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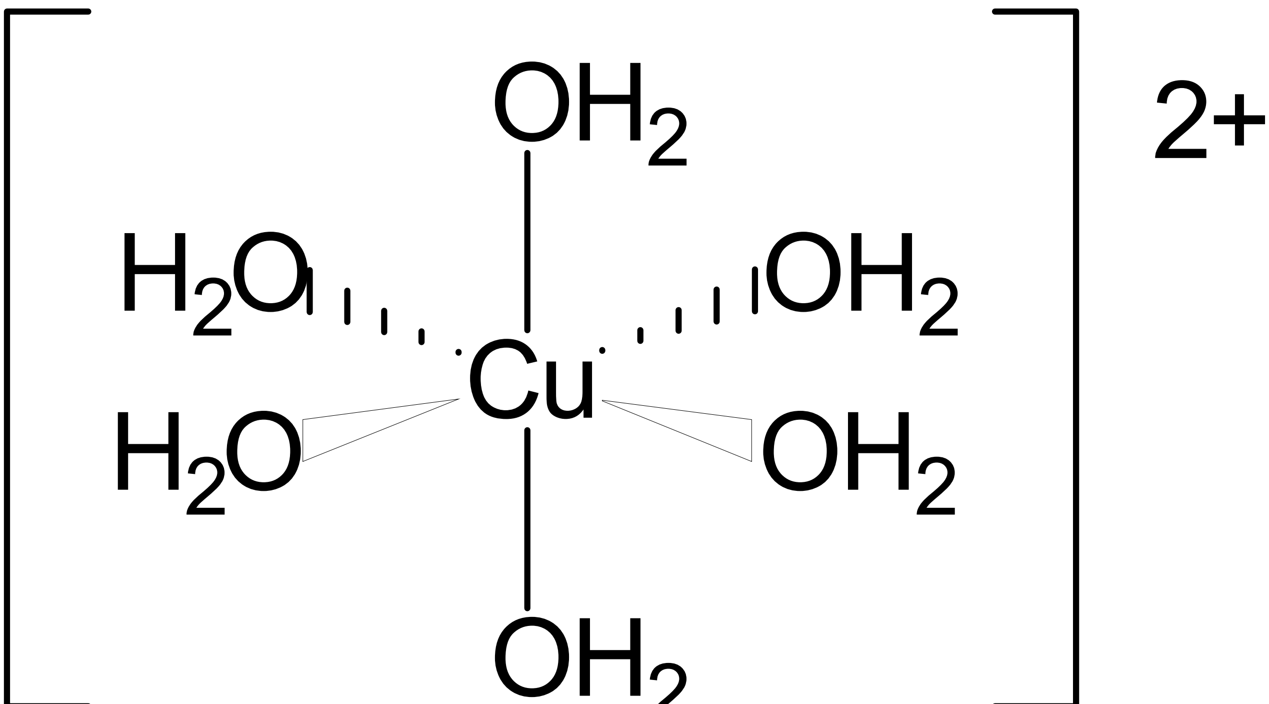
REACTIONS OF INORGANIC COMPLEXES

METAL AQUA IONS

METAL AQUA IONS

e.g. $[Cu(H_2O)_6]^{2+}$



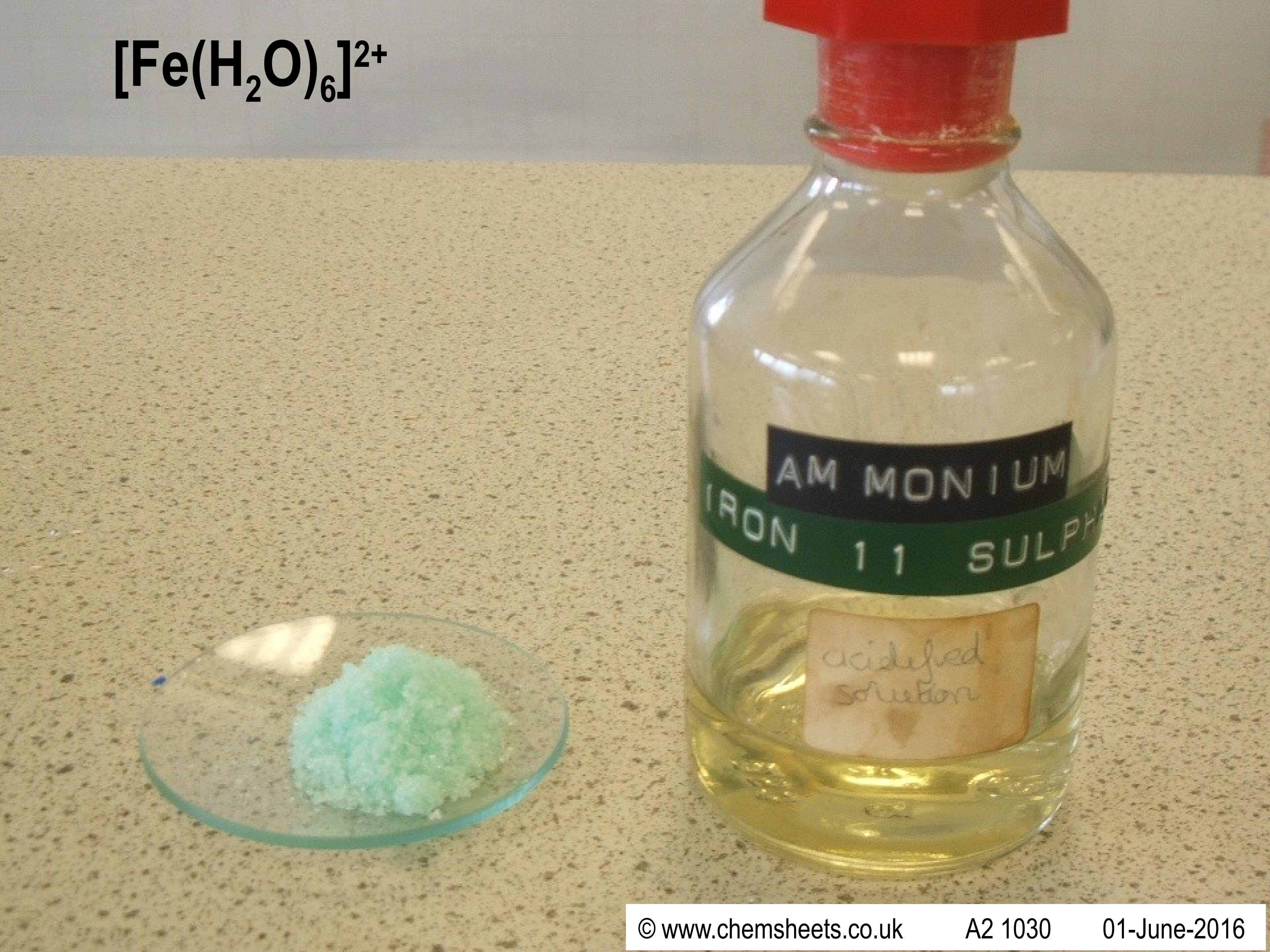
METAL AQUA IONS

complex	colour
$[Cu(H_2O)_6]^{2+}$	blue
$[Co(H_2O)_6]^{2+}$	pink
$[Fe(H_2O)_6]^{2+}$	green
$[V(H_2O)_6]^{2+}$	green
$[Cr(H_2O)_6]^{3+}$	violet*
$[Fe(H_2O)_6]^{3+}$	pale violet**
$[Al(H_2O)_6]^{3+}$	colourless

$[Cu(H_2O)_6]^{2+}$

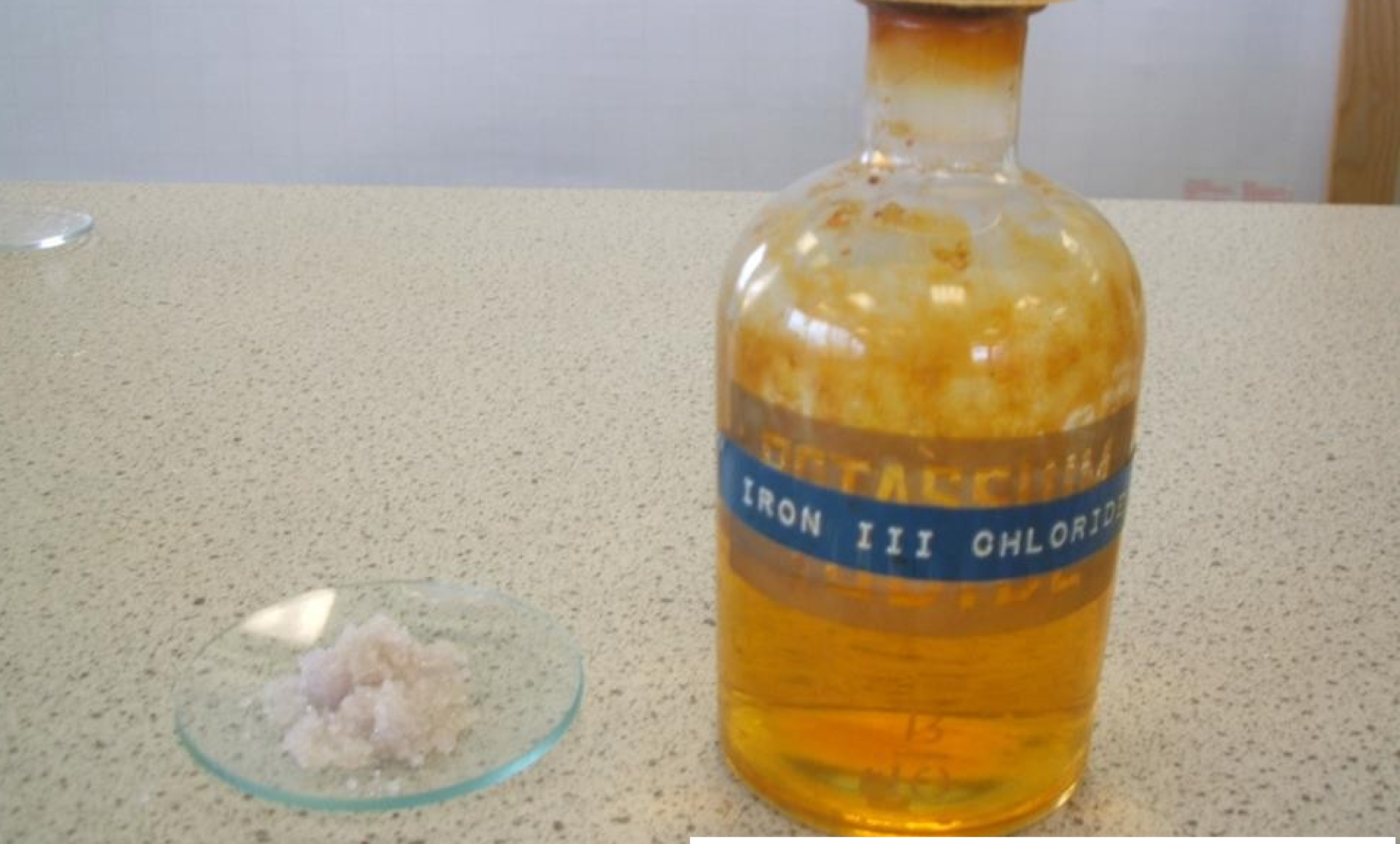
$[Co(H_2O)_6]^{2+}$

$[Fe(H_2O)_6]^{2+}$

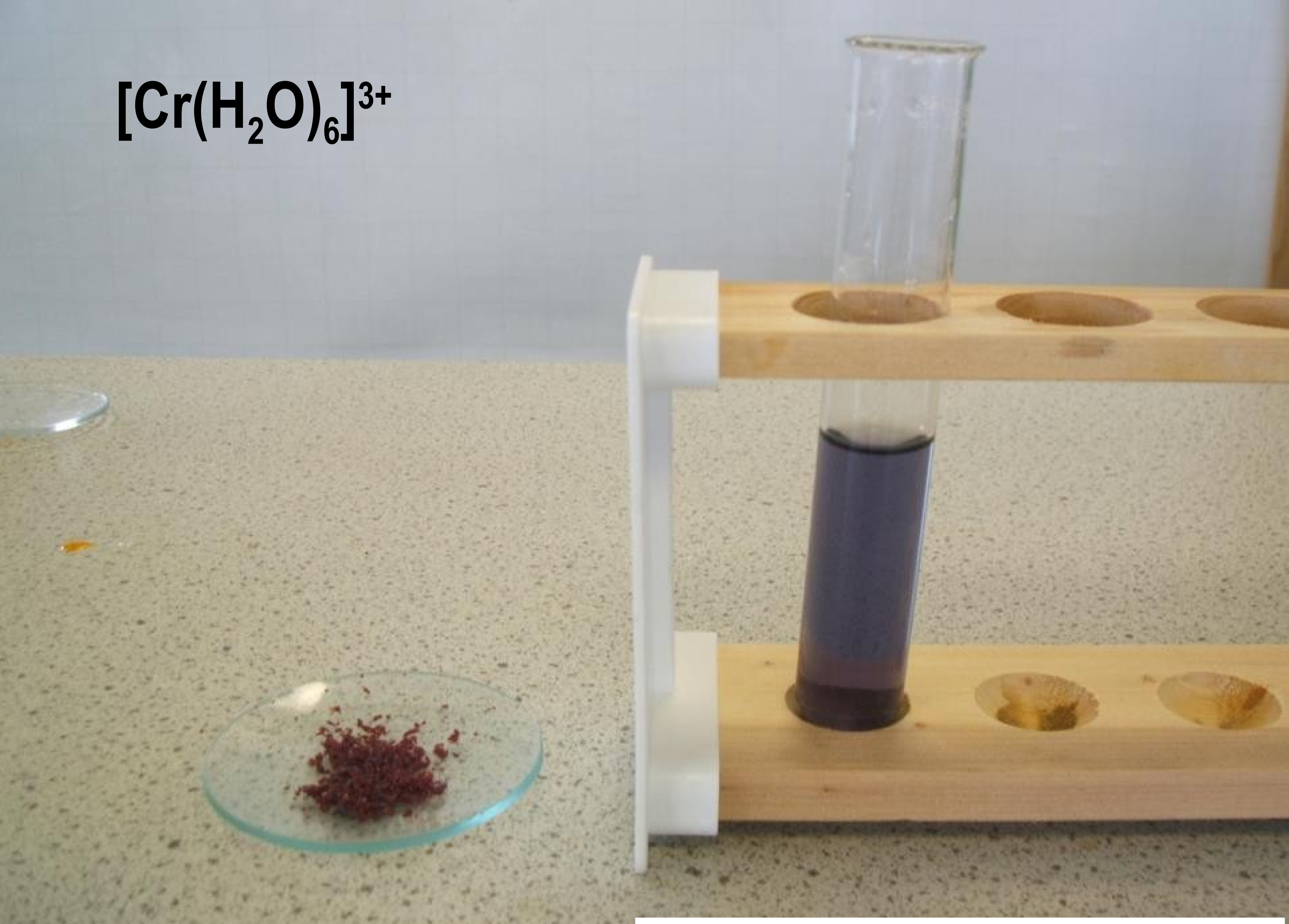


$[Al(H_2O)_6]^{3+}$

$[Fe(H_2O)_6]^{3+}$



$[Cr(H_2O)_6]^{3+}$

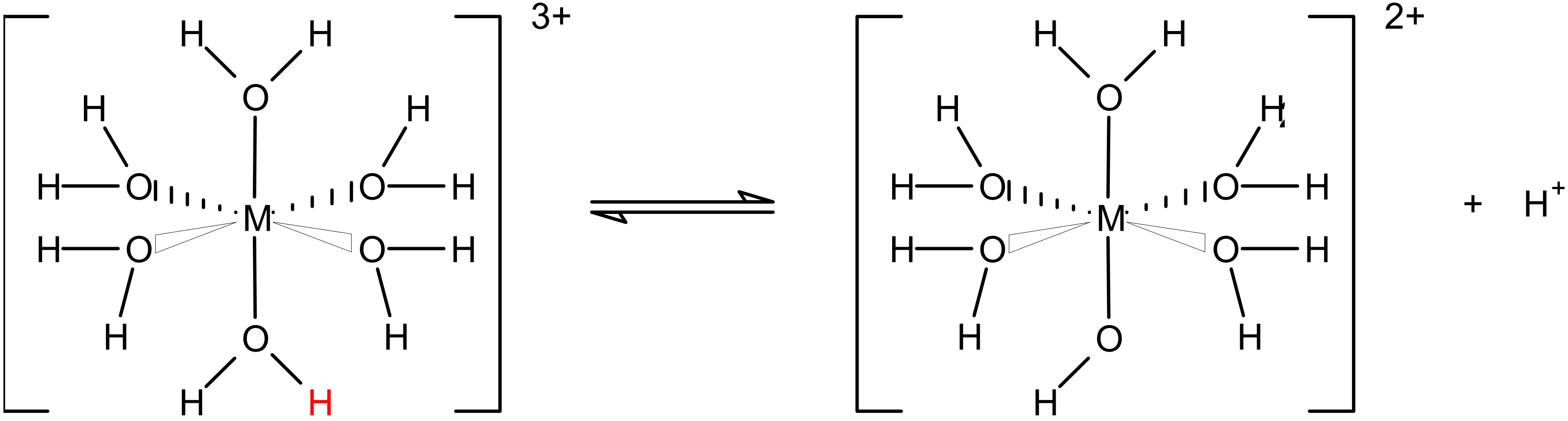


Reactions of METAL AQUA IONS

1)	Hydrolysis	O-H bond in H_2O ligand breaks
2)	Substitution	M-ligand bond breaks
3)	Redox	change in oxidation state of M

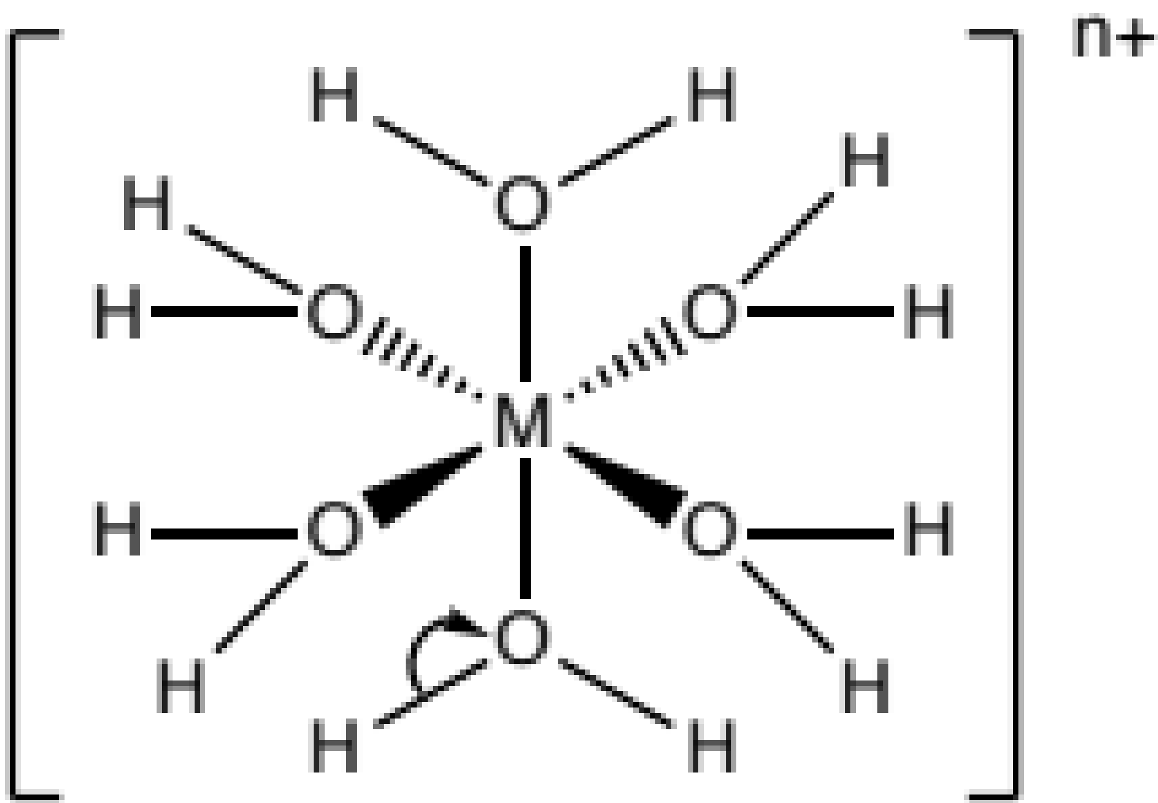
HYDROLYSIS of metal aqua ions

HYDROLYSIS OF $M^{n+}(aq)$



Aqua ion	$[M(H_2O)_6]^{+}$	$[M(H_2O)_6]^{2+}$	$[M(H_2O)_6]^{3+}$	$[M(H_2O)_6]^{4+}$
pH of typical solution	7	6	3	0

HYDROLYSIS OF $M^{n+}(aq)$



M^{3+} more acidic than M^{2+} due to:

M^{3+} smaller and greater charge than M^{2+} so O-H bond breaks more easily.

HYDROLYSIS OF $M^{n+}(aq)$

$$[M(H_2O)_6]^{2+} \rightleftharpoons [M(H_2O)_5(OH)]^{+} + H^{+}$$

$$[M(H_2O)_5(OH)]^{+} \rightleftharpoons [M(H_2O)_4(OH)_2] + H^{+}$$

$$[M(H_2O)_4(OH)_2] \rightleftharpoons [M(H_2O)_3(OH)_3]^{-} + H^{+}$$

$$[M(H_2O)_3(OH)_3]^{-} \rightleftharpoons [M(H_2O)_2(OH)_4]^{2-} + H^{+}$$

$$[M(H_2O)_2(OH)_4]^{2-} \rightleftharpoons [M(H_2O)(OH)_5]^{3-} + H^{+}$$

$$[M(H_2O)(OH)_5]^{3-} \rightleftharpoons [M(OH)_6]^{4-} + H^{+}$$

HYDROLYSIS OF $M^{n+}(aq)$

$$[M(H_2O)_6]^{3+} \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H^+$$

$$[M(H_2O)_5(OH)]^{2+} \rightleftharpoons [M(H_2O)_4(OH)_2]^{+} + H^+$$

$$[M(H_2O)_4(OH)_2]^{+} \rightleftharpoons [M(H_2O)_3(OH)_3] + H^+$$

$$[M(H_2O)_3(OH)_3] \rightleftharpoons [M(H_2O)_2(OH)_4]^{-} + H^+$$

$$[M(H_2O)_2(OH)_4]^{-} \rightleftharpoons [M(H_2O)(OH)_5]^{2-} + H^+$$

$$[M(H_2O)(OH)_5]^{2-} \rightleftharpoons [M(OH)_6]^{3-} + H^+$$

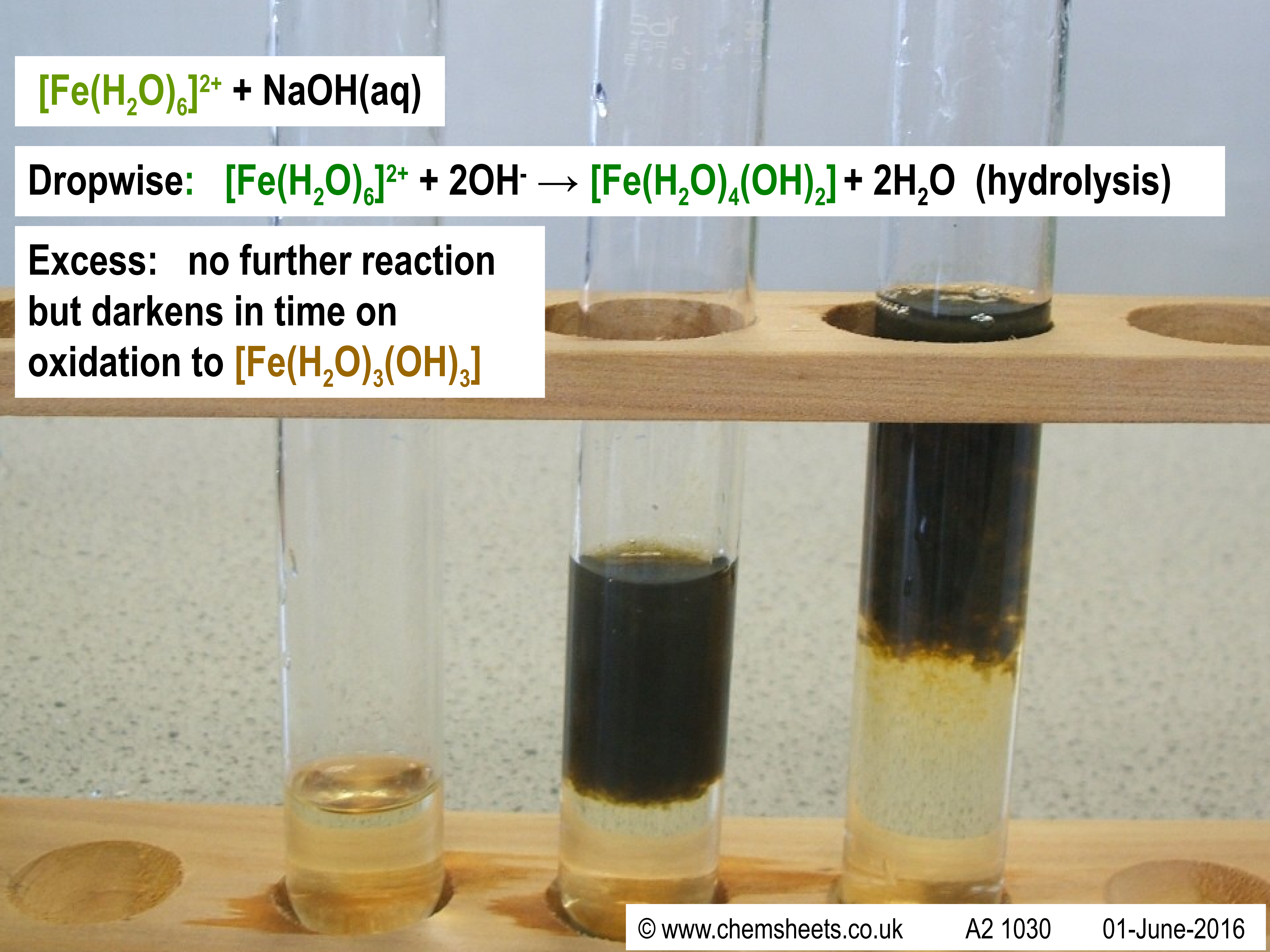
HYDROLYSIS of metal aqua ions

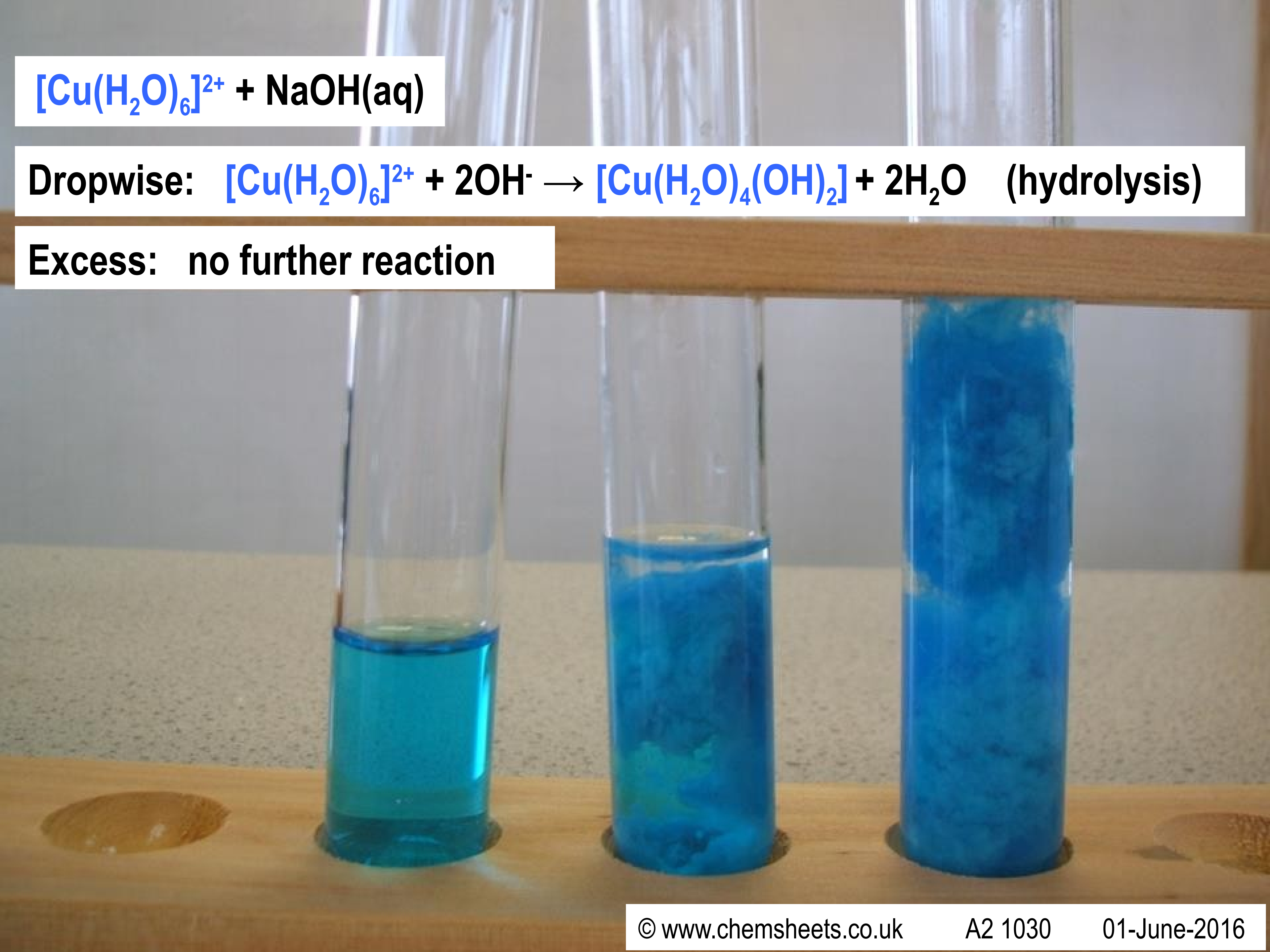
Reaction with $OH^-(aq)$

$[Fe(H_2O)_6]^{2+}$ + NaOH(aq)

Dropwise: $[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$ (hydrolysis)

Excess: no further reaction but darkens in time on oxidation to $[Fe(H_2O)_3(OH)_3]$





$[Cu(H_2O)_6]^{2+}$ + NaOH(aq)

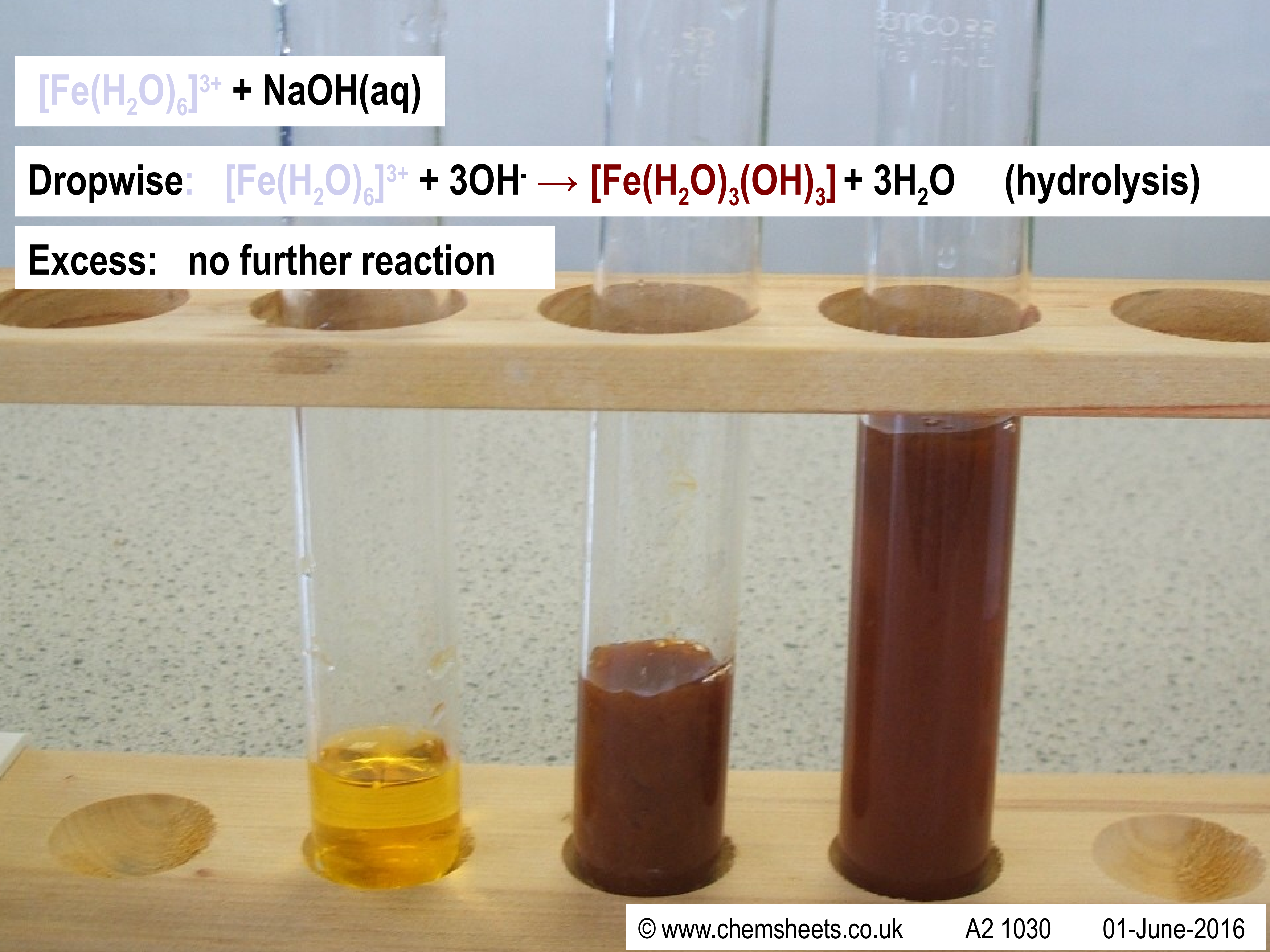
Dropwise: $[Cu(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$ (hydrolysis)

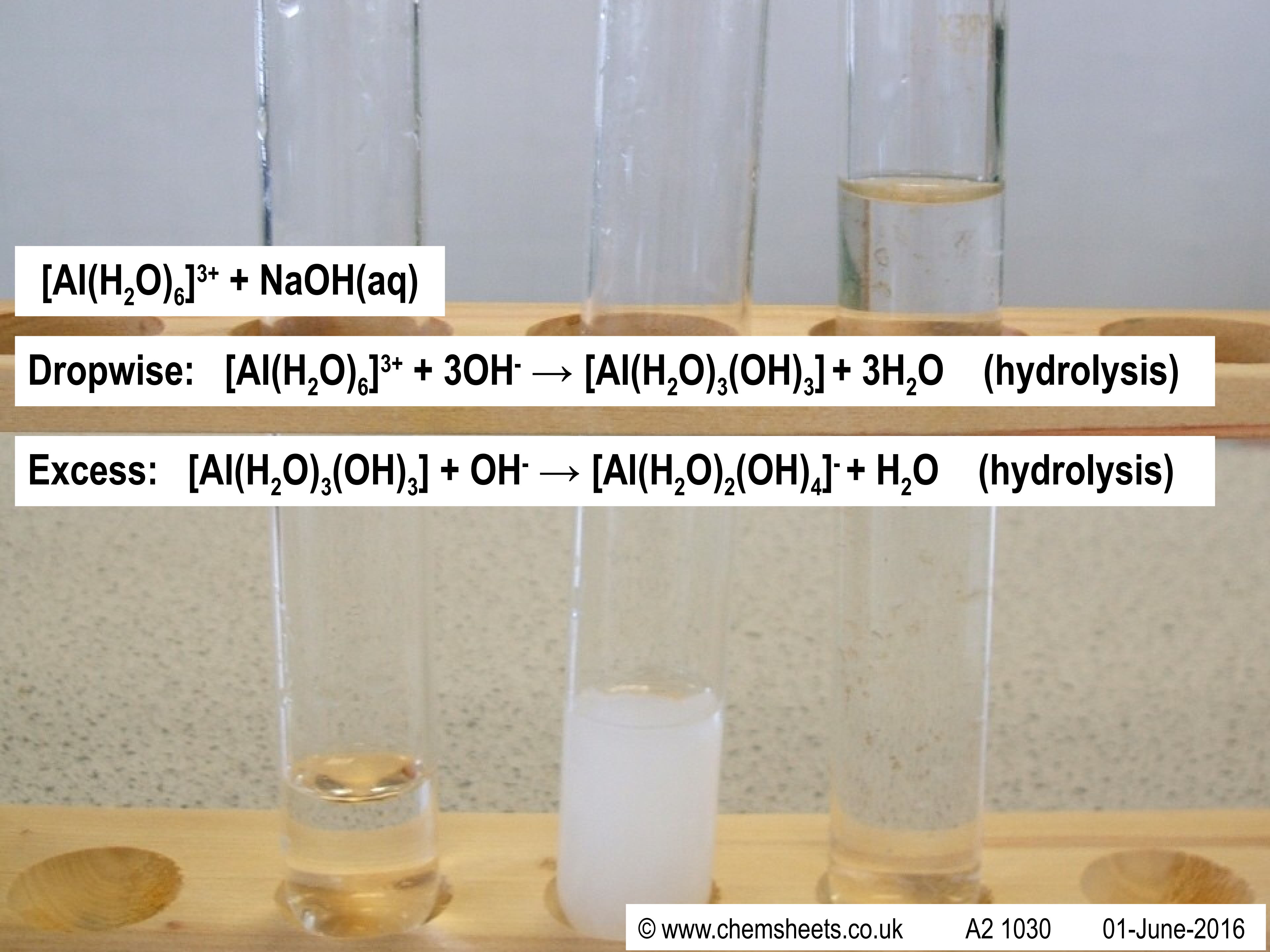
Excess: no further reaction

$[Fe(H_2O)_6]^{3+}$ + NaOH(aq)

Dropwise: $[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$ (hydrolysis)

Excess: no further reaction





$[Al(H_2O)_6]^{3+}$ + NaOH(aq)

Dropwise: $[Al(H_2O)_6]^{3+} + 3OH^- \rightarrow [Al(H_2O)_3(OH)_3] + 3H_2O$ (hydrolysis)

Excess: $[Al(H_2O)_3(OH)_3] + OH^- \rightarrow [Al(H_2O)_2(OH)_4]^- + H_2O$ (hydrolysis)

METAL AQUA IONS + $OH^-(aq)$

- Dropwise – precipitate of metal(II) hydroxide or metal(III) hydroxide forms

- Excess - $[Al(H_2O)_3(OH)_3]$ undergoes further hydrolysis to $[Al(H_2O)_2(OH)_4]^-$ and so 're-dissolves'

Acid-base character of metal hydroxides

ACID-BASE CHARACTER OF METAL HYDROXIDES

$$[Cu(H_2O)_6]^{2+} \xleftarrow{\text{XS } H^+} [Cu(H_2O)_4(OH)_2]$$

$$[Fe(H_2O)_6]^{2+} \longleftarrow [Fe(H_2O)_4(OH)_2]$$

$$[Fe(H_2O)_6]^{3+} \longleftarrow [Fe(H_2O)_3(OH)_3]$$

$$[Al(H_2O)_6]^{3+} \longleftarrow [Al(H_2O)_3(OH)_3] \xrightarrow{\text{XS } OH^-} [Al(H_2O)_2(OH)_4]^-$$

Basic

$[Cu(H_2O)_4(OH)_2]$

$[Fe(H_2O)_4(OH)_2]$

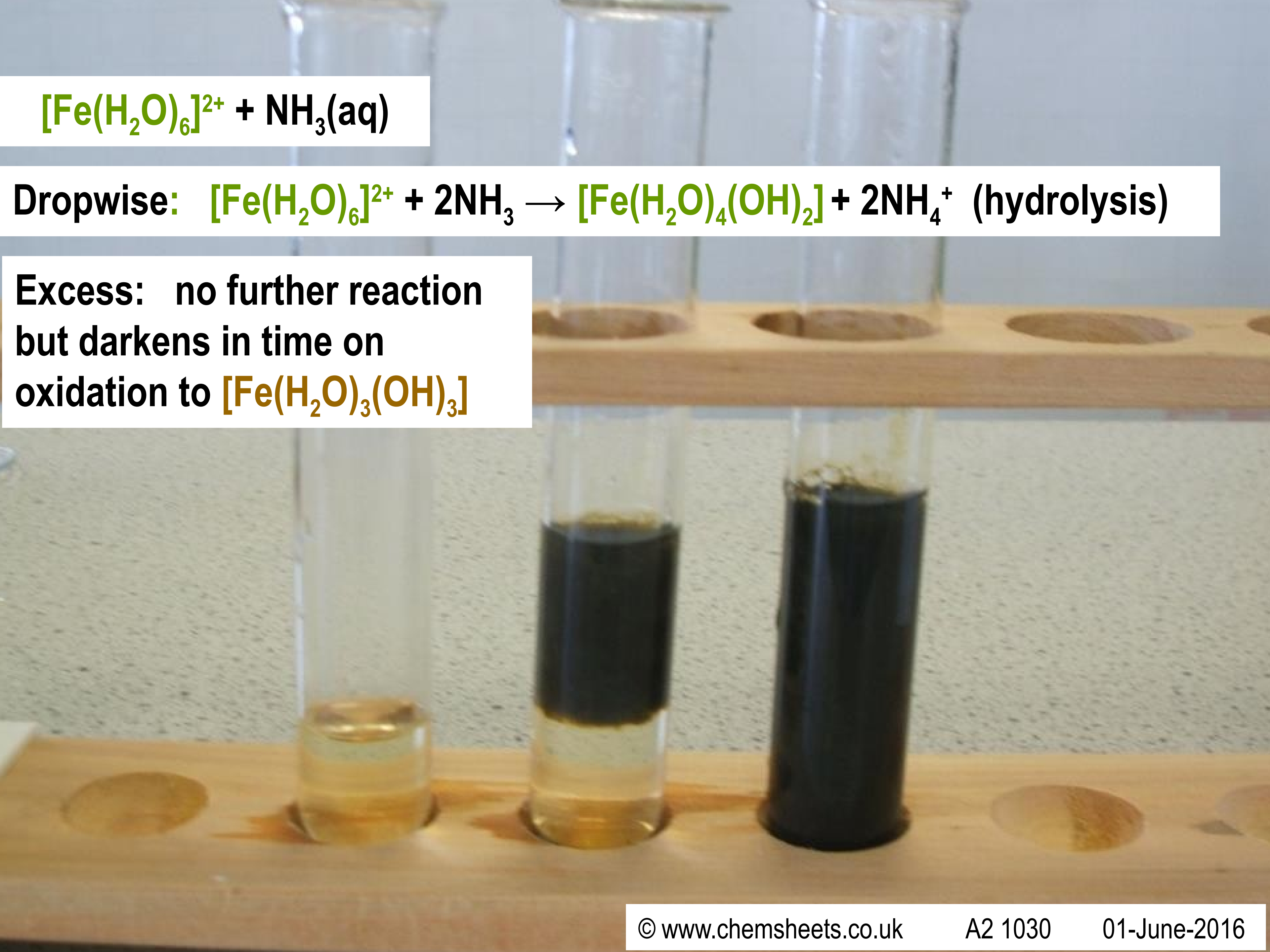
$[Fe(H_2O)_3(OH)_3]$

Amphoteric

$[Al(H_2O)_3(OH)_3]$

HYDROLYSIS of metal aqua ions

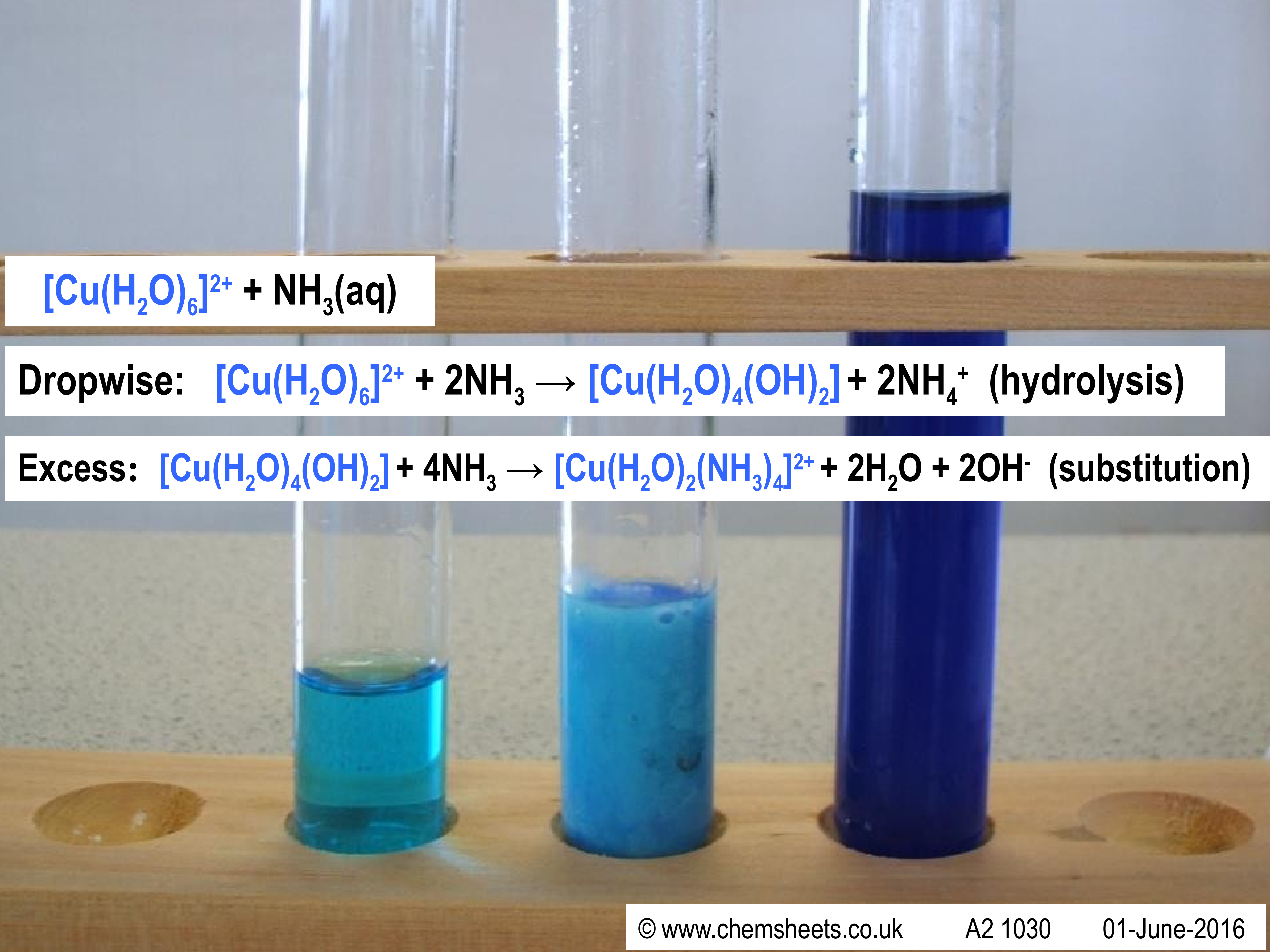
Reaction with $NH_3(aq)$



$[Fe(H_2O)_6]^{2+}$ + $NH_3(aq)$

Dropwise: $[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$ (hydrolysis)

Excess: no further reaction but darkens in time on oxidation to $[Fe(H_2O)_3(OH)_3]$



$[Cu(H_2O)_6]^{2+} + NH_3(aq)$

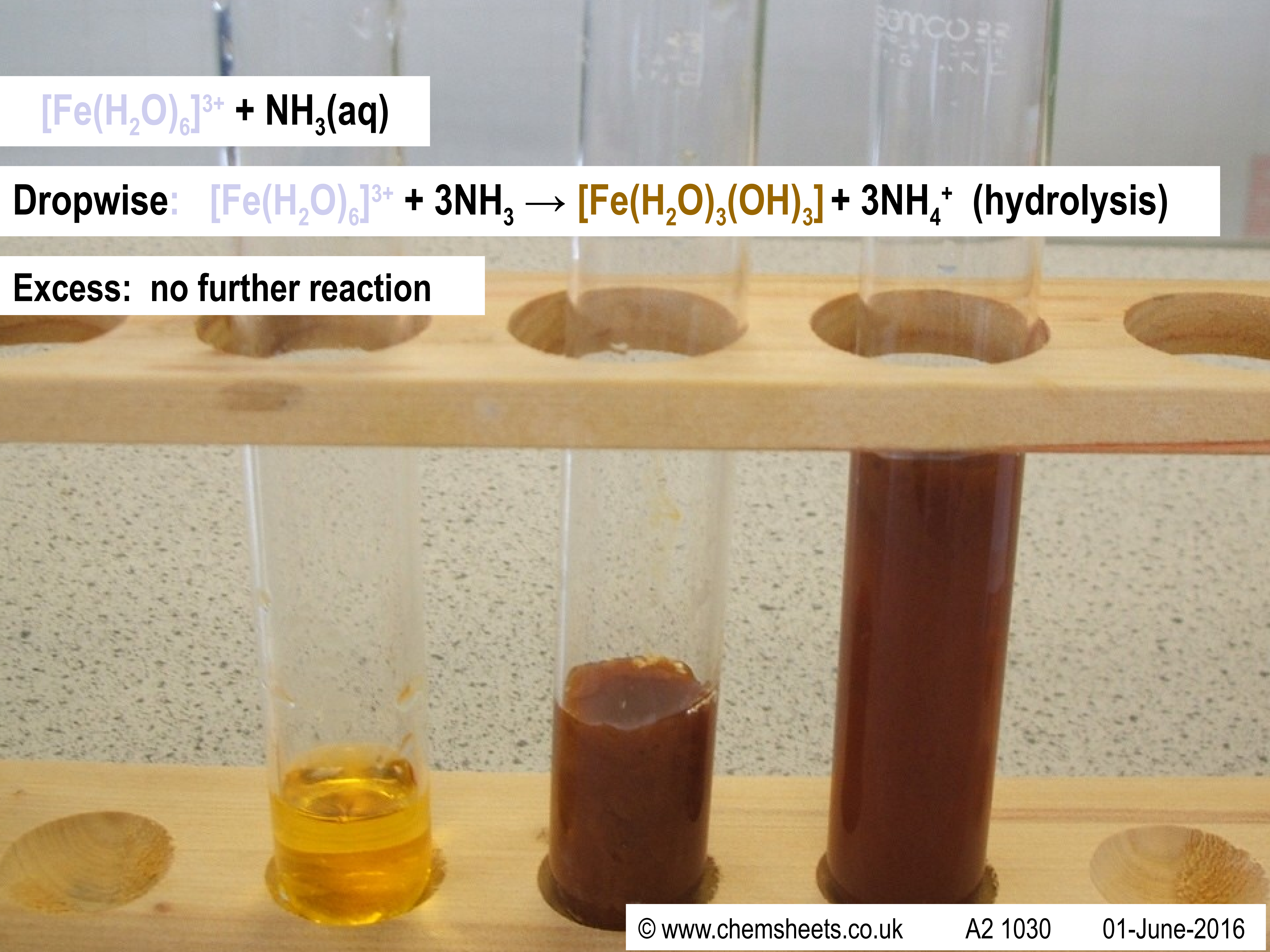
Dropwise: $[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$ (hydrolysis)

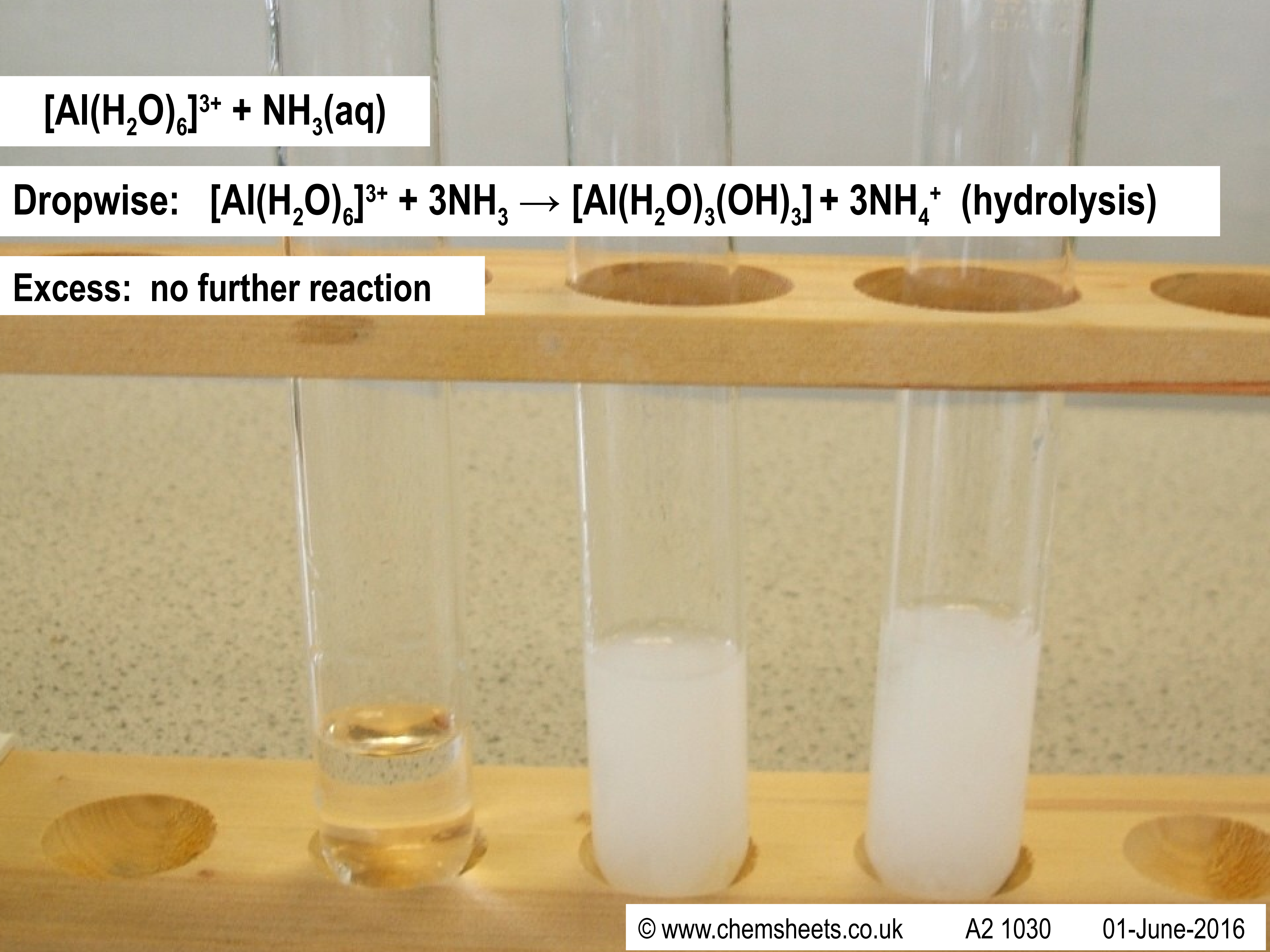
Excess: $[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O + 2OH^-$ (substitution)

$[Fe(H_2O)_6]^{3+} + NH_3(aq)$

Dropwise: $[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$ (hydrolysis)

Excess: no further reaction





$[Al(H_2O)_6]^{3+} + NH_3(aq)$

Dropwise: $[Al(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Al(H_2O)_3(OH)_3] + 3NH_4^+$ (hydrolysis)

Excess: no further reaction

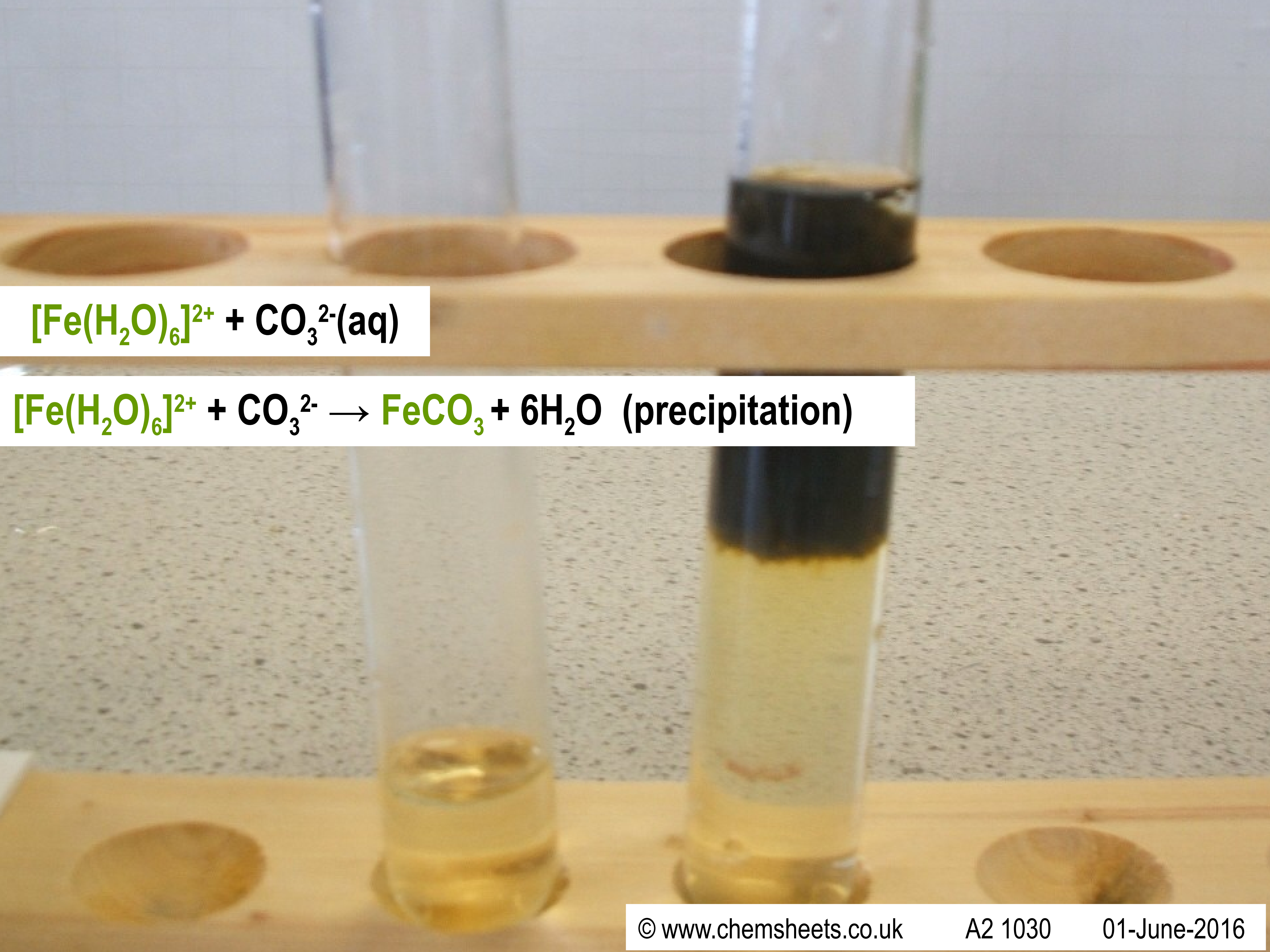
METAL AQUA IONS + NH_3(aq)

- Dropwise – precipitate of metal(II) hydroxide or metal(III) hydroxide forms

- Excess – $[Cu(H_2O)_4(OH)_2]$ undergoes ligand substitution to give $[Cu(H_2O)_2(NH_3)_4]^{2+}$

HYDROLYSIS of metal aqua ions

Reaction with $CO_3^{2-}(aq)$

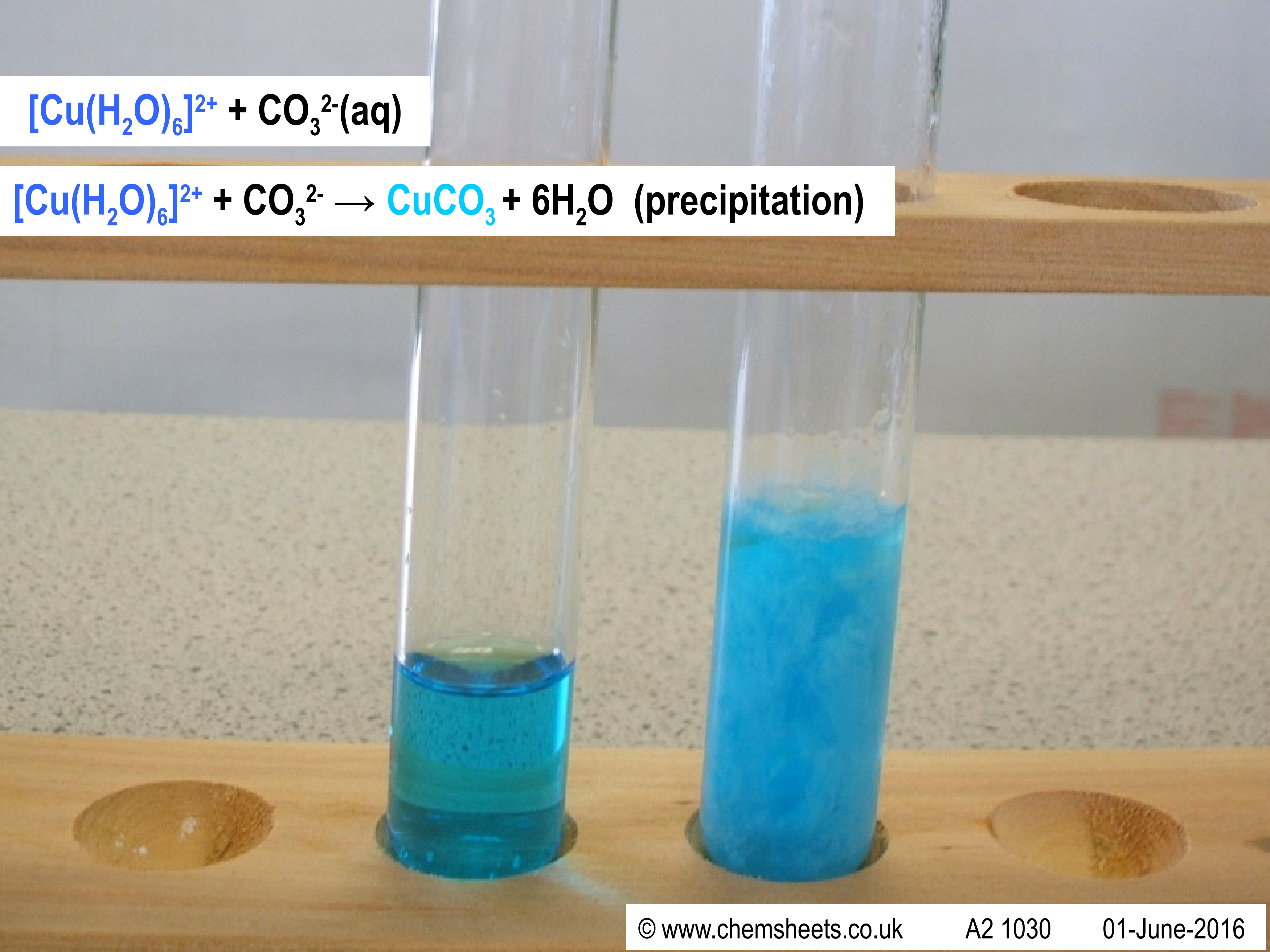


$[Fe(H_2O)_6]^{2+}$ + $CO_3^{2-}(aq)$

$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow FeCO_3 + 6H_2O$ (precipitation)

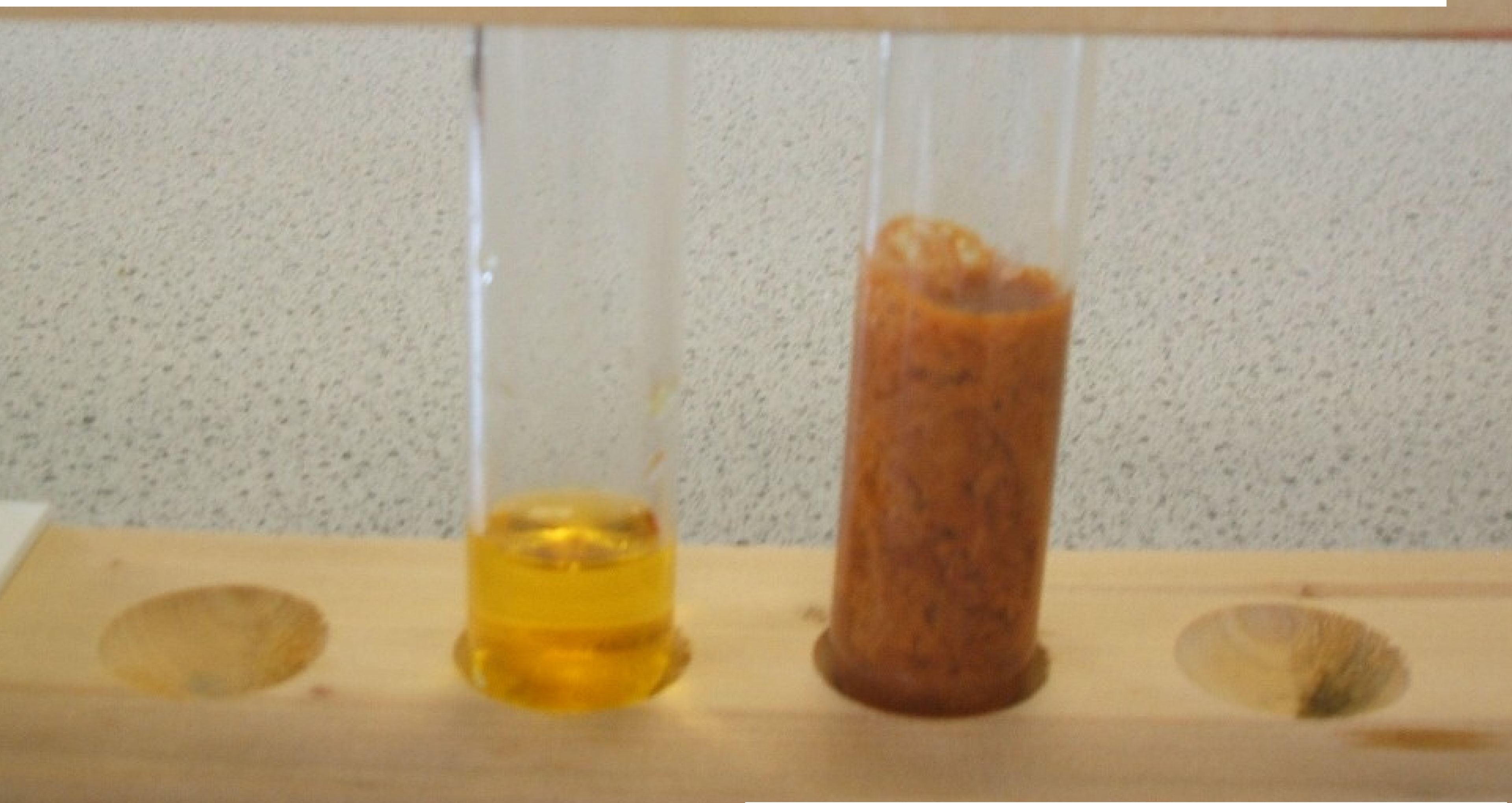
$[Cu(H_2O)_6]^{2+} + CO_3^{2-}(aq)$

$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow CuCO_3 + 6H_2O$ (precipitation)



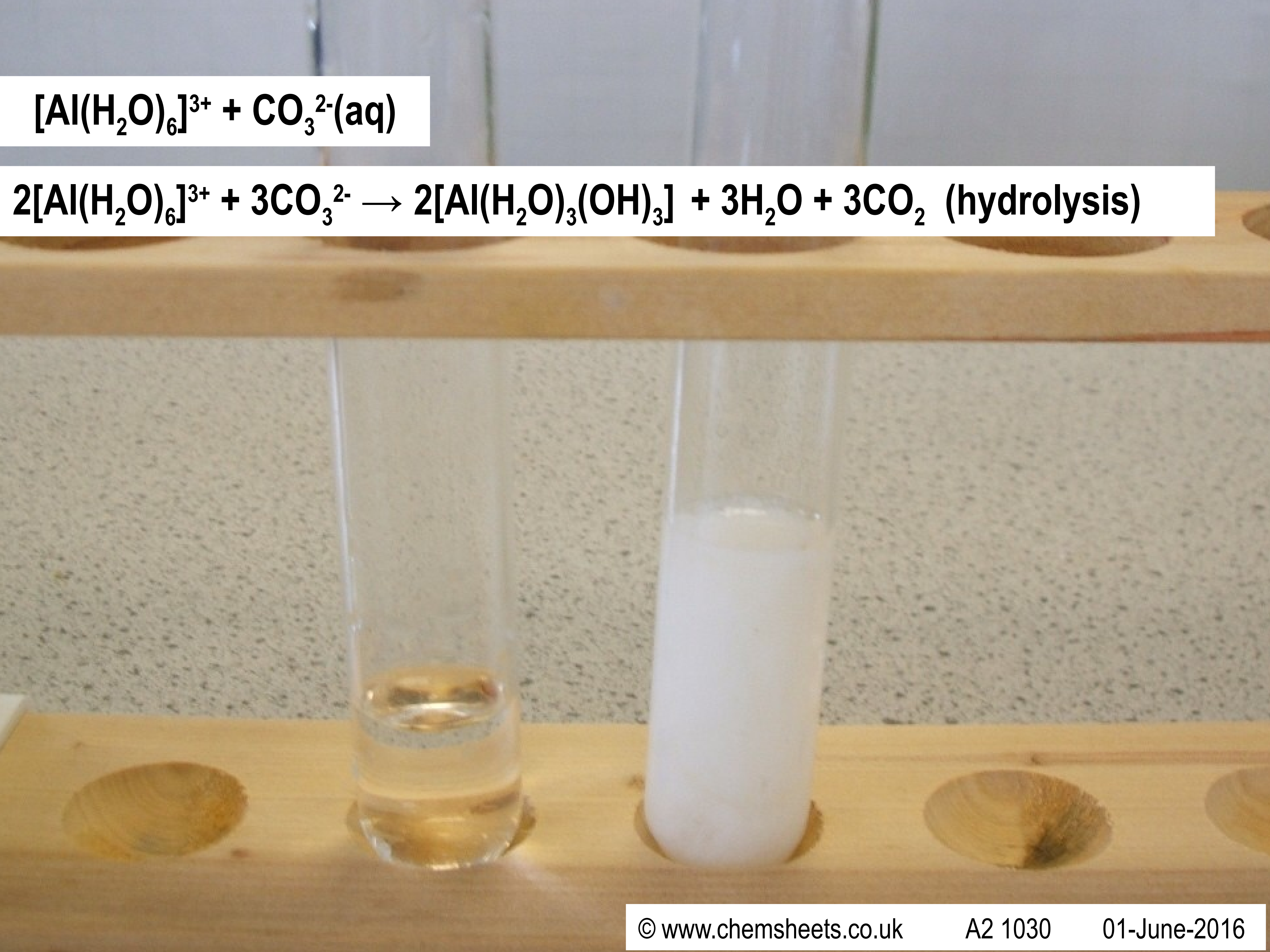
$[Fe(H_2O)_6]^{3+} + CO_3^{2-}(aq)$

$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Fe(H_2O)_3(OH)_3] + 3H_2O + 3CO_2$ (hydrolysis)



$[Al(H_2O)_6]^{3+} + CO_3^{2-}(aq)$

$2[Al(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow 2[Al(H_2O)_3(OH)_3] + 3H_2O + 3CO_2$ (hydrolysis)



METAL AQUA IONS + CO_3^{2-}(aq)

- $[M(H_2O)_6]^{2+}$ forms MCO_3 as precipitate (it is not acidic enough to release CO_2 from Na_2CO_3)
- $[M(H_2O)_6]^{3+}$ is more acidic and undergoes hydrolysis to form $[M(H_2O)_3(OH)_3]$ as a precipitate and gentle fizzing as CO_2 is formed

LIGAND SUBSTITUTION

Reaction with conc HCl

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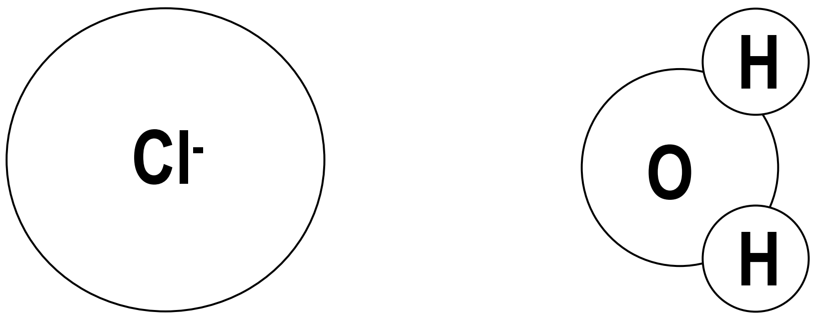
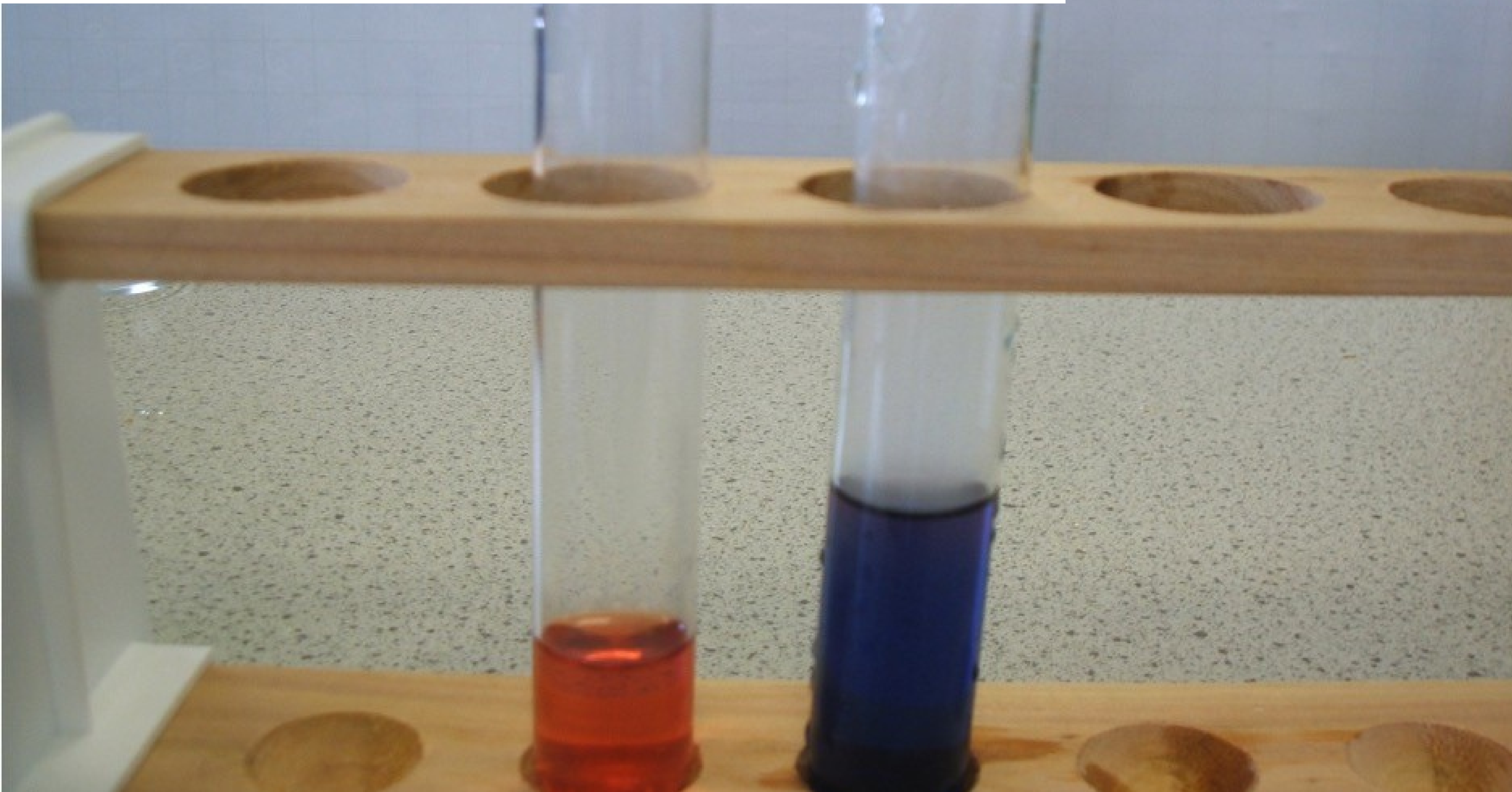
SUBSTITUTION by larger ligands

Cl^- bigger than O of H_2O – only four Cl^-'s fit around M^{n+}



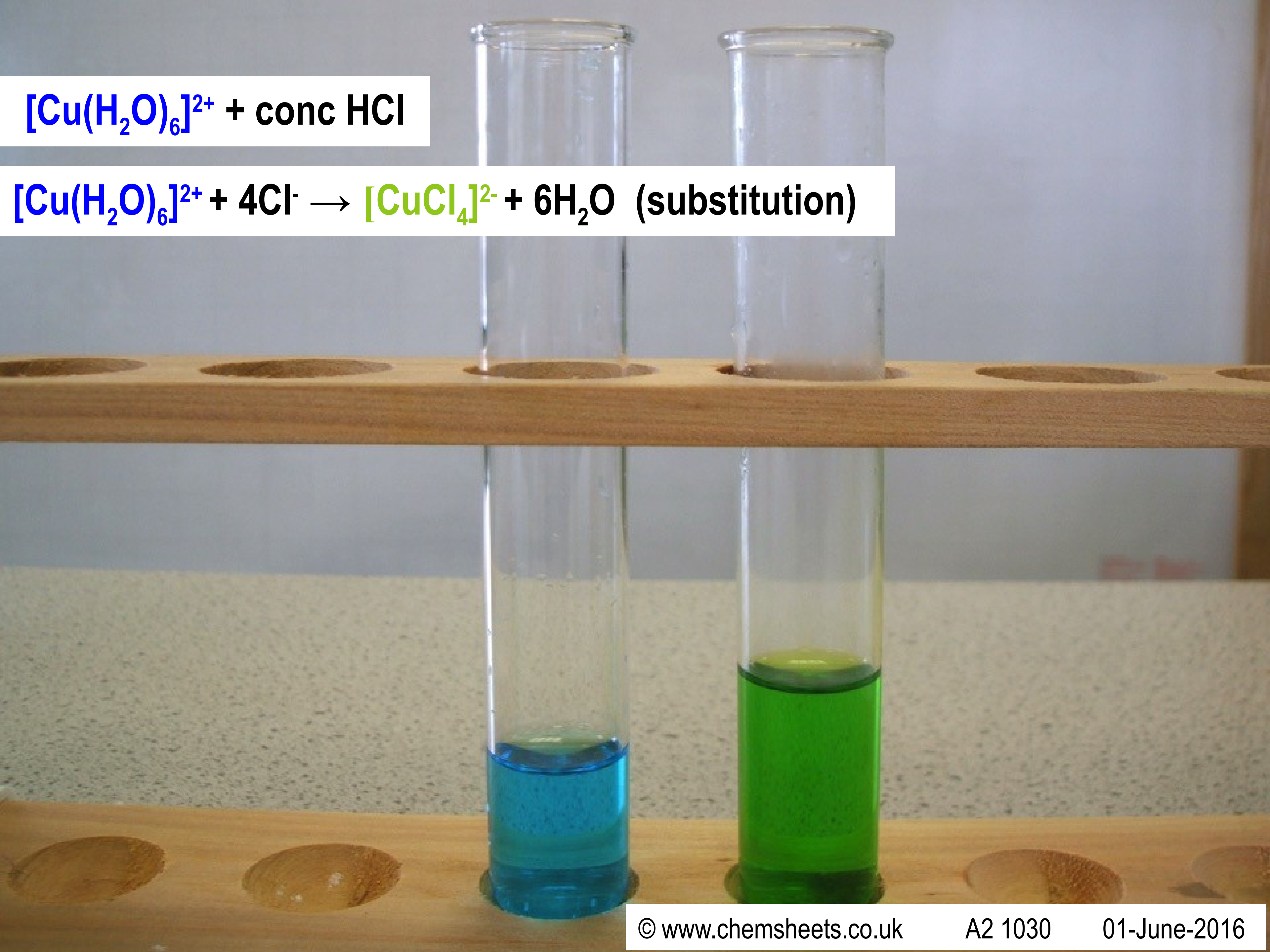
$[Co(H_2O)_6]^{2+}$ + conc HCl

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



$[Cu(H_2O)_6]^{2+}$ + conc HCl

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

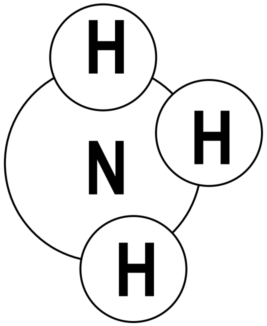


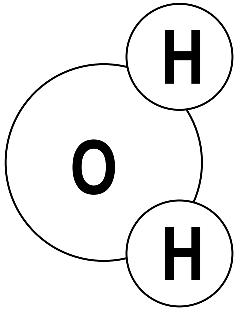
LIGAND SUBSTITUTION

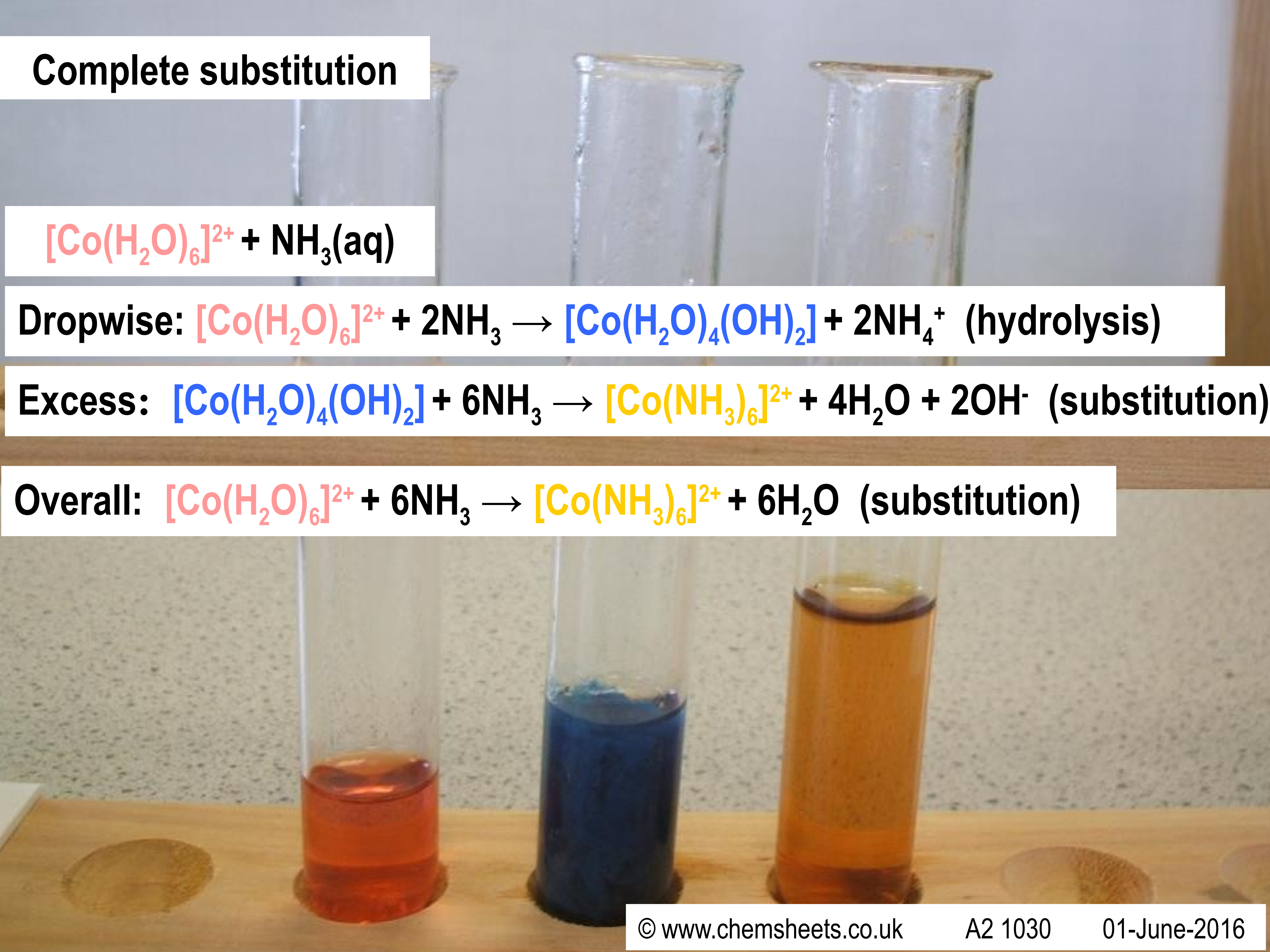
Reaction with $NH_3(aq)$

SUBSTITUTION by similar sized ligands

N of NH_3 similar size to O of H_2O







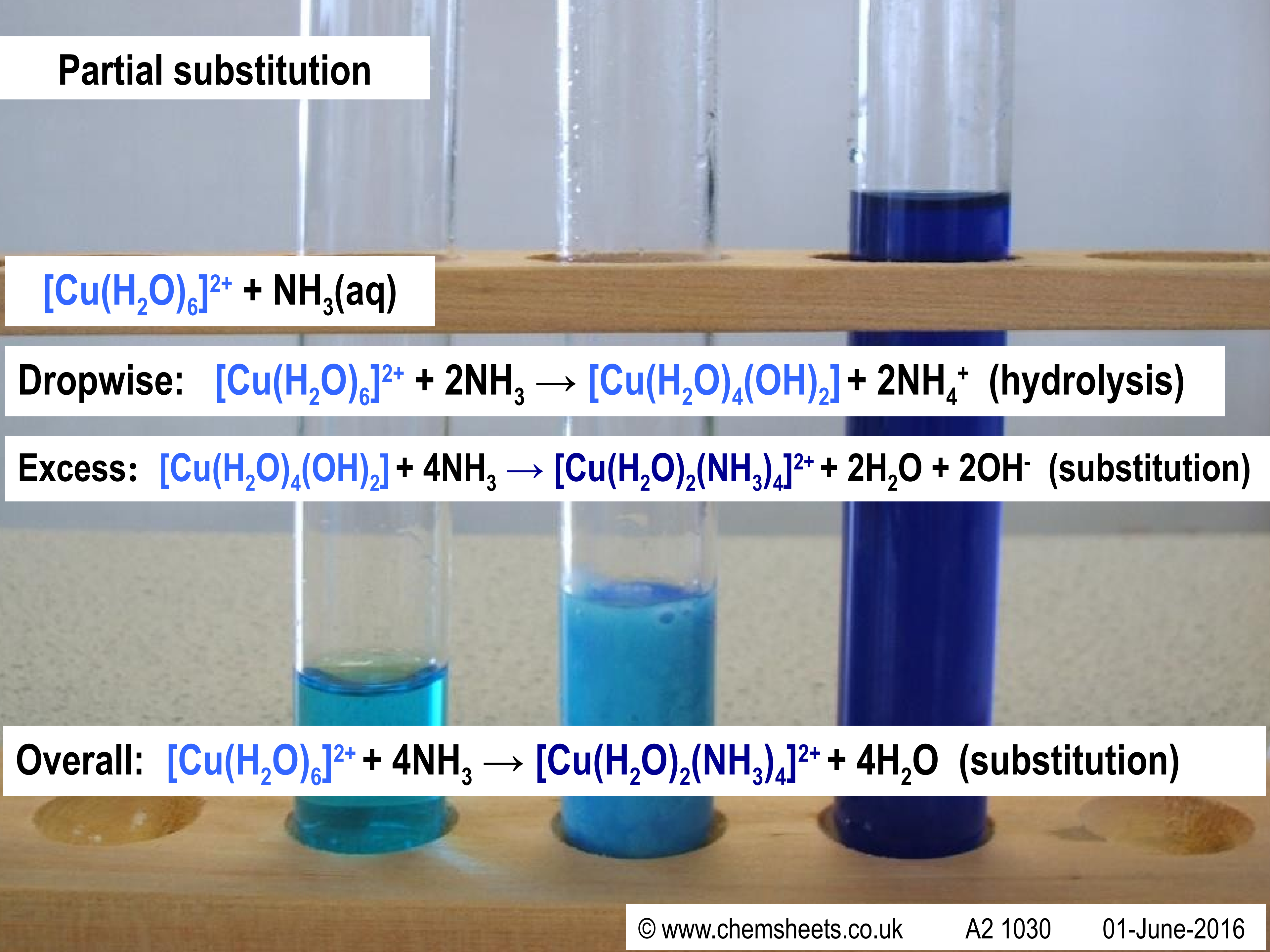
Complete substitution

$[Co(H_2O)_6]^{2+}$ + NH_3(aq)

Dropwise: $[Co(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Co(H_2O)_4(OH)_2] + 2NH_4^+$ (hydrolysis)

Excess: $[Co(H_2O)_4(OH)_2] + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 4H_2O + 2OH^-$ (substitution)

Overall: $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ (substitution)



Partial substitution

$[Cu(H_2O)_6]^{2+}$ + $NH_3(aq)$

Dropwise: $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$ (hydrolysis)

Excess: $[Cu(H_2O)_4(OH)_2] + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O + 2OH^-$ (substitution)

Overall: $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$ (substitution)

LIGAND SUBSTITUTION

Chelate Effect

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CHELATE EFFECT

$$[Cr(H_2O)_6]^{3+} + 3C_2O_4^{2-} \rightarrow [Cr(C_2O_4)_3]^{3-} + 6\ H_2O$$

4 particles → 7 particles

$$[Cr(H_2O)_6]^{3+} + EDTA^{4-} \rightarrow [Cr(EDTA)]^{-} + 6\ H_2O$$

2 particles → 7 particles

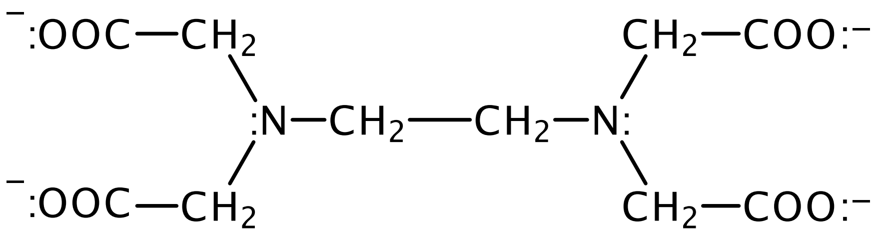
- ΔH negligible (similar number and type of bonds broken/formed)
- ΔS +ve (big increase in entropy).
- $\therefore$ reaction has large –ve ΔG $\therefore$ feasible

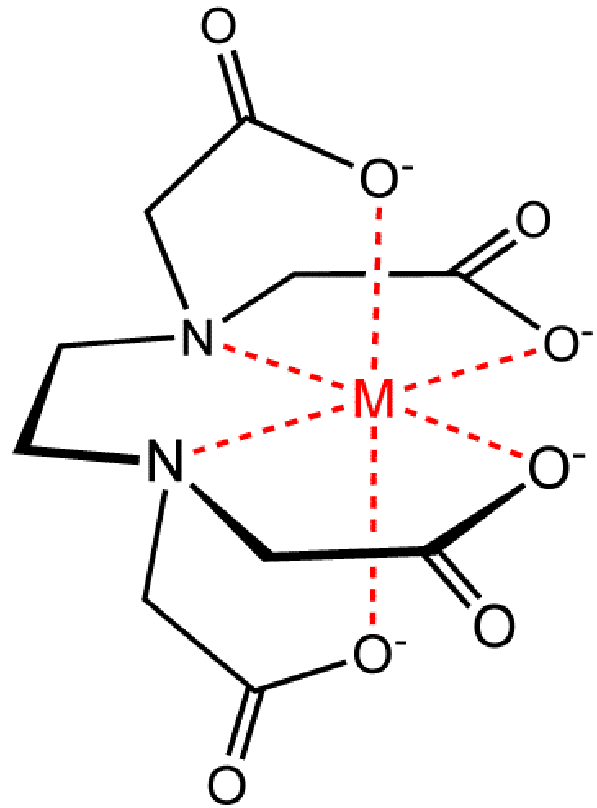
CHELATE EFFECT

- When replace ligands with those that form more co-ordinate bonds reaction is feasible (driven by increase in entropy)
- Reverse reaction is NOT feasible due to large–ve ΔG caused by big decrease in entropy

chela (latin) = claw / pincer

CHELATE EFFECT



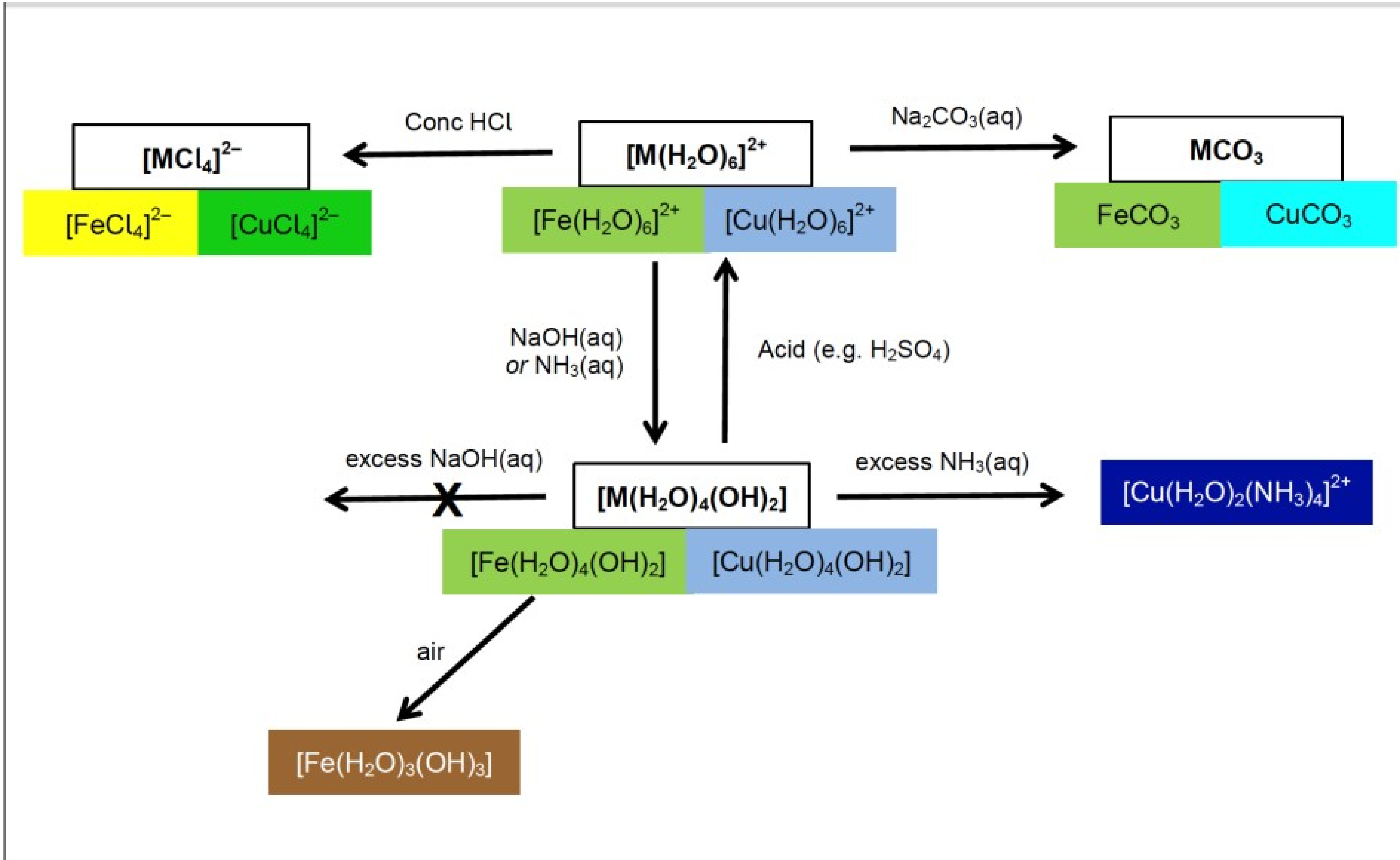


$EDTA^{4-}$ is an example of a chelating agent used to prevent poisoning by metal ions (e.g. Pb^{2+})

SUMMARY

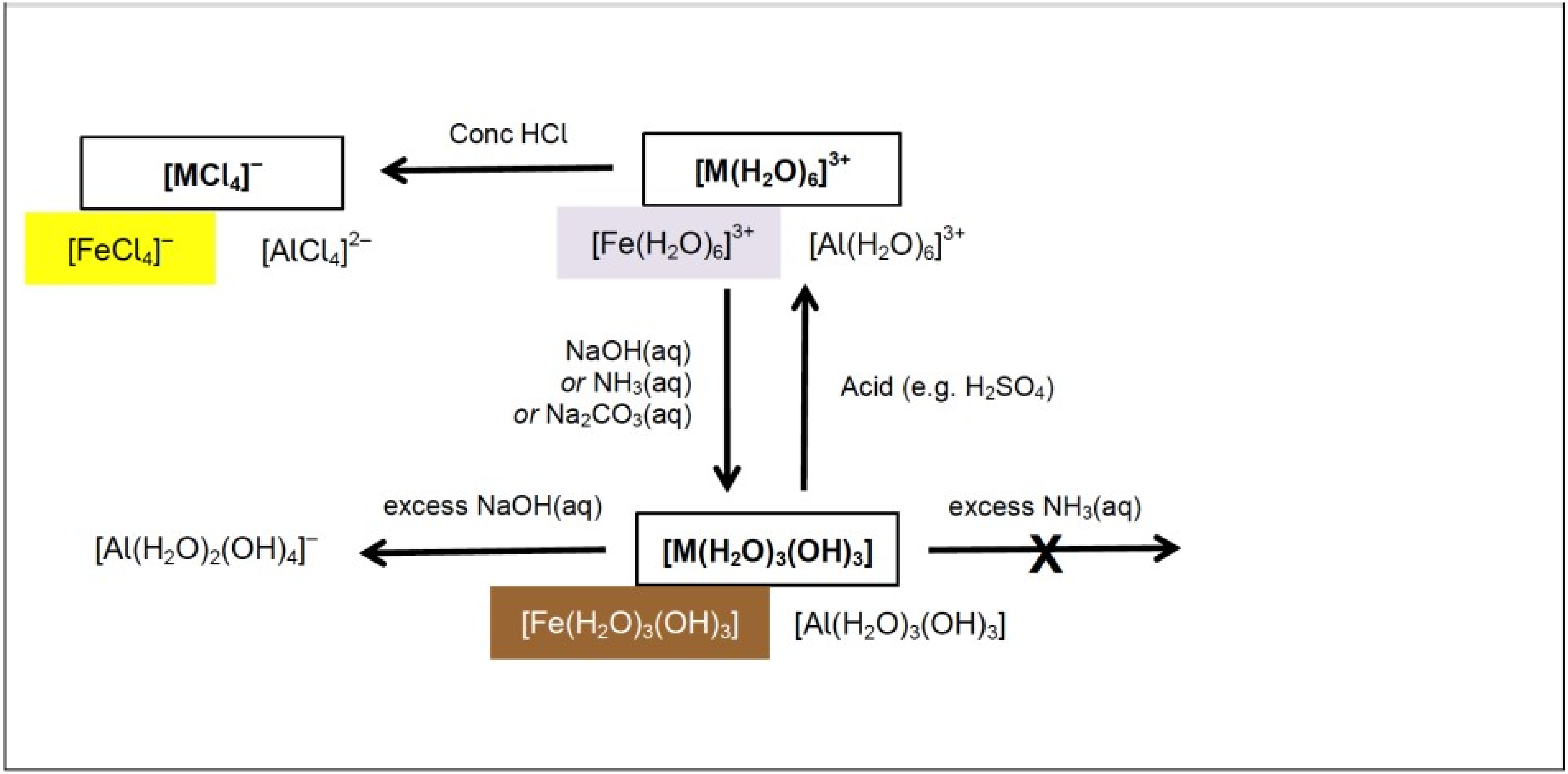
SUMMARY $M^{2+}(aq)$

(aq)



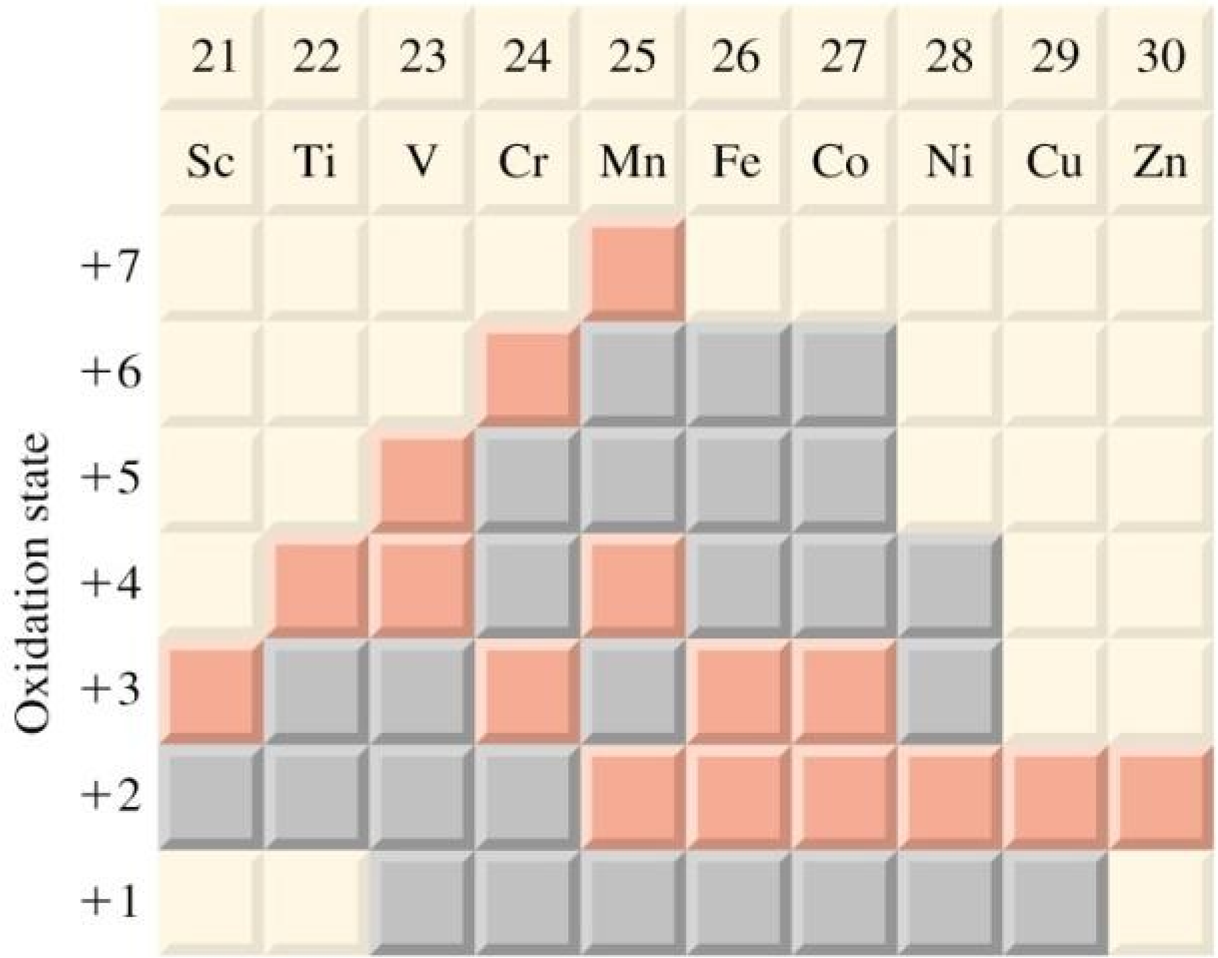
SUMMARY $M^{3+}(aq)$

(aq)



REDOX REACTIONS

VARIABLE OXIDATION STATES

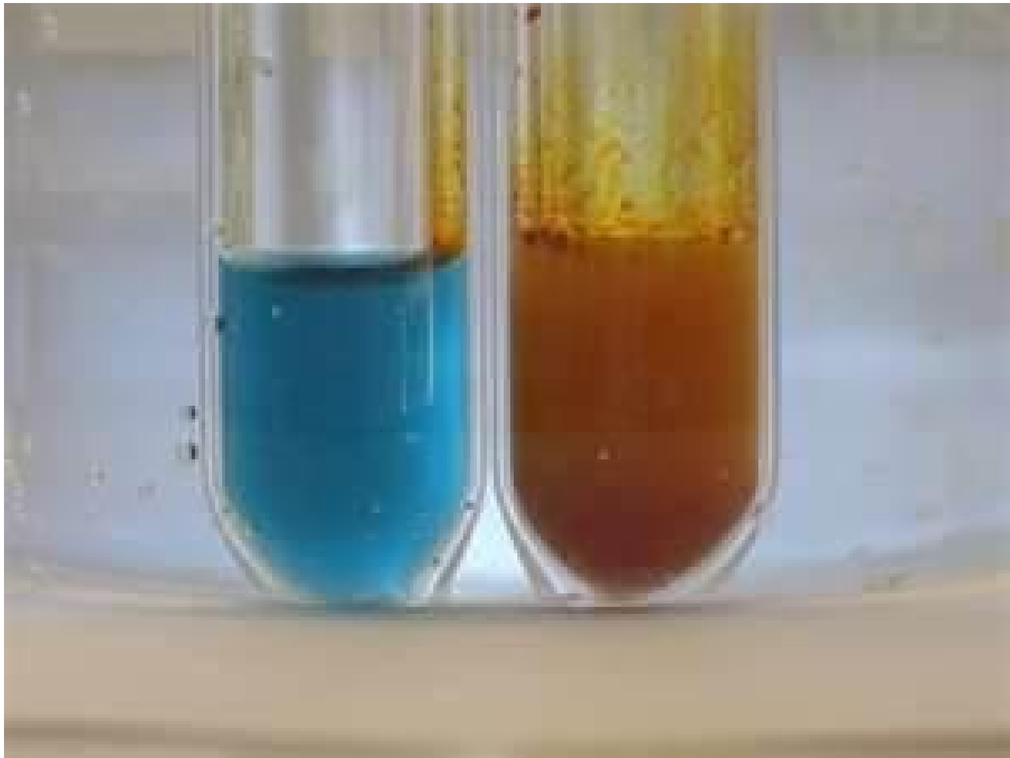


USES OF VARIABLE OXIDATION STATES

- Tollen's reagent, contains $[Ag(NH_3)_2]^+$
- Used to test for aldehydes – gives silver mirror
- Reduced from Ag(+1) to Ag(0)

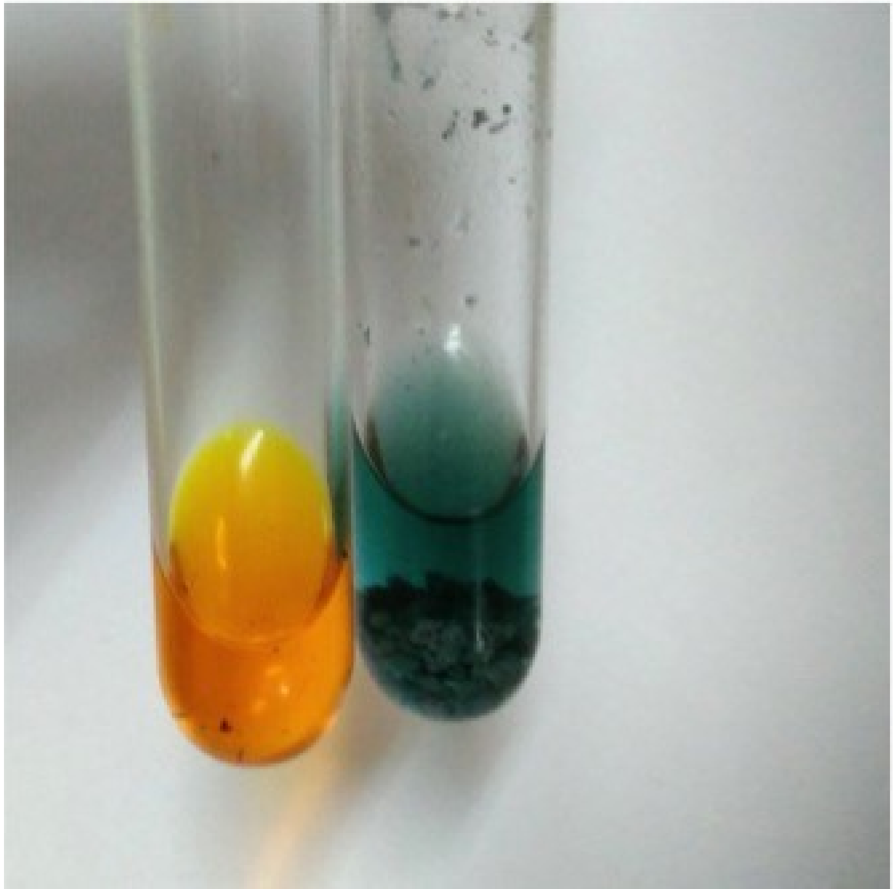
USES OF VARIABLE OXIDATION STATES

- Fehling's solution, contains Cu(+2)
- Used to test for aldehydes – gives brick-red precipitate of Cu_2O
- Reduced from Cu(+2) to Cu(+1)



USES OF VARIABLE OXIDATION STATES

- Acidified potassium dichromate, contains $Cr_2O_7^{2-}$
- Used to test for alcohols (1^y and 2^y) & aldehydes – goes from orange $Cr_2O_7^{2-}$ to green Cr^{3+}
- Reduced from Cr(+6) to Cr(+3)

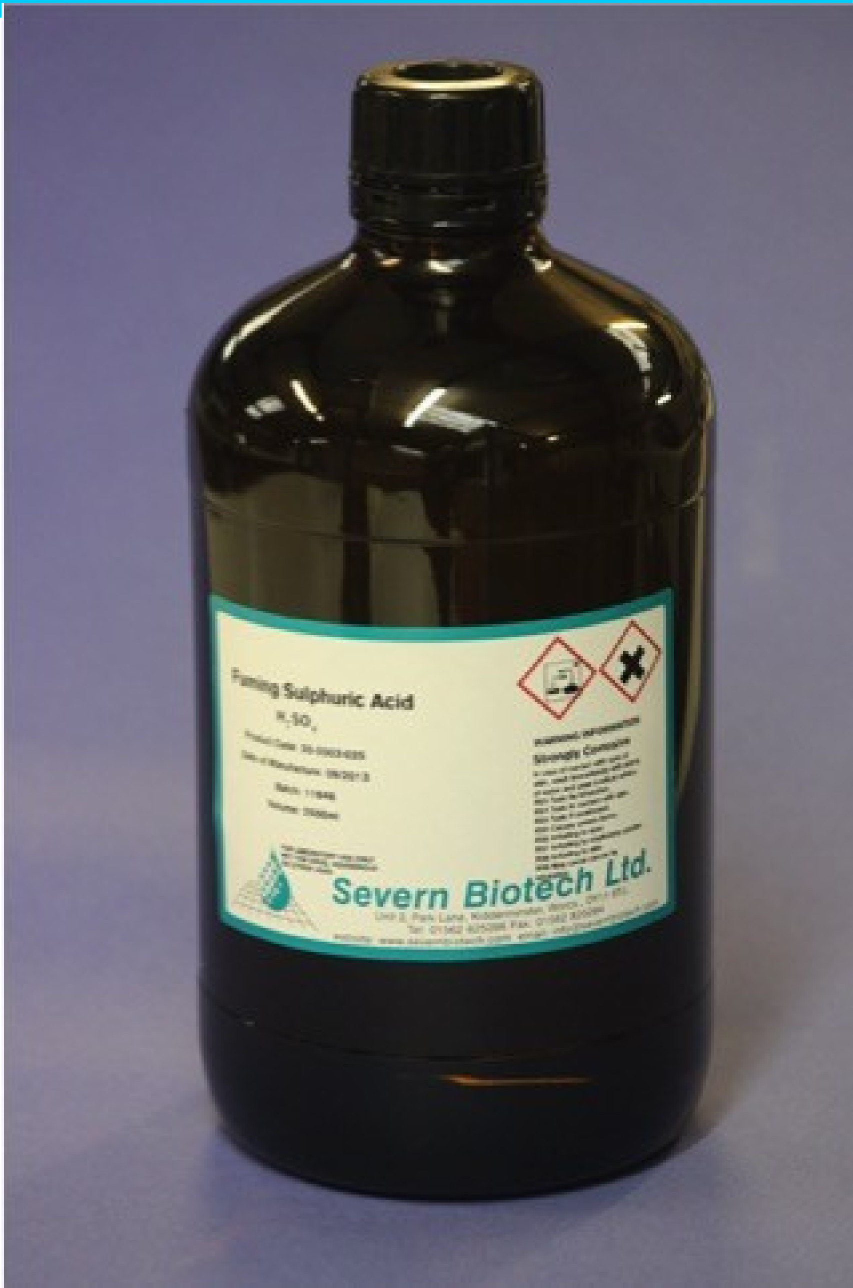


USES OF VARIABLE OXIDATION STATES

- Redox titrations
- e.g. acidified $KMnO_4$ to analyse Fe^{2+}

USES OF VARIABLE OXIDATION STATES

- Catalysts
- e.g. V_2O_5 in Contact process to make SO_3 (to make sulfuric acid)



HOW pH & LIGANDS AFFECT REDOX REACTIONS

oxidising agent
in alkaline conditions

Lower oxidation state ⇄ **Higher oxidation state**

reducing agent
in acidic conditions

effect of pH

e.g. Cr(+6) to/from Cr(3)

$CrO_4^{2-} + 7H_2O + 3e^- \rightleftharpoons [Cr(H_2O)_3(OH)_3] + 5OH^-$ $E° = -0.13$ V (in alkali)

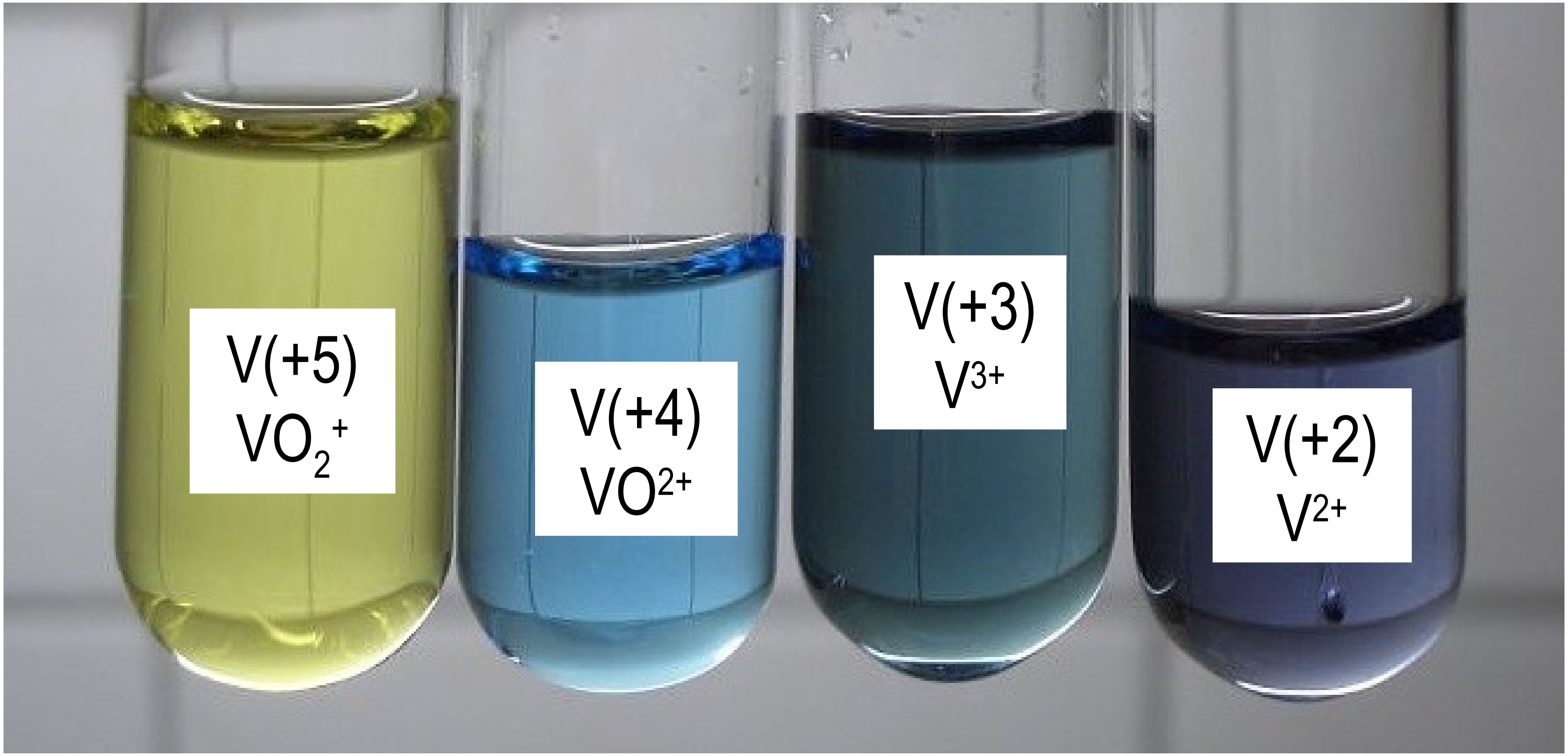
$\frac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e^- \rightleftharpoons [Cr(H_2O)_6]^{3+} + 3\frac{1}{2}H_2O$ $E° = +1.33$ V (in acid)

<u>much</u> easier to reduce $Cr_2O_7^{2-}$ (present in acid) than CrO_4^{2-} (present in alkali)

<u>much</u> easier to oxidise $[Cr(H_2O)_3(OH)_3]$ (present in alkali) than $[Cr(H_2O)_6]^{3+}$ (present in acid)

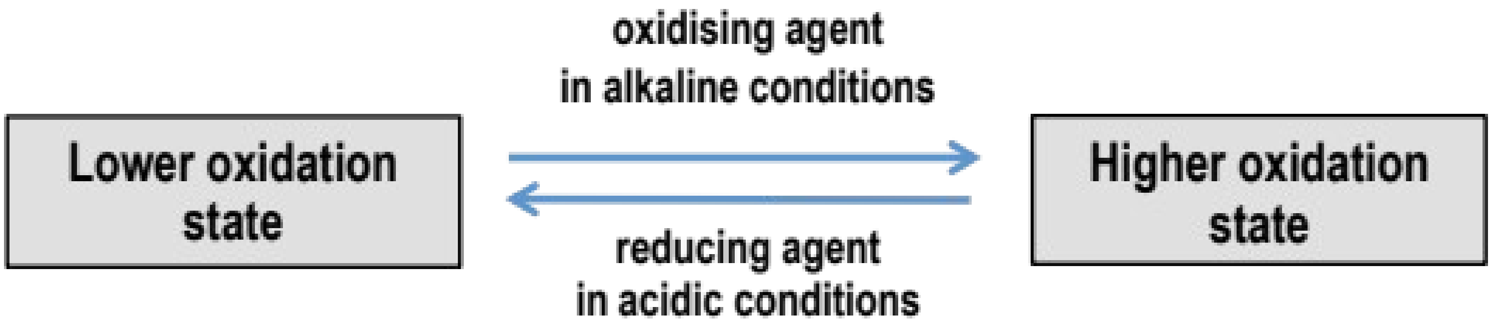
REDUCTION OF V(+5) to V(+2)

- V(+5) is reduced to V(+2) by Zn in acid



From: http://woelen.homescience.net/science/index.html Author W. Oelen

HOW pH & LIGANDS AFFECT REDOX REACTIONS



effect of ligand and pH

e.g. Fe(+3) to/from Fe(+2)

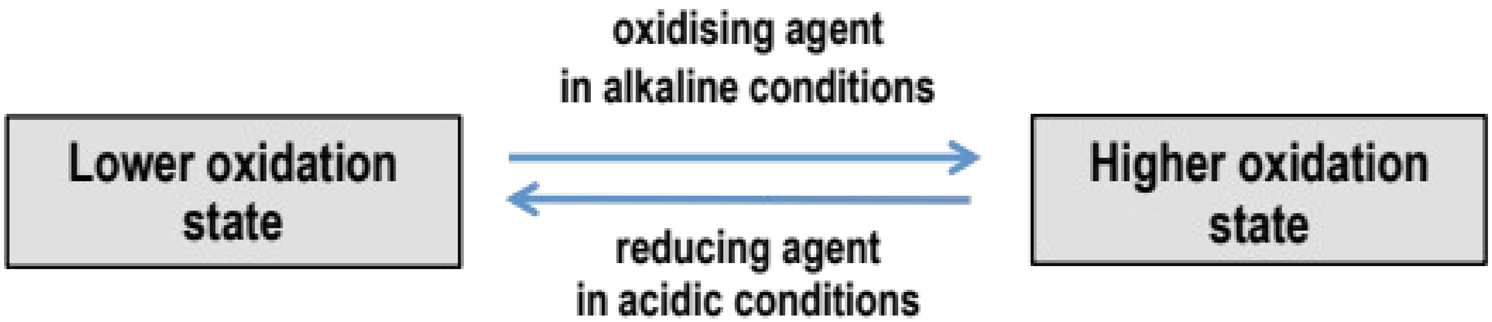
$[Fe(H_2O)_3(OH)_3] + H_2O + e^- \rightleftharpoons [Fe(H_2O)_4(OH)_2] + OH^-$ $E° = –0.56$ V (in alkali)

$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$ $E° = +0.77$ V (in acid)

<u>much</u> easier to reduce $[Fe(H_2O)_6]^{3+}$ (present in acid) than $[Fe(H_2O)_3(OH)_3]$ (present in alkali)

<u>much</u> easier to oxidise $[Fe(H_2O)_4(OH)_2]$ (present in alkali) than $[Fe(H_2O)_6]^{2+}$ (present in acid)

HOW pH & LIGANDS AFFECT REDOX REACTIONS



effect of ligand

e.g. Co(+2) to/from Co(0)

$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$ $E° = -0.43$ V

$[Co(H_2O)_6]^{2+} + 2e^- \rightleftharpoons Co + 6H_2O$ $E° = -0.28$ V

easier to reduce $[Co(H_2O)_6]^{2+}$ than $[Co(NH_3)_6]^{2+}$