
 University
of Idaho

GEOL578
Advanced Geochemistry of Natural Waters
LESSON 5
Aqueous Complexes
(Coordination Chemistry)

MODULE 1
Definitions and General Concepts

Start Audio Lecture!

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WHY IS CHEMICAL SPECIATION SO IMPORTANT?

- The biological availability (bioavailability) of metals and their physiological and toxicological effects depend on the actual species present.
 - Example: CuCO_3^0 , $\text{Cu}(\text{en})_2^0$, and Cu^{2+} all affect the growth of algae differently
 - Example: Methylmercury (CH_3Hg^+) is readily formed in biological processes, kinetically inert, and readily passes through cell walls. It is far more toxic than inorganic forms.
- Solubility and mobility depend on speciation.

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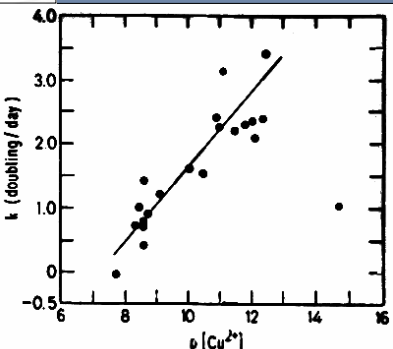


Figure 6-20 from Stumm & Morgan:
Effect of free Cu^{2+} on growth of algae in seawater.

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DEFINITIONS - I

Coordination (complex formation) - any combination of cations with molecules or anions containing free pairs of electrons. Bonding may be electrostatic, covalent or a mix.

Central atom (nucleus) - the metal cation.

Ligand - anion or molecule with which a cation forms complexes.

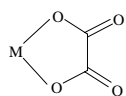
Multidentate ligand - a ligand with more than one possible binding site.

Chelation - complex formation with multidentate ligands.

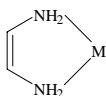
Multi- or poly-nuclear complexes - complexes with more than one central atom or nucleus.

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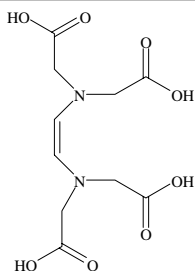
MULTIDENTATE LIGANDS



Oxalate (bidentate)



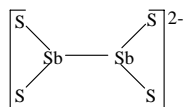
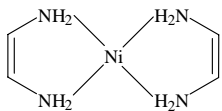
Ethylenediamine (bidentate)



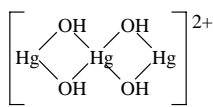
Ethylenediaminetetraacetic acid or EDTA (hexadentate)

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Chelation



$Sb_2S_4^{2-}$



$Hg_3(OH)_4^{2+}$

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DEFINITIONS - II

Species - refers to the actual form in which a molecule or ion is present in solution.
Coordination number - total number of ligands surrounding a metal ion.
Ligation number - number of a specific type of ligand surrounding a metal ion.
Colloid - suspension of particles composed of several units, whereas in true solution we have hydration of a single molecule, atom or ion.

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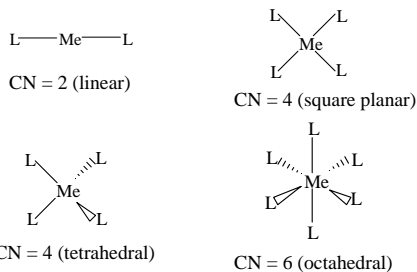
FORMS OF OCCURRENCE OF METAL SPECIES

← 10 Å ← 100 Å ← 1000 Å

Free metal ion	Inorganic ion pairs and complexes	Organic complexes, chelates	Metals bound to high mol. wt. species	Highly dispersed colloids	Metals sorbed on colloids
Cu ²⁺	Cu ₂ (OH) ₂ ²⁺	Me-SR	Me-lipids	FeOOH	Me _n (OH) _n
Fe ³⁺	PbCO ₃ ⁰	Me-OOCR	Me-humic acid	Fe(OH) ₃	MeCO ₃ , MeS, etc. on clays
Pb ²⁺	CuCO ₃ ⁰			Mn(IV) oxides	FeOOH or Mn(IV) on oxides
Na ⁺	AgSH ⁰			Ag ₂ S	
Al ³⁺	CdCl ⁻				
Zn ²⁺	CoOH ⁺				

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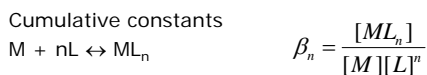
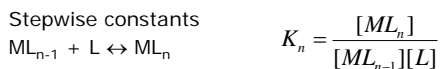
Coordination numbers



Coordination numbers 2, 4, 6, 8, 9 and 12 are most common for cations.

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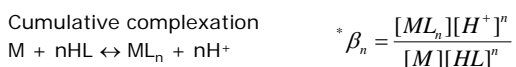
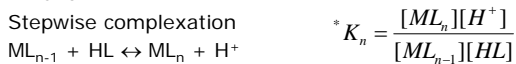
STABILITY CONSTANTS MEASURE THE STRENGTH OF COMPLEXATION



$$\beta_n = K_1 \cdot K_2 \cdot K_3 \cdots K_n$$

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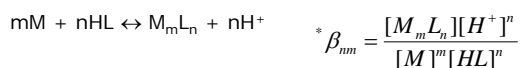
For a protonated ligand we have:



The larger the value of the stability constant, the more stable the complex, and the greater the proportion of the complex formed relative to the simple ion.

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STABILITY CONSTANTS FOR POLYNUCLEAR COMPLEXES



If $m = 1$, the second subscript on β_{nm} is omitted and the expression simplifies to the previous expressions for mononuclear complexes.

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METAL-ION TITRATIONS

- Metal ions can be titrated by ligands in the same way that acids and bases can be titrated.
- According to the Lewis definition, metal ions are *acids* because they accept electrons; ligands are *bases* because they donate electrons.

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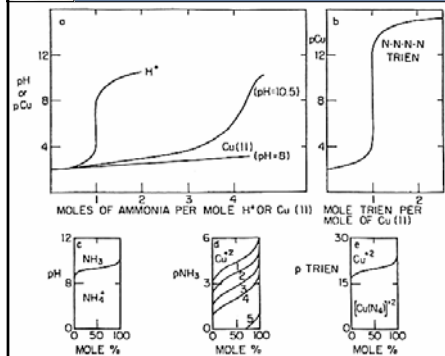


Figure 6-3 from Stumm & Morgan: Titration of H^+ and Cu^{2+} with ammonia and tetramine (trien)

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