

# A Novel Method for Synthesizing Crystalline Copper Carbodiimide, CuNCN. Structure Determination by X-Ray Rietveld Refinement

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Well-crystallized copper carbodiimide, CuNCN, was synthesized by the slow oxidation of a copper(I) cyanamide precursor under aqueous conditions. The X-ray powder data evidence the orthorhombic system and space group *Cmcm* with  $a = 2.9921(1)$ ,  $b = 6.1782(1)$ ,  $c = 9.4003(2)$  Å,  $V = 173.769(5)$  Å<sup>3</sup> and  $Z = 4$ . There is a strongly distorted octahedral Cu<sup>2+</sup> coordination reflecting a typical first-order Jahn-Teller effect, with interatomic distances of  $4 \times \text{Cu-N} = 2.001(2)$  Å and  $2 \times \text{Cu-N} = 2.613(3)$  Å; the NCN<sup>2-</sup> unit adopts the carbodiimide shape with C-N = 1.227(4) Å. Despite the formal  $d^9$  electron count of Cu<sup>2+</sup>, CuNCN exhibits a small temperature-independent paramagnetism and is likely to be a metallic conductor.

**Key words:** Copper, Cyanamide, Carbodiimide, Rietveld Refinement, Jahn-Teller Distortion

## Introduction

The design and synthesis of new classes of magnetic materials starting from the combination of paramagnetic transition-metal centers with diamagnetic, bidentate bridging ligands to generate extended networks is a very attractive goal for solid-state and coordination chemists. As small nitrogen-containing ligands, the basic anions (NCNH<sup>-</sup>, NCN<sup>2-</sup>) of the cyanamide (H<sub>2</sub>NCN) molecule have been successfully used to prepare a large number of salts comprising alkali metals [1–3], alkaline-earth metals [4–7], main-group elements [8–11],  $d^{10}$  transition metals [12–18], and also rare-earth metals [19–21] *via* widely differing synthetic routes. Nonetheless, the synthesis of cyanamides or carbodiimides of the genuine magnetic transition metals with a *non- $d^{10}$*  electron count appeared as a great challenge, even more so because the structure elucidation and further characterization of the products was expected to broaden our basic knowledge of such a novel class of materials.

According to our experience, transition-metal M<sup>2+</sup> ions ( $d^4 - d^9$ ) prefer to form metal-cyanamide *complexes* such as [M(NCNH<sub>2</sub>)<sub>4</sub>]<sup>2+</sup> ions in aqueous solution, and it is very difficult to further remove the hydrogen atoms from the complex ions in order to yield “MNCN” compounds [22, 23]. Other plausible high-temperature routes are also unsuitable because they

lead to the metal, metal nitride, C and gaseous N<sub>2</sub> but not to “MNCN” phases. To look at this synthetic problem from an alternative point of view, we have recently finished an extensive quantum-chemical study of the complete set of “MNCN” (M = Mn, Fe, Co, Ni, Cu) hypothetical phases [24] from density-functional theory (GGA), and this approach rendered *all* quasi-binary compounds as *unstable* in terms of both formation enthalpy  $\Delta H_f$  and Gibbs formation energy  $\Delta G_f$ . Using that information, we have recently accomplished the successful synthesis of the first magnetic carbodiimide, MnNCN, using a metathesis route involving zinc carbodiimide and manganese(II) chloride as starting materials. The synthetic idea lies in the low melting and also sublimation temperature of the product ZnCl<sub>2</sub> because the latter can be removed from the equilibrium directly upon formation, thereby enforcing MnNCN formation [25].

Because CuNCN has been predicted to be *more* unstable than MnNCN, even softer chemical routes had to be found for a successful synthesis. As mentioned before, Cu<sup>2+</sup> cations merely form coordination complexes such as [Cu(NCNH<sub>2</sub>)<sub>4</sub>]<sup>2+</sup> from which hydrogen atoms can not be abstracted; the alternative reaction of an aqueous copper(II) solution with anionic cyanamide units yields a black material whose amorphous nature renders its structure determination impossible [26, 27]. Fortunately, we have recently pre-

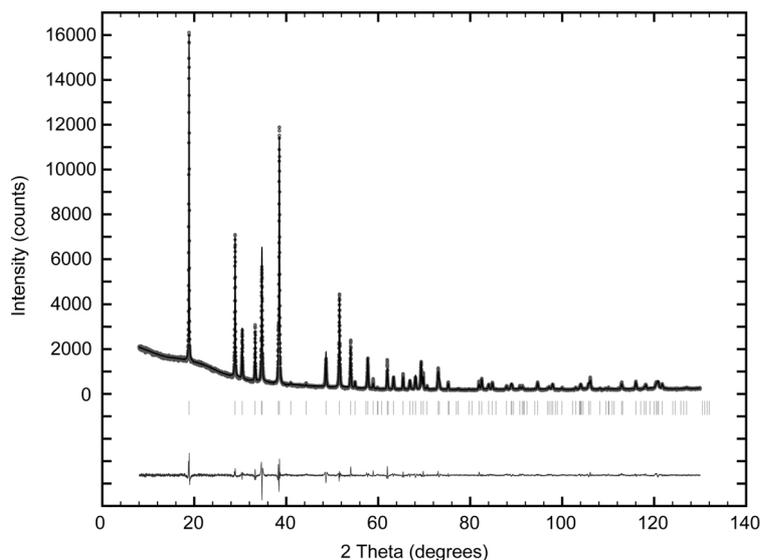


Fig. 1. Observed, calculated, and difference intensities for the X-ray Rietveld refinement of CuNCN. The vertical markers show the positions of the Bragg reflections.

pared a novel ammine copper(I) cyanamide compound,  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  [18], which appeared as a lucrative oxidizable substrate for the target phase CuNCN. Indeed, a slightly modified synthetic route for  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  using a large excess of cyanamide within an ammonia solution leads to perfectly crystalline CuNCN.

### Experimental Section

A clear dark-green aqueous solution (5 ml) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.70 g, 10 mmol) and  $\text{H}_2\text{NCN}$  (0.82 g, 20 mmol) was prepared in a round-bottom flask, and 5 ml of a solution of  $\text{Na}_2\text{SO}_3$  (1.26 g; 10 mmol) was added with stirring; the solution became light-green. Then, a concentrated ammonia solution (25 wt.%) was used to attain a pH around 9 whereupon pale white  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  precipitated. Upon stirring the suspension over night,  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  was slowly oxidized at room temperature by atmospheric oxygen to yield the black CuNCN. It was separated by filtration, washed with water, and dried *in vacuo*. The microcrystalline CuNCN was very well suited for powder X-ray diffraction. Yield: 0.84 g (80% with respect to  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). Analytical data for CuNCN (103.55): calcd. Cu 61.37, C 11.60, H 0, N 27.05; found Cu 61.30, C 11.62, H 0.14, N 27.00. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{NCN}) = 2035$  (s),  $\delta(\text{NCN}) = 595$  (s) and 690 (m).

The X-ray diffraction data of CuNCN were recorded at room temperature by means of a calibrated STOE STADI-P powder diffractometer with strictly monochromatized  $\text{Cu-K}\alpha_1$  radiation and a linear position-sensitive detector (PSD) with a flat sample holder; because of the excellent crystallinity, the range of measurement was a very wide 8–130°

Table 1. Crystallographic data and structure refinement for CuNCN.

Formula; molar mass:	CuNCN; 103.55 g/mol
Crystal color and form:	black powder
Lattice parameters:	$a = 2.9921(1) \text{ \AA}$ $b = 6.1782(1) \text{ \AA}$ $c = 9.4003(2) \text{ \AA}$
Cell volume:	$173.769(5) \text{ \AA}^3$
Space group; formula units:	$Cmcm$ (no. 63); 4
Number of reflections:	98
$R_p$ , $R_{wp}$ , $R_{\text{Bragg}}$ :	0.054, 0.079, 0.045

Table 2. Positional and isotropic displacement parameters for CuNCN with standard deviations in parentheses.

Atom	Wyckoff site	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
Cu	4a	0	0	0	1.35(2)
N	8b	0	0.3826(4)	0.3815(3)	0.77(7)
C	4c	0	0.3889(8)	1/4	0.66(11)

in  $2\theta$  with individual steps of  $0.01^\circ$ . The X-ray powder diagram was indexed using an orthorhombic unit cell with space group  $Cmcm$ . The primary structural model (atomic positions) came from a theoretical prediction [24]. The background of the data set was manually subtracted by linear interpolation, and the FULLPROF program package [28] was used for the Rietveld refinement with a pseudo-Voigt profile function. Using isotropic displacement parameters for all atoms, the residual values arrive at 0.054 ( $R_p$ ), 0.079 ( $R_{wp}$ ), and 0.045 ( $R_{\text{Bragg}}$ ) for a total of 15 variables and 98 Bragg reflections. Tables 1 and 2 contain all important crystallographic data. Additional structural details may be obtained from FIZ Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-415 220. The course of the final Rietveld refinement is shown in Fig. 1.

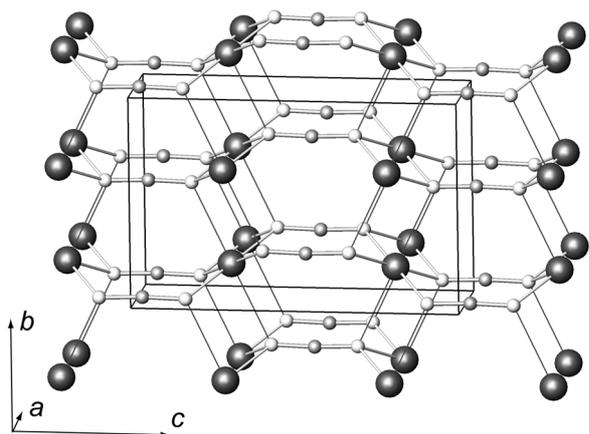
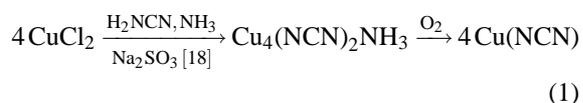


Fig. 2. View of the CuNCN structure along the  $a$  axis with Cu atoms in black, N in white and C in grey. The bond lengths (Å) and angles ( $^{\circ}$ ) are: Cu–Cu = 2.992(1) and 3.432(1),  $4 \times$  Cu–N = 2.001(2),  $2 \times$  Cu–N = 2.613(3), C–N = 1.227(4), N–C–N = 176.4(5), N–Cu–N = 180, N–Cu–N = 95.2(1), N–Cu–N = 84.8(1), N–Cu–N = 96.8(1), N–Cu–N = 83.2(1), and C–N–Cu = 117.0(3).

## Results and Discussion

The title compound has been prepared employing the procedure presented in eq. (1). Black crystals were obtained in 80% yield and their structure determined by powder X-ray diffraction and Rietveld refinement.



The crystal structure of CuNCN (Fig. 2) may be considered a layer structure in which each corrugated layer consists of alternating  $\text{Cu}^{2+}$  and  $\text{NCN}^{2-}$  ions, somewhat similar to the situation in MnNCN. In an alternative description, the  $\text{Cu}^{2+}$  ions form cationic sheets parallel to the  $ab$  face with Cu–Cu distances of 2.992(1) and 3.432(1) Å. Each  $\text{Cu}^{2+}$  ion is coordinated by six nitrogen atoms in the spirit of a typical first-order Jahn-Teller effect ( $4 \times$  Cu–N = 2.001(2) Å,  $2 \times$  Cu–N = 2.613(3) Å). Methods to computationally model the Jahn-Teller effect found for Cu(II) compounds (tetragonally distorted octahedral coordination *vs.* square planar coordination) have been suggested [29]. The  $\text{NCN}^{2-}$  units (Fig. 3) run parallel with the  $c$ -axis, and the complex anion is practically linear (N–C–N = 176.4(5) $^{\circ}$ ). The C–N bond length arrives at 1.227(4) Å, and because the central C atom coincides with the two-fold axis, the

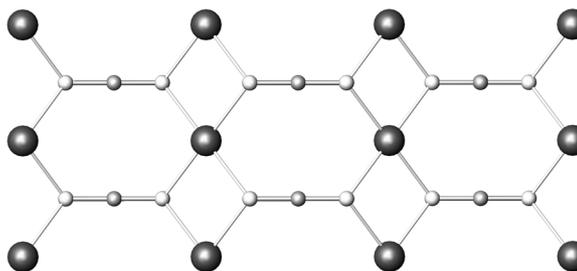


Fig. 3. Top view of a corrugated layer of  $\text{Cu}^{2+}$  and  $\text{NCN}^{2-}$  ions with a square planar  $\text{Cu}^{2+}$  coordination by nitrogen atoms.

two nitrogen atoms are generated by only one crystallographic N site; the anionic shape is very close to  $D_{\infty h}$  (carbodiimide) symmetry. In accord with that, the infrared spectrum of CuNCN exhibits only a strong carbodiimide-type asymmetrical vibration,  $\nu_{\text{as}}(\text{NCN}) = 2035 \text{ cm}^{-1}$ , plus a strong deformation vibration,  $\delta(\text{NCN}) = 595/690 \text{ cm}^{-1}$ . In contrast, no symmetrical  $\nu_{\text{s}}$  band (around  $1200 \text{ cm}^{-1}$ ) is observed because such a breathing mode is IR-forbidden for the  $[\text{N}=\text{C}=\text{N}]^{2-}$  carbodiimide unit although it would be allowed for a cyanamide  $[\text{N}-\text{C}\equiv\text{N}]^{2-}$  anion.

In previous contributions [11, 25] we have discussed the influence of the cationic hardness on the shape of the  $\text{NCN}^{2-}$  anion. While chemically hard cations (*e.g.*,  $\text{Ca}^{2+}$ ) favor ionic bonding to the symmetrical  $[\text{N}=\text{C}=\text{N}]^{2-}$  anion, softer cations (*e.g.*,  $\text{Pb}^{2+}$  or  $\text{Ag}^{+}$ ) bind covalently to one side of the  $\text{NCN}^{2-}$  unit and induce the less symmetrical  $[\text{N}-\text{C}\equiv\text{N}]^{2-}$  cyanamide shape, a finding easily rationalized by Pearson's HSAB concept [30]. Just like for MnNCN, however, the soft  $\text{Cu}^{2+}$  ion in CuNCN induces the *carbodiimide* shape, the second exception from the above shape rule. Further research is needed to clarify whether or not the presence of spin polarization (high-spin  $d^5$  for  $\text{Mn}^{2+}$ ) or metallicity ( $d^9$  for  $\text{Cu}^{2+}$ , see below) has a decisive influence on the shape of the  $\text{NCN}^{2-}$  unit.

The magnetic susceptibility of CuNCN has been determined by SQUID magnetometry (MPMS-5S, Quantum Design, San Diego, USA) in the temperature range between 100 and 300 K at an applied field of  $B_0 = 0.5 \text{ T}$ . Allowing for corrections by diamagnetic increments of  $\text{Cu}^{2+}$  and  $\text{NCN}^{2-}$  ( $-40 \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$  in SI units), a small temperature-independent paramagnetic contribution of  $20(3) \times 10^{-11} \text{ m}^3 \text{ mol}^{-1}$  results which is on the order of the magnitude of temperature-independent paramagnetism (TIP) and spin paramagnetism of the conduction electrons. The black appear-

ance of the material also points towards metallicity which certainly comes as a surprise. Presently, the magnetic behavior below 100 K and the field dependence of the magnetic susceptibility as well as the electronic structure by first-principles methods are under thorough investigation.

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