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Structure 3.1 HL

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Exceptions to the trend in ionisation energy

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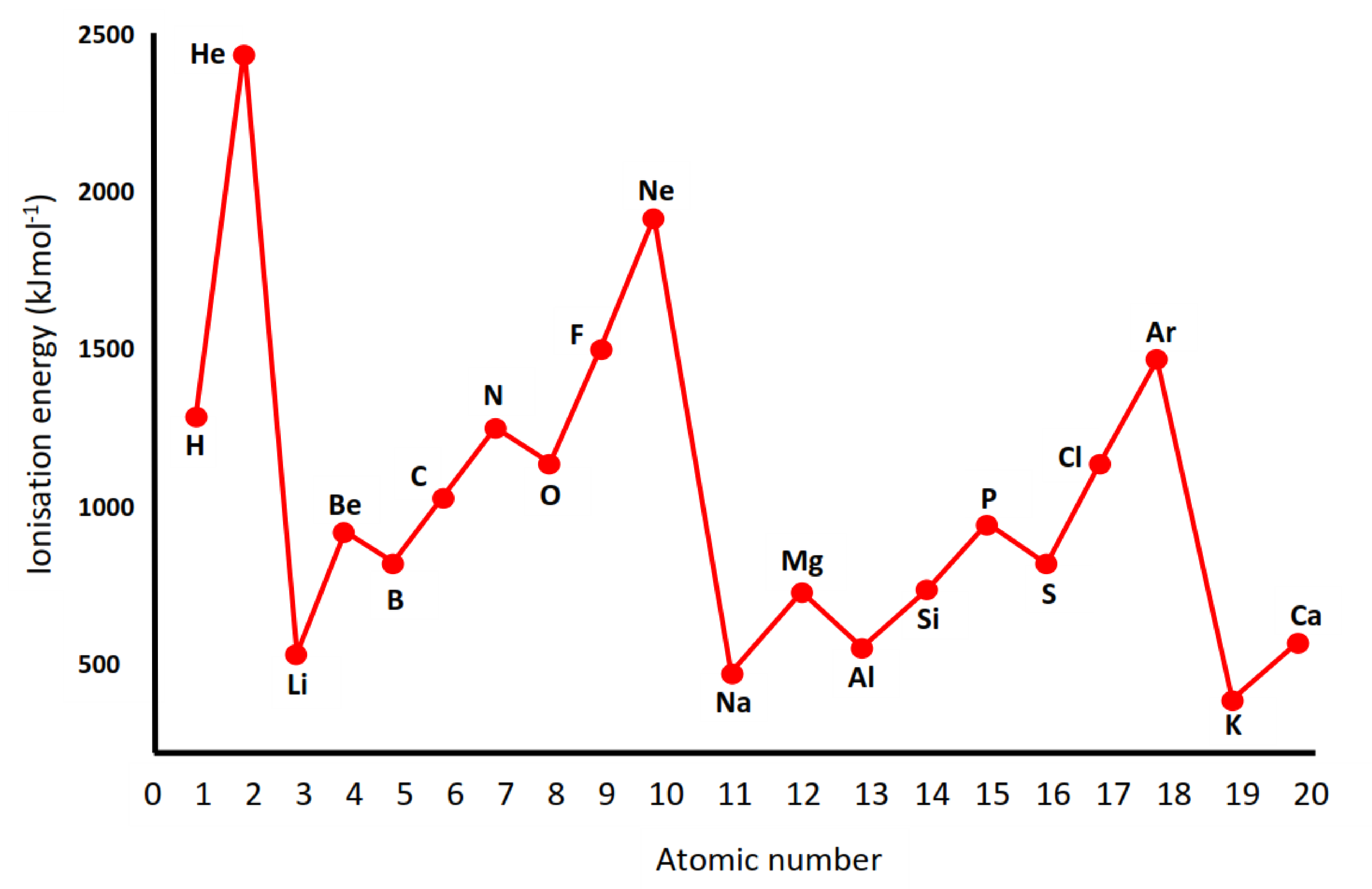
Ionisation energy



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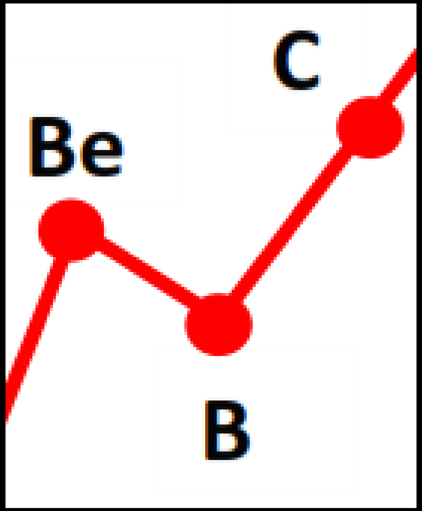
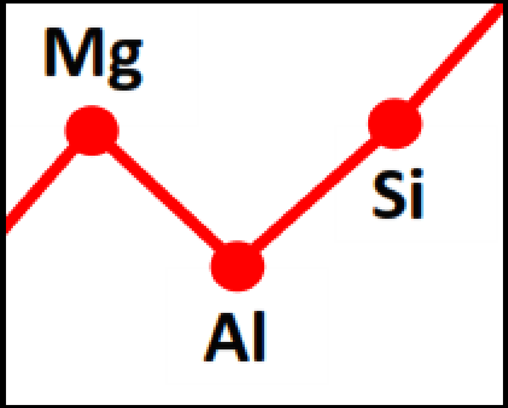
Ionisation energy



Be has the electron configuration $1s^2\,2s^2$

B has the electron configuration $1s^2\,2s^2\,2p^1$

Electrons in p orbitals are slightly higher in energy and further from the nucleus than electrons in s orbitals, therefore they require less energy to remove.



A similar explanation can be applied for the decrease in ionisation energy from Mg to Al, except that the electron configurations are $1s^2\,2s^2\,2p^6\,3s^2$ and $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$

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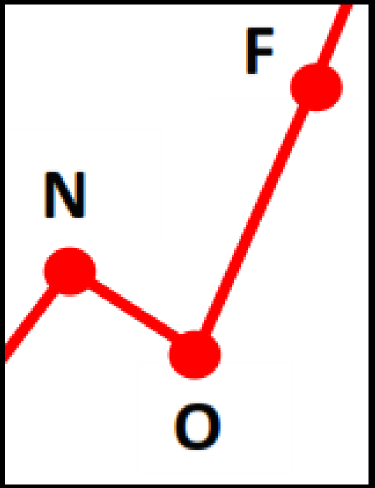
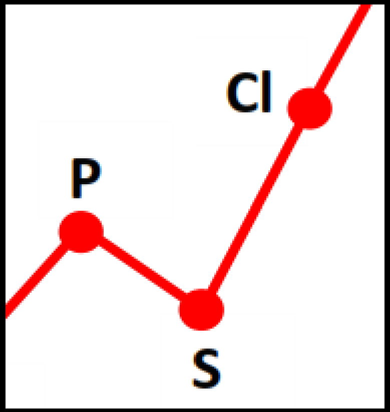
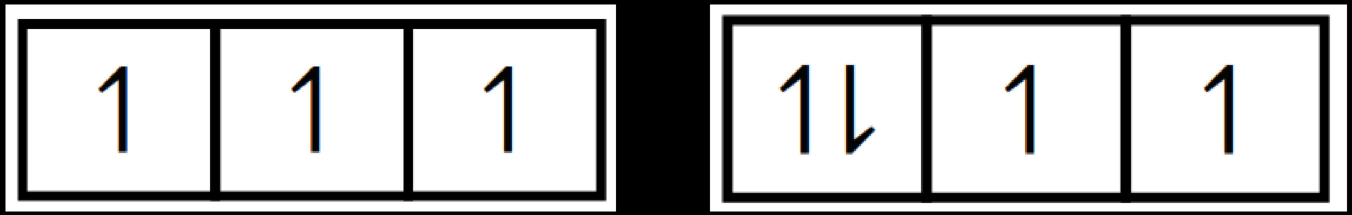
Ionisation energy





N has the electron configuration $1s^2 2s^2 2p^3$

O has the electron configuration $1s^2 2s^2 2p^4$



In oxygen, the electron is removed from a doubly occupied p orbital.

An electron in a doubly occupied orbital is repelled by the other electron and requires less energy to remove than an electron in a half-filled orbital.

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Transition elements

Transition elements

An element whose atom has an incomplete d sub-level, or can form positive ions with an incomplete d sub-level.

First row d-block elements

21	22	23	24	25	26	27	28	29	30
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
44.96	47.87	50.94	52.00	54.94	55.85	58.93	58.69	63.55	65.38

Zinc is not considered to be a transition element as it does not have an incomplete d sub-level as an atom or an ion.

Transition elements

First row d-block element	Electron configuration of atom	Ion formed	Electron configuration of ion
Sc	[Ar] $4s^2\ 3d^1$	Sc^{3+}	[Ne] $3s^2\ 3p^6$
Ti	[Ar] $4s^2\ 3d^2$	Ti^{2+}	[Ar] $3d^2$
V	[Ar] $4s^2\ 3d^3$	V^{2+}	[Ar] $3d^3$
Cr	[Ar] $4s^1\ 3d^5$	Cr^{3+}	[Ar] $3d^3$
Mn	[Ar] $4s^2\ 3d^5$	Mn^{4+}	[Ar] $3d^3$
Fe	[Ar] $4s^2\ 3d^6$	Fe^{3+}	[Ar] $3d^5$
Co	[Ar] $4s^2\ 3d^7$	Co^{2+}	[Ar] $3d^7$
Ni	[Ar] $4s^2\ 3d^8$	Ni^{2+}	[Ar] $3d^8$
Cu	[Ar] $4s^1\ 3d^{10}$	Cu^{2+}	[Ar] $3d^9$
Zn	[Ar] $4s^2\ 3d^{10}$	Zn^{2+}	[Ar] $3d^{10}$

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Transition elements

Physical properties	Chemical properties
High electrical and thermal conductivity	Have more than one oxidation state in compounds
High melting points	Form complex ions
Malleable and ductile	Form coloured compounds in solution
High tensile strength	Can act as catalysts
Show magnetic properties	

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Magnetism in transition elements


Neodymium magnet
MnO_2
$Ni(NO_3)_2$
$CuSO_4$
$Zn(NO_3)_2$

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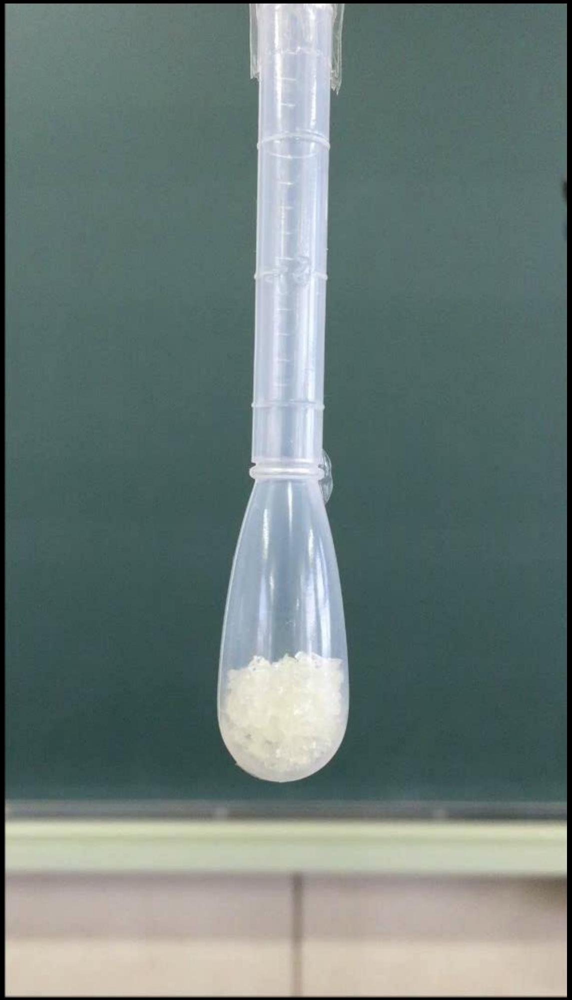
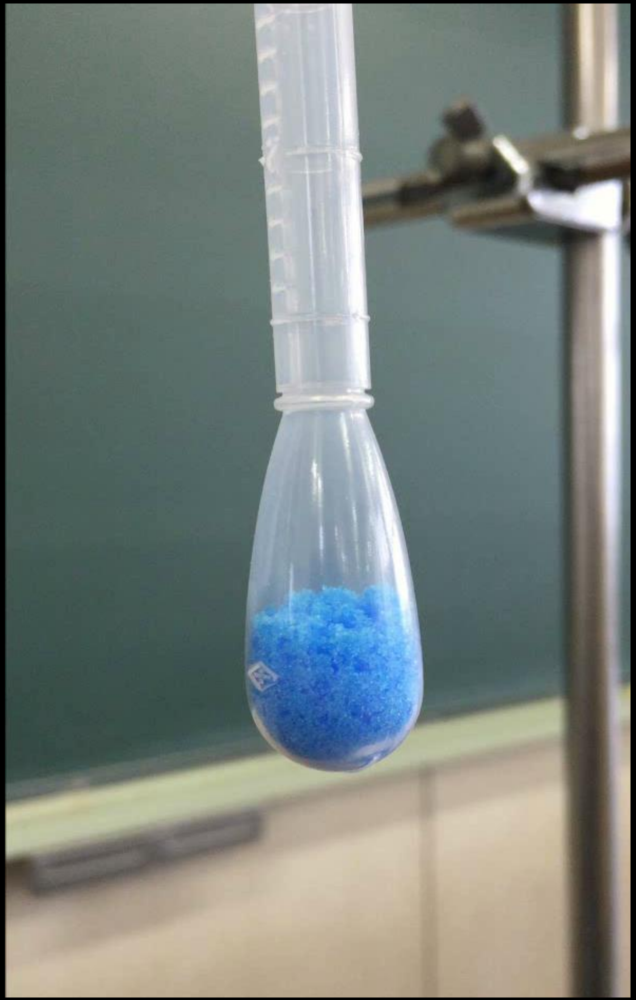
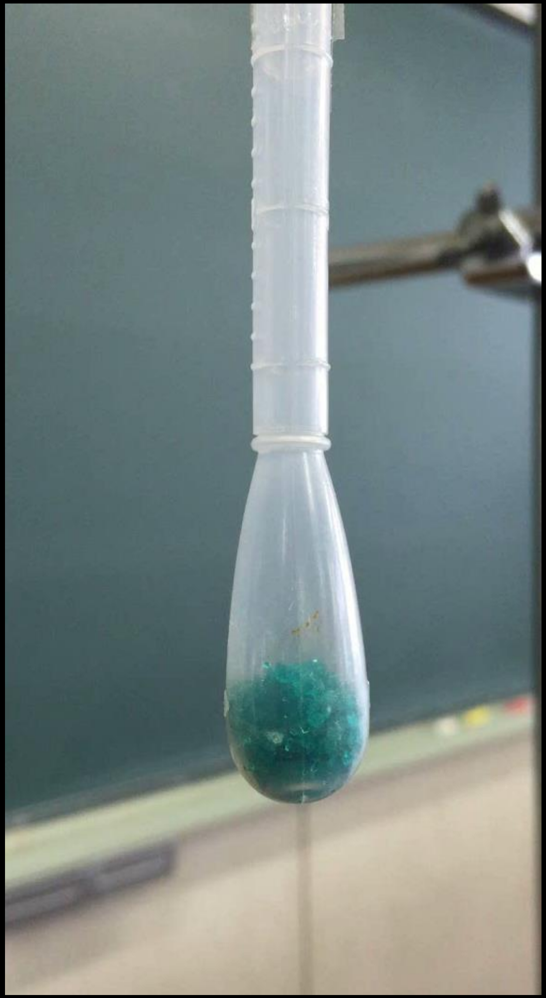
Magnetism of the transition elements



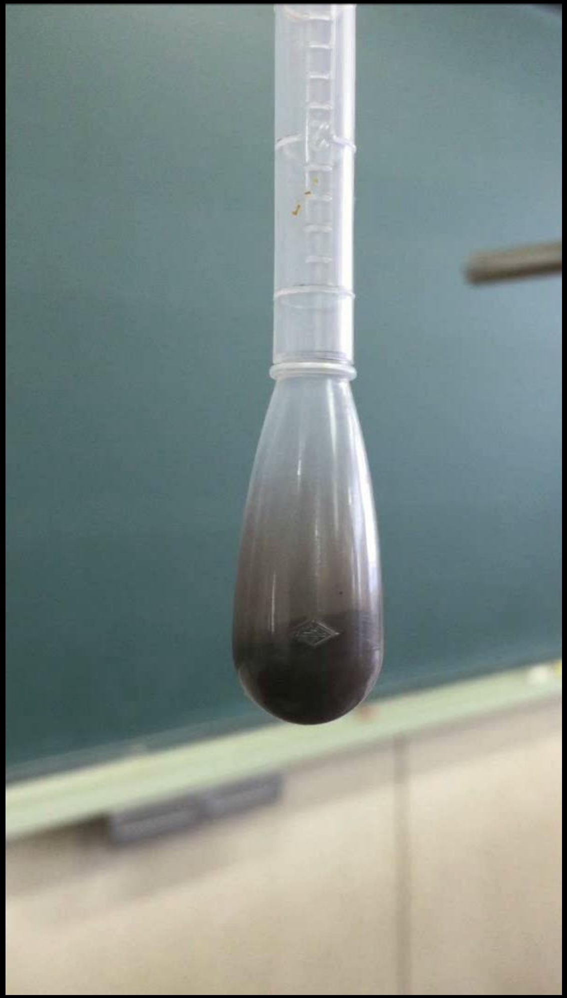
$Zn(NO_3)_2$



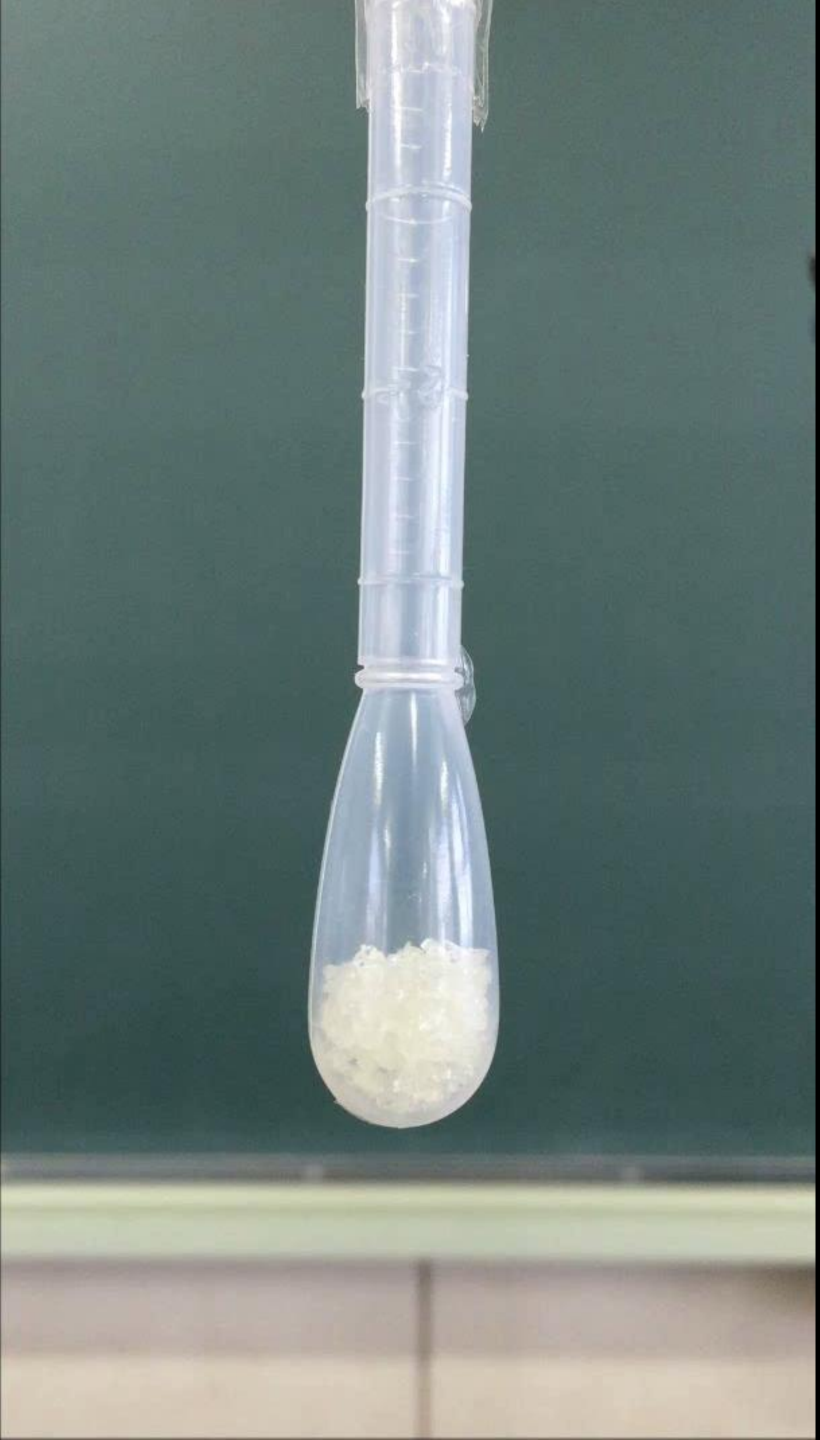
$CuSO_4$



$Ni(NO_3)_2$

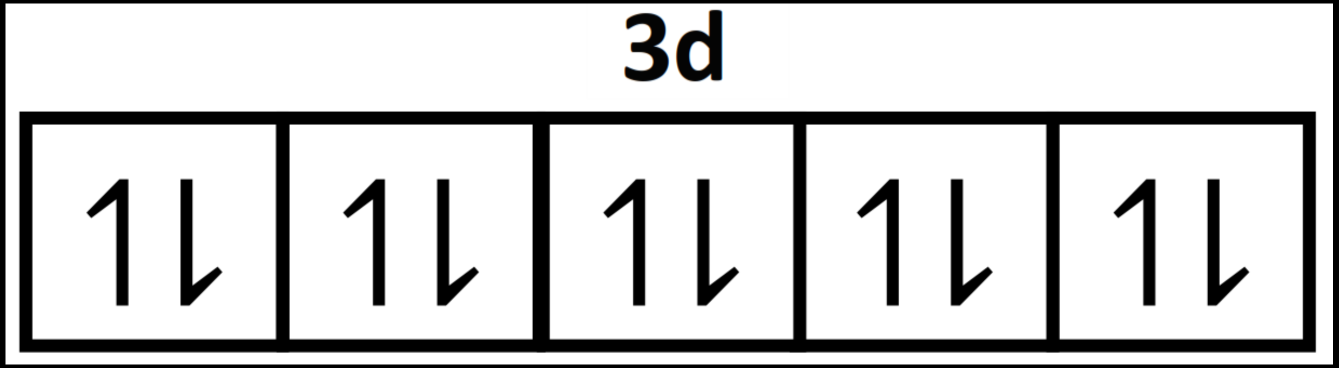


MnO_2

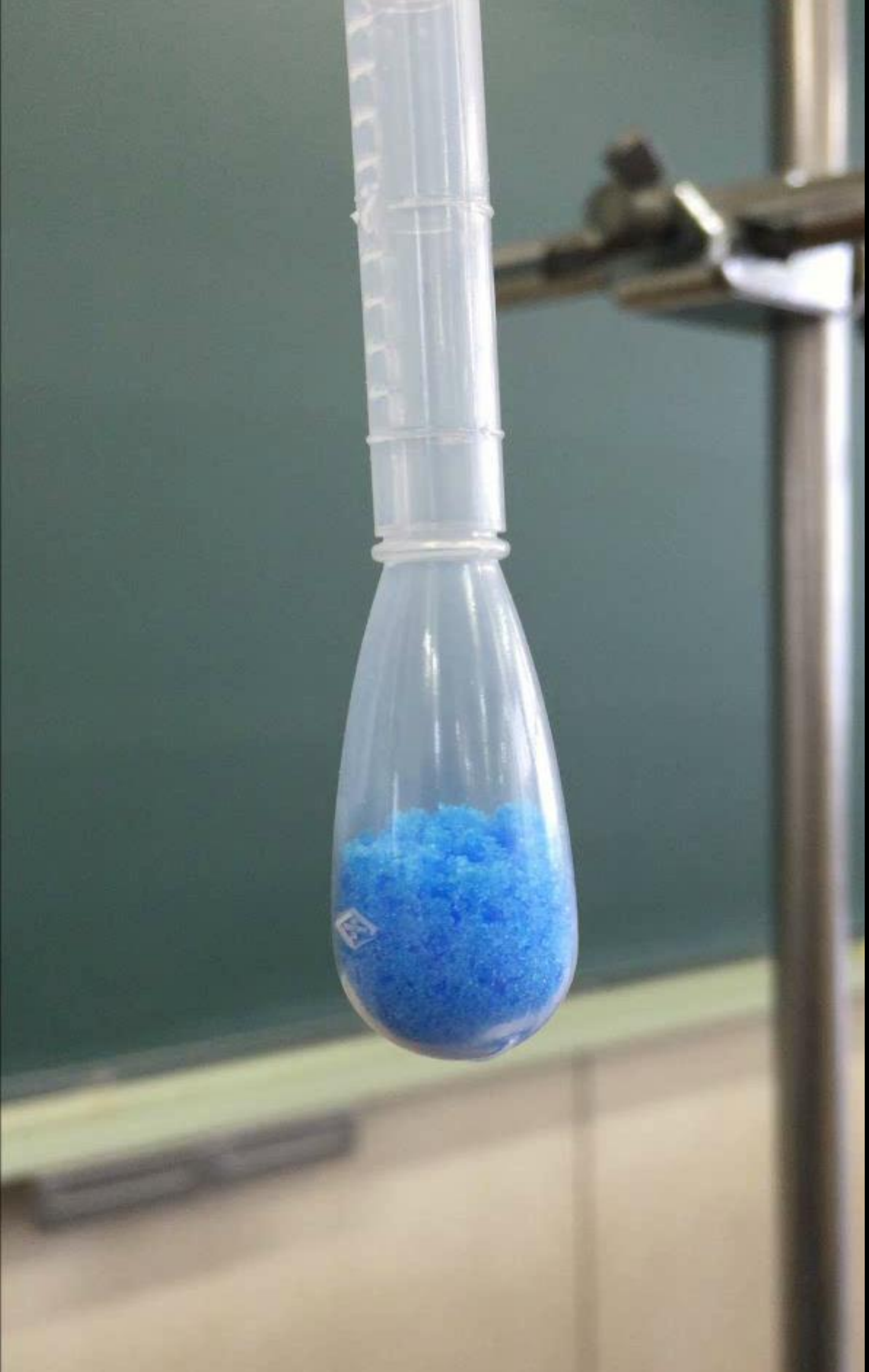


Zn^{2+} ion

Electron configuration of Zn^{2+} $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$



No unpaired 3d electrons



Cu^{2+} ion

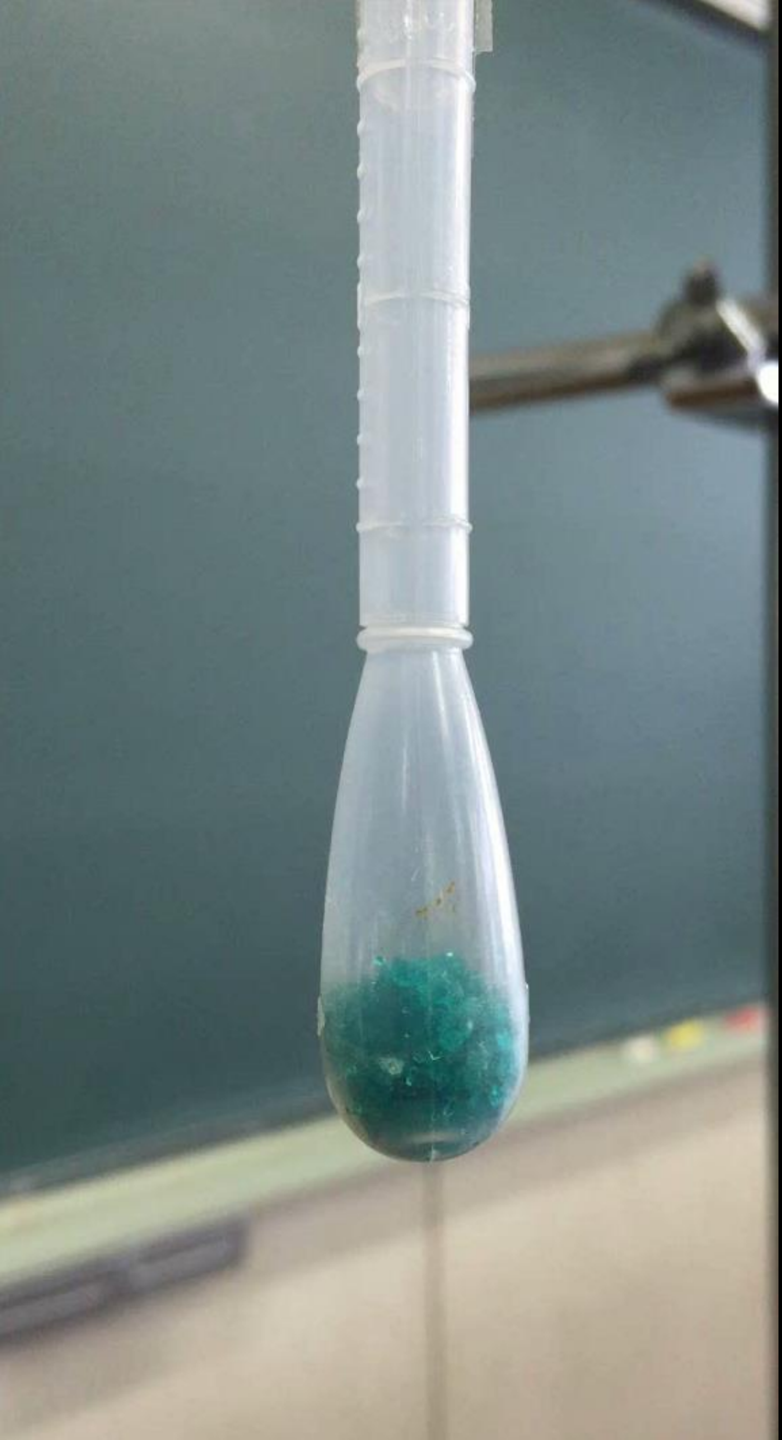
Electron configuration of Cu^{2+}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

3d

↑↓	↑↓	↑↓	↑↓	↑

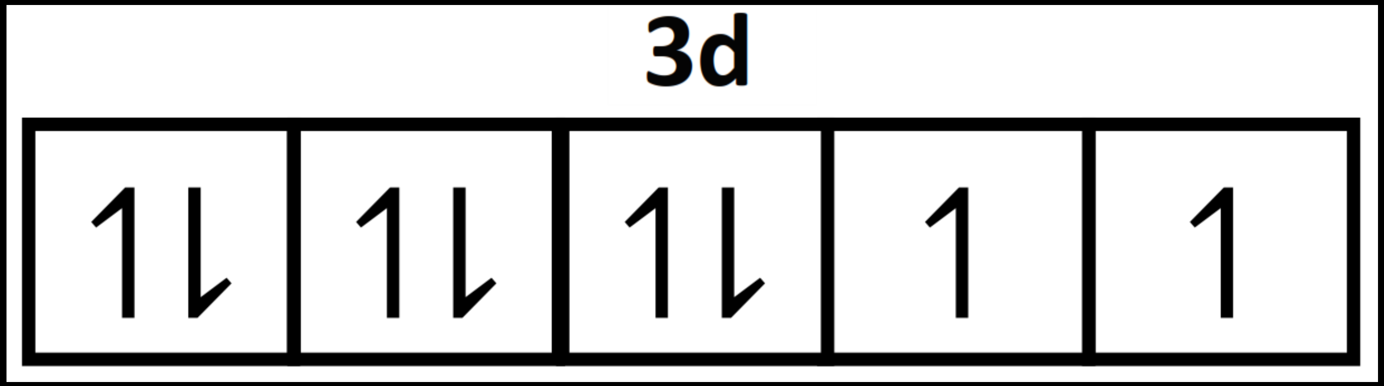
One unpaired 3d electron



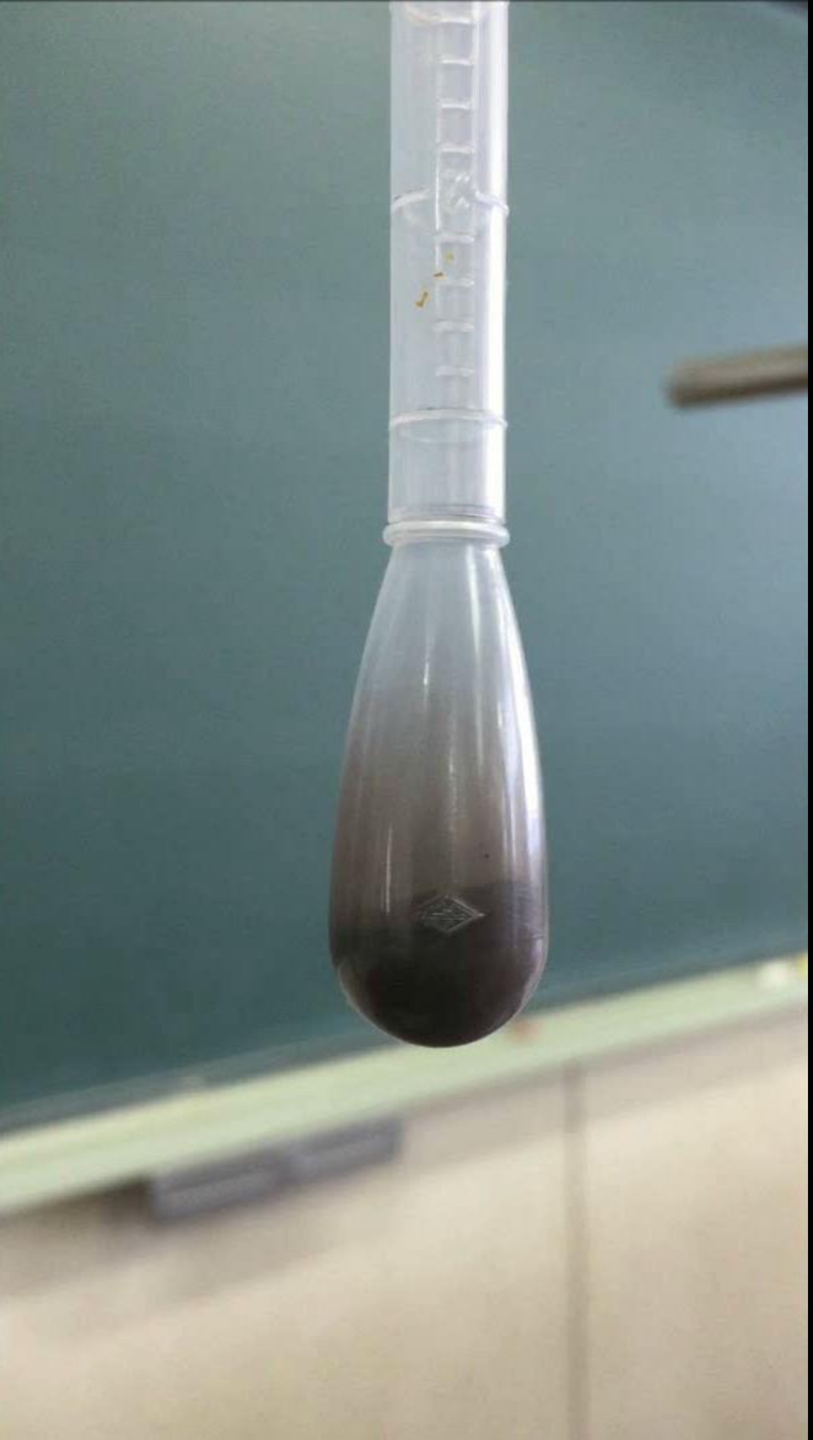
Ni^{2+} ion

Electron configuration of Ni^{2+}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$



Two unpaired 3d electrons



Mn^{4+} ion

Electron configuration of Mn^{4+}

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

3d				
1	1	1		

Three unpaired 3d electrons

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Summary

Ion	Effect in external magnetic field	Unpaired 3d electrons
Zn^{2+}	No effect*	3d: ↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Cu^{2+}	Weak effect	3d: ↑↓ ↑↓ ↑↓ ↑↓ ↑
Ni^{2+}	Stronger effect	3d: ↑↓ ↑↓ ↑↓ ↑ ↑
Mn^{4+}	Strongest effect	3d: ↑ ↑ ↑ [ ] [ ]

Increasing effect in magnetic field as number of unpaired 3d electrons increases.

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Complex ions

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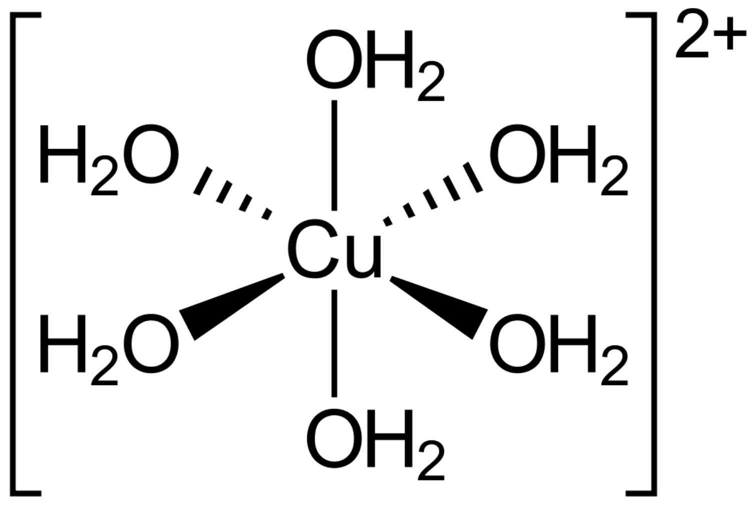
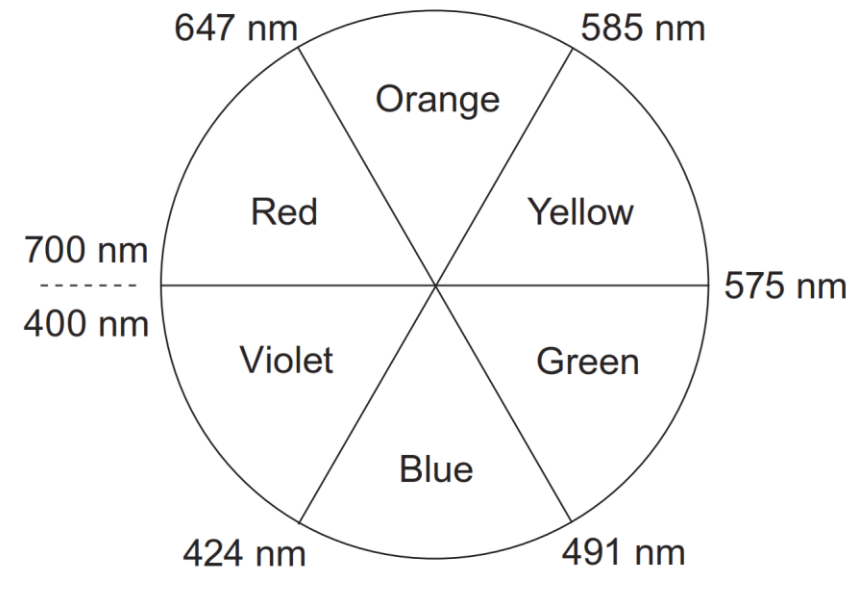
Complex ions

Complex ions are formed when the ions of a transition element bond with species called ligands.

$$Cu^{2+}_{(aq)} + 6H_2O_{(l)} \rightleftharpoons [Cu(H_2O)_6]^{2+}_{(aq)}$$

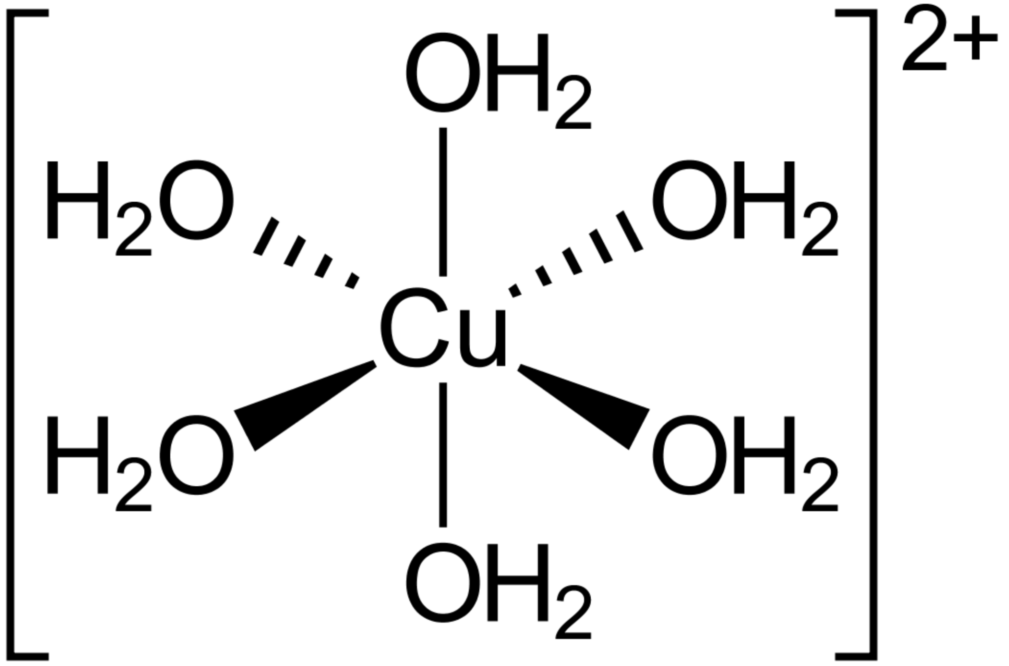


$[Cu(H_2O)_6]^{2+}$



Complex ions

Complex ions consist of a central metal ion bonded to ligands by coordinate covalent bonds.

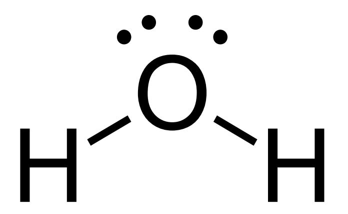


$[Cu(H_2O)_6]^{2+}$

Central metal ion: Cu^{2+}

Ligands: H_2O

Ligands supply the bonding electrons forming a coordinate covalent bond with the central metal ion



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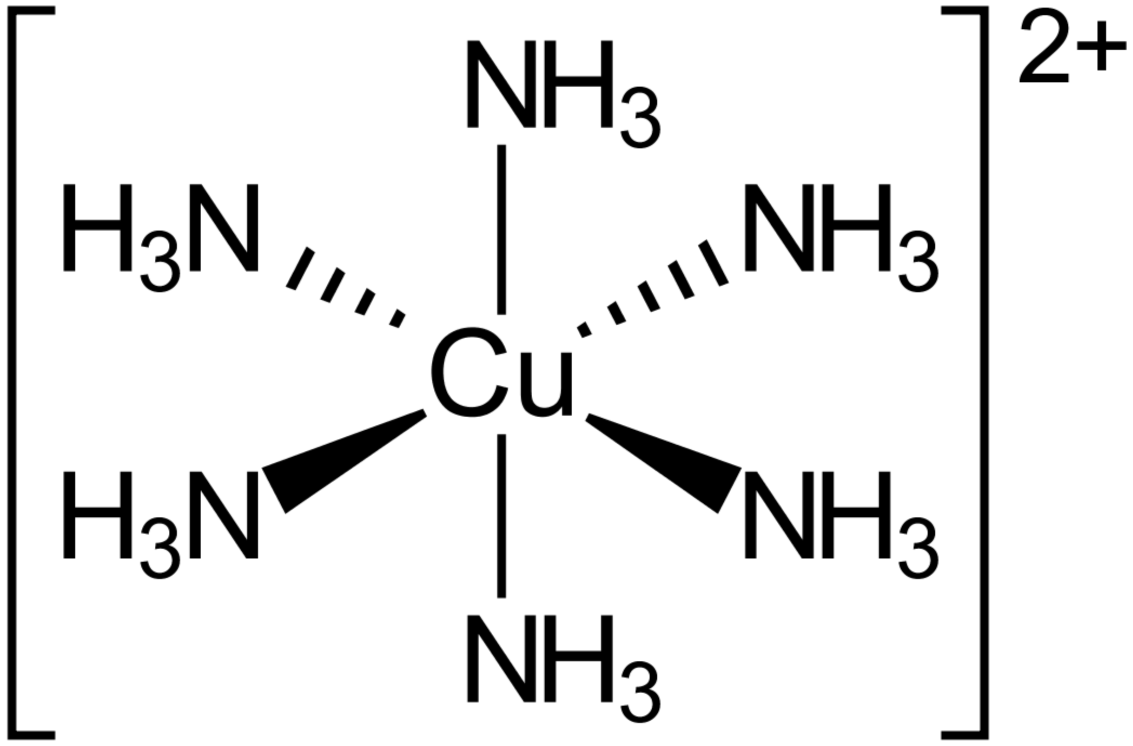
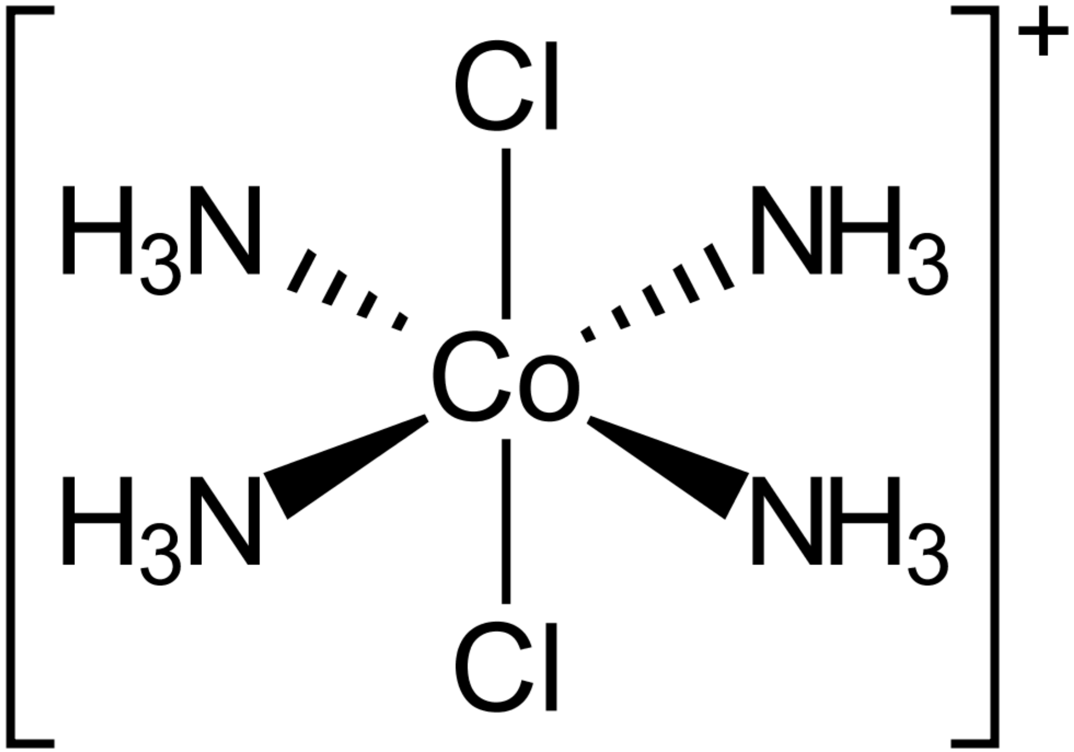
Complex ions



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



$[Co(NH_3)_4Cl_2]^{+}$

Central metal ion: Cu^{2+}

Ligands: NH_3

Central metal ion: Co^{3+}

Ligands: NH_3 /Cl^-

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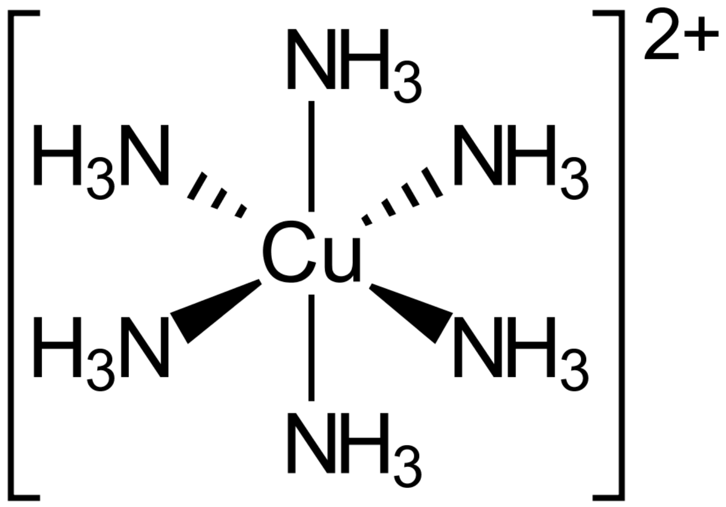
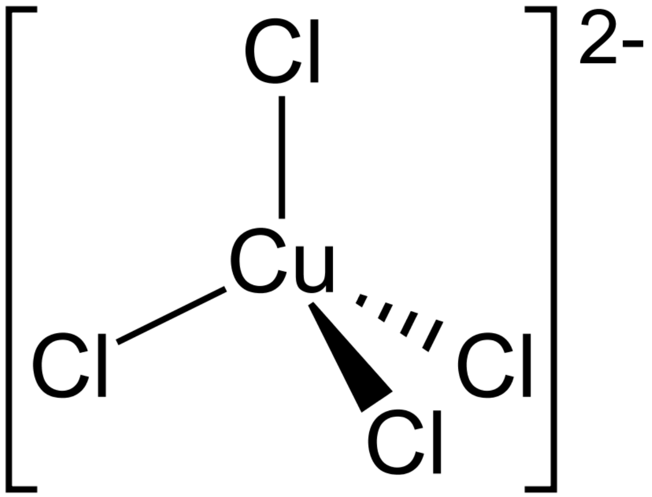
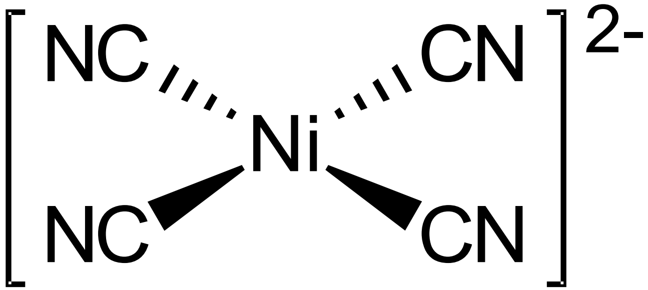
Complex ions



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



$[CuCl_4]^{2-}$



$[Ni(CN)_4]^{2-}$

$[CuCl_2]^{-}$

Complex ion	Coordination number	Geometry
$[Cu(NH_3)_6]^{2+}$	6	octahedral
$[CuCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$	4	tetrahedral/square planar
$[CuCl_2]^{-}$	2	linear

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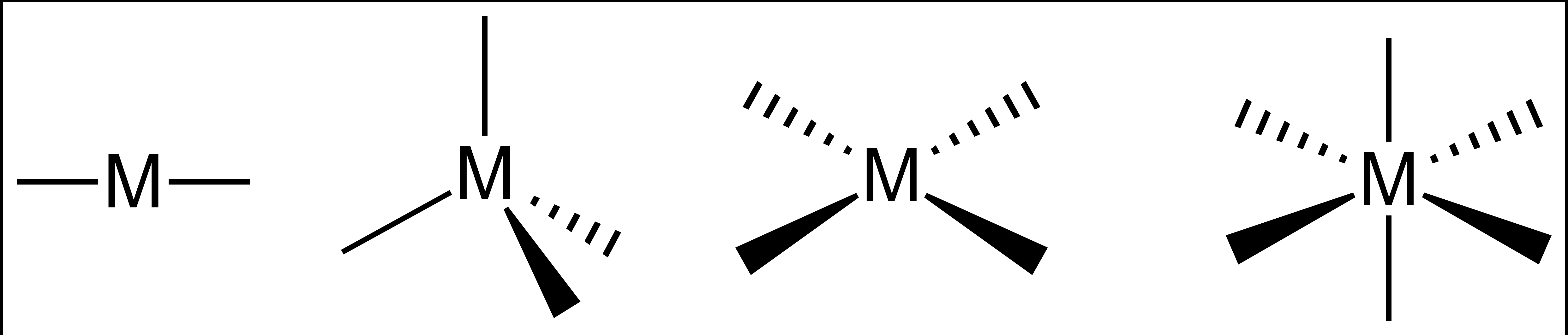
Complex ions



Complex ion	Coordination number	Geometry
$[Cu(NH_3)_6]^{2+}$	6	octahedral
$[CuCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$	4	tetrahedral/square planar
$[CuCl_2]^{-}$	2	linear

Coordination compounds

Coordination compounds consist of:

- a complex ion - central metal ion with ligands bonded by coordinate covalent bonds
- counter ions - ions that balance out the charge on the complex ion

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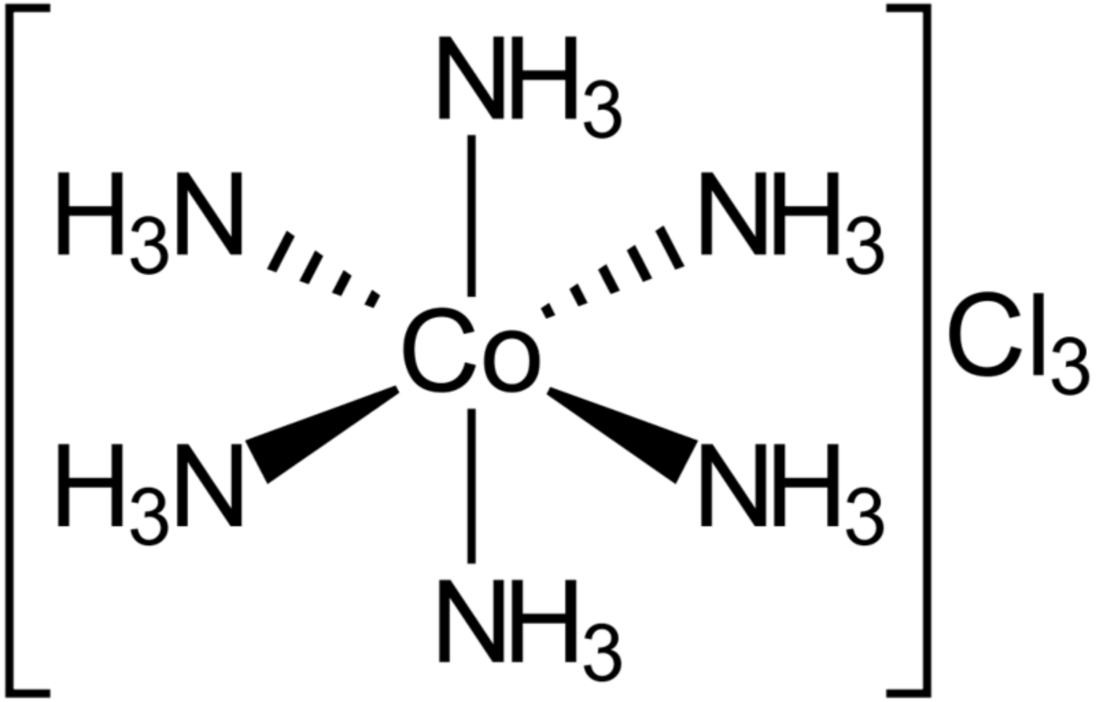
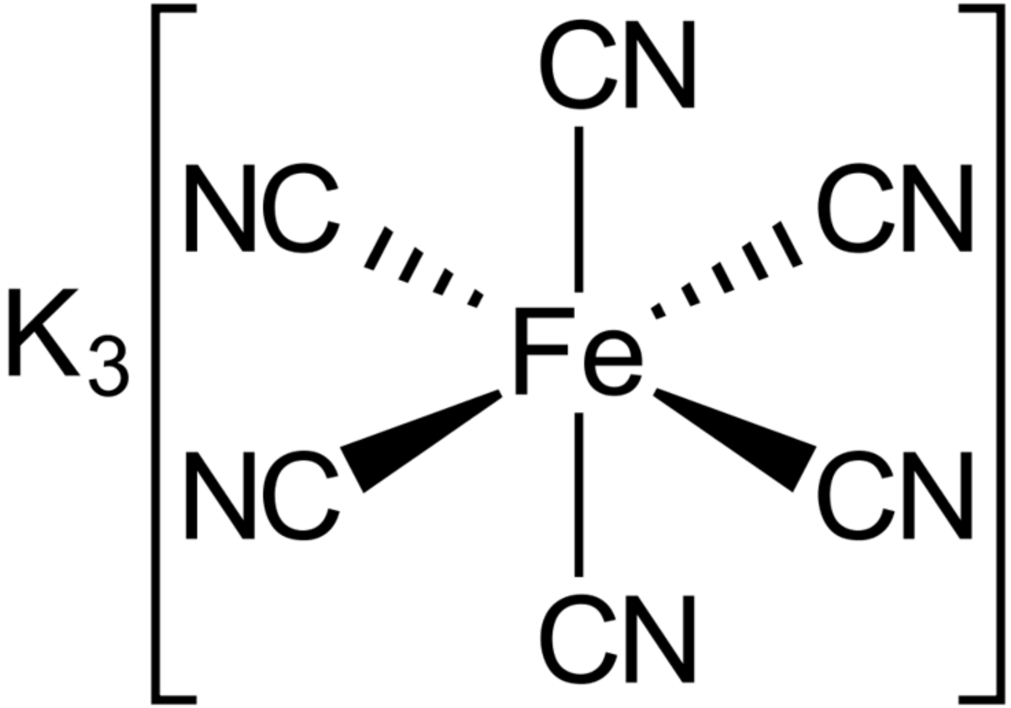
Coordination compounds



$[Co(NH_3)_6]Cl_3$



$K_3[Fe(CN)_6]$

Complex ion: $[Co(NH_3)_6]^{3+}$
Counter ions: $3Cl^-$

Complex ion: $[Fe(CN)_6]^{3-}$
Counter ions: $3K^+$

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Ligands

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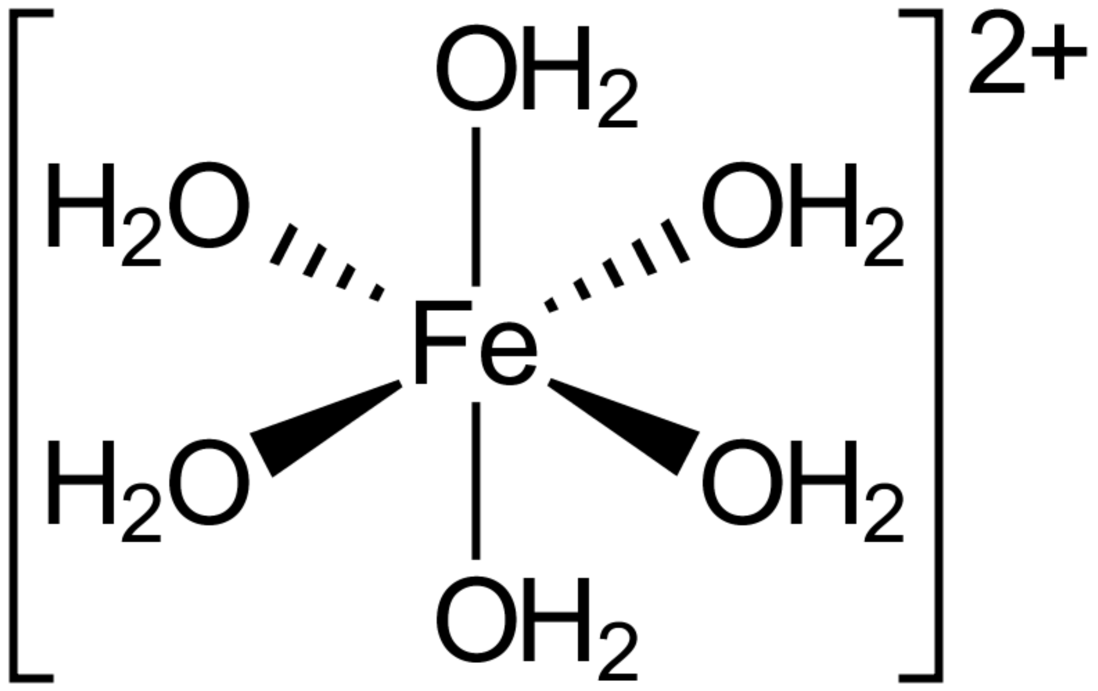
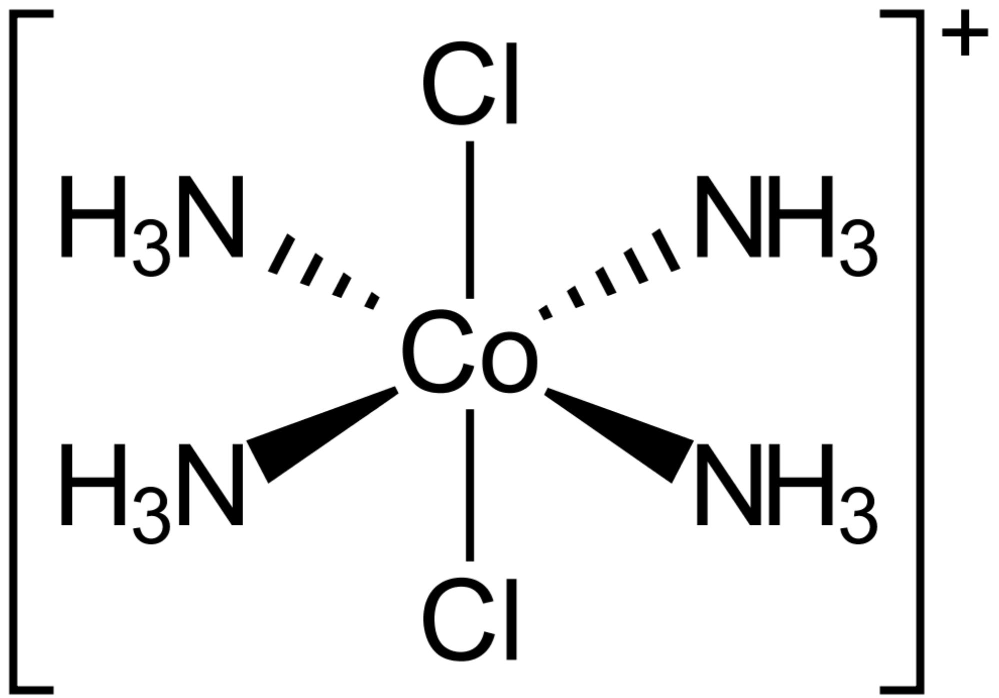
Ligands

Complex ions consist of a central metal ion bonded to ligands by coordinate covalent bonds.



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



$[Co(NH_3)_4Cl_2]^{+}$

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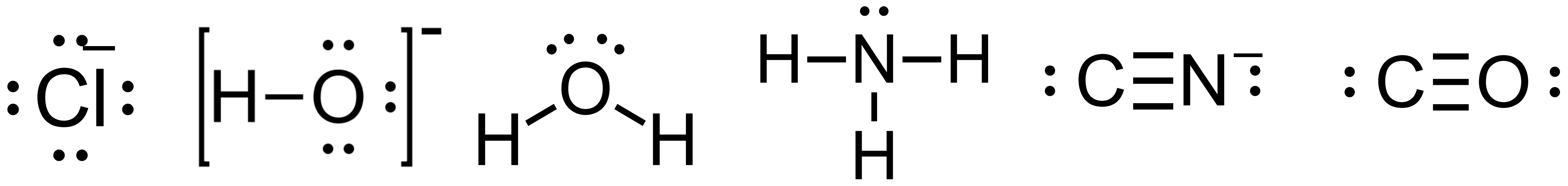
Ligands

Ligands are species with lone pairs of electrons that form coordinate covalent bonds with a central metal ion (ligands are also Lewis bases).

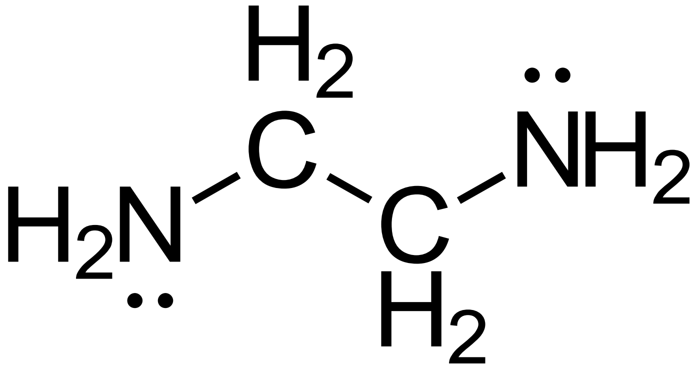
$$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < CN^- \approx CO$$



Monodentate ligands use only one lone pair of electrons to bond to a central metal ion.

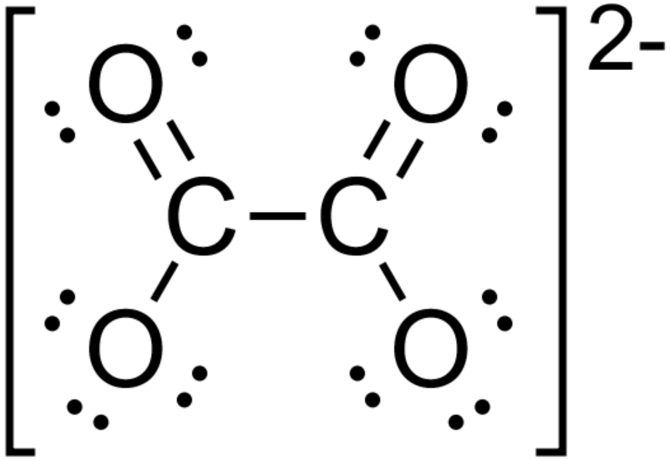
Ligands

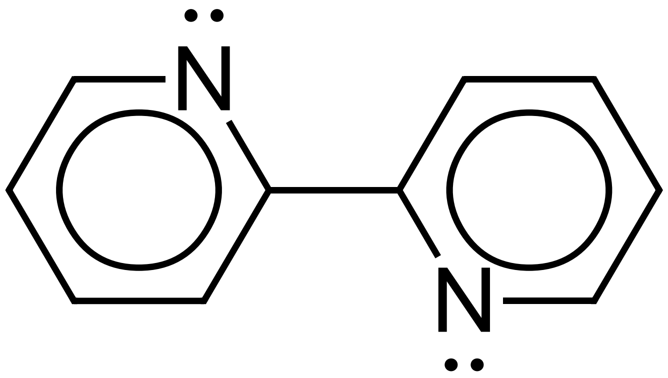
Bidentate ligands use two lone pairs of electrons to bond to a central metal ion.



1,2-ethanediamine

Ethanedioate ion

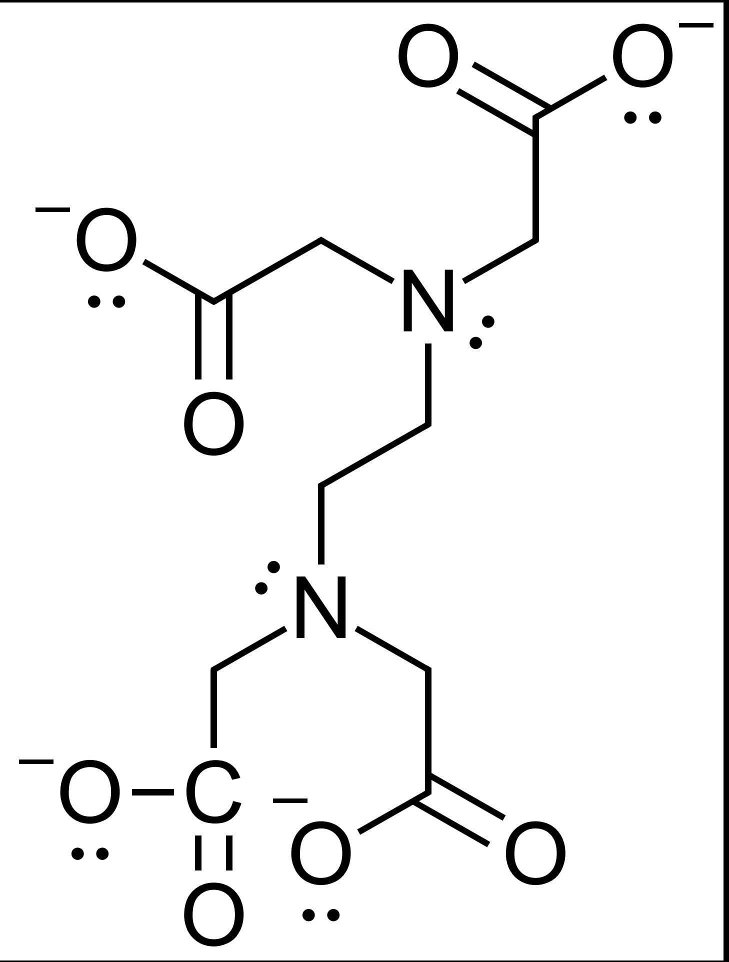




Bipyridine

Ligands

Polydentate ligands use multiple lone pairs of electrons to bond to a central metal ion.



$EDTA^{4-}$ is a hexadentate ligand; it uses six lone pairs of electrons to form six coordinate covalent bonds to a central metal ion.

$EDTA^{4-}$ is used as a food preservative as it binds to metal ions in enzymes that catalyse chemical reactions.

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Deduce the charge on a central metal ion

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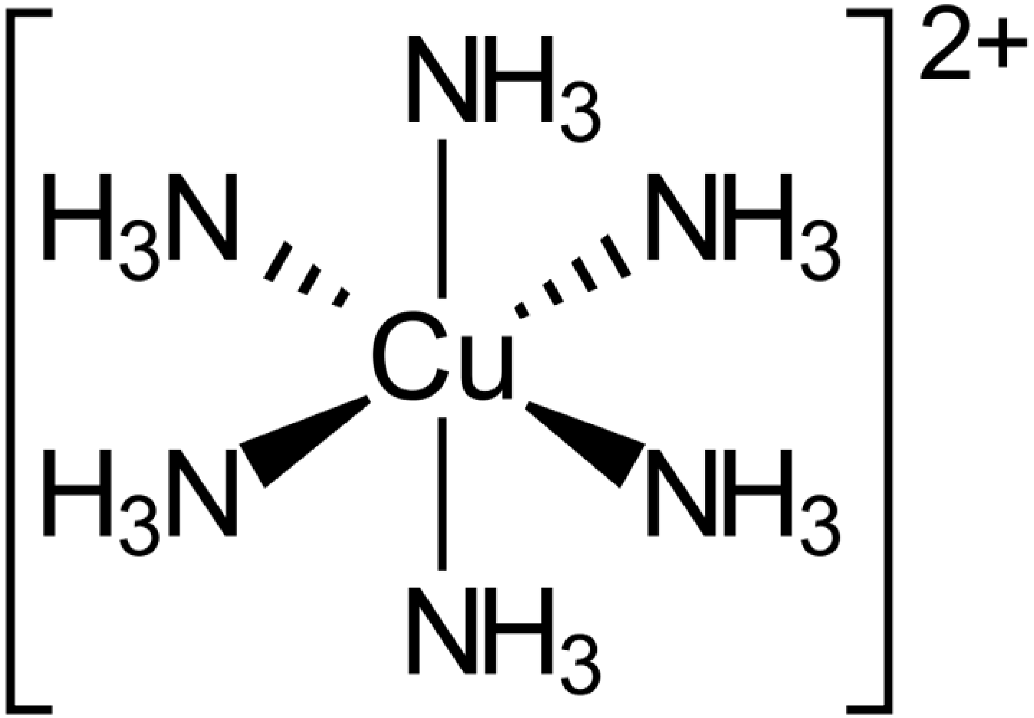
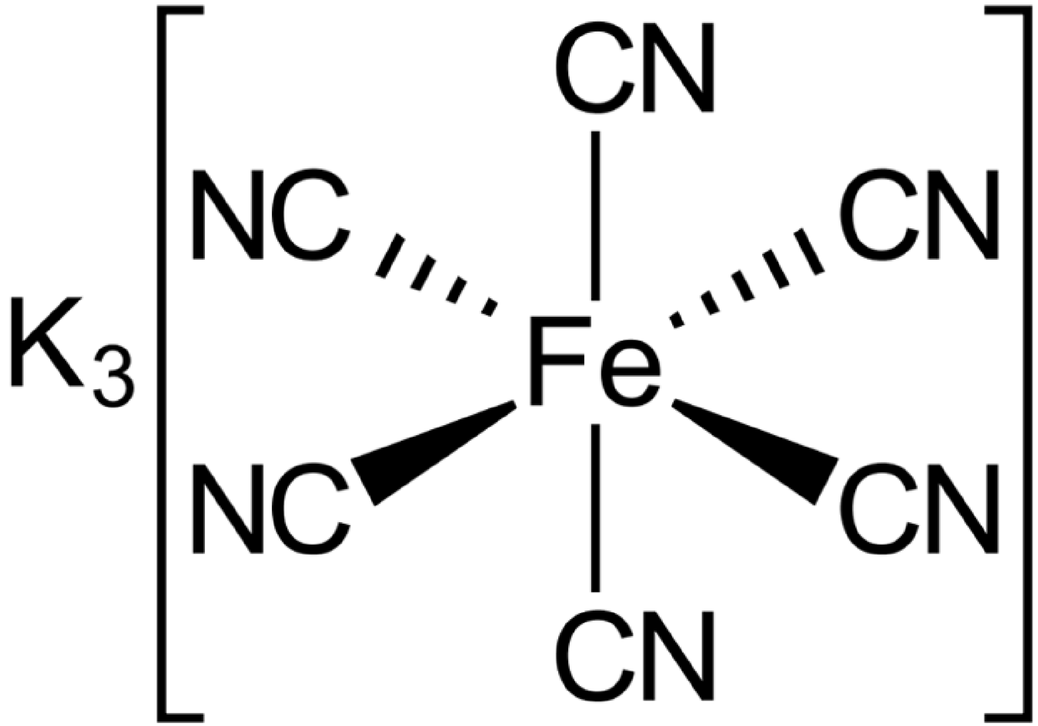
Charge on a central metal ion

Complex ion



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

Coordination compound

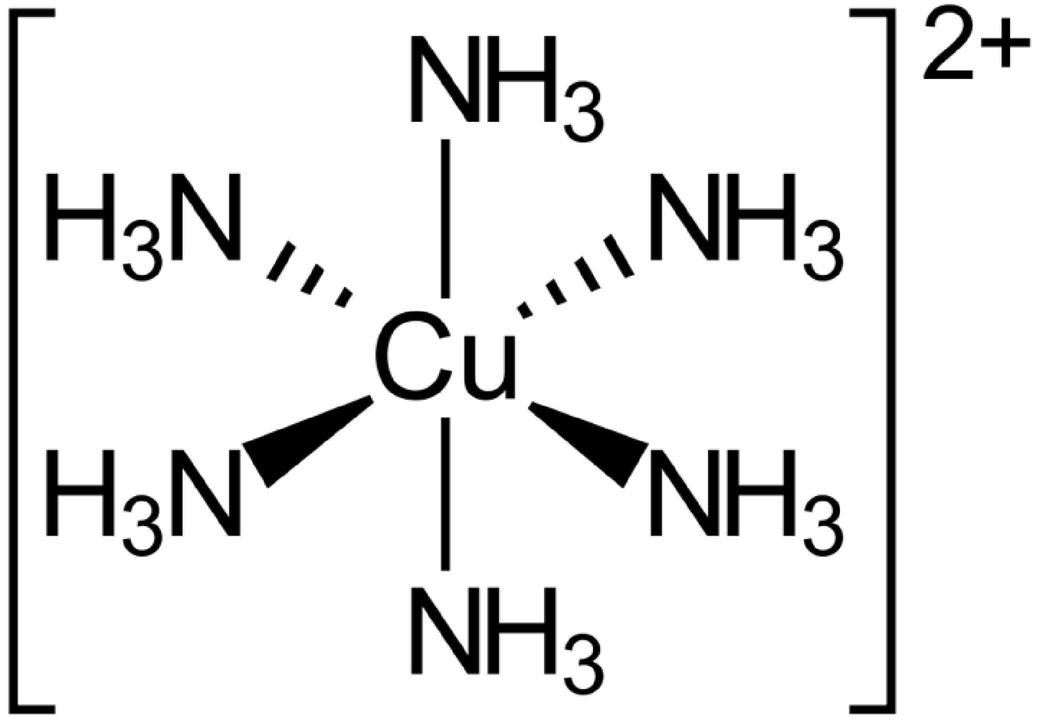


$K_3[Fe(CN)_6]$

Charge on a central metal ion

Transition element	Common ions formed	Oxidation state
Chromium	Chromium(II) Cr^{2+} Chromium(III) Cr^{3+}	+2 +3
Cobalt	Cobalt(II) Co^{2+} Cobalt(III) Co^{3+}	+2 +3
Copper	Copper(I) Cu^{+} Copper(II) Cu^{2+}	+1 +2
Iron	Iron(II) Fe^{2+} Iron(III) Fe^{3+}	+2 +3
Nickel	Nickel(II) Ni^{2+}	+2

Charge on a central metal ion



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

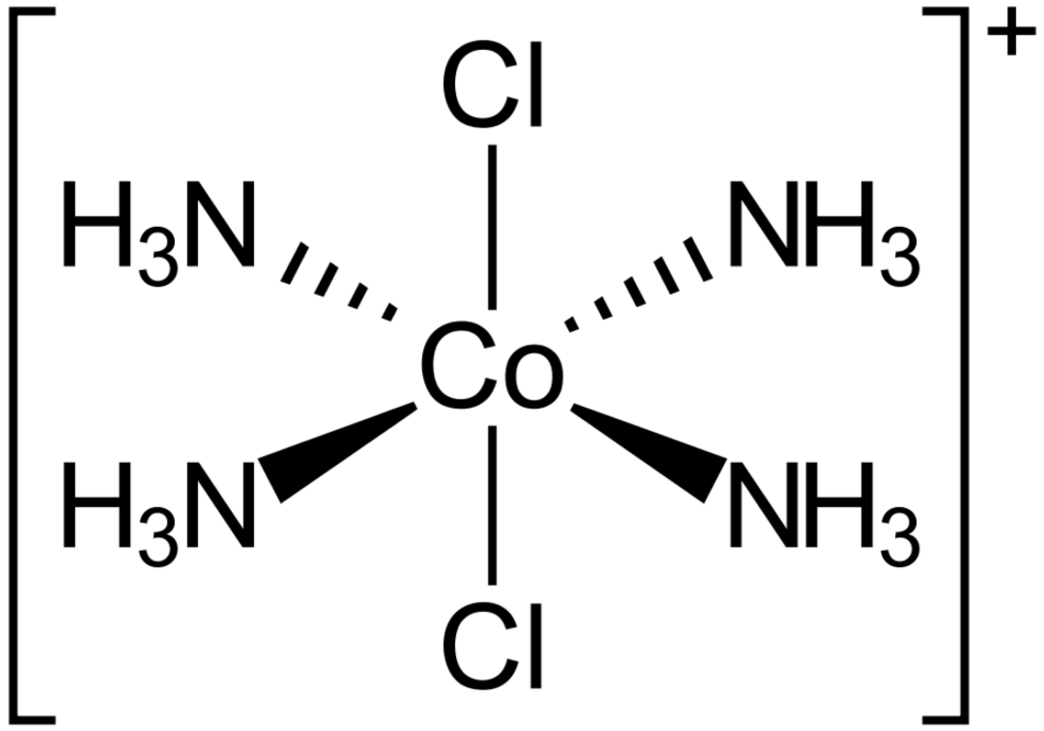
Central metal ion: Cu^{x+}

Ligands: $6NH_3$ molecules

If the ligands are neutral, the charge on the complex ion is the same as the charge on the central metal ion.

The central metal ion is the Cu^{2+} ion (oxidation state +2).

Charge on a central metal ion



$[Co(NH_3)_4Cl_2]^+$

If the ligands are negatively charged, subtract the total charge of the ligands from the charge on the complex ion.

The central metal ion is the Co^{3+} (oxidation state +3).

Central metal ion: Co^{x+}

Ligands: $4NH_3$ molecules, $2Cl^-$ ions

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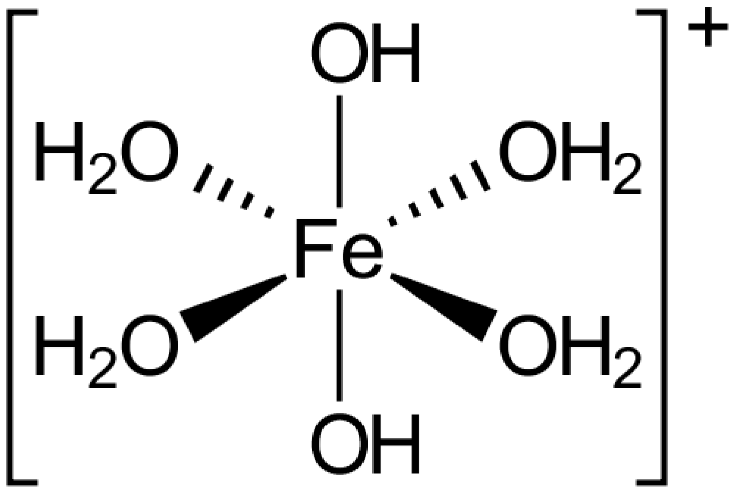
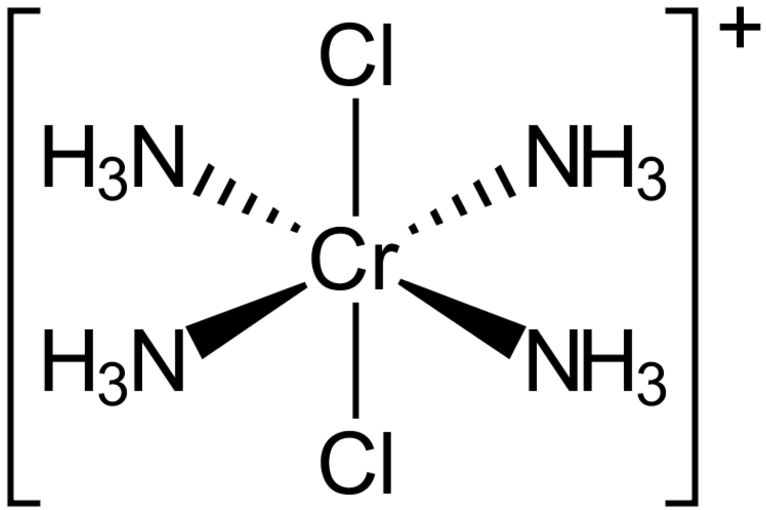
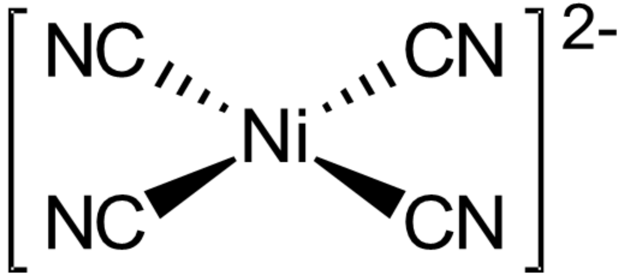
Charge on a central metal ion



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



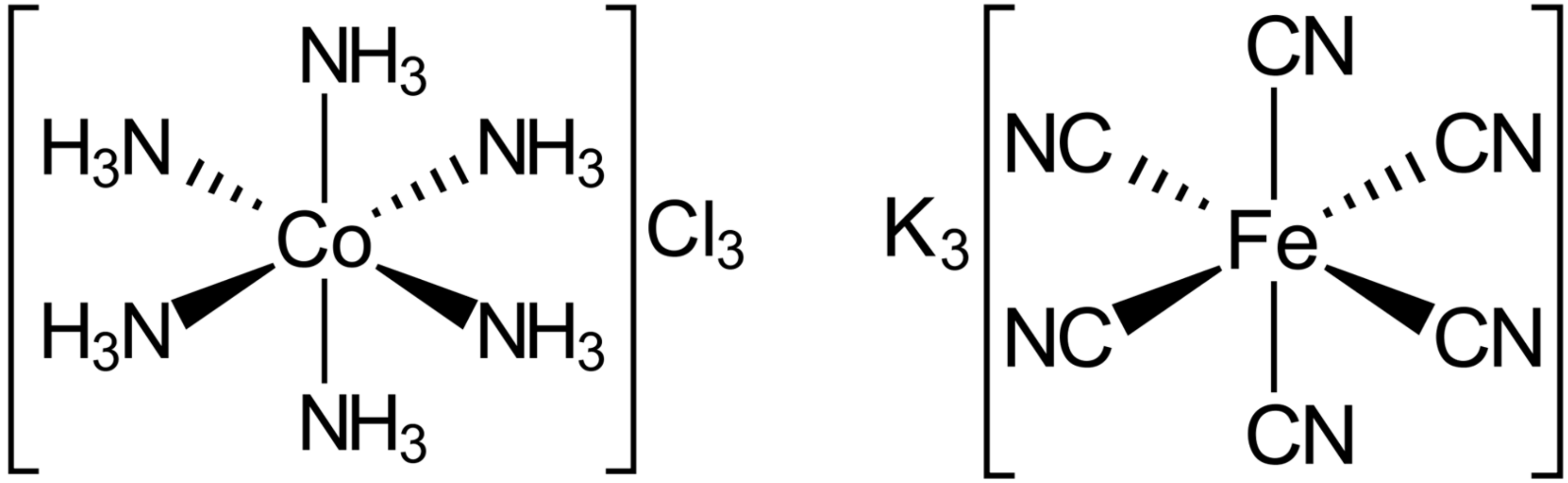
$[Cr(NH_3)_4Cl_2]^+$



$[Ni(CN)_4]^{2-}$

Complex ion	Ligands	Central metal ion	Oxidation state
$[Fe(OH)_2(H_2O)_4]^+$	$4H_2O$ $2OH^-$	Fe^{3+}	+3
$[Cr(NH_3)_4Cl_2]^+$	$4NH_3$ $2Cl^-$	Cr^{3+}	+3
$[Ni(CN)_4]^{2-}$	$4CN^-$	Ni^{2+}	+2

Charge on a central metal ion



$[Co(NH_3)_6]Cl_3$ $K_3[Fe(CN)_6]$

Coordination compound	Complex ion / counter ions	Ligands	Central metal ion	Oxidation state
$[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]^{3+}$ $3Cl^-$	$6NH_3$	Co^{3+}	+3
$K_3[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$ $3K^+$	$6CN^-$	Fe^{3+}	+3

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Oxidation states of the transition elements

Oxidation states

Transition elements show variable oxidation states in compounds.

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

All transition elements (except Sc) can have an oxidation state of +2.

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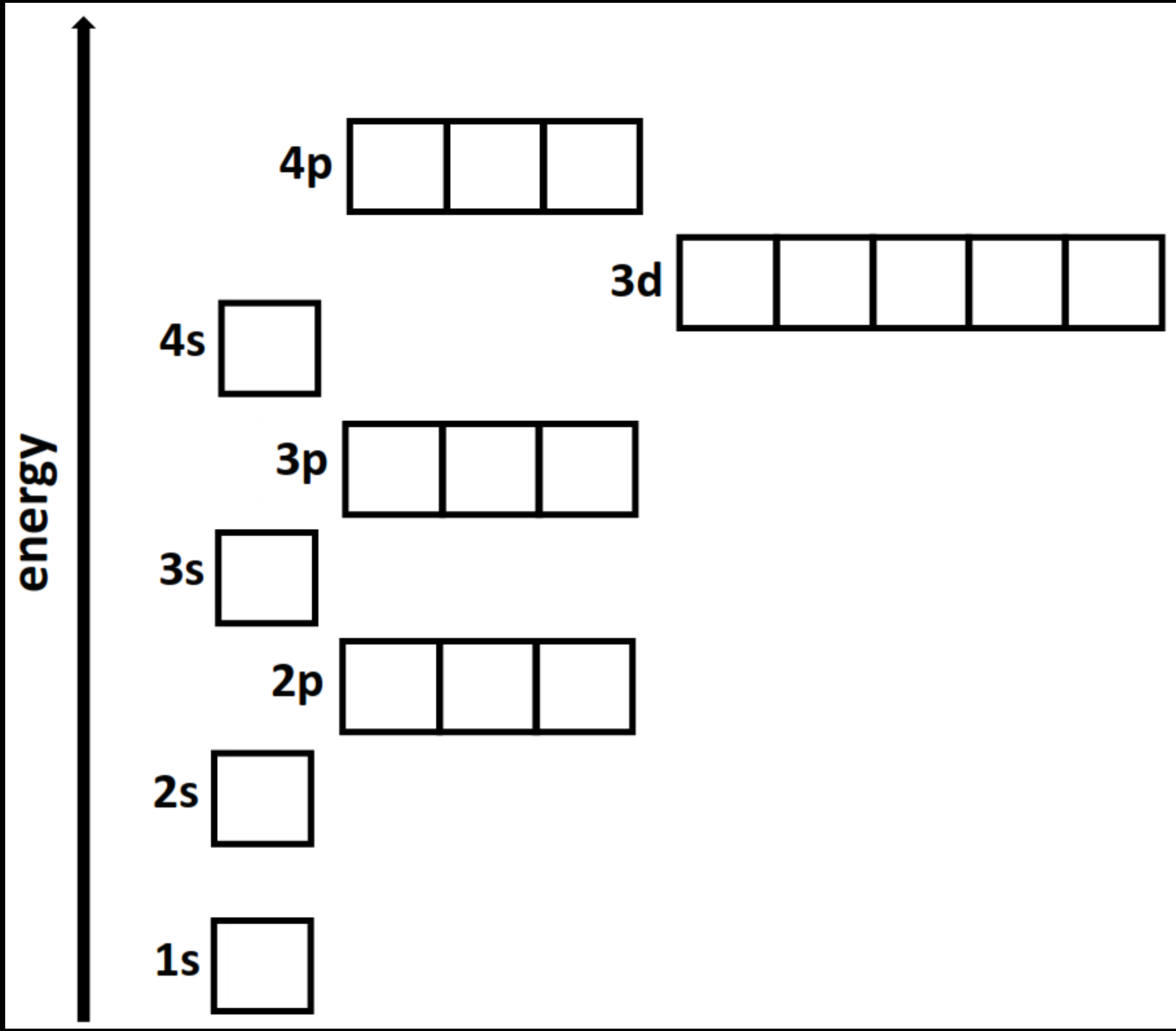
Transition element	Known oxidation states	Electron configuration	Orbital diagram (4s and 3d sub-levels only)
Sc	+3	[Ar] $4s^2\,3d^1$	4s [↑↓] 3d [↑][ ][ ][ ][ ]
Ti	+2 +3 +4	[Ar] $4s^2\,3d^2$	4s [↑↓] 3d [↑][↑][ ][ ][ ]
V	+1 +2 +3 +4 +5	[Ar] $4s^2\,3d^3$	4s [↑↓] 3d [↑][↑][↑][ ][ ]
Cr	+1 +2 +3 +4 +5 +6	[Ar] $4s^1\,3d^5$	4s [↑] 3d [↑][↑][↑][↑][↑]
Mn	+1 +2 +3 +4 +5 +6 +7	[Ar] $4s^2\,3d^5$	4s [↑↓] 3d [↑][↑][↑][↑][↑]
Fe	+1 +2 +3 +4 +5 +6	[Ar] $4s^2\,3d^6$	4s [↑↓] 3d [↑↓][↑][↑][↑][↑]
Co	+1 +2 +3 +4 +5	[Ar] $4s^2\,3d^7$	4s [↑↓] 3d [↑↓][↑↓][↑][↑][↑]
Ni	+1 +2 +3 +4	[Ar] $4s^2\,3d^8$	4s [↑↓] 3d [↑↓][↑↓][↑↓][↑][↑]
Cu	+1 +2 +3	[Ar] $4s^1\,3d^{10}$	4s [↑] 3d [↑↓][↑↓][↑↓][↑↓][↑↓]

Oxidation states



Transition elements lose their 4s and 3d electrons when they form ions.

The 3d and 4s orbitals are close in energy.

Successive ionisation energies of the transition elements show a gradual increase.

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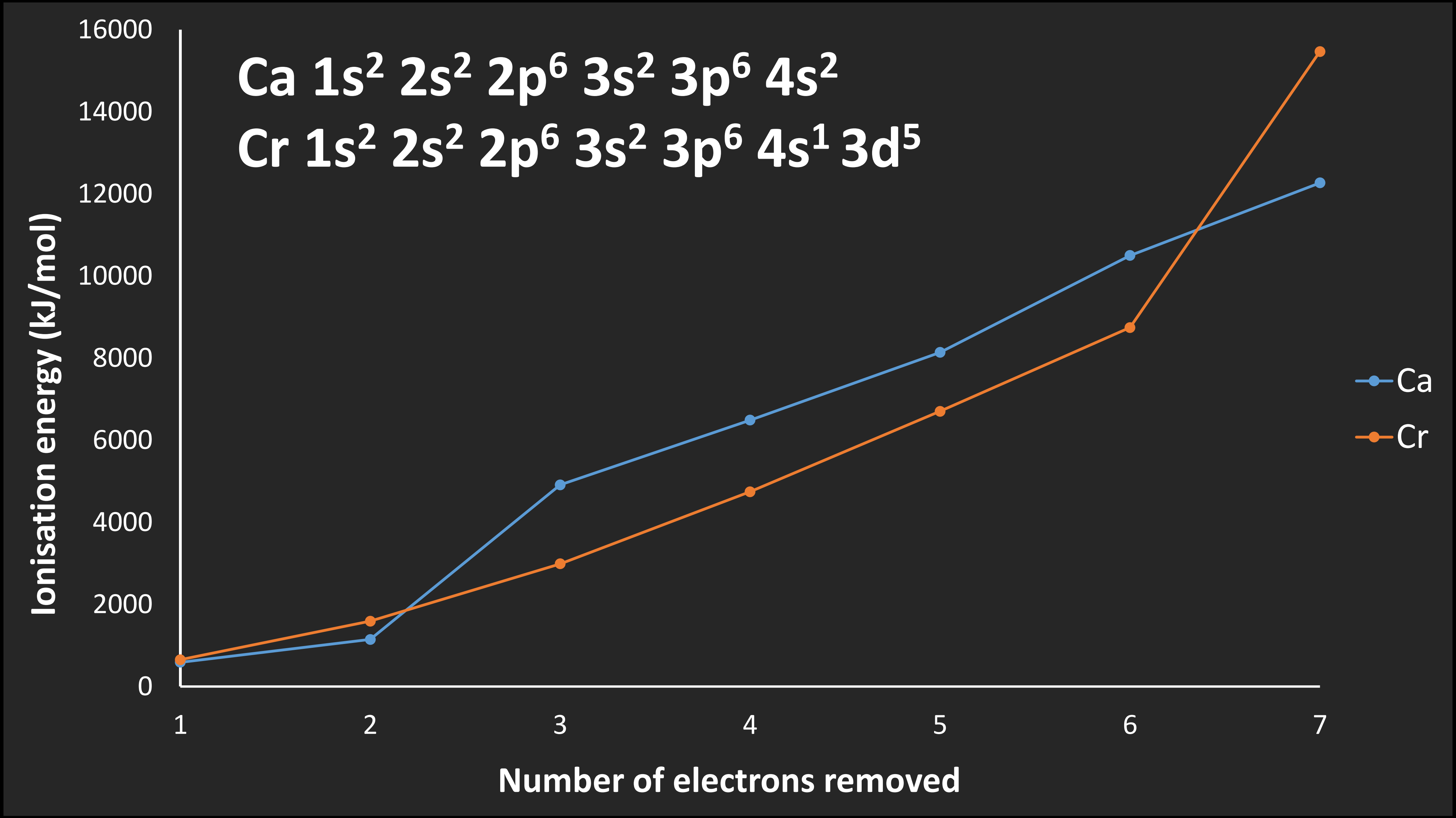
Oxidation states



Oxidation states

Transition elements have variable oxidation states.
Almost all transition elements have a +2 oxidation state because they lose their 4s electrons first.
The 4s and 3d orbitals are close in energy which results in a gradual increase in successive ionisation energies.
Group 1 and 2 elements only have one oxidation state (+1 and +2) because of the large increase in IE after the valence electrons are removed.

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Colour of complex ions

Colour of complex ions

Transition elements form coloured compounds.

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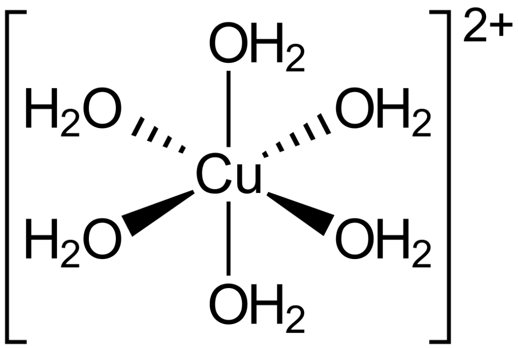
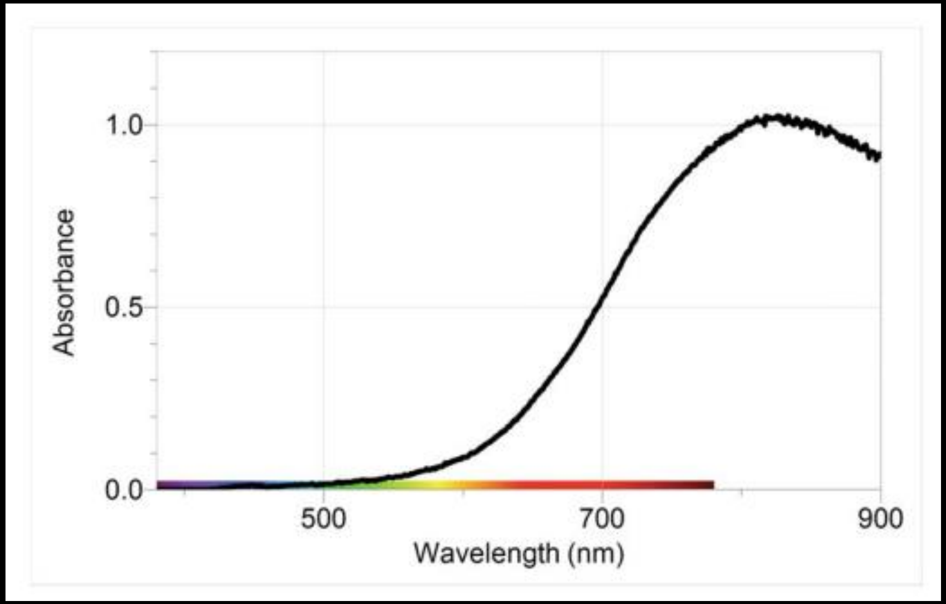
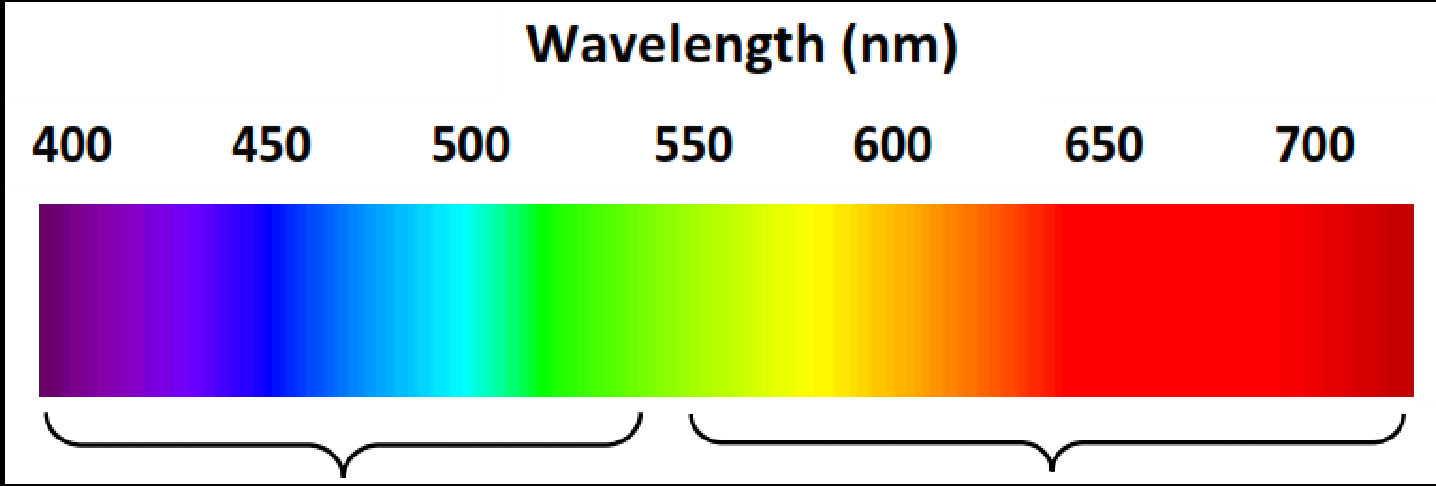
Colour of complex ions



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





These wavelengths are transmitted

These wavelengths are absorbed

Colour of complex ions

Crystal field theory states that the properties of complex ions are caused by the splitting of the d orbitals into two sets of different energies.

The splitting occurs when ligands approach the central metal ion; this causes repulsion between the lone pairs of electrons on the ligands and the electrons in the five d orbitals of the central metal ion.

The d electrons are repelled unequally which causes splitting, with two d orbitals of higher energy and three d orbitals of lower energy.

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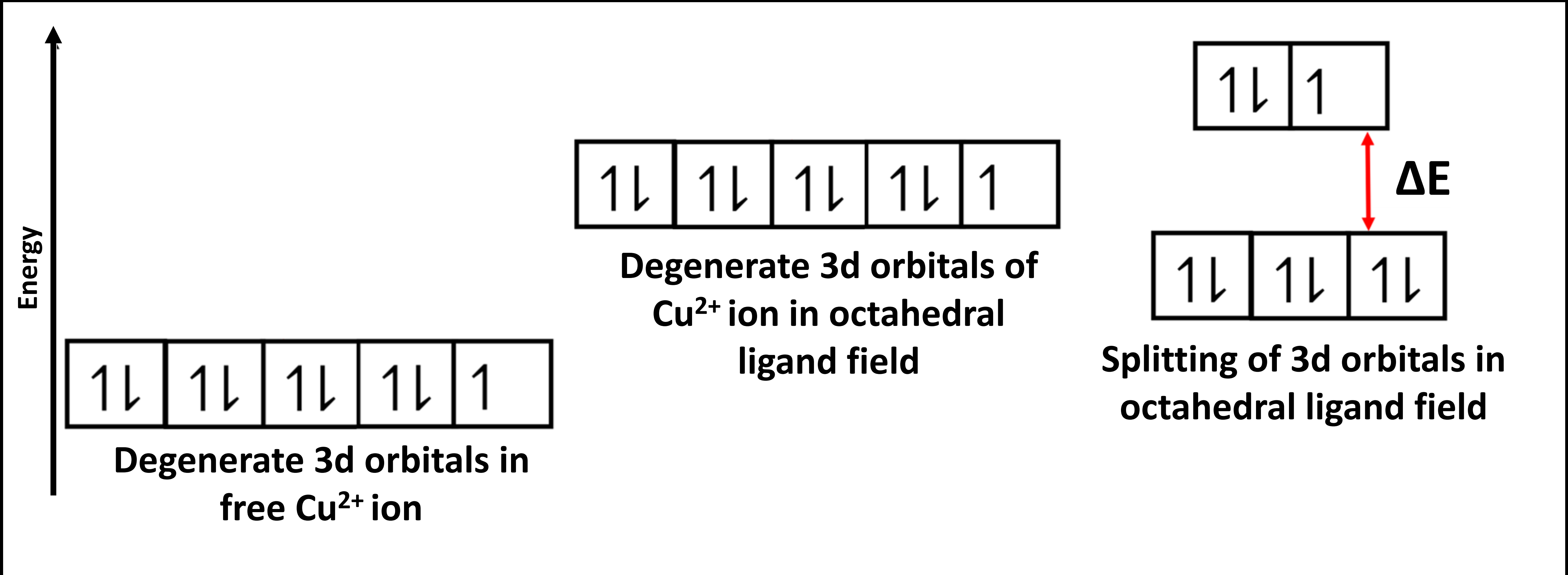
Colour of complex ions

Crystal field splitting in an octahedral field of ligands



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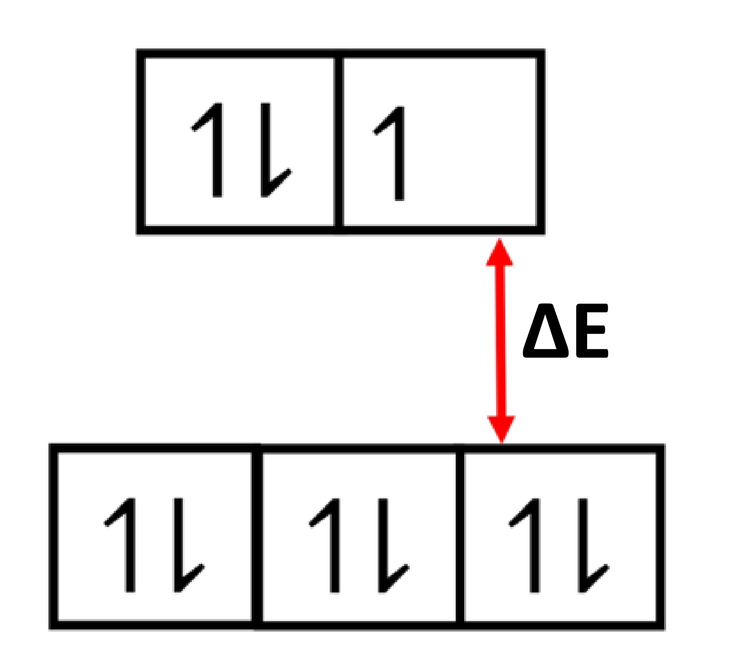
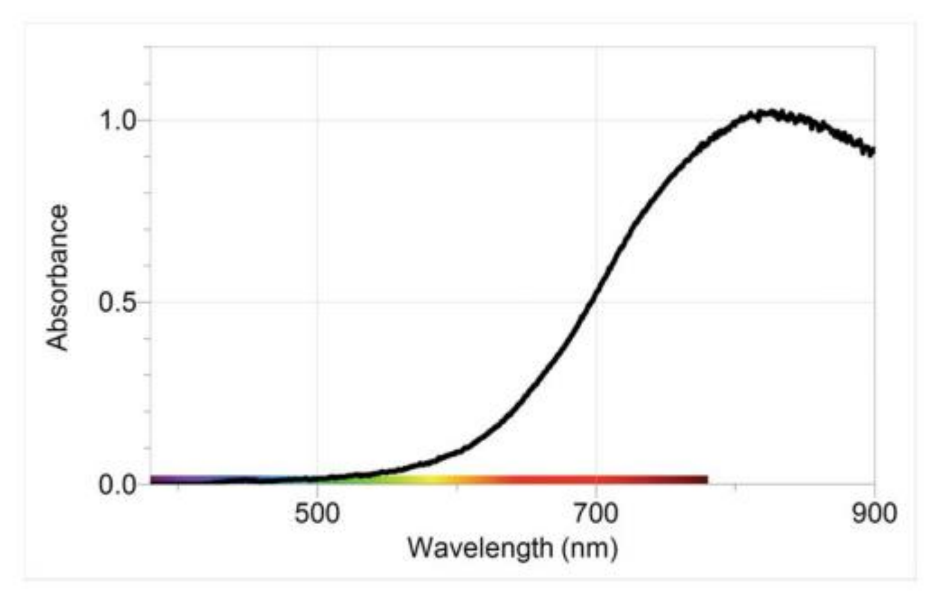
Colour of complex ions



An electron from the lower set of d orbitals can transition to the higher set of d orbitals by absorbing energy (d-d transitions).

The energy absorbed by the electron corresponds to the wavelengths of visible light.



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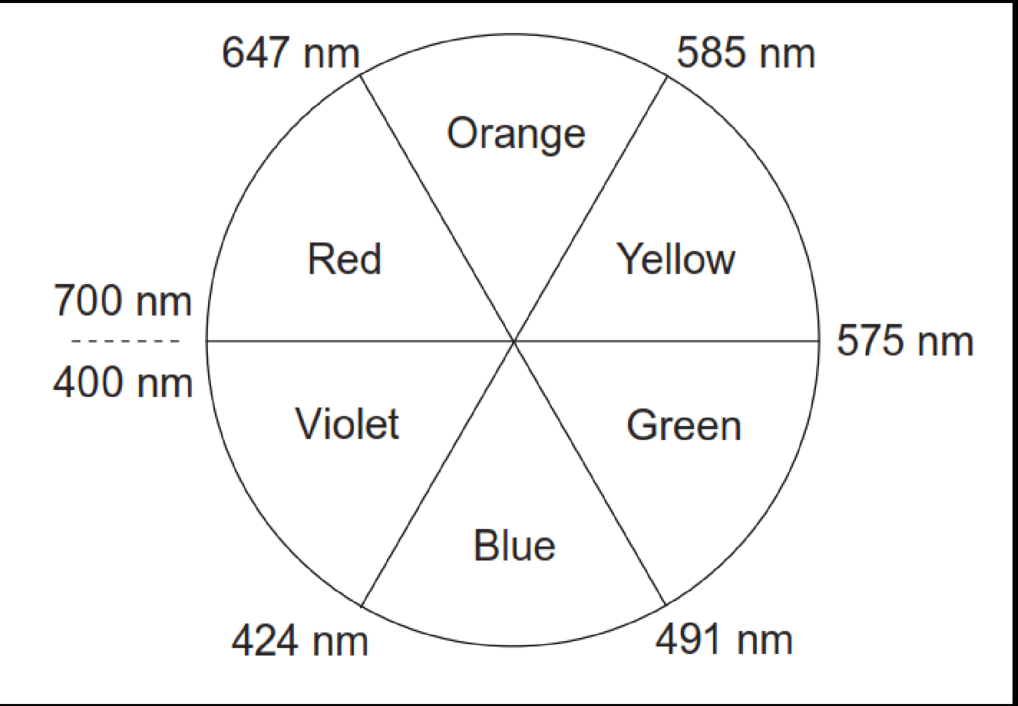
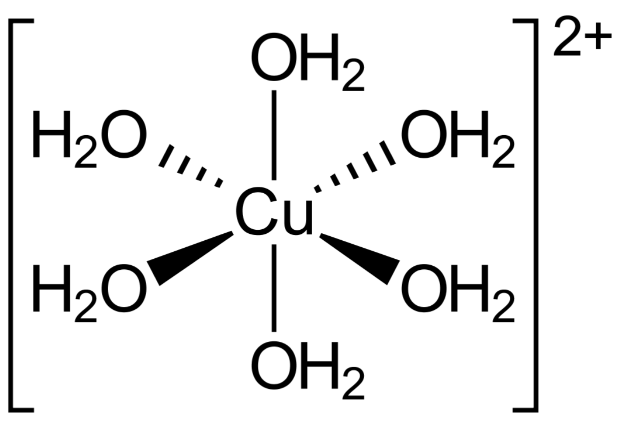
Colour of complex ions





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

The hexaaquacopper(II) ion appears blue because it absorbs orange light and transmits blue light.

The colour observed is complementary to the colour that is absorbed.

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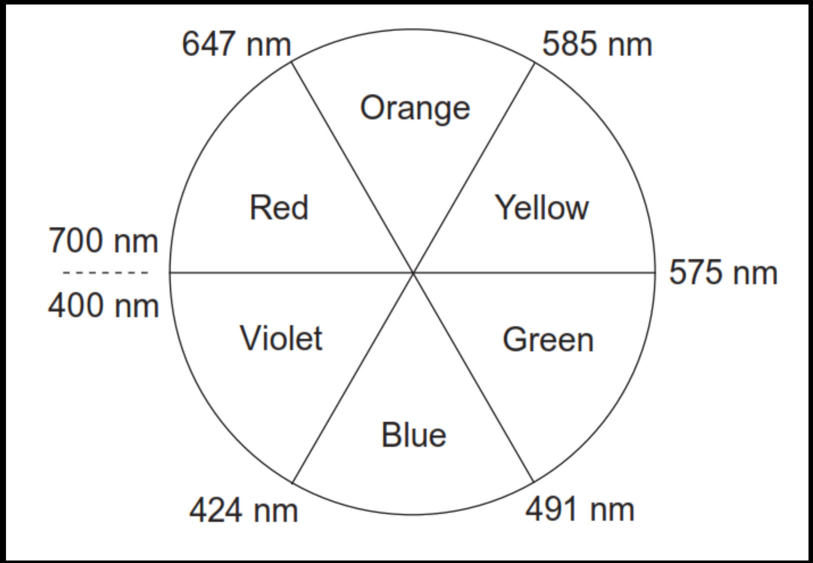
Colour of complex ions



Complex ion	Colour observed	Colour absorbed
$[Cr(H_2O)_6]^{3+}$	Green	Red
$[Co(H_2O)_6]^{2+}$	Red	Green

Colour of complex ions

Transition elements have incomplete d orbitals.

The d orbitals split into two sets of higher and lower energy when the ligands bond to the central metal ion.

The energy gap between the two sets of d orbitals corresponds to the wavelengths of visible light.

Electrons can transition from the lower to higher set of d orbitals by absorbing certain wavelengths of visible light.

The colour observed is complementary to the colour that is absorbed.

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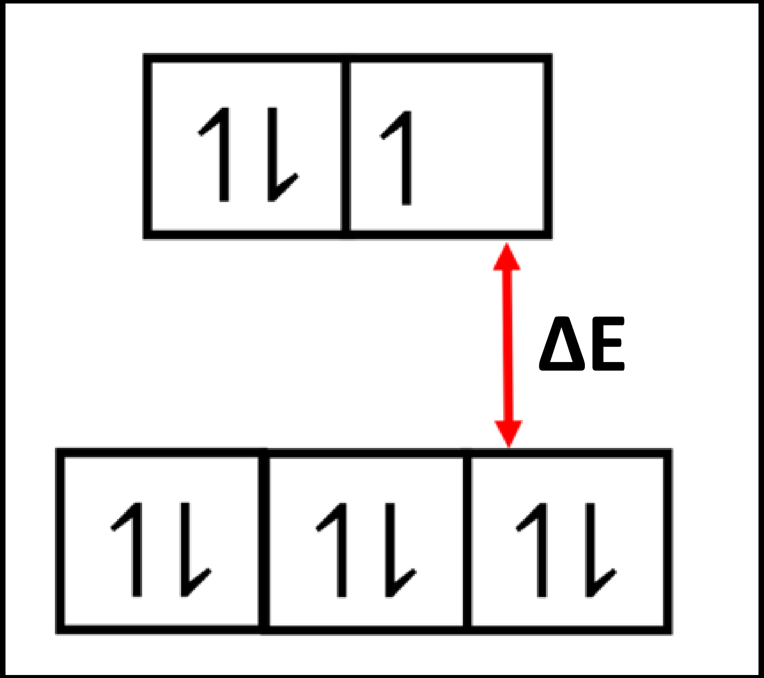
Factors that affect the colour of complex ions

Factors that affect the colour of complex ions



Any factor that changes the difference in energy (ΔE) between the two sets of d orbitals will change the wavelength of light that is absorbed when electrons transition from the lower set to higher set, and therefore the colour of the complex ion.

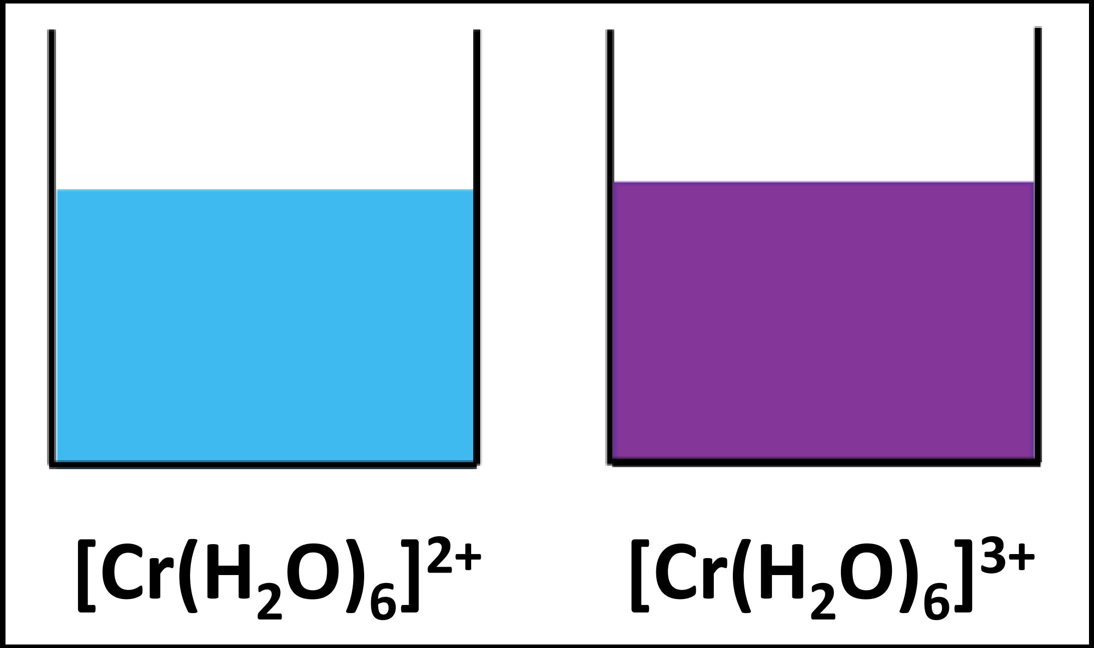
Identity of the central metal ion

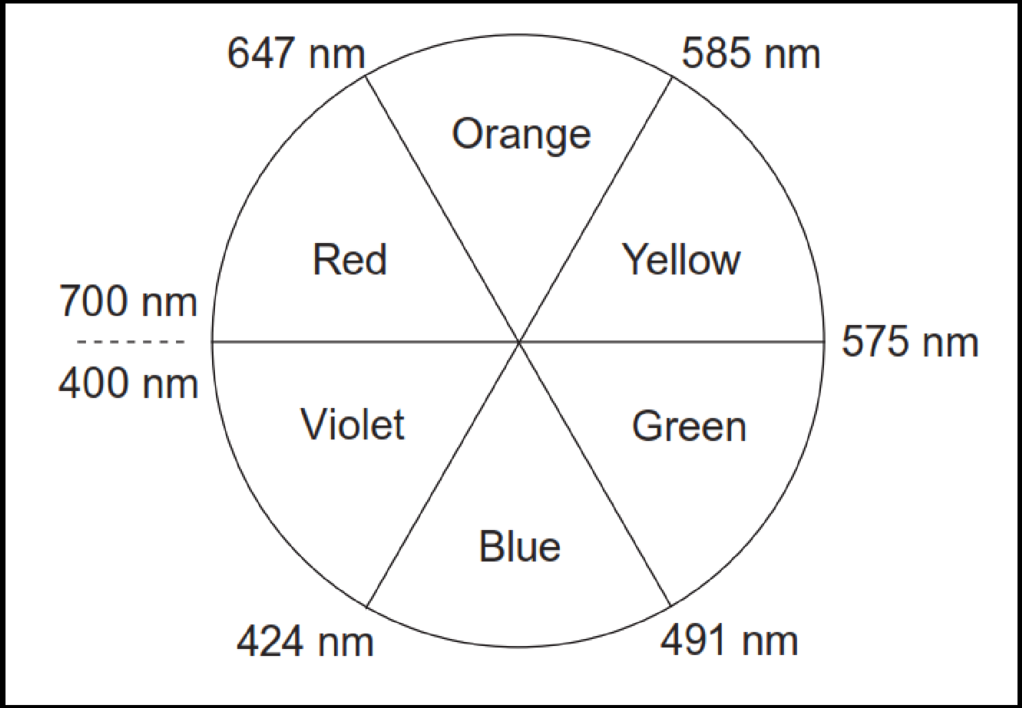
Oxidation state of the central metal ion

Geometry of the complex ion

Identity of the ligands (spectrochemical series)

Factors that affect the colour of complex ions

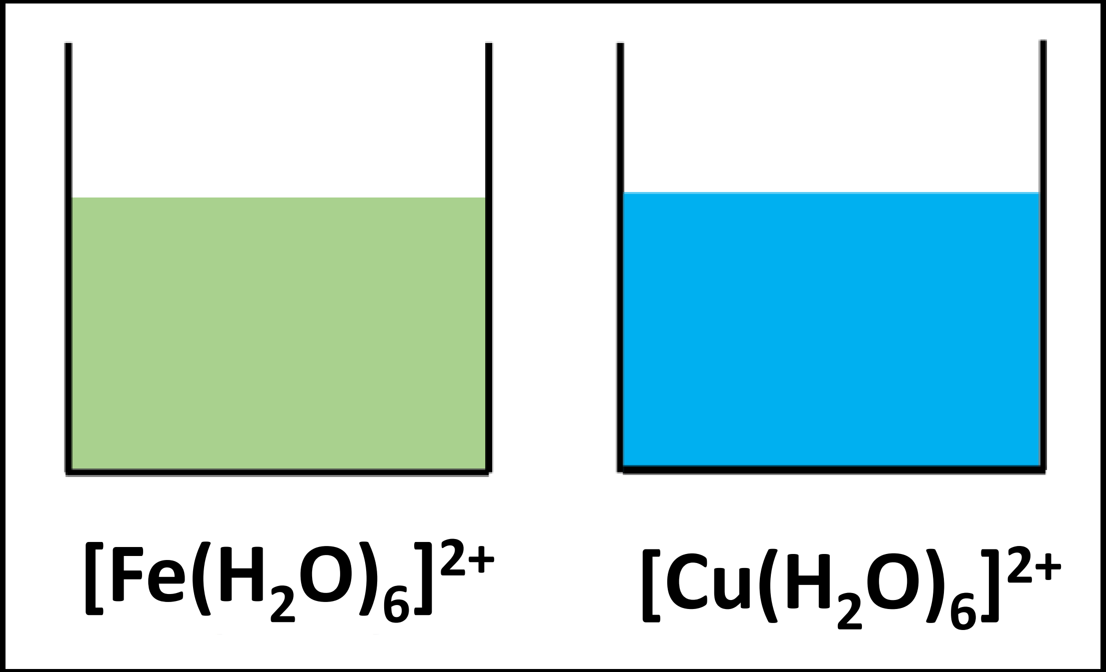


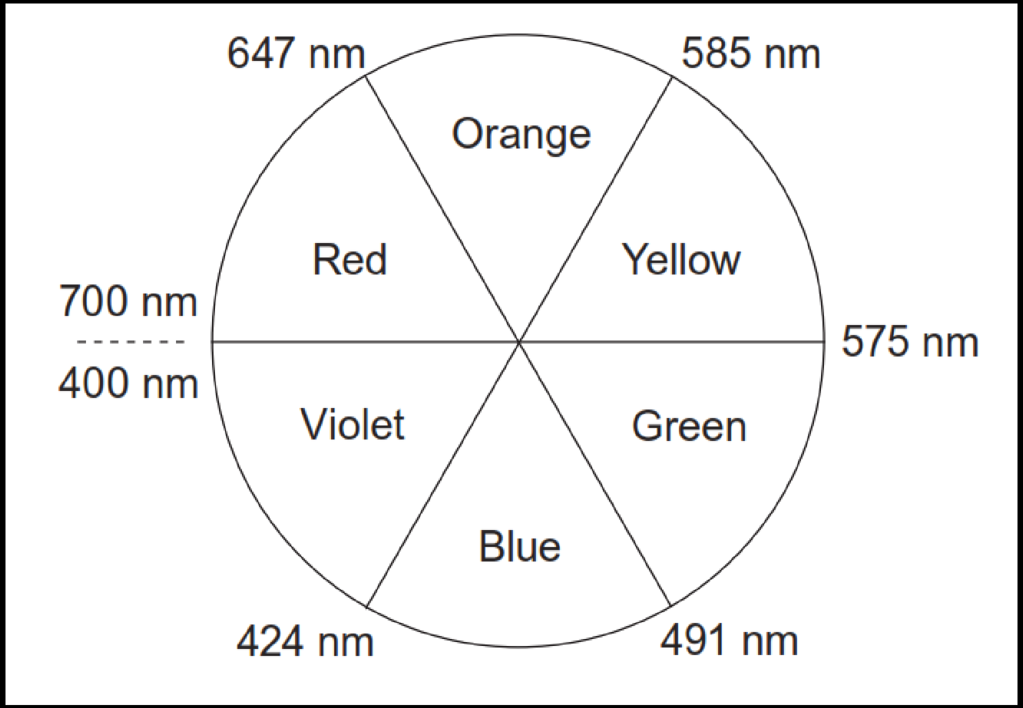


An increase in the oxidation state of the central metal ion increases the energy difference between the two sets of d orbitals.

The wavelength of the light absorbed decreases.

Factors that affect the colour of complex ions





The change in the identity of the central metal ion causes a difference in the wavelength of light absorbed.

The Cu^{2+} ion causes a larger energy gap and a shorter wavelength of light to be absorbed.

Factors that affect the colour of complex ions

Identity of the central metal ion

Oxidation state of the central metal ion

Geometry of the complex ion

Identity of the ligands (spectrochemical series)

$$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < CN^- \approx CO$$

The spectrochemical series arranges ligands in order of their ability to split d-orbitals in an octahedral complex ion.