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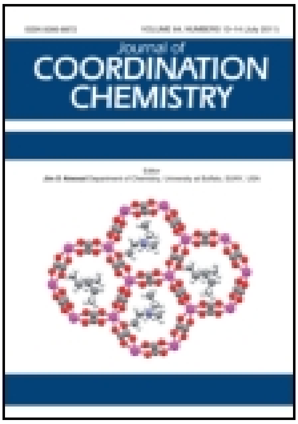

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Energetic cuprous azide complex: synthesis, crystal structure, and characterization

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Energetic cuprous azide complex: synthesis, crystal structure, and characterization

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An energetic cuprous azide complex, $[Cu_2(2apyz)(N_3)_2]_n$ (**1**) (2apyz = 2-aminopyrazine), has been synthesized through hydrothermal method by utilizing the reducibility of H_3PO_3 and structurally characterized by single-crystal X-ray diffraction. Complex **1** has a 2-D layer structure constructed from copper(I) bridged by azide and pyrazine. Catalysis research shows **1** can promote the burning rate of the main component of rocket propellant.

Keywords: Energetic complex; Cuprous azide; Crystal structure; Catalysis action

1. Introduction

Nitrogen-rich compounds are high-energy density materials and environmentally acceptable, which relies on their highly efficient gas production and also on their high heat of formation for energy release [1–6]. Inorganic metal azides are potential energetic materials for having high nitrogen content and positive formation enthalpy, but metal azides are not applied as energetic materials except lead azide and mercury azide because of their extreme sensitivity [7, 8]. Developing metal azides with suitable sensitivity has been particularly challenging.

Cuprous azide does not have practical applications due to its extreme sensitivity, $2.66\,N{\cdot}cm^{-2}$ [9], even more than lead azide or lead styphnate [10], but copper is less toxic than lead, reducing the risk to human health and the environment. Thus, cuprous azide could be a suitable energetic material if its sensitivity can be appropriately decreased.

Azide can afford a variety of coordination modes to link one or more transition metal ions to form 0-D, 1-D, 2-D, and 3-D complexes [11–17]; Cartwright's research reveals that there is a strong correlation between non-bonded N–N distance of azide ion and impact sensitivity in inorganic azides: the closer together non-bonded nitrogen atoms are the more sensitive the compound [7], suggesting design of safer energetic cuprous azide complex through adjusting and controlling non-bonded N–N distance with rigid N-containing facilitating ligands, such as pyrazine or 4,4′-bipyridine. In our previous

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work, we reported three cuprous azide complexes with pyrazine, 4,4′-bipyridine and 1,2-bipyridylethylene as facilitating ligand [15], which promote the burning rate of the main component of rocket propellant. In this article, we prepare an energetic cuprous azide complex with 2-aminopyrazine as facilitating ligand and report its catalytic properties on promoting the burning rate of the main component of rocket propellant.

2. Experimental

2.1. *Instruments and reagents*

2-Aminopyrazine was purchased from Acros. HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) was obtained from Xi'an Modern Chemistry Research Institute. All other starting materials were of analytical grade and purchased commercially. Elemental analysis (C, H, N) was performed on a Vario EL III analyzer. Thermogravimetric analysis was performed on a NETZSCH STA 449C thermogravimetric instrument.

2.2. *Synthesis of $[Cu_2(2apyz)(N_3)_2]_n$ (1)*

The red **1** was obtained by hydrothermal synthesis of a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.1211 g, 0.5 mmol), 2-aminopyrazine (0.0492 g, 0.5 mmol), and 0.5 mL H_3PO_3 in 10 mL H_2O, sealed in a Teflon-lined stainless container, heated at 90°C for 24 h and slowly cooled to room temperature at 5°C per hour. Yield: 54%. Anal. Calcd for **1**, $C_4H_4Cu_2N_9$ (%): C, 15.74; H, 1.32; N, 41.30. Found (%): C, 15.71; H, 1.36; N, 41.33. Complex **1** is very stable when exposed to air, water, and organic solvents such as methanol, alcohol, acetone and THF at room temperature.

2.3. *X-ray crystallography*

All single-crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scan mode. The single crystal structure of **1** was solved by direct methods (SHELXS-97 [18]) and refined with full-matrix least-squares based on F^2 using SHELXL-97 [19]. Hydrogen atoms of organic ligands were generated geometrically. Other details of crystal data, data collection parameters, and refinement statistics are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis chemistry*

Chambers indicated that H_3PO_3 was a reducing agent with reductibility greater with a rise in temperature [20]. In acid solution, the standard electrode potentials for the following half-reactions are −0.276 V and +0.153 V, respectively: (1) H_3PO_3

Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_4H_4Cu_2N_9$
Formula weight	305.24
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	5.2329(19)
b	5.905(2)
c	14.752(5)
α	90.00
β	105.816(12)
γ	90.00
Volume (Å^3), Z	438.6(3), 2
Calculated density (g cm^{-3})	2.311
Absorption coefficient (mm^{-1})	4.827
$F(000)$	298
Reflection collected	1996
Independent reflection	759
T_{max}/T_{min}	0.7944/0.6439
Data/restraint/parameters	7592/0/74
Goodness-of-fit on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0582$; $wR_2 = 0.\ 1359$
R indices (all data)	$R_1 = 0.0892$; $wR_2 = 0.\ 1628$
Largest difference peak and hole (e Å^{-3})	0.974 and −0.656

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(1)	1.957(7)	Cu(1)–N(2)	2.049(8)
Cu(1)–N(4)#1	2.105(3)	Cu(1)–N(2)#2	2.189(7)
N(4)#1–Cu(1)–N(1)	124.4(3)	N(4)#1–Cu(1)–N(2)	106.7(3)
N(1)–Cu(1)–N(2)	111.9(3)	N(4)#1–Cu(1)–N(2)#2	104.2(3)
N(1)–Cu(1)–N(2)#2	94.4(3)	N(2)–Cu(1)–N(2)#2	114.72(13)

Symmetry transformations:- #1: $-x+2$, $y-1/2$, $-z+1/2$; #2: $-x+1$, $y-1/2$, $-z+1/2$.

(aq) + $H_2O = H_3PO_4$ (aq) + $2H^+ + 2e^-$; (2) $Cu^{2+} + e^- = Cu^{1+}$, and we conclude that the electrodynamic potential is above 0 V when the two half-cells construct a primary cell. So, H_3PO_3 has the ability of reducing Cu^{2+} to Cu^+.

Complex **1** has been rationally designed according to the reductibility of H_3PO_3 under mild hydrothermal conditions (90°C, 24 h), and the characteristic red color of **1** indicates that it is possibly cuprous azide, confirmed by single-crystal X-ray diffraction analysis.

3.2. *Description of structure*

Single-crystal X-ray diffraction analysis reveals that **1** belongs to monoclinic, $P2_1/c$ space group, and displays a 3-D layer structure constructed from CuN_3 units bridged by 2-aminopyrazine. The amino substituent for 2-aminopyrazine is disordered, and the occupancies are 50% for N(5) and N(5A).

The asymmetric unit for **1** consists of eight non-hydrogen atoms as shown in figure 1. In this case, copper(I) shows a distorted tetrahedral geometry coordinated by three

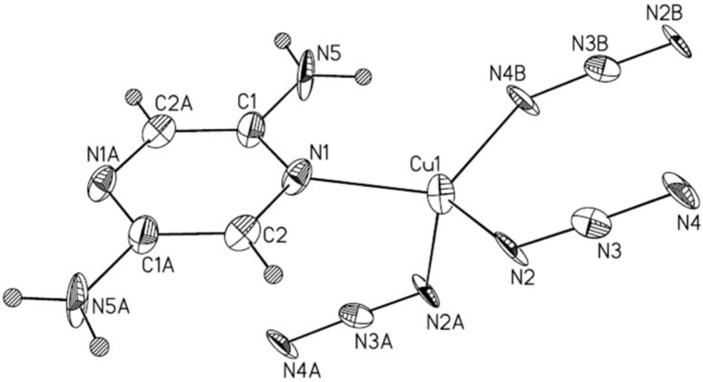

Figure 1. Molecular structure for **1**.

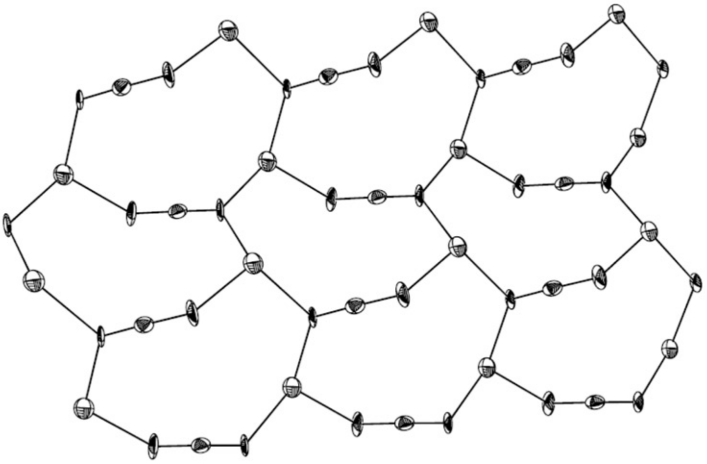

Figure 2. 2-D layer structure for $[CuN_3]_n$ units bridged by azide.

azides with μ-1,1,3 coordination, and an aromatic 2-apyz N-donor (see figure 1). The distances of Cu(1)–N(1), Cu(1)–N(2), Cu(1)–N(2A), Cu(1)–N(4B) are 1.985(3), 2.089(3), 2.375(3), 1.919(3)Å, respectively. The angles of N–Cu–N are in the range 91.68(9)–134.91(11)°. In contrast with $[Cu_2(heae)(N_3)_2]_n$ (heae = N,N'-bis(N-hydroxyethylaminoethyl)oxamide) [21], $[Cu_2(N_3)_2(PP)_2)] \cdot 2ClO_4$ (PP = 2,6-dipyrazol-1-ylpyridine) [22] and $[Cu_2(N_3)(N_3)(pmp)_2(ClO_4)]ClO_4$ (pmp = 2-((pyridin-2-yl)methoxy)-1, 10-phenanthroline) [23], the azides in $[Cu_2(heae)(N_3)_2]_n$ and $[Cu_2(N_3)_2(PP)_2)] \cdot 2ClO_4$ adopted μ-1,1 coordination mode, whereas the azide ligand in $[Cu_2(N_3)(N_3)(pmp)_2(ClO_4)]ClO_4$ adopted μ-1,3 coordination mode.

Figure 2 shows the μ-1,1,3 bridging model for azide ligands in **1**. Each Cu(I) coordinates with three nitrogen atoms from three μ-1,1,3 azides, leading to the 2-D plane structure, composed of a 10-membered ring with the formation of –Cu–N3–Cu–N3–Cu–N3–Cu–N3– and can be considered to adopt a pseudo-boat conformation. The rings are joined through CuN "edges" giving 2–D sheets of $[CuN_3]_n$. Furthermore, each

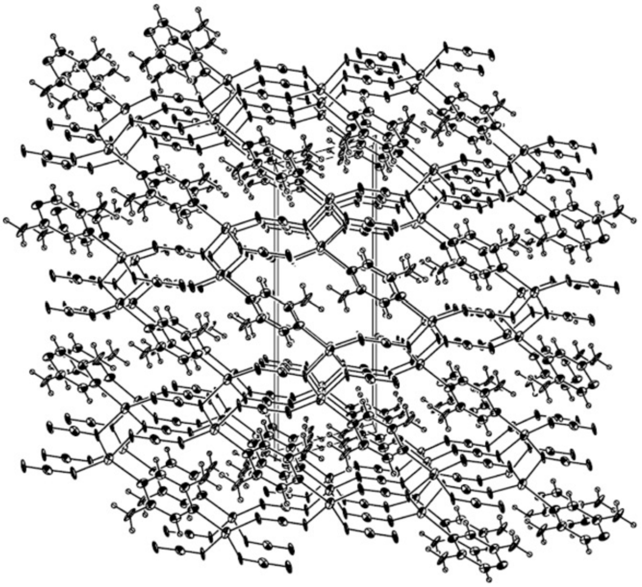

Figure 3. 3-D structure for **1**.

Cu(I) is linked by 2-aminopyrazine bidentate bridging ligand to afford a 3-D configuration (figure 3).

3.3. *Sensitivity performance*

In order to evaluate the sensitivity, impact sensitivity, friction sensitivity, and sensitivity to flame complex **1** has been tested. The results reveal: (1) **1** never ignites under flame sensitivity test conditions, (2) **1** never ignites under the impact sensitivity test conditions with a 1.0 kg hammer, (3) the igniting rate for **1** was 24% under friction sensitivity test conditions of pivot angle of 90° and gage pressure of 1.96 MPa, which shows **1** having friction sensitivity and may be expected to become an insensitive energetic material.

3.4. *Effect on the thermal decomposition of HMX*

Complex **1** is a rich nitrogen and high-density energetic compound because its nitrogen content is 41.30% and density is 2.311 $\mathrm{g\,cm^{-3}}$, with potential applications as energetic material. In this article, we studied its catalytic action on thermal decomposition of HMX.

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is the main component of rocket propellant, and change of its peak temperature of thermal decomposition can influence the burning rate of rocket propellant.

Figure 4 is the DSC curves for HMX and the mixture of HMX and **1** with a mass ratio of 100 : 1. The peak temperature of HMX containing **1** decreases from 293°C to 267°C, suggesting that **1** can catalyze the thermal decomposition of HMX.

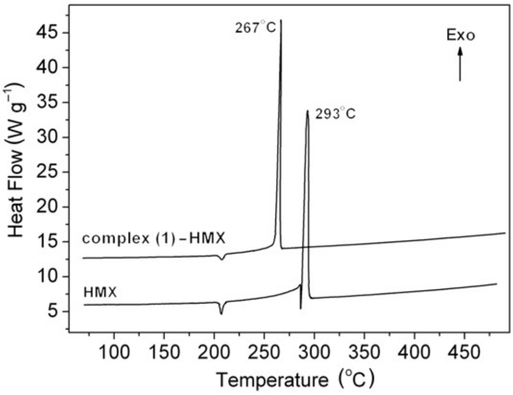

Figure 4. The DSC curves of HMX and mixtures.

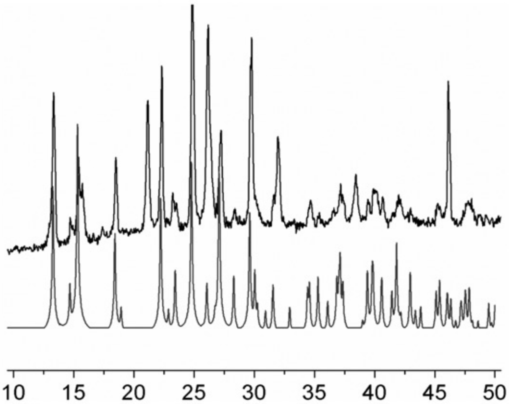

Figure 5. X-ray powder diffraction patterns for **1** (up: actual measurement; down: the simulated).

Therefore, the decomposition process of HMX is accelerated in the presence of **1**, indicating **1** can promote the burning rate of rocket propellant.

3.5. *Other physical data*

The X-ray powder diffraction patterns of the simulated and actual measurement for **1** (figure 5) agree with each other, indicating **1** is a pure phase.

4. Conclusion

We report the hydrothermal synthesis, crystal structure, and catalytic properties of $[Cu_2(2apyz)(N_3)_2]_n$ (**1**). This complex promotes the burning rate of rocket propellant and has potential application in the field of burning catalyst for rocket propellant. Sensitivity testing shows **1** has friction sensitivity and may be expected to become insensitive energetic material.

Supplementary material

Crystallographic data for **1** has been deposited with the Cambridge Crystallographic Data Center as supplementary publications with CCDC No. 819390. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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