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) Å³ and Z = 4. There is a strongly distorted octahedral Cu²⁺ coordination reflecting a typical first-order Jahn-Teller effect, with interatomic distances of $4 \times \text{Cu}-\text{N} = 2.001(2)$ Å and $2 \times \text{Cu}-\text{N} = 2.613(3)$ Å; the NCN²⁻ unit adopts the carbodiimide shape with C–N = 1.227(4) Å. Despite the formal d^9 electron count of Cu²⁺, 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⁻, NCN²⁻) of the cyanamide (H₂NCN) molecule have been successfully used to prepare a large number of salts comprising alkali metals [1-3], alkaline-earth metals [4-7], maingroup 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^{2+} ions $(d^4 - d^9)$ prefer to form metal-cyanamide *complexes* such as $[M(NCNH_2)_4]^{2+}$ 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 hightemperature routes are also unsuitable because they

lead to the metal, metal nitride, C and gaseous N2 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 $\Delta H_{\rm f}$ and Gibbs formation energy $\Delta G_{\rm f}$. 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 ZnCl₂ 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^{2+} cations merely form coordination complexes such as $[Cu(NCNH_2)_4]^{2+}$ 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-

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pared a novel ammine copper(I) cyanamide compound, $Cu_4(NCN)_2NH_3$ [18], which appeared as a lucrative oxidizable substrate for the target phase CuNCN. Indeed, a slightly modified synthetic route for $Cu_4(NCN)_2NH_3$ 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 CuCl₂. 2H₂O (1.70 g, 10 mmol) and H₂NCN (0.82 g, 20 mmol) was prepared in a round-bottom flask, and 5 ml of a solution of Na₂SO₃ (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 Cu₄(NCN)₂NH₃ precipitated. Upon stirring the suspension over night, Cu₄(NCN)₂NH₃ 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 $CuCl_2 \cdot 2H_2O$). 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, cm⁻¹): $v_{as}(NCN) = 2035$ (s), $\delta(NCN) = 595$ (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 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 $8-130^{\circ}$

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.

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) Å
	b = 6.1782(1) Å
	c = 9.4003(2) Å
Cell volume:	173.769(5) Å ³
Space group; formula units:	<i>Cmcm</i> (no. 63); 4
Number of reflections:	98
$R_{\rm p}, R_{\rm wp}, R_{\rm Bragg}$:	0.054, 0.079, 0.045

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

Atom	Wyckoff site	x	у	z	$B_{\rm iso}$ (Å ²)
Cu	4a	0	0	0	1.35(2)
Ν	8b	0	0.3826(4)	0.3815(3)	0.77(7)
С	4c	0	0.3889(8)	1/4	0.66(11)

in 2 θ with individual steps of 0.01°. 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_{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 (°) 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.

$$4\operatorname{CuCl}_{2} \xrightarrow[Na_{2}SO_{3}[18]]{} \operatorname{Cu}_{4}(NCN)_{2}NH_{3} \xrightarrow{O_{2}} 4\operatorname{Cu}(NCN)$$
(1)

The crystal structure of CuNCN (Fig. 2) may be considered a layer structure in which each corrugated layer consists of alternating Cu²⁺ and NCN²⁻ ions, somewhat similar to the situation in MnNCN. In an alternative description, the Cu²⁺ ions form cationic sheets parallel to the ab face with Cu-Cu distances of 2.992(1) and 3.432(1) Å. Each Cu²⁺ 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, $2 \times \text{Cu-N} = 2.613(3)$ 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 NCN²⁻ 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 Cu^{2+} and NCN^{2-} ions with a square planar 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, $v_{as}(NCN) = 2035 \text{ cm}^{-1}$, plus a strong deformation vibration, $\delta(NCN) = 595/690 \text{ cm}^{-1}$. In contrast, no symmetrical v_s band (around 1200 cm⁻¹) is observed because such a breathing mode is IR-forbidden for the $[N=C=N]^{2-}$ carbodiimide unit although it would be allowed for a cyanamide $[N-C\equiv N]^{2-}$ anion.

In previous contributions [11, 25] we have discussed the influence of the cationic hardness on the shape of the NCN²⁻ anion. While chemically hard cations $(e.g., Ca^{2+})$ favor ionic bonding to the symmetrical $[N=C=N]^{2-}$ anion, softer cations $(e.g., Pb^{2+} \text{ or } Ag^+)$ bind covalently to one side of the NCN²⁻ unit and induce the less symmetrical $[N-C\equiv N]^{2-}$ cyanamide shape, a finding easily rationalized by Pearson's HSAB concept [30]. Just like for MnNCN, however, the soft 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 Mn²⁺) or metallicity (d^9 for Cu²⁺, see below) has a decisive influence on the shape of the NCN²⁻ 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 $B_0 = 0.5$ T. Allowing for corrections by diamagnetic increments of Cu²⁺ and NCN²⁻ (-40×10^{-11} m³ mol⁻¹ in SI units), a small temperature-independent paramagnetic contribution of $20(3) \times 10^{-11}$ m³ 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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