, the following resonance structure is best.

$$\left[:N{\equiv}C{-}\ddot{\underset{..}{S}}: \right]^-$$
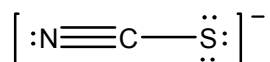
The N in this resonance structure is sp hybridized. Because the sp hybrid orbitals are $180°$ apart, one would expect that when the lone pair in an sp hybrid orbital on N is donated to the Cr^{3+} ion, the $180°$ bond angle would stay intact between Cr, N, C, and S.

Similar to $Co(en)_2Cl^{2+}$ discussed in Figures 21.16 and 21.17 of the text, $[Co(en)_2(NCS)_2]^+$ would exhibit cis-trans isomerism (geometric isomerism), and only the cis form would exhibit optical isomerism. For $[Co(en)_2(NCS)_2]^+$, NCS^- just replaces the Cl^- ions in the isomers drawn in Figures 21.16 and 21.17. The trans isomer would not exhibit optical isomerism.

101. i. $0.0203 \text{ g CrO}_3 \times \dfrac{52.00 \text{ g Cr}}{100.0 \text{ g CrO}_3} = 0.0106 \text{ g Cr};$ $\% \text{ Cr} = \dfrac{0.0106 \text{ g}}{0.105 \text{ g}} \times 100 = 10.1\% \text{ Cr}$

   ii. $32.93 \text{ mL HCl} \times \dfrac{0.100 \text{ mmol HCl}}{\text{mL}} \times \dfrac{1 \text{ mmol NH}_3}{\text{mmol HCl}} \times \dfrac{17.03 \text{ mg NH}_3}{\text{mmol}} = 56.1 \text{ mg NH}_3$

   $\% \text{ NH}_3 = \dfrac{56.1 \text{ mg}}{341 \text{ mg}} \times 100 = 16.5\% \text{ NH}_3$

   iii. $73.53\% + 16.5\% + 10.1\% = 100.1\%;$ the compound must be composed of only Cr, NH_3, and I.

   Out of 100.00 g of compound:

   $10.1 \text{ g Cr} \times \dfrac{1 \text{ mol}}{52.00 \text{ g}} = 0.194 \text{ mol};$ $\qquad$ $\dfrac{0.194}{0.194} = 1.00$

   $16.5 \text{ g NH}_3 \times \dfrac{1 \text{ mol}}{17.03 \text{ g}} = 0.969 \text{ mol};$ $\qquad$ $\dfrac{0.969}{0.194} = 4.99$

   $73.53 \text{ g I} \times \dfrac{1 \text{ mol}}{126.9 \text{ g}} = 0.5794 \text{ mol};$ $\qquad$ $\dfrac{0.5794}{0.194} = 2.99$

   $Cr(NH_3)_5I_3$ is the empirical formula. Cr^{3+} forms octahedral complexes. So compound A is made of the octahedral $[Cr(NH_3)_5I]^{2+}$ complex ion and two I^- ions as counter ions; the formula is $[Cr(NH_3)_5I]I_2$. Lets check this proposed formula using the freezing-point data.

   iv. $\Delta T_f = iK_f m;$ for $[Cr(NH_3)_5I]I_2$, $i = 3.0$ (assuming complete dissociation).

   $\text{Molality} = m = \dfrac{0.601 \text{ g complex}}{1.000 \times 10^{-2} \text{ kg H}_2\text{O}} \times \dfrac{1 \text{ mol complex}}{517.9 \text{ g complex}} = 0.116 \text{ mol/kg}$
   $\Delta T_f = 3.0 \times 1.86 \text{ °C kg/mol} \times 0.116 \text{ mol/kg} = 0.65\text{°C}$

   Because ΔT_f is close to the measured value, this is consistent with the formula $[Cr(NH_3)_5I]I_2$.

Marathon Problem

102. $CrCl_3 \cdot 6H_2O$ contains nine possible ligands, only six of which are used to form the octahedral complex ion. The three species not present in the complex ion will either be counter ions to balance the charge of the complex ion and/or waters of hydration. The number of counter ions for each compound can be determined from the silver chloride precipitate data, and the number of waters of hydration can be determined from the dehydration data. In all experiments, the ligands in the complex ion do not react.

Compound I:

$$\text{mol CrCl}_3\text{\textbullet}6\text{H}_2\text{O} = 0.27 \text{ g} \times \frac{1 \text{ mol}}{266.5 \text{ g}} = 1.0 \times 10^{-3} \text{ mol CrCl}_3\text{\textbullet}6\text{H}_2\text{O}$$

$$\text{mol waters of hydration} = 0.036 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 2.0 \times 10^{-3} \text{ mol H}_2\text{O}$$

$$\frac{\text{mol waters of hydration}}{\text{mol compound}} = \frac{2.0 \times 10^{-3} \text{ mol}}{1.0 \times 10^{-3} \text{ mol}} = 2.0$$

In compound I, two of the H_2O molecules are waters of hydration, so the other four water molecules are present in the complex ion. Therefore, the formula for compound I must be $[Cr(H_2O)_4Cl_2]Cl\text{\textbullet}2H_2O$. Two of the Cl^- ions are present as ligands in the octahedral complex ion, and one Cl^- ion is present as a counter ion. The AgCl precipitate data that refer to this compound are the one that produces 1430 mg AgCl:

$$\text{mol Cl}^- \text{ from compound I} = 0.1000 \text{ L} \times \frac{0.100 \text{ mol }[Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O}{L}$$

$$\times \frac{1 \text{ mol Cl}^-}{\text{mol }[Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O} = 0.0100 \text{ mol Cl}^-$$

$$\text{mass AgCl produced} = 0.0100 \text{ mol Cl}^- \times \frac{1 \text{ mol AgCl}}{\text{mol Cl}^-} \times \frac{143.4 \text{ g AgCl}}{\text{mol AgCl}} = 1.43 \text{ g}$$
$$= 1430 \text{ mg AgCl}$$

Compound II:

$$\frac{\text{mol waters of hydration}}{\text{mol compound}} = \frac{0.018 \text{ g H}_2\text{O} \times \dfrac{1 \text{ mol}}{18.02 \text{ g}}}{1.0 \times 10^{-3} \text{ mol compound}} = 1.0$$

The formula for compound II must be $[Cr(H_2O)_5Cl]Cl_2\text{\textbullet}H_2O$. The 2870-mg AgCl precipitate data refer to this compound. For 0.0100 mol of compound II, 0.0200 mol Cl^- is present as counter ions:

$$\text{mass AgCl produced} = 0.0200 \text{ mol Cl}^- \times \frac{1 \text{ mol AgCl}}{\text{mol Cl}^-} \times \frac{143.4 \text{ g}}{\text{mol}} = 2.87 \text{ g}$$
$$= 2870 \text{ mg AgCl}$$

Compound III:

This compound has no mass loss on dehydration, so there are no waters of hydration present. The formula for compound III must be $[Cr(H_2O)_6]Cl_3$. 0.0100 mol of this compound produces 4300 mg of AgCl(s) when treated with $AgNO_3$.
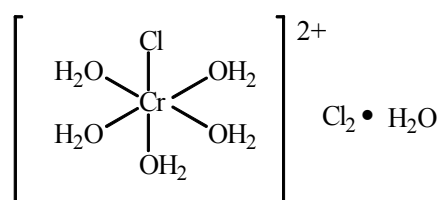
$$0.0300 \text{ mol Cl}^- \times \frac{1 \text{ mol AgCl}}{\text{mol Cl}^-} \times \frac{143.4 \text{ g AgCl}}{\text{mol AgCl}} = 4.30 \text{ g} = 4.30 \times 10^3 \text{ mg AgCl}$$
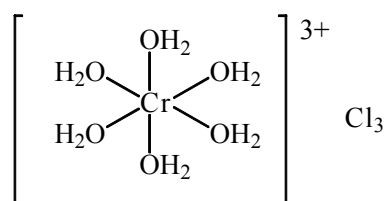
The structural formulas for the compounds are:

Compound I

$$Cl \cdot 2\,H_2O \quad \text{or}$$

$$Cl \cdot 2\,H_2O$$
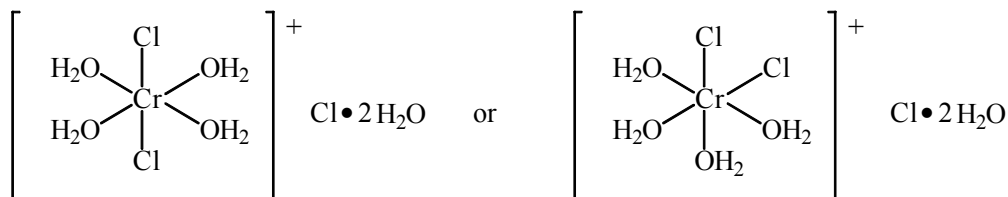
Compound II   Compound III

$$Cl_2 \cdot H_2O$$

$$Cl_3$$

From Table 21.16 of the text, the violet compound will be the one that absorbs light with the shortest wavelength (highest energy). This should be compound III. H_2O is a stronger-field ligand than Cl^-; compound III with the most coordinated H_2O molecules will have the largest d-orbital splitting and will absorb the higher-energy light.

The magnetic properties would be the same for all three compounds. Cr^{3+} is a d^3 ion. With only three electrons present, all Cr^{3+} complexes will have three unpaired electrons, whether strong field or weak field. If Cr^{2+} was present with the d^4 configuration, then the magnetic properties might be different for the complexes and could be worth examining.