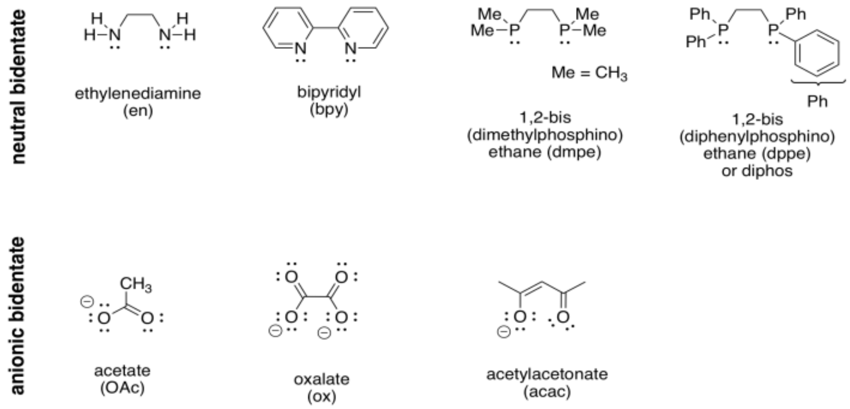
11.4: Chelation

Each ligand that binds to a transition metal donates a pair of its electrons to the metal, sharing those electrons in a metal-ligand bond. Counting the total number of electrons in the metal's valence shell is fairly easy when you know that each ligand contributes two electrons.

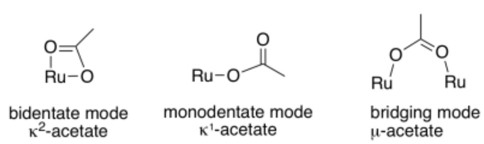
But what if a ligand could contribute more than two electrons? Take a look at the following table. Each of the ligands shown here can bind to a metal twice. The ligand forms two bonds to the metal, donating two pairs of electrons. It might seem obvious, but forming two bonds to the metal means the ligand binds more tightly to the metal. Remember the lego-like nature of transition metal complexes: ligands can come and go, but these ligands are less likely to go; they hold on.



These ligands are called bidentate ligands. That means, literally, that they have two teeth. That does not sound like much, but the ligands we have seen previously are described as monodentate; they have only one tooth. Bidentate ligands can bite into the metal, and hold onto it, more strongly than monodentate ones.

Another term used for these kinds of ligands is derived from the Greek *chele*, for claw. These ligands grab onto the metal like the claw of a lobster or crab; they *chelate*. The "chelate effect" is the tendency of these ligands to bind firmly to a metal, whereas monodentate ligands might come off more easily.

Now, just because a ligand could be bidentate does not mean that it always binds that way. That's often true with the acetate ligand, for example, because the four-membered ring that forms when it binds through both oxygens is a little too strained. Consequently, there are examples binding through both oxygen atoms, and there are also examples of binding through only one. Sometimes, acetate uses one oxygen to bind to one metal atom and the other oxygen to bind to a second metal atom, forming a bridge.



Usually, if a ligand is capable of chelation, assume it binds that way. However, there may be cases in which you are asked specifically to draw it binding in one way or another.

Exercise 11.4.1

Determine the denticity of each ligand in the following complexes.

a) $[Cu(en)_2(OH)_2]$ b) $[RuCl_2(dmpe)(bpy)]$ c) $[Ni(acac)_2(OH_2)_2]$ d) $K_2[Cu(ox)_2(OH_2)_2]$

e) $[FeH_2(dmpe)_2]$ f) $[RuH(OAc)(PPh_3)_3]$ g) $[Co(en)_2Cl_2]BF_4$ h) $[Ru(bpy)_2(HOCH_2CH_3)_2](ClO_4)_2$

Answer a:

en = bidentate; OH = monodentate

Answer b:

dmpe = bidentate; bpy = bidentate; Cl = monodentate

Answer c:

acac = bidentate; H_2O = monodentate

Answer d:

ox = bidentate; H_2O = monodentate

Answer e:

dmpe = bidentate; H = monodentate

Answer f:

H = monodentate; PPh3 = monodentate; OAc = bidentate. In this case, the acetate gets the complex to 18 electrons by binding twice.

Answer g:

en = bidentate; Cl = monodentate

Answer h:

bpy = bidentate; $HOCH_2CH_3$ = monodentate

Exercise 11.4.2

Determine the charges (or oxidation states) on the metals in the following complexes:

a) $K[Cr(ox)_2(OH_2)_2]$ b) $K[Mn(acac)_3]$ c) $[Cr(en)_2Cl_2]PF_6$ d) $[Co(en)_2(OH)Cl]ClO_4$

e) $Na_3[Mn(ox)_3]$ f) $K_3[Cr(ox)_3]$ g) $Na[Au(bpy)(CN)_2]$

Answer a:

Overall charge = 1-; ligands charge = 4-; charge on Cr = 3+

Answer b:

Overall charge = 1-; ligands charge = 3-; charge on Mn = 2+

Answer c:

Overall charge = 1+; ligands charge = 2-; charge on Cr = 3+

Answer d:

Overall charge = 1+; ligands charge = 2-; charge on Co = 3+

Answer e:

Overall charge = 3-; ligands charge = 6-; charge on Mn = 3+

Answer f:

Overall charge = 3-; ligands charge = 6-; charge on Cr = 3+

Answer g:

Overall charge = 1-; ligands charge = 2-; charge on Au = 1+

Exercise 11.4.3

Determine the electron count on the metal in each of the complexes from the previous problem.

Answer a:

Cr = d^6; Cr^{3+} = d^3; ox = 2 x 4e^- = 8 e^-; water = 2 x 2e^- = 4 e-; total = 15 e^-

Answer b:

$Mn = d^7$; $Mn^{2+} = d^5$; acac = 3 x 4e$^-$ = 12 e$^-$; total = 17 e$^-$

Answer c:

$Cr = d^6$; $Cr^{3+} = d^3$; en = 2 x 4e$^-$ = 8 e$^-$; Cl = 2 x 2e$^-$ = 4 e-; total = 15 e$^-$

Answer d:

$Co = d^9$; $Co^{3+} = d^6$; en = 2 x 4e$^-$ = 8 e$^-$; OH = 2e$^-$; Cl = 2 e-; total = 15 e$^-$

Answer e:

$Mn = d^7$; $Mn^{3+} = d^4$; ox = 3 x 4e$^-$ = 12 e$^-$; total = 16 e$^-$

Answer f:

$Cr = d^6$; $Cr^{3+} = d^3$; ox = 3 x 4e$^-$ = 12 e$^-$; total = 15 e$^-$

Answer g:

$Au = s^1d^{10}$; $Au^{1+} = d^{10}$; bpy = 2 x 2e$^-$ = 4 e$^-$; cyanide = 2 x 2e$^-$ = 4 e-; total = 18 e$^-$

See a more in-depth discussion of coordination complexes in a later course.
