Synthesis and Characterization of a Three-dimensional Coordination Polymer Based on Copper(II) Nitrate and a Tridentate Tetrazole Ligand

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Tris(2-(1H-tetrazol-1-yl)ethyl)amine (1) was synthesized as gas-generating agent and characterized by vibrational (IR) and NMR spectroscopy. The energetic properties were determined by bomb calorimetric measurements along with calculations using the EXPLO5 software. Tris(2-(1H-tetrazol-1-yl)ethyl)amine (1) was used for further reactions with copper(II) nitrate to form a three-dimensional coordination polymer 3. Both compounds were characterized by single crystal X-ray diffraction. The thermal stability was determined by DSC measurements and the physical stability by BAM standards. Tris(2-(1H-tetrazol-1-yl)ethyl)amine (1) proved to be suitable as gas-generating agent with sufficient physical and thermal stabilities. The low thermal stability of the copper complex 3 disqualifies it as potential colorant agent for pyrotechnical applications.

Key words: Coordination Polymer, Tetrazole, Energetic, Gas Generating

Introduction

Throughout heterocyclic chemistry, heterocycles possessing a large number of heteroatoms are a fascinating field of research. Among nitrogen-rich heterocycles, tetrazoles peak out with a high content of nitrogen (79 %) along with a sufficiently high thermal stability [1]. The application of tetrazoles ranges from pharmaceuticals [2] and biomedical applications [3] to energetic materials [4] and gas-generating agents for civil applications [5]. Beside the usage as neutral compounds, salts and complexes based on tetrazoles are sought compounds. Especially nitrogen-rich salts which contain aminoguanidinium, diaminoguanidinium or triaminoguanidinium cations and tetrazolates as anions are useful compounds regarding an application as gas-generating agents [6]. Further applications involve complexes containing cations of copper [7], strontium [8], barium or lithium [9] as colorant agents in pyrotechnical compositions.

Another feature of tetrazoles is their ability to form various complexes as anionic counterpart or neutral ligand. Copper complexes of nitriminotetrazolate showing weak antiferromagnetic interactions [10] or potential new contrast agents based on lanthanide(III) cations and 5-(2-pyridyl)tetrazolate or 5-(2-pyridyl-1-oxide)tetrazolate [11] are examples. Beside mononuclear or dinuclear complexes based on tetrazoles, polymers are an interesting topic. One example of coordination polymers containing copper and silver cations was contributed by Schmidbaur by using paracyclophane as bridging ligand [12]. With regard to the preparation of a three-dimensional polymeric network of tetrazole and copper(II), a tridentate tetrazole ligand was synthesized.

Results and Discussion

The synthesis of tris(2-(1H-tetrazol-1-yl)ethyl)amine (1) was carried out according to common methods. Instead of the substitution reaction of the highly toxic tris(2-chloroethyl)amine with 1H-tetrazolates [13], the commercially available tris(2-aminoethyl)amine (2) was used. The amine groups were converted into the tetrazole moieties by ethyl orthoformate and sodium azide in acetic acid [14] (Scheme 1).

The yield of the reaction is very low (10 %), compared to common yields of the reaction (40 – 60 %). An explanation could be found in intramolecular reactions of the amine groups and the ethyl orthoformate leading to polymers and ring systems. A closer investigation of the formed compounds was not carried out.
The remaining amine group of \textbf{1} was tried to be used as base in acid-base reactions with energetic acids like perchloric acid and nitric acid. Despite being well soluble in acidic media, only starting materials could be isolated instead of the expected salts. An explanation for the low basicity of the amine moiety could be found in the steric hindrance of the tetrazolyethyl moieties.

The copper complex \textbf{3} was synthesized by the reaction of \textbf{1} with copper(II) nitrate in 2 N nitric acid. Complex \textbf{3} precipitates from the aqueous solution and was obtained by filtration. The fast precipitation, achieved by the addition of a hot saturated solution of \textbf{1} to a concentrated copper(II) nitrate solution (both in 2 N nitric acid) yields a light-turquoise powder. If a diluted solution of \textbf{1} and copper(II) nitrate in water is heated to 100 \textdegree C, followed by the addition of 2 N nitric acid, \textbf{3} does not precipitate, but crystallizes within 12 h. The formed copper compounds are identical regarding their elemental analysis.

Compound \textbf{1} crystallizes in the monoclinic space group \emph{P}2\textsubscript{1}/c with four molecular formulas per unit cell (Fig. 1). The tetrazole moieties are oriented in such a manner that a ball-like conformation of \textbf{1} is achieved. The free electron pair of the amine nitrogen atom N13 points towards the center of the sphere. This conformation explains the low basicity of the nitrogen atom, due to the high sterical hindrance of the free electron pair by the substituents. The structure is stabilized by two intramolecular hydrogen bridges. The first is formed between C1–H1 as donor and N12 as acceptor, the second between C2–H2 as donor and N4 as acceptor [15]. \textbf{1} does not possess the expected three-fold rotational symmetry, because of a disarrangement of the tetrazole moiety containing C3 and N9 to N12.

The copper complex \textbf{3} crystallizes in the triclinic space group \emph{P}1 with two molecular formulas ([C\textsubscript{9}H\textsubscript{15}N\textsubscript{13}Cu](NO\textsubscript{3})\textsubscript{2}) per unit cell. The investigation of the conformation of the tristetrazole \textbf{1} and the tristetrazole moiety of \textbf{3} shows significant differences. Due to the coordination to the copper cation, the ball-like conformation of \textbf{1} is spread, and the tetrazolyl ethyl substituents are oriented away from N13 (Fig. 2). But in spite of the spread character of the nitrogenatom N13, only the complex of the neutral ligand instead of the corresponding nitrate salt was formed although 2 N nitric acid was used as solvent. This behavior is another proof of the low basicity of N13. Another difference between \textbf{1} and the tristetrazole moiety of \textbf{3} is the coordination geometry of the nitrogenatom N13. In case of \textbf{1}, the three angles between the alkyl moieties are equal (111.6\textdegree), whereas the values of the angles of \textbf{3} vary by 1.6\textdegree (114.9\textdegree, 114.3\textdegree and 113.3\textdegree). The sum of the angles of \textbf{1} is 334.8\textdegree,
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Fig. 3. Coordination of the amine nitrogen atom of 1 as free ligand (left) and in the copper complex 3 (right).

and the sum of the angles of the tristetrazole moiety of 3 is 342.5°. This finding shows, that the amine nitrogen of 3 is more planar than the amine nitrogen of 1 (Fig. 3).

The copper cation of 3 is coordinated distorted octahedrally by six tetrazole groups of six different tristetrazole moieties (Fig. 4). The tetrazole units are all coordinated to the copper cation with the nitrogen atom next to the tetrazole carbon atom (N4, N8 and N12). The distances to the equational tetrazole moieties are 2.02 Å, whereas the distance to the axial tetrazole moieties is significantly longer (2.44 Å). These distances lead to the expected distorted octahedral coordination. The nitrate anion is integrated into the structure by two different non-classical hydrogen bonds. The first is formed between C1–H1 as donor and O3 of the nitrate anion as acceptor (D···A: 3.282 Å, angle: 171.2°), the second between C2–H2 as donor and O2 of the nitrate anion as acceptor (D···A: 3.194 Å, angle: 148.6°).

The tristetrazole moieties and the copper cation form a threedimensional network, and the existing channels within the porous network are filled with the nitrate anion (Fig. 5).

In order to analyze a potential application of 1 as gas-generating agent or of 3 as colorant agent in py-
rotechnical applications, the thermal and physical stability of 1 and 3 was determined.

The sensitivity towards impact of 1 (25 J) was slightly higher than that of 3 (10 J). The sensitivity towards friction of both compounds was higher than 360 N. Thus, according to the UN Recommendations on the Transport of Dangerous Goods [16] both compounds are insensitive towards friction and sensitive towards impact.

The thermal stability of 1 and 3 was determined using DSC measurements (Fig. 6). Compound 1 melts at 142 °C and decomposes at 199 °C. The difference of nearly 60 °C between the melting point and decomposition point allows an application as melt-castable explosive. Compound 3 does not possess any melting point. Instead, three points of decomposition can be found at 135, 168 and 190 °C. The analysis of the thermal stability of 3 reveals its disadvantage: For an application, the explosive compound should reach at least a thermal stability of 200 °C to grant a safe handling.

The energetic properties of 1 were determined experimentally along with calculations using the EXPLO5 software [17]. The energy of combustion ($\Delta H_{\text{comb}}$) was determined by bomb calorimetric measurements. The enthalpy of formation was calculated using the Hess thermochemical cycle as reported in literature [18]. The energetic properties of 1 are summarized in Table 2.

In order to classify the explosion performance of 1, a comparison of 1 and common explosives (TNT, RDX and nitrocellulose) is given in Table 2. In comparison with these compounds, 1 proves to be a moderate explosive. The advantage of 1 compared to TNT, RDX or nitrocellulose is its environmental compatibility. TNT, RDX as well as nitrocellulose bear nitro groups or nitric esters as energetic moieties. The toxicity of nitroaromatic compounds [20] or explosives containing nitro functions (nitro group, nitric ester) [21] was intensively studied and the importance of environment-friendly explosives realized. Compound 1 possesses enhanced energetic properties compared with TNT, but does not contain any toxic moieties like nitro or azide groups.

### Conclusion

Tris(2-(1H-tetrazol-1-yl)ethyl)amine 1 and the corresponding complex of two tris(2-(1H-tetrazol-1-yl)ethyl)amine and one copper(II) nitrate 3 were syn-

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**Table 2. Energetic properties of 1.**

<table>
<thead>
<tr>
<th>Property</th>
<th>1</th>
<th>TNT*</th>
<th>RDX*</th>
<th>Nitrocellulose*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$\text{C}<em>9\text{H}</em>{15}\text{N}_{13}$</td>
<td>$\text{C}_3\text{H}_6\text{N}_2\text{O}_6$</td>
<td>$\text{C}_6\text{H}_5\text{N}_2\text{O}_5$</td>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_{10}\text{N}_8$</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>305.31</td>
<td>227.1</td>
<td>222.1</td>
<td>285</td>
</tr>
<tr>
<td>Density, g cm$^{-3}$</td>
<td>1.45</td>
<td>1.65</td>
<td>1.82</td>
<td>1.3–1.7</td>
</tr>
</tbody>
</table>

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*a Obtained from the database of EXPLO5 V5.02; b estimated from a structure determination; c experimental (constant volume) combustion energy; d experimental molar enthalpy of combustion; e molar enthalpy of formation; f energy of explosion; g explosion temperature; h detonation pressure; i detonation velocity; j assuming only gaseous products; k specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion); l specific impulse of a mixture containing 70% ammonium dinitramide as oxidizer.

and CO$_2$ (g) ($-394$ kJ mol$^{-1}$) were obtained from literature [19]. The energetic properties of 3 could not be calculated by the EXPLO5 software, because copper is not implemented in the software. The energetic properties of 1 are summarized in Table 2.

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**Fig. 6. DSC data of 1 and 3.**
thesized. Both compounds are insensitive towards friction and sensitive towards impact. Compound 1 possesses a point of decomposition of 199 °C and a melting point of 142 °C. The difference of 60 °C between the melting point and decomposition point renders this compound into a useful melt-castable explosive. Moreover, a comparison between common explosives and 1 showed its moderate energetic properties along with its improved environmental compatibility. In case of 3, the low thermal stability prevents this compound from being used as colorant agent in pyrotechnical applications. Both compounds were characterized by vibrational spectroscopy (IR), and their crystal structures were determined by single crystal X-ray diffraction.

**Experimental Section**

**CAUTION!** Tetrazoles, bromotetrazoles, tetracyclohydrazines and azidotetrazoles are highly energetic compounds with sensitivity towards heat and impact. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used when undertaking work involving these compounds.

**General**

All chemical reagents and solvents of analytical grade were obtained from Sigma–Aldrich or Acros Organics and used as supplied. 1H, 13C and 15N NMR spectra were recorded using a JEOL Eclipse 400 instrument. The spectra were measured in [D6]DMSO. The chemical shifts are given relative to tetramethylsilane (1H, 13C) as external standard. Coupling constants (J) are given in Hz. Infrared (IR) spectra were recorded using a Perkin–Elmer Spectrum One FT-IR instrument and KBr pellets at r.t. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Melting points were determined using a Linseis DSC PT-10 instrument. Measurements were performed at a heating rate of 5 °C min⁻¹ in closed aluminum containers with a hole (1 μm) on the top for gas release with a nitrogen flow of 5 mL min⁻¹. The reference sample was a closed aluminum container. The sensitivity data were performed using a BAM drophammer and a BAM friction tester. The crystallographic data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). The structure was solved using Direct Methods (SHELXS-97) [22] and refined using SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically. ORTEP [24] plots were drawn with displacement ellipsoids with 50 % probability for the non-hydrogen atoms.

CCDC 746454 (1) and 746453 (3) contain 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.

**Synthesis of tris(2-(1H-tetrazol-1-yl)ethyl)amine (1)**

Tris(2-aminoethyl)amine (20.0 g, 136 mmol) was suspended in triethyl orthoformate (101.5 mL). Sodium azide (31.7 g, 488 mmol) was added to the reaction mixture, and acetic acid (81 mL) was added dropwise at 0 °C. The reaction mixture was heated at 100 °C for 8 h. Afterwards concentrated hydrochloric acid (40 mL) was added at ambient temperature, and the solvent was removed under reduced pressure. The residue was neutralized by sodium hydroxide and extracted with ethyl acetate. The product precipitated after one day from the aqueous solution (4.1 g, 13 mmol, 10 %). M. p. 142 °C, dec. 199 °C. – IR (KBr, cm⁻¹): ν = 3441 (m), 3145 (m), 3014 (w), 2977 (w), 2951 (w), 2899 (w), 2847 (m), 2831 (m), 1734 (w), 1688 (w), 1635 (w), 1483 (s), 1454 (m), 1435 (s), 1384 (m), 1351 (m), 1303 (m), 1281 (m), 1253 (m), 1202 (w), 1174 (m), 1153 (m), 1118 (s), 1100 (vs), 1046 (m), 1030 (m), 995 (m), 966 (m), 975 (m), 877 (m), 871 (m), 737 (w), 723 (w), 677 (m), 645 (m), 536 (m). – 1HNMR ([D6]DMSO): δ = 3.02 (t, 2H, 3J = 6.5 Hz, CH2), 4.42 (t, 2H, 3J = 6.5 Hz, CH2), 9.15 (s, 1H, CH). – 13C NMR ([D6]DMSO): δ = 45.9 (CH2), 52.6 (CH2), 144.5 (Cq). – MS (DCI): m/z (M+H)+ = 306, 278, 253, 230, 228, 208, 180. – C9H15N13 (305.1737): calc. C 27.09, H 3.79, N 49.14; found C 26.81, H 3.67, N 49.21.

**Synthesis of [(C9H15N13)2Cu](NO3)2 (3)**

Tris(2-(1H-tetrazol-1-yl)ethyl)amine (2.0 g, 7 mmol) was dissolved in 2 N nitric acid, and a solution of copper(II) nitrate trihydrate (3.0 g, 12 mmol) in 2 N nitric acid was added. The copper complex precipitated within 6 to 12 h from the acidic solution (4.0 g, 5 mmol, 71 %). Dec. 135, 168, 190 °C. – IR (KBr, cm⁻¹): ν = 3142 (vw), 2986 (w), 2426 (vw), 1668 (vw), 1630 (w), 1506 (w), 1436 (m), 1384 (vs), 1321 (m), 1262 (w), 1171 (m), 1107 (m), 1038 (w), 1004 (w), 991 (w), 978 (w), 935 (vw), 906 (vw), 888 (vw), 829 (vw), 783 (vw), 772 (vw), 717 (vw), 674 (vw), 662 (w), 644 (vw), 554 (wv). – C18H30CuN23O6: calc. C 27.09, H 3.79, N 49.14; found C 26.81, H 3.67, N 48.91.

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codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work. We also thank Mr. Stefan Huber for sensitivity measurements.

[21] a) H. Stucki, Chimia 2004, 58, 409; b) M. M. Percher-
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