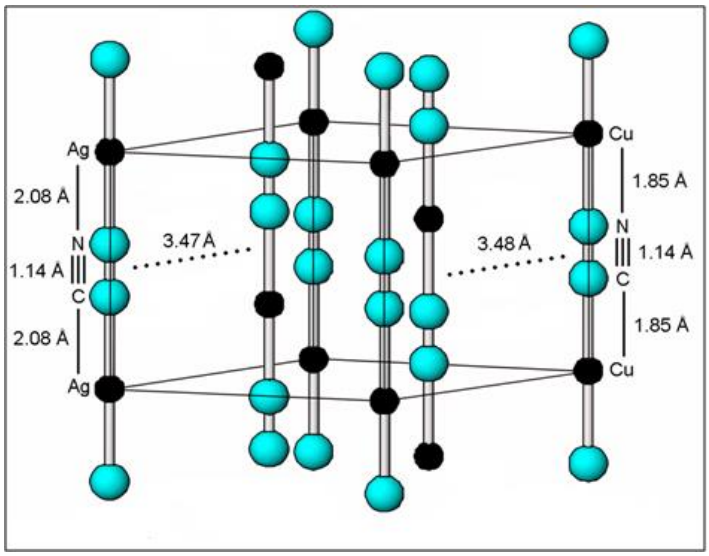
Transition-metal cyanides

This area of research has recently become very topical; many groups throughout the world are exploiting the fact that cyanide units can be linked together to form novel framework materials. These materials are of interest in a number of fields including supermolecular chemistry, hydrogen storage and crystal engineering. They show curious physical properties such as negative thermal expansion (i.e., they shrink when heated), negative compressability under pressure and luminescence – all of which are exciting to study!

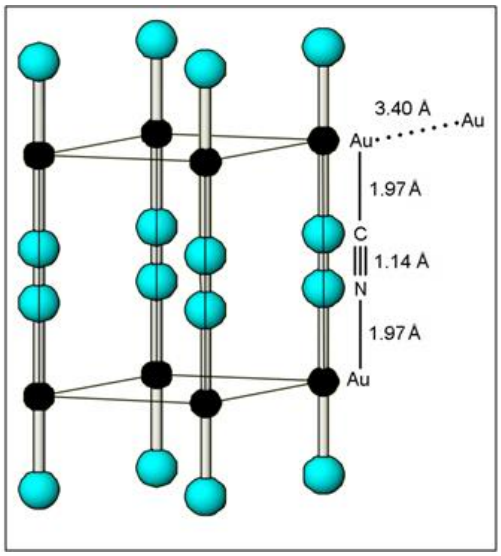
We employ chemical design to assemble one- two- and three-dimensional cyanide structures.

One-dimensional chain structures:

Although these have simple formulae, they can be structurally complex. For example, the group 11 cyanides, high-temperature CuCN,[1] AgCN[2] and AuCN[3] are all constructed from linear metal-cyanide chains, $[M{-}C{\equiv}N{-}]_n$ packed together. They are highly disordered crystalline solids and their structure solution has involved the use of both X-ray and neutron Bragg and total scattering experiments.



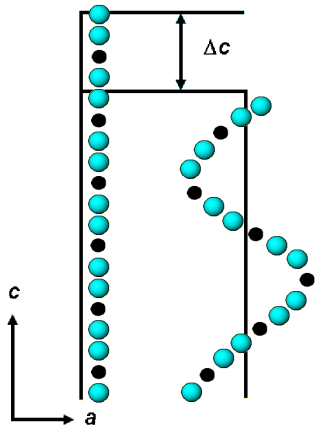
AgCN and HT- CuCN



AuCN

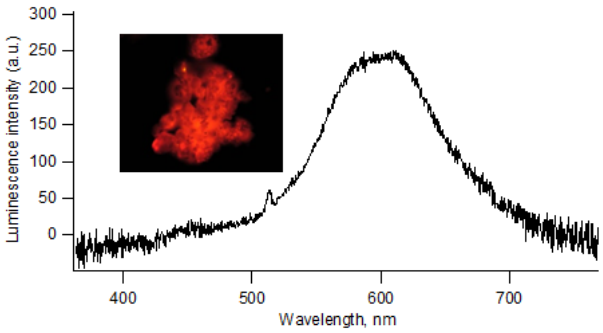
M
C/N

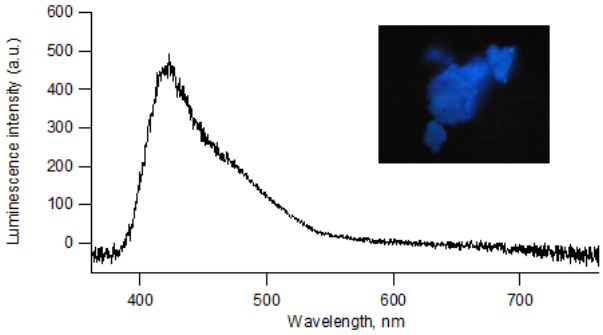
On heating these materials, they contract along the chain axis (*c* direction) i.e. show 1-D negative thermal expansion.[4] A simple model to account for this behaviour is shown on the right. As the temperature is increased, there is an increase in amplitude of the transverse motions perpendicular to the chain axis leading to a kinking of the chains and a decrease in length along *c*.



Low temp High temp

Mixed-metal compounds such as $Cu_{1/2}Au_{1/2}(CN)$ and $Ag_{1/2}Au_{1/2}(CN)$ can be prepared[5] enabling physical properties to be tailored. For example, under excitation using a 343nm laser, these compounds show very different luminescent behaviour.





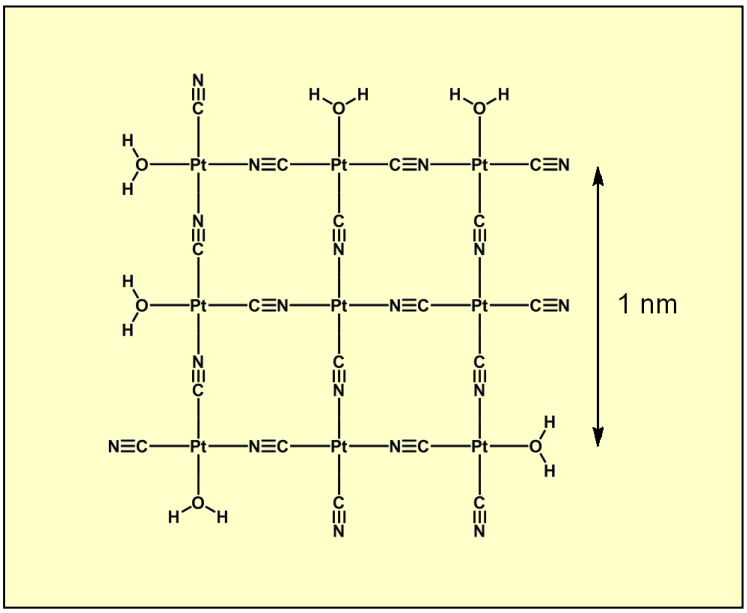
$Cu_{1/2}Au_{1/2}(CN)$ $Ag_{1/2}Au_{1/2}(CN)$

contain ordered chains:

− Cu− N≡C − Au − C≡N − − Ag− N≡C − Au − C≡N −

Two-dimensional sheet structures:

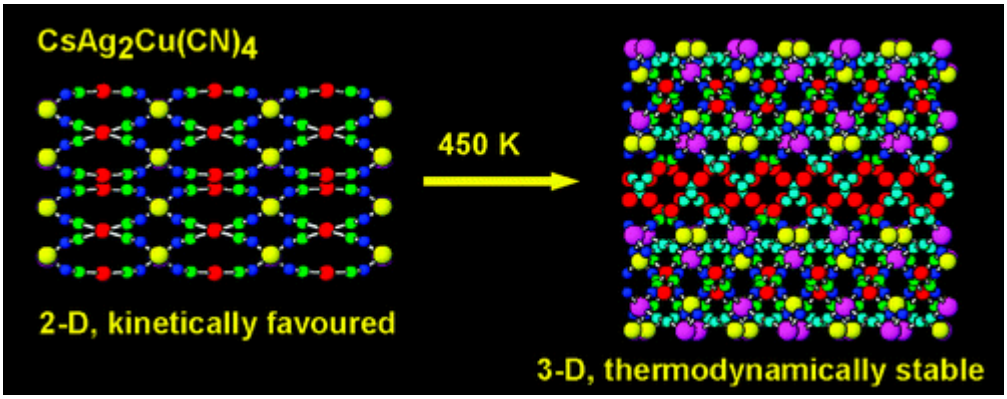
The group 10 cyanides, $Ni(CN)_2$,[6-8] $Pd(CN)_2$[9] and $Pt(CN)_2$[9] all have layered structures based on the 4,4' square net below with each metal having square-planar coordination geometry (as expected for metals ions with d^8 electron configuration). These sheets contract on heating (i.e. show 2-D negative thermal expansion behaviour). The stacking of the layers is highly disordered in these types of materials.[7,9]



Note that for the palladium and platinum cyanides, the sheet sizes are very small and they are said to be nanomaterials. The figure above shows the actual size of the sheets found in $Pt(CN)_2.0.67H_2O$.[9]

Three-dimensional framework structures:

Beyond these ‘simple’ materials the group has been active in preparing more complicated cyanide frameworks which demonstrate interesting stuctural features such as topological isomerism, polymorphism, and interpenetration, in which copies of the framework nest inside each other.[10-12] These materials can be prepared by solvothermal synthesis. The products are highly crystalline and their structures can be solved using single-crystal X-ray diffraction.



Above is shown the astonishing conversion between the two polymorphs of $CsAg_2Cu(CN)_4$. This conversion, which involves a major change in connectivity and topology, occurs at 180 °C as a single-crystal to single-crystal transformation.

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