



Synthesis and explosive properties of copper(II) chlorate(VII) coordination polymer with 4-amino-1,2,4-triazole bridging ligand

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ARTICLE INFO

Article history:

Received 28 July 2009

Received in revised form

30 November 2009

Accepted 1 December 2009

Available online 4 December 2009

Keywords:

4-Amino-1,2,4-triazole

Complex chlorate(VII) copper(II)

Primary explosive

ABSTRACT

Copper(II) chlorate(VII) coordination polymer with 4-amino-1,2,4-triazole as bridging ligand was prepared and characterized by elemental analysis, IR spectra and TG/DTA analyses. Sensitivity and detonator tests were also performed. The compound has a 1D chain structure in which Cu(II) ions are linked by triple triazole N1,N2 bridges. It is a detonator with performance close to that of lead azide, but at the same time it shows moderate sensitivity to thermal (explosively decomposes above 250 °C) and mechanical stimuli (sensitivity to friction 10N).

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1. Introduction

For more than 100 years, mercury fulminate (MF), lead azide (LA) and lead styphnate (LS) have been used as primary explosives. They are very good initiatory explosives but they also suffer from serious drawbacks, such as: (i) extremely high sensitivity to mechanical stimuli, (ii) thermal, hydrolytic, chemical instability or lack of resistance to light, (iii) incompatibility with metals commonly used in initiating devices, and (iv) high toxicity of the compounds themselves and their decomposition products [1].

The ongoing search for new primary explosives is aimed at finding materials safer in production and use which do not contain heavy metals and with better initiating performance than the multicomponent compositions being used now. The replacements of the present primaries should be more resistant to accidental stimuli (electrostatic discharge, impact, friction), but they must reliably inflame or detonate, e.g. upon exposure to flame, electrically heated wire or strike with a firing pin in stab and percussion initiators. However their thermal stability should not be too low in order to avoid unexpected explosions of ammunition exposed to heat flow from a fire. On the other hand some of the materials (detonants) must be capable of fast transition from deflagration to detonation. It is not easy to reconcile so many contradictory demands, but from

the recently published papers, it follows that it may be possible [1–20].

It has been confirmed many times that some complex compounds with a general formula of $M_x(L)_y(An)_z$ where M denotes a transition metal cation, L is a nitrogen rich ligand molecule, and An is an oxygen containing anion are effective primary explosives. The cation plays structure-creating role (i.e. coordinates other molecules) providing stability of the compound and the required level of safety. Usually it is also a catalyst of the first stage of decomposition which assures a rapid deflagration to detonation transition—inherent feature of primary explosives. In order to maximize the heat effect of decomposition, the oxygen balance of the compounds ought to be close to zero. Thanks to this the initiating performance of the new primaries may be higher than that of azides and flumintaes [1–20].

In the present work, copper(II) chlorate(VII) coordination polymer with 4-amino-1,2,4-triazole (4-AT, $C_2H_4N_4$) as bridging ligand was prepared and tentatively characterized from the point of view of its explosive properties. The copper ions are linked together by three triazole ligands (N1,N2 bridging mode) and the triple bridged Cu^{2+} chain is surrounded in the external zone with chlorate(VII) anions $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$. The composition and structure of the compound [21,22] was confirmed using results of elemental analysis and infrared spectra. Its explosive properties were characterized by measuring sensitivity to friction and impact, thermal stability (TG/DTA analyses), detonation velocity and performing detonator feasibility firing in a commercial detonator containing 1.2 g of pressed PETN as a secondary charge.

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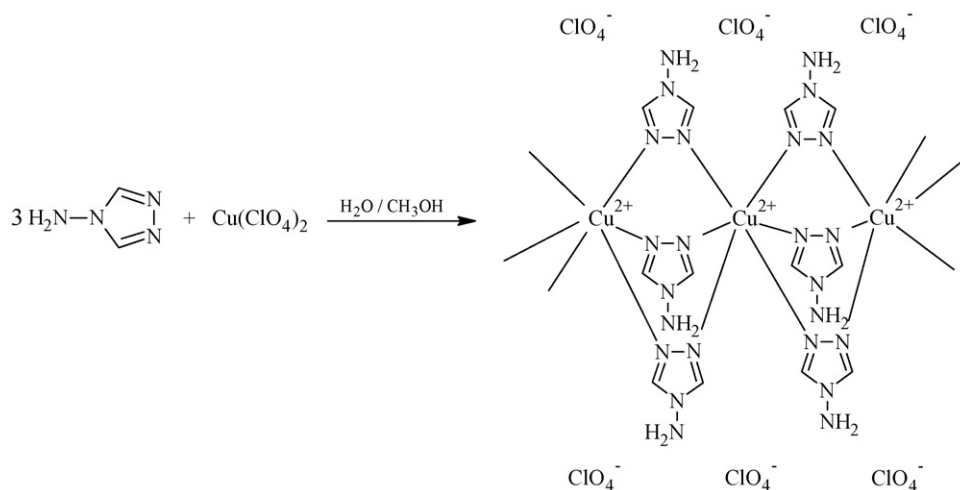


Fig. 1. Synthesis and structure of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$.

2. Experimental

2.1. Synthesis of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$

The scheme of synthesis and structure of the coordination polymer $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ are shown in Fig. 1.

One gram of 4-amino-1,2,4-triazole (Fluka, Cat. No. 09550) was dissolved in a solution of 20 cm³ of water and 15 cm³ of methanol, with stirring. After dissolving, 4.41 g of hydrated copper(II) chlorate(VII) ($\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, Aldrich Cat. No. 215392) was added. The resulting solution was stirred for 2.5 h at room temperature. The precipitate was filtered off, washed with water and methanol and dried at 40 °C. The final product was in the form of pale-blue, fine powder with mass of 1.24 g (yield of ca. 60%).

2.2. Characterization

Elemental analyses were performed with Analyzer CHNS Vario EL III (Elementar Analysensysteme GmbH). Atomic emission spectrophotometer Spectroflame-ICP M (Spectro Analytical Instruments) was used to determine the copper content of the complex. FTIR spectra were collected on a Nicolet iS10 (ThermoScientific) spectrometer using the potassium bromide pellet method (sample concentration of ca. 0.7%). Simultaneous thermal gravimetric and differential analyses (TG/DTA) were carried out using

LabSys-TG/DTA apparatus (Setaram). Samples of ca. 1 mg were heated from 20 to 500 °C, at a rate of 5 °C/min, in nitrogen atmosphere. Friction sensitivity measurements were made on Julius Peters apparatus according to the Polish standards (BAM method). The impact sensitivity was determined by the Fall Hammer Method using 1 kg drop hammer. Sensitivity to flame and detonating performance were assessed in a detonator test. To this end, 0.2 or 0.3 g of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ was pressed (30 MPa) above a 1.2 g pentaerythritol tetranitrate (PETN) charge in an aluminum cup of a commercial detonator (6.4/6.9 mm in the internal/external diameter). The detonator was fixed vertically on a 5-mm lead plate and its detonation was initiated with a standard electric match or safety fuse. The commercial detonator containing 0.3 g of lead azide and lead styphnate mixture (pressed under the same conditions) and 1.2 g of PETN was used as a reference. The mean values of detonation velocity of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ at a density of ca. 0.2, 1.1 and 1.4 g/cm³ were measured using short-circuit sensors and a time recorder. The charges were 10 mm in diameter, and they were placed in thin-walled paper tubes.

3. Results and discussion

The content of copper, carbon, hydrogen and nitrogen in $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ is as follows: Cu, 12.35%; C, 14.00%; H, 2.35%; N, 32.66%. The average results of elemental analyses are 11.6 ± 0.5 , 14.17; 2.25 and 31.97%, respectively. So that the elemen-

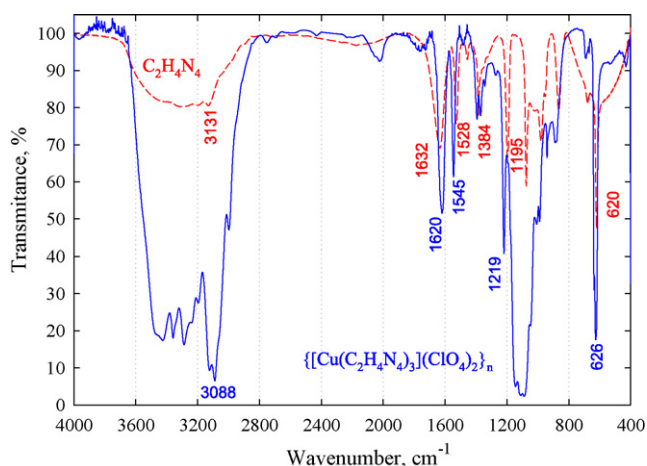


Fig. 2. FTIR spectra of 4-amino-1,2,4-triazole and $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$.

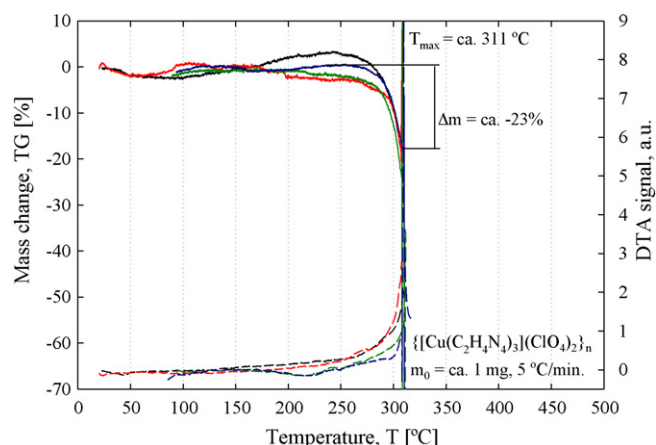


Fig. 3. TG/DTA curves of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$.

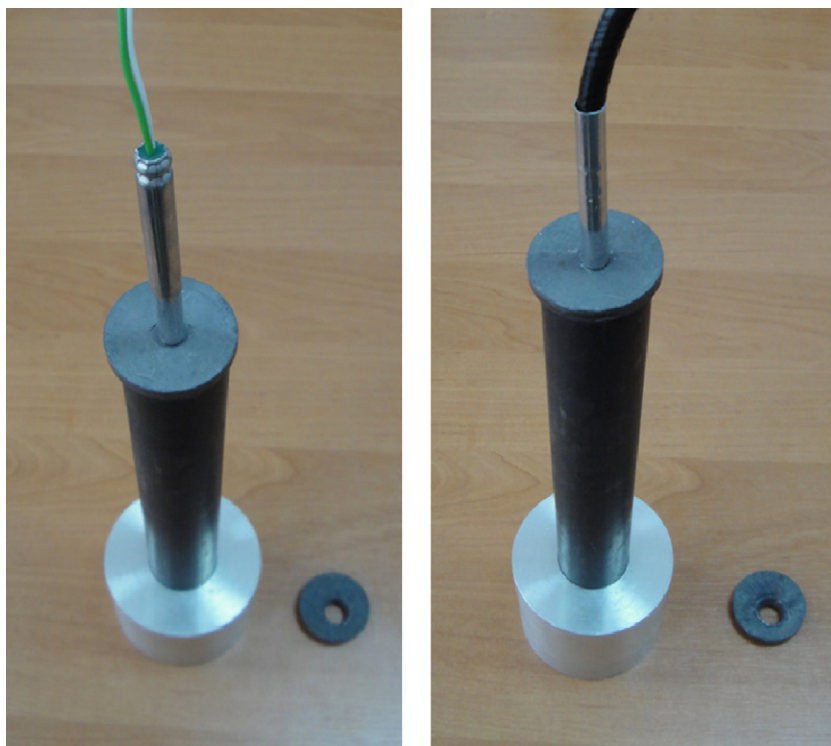


Fig. 4. Photographs of the tested detonators and the witness plates after firing.

tal composition of the obtained compound confirms its predicted structure.

FTIR spectra of 4-AT and $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ are shown in Fig. 2. The wide band above 3000 cm^{-1} is assigned to the stretching vibration of N–H and C–H linkage. In a range of $1700\text{--}600\text{ cm}^{-1}$, there are observed characteristic bands of stretching and deformation vibrations of the triazole ring and the external amino group, i.e. deformation vibrations of NH_2 (1632 cm^{-1}), stretching vibrations of the heterocyclic ring (1528 and 1384 cm^{-1}), stretching vibrations of the exocyclic N–N bond (1195 cm^{-1}) and deformation vibrations of the triazole ring ($700\text{--}600\text{ cm}^{-1}$).

In the IR spectrum of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$, a wide band appears in a range of $1200\text{--}1000\text{ cm}^{-1}$, which may be attributed to chlorate(VII) anion frequencies. The absorption of stretching vibrations of the triazole ring (1545 cm^{-1}) and N–N bond (1219 cm^{-1}) is shifted to higher wavenumber compared to the free ligand, whereas absorption resulting from deformation vibrations of NH_2 group appears at a lower frequency (1620 cm^{-1}). Such changes of 4-amino-1,2,4-triazole IR spectrum confirm that the molecule is coordinated in the N1N2 mode [22]. In this case, the triazole ring is polarized (electrons are shifted to copper ion) and becomes more rigid. This causes that the energy of ring vibrations and N–N bond (between triazole ring and NH_2 group) increases and the energy of N–H bond in the external amino group decreases.

Typical TG/DTA curves of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ are shown in Fig. 3. Samples as small as 1 mg detonates at ca. 311°C when heated up at a rate of $5^\circ\text{C}/\text{min}$ in open crucibles made of Al_2O_3 . In each case, detonation completely destroyed the crucible.

From the thermograms (Fig. 3), it follows that under the experimental conditions, the decomposition process starts above 250°C . At lower temperatures, the sample does not undergo any changes which are accompanied by mass or energy exchange. Detonation follows a slow decomposition stage during which the sample losses ca. 23% of its mass.

The results of friction sensitivity measurements (BAM method) have shown that $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ does not react up to pis-

til load of 8.8 N. When the load was 9.8 N, 10% of explosions (50 trials) were observed. First explosions in the impact sensitivity test happened, at an impact energy of 1 J (drop height 10 cm). It should be mentioned that pure lead azide was always initiated in comparative experiments.

The feasibility demonstration firings in the commercial detonator (Fig. 4) have shown that both 0.3 and 0.2 g pressed charges of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ detonate upon exposure to flame generated by the standard electric match or safety fuse and initiate detonation of pressed PETN used as an output charge.

In each case (10 trials) the detonator punched a hole (ca. 10 mm in diameter) on the 5 mm thick lead witness plate, equivalent to that of produced by a standard detonator (containing 0.3 g of lead azide and lead styphnate mixture as a priming charge).

The charges of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ in the tested detonators were 6.4 mm in diameter and had a density of ca. $1.4\text{ g}/\text{cm}^3$. The mass of minimum priming charge to PETN was found to be ca. 0.2 g, so that the deflagration to detonation distance in the detonator assembly is not longer than 4.5 mm.

At a bulk density of about $0.2\text{ g}/\text{cm}^3$, the tested explosive detonates at a velocity of 2.8 km/s when initiated with flame generated by a standard electric match. The detonation velocity measured in unconfined pressed charges with density of ca. 1.1 and $1.4\text{ g}/\text{cm}^3$ was ca. 5.5 and 6.5 km/s, respectively.

4. Conclusions

Coordination polymer with formula of $\{[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3](\text{ClO}_4)_2\}_n$ built of copper cations linked together by triple triazole bridges and surrounded with chlorate(VII) anions in the external zone was synthesized. To the best of our knowledge, the compound has been confirmed, for the first time, to be a primary explosive with very interesting properties. It can be characterized as a comparatively stable low-sensitive to friction (10 N), thermally resistant (decomposes above 250°C) and high energetic detonat ($6.5\text{ km}/\text{s}$ at $1.4\text{ g}/\text{cm}^3$). Upon exposure to flame, it detonates in pressed charges

of 200 mg in mass and initiates detonation of PETN charges. So that the compound may be used as an environmentally friendly and safe replacement of lead azide and lead styphnate. Its synthesis is very simple and starts from cheap, available substances.

The good properties of the compound result from its composition. Copper cation has high ion potential (the ratio of electric charge to ion radius) and thanks to this creates stable coordination compounds. What is more it is known as a catalyst of the first stage of decomposition of such compounds, because it activates ligands oxidizing them to reactive radicals [3]. Chlorate(VII) anion is rich in active oxygen and its redox potential is quite high ($\text{Cl}_2/\text{ClO}_4^-$, 1.39 V). 4-Amino-1,2,4-triazole is a stable compound and has the possibility of linking metal ions together because its two neighboring donor atoms are situated in the five-membered ring. As a result the preferred geometry is the coordination polymer in which metal cations are linked together by triple triazole bridges [23]. Strong, triple bonds between central ions and complete filling of their coordination zone are conducive to the complex stability, because separation of a ligand needs breaking two bonds and the copper ions cannot coordinate water molecules.

Acknowledgement

This research was supported by the Ministry of Science and Higher Education through Military University of Technology, Grant O R00 0011 06.

References

- [1] M.H.V. Huynh, M.A. Hiskey, T.J. Meyer, M. Wetzler, Green primaries: environmentally friendly energetic complexes, *PNAS* 103 (2006) 5409–5412.
- [2] M.H.V. Huynh, M.D. Coburn, T.J. Meyer, M. Wetzler, Green primary explosives: 5-nitrotetrazolato-N₂-ferrate hierarchies, *PNAS* 103 (2006) 10322–10327.
- [3] A.E. Fogelzang, V.P. Sidnitsky, V.Y. Egorshv, V.V. Serushkin, Effect of structure of energetic materials on burning rate, *Mater. Res. Soc. Symp. Proc.* 418 (1996) 151–161.
- [4] M.A. Ilushin, I.V. Teslynsky, Primary explosives, the present and prospects, *Russ. J. Chem.* 41 (1997) 3–13 (in Russian).
- [5] V.P. Sidnitsky, A.E. Fogelzang, Energetic materials based on co-ordination compounds, *Russ. J. Chem.* 41 (1997) 74–80 (in Russian).
- [6] M.A. Ilushin, Light-sensitive explosives and compositions and their laser ignition, *Russ. J. Chem.* 41 (1997) 81–88 (in Russian).
- [7] M.A. Ilushin, I.V. Teslynsky, Energetic metal complexes in primer detonators, *Russ. J. Chem.* 45 (2001) 72–78 (in Russian).
- [8] M.A. Ilushin, I.V. Teslynsky, Laser initiation of high-energy-capacity compounds in science and technology, *Russ. J. Appl. Chem.* 73 (2000) 1305–1312.
- [9] M.B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A.K. Sikder, B.R. Gandhe, A. Subhananda Rao, Environmentally compatible next generation green energetic materials (GEMs), *J. Hazard. Mater.* 161 (2009) 589–607.
- [10] J.-J. Liu, X. He, M. Shao, M.-X. Li, Syntheses, crystal structures and characterizations of the three new copper(II) azide coordination polymers with 1,2,4-triazole ligands, *J. Mol. Struct.* 919 (2009) 189–195.
- [11] Z. Liu, T. Zhang, J. Zhang, S. Wang, Studies on three-dimensional coordination polymer $[\text{Cd}_2(\text{N}_2\text{H}_4)_2(\text{N}_3)_4]_n$: crystal structure, thermal decomposition mechanism and explosive properties, *J. Hazard. Mater.* 154 (2008) 832–838.
- [12] M.B. Talawar, A.P. Agrawal, J.S. Chhabra, S.N. Asthana, Studies on lead-free initiators: synthesis, characterization and performance evaluation of transition metal complexes of carbohydrazide, *J. Hazard. Mater.* A 113 (2004) 57–65.
- [13] D.M. Badgujar, M.B. Talawar, S.N. Asthana, P.P. Mahulikar, Advances in science and technology of modern energetic materials: an overview, *J. Hazard. Mater.* 151 (2008) 289–305.
- [14] M. Friedrich, J.C. Glvez-Ruiz, T.M. Klapotke, P. Mayer, B. Weber, J.J. Weigand, BTA copper complexes, *Inorg. Chem.* 44 (2005) 8044–8052.
- [15] M.A.M. Taha, Use of 1,5-diaminotetrazole in the synthesis of some fused heterocyclic compounds, *J. Indian Chem. Soc.* 82 (2005) 172–174.
- [16] Y.-Q. Huang, B. Ding, H.-L. Gao, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, Syntheses, structures and characterization of novel cobalt(II) mono- and bi-triazole complexes, *J. Mol. Struct.* 743 (2005) 201–207.
- [17] M.B. Talawar, A.P. Agrawal, S.N. Asthana, Energetic co-ordination compounds: synthesis, characterization and thermolysis studies on bis-(5-nitro-2H-tetrazolato-N₂)tetraammine cobalt(III) perchlorate (BNCP) and its new transition metal (Ni/Cu/Zn) perchlorate analogues, *J. Hazard. Mater.* A 120 (2005) 25–35.
- [18] S. Zhu, Y. Wu, W. Zhang, J. Mu, Evaluation of a new primary explosive: nickel hydrazine nitrate (NHN) complex, *Propell. Explos. Pyrot.* 22 (1997) 317–320.
- [19] V.V. Andreev, A.G. Nekljudov, S.A. Pozdnjakov, A.E. Fogelzang, V.P. Sinditskiy, V.V. Serushkin, V. Ju. Egorshv, V.I. Kolesov, Primer detonator (variants), *Russ. Patent* 2,104,466 C1, February 10 (1998).
- [20] M. Hang, V. Huynh, Lead-free primary explosives, *US Patent Application Publication*, US 2008/0091029 A1, April 17 (2008).
- [21] L.G. Lavrenova, S.V. Larionov, S.A. Grankina, The metal complexes with 4-amino-1,2,4-triazole, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.* 5 (1979) 88–92 (in Russian).
- [22] V.P. Sidnitsky, V.I. Sokol, A.E. Fogelzang, M.D. Lutov, V.V. Serushkin, M.A. Poray-Koshitz, B.C. Svetlov, Vibration spectra and structure of coordination compounds with 4-amino-1,2,4-triazole as didentate ligand, *Russ. J. Inorg. Chem.* 32 (1987) 1950–1955 (in Russian).
- [23] J.G. Haasnoot, Mononuclear, oligonuclear and polynuclear metal coordination compounds with 1,2,4-triazole derivatives as ligands, *Coord. Chem. Rev.* 200–202 (2000) 131–185.