

Copper Bis(1-methyl-5-nitriminotetrazolate): A Promising New Primary Explosive

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Copper bis(1-methyl-5-nitriminotetrazolate) (**1**) was synthesized and investigated as a new primary explosive. Compound **1** was obtained by dehydration of diaquabis(1-methyl-nitriminotetrazolato)copper(II) dihydrate (**2**) or diaquabis(1-methylnitriminotetrazolato)copper(II) (**3**) at 120 °C. Complexes **2** and **3** are easily formed by the reaction of 1-methyl-5-nitrimino-1,2,3,4-tetrazole (**4**) with copper(II) nitrate in aqueous solution in high yields. Single crystals of **1** were obtained by recrystallization from dry methanol, whereas wet methanol favors the yield of diaquabis(1-methyl-nitriminotetrazolato)copper(II) dimethanolate (**5**). Compound **1** was characterized by using single-crystal X-ray diffraction, IR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). The sensitivities were investigated by using the BAM drophammer and friction tests, and the heat

of formation was calculated on the basis of electronic energies at the B3LYP/SDD level of theory. Compound **1** shows an impact sensitivity that is five times higher and a friction sensitivity that is ten times lower than that of lead azide, which is appropriate. In addition, the long-term stability of **1** at higher temperatures was tested by using isothermal safety calorimetry (TSC). Compounds **2** and **3** were characterized by single-crystal X-ray diffraction, IR spectroscopy, elemental analysis, DSC, bomb calorimetry, and BAM sensitivity tests. In addition, compound **5** was characterized by single-crystal X-ray diffraction and elemental analysis. The dehydration of **2** was determined by using thermal gravimetry (TG) to occur by the loss of crystal water in one discrete step. (© WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Commonly used primary explosives^[1,2] still include poisonous and polluting compounds (illustrated in Figure 1) like lead azide [Pb(N₃)₂],^[3–5] and lead styphnate (2,4,6-trinitroresorcinat),^[6] which replaced mercury fulminate [Hg(CNO)₂]^[7] early in the last century. Primary explosives are highly sensitive and are characterized by detonation velocities of 3500–5500 ms^{–1}. The discovery of suitable new substitutes for lead-containing primary explosives is an important aspect of current energetic materials research. Primary explosives consisting only of C, N, and H such as tetrazene,^[8] which is used as a sensitizer, exist but are often difficult to synthesize.

A recently employed idea is the formation of nontoxic metal complexes containing zinc or copper instead of toxic heavy metals.^[9] Because several tetrazoles^[10,11] and tetrazolates^[12,13] are known to be promising energetic compounds^[14] with appropriate properties such as high densities, a positive heat of formation, and a high nitrogen content, one possible alternative for the development of new primary explosives is the use of copper tetrazole complexes.^[15–17]

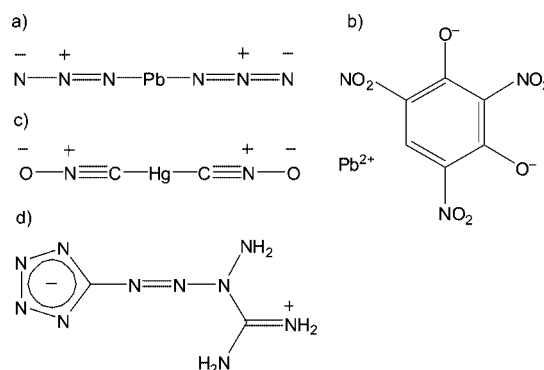


Figure 1. Common primary explosives: (a) lead azide, (b) lead styphnate, (c) mercury fulminate, and (d) tetrazene.

Copper tetrazole complexes are also suitable materials for modern pyrotechnical compositions. Common pyrotechnic compositions are nonexplosive combustible mixtures consisting of fuels and oxidizers, which generate bright-colored light, heat, or acoustic effects.^[18] High-nitrogen materials have been investigated for use in pyrotechnic compositions in order to reduce smoke production.^[19] A low-smoke pyrotechnic composition should include a nitrogen-rich energetic material (e.g. tetrazoles) with a low carbon content, an oxidizer, and a colorant. Copper(II) 1-

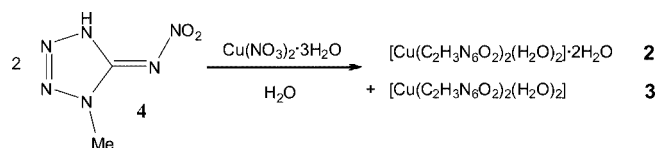
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methyl-5-nitriminotetrazolates **2** and **3** are suitable new compounds for use as green-coloring pyrotechnic materials acting as substitutes for toxic barium salts.

Results and Discussion

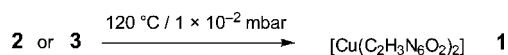
Synthesis

The copper complexes $[\text{Cu}(\text{C}_2\text{H}_3\text{N}_6\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{C}_2\text{H}_3\text{N}_6\text{O}_2)_2(\text{H}_2\text{O})_2]$ (**3**) were synthesized according to Scheme 1 by the addition of an aqueous solution of copper nitrate trihydrate to an aqueous solution containing two equivalents of 1-methyl-5-nitriminotetrazole (**4**)^[20] at 80 °C. Compound **2** was observed as the main product (85% yield), whereas **3** was obtained when the mother liquor was allowed to stand for a few days. Compound **4** was synthesized by the nitration of 1-methyl-5-aminotetrazole^[21,22] by using fuming HNO_3 .



Scheme 1. Synthesis of compounds **2** and **3**.

The highly explosive $[\text{Cu}(\text{C}_2\text{H}_3\text{N}_6\text{O}_2)_2]$ (**1**), which does not contain crystal water, was obtained by dehydration of **2** by using high vacuum (1×10^{-2} bar) at 120 °C for two hours (Scheme 2). To remove the four water molecules, heating to 120 °C is sufficient but it requires twice the time. Single crystals of **1** were obtained by recrystallization of **1** from dry methanol, whereas recrystallization from wet methanol led to the formation of crystals of compound **5**, which contains two coordinated water molecules and two free methanol molecules.



Scheme 2. Synthesis of **1** by dehydration of **2** or **3**.

Molecular Structures

The single-crystal X-ray diffraction data were collected with an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. Data collection was undertaken by using the CrysAlis CCD software,^[23] and the data reductions were performed with the CrysAlis RED software.^[24] The structures were solved by using SIR-92^[25] and refined with SHELXL-97^[26] and finally checked with PLATON.^[27] In the structures, the hydrogen atoms were located and refined. The absorptions of **1**, **2**, **3**, and **5** were corrected by using the SCALE3 ABSPACK multiscan method.^[28] Selected data

from the X-ray data collections and refinements are given in Table 3. Further information regarding crystal structure determination was deposited with the Cambridge Crystallographic Data Centre.^[29]

Primary explosive **1** crystallizes in the monoclinic space group $P2_1/c$ with 2 molecules in the unit cell and a density of 2.067 g cm^{-3} . The copper cations lay on the center of inversion and are coordinated in a distorted octahedral arrangement by two nitrogen atoms [$d(\text{Cu}-\text{N}4) = 1.923(2) \text{ \AA}$], which is also found in copper nitrogen complexes such as $[\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2]$,^[30] and four oxygen atoms [$d(\text{Cu}-\text{O}1) = 1.974(2) \text{ \AA}$, $d(\text{Cu}-\text{O}4^i) = 2.589(2) \text{ \AA}$ ($i: 2 - x, -0.5 + y, 1.5 - z$)]. The shorter coordination distances Cu–N4 and Cu–O1 are between one chelating 1-methyl-5-nitriminotetrazolato ligand, whereby a longer coordination to the other oxygen atom of the nitro group is also observed, which is longer than in typical Jahn–Teller distorted d^9 copper complexes (see structures of **2**, **3**, and **5**). Accordingly, every nitro group participates in coordination with two copper centers, which results in an endless 3-dimensional network. The extended molecular structure of **1**, which illustrates the coordination of the nitro groups in the crystalline state, is shown in Figure 2.

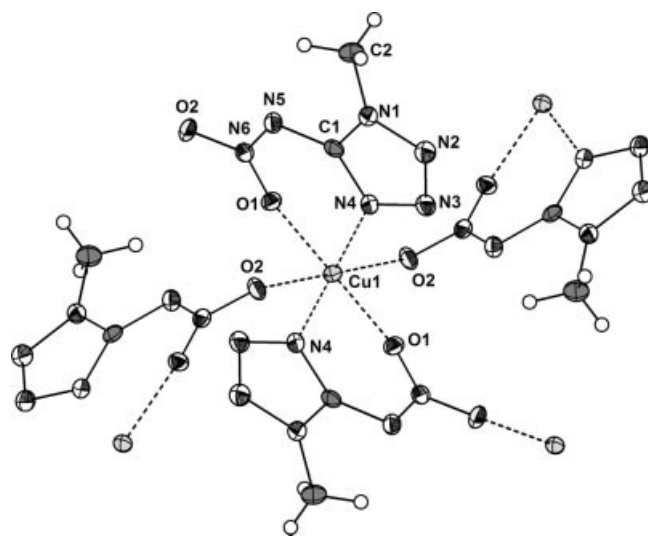


Figure 2. Crystal structure of **1** showing an extended molecular unit and atom-labeling scheme. Ellipsoids represent 50% probability.

The reaction of ligand **4** with copper(II) nitrate yields two different compounds $\{[\text{Cu}(\text{C}_2\text{H}_3\text{N}_6\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{C}_2\text{H}_3\text{N}_6\text{O}_2)_2(\text{H}_2\text{O})_2]$ (**3**), which can be easily distinguishable by their color. Blue-colored main product **2** is characterized by the inclusion of two water molecules that do not participate in the coordination sphere. In these two structures, the effects of the inclusion of water can clearly be seen for example in the variation of the density (**2** 1.870 g cm^{-3} , **3** 2.035 g cm^{-3}). Both compounds crystallize with two molecules in the unit cell in the monoclinic crystal system: **2** in the space group $P2_1/c$ and **3** in the alternative

setting $P2_1/n$. The coordination geometry of the copper cations is characterized by an elongated octahedral arrangement due to the Jahn–Teller effect. This coordination geometry is typical for transition-state metals with d^9 valence electron configurations distorted by the Jahn–Teller^[31] effect and is similar to those found for other complexes of both 2-substituted and 1-substituted tetrazoles.^[32] The Cu–N bond lengths show considerable variation. Whereas a typical Cu–N4 distance of 1.997(1) Å is found in **2**, which is comparable to complexes with ligand systems such as 1,10-phenanthroline,^[33] in compound **3** the distance Cu–N4 of 1.919(2) Å is importantly shorter. The differences in the Cu–O bond lengths are, however, less significant [**2**: $d(\text{Cu–O3}) = 1.971(1)$ Å, $d(\text{Cu–O1}) = 2.393(1)$ Å, **3**: $d(\text{Cu1–O1}) = 2.048(2)$ Å, $d(\text{Cu1–O3}) = 2.337(2)$ Å]. The geometries of the 1-methyl-5-nitriminotetrazolate moieties in **2** and **3** are essentially unaffected by the inclusion of water in **3**. In Figures 3 and 4 the molecular moieties of complexes **2** and **3** are shown.

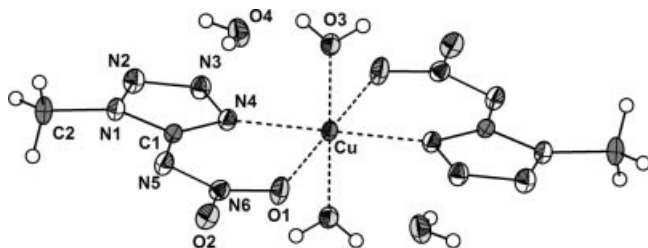


Figure 3. Crystal structure of **2** showing the molecular unit and atom-labeling scheme. Ellipsoids represent 50% probability.

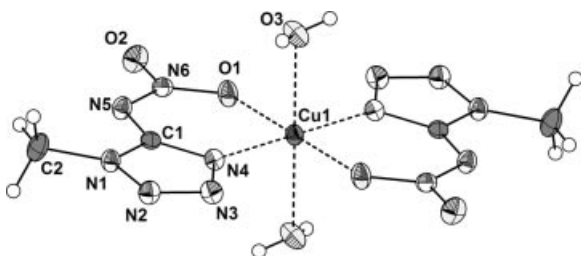


Figure 4. Crystal structure of **3** showing the molecular unit and atom-labeling scheme. Ellipsoids represent 50% probability.

Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell and the lowest density of 1.74 g cm^{−3} observed in this work. The structure is analogous to that of **2**; however, instead of two water molecules in **2**, two methanol molecules complete the packing of compound **5**. The methanol is not coordinated to any copper centers; therefore, it is not further discussed. The molecular structure of **5** in the crystalline state is shown in Figure 5.

The bond lengths and bond lengths of the discussed crystal structures **1**, **2**, **3**, and **5** are given in Table 1.

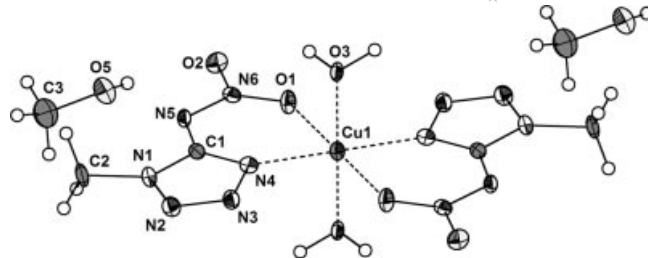


Figure 5. Crystal structure of **5** showing the molecular unit and atom-labeling scheme. Ellipsoids represent 50% probability.

Table 1. Bond lengths and angles.

Atoms A–B	1 <i>d</i> [Å]	2 <i>d</i> [Å]	3 <i>d</i> [Å]	5 <i>d</i> [Å]
Cu–O3	–	1.971(1)	2.337(2)	1.998(2)
Cu–N4	1.923(2)	1.997(1)	1.919(2)	1.960(2)
Cu–O1	1.974(2)	2.393(1)	2.048(2)	2.326(2)
O2–N6	1.248(3)	1.261(2)	1.241(3)	1.252(2)
O1–N6	1.291(3)	1.246(2)	1.284(3)	1.255(2)
N1–C1	1.340(3)	1.347(2)	1.344(3)	1.339(3)
N1–N2	1.352(3)	1.349(2)	1.352(3)	1.353(3)
N1–C2	1.467(4)	1.462(2)	1.467(3)	1.466(3)
N5–N6	1.306(3)	1.324(2)	1.311(3)	1.328(3)
N5–C1	1.362(3)	1.365(2)	1.366(3)	1.361(3)
N2–N3	1.287(3)	1.294(2)	1.293(3)	1.288(3)
N3–N4	1.365(3)	1.365(2)	1.365(3)	1.365(3)
N4–C1	1.334(3)	1.343(2)	1.337(3)	1.343(3)
Atoms A–B–C	Angle [°]	Angle [°]	Angle [°]	Angle [°]
O3–Cu–N4	–	89.84(6)	87.08(9)	89.27(8)
O3–Cu–O1	–	88.97(5)	91.39(8)	88.35(7)
N4–Cu–O1	86.23(8)	76.57(5)	85.57(8)	78.18(7)
C1–N1–N2	108.8(2)	109.5(1)	109.4(2)	109.8(2)
C1–N1–C2	129.5(2)	128.8(1)	129.2(2)	128.4(2)
N2–N1–C2	121.7(2)	121.7(1)	121.1(2)	121.8(2)
N6–N5–C1	117.5(2)	117.8(2)	118.3(2)	118.5(2)
N3–N2–N1	107.4(2)	106.6(1)	107.0(2)	107.1(2)
O1–N6–O2	117.8(2)	120.8(1)	117.6(2)	121.0(2)
O1–N6–N5	125.2(2)	124.9(1)	125.1(2)	124.0(2)
O2–N6–N5	116.9(2)	114.3(1)	117.4(2)	115.0(2)
N2–N3–N4	109.6(2)	110.6(1)	109.7(2)	109.5(2)
C1–N4–N3	107.1(2)	106.5(1)	107.4(2)	107.7(2)

Thermogravimetry

Thermogravimetry was used to investigate the dehydration step and was performed with a Setaram TG-DTA 92-16^[34] under a helium atmosphere with a heating rate of 1° min^{−1} to a maximum temperature of 350 °C. For the measurement, 5.351 mg of a pulverized sample in an aluminum oxide pan was used. The TG curve as well the DTA curve are shown in Figure 6, and they show that the loss of water occurs over a wide range that starts before 50 °C and ends at about 85 °C. The loss of water depends on the heating rate and occurs at higher temperatures when higher heating rates are used (see DSC measurements). The loss of 0.878 mg weight corresponds to the loss of all four water molecules in compound **2**, and therefore, it was not possible to stop the dehydration at compound **3**. In the second step

at about 245 °C, a mass of 3.932 mg was lost, which is more than the expected mass for the remaining copper(II) oxide as solid residues. Through the explosion that releases a huge amount of nitrogen, some of the Cu^{II}O must be removed from the open setup.

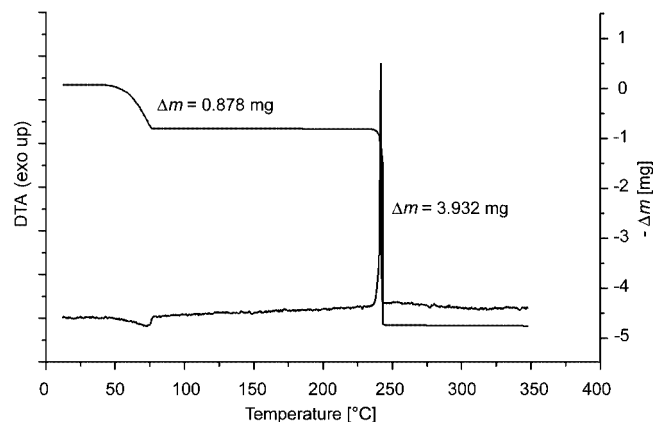


Figure 6. Thermogravimetry plot of compound **2** showing the loss of mass (right axis) and the DTA curve (left axis).

Energetic Properties

Differential Scanning Calorimetry (DSC)

DSC measurements used to determine the thermal behavior of the copper(II) 1-methyl-5-nitriminotetrazolate complexes were performed in covered Al containers with a nitrogen flow of 20 mL min⁻¹ with a Perkin–Elmer Pyris 6 DSC,^[35] which was calibrated by standard pure indium and zinc at a heating rate of 5 °C min⁻¹. Compound **1** decomposes at a temperature of 252 °C at a heating rate of 5 °C min⁻¹ and at 248 °C at a heating rate of 2 °C min⁻¹. The DSC plots in Figure 7 show the thermal behavior of ca. 1.5 mg of **1–3** in the temperature range from 50 to 300 °C. Interestingly, the deprotonation in combination with the coordination to the copper(II) centers results in a substantial increase in the decomposition points in relative to neutral ligand **4**, which decomposes at temperatures above 125 °C.

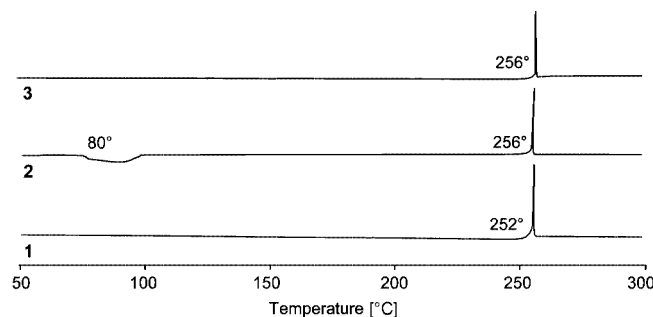
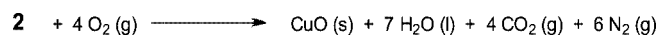


Figure 7. DSC plots of compounds **1**, **2**, and **3** (heating rate 5 °C min⁻¹).

To determine the heats of decomposition, a Linseis DSC PT10^[36] instrument was used. Three samples (ca. 1 mg) were heated with a heating rate of 2 °C min⁻¹ and a fixed nitrogen flow of 5 L h⁻¹ over the decomposition peaks. The surface was integrated by using Linseis software, and the average of three measurements was used to calculate the heats of decomposition: for **1** $\Delta_{\text{dec.}}H_{\text{m}}^{\circ} = 2739 \text{ J g}^{-1}$ (958 kJ mol⁻¹) and for **2** $\Delta_{\text{dec.}}H_{\text{m}}^{\circ} = 2218 \text{ J g}^{-1}$ (936 kJ mol⁻¹).

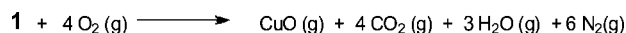
Bomb Calorimetry

As a result of its explosive character, it was not possible to combust compound **1** completely in the bomb calorimeter; therefore, only complex **2** was investigated by using bomb calorimetry (Scheme 3). For the calorimetric measurements of **2**, a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb for the combustion of highly energetic materials was used.^[37] The reported value of the energy of combustion $\Delta U_{\text{c}} = -1610 \text{ cal g}^{-1}$ (–2841 kJ mol⁻¹) is the average of three single measurements. The calorimeter was calibrated by combustion of certified benzoic acid (SRM, 39i, NIST) under an oxygen atmosphere at a pressure of 3.05 MPa. The standard molar enthalpy of combustion ($\Delta_{\text{c}}H^{\circ}$) was derived from $\Delta_{\text{c}}H^{\circ} = \Delta U_{\text{c}} + \Delta nRT$ [$\Delta n = \Delta n_{\text{i}}$ (products, g) – Δn_{i} (reactants, g); where Δn_{i} is the total molar amount of gases in the products or reactants]. The enthalpy of formation, $\Delta_{\text{f}}H^{\circ}$, of –904 kJ mol⁻¹ for **2** was calculated at 298.15 K by using the Hess thermochemical cycle and the combustion reaction outlined in Scheme 3. After combustion, only a brown compound was left in the bomb, which was identified as copper(II) oxide.



Scheme 3. Combustion equation of **2**.

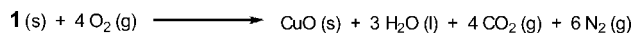
To estimate the heat of formation of solid [Cu(C₂H₃N₆O₂)₂] (**1**), we calculated^[38] the electronic energies of all species involved in the gas-phase reaction (Scheme 4) at the B3LYP/SDD level of theory to be $\Delta E^{\text{el}}(\mathbf{1}) = -1859 \text{ kJ mol}^{-1}$.



Scheme 4. Gas-phase combustion equation of **1**.

This gas-phase electronic energy was converted after correction for the work term and the vibrational, translational, and rotational corrections into the gas-phase enthalpy of $\Delta H(\mathbf{1}) = -1883.4 \text{ kJ mol}^{-1}$.

With the known enthalpy of sublimation for CuO of $\Delta H_{\text{sub}}(\text{CuO}) = 462.7 \text{ kJ mol}^{-1}$ ^[39] and the estimated heat of sublimation for **1** of $\Delta H_{\text{sub}}(\mathbf{1}) = 175.9 \text{ kJ mol}^{-1}$ [this value was taken to be equal to the enthalpy of sublimation of the Cu(salen) complex,^[40] the enthalpy of combustion of **1** according to the equation in Scheme 5 could be calculated to be $\Delta H_{\text{comb.}}(\mathbf{1}, \text{s}) = -2169.3 \text{ kJ mol}^{-1}$.

Scheme 5. Combustion equation of solid **1**.

The enthalpy of formation was then calculated by using the known literature^[41] values for the enthalpies of formation of water [$\Delta H^\circ_f(\text{H}_2\text{O}, \text{g}) = -242 \text{ kJ mol}^{-1}$] and carbon dioxide [$\Delta H^\circ_f(\text{CO}_2, \text{g}) = -393 \text{ kJ mol}^{-1}$] to be $\Delta H^\circ_f(\mathbf{1}, \text{s}) = -83.7 \text{ kJ mol}^{-1}$.

Sensitivities

For initial safety testing, the impact and friction sensitivities were tested according to BAM methods^[42,43] with the “BAM Fallhammer” and “BAM friction tester”. Compound **1** is very sensitive towards impact (0.7 J) and friction (40 N), and because the value is comparable with lead azide, it should be considered to be a primary explosive; it should therefore only be handled with appropriate precautions. Compounds **2** and **5** are not sensitive towards impact (<100 J) and friction (<360 N). Compound **3** shows only a very low impact sensitivity (>55 J) and is not sensitive towards friction.

Comparison with Lead Azide

Because lead azide is still used in modern priming charges and the U. S. army alone consumes more than 1000 lbs of it,^[9] a comparison of its properties with those of compound **1** is shown in Table 2.

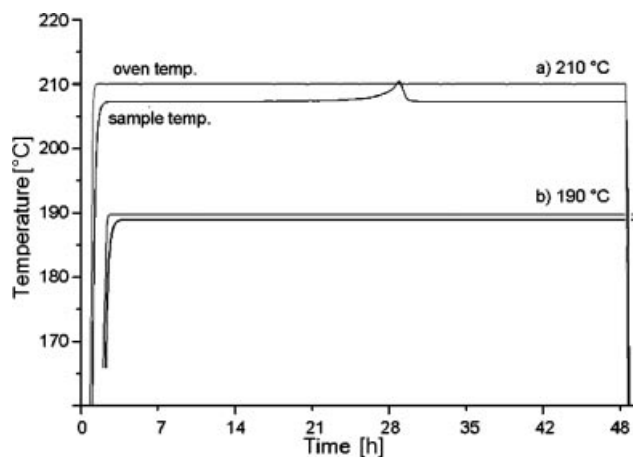
Table 2. Energetic properties of **1** and lead azide.

	1	Lead azide
Impact sensitivity	>0.7 J	2.5–4.0 J (pure) 3.0–6.5 J (techn.)
Friction sensitivity	>40 N	0.1–1 N
Decomposition temperature	252 °C	>315 °C

Long-Term Stability Tests

The long-term stability test of **1** was performed with a Systag FlexyTSC^[44] (thermal safety calorimetry) in combination with a RADEX V5 oven and the SysGraph software. The test was undertaken as long-term isoperibolic evaluations in glass test vessels at atmospheric pressure with 500 mg of the compound. It was shown that tempering the substance for 48 h at 40 °C below the decomposition point results in storage periods that are over 50 years at room temperature. Initially, for **1** a temperature of 210 °C was chosen and possible occurrences of exo- or endothermic behavior were investigated over period of 48 h (Figure 8). Compound **1** was not stable for 48 h at a temperature of 210 °C. After 25 h there was an explicit increase in the temperature that was passed again after a few hours. After 48 h the compound in the test vessel was mainly brown-colored Cu^{II}O. The second test was performed at a temperature of

190 °C, and the compound was completely stable during this period. It can therefore be reasoned that the compound shows long-term stability even at higher temperatures, which is a basic requirement for possible applications.

Figure 8. TSC plots of compound **1** over a period of 48 h at (a) 210 °C and (b) 190 °C (the upper curve represents the oven temperature, the curve below the sample temperature).

Conclusions

From this experimental study the following conclusions can be drawn: (1) 1-Methyl-5-nitriminotetrazole can be used as a bidentate ligand in novel copper complexes forming compounds with different amounts of crystal water depending on the reaction conditions. The crystal water can be completely removed at higher temperatures to form highly explosive bis(1-methyl-5-nitriminotetrazolate) copper(II) (**1**). The dehydration proceeds in discrete steps and is determined by differential thermo gravimetry. (2) Bis(1-methyl-5-nitriminotetrazolato) copper(II) is a primary explosive due to its high sensitivity towards impact (0.7 J), but it shows a lower sensitivity towards friction (40 N) relative to common primary explosives. It is stable up to 250 °C and even shows long-term stability when tested at a temperature of 190 °C. In comparison with the commonly used lead azide, it shows suitable properties, in particular, its friction and impact sensitivities and its lower toxicity. The thermal decomposition provides a heat of decomposition of 2730 J g^{-1} , which was measured by using differential scanning calorimetry. (3) The crystal structures presented show common copper coordinations that are characterized by a Jahn–Teller distorted elongated octahedral coordination sphere.

Experimental Section

All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting points were measured with a Perkin–Elmer Pyris6 DSC apparatus by using a heating rate of 5° min^{-1} . Otherwise, melting points were determined with a Büchi melting point B-450 apparatus and are not corrected.

Infrared (IR) spectra were recorded with a Perkin–Elmer Spectrum One FTIR instrument. Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. Bomb calorimetry was done with a Parr 1356 bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were performed with a BAM drophammer and a BAM friction tester.

CAUTION!

Compounds **1** and **4** are highly energetic materials that show increased sensitivities towards various stimuli. Proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar gloves and ear plugs) should be used when handling these compounds, especially when compound **1** is prepared on a larger scale.

[Cu(C₂H₃N₆O₂)₂] (1): The highly explosive copper complex **1** was obtained by dehydration of powdered **2** at 120 °C and reduced pressure (1×10^{-2} mbar) for 2 h. Single crystals suitable for X-ray diffraction were grown from dry methanol. M.p. 252 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3498 (m), 3456 (m), 3223 (m), 2861 (m), 2926 (m), 2346 (w), 1618 (m), 1528 (m), 1494 (m), 1477 (m), 1438 (m), 1384 (m), 1339 (s), 1303 (s), 1245 (m), 1229 (m), 1120 (m), 1037 (w), 1001 (m), 873 (m), 776 (w), 733 (w), 698 (w), 588 (w), 512 (w) cm⁻¹. C₄H₆CuN₁₂O₄ (349.71): calcd. C 13.74, H 1.73, N 48.06; found C 13.77, H 1.83, N 48.29.

[Cu(C₂H₃N₆O₂)₂ (H₂O)₂]·(H₂O)₂ (2): Copper(II) nitrate trihydrate (240 mg, 1.0 mmol) was dissolved in hot water (2 mL) and combined with a hot solution of 1-methyl-5-nitriminotetrazole (288 mg,

2 mmol) in water (15 mL) and heated at reflux for 5 min. After cooling to room temperature and standing for 24 h, blue crystals of **2** started to precipitate (299 mg, 71%). After filtration, the mother liquid was left, whereby green crystals of **3** were obtained (39 mg, 10%). M.p. 256 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3504 (m), 3461 (m), 3220 (m), 2963 (m), 2148 (w), 1801 (w), 1662 (w), 1526 (m), 1476 (s), 1398 (m), 1384 (m), 1339 (s), 1305 (s), 1256 (m), 1120 (m), 1037 (m), 1010 (w), 929 (w), 887 (w), 859 (w), 776 (w), 737 (w), 654 (w), 585 (w) cm⁻¹. C₄H₁₄CuN₁₂O₈ (421.78): calcd. C 11.39, H 3.35, Cu 15.07, N 39.85, O 30.35; found C 11.32, H 3.38, N 39.69.

[Cu(C₂H₃N₆O₂)₂(H₂O)₂] (3): M.p. 251 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3481 (m), 2963 (w), 1798 (w), 1628 (m), 1539 (m), 1487 (m), 1417 (s), 1404 (s), 1385 (s), 1339 (m), 1298 (s), 1247 (m), 1125 (m), 1030 (m), 877 (w), 772 (w), 757 (w), 734 (m), 701 (m), 537 (w) cm⁻¹. C₄H₁₀CuN₁₂O₆ (385.75): calcd. C 12.45, H 2.61, Cu 16.47, N 43.57; found C 12.28, H 2.71, N 43.11.

4: 1-Methyl-5-nitriminotetrazole was obtained by the nitration of 1-methyl-5-aminotetrazole by using fuming HNO₃. The nitration reaction was quenched with ice water, and the solvent was removed by using high vacuum until the product started to precipitate.

[Cu(C₂H₃N₆O₂)₂ (H₂O)₂]·(MeOH)₂: The light-blue colored methanol containing complex **5** was obtained by recrystallization of **1** from a wet methanol solution. C₆H₁₈CuN₁₂O₈ (449.83): calcd. C 16.02, H 4.03, N 37.37; found C 15.8, H 3.92, N 37.65.

Table 3 contains the parameters and data obtained from the single-crystal X-ray determinations.

Table 3. Crystallographic data.

	1	2	3	5
Formula	Cu ₄ H ₆ N ₁₂ O	Cu ₄ H ₁₄ N ₁₂ O ₈	Cu ₄ H ₁₀ N ₁₂ O ₆	C ₆ H ₁₈ CuN ₁₂ O ₈
Formula weight	349.75	421.81	385.78	449.87
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)
Color / habit	green / rods	blue / rods	green / plates	light blue / needles
Size [mm]	0.03 × 0.04 × 0.10	0.08 × 0.17 × 0.18	0.08 × 0.12 × 0.16	0.03 × 0.05 × 0.12
<i>a</i> [Å]	9.1982(5)	5.9934(4)	5.7451(6)	6.9382(3)
<i>b</i> [Å]	6.7004(3)	14.3068(8)	9.482(1)	12.1607(7)
<i>c</i> [Å]	9.3453(4)	8.9967(6)	11.574(1)	10.1950(5)
<i>α</i> [°]	90.0	90.0	90.0	90.0
<i>β</i> [°]	102.653(5)	103.753(6)	92.935(9)	93.188(5)
<i>γ</i> [°]	90.0	90.0	90.0	90.0
<i>V</i> [Å ³]	561.98(5)	749.32(8)	629.7(1)	858.86(7)
<i>Z</i>	2	2	2	2
$\rho_{\text{calcd.}}$ [g cm ⁻³]	2.067	1.870	2.035	1.740
μ [mm ⁻¹]	1.991	1.529	1.799	1.340
<i>F</i> (000)	350	430	390	462
$\lambda_{\text{Mo-K}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	100(2)	120(2)	200(2)	100(2)
θ min, max [°]	3.8, 26.0	4.5, 26.5	4.1, 26.5	3.7, 26.0
Data set	–11/11; –8/8; –11/11	–7/7; –17/17; –11/11	–7/7; –11/11; –14/14	–8/8; –13/15; –12/12
Reflections collected	5473	7776	6422	4363
Indep. reflections	1102	1551	1295	1689
<i>R</i> _{int}	0.044	0.025	0.038	0.041
Observed reflections	837	1473	1170	1060
No. parameters	109	143	126	160
<i>R</i> ₁ (obs)	0.0267	0.0254	0.0352	0.0291
<i>wR</i> ₂ (all data)	0.0669	0.0616	0.0782	0.0612
GooF	0.96	1.12	1.16	0.88
Min./Max. Resd. [e Å ⁻³]	–0.32, 0.42	–0.24, 0.34	–0.31, 0.39	–0.33, 0.41
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multiscan	multiscan	multiscan	multiscan
CCDC No.	642162	641972	641973	642161

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- [1] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, p. 174.
- [2] K. Karaghiosoff, T. M. Klapötke, A. N. Michailovski, H. Nöth, M. Suter, G. Holl, *Propellants Explos. Pyrotech.* **2003**, *28*, 1.
- [3] a) G. Pfefferkorn, *Z. Naturforsch., Teil A* **1948**, *3*, 364; b) B. Reitzner, R. P. Manno, *Nature* **1963**, *198*, 4884; c) C. M. Ho, S. T. Lee, P. C. Chen, G. H. Wei, J. S. Shiao, P. H. Chen, H. C. Fan, J. Y. Huan, *Huoyao Jishu* **1992**, *8*, 31; d) G. L. Glen, *J. Am. Chem. Soc.* **1963**, *85*, 3892.
- [4] a) M. Stammer, J. E. Abel, R. C. Ling, *Nature* **1961**, *192*, 626; b) M. Stammer, J. E. Abel, J. V. R. Kaufman, *Nature (London, U.K.)* **1960**, *185*, 4560; c) J. Roth, *J. Chem. Phys.* **1964**, *41*, 1929; d) G. Todd, E. Parry, *Nature* **1962**, *196*, 250.
- [5] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, p. 54.
- [6] a) A. Stettbacher, *Nitrocellulose* **1937**, *8*, 3–6; A. Stettbacher, *Nitrocellulose* **1937**, *8*, 21–27; b) J. R. Payne, *Thermochim. Acta* **1994**, *242*, 13; c) H. C. J. Saint, J. Hewson, *Analyst* **1959**, *84*, 183; d) F. C. Tompkins, D. A. Young, *J. Chem. Soc.* **1956**, 3331; e) W. C. McCrone, O. W. Adams, *Anal. Chem.* **1955**, *27*, 2014; f) J. F. Hobbs, W. Melville, *Ger. Offen.* **1974**.
- [7] a) S. Singh, *J. Phys. Soc. Jpn.* **1959**, *14*, 540; b) L. Wohler, A. Berthmann, *Angew. Chem.* **1930**, *43*, 59; c) A. Langhans, *J. Soc. Chem. Ind. (London)* **1918**, *38*, 389A; d) M. E. Brown, G. M. Swallowe, *Thermochim. Acta* **1981**, *49*, 333.
- [8] a) S. H. Patinkin, J. P. Horwitz, E. Lieber, *J. Am. Chem. Soc.* **1955**, *77*, 562; b) J. R. C. Duke, *J. Chem. Soc. Sect. D* **1971**, *1*, 2; c) G. C. Mei, J. W. Pickett, *Propellants Explos. Pyrotech.* **1998**, *23*, 172.
- [9] M. H. V. Huynh, M. A. Hiskey, T. J. Meyer, M. Wetzler, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 5409.
- [10] R. P. Singh, R. D. Verma, D. J. Meshri, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2006**, *45*, 3584.
- [11] T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *Propellants Explos. Pyrotech.* **2004**, *29*, 325.
- [12] A. Hammerl, M. A. Hiskey, G. Holl, T. M. Klapötke, K. Polborn, J. Stierstorfer, J. J. Weigand, *Chem. Mater.* **2005**, *17*, 3784.
- [13] C. Ye, J.-C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* **2005**, *21*, 2750.
- [14] T. M. Klapötke in *Moderne Anorganische Chemie* (Ed.: E. Riedel), 2nd ed., Walter de Gruyter, Berlin, New York, **2003**, pp. 95–100.
- [15] a) T. M. Klapötke, P. Mayer, K. Polborn, J. Stierstorfer, J. J. Weigand, *New Trends in Research of Energetic Materials, Proceedings of the Seminar*, 9th ed., Pardubice, Czech Republic, **2006**, vol. 2, p. 641; b) T. M. Klapötke, P. Mayer, K. Polborn, J. Stierstorfer, J. J. Weigand, *37th International Annual Conference of ICT*, Karlsruhe, Federal Republic of Germany, **2006**.
- [16] a) P. N. Gaponik, M. M. Degtyarik, A. S. Lyakhov, V. E. Matulis, O. A. Ivashkevich, M. Quesada, J. Reedijk, *Inorg. Chim. Acta* **2005**, *358*, 3949; b) A. S. Lyakhov, P. N. Gaponik, M. M. Degtyarik, L. S. Ivashkevich, *Acta Crystallogr., Sect. C* **2003**, *59*, 204; c) A. F. Stassen, H. Kooijman, A. L. Spek, L. Jos de Jongh, J. G. Haasnoot, J. Reedijk, *Inorg. Chem.* **2002**, *41*, 6468; d) T. Wu, B.-H. Yi, D. Li, *Inorg. Chem.* **2005**, *44*, 4130.
- [17] M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 8044.
- [18] J. Köhler, R. Meyer, *Explosivstoffe*, 9th ed., Wiley-VCH, Weinheim, **1998**, p. 138.
- [19] a) D. E. Chavez, M. A. Hiskey, M. H. Huynh, D. L. Naud, S. F. Son, B. C. Tappan, *J. Pyrotech.* **2006**, *23*, 70; b) D. E. Chavez, M. A. Hiskey, D. L. Naud, *J. Pyrotech.* **1999**, *10*, 17; c) M. A. Hiskey, D. E. Chavez, D. L. Naud, *U. S. patent* **2001**, US 6214139.
- [20] T. M. Klapötke, J. Stierstorfer, *New Trends in Research of Energetic Materials*, Proceedings, Pardubice, **2007**, 674–690.
- [21] R. A. Henry, W. G. Finnegan, *J. Am. Chem. Soc.* **1954**, *76*, 923.
- [22] R. M. Herbst, C. W. Roberts, E. J. Harvill, *J. Org. Chem.* **1951**, *16*, 139.
- [23] *CrysAlis CCD*, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01–04–2005 CrysAlis171.NET) (compiled Apr 1 **2005**, 17:53:34).
- [24] *CrysAlis RED*, Oxford Diffraction Ltd., Version 1.171.27p5 beta (release 01–04–2005 CrysAlis171.NET) (compiled Apr 1 **2005**, 17:53:34).
- [25] SIR-92, *A Program for Crystal Structure Solution*: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.
- [26] G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1994**.
- [27] A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1999**.
- [28] *SCALE3 ABSPACK: An Oxford Diffraction Program* (1.0.4, gui:1.0.3) (C), Oxford Diffraction Ltd., **2005**.
- [29] CCDC-642162 (for **1**), -641972 (for **2**), -641973 (for **3**), and -642161 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [30] B. Morosin, *Acta Crystallogr., Sect. B* **1976**, *32*, 1237.
- [31] E. Riedel, *Anorganische Chemie*, 4th ed., de Gruyter, Berlin, **1999**, p. 677 and 722.
- [32] a) R. Prins, M. Biagini-Cingi, R. A. G. De Graff, J. Haasnoot, A.-M. Manotti-Lanfredi, P. Rabu, P. Reedijk, E. Ugozzoli, *Inorg. Chim. Acta* **1996**, *248*, 35; b) R. Bronisz, *Inorg. Chim. Acta* **2004**, *357*, 396; c) P. Börsting, J. J. Steel, *Eur. J. Inorg. Chem.* **2004**, 376; d) P. E. M. Wijnands, J. S. Wood, J. Reedijk, W. J. A. Maaskant, *Inorg. Chem.* **1996**, *35*, 1214.
- [33] a) H. Nakai, Y. Deguchi, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2557; b) H. E. Heldal, J. Sletten, *Acta Chem. Scand.* **1997**, *51*, 122.
- [34] <http://www.setaram.com>.
- [35] <http://www.perkinelmer.com>.
- [36] <http://www.linseis.com>.
- [37] <http://www.parrinst.de>
- [38] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W.

- Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision A.1, Gaussian Inc., Pittsburgh, PA, **2003**.
- [39] CuO: $C_{\infty v}$, $E = -272.499622$ a.u., $zpe = 0.9$ kcal mol⁻¹; O₂: $D_{\infty h}$, $E = -150.315318$ a.u., $zpe = 2.1$ kcal mol⁻¹; CO₂: $D_{\infty h}$, $E = -188.541219$ a.u., $zpe = 6.8$ kcal mol⁻¹; H₂O: C_{2v} , $E = -76.414392$ a.u., $zpe = 13.0$ kcal mol⁻¹; N₂: $D_{\infty h}$, $E = -109.481395$ a.u., $zpe = 3.2$ kcal mol⁻¹; A: C_i , $E = -1310.826700$ a.u., $zpe = 102.7$ kcal mol⁻¹.
- [40] M. D. M. C. Ribeiro da Silva, J. M. Goncalves, A. L. R. Silva, P. C. F. C. Oliveira, B. Schröder, M. A. V. Ribeiro da Silva, *J. Mol. Catal. A Chem.* **2004**, 224, 207.
- [41] NIST Chemistry WebBook, *NIST Standard Reference Database Number 69*, Release: June **2005**. <http://webbook.nist.gov/chemistry/>.
- [42] a) M. Suceska, *Test Methods for Explosives*, Springer, New York, **1995**, p. 21 (impact), p. 27 (friction); b) <http://www.bam.de>
- [43] Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N (according to the UN Recommendations on the Transport of Dangerous Goods).
- [44] <http://www.systag.ch>

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