

Poster Presentations

[MS27-P02] CuNi(CN)₄: A 2-D Cyanide Framework Containing Cu(II) in a Square-Planar Environment.

Ann M. Chippindale, Simon J. Hibble and Elena Marelli;

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK.

Email: a.m.chippindale@rdg.ac.uk

The binary cyanide, Cu(CN)₂, does not exist. However, copper(II) can be stabilised in a cyanide-only environment in the stoichiometric, mixed copper-nickel cyanide, CuNi(CN)₄, and in the solid-solution, Cu_{1-x}Ni_{1+x}(CN)₄ ($\frac{1}{2} \leq x < 1$).

The atomic structure of the layers in CuNi(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 perfectly square-planar [Ni(CN)₄] and [Cu(NC)₄] units linked by shared cyanide groups *i.e.* both the metal and cyanide groups are perfectly ordered with Cu(II) coordinated to the nitrogen end of the cyanide group and Ni(II) to the carbon end. The layered structure of this new mixed-metal cyanide is related to those of Ni(CN)₂, which forms more extended sheets [1, 2], and Pd(CN)₂·xNH₃ and Pt(CN)₂·xH₂O, which form nanosheets [3].

The overall appearance of the powder X-ray diffraction pattern, including the unusual peak shapes of the observed Bragg reflections, has been successfully explained using models incorporating stacking disorder between next nearest neighbour layers. CuNi(CN)₄ shows similar thermal expansion behaviour to that observed previously for Ni(CN)₂ [1,4] with negative thermal expansion within the layers ($\alpha_a = -9.7 \text{ MK}^{-1}$) and positive thermal expansion between the layers ($\alpha_c = +89 \text{ MK}^{-1}$) measured over the temperature range 200-540 K.

The stability of Cu(II) atoms in a cyanide-only environment has been investigated by varying the ratio of the Cu²⁺ and Ni²⁺ ions used in the synthesis. Using a Cu:Ni ratio of 1:1, the

anhydrous phase, CuNi(CN)₄, is precipitated directly. For Cu:Ni ratios less than one, hydrates of the form Cu_{1-x}Ni_{1+x}(CN)₄·yH₂O ($\frac{1}{2} \leq x < 1$; $y \leq 6$) are produced which can be dehydrated to form the corresponding anhydrous compounds, Cu_{1-x}Ni_{1+x}(CN)₄. These compounds readily rehydrate. Replacement of Cu²⁺ by Ni²⁺, which occurs when the Cu:Ni ratio is less than one, leads to the creation of [Ni(NC)₄] units. These in turn readily hydrate to form six-coordinated [Ni(NC)₄(H₂O)₂] groups similar to those found in nickel-cyanide hydrates, such as Ni(CN)₂·3H₂O [1,5]. [Ni(CN)₄] units do not hydrate; hence CuNi(CN)₄, which contains such units, is not found in a hydrated form. With Cu:Ni ratios above one, partial reduction of the Cu(II) occurs to form LT-CuCN [6], in addition to CuNi(CN)₄. This result further confirms that Cu(II) ions can only be stabilised when connected to the nitrogen ends of bridging cyanide ligands and are unstable when connected to the carbon ends. Hence Cu(CN)₂ is unstable.

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