Chem 241

Lecture 9

Recap

- Should be able to assign a Point Group
- Use point groups to determine chiral molecules and polarity.

Character Table

Table 7.3 The components of a character table

Name of point group*	Symmetry operations R arranged by class (E, C_n, etc.)	Functions	Further functions	Order of group, h
Symmetry species (Γ)	Characters (χ)	Translations and components of dipole moments (x, y, z), of relevance to IR activity Rotations (about axes x, y, z)	Quadratic functions such as z^2, xy, etc., of relevance to Raman activity	

* Schoenflies symbol.

Table 7.4 The C_{2v} character table

C_{2v}	E	C_2	$\sigma(zx)$	$\sigma'(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yx

MO polyatomic

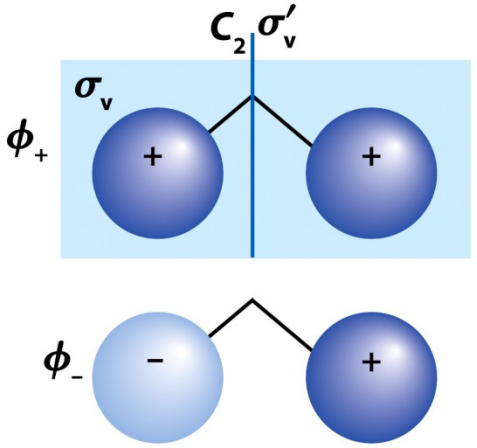
Consider H_2O

a. Point group = C_{2v}

b. 2 1s orbitals on equivalent H atoms generate 2 SALCs

$\psi_1 = 1s\ (H_a) + 1s\ (H_b)$

$\psi_2 = 1s\ (H_a) - 1s\ (H_b)$



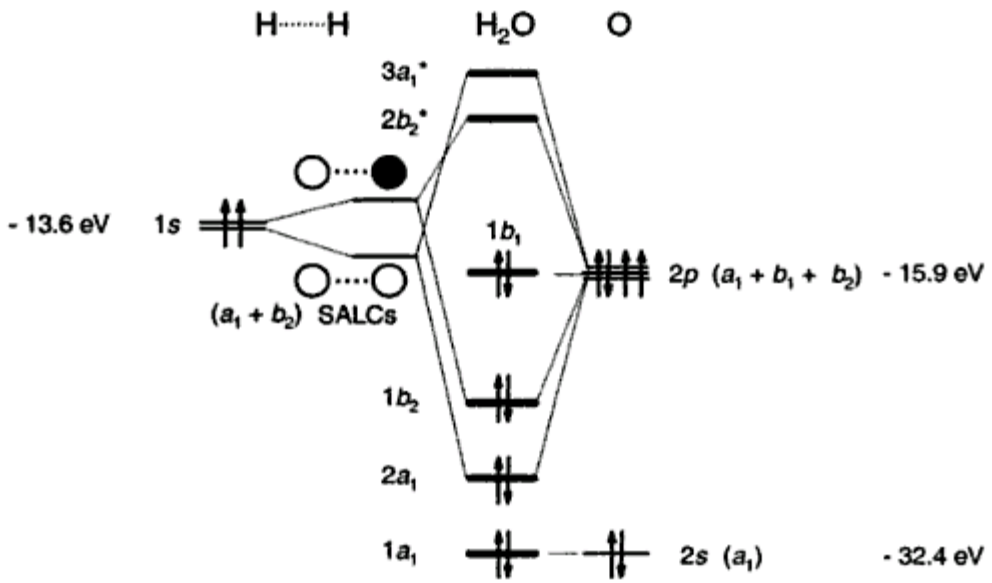
c. What symmetries do these SALCs have? (perform symmetry ops for the group, assign "1" if unchanged, "-1" if inverted.)

Can look up O AO symmetries (s, p_z–A_1; p_x–B_1; p_y–B_2)

d. Combine SALCS of the same symmetry

Symmetry

- MO diagram for H_2O



A little more complex

- Consider NH_3
  a. Point group = C_{3v}
  b. 3 1s orbitals on equivalent H atoms generate 3 SALCs

     $\phi_1 = 1s\ (H_a) + 1s\ (H_b) + 1s\ (H_c)$ ---A_1

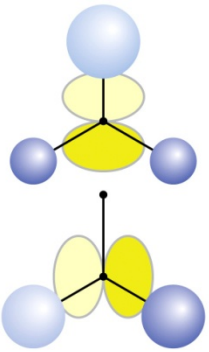
     $\phi_2 = 2\ 1s\ (H_a) - 1s\ (H_b) - 1s\ (H_c)$ ----E

     $\phi_3 = \ \ 1s\ (H_b) - 1s\ (H_c)$ ----E

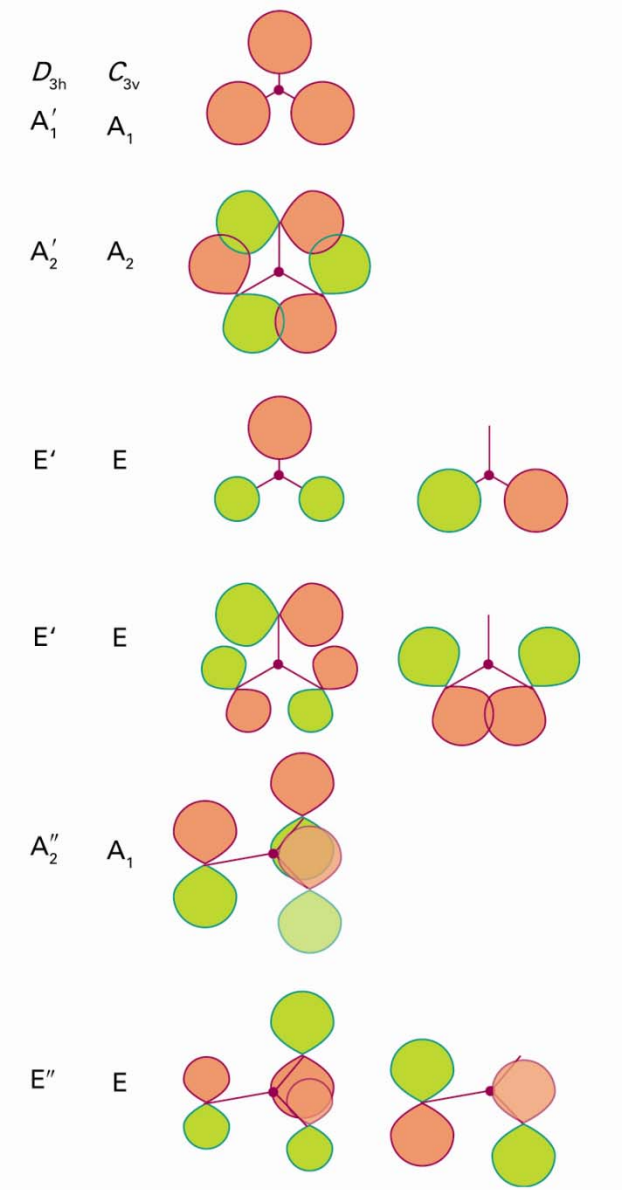
  c. What symmetries do these SALCs have? (perform symmetry ops for the group, assign "1" if unchanged, "-1" if inverted.

     Can look up O AO symmetries (s, p_z–A_1; p_x– E; p_y–E)

  d. Combine SALCS of the same symmetry



A little more complex

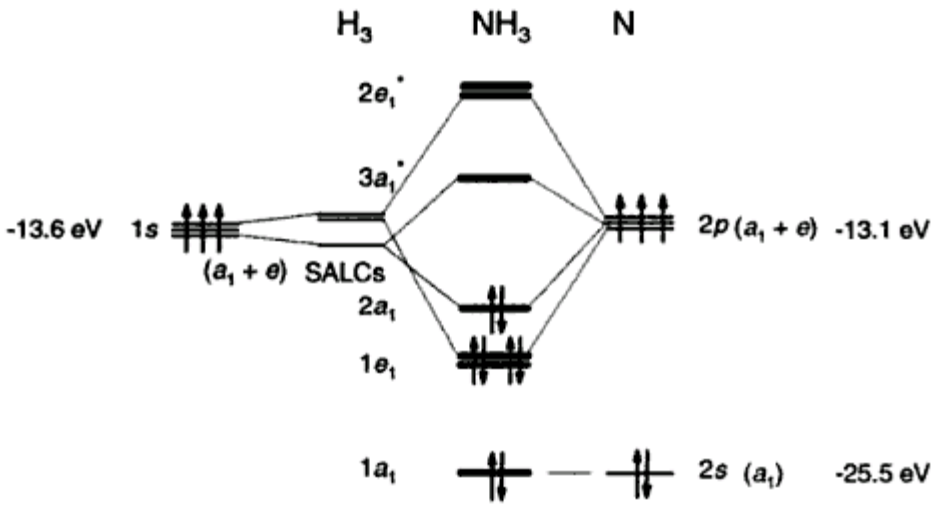


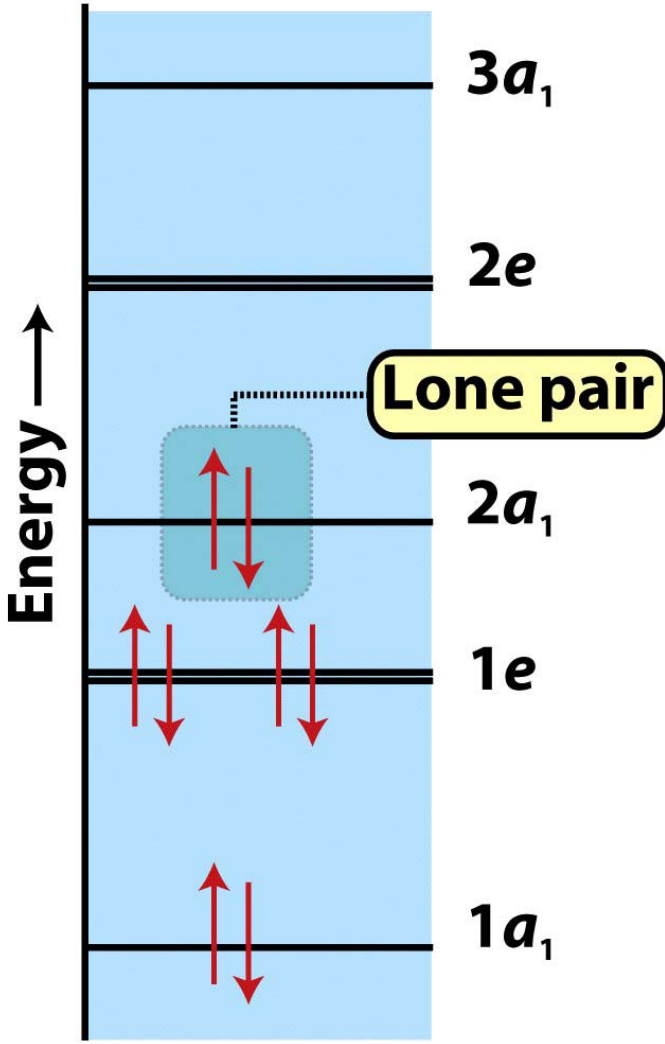
Symmetry

- MO diagram for NH_3

Table 7.5 The C_{3v} character table

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x,y) (R_x, R_y)	(zx, yz) $(x^2 - y^2, xy)$





MO diagrams for polyatomics

- a. Assign the molecule to a point group
- b. use the character table of that point group to generate SALCs for equivalent atoms, or look them up (see resource section 4/5 in Shriver)
- c. arrange the SALCs for each fragment in order of increasing energy, given issues of whether they derive from s, p or d etc. orbitals, and then the number of nodes in the wavefunction.
- d. Combine SALCs of the same symmetry type from the two fragments (equivalent atoms and central atom). (Remember N AOs generate N SALCs, which generate N MOs.)
- e. Confirm, correct, and revise the qualitative energy order by experiment (*e.g.,* PES) or by carrying out a calculation.

Homework

- Chapter 7, 8

Exercises: 7.2, 7.3, 7.6

Problem: 7.1

We will stop our discussion of symmetry at spectroscopic applications (section 7.8).

Additional courses that advance this material include Chem 546 (Advanced Inorganic) and Chem 648 (Coordination Chemistry)

Coordination Compounds

- Metal complexes, in which a single metal ion is surrounded by several ligands, is chemistry that is typical of d-block and f-block elements,

- The modern view of coordination compounds stems from the work of Alfred Werner, who was intrigued by the colors of metal complexes and won a Nobel Prize in 1913. (He proposed that all ligand molecules are bound directly to the metal ion, contrary to existing bonding theory.)

The Dilema

Complex	Color	Early Name	Excess Ag^+
$CoCl_3(NH_3)_6$	Yellow	*Luteo* complex	3 AgCl
$CoCl_3(NH_3)_5$	Purple	*Purpureo* complex	2 AgCl
$CoCl_3(NH_3)_4$	Green	*Praseo* complex	1 AgCl
$CoCl_3(NH_3)_4$	Violet	*Violeo* complex	1 AgCl

- Compounds $M(NH_3)_6X_3$ are derived from compounds by loss of one ammonia molecule

Some Definitions

1. Coordination compounds (complexes) result from the combination of Lewis acids and bases. The central metal is a Lewis acid (acceptor atom) the ligands are Lewis bases (donor atom).

   An example: $[Co(NH_3)_6]Cl_3$

Hexamine cobalt(III) chloride is a salt that contains the complex cation, $[Co(NH_3)_6]^{3+}$ and chloride **counterions**.

2. In the cation, Co(III) is the Lewis acid and NH_3 is the Lewis base, or **ligand**. The number of ligands is the **coordination number**.

3. The ligand **donor atoms** (in this case N atom) are bonded to the metal.

Coordination Compounds

4. The sum of all the ligands constitutes the **primary coordination sphere** of the metal. The [] in formulas are used to define the primary coordination sphere.

   What is $NiCl_2 \cdot 6H_2O$? $[Ni(H_2O)_6]Cl_2$

   What is $CoCl_2 \cdot 6H_2O$? $[Co(Cl)_2(H_2O)_4] \cdot 2H_2O$

In the first case, the choride anions outer sphere, in the second case they are inner sphere.

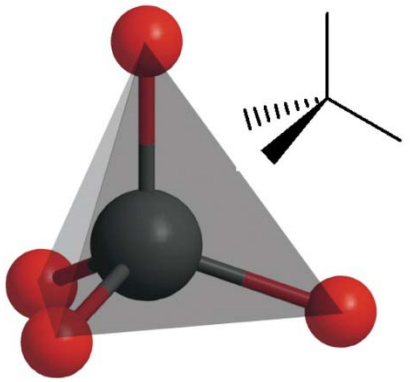
5. The additional solvent molecules in the outer sphere of $[Co(Cl)_2(H_2O)_4] \cdot 2H_2O$ are **solvent of crystallization**.

Low Coordination

- 1. Low coordination numbers (CN = 2, 3). Most common for electron rich metals, d^{10} ions like Cu(I), Ag(I), Au(I), Hg(II) with small ligands
- Three coordination is rare and typically occurs with bulky ligands. Many low coordinate complexes readily add additional ligands.

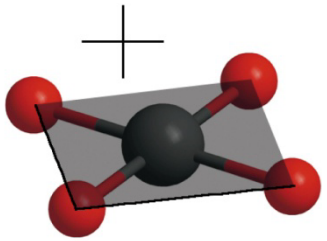
4 - Coordinate Compounds

- Two common 4-coordinate geometries: tetrahedral and square-planar.



- Tetrahedral complexes are favored by sterics. are common when the metal ion is small (right side and third row) and when the ligands are large.

- Square planar complexes result from electronics (common in d^8 metals) or from constraints.



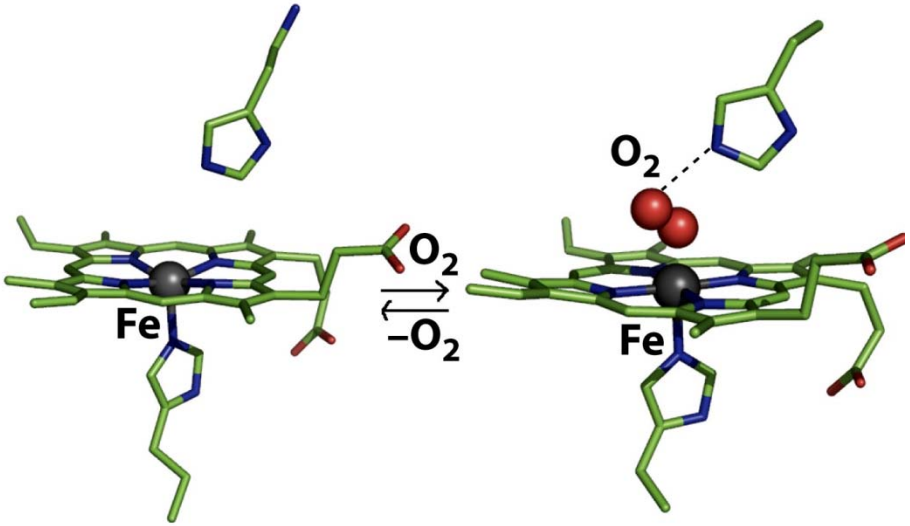
- **geometrical isomers**

- Consider complexes of ML_3X and M_2L_2

5 - Coordinate Compounds

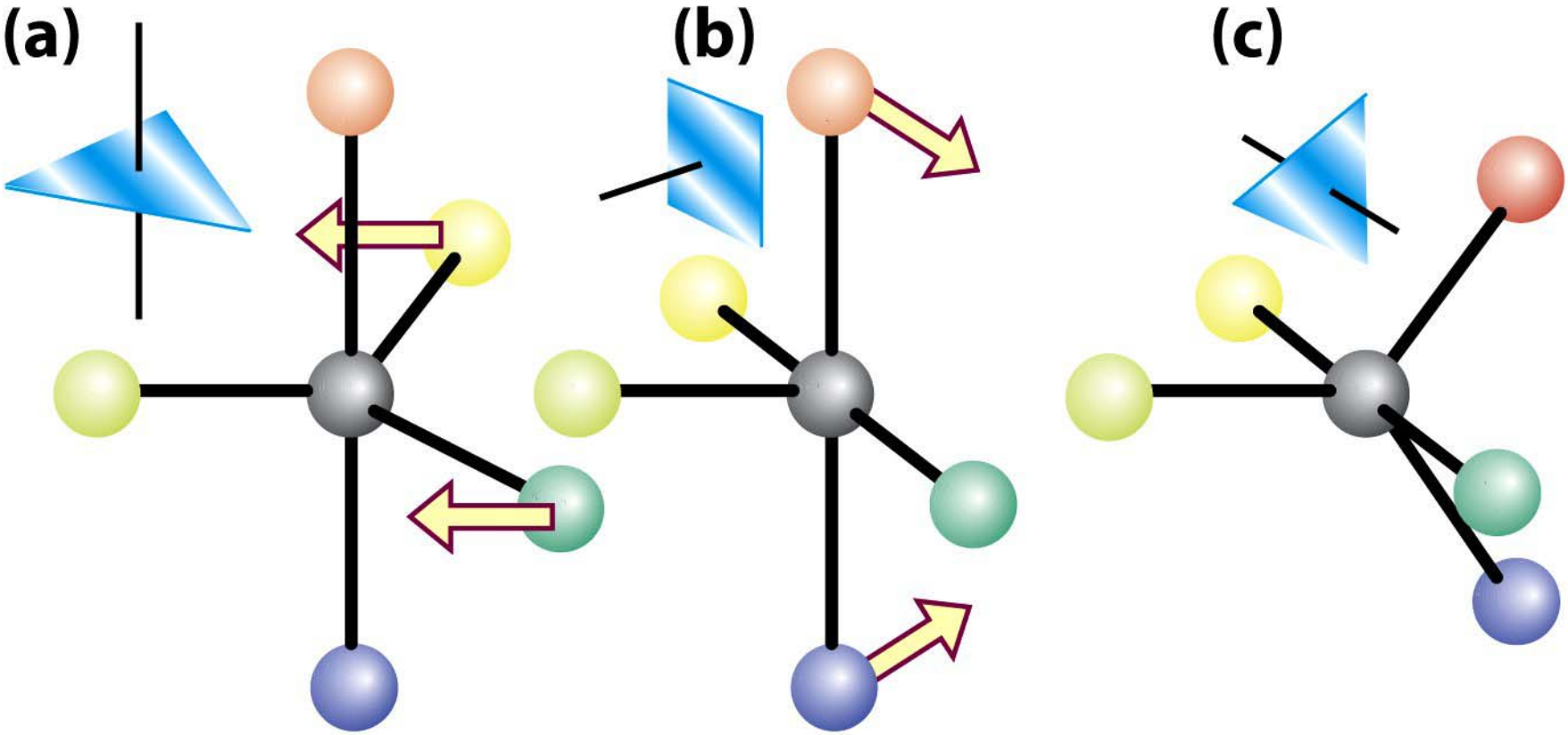
- Square planar geometry can also be forced by ligands that have an inflexible ring of four donor atoms, (e.g, macrocycles such as porphyrins).

c. Five-coordinate (CN=5) complexes have two limiting geometries, trigonal bipyramidal and square pyramidal, that often differ little in energy and are thus fluxional.



Coordination Compounds

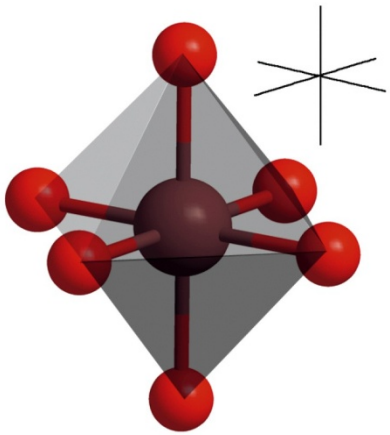
- Fluxional behavior can equilibrate all five ligands via a Berry pseudo-rotation mechanism.



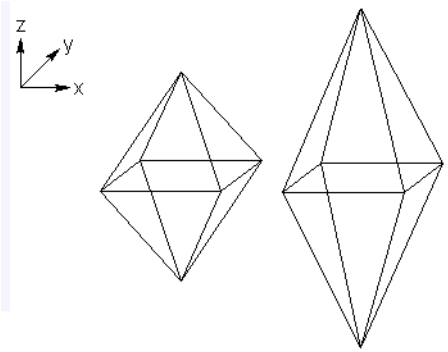
5 - Coordinate Compounds

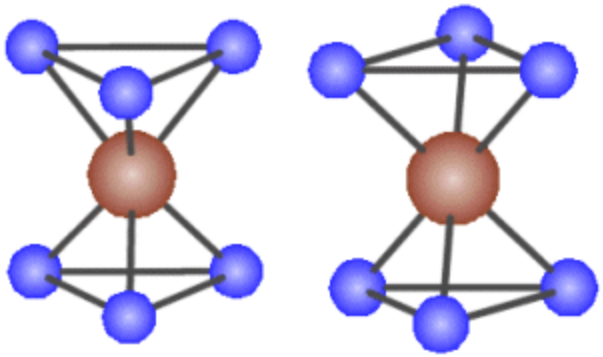
- d. Six-coordinate complexes are the most comm

  Most have octahedral thereof. (e.g., tetragonal, trigonal, rhombic).



13 Octahedral complex, O_h





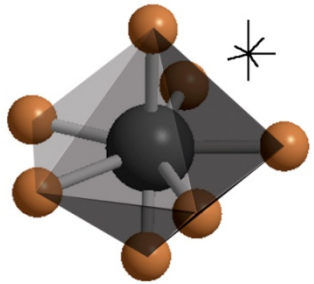
Trigonal Prism

Trigonal Antiprism

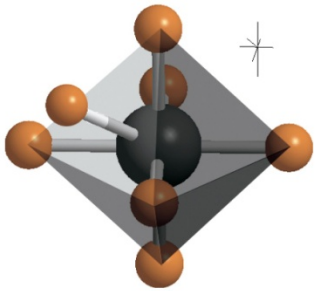
7 & 8 Coordinate

- Higher coordination numbers (more common for 4th and 5th row M(s)).

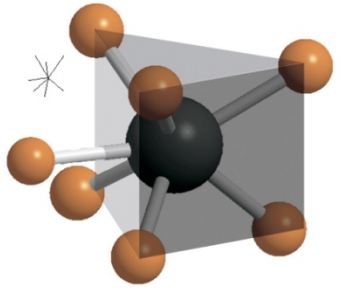
CN = 7



16 Pentagonal bipyramid, D_{5h}



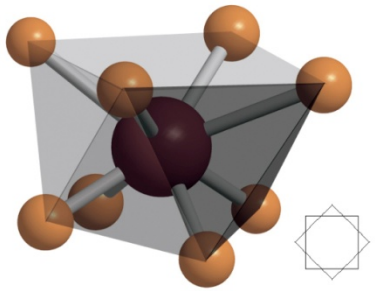
17 Capped octahedron



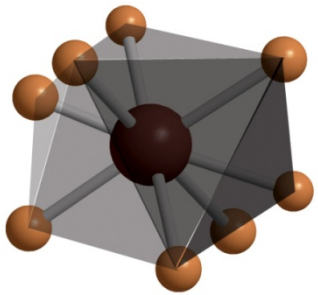
18 Capped trigonal prism

+

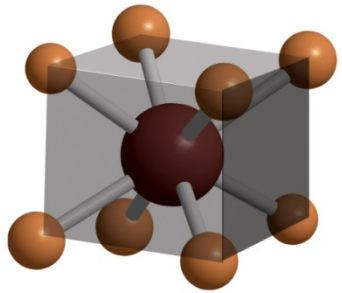
CN = 8 (also sterochemically non-rigid)



20 Square antiprism, D_4



21 Dodecahedron



24 Cube

rare

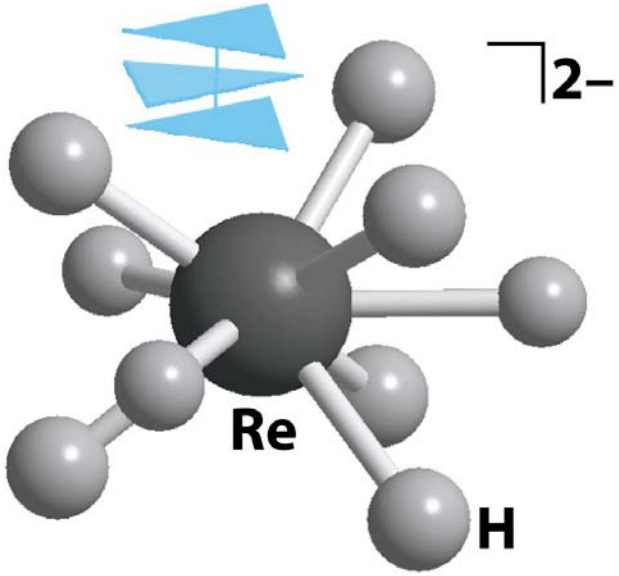
$[Mo(CN)_8]^{3-}$

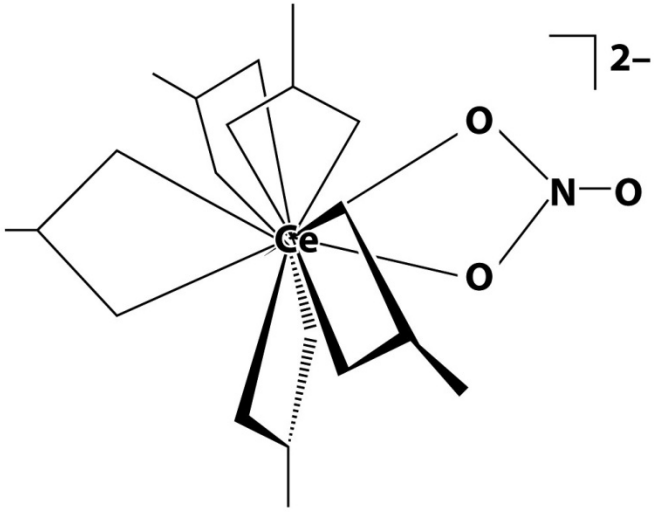
Coordination Compounds

CN = 9

More common in f block (e.g., $[Nd(OH_2)_9]^{3+}$)

Important d-block compound- $[ReH_9]^{2-}$ (note small L)





26 $[Ce(NO_3)_6]^{2-}$

CN = 10, 12 also known for f-block elements, e.g., $[Ce(NO_3)_6]^{2-}$