

Short Note

# Poly[1,3-Dimethyltetrahydropyrimidin-2(1*H*)-iminium [tri- $\mu_2$ -cyanido- $\kappa^6$ C:N-dicuprate(I)]]

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**Abstract:** The title compound contains a guanidinium cation that was unexpectedly found during X-ray single crystal analysis of a copper(I) cyanide network expected to contain protonated *N,N'*-dimethyl-1,3-diaminopropane. The cation was presumably formed by reaction of the amine with cyanide ions in the aqueous sodium cyanide/copper cyanide mixtures used in the synthesis. The structure of the network solid features the guanidinium cation as a guest in an anionic two-dimensional polymeric framework with stoichiometry  $\text{Cu}_2(\text{CN})_3^-$ . Confirmation of the structure was provided by analytical, thermal gravimetric and infrared data.

**Keywords:** copper; cyanide; network; guanidinium; unexpected iminium cation

## 1. Introduction

Polymeric copper(I) cyanide networks with guest cations continue to attract interest in light of their varied topologies and interesting physical properties, including chemiluminescence [1–5]. Our own work on CuCN complexes with amine bases, which initially sought to incorporate  $\text{Cu}^{\text{II}}$  into these  $\text{Cu}^{\text{I}}$  networks to provide neutral polymeric networks, has led to the characterization of both mixed valence CuCN compounds [6] and  $\text{Cu}^{\text{I}}\text{CN}$  networks with protonated amines as guests [7]. We report here the unexpected formation of the cyclic guanidinium complex poly[1,3-dimethyltetrahydropyrimidin-2(1*H*)-iminium [tri- $\mu_2$ -cyanido- $\kappa^6$ C:N-dicuprate(I)]], **1**, during an attempted synthesis of a copper cyanide polymer involving the diamine *N,N'*-1,3-dimethyldiaminopropane. We had originally hoped for the formation of a crystalline mixed valence  $\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}$  cyanide polymer with the  $\text{Cu}^{\text{II}}$  atoms stabilized by coordination of the bidentate amine ligands. The lack of color in the crystalline product indicated, however, that only  $\text{Cu}^{\text{I}}$  was involved, so we suspected that the amine base would be present as its conjugate acid, to provide charge neutrality for an anionic  $\text{Cu}^{\text{I}}\text{CN}$  network, as in the structure reported in reference [6]. Single crystal X-ray diffraction analysis, however, indicated that reaction of the diamine with cyanide had occurred with formation of a cyclic guanidinium cation. Lin et al. have reported a similar structure featuring the unexpected formation of the unsubstituted guanidinium cation [8]. We report here the crystal and molecular structure of **1**, together with chemical analyses, thermal decomposition and infrared data.

## 2. Results

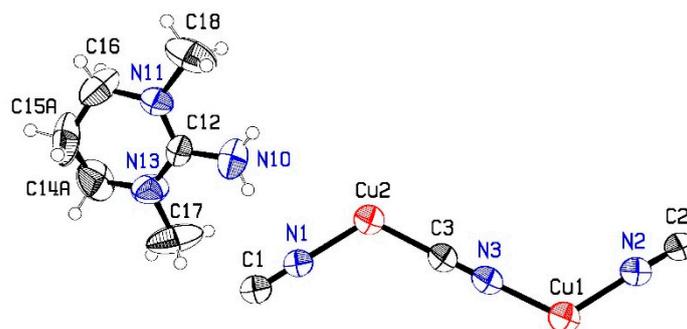
### 2.1. Synthesis

In a typical synthesis: 0.246 g NaCN (5.0 mmol) was dissolved in 2–3 mL water, 0.279 g (3.1 mmol) CuCN was added and the mixture was stirred until all solid had dissolved. Separately, 0.431 g *N,N'*-dimethyl-1,3-diaminopropane was dissolved in 2–3 mL water, and the solution was added slowly

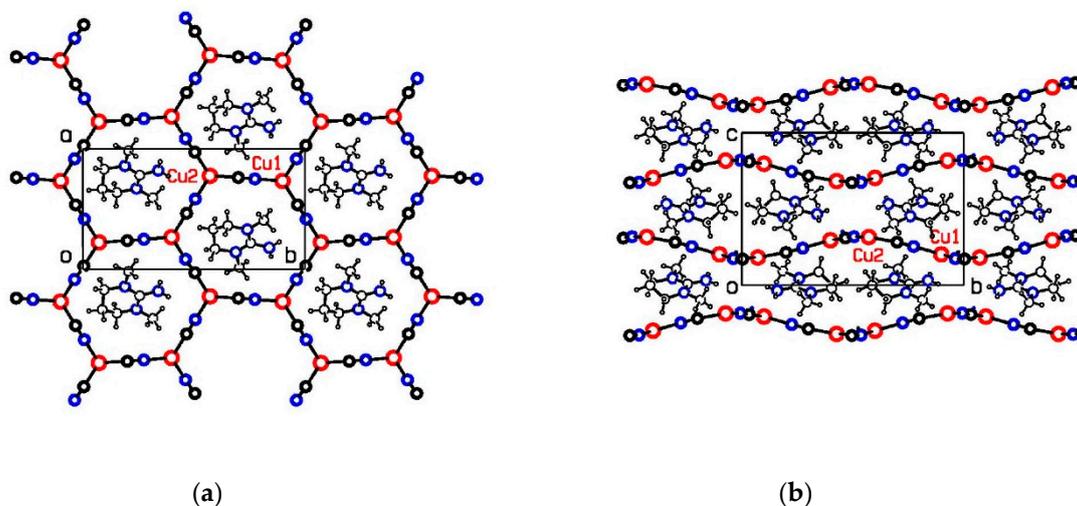
to the NaCN/CuCN mixture. Colorless crystals were usually obtained within a week after filtration and water washing.

## 2.2. X-ray Structure

The single crystal structure indicates a molecular formula  $[\text{LH}][\text{Cu}_2(\text{CN})_3]$ , where  $\text{LH}^+$  is the cyclic guanidinium cation. The asymmetric unit showing thermal ellipsoids and atom numbering is given in Figure 1. The compound crystallizes as a two-dimensional CuCN network with the cations as guests; see Figure 2.



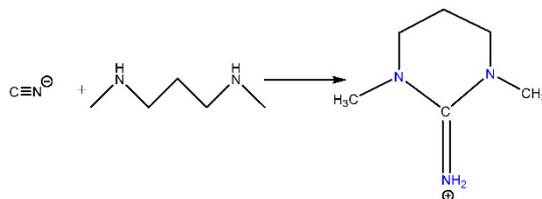
**Figure 1.** Asymmetric unit for compound **1**, showing thermal ellipsoids with 50% probability. Only one orientation of the disordered CN groups is shown. C14 and C15 are also disordered; only the major component is shown.



**Figure 2.** Packing Diagrams for **1**. (a) One CuCN sheet and one cation layer, viewed down the *c* axis. (b) Sheet edges, viewed down the *a* axis. Nitrogen atoms are shown in blue, carbon and hydrogen atoms in black and copper atoms in red. Cu1 and Cu2 are labeled in their reference positions.

The CuCN sheets are made up of 18-membered CuCN rings in a honeycomb arrangement. They are deformed from planarity, evidently in order to accommodate the guanidinium cations and in contrast to the planar sheets found in our earlier work on a similar structure [7]. The sheet deformation occurs with minimum deviation from ideal geometry for the trigonal planar Cu atoms: Cu1 and Cu2 lie only 0.035(2) and 0.073(2) Å above the plane through the three atoms bonded to them, and the angles at the Cu atoms differ from 120° by at most 2.4(1)°. Bonding at the bridging CN groups deviates from linearity by an average of 4.1(1)°, with a maximum of 8.1(2)°.

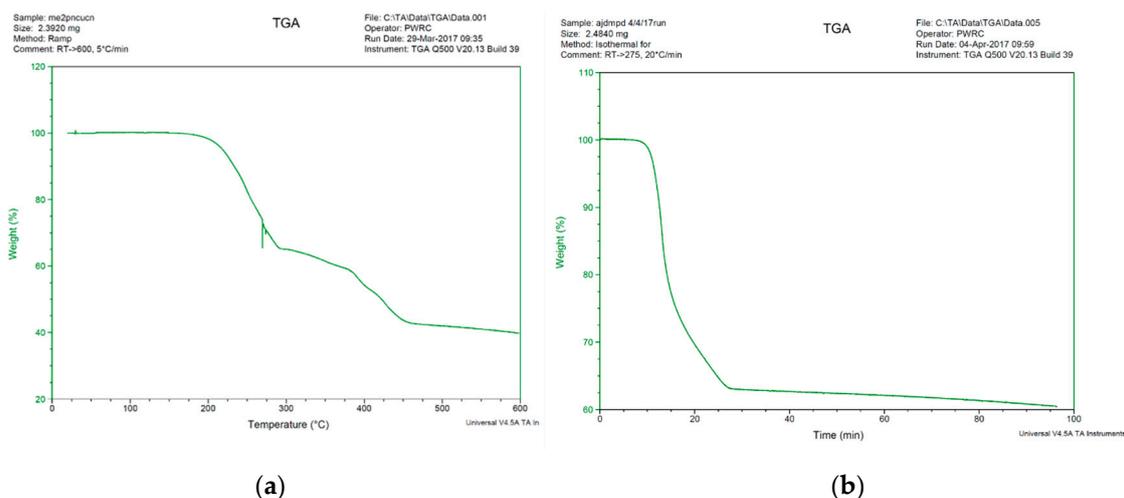
The cation is the cyclic guanidinium cation shown in Figure 1 and not the expected conjugate acid of the base. The new cation appears to have been formed by an oxidation reaction between the cyanide ion and the diamine base:



Perhaps the reaction involves a  $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$  cyanide system as catalyst—the faint blue color of the solutions during slow formation of the product indicated some  $\text{Cu}^{\text{II}}$  being present, presumably from air-oxidation. The central  $\text{CN}_3$  group of the guanidinium cation is rigidly planar, and the C–N bond lengths average 1.318(7) Å, which is close to the expected value. For example, the average C–N distance in a series of some 50 structures containing the guanidinium cation  $\text{CH}_6\text{N}_3^+$  [9] is 1.321 Å. There does not appear to be any significant hydrogen-bonding or other intermolecular interaction between the guanidinium cations and the anionic sheets. The thermal ellipsoids in Figure 1 imply rigid body vibration is occurring about an axis perpendicular to the plane of the molecule, a vibration that would be hampered if the iminium group were involved in significant hydrogen bonding.

### 2.3. Thermal Gravimetric Analysis

On heating a sample of **1** under nitrogen at 50 °C/min to 600 °C, the sample suffered a 38% mass loss by 300 °C, and then further losses in a complex fashion as the mass tended towards the 38% expected for residual  $\text{CuCN}(\text{s})$ ; see Figure 3a. Similarly, a sharp drop in mass of 38% was observed when separate samples were heated rapidly to 225 °C or to 275 °C (Figure 3b) and held at those temperatures for an hour and a half, during which there was only 1–2% further loss.



**Figure 3.** Thermal gravimetric analysis for **1**: (a) 0–600 °C at 50 °C/min, (b) 0–275 °C at 20 °C/min and hold 90 min.

Since the molar mass of  $[\text{LH}][\text{Cu}_2(\text{CN})_3]$  where L is the guanidine base is 333.3 u, the 38% mass loss corresponds to a loss of 127 u, suggesting that the guanidinium cation in **1** loses a proton to form the cyclic guanidine L, with mass 127 u, which is then released. If the cation were the expected protonated dimethylpropanediamine, the mass loss would have been very different. The nature of the remaining solid at 225 or 275 °C is not clear. In similar experiments with an *N*-methylethanolamine complex [10], the sample lost methylethanolamine and HCN gas separately at 200 °C to leave behind  $\text{CuCN}$ , but the  $\text{CuCN}$  in the present case is not formed until much higher temperatures.

#### 2.4. Spectroscopy and Analyses

The infrared spectrum of **1** shows strong absorptions at 2110  $\text{cm}^{-1}$  ( $\text{C}\equiv\text{N}$  stretch) and 3406 and 3497  $\text{cm}^{-1}$  ( $\text{N-H}$  stretch). As expected, the  $\text{C}\equiv\text{N}$  stretches are close to those observed in similar compounds. The  $\text{N-H}$  stretching frequencies are shifted from values in the region 3100–3200  $\text{cm}^{-1}$  found in a number of similar network solids we have made containing protonated amines. Data on infrared data on iminium cations in the literature are sparse, but reference [8] gives  $\text{N-H}$  frequencies at 3427(s), 3325(m), and 3268(m)  $\text{cm}^{-1}$  for the unsubstituted guanidinium cation. A lower value of 3115  $\text{cm}^{-1}$  was quoted for the asymmetric  $\text{N-H}$  stretch in methyl formimidate hydrochloride [11], but the author commented that the low value was likely due to strong  $\text{N-H}\dots\text{Cl}$  hydrogen-bonding. We synthesized the hydrochloride salt of 1,1,3,3-tetramethylguanidine, **2**, by titration of this base with HCl, since the iminium group in this salt should have a similar molecular environment to the iminium cation in **1**. The  $\text{N-H}$  stretches found for **2** were 3107 and 3281  $\text{cm}^{-1}$ . The significant differences in  $\text{N-H}$  frequencies for **1** and the model compound **2** perhaps again reflect  $\text{N-H}\dots\text{Cl}$  hydrogen bonding in **2** compared with the lack of hydrogen bonding to the iminium group in **1**. The presence of the host CuCN network could also affect the IR spectrum of **1**.

Elemental analysis of **1** gave 32.59% $\text{C}$ , 3.68% $\text{H}$  and 25.19% $\text{N}$ , which are comparable with the values calculated for the new product,  $\text{C}_9\text{H}_{14}\text{Cu}_2\text{N}_6$ —32.43% $\text{C}$ , 4.23% $\text{H}$  and 25.22% $\text{N}$ , and differ significantly from values of 31.06% $\text{C}$ , 5.21% $\text{H}$  and 22.64% $\text{N}$  calculated for the expected product  $\text{C}_8\text{H}_{16}\text{Cu}_2\text{N}_5$ , which would have contained the conjugate acid of the dimethyldiaminopropane. Further confirmation of the presence of the guanidinium cation in **1** was found in the density of the crystals, which was found by flotation methods to be 1.692(8)  $\text{g}/\text{cm}^3$ , the same as the value of 1.698  $\text{g}/\text{cm}^3$  calculated from the X-ray data for **1**.

### 3. Experimental

Crystal Data for  $\text{C}_9\text{H}_{14}\text{Cu}_2\text{N}_6$  ( $M = 333.34$  g/mol), crystals cut from colorless rods, monoclinic, space group  $\text{P}2_1/c$  (no. 14),  $a = 8.5598(14)$  Å,  $b = 14.825(4)$  Å,  $c = 10.853(2)$  Å,  $\beta = 108.570(13)^\circ$ ,  $V = 1305.5(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 300(2)$  K,  $\mu(\text{MoK}\alpha) = 3.249$   $\text{mm}^{-1}$ ,  $D_{\text{calc}} = 1.698$   $\text{g}/\text{cm}^3$ ,  $D_{\text{meas}} = 1.692(8)$   $\text{g}/\text{cm}^3$ , 21,730 reflections measured from four crystals ( $2.4^\circ \leq \Theta \leq 27.67^\circ$ , cell dimensions averaged from the four crystals), 3009 unique ( $R_{\text{int}} = 0.052$ ), which were used in all calculations. The final  $R_1$  was 0.0340 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0951 (all data) for 166 variables. The structure was solved by the heavy atom method from a Patterson map calculated with SHELXS and refined with SHELXL Version 2017 [12]. The CN groups were modeled with 50% disorder in their orientation, and a disordered model was also used for two of the three propane C atoms, with restraints on the geometry and temperature factors for atoms at alternative sites; refined occupancies for the A and B occupancies were 65(1)% and 35(1)%. Hydrogen atoms were constrained at idealized positions, riding on the carbon atoms, with C–H distances of 0.96 Å for methyl groups and 0.97 Å for methylene groups, and isotropic temperature factors were 50% larger than the  $U_{\text{eq}}$  of the bonded C atoms. Attempts to refine the iminium H atoms were not successful, so they too were constrained in ideal positions, with N–H distances of 0.86 Å, and  $U_{\text{iso}}$  was again 50% of the  $U_{\text{eq}}$  of the N atom. The cif file for this structure is included in the Supplementary Material for this article and has also been deposited with the Cambridge Crystallographic Data Center as CCDC 2035041. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

### 4. Discussion

This study shows that an unexpected reaction between cyanide ion and  $N,N'$ -dimethyl-1,3-diaminopropane occurred to form a cycle guanidinium cation under the preparative conditions used. We have not found reference elsewhere to the preparation of this cation or to the conjugate base. When syntheses were carried out at lower pH values, a different crystalline

product was obtained, for which X-ray diffraction analysis showed an anionic 3D CuCN network, not 2D, as in this case, the expected protonated diamine was a guest, rather than the guanidinium cation found in the present work. This work will be published elsewhere. Further studies will explore the conditions favoring the reaction described here, and a possible mechanism.

## 5. Materials and Methods

Chemicals were used as obtained from suppliers without further purification. Chemical analysis was performed by Robertson MicroLit (Ledgewood, NJ, USA). FTIR data were obtained with a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), and thermal gravimetric analyses were carried out under nitrogen with a TGA-Q500 instrument (TA Instruments, New Castle, DE, USA). The X-ray structure was determined with diffraction data collected with a Nonius Kappa CCD system (Bruker Axis LLC, Madison, WI, USA) using graphite monochromated MoK $\alpha$  radiation with  $\lambda = 0.7107 \text{ \AA}$ .

**Supplementary Materials:** The following are available online. Figure S1: Checkcif Report, Table S1: MOL File, Table S2: cif file, Figure S2: Infrared spectrum of title compound.

**Author Contributions:** P.W.R.C.: Designed the experiments, carried out the X-ray analysis, analyzed the results and wrote the manuscript. J.R.D.: Carried out the syntheses, thermal analyses, infrared spectra, and the preparation and infrared spectrum of tetramethylguanidinium chloride, **2**. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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