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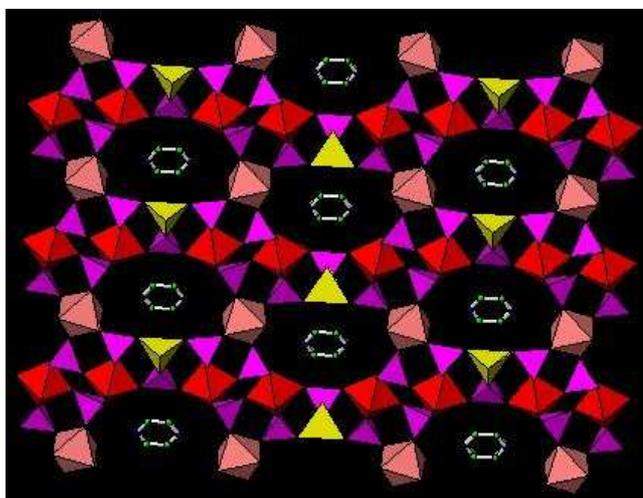


My research aims are to prepare new solid-state materials with interesting structural, chemical and physical properties. My main area of interest is the preparation and structural characterisation of ‘open-framework’ materials – materials with framework structures containing regular arrays of pores or channels of suitable size to accommodate small molecules – with the idea of performing chemical reactions inside the pores. A number of these types of material occur in Nature, including a class of aluminosilicate minerals called zeolites, which, by virtue of their open structures, have a range of uses from water softeners in washing powders to catalysts in petrochemical refining. I am exploring open-framework metal phosphates, sulphides and cyanides, which are synthetic materials that can mimic, and in some cases, outperform the natural zeolites.

Solvothermal techniques are used for the synthesis of most metal phosphates, cyanides and sulphides. A gel precursor, containing sources of the framework building elements (M, P, ‘CN’ or S), a solvent (aqueous or non aqueous) and a structure-directing agent or ‘template’ (most commonly an organic amine or alkali-metal cation), is heated in an autoclave at low temperature (<473 K). As the gel is heated, the metal and phosphate, cyanide or sulphur components assemble around the ‘templating’ species to form an open inorganic framework containing amine- or alkali-metal- filled pores. Thermodynamically metastable compounds can be formed by this approach and these are not accessible through conventional solution or solid-state synthesis techniques. A recent synthetic highlight has been the preparation of TiGaPO-1 (Fig. 1), the first example of a titanium gallophosphate with a 3-D framework structure, which undergoes topotactic oxidation at low temperatures in a single-crystal-to-single-crystal transformation.

Fig 1: TiGaPO-1.  $\text{Ti}^{\text{III}}\text{O}_4(\text{H}_2\text{O})_2$  (pink),  $\text{Ti}^{\text{IV}}\text{O}_6$  (red),  $\text{GaO}_4$  (yellow) and  $\text{PO}_4$  (magenta) units link to form a 3-D octahedral-tetrahedral hybrid framework containing a 1-D pore network in which pyridinium cations reside.

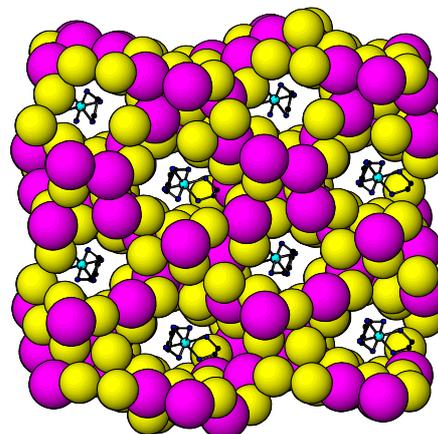
A.M. Chippindale, M.R. Grimshaw, A.R. Cowley and A.V. Powell, *Inorg. Chem.*, **44**, 4121 (2005).



Organically templated antimony sulphides have also been prepared by solvothermal methods in collaboration with Prof. AV Powell, Heriot Watt University. Antimony sulphides commonly exhibit low-dimensional structures and contain structural motifs based on  $\text{SbS}_3$  pyramidal units linked into chains or layers. We have recently prepared and characterised the first examples of truly three-dimensional structures. One material,  $[\text{M}(\text{en})_3][\text{Sb}_{12}\text{S}_{19}]$  ( $\text{M} = \text{Co}, \text{Ni}$ ) (Fig. 2), represents the first sulphide-based zeolite-like structure. This remarkable framework contains one-dimensional circular channels with a cross-section of *ca.*  $5\text{\AA}$ , a distance comparable with the dimensions of the channels in the commercially important zeolite, ZSM-5.

Fig 2:  $[\text{Co}(\text{en})_3][\text{Sb}_{12}\text{S}_{19}]$ .<sup>3</sup> Space filling representation of a 3-D antimony-sulphide framework showing the 1-D pore network in which transition-metal complex cations reside.

P. Vaqueiro, A.M. Chippindale, and A.V. Powell, *Inorg. Chem.*, **43**, 7963 (2004).



A further area of great current interest is transition-metal cyanide chemistry. Work in this field is carried out in collaboration with Dr Simon Hibble.

## Recent Publications

- **A.M. Chippindale, L.E. Head and S.J. Hibble**, Simple Linear Asymmetrical Complexes of Silver(I):  $\text{NC-Ag-NH}_3$  and  $\text{Br-Ag-NH}_3$ , *Chem. Commun.*, article online May 2008. DOI: [10.1039/b803500h](https://doi.org/10.1039/b803500h).
- **F.O.M. Gaslain, K.E. White, A.R. Cowley and A.M. Chippindale**, Control of framework stoichiometry in MeGaPO laumontites using 1-methylimidazole as structure-directing agent, *Microporous and Mesoporous Materials*, **112**, 2008, 368.
- **A.V. Powell, R.J.E. Lees and A.M. Chippindale**, Structure determination, magnetic and optical properties of a new chromium(II) thioantimonate,  $[\text{Cr}(\text{tren})]\text{Sb}_4\text{S}_7$ , *J. Phys. Chem. Solids*, **69**, 2008, 1000.
- **S.J. Hibble, A.M. Chippindale, A.H. Pohl and A.C. Hannon**, Surprises from a simple material - the structure and properties of nickel cyanide, *Angew. Chemie Int. Ed.*, **46**, 2007, 7116-7118.
- **F.O.M. Gaslain and A.M. Chippindale**, *Catena*-Poly[bis(ethane-1,2 diammonium)[manganese(II)-di- $\mu$ phosphato- $k^4\text{O}:\text{O}']$ : a one-dimensional manganese phosphate, *Acta Cryst.*, **C63**, 2007, m537-m540.
- **R.J. Lees, A.V. Powell, and A.M. Chippindale**, The Synthesis and Characterisation of Four New Antimony Sulphides Incorporating Transition-Metal Complexes, *J. Phys. Chem. Solids*, **68**, 2007, 1215-1219.
- **A.M. Chippindale**, Poly(2,2'-bipyridine- $\kappa^2 N,N'$ )( $\mu_2$ -hydrogen phosphato)( $\mu_2$ -dihydrogen phosphato)-aluminium(III),  $\text{Al}(2,2'\text{-bipy})(\text{HPO}_4)(\text{H}_2\text{PO}_4)$ , a layered inorganic-organic hybrid material, *Acta Cryst.*, **C62**, 2006, m372-m374.

- **Chippindale, A.M., Hibble, S.J., Pohl, A.H. and Bilbé, E.J.** Dicaesium pentacyanotricuprate(I),  $\text{Cs}_2\text{Cu}_3(\text{CN})_5$ . *Acta Cryst.*, **E62**, 2006, i140-i142.
- **Chippindale, A.M.** Poly(2,2'-bipyridine- $\kappa_2$  N,N')(  $\mu_2$ -hydrogen phosphato)(  $\mu_2$ -dihydrogen phosphato)-aluminium(III),  $\text{Al}(2,2'\text{-bipy})(\text{HPO}_4)(\text{H}_2\text{PO}_4)$ , a layered inorganic-organic hybrid material. *Acta Cryst.*, **C62**, 2006, m372-m374.
- **Lees, R.J., Powell, A.V. and Chippindale, A.M.** 1,4,8,11-Tetracyclotetradecane antimony(III) sulfide. *Acta Crystallography*, **C63**, 2006, m27-m28.
- **Pohl, A.H., Chippindale, A.M. and Hibble, S.J.** New Copper (I) Cyanide Networks: Interpenetration, Self-Penetration and Polymorphism. *Solid State Science*, **8**, 2006, 379-387.
- **Powell, A.V., Lees, R.J. and Chippindale, A.M.** Macrocyclic amines as structure directing agents for the synthesis of 3-D antimony-sulfide frameworks. *Inorganic Chemistry*, **45**, 2006, 4261-4267.
- **Hibble, S.J. and Chippindale, A.M.** , The threading of  $[(\text{CuCN})_2(\mu\text{-}4,4'\text{-bipyridyl})]$  sheets by CuCN chains, *Z. Anorg. Allg. Chem.*, **631**, 2005, 542-545.
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- **Puls, A., Schaefer, M., Nather, C., Bensch, W., Powell, A.V., Boissière, S., and Chippindale, A.M.**, Solvothermal syntheses, crystal structures and properties of five new thioantimonates(III) containing the  $[\text{Sb}_4\text{S}_7]^{2-}$  anion, *J. Solid State Chem.*, **178**, 2005, 1171.
- **Chippindale, A.M., Grimshaw, M.R., Cowley, A.R., and Powel, A.V.** , Topotactic oxidation of TiGaPO-1, a pyridine-templated titanium gallophosphate with a new octahedral-tetrahedral 3-D framework structure containing  $\text{Ti}^{\text{III}}/\text{Ti}^{\text{IV}}$ , *Inorg. Chem.*, **44**, 2005, 4121-4123.
- **Lees, R.J.E., Powell, A.V. and Chippindale, A.M.**, The synthesis and characterisation of two new iron thioantimonates:  $[\text{Fe}(\text{en})_3]_2\text{Sb}_2\text{S}_5 \cdot 0.55\text{H}_2\text{O}$  and  $[\text{Fe}(\text{en})_3]_2\text{Sb}_4\text{S}_8$ , *Polyhedron*, **24**, 2005, 1941-1948.
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- **A.M. Chippindale and S.J. Hibble**, Bending, twisting and breaking CuCN chains to produce framework materials: the reactions of CuCN with alkali-metal halides, *Inorganic Chemistry*, **43**, 2004, 8040-8048.
- **Vaqueiro, P., Darlow, D.P., Powell, A.V. and Chippindale, A.M.** Solvothermal synthesis of novel antimony sulphides containing  $[\text{Sb}_4\text{S}_7]^{2-}$  units. *Solid State Ionics*, **172**, 2004, 601.
- **Hibble, S.J., Eversfield, S.G., Cowley, A.R., and Chippindale, A.M.** Copper (I) Cyanide: a Simple Compound with a Complicated Structure and Surprising Room-Temperature Reactivity, *Angew. Chem. Int Ed.*, **43**, 2004, 628-630.