Semester IV

CHE-HC-4014: INORGANIC CHEMISTRY-III

Topic: Coordination Chemistry

Inert and Labile Complexes

Rates of ligand substitution

- Ligand substitution is an important step in many reactions of coordination complexes.

$$\underset{\text{green}}{[Ni(H_2O)_6]^{2+}} + 6\,NH_3 \rightleftharpoons \underset{\text{blue}}{[Ni(NH_3)_6]^{2+}} + 6\,H_2O$$

$$\underset{\text{very pale violet}}{[Fe(H_2O)_6]^{3+}} + SCN^- \rightleftharpoons \underset{\text{red}}{[Fe(H_2O)_5(SCN)]^{2+}} + H_2O$$

- The rate at which one complex converts into another is governed by the height of the activation energy barrier that lies between them (**kinetic factor**).
- Complexes that undergoes exchange of one ligand for another within the time of mixing the reactants, are classified as **labile**.
- A **labile complex** has a very **low activation energy** for ligand substitution.
- Taube suggested a reaction half-life of one minute or less as the criterion for lability.
- Complexes that survive for long periods (by convention, at least a minute) are commonly called ‘inert’ or nonlabile.
- A **nonlabile** complex has a **higher activation energy** for ligand substitution.

Examples

$$[M(H_2O)_m]^{n+} + H_2{}^{18}O \rightleftharpoons [M(H_2O)_{m-1}(H_2{}^{18}O)]^{n+} + H_2O$$

Rate Constants for Water Exchange in $[M(H_2O)_6]^{n+}$

Complex	$k(s^{-1})$ (298 K)	Electronic Configuration*
$[Ti(H_2O)_6]^{3+}$	1.8×10^5	$t_{2g}{}^1$
$[V(H_2O)_6]^{3+}$	5.0×10^2	$t_{2g}{}^2$
$[V(H_2O)_6]^{2+}$	8.7×10^1	$t_{2g}{}^3$
$[Cr(H_2O)_6]^{3+}$	2.4×10^{-6}	$t_{2g}{}^3$
$[Cr(H_2O)_6]^{2+}$	$> 10^8$	$t_{2g}{}^3 e_g{}^1$
$[Fe(H_2O)_6]^{3+}$	1.6×10^2	$t_{2g}{}^3 e_g{}^2$
$[Fe(H_2O)_6]^{2+}$	4.4×10^6	$t_{2g}{}^4 e_g{}^2$
$[Co(H_2O)_6]^{2+}$	3.2×10^6	$t_{2g}{}^5 e_g{}^2$
$[Ni(H_2O)_6]^{2+}$	3.2×10^4	$t_{2g}{}^6 e_g{}^2$
$[Cu(H_2O)_6]^{2+}$	4.4×10^9	$t_{2g}{}^6 e_g{}^3$
$[Zn(H_2O)_6]^{2+}$	$> 10^7$	$t_{2g}{}^6 e_g{}^4$

*These configurations assume octahedral geometry, even in cases where Jahn–Teller distortion is anticipated.

A Few Generalizations

- All complexes of s-block ions except the smallest (Be^{2+} and Mg^{2+}) are very labile.
- Complexes of the M(III) ions of the f block are all very labile.
- Complexes of the d^{10} ions (Zn^{2+}, Cd^{2+}, and Hg^{2+}) are normally very labile.
- Across the 3d series, complexes of d-block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
- Complexes of d-block M(III) ions are distinctly less labile than d-block M(II) ions.
- *d-Metal complexes with d^3 and low-spin d^6 configurations (for example Cr(III), Fe(II), and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as $[Fe(phen)_3]^{2+}$, are particularly inert.*
- Nonlability is common among the complexes of the 4d and 5d series, which reflects the high LFSE and strength of the metal-ligand bonding.

Slow Reactions (Inert)	Moderate Rate	Fast Reactions (Labile)
d^3, low-spin d^4, d^5, and d^6		d^1, d^2, high-spin d^4, d^5, and d^6
Strong-field d^8 (square planar)	Weak-field d^8	d^7, d^9, d^{10}

Representative timescales of chemical and physical processes

Timescale*	Process	Example
10^8 s	Ligand exchange (inert complex)	$[Cr(OH_2)_6]^{3+} - H_2O$ (*c.* 6 days)
60 s	Ligand exchange (nonlabile complex)	$[V(OH_2)_6]^{3+} - H_2O$ (50 s)
1 ms	Ligand exchange (labile complex)	$[Pt(OH_2)_4]^{2+} - H_2O$ (0.4 ms)
1 μs	Intervalence charge transfer	$(H_3N)_5Ru^{II}-N$ ⟨⟩ $N-Ru^{III}(NH_3)$ (0.5 μs)
1 ns	Ligand exchange (labile complex)	$[Ni(OH_2)_5(py)]^{2+} - H_2O$ (1 ns)
10 ps	Ligand association	$Cr(CO)_5$ + THF (10 ps)
1 ps	Rotation time in liquid	CH_3CN (1 ps)
1 fs	Molecular vibration	Sn—Cl stretch (300 fs)

* Approximate time at room temperature.

IMPORTANT NOTE

Labile and ***nonlabile*** (inert) are kinetic terms and must be distinguished from the thermodynamic descriptions **stable** and **unstable**