Detonation and Decomposition Characteristics of Dichlorate(VII) *μ*-Tris(4-amino-1,2,4-triazole)copper(II)

Stanisław CUDZIŁO*, Waldemar A. TRZCIŃSKI,
Józef PASZULA, Marcin NITA

*Military University of Technology,
Kaliskiego 2, 00-908 Warsaw, Poland*
E-mail: scudzilo@wat.edu.pl

Abstract. Dichlorate(VII) *μ*-tris(4-amino-1,2,4-triazole)copper(II) is an explosive with a performance close to that of lead azide. However, it is quite stable and has moderate sensitivity to thermal and mechanical stimuli. In order to fully characterize it as a primary explosive, its thermal decomposition kinetics were studied and some important detonation and explosion parameters (detonation heat and velocity, acceleration ability, water shock wave overpressure, and energy) were measured and/or calculated.

Keywords: 4-amino-1,2,4-triazole, complex copper compound, primary explosive, detonation parameters

1 Introduction

Dichlorate(VII) *μ*-tris(4-amino-1,2,4-triazole)copper(II) ($\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$) has recently been identified as an interesting primary explosive that combines moderate sensitivity to thermal and mechanical stimuli with high performance [1]. This compound's beneficial properties result from its elemental composition and structure. It is a coordination polymer in which the Cu(II) ions are linked by triple triazole N1,N2 bridges [2, 3]. The bidentate coordination mode and complete filling of the coordination zone provide stability to the complex, because separating a ligand requires the breaking of two bonds and the copper ions cannot coordinate water molecules.

The present work includes the measurement and calculation of some

decomposition and detonation parameters of dichlorate(VII) μ-tris(4-amino-1,2,4-triazole)copper(II). The non-isothermal kinetics of the thermal decomposition was studied first, and the heats of explosion in an argon and an oxygen atmosphere were then measured. The results of these tests provided the basis for calculating the enthalpy of formation. Knowing the elemental composition, theoretical density, and enthalpy of formation, it was possible to compute the detonation velocity, pressure, temperature, and energy at different densities using the Cheetah code. The detonation velocity at densities ranging from 0.25 to 1.40 $g \cdot cm^{-3}$ was also measured. Finally, the explosive was tested using the cylinder test and the underwater detonation test for charges having different masses that were pressed into a metal cup. Important explosion parameters, such as the accelerating ability of the explosive, the shock wave overpressure, the shock wave energy, and the bubble energy, were determined and compared to those of TNT, phlegmatized RDX (RDXph), a lead azide/lead styphnate (LA/LS) mixture.

2   Experimental

2.1 Materials and test methods

To synthesize $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$, 4-amino-1,2,4-triazole ($C_2H_4N_4$, Fluka, Cat. No. 09550) and hydrated copper(II) dichlorate(VII) ($Cu(ClO_4)_2 \cdot 6H_2O$, Sigma-Aldrich Cat. No. 215392) were used as supplied.

Elemental analyses were performed using an Analyzer CHNS Vario EL III, (Elementar Analsensysteme GmbH), and the copper content of the complex was determined using an atomic emission spectrophotometer Spectroflame-ICP M (Spectoro Analytical Instruments). TG and DSC analyses were conducted using a Universal V4.2E apparatus (TA Instruments). Samples of approximately 0.1 mg in mass were heated from 20 to 500 ºC at different heating rates (2, 5, 10, and 15 ºC·min^{-1}) in a nitrogen atmosphere with a flow rate of 50 mL·min^{-1}.

The mean values of the detonation velocity of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ at densities of 0.25, 1.05, and 1.40 $g \cdot cm^{-3}$ were measured using short circuit sensors and a time recorder. The charges were 10 mm in diameter and were contained in thin-walled paper tubes.

A water calorimeter (static jacket) equipped with an oxygen bomb was used for the calorimetric measurements. Samples of approximately 0.5 g were loaded in open quartz crucibles and initiated with an electrically heated wire. The calorimeter was calibrated by combusting certified benzoic acid in an oxygen atmosphere at a pressure of 2.5 MPa. The reported values are the average of three

single measurements. The enthalpy of formation was calculated at 298.15 K using a designed Hess thermochemical cycle.

A standardized [4] underwater detonation test was used to measure the energy released by detonating explosive charges with masses of 0.3 and 0.5 g. The charges were pressed to a density of approximately 1.4 $g \cdot cm^{-3}$ in the aluminum cup of a commercial detonator (6.4/6.9 mm internal/external diameter). For comparison, analogical detonators containing 0.3, 0.5, 1.0, and 1.5 g of a mixture of lead azide (LA) and lead styphnate (LS) (LA/LS = 4/1 mass ratio) were prepared and tested under the same conditions. The shock wave-time profiles and the bubble pulse period at a distance 0.4 m from the detonator were recorded using piezoelectric pressure gauges (PCB, series 138) and a digital oscilloscope. These test results provided the basis for calculating the shock wave energy and the bubble energy. These calculations used the equations cited by Bjarnholt and Holmberg [5].

A cylinder expansion test was performed to estimate the accelerating capability of the explosive. The explosive charge was placed inside a copper tube 200 mm long with an inner diameter and wall thickness of 13 and 1 mm, respectively. The expansion of the tube, driven by the detonation products, was recorded using a SANDIFLASH X-ray apparatus. Images were recorded when the detonation front was 5 mm from the end of the charge. Two tests were performed for charges having a density of approximately 0.8 and 0.9 $g \cdot cm^{-3}$. The detonation velocity of the charges was measured simultaneously using short circuit sensors. Considering that the tube geometry affects the value of an explosive's Gurney energy [6], the test was repeated under the same conditions for TNT ($\rho_0 = 1.58$ $g \cdot cm^{-3}$) and RDXph ($\rho_0 = 1.67$ $g \cdot cm^{-3}$).

2.2 Synthesis

4-Amino-1,2,4-triazole (3.03 g, 0.036 mol) was dissolved in ethanol (25 mL) by stirring at room temperature. A solution of copper(II) perchlorate hexahydrate (4.41 g, 0.012 mol) in ethanol (45 mL) was then added in small portions. The reaction mixture was stirred for 2.5 hours at room temperature. The precipitate was filtered off, washed with ethanol, and dried at 40 ºC. The final product was a pale blue, fine powder (6.0 g, approximately 97% yield). The crude material was recrystallized from boiling water to yield needle-shaped crystals (Figure 1).
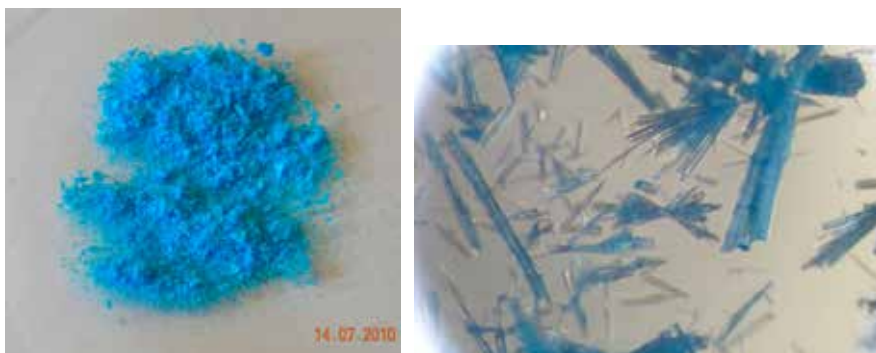
Figure 1.   Optical microscopic images of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ crystals grown from water. Left: general view. Right: crystal shape at $100\times$ magnification.

The copper, carbon, hydrogen, and nitrogen contents in $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ are calculated as: Cu 12.35, C 14.00, H 2.35, and N 32.65%. The averaged results from the elemental analyses of the crystallized product were 12.4 ±0.6, 14.17, 2.25, and 31.97%, respectively.

3   Results and Discussion

### 3.1 Non-isothermal kinetics analysis

Kissinger's method [7] was applied to study the decomposition kinetics of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$. The sample mass was kept small (approximately 0.1 mg) to minimize the temperature gradients within the sample and to prevent destruction of the equipment. DSC thermograms of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ at different heating rates (β = 2, 5, 10, and 15 ºC·min⁻¹) are presented in Figure 2. It is seen that the temperature of the exothermic maximum increases with increasing heating rate, which allows the kinetic parameters of the thermal decomposition to be determined.

Using the main exothermic peak temperatures, the apparent activation energy E_a and pre-exponential factor A were estimated to be 182.6 kJ·mol⁻¹ and $1.8268\cdot10^{11}$ s⁻¹, respectively, with correlation coefficient r^2 = 0.993. The Arrhenius equation can be expressed in E_a and $\ln A$ as follows:

$$\ln k = 25.93 - 182600/RT$$

This equation can be used to calculate the rate constant k at different temperatures T and to assess the potential of the material for thermal explosion. Relatively high values of the E_a indicate good thermal stability for the complex.
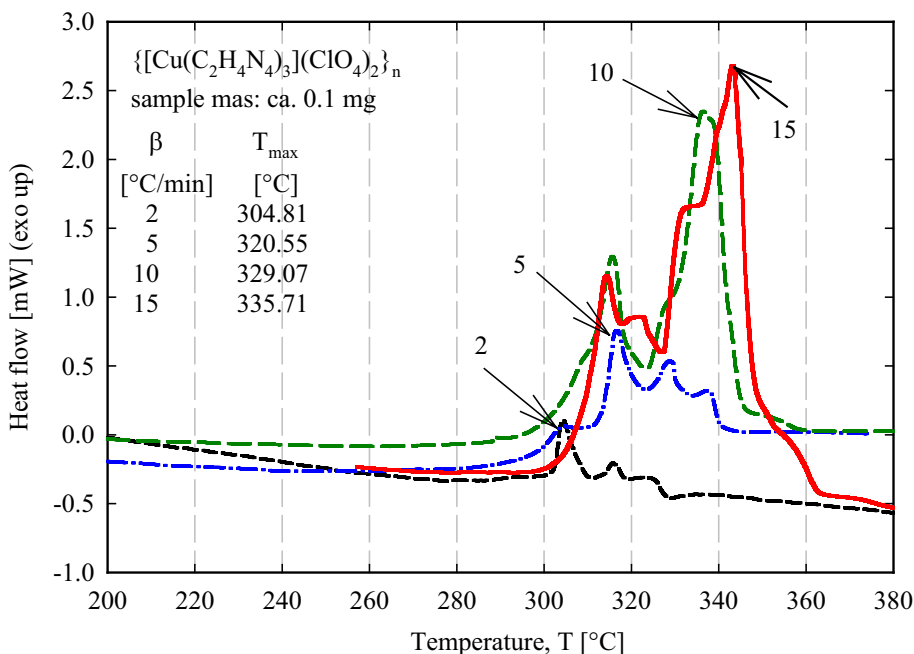
Figure 2. DSC curves of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ samples at different heating rates.

3.2 Thermodynamic aspects

The heat of combustion (explosion) of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ in an oxygen atmosphere was determined experimentally, and the values of the molar enthalpy of formation ($\Delta_f H°$) were calculated from a designed Hess thermochemical cycle according to reaction (1).

$$[Cu(C_2H_4N_4)_3](ClO_4)_2 + 5\,O_2 \longrightarrow CuO + 6\,CO_2 + 5\,H_2O + 2\,HCl + 6\,N_2 \quad (1)$$
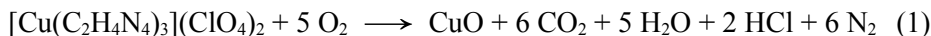
The results are summarized in Table 1. The enthalpy criteria of energetic materials are governed by their molecular structure. Therefore, the presence in the complex of three triazole ligands with high nitrogen content results in a quite high $\Delta_f H°$ (801.5 kJ·mol^{-1}). It should be mentioned that the formation enthalpies of a family of coordination compounds of 4-amino-1,2,4-triazole with metal

nitrates and perchlorates were previously determined with reaction calorimetry by measuring the heat of dissolution of the coordination compounds and the starting materials in an acid solution [8]. The enthalpy of formation of $[Cu(C_2H_4N_4)_3]$ $(ClO_4)_2$ was found to be 382.2 $kJ \cdot mol^{-1}$. The reason for the discrepancy in the values may be that the composition of the combustion products differed from that assumed in Equation (1). Different compositions of the tested samples cannot be excluded.

Table 1.   Physicochemical properties of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$.

Parameter	Value
Formula	$C_6H_{12}N_{12}O_8Cl_2Cu$
Molar mass	514.69
Nitrogen content, [%]	32.66
Oxygen balance, [%]	-27.98
Activation energy, [$kJ \cdot mol^{-1}$]	182.6
Heat of combustion in oxygen atmosphere, [$kJ \cdot kg^{-1}$]	9600 ±300
Molar enthalpy of formation, [$kJ \cdot mol^{-1}$]	801.5

3.3 Combustion and detonation parameters

The heat of combustion of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ in an argon atmosphere is presented in Table 2. The Table also contains the values of the detonation velocity measured at three different densities.

**Table 2.**   Combustion and detonation properties of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$.

Parameter	Value	
	Experimental	Calculated
Heat of combustion in argon atmosphere, [$kJ \cdot kg^{-1}$]	3850 ±70	4204
Detonation energy at 0.25 $g \cdot cm^{-3}$, [$kJ \cdot kg^{-1}$]	-	4276
Detonation velocity at 0.25 $g \cdot cm^{-3}$, [$m \cdot s^{-1}$]	2900 ±150	3173
Detonation velocity at 1.05 $g \cdot cm^{-3}$, [$m \cdot s^{-1}$]	5380 ±150	5494
Detonation velocity at 1.40 $g \cdot cm^{-3}$, [$m \cdot s^{-1}$]	6280 ±150	6327
Detonation pressure at 1.40 $g \cdot cm^{-3}$, [GPa]	-	15.3

The Cheetah code [9] was used to theoretically estimate the combustion and detonation parameters of the tested explosive. The BKW EOS was assumed to characterize the physical properties of the gaseous products. The BKWS set of parameters, with $\alpha = 0.5$, $\beta = 0.298$, $\kappa = 10.50$, and $\Theta = 6620$ [10], as well as the experimental value of the formation enthalpy $\Delta H_f^\circ = 801.5$ $kJ \cdot mol^{-1}$, were used in the calculations.

The calculated heat of combustion in an argon atmosphere is shown in Table 2. The Chapman-Jouguet (CJ) characteristics, *i.e.* detonation velocity D, pressure p_{CJ}, temperature T_{CJ}, and energy of detonation E_d, were determined as a function of the density of the explosive (Figures 3 and 4). The detonation energy calculated with the Cheetah code is the sum of the mechanical and thermal energies. The mechanical energy represents the amount of energy available to do mechanical work and is equal to the expansion work of the detonation products. It is determined for the volume of the detonation products corresponding to a pressure of $p = 1$ atm. The thermal energy represents the heat content in the detonation products at $p = 1$ atm [9]. In the calculations, the composition of the detonation products was frozen at a temperature of 1800 K on the isentrope starting at the CJ point. For ideal explosives the Cheetah detonation energy is close to the calorimetric heat of detonation [11]. The experimental detonation velocities presented in Figure 3 were obtained for unconfined (paper tube) and confined (copper tube) charges (values measured during the cylinder test).
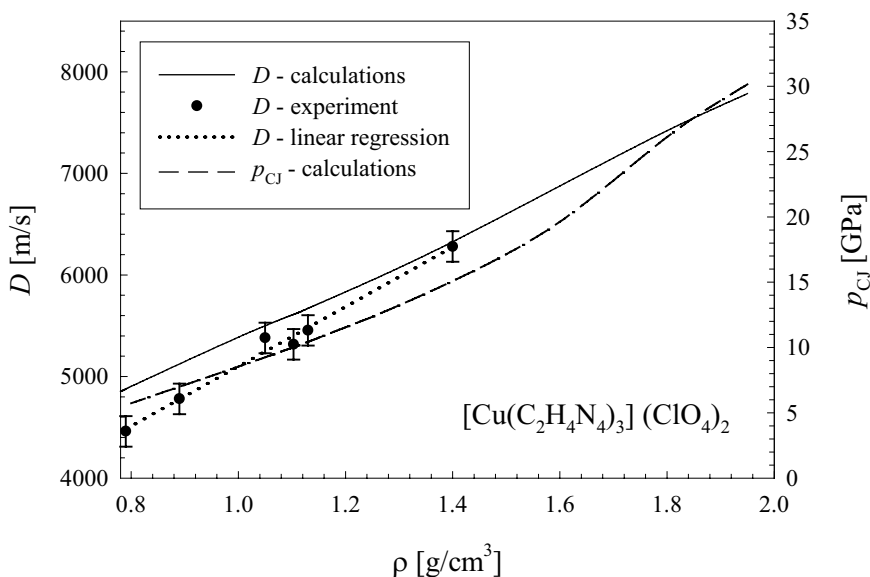
Figure 3.   Dependence of the detonation velocity and detonation pressure on density.
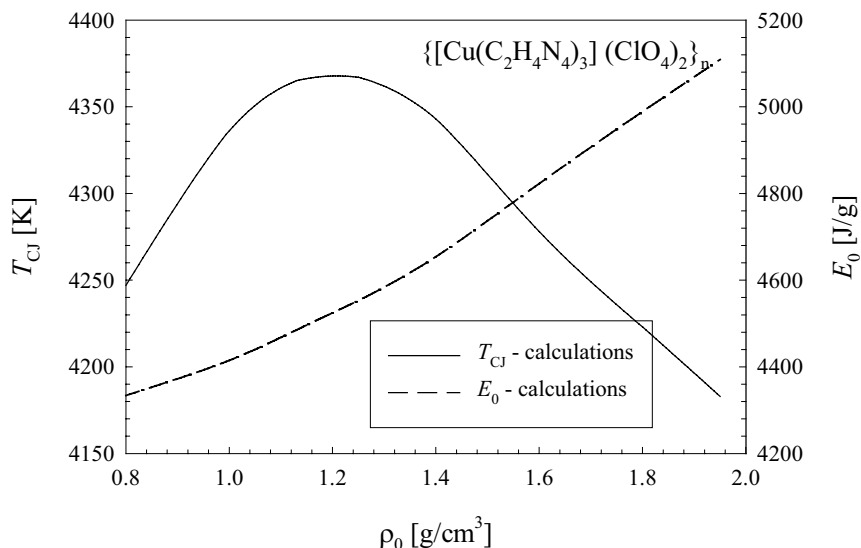
Figure 4.   Dependence of the detonation temperature and energy on density.

It follows from the analysis of the calculated detonation parameters (Table 1 and Figures 3 and 4) that the tested material can be included in the group of high explosives. However, the theoretical characteristics should be validated with those obtained by experiment. The explosion heat measured in a calorimetric bomb filled with argon (approximately 3850 $kJ \cdot kg^{-1}$) is lower by about 10% than the detonation energy calculated at a density of 0.25 $g \cdot cm^{-3}$ (4280 $kJ \cdot kg^{-1}$). The measured and calculated detonation velocities are also comparable, especially at densities greater than 1 $g \cdot cm^{-3}$ (Table 1 and Figure 2). Quite good conformity between the experimental and theoretical characteristics indicates that the other calculated parameters are also correct.

3.4 Cylinder test results

Cylinder test data can be used to determine some important characteristics of explosives. For example, the expansion velocity of the liner can be determined from the radial displacement of the external cylinder wall versus the axis coordinate; furthermore, the Gurney energy of the tested explosive [12] can also be determined.

Figure 5 shows a photograph of the copper tube driven by the detonation products of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$. The dependence of the outer radius of the tube on the axial coordinate was determined from the photograph using graphical computer processing. The examined range of the axial coordinate was limited

to those locations where the volume of the detonation products was 6-7 times larger than the initial volume. These dependences, along with the values of the detonation velocity (4470 and 4780 $m \cdot s^{-1}$ at densities of 0.79 and 0.89 $g \cdot cm^{-3}$, respectively), were used to determine the explosive performance.
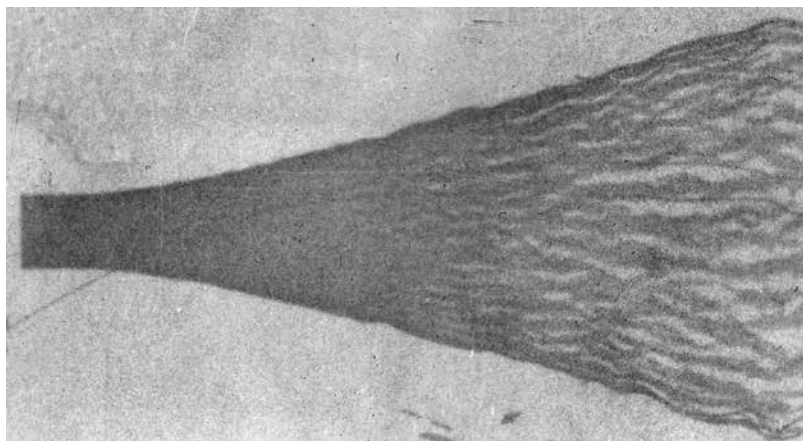
Figure 5. X-ray photograph of the copper tube driven by the detonation products of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ (test 1).

A detailed procedure for determining the cylinder velocity is given in [12]. It uses the dependence of the position of the cylinder external surface on the axial coordinate, as recorded in a cylinder test. The calculated dependencies of the Gurney energies on the relative volume of the detonation products are presented in Figure 6. For comparison, the Figure also shows the Gurney energies of TNT ($\rho_0 = 1.58$ $g \cdot cm^{-3}$) and RDXph ($\rho_0 = 1.67$ $g \cdot cm^{-3}$) determined with the same set up.

The final values of the Gurney energy, at the relative volume $v/v_0 = 7$, are 2160 and 2410 $J \cdot g^{-1}$ for test 1 and test 2, respectively. Under the same conditions, the performances of RDXph (4210 $J \cdot g^{-1}$) and TNT (3070 $J \cdot g^{-1}$) are much higher (by a factor of about 2 and 1.5, respectively). However, both of these explosives were pressed to densities about twice as high as the density of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$, and the density of an explosive significantly affects its Gurney energy [6].
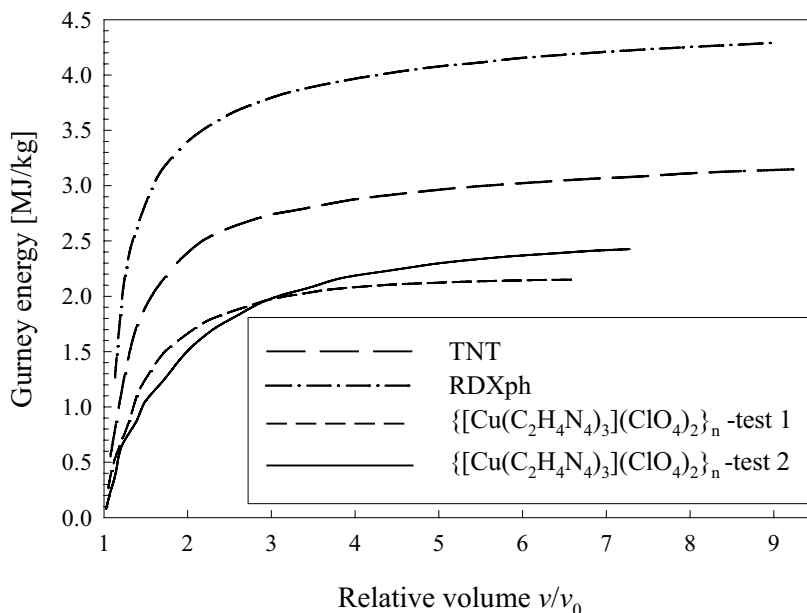
Figure 6.   Gurney energy *vs.* the relative volume of the detonation products.

To summarize, although the accelerating ability of the tested compound is much lower than that of high explosives, it seems to be quite suitable as a primary explosive.

3.5 Underwater test results

An underwater detonation test was performed to complement the energetic parameters of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ and to provide more insight into its initiating capability. Detonators containing the tested or reference explosive (LA/LS mixture) were located 400 mm from the pressure sensor and 400 mm under the water surface. Typical records of the overpressure in the first shock wave and the entire pressure curve are presented in Figure 7.
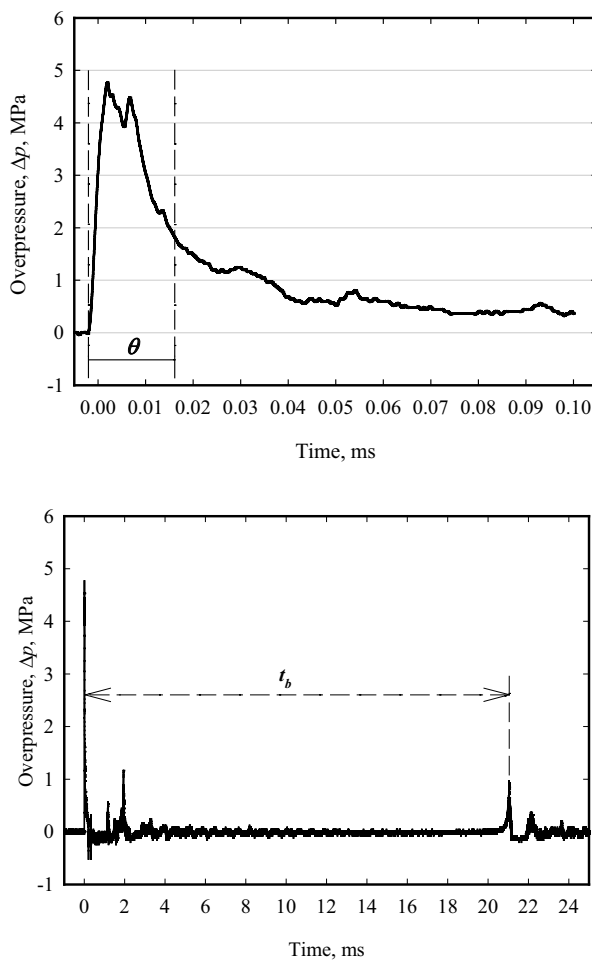
Figure 7. Shock wave-time profiles recorded after the initiation of a detonator containing 0.5 g of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$, pressed to a density of 1.4 g/cm^3. θ - integration region, t_b - bubble pulsing period.

Table 3 lists the experimental shock wave parameters (θ, t_b, and Δp), the shock wave energy E_S, and the bubble energy E_b (calculated according to the method in [5]). θ is the time when the maximum overpressure (Δp) has decreased by a factor of $e = 2.7183$ (it is also the range of (Δp)^2 integration), and t_b is the bubble pulsing period.

Table 3.   Shock wave parameters and calculated results.

Explosive	Mass [g]	θ [μs]	t_b [ms]	Δp [MPa]	E_S [J]	E_b [J]
Lead azide / Lead styphnate 4/1 (by mass)	0.3	12.55 ± 0.70	15.63 ± 0.02	3.82 ± 0.09	165 ± 5	297 ± 1
	0.5	12.51 ± 0.08	15.83 ± 0.02	3.81 ± 0.09	168 ± 6	309± 1
	1.0	15.30 ± 0.60	18.89 ± 0.06	4.96 ± 0.20	355 ± 15	525 ± 5
	1.5	14.10 ± 1.10	20.79 ± 0.11	6.14 ± 0.14	355 ± 15	670 ± 11
$\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$	0.3	15.93 ± 0.79	18.28 ± 0.14	4.22 ± 0.11	245 ± 5	475 ± 11
	0.5	17.58 ± 0.38	20.98 ± 0.05	4.89 ± 0.19	425 ± 20	718 ± 5

Figure 8 shows that the total energy of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$, obtained as the sum of the E_S and E_b, is very high compared to that of the standard initiating mixture of LA/LS = 4/1.
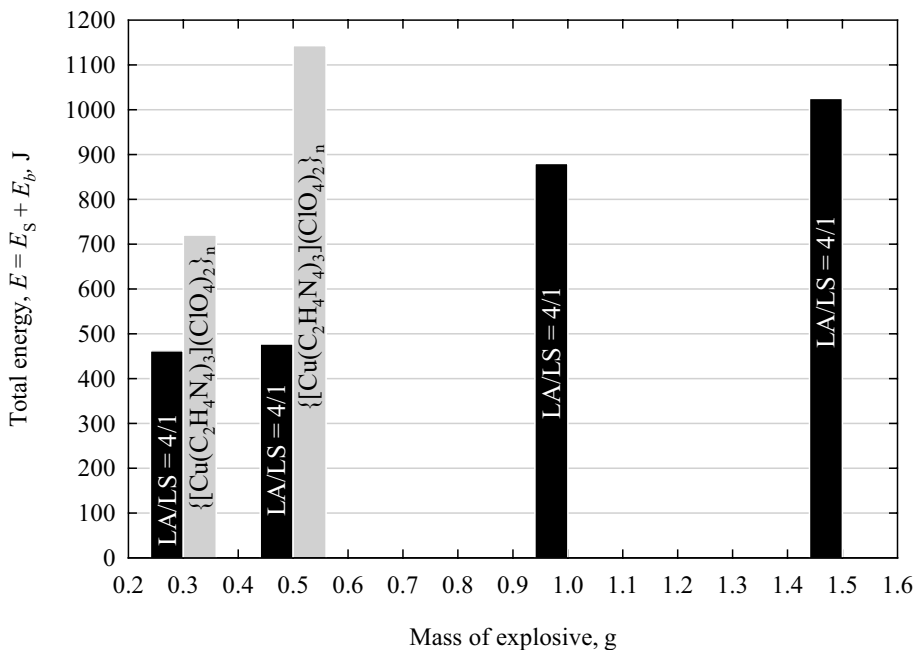
Figure 8.   Influence of the charge mass on the total energy of the tested explosives.

From the data presented in Figure 8, it follows that the energy equivalent of the tested compound equals 2.5-3 if the LA/LS mixture is used as the reference explosive, probably due to the differences in the heats of detonation of the explosives. In the case of the LA/LS composition, this parameter is approximately

1600 J·g^{-1} [13], whereas an explosion of 1 g of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ in argon produces 3850 J·g^{-1} of energy (Table 2). The ratio of the two heat effects is approximately 2.4. Moreover, the volume of gas produced during an explosion of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ is much higher than that from the LA/LS mixture, at 0.80 and 0.24 dm^3·g^{-1}, respectively.

4   Conclusions

The thermally stable compound dichlorate(VII) μ-tris(4-amino-1,2,4-triazole) copper(II) has been synthesized and characterized. It decomposes explosively during heating in a nitrogen atmosphere above 300 ºC. The activation energy of decomposition is about 183 kJ·mol^{-1}, and the detonation parameters of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ are quite high. The heat of explosion is approximately 3850 kJ·kg^{-1}, and it detonates at around 6.3 km·s^{-1} in unconfined charges pressed to a density of 1.4 g·cm^{-3}. Its accelerating ability (the Gurney energy at 2300 J·g^{-1}) is lower by a factor of 1.5-2 than that of high explosives. However, the performance of $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ is very high as a primary explosive. In underwater detonation tests, it produces effects comparable to those from charges of an LA/LS mixture with masses higher by a factor of 2.5-3.

The complex $\{[Cu(C_2H_4N_4)_3](ClO_4)_2\}_n$ is of interest as a replacement for lead azide, as it shows promise with respect to its thermal stability and energetic properties.

5   References

[1] Cudziło S., Nita M., Synthesis and Explosive Properties of Copper(II) Chlorate(VII) Coordination Polymer with 4-Amino-1,2,4-triazole bridging Ligand, *J. Hazard. Mater*., **2010**, *177*, 146-149.

[2] Lavrenova L.G., Larionov S.V., Grankina S.A., The Metal Complexes with 4-Amino-1,2,4-triazole (in Russian), *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim*., **1979**, *5*, 88-92.

[3] Sinditskii V.P., Sokol V.I., Fogelzang A.E., Dutov M.D., Serushkin V.V., Porai-Koshits M.A., Svetlov B.C., Vibration Spectra and Structure of Coordination Compounds with 4-Amino-1,2,4-triazole as Didentate Ligand (in Russian), *Zh. Neorg. Khim*., **1987**, *32*, 1950-1955.

[4] *Explosives for civil uses – Detonators and delays – Part 15: Determination of equivalent initiating capability*, European Standard EN-13763-15, **2004**.

[5] Bjarnholt G., Holmberg R., Explosive Expansion Works in Underwater Detonations,

6th Symposium (Int*.) on Detonation*, Coronado, August 24-27, **1976**, 325-330.

[6] Backofen J.E., The Influence of Geometry and Material Properties on an Explosive's Gurney Velocity and Energy, *New Trends Res. Energ. Mater., Proc. Semin., 9th*, Pardubice, **2006**, 256-261.

[7] Kissinger H.E., Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.*, **1957**, *29*, 1702-1706.

[8] Konkova T.S., Matyushin Y.N., Sinditskii V.P., Fogelzang A.E., Enthalpies of Formation of 4-Amino-1,2,4-triazole Coordination Compounds, *Chem. Phys. Reports*, **1995**, *14*, 858-864.

[9] Fried L.E., *CHEETAH 1.39 User's Manual*, UCRL-MA-117541, Rev. 3, Lawrence Livermore National Laboratory, **1996**.

[10] Hobs M.L., Baer M.R., Nonideal Thermoequilibrium Calculations Using a Large Product Species Data Base, *Shock Waves*, **1992**, *177*, 2-12.

[11] Trzciński W.A., Cudziło S., Paszula J., Studies of Free Field and Confined Explosions of Aluminium Enriched RDX Compositions, *Propellants Explos. Pyrotech.*, **2007**, *32*(6), 502-508.

[12] Trzciński W.A., Application of a Cylinder Test for Determining Energetic Characteristics of Explosives, *J. Techn. Phys.*, **2001**, *42,* 165-176.

[13] Meyer R., Kohler J., Homburg A., *Explosives*, Wiley-VCH, Weinheim, **2002**.