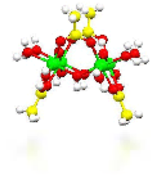


Chapter 22

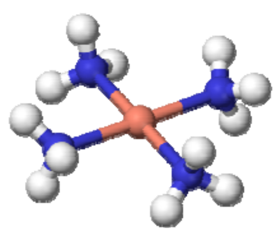
COORDINATION CHEMISTRY

(Part I)

21.1

Coordination Compounds

- ***Coordination compounds*** contain *coordinate covalent* bonds formed between metal ions with groups of *anions* or *polar molecules.*
  - Metal ion : Lewis acid (e^- acceptor)
  - Bonded groups : Lewis base (e^- donors)
- C***omplex ions***
  - They are ions in which the metal cation is covalently bound to one or more molecules or ions.
  - A pair of electrons is donated by the group (an ion or a polar molecule) to form a bond with the metals. ← *Coordinate covalent* bonds



Tetraamminecopper(II) ion $Cu(NH_3)_4^{2+}$

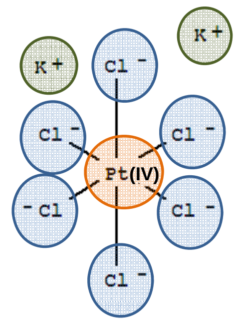
21.1

Coordination Compounds

- Components of a coordination compound:
  1. Complex ion (enclosed in square brackets)

$K_2[PtCl_6]$

  2. Counter ions
  3. Ligands
  4. Metal: Most of the metals that form complexes are ***transition metals***.



- Some coordination compounds do not contain a complex ion.

$Fe(CO)_5$

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Transition Metals

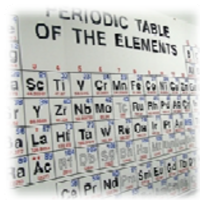
They (as well as their ions) have incompletely filled *d* subshells.

Based on the definition above, **Zn**, **Cd** and **Hg** are not considered to be transition metals.

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	(117)	118

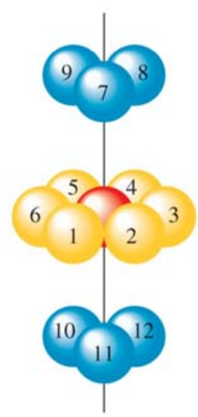
Properties of Transition Metals

- The incompletely filled *d* orbitals in transition metals give them some properties, such as:
  - Paramagnetism.
  - Catalytic activity.
  - Tendency to form complex ions.
  - Distinctive colors of the solutions formed by their ions.



Properties of Transition Metals

- Transition metal atoms normally have *close-packed structure* where a metals atom has 12 neighboring atoms. This fact results in many ***unique*** properties for metals, such as:
  - small atomic radii.
  - strong metallic bonding.
  - high densities.
  - high melting and boiling point.



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Properties of Transition Metals

- Transition metals exhibit variable oxidation states in their compounds.

				+7				
			+6	+6	+6			
		+5	+5	+5	+5			
	+4	+4	+4	+4	+4	+4		
+3	+3	+3	+3	+3	+3	+3	+3	+3
	+2	+2	+2	+2	+2	+2	+2	+2
								+1
Se	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**

- Oxidation states shown in red are the most stable ones for specific metals.
- Metals ions have higher oxidation states when coordinated to highly electronegative elements such as oxygen.
  - Mn_2O_7
  - V_2O_5

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Properties of Transition Metals

TABLE 22.1 Electron Configurations and Other Properties of the Fourth-Period Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configuration									
M	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$
M^{2+}	—	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9
Ionization energy (kJ/mol)									
First	631	658	650	652	717	759	760	736	745
Second	1235	1309	1413	1591	1509	1561	1645	1751	1958
Third	2389	2650	2828	2986	3250	2956	3231	3393	3578
Radius (pm)									
M	162	147	134	130	135	126	125	124	128
M^{2+}	—	90	88	85	80	77	75	69	72
M^{3+}	81	77	74	64	66	60	64		

Properties of Transition Metals

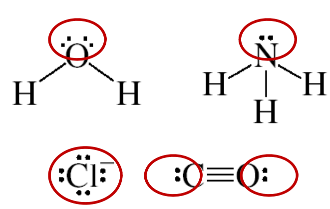
- Physical properties of transition metals vary greatly from those of the main group elements and the 2B group elements.

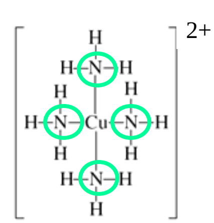
TABLE 22.2 Physical Properties of Elements K to Zn

	1A	2A	Transition Metals									2B
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius (pm)	235	197	162	147	134	130	135	126	125	124	128	138
Melting point (°C)	63.7	838	1539	1668	1900	1875	1245	1536	1495	1453	1083	419.5
Boiling point (°C)	760	1440	2730	3260	3450	2665	2150	3000	2900	2730	2595	906
Density (g/cm^3)	0.86	4.51	3.0	4.51	6.1	7.19	7.43	7.86	8.9	8.9	8.96	7.14

Ligands

- ***Ligands*** are the polar molecules or ions that surround the transition metal ion in a complex ion.
- A ligand:
  - must contain at least one *unshared pair of valence electrons*.
  - acts as a *Lewis base*, while the metal ion acts as a Lewis acid.
  - contains *donor atoms* which are the atoms that are directly bonded to the metal atom.





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Common Ligands

- A ***monodentate ligand*** has only *one donor atom*.

Name	Structure
Monodentate	
Ammonia	H—N̈—H (with H below N)
Carbon monoxide	:C≡O:
Chloride ion	$[:\ddot{Cl}:]^-$
Cyanide ion	$[:C≡N:]^-$
Thiocyanate ion	$[:\ddot{S}—C≡N:]^-$
Water	H—Ö—H

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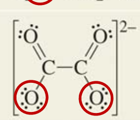
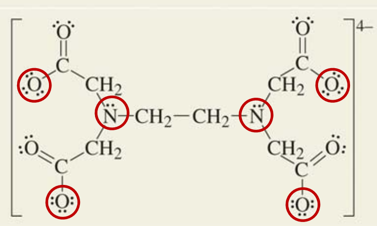
Common Ligands

- A ***bidentate ligand*** has *two donor atoms*.
- A ***polydentate ligand*** has *more than two donor atoms*.

Bidentate	
Ethylenediamine (en)	$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$
Oxalate ion	
Polydentate	
Ethylenediaminetetraacetate ion (EDTA)	

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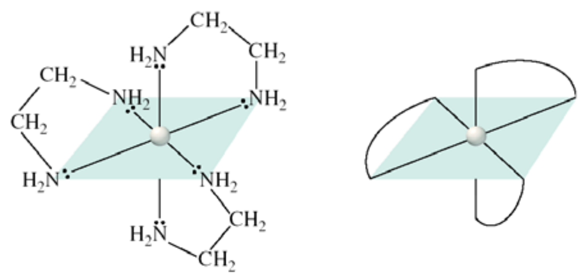
Chelating Agents

- ***Chelating agents*** is another name for *bidentate* or *polydentate* ligands.

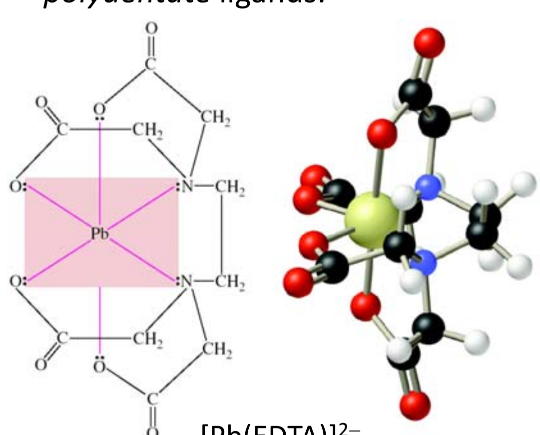


Each ***ethylenediamine (en)*** molecule provides two N donor atoms. Thus, en is a ***bidentate ligand***.

$[Co(en)_3]^{2+}$

Chelating Agents

- ***Chelating agents*** is another name for *bidentate* or *polydentate* ligands.



A single ***EDTA*** ion provides six donor atoms. Thus, EDTA is a ***polydentate ligand***.

• The EDTA ion has 4– charge,
• while the overall charge of the complex ion is 2–.
• So the Pb ion must adopt an oxidation state of +2.
Pb(II)

$[Pb(EDTA)]^{2-}$

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Determination of Oxidation Numbers

- Example (1):
  What is the oxidation state of the Pt ion in $K_2[PtCl_6]$?
  - Because the overall charge on the compound is zero, the complex ion is $[PtCl_6]^{2-}$.
  - There are *six ligands* each with a *−1 charge*, making the total negative charge *− 6*.
  - So the charge on the platinum ion *must be +4*.
- Example (2):
  What is the oxidation state of the Au ion in $[Au(NH_3)_2(OH)_2]^{-1}$?

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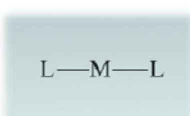
Coordination Number

- A ***coordination number*** refers to the number of donor atoms surrounding the central metal atom in a coordination compound.
- Most of common coordination numbers are 4 and 6, and to less extent, 2 and 5.



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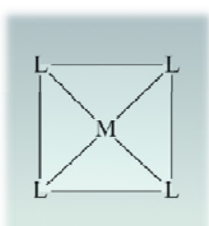

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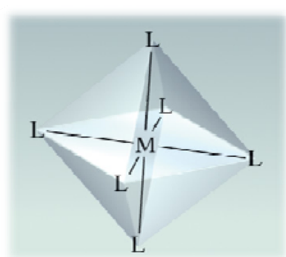

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Naming Coordination Compounds

1. The *cation* is named ***before*** the *anion*, as in other ionic compounds.
2. Within *a complex ion*, the *ligands* are named ***first***, in an alphabetical order, and the *metal ion* is named ***last***.
3. The names of ***anionic ligands*** end with the letter ***o***, whereas ***neutral ligands*** are usually called by the *same names* of the molecules.
   Exceptions are H_2O (aquo), CO (carbonyl) and NH_3 (ammine).

$K[Co(NH_3)_2Cl_4]$

$[Co(NH_3)_2Cl_4]^-$

Chlor***o***

Ammine

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Naming Coordination Compounds

TABLE 22.4 Names of Common Ligands in Coordination Compounds

Ligand	Name of Ligand in Coordination Compound
Bromide, (Br^-)	Bromo
Chloride, (Cl^-)	Chloro
Cyanide, (CN^-)	Cyano
Hydroxide, (OH^-)	Hydroxo
Oxide, (O^{2-})	Oxo
Carbonate, (CO_3^{2-})	Carbonato
Nitrite, (NO_3^-)	Nitro
Oxalate, ($C_2O_4^{2-}$)	Oxalato
Ammonia, (NH_3)	Ammine
Carbon monoxide, (CO)	Carbonyl
Water, (H_2O)	Aquo
Ethylenediamine	Ethylenediamine (en)
Ethylenediaminetetraacetate	Ethylenediaminetetraacetate (EDTA)

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Naming Coordination Compounds

4. When two or more of the same ligand are present, use Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* to specify their number. (Prefixes are not included in determining the alphabetical order.)
   - *When the name of the ligand contains a Greek prefix, a different set of prefixes are used for the ligand: 2 = bis-, 3 = tris-, 4 = tetrakis-.*

$K[Co(NH_3)_2Cl_4]$

$[Co(NH_3)_2Cl_4]^-$

diamminetetrachloro

⇨ $[Co(en)_3]^{2+}$ *tris*(ethylenediamine)

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Naming Coordination Compounds

5. The oxidation number of the metal is indicated with ***Roman numerals*** immediately following the name of the metal.
6. If the complex is an anion, its name ends with ***-ate***. (Roman numeral indicating the oxidation state of the metal *follows* the suffix *-ate*)

$K[Co(NH_3)_2Cl_4]$

(III)

$[Co(NH_3)_2Cl_4]^-$

diamminetetrachlorocobalt***ate***(III)

⇧

No space is there between the ligand names, the metal name and Roman number.

<u>The final name:</u>

Potassium diamminetetrachlorocobaltate(III)

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Naming Coordination Compounds

TABLE 22.5 Names of Anions Containing Metal Atoms

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

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Naming Coordination Compounds

- Example (1):

  Give the correct name for $[Cr(H_2O)_4Cl_2]Cl$.

  Tetraaquodichlorochromium(III) chloride

- Example (2):

  Write the formula for *tris*(ethylenediamine)cobalt(III) sulfate.

  $[Co(en)_3]_2(SO_4)_3$

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Naming Coordination Compounds

(1) Select the correct name for the compound $[Cu(NH_3)_4]Cl_2$.

a) Coppertetraammine dichloride
b) Tetraamminecopper(II) chloride
c) Tetraaminedichlorocuprate(II)
d) Dichlorotetraaminecopper(II)
e) Tetraaminedichlorocopper(II)

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Naming Coordination Compounds

(2) Select the correct formula for pentaaminenitrocobalt(III).

a) $[Co(NH_3)_5NO_3]^{3+}$
b) $[Co(NH_3)_5NO_3]^{2+}$
c) $Co(NH_3)_5NO_3$
d) $[Co(NH_3)_5](NO_3)$
e) $[Co(NH_3)_5](NO_3)_2$

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Naming Coordination Compounds

(3) Select the correct name for the compound $K_3[FeF_6]$.

a) Tripotassiumironhexafluoride
b) Hexafluorotripotassiumferrate(III)
c) Hexafluoroiron(III) potassium
d) Potassium hexafluoroferrate(III)
e) Potassium ironhexafluorate

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Naming Coordination Compounds

(4) Select the correct formula for tetraaquodichlorochromium(III) chloride.

a) $[Cr(H_2O)_4Cl_2]Cl_3$
b) $[Cr(H_2O)_4Cl_2]Cl_2$
c) $[Cr(H_2O)_4Cl_2]Cl$
d) $[Cr(H_2O)_4]Cl_3$
e) $[Cr(H_2O)_4]Cl_2$

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Naming Coordination Compounds

(1) Select the correct name for the compound $[Cu(NH_3)_4]Cl_2$.

a) Coppertetraammine dichloride
✓ b) Tetraamminecopper(II) chloride
c) Tetraaminedichlorocuprate(II)
d) Dichlorotetraaminecopper(II)
e) Tetraaminedichlorocopper(II)

Naming Coordination Compounds

(2) Select the correct formula for pentaaminenitrocobalt(III).

a) $[Co(NH_3)_5NO_3]^{3+}$
✓ b) $[Co(NH_3)_5NO_3]^{2+}$
c) $Co(NH_3)_5NO_3$
d) $[Co(NH_3)_5](NO_3)$
e) $[Co(NH_3)_5](NO_3)_2$

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Naming Coordination Compounds

(3) Select the correct name for the compound $K_3[FeF_6]$.

a) Tripotassiumironhexafluoride

b) Hexafluorotripotassiumferrate(III)

c) Hexafluoroiron(III) potassium

✓ d) Potassium hexafluoroferrate(III)

e) Potassium ironhexafluorate

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Naming Coordination Compounds

(4) Select the correct formula for tetraaquodichlorochromium(III) chloride.

a) $[Cr(H_2O)_4Cl_2]Cl_3$

b) $[Cr(H_2O)_4Cl_2]Cl_2$

✓ c) $[Cr(H_2O)_4Cl_2]Cl$

d) $[Cr(H_2O)_4]Cl_3$

e) $[Cr(H_2O)_4]Cl_2$