Copper(II) Dicyanamide Complexes with \(N\)-Substituted Tetrazole Ligands – Energetic Coordination Polymers with Moderate Sensitivities

Maximilian H. H. Wurzenberger, Jasmin T. Lechner, and Jörg Stierstorfer

Following the useful concept of energetic coordination compounds (ECC), copper(II) dicyanamide was used as a building block for the synthesis of eight new complexes. As ligands, six different \(N\)-substituted tetrazoles were applied, leading to the formation of high-nitrogen containing complexes. The obtained compounds were characterized in detail by single crystal as well as powder XRD, IR, EA, DTA, and TGA. In addition, the sensitivities towards impact and friction were determined with BAM standard techniques as well as the sensitivity towards electrostatic discharges. All compounds show moderate sensitivities (\(IS > 6, FS > 80\ N\)) and energetic properties but differ in their polymeric structures forming polymeric chains or layers up to 3D networks.

Introduction

The dicyanamide moiety belongs to the class of cyanamides, which have manifold applications and are used as precursors or intermediates in industry. Sodium dicyanamide (NaDCA) can be easily obtained by reacting cyanamide with cyanogen chloride and sodium hydroxide.\(^{[1]}\)

Dicyanamides can be used as starting materials for the synthesis of many different materials such as heterocycles, ionic liquids or transition metal complexes.\(^{[1]}\) An interesting hetero-

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showing a moderate positive heat of formation. For the DCA anion, both the pure copper(I) and copper(II) salts are stable at ambient conditions.\textsuperscript{[10]} While many copper(II) dicyanamide complexes were investigated, nitrogen-rich representatives are very rare in literature. Solely the 1,5-diaminotetrazole compound is mentioned as an energetic combustion catalyst for propellant systems, indicating their potential as possible ECC.\textsuperscript{[11]} Therefore, in this work, new copper(II) coordination polymers based on dicyanamide and tetrazole ligands were synthesized and their energetic properties investigated.

Results and Discussion

Synthesis

The copper(II) dicyanamide compounds were synthesized using six different tetrazole ligands and started with a metathesis reaction. Therefore, the corresponding copper(II) nitrate complexes were generated \textit{in situ} and further reacted with aqueous sodium dicyanamide solutions (Scheme 1). The used ligands were available in the research group and prepared according to literature known syntheses.\textsuperscript{[12]} All eight complexes possess polymeric structures due to the bridging nature of the DCA anion and therefore crystallize quickly after the synthesis.

During the synthesis of 6\textsubscript{a}, sometimes the formation of a second species in very small traces was observed. The side-species \textit{6b} represents a monohydrate of 6\textsubscript{a} and is the only water-containing compound. All other complexes were obtained as anhydrous substances. Similar to \textit{6b} only some single-crystals of complex 3 were able to be obtained. Therefore, both compounds could not be further characterized. The pure copper(II) dicyanamide (7) was obtained as the main product during the attempted synthesis of 3 and as the only product when 2-amino-5-methyltetrazole was applied as ligand.

Crystal Structures

All compounds were characterized by low-temperature single-crystal X-ray diffraction and details on the measurement and refinement data are given in the Supporting Information (Table S1–3).\textsuperscript{[13]}

In all eight complexes, the central Cu\textsuperscript{2+} cations are octahedrally coordinated and show typical d\textsuperscript{9} Jahn-Teller distortions. Due to the bridging dicyanamide anion, all structures are multidimensional. The spatial structures of compounds 1, 2 and 3 with the ligands 1-MTZ (1), AET (2) and 1-AMT (3) are quite similar. The copper atoms are all coordinated by two tetrazole ligands in equatorial positions and four bridging dicyanamido anions. The MTZ complex 1 is crystalizing in the monoclinic space group \textit{P}2\textsubscript{1}/\textit{n} and compounds 2 and 3 in the triclinic space group \textit{P}–\textit{1} (Figure 2). They show comparable densities between 1.735 and 1.772 g cm\textsuperscript{–3}.

In all three cases, the bridging leads to the formation of one-dimensional chains (Figure 3), which are caused by the binding of the two outer nitrogen atoms of the DCA to the central metals. Two anions each bridging between the same two cations. The heterocycles all bind to the copper via the N4 atom which is located next to the carbon atom. The bond lengths between the Cu and the N4 atom are almost the same for all three complexes. The copper complex 4 with 1-AT as ligand has a nearly similar coordination environment as the previously described complexes 1–3. The central copper atom is coordinated by two 1-AT ligands via N4, and 4 DCA anions again via the outer two nitrogen atoms (Figure 4). It crystallizes in the monoclinic space group \textit{P}2\textsubscript{1}/\textit{c} with two formula units per unit cell and a calculated density of 1.860 g cm\textsuperscript{–3} at 143 K.

However, the compounds differ in their polymeric structure. While in complexes 1–3 the dicyanamide anions are bridging always between the same two central metals, the four DCAs in compound 4 link to four different copper cations. This creates a two-dimensional polymeric layer (Figure 5).

The coordination polymers of copper(II) dicyanamide with 2-amino(tetrazol-1-yl)ethane can be obtained in two different polymorphs.
5a and 5b. Similar to 4, both compounds show a coordination structure with the copper central atom bound to two 2-AT ligands via the N4 atom. Furthermore, four dicyanamide anions bind to the Cu(II), but this time each via one outer and the middle nitrogen atom. While 5a crystallizes in a monoclinic space group (P2_1/c), 5b is present in an orthorhombic one (Pbca; Figure 6). Interestingly, they show a difference in density of about 0.1 g cm\(^{-3}\), whereby 5a has 1.858 g cm\(^{-3}\) at 127 K and 5b 1.757 g cm\(^{-3}\) at 143 K.

Both compounds show a comparable coordination behavior with the dicyanamido ligands linking the central metals to four different copper atoms forming two-dimensional polymers. Upon closer examination, it becomes clear that the only
difference between the two is the arrangement of the tetrazole ligands. While in 5b the heterocycles of one side all point to the same side in 5a they alternate, allowing a denser packing and explaining the higher density (Figure 7).

Compared to the other complexes, the structures of 6a and 6b are outstanding due to the insertion of an additional bridging ligand. The anhydrous compound 6a crystallizes in the triclinic space group P\(-\)1 with a density of 1.817 g cm\(^{-3}\) (110 K) and the monohydrate in the monoclinic space group \(\text{C}2/c\) with a slightly lower density (1.752 g cm\(^{-3}\)) @ 127 K. In both cases, the central metals are coordinated by two tetrazoles and four DCA nitrogen atoms. Like in 5a and 5b, the anions are binding with one outer and the middle nitrogen atom. The molecular unit of 6b is completed by an additional crystal water molecule (Figure 8).

Nevertheless, 6b is not just simply the monohydrate of 6a. A closer examination of the crystal structures reveals the difference of 6a forming a two-dimensional and 6b a three-dimensional structure. Similar to compounds 1–3, in 6a two anions each are bridging between the same two central metals leading to the formation of polymeric chains. The additional linking of the ditetrazolyl ligand is causing an enhancement of the dimension to polymeric layers (Figure 9).

The dte ligand is also increasing the dimension in complex 6b, but here the DCA anions are already forming 2D-layers, similar to complex 5a and 5b. This results in a three-dimensional polymeric structure of 6b (Figure 10). The structure favors the storage of water, which is why 6b crystallizes as monohydrate.

**Physiochemical Properties**

All synthesized compounds, except 3 and 6b, were investigated regarding their thermal properties and sensitivities towards external stimuli. In order to check the isomeric purity of compounds 5a and 5b, they were further investigated by powder X-ray diffraction.

**Thermal Analysis**

Compounds 1, 2, 4, 5a, 5b, and 6a were characterized by differential thermal analysis (DTA) with a linear heating rate of
\[ \beta = 5^\circ \text{Cmin}^{-1} \]

in the range of 30 to 400 °C. The DTA plots are shown in Figures 11 and S3.

The experiments (Table 1) reveal that all complexes possess lower decomposition points (126–193 °C) compared to pure Cu (DCA)\(_2\) (254 °C). Furthermore, compound 2 is the only one showing an endothermic event right before its decomposition. Closer examination using thermogravimetric analysis (TGA) proves the compounds' stability up to their corresponding exothermic decomposition temperatures, revealing a melting point for complex 2 at 126 °C (Figures 12 and S4).

### Sensitivities

Except for 3 and 6b, the energetic properties of all compounds were investigated. The sensitivities towards impact, friction, and electrostatic discharge are summarized in Table 1. The impact sensitivities are in the range of 6–10 J and therefore, the complexes have to be classified as sensitive according to the UN Recommendations on the Transport of Dangerous Goods. Only the salt 7 is classified as less sensitive with a value of 40 J.

Concerning the friction sensitivities, compounds 1, 6a and 7 can be classified as insensitive (>360 N). In contrast, complexes 2, 4, 5a and 5b have to be classified as sensitive, with values between 80 N (5a, 5b) and 192 N (2). It can be seen that the energetic character of pure copper(II) dicyanamide is getting increased through the coordination of nitrogen-rich ligands. Interestingly the two different polymorphs 5a and 5b do not show major aberrations in their energetic properties.

### Powder diffraction

For a more detailed investigation, compounds 5a and 5b were applied to X-ray powder diffraction measurements (Figure 13). Small variations in the orthorhombic species 5b can be attributed to the temperature differences of single-crystal and powder X-ray diffraction. Therefore, it is possible to synthesize 5b isomerically pure. However, in the case of 5a contamination with the second polymorph are observable and further research is necessary for selective synthesis of it.

### Conclusion

In this work, eight new nitrogen-rich copper(II) dicyanamide complexes based on N-substituted tetrazole ligands were synthesized. Due to the good coordination behavior of dicyanamide, they can all be obtained without the inclusion of water. Only the formation of a 3D-polymeric side-species allows the inclusion of guest solvent molecules. All complexes were investigated by low-temperature single-crystal X-ray experiments and their polymeric structure examined in detail. The energetic properties and thermal behavior of the low watersoluble six ECC were determined and showed moderate sensitivities (IS > 6, FS > 80 N). This allows the safe handling of...
Figure 13. Powder diffraction experiments (comparison (blue) of the measured (red) and calculated (black) data) of compounds 5a (top) and 5b (bottom).

the complexes, which could be used as potential energetic additives e.g. burn rate catalysts. Also, a non-energetic use as magnetic switches could be possible. Especially compounds 4 and 5b show promising properties for the use as energetic metal-organic frameworks (EMOF).

Experimental Section

Caution! All investigated compounds are energetic materials, which partly show increased sensitivities towards various stimuli (e.g. elevated temperatures, impact, friction or electronic discharge). Although no incidents occurred, proper security precautions (safety glasses, face shield, earthed equipment and shoes, leather jacket, Kevlar sleeves, and earplugs) have to be worn while synthesizing and handling the described compounds.

Detailed information on chemicals, syntheses, as well as analytical data and methods of 1–6 can be found in the Supplementary Information.

General procedure for the preparation of copper(II) dicyanamide complexes (1–5a and 6a): To a solution of copper(II) nitrate trihydrate (60.4 mg, 0.25 mmol, 1 eq) in water (1 mL) the corresponding ligand (1: 1-methyl-SH-tetrazole (42.0 mg, 0.5 mmol, 2 eq); 2: 1-azidoethyl-SH-tetrazole (69.6 mg, 0.5 mmol, 2 eq); 3: 1-amino-5-methyltetrazole (49.6 mg, 0.5 mmol, 2 eq); 4: 1-amino-SH-tetrazole (42.5 mg, 0.5 mmol, 2 eq); 5a: 2-amino-SH-tetrazole (42.5 mg, 0.5 mmol, 2 eq); 6a: 1,2-ditetrazol-1-yl)ethane (41.55 mg, 0.25 mmol, 1 eq)) was added. After stirring for a minute, an aqueous solution (1 mL) of sodium dicyanamide (44.5 mg, 0.5 mmol, 2 eq) was added, the mixture was stirred for one more minute at room temperature and left for crystallization. After formation of the crystalline products, the compounds were filtered off, washed with cold ethanol and dried in air. All compounds were obtained in the form of single crystals suitable for X-ray diffraction.

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Conflict of Interest

The authors declare no conflict of interest.

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[13] CCDC 1986804 (1), 1986806 (2), 1986801 (3), 1986805 (4), 1986800 (5a), 1986803 (5b), 1986802 (6a) and 1986807 (6b) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.