Polymorphs of CuCN

Copper(I) Cyanide: A Simple Compound with a Complicated Structure and Surprising Room-Temperature Reactivity**

Simon J. Hibble, Sharon G. Eversfield, Andrew R. Cowley, and Ann M. Chippindale**

The structural chemistries of CuCN, AgCN, and AuCN are much more complex than might be anticipated for compounds of such simple formulae. This is particularly true for the first member of the group, CuCN, for which the situation has been complicated by the existence of more than one polymorph and the mistaken identification in the literature of copper(I) cyanide hydrates as additional polymorphs. The structure of solid CuCN has long been presumed to consist of -Cu–CN–Cu–CN- chains, by analogy with the structures of the other group 11 cyanides[1–3] and with supporting evidence from a wide range of techniques including NMR spectroscopy,[4] nuclear quadrupole resonance (NQR),[4] extended X-ray absorption fine-structure spectroscopy (EXAFS)[5] and vibrational spectroscopy.[3] However, it was not until 2002 that the structure of what is now known to be the high-temperature form of CuCN (HT-CuCN) was determined.[6–8] This phase can, under certain conditions, be prepared at room temperature[8] and is also formed irreversibly from the low-temperature polymorph (LT-CuCN) at 563 K. HT-CuCN is isomorphous with AgCN[3,9] and structurally related to AuCN,[3,10] and consists of hexagonally packed infinite linear -(Cu–CN)- chains with adjacent chains displaced by $\pm 1/3$ along the chain axis. Although the basic structures of all three materials are simple, disorder, which includes large static and thermal displacements of the chains and "head-to-tail disorder" of the CN groups (that is, NC versus CN), made the structure determinations problematical. Nevertheless, using total diffraction[8–10] and NMR spectroscopy experiments,[4,11] the average and local structures of these three cyanides has now been well determined.

Surprisingly, the structure of LT-CuCN, which is sold as "copper(I) cyanide" by chemical companies, such as Fluka and Aldrich, has so far proved elusive, even though a report of the preparation of single crystals appeared as long ago as 1957.[12] Herein we report for the first time the structure of LT-CuCN and the interconversion of LT- and HT- forms at room temperature via an isolable intermediate phase, $KCu_2(CN)_2Br\cdot H_2O$. The relationship between all three structures is discussed.

Single crystals of LT-CuCN were grown from polycrystalline LT-CuCN under hydrothermal conditions at 433 K employing KCN as a mineralizer.[13] The structure is curious and consists of infinite CuCN chains, each containing five crystallographically distinct Cu atoms, which form waves with a repeat corresponding to nine CuCN units (Figure 1).

Refinement of C and N occupancies was possible and indicated "head-to-tail" disorder of the cyanide groups, as observed in related materials.[4,10,11] The bond lengths appear reasonable (Cu–C/N 1.839(9)–1.872(12) Å, C≡N 1.148(12)–1.177(13) Å) and are in good agreement with those found in HT-CuCN.[8] Unlike in HT-CuCN, where the bond angles are fixed by symmetry at 180°, in LT-CuCN they deviate slightly from linearity (N/C-Cu-C/N 176.7(3)–179.0(5)°, C-N-Cu 174.0(8)–179.3(7)°). The combination of these small local deviations leads to significant divergence from linearity for the chain as a whole. The chains stack parallel to each other with the waves "in phase" to form layers lying in the *ac* plane. The chain axes in adjacent layers are rotated by 49° (Figure 2a and b). As the local geometries (i.e. the bond lengths and angles around the Cu, C, and N atoms) in LT-CuCN are very similar to those in HT-CuCN,[7,8] the infrared and Raman spectra are therefore almost identical. A notable feature of LT-CuCN is that it shows negative thermal expansion of the *a* axis reflecting the strength and nature of the bonding within the chains. We have observed similar effects in HT-CuCN, AgCN, and AuCN.[10,17] It is a curiosity that the cell volumes per CuCN unit are, within experimental error, identical over the temperature range 150–300 K, which is in contrast to the assumption that the more thermodynamically stable phase will have the lower volume.

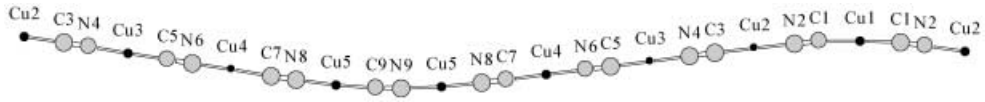

Figure 1. A portion of a single -(Cu–CN)- chain in LT-CuCN showing the repeat distance of the wave. In reality there is "head-to-tail" disorder of C≡N groups and one possible arrangement is shown.

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The conversion of the LT-CuCN into HT-CuCN requires a major reorganization of the structure to make all the -(Cu–CN)- chains lie parallel and can be achieved by heating above 563 K.[6,7] Interestingly, this transformation can also be carried out at room temperature by stirring polycrystalline LT-CuCN in concentrated aqueous KBr (or NH_4Br) followed by washing with copious amounts of cold water (Scheme 1). Limiting the amount of water used in washing leads to recovery of CuCN predominantly in the low-temperature form. The reactions proceed without dissolution of the CuCN containing species via an intermediate, highly crystalline powdered phase, which undergoes immediate flocculation on

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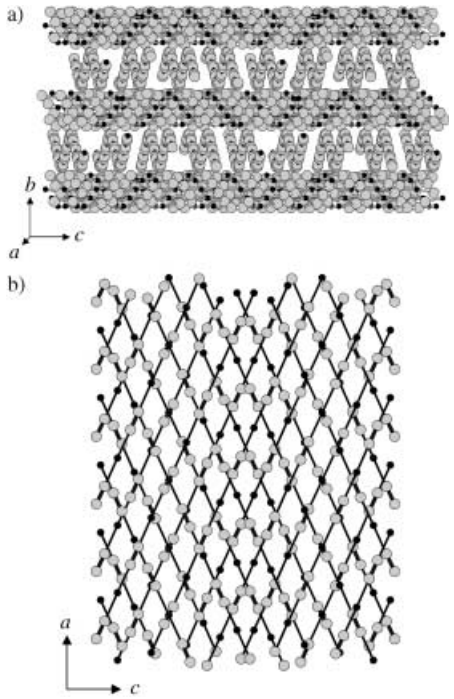
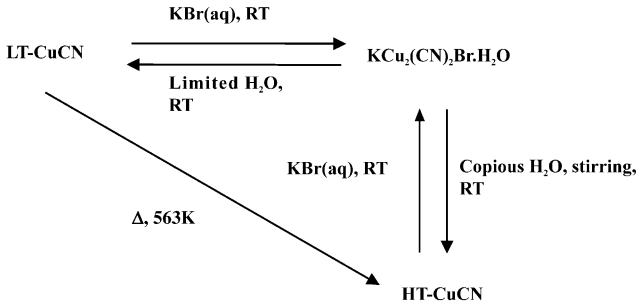


Figure 2. a) A view showing layers of -(Cu–CN)- chains, which lie in the [150] direction. Small black circles represent Cu and large gray circles disordered C/N atoms. b) A view along the *b* axis showing that the -(Cu–CN)- chains in the layers shown in Figure 2a are identical, but are rotated by 49° between adjacent layers (key as in Figure 2a).



Scheme 1. Interconversion of LT- and HT-CuCN.

treatment with water. Stirring HT-CuCN with concentrated aqueous KBr (or NH_4Br) produces the same intermediate. It has proved possible to grow single crystals of the intermediate by heating either HT- or LT-CuCN in concentrated aqueous KBr under hydrothermal conditions at 433 K for a few hours and it has the formula $KCu_2(CN)_2Br{\cdot}H_2O$. The reclamation of CuCN after reactions with aqueous KBr and KI has been studied previously by Bowmaker et al.,[18] but neither the polymorphs of CuCN, nor the nature of the intermediates, were identified. The phase of CuCN that is formed is clearly sensitive to reaction conditions. The work of Wang et al.[6] shows that LT-CuCN is the thermodynamically stable phase below 563 K. In that work[6] it is also shown that HT-CuCN does not convert back into LT-CuCN on cooling. This is not surprising as we can prepare both forms at room temperature. As might be expected more rapid formation of CuCN from $KCu_2(CN)_2Br{\cdot}H_2O$ produces the more highly disordered HT-CuCN form of CuCN.

$KCu_2(CN)_2Br{\cdot}H_2O$ is structurally interesting in its own right for its zeolite-like framework[19] (Figure 3) as well as for its role in the interconversion of LT- and HT-CuCN. The

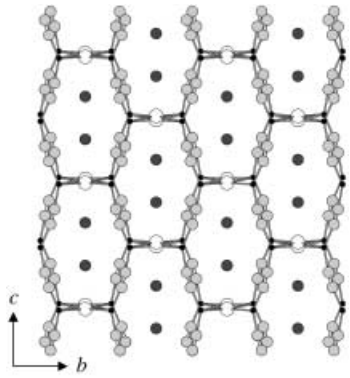


Figure 3. View along the *a* axis of $KCu_2(CN)_2Br{\cdot}H_2O$ showing the open 3D structure generated by linking of -(Cu–CN)- chains (key as in Figure 2) by Br atoms (open circles). K^+ ions (large black circles), and water (not shown) reside in the pores.

-(Cu–CN)- chains observed in both forms of CuCN are retained in this intermediate compound and similarly exhibit "head-to-tail" disorder in the cyanide groups (Cu–C/N 1.892(3) and 1.884(4) Å, C≡N 1.158(5) Å). Additional bonding to two bromine atoms gives rise to distorted tetrahedral coordination around the Cu atom (Cu–Br 2.6643(6) and 2.7014(6) Å, Br-Cu-Br′ 88.564(14)°) and severe bending of the -(Cu–CN)- chains (N/C-Cu-C/N 147.10(15)°; Figure 4). The bromine atoms serve to link adjacent -(Cu–CN)- chains together to generate a 3D framework of formula $[Cu_2(CN)_2Br]^-$ containing pores in which K^+ and H_2O reside. The K^+ ion is coordinated by two water molecules (K···O 2.803(5) and 2.896(5) Å) and one framework bromine atom (K···Br 3.299(1) Å), with additional rather weak interactions to nitrogen (K···N separations lie in the range 3.272(3)–3.387(4) Å). Given the rather poor coordination around the K^+ ion, it is not too surprising that this ion can be "washed out" together, by necessity, with the Br^- ion. Remarkably, it appears that the -(Cu–CN)- chains are retained during this process.

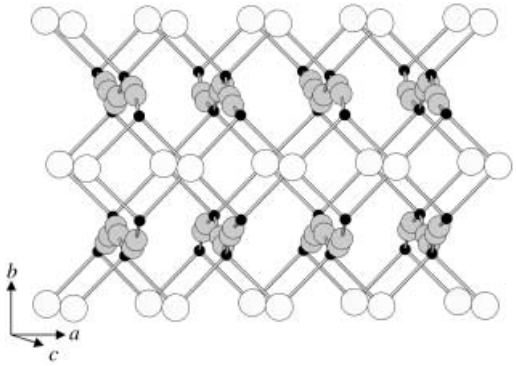


Figure 4. A view of the CuCNBr framework of $KCu_2(CN)_2Br{\cdot}H_2O$ showing the -(Cu–CN)- chains and the square planar arrangement of Cu atoms around each Br atom (key as in Figure 3).

In summary, the structure of the most commonly occurring form of CuCN has been solved. The chemical interconversion between this and the high-temperature disordered form of CuCN has been achieved at room temperature using aqueous KBr and the structure of the open framework intermediate, $KCu_2(CN)_2Br.H_2O$, determined. Further work will include using total neutron diffraction to determine whether dynamic wavelike motions of -(Cu–CN)- chains, similar in form to the static waves found in LT-CuCN, account for the negative thermal expansion in the chain direction in HT-CuCN.[7]

Experimental Section

LT-CuCN. Small colorless crystals (too small for X-ray analysis) were obtained on heating CuCN (0.5 g, 55 mmol, polycrystalline LT-CuCN, Fluka) with KCN (0.02 g, 0.3 mmol) in H_2O (10 mL) in a Teflon liner in an autoclave at 433 K for 6 days. Addition of further KCN (0.02 g) and reheating for 14 days produced a mixture of products including colorless blocks. These blocks were very fragile and broke into plates when touched with a steel needle. One of these plates was used for the single-crystal X-ray study.[13] The powder X-ray pattern generated from this structural study is in excellent agreement with the pattern measured for both commercial and laboratory-prepared polycrystalline LT-CuCN (see Supporting Information).

Vibrational spectra for polycrystalline samples of copper cyanide: LT-CuCN. IR (Nujol): ν(CN) 2166(vs), 2118 cm^{-1} (m); Raman: ν(CN) 2177(vs), 2114 (vvw); δ(MCN) 332 (vw, sh), 321 cm^{-1} (w); HT-CuCN. IR (Nujol): ν(CN) 2167(vs), 2120 cm^{-1} (m, sh); Raman: ν(CN) 2177(vs), 2121(vvw); δ(MCN) 332(vw, sh), 321 cm^{-1} (w).

$KCu_2(CN)_2Br{\cdot}H_2O$. Single crystals of $KCu_2(CN)_2Br{\cdot}H_2O$ were obtained from either LT- or HT-CuCN under hydrothermal conditions. CuCN (0.19 g, 21 mmol) was added to a KBr solution (10 mL, 3.2 M) and heated in an autoclave at 433 K for 24 h. The sample was collected by filtration and allowed to dry without washing. The solid product consisted of colorless hexagonal plates of $KCu_2(CN)_2Br{\cdot}H_2O$, suitable for diffraction studies[19] as the majority phase. Beige polycrystalline samples, were prepared by stirring CuCN (0.75 g, 82 mmol, LT- or HT-) in a KBr solution (25 mL, 3.2 M) for 2 h, at room temperature, filtering, and washing with further KBr solution. Powder X-ray patterns could be fully indexed on the basis of the unit cell determined in the single-crystal study[19] with additional lines from KBr confirming that the products from LT- or HT-CuCN are identical (see Supporting Information); IR (Nujol): $\tilde{\nu} = \nu$(OH) 3580(w), 3553(vw); ν(CN) 2112(s); $\delta(OH_2)$ 1607(s); $\rho(OH_2)$ 524 cm^{-1} (s).

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[13] Crystal Data for LT-CuCN: $C_9Cu_9N_9$, $M_r = 806.13$, $\rho_{calcd} = 2.988\ mg\,m^{-3}$, orthorhombic, $C\ 222_1$, $Z = 4$, $a = 7.9024(5)$, $b = 12.6403(8)$, $c = 17.9364(13)$ Å, $V = 1791.6$ Å^3 at 150 K (Cell parameters at 293 K: $a = 7.8418(6)$, $b = 12.8045(10)$, $c = 18.1450(14)$ Å, $V = 1821.6$ Å^3). X-ray data collected at 150 K for a colorless rectangular plate (dimensions: $0.03 \times 0.08 \times 0.20$ mm) using an Enraf Nonius Kappa CCD diffractometer (graphite monchromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The data were processed using DENZO/SCALEPACK[14] and a multi-scan absorption correction applied (data range: $(5.160 < \theta < 27.459)°$, 2027 measured reflections, 2017 independent, $T_{min} = 0.38$, $T_{max} = 0.73$). The structure was solved by direct methods[15] and the model refined by full-matrix least-squares analysis.[16] "Head-to-tail" disorder of the C and N atoms of each cyanide group was included in the refinement. 128 parameters were refined, including anisotropic temperature factors for all atoms and the Flack parameter (0.44(7), racemic twin) ($R(F) = 0.0365$ $wR(F) = 0.0416$ using 1391 reflections with $I > 3\sigma(I)$). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-391243.
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[19] Crystal Data for $KCu_2(CN)_2Br{\cdot}H_2O$: $C_2H_2BrCu_2KN_2O$, $M_r = 316.16$, $\rho_{calcd} = 2.887\ mg\,m^{-3}$, orthorhombic, *Pnma*, $Z = 4$, $a = 7.4699(5)$, $b = 10.3199(5)$, $c = 9.4336(5)$ Å, $V = 727.2$ Å^3 at 150 K (Cell parameters at 293 K: $a = 7.5522(4)$, $b = 10.4461(5)$, $c = 9.3825(5)$ Å, $V = 740.2$ Å^3). X-ray data collection and processing as above[13] for a colorless hexagonal plate (dimensions: $0.01 \times 0.08 \times 0.10$ mm, data range: $(5.112 < \theta < 27.473)°$, 1652 measured reflections, 875 independent, $T_{min} = 0.33$, $T_{max} = 0.89$). The hydrogen atom of the water molecule was located in a difference Fourier map. "Head-to-tail" disorder of the C and N atoms of each cyanide group was modeled in the refinement. 51 parameters, including anisotropic temperature factors for all non-hydrogen atoms, were refined ($R(F) = 0.0316$ $wR(F) = 0.0355$ using 671 reflections with $I > 3\sigma(I)$). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413310.

