

New Energetic Complex of Copper(II) Dinitramide Based Nitrogen-rich Ligand Aminoguanidine(CH₆N₄): Synthesis, Structural and Energetic Properties

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Abstract: The crystal structure of the energetic complex bis (aminoguanidine)copper(II) dinitramide [Cu(AG)₂][DN]₂ (I), has been determined at 298 K using single-crystal X-ray diffraction technique. The Cu(II) atom is four-coordinated by two imine N atoms and two amine N atoms from two aminoguanidine ligands, forming a slightly distorted square-planar coordination. In the crystal structure, molecules are linked through intermolecular N–H...O hydrogen bonds, forming a network. The infrared spectrum showed a sharp peaks at 1650 and 1010 cm⁻¹ which are typical of the conjugated C=N stretching due to the coordination of the

imine nitrogen and NNN stretching dinitramide counterion, respectively. The thermal decomposition process of this complex was investigated through differential scanning calorimetry (DSC) and the sensitivities toward impact and friction were assessed using a BAM drophammer and a BAM friction tester. In the measurement of I a violent explosion appeared destroying the setup. This may be a reason, due to the copper complex (I), which crystallizes water free. The power of powder and single crystal of I was measured by the Trauzl test are 425 and 427 cm⁻³ for 10 g I (142% TNT and 88% RDX).

Keywords: Aminoguanidin · Dinitramide ion · Energetic complexes · Violent explosion

1 Introduction

Guanidine chemistry has evolved into an extremely wide ranging field of applications starting from bioorganic chemistry and biochemistry [1–3] to inorganic chemistry, which most importantly can be traced back to a vast variability of derivatization of the guanidine moiety itself. In recent years there has been a great interest in the development of new solid energetic materials, especially propellants with low signatures. Desired properties for this class of compounds are a halogenfree, nitrogen- and oxygen-rich molecular composition, high densities and a high heat of formation. A breakthrough in this area of chemistry came in 1991 with the first reports on dinitraminic acid, NH(NO₂)₂, and its dinitramide salts [4, 5]. The ability of the dinitramide anion, N₃O₄⁻, to form stable oxygen-rich salts with high densities with a variety of cations makes it a promising candidate in the development of energetic oxidizers for solid propellants [6]. Dinitramide salts form molecular complexes with many ligands. Complexes with nitrogen containing ligands such as pyridine [7], 3-Amino-1-nitroguanidine [8] and 5-(1-Methylhydrazinyl)-1H-tetrazole [9] were also prepared. Trammell et al. reported a rhenium metal complex with bipyridyl and carbonyl units and identified its structure by X-ray methods. The X-ray crystal structure indicates that the coordination occurs at the central nitrogen atom of the dinitramide [10]. Metal complexes of nickel(II), zinc(II), copper(II) and cadmium(II) with ethylenediamine (en) were prepared by Varand et al. [11]. Lukya-

nov et al. reported *syntheses* of mercury(II) dinitramide contain aniline, pyridine, triphenylphosphine and dimethylsulfide [12]. The prepared complexes were studied by element analysis, UV spectroscopy and DSC. Melting point of these complexes are 145 °C (decomp.), 176 °C (decomp.), 165 °C and 133 °C (decomp.), respectively. Fischer et al. reported on the synthesis of a Co(II), Ni(II) and Ag(I) complexes bearing 3-Amino-1-nitroguanidine as a ligand and dinitramide as the counterion and its use as laser ignitable primary explosives [8]. DN salts are used in gas-generating and other pyrotechnical formulations [13]. Tetraaminocopper(II) dinitramide is suggested to use nitrogen-rich metal-complex salts of DN, instead of GUS (Guanylurea Sulfate). For example, a mixture of 26.2% guanidine nitrate and 73.8% dinitraze salt of tetramminocopper(II), [Cu(NH₃)₄]²⁺ 2 N(NO₂)₂²⁻, yields in combustion 3.65 mol of gases per 100 g [14]. The present paper describes the preparation, single crystal X-ray structure and energetic properties of bis (aminoguanidine)copper (II) dinitramide (I).

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2 Experimental Section

Caution! The herein described metal complexes of dinitramide (DN) are energetic materials with increased sensitivities toward shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

2.1 Materials and Physical Measurements

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). Infrared spectra were measured using a Perkin-Elmer Spectrum One FT-IR spectrometer as KBr pellets. The UV/Vis/NIR reflectance of the solid samples was measured with a Varian Cary 500 spectrometer in the wavelength range 350–1300 nm. The impact and friction sensitivity tests were performed according to standard methods by using a BAM (Bundesanstalt für Materialforschung) drop hammer and a BAM friction tester. Additionally, these compounds were tested upon the sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.

2.2 Synthesis of ADN

A three-necked glass flask with mechanical stirrer assembly was fitted over a cryobath with a thermometer and an addition funnel. Conc. HNO_3 (98%, 110 mL) was put into the flask and the cryobath was cooled to 45 °C and conc. H_2SO_4 (98%, 40 mL) was added dropwise whilst stirring (400 rpm). Potassium sulfamate (48 g, 0.36 mol) was added in small portions to the nitrating mixture for a period of 25 min whilst stirring (500 rpm) with constant monitoring the temperature (−20 to −40 °C), during the addition of potassium sulfamate. Ice cold water (100 mL) was given in an open glass bowl fitted with a mechanical stirrer. Cyanoguanidine (24 g, 0.29 mol) was suspended in ice cold water (100 mL) and the temperature was maintained at 15 °C. The nitration mixture was quenched with the aqueous suspension (containing cyanoguanidine) under constant stirring (300 rpm). The reaction was robust. The color of the mixture turned to yellow and the suspension was allowed to attain ambient temperature under constant stirring (300 rpm). After cooling, a crystalline white solid (GUDN) separated from the reaction mixture. GUDN was filtered under vacuum and washed with ice cold water and dried at 40 °C for about 2 h. DSC (dec. temperature) 214 °C (Ref. [15]: 212 °C). Part of the recovered guanylurea dinitramide (GUDN) was used for preparation of potassium dinitramide (KDN). A solution containing about 30% by weight of water, 60% by weight of ethanol and 10% by weight of KOH was heated to about 50 °C, and guanylurea dinitramide was dissolved in this solution during continued heating. After about 15 min, the

solution contained 30% by weight of dissolved guanylurea dinitramide, and cooling of the solution was started. KDN began to crystallise and the mixture was further cooled to 15–20 °C, after which crystallised KDN was filtered off and washed with ethanol. DSC (melt. temperature) 127 °C (Ref. [16]: 128 °C). Part of the ethanol-moist potassium dinitramide from filtration was used immediately for preparation of ammonium dinitramide (ADN). 0.5 g KDN was dissolved in 1 ml water and 0.5 g $(\text{NH}_4)_2\text{SO}_4$ was dissolved in 1 ml water. The solutions were mixed with each other and a white precipitate of K_2SO_4 formed. 10 ml 2-propanol was added. K_2SO_4 was filtered off, and the solution was roller-evaporated. The slightly 15 moist products from the roller-evaporation was dissolved in 2-propanol and the undissolved solid was filtered off. The filtrate was concentrated under reduced pressure to yield ammonium dinitramide (ADN) and dried for 2 days at 50 °C. DSC (melt. temperature) 93 °C (Ref. [17]: 92.71 °C).

2.3 Synthesis of $[\text{Cu}(\text{AG})_2][\text{DN}]_2$ (I)

At ambient temperature, a water solution (5 mL) of sodium carbonate (20 mg) was added to aminoguanidine hemisulfate (AGHS) (1 g, 4 mmol) in water (10 mL) with stirring. After half an hour, a mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1 g, 4 mmol) and ammonium dinitramide (ADN) (1 g, 8 mmol) in water (5 mL) was added to the above solution, which was stirred for an additional 20 min. Slow evaporation of the solvent gave the title complex (I) as dark violet crystals (> 500 μm). For the preparation of powder (I), solution cooled to 0 °C and solid product (violet) was filtered (< 50 μm) and dried in a desiccator. Anal. Calc. for $\text{C}_2\text{H}_{12}\text{CuN}_{14}\text{O}_8$ (%): C, 5.67; N, 46.28; H, 2.85; Found C, 5.71; N, 46.10; H, 2.97.

2.4 X-ray Crystal Structure Determination

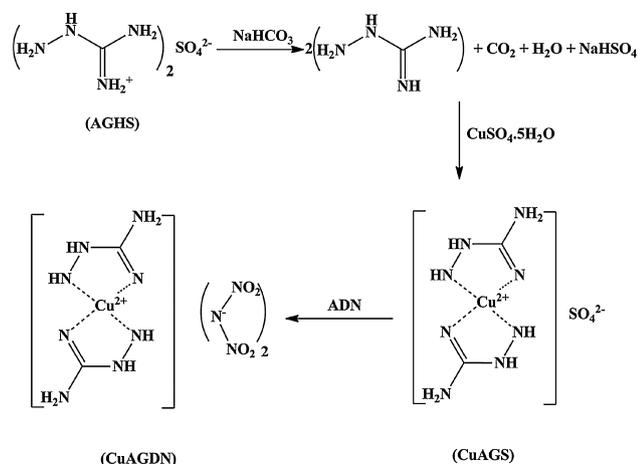
Single-crystal diffraction for (I) were measured at 298 K on a Stoe IPDS-II diffractometer with Mo-K_α radiation (0.71073 Å); absorption corrections were based on repeated and symmetry-equivalent data. The structure was solved by direct methods and refined on all unique F^2 values, with anisotropic displacement parameters and with constrained riding isotropic H atoms. Violet crystal, 0.36 × 0.29 × 0.21 mm; $\text{C}_2\text{H}_{12}\text{CuN}_{14}\text{O}_8$, $M = 423.80$; triclinic, space group $P-1$, $a = 6.9529(14)$, $b = 6.9650(14)$, $c = 8.7967(18)$ Å, $\alpha = 70.83(3)$, $\beta = 89.09(3)$, $\gamma = 62.32(3)^\circ$, $V = 351.54(19)$ Å³, $Z = 1$. 3895 reflections measured, 1868 unique, $R_{\text{int}} = 0.0316$, 1868 reflections with $F^2 > 2\sigma$, data 98.8% complete to $\theta = 29.17^\circ$. 119 refined parameters, $R [F, F^2 > 2r] = 0.0477$, $R_w [F^2, \text{all data}] = 0.1648$, goodness of fit = 1.160 on F^2 , final difference map extremes +0.615 and −0.727 e Å^{−3}. Computer Programs was X-Area for data collection and processing, SHELXTL for structure solution, refinement and graphics [18, 19]. Crystallographic data have been deposited with the

Cambridge Crystallographic Data Centre, CCDC No. 1416456 for (I). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3 Results and Discussion

3.1 Synthesis

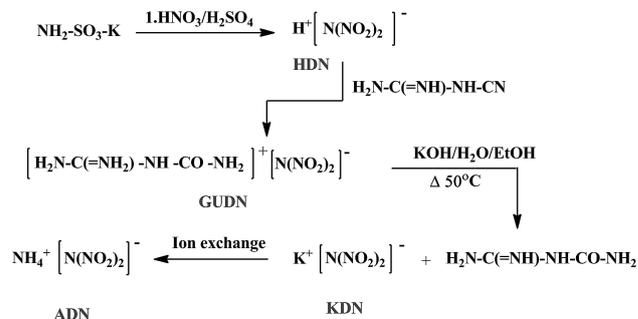
The reaction of aminoguanidine hemisulfate (AGHS) in the presence of sodium bicarbonate (NaHCO_3), with copper(II) sulfate and ammonium dinitramide (ADN) in 1:1:2 molar ratio, afforded the bis(aminoguanidine)copper(II) dinitramide (I) product. As shown in Scheme 1, the bidentate



Scheme 1. Synthesis of $[\text{Cu}(\text{AG})_2][\text{DN}]_2$ (I).

ligand aminoguanidine forms a chelate complex with the copper ion. Chelation results in the formation of a five-membered CuN_4 ring. To dissolve the AGHS, the pH of the solution was raised to 8.5 by adding several drops of an aqueous solution of sodium bicarbonate.

Ammonium dinitramide (ADN) was synthesized from salts of sulfamic acid [20]. In a typical reaction, potassium sulfamate was nitrated using fuming $\text{HNO}_3/\text{con. H}_2\text{SO}_4$ mixture. The mixture was then treated with cyanoguanidine to give guanylurea dinitramide (GUDN). The precipitated GUDN was removed by filtration and dried in vacuum. In order to obtain ADN, the formed GUDN was treated with aqueous KOH solution at 50°C until no solids remained and upon cooling, potassium dinitramide (KDN) precipitated from the solution. A double decomposition or ion exchange reaction of potassium dinitramide gave ADN. The reaction is shown in scheme 2. Using potassium dinitramide instead is disadvantageous because of the simultaneous precipitation of both potassium sulfate and the $[\text{Copper}(\text{AG})_2][\text{DN}]_2$.



Scheme 2. Synthesis of ammonium dinitramide (ADN) from potassium sulfamate using cyanoguanidine as neutralizing agents.

3.2 Spectral Characterization

UV spectrum of ADN and complex (I) were recorded in water solution (Figure 1). In this spectra, there are two intense peaks at 216 and 281 nm which are identified as characteristic $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ absorption bonds of dinitramide (DN) anion in solution [21]. The $d-d$ transition spectra of the complex show broad band centered at 587 nm, being suggestive of approximate squareplanar geometry at Cu [22–25]. The ligand (AGHS) and its dinitramide copper(II) complex have been characterized in detail by recording their IR spectra. The IR spectrum of the free ligand (AGHS) exhibits the characteristic band of an imine, which appears at 1683 cm^{-1} . This band is shifted to lower frequencies in the IR spectra of complex due to the coordination of the imine nitrogen (Figure 2) [26]. As a result of complexation, typical dinitramide vibrations of I ($\nu_{\text{as}}(\text{NO}_2) = 1513\text{ cm}^{-1}$, $\nu_{\text{s}}(\text{NO}_2) = 1169\text{ cm}^{-1}$, and $\nu_{\text{as}}(\text{N}_3) = 1010\text{ cm}^{-1}$) are redshifted compared to those of noncoordinating dinitramide anions [27].

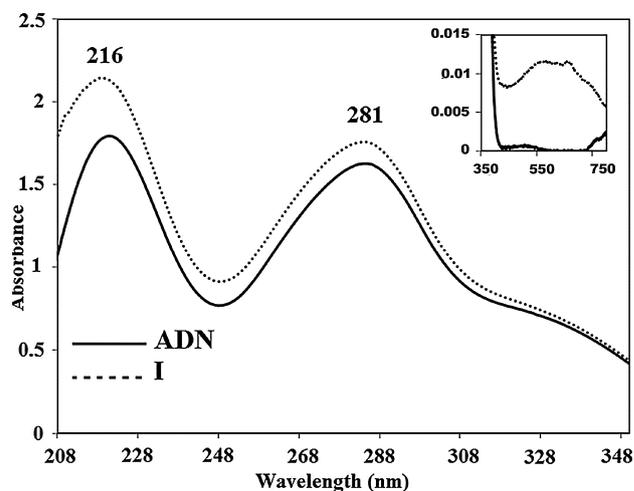


Figure 1. UV spectrum of ADN and I in water.

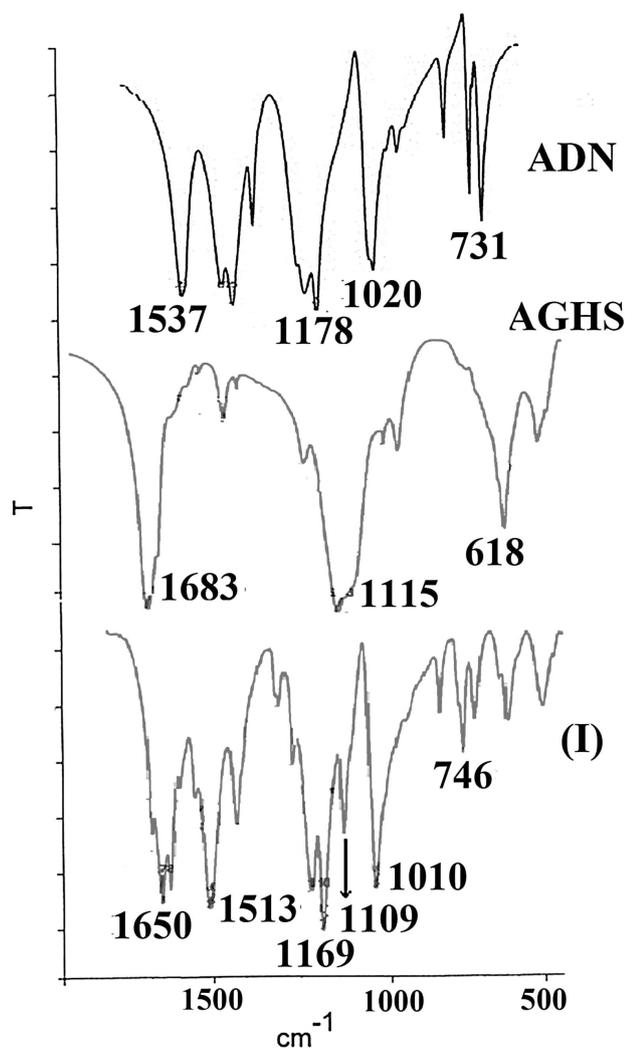


Figure 2. IR spectra of ADN, AGHS and $[\text{Cu}(\text{AG})_2][\text{DN}]_2$ (I).

3.3 Structure Description

The molecular structure of I illustrated in Figure 3, and selected bond distances and angles are given in table 1. In

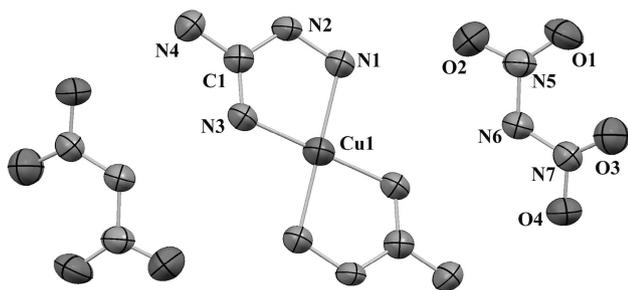


Figure 3. Molecular structure and labeling scheme for the complex (I), hydrogen is omitted for clarity and thermal ellipsoids are shown at the 50% probability level.

Table 1. Selected geometric parameters (\AA , $^\circ$) for I.

| Bond lengths | \AA | Bond angle | |
|--------------|--------------|--------------------------------|------------|
| Cu(1)–N(1) | 2.019(3) | N(3)–Cu(1)–N(3) ^[a] | 180.00(17) |
| Cu(1)–N(3) | 1.923 (3) | N(1)–Cu(1)–N(1) ^[a] | 180.000(1) |
| C(1)–N(3) | 1.295(4) | N(3)–Cu(1)–N(1) ^[a] | 97.82(11) |
| C(1)–N(4) | 1.335(4) | N(3)–C(1)–N(2) | 118.5(3) |
| C(1)–N(2) | 1.362(4) | N(3)–C(1)–N(4) | 124.8(3) |
| N(6)–N(7) | 1.364(4) | N(4)–C(1)–N(2) | 116.7(3) |
| N(6)–N(5) | 1.383(4) | N(7)–N(6)–N(5) | 115.8(3) |
| N(5)–O(2) | 1.229(4) | O(1)–N(5)–O(2) | 122.3(3) |
| N(5)–O(1) | 1.225(4) | | |
| N(2)–N(1) | 1.413(4) | | |

[a] Symmetry code: $-x+1, -y, -z+1$.

the cation of I, the Cu^{II} atom is four-coordinated by two imine N and two amine N atoms from two aminoguanidine (AG) ligands. The four coordinating atoms around Cu are approximately coplanar, giving a square-planar coordination. The two Trans angles at Cu1 are 180° and the other angles are ranging from 82.19 to 97.81° , which indicates a slightly distorted square-planar coordination of the Cu atom (Figure S1). The N3–C1 bond length is 1.296 \AA , which is typical of C=N bonds. The Cu1–N1 bond (Table 1) is comparable to the corresponding value [1.982 \AA] observed in $[\text{Cu}(\text{ANQ})_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2$ [8]. However, Cu1–N3 is slightly smaller than the corresponding value [2.032 \AA]. The dihedral angle between the N1/Cu1/N3 and N3/C1/N2/N1 planes is 5.92° , showing that there is a significant coplanarity of the CuN₄ plane and the five-membered chelate ring. The dihedral angle between the two ligand coordination planes [Cu1/N1/N3 and Cu1/N1¹/N3¹; Symmetry code: (i) $-x+1, -y, -z+1$] is 0.0° . The molecule of the title copper (II) complex exist as monomer, with Cu...Cu separation of 6.965 \AA , leading to no dimeric interaction. The N6–N7, N5–O2 bond lengths and N5–N6–N7 angle are $1.364(4)$, $1.229(4) \text{ \AA}$ and $115.8(3)^\circ$, respectively in the dinitramide counterion. In these and other respects there are no major differences between the dinitramide structures, the bond lengths and angles are similar to those of related salts found in the Cambridge Structural Database [28,29]. The dinitramide anions are not planar and follow the twisted structure observed for, for example, lithium and potassium dinitramide [30]. In summarizing the metrical parameters it is noted that in no case are the N–N bonds (dinitramide) as short as a N=N double bond (1.245 \AA) nor as long as a N–N single bond (1.454 \AA) [31]. These results indicate some degree of delocalization and are reflected in the N–N–N angles which are intermediate between expected sp^2 and sp^3 values at $115.8(3)^\circ$. From our results, I crystallizes in triclinic space group $P\bar{1}$ with $a=6.9529(14)$, $b=6.9650(14)$, $c=8.7967(18) \text{ \AA}$, $\alpha=70.83(3)$, $\beta=89.09(3)$, $\gamma=62.32(3)^\circ$, $V=351.54(19) \text{ \AA}^3$, $Z=1$. In I each dinitramide anion is surrounded by five nearest copper^{II} cation so that each oxygen and central nitrogen atom of dinitramide (DN) is hydrogen bonded to one or two hydrogen atoms (Figure S2). Con-

versely, in **I** each copper^{II} cation is surrounded by eight nearest dinitramide (DN) so that each hydrogen atoms of copper^{II} cation is hydrogen bonded to one or two nitrogen atoms (Figure S3). In the crystal packing, the ions are linked via N–H...O hydrogen bonds, involving uncoordinated dinitramide (DN) anions and NH, NH₂ groups of AG, to form a three-dimensional network (Table 2, Figure S4 and S5).

3.4 Energetic Properties

DSC measurements for determining the thermal behavior of the powder and single crystal of **I** were performed in covered Al-containers with a nitrogen flow of 20 mL min⁻¹ on a Perkin-Elmer Pyris 6 DSC, at a heating rate of 5 °C min⁻¹. The compounds decompose/explode violently mostly without prior melting points. **I** (powder) show a well-defined decomposition point at 130 °C (Figure 4), while the neutral ADN and AGHS melts at an onset temperature of 92 and 200 °C [32,33]. In the measurement of **I** (single crystal) a violent explosion appeared destroying the setup, which can be seen on its thermo plot (Figure 5). Fischer et al. report the structural of dinitramide-based 3-Amino-1-Nitroguanidium complexes (Co and Ni) [8]. These complexes crystallize isotypically as tetrahydrates in the monoclinic crystal system. Two water molecules participate in the coor-

Table 2. Distances and angles of selected hydrogen bonds in **I**.

| D–H...A ^[a] | D–H [Å] | H...A [Å] | D...A [Å] | D–H...A [°] |
|----------------------------------|---------|-----------|-----------|-------------|
| N(2)–H(2)...O(2) ^[b] | 0.860 | 2.270 | 3.060 | 152.70 |
| N(4)–H(4A)...O(4) ^[b] | 0.860 | 2.159 | 2.998 | 165.05 |
| N(4)–H(4B)...O(4) ^[c] | 0.860 | 2.543 | 2.996 | 113.88 |
| N(1)–H(1A)...O(3) ^[d] | 0.900 | 2.198 | 2.951 | 140.85 |

[a] Symmetry codes; [b] –x, 1–y, 1–z; [c] –1+x, y, z; [d] 1–x, –y, 2–z.

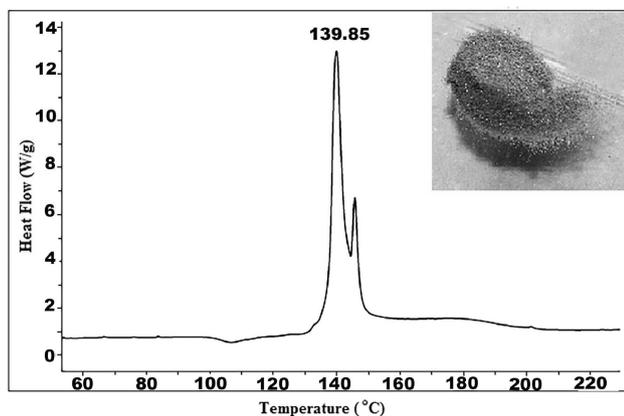


Figure 4. DSC spectrum of **I** (powder) at a heating rate of 5 °C min⁻¹ in N₂ atmosphere.

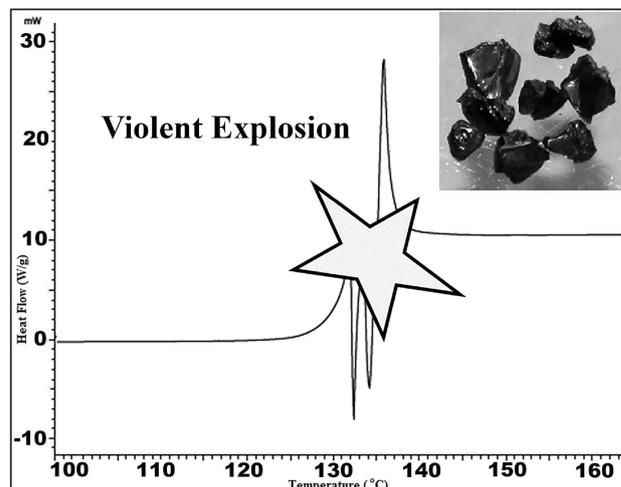


Figure 5. DSC spectrum of **I** (single crystal) at a heating rate of 5 °C min in N₂ atmosphere.

dination sphere, while the others are connected to the dinitramide anions by formation of hydrogen bonds. The crystal water containing complexes (Co and Ni) can be dehydrated after heating, indicated by an endothermic peak in the DSC curve, which is well-separated from the exothermic decomposition event. One of the most important properties for new energetic materials is sensitivity. The drop weight sensitivities for powder and single crystal of **I** are 3.5 and 10 J respectively. In this measurement, we found that the impact sensitivity of **I** (powder) is of the same magnitude of ADN (4J) and also indicated that the RDX is nearly twice insensitive than the neat powder of **I** [34]. A summary of the impact and friction sensitivity of **I** is given in Table 3. The friction sensitivity results for powder and single crystal of **I** is 40 N. The observation shows that the friction sensitivity of **I** is much more than that of RDX (157 N) and ADN (72 N) [34,35]. Interestingly, the cobalt and nickel ANQ dinitramide complexes, while still being comparatively sensitive, do not reach the high sensitivity level of **I** in term of impact as well as friction sensitivity, presumably because of the inclusion of four molecule of crystal

Table 3. Sensitivities and thermal behavior.

| Complexes | IS (J) | FS (N) | ESD (J) | T _{dehydr} (°C) | T _{dec} (°C) |
|--|--------|--------|---------|--------------------------|-----------------------|
| [Cu(AG) ₂](N(NO ₂) ₂) ₂ (I), Single Crystal | 10 | 40 | 0.25 | – | 130 ^[c] |
| [Cu(AG) ₂](N(NO ₂) ₂) ₂ (I), Powder | 3.5 | 40 | 0.25 | – | 130 |
| [Co(ANQ) ₂ (H ₂ O) ₂](N(NO ₂) ₂) ₂ ^[8] | 5 | 80 | 0.70 | 85 | 118 |
| [Ni(ANQ) ₂ (H ₂ O) ₂](N(NO ₂) ₂) ₂ ^[8] | 3 | 80 | 0.60 | 138 ^[a] | 142 |
| [Ag(N(NO ₂) ₂ (ANQ))(H ₂ O) ^[8] | 2 | 7 | 0.10 | 71 | 108 |

[a] Decomposition (exothermic) occurs immediately after dehydration (endothermic); [b] 3-amino-1-nitroguanidine; [c] Violent explosion.

water per formula unit (Table 3). Low sensitivities and violent explosion (DSC) may be a reason, due to the copper complex (I), which crystallize water free. The power of powder and single crystal of I measured by the Trauzl test are 425 and 427 cm⁻³ for 10 g I (142% TNT and 88% RDX) [36].

4 Conclusions

The title complex, bis(aminoguanidine)copper (II) didinitramide (C₂H₁₂CuN₁₄O₈) (I), has been synthesized by reaction of aminoguanidine hemisulfate (AGHS) in the presence of KOH, with copper (II) sulfate and ammonium dinitramide (ADN) in 1:1:2 molar ratios. The crystal structure has been investigated by a single-crystal X-ray diffraction study at 298 K. A dinitramide containing complex crystallizes water free. The copper (II) complex decomposes at relatively low temperature (130 °C, Violent explosion). This complex bearing energetic counterion show enhanced sensitivities toward impact and friction, which especially applies to the solvate water free copper complex with values of 10J (IS) and 40N (FS). The power of powder and single crystal of I measured by the Trauzl test are 425 and 427 cm⁻³ for 10 g I (142% TNT and 88% RDX).

Acknowledgements

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