

To Be or Not To Be Protonated: cyclo-N_5^- in Crystal and Solvent

Wei Chen,^{‡,§} Zhiqiang Liu,^{‡,§} Yinghe Zhao,^{‡,§} Xianfeng Yi,[‡] Zhongfang Chen,^{*,†,§}
and Anmin Zheng^{*,‡,§}

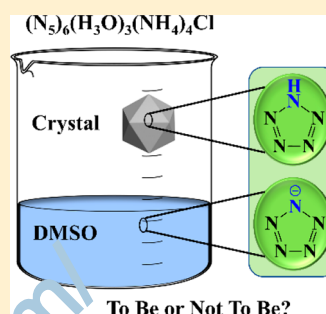
[‡]State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, National Center for Magnetic Resonance in Wuhan, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P.R. China

[†]Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico 00931, United States

[§]University of Chinese Academy of Sciences, Beijing 100049, P.R. China

S Supporting Information

ABSTRACT: Pentazole (HN_5) and its anion (cyclo-N_5^-) have been elusive for nearly a century because of the unstable N_5 ring. Recently, Zhang et al. reported the first synthesis and characterization of the pentazolate anion cyclo-N_5^- in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ salt at ambient conditions (*Science* 2017, 355, 374). However, whether the cyclo-N_5^- in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ salt is protonated or not has been debated (Huang and Xu, *Science*, 2018, 359, eaao3672; Jiang et al. *Science*, 2018, 359, aas8953). Herein, we employed ab initio molecular dynamics (AIMD) simulations, which can well present the dynamic behavior at realistic experimental conditions, to examine the potential protonated state of cyclo-N_5^- in both crystal and dimethyl sulfoxide (DMSO) solvent. Our simulations revealed that the protonation reaction of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl} \rightarrow (\text{N}_5)_5(\text{N}_3\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$ is thermodynamically spontaneous according to $\Delta G < 0$, and the small energy barrier of 12.6 kJ/mol is not enough to prevent the partial protonation of cyclo-N_5^- due to the temperature effect; consequently, both deprotonated and protonated cyclo-N_5^- exist in the crystal. In comparison, the DMSO solvent effect can remarkably reduce the difference of proton affinities among cyclo-N_5^- , H_2O , and NH_3 , and the temperature effect can finally break these hydrogen bonds and lead to the deprotonated cyclo-N_5^- in DMSO solvent. Our AIMD simulations reconcile the recent controversy.



Pentazole (HN_5) and its anion (cyclo-N_5^-) are the potential constituents of energetic materials and can be applied in both military and civilian contexts.^{1–5} In January 2017, Zhang et al.⁶ reported the first synthesis and characterization of the pentazolate anion, cyclo-N_5^- , in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ salt at ambient conditions and concluded that cyclo-N_5^- is stabilized by hydrogen bonding from adjacent H_3O^+ and NH_4^+ counterions. Encouraged by this exciting experimental achievement, various complexes and salts containing cyclo-N_5^- have been developed as new high-energy-density materials. cyclo-N_5^- can interact with metal ions (Mn^{2+} , Co^{2+} , Fe^{2+} , Mg^{2+} , Ag^+ , Na^+ , Zn^{2+} , Li^+ , and Rb^+)^{1–5,7–12} to form metal complexes, coordination polymers, and metal–organic frameworks; it can also be stabilized by nanocages ($\text{Na}_{24}\text{Si}_{30}$ and $\text{Na}_{24}\text{N}_{60}$),¹³ nanotubes (CNT),¹⁴ and organic ions.¹⁵ Moreover, new materials such as metal pentazolate frameworks¹⁶ have been theoretically predicted. It is noteworthy that very recently Yu et al. investigated the stabilities and possible formation pathways of the pentazolate anion at the B3LYP/6-311++G** and CCSD(T)/CBS levels.¹⁷ These results have been illuminating the paths of theoretical and experimental studies on pentazolate.

However, the precise characterization of cyclo-N_5^- is difficult because of the explosive hazard of the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal as the energetic material and the inability of experimental analysis to confirm the position of hydrogen atoms. Modern quantum chemical computations offer an

alternative and also are powerful tools to investigate the structures and properties of materials. In this regard, in March 2018, Huang and Xu¹⁸ challenged Zhang's structural characterization. Their density functional theory (DFT) computations and wave functional analysis based on static cluster models in the gas phase suggested that the cyclo-N_5^- anion does not exist in the synthesized crystal; instead, its neutral protonated HN_5 would be favored over the anion in the reported pentazolate salt via proton transfer. In response, Jiang et al.,¹⁹ the research team receiving the comment, insisted on the existence of cyclo-N_5^- , arguing that Huang et al.¹⁸ used an improper method to access the proton transfer in a solid crystal structure, because the result in the gas phase cannot explain the phenomenon in crystal. Moreover, Jiang et al.¹⁹ also performed the static periodic DFT calculations and liquid NMR spectroscopy to confirm the existence of cyclo-N_5^- in the crystal structure. Note that external conditions, especially temperature, could greatly influence the proton transformation in the solid, and the liquid NMR spectrum might not well explain the situation in the crystal structure. Nevertheless, the effects of temperature and solvents have not been considered by Jiang et al.¹⁹ in the above debate. To date, the controversy has not been reconciled, and

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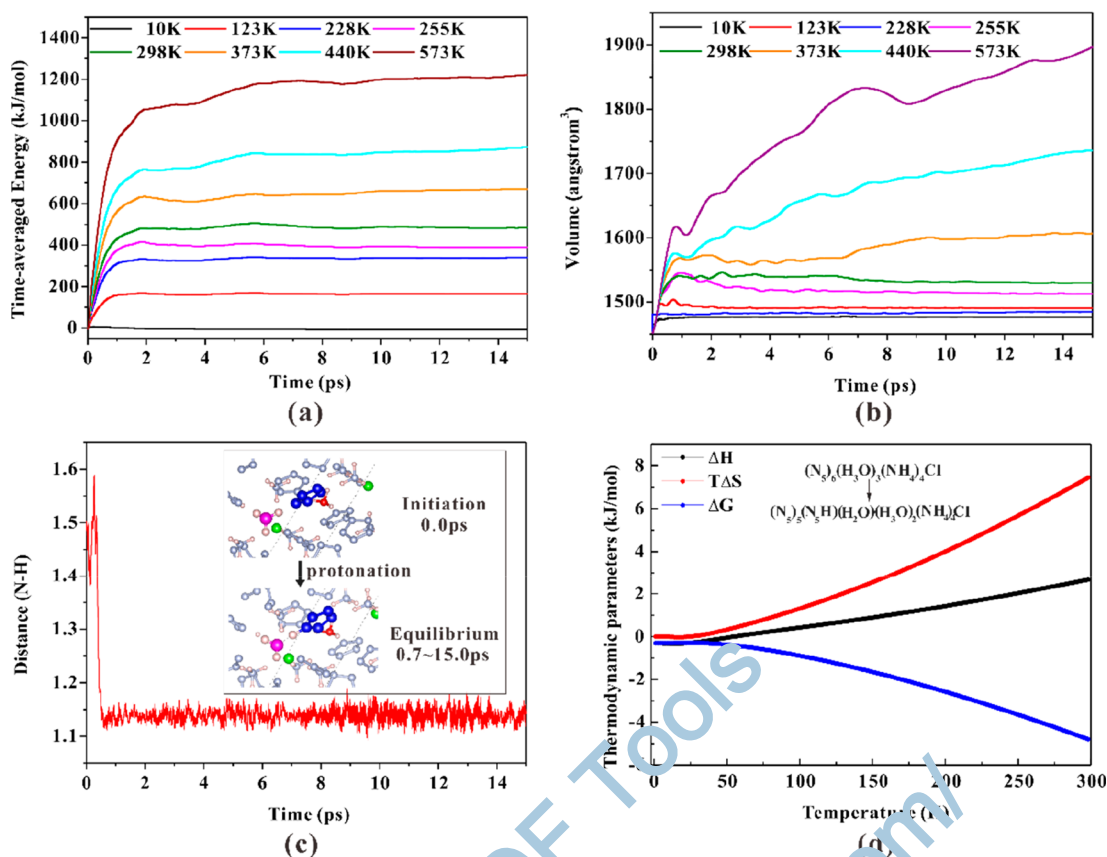


Figure 1. AIMD simulations of NPT ensemble on $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal under different temperatures (10, 123, 228, 255, 298, 373, 440, and 573 K) and 1 bar. (a) Time-averaged energy curve, (b) volume curve with timeline, (c) the protonation process from $\text{N}_5^- \cdots \text{H}_3\text{O}^+$ to $\text{N}_5\text{H} \cdots \text{H}_2\text{O}$ at 123 K, and (d) thermodynamic parameters of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl} \rightarrow (\text{N}_5)_5(\text{N}_5\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$ based on static periodic DFT calculations.

the question of whether the *cyclo*- N_5^- in the crystal structure and DMSO solvent is protonated is still open.

Ab initio molecular dynamics (AIMD) is a powerful computational technique that can better reflect dynamic behaviors at realistic experimental conditions as compared with static DFT calculations.^{20–22} Herein, to answer the titular question, we performed comprehensive AIMD simulation, which can account for temperature and solvent effect, to explore the form of *cyclo*- N_5^- in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal and DMSO solvent.

Protonated State of *cyclo*- N_5^- in Crystal. In the crystal, the initial structures and cell parameters were first optimized. Our optimized cell parameters are in good agreement with the experimental data (Table S1). The same as reported by Jiang et al.,¹⁹ we also found that the *cyclo*- N_5^- is not spontaneously protonated by H_3O^+ and NH_4^+ by static periodic DFT calculation. Starting from the optimized initial structure, the system was simulated in the NPT ensemble at a pressure of 1 bar and eight important experiment temperatures, namely, 10 K (ultralow temperature), 123 K (XRD temperature), 228 K (reaction temperature), 255 K (sample rest temperature), 298 K (room temperature), 373 K (first decomposition temperature), 440 K (second decomposition temperature), and 573 K (final decomposition temperature), for 15 ps.

When the temperature is below 298 K, as indicated by the averaged energy and volume fluctuations (Figure 1a,b), the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ system can rapidly reach an equilibrium state. The MD trajectories at 123 K (XRD temperature)

revealed that two *cyclo*- N_5^- have been protonated to HN_5 at the beginning of the simulations, as illustrated in Movie 1. In other words, the protonation of *cyclo*- N_5^- in $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ at 123 K is spontaneous (Figure 1b), which is qualitatively in agreement with Huang's conclusion obtained by using a static gas-phase cluster model¹⁷ and indicates that the extensive hydrogen-bonding interactions between the cations and anions in the crystal¹⁹ are not sufficient to retain all hydrogen atoms in H_3O^+ (see the detailed trajectory in the Supporting Information).

When the temperature reaches 298 K, the temperature effect on the proton-transfer process becomes significant: continuous proton transformation between one H_3O^+ and three *cyclo*- N_5^- can be observed (see Figure S1 and Movie 2), and the volume change of the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal is within 5.5% (Figure 1b). Further increasing the temperature resulted in the collapse of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal with over 10.7% volume expansion, in agreement with experimental observations. Note that the HN_5 can be observed at all these temperatures (see Figure S2). Note that the quantum effect and long-range correlation could influence the proton motion. To consider these effects, we performed ab initio path integral molecular dynamics (AI-PIMD) calculations at 10 K and also performed AIMD simulations using a larger simulation box (i.e., $2 \times 1 \times 1$, $1 \times 2 \times 1$, and $1 \times 1 \times 2$) at 123 K. However, our computations showed that including these factors does not have a significant effect, and our original conclusion holds true (see Figures S3 and S4, and Movie 3).

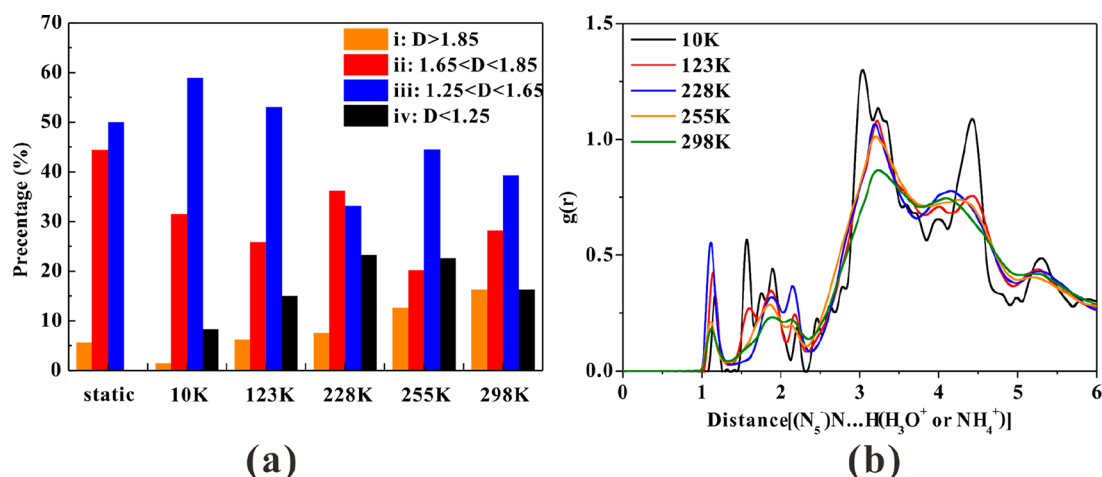


Figure 2. (a) N–H distance distributions and (b) $g(r)$ between hydrogen atoms and the nitrogen atoms of cyclo-N_5^- by AIMD simulations under NVE ensemble in the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal at different temperatures.

To investigate the temperature effect, we carried out the thermodynamic analysis of the proton-transfer process, i.e., $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl} \rightarrow (\text{N}_5)_5(\text{N}_5\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$ (Figure 1d). The instantaneous proton transfer to N_5^- found in MD simulations can be fully understood from both the negative Gibbs free-energy change (ΔG , $\Delta G = \Delta H - T\Delta S$) of this process and the very low energy barrier of 12.6 kJ/mol obtained by static computations. Notably, the ΔG value becomes more negative with increasing temperature because of the positive ΔS value. Thus, from the thermodynamic viewpoint, it is a spontaneous reaction that the proton transfers from H_3O^+ to cyclo-N_5^- to form pentazole. The thermodynamically spontaneous process and the small energy barrier (12.6 kJ/mol) for the protonation reaction, $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl} \rightarrow (\text{N}_5)_5(\text{N}_5\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$, allow the transformation between N_5 and HN_5 in the crystalline environment even under very low temperature (e.g., 10 K).

Our AIMD simulations at the NPT ensemble revealed the existence of HN_5 in the crystal. To certify the presence of HN_5 and examine the behavior and stability of HN_5 under 298 K, we further performed 30 ps AIMD simulations under NVT ensemble at the temperatures of 10, 123, 228, 255, and 298 K to equilibrate the crystal.

To examine the state of N_5^- and hydrogen bond in $\text{H}_3\text{O}^+\cdots\text{N}_5^-$, we employed the atom in molecule (AIM) method²³ to analyze the interaction between N and H using Multiwfn software.²⁴ The interaction between N and H can be divided to four categories^{25,26} (for detailed classification, see Table S2). As displayed in Figure 2a, the static results (0 K) revealed that the $(\text{N}_5^-)\cdots\text{H}(\text{H}_3\text{O}^+)$ is mainly categorized as ii and iii, e.g., the weak and medium hydrogen bonds, and protonated HN_5 does not exist, which is in agreement with Jiang et al.'s periodic DFT computations.¹⁹ With increasing temperature from 10 to 298 K, the cyclo-N_5^- species (HN_5) begins to emerge: the percentage of covalent N–H bond (iv) increases to 15.0% at 123 K, reaches a maximum value of 23.2% at 228 K, up to 22.6% at 255 K, and then declines to 16.3% at 298 K. Such increasing percentage of covalent N–H bond from 10 to 255 K can be explained by the more negative ΔG with the rising of temperature in Figure 1d, because the more negative ΔG will lead to the higher transformed tendency from N_5^- to HN_5 in the crystal.

To get a full picture of the protonation of cyclo-N_5^- , we plotted the radial distribution function $g(r)$ between nitrogen atoms of cyclo-N_5^- and all the hydrogen atoms (Figure 2b), which helps visualize the distribution of N–H distances. In general, distinct $g(r)$ peaks corresponding to the covalent N–H bond (iv: 0.95–1.25 Å) in HN_5 appear at all temperatures (Figure 2b), indicating that the protonated HN_5 is a permanent and ineradicable species under the temperatures we studied. Note that the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ salt is very similar to the substance in the lithium imide/amide systems; the possible existence of Frenkel defects could affect the protonated states of cyclo-N_5^- in the crystal because the number of groups (i.e., NH_4^+ , H_3O^+ , and Cl^-) around cyclo-N_5^- .²⁷

Protonated State of cyclo-N_5^- in Dimethyl Sulfoxide (DMSO) Solvent. Our AIMD simulations strongly confirmed the dominance of N_5^- and the existence of HN_5 in the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal under experimental conditions. Then, how about the situation in a solvent?

To address this question, we performed molecular dynamics simulations with explicit solvent models. In our model, there are 30 DMSO solvent molecules in a $15 \times 15 \times 15$ cubic box. The $\text{HN}_5\text{H}_2\text{O}$, $\text{N}_5^-\text{H}_3\text{O}^+$, and $\text{N}_5^-\text{NH}_4^+$ complexes, whose existence was revealed by our AIMD simulations in the crystal, were put separately into the solvent system. Note that DMSO solvent can easily dissolve the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal, as indicated by the very narrow ^{15}N NMR.⁶ Moreover, the $\text{N}_5/\text{H}_3\text{O}^+/\text{NH}_4^+$ fragments and DMSO solvent can form good hydrogen-bonding networks (Figure S6). Therefore, the rest of the components in the crystal can be approximately ignored in the theoretical calculations because of their insignificance and the limitation of the current computational resources. The initial structures were first simulated by 1 ns MD simulation in the NVT ensemble at 298 K based on the Dreiding force field,²⁸ i.e., MM/MD, and further optimized and dynamically simulated at the PBE-D3/DZVP level of theory.

According to our MM/MD simulations, the strong electrostatic interaction between charged species drives H_3O^+ or NH_4^+ surrounding the cyclo-N_5^- in $\text{N}_5^-\text{H}_3\text{O}^+$ and $\text{N}_5^-\text{NH}_4^+$ systems, while in the $\text{HN}_5\text{H}_2\text{O}$ system, the neutral H_2O and HN_5 interact by $(\text{H}_2\text{O})\cdots\text{H}(\text{HN}_5)$ hydrogen bonding. Note that the $\text{N}_5^-\text{H}_3\text{O}^+$ complex can adopt two different configurations: In the first configuration, denoted as

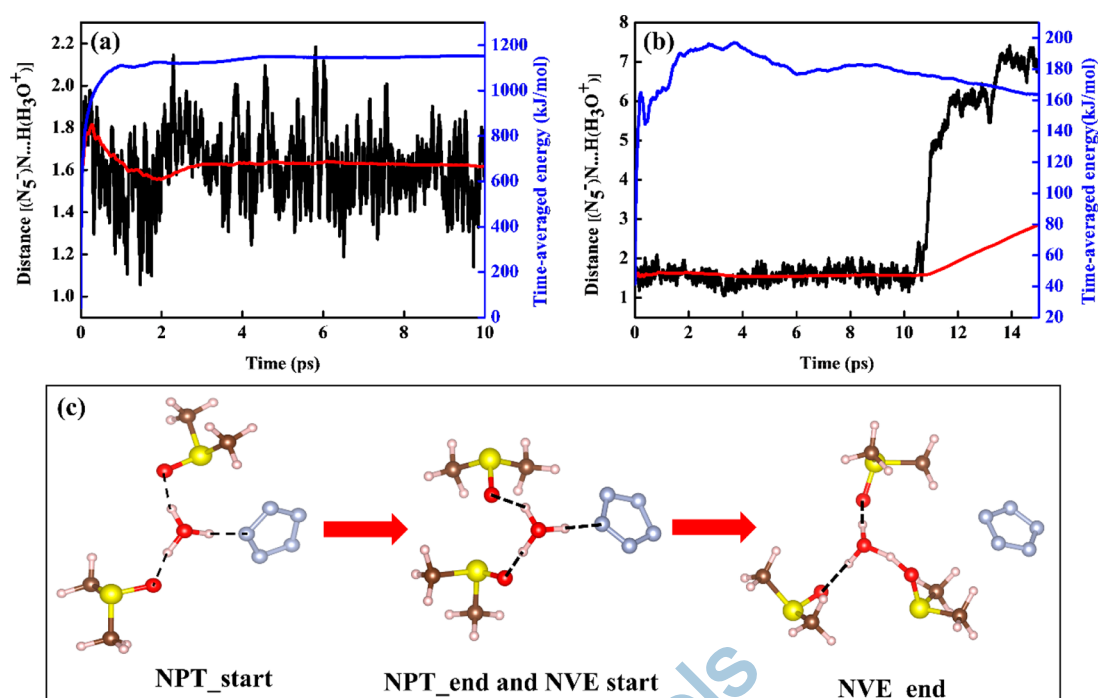


Figure 3. Time-averaged energy (blue) and $[(N_5^-)N \cdots H(H_3O^+)]$ distances (black: instantaneous values, red: time-averaged values) of $N_5^- \cdots H_3O^+$ complexes in (a) *NPT* and (b) subsequent *NVE* ensembles with 30 DMSO molecules by AIMD simulations, (c) snapshots of configurations at the start and end of simulations in *NPT* and *NVE* ensembles, the black dashed lines are hydrogen bonds. (other DMSO molecules are not shown for clarity).

$N_5^- \cdots H_3O^+$, H_3O^+ interacts with *cyclo*- N_5^- by hydrogen bonding. In the second configuration, denoted as $N_5^- \cdots OH_3^+$, H_3O^+ is tightly captured by three DMSO molecules via $(H_3O^+)H \cdots O(DMSO)$ hydrogen bond interactions; consequently, the *cyclo*- N_5^- could interact only with the C atom of H_3O^+ , rather than H atoms. Thus, four systems containing these complexes, namely, $N_5^- \cdots H_3O^+$, $N_5^- \cdots OH_3^+$, $N_5^- \cdots H_3O^+$, and $N_5^- \cdots NH_4^+$ (detailed structure of these four initial structures are provided in Figure S6) were subsequently investigated by the precise AIMD simulations in the *NPT* ensemble.

The system initially containing the $N_5^- \cdots H_3O^+$ complex can quickly reach equilibrium at 298 K (Figure 3a), and the curve of $[(N_5^-)N \cdots H(H_3O^+)]$ distance reveals that the interactions are mostly strong hydrogen bonding, with only a few N–H covalent bonding (with N–H distances < 1.25 Å). However, the stability of this hydrogen bond-containing system is rather low, as revealed by our subsequent 15 ps *NVE* simulations. This hydrogen bond can remain stable for only ~ 10 ps and finally breaks with obvious energy increase (Figure 3b), leaving one hydrogen of H_3O^+ taken away by DMSO (Figure 3c; see Movie 4 for details). Similarly, for the system initially containing the $N_5^- \cdots OH_3^+$ complex, the *cyclo*- N_5^- cannot take hydrogen away from the H_3O^+ , which is hydrogen bonded with DMSO, as seen from the snapshots in Figure 4 and the over 6 Å N–O distance in Figure S4. Thus, because of the strong ability of DMSO to capture H_3O^+ , the chance for *cyclo*- N_5^- to interact with H_3O^+ to form either $N_5^- \cdots H_3O^+$ or $N_5^- \cdots OH_3^+$ complexes is rather slim.

Can the HN_5 originally existing in the $(N_5)_6(H_3O)_3(NH_4)_4Cl$ crystal preserve its protonated form in DMSO solution? Our AIMD simulations on the $HN_5 \cdots H_2O$ system in the *NPT* ensemble revealed that the covalent N–H bond quickly breaks; the lost H first forms a hydrogen bond

$[(N_5^-)N \cdots H(H_3O^+)]$ with H_3O^+ ; finally this hydrogen bond is broken by the effect of temperature, and *cyclo*- N_5^- departs from H_3O^+ similar to what occurs in $N_5^- \cdots H_3O^+$ and $N_5^- \cdots OH_3^+$ systems (Figure 4).

We also examined the possibility for the $N_5^- \cdots NH_4^+$ complex. Note that Jiang et al.¹⁹ pointed out that the NH_3 molecule has a stronger proton affinity than H_2O , indicating the higher difficulty for *cyclo*- N_5^- to be protonated by NH_4^+ . This expectation was confirmed by AIMD simulations: the N_5^- and NH_4^+ units separate from each other along the simulations (Figures 4 and S5).

Our AIMD simulations showed that *cyclo*- N_5^- can be protonated in the crystal, but it preserves the free anion form in the DMSO solvent; in other words, there is *cyclo*- N_5^- of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ in DMSO solution (Table 1). Why can the *cyclo*- N_5^- not be protonated by H_3O^+ or NH_4^+ in the DMSO environment? To gain further insights into the different behavior in the crystal and solvent, we calculated the proton affinities (PAs) in both the gas phase and DMSO solvent (Table 2; see Supporting Information for details).

Our used theoretical levels (M06-2X-D3 and PBE-D3) can reproduce the experimental PA values for NH_3 , H_2O , and DMSO in the gas phase (the error between experiment and calculation is less than 9 kJ/mol) and are expected to well predict PA values of other related systems in this work. *cyclo*- N_5^- (PA = 1332.8 kJ/mol) has a much higher PA than H_2O (691.9 kJ/mol) and NH_3 (845.0 kJ/mol at M06-2X-D3 level of theory), which can explain qualitatively the protonated HN_5 in the isolated gas-phase $H_3O^+ \cdots N_5^-$ complex model reported by Huang et al.¹⁸ and the appearance of HN_5 in $(N_5)_6(H_3O)_3(NH_4)_4Cl$ crystal revealed by our AIMD simulations. Note that proton affinity is a reliable parameter to determine the basicity of a neutral atom or molecule or an anion in the free state. However, the PA computations can

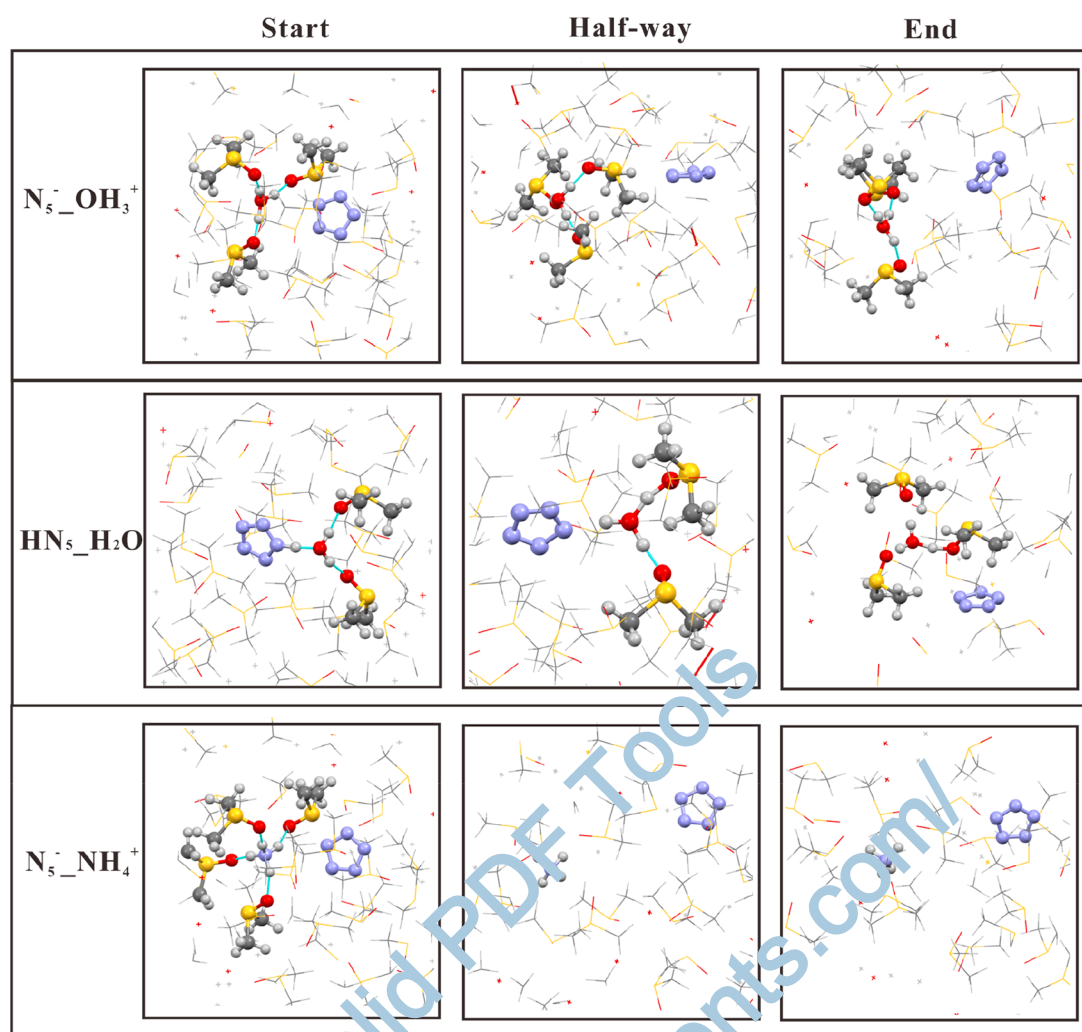


Figure 4. Snapshots of $N_5^-OH_3^+$, $HN_5^-H_2O$, and $N_5^-NH_4^+$ systems in NPT ensemble at 298 K. The hydrogen bonds are denoted by cyan lines.

Table 1. Summary of Protonated State in Different Systems in DMSO Solvent after AIMD Simulations at 298 K in NPT and the Subsequent NVE Ensembles

system	Initial interaction ^a	NPT ^b	NVE ^c
$N_5^-H_3O^+$	H-bonding	a few protonations, mostly H bonding	no protonation
$N_5^-OH_3^+$	van der Waals interaction	no protonation	protonation
$HN_5^-H_2O$	covalent bond	a few protonations, mostly H bonding	no protonation
$N_5^-NH_4^+$	van der Waals interaction	no protonation	no protonation

^aThe initial interaction between nitrogen of *cyclo*- N_5^- and hydrogen of H_3O^+ or NH_4^+ . ^bThe protonated state of *cyclo*- N_5^- .

provide only a qualitative order for the relative basicity of H_2O , NH_3 , and N_5^- but cannot give a quantitative result because the charge of N_5^- anion is not exactly -1 in the crystalline environment. Thus, to quantitatively describe the proton transfer in crystal, we provided the thermodynamic data (enthalpies, entropies, and Gibbs free energies) under the crystalline environment (Figure 1d). The narrow range of ΔH (-0.31 to 2.66 kJ/mol) and the negative ΔG values are attributed to the proton transfer in the crystal.

Because the PA values in the gas phase might differ significantly from those in the liquid phase because of the solvent effect, we computed their PA values in the solvent using both the implicit SMD solvation model and the explicit model.²⁹ This implicit model can increase the PA values of NH_3 , H_2O , and DMSO (by ca. 230–370 kJ/mol), while it decreases the PA value of *cyclo*- N_5^- by ca. 210 kJ/mol, consequently reducing the PA difference between H_2O and *cyclo*- N_5^- from ca. 640 kJ/mol in the gas phase to ca. 64 kJ/mol in the solvent at the M06-2X-D3 level of theory (Table 2). To deeply investigate the influence of the realistic hydrogen-bonding interactions between the solvent (DMSO) and solutes (NH_3 , NH_4^+ , H_2O , and H_3O^+),³⁰ besides the empirical implicit solvation model, we also calculated the PA values of H_2O and NH_3 combined with different numbers ($n = 1-3$) of DMSO solvent molecules to approach the explicit solvent model as much as possible. As the number of DMSO molecules increase, the PA values of both H_2O and NH_3 increase, confirming that the DMSO solvent can increase the PA of H_2O and NH_3 , as found in the implicit solvent model. Thus, the solvent effect of DMSO is responsible for the greatly reduced PA differences among *cyclo*- N_5^- , H_2O , NH_3 , and DMSO species.

More specifically, for the $N_5^-H_3O^+$ complex, the minimum on the potential energy surface (PES) along the $(N_5^-)N \cdots H(H_3O^+)$ distance in the gas phase significantly differs from

Table 2. Proton Affinity (kJ/mol) of *cyclo*-N₅[−], H₂O, NH₃, and DMSO Calculated in the Gas Phase and in the Solvent Using Implicit SMD and Explicit Solvent Models^a

species	gas phase		implicit solvent	number of DMSO in explicit model ^c		
	exptl ^b	calc ^c	calc ^c	1	2	3
<i>cyclo</i> -N ₅ [−]		1332.8/1351.1	1124.3/1140.6			
H ₂ O	691.0	691.9/696.9	1060.0/1068.2	947.3/946.3	1014.2/1021.2	
NH ₃	853.6	845.0/854.1	1175.3/1185.1	992.4/999.2	1049.0/1063.3	1083.4/1090.1
DMSO	884.4	886.6/880.4	1109.9/1110.1			

^aThe number of DMSO molecules in the explicit model ($n = 1-3$) of DMSO is also given. ^bExperimental values reported by Hunter et al.³¹

^cCalculated values at the M06-2X-D3 (in roman type) and PBE-D3 (in bold) levels of theory.

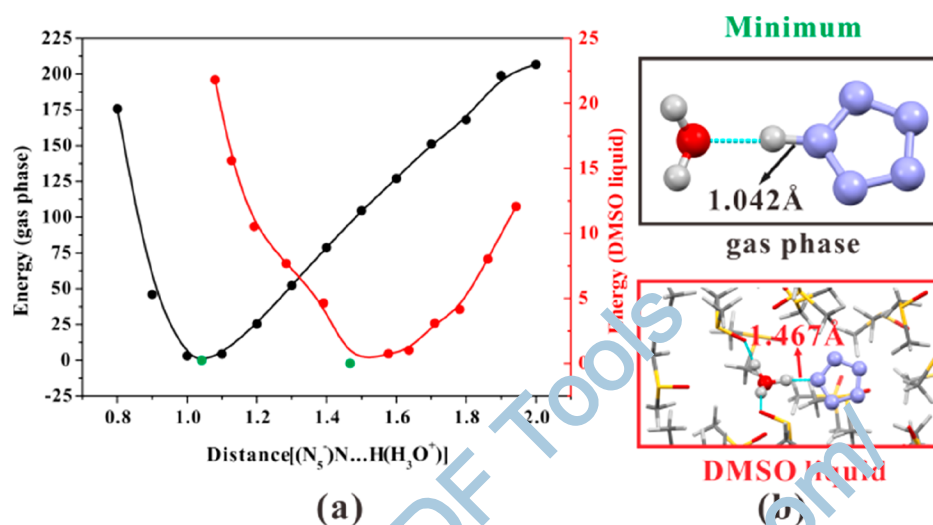


Figure 5. (a) Potential energy surface curve along the direction of (N₅[−])N...H(H₃O⁺) distance in the N₅[−]-H₃O⁺ system in the gas phase (black) and DMSO liquid (red); (b) minimum energy structures (hydrogen bonds are denoted by dashed lines) (unit: kJ/mol).

that in DMSO solvent: in the gas phase, there is a 1.042 Å covalent N–H bond as the minimum, whereas in the DMSO solvent, the minimum with 1.467 Å distance of (N₅[−])N...H(H₃O⁺) (explicit solvent model) indicates a hydrogen bond (Figure 5). Moreover, this potential energy curve also reveals that the deprotonated process of HN₅ in DMSO solvent is much easier than that in the gas phase. Very similar behavior was also observed for the N₅[−]-NH₄⁺ system (Figure S6). These phenomena are attributed to the solvent effect: in the DMSO solvent, the PA differences between *cyclo*-N₅[−] and H₂O, NH₃, and DMSO species are significantly reduced. Thus, the proton transfer from H₃O⁺ and NH₄⁺ to *cyclo*-N₅[−] does not occur, or the formed hydrogen bond cannot persist upon temperature increase (as seen in the case of the N₅[−]-H₃O⁺ system in Figure 3).

In summary, to understand and potentially reconcile the recent controversy about the protonated state of *cyclo*-N₅[−], we performed AIMD simulations that can better model the realistic conditions of (N₅)₆(H₃O)₃(NH₄)₄Cl in the crystalline environment and DMSO solvent. The presence of the *cyclo*-N₅[−] differs significantly in the crystal and liquid states. In (N₅)₆(H₃O)₃(NH₄)₄Cl crystal, because of the synergistic interactions between the thermodynamically favored proton transfer and the temperature effect, the dominant unprotonated *cyclo*-N₅[−] coexists with its protonated N₅H even at the super low temperature of 10 K; the protonated HN₅ has 15% at 123 K and can reach a maximum percentage of 23.2% at 228 K. In contrast, in the DMSO solvent, the solvent effect significantly narrows the proton affinity difference between *cyclo*-N₅[−] and H₂O (or NH₃), and the temperature effect

further drives the existence of only unprotonated *cyclo*-N₅[−], which was unambiguously identified by the single ¹⁵N peak in the liquid NMR experiment. Our AIMD simulations not only reconcile the recent controversy but also call for more attention to considering external conditions, such as temperature and solvent, for structural elucidations and property studies in both experimental and theoretical investigations.

COMPUTATIONAL METHODS

CP2K software³² was employed to explore the dynamic behavior of (N₅)₆(H₃O)₃(NH₄)₄Cl in solid and liquid states. All the density functional theory computations were carried out using the PBE-D3 method.^{33,34} For (N₅)₆(H₃O)₃(NH₄)₄Cl in the solid state, the triple-ζ valence plus polarization (TZVP) basis set³⁵ and the Goedecker–Teter–Hutter (GTH) pseudopotentials^{36,37} were used, while the smaller basis set, namely, double-ζ valence plus polarization (DZVP),³⁵ was used for the much larger liquid systems, which contain 30 DMSO molecules and four complexes (N₅[−]-H₃O⁺, N₅[−]-OH₃⁺, HN₅-H₂O, and N₅[−]-NH₄⁺) within a 15 × 15 × 15 cubic box. During the SCF procedure, a 360 Ry density CUTOFF criterion with the finest grid level was employed, together with multigrids number 4 (NGRID 4 and REL CUTOFF 70).

The time steps in liquid and solid states were both set to 1 fs. In the solid, (N₅)₆(H₃O)₃(NH₄)₄Cl was simulated in the 15 ps NPT ensemble (constant temperature and pressure using a flexible cell) at temperatures of 10, 123, 228, 255, 298, 373, 440, and 573 K, which rely on a canonical sampling through

velocity rescaling (CSVR) thermostat³⁸ with a time constant of 100 fs to ensure fast thermal equilibration; afterward, 30 ps MD simulations of the NVE ensemble at several temperatures (10, 123, 228, 255, and 298 K) were used to count the percentage of HN_5 . The quantum effects could influence the proton motion, especially at ultralow temperature, and the ab initio path integral molecular dynamics (AI-PIMD) was employed to consider the quantum effects at 10 K. In liquid systems, $\text{N}_5^- \text{H}_3\text{O}^+$, $\text{N}_5^- \text{OH}_3^+$, $\text{HN}_5 \text{H}_2\text{O}$, and $\text{N}_5^- \text{NH}_4^+$ complexes in DMSO environment were performed starting with a 10 ps equilibration run to initialize the systems, followed by the production run of 15 ps to obtain a sufficient sampling of the phase space.

To obtain the energy barrier of the proton transfer in the solid, i.e., the process of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl} \rightarrow (\text{N}_5)_5(\text{N}_5\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$, the transition state was optimized by the Dimer method.³⁹ On the basis of the optimized structures and frequencies of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ and $(\text{N}_5)_5(\text{N}_5\text{H})(\text{H}_2\text{O})(\text{H}_3\text{O})_2(\text{NH}_4)_4\text{Cl}$, the thermodynamic analysis of this process was carried out by TAMkin software.⁴⁰

The proton affinity calculations were performed at the PBE³³ and M06-2X⁴¹ level of theory with consideration of Grimme's dispersion correction (DFT-D3)³⁴ using Dunning basis sets cc-PVTZ.^{42,43} The PA values in the gas phase were directly calculated according to the equation

$$\text{PA}(\text{gas}) = E(\text{X}) - E(\text{HX}^+)$$

$$(\text{X} = \text{N}_5^-, \text{H}_2\text{O}, \text{NH}_3, \text{ and DMSO})$$

In liquid, the implicit solvent model, SMD,⁴⁴ was used to describe the species, and the corresponding PA values were calculated following the equation

$$\text{PA}(\text{liquid}) = E(\text{X_SMD}) - E(\text{HX}^+ \text{_SMD})$$

$$(\text{X} = \text{N}_5^-, \text{H}_2\text{O}, \text{NH}_3, \text{ and DMSO})$$

where $E(\text{X_SMD})$ and $E(\text{HX}^+ \text{_SMD})$ are the total energies of X and HX^+ in the SMD solvent model, respectively.

Moreover, different numbers of DMSO molecules combined with H_2O and NH_3 were used to realize the explicit solvent model as much as possible, and the PA equation can be written as

$$\text{PA}(\text{liquid}) = E(\text{X_nDMSO}) - E(\text{HX}^+ \text{_nDMSO})$$

$$(\text{X} = \text{H}_2\text{O} \text{ and } \text{NH}_3; n = 1-3)$$

where $E(\text{X_nDMSO})$ and $E(\text{HX}^+ \text{_nDMSO})$ are the total energies of X and HX^+ , respectively, combined with different numbers (n) of DMSO molecules. All these PA calculations were performed using Gaussian 09 (version B.01).⁴⁵

Similar to the PA calculations, the potential energy surface (PES) was scanned along the direction of N–H bond in $\text{N}_5^- \text{H}_3\text{O}^+$ and $\text{N}_5^- \text{NH}_4^+$ complexes under three conditions, i.e., gas phase, implicit solvent model (SMD), and explicit solvent model. The first two conditions can be easily carried out by Gaussian 09,⁴⁵ and the explicit solvent model was represented by 30 DMSO molecules in a $15 \times 15 \times 15$ box via VASP code.⁴⁶ To realize the PES scan in the explicit solvent model, $\text{N}_5^- \text{H}_3\text{O}^+$ and $\text{N}_5^- \text{NH}_4^+$ complexes were first optimized to minima without any constraints in DMSO solution. Subsequently, a series of structures with N–H distance ranging from 0.8 to 2.0 Å were optimized. During the

optimization, the N–H distance was fixed by freezing N and H atoms, but other atoms were relaxed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b02841.

Additional calculation details and results (PDF)

Movie 1: Trajectory for the proton transfer between H_3O^+ and *cyclo*- N_5^- in the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal at 123 K (XRD temperature) and 1 bar (MPG)

Movie 2: Trajectory for the proton transfer between H_3O^+ and *cyclo*- N_5^- in the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal at 298 K (room temperature) and 1 bar (MPG)

Movie 3: Trajectory for the proton transfer between H_3O^+ and *cyclo*- N_5^- in the $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ crystal at 10 K (super low temperature) and 1 bar (MPG)

Movie 4: Trajectory for the $\text{HN}_5 \text{H}_2\text{O}$ complex in DMSO solvent at 298 K (room temperature) and 1 bar (MPG)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhenganm@wipm.ac.cn

*E-mail: zhongfangchen@163.com

ORCID

Zhiqiang Liu: 0000-0003-2872-0125

Yinghe Zhao: 0000-0002-2331-8973

Zhongfang Chen: 0000-0002-1445-9184

Anmin Feng: 0000-0001-7115-6510

Notes

The authors declare no competing financial interest.

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