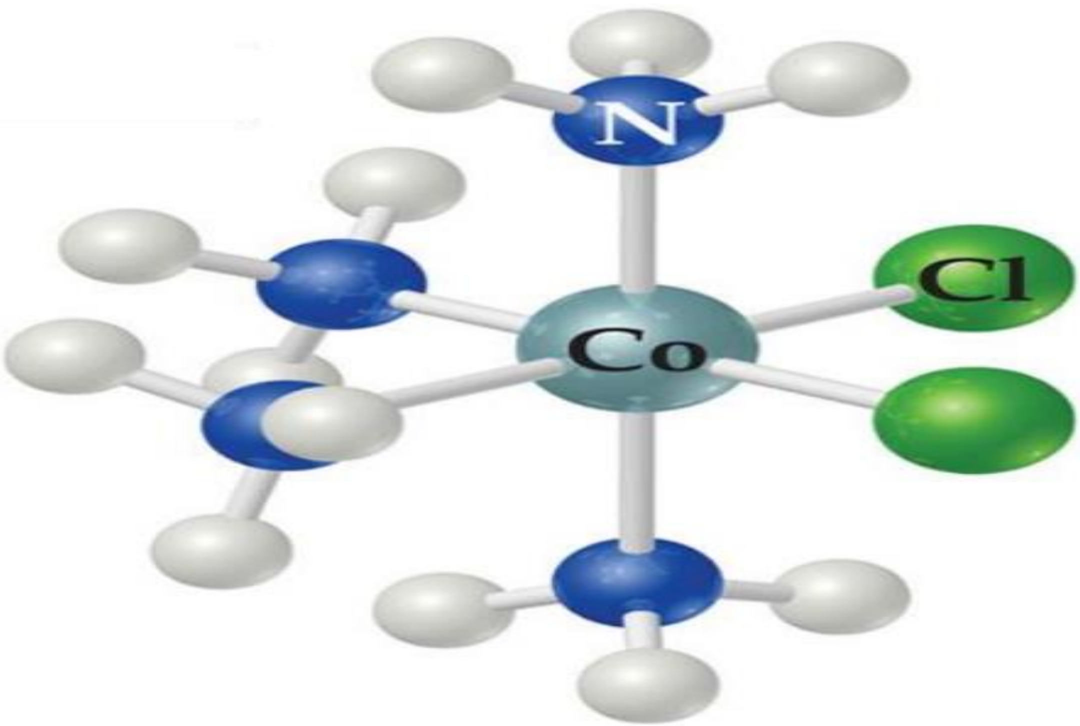
Coordination Compounds and Complexation

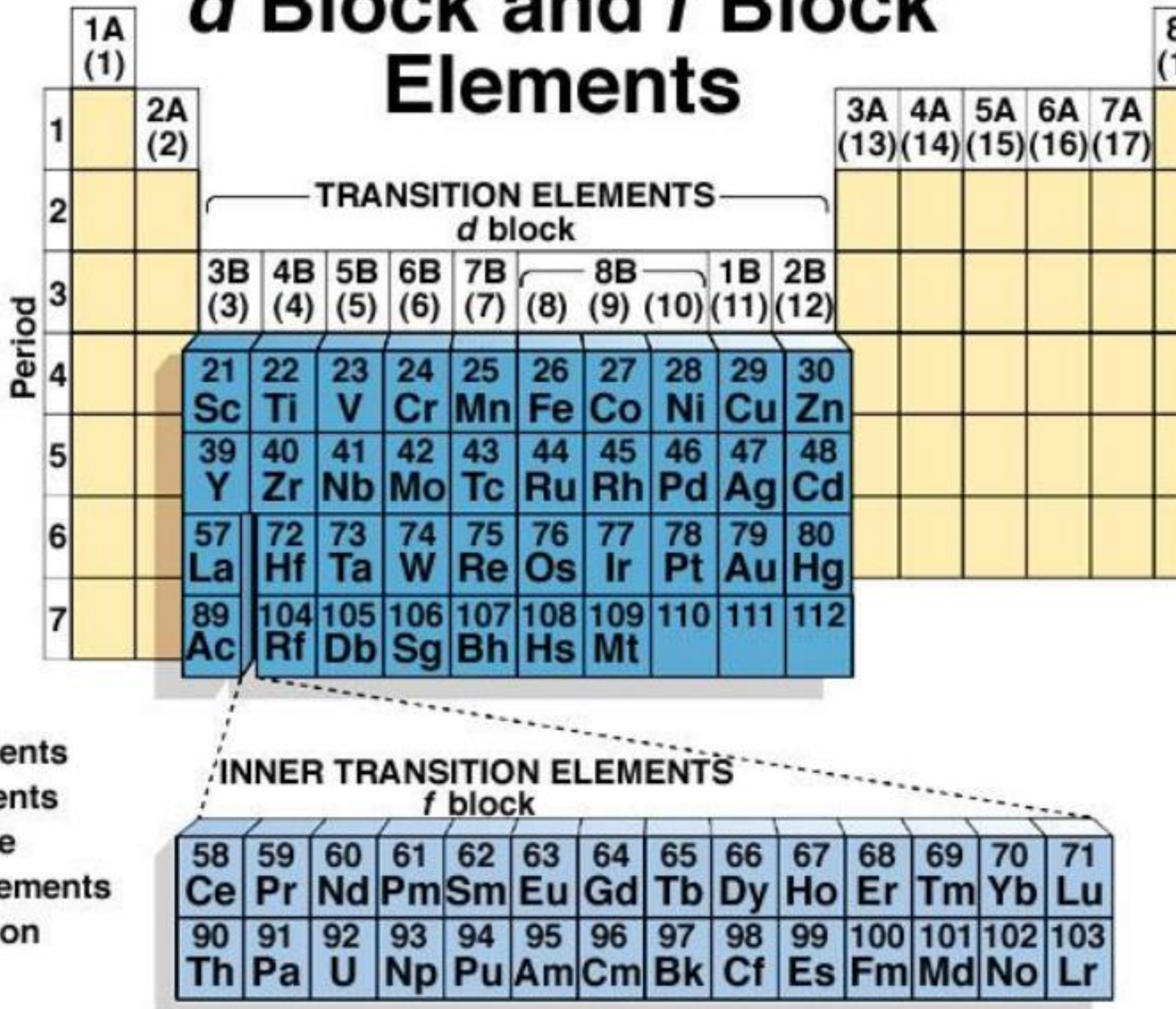
Lecture 3



Electron Configuration Exceptions

- Electrons are removed from 4s orbital before they are taken out of 3d
- 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

d Block and *f* Block Elements



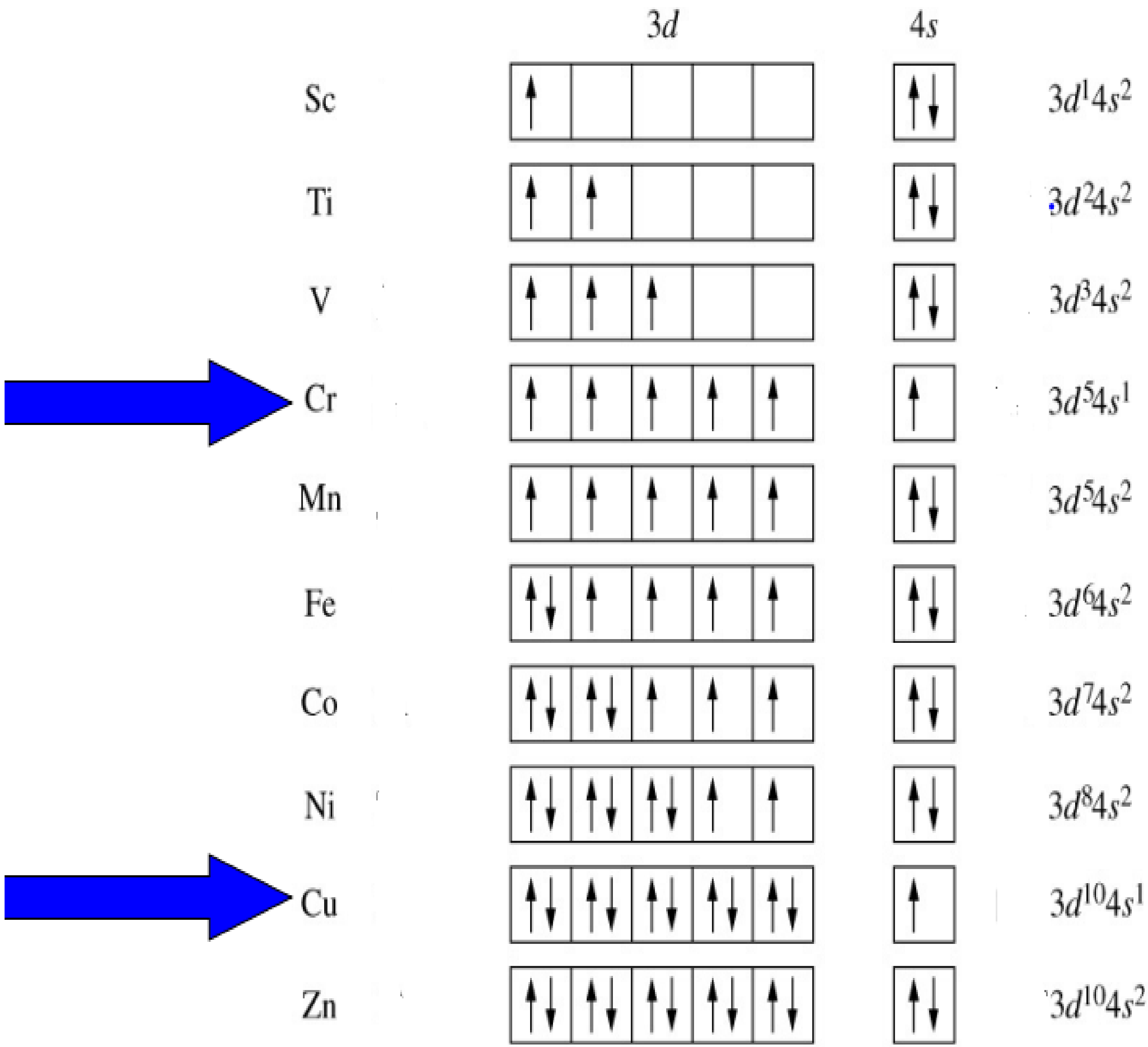
d block elements

f block elements

Periodic table

Transition elements

Inner transition elements


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

Definitions

Coordination compound Consist from complex ion and counter ions and are neutral

Complex ion – Consist from central transition metal which attached to ligands

Properties:

-Has net charge (+/-)

-Complex is set off in brackets that isolate it from the rest of compound

-Ions outside brackets-free (uncomplexed) ions (counter ion)

Metal cation-central atom

Counter ions Anions/cations needed to balance charge so it has no net charge

Ligand (complexing agent) Neutral molecule(lone pair) or anion that can be used to form bond to central metal ion

Normally either negative ion/polar molecule Must contain at least one lone pair of electrons that can serve as electron-pair donors or

Lewis bases

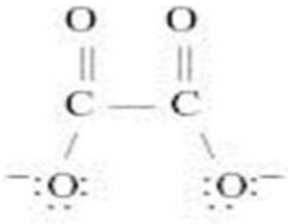
Metal ions (particularly transition metal ions) have vacant valence orbitals which can serve as electron-pair acceptors or **Lewis acids**

(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

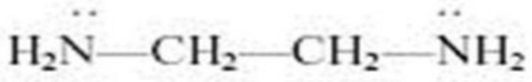
Halide ions, SCN- (thiocyanate ions), anions of weak acids

Bidentate ligand 2 donor atoms present and can occupy 2 coordination sites (2 bonds to metal ion)

Most common diamines (neutral)/anions of diprotic organic acids)

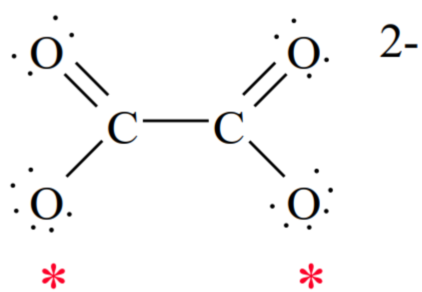


Oxalate ion (ox), $C_2O_4^{2-}$

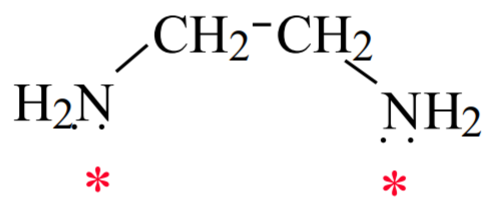


Ethylenediamine (en)

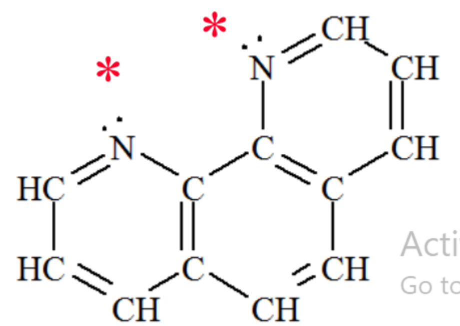
oxalate ion



ethylenediamine



ortho-phenanthroline



Donor Atoms

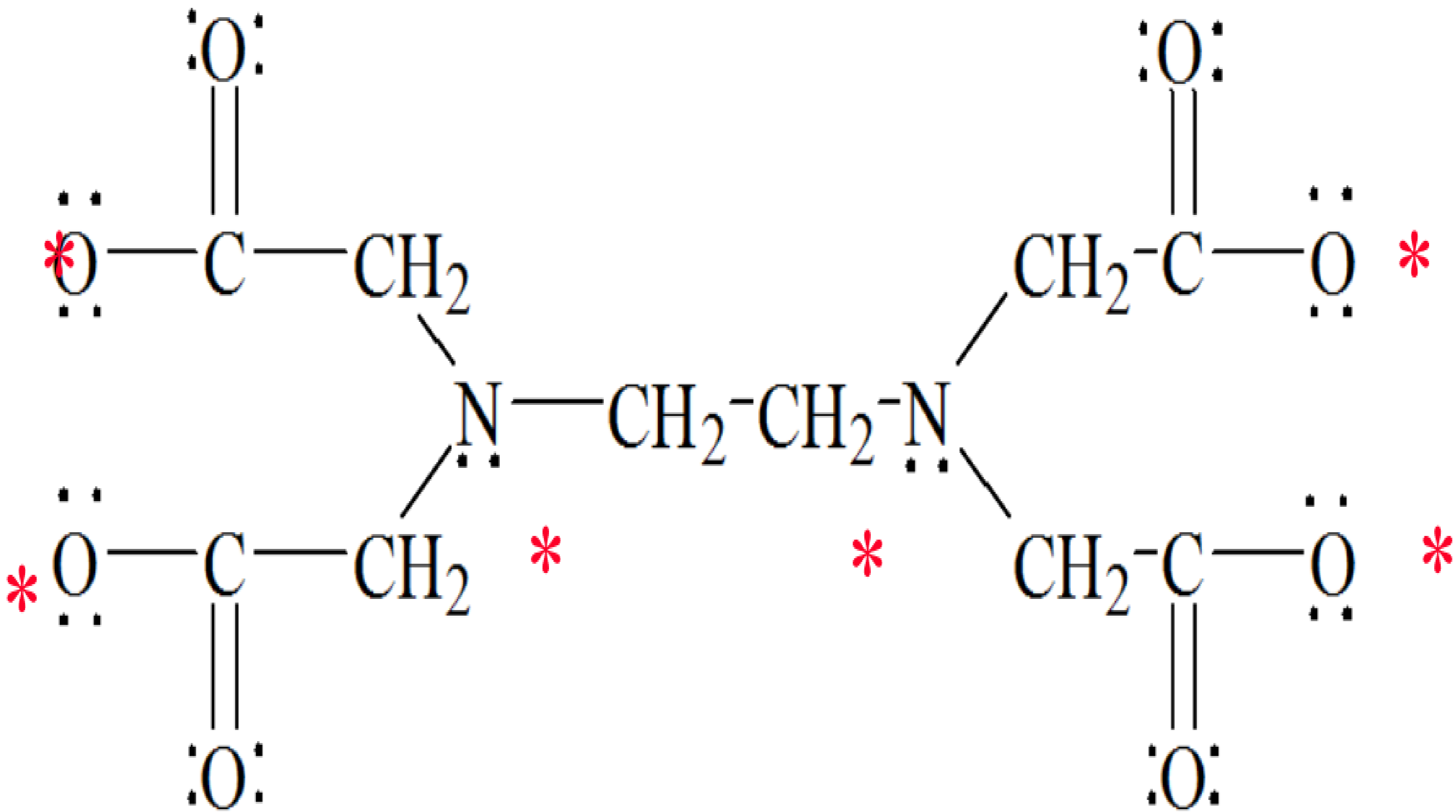
polydentate ligands-chelating ligands Can form more than two bonds to metal ion. Appear to grasp metal between 2 or more donor atoms, called chelating agents

- 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

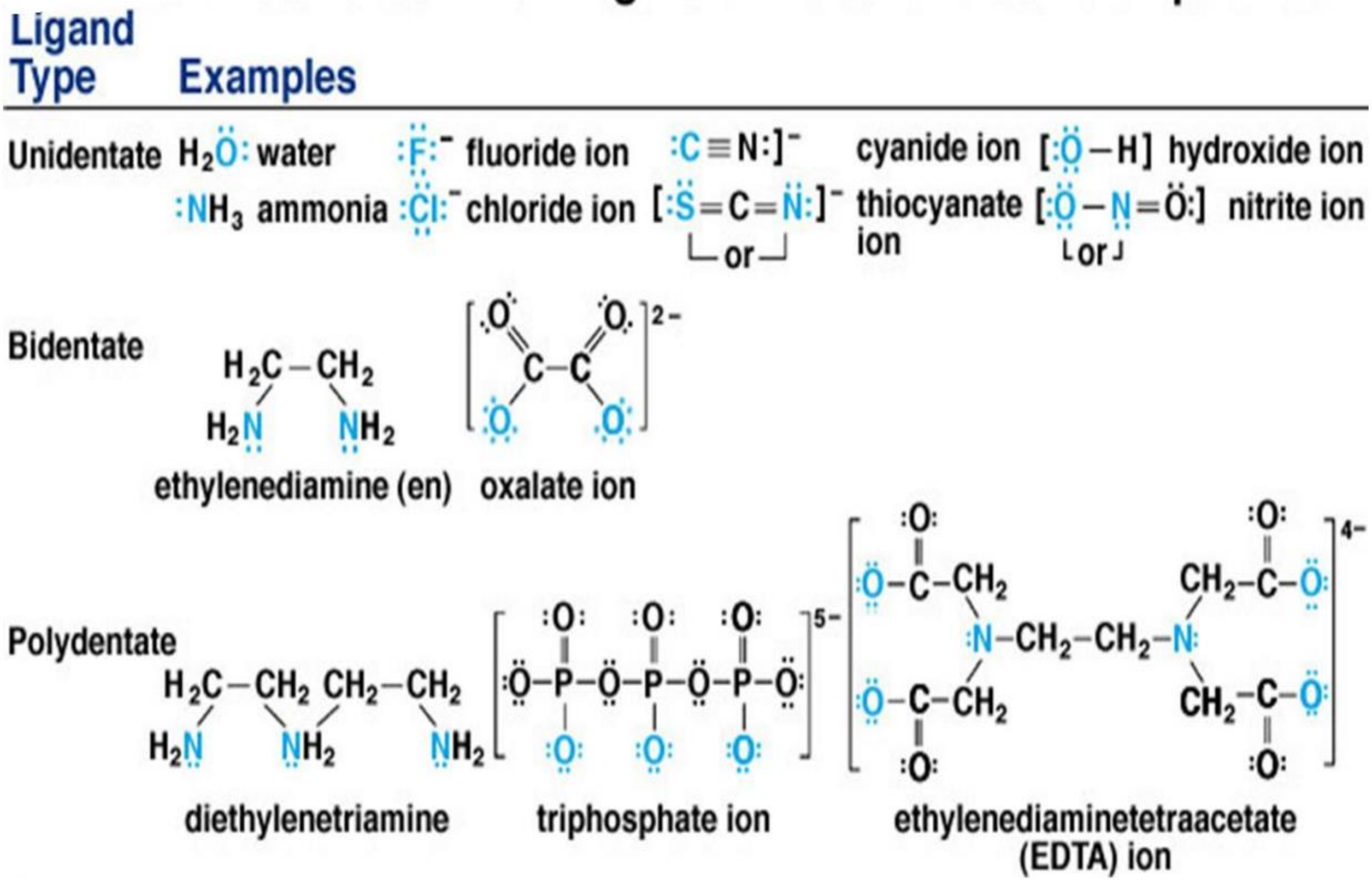
Found in many cosmetics, drugs, foods as preservative by forming complexes with metal ions, acts as catalysts to promote oxidation

EDTA



Donor Atoms

Some Common Ligands in Coordination Compounds



Part of ligand that bonds directly with metal called donor atom

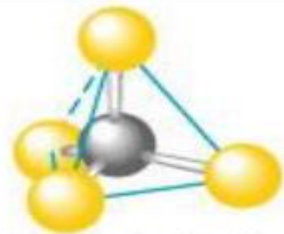
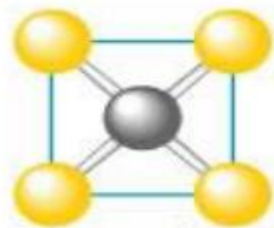
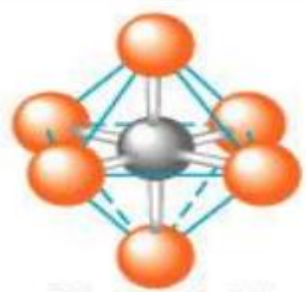
$[Co(NH_3)_5Cl]^{2+}$ (5) N atoms and 1 Cl atom serve as donor atoms for Co

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: Number of bonds formed by metal ions to ligands in complex ions varies from 2-8 depending on;

1.size, 2.charge, 3.electron configuration of transition metal ion

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

Coordination number	Geometry
2	 Linear
4	 Tetrahedral  Square planar
6	 Octahedral

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

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^{3+} in $[Co(NH_3)_6]^{3+}$ is 6

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

Write formula for complex ion tetra ammine cuprate (II)

- Identify central metal ion : copper, Cu
- Identify charge on central metal ion in (II): 2+
- Identify ligands: ammine = NH3 (neutral species)
- Identify number of 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)