

# Synthesis, Thermal and X-Ray Investigations of the High-Temperature Phase of Copper(I) Cyanide

Olaf Reckeweg<sup>a</sup>, Cora Lind<sup>a</sup>, Arndt Simon<sup>b</sup>, and Francis J. DiSalvo<sup>a</sup>

<sup>a</sup> Baker Laboratory, Department of Chemistry and Chemical Biology Cornell University, Ithaca, NY 14853-1301, USA

<sup>b</sup> Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart

Reprint requests to Dr. O. Reckeweg. E-mail: olaf.reykvjavik@gmx.de

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CuCN was investigated by chemical analysis, IR spectroscopy and powder X-ray diffraction. A high-temperature phase of CuCN was identified and structurally characterized by Rietveld refinement. HT-CuCN is isotypic to AgCN (*R* $\bar{3}m$  (No. 166), *Z* = 3, *a* = 597.109(8), *c* = 484.33(5) pm, Cu (3a), C/N (6c), *z* = 0.3915(10) at 77 K) with head-tail disorder of the cyanide anions.

**Key words:** Copper, Cyanide, Structure Elucidation, Thermal Properties, Optical Spectroscopy

## Introduction

It is rather hard to believe that the quest for the structure of a “textbook compound” like CuCN (which was first reported almost 200 years ago [1]!) is still not at its successful end. Extensive NMR experiments [2] showed that the structure contains linear chains with ‘head-tail’ disordered cyanide anions. Recently, Raman, TG/DTA and X-ray experiments were performed on CuCN that was freshly precipitated from aqueous solution [3]. In this paper, the symmetric C $\equiv$ N stretching frequency is given with  $\nu = 2172\text{ cm}^{-1}$ , which is in good agreement with previous literature data ( $\nu = 2169\text{ cm}^{-1}$  [4] and  $\nu = 2173\text{ cm}^{-1}$  [2], respectively). All X-ray powder patterns indicate that the structure has low symmetry. The data closely resemble the two previously reported patterns [5,6], the resolution is improved compared to the older data probably due to somewhat improved crystallinity of the material. However, complete structure elucidation was not possible because of the still poor crystallinity of the material. No improvement in crystallinity was achieved by attempts to use solvothermal methods to recrystallize CuCN since this always seems to result in the formation of adducts [7].

While it seems reasonable to assume that CuCN would adopt a structure similar to AgCN and AuCN on the basis of the NMR data, none of the diffraction patterns reported in the literature could be completely indexed on the basis of a trigonal cell. Some authors attributed this difficulty to the presence of a second phase

of CuCN or of a hydrate (CuCN) $_3\cdot\text{H}_2\text{O}$  [8]. However, in TG/DTA experiments on as precipitated CuCN no mass loss is observed below 600 K. The DTA curve displayed two endothermic effects at 565 K and 754 K with no mass loss in the first case and 23% loss in the second step. The second effect at 754 K agreed well with the reported decomposition temperature of 750 K [5], while the effect at 565 K seemed to correspond to a reversible phase transition which, however, is kinetically hindered in the reverse direction. The two phases below and above 565 K will be referred to as LT-CuCN and HT-CuCN throughout this paper.

The only previous attempt to elucidate the structure of CuCN using powder data was carried out with total neutron diffraction by Hibble *et al.* on as precipitated material [8]. The data showed that the HT-CuCN phase was already present to a certain degree, but the refinement was of poor quality indicating either the presence of yet another phase or a different structure. Here we report the results of our efforts to determine the crystal structure of HT-CuCN from powder data.

## Experimental Section

NaCN (Merck, p.a.), CuSO $_4\cdot 5\text{H}_2\text{O}$  (Alfa, 99%), Na $_2\text{S}_2\text{O}_5$  (Sigma-Aldrich, > 99%) and CuCN (Aldrich, 99.99%) were commercially available and used as received.

To prepare CuCN, we used a procedure similar to that described in the literature [2, 3]. No differences in color or behavior were observed between our sample and the commercially available CuCN. The compound showed a faint

greenish tint. The material precipitated at room temperature was transformed into HT-CuCN by heating a 250 mg sample (sealed under vacuum in a fused silica ampoule) to 600 K for 12 h, and then quenching to RT. The color of the sample changed during this process from faint green to greyish-white.

Chemical analyses were performed on LT-CuCN using ICP-OES for Cu, hot-extraction analyses for O<sub>2</sub> and N<sub>2</sub>, and combustion analyses in an O<sub>2</sub> stream for C. The calculated contents of CuCN (Cu/C/N = 71.0/13.4/15.6 wt.%) agreed reasonably well with the analytical data given by the vendor of the commercially available CuCN (Cu = 70.67%, C and N content not analyzed) and in principal with our results (commercial sample: 70.8(7)/15.0(45)/9.0(45) wt.%, sample synthesized for this work: 70.2(7)/15.0(45)/10.5(45) wt.%). The O content proved in both cases to be less than 0.02 mol O per mol CuCN. Thus, the composition of the material we used is indicated by the analyses as Cu<sub>1.0</sub>C<sub>1.1</sub>N<sub>0.7</sub>. The N content deviated from the expected value probably due to the formation of (CN)<sub>2</sub> or N<sub>2</sub> during the extraction process. It is apparent that the analytical technique is not optimized for C or N analyses of such samples.

IR spectra were recorded on the LT-CuCN and HT-CuCN on a Mattson Polaris FT-IR spectrometer (KBr pellet and diffuse reflectance technique).

*In situ* X-ray data were collected on an as precipitated CuCN sample sealed in a 0.2 mm thin-walled quartz glass capillary under argon on a Guinier-Simon camera [9] equipped with a flexible image plate in the temperature range from 293 to 723 K. The temperature was raised smoothly, and the image plate was moved continuously while ramping the temperature.

X-ray powder data were also collected on CuCN flatbed samples with silicon as an internal standard on a Scintag XDS-2000 powder diffractometer with a Scintag Low-High Temperature stage. Data were obtained between 77 and 573 K. A refinement scan was collected at 77 K to minimize thermal disorder.

## Results

Our previous TG/DTA results, which showed that the samples did not contain a hydrated copper cyanide phase, but only very small amounts of superficially adsorbed water, was corroborated by the results of chemical analyses.

IR spectroscopy showed also no indication of water being present. The symmetric stretching mode was found at the very same wavenumber for LT- and HT-CuCN. By diffuse reflectance spectroscopy we found the frequency to be  $\nu_s = 2171 \text{ cm}^{-1}$ , by the KBr technique it was determined to be  $\nu_s = 2168 \text{ cm}^{-1}$ .

Table 1. Results from Rietveld analysis of the 77 K X-ray powder diffraction data for HT-CuCN.

Compound	CuCN
Space group; Z	$R\bar{3}m$ , (166), 3
Lattice constants $a, c$ [pm]	597.109(8), 484.33(5)
Density [gcm <sup>-3</sup> ]	2.983
Diffractometer; temperature	Scintag XDS-2000; 77.0(1) K
Monochromator; radiation	None, Cu-K $\alpha_1$
Refinement range [°]	$15 \leq 2\theta \leq 110$
Datapoints	4750
Observed reflections	32
Fitted parameters	36
$R_P, R_{wp}, R(F^2) / \%; \chi^2$	2.9, 4.2, 8.9; 5.9

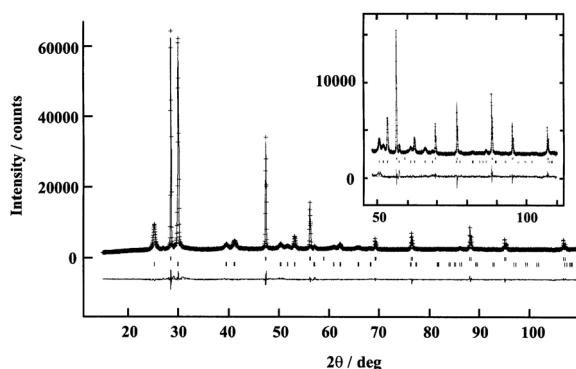


Fig. 1. Rietveld refinement results for HT-CuCN. Crosses represent observed data, the solid line the calculated fit, and the tick marks correspond to the reflection positions for Si (upper marks) and HT-CuCN (lower marks). The difference curve is plotted at the bottom.

Investigations on LT-CuCN with a Guinier Simon camera showed a phase transition to HT-CuCN around 550 K. At higher temperatures, decomposition was observed as evidenced by peak broadening and the evolution of an amorphous hump. The patterns observed above  $\sim 570$  K were identical to those of a sample that had been annealed at 573 K and quenched.

The X-ray patterns could be indexed on the basis of a trigonal cell with lattice constants  $a = 597.11$  and  $c = 484.33$  pm at 77 K, suggesting that the compound is isostructural to AgCN [3,10]. The published structural parameters for AgCN were used as a starting model for Rietveld refinements with the program GSAS [11]. The initial fit was poor. A convincing fit to the data could be obtained using the anisotropic peak broadening options supplied by the GSAS program suite. The results of the Rietveld refinement of the 77 K data for HT-CuCN are given in Fig. 1 and Tables 1–3.

Atoms	Wyckoff-site	$x/a$	$y/a$	$z/a$	$U_{\text{iso}} [\text{\AA}]$
Cu	3a	0	0	0	0.715(15)
C / N	6c	0	0	0.3915(10)	0.025(22)
Atoms	d [pm]	Atoms	d [pm]	Atoms	d [pm]
Cu-C/N	189.6(5)	Cu-Cu	380.7(8)	C/N-C/N	105.1(10)

Table 2. Atomic positions, isotropic displacement factors and selected distances of HT-CuCN

Table 3. Temperature dependence of the lattice constants of HT-CuCN. The values for 10 K are taken from [8].

$T$ [K]	$a$ [pm]	$c$ [pm]	$V$ [ $10^6 \cdot \text{pm}^3$ ]
10	591.2(3)	486.107(3)	147.1
77	596.02(2)	484.7(1)	149.1
173	597.64(2)	484.2(1)	149.8
273	601.56(2)	483.0(1)	151.4
323	604.38(3)	483.1(1)	152.8
373	605.81(2)	481.3(1)	153.0
423	608.26(2)	480.7(1)	154.0
473	610.59(3)	480.0(2)	155.0
523	613.18(5)	479.6(3)	156.2
573	615.09(5)	478.8(4)	156.9

No structural changes were observed between the room temperature and 77 K data for HT-CuCN. However, the peak movements indicated highly anisotropic expansion behavior. Analysis of variable temperature X-ray data collected between 77 and 573 K confirmed that HT-CuCN shows normal positive expansion along  $a$  and small negative expansion along the  $c$  axis, leading to an overall positive volume expansion.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49(0)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412668 (HT-CuCN).

## Discussion

As in AgCN, the structure of HT-CuCN consists of linear  $\text{—Cu—X}\equiv\text{X—Cu—}$  chains (X stands for disordered C/N) with 'head-tail' disorder of the cyanide anions. Each chain is surrounded by six other chains which are shifted relative to each other by  $1/3c$  (see Figure 2). The closest Cu—Cu contact is 383.3 pm. This structure is also very similar to that of AuCN [4], which is made up of linear polymeric  $\text{—Au—X}\equiv\text{X—Au—}$  chains with possible 'head-tail' disorder, but without a relative shift of the chains. The Au atoms form 2D close packed layers which are held together by the cyanide anions. The closest Au—Au contact is 339.6 pm.

The high-temperature form of CuCN must be closely related to the room-temperature form since it

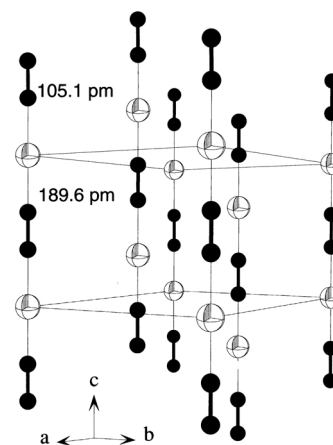


Fig. 2. Crystal structure of HT-CuCN.

has been established by NMR-experiments [2] that LT-CuCN also contains  $\text{—Cu—X}\equiv\text{X—Cu—}$  chains with 'head-tail' disorder of the cyanide anions. This is backed up by the fact that both forms show only one symmetric  $\text{C}\equiv\text{N}$  stretching mode at virtually the same wavenumber. It seems possible that LT-CuCN exhibits a lower symmetry 3D arrangement of these chains with significant disorder, which would explain the poor crystallinity of the LT phase. This is supported by the good fit that Hibble *et al.* could obtain for their total correlation function, which only measures interatomic distances (*e.g.* local environments, which should be similar in both phases), while the agreement between their diffraction data and a fit based on the AgCN structure was not convincing [8]. According to the presented X-ray data their sample contained a mixture of HT- and LT-CuCN. Their lattice constants for HT-CuCN measured at 10 K fit well into our refined values (see Table 3).

It is interesting to note that the  $a$  lattice constant and the cell volume of HT-CuCN increase with temperature as expected, whereas the  $c$  lattice constant decreases. This behaviour can be associated with a pronounced precession of the disordered cyanide anions around  $(0,0,1/2)$ , leading to expansion perpendicular to the  $\text{Cu—X}\equiv\text{X—Cu}$  chains and contraction along the  $\text{Cu—X}\equiv\text{X—Cu}$  chains. Similar behavior has been

observed, *e. g.* for  $C_2^{2-}$  [12]. The structure of LT-CuCN remains elusive.

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