Aquation + Acidity of Metal Cations - Chapter 7

Lewis Acid ⟹ e^- pair acceptor

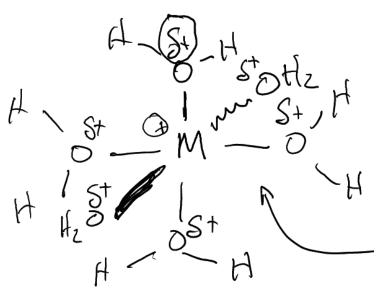
Lewis Base ⟹ e^- pair donor

Metals ions in aqueous solution:

$NaCl \xrightarrow[H_2O]{}$ Hydration (Solvation by water solvent)

$[Na(OH_2)_6]^+ + Cl^-$

↳ sodium ion within its first hydration shell



⟹ Simple coordination complex

M–O bond has partial ionic + covalent character

H_2O = Lewis Base M^+ = Lewis Acid

$$[M(OH_2)_6]^{n+}_{(aq)} + H_2O_{(l)} \overset{K}{\rightleftharpoons} [H_3O]^+_{(aq)} + [M(OH_2)_5(OH)]^{(n-1)+}_{(aq)}$$

↳ Acts as a Brönstead Acid

The position of K depends on charge density (ρ) of M^{n+}

↳ Determines the extent O–H polarization.

$$\text{Charge Density } (\rho) = \frac{(\text{Charge of } M^{n+})}{\text{Surface area of ion}}$$

$SA = 4\pi r^2$

↑ r is the ionic Radius.

Larger Charge Density ⟹ More acidic $[M(OH_2)_6]^{n+}$

$$[M(OH_2)_6]^{n+} + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} [H_3O]^+ + [M(OH_2)_5(OH)]^{(n-1)+}$$

Metal ion	Ka	Metal ion	Ka
Fe^{3+}	6.7 e-3	Fe^{2+}	5 e-9
Cr^{3+}	1.6 e-4	Cu^{2+}	5 e-9
Sc^{3+}	1.1 e-5	Ni^{2+}	5 e-9
		Zn^{2+}	2.5 e-9

In general:

M^{2+} ions are weakly acidic

M^{3+} ions are moderately acidic

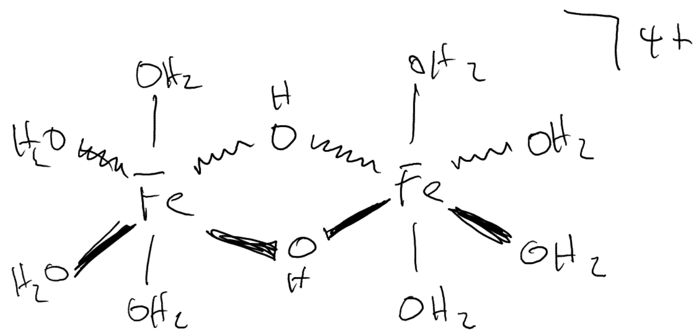
M^{4+} ions are highly acidic (only exist as oxygenated anions)

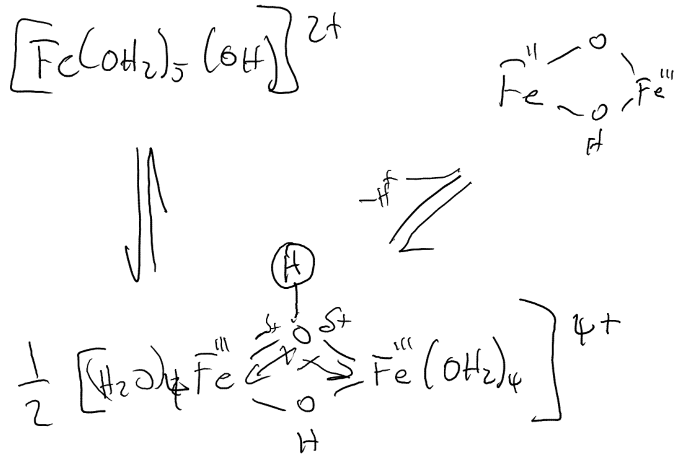
MnO_2, VO_2

In some cases we can have multiple equilibria:

* $$[Fe(OH_2)_6]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Fe(OH_2)_5(OH)]^{2+} \quad pka=2$$
(purple) (yellow)

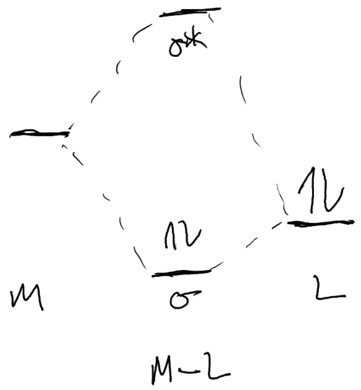
* $$[Fe(OH_2)_5(OH)]^{2+} + H_2O \rightleftharpoons H_3O^+ + [Fe(OH_2)_4(OH)_2]^{+} \quad pka=3.3$$
(brown)





Coordination Chem – Chapter 9

Any e^- pair donor can act as a ligand + bond to a metal center

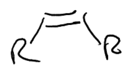


Ligands – Any e^- pair donor that can bond to a metal

→ Lewis Base Fragment

Cationic $2e^-$ – $:NO^{+}$ Isoelectronic w/ $C^{-}\equiv O^{+}$

Neutral $2e^-$ – CO, $:PR_3$, OH_2, NH_3, $:C\equiv N-R$

, $R-\equiv-R$, $N\equiv C-R$, etc...

Anionic $2e^-$ – X^-, OH^-, NR_2^-, OR^-, H^-, CN^-, CH_3^-, Ph^-, $^{-}C(O)R$, SR, $:PR_2^-$

Anionic $4e^-$ O^{2-}, S^{2-}, NR^{2-}, PR^{2-}, CR_2^{2-}, allyl ($C_3H_5^-$)

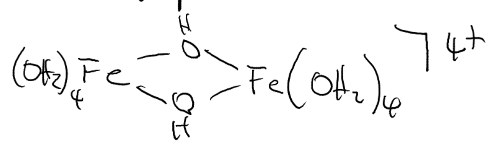
Anionic $6e^-$ O^{2-}, N^{3-}, P^{3-}, CR^{3-}, 

Nomenclature of M–L interactions

① hapticity  interacts through 1, 3, 5 η^x (eta)

η^1–Cp	η^3–Cp	η^5–Cp
$2e^-$	$4e^-$	$6e^-$

② Cases where multiple metals can interact w/ a ligand

OH^- 

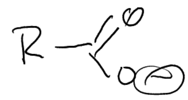
μ_x (mu) M — O — M

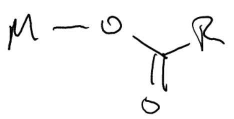
$\mu_2 - O$ (2 metals bridged)

$\mu_3 - O$

(3 metals bridged)

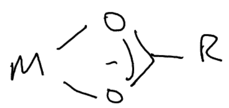
③ Ligands containing heteroatoms can interact w/ metals in multiple ways (ambidentate ligands)

Carboxylates 



$2e^-$ donor

$\kappa^1 - O_2CR$



$4e^-$ donor

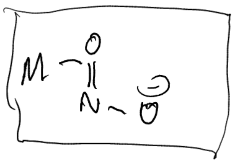
$\kappa^2 - O_2CR$

κ^x (Kappa)

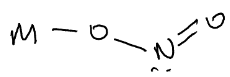
Linkage Isomerism

Nitrite NO_2^-

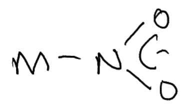
uncommon



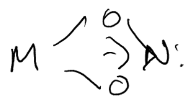
$\eta^2 - NO_2$



$\kappa^1 - O_2N$



$\kappa^1 - NO_2$



$\kappa^2 - O_2N$

Electron Counting

① Donor-Pair Model

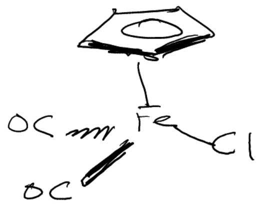
Must Remove ligands as closed shell ions

Cp^-	$6e^-$
Cl^-	$2e^-$
$2 \times CO$	$4e^-$
Fe^{II}	$6e^-$

$18e^-$

(2) Neutral Ligand Model ~ Considers each ligand as a neutral species

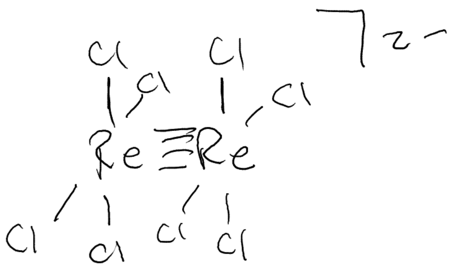
Ligands are considered to donate the # of e^- associated w/ their free ions



Cp	$5e^-$	
Cl	$1e^-$	$18e^-$
2 CO	$4e^-$	
Fe	$8e^-$	

Complexes that contain M–M bonds

M–M	M=M	M≡M	M≣M
$1e^-$	$2e^-$	$3e^-$	$4e^-$



Re^{III}	$4e^-$
4 Cl^-	$8e^-$
$Re \overset{4}{-} Re$	$4e^-$
Valance electron Count	$16e^-$