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CuCN: A Polymorphic Material. Structure of One Form Determined from Total Neutron Diffraction

Simon J. Hibble,*,† Simon M. Cheyne,† Alex C. Hannon,‡ and Sharon G. Eversfield†

Department of Chemistry, University of Reading, Reading RG6 6AD, U.K., and ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, U.K.

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CuCN has been found to be polymorphic. The structure of one form, which is isomorphous with AgCN, has been determined using the information provided by Bragg and diffuse neutron scattering. The polymorph of CuCN formed has been found to depend on the Cu/CN ratio used in its preparation.

In an age when structure solution appears to have become routine, even for complex biological molecules, it is humbling to discover that there are many "simple" inorganic compounds whose structures remain unknown. Copper cyanide, CuCN, is an example of such a material. It would seem reasonable to suppose that it should adopt a structure related to those of AgCN and AuCN,[1,2] which contain one-dimensional linear M$-$(CN)$-$M$-$(CN)$-$M$-$(CN) chains, and there is evidence to support this from EXAFS,[3] NMR and NQR,[4] and infrared spectroscopy studies.[1] There is, however, no crystal structure determination to confirm this, or to define the relationship between the MCN chains, which differentiates the structures of AgCN and AuCN. This is despite the fact that there were early reports of the preparation of single crystals of CuCN.[5,6] CuCN, as prepared by Bowmaker et al.[1] and us, is a highly disordered material, and polycrystalline samples of CuCN yield only poor quality Bragg diffraction data unsuitable for simple Rietveld analysis. However, as we report here, total neutron diffraction, in which the complete diffraction pattern is Fourier transformed to produce an interatomic correlation function, can be used in combination with the information available from Bragg diffraction to determine the structure of CuCN. We recently applied this method to determine accurate interatomic distances in AgCN,[2] which is also a highly disordered material, and for which Rietveld analysis on its own had not yielded a satisfactory description of the structure. Others, for example, Egami,[7] have also used total diffraction data to study disordered crystalline materials.

Copper cyanide was synthesized using the method of Bowmaker et al.[1] The infrared spectrum, collected as a Nujol mull over the range 400$-$4000 cm^{-1}, was in agreement with that of Bowmaker et al.,[1] with an intense absorption due to the CN stretch at 2170 cm^{-1}. The powder X-ray diffraction pattern collected at room temperature was typical of a poorly crystalline material, and the most distinctive feature was an intense reflection with $d = 3.012$ Å. The position of this reflection, along with a number of much weaker reflections with $d = 3.729$, 3.189, 3.153, 2.605, and 2.353 Å, was in agreement with the d-values reported for CuCN in the powder diffraction file.[8] However, these weaker peaks had much lower relative intensities, when compared to the peak with $d = 3.012$ Å, than reported previously, and there were additional weak reflections observed at $d = 3.538$, 2.189, 1.738, and 1.605 Å. Neutron diffraction data were collected at room temperature and 10 K on the time-of-flight neutron diffractometer GEM[9] at the ISIS Facility (Rutherford Appleton Laboratory). Rietveld analysis was carried out using data from the 90° detector bank over the d-spacing range 0.53$-$3.09 Å. These data are shown in Figure 1, along with the calculated profile for our final Rietveld model.

The distinct scattering, $i(Q)$, for CuCN was obtained by merging the data from detector banks at 20°, 60°, and 90° (up to a maximum Q of 40 Å^{-1}) which had been normalized to absolute scattering units, after correcting for multiple scattering, attenuation, and inelasticity using the ATLAS suite

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* To whom correspondence should be addressed. E-mail s.j.hibble@rdg.ac.uk.

† University of Reading.

‡ Rutherford Appleton Laboratory.

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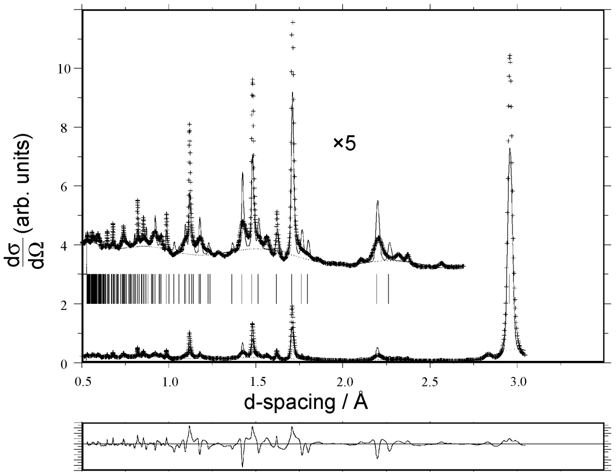

Figure 1. Final fitted profiles (+, observed; −, calculated) from Rietveld refinement for CuCN at 10 K shown in upper frame. Vertical tick lines indicate the positions of the allowed reflections. The lower frame shows the residuals (($I_{\mathrm{obs}} - I_{\mathrm{calcd}}$)/s.u.) for the fit.

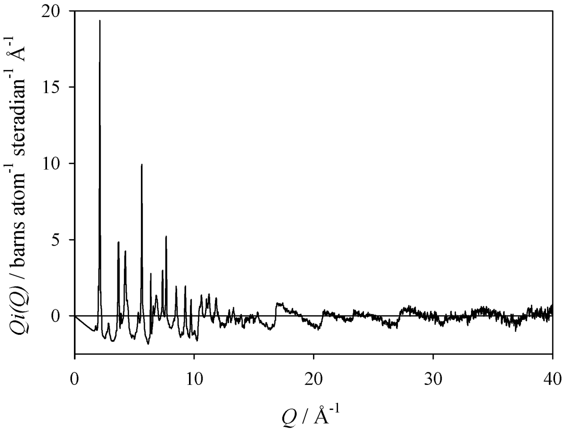

Figure 2. Interference function, $Qi(Q)$, for CuCN at 10 K.

of programs.[10] A fuller description of the reduction and analysis of total neutron diffraction data can be found elsewhere.[9,11] Figure 2 shows the interference function, $Qi(Q)$, for CuCN ($Q = 2\pi/d$). The Bragg diffraction peaks are clearly visible, and a saw-tooth-like diffuse scattering can also be seen, particularly at higher Q.

Cooling from room temperature to 10 K has a very large effect on the Bragg diffraction pattern of CuCN, and many more Bragg peaks were visible at low temperature. By comparing the 10 K data set with that previously obtained for AgCN, we were able to index all but one of the sharp peaks in the diffraction pattern as the *hk*0 reflections of a hexagonal unit cell. These reflections had all moved to smaller *d*-spacings on cooling. The remaining sharp peak at $d = 1.64$ Å, which had moved in the opposite sense, was indexed as the 003 reflection. This information allowed us to determine the unit cell parameters for CuCN. Further information was obtained from the total correlation function, $T(r)$, obtained via a Fourier transformation of the interference function. Peaks in $T(r)$ correspond to frequently occurring interatomic distances in the sample.[10] Figure 3 shows the experimental total correlation function, $T(r)_{\mathrm{exp}}$, for CuCN at 10 K.

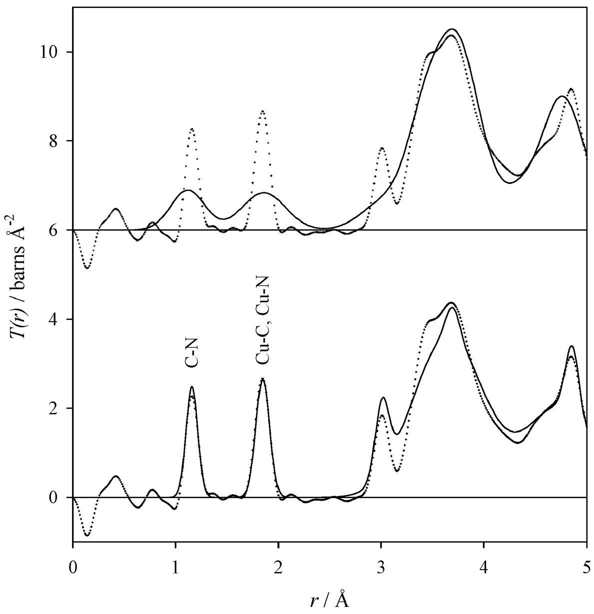

Figure 3. Top: $T(r)_{\mathrm{exp}}$ for CuCN (···), and $T(r)_{\mathrm{Riet}}$ (—) for our Rietveld model. Bottom: $T(r)_{\mathrm{exp}}$ for CuCN (···), and $T(r)_{\mathrm{model}}$ (—) for our final model incorporating both Rietveld and $T(r)$ information.

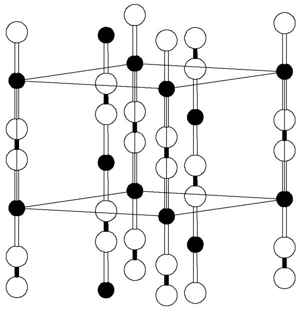

Figure 4. Structure of CuCN (●, Cu; ○, C/N). Light lines indicate the unit cell, and the *c*-axis lies up the page.

The peak centered at 1.17 Å corresponds to the C−N distance in the cyanide ion, and the peak centered at 1.85 Å, to Cu−C and Cu−N distances. Using this information and the unit cell derived from Bragg diffraction, we constructed a model in the space group $R\bar{3}m$, which we have previously used to describe the structure of AgCN. Figure 4 shows the structure of CuCN, which is isostructural with AgCN.[1,2] The top part of Figure 3 shows the correlation function, $T(r)_{\mathrm{Riet}}$, calculated[12] using only the parameters derived from Rietveld refinement. Clearly, the Rietveld thermal parameters lead to gross overestimates of the widths of the sharper peaks in $T(r)$. This discrepancy in widths arises, as for AgCN,[2] because there is a large degree of interchain disorder, even at 10 K. The bottom part of Figure 3 shows a model correlation function, $T(r)_{\mathrm{model}}$, which is based on the structure from Reitveld refinement, except that the C≡N correlation, the other intrachain correlations, and the interchain correlations have been broadened with root-

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Table 1. Structural Parameters[a] Obtained in the Rietveld Refinement[b] and Used to Produce the Total Correlation Function, $T(r)_{\text{model}}$, for CuCN in $R\bar{3}m$, and Selected Bond Distances

	Rietveld 10 K	$T(r)$ modeling 10 K
$z_{\text{C/N}}$	0.3847(7)	0.3797
$r_{\text{Cu-C/N}}$/Å	1.870(3)	1.846
$r_{\text{C-N}}$/Å	1.121(5)	1.170

[a] $a = 5.912(3)$ Å, $c = 4.86107(3)$ Å; Cu at (0,0,0); C and N at (0,0,z); $B_{\text{Cu}} = 2.3(2)$ Å^2; $B_{\text{C/N}} = 1.0(2)$ Å^2; $Z = 3$. [b] $R_{\text{wp}} = 0.3031$, $R_{\text{exp}} = 0.0079$ and $R_{\text{I}} = 0.3155$, background Chebyshev polynomials, 143 reflections.

mean-square displacements, $\langle u^2\rangle^{1/2}$, of 0.019, 0.044, and 0.276 Å, respectively. The large difference between the $\langle u^2\rangle^{1/2}$ values for the intra- and interchain correlations arises from the large degree of disorder between the chains. Table 1 contains details of our model.

The correlation functions $T(r)_{\text{exp}}$ and $T(r)_{\text{model}}$ are in good agreement, showing that the local structure in CuCN is well described by our model. A notable feature of the structure is that the M−N and M−C distances must be nearly identical in this material, in agreement with previous EXAFS[3] and NMR studies,[4] and as we also found in AgCN.[2] Unfortunately, this makes it impossible to obtain information from our $T(r)$ data on the head-to-tail disorder of the CN groups found by Kroeker et al. using NMR and NQR.[4] This type of disorder, along with the large degree of static disorder between the chains, leads to the very high and physically unrealistic atomic thermal factors we find when we fit the Bragg diffraction using Rietveld refinement. However, the most serious problem with Rietveld refinement is that it yields positional and thermal parameters that are incorrect because they do not account for $T(r)_{\text{exp}}$; see Table 1 and Figure 3.

Close inspection of the Rietveld fit to the Bragg diffraction data shows a number of unexplained weak Bragg peaks, two of which accord with the weak peaks assigned to CuCN in two early reports on CuCN crystals[6,7] and are also seen in our room-temperature powder X-ray pattern at $d = 2.605$ and 2.353 Å. We therefore wondered if these extra weak Bragg peaks could arise from another form of CuCN. If this were correct, it would explain why no unexplained features were found in $T(r)$, because the distances found at low r might be expected to be similar in different polymorphs of the same compound. Any small differences would be very difficult to detect when the second phase is present only as a minor impurity. In an attempt to determine more about the nature of the impurity in our sample of CuCN, we repeated our preparation but varied the Cu/CN ratio. We found that when excess cyanide was present we obtained a product which gave a powder X-ray pattern in agreement with those reported in the powder diffraction file[7] and with single-crystal measurements reported previously.[6,7] This product also appears identical to that sold by Fluka as CuCN. Comparison of the powder X-ray patterns of the two forms of CuCN, Figure 5, shows that our neutron sample is composed predominantly of a poorly crystalline form of CuCN, α-CuCN, which is isostructural with AgCN, contaminated with a small quantity of the more highly crystalline form β-CuCN.

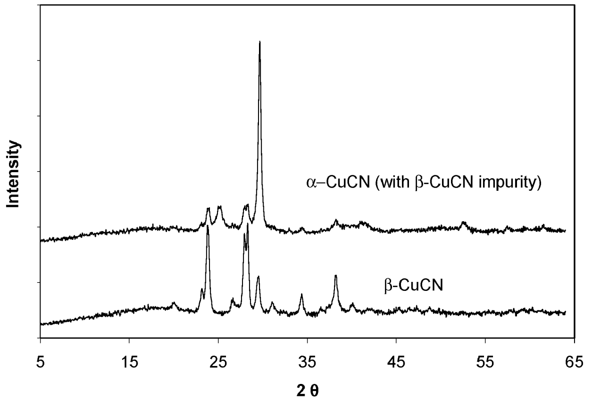

Figure 5. Powder X-ray patterns of the two polymorphs of CuCN collected at room temperature using Cu Kα radiation.

β-CuCN corresponds to the phase whose powder X-ray pattern has been reported previously. The observed density of β-CuCN[6] of 2.97 g cm^{-3} is close to that of 3.03 g cm^{-3} calculated for α-CuCN from our low-temperature neutron diffraction results. Although this suggests a close structural similarity of the two forms of CuCN, we have not yet been able to determine the structure of β-CuCN.

Note Added in Proof. After submission of this manuscript, Wang et al.[13] determined a structure for α-CuCN in space group $R3m$ by Bragg X-ray diffraction. Although their conclusion that α-CuCN has a chain structure is correct, the derived Cu−C and Cu−N bond lengths are at variance with the equal distances determined here. This is due to the limitations of using Bragg diffraction in isolation to study the structure of disordered crystalline materials. The choice of space group to describe the structure of CuCN is problematical because local symmetry depends on the orientation of the CN groups around Cu. Our description of the average structure in $R\bar{3}m$, with C and N having 50/50 occupancies of the same site, has the advantage of emphasizing the equivalence of the Cu−C and Cu−N bond lengths.

Supporting Information Available: Full experimental details of sample preparation and further details of the Rietveld refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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