[LiNa(N₅)₂(H₂O)₄]·H₂O: a novel heterometallic *cyclo*-N₅[−] framework with helical chains

Juecheng Li¹, Kangcai Wang¹, Siwei Song¹, Xiujuan Qi², Wenquan Zhang^{1*}, Mucong Deng¹ and Qinghua Zhang^{1*}

Over the past decades, there has been an intensive quest for theoretical studies and experimental detection of polynitrogen species (e.g., N₄, N₅⁺, N₈, *cyclo*-N₅[−], and polymeric nitrogen, etc.) that are potentially stable in the condensed phase [1–4]. As a class of representative polynitrogen species, *cyclo*-pentazolate (*cyclo*-N₅[−]) compounds have received significant interest from synthetic chemists. Despite traditional arylpentazole compounds were discovered in 1956 [5], the experimental synthesis of stable *cyclo*-N₅[−] species has encountered great difficulties for subsequent decades. The major challenge is the selective cleavage of C–N bond in the arylpentazoles while keeping the N=N and N–N bonds of *cyclo*-N₅[−] ring undamaged [6–8]. Tremendous efforts were devoted to the synthesis of stable *cyclo*-N₅[−] materials [9–14]; however, the quest for efficient cleavage strategy remains a great challenge.

Recently, the synthesis of stable *cyclo*-N₅[−] salt was achieved through an oxidative cleavage strategy by Zhang *et al.* (Fig. 1a) [15]. A series of *cyclo*-N₅[−]-based metal salts including [Na(H₂O)(N₅)]·2H₂O (Fig. 1b), [M(H₂O)₄(N₅)₂]·4H₂O (M = Zn, Mn, Fe and Co, Fig. 1c) and [Mg(H₂O)₆(N₅)₂]·4H₂O (Fig. 1d) were prepared [16–18]. Benefitting from versatile and multiple coordination modes, the *cyclo*-N₅[−] anion opens a new avenue to synthesize metal-pentazolate frameworks (MPFs) with intriguing structures. For example, a series of *cyclo*-N₅[−] metal salts including [Na₈(N₅)₈(H₂O)₃]_n, [Ag(N₅)]_n, [Cu(N₅)(N₃)]_n and metal-free *cyclo*-N₅[−] nitrogen-rich salts were synthesized [19–23]. Moreover, we recently reported a zeolitic *cyclo*-N₅[−] open-framework (MPF-1) containing two types of nano-cages (Na₂₀N₆₀ and Na₂₄N₆₀) [24]. Lu *et al.* [19] reported a barium-containing *cyclo*-N₅[−] compound with the formula of [NaBa₃(N₅)₆(NO₃)(H₂O)₃]_n, in

which only barium ions were contained in the framework. Despite tremendous theoretical and synthetic efforts towards monometallic *cyclo*-N₅[−] complexes [25–27], the attempts to construct new heterometallic *cyclo*-N₅[−] frameworks are very rare so far.

In our continuous efforts to synthesize new *cyclo*-N₅[−] materials, here we present the synthesis of an interesting heterometallic *cyclo*-N₅[−] framework with layered structure, i.e., [LiNa(N₅)₂(H₂O)₄]·H₂O (**1**, Fig. 2). The synthetic details are provided in the Supplementary information (Experimental Section, Fig. S1). Crystal of **1** suitable for single crystal X-ray diffraction (XRD) was obtained by recrystallization in ethyl alcohol (Fig. S2). The crystal structures were resolved and refined by direct methods and full-matrix least-squares methods on F² using SHELXTL program package, respectively (Table S1–S3). Compound **1** crystallizes in monoclinic C2/c space group with a density of 1.547 g cm^{−3} at 173 K. There are one independent Li(I) ion, one Na(I) ion, two *cyclo*-N₅[−] anions, and four and two halves water molecules contained in the asymmetric unit of **1** (Fig. 2a). Each lithium ion is connected with two different *cyclo*-N₅[−] anions and two water molecules to form a two-connected tetrahedral configuration, while each sodium ion is coordinated to two adjacent *cyclo*-N₅[−] anions and four water molecules to construct an octahedral structure. The bond length of Li–N and Na–N are in the range of 2.0440(3)–2.0680(3) Å and 2.5406(14)–2.6185(14) Å, respectively (Table S2). The adjacent lithium and sodium ions are connected to each other by *cyclo*-N₅[−] anions to form an inorganic chain {LiNa(H₂O)₂(N₅)₂}_n, while the lithium and sodium ions are alternating in the hybrid chain strictly (Fig. 2b). The adjacent and parallel hybrid chains are further connected by the bridged water molecules, forming the layered

¹ Research Center of Energetic Material Genome Science, Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang 621900, China

² Southwest University of Science and Technology, Mianyang 621010, China

* Corresponding authors (emails: zhangwq-cn@caep.cn (Zhang W); qinghuazhang@caep.cn (Zhang Q))

Figure 1 Several reported structures of *cyclo*-N₅[−]-containing salts.

structure of **1** (Fig. 2d). The layered structure of **1** can also be understood as a smart construction from the inorganic chain building block of $\{Na(H_2O)_2\}_n$ (Fig. 2c) and trimer building block of $\{Li(H_2O)_2(N_5)_2\}$ (Fig. 2b). This inorganic chain of $\{Na(H_2O)_2\}_n$ can also be observed in the reported *cyclo*-N₅[−] salt of $[Na(H_2O)(N_5)] \cdot 2H_2O$, however, the coordination mode of this inorganic chain with *cyclo*-N₅[−] anions in **1** is much different from that in $[Na(H_2O)(N_5)] \cdot 2H_2O$. In compound **1**, each *cyclo*-N₅[−] anion is connected with only one sodium ion, while in $[Na(H_2O)(N_5)] \cdot 2H_2O$, the *cyclo*-N₅[−] anion acts as a bridge linker to connect two adjacent sodium ions [16].

Compound **1** has a 3D supramolecular structure constructed through extensive hydrogen bonds among $\{Li(H_2O)_2(N_5)_2\}$ trimmers and crystal water molecules (Fig. S3). A notable feature in this supramolecular structure is the existence of left- and right-handed helical

chains along *b* axis (Fig. 2e, g), which are formed by $\{Li(H_2O)_2(N_5)_2\}$ trimmers through hydrogen bonds of O–H...N (Table S4). The pitch of the helical is about 3.55 (Å). It is worth noting that the helical chains contained in **1** are first observed in reported *cyclo*-N₅[−] materials. In this aesthetic structure, the nearby left- and right-handed helical chains interacted with each other by hydrogen bonds of O–H...N, while the same helical chains were connected by crystal water molecules (Fig. 2f). Consequently, a negative supramolecular structure with 1D channel along *b* axis was constructed through those hydrogen-bonding interactions, while the channels were occupied by finite inorganic chains $\{Na(H_2O)_2\}_n$ (Fig. 2f). With the aim of gaining a deep insight into these hydrogen-bonding interactions, Hirshfeld surfaces and 2D fingerprint spectra of **1** were studied. On the Hirshfeld surface, the red and blue spots represent the high and low

Figure 2 (a) The asymmetric unit of compound **1**; (b) the inorganic hybrid chain $\{\text{LiNa}(\text{H}_2\text{O})_2(\text{N}_5)_2\}_n$ contained in **1**; (c) the inorganic chain $\{\text{Na}(\text{H}_2\text{O})_2\}_n$ contained in **1**; (d) the 2D layer structure of **1**; (e, g) left- and right-handed helical chains contained in the supramolecular structure of **1** along b axis; (f) the supramolecular structure of **1** view along b axis.

close contact populations, respectively. As can be seen from Fig. 3, the red spots denote the strong hydrogen bonds of $\text{O}\cdots\text{H}\cdots\text{N}$, while the red spots are around the edge of Hirshfeld surface of the trimmer structure of $\{\text{Li}(\text{H}_2\text{O})_2(\text{N}_5)_2\}$. The arrangements of red spots on Hirshfeld surface are in good accordance with the characteristics of supramolecular structure of **1**. Three sharp spikes are observed from fingerprint spectra of **1**, which belong to the interactions of $\text{N}\cdots\text{H}$, $\text{N}\cdots\text{H}$, and $\text{O}\cdots\text{H}$, respectively. Notably, the total interactions of $\text{N}\cdots\text{H}$ are up to 59.5%, while the $\text{O}\cdots\text{H}$ interactions are only 5.9% (the total Hirshfeld surface is 100%). The high percentage of $\text{N}\cdots\text{H}$ interactions demonstrate the existence of extensive hydrogen bonds in the crystal structure of **1**. These extensive $\text{N}\cdots\text{H}$ interactions are very helpful to stabilize the *cyclo*- N_5^- anions [15].

The Raman and infrared spectra of **1** are shown in Figs S4 and S5 in the Supplementary information. Previous studies have demonstrated that the stretching mode of *cyclo*- N_5^- span includes $\text{A}_1' + \text{E}_1' + 2\text{E}_2' + \text{E}_2''$ [15,16], in which only A_1' and E_2' are Raman-active and only E_1' is IR-active. The Raman spectrum of **1** showed three typical *cyclo*- N_5^- bands, i.e., $1,187\text{ cm}^{-1}$ (A_1'), $1,117\text{ cm}^{-1}$ (E_2'), $1,025\text{ cm}^{-1}$ (E_2'), which are in accordance with reported *cyclo*- N_5^- salts. The IR signal of *cyclo*- N_5^- anion in compound **1** is also observed in $1,245\text{ cm}^{-1}$ (E_1'), which responds to the strong N–N stretching vibration.

The thermal stability of **1** was evaluated by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. From the DSC curve (red line) in Fig. 4, two endothermic peaks and two exothermic peaks were observed in the temperature range from 50 to 500°C . Ac-

Figure 3 The 2D fingerprint spectra of **1**; insert: Hirshfeld surfaces.

Figure 4 TG-DSC curve at rate of 10 K min⁻¹.

cordingly, the TG curve (blue line) reveals that **1** underwent four stages of weight losses as well. In the initial stage of heating process, two endothermic peaks with two stages of weight losses are observed (about 20 wt%) under 100°C, indicating the possible escaping of H₂O molecules from the framework of **1**. A sharp weight loss (about 20 wt%) is followed at 106.1°C, and the corresponding exothermic peak temperature is 142.7°C and 160.2°C, which correspond to the thermal decomposition of *cyclo*-N₅⁻ anions, suggesting a complex thermal degradation process.

Associated with structure characteristic of two independent *cyclo*-N₅⁻ anions contained in asymmetric unit of **1**, two exothermic peaks at 142.7 and 160.2°C observed from the DSC curve may indicate that different chemical environments of *cyclo*-N₅⁻ anions in the framework have

significant effects on the thermal stability. Obviously, the *cyclo*-N₅⁻ anions with different coordination modes showed different thermal stabilities, e.g., the onset decomposition temperatures of *cyclo*-N₅⁻ anions contained in (N₅)₆(H₃O)₃(NH₄)₄Cl [15], [Mn(H₂O)₄(N₅)₂].4H₂O [16] and [Ag(NH₃)]⁺[Ag₃(N₅)₄]⁻ [21] are 117, 104.1 and 90.0°C, respectively. Therefore, the construction of novel coordination structures would be an effective strategy to improve the thermo stability of *cyclo*-N₅⁻ anion. Moreover, at the first exothermic stage, the thermal decomposition of *cyclo*-N₅⁻ species in **1** produced the N₂ and N₃ species, which was the same as known *cyclo*-N₅⁻ salts. At the second stage, a tremendous exothermic peak was observed at 306.1°C (the exothermic peak temperature is 327.5°C), probably due to the drastic explosion of N₃-containing residues.

In summary, a novel bimetallic *cyclo*-N₅⁻ framework [LiNa(N₅)₂(H₂O)₄].H₂O (**1**) was reported. It is notable that compound **1** has a 3D supramolecular structure with left- and right-handed helical chains. This is a promising example of stable bimetallic *cyclo*-N₅⁻ frameworks with helical chain structure. The extensive hydrogen-bond interactions of N...H and O...H in this framework structure should play vital roles in stabilizing the *cyclo*-N₅⁻ species. Thermal analysis indicates that the stability of *cyclo*-N₅⁻ is below 110°C based on TG-measured onset decomposition temperature. This work opens a door to explore new bimetallic *cyclo*-N₅⁻ frameworks with interesting structures and specific functions.

Received 5 July 2018; accepted 8 August 2018;
published online 22 August 2018

- Samartzis PC, Wodtke AM. All-nitrogen chemistry: how far are we from N₆₀? *Int Rev Phys Chem*, 2006, 25: 527–552
- Christe KO. Recent advances in the chemistry of N₅⁺, N₅⁻ and high-oxygen compounds. *Prop Explos Pyrotech*, 2007, 32: 194–204
- Lu M. Opinion on the energy level of metal-free pentazolate salts. *Chin J Energ Mater*, 2017, 25: 530–532
- Christe KO, Wilson WW, Sheehy JA, *et al*. N₅⁺: A novel homoleptic polynitrogen ion as a high energy density material. *Angew Chem Int Ed*, 1999, 38: 2004–2009
- Huisgen R, Ugi I. Zur Lösung eines klassischen Problems der organischen Stickstoff-Chemie. *Angew Chem*, 1956, 68: 705–706
- Zhang C, Sun C, Hu B, *et al*. Investigation on the stability of multisubstituted arylpentazoles and the influence on the generation of pentazolate anion. *J Energetic Mater*, 2016, 34: 103–111
- Carlqvist P, Östmark H, Brinck T. The stability of arylpentazoles. *J Phys Chem A*, 2004, 108: 7463–7467
- Geiger U, Elyashiv A, Fraenkel R, *et al*. The Raman spectrum of dimethylaminophenyl pentazole (DMAPP). *Chem Phys Lett*, 2013, 556: 127–131
- Vij A, Pavlovich JG, Wilson WW, *et al*. Experimental detection of the pentaazacyclopentadienide (pentazolate) anion, *cyclo*-N₅⁻. *An-*

- gew Chem Int Ed, 2002, 41: 3051–3054
- 10 Butler RN, Stephens JC, Burke LA. First generation of pentazole (HN_5 , pentazolic acid), the final azole, and a zinc pentazolate salt in solution: A new *N*-dearylation of 1-(*p*-methoxyphenyl) pyrazoles, a 2-(*p*-methoxyphenyl) tetrazole and application of the methodology to 1-(*p*-methoxyphenyl) pentazole. *Chem Commun*, 2003, 1016–1017
 - 11 Bazanov B, Geiger U, Carmieli R, *et al.* Detection of *cyclo*- N_5^- in THF solution. *Angew Chem*, 2016, 128: 13427–13429
 - 12 Butler RN, Hanniffy JM, Stephens JC, *et al.* A ceric ammonium nitrate *N*-dearylation of *N*-*p*-anisylazoles applied to pyrazole, triazole, tetrazole, and pentazole rings: Release of parent azoles. generation of unstable pentazole, HN_5/N_5^- , in solution. *J Org Chem*, 2008, 73: 1354–1364
 - 13 Bazanov B, Geiger U, Grinstein D, *et al.* N_5^- in solution: isotopic labeling and further details of its synthesis by phenyl pentazole reduction. *J Phys Chem A*, 2017, 121: 6727–6731
 - 14 Schroer T, Haiges R, Schneider S, *et al.* The race for the first generation of the pentazolate anion in solution is far from over. *Chem Commun*, 2005, 38: 1607–1609
 - 15 Zhang C, Sun C, Hu B, *et al.* Synthesis and characterization of the pentazolate anion *cyclo*- N_5^- in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$. *Science*, 2017, 355: 374–376
 - 16 Xu Y, Wang Q, Shen C, *et al.* A series of energetic metal pentazolate hydrates. *Nature*, 2017, 549: 78–81
 - 17 Xu Y, Wang P, Lin Q, *et al.* A carbon-free inorganic–metal complex consisting of an all-nitrogen pentazole anion, a Zn(II) cation and H_2O . *Dalton Trans*, 2017, 46: 14088–14093
 - 18 Zhang C, Yang C, Hu B, *et al.* A symmetric $\text{Co}(\text{N}_5)_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ high-nitrogen compound formed by cobalt(II) cation trapping of a *cyclo*- N_5^- anion. *Angew Chem Int Ed*, 2017, 56: 4512–4514
 - 19 Xu Y, Lin Q, Wang P, *et al.* Syntheses, crystal structures and properties of a series of 3D metal-inorganic frameworks containing pentazolate anion. *Chem Asian J*, 2018, 13: 1669–1673
 - 20 Sun C, Zhang C, Jiang C, *et al.* Synthesis of AgN_5 and its extended 3D energetic framework. *Nat Commun*, 2018, 9: 1269
 - 21 Xu Y, Lin Q, Wang P, *et al.* Stabilization of the pentazolate anion in three anhydrous and metal-free energetic salts. *Chem Asian J*, 2018, 13: 924–928
 - 22 Xu Y, Wang P, Lin Q, *et al.* Self-assembled energetic 3D metal–organic framework $[\text{Na}_8(\text{N}_5)_8(\text{H}_2\text{O})_3]_n$ based on *cyclo*- N_5^- . *Dalton Trans*, 2018, 47: 1398–1401
 - 23 Christe KO. Polynitrogen chemistry enters the ring. *Science*, 2017, 355: 351
 - 24 Zhang W, Wang K, Li J, *et al.* Stabilization of the pentazolate anion in a zeolitic architecture with $\text{Na}_{20}\text{N}_{60}$ and $\text{Na}_{24}\text{N}_{60}$ nanocages. *Angew Chem Int Ed*, 2018, 57: 2592–2595
 - 25 Steele BA, Stavrou E, Crowhurst JC, *et al.* High-pressure synthesis of a pentazolate salt. *Chem Mater*, 2017, 29: 735–741
 - 26 Laniel D, Weck G, Gaiffe G, *et al.* High-pressure synthesized lithium pentazolate compound metastable under ambient conditions. *J Phys Chem Lett*, 2018, 9: 1600–1604
 - 27 Wang PC, Xu YG, Wang Q, *et al.* Self-assembled energetic coordination polymers based on multidentate pentazole *cyclo*- N_5^- . *Sci China Mater*, 2018, doi:10.1007/s40843-018-9268-0
- Acknowledgements** This work was supported by the National Natural Science Foundation of China (21602211 and 11472251), the Thousand Talents Plan (Youth), Development Foundation of CAEP (2015B0302057 and 2015B0302056), and the Science Challenge Project (TZ2018004).
- Author contributions** Zhang W, Zhang Q and Li J conceived the idea, designed the experiments and co-wrote the manuscript. Li J conducted the synthetic experiments and performed the DSC and TGA measurements. Qi X assisted the calculations. Song S and Deng M assisted the synthetic experiments. Wang K performed the single-crystal XRD measurements. All authors contributed to the general discussion and article revision.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Experimental details and supporting data are available in the online version of the paper.

Juecheng Li was born in 1993. He joined Prof. Zhang's group as a master candidate in 2016. His research interest focuses on the design and synthesis of energetic materials.

Wenquan Zhang obtained his BSc in 2008 and PhD in 2013 from the University of Science and Technology of China. From 2014 to 2016, he worked as a postdoctoral fellow at the Institute of Chemical Materials (ICM), China Academy of Engineering Physics (CAEP). Now he is working as an associate professor in ICM. His research interest includes the synthesis of high energy-density materials, hypergolic ionic liquids, and polynitrogen compounds.

Qinghuang Zhang received his PhD from Lanzhou Institute of Chemical Physics in 2008. From 2010 to 2012, he worked as a CNRS associate researcher at the University of Poitiers, France. From 2012 to 2013, he worked as a postdoctoral fellow at the University of Idaho, USA. Now he is working as a professor in the Institute of Chemical Materials, China Academy of Engineering Physics. His research interest focuses on the synthesis of new high-energy-density materials, polynitrogen compounds, and energetic ionic liquids.

$[\text{LiNa}(\text{N}_5)_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$: 一种含螺旋链的新型双金属五唑骨架

李珏成¹, 王康才¹, 宋思维¹, 乔秀娟², 张文全^{1*}, 邓沐聪¹, 张庆华^{1*}

摘要 过去一个世纪以来, 探索合成含有五唑阴离子(*cyclo*- N_5^-)的聚氮化合物吸引了科学家们的极大兴趣. 本论文报道了一例基于异质双金属的五唑骨架, $[\text{LiNa}(\text{N}_5)_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (**1**), 并对其结构和热性质进行了表征. 单晶X射线衍射表明化合物**1**具有三维超分子结构, 其中相邻的 $\{\text{Li}(\text{H}_2\text{O})_2(\text{N}_5)_3\}$ 三聚体之间通过 $\text{O} \cdots \text{H} \cdots \text{N}$ 氢键作用形成左手型和右手型螺旋链结构. 化合物**1**在室温条件下具有良好的热稳定性, 五唑环在106.1°C开始分解. 本研究对于探索五唑阴离子的配位化学以及相关聚氮材料提供了新思路.