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Beyond Bragg Scattering: The Structure of AgCN Determined from Total Neutron Diffraction

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Total neutron diffraction has yielded accurate bond lengths, Ag–C = Ag–N = 2.06 Å and C–N = 1.16 Å, for the disordered crystalline solid AgCN. This information cannot be obtained from analysis of Bragg scattering studies, because the $(-Ag-CN-)_n$ chains are randomly displaced along the chain axis relative to each other by a root-mean-square displacement of 0.24 Å at 10 K. These results show the power of total neutron diffraction for determining structure in disordered systems.

It is always surprising to find that the structures of simple compounds are unknown or that the published structures contain serious deficiencies. The group 11 cyanides AgCN, CuCN, and AuCN are examples of such materials. All three materials are believed to contain one-dimensional linear M−(CN)−M−(CN)−M−(CN)− chains,[1,2] and this has been confirmed for AgCN and AuCN, in a recent powder neutron diffraction study published in *Inorganic Chemistry* by Bowmaker et al.[3] Figure 1 shows the basic structure of AgCN.

However, the three cyanides are highly disordered, and we have found that the published bond lengths are wrong. We attribute this to the fact that Bragg scattering studies on their own, as used in the work of Bowmaker,[3] are incapable of yielding the correct interatomic distances in highly disordered compounds. In this work we demonstrate how total neutron diffraction (in which both the Bragg and diffuse scattering are Fourier transformed to produce an interatomic correlation function) can, in combination with conventional Bragg scattering studies, yield more accurate interatomic distances and a more complete structural description of AgCN.
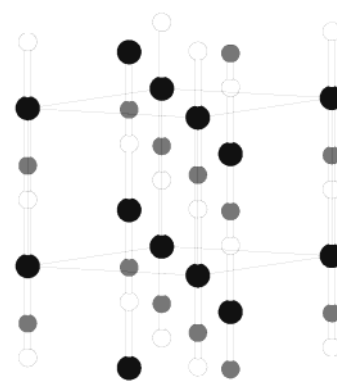

Figure 1. The structure of AgCN (open circles C, solid circles Ag, gray circles N) after Bowmaker.[3] Light lines indicate the unit cell, and the *c* axis lies up with the page.

Silver cyanide was synthesized using the method described by Bowmaker et al.[3] Neutron diffraction data were collected at room temperature and 10 K on the time-of-flight neutron diffractometer GEM at the ISIS Facility (Rutherford Appleton Laboratory). Data for total neutron diffraction were obtained by merging the data from detector banks at 20°, 60°, and 90° (up to a maximum Q of 35 Å^{-1}) normalized to absolute scattering units, after correcting for detector dead-time, multiple scattering, attenuation, and inelasticity using the ATLAS suite of programs.[4] A fuller description of the reduction and analysis of total neutron diffraction data can be found elsewhere.[5] Data for Rietveld analysis were obtained by focusing the data from the 90° detector bank. Figure 2 shows the interference function, $Qi(Q)$, for AgCN ($Q = 2\pi/d$). The Bragg diffraction peaks are clearly visible, and the sawtooth-like diffuse scattering can also be seen, particularly at higher Q.

The total correlation function, $T(r)$, may be obtained via a Fourier transformation of the interference function. Peaks in $T(r)$ correspond to frequently occurring interatomic distances in the sample.[5] Figure 3 (top) shows the experimental total correlation function, $T(r)_{exp}$, for AgCN, com-

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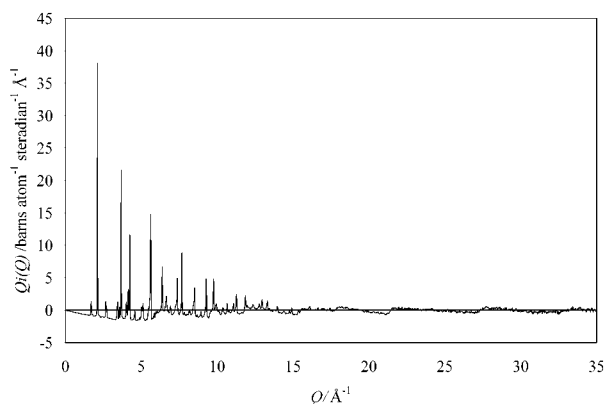
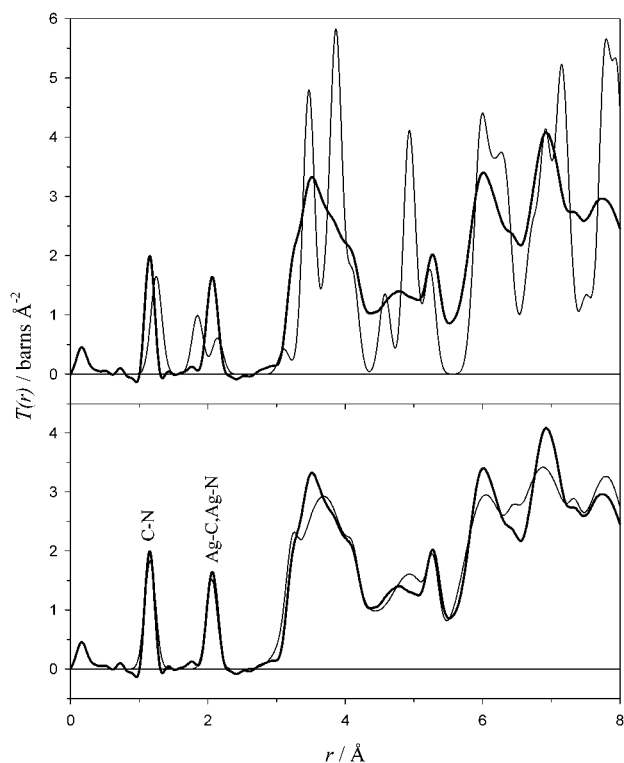**Figure 2.** The interference function, $Qi(Q)$, for AgCN at 10 K.

Table 1. Structural Parameters Used To Produce the Total Correlation Function, $T(r)_{model}$, for the Different Models,[a] and Selected Bond Distances

	this work 10 K		
	Rietveld		$T(r)$ modeling
space group	$R3m$	$R\bar{3}m$	$R\bar{3}m$
a/Å	5.9021	5.9032	5.9032
c/Å	5.2842	5.2829	5.2829
z_C	0.4221	0.3837^b	0.3899^b
z_N	−0.3635		
d_{Ag-C}/Å	2.230	2.027	2.06
d_{Ag-N}/Å	1.920	2.027	2.06
d_{C-N}/Å	1.133	1.229	1.16

[a] Ag at (0,0,0); C and N at (0,0,z). [b] 50/50 C/N.

Figure 3. Top: $T(r)_{exp}$ for AgCN (bold line), and $T(r)_{model}$ (light line) from Bowmaker et al.'s crystal structure. Bottom: $T(r)_{exp}$ for AgCN (bold line), and $T(r)_{model}$ (light line) for our model.

structure in AgCN, see Table 1. Head to tail disorder of cyanide groups, as has been found in CuCN,[2] appeared to us to be a likely source of disorder in AgCN. We incorporated this type of disorder into our modeling by carrying out Rietveld refinements in space group $R\bar{3}m$. This was only partially successful; although these refinements produced a slightly more physically reasonable structural model, the final parameters still did not yield interatomic distances in agreement with $T(r)_{exp}$. Furthermore, in all our Rietveld refinements, the anisotropic temperature factors along the chain axis were unphysically large, as were Bowmaker et al.'s isotropic temperature factors.[3]

We produced a much better structural model by taking the basic structural framework determined from analysis of the Bragg scattering and adjusting the atomic z parameter for C and N to fit $T(r)_{exp}$, see Table 1. The success of this approach can be seen in Figure 3 (top), in which $T(r)_{model}$ was produced by broadening the intrachain and interchain correlations with root-mean-square displacements, $\langle u^2 \rangle^{1/2}$, of 0.056 and 0.24 Å respectively. The large difference between the $\langle u^2 \rangle^{1/2}$ values for the two types of correlation show that there is a large degree of disorder between the chains even at 10 K. This disorder, combined with head to tail disorder, leads to the very high temperature factors found in Bragg diffraction studies, and the impossibility of using such studies in isolation to determine the true local structure in AgCN. Interchain disorder becomes extremely high at 300 K, because of the weak interactions between the chains, and features due to these correlations become very broad. However, the peaks due to intrachain correlations remain reasonably sharp, and there is little change in $d_{Ag-C/N}$ and d_{C-N} with temperature. The 10 K data set is presented here since it presents a more stringent test of our model due to the sharper correlation function peaks.

There are other techniques, such as extended X-ray absorption fine structure (EXAFS) or magnetic resonance, which can yield information on local structure. However, the random displacements of the chains in the direction of the chain axis would not be apparent in the results of an EXAFS experiment, because of the relatively large interatomic distances and the very large displacements involved. Total diffraction has the advantage that it can probe correlations over a large range of length scales and, because it measures data closer to the origin of reciprocal space (i.e.,

pared to a model correlation function, $T(r)_{model}$, calculated using the space group, positional parameters, and lattice parameters of Bowmaker et al., Table 1. The calculated correlation function, $T(r)_{model}$, has been broadened assuming a root-mean-square atomic displacement, $\langle u^2 \rangle^{1/2}$, of 0.056 Å. $T(r)_{exp}$ is model independent and yields information on interatomic distances without recourse to any ordered crystalline model. In this "simple" material the peak around 1.15 Å can be ascribed to the C−N distance and that around 2.07 Å to both Ag−C and Ag−N correlations. It is clear that the structure determined by Bowmaker using only Bragg diffraction data is in error; the C−N and Ag−C distances are too long, and the Ag−N distance is too short.

As with Bowmaker et al.'s work,[3] Rietveld refinement of our powder neutron diffraction data at both 10 and 300 K in space group $R3m$ yielded an incorrect description of the local

low Q), it is not nearly so adversely affected by large thermal and static displacements. CuCN has been profitably studied by a combination of NMR and NQR,[2] showing that there is head−tail C−N disorder, but this study did not yield accurate information on interatomic distances or any information on the interchain structural relationship. It would be interesting to study AgCN using magnetic resonance to gain further information on head to tail disorder in this material.

By modeling the results from total neutron diffraction studies of AgCN, we have found that the Ag−C and Ag−N bond lengths must be nearly identical and equal to 2.06 Å, in contrast to previous work[3] in which the Ag−C and Ag−N bond lengths were reported to be 2.15 and 1.86 Å, respec-

tively. The C−N bond length of 1.16 Å is comparable to the value, 1.15 Å, found in the $Ag(CN)_2^-$ ion in $Na Ag(CN)_2$[6] and much more realistic than the value of 1.26 Å found by Bowmaker et al. Accurate bond lengths for AgCN and the other group 11 cyanides are essential if we wish to discuss the bonding and understand the vibrational spectra of these materials. We are at present determining the structures of the related cyanides, CuCN and AuCN, using total neutron diffraction.

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