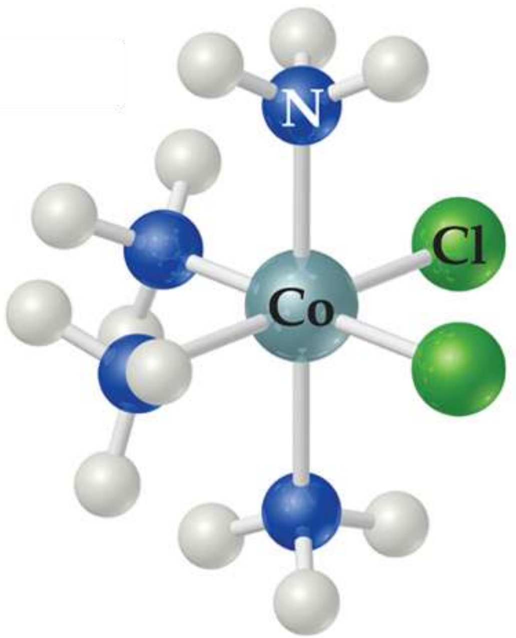
Coordination Compounds and Complexation



Assist.Prof.Dr. Mohammed Hassan

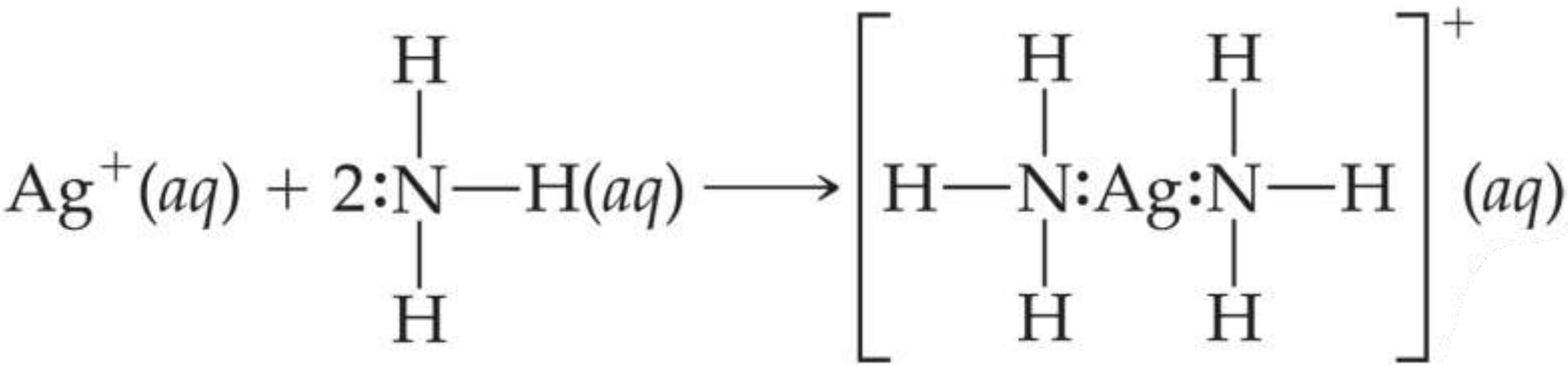
Lecture 4

- metal complex: A central metal atom bonded to a group of molecules or ions
- If the complex bears a charge, it is a complex ion.
- coordination compounds: Compounds containing complexes.

- The molecules or ions coordinating to the metal are the ligands.
- They are usually anions or polar molecules.

Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
  - The ligands (Lewis bases) have nonbonding electrons.
  - The metal (Lewis acid) has empty orbitals.



Oxidation Numbers

or Complex charge

Complex charge = sum of charges on the metal and the ligands

$[Fe(CN)_6]^{3-}$

+3

6(-1)

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions

$[Co(NH_3)_6]Cl_2$

+2 6(0) 2(-1)

neutral compound

Electron Configuration Exceptions

- Electrons are removed from *4s* orbital before they are taken out of *3d*
  - Energies of *3d/4s* orbitals are not as close together in ions of transition metals as in neutral atoms
  - In ions of transition elements, *3d* orbitals are lower in energy than *4s* orbitals
  - Therefore, electrons most easily lost are those in outermost principal energy level, the ns
  - Additional electrons may then be lost from *(n – 1)d* orbital

		3*d*					4*s*	
Sc	[Ar]	↑					↑↓	[Ar]$3d^1 4s^2$
Ti	[Ar]	↑	↑				↑↓	[Ar]$3d^2 4s^2$
V	[Ar]	↑	↑	↑			↑↓	[Ar]$3d^3 4s^2$
Cr	[Ar]	↑	↑	↑	↑	↑	↑	[Ar]$3d^5 4s^1$
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar]$3d^5 4s^2$
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar]$3d^6 4s^2$
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar]$3d^7 4s^2$
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar]$3d^8 4s^2$
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar]$3d^{10} 4s^1$
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	[Ar]$3d^{10} 4s^2$

Complex Ions

Ligands

Definitions:

- **Coordination compound**
  - Complex ion and counter ions
  - Are neutral
- **Complextion**
  - Central transition metal with attached ligands
  - Has net charge (+/-)
  - Complex is set off in brackets that isolate it from the rest of compound
  - Ions outside brackets-free (uncomplexed) ions
  - Metal cation-**central atom**
- **Counter ions**
  - Anions/cations needed to balance charge so it has no net charge

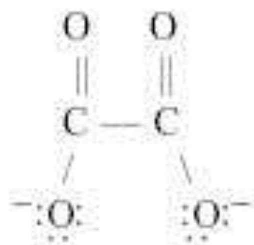
- **Ligand (complexing agent)**
  - Neutral molecule or anion w/**lone pair** that can be used to form bond to central metal ion
- **(Mono)Unidentate ligand**
  - Can form one bond to metal ion
  - One donor atom present and can occupy only one site in coordination sphere
    - Even if more than one pair of electrons available, if donation of one pair does not allow for proper positions to make additional bonds, other pairs don't bond
  - Halide ions, SCN- (thiocyanate ions), anions of weak acids

H_2O, CN^-, NH_3, NO^{2-}, SCN^-, OH^-, X^- (halide ions), CO, O^{2-}

Bidentate ligand

- 2 donor atoms present and can occupy 2 or more coordination sites (2 bonds to metal ion)
- Most common (diamines/anions of diprotic organic acids)

- examples: oxalate ion (ox), $C_2O_4^{2-}$; ethylenediamine (en), $NH_2CH_2CH_2NH_2$

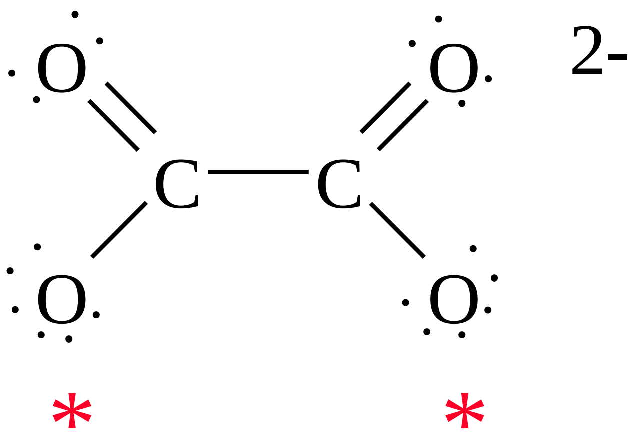


Oxalate ion (ox), $C_2O_4^{2-}$

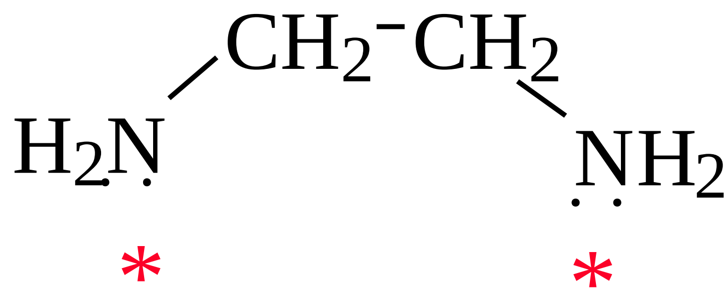
$H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$

Ethylenediamine (en)

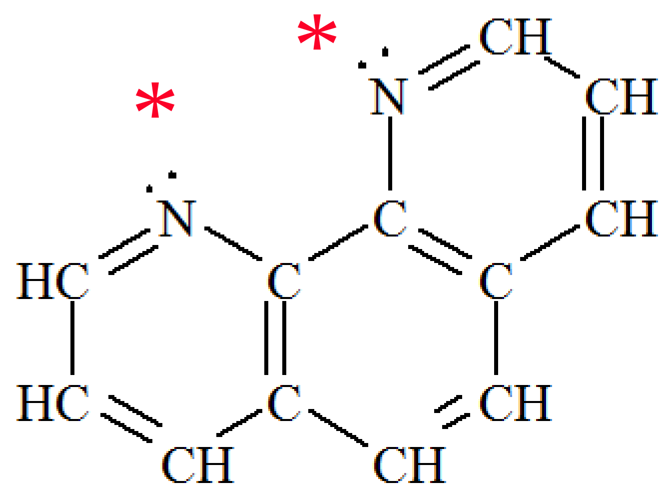
oxalate ion



ethylenediamine

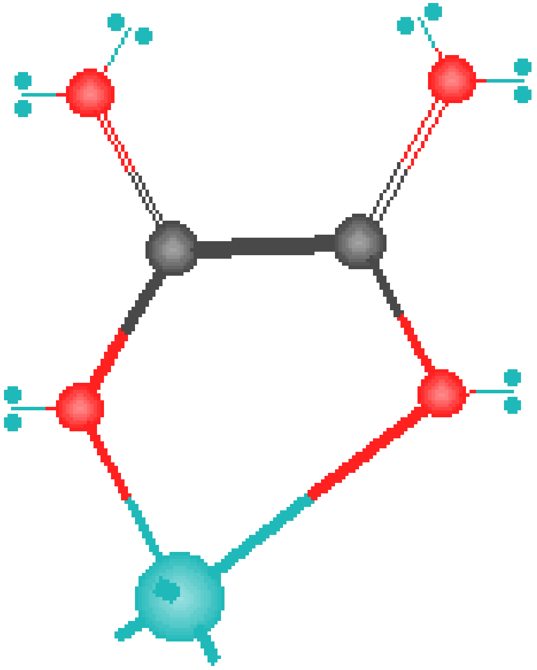


ortho-phenanthroline

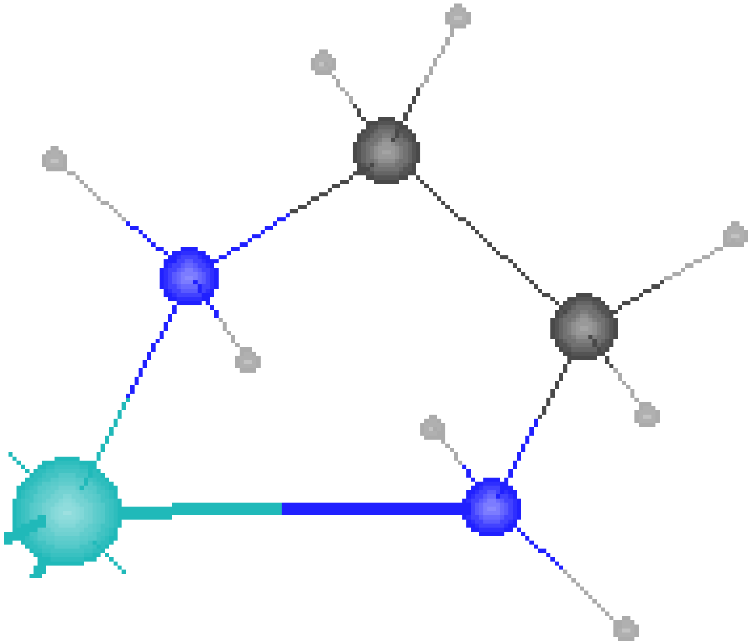


Donor Atoms

oxalate ion



ethylenediamine



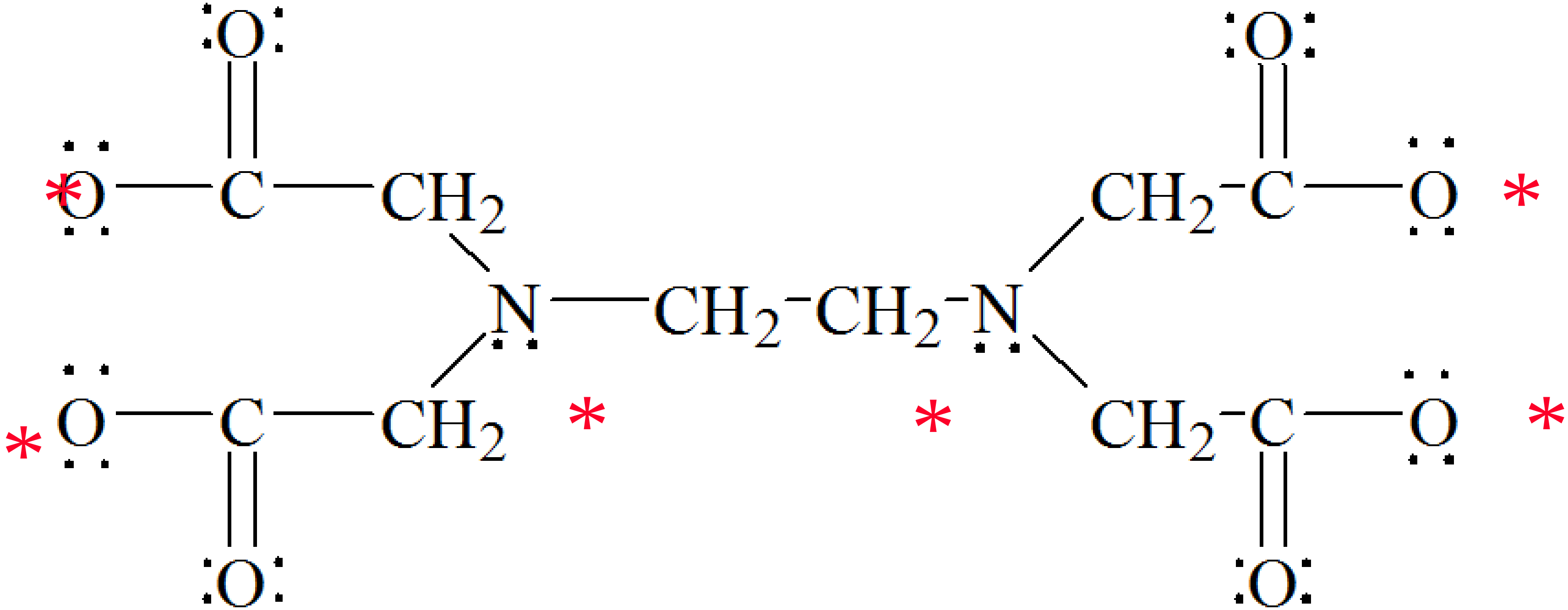
polydentate ligands-**chelating ligands**

- Can form more than two bonds to metal ion. Appear to grasp metal between 2 or more donor atoms, called chelating agents (Greek “claw”)

▸ example: ethylenediaminetetraacetate ion ($edta^{4-}$)

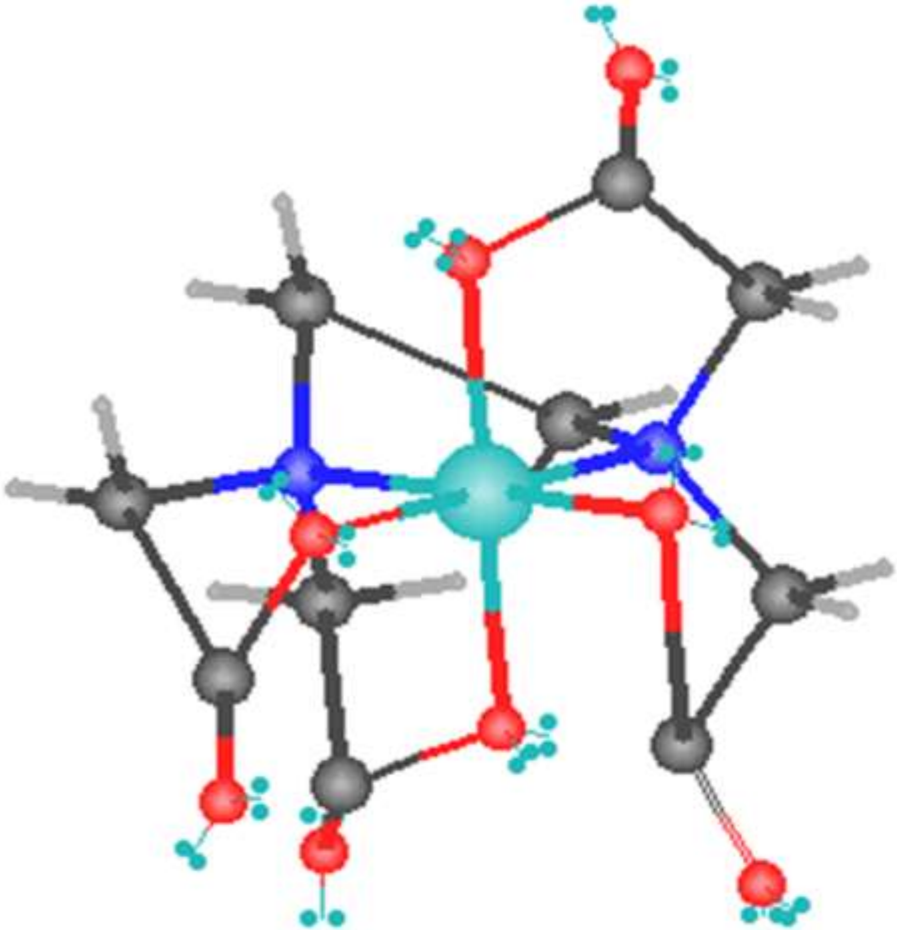
- Extra stable because two bonds must be broken to separate metal from ligand
  - Excellent chelating ligand
  - Has 6 pairs of electrons to donate
    - Molecule flexible enough to allow each of 6 pairs to form bonds with metal ion
  - Important for chemical analysis of metal ions using simple titration methods, found in many cosmetics, drugs, foods as preservative by forming complexes with metal ions, acts as catalysts to promote oxidation

EDTA



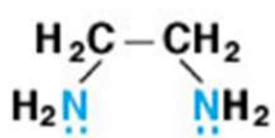
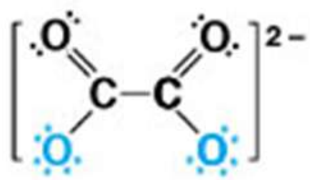
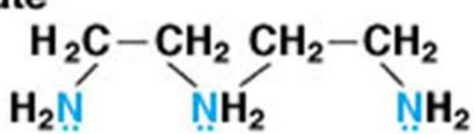
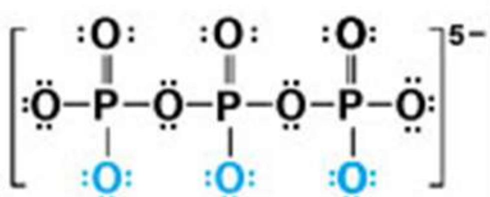
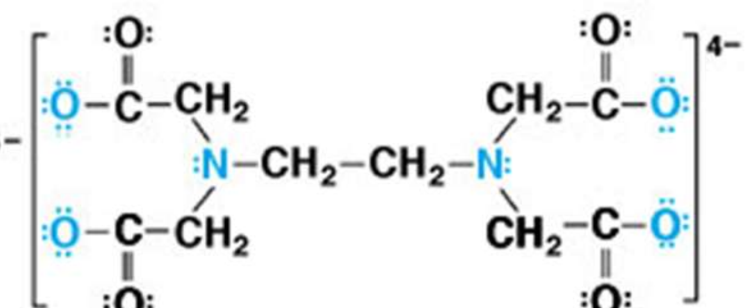
Donor Atoms

EDTA



Ligands in Coordination Compounds

Table 23.7 Some Common Ligands in Coordination Compounds

Ligand Type	Examples
Unidentate	$H_2\ddot{O}:$ water; $:\ddot{F}:^-$ fluoride ion; $[:C\equiv N:]^-$ cyanide ion; $[:\ddot{O}-H]^-$ hydroxide ion; $:NH_3$ ammonia; $:\ddot{Cl}:^-$ chloride ion; $[:\ddot{S}=C=\ddot{N}:]^-$ thiocyanate ion (S or N); $[:\ddot{O}-\ddot{N}=\ddot{O}:]^-$ nitrite ion (O or N)
Bidentate	 ethylenediamine (en);  oxalate ion
Polydentate	 diethylenetriamine;  triphosphate ion;  ethylenediaminetetraacetate (EDTA) ion

- **Coordination number**:
  - $[Co(NH_3)_5Cl]^{2+}$-5 N atoms and 1 Cl atom serve as donor atoms for Co
- Number of donor atoms surrounding central metal atom-**coordination number** of the metal
  - Above, there are 6 donor atoms, so Co has a coordination number of 6
  - **Coordination number of a metal is equal to twice its charge**-there are many exceptions to this rule,

Number of bonds formed by metal ions to ligands in complex ions varies from 2-8 depending on size, charge, electron configuration of transition metal ion –

Many metal ions have more than one –

2 ligands give linear structure, 4-tetrahedral or square planar, 6-octahedral –

Typical Coordination #s for some common metal ions

M^{3+}	Coor. #s	M^{2+}	Coor. #s	M^{+}	Coor. #s
6	Sc^{3+}	4, 6	2, 4	Mn^{2+}	Cu^{+}
6	Cr^{3+}	6	Fe^{2+}	2	Ag^{+}
6	Co^{3+}	4, 6	Co^{2+}	2, 4	Au^{+}
4	Au^{3+}	4, 6	Ni^{2+}		
		4, 6	Cu^{2+}		
		4, 6	Zn^{2+}		

Examples

- $[Ag(NH_3)_2]Cl$ and $K_3[Fe(CN)_6]$
  - Complex ion is shown enclosed in brackets
  - In the silver compound, Cl^- is a free chloride ion, and in the iron compound each K^+ is a free potassium ion
- K^+ and Cl^- ions are examples of **counter ions** which serve to balance or neutralize the charge of the complex ion
  - Coordination number of Pt^{2+} in $[Pt(NH_3)_4]^{2+}$ is 4, and that of Co^{2+} in $[Co(NH_3)_6]^{2+}$ is 6.

Common ligands

	Polar molecules:
H_2O	Aquo
NH_3	Ammine
CO	Carbonyl
NO	Nitrosyl
	Neutral Molecules:
CH_3NH_2	Methylamine
$H_2NCH_2CH_2NH_2$	Ethylenediamine (en)
	Anions:
$F^-/Cl^-/Br^-/I^-$	Fluoro-/chloro-/bromo-/iodo-
CN^-	Cyano
OH^-	Hydroxo
$S_2O_3^{2-}$	Thiosulfato
CO_3^{2-}	Carbonato
$C_2O_4^{2-}$	Oxalato

Naming complex ions

- Ligands named before central metal atom
- Anionic ligands names end in “o”
  - ide → o
    chloride → chloro
  - ate → ato
    sulfate → sulfato
- Neutral ligands named as molecule except
  - H_2O → aquo/NH_3 → ammine/CO → carbonyl
- # ligands in complex use Greek prefixes
  - di for 2/tri for 3/tetra for 4/penta for 5/hex for 6
  - Prefixes bis-, tris-, tetrakis-, etc. used when other are already used

- Name of cationic complex ion ends in name of central metal ion w/oxidation state shown as Roman numeral in () at end of metal's name
- Name of anionic complex ion ends in "ate," sometimes Latin name used

chromium(II) → chromate(II) –
nickel(II) → nickelate(II) –
platinum(II) → platinate(II) –
Iron(II) → ferrate(II) –
Copper(I) → cuprate(I) –
Lead(II) → plumbate(II) –
silver=argentate –
Gold(I) → aurate(I) –
Tin(IV) → stannate(IV) –

Name complex ion w/formula $Fe(CN)_6^{3-}$

- Anionic ligands have names ending in 'o'
  - CN^- named as cyano
- # ligands in complex specified using Greek prefix
  - 6 ligands = hexa → hexacyano
- Oxidation state of central metal atom shown w/Roman numeral in parantheses at end of metal's name
  - Central metal ion is iron
  - Charge on iron: 3- = x + (6 x 1-)
  - 3- = x -6
  - x = 3+
  - Central metal ion: iron (III)
- Complex ion is anion, therefore name will end in ferrate (III)
- Ligands named before central metal ion:
  - hexacyanoferrate (III)

Formula	Ligand Name	No. of Ligands and prefix	Central Ion Name	Complex Ion Name
$Ag(NH_3)_2^+$	ammine	2 → di	silver (I) (+1= x + 2(0), x = +1)	diamminesilver (I) ion (complex is a cation)
$Ag(CN)_2^-$	cyano	2 → di	silver (I) → argentate (I) (-1= x + 2(-1), x = +1)	dicyanoargentate (I) ion (complex is an anion)
$Cu(H_2O)_6^{2+}$	aquo	6 → hexa	copper (II) (+2= x + 6(0), x = +2)	hexaaquocopper (II) ion (complex is a cation)
$CuCl_4^{2-}$	chloro	4 → tetra	copper (II) → cuprate (II) (-2= x + 4(-1), x = +2)	tetrachlorocuprate (II) ion (complex is an anion)

Writing Formula of a Complex

Identify central metal ion .1

Identify charge on central metal ion in () .2

Identify ligands .3

Identify # ligands .4

Calculate total chare on ligands .5

Calculate charge on complex ion .6

Charge on metal ion + total charge on ligands –

Ligands written first, then central metal ion .7

When more than one type of ligand present, .8
name alphabetically (prefixes don't affect order)

Write formula for complex ion tetraamminecopper (II)

- Identify central metal ion : copper, Cu
- Identify charge on central metal ion in (): 2+
- Identify ligands: ammine = NH_3 (neutral species)
- Identify # ligands: tetra = 4
- Calculate total charge on ligands = 4 x 0 = 0
- Calculate charge on complex ion = charge on metal ion + total charge on ligands = 2+ + 0 = 2+
- Write formula giving central metal ion first followed by ligands : $Cu(NH_3)_4^{2+}$

Name	Central Ion Formula	Ligand Formula	No. of Ligands	Complex Ion Formula
hexaaquocobalt (II) ion	Co^{2+} (charge in parentheses)	H_2O (aquo = H_2O)	hexa = 6	$Co(H_2O)_6^{2+}$ (4 x 0 +2 = +2)
tetrachlorocobaltate (II) ion (ate = anion)	Co^{2+} (charge in parentheses)	Cl^- (chloro = Cl^-)	tetra = 4	$CoCl_4^{2-}$ (4 x -1 + 2 = -2)
tetracarbonylnickel (II) ion	Ni^{2+} (charge in parentheses)	CO (carbonyl = CO)	tetra = 4	$Ni(CO)_4^{2+}$ (4 x 0 + 2 = +2)
tetracyanonickelate (II) ion (ate = anion)	Ni^{2+} (charge in parentheses)	CN^- (cyano = CN^-)	tetra = 4	$Ni(CN)_4^{2-}$ (4 x -1 +2 = -2)

$K_2[Ni(CN)_4]$

- Name cation-potassium
- Name anion-potassium tetracyano
- Oxidation state of central atom-potassium tetracyanonickelate(II)

$[Co(NH_3)_2(en)_2]Cl_2$

- Name ligands first in alphabetical order- diamminebis(ethylenediamine)
- Name central atom w/oxidation number- diamminebis(ethylenediamine)cobalt(II)
- Name anion- diamminebis(ethylenediamine)cobalt(II)chloride

- $[CoI(NH_3)_5]Cl_2$
- pentaammineiodocobalt(III) chloride
- $[Cu(NH_3)_4]SO_4$
- tetraamminecopper(II) sulfate
- $[CrCl(en)_2(H_2O)]Cl_2$
- aquachlorobis(ethylenediamine)chromium(III) chloride
- $(NH_4)_2[CdCl_4]$
- ammonium tetrachlorocadmate(II)
- Na[Rh(EDTA)]
- sodium ethylenediaminetetraacetatorhodate(III)
- $[Pd(en)_2][CrCl_4(NH_3)_2]$
- bis(ethylenediamine)palladium(II)diamminetetrachlorochromate(III)
- $K_3[Fe(ox)(ONO)_4]$
- potassium tetranitritooxalatoferrate(III)

- $Ag(NH_3)_2]^+$
- diamminesilver(I)
- $[RuCl5(H_2O)]^{2-}$
- aquapentachlororuthenate(III)
- $[Fe(CN)_6]^{4-}$
- hexacyanoferrate(II)
- $Na_4[Ni(C_2O_4)_3]$
- sodium tris(oxalato)nickelate(II)
- $(NH_4)_2[CuBr_4]$
- ammonium tetrabromocuprate(II)
- $[Co(NH_3)_5Cl](NO_3)_2$
- pentaamminechlorocobalt(III) nitrate
- $[Co(H_2O)_6]I_3$
- hexaaquacobalt(III) iodide
- $K_2[PtCl_4]$
- potassium tetrachloroplatinate(II)

- Potassium hexafluorocobaltate (III)
- $K_3[CoF_6]$
- tetraamminechloronitrocobalt(III) chloride
- $[CoClNO_2(NH_3)_4]Cl$
- tris(ethylenediamine)nickel(II) sulfate
- $[Ni(en)_3]SO_4$
- tetramminedichloroplatinum(IV) tetrachloroplatinate(II)
- $[PtCl_2(NH_3)_4][PtCl_4]$
- tris(ethylenediamine)cobalt(II) nitrate
- $[Co(en)_3](NO_3)_2$
- cobalt(II) hexanitrocobaltate(III)
- $Co_3[Co(NO_2)_6]_2$
- ammineaquadicarbonyldicyanoiron(III)
- $[Fe(CN)_2(NH_3)(H_2O)(CO)_2]^+$

- Sodium tetracyanoosmium(III)
- $Na[Os(CN)_4]$
- Tris(ethylenediamine)nickel(II) tetraoxomanganate(II)
- $[Ni(en)_3]_3[MnO_4]$
- Hexaamminezinc(II) tris(oxalato)chromate(III)
- $[Zn(NH_3)_6]_3[Cr(ox)_3]_2$
- tris(oxalato)vanadate(II)
- $[V(ox)_3]^{4-}$
- sodium dihydroxodinitritomercurate(II)
- $Na_2[Hg(OH)_2(ONO)_2]$
- ammonium tetrabromoaurate(II)
- $(NH_4)_2[AuBr_4]$
- Potassium ethylenediaminetetraacetatoferrate(II)
- $K_2[Fe(EDTA)]$
  diaquabis(ethylenediamine)iridium(III) chloride
- $[Ir(H_2O)_2(en)_2]Cl_3$

In complexation reactions, Lewis bases have many names

- Ligands, complexing agents, chelates, sequestering agents
- Most ligands have one pair of electrons to donate (ammonia)
- Some have two pairs of elections and some up to six pairs
- Ligands that provide more than one electron pair in forming a complex must be large, flexible molecules so that each pair of electrons can be oriented properly to form a bond

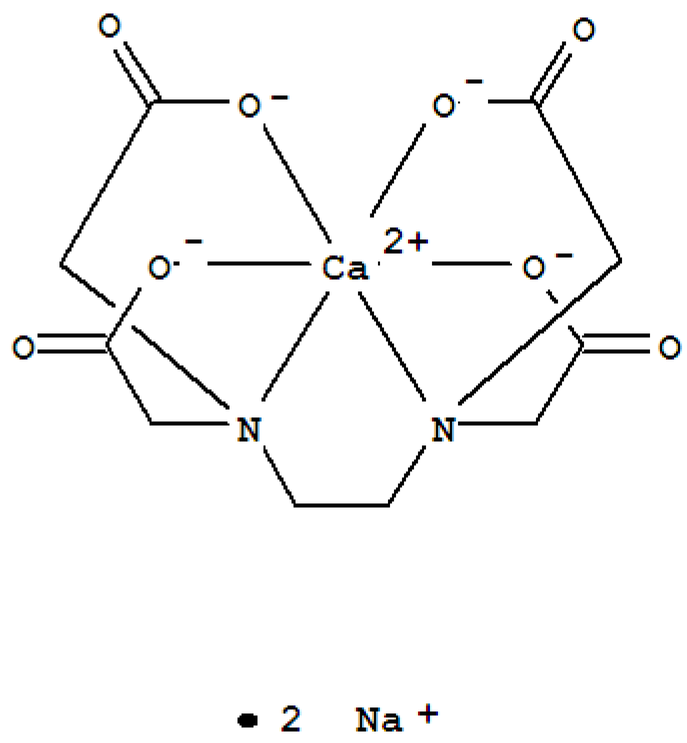
- Complexation reactions can be written generally as
  - $M^{n+} + xL^{m-} \leftrightharpoons ML_x^{n-mx}$ where M^{n+} is a metal ion with a charge of +n and L^{m-} is a liquid with a charge of –m
  - Ag tends to accept two electron pairs
  - Cu accepts four electron pairs
  - Other metal ions tend to accept six electron pairs in complexes
  - This information allows us to accurately write most complexation reactions once the number of electron pairs that a ligand can donate has been determined

Shapes (Geometry) of Some Complex Ions

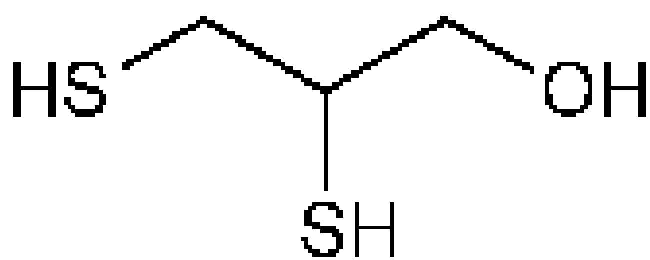
Coordination number = # ligands = 2 → linear
Coordination number = # ligands = 4 → tetrahedral or square-planar
Coordination number = # ligands = 6 → octahedral
(octahedral geometry is most common for transition metal complexes)

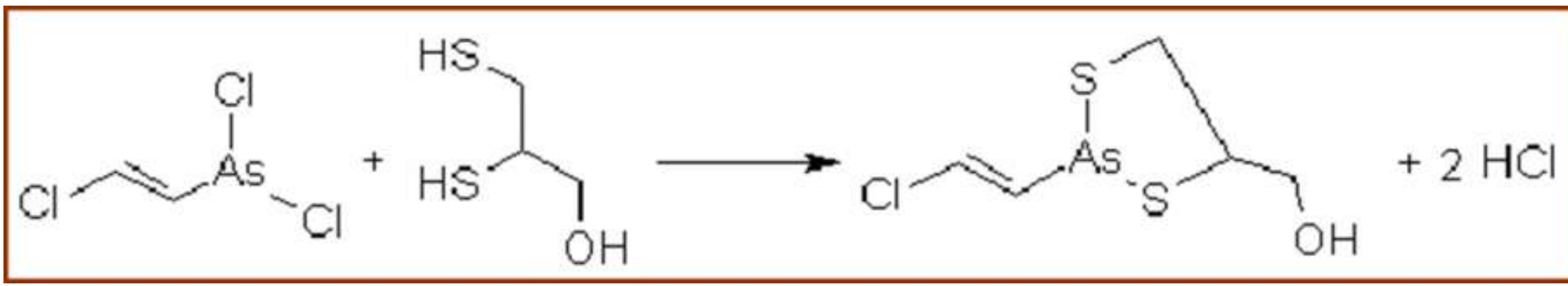
Complex Ion Formula	No. of Ligands	Coordination Number	Shape
$Ag(NH_3)_2^+$	2	2	linear
$CuCl_2^-$	2	2	linear
$Cr(NH_3)_6^{3+}$	6	6	octahedral
$Fe(CN)_6^{3-}$	6	6	octahedral

EDTA calcium disodium: use for treatment heavy metal poisoning Such as lead which form water soluble complex that excreted From kidney

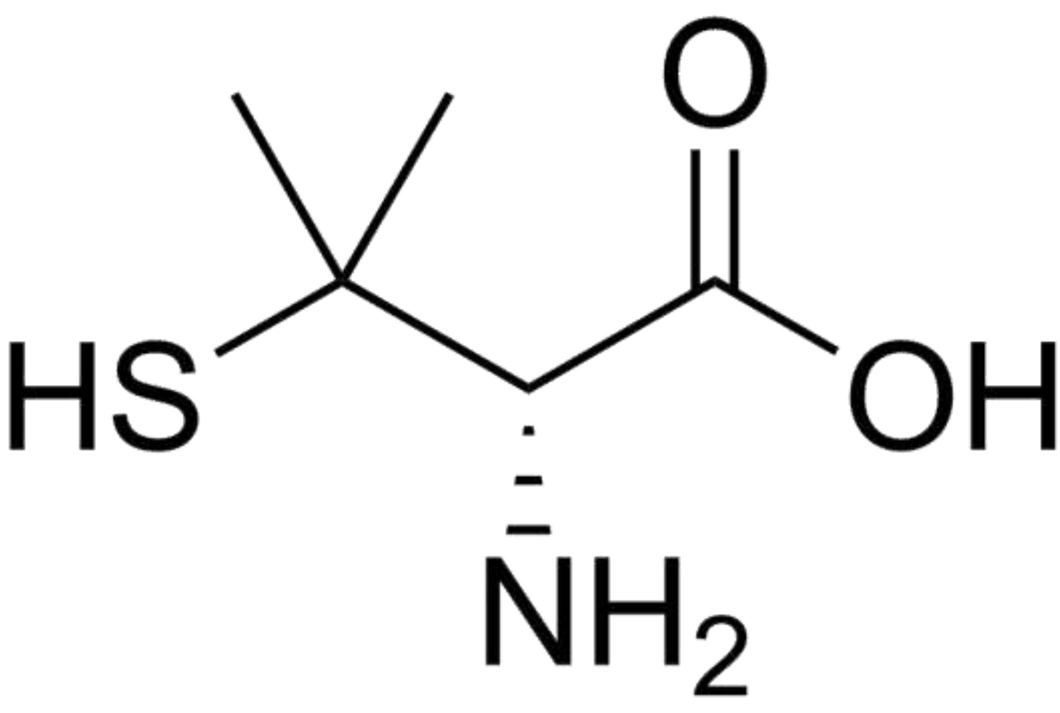


Dimercaprol is indicated as a chelating agent in arsenic, gold, and mercury



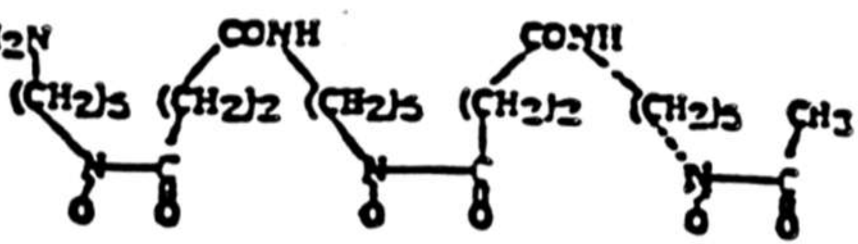

Cl
As
Cl
Cl
+
HS
HS
OH
S
Cl
As
S
OH
+ 2 HCl

Penicillamine is cabaple of forming complex with heavy metal Such as copper,iron ,mercury ,lead ,gold.

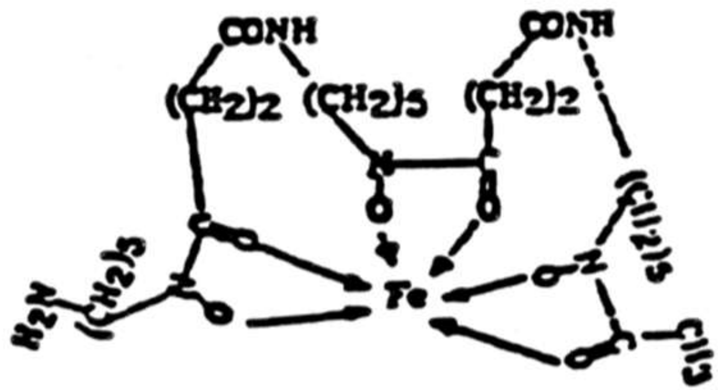


4. Deferoxamine

A. Structure



Complex



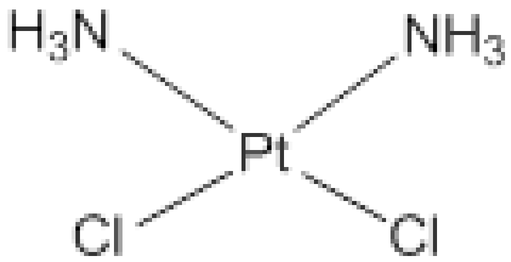
b. Uses

iron (Fe^{3+}) poisoning IM or slow IV. It has also been used orally to chelate iron poiso

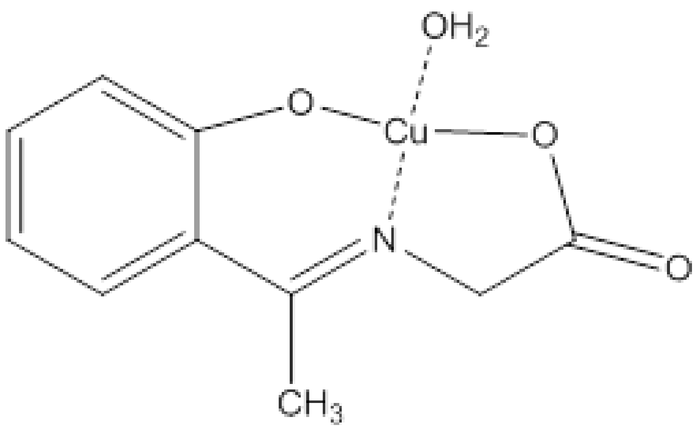
c. Toxicity

1. skin rash
2. histamine release with reduced blood pressure (shock)
3. cataracts

complexes as anticancer agents



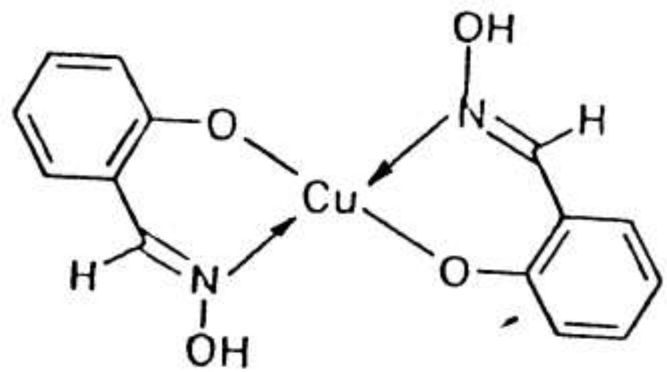
cisplatin, *cis*-diamminedichloroplatinum(II)



Copper *N*-(2-hydroxyacetophenone) glycinate

Induces reactive oxygen species (ROS) generation.

ROS have multiple functions and are implicated in tumor initiation and progression as well as in induction of apoptosis of various cancer cells, drug resistant cancers.



copper salicylaldoxime

Inhibits topoisomerase II catalytic activity.