

Poster Presentation

MS55.P05

2-D cyanides from square planar $M(\text{CN})_4$ units ($M(\text{II}) = \text{Ni}, \text{Pd}, \text{Pt}, \text{Cu}$)

A. Chippindale¹, S. Hibble¹, E. Marelli¹

¹Reading University, Department of Chemistry, Reading, UK

The binary cyanide, $\text{Cu}(\text{CN})_2$, has never been synthesised. However, by using $\text{Ni}(\text{CN})_4^{2-}$ as a structural synthon, copper(II) can be stabilised in a cyanide-only environment in $\text{CuNi}(\text{CN})_4$ and in the solid-solution $\text{Cu}_x\text{Ni}_{1-x}(\text{CN})_2$ ($0 \leq x < 1/4$). The atomic structure of the layers in $\text{CuNi}(\text{CN})_4$ and the stacking relationship between nearest-neighbour layers have been determined from total neutron diffraction studies at 10 and 300 K. The structure consists of flat layers of square-planar, ordered $[\text{Ni}(\text{CN})_4]$ and $[\text{Cu}(\text{CN})_4]$ units. (NB it is very unusual to find Cu(II) in a genuine square-planar environment within an extended solid). The layered structure of this new material is closely related to those of the Group 10 cyanides, $\text{Ni}(\text{CN})_2$, $\text{Pd}(\text{CN})_2 \cdot x\text{NH}_3$ and $\text{Pt}(\text{CN})_2 \cdot x\text{H}_2\text{O}$, except that these are generated from vertex-sharing square-planar metal-cyanide units with head-to-tail disorder of the $\text{C}\equiv\text{N}$ groups. The overall appearance of the powder X-ray diffraction pattern of $\text{CuNi}(\text{CN})_4$, including the unusual peak shapes of the observed Bragg reflections, has been successfully explained using models incorporating stacking disorder between next nearest neighbour layers. $\text{CuNi}(\text{CN})_4$ forms less extended sheets than $\text{Ni}(\text{CN})_2$ [1, 2], but larger sheets than those found in $\text{Pd}(\text{CN})_2 \cdot x\text{NH}_3$ and $\text{Pt}(\text{CN})_2 \cdot x\text{H}_2\text{O}$, which are nanocrystalline [3]. $\text{CuNi}(\text{CN})_4$, like $\text{Ni}(\text{CN})_2$ [1], shows interesting thermal expansion behavior i.e. intralayer negative thermal expansion ($\alpha_a = -9.7 \text{ MK}^{-1}$) and interlayer positive thermal expansion ($\alpha_c = +89 \text{ MK}^{-1}$). $\text{CuNi}(\text{CN})_4$ forms as an anhydrous material from aqueous solution, unlike $\text{Ni}(\text{CN})_2$, which can form hydrates such as $\text{Ni}(\text{CN})_2 \cdot n\text{H}_2\text{O}$ ($n = 3, 3/2, 2, 1$). However, on investigating the Cu-Ni-CN phase diagram, it is found that nickel-rich compounds, $\text{Cu}_x\text{Ni}_{1-x}(\text{CN})_2$ ($0 \leq x < 1/4$), can be formed via hydrated phases, $\text{Cu}_x\text{Ni}_{1-x}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$, and readily rehydrate. Attempts to form copper-rich phases results in partial reduction of Cu(II) with the formation of copper(I) cyanide, CuCN , in addition to $\text{CuNi}(\text{CN})_4$, suggesting that Cu(II) ions are stable in a cyanide environment only when connected to the nitrogen ends of bridging $\text{C}\equiv\text{N}$ ligands. Hence the non existence of $\text{Cu}(\text{CN})_2$ can now be explained.

[1] Hibble S. J., Chippindale A. M., et al. (2007). *Angew. Chem. Int. Ed.*, 46, 7116-7118., [2] Goodwin A. L., Dove M. T.; et al. (2009). *Phys. Rev. B: Condens. Matter*, 80, 054101/1-054101/7., [3] Hibble S. J., Chippindale A. M., et al. (2011) *Inorg. Chem.* 50, 104-113.

Keywords: total neutron diffraction, mixed-metal cyanide, negative thermal expansion