

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

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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]

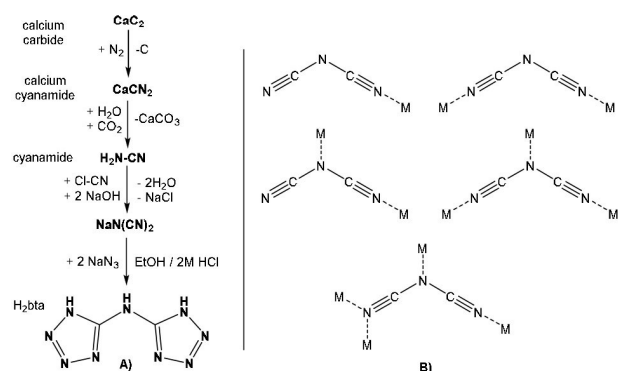


Chart 1. A) Synthesis of the di-heterocyclic compound bis(tetrazolyl)amine H_2bta starting from sodium dicyanamide (NaDCA), which can be produced from calcium carbide; **B)** Different coordination modes of the DCA anion reported in the literature.^[2]

Dicyanamides can be used as starting materials for the synthesis of many different materials such as heterocycles, ionic liquids or transition metal complexes.^[3] An interesting hetero-

cycle with regards to its very high nitrogen content on the one hand side and its perfect stability and facile accessibility on the other hand side is 5,5'-bis(1*H*-tetrazol-5-yl)amine (H_2bta). It can easily be prepared by a one-step reaction starting with NaDCA (Chart 1 A). The neutral compound and its metal salts were discussed for different applications, especially for the use as energetic materials, e.g. as burn rate modifiers due to their moderate sensitivities.^[4] Another important use of the DCA anion is its application in transition metal complexes. Due to its manifold coordination modes and bridging character it can connect between several metal centers forming polymeric compounds with unique features (Chart 1 B).^[2] An innumerable amount of complexes mainly based on 3d transition metals are discussed in literature for different applications such as magnetic switches.^[5] Besides the commonly used central metals copper and cobalt there can also be found more exotic ones, like silver or uranium.^[6]

In the past, strong oxidizing anions such as nitrate or perchlorate were often used for the synthesis of energetic coordination compounds (ECC). The obtained complexes are powerful compounds with great performance but also come along with high sensitivities making their handling considerably more difficult.^[7] In recent years, the focus of new energetic compounds shifted strongly towards substances that are safer to use and therefore possess decreased sensitivities.^[8] For the synthesis of novel ECC, we focused on small anions with positive heat of formation (ΔH_f°). Most of the anions such as (per)chlorate, nitrate, etc. are formed exothermically in the gas phase (Figure 1). In contrast cyanide, fulminate, azide, and dicyanamide have different positive calculated ΔH_f° 's and allow therefore the tuning of the desired properties.

In the case of copper(II) complexes the choices are considerably narrowed. Both, fulminates and cyanides are leading to the reduction to Cu^+ , while copper azides are extremely sensitive and dangerous to handle. The optimal compromise for the synthesis of energetic copper complexes with moderate sensitivities is thus the dicyanamide anion

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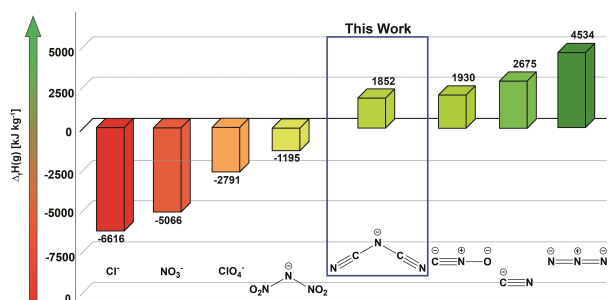


Figure 1. Comparison of the calculated gas-phase enthalpies of formation^[9] for several simple negatively charged anions showing positive heat of formation for the DCA anion.

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.^[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.^[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

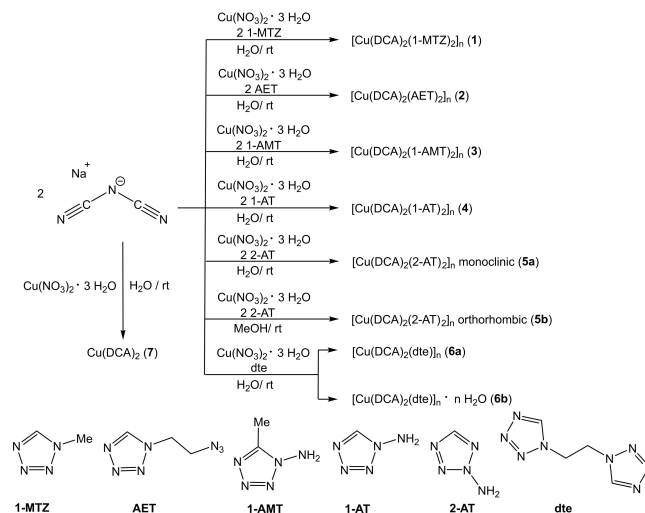
Synthesis

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 *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.^[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 **6a**, sometimes the formation of a second species in very small traces was observed. The side-species **6b** represents a monohydrate of **6a** and is the only water-containing compound. All other complexes were obtained as anhydrous substances. Similar to **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



Scheme 1. Syntheses of the coordination compounds **1–6** and the pure copper(II) salt **7** (top). Structures of the used ligands (bottom). 1-MTZ: 1-methyl-5H-tetrazole; AET: 1-azidoethyl-5H-tetrazole; 1-AMT: 1-amino-5-methyltetrazole; 1-AT: 1-amino-5H-tetrazole; 2-AT: 2-amino-5H-tetrazole; dte: 1,2-di(tetrazol-1-yl)ethane.

refinement data are given in the Supporting Information (Table S1–3).^[13]

In all eight complexes, the central Cu²⁺ cations are octahedrally coordinated and show typical d⁹ 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 crystallizing in the monoclinic space group *P*₂₁/*n* and compounds **2** and **3** in the triclinic space group *P*–1 (Figure 2). They show comparable densities between 1.735 and 1.772 g cm^{–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 Cu1 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 *P*₂₁/*c* with two formula units per unit cell and a calculated density of 1.860 g cm^{–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-aminotetrazole can be obtained in two different polymorphs

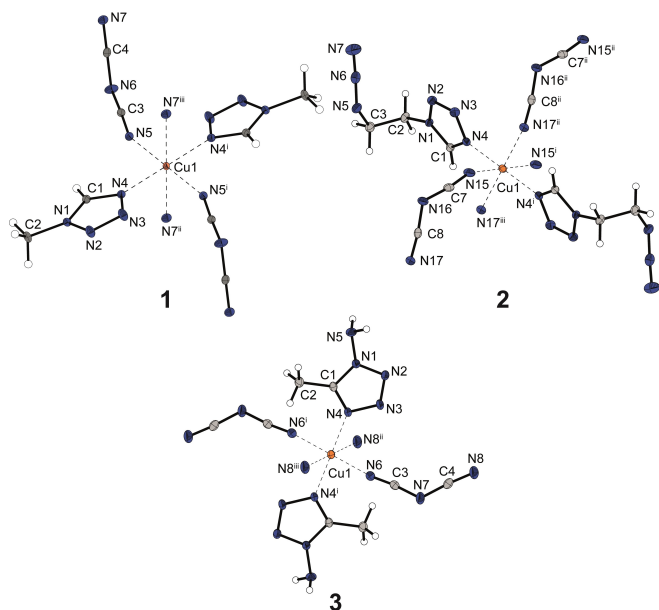


Figure 2. Copper(II) coordination environment of **1** (top left), **2** (top right) and **3** (bottom). Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected bond lengths of **1** (Å): Cu1–N4 2.0179(13), Cu1–N5 1.9892(14), Cu1–N7ⁱⁱ 2.4717(14). Selected bond angles of **1** (°): N4–Cu1–N5 89.07(6), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N7ⁱⁱ 85.17(5). Symmetry codes of **1**: i) 1-x, 1-y, 1-z; ii) x, -1+y, z; iii) 1-x, 2-y, 1-z. Selected bond lengths of **2** (Å): Cu1–N4 2.013(2), Cu1–N15 2.459(2), Cu1–N17ⁱⁱ 1.991(2). Selected bond angles of **2** (°): N4–Cu1–N15 90.28(8), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N17ⁱⁱ 90.83(9). Symmetry codes of **2**: i) 2-x, -y, 1-z; ii) -1+x, y, z; iii) 3-x, -y, 1-z. Selected bond lengths of **3** (Å): Cu1–N4 2.0459(16), Cu1–N6 1.944(2), Cu1–N8ⁱⁱ 2.544(2). Selected bond angles of **3** (°): N4–Cu1–N6ⁱ 90.55(8), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N8ⁱⁱ 89.23(6). Symmetry codes of **3**: i) -x, -y, -z; ii) -1+x, y, z; iii) 1-x, -y, -z.

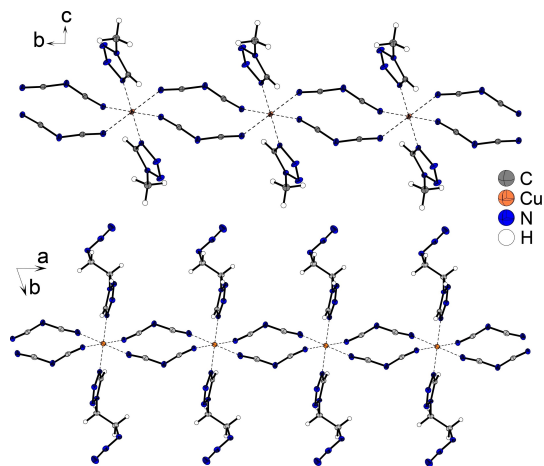


Figure 3. One-dimensional polymeric structure of **1** (top) and **2** (bottom).

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 (*P2₁/c*), **5b** is present in an orthorhombic one (*Pbca*; Figure 6. Interestingly, they show a difference in density

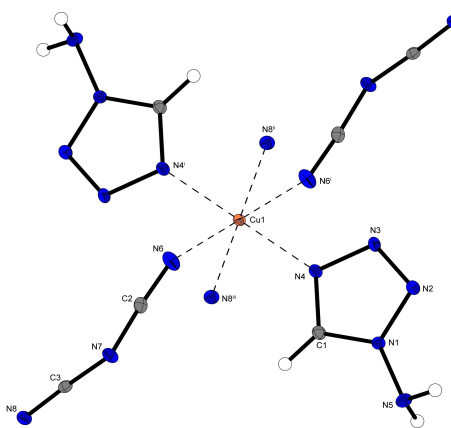


Figure 4. Copper(II) coordination environment of **4**. Selected bond lengths (Å): Cu1–N4 2.0191(12), Cu1–N6 2.3986(14), Cu1–N8ⁱⁱ 1.9884(14). Selected bond angles (°): N4–Cu1–N6ⁱ 90.69(5), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N8ⁱⁱⁱ 89.55(5). Symmetry codes: i) x, 2-y, -z; ii) x, 0.5+y, -0.5-z; iii) x, 1.5-y, 0.5+z.

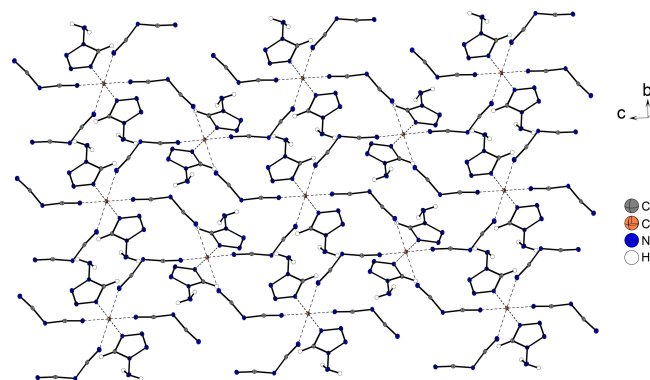


Figure 5. Two-dimensional polymeric structure of **4**, view along the *a* axis.

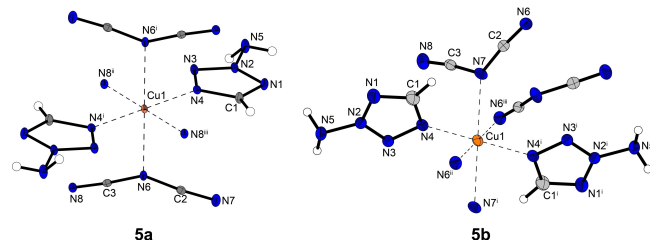


Figure 6. Copper(II) coordination environment of **5a** (left) and of **5b** (right). Selected bond lengths of **5a** (Å): Cu1–N4 2.0321(14), Cu1–N6 2.4280(13), Cu1–N8ⁱⁱ 1.9803(14). Selected bond angles of **5a** (°): N4–Cu1–N6ⁱ 92.51(5), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N8ⁱⁱⁱ 89.13(5). Symmetry codes of **5a**: i) -x, 1-y, 1-z; ii) x, 1.5-y, 0.5+z; iii) -x, -0.5+y, 0.5-z. Selected bond lengths of **5b** (Å): Cu1–N4 2.0311(18), Cu1–N6ⁱ 1.956(2), Cu1–N7 2.464(2). Selected bond angles of **5b** (°): N4–Cu1–N6ⁱⁱ 89.77(8), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N7 86.19(7). Symmetry codes of **5b**: i) 1-x, 1-y, -z; ii) -0.5+x, 0.5-y, -z; iii) 1.5-x, 0.5+y, z.

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 $P\bar{1}$ with a density of 1.817 g cm^{-3} (110 K) and the monohydrate in the monoclinic space group $C2/c$ 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).

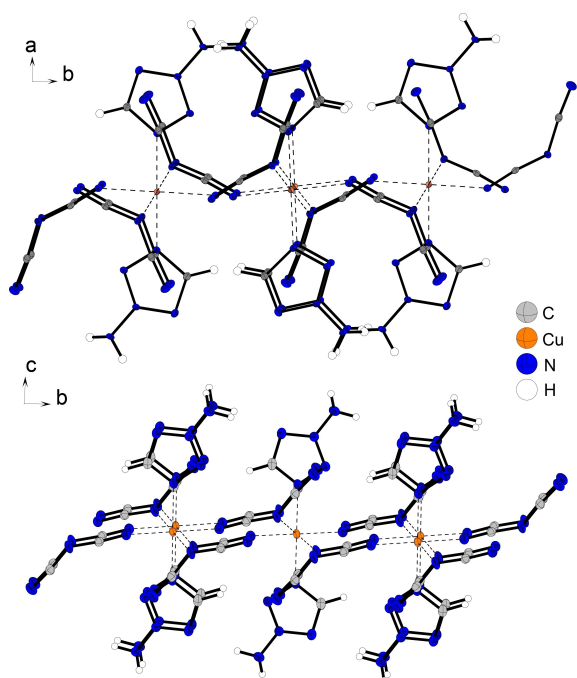


Figure 7. Two-dimensional polymeric structure of **5a** (top) and **5b** (bottom).

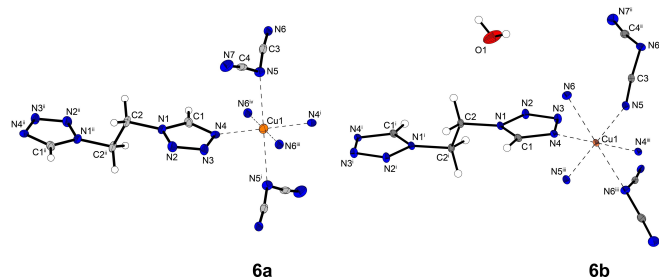


Figure 8. Copper(II) coordination environment of **6a** (left) and of **6b** (right). Selected bond lengths of **6a** (Å): Cu1–N4 2.027(3), Cu1–N5 2.438(3), Cu1–N6ⁱⁱⁱ 1.958(3). Selected bond angles of **6a** (°): N4–Cu1–N5ⁱ 93.14(12), N4–Cu1–N4ⁱ 180.00, N4–Cu1–N6^{iv} 90.82(13). Symmetry codes of **6a**: i) 2–x, –y, –z; ii) 2–x, –1–y, 1–z; iii) 1–x, –y, –z; iv) 1+x, y, z. Selected bond lengths of **6b** (Å): Cu1–N4 2.0094(14), Cu1–N5 1.9619(14), Cu1–N6 2.4851(15). Selected bond angles of **6b** (°): N4–Cu1–N6 86.20(5), N4–Cu1–N4ⁱⁱⁱ 180.00, N4–Cu1–N5ⁱⁱⁱ 90.22(6). Symmetry codes of **6b**: i) –x, –y, 1–z; ii) x, 1–y, 0.5+z; iii) 0.5–x, 0.5–y, 1–z.

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.

Physicochemical 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

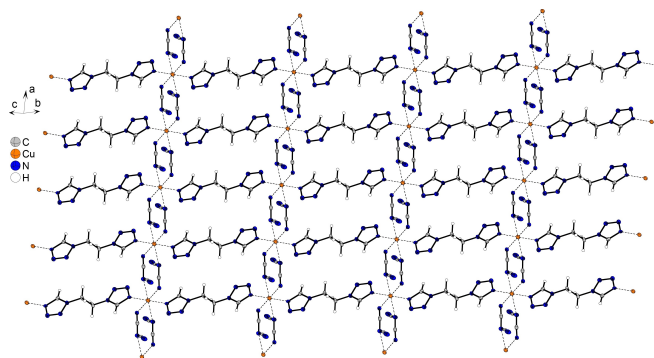


Figure 9. Two-dimensional polymeric structure of **6a**.

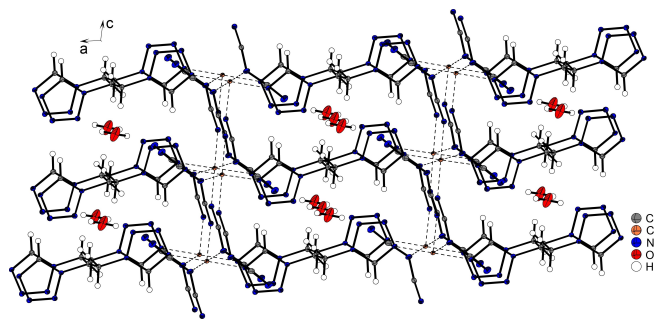


Figure 10. View along the *b* axis of three-dimensional polymeric structure of **6b**.

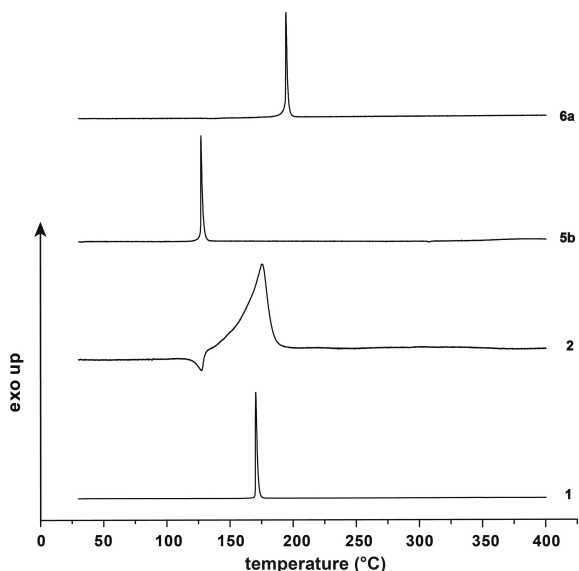


Figure 11. DTA plots of compounds 1, 2, 5b and 6a.

$\beta = 5^\circ\text{C min}^{-1}$ 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

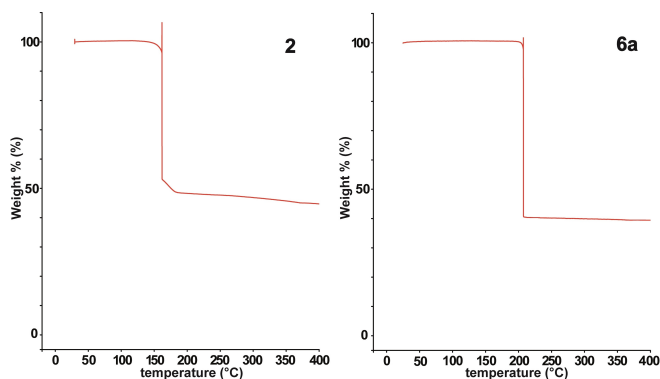


Figure 12. TGA plots of compounds 2 and 6a.

Table 1. Thermal stability measurements by DTA^[a], as well as sensitivities towards impact, friction and ESD of compounds 1–7.^[b]

	$T_{\text{exo}}^{[c]}$ (°C)	$IS^{[d]}$ (J)	$FS^{[e]}$ (N)	$ESD^{[f]}$ (mJ)
1	170	8	> 360	> 1500
2	131	6	192	1500
4	141	6	144	1350
5a	129	9	80	540
5b	126	9	80	540
6a	193	10	> 360	1220
7	254	40	> 360	630

[a] Onset temperatures at a heating rate of 5°C min^{-1} . [b] Determined at a grain size < 100 μm . [c] Exothermic peak, which indicates decomposition. [d] Impact sensitivity according to the BAM drop hammer (method 1 of 6). [e] Friction sensitivity according to the BAM friction tester (method 1 of 6). [f] Electrostatic discharge sensitivity (OZM XSpark10 ESD tester); impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, and very sensitive ≤ 3 J; friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N and > 80 N, very sensitive ≤ 80 N, and extremely sensitive ≤ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods.

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 water-soluble six ECC were determined and showed moderate sensitivities ($IS > 6$, $FS > 80$ N). This allows the safe handling of

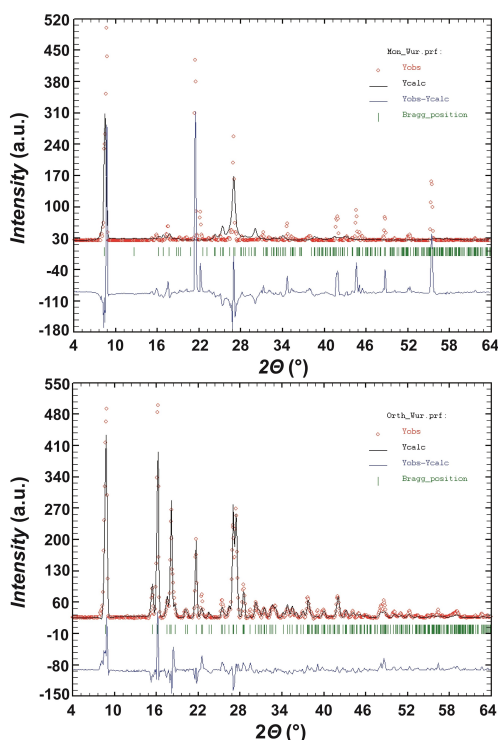


Figure 13. Powder diffraction experiments (comparison (blue) of the measured (red) and calculated (black) data) of compounds **5a** (top) and **5b** (bottom).

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-5H-tetrazole (42.0 mg, 0.5 mmol, 2 eq); 2: 1-azidoethyl-5H-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-5H-tetrazole (42.5 mg, 0.5 mmol, 2 eq); 5a: 2-amino-5H-tetrazole (42.5 mg, 0.5 mmol, 2 eq); 6a: 1,2-di(tetrazol-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.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: bridging ligands · copper · dicyanamides · energetic materials · nitrogen heterocycles

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