

# Crystal Structure and Properties of an Energetic Perchlorate Complex Compound with Copper and Cytosine

 Rafał Lewczuk,<sup>\*[a]</sup> Judyta Rećko,<sup>[b]</sup> and Sławomir Wojtulewski<sup>[c]</sup>

**Abstract:** A coordination compound from copper(II) perchlorate with cytosine was synthesized. The molecule contains copper(II) cation, four cytosine ligands, and two perchlorate anions. The single crystals of the compound were grown from the methanol solution. The crystal structure was determined by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic system (*Pbcn* space group) with crystal parameters:  $a=19.454(2)$  Å,  $b=10.185(2)$  Å,  $c=13.604(1)$  Å,  $V=2695.83(5)$  Å<sup>3</sup>,  $Z=4$ , and  $F(000)=1508$  as a solvate with one methanol molecule in

the asymmetric unit. It was characterized with elemental analysis, differential scanning calorimetry (temperature of decomposition – 270.1 °C), differential thermal analysis, infrared spectroscopy. Small-scale safety testing was done to determine the impact and friction sensitivity. The title compound has sensitivity typical to secondary explosives (7.5 J, 230 N). Measured density and enthalpy of formation were used to calculate detonation parameters. With detonation velocity and pressure of 6132 m/s and 14.6 GPa, respectively, it has the moderate performance.

**Keywords:** Energetic coordination compounds · Explosive properties · X-Ray crystal structure

## 1 Introduction

Through the years of development of energetic materials, many classes of chemical compounds have shown potential for violent decomposition in the absence of atmospheric oxygen. Organic heterocycles (e.g. benzotrifuroxane), as well as inorganic salts (e.g. lead(II) azide), can undergo explosive reactions. One distinctive group of energetics is formed by coordination (or complex) compounds. In their structure, the oxidizers (deprotonated oxyacids) are located next to a fuel (e.g. organic or inorganic amines) in the distance of molecular bond. Metal cation in the centre plays the structure-forming role. Complexes made from metal perchlorates are among the famous ones.

As a model example of perchlorate complex compound tetraamminecopper(II) perchlorate (TACP) can be used. It is known for more than hundred years [1] but its explosive properties have been well described recently [2]. Its synthesis is cheap and straightforward. It involves reaction of copper(II) perchlorate hexahydrate with aqueous ammonia. TACP has a sensitivity to mechanical stimuli similar to PETN. Its detonation velocity at a density of  $0.9 \text{ g cm}^{-3}$  was found to be  $3230 \text{ m s}^{-1}$ .

Another interesting coordination compound is copper (II) perchlorate complex with 4-amino-1,2,4-triazole and water [3]. Its sensitivity to impact and friction was found to be 5 J and 50 N, respectively. The detonation parameters are quite high. Detonation heat equals  $3480 \text{ kJ kg}^{-1}$  and it detonates with  $6.6 \text{ km s}^{-1}$  at a density of  $1.6 \text{ g cm}^{-3}$ . Pressed charges of the material (0.3 g in mass) deflagrate when exposed to flame. The complex is of interest as an additive in pyrotechnics, ammonium perchlorate-based propellants, or

in other applications, as it shows promising energetic properties.


The use of various perchlorates and nitrogen bases presents many opportunities for modification of chemical and explosive properties. Next to the above-mentioned examples, there are such compounds as bis(ethylenediamine) copper(II) perchlorate, which causes a strong increase in burning rate of HTPB/AP composite propellants [4], tris(carbohydrazide)cobalt(II) perchlorate – possible filler for lead-free detonators [5], and nickel hydrazine perchlorate (NHP) [6]. In the latter, bridging ligands join adjacent metal centres to form coordination polymer. NHP proved to be very powerful primary explosive.

Numerous advantages of coordination perchlorate compounds encouraged us to continue research in this area. We have found that salts with nucleobases, namely with 4-ami-

[a] R. Lewczuk  
Department of High Energetic Materials  
Łukasiewicz Research Network – Institute of Industrial Organic Chemistry  
Annopol 6, 03-236 Warsaw, Poland  
\*e-mail: rafal.lewczuk@ipo.lukasiewicz.gov.pl

[b] J. Rećko  
Department of Explosives  
Military University of Technology  
Gen. S. Kaliskiego 2, 00-908 Warsaw, Poland

[c] S. Wojtulewski  
Department of Chemistry  
University of Białystok  
Ciołkowskiego 1 K, 15-245 Białystok, Poland

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no-1*H*-pyrimidine-2-one (cytosine) and 9*H*-purin-6-amine (adenine), are characterized by low mechanical sensitivity and good thermal stability [7]. Therefore, we made an attempt to synthesis perchlorate complex compound with copper and cytosine – tetrakis(4-amino-1*H*-pyrimidine-2-one)copper(II) perchlorate (CCPL). It was obtained before [8] but the crystallographic data of the methanol solvate were never published.

In this contribution, we report the synthesis and structural characterization of CCPL-MeOH. For the methanol-free compound, some physicochemical properties (e.g. thermal analysis, standard molar enthalpy of formation) and energetic characteristics (sensitivity to mechanical stimuli, detonation parameters) were explored. Experimental results suggest the title compound is possible to be utilized as a high-energetic material.

## 2 Experimental

### 2.1 Materials and Methods

In the synthesis of CCPL, copper(II) perchlorate hexahydrate (Sigma-Aldrich, Cat. No. 215392), cytosine (Sigma-Aldrich, Cat. No. C3506), and methanol (puriss p.a.) were used as supplied.

Elemental analysis of CCPL sample was performed with Analyzer CHNS–O–Cl, type VarioEl Cube in the CHN mode.

The Fourier transform infrared spectroscopy (FTIR) analysis was performed using Thermo Scientific NICOLET 6700 spectrometer (Waltham, MA, USA) with ATR unit. The FTIR spectrum was recorded in the wave number range: 400–4000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ .

DTA/TG analysis was performed using Setaram Labsys™ Evo calorimeter. The measurement was done in open aluminum crucible in an argon atmosphere. The mass of the sample was  $5.0 \pm 0.2$  mg. Differential Scanning Calorimetry was carried out by Netzsch STA 449F1 calorimeter. Sample of approx. 1.5 mg was placed in an aluminum pan (Concavus® type) and the measurement was taken under a nitrogen atmosphere with a gas flow of 70  $\text{mL min}^{-1}$ . The heating rate in both measurements was 5  $^{\circ}\text{C min}^{-1}$ .

A water calorimeter equipped with an oxygen bomb was used for the calorimetric measurements. Pressed samples were loaded into open quartz crucibles and initiated with an electrically heated wire. The atmosphere was oxygen at 3.0 MPa.

The mechanical sensitivity was determined by using standard BAM fall hammer for the impact sensitivity (IS) and BAM friction tester for friction sensitivity (FS). The results correspond to the lowest value of impact energy or friction force for which at least one positive reaction was observed in six trials.

Detonation parameters were computed using the EXPLO5 V6.05 thermochemical computer code [9]. The Becker-Kistiakowsky-Wilson equation of state (BKW EOS, with the

following sets of constants:  $\alpha = 0.5$ ,  $\beta = 0.38$ ,  $\kappa = 9.41$ , and  $\Theta = 4250$  for gaseous detonation products) and the Murnaghan equation of state for condensed products (compressible solids and liquids) were applied. The density of the methanol solvate was used in the calculation of detonation parameters of the methanol-free compound because the exact density of the latter was not known.

### 2.2 Synthesis

A solution of 2.04 g of copper(II) perchlorate hexahydrate (5.5 mmol) in 20 mL of methanol was added dropwise to 2.22 g of cytosine (20 mmol) dissolved in 30 mL of methanol at 45  $^{\circ}\text{C}$ , with stirring. The solution was allowed to cool slowly to ambient temperature. It was left for three days for product to crystallize. The purple precipitate was filtered off, washed with methanol, and dried at 80  $^{\circ}\text{C}$  for one hour to completely remove solvent from the crystals. The yield of the methanol-free product was 2.39 g (67.7%) The product after filtration is shown in Figure 1.

FT-IR results for CCPL ( $\text{cm}^{-1}$ ): 3330 ( $\nu_s$  -NH<sub>2</sub>); 3224 ( $\nu_{as}$  -NH<sub>2</sub>); 1616 ( $\nu$  C=O); 1511 ( $\nu$  pyrimidine ring); 1443, 1280, 1224 (ring modes); 1058 ( $\nu_{as}$  ClO<sub>4</sub><sup>-</sup>); 781; 728; 618.

Elemental analysis results for CCPL: Calc. for Cu-(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>O)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, CH<sub>3</sub>OH (%): C 27.19, H 2.85, N 23.78. Found: C 27.35, H 2.94, N 23.59.

### 2.3 X-Ray Crystallography

After several attempts, we have failed to obtain single crystals of the solvent-free compound suitable for X-ray crystallography. Single crystals for the measurement were obtained by slow evaporation of the methanol solution of CCPL. A suitable crystal was mounted on a fiber loop and used for X-ray measurement. X-ray data were collected on the Oxford Diffraction SuperNova DualSource diffractometer with use of the monochromated CuK $\alpha$  X-ray source

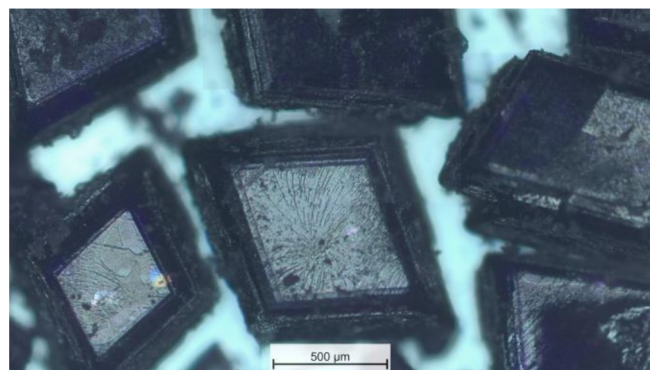


Figure 1. Picture of CCPL-MeOH crystallized from methanol solution.

( $\lambda = 1.54184$ ). The crystals were kept at 100 K during data collection. Data reduction and analytical absorption correction were performed with CrysAlis PRO [10]. Using OLEX2 [11], the structures were solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization [12]. The molecular geometry was calculated by Mercury 3.10 [13].

The non-hydrogen atoms were refined anisotropically. The positions of the NH hydrogen atoms were found on a Fourier difference map and isotropically refined without any restraints. The hydrogen CH atoms were introduced in calculated positions with idealized geometry and constrained using a rigid body model. The isotropic displacement parameters were fixed to 1.2 and 1.5 times the equivalent displacement parameters of the parent atoms.

The CCDC 1897361 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

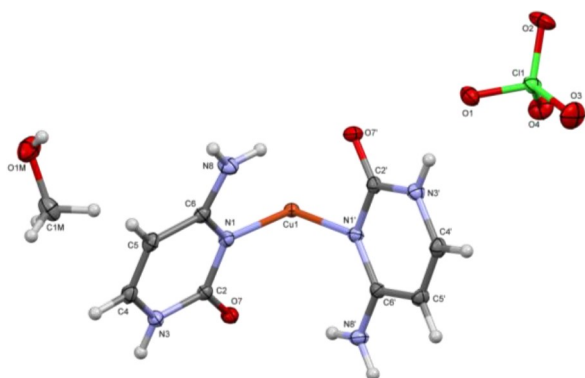


Figure 2. Asymmetric unit of complex CCPL in the crystal.

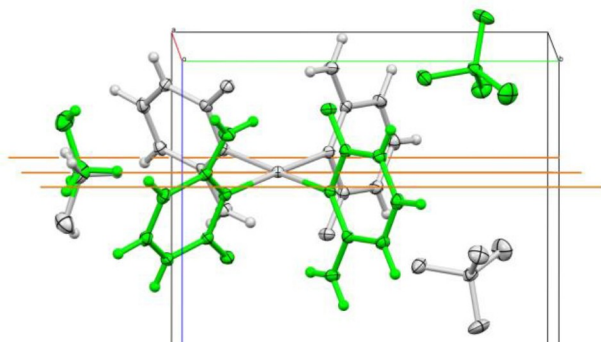


Figure 3. Molecular structure of complex CCPL in the crystal. The symmetry-equivalent atoms are the same color, orange lines represent crystallographic 2-fold rotation axis along the crystallographic direction [0 1 0].

## 3 Results and Discussion

### 3.1 Crystal Structure

The synthesized copper complex crystallizes in the orthorhombic *Pbcn* space group as a solvate. The asymmetric unit of the complex CCPL is presented in Figure 2. It contains half of molecular complex and one methanol molecule. Selected geometric parameters were shown in Table S1 in Supporting Information.

The carbon atom of the methanol molecule and copper atom lie on the crystallographic 2-fold rotation axis along the crystallographic direction [0 1 0] (Figure 3). Therefore, the methanol molecule was introduced as a rigid body with idealized methyl and OH groups refined as rotating groups with the occupancy 0.5.

The copper Cu1 atom is bonded to the four 4-aminopyrimidin-2(1*H*)-one molecule. The bond lengths Cu1-N1 and Cu1-N1' are equal to 2.029 Å and 2.013 Å, respectively. The valence angles N1-Cu1-N1', N1-Cu1-N1<sup>(1)</sup> are close to 90 degrees and angle N1-Cu1-N1<sup>(1)</sup> is close to 180 degrees. Moreover, the dihedral angle N1-N1<sup>(1)</sup>-N1<sup>(1)</sup>-N1' is -4.06 degrees. Hence, the overall coordination sphere around copper can be described as a square planar slightly distorted.

The distortion of the coordination sphere is caused by the six intramolecular hydrogen bonds N-H...O7(O7') type (Figure S1 in Supporting Information) and two intermolecular charge assisted hydrogen bonds N-H...O1(-) type (Figure S2 in Supporting Information). Additionally, the cyclic N3-H3...O7 hydrogen bond between two complex molecules can be observed (Figure S3 in Supporting Information).

The geometrical parameters of all seven hydrogen bonds are presented in Table S2 in Supporting Information. A summary of relevant crystallographic data is given in Table 1.

### 3.2 Thermal Analysis

The basic thermal stability of CCPL was measured with DTA/TG and DSC. During DTA/TG experiment mass loss of CCPL proceeded in one step. It began at approx. 233 °C. The exothermic signal was observed on a DTA curve at 275.5 °C (maximum peak temperature) with the onset point at 271.5 °C. It was connected with thermal decomposition. The peak temperature on the DSC thermogram was 280.8 °C. The temperature of decomposition, the onset point of the peak during DSC measurement, was 270.1 °C. Described thermograms are shown in Figure 4.

### 3.3 Thermodynamic Aspects

The heat of combustion of CCPL in oxygen atmosphere was averaged from three measurements in a calorimetric bomb.

Table 1. Crystal data and structure refinement.

Parameter	Value
Empirical formula	Cu(C <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O) <sub>4</sub> (ClO <sub>4</sub> ) <sub>2</sub> , CH <sub>3</sub> OH
Formula weight [g/mol]	738,93
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions:	a = 19.454(2) Å, α = 90° b = 10.185(2) Å, β = 90° c = 13.604(1) Å, γ = 90°
Volume [Å <sup>3</sup> ]	2695.83(5)
Z	4
Density [g/cm <sup>3</sup> ]	1.821
Absorption coefficient [mm <sup>-1</sup> ]	3.787
F(000)	1508
Analytical absorption T limits	T <sub>min</sub> = 0.471, T <sub>max</sub> = 0.802
2θ range for data collection	9.092°–153.518°
Index ranges:	–24 ≤ h ≤ 14 –12 ≤ k ≤ 12 –17 ≤ l ≤ 17
Reflections collected	15135
Independent reflections	2835 [R <sub>ind</sub> = 0.0248, R <sub>sigma</sub> = 0.0170]
Data/restraints/parameters	2835/9/239
Goodness-of-fit on F <sup>2</sup>	1.068
Final R indexes [I > 2σ (I)]	R <sub>1</sub> = 0.0293, wR <sub>2</sub> = 0.0789
Final R indexes [all data]	R <sub>1</sub> = 0.0332, wR <sub>2</sub> = 0.0824
Largest diff. peak/hole [e Å <sup>-3</sup> ]	0.39/–0.59

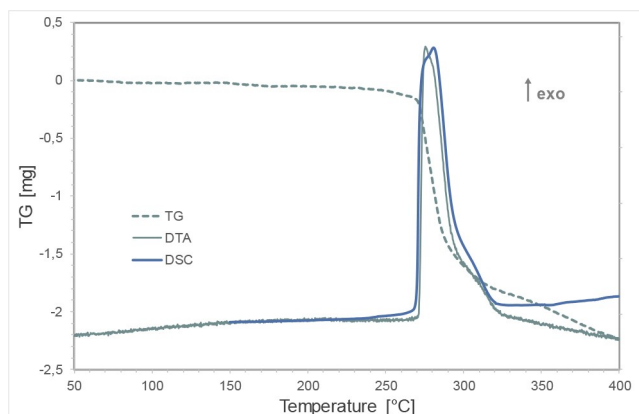


Figure 4. DTA/TG and DSC thermograms of CCPL.

It was determined as  $-5359$  kJ/mol. The standard molar enthalpy of formation ( $\Delta_f H^\circ$ ) was calculated at 298.15 K using a Hess thermochemical cycle with the known assumption that the combustion products contained only carbon dioxide, water, nitrogen, and copper(II) chloride [3]. The obtained value is equal to  $-937$  kJ/mol. The enthalpy of formation of CCPL is very low in comparison to most of the energetic materials; some of the nitrates have lower  $\Delta_f H^\circ$  – dipentaerythritol hexanitrate ( $-979.5$  kJ/mol) and saccharose octanitrate ( $-1364.9$  kJ/mol) [14]. Nevertheless, negative enthalpy of formation is typical for perchlorate salts and energetic coordination compounds.

### 3.4 Sensitivity and Performance

Determination of the sensitivity to mechanical stimuli is very important in manufacturing and using context. The impact sensitivity of CCPL is 7.5 J, which is similar to RDX. The friction sensitivity is 230 N, which is quite low as compared to other perchlorate complex compounds. In the term of sensitivity criteria, CCPL is a secondary explosive.

In regards to explosive properties, CCPL has moderate performance. The velocity of detonation 6.1 km/s and detonation pressure 14.6 GPa are lower than for TNT. Many coordination explosives, especially with nitrogen-rich ligands, have higher detonation parameters. For example, cobalt hydrazine perchlorate (CHP) at density 1.948 g/cm<sup>3</sup> has velocity, pressure, and heat of detonation equal to 7.5 km/s, 25.1 GPa, and 5230 kJ/kg, respectively [6].

Low detonation parameters of CCPL are connected with negative enthalpy of formation and disadvantageous oxygen balance. On the other hand, lower performance means higher safety during handling, in that case. The properties which were described above are listed in Table 2.

## 4 Conclusion

As many coordination compounds, tetrakis(4-amino-1H-pyrimidine-2-one)copper(II) perchlorate was easily synthesized from relatively inexpensive substrates. It crystallizes from the methanol solution as a methanol solvate. The purple crystals were suitable for X-ray diffraction. The crystal structure shows the copper atom is coordinated by four nitrogen atoms, with cytosine oxygen atoms above and below the plane.

The solvent moiety can be removed by simple heating at 80 °C. The thermal analysis of the product showed that the decomposition temperature is high in comparison to most of the energetic materials. From the calorimetric measurements, it follows that CCPL is a thermodynamically stable compound with a negative value of standard molar enthalpy of formation. Low  $\Delta_f H^\circ$  contributes to results of

Table 2. Physicochemical and explosive properties of CCPL.

Parameter	Value
Oxygen balance <sup>[a]</sup> [%]	–65.0
Temperature of decomposition [°C]	270.1
Standard molar enthalpy of formation [kJ/mol]	–937
Impact sensitivity [J]	7.5
Friction sensitivity [N]	230
EXPLO5V6.05 <sup>[b]</sup>	
Heat of detonation [kJ/kg]	–2341
Detonation temperature [K]	2089
Detonation pressure [GPa]	14.6
Detonation velocity [m/s]	6132

<sup>[a]</sup> Calculated as if the fully oxidized products were CO<sub>2</sub>, H<sub>2</sub>O, and CuCl<sub>2</sub>. <sup>[b]</sup> Calculated for density 1.821 g/cm<sup>3</sup>.

calculation of detonation parameters, which are lower than for TNT. As it comes to mechanical sensitivity, it is typical for secondary explosives, which means safe handling.

Taking all this into account, CCPL is an interesting coordination compound. It can be also explored as a catalyst in solid heterogeneous rocket propellants or as an ingredient in pyrotechnic mixtures, due to the copper content. The results of this work support further efforts in this area.

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## Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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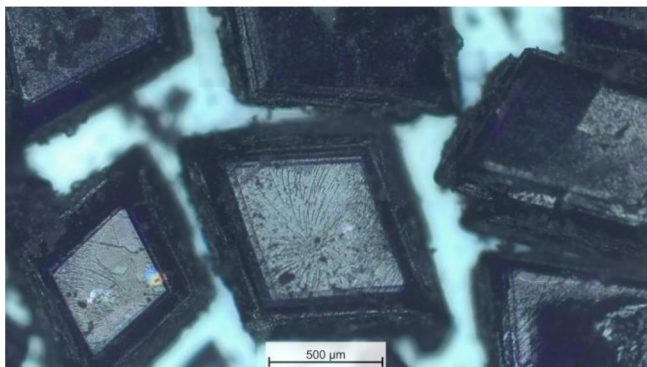
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## FULL PAPER

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*R. Lewczuk\*, J. Rećko, S. Wojtulewski*

1 – 6

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