Coordination Compounds

Compounds in which a central metal atom or ion is bonded to a fixed number of ions or molecules (~~called~~ ligands) by coordinate (dative) bonds. e.g. $[Cu(NH_3)_4]SO_4$.

Important : chlorophyll (Mg), haemoglobin (Fe), vitamin B12 (Co) - all complexes.

Werner's Theory (1898)

Studied $CoCl_3 \cdot xNH_3$ series :

$CoCl_3.6NH_3$ (yellow) -> 3 AgCl ppt
$CoCl_3.5NH_3$ (purple) -> 2 AgCl ppt
$CoCl_3.4NH_3$ (green) -> 1 AgCl ppt

Postulates

1. Two valences : primary & secondary.
2. Primary = ionisable, satisfied by negative ions (e.g. Cl^- outside).
3. Secondary = non-ionisable, fixed in number = coordination number.
4. Secondary valences are directed in space - give definite geometry.

Important Terms

Coordination entity

Central metal + bonded ligands within [ ] .

e.g. $[Ni(CO)_4]$, $[Fe(CN)_6]^{4-}$.

Central atom / ion

Atom to which ligands are bonded; acts as a Lewis acid (electron-pair acceptor).

Ligand

Ion / molecule that donates an e- pair.

Acts as a Lewis ~~acid~~ base.

Types based on no. of donor atoms :

- Unidentate : Cl^-, NH_3, H_2O
- Didentate : en, $C_2O_4^{2-}$ (oxalate)
- Polydentate : $EDTA^{4-}$ (hexadentate)
- Ambidentate : NO_2^- , SCN^- .

Coordination number (CN)

No. of donor atoms sigma-bonded to the central metal. (pi-bonds NOT counted)

e.g. $[PtCl_6]^{2-}$ CN = 6 ; $[Ni(NH_3)_4]^{2+}$ CN = 4 ; $[Co(en)_3]^{3+}$ CN = 6 (en is didentate, so each en counts twice).

Oxidation Number & Nomenclature

Oxidation no. of central atom

Charge it would carry if all ligands left with their shared e- pairs. Roman in ( ).

$K_4[Fe(CN)_6]$ → Fe is Fe(II)

$\leftarrow 4(+1) + x$
$\leftarrow + 6(-1) = 0$

IUPAC Naming Rules

(i) Cation named before anion.

(ii) Ligands alphabetical, BEFORE metal.

(iii) Anionic ligands end in -o : Cl^- = chlorido, CN^- = cyanido, OH^- = hydroxido.
Neutral : H_2O = aqua, NH_3 = ammine, CO = carbonyl, NO = nitrosyl.

(iv) Prefixes di, tri, tetra ... for no.
If ligand name has di/tri itself, use bis, tris, tetrakis ( ).

(v) Metal in cation → English name ; in anion → -ate suffix (ferrate, cuprate, ~~aluminate~~ aluminate).

Worked example

$[Cr(NH_3)_3(H_2O)_3]Cl_3$ = triammine-triaqua chromium(III) chloride.

Isomerism in Complexes

Same formula, different arrangement.

Two classes : Stereo and Structural.

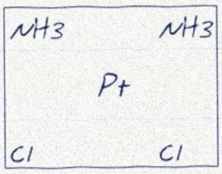
1. Geometrical (cis-trans)

Found in square planar and octahedral complexes with two kinds of ligands.

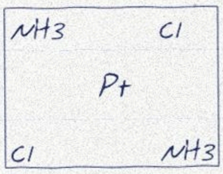
Square planar Ma_2b_2 : cis & trans.

e.g. $[Pt(NH_3)_2Cl_2]$ - cis-platin (anti tumour drug) ; trans-platin (inactive).

cis



trans



Octahedral Ma_4b_2 : cis & trans. Ma_3b_3: Facial (fac) & meridional (mer) forms.

2. Optical (d and l)

Non-superimposable mirror images that rotate plane-polarised light. Shown by $[Co(en)_3]^{3+}$ and cis-$[Co(en)_2Cl_2]^+$; trans form is optically inactive.

Structural Isomerism

(a) Linkage isomerism

Ambidentate ligand binds via different donor atoms. e.g. NO_2^- - via N or O.

$\boxed{[Co(NH_3)_5(NO_2)]^{2+} \; / \; [Co(NH_3)_5(ONO)]}^{2+}$

nitrito-N vs nitrito-O

(b) Coordination isomerism

Interchange of ligands between cationic and anionic complex ions of same compound.

e.g. $[Co(NH_3)_6][Cr(CN)_6]$ and

$[Cr(NH_3)_6][Co(CN)_6]$.

(c) Ionisation isomerism

Counter ion in complex salt is itself a potential ligand. ~~Different~~ Give different ions in solution.

$\boxed{[Co(NH_3)_5(SO_4)]Br \; / \; [Co(NH_3)_5Br]SO_4}$

Br^- free vs SO_4^{2-} free in soln.

(d) Solvate (hydrate) isomerism

H_2O is in / out of coord. sphere.

$[Cr(H_2O)_6]Cl_3$ (violet), $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (blue-green).

Valence Bond Theory (VBT)

Metal ion hybridises (n-1)d, ns, np or ns, np, nd orbitals to give equivalent hybrid orbitals. Ligands donate lone pairs into these vacant hybrid orbitals (datively).

Hybridisation vs Geometry

CN	Hybrid.	Geometry
4	sp3	tetrahedral
4	dsp2	square planar
5	sp3d	trig. bipyramidal
6	sp3d2 (outer)	octahedral
6	d2sp3 (inner)	octahedral

Inner vs Outer orbital complex

Inner = d2sp3 - uses (n-1)d - low spin, spin-paired - strong field ligand.

Outer = sp3d2 - uses nd - high spin, spin-free - weak field ligand.

[Co(NH3)6] 3+ -> d2sp3 (LS, dia.) <inner) orbital

[CoF6] 3- -> sp3d2 (HS, para.) <outer) orbital

mu = sqrt[n(n+2)] BM

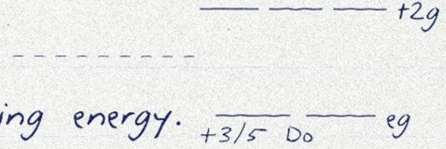
Crystal Field Theory (CFT)

Electrostatic model : M-L bond purely ionic. Ligands = point charges / dipoles. Degenerate d orbitals split in presence of ligand field. Pattern depends on geometry.

Octahedral splitting

eg (dx2-y2, dz2) : raised by 3/5 Do .

t2g (dxy, dyz, dxz) : lowered by 2/5-2/DoDo



Do = crystal field splitting energy.

Spectrochemical series

I- < Br- < SCN- < Cl- < F- < OH-
< C2O4 2- < H2O < NCS- < edta 4-
< NH3 < en < CN- < CO (~~weak~~ strong)

High vs Low spin (octahedral d4-d7)

Compare Do with pairing energy P :

Do < P -7 high spin (t2g 3 eg<-weak) field

Do > P -7 low spin (t2g 4 eg: strong) field

Tetrahedral : Dt = (4/9) Do , inverted ;

Colour, Carbonyls & Applications

Colour in complexes

d-d transition : e- excited from t_{2g} -> e_g by absorbing visible light (h.nu = Do). Observed colour = complementary of the colour ~~emitted~~ absorbed.

$[Ti(H_2O)_6]^{3+}$ absorbs 498 nm (green) -> appears violet. d^0 / d^{10} ions are colourless (no d-d transition).

Metal carbonyls

Homoleptic CO complexes. M oxidn = 0. $Ni(CO)_4$ - tetrahedral ; $Fe(CO)_5$ - trig. bipy. ; $Cr(CO)_6$ - octahedral.

M-C bond : has sigma + pi character.
sigma : CO lone pair -> empty M orbital.
pi : filled M d-orbital -> pi* of CO.

Synergic bonding strengthens M-C

<- back-
<- donation

Applications

EDTA - water hardness ; cis-platin - anti-tumour ; chlorophyll, Hb, B12 - life !