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Metal–Organic Frameworks

A Highly Energetic N-Rich Metal–Organic Framework as a New High-Energy-Density Material

Huabin Zhang ,[a, b] Mingjian Zhang,[a] Ping Lin,[a] Victor Malgras,[b] Jing Tang,[b, c] Saad M. Alshehri,[d] Yusuke Yamauchi ,*[a, c, d] Shaowu Du,*[a] and Jian Zhang*[a]

Abstract: Metal–organic framework (MOF)-based energetic material $[Cu_3(MA)_2(N_3)_3]$ (**1**; MA = melamine) was synthesized and structurally characterized (47.55 % N). The structural analysis revealed the existence of unusual multiwalled tubular channels and interweaving of single and double helical units in **1**. The standard molar enthalpy of formation was found to be 1788.73 $kJ\,mol^{-1}$, which is the highest value among previously reported MOF-based energetic materials. The calculated detonation properties showed that **1** can be used as a potential explosive. Sensitivity tests revealed that **1** is insensitive and thus can function as a high-energy-density material with a favorable level of safety.

Introduction

Metal–organic frameworks (MOFs) and porous coordination polymers (PCPs) have been extensively studied as a new family of hybrid materials.[1–2]In general, they can be readily prepared through coordination bonds between the metal center and organic linkers.[3] Of major interest is the exploration of highly symmetrical multitopic ligands, which may adopt various coordination modes to satisfy the requirements of the assembly process to lead to interesting structural motifs, especially those with high symmetry and elegant design.[4] Tubular architectures have mushroomed in the fields of materials science, nanotechnology, molecular sieves, ion sensors, and fluidic transport systems.[5] Much effort has been made in inorganic and organic tubular structures, but the corresponding architectures of coordination frameworks are still rarely observed. Although coordination networks with large and single-walled tubes have been documented, those with multiwalled tubes remain largely unexplored up to now.[6]

Because of their intriguing structures and unique properties, porous MOFs are currently being pursued in diverse applications but remain essentially unexplored in the field of energetic materials. A porous structure may produce two-phase flow effects due to the reaction between gas flow and unburned porous solid, which is significant for convective transport and produces confinement effects and thus will influence the energetic performance.[1e,7] Recently, the possibility of using nitrogen-rich MOFs as high explosives, particularly because of their high density and high heat of detonation, was demonstrated.[8] Although they remain to be systematically exploited, the exceptional energetic performance of several reported MOFs has revealed their great potential as new-generation high explosives. For example, Pang and co-workers recently reported 4,4′-azo-1,2,4-triazole (atrz)-based MOF $[Cu(atrz)_3(NO_3)_2]_n$, which is possibly the most powerful metal-based energetic material known to date, with a heat of detonation higher than that of hexanitrohexaazaisowurtzitane (CL-20, ca. 1.5 $kcal\,g^{-1}$).[8h]

Despite these advances, current energetic MOFs are mostly limited to 1D or 2D structures, in which the contradiction between sensitivity and high energy is still obvious. Compared with 1D linear and 2D layered structures, 3D frameworks have more complicated connection modes, which could further enhance the structural reinforcement and hence improve both stability and energetic properties. On the other hand, recent concerns about the environmental impact of energetic materials have nowadays led to a renaissance in the synthesis of green energetic materials, which are based on a high nitrogen content that releases mainly environmentally friendly N_2 after decomposition or degradation. As an environmentally compatible, green energetic material, the azido ion (N^{3-}) has attracted considerable attention due to its explosive nature. Its various

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[a] Dr. H. Zhang ,+ Dr. M. Zhang,+ Prof. P. Lin,+ Prof. Y. Yamauchi , Prof. S. Du,
Prof. J. Zhang
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
The Chinese Academy of Sciences Fuzhou
Fujian, 350002 (P. R. China)
E-mail: yamauchi.yusuke@nims.go.jp
swdu@fjirsm.ac.cn
zhj@fjirsm.ac.cn

[b] Dr. H. Zhang ,+ Dr. V. Malgras, Dr. J. Tang
World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA)
National Institute for Materials Science (NIMS)
1-1 Namiki, Tsukuba, Ibaraki 305-0044 (Japan)

[c] Dr. J. Tang, Prof. Y. Yamauchi
Faculty of Science and Engineering, Waseda University
3-4-1 Okubo, Shinjuku, Tokyo 169-0072 (Japan)

[d] Prof. S. M. Alshehri, Prof. Y. Yamauchi
Department of Chemistry, College of Science, King Saud University
Riyadh 11451 (Saudi Arabia)

[+] These authors contributed equally to this work.

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coordination modes have also provided a platform for the construction of elegant frameworks with high-dimensional structures. The rigid melamine (MA) ligand, having a high nitrogen content (66.64 %) and energetic C–N bonds, has three N donor sites located in one plane at 120° relative to each other and is expected to be a good candidate for the construction of high-symmetry coordination frameworks with high energy. However, transition metal MA complexes have rarely been mentioned and no MA-based MOFs as energetic materials have been reported until now.[9] Given the above challenges and considerations, herein we report the synthesis, structural determination, and analysis of a Cu-based energetic material in which MA and N^{3-} bridging ligands join adjacent metal centers to form 3D MOF $[Cu_3(MA)_2(N_3)_3]$ (**1**). We disclose that the structure of **1** is characterized by unusual multiwalled tubular channels and the interweaving of single and double helical units; these features have rarely been observed in MOF materials. Furthermore, owing to the high nitrogen content of the MA and N_3^- ligands, which have the environmental benefit of releasing mainly N_2 upon decomposition, compound **1** exhibits high formation enthalpy, moderate detonation performance, and low sensitivity. Thus, **1** can function as a high-energy-density material with favorable levels of safety.

Table 1. Crystallographic data and structure refinement details for **1 P** and **1 M**.

Compound	1 P	1 M
empirical formula	$C_3H_6Cu_3N_{15}$	$C_3H_6Cu_3N_{15}$
formula weight	442.85	442.85
crystal system	hexagonal	hexagonal
space group	$P6_122$	$P6_522$
a [Å]	11.4719(3)	11.4708(6)
b [Å]	11.4719(3)	11.4708(6)
c [Å]	18.4685(1)	18.4672(1)
V [Å^3]	2104.9(1)	2104.4(2)
Z	6	6
ρ_{calcd} [g cm^{-1-3}]	2.096	2.097
μ [mm^{-1}]	4.524	4.526
$F(000)$	1296	1296
reflns collected	24084	29401
reflns unique	6669	8546
reflns with $I > 2\sigma(I)$	6460	7340
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0366$ $wR_2 = 0.1384$	$R_1 = 0.0391$ $wR_2 = 0.1383$
R indices (all data)	$R_1 = 0.0376$ $wR_2 = 0.1384$	$R_1 = 0.0407$ $wR_2 = 0.1396$
goodness of fit	1.211	1.076
Flack parameter	0.0146	0.0768

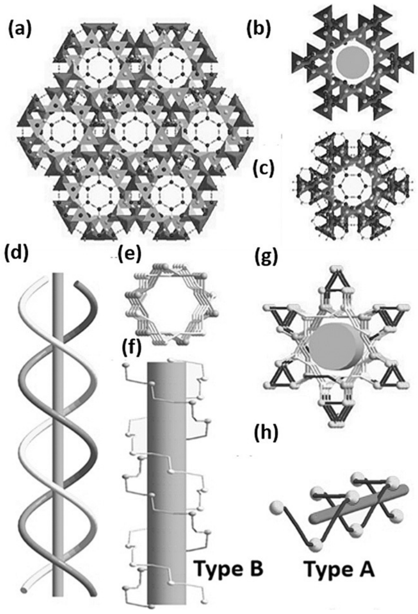

Figure 1. a) View of the whole network along the c axis. b) and c) View of the multiwalled tubular channel in **1 M**. d), e), and f) Idealized and ball-and-stick models of the left-handed double helix in **1 M**. g) View of the combination of single helix and double helix with the same handedness. h) View of a single helix.

Results and Discussion

Dark gray crystals of **1** were hydrothermally synthesized from a mixture of $Cu(NO_3)_2 \cdot 4H_2O$, MA, and NaN_3 in MeOH/acetonitrile (8 mL, 1:1 v/v) at 115 °C for 72 h (see Experimental Section and Supporting Information, Figure S1). The structure of **1** was determined by single-crystal X-ray diffraction, which showed that **1** contains enantiomers **1 M** and **1 P** with the chiral space groups $P6_522$ and $P6_122$, respectively, indicating the occurrence of spontaneous resolution during the crystal growth process (Table 1). The fundamental building units for **1 M** and **1 P** consist of 1.5 unique independent Cu^+ ions, 0.5 MA ligands, and 1.5 azido anions for charge balance (Figure S2, Supporting Information). Taking **1 M** as an example, there are two kinds of Cu cations: the Cu1 atom is in a heavily distorted tetrahedral geometry, whereas the Cu2 atom is pentacoordinated and adopts a distorted trigonal-bipyramidal configuration. The Cu–N bond lengths are in the range of 1.946(5)–2.415(5) Å. The azido anions can be divided into two types in terms of their coordination modes: μ_3-1,1,3 (mode A) and μ_4-1,1,3,3 (mode B; Figure S3, Supporting Information). These bridging azido ligands connect the crystallographically unique Cu^+ ions in turn to form an infinite helical motif, which is interwoven by a double helix and a single helix with the same handedness and creation of helical tubular channels along the c axis (Figure 1). The MA ligand overcomes different kinds of restrictive factors and uses all three ring nitrogen atoms to connect three identical helical motifs through Cu–N bonds, which further stabilize the 3D framework. Notably, only one compound containing such a μ_3-bridging MA ligand has been reported in the literature, and compound **1** is the first example of a 3D framework based on the MA ligand.[9a] Compared with the rare examples of interweaving of different helical ribbons, this helical motif may be one of the most complicated entanglement structures ever found in helical coordination chemistry.

To interpret the whole framework of **1 M** (or **1 P**) clearly, it is necessary to describe each individual helical chain in more detail and investigate the linkage between them. The double helix consists of two intertwined helical chains, each of which is made up of Cu1 and mode B azido anions with equal pitch to the single helix. In this double helix, the two $\{Cu1\text{-}N_3\text{-}Cu1\}_n$

chains spiral around each other along a sixfold screw axis, which is similar to the double helix of DNA (Figure 1 d and f). When viewed down the *c* axis, they are arranged as two homocentric hexagrams interleaved with each other (Figure 1 e). Apparently, this is exceptional for common multiple helical structures, in which the single helixes are usually arranged in a parallel way or intertwisted by low-fold helical axles. The Cu2 atoms and mode A azido anions give rise to an infinite left-handed helical chain $\{Cu2\text{-}N_3\text{-}Cu2\}_n$ along the threefold screw axis, with a long pitch of 18.467 Å based on the repeat units, each containing three Cu2 centers and three azido ligands (Figure 1 h). The interweaving of single and double helical chains of **1 M** leads to an unprecedented 3D network. Through the connection between Cu1 and Cu2, each single helix is linked to three surrounding double helices, and each double helix is connected to six neighboring single helices (Figure 1 g). Another remarkable structural characteristic of **1 M** is the existence of one-dimensional multiwalled tubular open-ended channels along the crystallographic *c* axis (the minimum internal diameter is ca. 5.2 Å without considering the van der Waals contacts; Figure S4, Supporting Information). A cross section shows that the outer shell of the channel is composed of six single helixes arranged in a hexagonal pattern, whereas the inner shell is supported by a double helix (Figure 1 b). Finally, the tubular channels are connected through the ring nitrogen atoms of the MA ligands running perpendicular to the *c* axis, which further consolidates the whole 3D framework. Open frameworks with monowalled tubular channels have been reported in the literature, but, to the best of our knowledge, those with multiwalled hexagonal tubular channels are quite rare.[6]

Before measurement, the compound was washed thoroughly with CH_3OH. The peak positions of the simulated and experimental patterns are in agreement with each other, which indicates good phase purity of the as-synthesized sample (Figure S5, Supporting Information). The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) curves of compound **1** were performed with a linear heating rate of 10 °C min^{-1} under nitrogen and are shown in Figure 2. The DSC curve shows two main successive endothermic processes, with peaks located at 178 and 242 °C, respectively. Upon further heating, endothermic stages also occur in the range of 293.2–314.5 °C, with a maximum at 301.6 °C. The TGA curve shows a mass loss of 34.6 % from 170 to 260.0 °C, which corresponds to the loss of N^{3-}. The last 23.9% mass-loss stage is a relatively slow process.

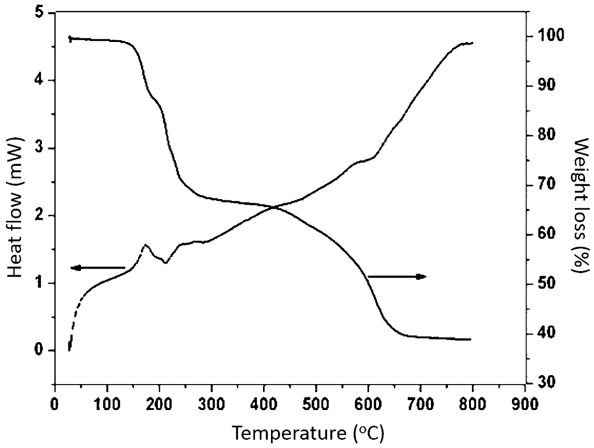

Figure 2. DSC and TGA curves of compound **1**.

Nitrogen-rich compounds are traditional sources of energetic materials because they have a large number of energetic N–N and C–N bonds. Compound **1** has a high nitrogen content (47.55 %) and moderate thermal stability, which make it a prospective high-energy material. To study the energy of combustion and enthalpy of formation of **1**, the constant-volume energy of combustion Q_v was measured by oxygen bomb calorimetry, and was determined to be 9.76 MJ kg^{-1}. The bomb equation [Eq. (1)] is as follows:

$$\begin{aligned} &C_3H_6Cu_3N_{15}(s) + 6\,O_2(g) \rightarrow \\ &3\,CO_2(g) + 3\,H_2O(l) + 3\,CuO(s) + 7.5\,N_2(g) \end{aligned} \tag{1}$$

The energy of combustion is given by Equation (2)

$$\Delta_c H^\circ(\mathbf{1}) = Q_p = Q_v + \Delta nRT = -9.73\ \mathrm{MJ\,kg^{-1}} \tag{2}$$

where Δn is the change in the number of gas constituents in the reaction process. The energy of combustion of **1** is lower than that of TNT (2,4,6-trinitrotoluene), but comparable to that of RDX (cyclotrimethylenetrinitramine) and HMX (cyclotetramethylenetetranitramine).[10] It is much higher than that of 1D Zn^{II} MOF $ZnN_2H_4(N_3)$ and aminotetrazolate-based Cd^{II} MOF CdATZ, but lower than that of amino acid/tetrazole-based Zn^{II} MOF ZnTZET.[11] (Table 2) The standard enthalpy of formation of **1** was back-calculated from the energy of combustion on the basis of Equation (1) and with the Hess law, as given in Equation (3). With the known enthalpies of formation of CuO(s) (−155.2 kJ mol^{-1}), CO_2(g) (−393.5 kJ mol^{-1}), and H_2O(l) (−285.8 kJ mol^{-1}), the enthalpy of formation of **1** ($\Delta_f H^\circ_{298}\{[Cu_3(MA)(N_3)_3](s)\}$) can be calculated to be 1788.73 kJ mol^{-1} by means of Equation (3).

Table 2. Comparison of thermochemical properties for compound **1** and HMX, RDX, TNT, and related energetic MOFs.

Compound	M_r [g mol^{-1}]	N[a] [%]	Density[b] [g cm^{-3}]	$\Delta_c H$ [kJ g^{-1}]	$\Delta_f H^\circ$ [kJ mol^{-1}]
HMX[10]	292.16	37.84	1.91	−9.60	105
RDX[10]	222.12	34.31	1.82	−9.61	93
TNT[10]	227.13	18.5	1.65	−16.27	−67
1	442.85	47.55	2.096	−9.73	1788.73
CdATZ[11b]	1894.73	30.31	2.530	−6.672	−102.27
$ZnN_2H_4(N_3)$[11a]	213.53	65.6	2.083	−5.45	−327.62
ZnTZET[11c]	328.66	21.31	1.716	−14.16	−1271.8
CoBTA[8b]	2922.31	51.78	1.975	−5.92	859.66

[a] N content of the framework. [b] Density calculated from X-ray diffraction data.

$$\begin{aligned}\Delta_f H^\circ_{298}\{[Cu_3(MA)(N_3)_3](s)\} &= 3\Delta_f H^\circ_{298}[CuO(s)] \\ &+3\Delta_f H^\circ_{298}[H_2O(l)] + 3\Delta_f H^\circ_{298}[CO_2(g)] \\ &-\Delta_c H^o\{[Cu_3(MA)(N_3)_3](s)\}\end{aligned} \tag{3}$$

This value is not only higher than those of traditional energetic materials such as HMX, RDX, and TNT, but is also higher than those of previously reported energetic MOFs.[11] The enthalpy criteria of energetic materials are governed by their molecular structures and nitrogen content. For heterocycles, as the nitrogen content increases, for example, moving from imidazole ($\Delta_f H^\circ_{cryst} = 14.0$ kcal mol^{-1}) to 1,2,4-triazole ($\Delta_f H^\circ_{cryst} = 26.1$ kcal mol^{-1}) to tetrazole ($\Delta_f H^\circ_{cryst} = 56.7$ kcal mol^{-1}), the heat of formation increases significantly.[8b,12] Therefore, strong structural reinforcement and extensive coordination networks, as well as the high nitrogen content of the MA ligand in this 3D framework, may be responsible for the high heat of formation of the final compound.

To estimate the heat of detonation ΔH_{det} for comparison with those of energetic MOFs and classical energetic materials, DFT was used to calculate the energy of detonation ΔE_{det}, from which ΔH_{det} is estimated by using a linear correlation equation developed from known ΔH_{det} data for eleven commonly used high explosives (Table S1, Supporting Information). Nitrogen, carbon, and ammonia are assumed to be the decomposition products of the organic component of **1**, and the formation of the metal is assumed owing to the deficiency of oxygen. All the non-metal-containing products are treated as gases. The detonation reaction considered for the compound is described by Equation (4).

$$C_{18}H_{36}Cu_{18}N_{90}(s) \rightarrow 18\,C + 12\,NH_3 + 18\,Cu + 39\,N_2(g) \tag{4}$$

For **1**, $\Delta H_{det} = 2.473$ kcal g^{-1} (5.171 kcal cm^{-3}), which is superior to that reported for other energetic MOFs (e.g., ZnHHP,[8d] CHHP,[8d] CHP,[8c] and NHP,[8c]), comparable to that of Co-BTA,[8b] but lower than that of ATRZ-1, in which a large number of nitrate ions fill the channels.[8a] It is even higher than those of CL-20 (ca. 1.5 kcal g^{-1}) and octanitrocubane (ONC, ca. 1.8 kcal g^{-1}), which are the most energetically intense known organic explosives (Figure 3).[8h,i] The relatively high ΔH_{det} value of **1** is attributed to the nitrogen-rich heterocyclic ligand MA and the advantageous structural framework. The detonation pressure P and detonation velocity D of compound **1** were calculated to be 35.32 GPa and 8.47 km s^{-1} by means of Kamlet–Jacobs equations (Table S2, Supporting Information).[13] As hypothesized, the high strain energy fixed in the 3D MOF-based energetic material is released as extra energy during the detonation.

We also considered safety, and thus evaluated the friction and impact sensitivities of **1**. Twenty milligrams of **1** was compacted into a copper cap at pressures of 1.96 and 3.92 MPa. No impact sensitivity was observed. Friction sensitivity was investigated under the strike of 0.8 kg drop hammer, and the test results showed that the firing rate was zero. This reveals that **1** is insensitive to external stimuli due to the stabilized 3D covalent framework.

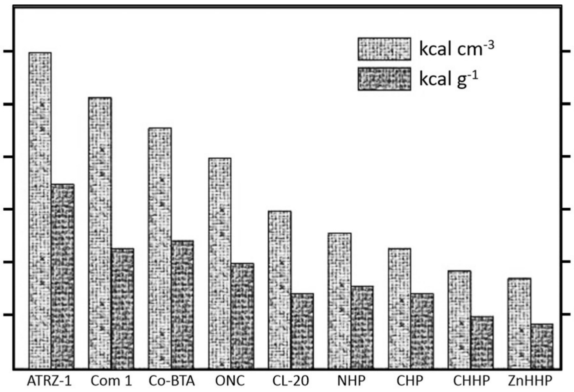

Figure 3. Bar chart representation of the literature ΔH_{det} values for common explosive materials, including ONC[8i] and CL-20.[8h] Previously reported values for energetic MOFs (ATRZ-1,[8e] Co-BTA,[8b] NHP,[8c] CHP,[8c] CHHP,[8d] and ZnHHP,[8d] along with the predicted ΔH_{det} value for compound **1** (Com 1).

Conclusion

We combined MA and N_3^- ligands in a framework and thus realized the construction of a new energetic MOF by self-assembly of highly energetic ligands with copper ions. Structural analysis revealed the existence of unusual multiwalled tubular channels and interweaving of single and double helical units in the 3D framework of **1**. The ordered framework exhibits high density, good thermal stability, excellent energetic performance, and low sensitivity. This work will provide a great opportunity to develop new green primary energetic materials with predictable properties and energetic performance.

Experimental Section

Materials and instrumentation

All starting materials were purchased commercially and were used as obtained from the supplier. Thermogravimetric analysis was performed with a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Elemental analyses were performed with a Vario EL III CHNO analyzer. Powder X-ray diffraction patterns were recorded with a RIGAKU DMAX2500 diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å). The sensitivity to impact was determined by the standard staircase method by using a fall-hammer apparatus with a 2 kg drop weight. The results were reported in terms of height for a 50% probability of explosion ($h_{50\%}$). The friction sensitivity was determined on a Julius Peter apparatus by following the BAM method. The combustion heats were measured by oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instruments Co., LTD, China).

Synthesis of $[Cu_3(MA)_2(N_3)_3]$ (1)

$Cu(NO_3)_2{\cdot}4H_2O$ (0.4 mmol), MA (1 mmol), and NaN_3 (0.3 mmol) were placed in a 20 mL Teflon-lined stainless steel vessel with 8 mL of CH_3CN/MeOH (v/v 1:1). The mixture was heated up to 115 °C over 4 h and kept at this temperature for 3 days. The reaction system was cooled slowly to room temperature over a further 2 days. Dark gray crystals of **1** were collected, washed thoroughly with CH_3OH, and dried in air at room temperature (yield: 56% based on $Cu(NO_3)_2{\cdot}3H_2O$). Elemental analysis calcd (%) for

$C_3H_6Cu_3N_{15}$ (442.85): C 8.10, H 1.26, N 47.55; found: C 8.26, H 1.30, N 47.69.

X-ray crystallography

Diffraction data for **1 P** and **1 M** were collected with a Mercury CCD area detector ($Mo_{K\alpha}$, $\lambda = 0.71073$ Å) at 298 K. Empirical absorption corrections were applied to the data with the CrystalClear program. The structures were solved by the direct method and refined by the full-matrix least-squares technique on F^2 with the SHELXTL-97 program.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model.

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Keywords: helical structures · high-energy materials · hydrothermal synthesis · metal–organic frameworks · N ligands

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