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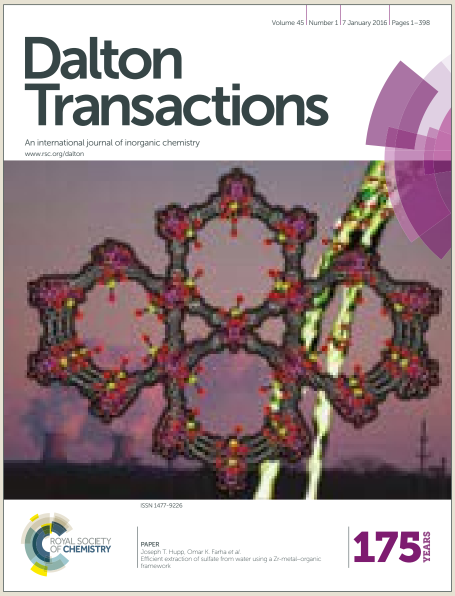

Volume 45 Number 1 7 January 2016 Pages 1–398

Dalton Transactions

An international journal of inorganic chemistry
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ISSN 1477-9226

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COMMUNICATION

Self-assembled energetic 3D metal-organic framework $[Na_8(N_5)_8(H_2O)_3]_n$ based on *cyclo*-N_5^-

Yuangang Xu,[a] Pengcheng Wang,*[a] Qiuhan Lin,[a] Xuefeng Mei[b] and Ming Lu*[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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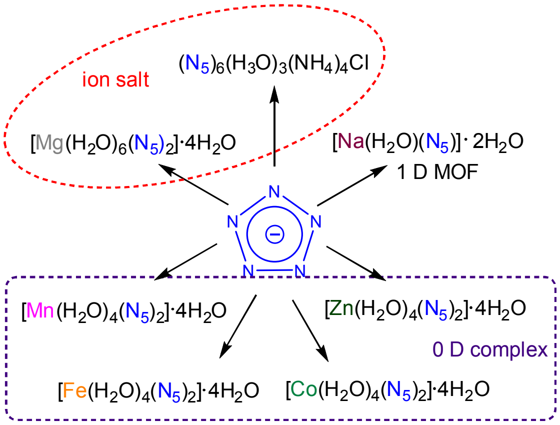
From a 1D sodium-N_5^- framework, a new zeolite-like metal-organic framework (MOF) with fascinating 3D structure was successfully constructed. It exhibited enhanced thermal stability with a decomposition temperature (onset) of 129 °C and enhanced coordination ability (five-coordination) of *cyclo*-N_5^- in weak alkaline conditions. The 3D MOF with bulky size offers new opportunities for not only the formation of porous materials but also control the balance between performance and stability of polynitrogen materials.

The seeking for new porous materials remains at the forefront of synthetic materials science as their intriguing molecular topologies and their potentially useful ion-exchange, catalytic, adsorption, fluorescence, and magnetic properties.[1-4] Inorganic zeolites and metal-organic frameworks (MOFs) are two families of functional porous materials. Combination of both zeolites and MOFs would allow the creation of a special class of zeolitic MOFs with unusual structures and potential functions.[5] Very recently, several studies have underscored the possibility to utilize the structural reinforcement of zeolitic MOFs as energetic materials.[6]

Energetic materials have been studied for nearly two centuries due to their military and civilian needs.[7] Polynitrogen materials containing nitrogen as the only element have been a hot topic in this field.[8] Among all kinds of energetic materials, metal-based energetic materials (e.g. lead azide) were early designed as initiating primary explosives because of their high sensitivities toward mechanical stimuli.[9] However, by coordinating with bidentate or multidentate nitrogen-rich ligands, metal ions can also be constructed as energetic zeolite-like MOFs which will be an emerging class of energetic materials because of their various advantages, including good stability, high security, controllable structures, and various modifiable functionalities[10].

A bulk material containing the pentazole anion, *cyclo*-N_5^- was reported which means polynitrogen chemistry enters the ring.[11] Recently, we have developed a series of metal-based pentazolate hydrates which illustrates the adaptability of the *cyclo*-N_5^- unit in terms of its ability to take part in ionic, coordination and hydrogen-bonding interactions (Scheme 1).[12] Especially, the structure of the 1D MOF $[Na(H_2O)(N_5)]\cdot 2H_2O$ (**1**) [12a] suggests that each nitrogen of *cyclo*-N_5^- has the potential to coordinate with the metal, indicating that it is possible to synthesize a 3D zeolite-like MOF of *cyclo*-N_5^-.



Scheme 1 Salts and complexes of cyclo-N_5^-.

As a continuous and innovative work, we report here a carbon-free 3D MOF, namely, $[Na_8(N_5)_8(H_2O)_3]_n$ (**2**) which features a new type zeolite-like porous framework with cages.

Colorless crystals of complex **2** was synthesized by mixing complex **1**, ammonia, 2M in methanol solvent at ambient temperature and pressure. Single-crystal X-ray diffraction (XRD) revealed that complex **2** crystallizes in the cubic $P_{m\text{-}3n}$ with an asymmetric unit that consists of four sodium ions, two water molecules, and six nitrogen atoms (Fig. S7). As shown in Fig. 1a and 1b, Na(I) ions have two coordination modes. Na3 features a four-pyramid geometry, coordinated to two oxygen atoms (O2) and two nitrogen atoms (N6) from different *cyclo*-N_5^- rings. The sodium atom Na3 is at the vertex of the quadrangular pyramid, O2 and N6 are coplanar formed the

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[a] School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, Jiangsu, China. E-mail: luming@njust.edu.cn (M. Lu); alexwpch@njust.edu.cn (P. Wang)
[b] Pharmaceutical Analytical & Solid-State Chemistry Research Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China.

† Electronic Supplementary Information (ESI) available: CCDC 1544793. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

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bottom of the pyramid (Fig. S8). While Na1 features a triangular pyramid geometry, coordinated to three nitrogen atoms from three different *cyclo*-N_5^- ligands (Fig. S9). The average Na-N bond length in this complex is ~2.456 Å which is shorter than that of complex **1** (2.523 Å). Each *cyclo*-N_5^- ligand is bonded to five sodium ions that means each nitrogen atom of every *cyclo*-N_5^- is bonded to a sodium ion (Fig. 1c). The five coordinated sodium ions are almost coplanar with the *cyclo*-N_5^- ring (Fig. S10). The average N-N bond length of the *cyclo*-N_5^- is 1.323 Å which is slightly longer than complex **1** (1.316 Å).

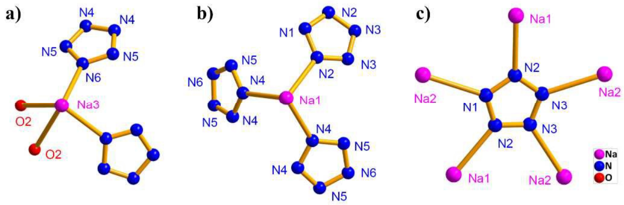

Fig. 1 (a, b) Coordination environment of Na (I). (c) Coordination model of *cyclo*-N_5^-.

Every twenty four sodium ions, twelve *cyclo*-N_5^- rings, and twelve oxygen atoms form a drum-like structure with one sodium ion in the center of the drum (Fig. 2a and 2c). The top and bottom of the drum are all coplanar hexagon which consisted of six oxygen atoms and six sodium ions (Fig. S11). Each drum shares its two planes with two neighboring drums. Along the direction of the three coordinate axes are connected in such a manner that holes in different directions do not penetrate each other. In this way, all of these cages give rise to the 3D framework of complex **2** with a new topology (Fig. S15). Fig. 3 shows two kinds of model for the 2*2*2 cells packing diagram along the c axis. The same structure exists along five other directions (such as a, b, a*, b*, c* axis) (Fig. S12-14).

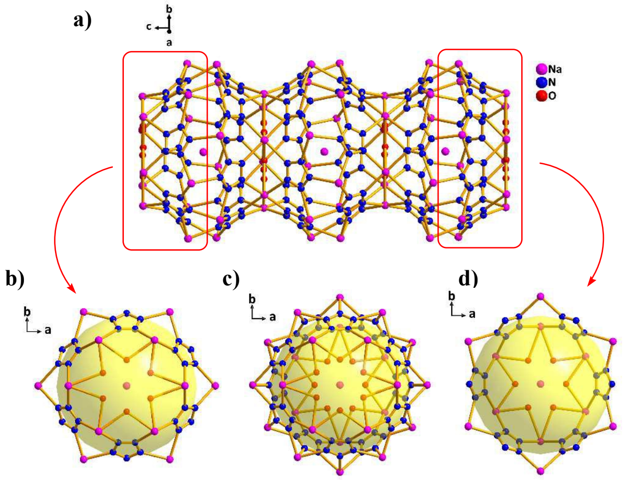

Fig. 2 (a) Selected three cages view along the a axis. (b) Half of a cage view along the c* axis. (c) Selected three cages view along the c axis. (d) Half of a cage view along the c axis.

Like most zeolites, complex **2** has a negatively charged framework. The charge-balancing sodium cations in the center of the cages were determined by single-crystal XRD, IR, elemental analysis, and thermal analysis. The contribution of the disordered solvent molecules was subtracted from the reflection data by SQUEEZE method as implemented in *PLATON*.[13] The solvent-accessible volume of **2** was estimated to be ~33.5% of the total crystal volume (6066 $Å^3$).

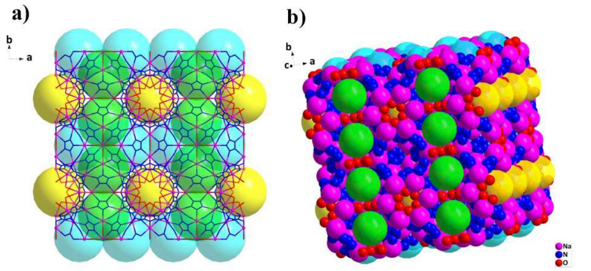

Fig. 3 3D framework of complex **2**. (a: sticks model; b: space-filling model; cages filled with a axis: blue, b axis: green, and c axis: yellow).

To understand the morphology of complex **2**, crystals were examined via 3D microscope and scanning electron microscopy (SEM). As can be observed from the images in Fig. S1 and S2, Complex **2** crystals exhibited the cube-like morphology with smooth surface and were well dispersed with an average size of ~500*500*300 μm^3.

The vibrational spectroscopy of **2** is further studied. The geometric parameters of the complex indicate that there are two different *cyclo*-N_5^-. Although both forms of *cyclo*-N_5^- have different bond lengths and bond angles, they are C_{2v} symmetry $[A_1 + (A_1 + B_2) + 2(A_1 + B_2) + (A_2 + B_1)]$ (Fig. S3). In addition to the two bands (3407, 1615 cm^{-1}) due to the H_2O, only one vibration (1231 cm^{-1}) can be detected and assigned (Fig. S4). Compared to complex **1**[12], the A_1 and B_2 mode are not clearly split apart. Due to the internal porous structure of zeolite-like MOF, multiple Raman tests show that the noise of spectra is large (Fig. S5). But the strong signal at ~1178 cm^{-1} is obvious and can be assigned to A_1 mode.

The thermal behaviors of **2** were investigated on a Mettler Toledo DSC-1 (differential scanning calorimeter) at heating rates of 5 °C min^{-1}. (Fig. 4) Even though complexes **1** and **2** contain the same ligand *cyclo*-N_5^-, the decomposition temperature (onset) of **2** (129 °C) is 18 °C higher than that of **1** (111 °C). The result of thermogravimetric analysis (TGA) for **2** was in good agreement with DSC (Fig. S6). This property can be attributed to the complex coordination, regular 3D structure, along with ring strain, chelation, bridging actions, and electrostatic forces in case of **2**.

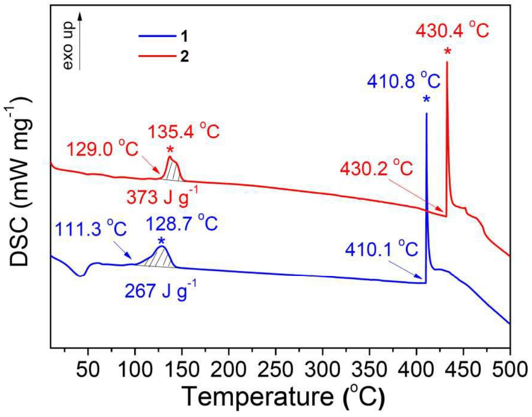

Fig. 4 DSC spectra of complex **1** and **2**.

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The constant-volume combustion energy (Q_v) of **2** was measured by an oxygen-bomb calorimeter, from which the standard molar enthalpy of combustion ($\Delta_c H_m^\vartheta$) is estimated by using an equation $\Delta_c H_m^\vartheta = \Delta_c U_m^\vartheta + \Delta n RT$. The standard enthalpy of formation for **2** is calculated via the known $\Delta_f H_m^\theta$ of the combustion products and $\Delta_c H_m^\vartheta$ of **2** (see the ESI†). The heat of formation (879 kJ mol^{-1}) for **2** is much higher than that of the traditional energetic materials[7] (TNT, RDX, and HMX).

Table 1 Physicochemical properties of **2** and some energetic materials.

Compound	ρ^a (g cm^{-3})	N^b (%)	$T_{dec}{}^c$ (°C)	Q^d (kcal g^{-1})	D^e (km s^{-1})	P^f (GPa)
2	1.301	70.19	129	0.664	5.011	8.76
HMX[10b]	1.950	37.80	280	1.320	8.900	38.39
RDX[10b]	1.806	37.80	210	1.386	8.600	33.92
TNT[10b]	1.654	18.50	244	0.897	7.178	20.50
ATRZ-1[17a]	1.680	53.35	243	3.618	9.160	35.68
ATRZ-2[17a]	2.160	43.76	257	1.381	7.773	29.70
$[Cu_4(Mtta)_5Na(CH_3CN)]_n$[17b]	1.975	40.08	384	2.366	7.225	24.43
$[Pb(tztr)_2(H_2O)]_n$[15b]	2.486	39.58	368	0.634	6.283	20.81
$[Cu(ntz)(N_3)(H_2O)]_n$[17c]	2.218	41.5	287	0.018	2.22	4.46
CHHP[17d]	2.000	23.58	231	0.750	6.205	17.96
ZnHHP[17d]	2.117	23.61	293	0.700	7.016	23.58

[a]From X-ray diffraction. [b]Nitrogen content. [c]Decomposition temperature. [d]The heat of detonation. [e]Detonation velocity. [f]Detonation pressure. HMX = octogen; RDX = cyclotrimethylenetrinitramine; TNT = trinitrotoluene; ATRZ = 4,4'-azo-1,2,4-triazole; CHHP = cobalt hydrazine hydrazinecarboxylate perchlorate; ZnHHP = zinc hydrazine hydrazinecarboxylate perchlorate.

Heat of detonation (Q), detonation velocity (D), and detonation pressure (P) are pivotal parameters for energetic MOFs. On the basis of the largest exothermic principle proposed by Kamlet-Jacobs (K-J),[14] We employed a widely used empirical method[15] proposed by Pang and coworkers[16] to investigate the detonation properties of **2**. The results are shown in Table 1. The Q of **2** is 0.664 kcal g^{-1}, which is comparable to the reported energetic MOFs $[Pb(tztr)_2(H_2O)]_n$, CHHP, and ZnHHP[17] and common explosive TNT[10b]. The D and P of **2** are calculated to be only 5011 m s^{-1} and 8.76 GPa, respectively. Its D is lower than that of most energetic MOFs. The poor detonation performance of **2** is attributed to its low density (1.26 g cm^{-3}, recalculated from low-temperature X-ray density). Therefore, increasing the densities of energetic MOFs based on *cyclo*-N_5^- is an effective way to improve their detonation performances.

In summary, through the self-assembly of sodium ions with *cyclo*-N_5^- ligands, a new 3D zeolite-like MOF containing cages has been successfully synthesized. It exhibited high nitrogen content of 70.19% and surprising thermal stability with a decomposition temperature (onset) of 129 °C. The enhanced stability and coordination ability of *cyclo*-N_5^- in weak alkaline conditions demonstrate that other new derivatives of *cyclo*-N_5^- would be obtained by following a similar synthetic strategy. This work will certainly provide new inspiration for polynitrogen chemistry.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 11702141, 21771108 and U1530101) for support of this work. The authors gratefully acknowledge Dongxue Li (College of Chemical Engineering, Nanjing Tech University) for her tests of the SEM and Raman spectra.

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DOI: 10.1039/C7DT04501H

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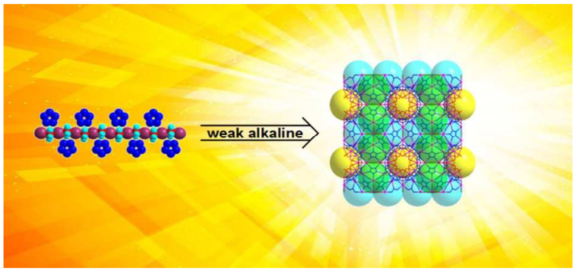
Manuscript ID: DT-COM-11-2017-004501

TITLE: Self-assembled energetic 3D metal-organic framework $[Na_8(N_5)_8(H_2O)_3]_n$ based on *cyclo*-N_5^-



A new 3D zeolite-like MOF $[Na_8(N_5)_8(H_2O)_3]_n$ with enhanced stability has been successfully synthesized by self-assembly of Na^+ with *cyclo*-N_5^- ligands.