# Stability of Transition Metal Complexes

(continued, see 7.12-7.13 H&S 3rd Ed.)

The *'chelate effect'*: observation that chelating ligands form more stable complexes (higher β values) than do an equivalent number of related monodentate ligands

| *Eg.* | Ion | L | Complex | log *β* |
|---|---|---|---|---|
| | $Cu^{2+}$ | $NH_3$ | $[Cu(NH_3)_4]^{2+}$ | 12.6 |
| | $Cu^{2+}$ | en | $[Cu(en)_2]^{2+}$ | 20.6 |
| | $Ni^{2+}$ | $NH_3$ | $[Ni(NH_3)_6]^{2+}$ | 8.7 |
| | $Ni^{2+}$ | en | $[Ni(en)_3]^{2+}$ | 18.0 |

*Why are chelate complexes preferred?*

$$[Cu(NH_3)_4]^{2+} + 2\ en \rightleftharpoons [Cu(en)_2]^{2+} + 4\ NH_3$$

$$\Delta G° = -RTlnK = \Delta H - T\Delta S$$
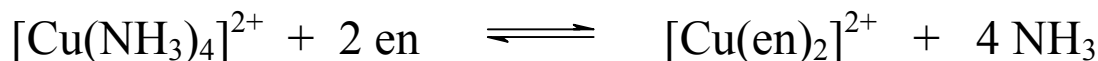
$$lnK = -\Delta H/RT + \Delta S/R \ \text{(Eyring Equation)}$$

plot of lnK vs. 1/T gives straight line
with slope $-\Delta H/R$ and intercept $\Delta S/R$

ΔH is dependent on the nature of the ligand and metal as well as ligand size *(see Hard-Soft Acid-Base section)*:

**but here $NH_3$ and en ($H_2NCH_2CH_2NH_2$) are very similar to one another so ΔH is unlikely to vary much**

*What about the other term in the equilibrium equation?*

*Will ΔS change much in the reaction shown above?*

- **Yes, we are going from a total of 3 particles to 5 as we displace two $NH_3$ for every en. This is a significant positive change in entropy and it makes ΔG negative for this reaction.**

- **Similarly, chelate ligands are far less likely to be displaced by water molecules, even in cases where water is a better ligand for the metal than the particular donor in the chelate, because binding 6 waters causes an unfavourable decrease in entropy.**

**Remember: the Chelate Effect is ENTROPY driven!!**

**The effect is even more pronounced for:**

- ligands capable of forming multiple chelate rings

*Eg.* **EDTA** complexes

$$[M(H_2O)_6]^{n+} \; + \; EDTA^{4-} \; \rightleftharpoons \; [M(EDTA)]^{(n-4)} \; + \; 6\,H_2O$$
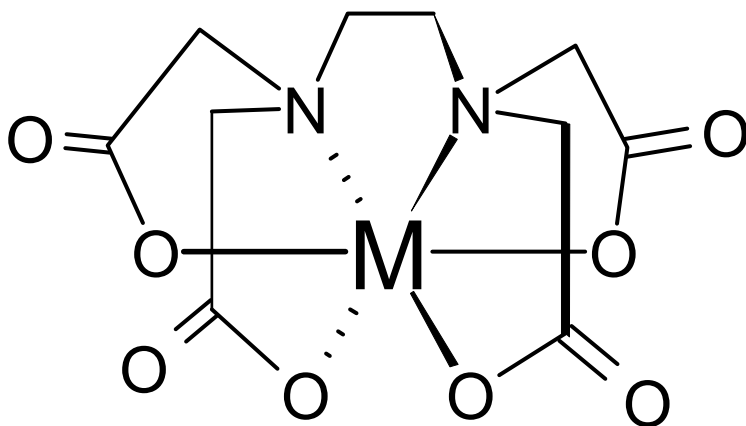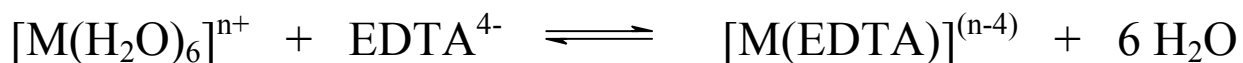


| M | log $K_1$ for M(EDTA) |
|---|---|
| $Ag^+$ | 7.3 |
| $Ca^{2+}$ | 10.8 |
| $V^{2+}$ | 12.7 |
| $Fe^{2+}$ | 14.3 |
| $Co^{2+}$ | 16.1 |
| $Ni^{2+}$ | 18.6 |
| $Cu^{2+}$ | 18.7 |
| $V^{3+}$ | 25.9 |
| $Fe^{3+}$ | 25.1 |
| $Co^{3+}$ | 36.0 |

- macrocycles *('macrocyclic effect')*: macrocyclic complexes are more stable (higher β) than **linear polydentate ligands OR monodentate ligands** of similar type
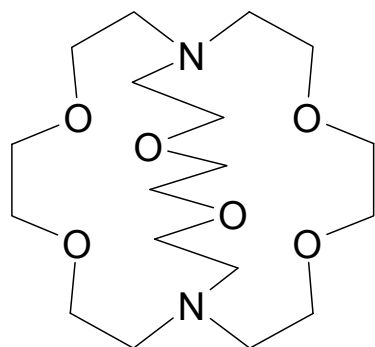
  - **besides entropy favouring a polydentate ligand over an equivalent number of monodentate donors, macrocycles are already tied into rings so there are fewer degrees of conformation freedom to lose on coordination**

  - **this effect is sometimes referred to as *'pre-organization'***



log $K_1$ = 23.9
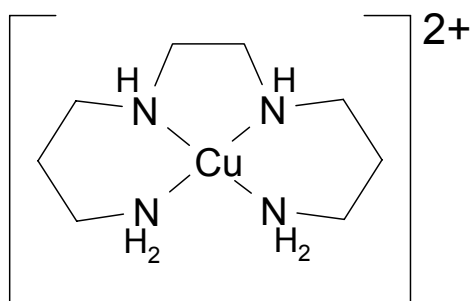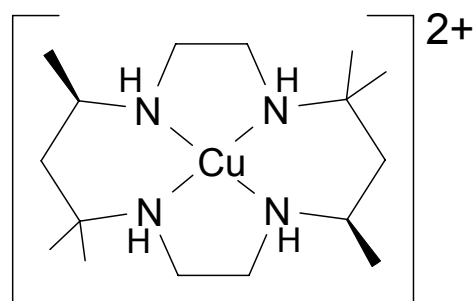
log $K_1$ = 28.0



2,2,2-crypt
(a cryptand ligand)

# Hard-Soft Acid-Base Theory (Pearson)

- a *qualitative* observation that certain metals bind with certain donors preferentially:

Hard (*Class a*) metals: high Q/r ratio, polarizing

s block, early to middle d block, f block

*prefer*

Hard donors: electronegative, not easily polarized

F, O, N, Cl, OH$^-$, $\pi$-donors

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Soft (*Class b*) metals: low Q/r ratio, not very polarizing

zero oxidation state or late d block, p block metals

*prefer*

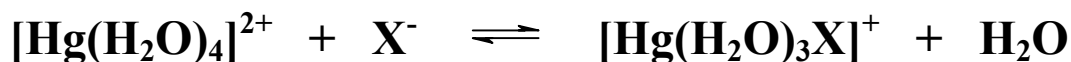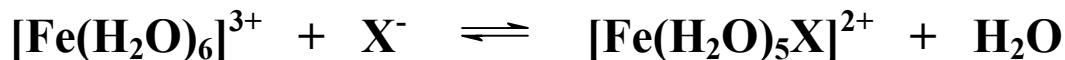Soft donors: medium electronegativity, easily polarized, $\pi$-acceptors

I, S, P, H$^-$, CO, alkenes

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Intermediate donors: Br$^-$, N$_3^-$, py

*Egs.*

$$[Fe(H_2O)_6]^{3+} \; + \; X^- \; \rightleftharpoons \; [Fe(H_2O)_5X]^{2+} \; + \; H_2O$$

$$[Hg(H_2O)_4]^{2+} \; + \; X^- \; \rightleftharpoons \; [Hg(H_2O)_3X]^{+} \; + \; H_2O$$

| $M^{n+}$ | $F^-$ | $\log K_1$ $Cl^-$ | $Br^-$ | $I^-$ | |
|---|---|---|---|---|---|
| $Fe^{3+}$ | 6.0 | 1.4 | 0.5 | ? | HARD |
| $Hg^{2+}$ | 1.0 | 6.7 | 8.9 | 12.9 | SOFT |

*Qualitative but useful:*

- **usually reliable in predicting thermodynamics of substitution reactions (but NOT the kinetics)**

- **correctly predicts that behaviour will be linked to oxidation state – higher OS are harder and most commonly found with O, N and F ligation while zero valent metal centres strongly prefer soft ligands like CO, alkenes and $I^-$**