Solutions to Module 2 Problems

7. Each of the chloride' carries a -1 charge and each of the ammonia's carries no charge. The cobalt must have a charge of +3 to give a neutral compound.

13. CuF_4^{2-} → coordination number is 4; charge on copper is +2 (each fluoride is -1)

    $Cr(CO)_6$ → coordination number is 6; charge on chromium is zero (CO is carbon monoxide, a neutral ligand)

    $Fe(CN)_6^{4-}$ → coordination number is 6; charge on iron is +2 (each cyanide is -1)

    $Pt(NH_3)_2Cl_2$ → coordination number is 4; charge on platinum is +2 (each chloride is -2)

30. $Cu(NH_3)_4^{2+}$ → tetraminecopper(II)

    $Mn(H_2O)_6^{2+}$ → hexaquomanganese(II)

    $Fe(CN)_6^{4-}$ → hexacyanoferrate(II)

    $Ni(en)_3^{2+}$ → tris(ethylenediamine)nickel(II)

    $Cr(acac)_3$ → triacetylacetonechromium(III)

31. $Pt(NH_3)_2Cl_2$ → diaminedichloroplatinum(II) *note: modular chapter indicates to arrange the name of ligands by doing anions first, then neutrals an then cations; I've seen both in use in the chemical literature—for our purposes, the order is not essential.*

    $Ni(CO)_4$ → tetracarbonylnickel(0)

    $Co(en)_3^{3+}$ → tris(ethylenediamine)cobalt(III)

32. $Na_3[Co(NO_2)_6]$ → sodium hexanitritocobaltate(III)

    $Na_2[Zn(CN)_4]$ → sodium tetracyanozincate(II)

    $[Co(NH_3)_4Cl_2]Cl$ → tetraminedichlorocobalt(III) chloride

    $[Ag(NH_3)_2]Cl$ → diaminosilver(I) chloride

33. $[Cr(NH_3)_6]Cl_3$

$[Cr(NH_3)_5Cl]Cl_2$

$[Cu(en)_3]Cl_3$

$K[Co(NO_2)_4(NH_3)_2]$

34. $Co(NH_3)_6^{3+}$ → no isomers; all ligands are identical

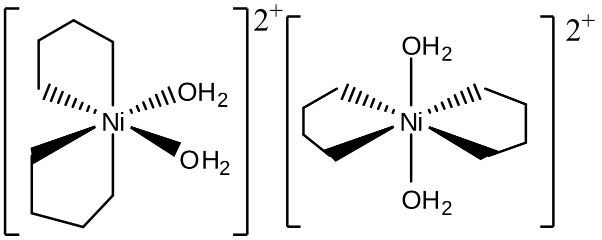
$Co(NH_3)_5Cl^{2+}$ → no isomers; a single ligand cannot be cis or trans to just itself

$Co(NH_3)_5(H_2O)^{3+}$ → no isomers; a single ligand cannot be cis or trans to just itself

$Co(NH_3)_4Cl^{+}$ → yes; the two chlorides can be either cis or trans to each other

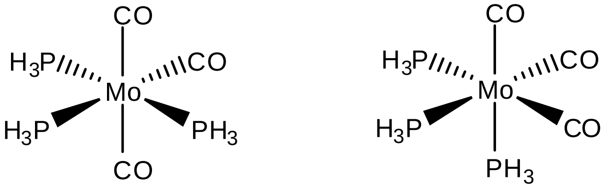
$Co(NH_3)_4(H_2O)_2^{3+}$ → yes; the two waters can be either cis or trans to each other

35. The two isomers are cis and trans:



cis trans

36. The two isomers are meridianal and facial:



meridinal facial

37. $Cu(NH_3)_4^{2+}$ → no isomers; a single ligand cannot be cis or trans to just itself

$Pt(NH_3)_2Cl_2$ → yes; the two chlorides (and the two amines) can be either cis or trans to each other

$RhCl_3(CO)$ → no isomers; a single ligand cannot be cis or trans to just itself

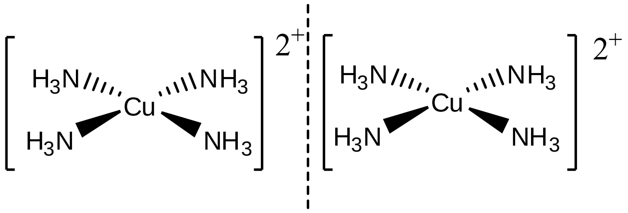
$IrCl(CO)(PH_3)_2$ → yes; the two phosphines can be either cis or trans to each other

38. In a square planar complex the two ligands X can be 90° apart or 180° apart; in a tetrahedral structure, however, the two ligands always be 109.5° apart.

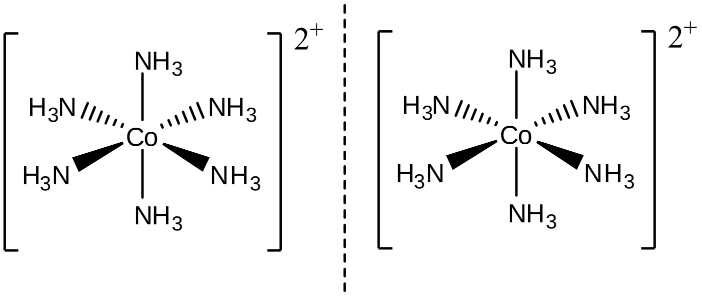
39. To form cis and trans isomers, there must be at least one pair of ligand; in the case of MX_3Y there is a single Y and three Xs.

40. It must be square planar—see answer to question 38 for an explanation.

41. The mirror images for $Cu(NH_3)_4^{2+}$, as shown below, are superimposible and, therefore, the complex is not optically active.



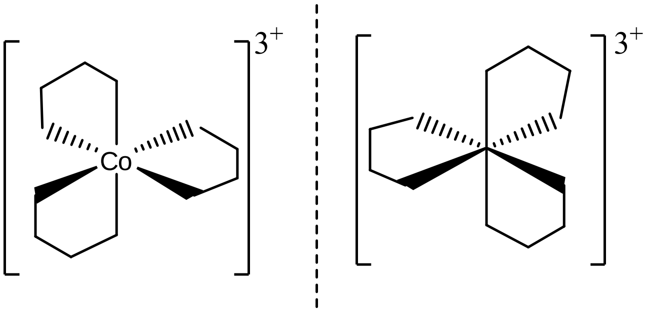
The mirror images for $Co(NH_3)_6^{2+}$, as shown below, are superimposible and, therefore, the complex is not optically active.



The mirror images for $Ag(NH_3)^+$, as shown below, are superimposible and, therefore, the complex is not optically active.

$[H_3H—Ag—NH_3]^+$ | $[H_3H—Ag—NH_3]^+$

The mirror images for $Co(en)_3^{3+}$, as shown below, are not superimposible and, therefore, the complex is optically active. If you have trouble seeing this, note that when you rotate the figure on the left by 180°, the bottom left ethylenediamine, which comes out toward you, ends up pointing away from you.



47. The valence bond approach assumes that the valence shell contains hybrid orbitals and d-orbitals with the hybrid orbitals determined by VSEPR. The "hint" means to assume that all the valence electrons for a metal with an oxidation state of zero are in the d-orbitals; that is, Sc, which we think of as $4s^23d^1$, is treated as being $3d^3$.

    $Ni(CO)_4$ → Nickel has an oxidation state of zero in this complex, and its valence shell of $4s^23d^8$ is taken as being $3d^{10}$. The remaining empty valence shell orbitals of one 4s and three 4p orbitals combine to make four sp^3 orbitals that point toward the corners of a tetrahedron; thus, we expect tetrahedral geometry for the complex.

    $Fe(CO)_5$ → Iron has an oxidation state of zero in this complex and its valence shell of $4s^23d^6$ is taken as being $3d^8$. This leaves empty valence shell orbitals of one 3d orbital, one 4s orbitals and three 4p orbitals, which combine to give five dsp^3 orbitals; thus, we expect trigonal bipyramidal geometry for the complex.

    $Cr(CO)_6$ → Chromium has an oxidation state of zero in this complex and its valence shell of $4s^23d^4$ is taken as being $3d^6$. This leaves empty valence shell orbitals of two 3d orbitals, one 4s orbital and three 4p orbitals, which combine to give six d^2sp^3 orbitals; thus, we expect octahedral geometry for the complex.

48. See answer for problem 47 for explanation.

49. A set of five d-orbitals, one s-orbital and three p-orbitals can hold 18 electrons. If we have four CO molecules that each contribute a lone-pair of electrons when bonding to iron, and the iron provides eight electrons, then we have accounted for 16 electrons. The charge of -2 provides the two additional electrons.

    For $Co(CO)_4^{x-}$, a similar argument indicates that there are eight electrons from CO and nine electrons from cobalt; the charge, therefore, must be -1.

$HFe(CO)_4^{x-}$ is the conjugate acid of $Fe(CO)_4^{2-}$; adding a H^+ means that the charge must one less, or -1.

52. The CO ligands provide 2 electrons apiece and the manganese provides 7, for a total of 17 electrons; a charge of -1 gives 18 electrons.

55. The valence shell electron configuration for Zn^{2+} is $3d^{10}$; thus, Zn^{2+} will accept four pairs of electrons from ligands to give a coordination number of four.

61. In an octahedral field the ligands interact more directly with the d_{z^2} and $d_{x^2-y^2}$ orbitals than the ligands in a tetrahedral field interact with the d_{xy}, d_{xz} and d_{yz} orbitals. In addition, six ligands provide more total electron density than with four ligands.

63. The value of Δ_o and Δ_t is always greater for metals in the second row of transition metals than it is for those metals in the first row of transition metals; Rh^{3+} is the only choice from the second row and, therefore, has the greatest value for Δ_o or Δ_t.

64. Cyanide, CN^-, is the strongest-field ligand and gives the largest Δ_o. A Lewis structure for cyanide shows that carbon carries the negative formal charge. Bonding through carbon, therefore, should be very strong because (a) this is not the most favorable atom in CN^- to carry the negative formal charge and (b) carbon has a strong desire to form four bond.

66. The are two factors—the energy Δ_o between the degenerate d-orbitals and the energy needed to add a second electron to an orbital that already contains one electron, which we can call E_{pair}. When $\Delta_o > E_{pair}$ then we get a low-spin complex and when $\Delta_o < E_{pair}$ then we get a high-spin complex.

68. CN^- is a stronger field ligand than H_2O; thus Δ_o for CN^- is larger and it will be the low-spin complex.

69. Because Δ_t is about 4/9 of Δ_o we are far more likely to find that Δ_t is less than E_{pair}, favoring high-spin complexes.

71. The value of Δ_o increases down a group.

74. The color we see is that portion of white light (all colors) that is not absorbed by the sample. If $Cu(NH_3)_4^{2+}$ absorbed blue light, then its solution will look to us as if it were white light without blue light, which is an orange color.

76. Bright yellow means that a wavelength of approximately 430 nm is absorbed, while an orange color means that a wavelength of about 480 nm is absorbed. Shifting to a longer wavelength means a smaller frequency as $c = \lambda\nu$.

77. Absorbing blue-green light (wavelength of approximately 500 nm) leaves a solution that is red.