

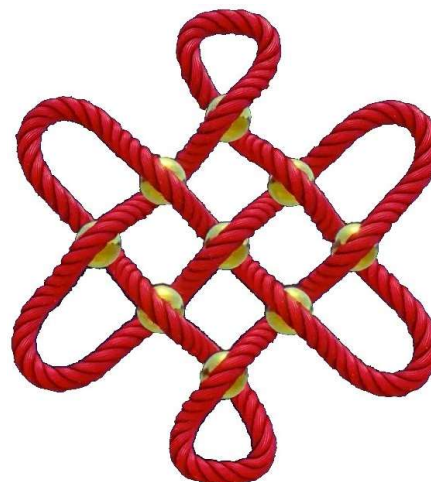
5. This question is about making the smallest Chinese knot

The 2022 International Chemistry Olympiad is being organised by Tianjin University in China. Traditional Chinese culture often features decorative knots tied from strands of cord or material. In 2021, researchers managed to tie a molecule into the smallest ever Chinese knot.

They first synthesised an organic ligand to act as the strands of thread. Coordination of atoms on these organic ligands to metal ions produced a (3 × 3) interwoven grid as shown below. The twelve strand ends were joined with a chemical reaction and the metal ions were then removed to give a purely organic Chinese knot.

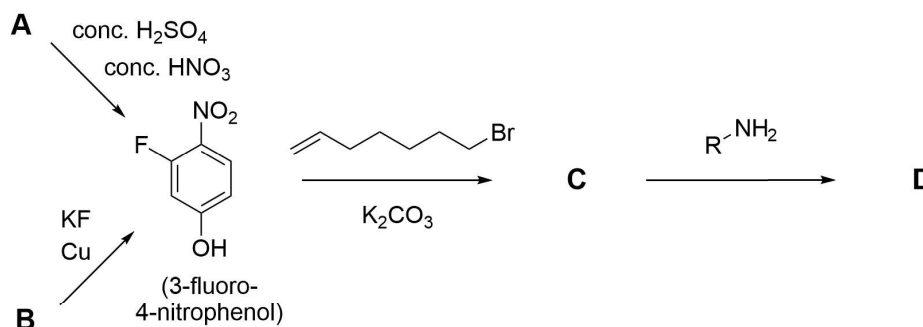


(3 × 3) grid



A Chinese knot from rope

The synthesis of one of the organic strands can begin from two different starting materials: **A** or **B** which can both be converted into 3-fluoro-4-nitrophenol.



- (a) (i) Draw the structure of **A**.
- (ii) Draw the structure of the active electrophile formed when **A** reacts to form 3-fluoro-4-nitrophenol.

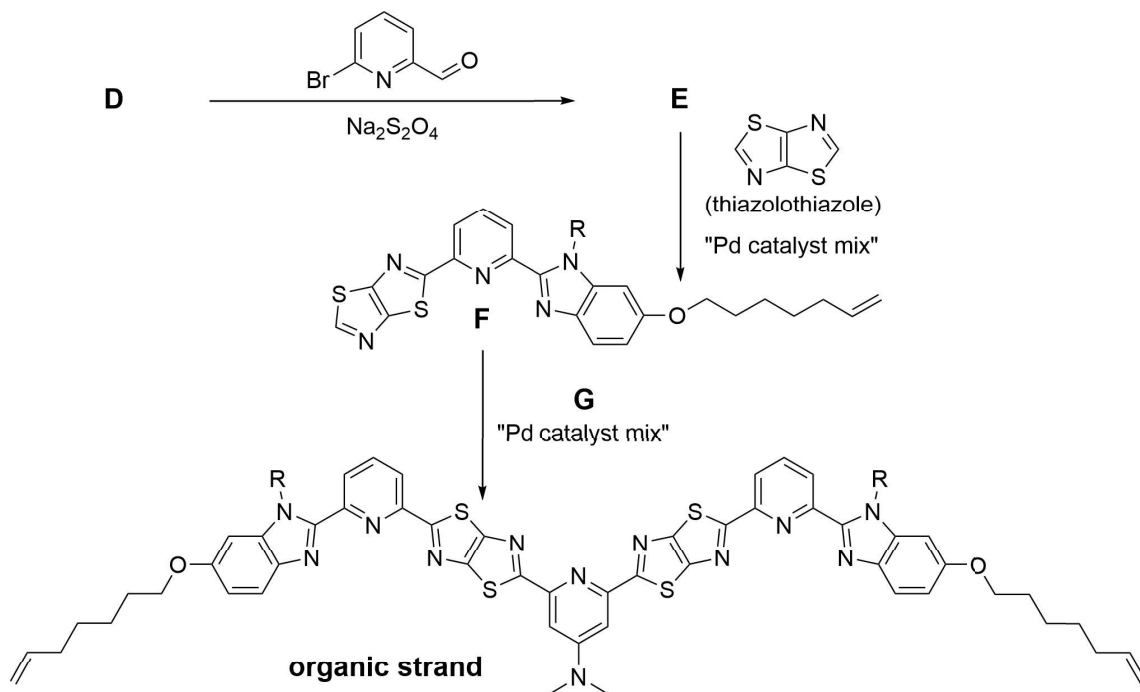
Elemental Analysis of **B** revealed: C 51.81%; H 3.62%; N 10.07%.

- (b) Draw the structure of **B**.

3-Fluoro-4-nitrophenol is converted into compound **D**. In the reaction of **C** to **D**, a primary amine (RNH₂) is used, where R is an alkyl group.

- (c) (i) Draw the structure of **C**.
- (ii) Draw the structure of **D**. Use the abbreviation R for the alkyl group from the primary amine.

Compound **D** is converted into the organic strand in three steps. The final two steps use the same palladium catalyst mix. Treating compound **E** and thiazolothiazole with this mix gives compound **F**. Treating compound **F** and reagent **G** with this mix gives the organic strand.



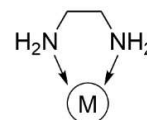
(d) Draw the structures of compound **E** and reagent **G**.

In the ^1H NMR spectrum of **D**, the signals from the alkyl group R are as follows:
 3.26 ppm (2H, doublet of triplets); 1.77 ppm (1H, multiplet); 1.63 ppm (2H, doublet of triplets)
 0.98 ppm (6H, doublet).

(e) Draw the structure of the primary amine (RNH_2) used to synthesise **D**.

Atoms in each strand coordinate to transition metal ions to form the (3×3) grid.

(f) On the structure of the strand in the answer booklet, draw in the place of the metal ions and show which atoms coordinate to each metal ion. Use the style of the picture on the right, where the metal ion is represented by a letter M in a circle, and the atoms which are coordinating have an arrow to show which metal they coordinate to.



(g) What is the overall coordination geometry around each metal ion in this 3×3 grid best described as? Tick the correct answer in the answer booklet.

tetrahedral

trigonal planar

square planar

octahedral

square pyramidal

hexagonal planar

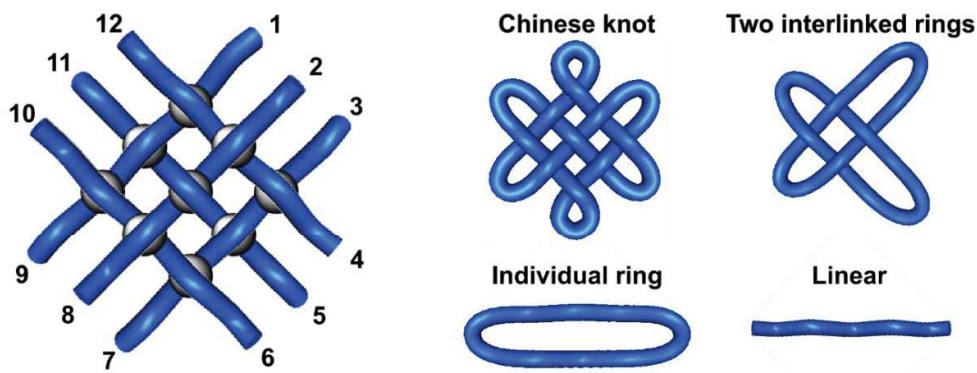
The formula of the metal salt added to form the grid can be written as $\text{MX}_2 \cdot 6\text{H}_2\text{O}$, where M^{2+} is a divalent cation of a first-row transition metal, X^- is a tetrahedral anion of charge -1 , and there are six molecules of water of crystallisation in the salt. Upon shaking the salt in aqueous sodium hydroxide, a green precipitate is formed that upon standing turns brown. Upon gentle heating of the salt, there is a 32.0% loss in mass. Anion X^- contains two different elements, neither of which is oxygen.

(h) Identify M^{2+} and draw the structure of anion X^- .

The 3×3 grid is then subjected to a reaction known as alkene metathesis, which joins two terminal alkenes into a disubstituted alkene, producing ethene as a by-product. Due to the rigid structure of the grid, only adjacent strands can be joined in this reaction.



Although this reaction only joins adjacent strand ends, there are still many possibilities of which ends can be joined. Depending on which ends join first, sometimes some ends are left too far away from other ends to be joined at all. Once the alkene metathesis reaction is complete, the metal ions are removed by addition of EDTA. After metal ion removal, four different types of organic structure remain, depending on which ends join: (i) Chinese knots; (ii) two interlinked rings; (iii) individual rings; (iv) linear organic molecules.



(i) In the answer booklet tick which of the four structures will be present after the following connections are made between the strand ends and then the metal ions removed.

- (i) (1,2) (3,4) (5,6) (7,8) (9,10) (11,12)
- (ii) (1,2) (4,5) (6,7) (8,9) (10,11) (3 and 12 remain unjoined)
- (iii) (1,2) (3,4) (5,6) (8,9) (10,11) (7 and 12 remain unjoined)
- (iv) (2,3) (4,5) (6,7) (8,9) (10,11) (12,1)