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# An Investigation of the Formation Mechanism of Copper(II) Carbodiimide

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*Dedicated to Professor Arndt Simon on the Occasion of his 70<sup>th</sup> Birthday*

## Abstract

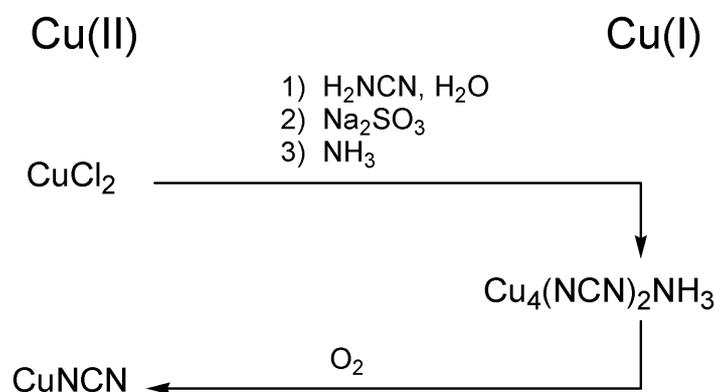
The formation mechanism of copper(II) carbodiimide in aqueous ammonia solution has been studied by synthetic and crystallographic means. The reduction of the starting Cu(II) solution leads to the synthesis of solid Cu(I) intermediates, and the crystal structures of the two new compounds Cu(NCNH<sub>2</sub>)Cl ( $a = 8.2925(4)$ ,  $b = 3.7275(1)$ ,  $c = 12.4534(4)$  Å, *Pnma*) and the iso-structural Cu(NCNH<sub>2</sub>)Br ( $a = 8.406(3)$ ,  $b = 3.9229(9)$ ,  $c = 12.656(3)$  Å, *Pnma*) have been elucidated. A further increase in pH value by adding more ammonia leads to the crystallization of two additional Cu(I) intermediates, Cu<sub>2</sub>NCN and the ammine adduct Cu<sub>4</sub>(NCN)<sub>2</sub>NH<sub>3</sub>. The former can be also made by the thermal decomposition of the latter whereas mild oxidation of Cu<sub>4</sub>(NCN)<sub>2</sub>NH<sub>3</sub> leads to the formation of perfectly crystalline CuNCN.

**Keywords:** carbodiimide / cyanamide / copper / crystal structure / reaction mechanism

## Introduction

The motivation for carrying out exploratory syntheses in the fields of carbodiimides and cyanamides of the divalent magnetic transition metals ( $d^5 - d^9$ ) is naturally linked with the structural and physical properties of these novel types of inorganic materials.<sup>[1-7]</sup> Among them, black powderous copper carbodiimide, CuNCN, stands for the nitrogen-based analogue of CuO,<sup>[2,5]</sup> and CuNCN was first made in large, phase-pure and well-crystallized quantities only five years ago.<sup>[2]</sup> The synthetic difficulty lies in the fact that aforementioned M<sup>2+</sup> transition-metal ions prefer to form cyanamide *complexes* in aqueous solution<sup>[8,9]</sup> such that, as a charac-

teristic example,  $\text{Cu}^{2+}$  cations merely form coordination complexes like  $[\text{Cu}(\text{NCNH}_2)_4]^{2+}$  from which the protons can not be fully removed. The brute-force alternative of a (strong) basic aqueous Cu(II) solution reacting with anionic cyanamide units, however, yields a black material whose amorphous nature renders its structure determination impossible.<sup>[10,11]</sup> As said before, we were fortunate to discover a new synthetic approach for perfectly crystalline CuNCN a while ago.<sup>[2]</sup> The two-step method is essentially based on an ammine Cu(I) cyanamide compound,  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$ , which can be obtained from the mild reaction of  $[\text{Cu}(\text{NH}_3)_2]^+$  and  $\text{H}_2\text{NCN}$  under aqueous ammonia conditions.<sup>[12]</sup> The likewise mild oxidation of  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  then yields the target phase CuNCN. Schematically, the entire procedure may be summarized as follows:



In order to come up with a less formal description, we have now examined the reaction mechanism of CuNCN formation in more detail. By doing so, the syntheses and crystal structures of two new solid-state copper(I) halide complexes have been accomplished, together with yet another new Cu(I) cyanamide solid-state material.

## Experimental Section

In order to elucidate possible reaction pathways, alternative syntheses were tested, namely a total of six different preparations.

**Experiment 1:** A mixture of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.71 g, 10 mmol) and cyanamide  $\text{H}_2\text{NCN}$  (0.84 g, 20 mmol) was stirred at room temperature in water (10 mL) under argon gas. A solution of  $\text{Na}_2\text{SO}_3$  (1.26 g, 10 mmol) in 10 mL water was added dropwise to the above mixture resulting in colorless needle-like crystals of the new phase  $\text{Cu}(\text{NCNH}_2)\text{Cl}$  (**1a**) which were then filtered and dried under vacuum. Analytical data (%) for  $\text{Cu}(\text{NCNH}_2)\text{Cl}$  (141.04 g/mol): Cu 44.76 (calc. 45.05); C 8.32 (8.52); H 2.01 (1.42); N 19.34 (19.86).

**Experiment 2:** It was analogous to experiment 1 but using  $\text{CuBr}_2$  (2.23 g, 10 mmol). The product crystallized as colorless needle-like crystals of the new phase  $\text{Cu}(\text{NCNH}_2)\text{Br}$  (**1b**) but with a small amount of a  $\text{CuBr}$  impurity detectable from X-ray powder diffraction data (XRPD). Fortunately, a single crystal of **1b** was isolated which turned out as suitable for single-crystal measurement as well as solution and refinement.

**Experiment 3:** When **1a** had been formed in experiment 1, adding 10 mL of a 25 wt.% ammonia solution ( $\text{NH}_3\cdot\text{H}_2\text{O}$ ) resulted in the precipitation of pure white  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  (**2**) which was filtered and dried under vacuum.<sup>[12]</sup>

**Experiment 4:** When **1a** had been formed in experiment 1, 10 mL of a one-molar  $\text{NH}_3\cdot\text{NH}_4\text{Cl}$  buffer solution were added. A pale-yellow precipitation was obtained, then filtered and dried under vacuum. XRPD analysis showed it to be a mixture of **2** and the new phase  $\text{Cu}_2\text{NCN}$  (**3**).

**Experiment 5:** 0.1 g of **2** was heated at 150 °C under vacuum for two days in one side of a long Schlenk glass. Yellow powderous **3** was obtained, and the presence of ammonia was verified in the attached cooling trap. **3** appeared as very well crystallized. XRPD analysis showed that **3** was a pure phase which could be indexed using an orthorhombic cell. Analytical data (%) for  $\text{Cu}_2\text{NCN}$  (167.09 g/mol): Cu 75.30 (calc. 76.06); C 7.20 (7.18); H 0.14 (0); N 17.0 (16.76). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{NCN}) = 2138$  and  $2193(\text{s})$ ,  $\nu_{\text{s}}(\text{NCN}) = 1183$  (s) and  $\delta(\text{NCN}) = 655$  (m).

**Experiment 6:** Upon stirring the suspension from experiment 3 over night, **2** was slowly oxidized at room temperature due to the presence of small amounts of atmospheric oxygen within the reaction flask, thereby yielding black crystalline  $\text{CuNCN}$ .<sup>[2]</sup>

## X-ray Crystallography

**Structure data of 1a.** The X-ray diffraction data were recorded at room temperature using a G670 Imageplate Guinier diffractometer (Huber, Rimsting) equipped with a Johansson Ge monochromator for  $\text{Cu K}\alpha_1$  radiation and a flat sample holder in the  $2\theta$  range between 6 and 100°. The XRPD pattern of **1a** indicated a pure phase such that its structure was determined using Rietveld analysis based upon the iso-structural model of **1b**. The FULLPROF program package<sup>[21]</sup> was used with a pseudo-Voigt profile function, and the background data were manually subtracted by linear interpolation. Because of strongly preferred orientation and likewise asymmetric Bragg peaks, the atomic distances of  $\text{Cu-N}$  and  $\text{C-N}$  and the  $\text{N-C-N}$  angle had to be soft-restrained to yield reasonable bond lengths and a more reliable refine-

ment. Likewise, all H positional parameters were fixed to N–H distances of 0.89 Å. Empirical formula  $\text{CH}_2\text{ClCuN}_2$ ,  $M_r = 141.04$ , orthorhombic,  $Pnma$ ,  $a = 8.2925(4)$ ,  $b = 3.7275(1)$ ,  $c = 12.4534(4)$  Å,  $V = 384.48(2)$  Å<sup>3</sup>,  $Z = 4$ . The residual values arrived at 0.072 ( $R_p$ ), 0.102 ( $R_{wp}$ ), and 0.18 ( $R_{Bragg}$ ) for a total of 22 variables, 4 restraints and 248 Bragg reflections.

**Structure data of 1b.** A complete set of X-ray intensities was collected with a Bruker SMART-CCD diffractometer using graphite-monochromatized Mo  $K\alpha$  radiation at  $T = 20(1)$  °C and with the aid of the SMART and SAINT software packages.<sup>[22]</sup> A total Ewald sphere was collected and carefully corrected with respect to absorption using the empirical SADABS method. The crystal structure was then solved by Direct Methods and refined by alternating cycles of difference Fourier syntheses and full-matrix least-squares refinements with SHELXS-97 and SHELXL-97.<sup>[23]</sup> All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were located by difference Fourier synthesis and refined using a riding model with restrained N–H distances of 0.86–0.89 Å and with  $U_{iso}(\text{H})$  values of  $1.2 \times U_{eq}(\text{N}_2)$ . Empirical formula  $\text{CH}_2\text{BrCuN}_2$ ,  $M_r = 185.49$ , orthorhombic,  $Pnma$ ,  $a = 8.406(3)$ ,  $b = 3.9229(9)$ ,  $c = 12.656(3)$  Å,  $V = 417.4(2)$  Å<sup>3</sup>,  $Z = 4$ , size =  $0.15 \times 0.05 \times 0.04$  mm<sup>3</sup>,  $\theta_{\text{range}} = 2.9$  to 24.8°, 3039 reflections ( $R_{\text{int}} = 0.126$ ), GOF = 0.862,  $R_1 (I > 2\sigma(I)) = 0.0639$ ,  $wR_2 (I > 2\sigma(I)) = 0.130$ ; CSD–420807. All important numerical details of the refinements of **1a** and **1b** may be found in Table 1. Positional and displacement parameters are listed in Table 2.

## Results and Discussion

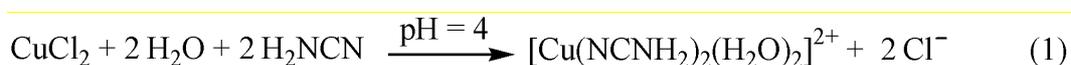
**Reaction procedure.** The reported synthesis of CuNCN is, in fact, a one-pot reaction. In this study, the synthetic procedure has been interrupted after each proposed intermediate species. In order to characterize these intermediates, additional reactions have been carried out.

At first,  $\text{Cu}^{2+}$  ions have been reduced by  $\text{Na}_2\text{SO}_3$  in an excess (two equimolar) of  $\text{H}_2\text{NCN}$  solution under inert atmosphere. For  $\text{CuCl}_2$  as a starting substance, the pure intermediate  $\text{Cu}(\text{NCNH}_2)\text{Cl}$  (**1a**) has been obtained. For the case of  $\text{CuBr}_2$ , the bromine analogue  $\text{Cu}(\text{NCNH}_2)\text{Br}$  (**1b**) has been found together with a small amount of  $\text{CuBr}$ . This finding may be a consequence of the 25 times smaller solubility product of  $\text{CuBr}$  ( $K_{sp} = 4.15 \times 10^{-8}$  mol<sup>2</sup> L<sup>-2</sup>) than that of  $\text{CuCl}$  ( $1.02 \times 10^{-6}$  mol<sup>2</sup> L<sup>-2</sup>). Fortunately, single crystals of **1b** have been isolated for crystal structure determination. Although **1a** was not obtained as a single crystal, the XRPD patterns for **1a** and **1b** clearly show that they are iso-structural.

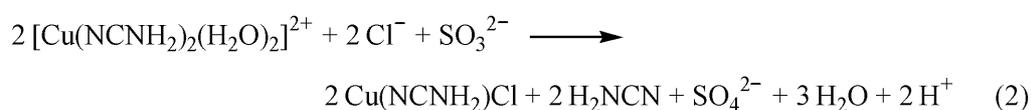
After reducing all Cu(II) in H<sub>2</sub>NCN solution by the use of Na<sub>2</sub>SO<sub>3</sub>, a concentrated ammonia solution was added until pH > 10 which resulted in the formation of white Cu<sub>4</sub>(NCN)<sub>2</sub>NH<sub>3</sub> (**2**). By careful observation it appears that, along with adding the ammonia, a yellow – instead of white – precipitation starts at the very beginning, which then rapidly changes to white. Thus, the attempt to isolate the yellow compound utilizes a buffer solution, that is, a one-molar NH<sub>3</sub>·NH<sub>4</sub>Cl mixture with a pH around 8–9, and this, in fact, leads to a solid mixture of **2** and Cu<sub>2</sub>NCN (**3**). The chemical similarity between **2** and **3** is obvious because the heat treatment of **2** (150 °C, vacuum, 48 h) leads to a pure yellow powder of **3**, together with NH<sub>3</sub> gas inside the cooling trap. Elemental analysis agrees with the theoretical composition of Cu<sub>2</sub>NCN. Comparing the infrared spectra of **3** with the compilation of metal-carbodiimides/cyanamides provided by *Reckeweg* and *Simon*,<sup>[7]</sup> it is obvious that **3** not only exhibits strong carbodiimide-type asymmetrical vibrations, ν<sub>as</sub>(NCN) = 2138/2193 cm<sup>-1</sup>, plus a strong deformation vibration, δ(NCN) = 655 cm<sup>-1</sup>, but also the symmetrical ν<sub>s</sub> band (1182 cm<sup>-1</sup>) which would be allowed for the less symmetrical cyanamide [N–C≡N]<sup>2-</sup> anion and IR-forbidden for the [N=C=N]<sup>2-</sup> carbodiimide unit. However, no good structural model has been found so far to allow for a reasonable crystal-structure refinement of the XRPD pattern.

In case a small amount of air was allowed to enter the mixture of **2** and the cyanamide solution, the solution itself changed rapidly to blue; the oxidation of the white precipitate **2**, however, proceeded very slowly to eventually give black CuNCN. The latter phase forms with an exceptionally good crystallinity over night (Figure 1).

**Mechanism discussion.** We have tried to reduce the surplus amount of H<sub>2</sub>NCN from four to two equimoles compared to that of Cu<sup>2+</sup> ions as described in experiment 1. Nonetheless, essentially the same results were observed with the only exception of a slightly reduced yield of CuNCN from lower-concentrated H<sub>2</sub>NCN solutions. If an equimolar relation of Cu<sup>2+</sup> and H<sub>2</sub>NCN was used at the very beginning, insoluble CuCl was found together with **1a**; the latter phase will not, however, influence the purity of final product simply because CuCl later also dissolves in concentrated ammonia solution. Taking into account that Cu(II) must be four-coordinated by electronegative atoms such as O and N – for example, as given in the complex [Cu(NCNH<sub>2</sub>)<sub>4</sub>]<sup>2+</sup> cation<sup>[9]</sup> – we therefore tentatively conclude that the complex ion [Cu(NCNH<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> has been formed:



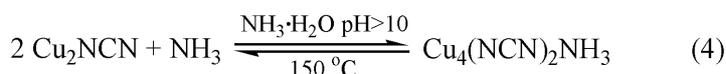
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3 The reduction of Cu(II) in the presence of coordinating ligands is an established method to  
4 obtain copper(I) complexes,<sup>[13,14]</sup> but such reactions are typically performed in organic sol-  
5 vents instead of aqueous solution because of the low equilibrium concentrations of Cu(I) and  
6 its instability with respect to disproportionation ( $2 \text{Cu}^{\text{I}} = \text{Cu}^0 + \text{Cu}^{\text{II}}$ ). The latter stability problem in  
7 aqueous solution depends very strongly on the nature of the ligand which should have  $\pi$ -  
8 acceptor character to stabilize  $\text{Cu}^+$ . In this respect,  $\text{H}_2\text{NCN}$  is indeed a suitable ligand being  
9 able to form the new solid-state halide complexes **1a** or **1b** under strongly acidic condition  
10 (reaction 2) and even to allow for the existence of the ammonia complex **2** under strongly  
11 basic conditions (reaction 4, see below).  
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27 The adjustment of the pH value plays a very important role in the entire procedure; in fact, the  
28 change of the pH value leads to the formation of four different compounds. While the pH  
29 value of the starting reaction mixture is about 4, the addition of the reducing agent leads to  
30 reaction 2 taking place in which the pH drops to about 1. Thus, the two solid-state complexes  
31 **1a** and **1b** can only exist under acidic conditions. Upon adding ammonia to the reaction solu-  
32 tion and thereby attaining weakly basic conditions, the  $\text{H}_2\text{NCN}$  species is deprotonated which  
33 leads to the synthesis of **3** as shown in reaction 3:  
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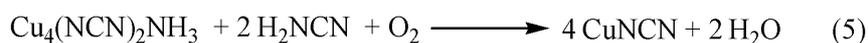


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45 When the pH value exceeds 10, only **2** exists, a consequence of the law of mass action. Alter-  
46 natively expressed, the structural stability of  $\text{Cu}_4(\text{NCN})_2\text{NH}_3$  (**2**) at room temperature exceeds  
47 the one of  $\text{Cu}_2\text{NCN}$  (**3**). Likewise, it is not difficult to understand that the application of  
48 higher temperatures leads to the removal of weakly coordinating  $\text{NH}_3$  from **2**, thereby forming  
49 **3** by thermal decomposition (reaction 4).  
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60 The final oxidation step takes place under strongly basic (aqueous ammonia) conditions  
which is more effective and ensures the purity of the final product  $\text{CuNCN}$  by forming

[Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>. As said before, *stable* copper(I) complexes are not very common although plenty of copper(I) compounds have been reported in recent years.<sup>[13–17]</sup> To the best of our knowledge, the use of a stable copper(I) complex to synthesize a copper(II) target compound is very rare. The main advantage of our method is that the oxidation of suspended **2** is taking place quite slowly in order to form well-crystallized CuNCN (reaction 5).

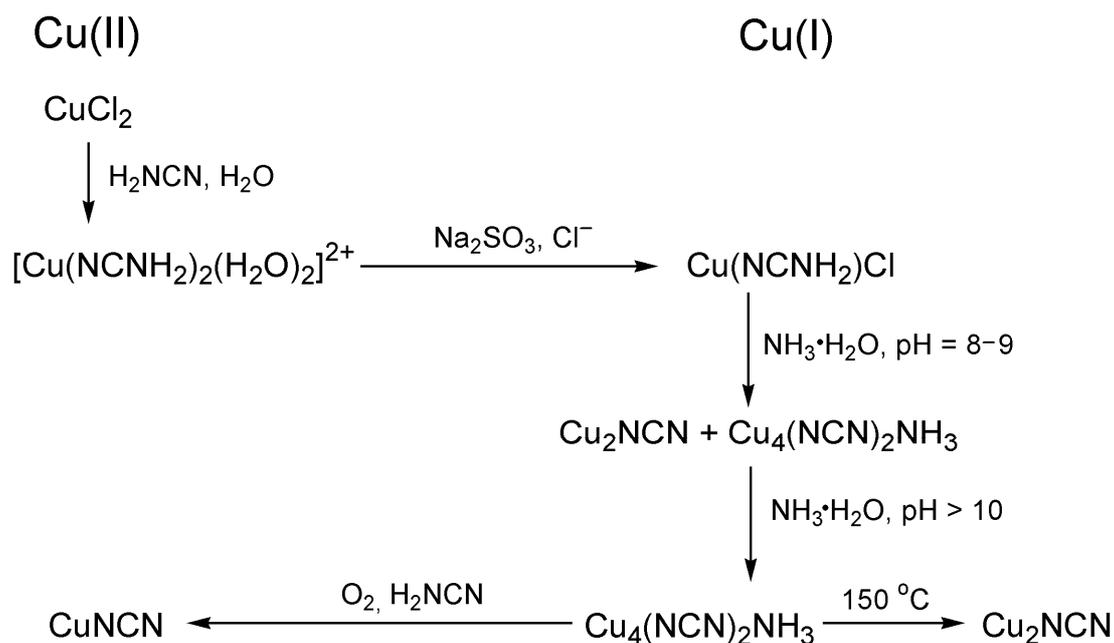


**Crystal structure.** A large number of different structures for Cu(I) halide complexes have been identified depending on the nature of ligand as well as the composition.<sup>[14–17]</sup> In the present case, the structures of **1a** and **1b** are of the same type, despite the fact that Cu(NH<sub>3</sub>)Cl forms linear NH<sub>3</sub>–Cu–Cl units whereas Cu(NH<sub>3</sub>)Br does not exist; instead, the phase [Cu(NH<sub>3</sub>)<sub>2</sub>]Br has been described.<sup>[14]</sup> The structures of **1a** and **1b** may be well compared with the one of copper(I) iodide pyridine, [CuI(NC<sub>5</sub>H<sub>5</sub>)<sub>4</sub>], with a four-coordinated Cu(I) to which three halides and one N from the ligand bonds.<sup>[18]</sup> In the case of **1a** and **1b**, one finds infinite one-dimensional chains of [–Cu(NCNH<sub>2</sub>)X–]<sub>n</sub> (see Figure 2) which consist of tetrahedrally coordinated Cu(I) ions, that is, bonded to three halide atoms (2 × 2.47(3) and 1 × 2.40(3) Å for Cu–Cl in **1a**; 2 × 2.536(2) and 1 × 2.510(3) Å for Cu–Br in **1b**) and to one nitrogen atom from the C–N single bond side (Cu–N = 2.04(3) in **1a** and 1.92(2) Å in **1b**) that stems from the cyanamide molecule (see Figure 3). The H<sub>2</sub>NCN unit shows the typical cyanamide shape with one single C–N bond of 1.35(2) Å and one triple bond of 1.11(2) Å refined for **1b**; for the **1a** Rietveld-based structure, the carbon-nitrogen bond lengths had to refined with restraints (1.10(4) and 1.27(4) Å) but the structure of H<sub>2</sub>NCN should not have too much deviation. As is evident from Table 3, there exist no strong hydrogen bonds in the crystals. Comparing with much shorter Cu–Cu distances of 2.979(1) Å in Cu(NH<sub>3</sub>)Cl<sup>[14]</sup> and 2.453(1) Å in Cu<sub>2</sub>(C<sub>7</sub>N<sub>3</sub>H<sub>12</sub>)<sub>2</sub>,<sup>[19]</sup> the Cu–Cu distances in **1a** and **1b** are about 3.0 Å and indicate nonbonding Cu–Cu interactions.<sup>[20]</sup>

It is quite interesting that the NCN cores of the cyanamide molecules exhibit different structures in the two intermediates **1a** and **2** as compared with CuNCN. In Cu(H<sub>2</sub>NCN)Cl, we have a cyanamide molecule with a single C–N and a triple C≡N bonds (see above), and the same is found for Cu<sub>4</sub>(NCN)<sub>2</sub>NH<sub>3</sub> despite containing an anion. In CuNCN, the “harder” Cu(II) atom bonds to the NCN<sup>2–</sup> unit which exists in the carbodiimide shape, namely with two double C=N bonds. Obviously, the molecular shape depends on the counter cation, the coordination motif and also the crystal packing.

## Conclusions

The reaction mechanism of the formation of copper(II) carbodiimide has been analyzed by using chemical and crystallographic means. The results indicate the presence of at least three new intermediates, two of which have been characterized in terms of their crystal structures. The crystal-structural determination of  $\text{Cu}_2\text{NCN}$  is still in progress. The entire reaction scheme may be formulated as follows:



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**Table 1.** Important structural parameters of **1a** and **1b** including characteristic bond lengths (Å) and angles (°).

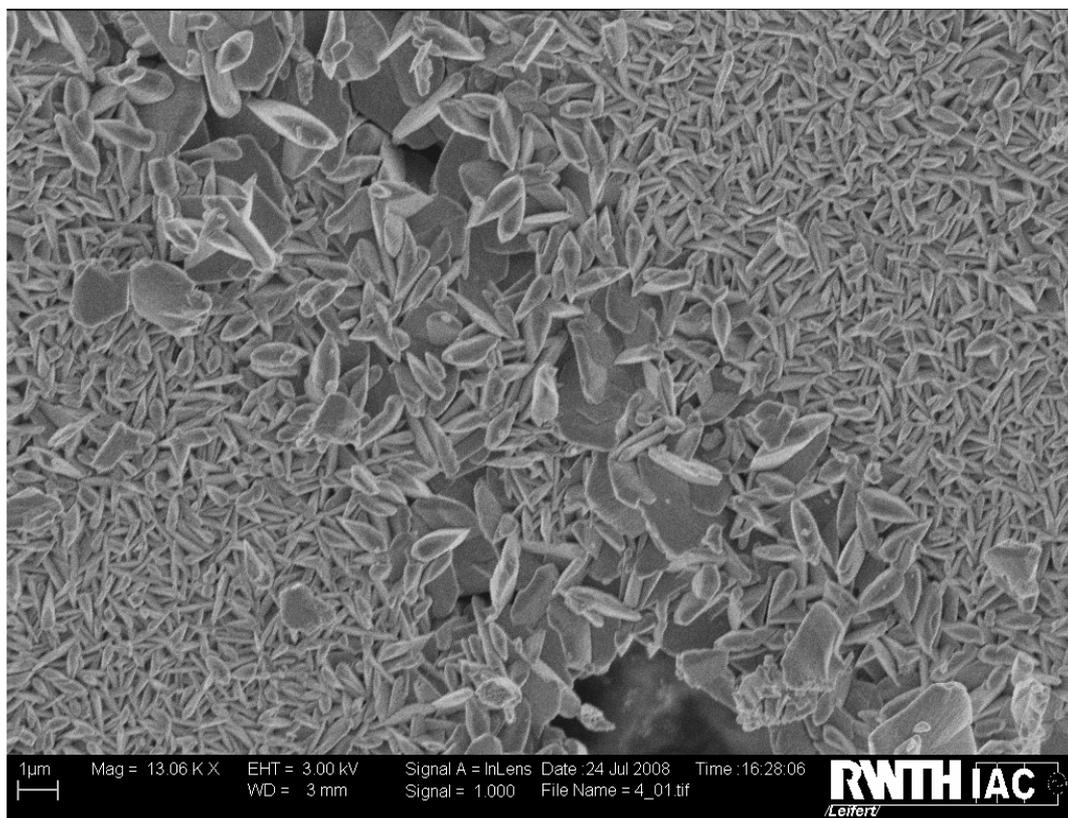
	Cu(NCNH <sub>2</sub> )Cl ( <b>1a</b> )	Cu(NCNH <sub>2</sub> )Br ( <b>1b</b> )
color, form	white needles	white needles
space group	<i>Pnma</i> (no. 62)	<i>Pnma</i> (no. 62)
<i>a</i> (Å)	8.2825(4)	8.406(3)
<i>b</i> (Å)	3.7275(1)	3.9229(9)
<i>c</i> (Å)	12.4534(4)	12.656(3)
<i>V</i> (Å <sup>3</sup> )	384.48(2)	417.4(2)
Cu–X	2.47(3) (2×); 2.40(3)	2.536(2) (2×); 2.510(3)
Cu–N1	2.04(3)	1.916(15)
N1–C, C–N2	1.10(4), 1.27(4)	1.11(2), 1.35(2)
Cu–N1–C	177(2)	177.2(19)
N1–C–N2	177 (2)	180(2)
N2–H2A, N2–H2B	0.89 (fixed)	0.882, 0.865 (restrained)

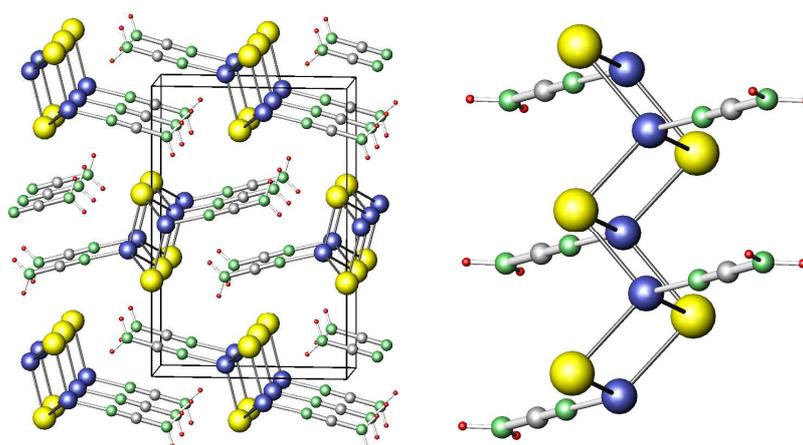
**Table 2** Positional parameters (all atoms on 4c,  $y \equiv 1/4$ ) and isotropic displacement parameters ( $U_{eq}$  in Å<sup>2</sup>) for **1a** and **1b** (X = Cl, Br) with standard deviations in parentheses.

atom	Cu(NCNH <sub>2</sub> )Cl ( <b>1a</b> )			Cu(NCNH <sub>2</sub> )Br ( <b>1b</b> )		
	<i>x</i>	<i>z</i>	$U_{eq}$	<i>x</i>	<i>z</i>	$U_{eq}$
Cu	0.1211(3)	0.5593(2)	0.0894(15)	0.1091(3)	0.5550(2)	0.0758(10)
X	0.0468(5)	0.3727(3)	0.0169(14)	0.0365(2)	0.36269(14)	0.0552(7)
N1	0.3555(10)	0.6110(11)	0.082(2)	0.3312(17)	0.5892(15)	0.076(5)
C	0.4833(11)	0.6340(18)	0.082(2)	0.458(3)	0.6131(13)	0.056(4)
N2	0.6290(10)	0.6665(11)	0.082(2)	0.6132(17)	0.6415(13)	0.073(5)
H2A	0.643	0.738	0.088	0.6433	0.7066	0.087
H2B	0.696	0.611	0.088	0.6903	0.5943	0.087

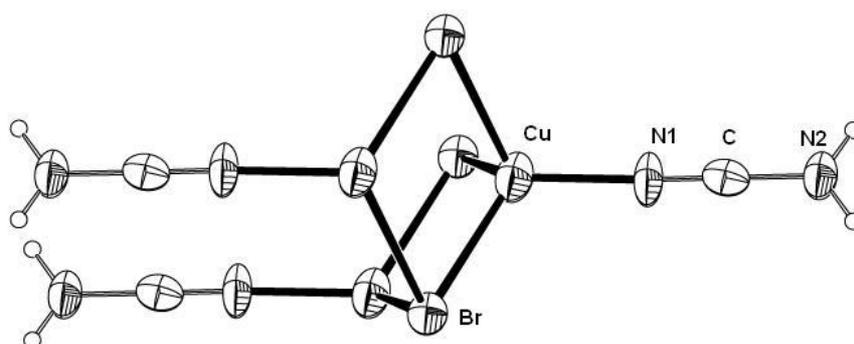
**Table 3** Hydrogen bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1a** and **1b**.

	D-H $\cdots$ A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
<b>1a</b>	N2-H2A $\cdots$ N1	0.89	2.58	3.346	144.0
<b>1b</b>	N2-H2A $\cdots$ N1	0.882	3.04	3.55	134.63

**Figure 1.** SEM micrograph of CuNCN. All micro-crystals appear as thin plates.

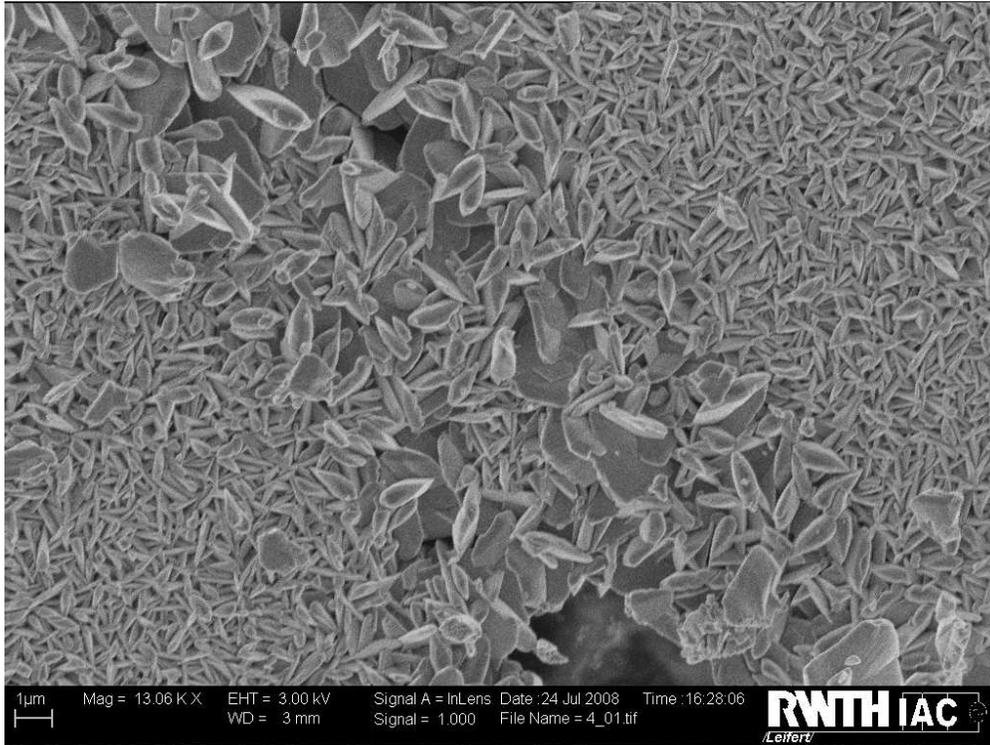


**Figure 2.** Packing diagram of the crystal structure of  $\text{Cu}(\text{NCNH}_2)\text{X}$  with  $\text{X} = \text{Cl}$  and  $\text{Br}$ . The left part shows a view along the crystallographic  $b$  axis, and the right part displays the quasi one-dimensional copper-halogen chain. Color scheme: Cu in blue, X in yellow, N in green, C in grey, and H in red.

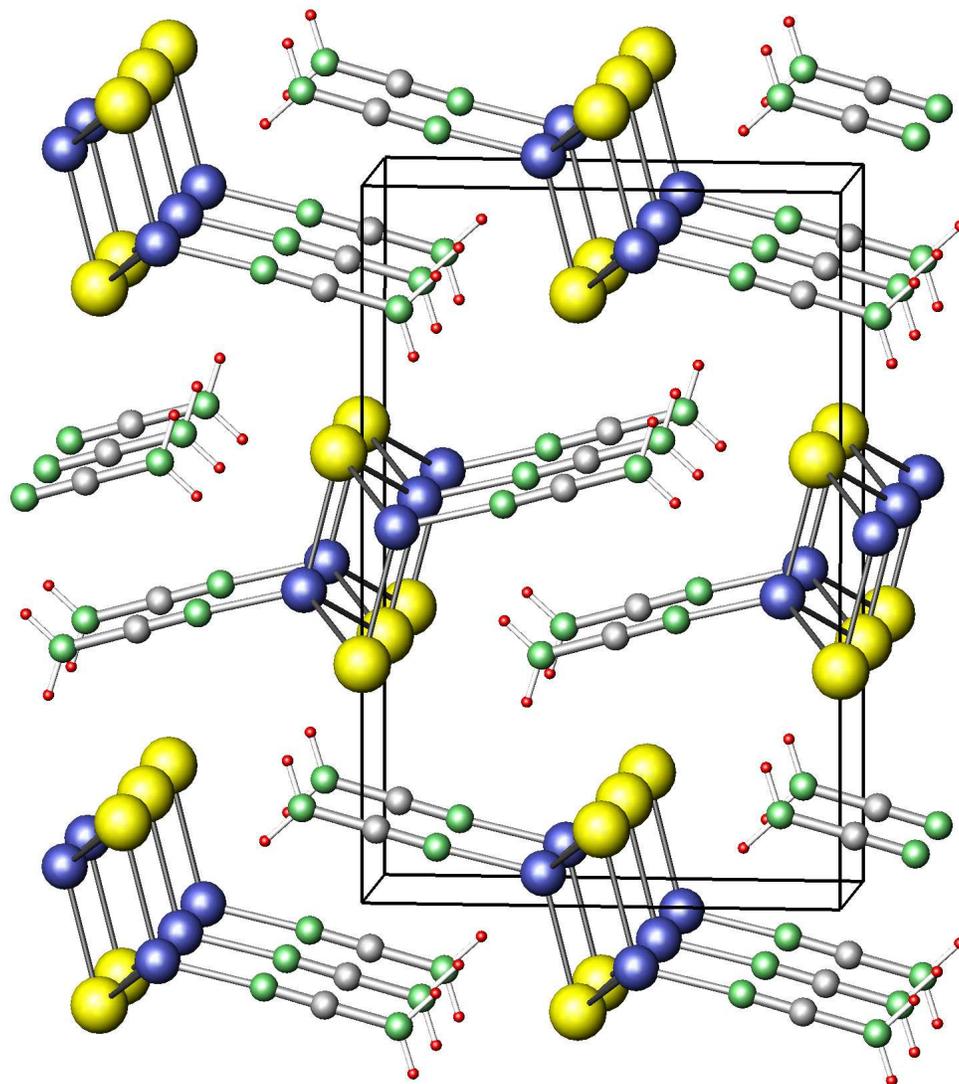


**Figure 3.** An ORTEP drawing of  $\text{Cu}(\text{NCNH}_2)\text{Br}$  with thermal ellipsoids at 30% probability level and H atoms as circles of arbitrary size.  $\text{Cu}(\text{NCNH}_2)\text{Cl}$  is iso-structural.

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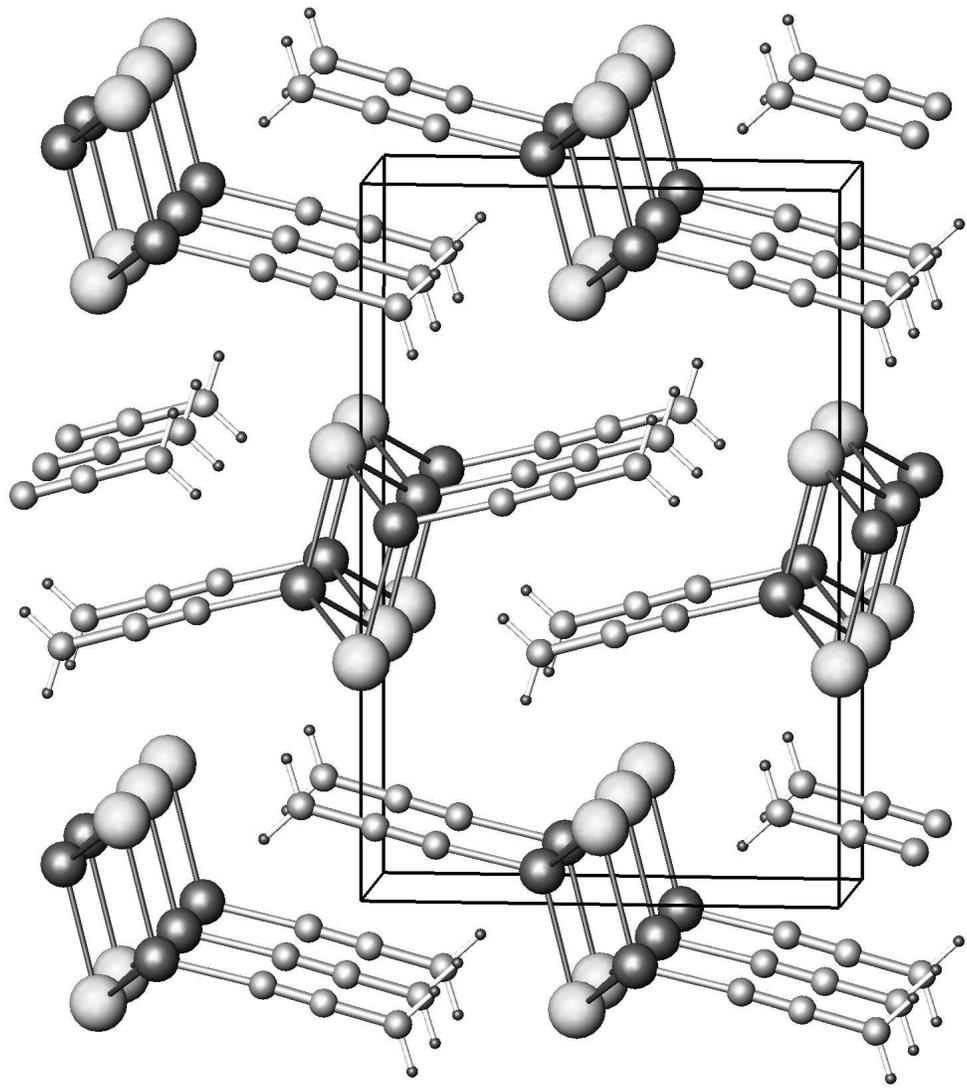


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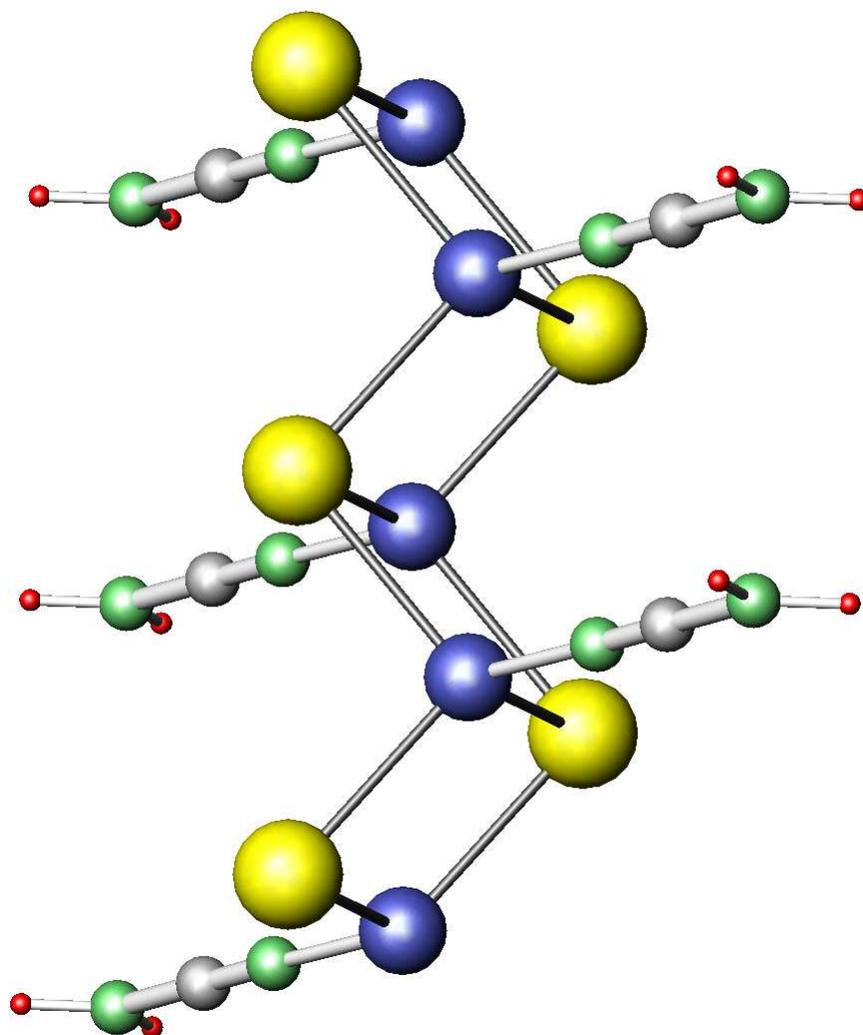


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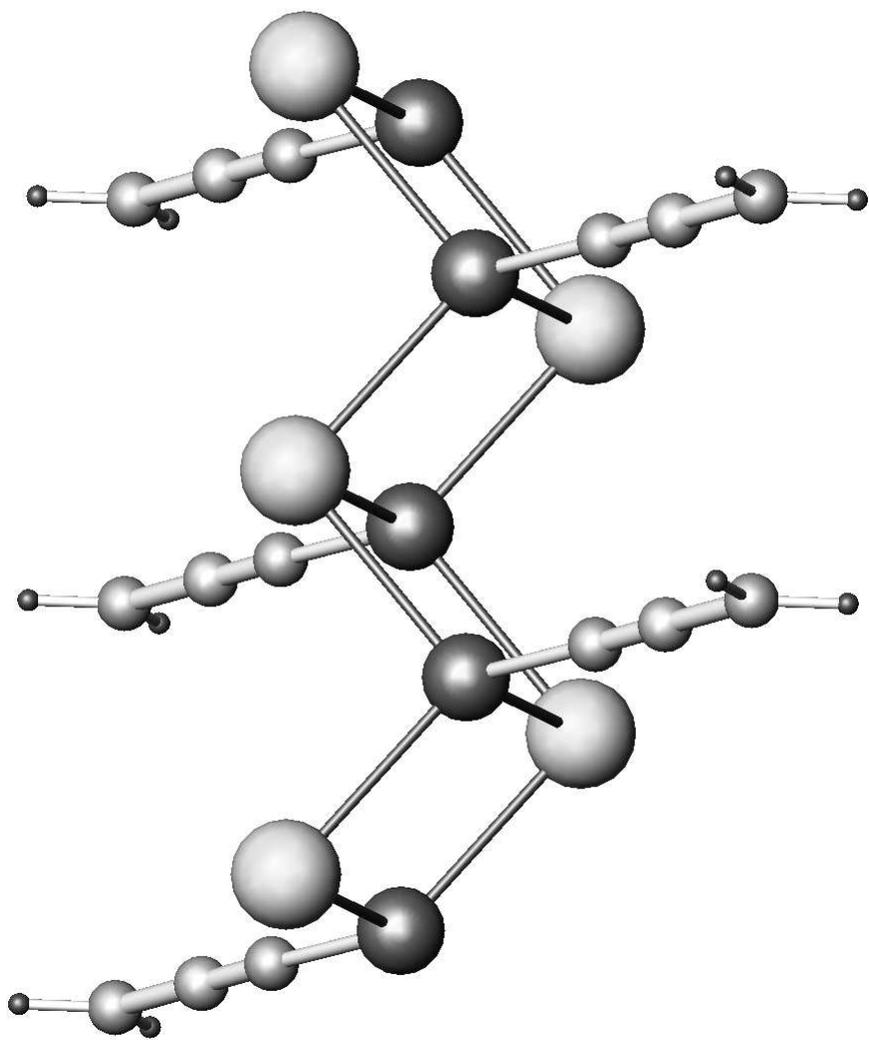


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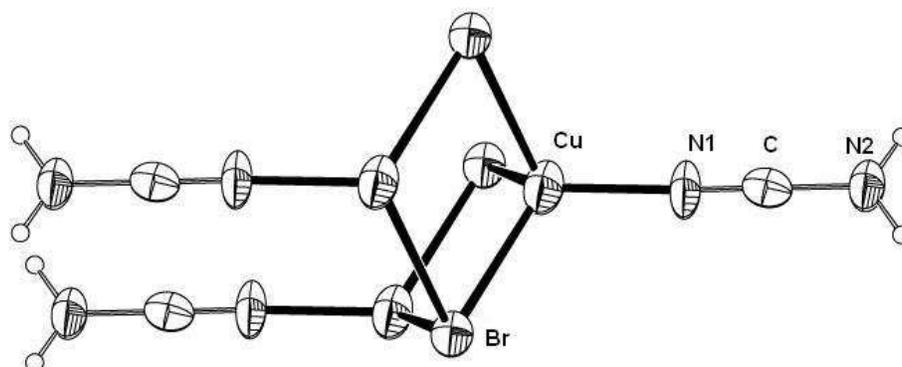


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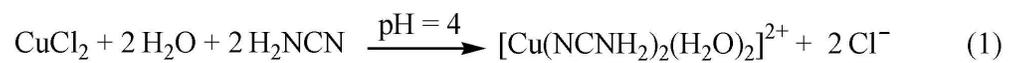
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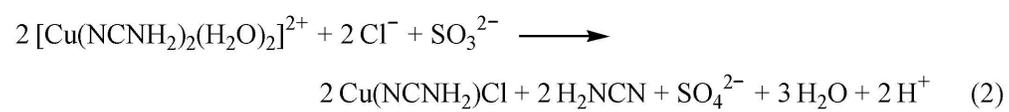
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190x82mm (96 x 96 DPI)



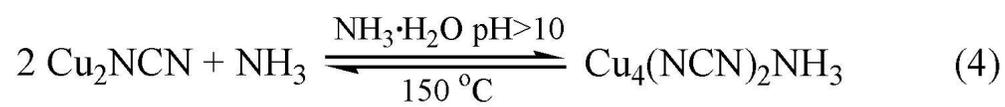
139x9mm (360 x 360 DPI)



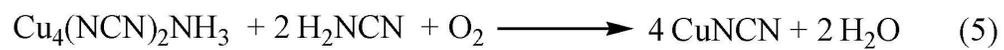
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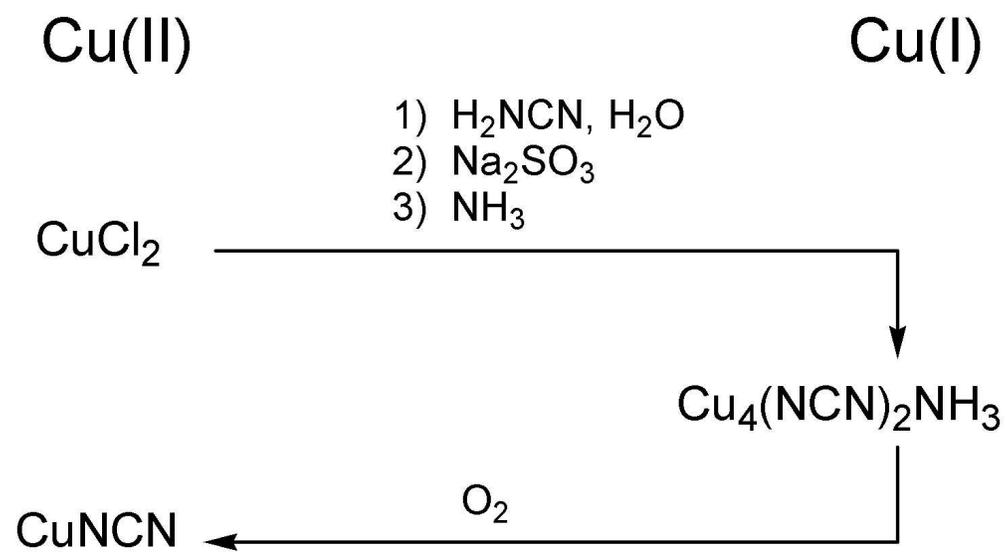
131x8mm (360 x 360 DPI)



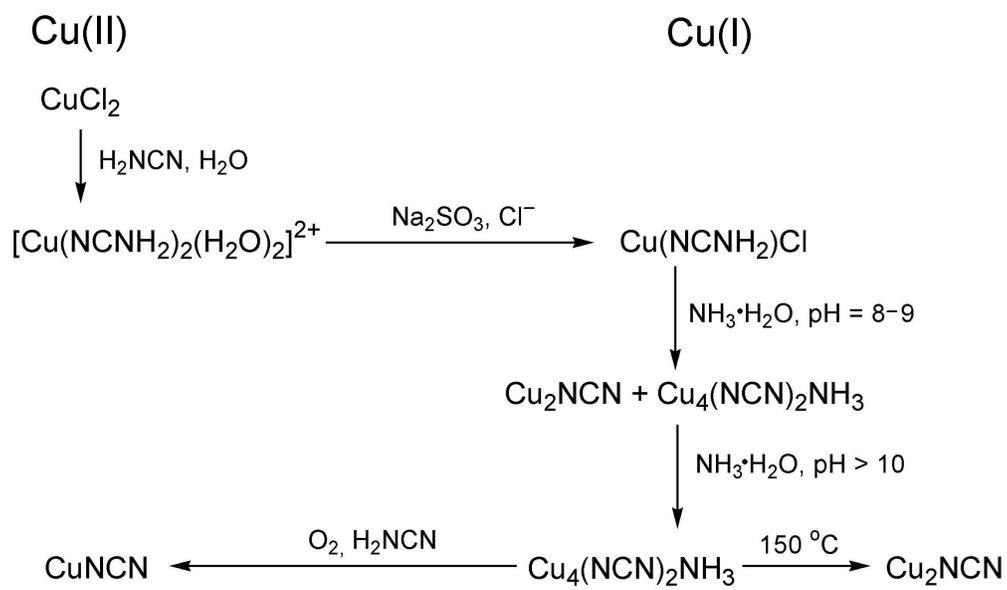
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