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CEE 680: Water Chemistry

Lecture #33
Coordination Chemistry: Practice
 (Stumm & Morgan, Chapt.6: pg.317-319)
Benjamin; Chapter 8.1-8.6

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Which ligands for which metals?

- Benjamin 2nd ed., pg 532

Table 10.1 Some important inorganic ligands and some metals to which they bind.

Ligand	Metals	Environment/Application
H ₂ O	All	Any aquatic system
OH ⁻	Virtually all	Any aquatic system
F ⁻	Fe ³⁺ , Al ³⁺	Some natural systems; industrial systems where HF is used to treat metal surfaces
Cl ⁻	Cu ²⁺ , Cu ⁺ , Pb ²⁺ , Cd ²⁺	Estuaries, seawater; corrosion of metals
CN ⁻	Fe ³⁺ , Fe ²⁺ , Cu ⁺ , Cu ²⁺ , Ni ²⁺ , Ag ⁺	Metal plating
NH ₃	Cu ⁺ , Cu ²⁺ , Cd ²⁺ , Ni ²⁺	Metal finishing
S ₂ O ₃ ²⁻	Ag ⁺	Photofinishing
P ₂ O ₇ ⁴⁻ , P ₃ O ₁₀ ⁵⁻	Ca ²⁺ , Mn ²⁺ , Fe ³⁺	Detergents, corrosion inhibitors

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Classification of Metals

- A and B type cations

A-Type Metal Cations	Transition-Metal Cations	B-Type Metal Cations
Electron configuration of inert gas; low polarizability; "hard spheres"; (H ⁺), Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Al ³⁺ , Sc ³⁺ , La ³⁺ , Si ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺	One to nine outer shell electrons; not spherically symmetric; V ²⁺ , Cr ²⁺ , Mn ²⁺ , Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Ti ³⁺ , V ³⁺ , Cr ³⁺ , Mn ³⁺ , Fe ³⁺ , Co ³⁺	Electron number corresponds to Ni ⁰ , Pd ⁰ , and Pt ⁰ (10 or 12 outer shell electrons); low electronegativity; high polarizability; "soft spheres"; Cu ⁺ , Ag ⁺ , Au ⁺ , Tl ⁺ , Ga ⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺ , Pb ²⁺ , Sn ²⁺ , Tl ³⁺ , Au ³⁺ , In ³⁺ , Bi ³⁺

From: Stumm & Morgan, Table 6.3, pg 284

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Pearson's Hard & Soft Acids

Hard Acids	Borderline	Soft Acids
All A-type metal cations plus Cr ³⁺ , Mn ³⁺ , Fe ³⁺ , Co ³⁺ , UO ²⁺ , VO ²⁺ Also species such as BF ₃ , BCl ₃ , SO ₃ , RSO ₂ ⁺ , RPO ₂ ⁺ , CO ₂ , RCO ⁺ , R ₃ C ⁺	All bivalent transition-metal cations plus Zn ²⁺ , Pb ²⁺ , Bi ³⁺ , SO ₂ , NO ⁺ , B(CH ₃) ₃	All B-type metal cations minus Zn ²⁺ , Pb ²⁺ , Bi ³⁺ All metal atoms, bulk metals I ₂ , Br ₂ , ICN, I ⁺ , Br ⁺
Preference for ligand atom: N >> P O >> S F >> Cl	Qualitative generalizations on stability sequence: Cations: Stability ∝ (charge/radius) Ligands: F > O > N = Cl > Br > I > S OH ⁻ > RO ⁻ > RCO ₂ ⁻ CO ₃ ²⁻ >> NO ₃ ⁻ PO ₄ ³⁻ >> SO ₄ ²⁻ >> ClO ₄ ⁻	P >> N S >> O I >> F Ligands: S > I > Br > Cl = N > O > F

From: Stumm & Morgan, Table 6.3, pg 284

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A Periodic Table

Element Symbol

Atomic Number, Z

Atomic Molar mass (g/mol)

Electronegativity

Valence Configuration

Element Name

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Me-ligand affinities

- Irving-Williams series

From: Stumm & Morgan, Figure 6.11, pg 286

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Periodic Table

Element Symbol

Atomic Number, Z — 1.008 — Atomic Molar mass (g/mol)

Electronegativity (Allred-Rewshaw if Pauling not avail.) — 2.20 — Valence Configuration

Element Name

1	2											3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																						
1	2											3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																						
H	He											B	C	N	O	F	Ne																																																
Li	Be											B	C	N	O	F	Ne																																																
Na	Mg											Al	Si	P	S	Cl	Ar																																																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																																																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																																																
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																																																
Fr	Ra	Lr	Unq	Unp	Unh	Uns	Uno	Uue																																																									
																		57	58	59	60	61	(145)	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	(259)
																		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb																																		
																		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No																																		

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