

## Mixed-Valence Copper Cyanide Polymers – Successes, Surprises and Disappointments

Our goal is the synthesis of mixed-valence copper cyanide frameworks with incorporation of  $\text{Cu}^{\text{II}}$  complexed with amine bases into the framework, leading to a neutral network able to accommodate small neutral guest molecules. We have synthesized and determined the X-ray structures of some 25 new compounds, characterized also by infrared spectroscopy, and in some cases by CHN analyses, thermal gravimetric analysis, and electron spin resonance. About two-thirds of our structures include both  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  atoms, with typical molecular formulas  $\text{Cu}_n(\text{CN})_{n+1}\text{L}_2$ , where L is a bidentate base. 3D mixed-valence frameworks occur in just a few cases. The majority of these mixed-valence structures involve either monomeric molecular complexes, 1D chains or ribbons, or 2D networks. The remaining structures involve anionic 2D or 3D  $\text{Cu}^{\text{I}}$  networks, with guest cations comprised of either protonated bases or  $\text{Cu}^{\text{II}}$  complex ions, and molecular formulas such as  $[\text{BH}][\text{Cu}_2(\text{CN})_3]$ . In one intriguing case, the base N,N'-dimethylpropylenediamine appears to have reacted with cyanide to form a cyclic guanidinium cation, in a reaction perhaps catalyzed by the copper cyanide moieties in the aqueous reaction mixture.

Peter Corfield  
Joseph Dayrit  
Michael Gleeson  
Christina Sheedy  
Thomas Stavola

Fordham University