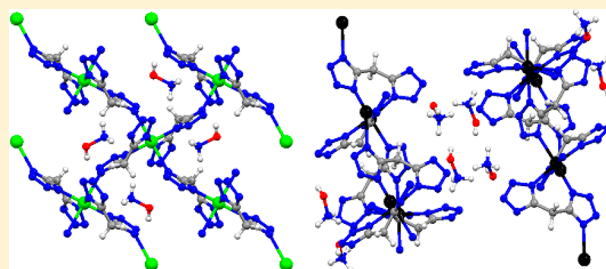


Energetic Metal–Organic Frameworks Incorporating  $\text{NH}_3\text{OH}^+$  for New High-Energy-Density MaterialsYongan Feng,<sup>†,‡</sup> Sitong Chen,<sup>†</sup> Mucong Deng,<sup>†</sup> Tonglai Zhang,<sup>\*,‡</sup> and Qinghua Zhang<sup>\*,†</sup><sup>†</sup>Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang, 621900, People's Republic of China<sup>‡</sup>School of Mechatronical Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

## Supporting Information

**ABSTRACT:** Energetic metal–organic frameworks (E-MOFs) have witnessed increasing development over the past several years. However, as a highly energetic cation,  $\text{NH}_3\text{OH}^+$  has never been explored to construct transition-metal-based E-MOFs. Herein, we report the first examples of  $\text{NH}_3\text{OH}^+$ -containing E-MOFs with bis(tetrazole)methane ( $\text{H}_2\text{btm}$ ) as a ligand and copper and manganese as central metal ions,  $[(\text{NH}_3\text{OH})_2(\text{Cu}(\text{btm})_2)]_n$  and  $[(\text{NH}_3\text{OH})_2(\text{Mn}(\text{btm})_2)]_n$ . Crystal structure determinations reveal that both E-MOFs show two-dimensional layered structures. Experimental results suggest that they have high thermal decomposition temperatures ( $>200\text{ }^\circ\text{C}$ ). Among them, Cu-based E-MOFs possesses outstanding thermal stability ( $T_{\text{dec}} = 230.3\text{ }^\circ\text{C}$ ), which surpasses those of known  $\text{NH}_3\text{OH}^+$ -containing compounds. They also have high energy density; in particular, the Cu-based E-MOF affords a high heat of combustion ( $11447\text{ kJ kg}^{-1}$ ) and high heat of detonation ( $713.8\text{ kJ mol}^{-1}$ ) beyond the most powerful organic explosives in use today. Additionally, the two E-MOFs show completely different sensitivity properties: the Mn-based E-MOF is an insensitive high-energy-density material ( $\text{IS} > 40\text{ J}$ ;  $\text{FS} > 360\text{ N}$ ;  $\text{EDS} > 20\text{ J}$ ), while the Cu-based E-MOF can be classified as a sensitive energetic material ( $\text{IS} = 13\text{ J}$ ;  $\text{FS} = 216\text{ N}$ ;  $\text{EDS} = 10.25\text{ J}$ ), demonstrating their diverse applications in different fields. Our research proposes a unique class of high-energy-density materials.



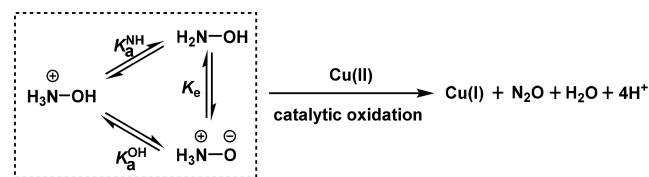
## INTRODUCTION

Energetic metal–organic frameworks (E-MOFs), as an emerging class of high-energy-density materials, are of current interest because of their potential applications as combustion catalysts, initiating substances, biocidal materials, pyrotechnic additives, and functional precursors of advanced carbon materials.<sup>1–14</sup> Up to now, a number of E-MOFs with fascinating structures, high thermal stabilities, and adjustable energetic performances have been prepared. Among them, transition-metal-based E-MOFs are the most typical due to their environmentally friendly characteristics and excellent energetic properties. On the other hand, hydroxylammonium ( $\text{NH}_3\text{OH}^+$ , in comparison with other nitrogen-rich cations, e.g.  $\text{NH}_4^+$ ,  $\text{NH}_2\text{NH}_3^+$ , guanidinium, triazolium, and tetrazolium) is an preferred energetic cation for the construction of high-energy-density materials, since  $\text{NH}_3\text{OH}^+$ -containing energetic salts nearly always show superior energetic performances over other analogues.<sup>15–19</sup> Therefore, E-MOFs that combine  $\text{NH}_3\text{OH}^+$  and transition metals are expected to possess unusual properties or performances. However, to our knowledge,  $\text{NH}_3\text{OH}^+$ -containing transition-metal E-MOFs have not been investigated so far.

In fact, there are great difficulties in the design and synthesis of transition-metal-based anionic E-MOFs. For instance, in a study involving a  $\text{NH}_4^+$ -containing E-MOF in 2017, Klapötke and co-workers stated “only a few single crystals could be picked...

The attempted synthesis of... in larger quantities failed unfortunately”, which hindered the study of its physicochemical property and energetic performance.<sup>20</sup> For the  $\text{NH}_3\text{OH}^+$ -containing Cu(II)-based E-MOFs, an additional major challenge is to overcome the instability of the  $\text{Cu}^{2+}/\text{NH}_3\text{OH}^+$  system,<sup>21–23</sup> despite the fact that this challenge has not been encountered in our previous study of an  $\text{AG}^+$ -containing Cu-based E-MOF.<sup>24</sup> Many nonenergetic  $\text{NH}_3\text{OH}^+$ -based transition-metal complexes (Mn, Co, Ni, Zn, Cd, etc.) have been prepared, but the undesirable  $\text{NH}_3\text{OH}^+ \rightleftharpoons \text{NH}_2\text{OH} + \text{NH}_3\text{O}^+$  equilibrium, along with the oxidation of hydroxylamine catalyzed by  $\text{Cu}^{2+}$  in solution (Scheme 1), makes the synthesis of Cu-based analogues difficult.<sup>25–28</sup> Until 2010, the only

## Scheme 1. Copper-Catalyzed Oxidation of Hydroxylammonium



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$\text{NH}_3\text{OH}^+$ -containing Cu(II)-based complex with a determined crystal structure,  $\{(\text{NH}_3\text{OH})_2\text{CuF}_4\}_n$ , was successfully prepared in 40% HF solution at room temperature.<sup>29</sup> In this complex, the catalytic oxidation was significantly inhibited in strongly acidic solution at low temperature. Despite these advances, the existing  $\text{NH}_3\text{OH}^+$ -containing transition-metal complexes are nonenergetic.

We herein present the first examples of  $\text{NH}_3\text{OH}^+$ -containing transition metal-based E-MOFs, i.e.,  $\{(\text{NH}_3\text{OH})_2[\text{Cu}(\text{btm})_2]\}_n$  (Cu-btm- $\text{NH}_3\text{OH}$ ) and  $\{(\text{NH}_3\text{OH})_2[\text{Mn}(\text{btm})_2]\}_n$  (Mn-btm- $\text{NH}_3\text{OH}$ ), where  $\text{H}_2\text{btm}$  denotes bis(tetrazole)-methane.  $\text{H}_2\text{btm}$  was chosen as the energetic ligand mainly on the basis of three reasons: (1)  $\text{H}_2\text{btm}$  is an environmentally friendly energetic compound with a high nitrogen content up to 73.7% and is insensitive to external stimuli and thus safe to handle and use; (2)  $\text{H}_2\text{btm}$  has a great potential to form anionic frameworks with transition metals and nitrogen-rich cations, which has been confirmed in our previous study;<sup>24</sup> (3)  $\text{H}_2\text{btm}$  has eight potential coordination N atoms and can coordinate to central ions with versatile coordination modes, which allows  $\text{H}_2\text{btm}$  to tightly chelate with  $\text{Cu}^{2+}$  and thus facilitate inhibiting the Cu(II)-catalyzed oxidation reaction mentioned above.

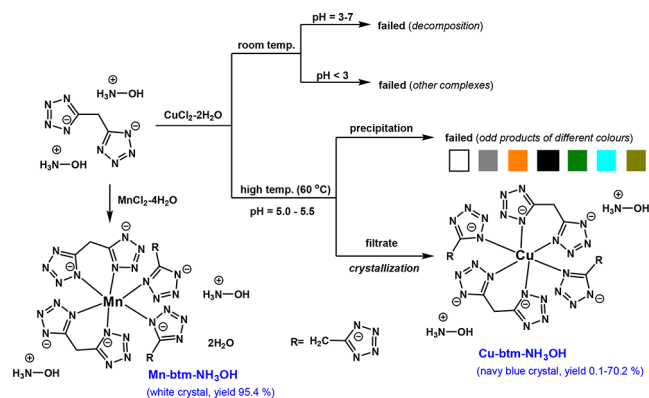
## RESULTS AND DISCUSSION

**Synthesis.** Since copper-catalyzed oxidations in solution are generally pronounced and rapid at high temperature, we initially tried to synthesize Cu-btm- $\text{NH}_3\text{OH}$  at room temperature by using our reported method for synthesizing two anionic MOFs.<sup>24</sup> This failed, however, even when the pH of the reaction system was adjusted to 3–4 (before the addition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). Catalytic decomposition occurs immediately in solution at the moment when  $\text{Cu}^{2+}$  cations are in contact with  $\text{NH}_3\text{OH}^+$  solution. In order to inhibit the copper-catalyzed oxidation, a lower pH (<3) system was employed, which, however, led to some cationic or neutral energetic complexes rather than an anionic complex due to the weak acidity of  $\text{H}_2\text{btm}$ .

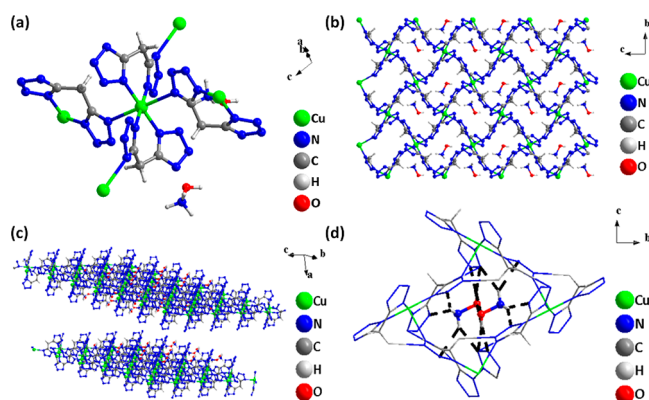
Incredibly, when the temperature was increased to about 60 °C, a clear dark blue solution was formed in the initial stage of the reaction. We judged that the target product should be formed. With the addition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (approximately 5%), an odd precipitate immediately appeared, indicating that catalytic decomposition occurred. The color of the solid product obtained in each experiment varies greatly, from white, to gray, orange, light blue, green, brown, or even black (Scheme 2). Occasionally, several dark blue block crystals of Cu-btm- $\text{NH}_3\text{OH}$  could be obtained in an extremely low yield of less than 0.1%, while the yield of Mn-btm- $\text{NH}_3\text{OH}$  under the same conditions is as high as 95.4%, demonstrating the great difficulty in producing energetic  $\text{NH}_3\text{OH}^+$  complexes of copper (Scheme 2). Fortunately, when the pH of the reaction system is adjusted to 5.0–5.5 (before the addition of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), the yield can sometimes be greatly increased to about 70.2%, but this does not always work. Five gram quantities of crystal products of Cu-btm- $\text{NH}_3\text{OH}$  and Mn-btm- $\text{NH}_3\text{OH}$  were finally collected for structure determination, thermal stability measurement, and performance testing.

**Crystal Structure.** The structure of Cu-btm- $\text{NH}_3\text{OH}$  was fully characterized by elemental analysis and X-ray photoelectron spectroscopy (XPS). The XPS spectrum of the crystalline sample showed an evident satellite peak of 933 eV, suggesting the presence of Cu(II) in Cu-btm- $\text{NH}_3\text{OH}$ . The

## Scheme 2. Synthesis of Cu-btm- $\text{NH}_3\text{OH}$ and Mn-btm- $\text{NH}_3\text{OH}$



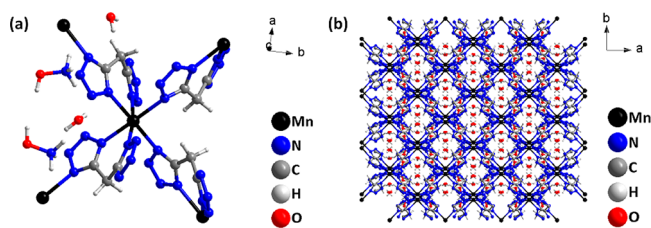
accurate structure of Cu-btm- $\text{NH}_3\text{OH}$  was confirmed by single-crystal X-ray diffraction. As shown in Figure 1, Cu-btm-



**Figure 1.** Crystal structure of Cu-btm- $\text{NH}_3\text{OH}$ : (a) molecular structure and coordination mode; (b) 2D networks and pores in the crystal; (c) 2D layered structure; (d) hydrogen bonding among the layers (black dashed lines).

$\text{NH}_3\text{OH}$  crystallizes in the monoclinic space group  $P2_1/c$  (Supporting Information). The asymmetric unit of Cu-btm- $\text{NH}_3\text{OH}$  consists of one  $\text{Cu}^{2+}$ , two  $\text{btm}^{2-}$ , and two  $\text{NH}_3\text{OH}^+$ . The central  $\text{Cu}^{2+}$  is hexacoordinated by six nitrogen atoms (N4, N5, and N8) from four  $\text{btm}^{2-}$  in a regular octahedral arrangement. Each  $\text{btm}^{2-}$  ligand exhibits a tridentate coordination pattern. N4 and N8 coordinate to  $\text{Cu}^{2+}$  with a chelating mode, while N5 coordinates with a bridging mode. Thus, infinitely expanded two-dimensional (2D) layered networks are formed. The networks are stacked layer-by-layer along the  $a$  axis via a large amount of hydrogen bonds among  $\text{btm}^{2-}$  and  $\text{NH}_3\text{OH}^+$ , forming a hydrogen-bonded 2D MOF. In the crystal structure of Cu-btm- $\text{NH}_3\text{OH}$ , the pores along the  $a$  axis are filled with  $\text{NH}_3\text{OH}^+$ . The layer spacing is calculated to be 1.032 Å. The lengths of hydrogen bonds between the layers are in the range of 1.86–2.83 Å (102 K), which may allow Cu-btm- $\text{NH}_3\text{OH}$  to be easily exfoliated into 2D nanosheets by top-down methods for diverse applications, just like the exfoliation of graphene, transition-metal dichalcogenides, and other 2D nanomaterials.<sup>30</sup>

The 2D structure of the hydrate of Mn-based E-MOF (Mn-btm- $\text{NH}_3\text{OH} \cdot \text{H}_2\text{O}$ ) was also revealed. As shown in Figure 2, the asymmetric unit of Mn-btm- $\text{NH}_3\text{OH} \cdot \text{H}_2\text{O}$  consists of one  $\text{Mn}^{2+}$ , two  $\text{btm}^{2-}$ , two  $\text{NH}_3\text{OH}^+$ , and four  $\text{H}_2\text{O}$ , which is

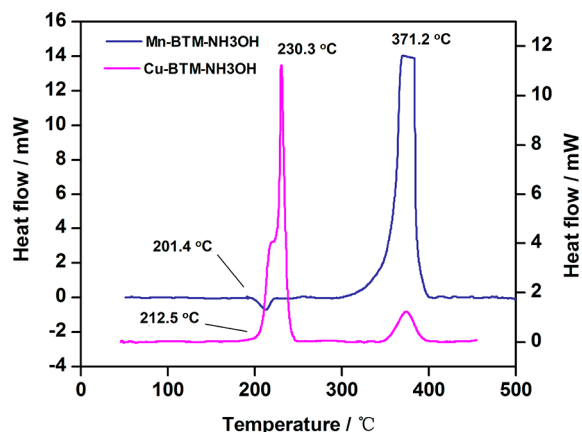


**Figure 2.** Crystal structure of Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O: (a) molecular structure and coordination mode; (b) 2D networks and pores in the crystal.

similar to that of Cu-btm-NH<sub>3</sub>OH. The central Mn<sup>2+</sup> is also hexacoordinated by six nitrogen atoms (N1, N5, and N8) from four btm<sup>2-</sup>. Each btm<sup>2-</sup> ligand exhibits the same tridentate coordination pattern as the btm<sup>2-</sup> ligands in Cu-btm-NH<sub>3</sub>OH. On the basis of this coordination mode, infinitely expanded two-dimensional (2D) layered networks are formed. The 2D layered networks are then stacked layer-by-layer along the *c* axis via a large amount of hydrogen bonds among btm<sup>2-</sup>, H<sub>2</sub>O, and NH<sub>3</sub>OH<sup>+</sup>, forming a hydrogen-bonded 2D MOF. However, different from Cu-btm-NH<sub>3</sub>OH, Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O crystallizes in the orthorhombic space group *Pbcn*, and the coordination structure is not as regular as that of Cu-btm-NH<sub>3</sub>OH. In comparison to that of Cu-btm-NH<sub>3</sub>OH, the spatial location of the bridging ligands in Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O changes significantly (Figure 2a), which results in the dihedral angle (N5–Cu–N5) formed by bridging atoms and metal ions in Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O to become 93.7°, from 180° in Cu-btm-NH<sub>3</sub>OH. Additionally, due to its different coordination structure, Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O presents a stacked pattern different from that of Cu-btm-NH<sub>3</sub>OH, as shown in Figure 2b. In the crystal structure of Mn-btm-NH<sub>3</sub>OH-H<sub>2</sub>O, the pores along the *c* axis are filled with H<sub>2</sub>O rather than NH<sub>3</sub>OH<sup>+</sup>. The layer spacing is calculated to be 3.306 Å, which is much larger than that of Cu-btm-NH<sub>3</sub>OH. The lengths of hydrogen bonds between the layers are in the range of 1.73–2.61 Å (153 K), which may indicate stronger intermolecular interactions and better sensitivity performance.

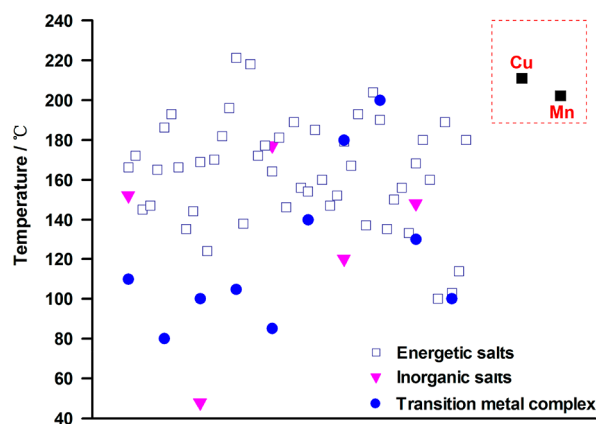
**Thermal Stability.** Thermal stability is crucial to energetic materials (EMs) because it reflects the difficulty of accidental combustion or explosion of EMs under an external thermal load. In general, a heat resistance above 200 °C is highly desirable for practical application.<sup>16</sup> Here, the thermal stability was investigated by using differential scanning calorimetry (DSC). As shown in Figure 3, Cu-btm-NH<sub>3</sub>OH exhibits an intense exothermic process with a decomposition onset ( $T_{\text{dec-onset}}$ ) of 212.5 °C and a peak temperature of 230.3 °C, indicating a violent decomposition reaction. Interestingly, when the dehydrated Mn-btm-NH<sub>3</sub>OH decomposes, it first shows a weak endothermic process with a decomposition onset of 201.4 °C and a peak temperature of 211.6 °C. This apparent discrepancy demonstrates the amazing thermal decomposition behavior of NH<sub>3</sub>OH<sup>+</sup>-containing transition-metal-based E-MOFs, indicating that the thermal properties of these materials could be adjusted in a large range via replacement of metal ions to meet a diverse set of applications.

Notably, although electrostatic interaction in salts is considered to be an effective method for improving the thermal stability of unstable compounds, almost all inorganic hydroxylammonium salts still have unsatisfactory thermal stability: for instance, (NH<sub>3</sub>OH)Cl (152 °C), (NH<sub>3</sub>OH)NO<sub>3</sub> (48 °C), (NH<sub>3</sub>OH)<sub>2</sub>SO<sub>4</sub> (177 °C), (NH<sub>3</sub>OH)ClO<sub>4</sub> (120 °C),



**Figure 3.** DSC curves of Cu-btm-NH<sub>3</sub>OH and Mn-btm-NH<sub>3</sub>OH.

and (NH<sub>3</sub>OH)<sub>3</sub>PO<sub>4</sub> (148 °C). Energetic hydroxylammonium salts, except for a few substances such as TKX-50 ( $T_{\text{dec-onset}} = 222$  °C),<sup>16</sup> also face the same problems ( $T_{\text{dec-onset}} < 200$  °C, Figure 4).<sup>31–34</sup>



**Figure 4.** Comparison of thermal stabilities of reported NH<sub>3</sub>OH<sup>+</sup>-containing substances: nonenergetic complexes (blue dots); inorganic salts (pink triangle); energetic salts (colorless boxes); two E-MOFs (black boxes).

Another method to improve thermal stability is to develop transition-metal complexes based on coordination bonds. However, as shown in Figure 4, few NH<sub>3</sub>OH<sup>+</sup>-containing complexes have a good thermal stability with  $T_{\text{dec-onset}}$  values higher than 200 °C. To the best of our knowledge, [NH<sub>3</sub>OH][Ni(HCOO)<sub>3</sub>], among the reported NH<sub>3</sub>OH<sup>+</sup>-containing complexes with a determined crystal structure, shows the highest decomposition onset, close to 200 °C,<sup>27</sup> which is still lower than those of Cu-btm-NH<sub>3</sub>OH and Mn-btm-NH<sub>3</sub>OH. The aforementioned {(NH<sub>3</sub>OH)<sub>2</sub>CuF<sub>4</sub>} has a very low thermal decomposition onset of 80 °C.<sup>29</sup> This demonstrates the outstanding thermal stability of NH<sub>3</sub>OH<sup>+</sup>-containing transition-metal-based E-MOFs.

**Energetic Properties.** The energy released during combustion and explosion, the heat of combustion ( $\Delta_c U$ ) and heat of detonation ( $Q$ ), are two critical parameters for assessing the performance of energetic materials. The  $\Delta_c U$  values in this study were tested by using a Parr-6200 bomb calorimeter, and the results for  $-\Delta_c U$  of Cu-btm-NH<sub>3</sub>OH and Mn-btm-NH<sub>3</sub>OH are 11447 and 11510 kJ kg<sup>-1</sup>, respectively, which are higher than those of RDX (9600 kJ kg<sup>-1</sup>) and HMX

**Table 1. Energetic Properties of Mn-btm-NH<sub>3</sub>OH, Cu-btm-NH<sub>3</sub>OH, RDX, and HMX**

compound	$d^a$ (g cm <sup>-3</sup> )	$T_d^b$ (°C)	$-\Delta_c U^c$ (kJ kg <sup>-1</sup> )	$\Delta_f H^d$ (kJ mol <sup>-1</sup> )	$Q^e$ (kcal g <sup>-1</sup> )
Cu-btm-NH <sub>3</sub> OH	1.89	230.3	11447	713.8	1.46
Mn-btm-NH <sub>3</sub> OH	1.70	211.6	11510	245.8	1.07
RDX	1.80	204.5	9600	80.0	1.48
HMX	1.89	279.0	9880	105.0	1.47

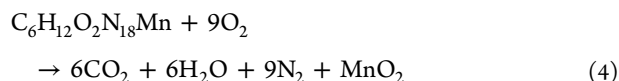
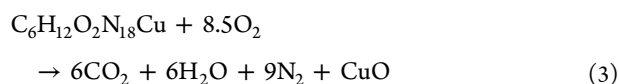
<sup>a</sup>Crystal density. <sup>b</sup>Thermal decomposition temperature. <sup>c</sup>Heat of combustion. <sup>d</sup>Heat of formation. <sup>e</sup>Heat of detonation.

(9880 kJ kg<sup>-1</sup>),<sup>35</sup> two of the most powerful organic explosives commonly in ammunition use (Table 1).

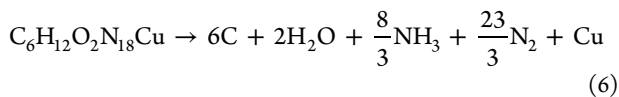
With respect to the heat of detonation ( $Q$ ), there are three common methods for the prediction of  $Q$ , including the Kamlet formula, density functional theory (DFT), and the commercial program EXPLOS. Given that the calculation results for metal-based energetic compounds achieved from several existing methods are quite different, we adapted a new method to calculate  $Q$  on the basis of measured  $\Delta_c U$  (for details see the Supporting Information).<sup>1,36–38</sup> Here, the standard molar enthalpies of combustion ( $\Delta_c H^\circ$ ) can be calculated on the basis of eq 1, and the heats of formation ( $\Delta_f H$ ) at 298 K were calculated via the Hess thermochemical cycle on the basis of eq 1 and the combustion reactions (eqs 3 and 4). As shown in Table 1, the calculated heats of formation for Cu-btm-NH<sub>3</sub>OH and Mn-btm-NH<sub>3</sub>OH are 713.8 and 245.8 kJ mol<sup>-1</sup>, respectively, which are also higher than those of RDX (80.0 kJ mol<sup>-1</sup>) and HMX (105.0 kJ mol<sup>-1</sup>).<sup>18,19</sup> With the heats of formation of both E-MOFs and combustion products, the heats of detonation can be calculated on the basis of the new method (eq 5) and decomposition reaction (eqs 6 and 7). The  $Q$  values for Cu-btm-NH<sub>3</sub>OH and Mn-btm-NH<sub>3</sub>OH are 1.46 and 1.07 kcal mol<sup>-1</sup>, respectively. Among them, Mn-btm-NH<sub>3</sub>OH has a relatively low heat of detonation, while Cu-btm-NH<sub>3</sub>OH shows a heat of detonation comparable to those of HMX and RDX, indicating a high energy density.

$$\Delta_c H^\circ = \Delta_c U + \Delta nRT \quad (1)$$

$$\Delta_f H_{\text{materials}} = \Delta_f H_{\text{products}} - \Delta_c H^\circ \quad (2)$$



$$Q = \frac{-[\Delta_f H^\circ(\text{products}) - \Delta_f H^\circ(\text{materials})]}{\bar{M}_{\text{materials}}} \quad (5)$$



**Mechanical Sensitivities.** From the perspective of safety and reliability, the sensitivities of energetic materials (EMs) to mechanical stimuli are of particular concern. For example, some EMs are sensitive to external stimuli, which makes them unusable as pyrotechnic additives or combustion catalysts because their production, transportation, storage, and handling are dangerous, while others are insensitive to external stimuli, which makes them impossible to use as initiating substances

due to low ignition reliability and high excitation energy. Here, by using related methods, the sensitivities of two NH<sub>3</sub>OH<sup>+</sup>-containing E-MOFs toward impact, friction, and electrostatic spark were tested. It is clearly seen from the data presented in Table 2 that Mn-btm-NH<sub>3</sub>OH is insensitive toward external

**Table 2. Sensitivities of Mn-btm-NH<sub>3</sub>OH, Cu-btm-NH<sub>3</sub>OH, NH<sub>4</sub>CuNT, and Their Corresponding Ligands H<sub>2</sub>btm and 5-Nitrotetrazole (5-NT)**

compd	IS <sup>a</sup> (J)	FS <sup>b</sup> (N)	EDS <sup>c</sup> (J)
H <sub>2</sub> btm	>40	>360	>20
Mn-btm-NH <sub>3</sub> OH	>40	>360	>20
Cu-btm-NH <sub>3</sub> OH	13	216	10.25
5-NT	<1	<5	<0.005
NH <sub>4</sub> CuNT	2.4	>8	>0.36

<sup>a</sup>Impact sensitivity. <sup>b</sup>Friction sensitivity. <sup>c</sup>Electrostatic spark sensitivity.

stimuli, with impact (IS), friction (FS), and electrostatic spark (EDS) sensitivities of >40 J, >360 N, and >20 J, respectively, which are comparable to those of the corresponding ligand (H<sub>2</sub>btm: IS > 40 J; FS > 360 N; EDS > 20 J). We think it may be used as a pyrotechnic additive, a combustion catalyst of a solid propellant, or even other advanced functional materials (e.g., gas separation/uptake).

Interestingly, Cu-btm-NH<sub>3</sub>OH is sensitive to impact, friction, and electrostatic spark, with IS = 13 J, FS = 216 N, and EDS = 10.25 J, respectively, which classifies it as a sensitive energetic material. Obviously, the Cu-based E-MOF is more sensitive than its ligand (Table 2). However, most reported energetic MOFs, in the absence of perchlorate (ClO<sub>4</sub><sup>-</sup>), are less sensitive than their ligands. This unusual sensitivity property has significant application potential for advanced energetic materials. To the best of our knowledge, most of the primary explosives in use are perchlorate-based transition-metal complexes, such as CP and BNCP.<sup>39,40</sup> However, the toxicity of perchlorates has aroused public and government concerns because they promote thyroid dysfunction and are teratogenic.<sup>2</sup> Although some newly reported transition-metal primary explosives, such as NH<sub>4</sub>CuNT, are free of perchlorate, their ligands (5-nitrotetrazole) are extremely sensitive (e.g., IS < 1 J) and are more sensitive than primary explosives (Table 2), which makes the production of both ligands and primary explosives very dangerous.<sup>41,42</sup> This means that, if a primary explosive with the desired sensitivities is needed, a powerful and extremely sensitive ligand will have to be employed. However, the study of the sensitivities of Cu-btm-NH<sub>3</sub>OH tells us that we could achieve some new green primary explosives with the desired sensitivities on the basis of NH<sub>3</sub>OH<sup>+</sup>-containing Cu-based complexes by using less sensitive ligands, which will allow the production of new primary explosives to be very simple and safe, highlighting the potential application

of  $\text{NH}_3\text{OH}^+$ -containing Cu-based energetic complexes for new green initiating substances.

## CONCLUSIONS

In summary,  $\text{NH}_3\text{OH}^+$  as a highly energetic component has been introduced into transition-metal-based energetic metal–organic frameworks (E-MOFs) for the first time, and two  $\text{NH}_3\text{OH}^+$ -containing E-MOFs have been synthesized as  $[(\text{NH}_3\text{OH})_2(\text{Cu}(\text{btm})_2)]_n$  (Cu-btm- $\text{NH}_3\text{OH}$ ) and  $[(\text{NH}_3\text{OH})_2(\text{Mn}(\text{btm})_2)]_n$  (Mn-btm- $\text{NH}_3\text{OH}$ ). Between them, Cu-btm- $\text{NH}_3\text{OH}$  is much more difficult to synthesize than Mn-btm- $\text{NH}_3\text{OH}$  due to the instability of the  $\text{Cu}^{2+}/\text{NH}_3\text{OH}^+$  solution system. Structural determinations suggest that both energetic compounds exhibit a two-dimensional layered structure with  $\text{NH}_3\text{OH}^+$  among the layers. A thermal analysis demonstrates that Cu-btm- $\text{NH}_3\text{OH}$  has a high thermal decomposition temperature (230.3 °C), which is higher than that of Mn-btm- $\text{NH}_3\text{OH}$  (211.6 °C). Especially, Cu-btm- $\text{NH}_3\text{OH}$  possesses an excellent thermal stability surpassing those of all reported  $\text{NH}_3\text{OH}^+$ -containing compounds. Additionally, experimental tests and thermodynamic calculations display that Cu-btm- $\text{NH}_3\text{OH}$  and Mn-btm- $\text{NH}_3\text{OH}$  have high heats of combustion ( $\Delta_c U$ ) and heats of detonation ( $Q$ ), with  $\Delta_c U$  values for Cu-btm- $\text{NH}_3\text{OH}$  and Mn-btm- $\text{NH}_3\text{OH}$  of 11447 and 11510  $\text{kJ kg}^{-1}$ , respectively, and  $Q$  values for Cu-btm- $\text{NH}_3\text{OH}$  and Mn-btm- $\text{NH}_3\text{OH}$  of 713.8 and 245.8  $\text{kJ mol}^{-1}$ , respectively, which are higher than those of HMX and RDX, the two most powerful organic explosives in use today. Interestingly, Cu-btm- $\text{NH}_3\text{OH}$  and Mn-btm- $\text{NH}_3\text{OH}$  show completely different sensitivity properties: Cu-btm- $\text{NH}_3\text{OH}$  (IS = 13 J; FS = 216 N; EDS = 10.25 J) is much more sensitive than its ligand, while Mn-btm- $\text{NH}_3\text{OH}$  (IS > 40 J; FS > 360 N; EDS > 20 J) has sensitivities comparable to those of its ligand, indicating their possible diverse applications. This study highlights the great potential of  $\text{NH}_3\text{OH}^+$ -containing E-MOFs (or complexes) for new high-energy-density materials.

## EXPERIMENTAL SECTION

**Safety Precautions.** The energetic metal–organic frameworks involved in this study are high-energy-density materials and tend to explode under certain conditions. All compounds should be handled with extreme care, and safety precautions should be taken at all times.

**Materials and Instruments.** All chemical reagents were used as supplied without further purification. Elemental analyses (C, H, O, and N) were performed on a Flash EA 1112 fully automatic trace element analyzer. The valence state of the Cu ion in the complex was confirmed by a Thermo ESCALAB 250Xi X-ray photoelectric spectrometer. DSC measurements were conducted on a CDR-4 instrument from Shanghai Precision & Scientific Instrument Co., Ltd. (heating rate 10 °C  $\text{min}^{-1}$ ). Impact sensitivities and friction sensitivities were determined by following the corresponding BAM methods, and electrostatic sensitivities were performed using a JGY-50(III) electrostatic test apparatus. The single-crystal X-ray diffraction data collections were carried out on a Rigaku AFC-10/Saturn 724+CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the multiscan technique, and structures were solved and refined using SHELXS-97.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01636.

Details of the syntheses, crystallographic data, and thermodynamic calculations (PDF)

### Accession Codes

CCDC 1430316 and 1540120 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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