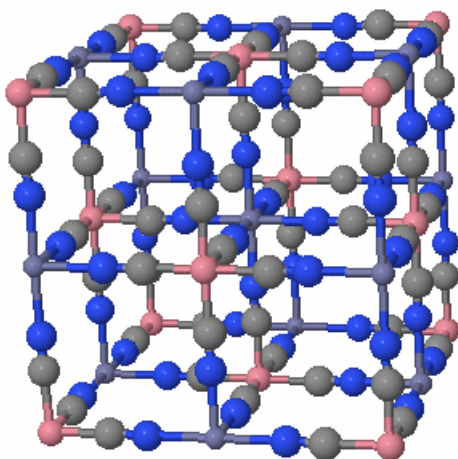


E40 MOLECULAR FRAMEWORKS

Prussian Blue

Molecules and solids with contain large enough holes to trap other molecules, atoms or ions are of considerable interest as nanomaterials. The 'hydrogen economy' relies on being able to safely carry highly explosive H_2 around in cars and release it when required. The holes or 'pores' in the molecular framework of some of these nanomaterials are capable of storing small molecules like H_2 . Others are able to trap unwanted pollutants such as cations of poisonous heavy metals and act as molecular sieves. The School of Chemistry is at the forefront of the development of these materials.

Prussian Blue was the first synthetic colour to be created, way back in the early 1700s. It is now being investigated as a possible nanomaterial for removing Tl^+ and Cs^+ ions in radioactive material. You have already made Prussian Blue this semester when you mixed potassium hexacyanoferrate(III) with an Fe^{2+} compound in 'E1 Chemistry with Light' (week 3) and you may remember its beautiful, deep blue colour. You will make it again this week and also make analogues of it with different M^{2+} metal ions. You will then test the ability of these nanomaterials to trap metal ions.



Prussian Blue itself has the framework structure shown below.

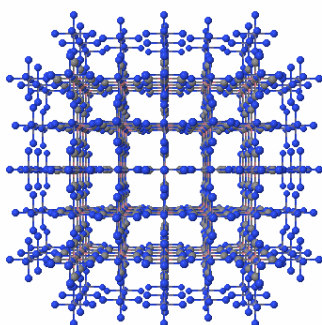
The structure contains Fe^{2+} (shown as grey spheres) and Fe^{3+} ions (shown as pink spheres).

In this experiment, you will also make frameworks in which Fe^{2+} is replaced by other M^{2+} transition metal ions.

These ions are connected together with ligands (see Glossary). In Prussian Blue, the ligand is cyanide (CN^-) (see Glossary) which is capable of bonding to two metals at once.

The framework structure with metal ions on the corners and cyanide spacers leads to large pores in which water molecules normally sit but into which other metal ions can be introduced.

The metal ions that are introduced into the pores are held sufficiently strongly that they are efficiently removed from the surrounding solution. Their absence from the solution following uptake by the framework can be detected using a flame test on the solution.



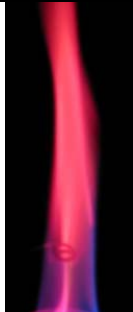




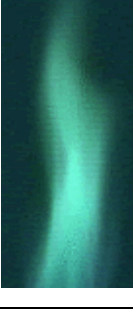




Each Fe^{2+} and Fe^{3+} ion is joined to six cyanide ligands so that the structure is made up of many of these cubes, to make an infinite network

The blue colour of Prussian Blue is due to **absorption** of light. The light causes an electron to transfer from Fe^{2+} to Fe^{3+} . As discussed in E1, the blue colour we see is the complementary colour (see Appendix) of the absorbed light.

Flame Tests

Flame tests are a quick and easy way of detecting the presence (or absence) of certain metal ions. In the heat of a flame, electrons are excited into orbitals in higher shells. When they 'relax' and return to their original energy level, they emit light. The energies of an atom's orbitals depend on its nuclear charge and on the shielding by the other electrons. As a result, each element has a characteristic emission spectrum that can be used to identify it. In part of the emission falls in the visible region, we see it as a colour. Although the actual wavelengths emitted are unique to each element, our eyes may not be able to detect small differences so that never every element has a unique colour in a flame. Nevertheless, flame tests are very useful for identifying certain elements. The table below shows some common metals and their corresponding flame colours.

Colour	Element
Red	Lithium, Strontium
Orange	Calcium
Yellow	Sodium
Yellowish-Green	Boron
Green	Barium, Copper
Blue	Copper (CuO, CuCO ₃ and halides)
Purple-Violet	Potassium
White-Silver	Aluminum, Magnesium, Titanium

				
lithium chloride	strontium chloride	calcium chloride	sodium chloride	borax (boron)
				
barium chloride	copper sulphate	copper(II) chloride	potassium chloride	magnesium turnings

The colour of the flame is due to the **emission** of light. Electrons are excited by the heat of the flame and emit light when they return to their normal energy. Both the metal ion and the metal atom contribute to the flame colour. The colour we see is the **same** as that emitted.

GLOSSARY

Ligand

Ligands are molecules or anions that bond to a metal. They have a lone pair that can be donated to a metal so that both the electrons in a metal-ligand bond come from the ligand: it is a 'coordinate' or 'dative' bond.

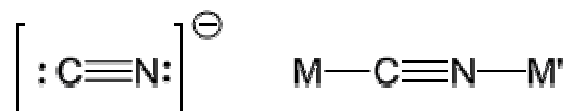
Common ligands include neutral molecules like H_2 and NH_3 and anions like the halides (F^- , Cl^- , Br^- and I^- , OH^- and cyanide (CN^-).



Cyanide

Cyanide is a very 'good ligand' meaning that it forms strong bonds with metals. Its toxicity arises due to the strength of the bonds it forms to Fe cations in enzyme: once these bonds are made they are very difficult to break and the enzyme is prevented from carrying out its normal tasks. Whilst free cyanide is very poisonous, its metal compounds, such as the $[Fe(CN)_6]^{3-}$ complex used in this experiment, are safe for the same reason - the strong bond prevents release of the free ligand.

Cyanide is unusual in that, as the Lewis structure below shows, it has a lone pair both ends. This enables it to bond to two metals at the same time to form linear M-C-N-M units that hold the framework together.



APPENDIX

Origin of colour

White light, such as sunlight, is a combination of all colours. Materials that are black absorb all the visible light which is shone on them. Materials that are white or colourless absorb no visible light.

The colours of other objects are due to the particular wavelengths of light that they absorb. A solid that absorbs red light and reflects all the other colours will appear green. We perceive a green colour when we see white light with the red part removed. Similarly, red wine absorbs green light and allows the other colours to pass through. White light with the green part removed is perceived by us as a red colour.

Red and green are examples of **complementary colours**. Complementary pairs include:

- red and green.
- blue and orange
- yellow and purple

Complementary colours have been known to artists for thousands of years. In Newton's colour wheel, complementary colours are on opposite sides of the wheel.

Newton's colour wheel

