Transition elements

Ca [Ar] $3d^0 4s^2$

		3d					4s
Sc	[Ar] $3d^1 4s^2$	↑					↑↓
Ti	[Ar] $3d^2 4s^2$	↑	↑				↑↓
V	[Ar] $3d^3 4s^2$	↑	↑	↑			↑↓
Cr	[Ar] $3d^5 4s^{1*}$	↑	↑	↑	↑	↑	↑
Mn	[Ar] $3d^5 4s^2$	↑	↑	↑	↑	↑	↑↓
Fe	[Ar] $3d^6 4s^2$	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar] $3d^7 4s^2$	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar] $3d^8 4s^2$	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar] $3d^{10} 4s^{1*}$	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar] $3d^{10} 4s^2$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Properties

> All transition elements, have to have a stable ion that has a partially filled d-orbital

> Transition elements have variable oxidation compounds

> They all have color.

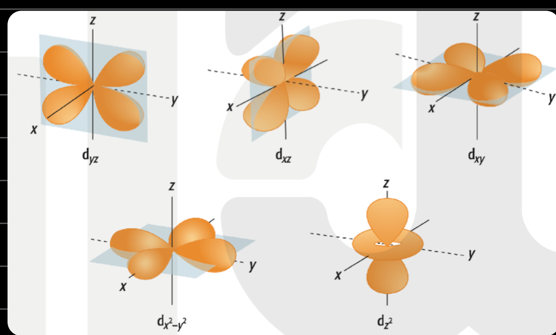
> Form complex ions.

Shapes of d-orbitals

> The 5 d-orbitals are divided into two types

Between axis: d_{xy}, d_{xz}, d_{yz}

Along axis: $d_{x^2-y^2}$, d_{z^2}



Physical and atomic properties

- Larger Density compared to s block, because their masses are greater while having smaller atomic radii

- High melting points compared to s and p blocks.

- Atomic radius and I E are almost constant, as even tho nuclear charge is increasing electrons are being added to inner shell, shielding effect increases too, cancelling out the attraction caused by increasing nuclear charge.

- Many oxidation states, Minimum oxidation state of all transition element is +2, except copper (min +1)
  Max oxidation state is equal to the number of unpaired electrons in 3d + 2

[Ar] $3d^5 4s^2$

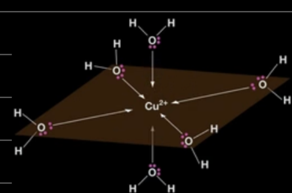
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
			+7				
		+6	+6	+6			
	+5	+5	+5	+5	+5		
+4	**+4**	+4	**+4**	+4	+4	+4	
+3	+3	**+3**	+3	**+3**	**+3**	+3	+3
+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**
		+1					**+1**

— = important / learn

Complex ions

- Bond with ligands

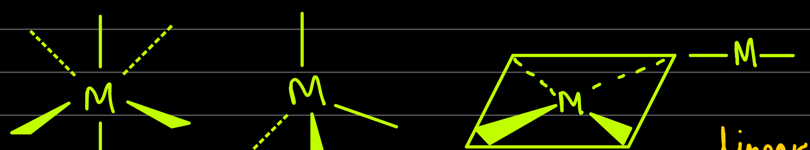
- octahedral: $[Cu(H_2O)_6]^{2+}$: Dative bonds between H_2O's and Cu,
  ligand; coordination number



- $[Ag(NO_3)_2]^+$: linear

> ligands
- Are lewis bases
- molecule or anion
- have to have one lone pair atleast
- make a dative bond with a transition element

Shapes of complex ions



octahedral　　tetrahedral　　square-planar　　linear

> Need to memorise

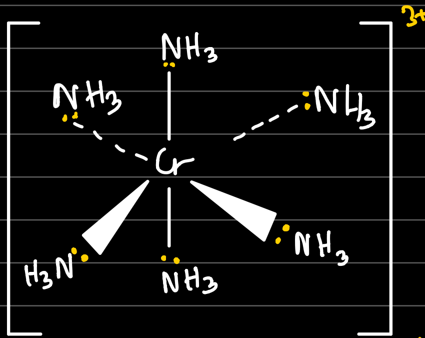
① linear

① $[CuCl_2]^-$: $Cl^-: \longrightarrow Cu^+ \longleftarrow :Cl^-$

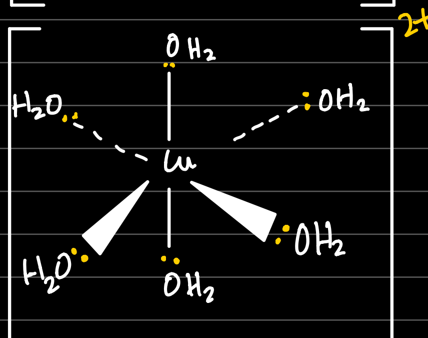
② $[Ag(NH_3)_2]^+$: $H_3N: \longrightarrow Ag^+ \longleftarrow : NH_3$

② octahedral

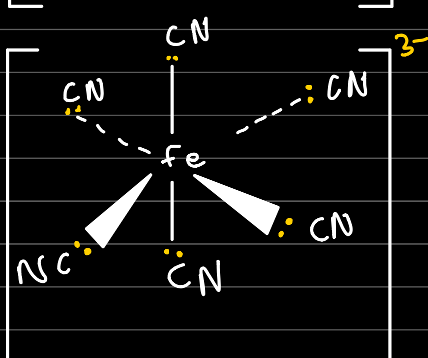
① $[Cr(NH_3)_6]^{3+}$:



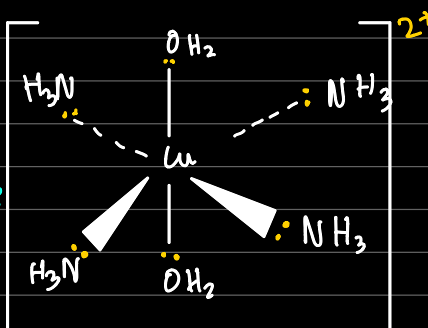
② $[Cu(H_2O)_6]^{2+}$:



③ $[Fe(CN)_6]^{3-}$:

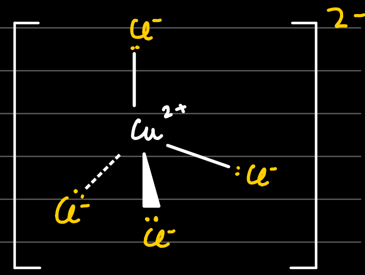


④ $[Cu(NH_3)_4(H_2O)_2]^{2+}$:

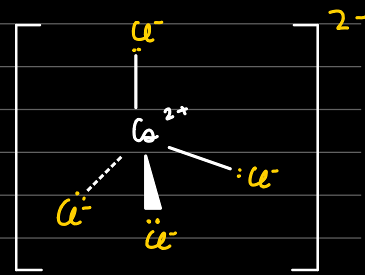


③ Tetrahedral

① $[CuCl_4]^{2-}$



② $[CoCl_4]^{2-}$

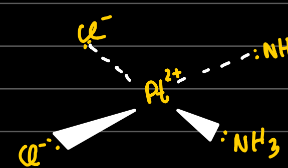


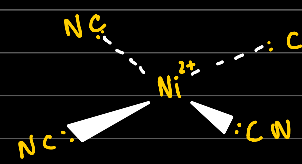
④ Square planar

① $PtCl_2(NH_3)_2$

make square planar

② $[Ni(CN)_4]^{2-}$





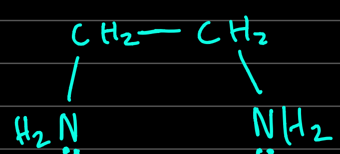
Types of ligands

① Monodentate ligands : H_2O, NH_3, Cl^-, $:CN^-$

② Polydentate ligands (Two types)

• Bidentate ligand

①



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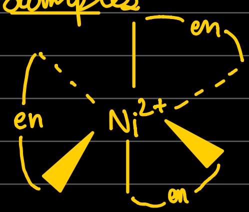
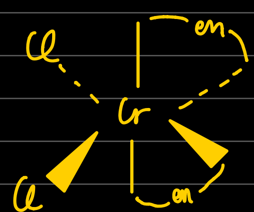
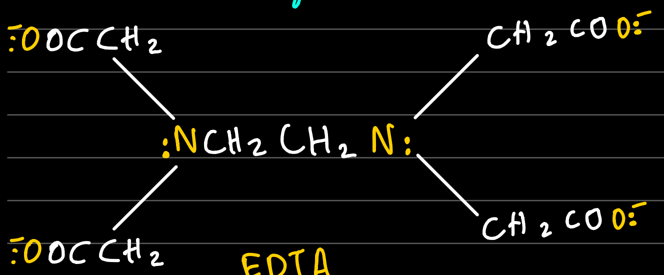
Examples



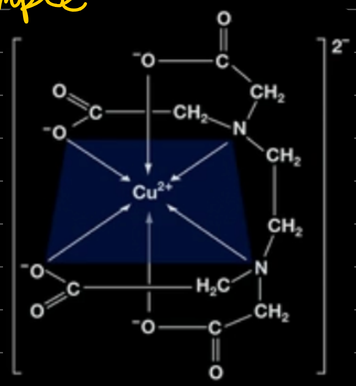


• Hexadented ligands



EDTA

Example



$[Cu(EDTA)]^{2-}$

Stereoisomerism

- cis-trans: square planar, octahedral
- optical: octahedral

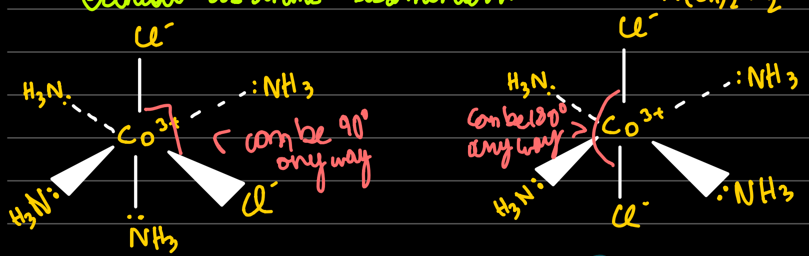
① cis-trans in square planar

> Square planars that have the form MA_2B_2 exhibit cis trans isomerism

cisplatin　　　transplatin

② cis-trans in octahedral

> Octahedrals that have the form MA_2B_4 | MA_4B_2 exhibit cis-trans isomerism
> └ or $M(en)_2A_2$

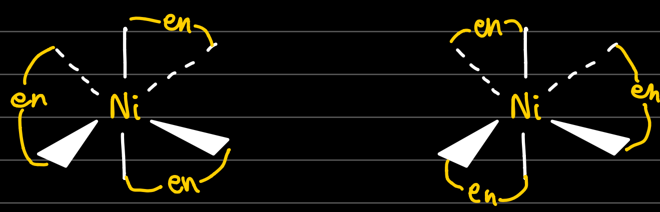


cis　　　trans

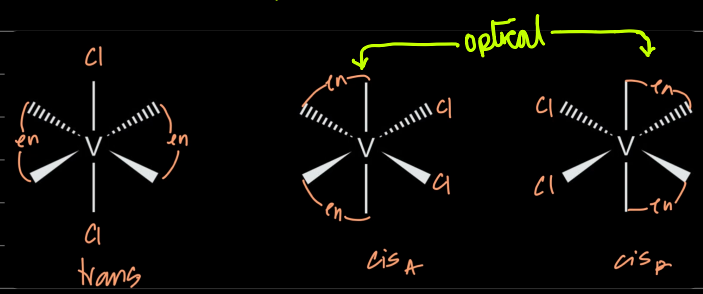
① Optical isomerism in octahedrals

> Needs to have atleast two bidented ligands

$[Ni(en)_3]^{2+}$



• A few more examples



Ligand exchange reactions

① $Cu^{2+}(aq) + NaOH(aq)$

- $Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$
- $[Cu(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons [Cu(H_2O)_4(OH)_2](s)$

blue solution　　　Pale blue ppt.

② $Cu^{2+}(aq) + NH_3(aq)$

- $[Cu(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons [Cu(H_2O)_4(OH)_2](s)$

Pale blue ppt.

then

- $[Cu(H_2O)_4(OH)_2](s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l) + 2OH^-$

dark blue solution

Overall

- $[Cu(H_2O)_6]^{2+} + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O$

blue solution　　　dark blue sol.

③ $Cu^{2+}(aq) + NH_3(l)$

- $[Cu(H_2O)_6]^{2+} + 6NH_3(aq) \rightleftharpoons [Cu(NH_3)_6]^{2+} + 6H_2O$

blue solution　　　dark blue sol.

④ Cu^{2+} with Cl^- / conc HCl / conc NaCl

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

blue solution　　　yellow solution

Cobalt's reactions:

⑤ $[Co(H_2O)_4]^{2+} + 2OH^- \rightleftharpoons [Co(H_2O)_4(OH)_2](s) + 2H_2O$

pink solution — blue ppt

$\downarrow$ excess NaOH + warm

pink/red. ppt

⑥ $[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$

pink solution — Brown solution

⑦ $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

pink solution — Blue solution

Stability constant, Kstab

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$

$$K_c = \frac{[[CuCl_4]^{2-}][H_2O]^6}{[[Cu(H_2O)_6]^{2+}][Cl^-]^4} \quad \therefore K_{stab} = \frac{[[CuCl_4]^{2-}]}{[[Cu(H_2O)_6]^{2+}][Cl^-]^4}$$

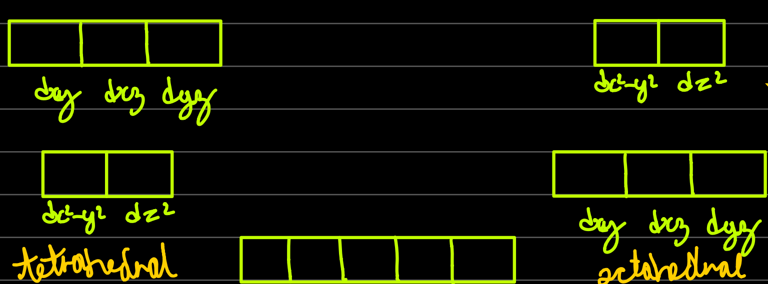
> The larger K stab, the more stable the complex ion

> The stronger the ligand's, the more stable the complex ion

> The larger the charge on cation, '2+ or 3+', the stronger the bond / more stable the complex ion.

Colors in complex ions

① forming complex ions, degenerate d orbitals are split into



ΔE ∝ ligand
∝ cation
∝ charge?

② e⁻ from lower energy level of 3d orbital absorb energy to jump to higher level.

③ energy corresponds to freq. of certain colors of UV light

④ the complementary color is seen.