Coordination Chemistry

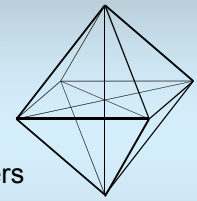
S.M.Jørgensen
1837-1914

1890's: $CoCl_2 \cdot 6H_2O + NH_3/NH_4^+$

Reacted with	Name (colour)	Formula
H_2O_2 + act. charcoal	Luteocobalt chloride	$Co(NH_3)_6Cl_3$
H_2O_2 (only)	Purpureocobalt chloride	$Co(NH_3)_5Cl_3$
Air, evapo-rate with HCl	Praseocobalt chloride	$Co(NH_3)_4Cl_3$
Heating the green one	Violeocobalt chloride	$Co(NH_3)_4Cl_3$

Coordination number 6

Octahedral geometry



- Cobalt(III) ion in centre
- Donor atoms (N, Cl) in corners

Very common geometry in coordination compounds

Coordination numbers

number	geometry	example
2	Linear	$Ag(NH_3)_2^+$
3	Trigonal planar	$Cu(CN)_3^-$
4	Tetrahedral Square planar	MCl_4^{n-} $PtCl_4^{2-}$
5	Trigonal bipyramide Square pyramidal	$CuCl_5^{3-}$ $W(V)Cl_4O^-$

Coordination numbers

number	geometry	example
6	Octahedral Trigonal prismatic(rare)	$Co(NH_3)_6^{3+}$ $W(CH_3)_6$
7	Capped or Pentagonal bipyramide	rare
8  	Square antiprism dodecahedron	$Mo(CN)_8^{4-}(aq)$ $Y(H_2O)_8^{3+}$
9	Tricapped prismatic	ReH_9^- $Pu(H_2O)_9^{3+}$

$Pu(H_2O)_9^{3+}$

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High-Yield Synthesis and Single-Crystal X-ray Structure of a Plutonium(III) Aquo Complex: $[Pu(H_2O)_9](CF_3SO_3)_3$

The aquo complex of Pu(III) is 9-coordinate with an ideal tricapped trigonal-prismatic geometry. The cation was crystallized as the triflate salt in quantitative yield from dissolution of Pu metal in triflic acid. Structural comparisons with analogous lanthanide aquo complexes are presented.

- (remember: aqua !) Naming important !

Names and formula

- Cationic part first, anionic part next, water of crystallisation etc. last
- From name to formula $[ML^1_xL^2_yL^3_z\ldots]$

Ligands alphabetic anionic, neutral, cationic

- From formula to name $L^1_xL^2_yL^3_z\ldots M$

Ligands strictly alphabetic (x,y,z as prefixes)
M-ate if $[----]^{n-}$

Special ligand names

Name	Formula	Ligand name as ligand
water	H_2O	aqua
ammonia	NH_3	ammine
(methyl)amine	$(CH_3)NH_2$	(methyl)amine
nitrogenmonoxide	NO	nytrosyl
carbonmonoxide	CO	carbonyl
dinitrogen	N_2	dinitrogen
dioxygen	O_2	dioxygen

Formula

- *cis*-Tetraaquadichlorochromium(III) chloride
- Potassium pentachloronitroosmate(IV)
- *mer*-trihydridotris(triphenylphosphin)ruthenium(III)
- Pentaamminechlorocobalt(III) nitrate
- Potassium trioxalatocobaltate(III)
- Bis(1,2-ethandiamine)diiodocobalt(III) perchlorate
- Dichlorobis(1,2-ethandiamine)cobalt(III) tetrafluoroborate
- Pentaamminedinitrogenruthenium(II) chloride
- Sodium pentacyanonitrosylferrate(II) dihydrate
- Pentaamminecobalt(III)-μ-cyanopentacyanocobaltate(III)

Names

- $[PtCl_2(NH_3)_2]$
- $[RhCl(NH_3)_5]Cl_2$
- $[Co(NH_3)_6]SO_4$
- $[Co(NH_3)_4(H_2O)_2](BF_4)_3$
- $Na_3[Fe(CN)_6]\cdot 2H_2O$,
- $[Ni(CO)_4]$,
- $[Co(CH_3COO)BrCl(NH_3)_2]$,
- $[Pt(py)_4]$ $[PtCl_4]$,
- $Na_2[PdCl_6]$,
- $(NEt_4)_3[AlF_6]$,
- $[Pt(acac)_2ClNH_3]Cl$

Isomerism** OBS fig 19.11

Structural isomerism (what is bound to what)	**Stereo**isomerism (spatial arrangement)
Hydration	Geometrical or diastereoisomeric
Ionisation	Optical or enantiomeric
Linkage	
Coordination	

Structural isomerism

Examples

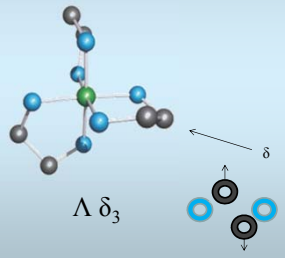
- Ionisation $Co(NH_3)_5SO_4Br$
- Hydration $Co(H_2O)_6Cl_3$
- Coordination $CoCr(NH_3)_6(CN)_6$
- Linkage $Co(NH_3)_5NO_2Cl_2$

Stereoisomerism**OBS fig 19.11

- Geometrical isomerism
  - cis-trans
  - fac-mer
  - (tetrahedral-square planar)
  - E - Z
- Optical isomerism
  - enantiomers
  - Diastereomers (obs: from organic chemistry)

Descriptors for chiral cases

- (+) - (-)
- d – l
- D - L
- R – S
- Δ - Λ
- δ – λ



Λ δ_3

Problems

- Draw sketches of the 10 possible octahedral MA_nB_{6-n}
- Draw sketches of the more than 10 possible prismatic MA_nB_{6-n}
- Draw sketches of possible octahedral complexes with 4 different monodentate ligands

Problems

- Draw the two different geometrical arrangements of an octahedral $M(A\text{-}B)_3$. Optical isomerism?
- Draw the different geometrical arrangements of an octahedral $M(A\text{-}B)_2X_2$ Optical isomerism?

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