Coordination Complexes

Some Miscellaneous Topics

- **Spectrochemical Series**

$I^- < Br^- < S_2^{2-} < SCN^- < Cl^- < N_3^-, F^- <$ urea, $OH^- <$ ox,

$O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-$

$C_6H_5^- < CN^- < CO$

Trends in values of Δ_{oct} lead to the conclusion that metal ions can be placed in a spectrochemical series which is independent of the ligands:

$$\underset{\text{increasing field strength}}{\xrightarrow{\quad Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV) \quad}}$$

Spectrochemical series are empirical generalizations and simple crystal field theory cannot account for the magnitudes of Δ_{oct} values.

- **Oxidation Potential Values**

$[Co(H_2O)_6]^{2+} \longrightarrow [Co(H_2O)_6]^{3+} + e^-$ $\quad E^0 = -1.83$

$[Co(ox)_3]^{4-} \longrightarrow [Co(ox)_3]^{3-} + e^-$ $\quad E^0 = -0.57$

$[Co(phen)_3]^{2+} \longrightarrow [Co(phen)_3]^{3+} + e^-$ $\quad E^0 = -0.42$

$[Co(edta)]^{2-} \longrightarrow [Co(edta)]^- + e^-$ $\quad E^0 = -0.37$

$[Co(en)_3]^{2+} \longrightarrow [Co(en)_3]^{3+} + e^-$ $\quad E^0 = -0.18$

$[Co(NH_3)_6]^{2+} \longrightarrow [Co(NH_3)_6]^{3+} + e^-$ $\quad E^0 = -0.11$

$[Co(CN)_5H_2O]^{3-} + CN^- \longrightarrow [Co(CN)_6]^{3-} + H_2O + e^-$ $\quad E^0 = +0.83$

- **Table:** Values of λ for spinels, $A^{II}B_2^{III}O_4$

B^{3+}/A^{2+}	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Al^{2+}	0	0	0	0	0.38	–	0
Cr^{2+}	0	0	0	0	0	0	0
Fe^{3+}	0.45	0.1	0.5	0.5	0.5	0.5	0
Mn^{3+}	–	0	–	–	–	–	0
Co^{3+}	–	–	–	0	–	–	0

⏩ **Table:** The nephelauxetic series of ligands and metal ions

Ligand	h	Metal	k	Ligand	h	Metal	k
F^-	0.8	Mn(II)	0.07	Cl^-	2.0	Rh(III)	0.28
H_2O	1.0	V(II)	0.1	CN^-	2.1	Ir(III)	0.28
Urea	1.2	Ni(II)	0.12	Br^-	2.3	Co(III)	0.33
NH_3	1.4	Mo(III)	0.15	N_3^-	2.4	Pt(IV)	0.6
en	1.5	Cr(III)	0.20	I^-	2.7	Pd(IV)	0.7
ox	1.5	Fe(III)	0.24				

⏩ **Table:** Radius Ratios

C.N.	Minimum radius ratio	Coordination polyhedron
4	0.225	Tetrahedron
6	0.414	Octahedron/square plane
6	0.528	Trigonal prism
7	0.592	Capped octahedron
8	0.645	Square antiprism
8	0.668	Dodecahedron (bisdisphenoid)
8	0.732	Cube
9	0.732	Tricapped trigonal prism
12	0.902	Icosahedron
12	1.000	Cuboctahedron

⏩ **Splliting of d-orbital in coordination number 8.**

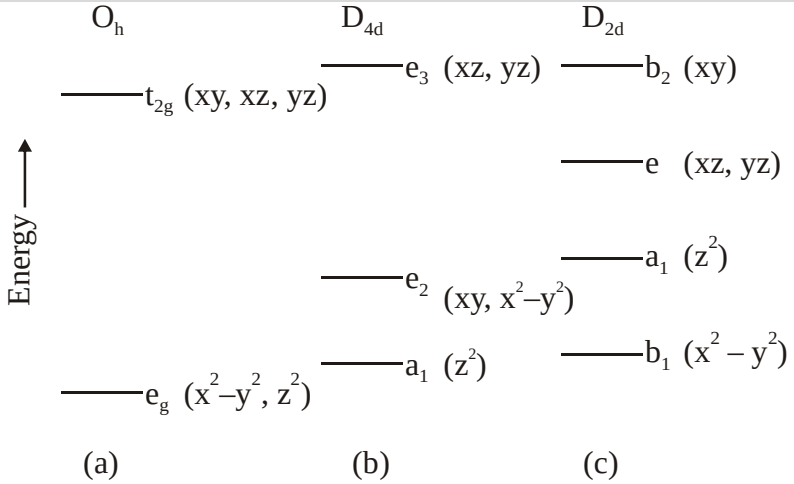


Figure: Energy level diagram for eight-coordination: (a) cubic (O_h); (b) square antiprismatic (D_{4d}); (c) dodecahedral (D_{2d})

⏩ **Stability of crowns in gas phase**

Gas-phase phase studies shows that crown-5 prefers Li^+ more than one other alkali metal cations:

crown-5: $Li^+ >> Na^+ > K^+ > Cs^+$

On the other hand crown-6 shows more affinity for Na^+ and crown-7 prefers K^+:

crown-6: $Na^+ \geq K^+ > Li^+ > Rb^+ > Cs^+$

crown-7: $K^+ > Na^+ \geq Rb^+ > Li^+ > Cs^+$

Table: Thermodynamic contributions to the macrocyclic effect in complexes of 18-crown-6 and pentaglyme, $CH_3(OCh_2CH_2)_5OCH_3$, in methanol

		Na^+	K^+	Ba^{2+}
log K_1	18-crown-6	4.36	6.06	7.04
	pentaglyme	1.44	2.1	2.3
	log K difference	2.92	3.96	4.74
ΔH	18-crown-6	–35.1	–56.0	–43.5
	pentaglyme	–16.7	–36.4	–23.8
	ΔH difference	–18.4	–19.6	–19.7
ΔS	18-crown-6	–33	–71	–13
	pentaglyme	–29	–84	–33
	ΔS difference	–4	13	20

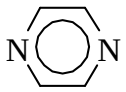
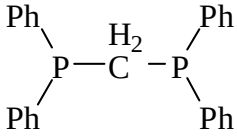
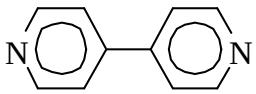
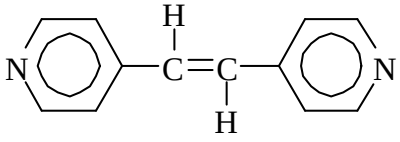
Table: Rate constants for the reactions of $[Co(NH_3)_5(H_2O)]^{3+}$ with X^{n-} in water at 45°C

X^{n-}	k (M^{-1} s^{-1})
NCS^-	1.3×10^{-6}
$H_2PO_4^-$	2.0×10^{-6}
Cl^-	2.1×10^{-6}
NO_3^-	2.3×10^{-6}
SO_4^{2-}	1.5×10^{-5}

Table: Rate constants for the reactions of $[Co(NH_3)_5X]^{m+}$ with H_2O

X^{n-}	k (s^{-1})
NCS^-	5.0×10^{-10}
$H_2PO_4^-$	2.6×10^{-7}
Cl^-	1.7×10^{-6}
NO_3^-	2.3×10^{-5}
SO_4^{2-}	1.2×10^{-6}

Table: Calculated rate constants for electron transfer in $[Ru(bpy)_2Cl]_2L$ – L complexes and distances (r) separating the metal centers

L – L	r_1 Å	k_r s^{-1}
	6.8	3×10^9
	7.1	1×10^8
	6.0	6×10^{10}
	11.3	1×10^8
	13.8	2×10^7