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Article

## Preparation and Crystal Structure of Diaqua( $\mu$ -5,5'-bistetrazolato- $\kappa^4N^1,N^2,N^5,N^6$ )copper(II)

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**Abstract:** The crystal structure of the coordination polymer diaqua( $\mu$ -5,5'-bistetrazolato- $\kappa^4N^1,N^2,N^5,N^6$ )copper(II) was determined by X-ray diffraction. The copper atoms are connected to chains over the bridging 5,5'-bistetrazolato ligand. The energetic properties of the compound were investigated, such as thermal behavior and sensitivities (shock, friction, electrical spark).

**Keywords:** energetic materials; 5,5'-bistetrazole; coordination polymer; copper

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### 1. Introduction

The research of environmental friendly primary explosives as replacements for lead azide and lead styphnate is of great interest. Lead containing explosives cause environmental problems because of the heavy metal contamination of e.g., shooting ranges. As it was shown in the past, nitrogen-rich heterocycles like tetrazoles in combination with less toxic metal cations like copper(II), zinc(II) or iron (II/III) seem to be alternatives for lead azide. One heterocycle of interest is 5,5'-bistetrazole (5,5'-H<sub>2</sub>BT).

Neutral 5,5'-bistetrazole (5,5'-H<sub>2</sub>BT) [1] and some of its salts (manganese, sodium) have been described in literature for a long time [2]. However, the potential of this compound as an energetic material was first recognized by W. Friederich in 1956 [3]. Hiskey and Chavez further investigated the copper(II) and some nitrogen-rich salts (diammonium, hydrazinium, hydroxylammonium *etc.*) of

5,5'-bistetrazole as low-smoke pyrotechnics and reported the synthesis of 5,5'-H<sub>2</sub>BT from sodium azide, sodium cyanide and manganese dioxide in water [4,5]. In addition, our research group pointed out the potential use of the barium and strontium salt in coloring pyrotechnical compositions and determined the crystal structures of all alkaline earth metal salts except radium (Be, Mg, Ca, Sr and Ba) [6]. However, the crystal structure of the diaqua( $\mu$ -5,5'-bistetrazolato- $\kappa^4 N^1, N^2, N^5, N^6$ )copper(II) (**2**) was not determined until now. In this work, the structure of **2** was determined by low temperature single crystal X-ray diffraction and the purity approved by vibrational spectroscopy and elemental analysis. The sensitivities were tested according to BAM (*Bundesanstalt für Materialforschung und-prüfung*) methods.

## 2. Results and Discussion

Due to lower sensitivities, the monosodium 5,5'-bistetrazolate trihydrate (**1**) (was synthesized instead of the neutral 5,5'-H<sub>2</sub>BT. The preparation was carried out using slight modifications to the method described in literature [4]. The intermediate manganese 5,5'-bistetrazolate was treated in a sodium carbonate solution with less hydrochloric acid to protonate only once. **1** was further reacted with a solution of copper(II) nitrate trihydrate in 2 M nitric acid, from which **2** precipitated after a few days as blue crystals.

Thermal ellipsoids in the structure depictions are drawn with 50% probability. Crystallographic data is given in Table 1.

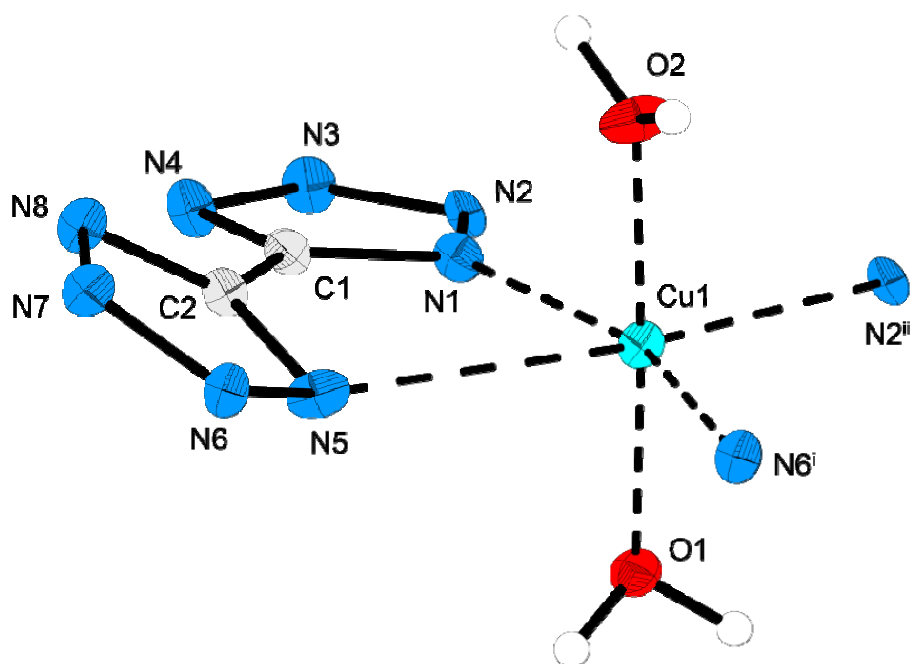
**2** crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in the unit cell and a calculated density of 2.335 g cm<sup>-3</sup> which is very high even for a copper complex. The copper(II) central atom has an octahedral coordination sphere (Figure 1) which is Jahn-Teller distorted along the N2<sup>ii</sup>-N5 axis and not along the water-copper bonds which would have been expected. The Cu1-N5 bond (2.76 Å) is a very long and weak coordinative bond. However, this bond length is in agreement with the Cu-N bond of the similar bis(5-amino-1,2,4-triazol-3-yl)copper(II) complex [7]. The Cu1-N2<sup>ii</sup> bond can be arranged as a normal coordinative bond but is with 2.27 Å still longer than the Cu1-O1, Cu1-O2, Cu1-N1 and Cu1-N6<sup>i</sup> bonds (all about 2.0 Å and similar to the Cu(II) complex in the literature [8]). The bond angle between O1, Cu1 and the according N-atoms in the N2<sup>ii</sup>-N6<sup>i</sup>-N5-N1 plane is about 90°. The N2<sup>ii</sup>-N6<sup>i</sup>-N5-N1 torsion angle (-2.3°) is small, indicating a planar coordination of the nitrogen atoms to Cu1. The N-Cu-N angles (e.g.,  $\angle(N1-Cu1-N2^{ii}) = 100.1^\circ$  and  $\angle(N1-Cu1-N5) = 72.2^\circ$ ) in the N2<sup>ii</sup>-N6<sup>i</sup>-N5-N1 plane deviate from 90° and indicate a distorted octahedral coordination sphere which is induced by the fixed geometry of the 5,5'-bistetrazolato ligand. The bond lengths of the ligand are in a typical range of 5,5'-bistetrazoles (about 1.30-1.35 Å for N-N bonds, 1.35 Å for C-N bond and 1.46 Å for the C-C bond). Supplementary the N-N bond length of 1.30-1.35 Å is between N-N single (1.48 Å) and N=N double bonds (1.20 Å) which together with the nearly planar tetrazole rings ( $\angle(N1-N2-N3-N4) = -0.7^\circ$ ) indicates an aromatic 6 $\pi$ -system [9]. However, the C-bridged tetrazole rings of the 5,5'-BT are twisted to each other ( $\angle(N1-C1-C2-N5) = 24.9^\circ$ ) due to sterical effects and the above mentioned weak bond between N5 and Cu1. Hydrogen bonds are formed between the water molecules and nitrogen atoms of neighbored 5,5'-BT ligands. All hydrogen bonds (Table 2) can be classified as moderate [10]. The strongest hydrogen bond is between O2<sup>v</sup> and N8 which is nearly linear ( $\angle(O2^v-H2B\cdots N8) = 178^\circ$ ) and has a short O-H $\cdots$ N contact of 1.85 Å.

The weakest O-H $\cdots$ N contact is between O1<sup>iv</sup> and N4 with a H $\cdots$ N distance of 2.06 Å and an O1<sup>iv</sup>-H1B $\cdots$ N4 angle of 135°.

**Table 1.** Crystallographic data for **2**.

X-ray parameter 1	2	X-ray parameter 2	2
Formula	C <sub>2</sub> H <sub>4</sub> CuN <sub>8</sub> O <sub>2</sub>	$\mu/\text{mm}^{-1}$	3.238
$M/\text{g mol}^{-1}$	235.68	$\theta$ range/°	4.76–26.24
Color	blue	Dataset ( $h$ ; $k$ ; $l$ )	–9:9; –9:9; –9:9
Habit	block	Reflections collected	3451
Crystal size /mm	0.19 × 0.18 × 0.07	Independent reflections	1342
Crystal system	triclinic	Observed reflections	1153
Space group	$P-1(2)$	$R_{\text{int}}$	0.0713
$a/\text{Å}$	7.4137(13)	Data	1342
$b/\text{Å}$	7.4890(13)	Restraints	4
$c/\text{Å}$	7.5391(14)	Parameters	134
$\alpha/^\circ$	118.928(19)	$R_1$ (obs.)	0.0448
$\beta/^\circ$	109.295(17)	$wR_2$ (all data)	0.1158
$\gamma/^\circ$	92.470(14)	$S$	1.090
$V/\text{Å}^3$	335.18(10)	Resd. dens./e Å <sup>-3</sup>	–0.787/1.311
$Z$	2	Solution	SIR92
$\rho_{\text{calc.}}/\text{g cm}^{-3}$	2.335	Refinement	SHELXL-97
$T/\text{K}$	173(2)	Absorption correction	multi-scan
$F(000)$	234	CCDC	880415

**Figure 1.** Coordination geometry of diaqua( $\mu$ -5,5'-bistetrazolato- $\kappa^4N^1,N^2,N^5,N^6$ )copper(II) (**2**). Symmetry codes: (i)  $1-x, -y, -z$ ; (ii)  $2-x, -y, 1-z$ .



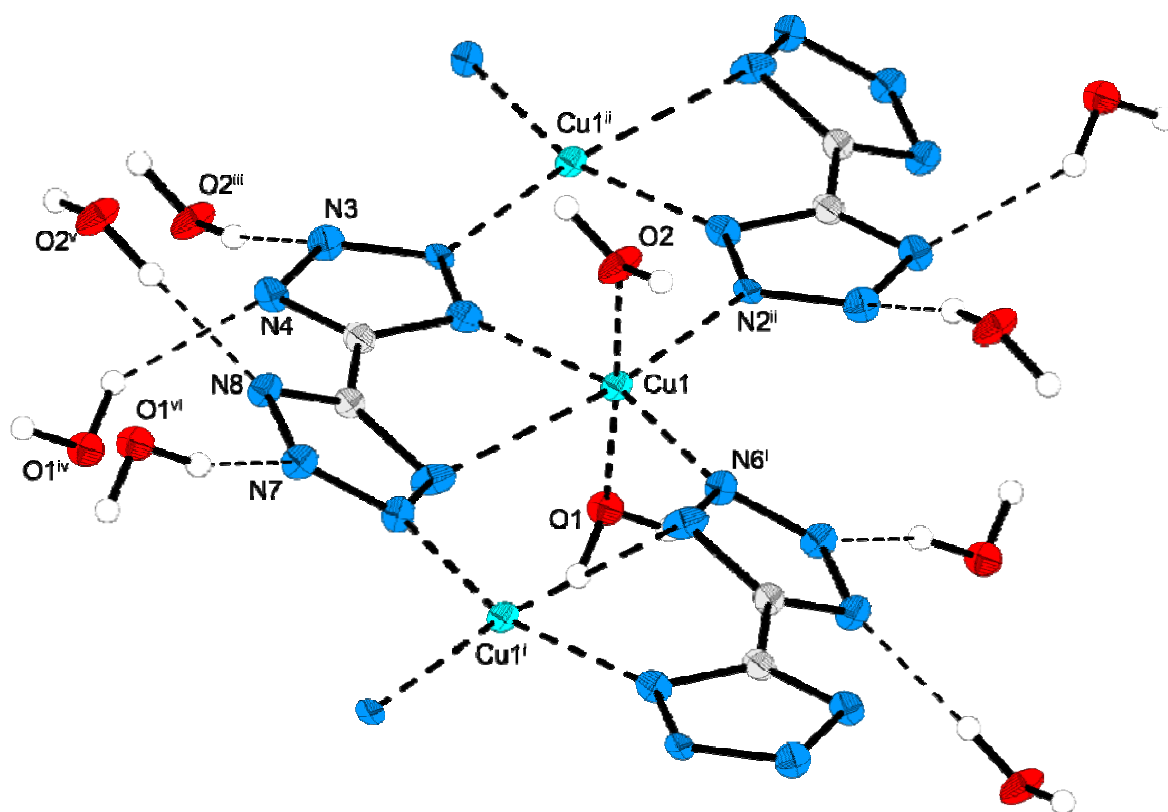
**Table 2.** Distances and angles of the hydrogen bonds of **2**.

D-H...A	<i>d</i> (D-H)/Å	<i>d</i> (H...A)/Å	<i>d</i> (D...A)/Å	< (D-H...A)/°
O2 <sup>iii</sup> -H2A...N3	0.89(6)	1.99(5)	2.876(6)	170(7)
O1 <sup>iv</sup> -H1B...N4	0.90(7)	2.06(6)	2.771(6)	135(8)
O2 <sup>v</sup> -H2B...N8	0.89(5)	1.85(5)	2.746(8)	178(7)
O1 <sup>vi</sup> -H1A...N7	0.90(5)	1.98(5)	2.812(6)	155(4)

Symmetry code: (iii)  $x, y, 1+z$ ; (iv)  $1-x, -y, 1-z$ ; (v)  $1-x, -1-y, -z$ ; (vi)  $-1+x, -1+y, -1+z$ .

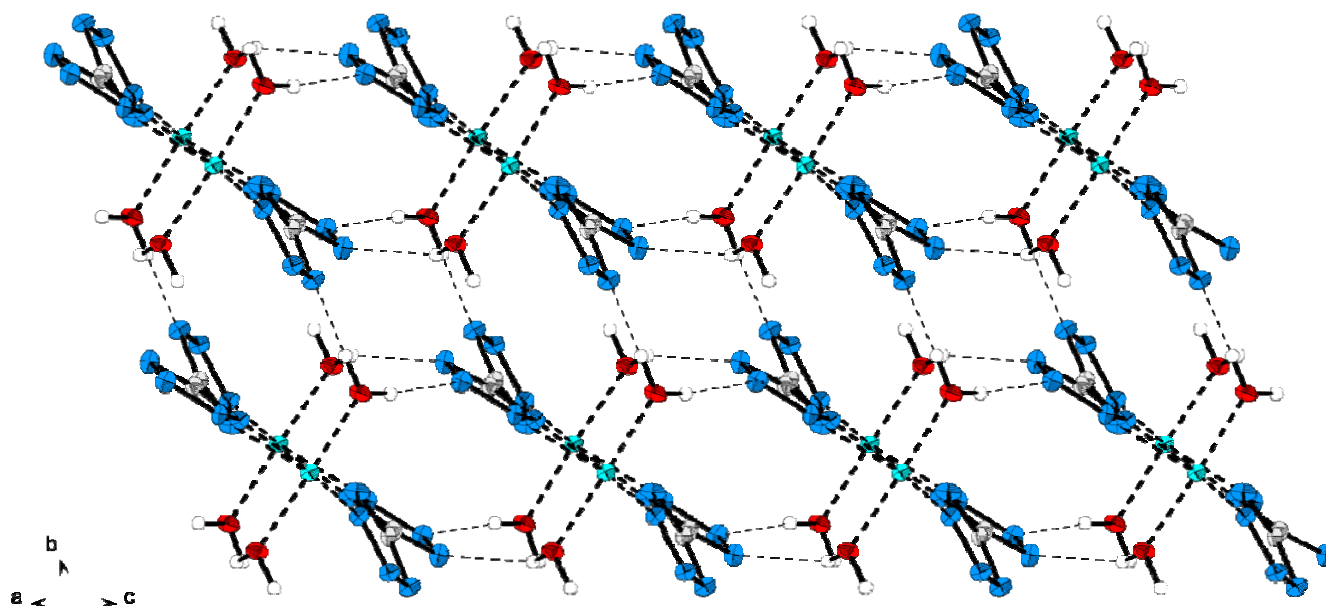
The copper atoms are connected by the 5,5'-bistetrazolato ligand to chains between the *a*- and the *c*-axis (Figure 2). The chains are stacked parallel along the *b*- and the *c*-axis. One chain is hexagonal surrounded (Figure 3). The chains are stabilized among each other with hydrogen bonds between the N atoms of a 5,5'-bistetrazolato ligand and coordinated water molecules of a neighbored complex unit, shown in Figure 3.

**Figure 2.** Hydrogen bonds of **2**. Symmetry codes: (i)  $1-x, -y, -z$ ; (ii)  $2-x, -y, 1-z$ ; (iii)  $x, y, 1+z$ ; (iv)  $1-x, -y, 1-z$ ; (v)  $1-x, -1-y, -z$ ; (vi)  $-1+x, -1+y, -1+z$ .



The energetic properties of compound **2** were also investigated. An impact sensitivity of 30 J, a friction sensitivity of 80 N and an electrostatic discharge of 50 mJ were determined. **2** loses its coordinative bound water at about 160 °C. Decomposition starts at 238 °C in the form of a detonation. The complex compound detonated on a hot-plate, while it was just deflagrating in flame with a green color.

**Figure 3.** Packing scheme of **2**. The parallel stacked chains are stabilized by hydrogen bonds among each other.



### 3. Experimental Section

All chemicals were used as supplied (AppliChem, Sigma-Aldrich, VWR).

NMR spectra were recorded using the spectrometer JEOL Eclipse 400. The measurements were conducted in regular glass NMR tubes ( $\varnothing$  5 mm) and at 25 °C. Tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) was used as external standard. IR spectra were recorded using a PerkinElmer BX FT IR spectrometer on a Smiths DuraSamplIR II diamond ATR unit with pure samples.

The UV-VIS-NIR reflectance of solid samples was measured with a *Varian Cary 500* spectrometer in a wavelength range of 350–1300 nm. The determinations of the carbon, hydrogen and nitrogen contents were carried out by combustion analysis using an Elementar Vario EL.

Decomposition temperatures were measured via differential thermal analysis (DTA) by using an *OZM Research DTA 552-Ex* instrument. The samples (~25 mg) were measured in open glass tubes ( $\varnothing$  4 mm, length about 47 mm) at a heating rate of 5 °C in a range of 15–400 °C.

Crystal structures were determined by single crystal X-ray diffraction on an Oxford Diffraction Xcalibur3 diffractometer with a Sapphire CCD detector, four circle kappa platform, Enhance molybdenum  $\text{K}_\alpha$  radiation source ( $\lambda = 71.073$  pm) and Oxford Cryosystems Cryostream cooling unit. Data collection and reduction were performed with the CRYALISPRO software [11]. The structures were solved with SIR92 [12], refined with SHELXL-97 [13] and checked with PLATON [14], all integrated in the WinGX software suite [15]. The finalized CIF files [16] were checked with checkCIF [17]. Intra- and intermolecular contacts were analyzed with Mercury [18]. Illustrations of molecular structures were drawn with Diamond [19].

The sensitivities against impact (IS) and friction (FS) were determined according to BAM [20] standards using a BAM drop hammer and a BAM friction apparatus [21–25]. The compounds were classified in compliance with UN guidelines [26]. The sensitivities against electrostatic discharge (ESD) were determined using an OZM Research ESD 2010 EN.

Caution: The compounds prepared herein are energetic compounds sensitive towards impact, friction and electric discharge. Therefore, proper protective measures (ear protection, Kevlar<sup>®</sup> gloves, face shield, body armor and earthed equipment) should be used.

### 3.1. Monosodium 5,5'-Bistetrazolate Trihydrate (**1**)

Compound (**1**) was prepared similar to the literature procedure [4]: To a solution of sodium cyanide (29.4 g, 600 mmol) and sodium azide (39.0 g, 600 mmol) in water (350 mL), manganese dioxide (33.0 g, 380 mmol) was added. A mixture of concentrated sulfuric acid (58.8 g, 600 mmol), glacial acetic acid (47.7 g, 795 mmol) and copper(II) sulfate pentahydrate (1.20 g, 4.81 mmol) in water (150 mL) was added dropwise over the course of 2.5 h to the suspension under cooling in an ice bath to keep the temperature below 25 °C. After complete addition the reaction mixture was stirred at 80 °C for 3 h and then cooled to room temperature over night. The brown solid was filtered off and suspended in water (350 mL). Sodium carbonate (45.0 g, 425 mmol) was dissolved in water (250 mL), poured to the suspension and stirred for 2 h at 90 °C. Afterwards the suspension was filtered hot and the slightly green filtrate acidified with conc. hydrochloric acid to pH 1. The precipitating white solid was filtered off and air dried. Concentration of the filtrate to half volume yielded more product. Total yield: 32.8 g (153 mmol, 51%).

DTA ( $T_{\text{onset}}$ , 5 °C min<sup>-1</sup>): 300 °C (dec.); IR (ATR, cm<sup>-1</sup>):  $\nu$  = 3531 (m), 3491 (m), 3480 (m), 3370 (vs), 3305 (s), 2981 (w), 2800 (w), 2739 (w), 2630 (m), 2451 (m), 2282 (w), 1897 (w), 1670 (m), 1619 (m), 1488 (w), 1444 (w), 1349 (s), 1293 (w), 1239 (w), 1206 (w), 1155 (w), 1105 (w), 1078 (w), 1052 (w), 1010 (m), 723 (w), 704 (w), 699 (w); <sup>1</sup>HNMR (*d*<sub>6</sub>-DMSO, 400 MHz, ppm):  $\delta$  = 4.97 (s, 1H, CN<sub>4</sub>H); <sup>13</sup>CNMR (*d*<sub>6</sub>-DMSO, 100 MHz, ppm):  $\delta$  = 149.9 (s, CN<sub>4</sub>); MS (FAB<sup>+</sup>): *m/z* = 23.0 (Na<sup>+</sup>); MS (FAB<sup>-</sup>): *m/z* = 137.0 (C<sub>2</sub>HN<sub>8</sub><sup>-</sup>); EA (C<sub>2</sub>H<sub>7</sub>N<sub>8</sub>NaO<sub>3</sub>, 214.12 g mol<sup>-1</sup>), calculated: C 11.22, H 3.30, N 52.33%, found: C 11.77, H 3.18, N 52.16%; Sensitivities (grain size: < 100 μm): IS: 40 J, FS: 288 N, ESD: 0.50 J.

### 3.2. Diaqua(μ-5,5'-bistetrazolato-κ<sup>4</sup>N<sup>1</sup>,N<sup>2</sup>,N<sup>5</sup>,N<sup>6</sup>)copper(II) (**2**)

Monosodium 5,5'-bistetrazolate trihydrate (**1**, 107 mg, 500 μmol) was dissolved in conc. nitric acid (7 mL) at 60 °C. A warm solution of copper(II) nitrate trihydrate (0.121 g, 500 μmol) in 2 M nitric acid (4 mL) was slowly added and the reaction mixture stirred for 10 min at 60 °C. The blue solution was reduced until a fine blue solid precipitated and then filled up with a large amount of water to dissolve the solid again. The solution was left at room temperature for crystallization. After a few days, **2** was obtained as blue crystals suitable for X-ray structure determination. The crystals were filtered off and washed with acetone. Yield: 110 mg (467 μmol, 93%).

DTA ( $T_{\text{onset}}$ , 5 °C min<sup>-1</sup>): 238 °C (dec.); IR (ATR, cm<sup>-1</sup>):  $\nu$  = 3177 (vs), 3016 (s), 2230 (w), 1623 (w), 1441 (w), 1360 (s), 1325 (m), 1235 (w), 1211 (m), 1184 (m), 1161 (w), 1129 (vw), 1113 (w), 1071 (m), 1024 (m), 780 (w), 735 (m), 675 (w), 662 (m); UV-VIS-NIR (nm):  $\lambda_{\text{max}}$  = 695, 1072; EA (C<sub>2</sub>H<sub>4</sub>CuN<sub>8</sub>O<sub>2</sub>, 235.65 g mol<sup>-1</sup>), calculated: C 10.19, H 1.71, N 47.55%, found: C 10.40, H 1.74, N 47.26%; Sensitivities (grain size: < 100 μm): IS: 30 J, FS: 80 N, ESD: 0.05 J (dec.).

#### 4. Conclusions

The coordination polymer diaqua( $\mu$ -5,5'-bistetrazolato- $\kappa^4 N^1, N^2, N^5, N^6$ )copper(II) (**2**) was prepared from copper(II) nitrate trihydrate and monosodium 5,5'-bistetrazolate trihydrate (**1**) in high yield and purity. The crystal structure could be determined and showed an interesting coordination polymer which forms parallel stacked chains. **2** is sensitive towards impact (IS: 30 J) and very sensitive towards friction (FS: 80 N). **2** only deflagrates in flame, whereas the hot-plate test showed detonation. The coordination polymer is nearly insoluble in water and insoluble in acetone. Permanent dehydration of **2** is not possible because the coordinated crystal water participates in the strong H-bond network and complements the octahedral coordination sphere of the copper(II) centres.

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#### Conflict of Interest

The authors declare no conflict of interest.

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