Inorganic Chemistry with Doc M.
Fall Semester, 2012
Day 16. Transition Metals Complexes:
Structure and Isomers

Name(s):	Element:

Topics:

1. Periodic trends and the transition metals
2. Lanthanide contraction
3. Ligands and transition metal complexes

4. Polydentate ligands
5. Diastereomers
6. Enantiomers

A. Periodic trends and the transition metals.

1. **Ionic radii decrease from left to right.** Just like with the atomic radii of neutral elements, ionic radii generally decrease from left to right as long as we are comparing ions of the same charge. There are some troublemakers, however.

2.

High spin*	Sc^{+2}	Ti^{+2}	V^{+2}	Cr^{+2}	Mn^{+2}	Fe^{+2}	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}
r_+(pm)	-	100	93	87	97	92	89	83	87	88

High spin*	Sc^{+3}	Ti^{+3}	V^{+3}	Cr^{+3}	Mn^{+3}	Fe^{+3}	Co^{+3}	Ni^{+3}	Cu^{+3}	Zn^{+3}
r_+(pm)	89	81	78	76	79	79	75	74	-	-

*discussed later

2. **Ionic radii decrease as the + charge increases.** For example, Fe^{+3} is smaller than Fe^{+2}.

	Ti^{+2}	Ti^{+3}	Ti^{+4}
r_+(pm)	100	81	75

High spin*	Fe^{+2}	Fe^{+3}
r_+(pm)	92	79

*discussed later

3. **Ionic radii increase from the first row transition metals to the second and third row transition metals.** The second and third row transition metals are more similar in terms of size than the first and second rows.

	r_+(pm)
V^{+3}	78
Nb^{+3}	86
Ta^{+3}	86

	r_+(pm)
Co^{+3}	69
Rh^{+3}	81
Ir^{+3}	82

	r_+(pm)
Ni^{+2}	83
Pd^{+2}	100
Pt^{+2}	94

4. Ionization energy increases from left to right. For example, the early transition metals are known in larger oxidation states such as Ti^{+4} ; the largest oxidation state for iron is Fe^{+3} and nickel, copper, and zinc can only form +2 as the largest oxidation states.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE (kJ/mol)	631	658	650	653	717	759	758	737	746	906

5. Higher oxidation states are more common for second and third row transition metals than for first row transition metals. It is easier to form larger + oxidation states for second and third row transition metals than for first row metals. For example, gold is known to have a +3 oxidation state, even though copper and silver do not. For cobalt, the +3 oxidation state is rare, for rhodium, +3 is the most common.

Sc 3	Ti 3, 4	V 2 – 5	Cr 2, 3, 6	Mn 2 – 4, 6, 7	Fe 2, 3	Co 2, 3	Ni 2, 3	Cu 1, 2	Zn 2
Y 3	Zr 4	Nb 3, 5	Mo 2 – 6	Tc 7	Ru 2, 3, 4, 6, 8	Rh 2, 3, 4	Pd 2, 4	Ag 1	Cd 2
La 3	Hf 4	Ta 5	W 2 – 6	Re -1, 2, 4, 6, 7	Os 2, 3, 4, 6, 8	Ir 2, 3, 4, 6, 8	Pt 2, 4	Au 1, 3	Hg 1, 2

Summary of General Periodic Trends:

Larger ionic radii

Early transition metals (left side)

Smaller + oxidation states

2nd and 3rd row metals

Smaller ionic radii

late transition metals (right side)

larger + oxidation states

1st row transition metals

Larger oxidation states

Early transition metals (left side)

2nd and 3rd row metals

Smaller oxidation states

late transition metals (right side)

1st row transition metals

6. Lanthanide contraction. This funny-sounding term describes what occurs between the second and third row transition metals: the lanthanides have occurred! In the electron configuration of every third row metal, there are fourteen 4f electrons. These extra electrons along with the 14 extra protons cause the third row metals to be more similar in size to the second row metals. The expected big increase in size in going from the 2nd to 3rd row is offset by the 14 slight decreases caused by the 4f elements. Consider the atomic radii of the copper triad: Cu: r = 157 pm; Ag: r = 175 pm; Au: r = 179 pm. Given the atomic radii of iron and ruthenium to be 172 pm and 189 pm, respectively, estimate the atomic radius of osmium.

The same is true for the ionization energies. Explain what is expected and how the 4f elements change that. Here are some data that may be useful to include in your discussion:

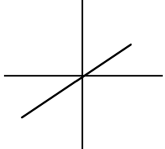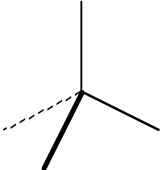|	IE (kJ/mol)
Fe	759
Ru	711
Os	839

B. Formation of transition metal complexes

1. Ligands are Lewis bases and metal cations are Lewis acids. The word *complex* is defined to be a "transition metal ion surrounded by ligands to form an ion or compound." A typical transition metal complex is $[Fe(NH_3)_6]SO_4$. The cation is the ***complex ion*** $Fe(NH_3)_6^{+2}$, sulfate is the anion. Note that the complex ion is often designated by the square brackets, [ ], around it. Other transition metal complexes such as $Fe(NH_3)_4Cl_2$ are neutral.

2. Ligands. All of the following are known ligands. Sketch the Lewis dot structure of these ligands. All of which are Lewis bases. Write "HB" by the hard bases and "SB" by the soft bases – look them up in your book.

Cl^-	CN^-	H_2O
OH^-	CO	NH_3
NH_2^-	SCH_3^-	NO_2^-

3. Transition metals tend to form cations and as such are Lewis acids. Sketch the Lewis acid-base interaction between one ammonia molecule and iron(II).

4. Transition metal complexes tend involve 3 – 8 Lewis bases with four and six being by far the most common. (a) In the case of the above ligands, this means that each transition metal complex 3 – 8 ligands with 4 or 6 ligands being the most common. When four Lewis bases are involved, the tetrahedron is usually obtained and when there are six ligands, the octahedron is the most common structure. Sketch the transition metal complex only for the following compounds, all of which are either tetrahedral or octahedral. Note that the actual complex is in square brackets when the complex is ionic. Thus, $Cr(NH_3)_4Cl_2$ is neutral and both NH_3 and Cl^- are ligands. Do not include the counterions in the sketches, but do use large brackets and include the charge when appropriate.

$[Fe(NH_3)_6]SO_4$	$(NH_4)_2[CoCl_4]$	$Cr(NH_3)_4Cl_2$
$K_4[Mn(CN)_6]$	$[Co(P(CH_3)_3)_4]_2(SO_4)_3$	$[Ni(H_2O)_6]Cl_2$

(b) Sketch the thiocyanate ligand, SCN^-, including *both* important resonance forms (there is a third one with unacceptable formal charges). Assign formal charges to every atom in each sketch. Both ends of thiocyanate turn out to be Lewis bases. One end is a soft base and one end is a hard base. Identify each end in your structure.

(c) Sketch the preferred arrangement for coordination when the thiocyanate ion coordinates with Cu^{+2} and Rh^{+1}, respectively. Only one ligand need be sketched in each case. Use formal charges to establish which resonance structure favors coordination to Cu^{+2} and which favors coordination to Rh^{+1}

(d) Some ligands, including pyridine, are typically abbreviated in their formulas. Sketch the pyridine ligand. It's abbreviation is "py."

(e) Determine the oxidation state on the transition metal in the following compounds.

$[V(H_2O)_6](NO_3)_3$	$(NH_4)_2[CoCl_4]$	$[Co(py)_4]Br_2$
$K_4[Mn(CN)_6]$	$[Co(P(CH_3)_3)_4]_2(SO_4)_3$	$Ni(NH_3)_4Cl_2$

5. Ligands that contain more than one Lewis base often coordinate with some or all of them.

(a) The simplest example is ethylenediamine, $NH_2CH_2CH_2NH_2$, which is basically two ammonia molecules tethered by a $-CH_2CH_2-$ backbone. Sketch the ligand by itself and then coordinated to some generic metal cation, M^+.

(b) Ligands that coordinate at two locations are called **bidentate**. Ethylenediamine is a bidentate ligand. It is abbreviated "*en*." Other ligands are tridentate, tetradentate, and so on. Sketch these lignands and decide if they are monodentate, bidentate, tridentate or tetradentate.

$N(CH_3)_3$	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

(c) Ligands that coordinate in more than one location are collectively called **chelates**. Thus, a chelate ligand is at least bidentate, but could be tridentate and so on. Entropy favors chelating ligands. Considering the

similarities in the Lewis acid-base interactions between the nitrogen's lone pair and the transition metal cation, predict ΔH and ΔS for this reaction which does lie far to the right.

$$Cr(NH_3)_6{}^{+3} + 3\ en \xrightleftharpoons{} Cr(en)_3{}^{+3} + 6\ NH_3 \qquad \Delta H\ (>\ \sim\ <)\ 0 \qquad \Delta S\ (>\ \sim\ <)\ 0$$

(d) Look up the structures of these other chelate ligands. Include electron pairs!

acac	ox	dppe

6. Transition metal complexes and writing their formulas. Put the following complexes

together to give the formula of the complex. Remember to use [ ] to identify the complex ion in ionic complexes. In cases where you need a counterion to produce a neutral compound, use either K^+ or $SO_4{}^{-2}$. Remember, that we normally list cation first, followed by anion for ionic compounds.

Metal/charge	Ligands	Formula
V^{+3}	Four H_2O and two SCN^-	$[V(H_2O)_4(SCN)_2]_2SO_4$
Co^{+2}	Four Br^-	
Ru^{+3}	Three oxalates	
Os^{+3}	Three dppe	
Ni^{+2}	Two Br^-, two NH_3, and two CN^-	
Fe^{+3}	Six CN^-	

B. Geometric Isomerism (diastereomers) of Octahedral Complexes. Ligands can coordinate in various ways with profound differences in the chemical properties of the compounds. Just as ortho, meta- and paradichlorobenzene are different compounds with unique physical and chemical properties, the same is true with transition metals isomers.

1.MA_4B_2. This is the simplest empirical formula for which geometric isomerism is possible. The B groups can be situated 90° or 180° apart. No matter how you sketch them on these sets of axes, there only two unique arrangements. In language familiar from organic chemistry, the terms *cis* and *trans* names are given to the 90° and 180° situations. Label your sketches cis and trans.
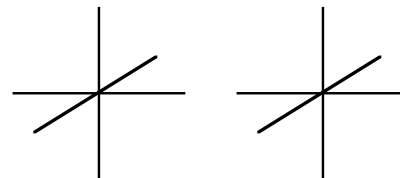
2.MA_3B_3. This has no analog in organic chemistry. Two ligands, three of each. There are only two ways to sketch them! They are called *fac* and *mer*. The term *fac* stands for facial as in the triangular face the octahedron makes when viewed down the C_3 axis. The term *mer* stands for meridian and describes the same ligands going around the "meridian of the octahedron."
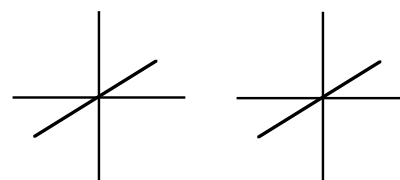
C. Optical Isomers of Octahedral Complexes. In organic chemistry you learned that it takes four different bonding groups to make a carbon center chiral. The explanation is based on the fact that with only three bonding groups, such as for $CABC_2$, there in an internal mirror plane, in this case a σ_v. For the octahedron, the minimum requirements for enantiomerism is 3 different groups! The simplest example would be *cis*-$MA_2B_2C_2$. Sketch this compound and its enantiomer using the coordinates.
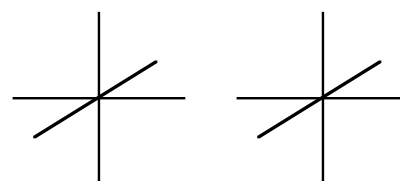
D. Stereoisomers. Geometric isomers (diastereomers) and optical isomers (enantiomers) are collectively referred to as *stereoisomers* or *configurational isomers*.

$MA_2B_2C_2$. Thinking in terms of *cis*, *trans*, *fac*, and *mer* is very helpful when trying to determine the number of isomers are possible for more complex situations. For example, consider the complex $MA_2B_2C_2$. If we start with the A ligands because we know they can be either *cis* or *trans*, we have simplified the problem considerably. (We could have started with the B or C ligands for the same reason.) Next we address the B ligands or C ligands and since there are two of each, we can do either one. Separately considering the two arrangements sketch above for the A ligands, what can the B ligands do? The C ligands are resigned to taking the remaining positions, so all together, there are _five_ geometric isomers (diastereomers) possible. Sketch them here. One of these five has a mirror image or enantiomer. If a structure has an internal mirror plane, σ_v or σ_h, the structure

does not have a mirror image. Use this fact to determine which of the five is enantiomeric. Circle the enantiometic structure and sketch its mirror image using the last coordinate system.
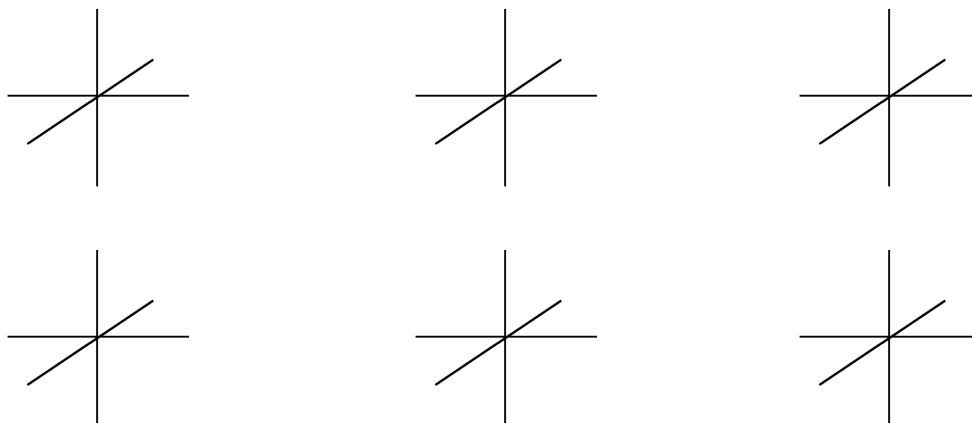
MA$_3$B$_2$C. How many geometric isomers are possible for MA$_3$B$_2$C? Sketch them. Remember it is useful to think in terms of *fac/mer* or *cis/trans*. This molecule allows for both. I recommend doing *fac/mer* prior to *cis/trans*.

Optional. Bored in the evenings? Try this optional one: How many structural isomers are possible for MA$_2$BCDE? Sketch them.

E. Chelates and geometric isomers. Bidentate ligands always bind *cis*. How many geometric isomers are possible for Fe(acac)(H$_2$O)$_4^{+2}$? Sketch them.

(b) There are three stereoisomers (two geometric and one pair of enantiomers) possible for

$Cr(ox)_2(H_2O)_2{}^{-2}$? Sketch them.
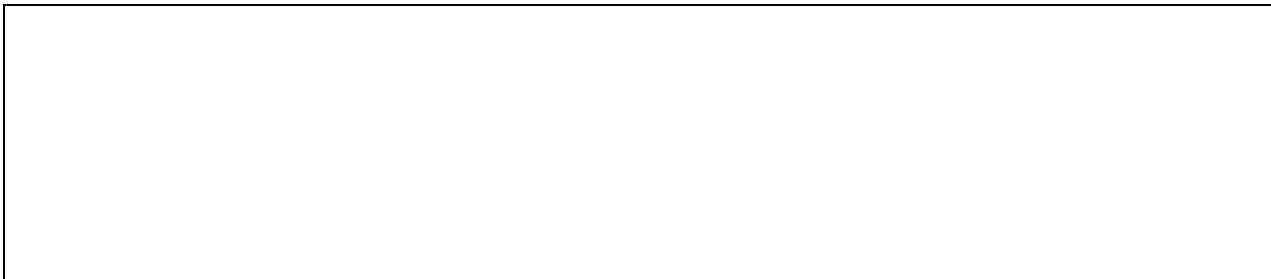
C. Optical Isomerism (enantiomerism) of Octahedral Complexes. As with the tetrahedron in organic chemistry, optical isomers exist if all the B groups are arranged in the same geometric arrangement, yet the mirror images are not super-imposable. With octahedral complexes, the simplest to visualize enantiomeric complex is M(bidentate)$_3$, shown below. For the sake of easier viewing, we start with the Cartesian coordinate system viewed down the C$_3$ rotation axis as shown in the left figure. In the two figures at right, the bidentate ligand is represented by an arc connecting two positions. The symbol Δ designates a right-handed rotation to the structure and Λ designates a left-handed rotation to the structure. Note that these designations to not necessarily correspond to the rotation of light caused by either isomer.

Δ   Λ
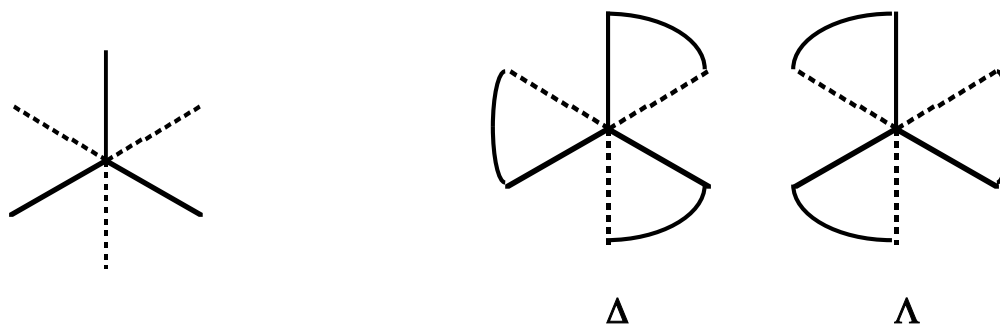
1. M(Bidentate)$_2$B$_2$. For this formula three isomers are possible, two geometric isomers and one of the two also exhibits optical isomerism. Sketch the three here.
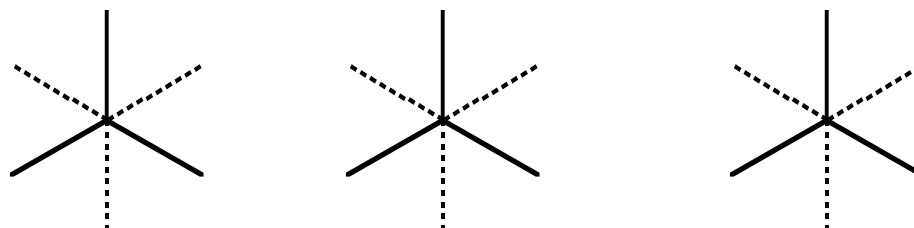
(a). Determine the number and type (geometric, optical) of isomers that occur in these compounds. Sketch them all.

$[Ni(NH_3)_4(H_2O)_2]SO_4$

$(NH_4)_2[Zr(SCN)_2Br_2(H_2O)_2]$

$(NH_4)_4[Fe(ox)_2(CN)_2]$
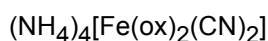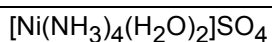
D. Linkage isomerism. We saw linkage isomerism earlier when he saw how thiocyanate could bind to a hard acid or soft acid through either the sulfur or nitrogen. This is not too common. Find another ligand that could exhibit linkage isomerism.

E. Coordination number 4

(a) The tetrahedron. Organic chemistry revisited! In Organic, you learned that enantiomerism occurs only when all four groups on a particular carbon are different, CBB'B''B'''. The same is true among tetrahedral inorganic compounds. If all four ligands are unique, the complex will be chiral. Geometric isomerism does not occur for the tetrahedron. Cu^{+2} is frequently involved in tetrahedral bonding. Create a Cu^{+2} complex that is optically active. Also sketch its mirror image.
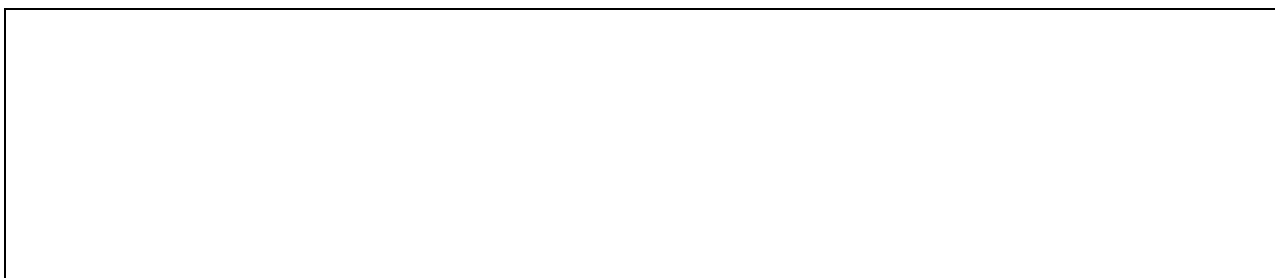
(b) The square plane. No metal-centered enantiomerism, but *cis/trans* geometric isomers are possible.

Sketch cis and trans square planar $Pt(NH_3)_2Cl_2$.

F. Periodic trends and coordination number. *Coordination number 6 is common for all transition metals of all charges.* We started this worksheet with a discussion of periodic trends across the transition metals. Ionic radii decreased from left to right. This has an impact on the coordination number expected for the metal ions. Early transition metals are rarely 4-coordinate, while late transition metals are more commonly 4-coordinate. Coordination numbers greater than 6 are more common for early transition metals and for 2nd and 3rd row metal cations. There are other factors affecting the coordination number, the most important one being the size of the ligand. Ligands such as cyanide take up relatively little room, while substituted amines or phosphines, NR_3 and PR_3, take up a huge amount of space. We expect large-volume ligands to favor lower coordination numbers.

G. Square planar complexes usually have metals with electronic configurations of d^8.

Examples include Ni^{+2}, Pd^{+2}, and Pt^{+2}. Also, Rh^{+1} and Ir^{+1}. The configuration d^8 can also be octahedral (6-coordinate), but when the coordination number is 4, d^8 configurations prefer square planar over tetrahedral geometries. We will learn why in an upcoming lesson. Predict which of these could also be square planar.

$AuCl_4^-$	$Co(NH_3)_4^{+3}$	$Cu(PPh_3)_4^{+2}$; Ph = C_6H_5

Review for ACS standardized final exam

1. Which of these compounds is most likely to be square planar?

   (a) $Co(NH_3)_4{}^{+2}$

   (b) $FeCl_4{}^{-2}$

   (c) $Ni(H_2O)_4{}^{+2}$

   (d) $Pt(en)_2{}^{+2}$

   (e) $TiCl_4$

2. What is the electronic configuration of cobalt in $K[Co(NH_3)_3(Cl)_3]$?

   (a) [Ar] $4s^2\ 3d^5$

   (b) [Ar] $4s^0\ 3d^7$

   (c) [Ar] $4s^0\ 3d^6$

   (d) [Ar] $4s^1\ 3d^5$

   (e) [Ar] $4s^2\ 3d^7$

3. Which estimation of ΔH and ΔS adequately explains the two reactions given below, both of which have large formation constants.

$$Ni(H_2O)_6{}^{+2} + 6\ NH_3 \longrightarrow Ni(NH_3)_6{}^{+2} + 6\ H_2O$$

$$Ni(NH_3)_6{}^{+2} + 3\ en \longrightarrow Ni(en)_3{}^{+2} + 6\ NH_3$$
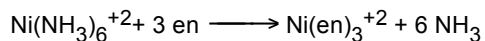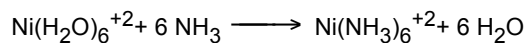
	First reaction		Second reaction	
(a)	ΔH < 0	ΔS < 0	ΔH < 0	ΔS < 0
(b)	ΔH < 0	ΔS = 0	ΔH = 0	ΔS < 0
(c)	ΔH > 0	ΔS < 0	ΔH = 0	ΔS > 0
(d)	ΔH < 0	ΔS = 0	ΔH = 0	ΔS > 0
(e)	ΔH = 0	ΔS < 0	ΔH < 0	ΔS = 0

4. Which of these compounds is chiral?

   (a) $Co(NH_3)_3(CN)_3{}^-$

   (b) $Cr(NH_3)_2(H_2O)_2(CN)_2{}^+$

   (c) $cis\text{-}Pd(NH_3)_2(Cl)_2$

   (d) $trans\text{-}Fe(en)_2(Cl)_2{}^+$

   (e) $cis\text{-}Mn(en)_2(Cl)_2$

5. What is the total number of stereoisomers possible for $Co(NH_3)_2(Br)_2(en)^+$?
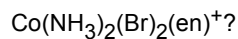
   (a) 3

   (b) 4

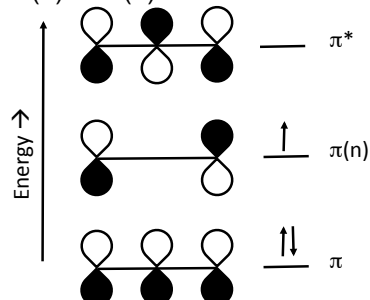   (c) 5

   (d) 6

   (e) 7

Answers: D, B, D, E, B

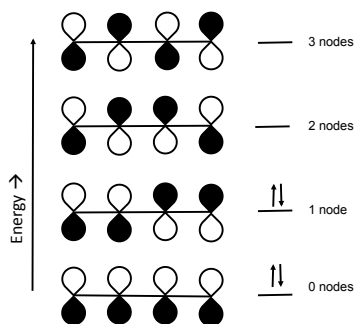# Answers to Day 15.

A. Conjugated ene systems.

1. The left one is bonding (0 nodes) and the right one is anti-bonding (1 node).
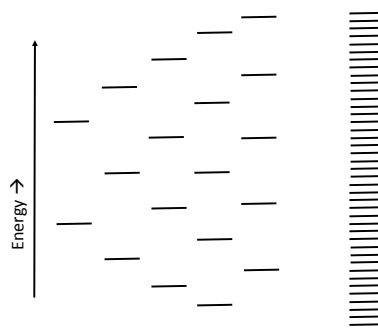
2. (a) and (d)

3.

(b) and (c)

	AO (C1)	AO (C2)	AO (C3)	sum
MO(π^*)	1/4	1/2	1/4	1
MO($\pi(n)$)	1/2	0	1/2	1
MO(π)	1/4	1/2	1/4	1
sum	1	1	1	

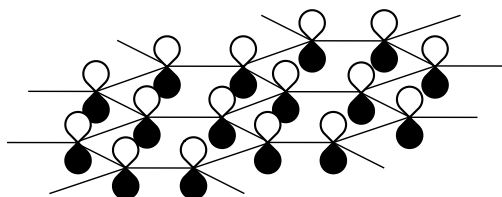(e) For the allyl radical, there is a node at C2. The radical electron is on C1 and C3

B. Extended conjugated ene systems. The lower half of each of these MO diagrams are filled.
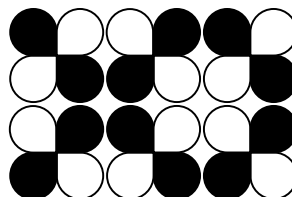

C. Network covalents.

2. (a) diamond NC (b) tin M (c) calcium carbide I

(d) silicon carbide NC (e) silicon SM (f) silicon tetrachloride CM

(g) sodium silicide I (h) graphite NC (g) copper M

3.

4.

D. Band theory. 2. From L → R: conductor, semi-conductor, insulator; 3. The MO diagrams were made from s and d orbitals (6 orbitals) per atom. They are, in order, Sc, Cr, Co, and Zn. The bond order is largest for the half-filled figure, and that corresponds to Cr. Chromium has a high melting point and is hard and strong. Zinc, cadmium and mercury must use p-orbitals as well in their valence manifold. This way they can have some bond order and be able to conduct electricity.

3. (a) Silicon be a non-conductor at 0 K. (b):
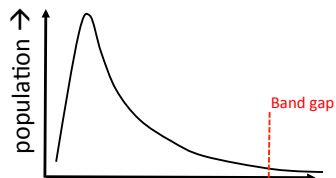
E. Semi-conductors. 1a.

population →

Band gap

F. Diodes: p-n junctions. 2a. The p-type is slightly **negative** and the n-type is slightly **positive**. (b) Left half is δ^-. 3. The energies of orbitals on cations are **lower** than on their neutral or negative counterparts.
4. When the voltage is applied in a forward bias situation, electrons flow as per the arrow. When the battery is switched, electrons do not flow. The diode "rectifies" alternating current, turning it into phased direct current

G. Photosensitive switches.

Photons

Photons cause excitation

DC

Applied voltage

H. Photovoltaic cells

Photons

Photons cause excitation

I. LEDs

LED

Photon emitted

DC

Electron flow