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Research paper Direct formation of [NH₄]N₃ from a pentazolate salt through single-crystal to single-crystal transformation



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1. Introduction

Polynitrogen ions (N_n , $n \ge 3$), as the potential top performer of high energy density materials, have become the focus of intensive research efforts by chemists due to their desirable attributes of fast energy release and eco-friendly detonation products [1–4]. Azide anion (N_3) is the first-known stable polynitrogen anion, which has a linear and symmetrical arrangement of three nitrogen atoms [5]. Ammonium azide ([NH₄]N₃) has been called one of the most remarkable azides on the basis of its high nitrogen content of 93.3%. Upon full decomposition, it is expected to give only environmentally friendly products. Over the past decades, considerable efforts have been devoted to the study of the structure of [NH₄] N₃ and its application in energetic material formulations [6–8]. Recently, increasing interest focused on its properties under high pressure, which are critical for the synthesis of polymeric nitrogen compounds from [NH₄]N₃ [9,10]. Furthermore, it has been predicted that [NH₄]N₃ can undergo a pressure-induced phase transition at 36 GPa to a hydronitrogen solid of $(NH)_4$ [11,12]. Although considerable studies have been carried out for [NH₄]N₃, many fundamental aspects of [NH₄]N₃ are still not well-understood because of its complex chemical behaviors.

The general methods for the preparation of ammonium azide rely on metathesis reactions between NaN_3 and $[NH_4]NO_3$ or

ABSTRACT

In the area of polynitrogen anions, the only stable species synthesized as yet are the azide anion (N_3^-) and the pentazolate anion (cyclo- N_5^-). We here describe an unprecedented example of a spontaneous single-crystal to single-crystal transformation from the pentazolate salt $[NH_4]_4[H_3O]_3(N_5)_6Cl$ to the known $[NH_4]N_3$ with concomitant release of N_2 and H_2O , which involves the cleavage of N–N bonds and a change in space group. This transformation is helpful for the understanding of the relationship between the long-known N_3^- and the recently synthesized cyclo- N_5^- polynitrogen anions.

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between HN₃ and [NH₄]OH [13,14]. In these methods, the special chemical properties of the raw materials have the potential to pose a threat to personal safety. Little information in synthesizing [NH₄] N₃ by other methods is available. Herein, a direct formation of [NH₄]N₃ via release of nitrogen molecules was found in the pentazolate salt, $[NH_4]_4[H_3O]_3(N_5)_6CI$.

2. Experiment section

2.1. Materials and chemicals

All reagents and solvents used were analytical grade without further purification obtained commercially and used as received.

2.2. Preparation of crystal [NH₄]₄[H₃O]₃(N₅)₆Cl

The $[NH_4]_4[H_3O]_3(N_5)_6Cl$ salt was synthesized according to the published procedures [15]. Colorless crystals were grown by dissolving the solid in a minimum amount of the mixed solution of ethanol and ethyl acetate held at -18 °C for two weeks. After filtration, the solid crystals were washed with ethyl acetate and collected.

2.3. Preparation of crystal [NH₄]N₃

 $[\rm NH_4]_4[\rm H_3O]_3(\rm N_5)_6Cl$ has a high lever solubility in polar solvents, including water, methanol, and acetonitrile, while is insoluble in

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solvents such as ethyl acetate and tetrahydrofuran. Interestingly, after the crystals were suspended in a small quantity of ethyl acetate and placed at 30 °C, the $[NH_4]_4[H_3O]_3(N_5)_6Cl$ salt gradually transformed into crystals $[NH_4]N_3$ over the course of two months.

3. Results and discussion

In 2017, we reported the unprecedented synthesis and characterization of the cyclo- N_5^- anion salt with the molecular formula of $[NH_4]_4[H_3O]_3(N_5)_6Cl$ [15]. Although cyclo-N₅⁻ anion was prepared at low temperature by the rupture of the C–N bond in 3,5dimethyl-4-hydroxyphenylpentazole (HPP) through treatment with m-chloroperbenzoic acid (m-CPBA) and ferrous bisglycinate $[Fe(Gly)_2]$, the salt was proved to be stable up to 117 °C through TGA analysis. Determined by single-crystal X-ray diffraction, the unit-cell of $[NH_4]_4[H_3O]_3(N_5)_6Cl$ is built by the stacking of closepacked layers of the cyclo-N₅⁻ anion and NH₄⁺, H₃O⁺ cations (Supporting Information, Figure S1). Interestingly, the block crystals of [NH₄]₄[H₃O]₃(N₅)₆Cl stored in ethyl acetate at 30 °C slowly transformed into crystals of $[NH_4]N_3$ over the course of two months (Scheme 1 and Fig. 1). From the mother liquid, ammonium chloride was identified as the other product (Supporting Information, Figure S2). This SCSC transformation of polynitrogen anions is accompanied by a large amount of energy release, resulting in direct change from $[NH_4]_4[H_3O]_3(N_5)_6Cl$ to $[NH_4]N_3$ [16]. As shown in Fig. 2, [NH₄]N₃ crystallized in the orthorhombic space group Pmna with a cell volume of 289.49(18) Å³. Relevant crystal data and refinement results are summarized in Table S1. Selected bond lengths and angles are listed in Table S2 and Table S3, and the data of hydrogen bonding are listed in Table S4. In contrast to the structure of $[NH_4]_4[H_3O]_3(N_5)_6Cl$, the unit-cell volume decreases by 95%, owing to the release of nitrogen and water molecules involving the structure change. The azide groups N(2)-N(3)-N(2)ⁱⁱ and N(4)-N(5)- $N(4)^{iii}$ are aligned along *a* axis and parallel to the plane (010), respectively. These distances between nitrogens in [NH₄]N₃ (1.180 and 1.178 Å) are shorter than the normal N=N double bond lengths (NH=NH, 1.252 Å) and longer than the bond length in free N_2 (N=N, 1.100 Å) [17,18] indicating the partial double-bond character for the N–N bonds. The average N–N bond length in [NH₄]N₃ crystal is 1.179 Å, which is much shorter than that of 1.315 Å in cyclo- N_5^- , suggesting that the superior stability for N_3^- is a wellfounded estimate compared to cyclo-N₅⁻. It is also in accordance with the prediction of the *ab initio* calculations that $cyclo-N_{5}^{-}$ is less stable than the N_3+N_2 fragments [19].

As found in the crystal of $[NH_4]_4[H_3O]_3(N_5)_6Cl$, hydrogen bonding plays a dominant role in strengthening the stability of cyclo-N₅⁻. The hydrogen bonding in $[NH_4]N_3$ are shown in Fig. 3. A perspective view of the unit cell shows that the azide anions and ammonium cations are broadly organized into two principal parallel layers, but half of the anions deviate out of the vertical plane allowing hydrogen to bond between the NH⁴₄ cation and the negative termini of the N₃⁻ ions. Fig. 3b indicates that each NH⁴₄ cation is surrounded by four N₃⁻ anions at approximately tetrahedral angles via the hydrogen bonding linkages, and each ammonium group consists of a pair H1A and a pair H1B both located at the identical Wyckoff position 8*i*, which are capable of engaging in hydrogen bonding with N2 and N4 in N₃⁻, respectively. By comparing the hydrogen bond N4-H4A···N2 (2.912 Å) in $[NH_4]_4[H_3O]_3(N_5)_6Cl$ with the corresponding N1-H1A···N2(2.103 Å) and N1-H1B···N4 (2.060



Fig. 1. The route of single-crystal transformation and optical microscopic photographs of (a) one single crystal of $[NH_4]_4[H_3O]_3(N_5)_6Cl$ and (b) one single crystal of $[NH_4]N_3$.



Fig. 2. X-ray crystallographic structure. (a) Ellipsoid plot of $[NH_4]N_3$ at 50% probability level, the occupancies of NH_4^+ , N_3^- are 1/2, 1/4, respectively. Symmetry codes: (i) 1.5-x, y, 0.5-z; (ii) 1-x, 1-y, 1-z; (iii) x, 1-y, z. (b) A packing diagram for $[NH_4]N_3$ along [1 1 1]plane.

Å) in $[NH_4]N_3$, a noticeable decrease, about 28%, is found in the length of hydrogen bonds during crystal transformation from $[NH_4]_4[H_3O]_3(N_5)_6Cl$ to $[NH_4]N_3$. Generally, the strength of a hydrogen bond depends almost linearly on its length [20]; It can be seen that the observed N4-H4A...N2 bond angle is 171° while the N1-H1A...N2 and N1-H1B...N4 bond angles are approximately 175° and 178°, respectively. They are all nearly linear in the case of ignoring the small deviations (less than 10°). As a consequence, the parameters of hydrogen bonds in $[NH_4]N_3$ crystal are indicative of stronger hydrogen bonds as compared to the hydrogen bond strength in $[NH_4]_4[H_3O]_3(N_5)_6Cl$.



Scheme 1. The decomposition product of the block crystals of [NH₄]₄[H₃O]₃(N₅)₆Cl.



Fig. 3. Schematic representation of the hydrogen-bonding in $[NH_4]N_3$. (a) Hydrogen-bonding around the NH_4^* cation, Symmetry codes: (i) 1.5-x, y, 0.5-z; (ii) 1.5-x, 1-y, -0.5 + z; (iii) 0.5 + x, y, 0.5-z; (iv) 1.5-x, 2-y, 0.5 + z; (v) 1.5-x, 1 + y, 0.5-z; (vi) x, 1-y, 1-z; (vii) 1.5-x, 1-y, 0.5 + z; (viii) 1-x, 1-y, 1-z; (ix) 1-x, y, z; (x) -0.5 + x, y, 0.5-z; (xi) x, 1 + y, z; (xii) x, 2-y, -z; (xiii) 1.5-x, 3-y, -0.5 + z; (vii) -0.5 + x, 3-y, -0.5 + z; (x) 1-x, 3-y, -z; (b) a view of packing along c axis.

In order to observe the NMR spectrum changes of crystal transformation, we heated a batch of ¹⁵N-labeled single crystal of $[NH_4]_4[H_3O]_3(N_5)_6Cl$ at 40 °C for 4 h under vacuum. The utilization of ¹⁵N-labeled cyclo- N_{5}^{-} ensured that the weak ¹⁵N signal of N_{3}^{-} came from the crystal transformation could be normally observed at natural abundance. The heat treatment process resulted in a new hybrid crystal that was dissolved in dimethyl sulfoxide (DMSO)-d₆ solvent and measured by ¹⁵N nuclear magnetic resonance (NMR) with CH₃NO₂ (¹⁵N) as an external standard. The results of chemical shift are shown in Fig. 4. By comparison with $[NH_4]_4[H_3O]_3(N_5)_6Cl$, a new signal appeared at -133.54 ppm in different runs and could be attributed to N_{3} , which is in excellent agreement with the value observed in ¹⁵N -labeled NaN₃ [21]. Consequently, by analogy with other SCSC transformation process, such as guest exchange, ligand exchange and thermally induced rearrangement reactions [22-25], it can be inferred that the process of obtaining [NH₄]N₃ crystal from the [NH₄]₄[H₃O]₃(N₅)₆Cl crystal should be rather slow.



Fig. 4. The ^{15}N NMR spectrum of crystal before and after heating at 40 °C for 4 h under vacuum.



Fig. 5. IR spectra of solid [NH₄]₄[H₃O]₃(N₅)₆Cl after heating at from 40 to 160 °C.

To study and monitor structure transformation on powder samples of $[NH_4]_4[H_3O]_3(N_5)_6Cl$, we also made an attempt to heat the solid [NH₄]₄[H₃O]₃(N₅)₆Cl under nitrogen from 40 to 160 °C (Caution! explosion at higher temperatures), and then the samples obtained above were characterized by infrared spectrometer. As displayed in Fig. 5, after complex [NH₄]₄[H₃O]₃(N₅)₆Cl was heated at 40, 60, 80, 100, 120, 140 and 160 °C for 4 h, respectively. The signal for cyclo-N₅ gradually became weak and eventually vanished but the signal at about 2100 cm⁻¹ became increasingly prominent. Significant transformation of N₅ occurred at 120 °C, and by comparison with the peaks, it could be deducted that the transformation process on powder samples of [NH₄]₄[H₃O]₃(N₅)₆Cl was at relatively slow speed, but could be facilitated via heating. In particular, it was worth mentioning that no melting process occurred even though [NH₄]₄[H₃O]₃(N₅)₆Cl was heated at 160 °C, accompanied by a color change from white to gray, suggesting that the compound may be undergoing strong reactions upon heating. Additionally, the signals of IR spectrum for products obtained at 160 °C were assigned comprehensively, which demonstrated the formation of impure [NH₄]N₃ phase. A low-frequency mode located at 638 cm⁻¹ was assigned as a N₃ bending mode, correspondingly, the intense band at 2109 cm^{-1} is clearly associated with the asymmetrical stretching motion of N_3 [26], The other peaks at 1405 cm⁻¹ and 1666 cm⁻¹, were assigned as the H–N–H bending motions (NH_4^+) . However, the stretching motions of NH_4^+ located at the 3000–3200 cm⁻¹, could not be observed in our measured spectrum. The absorption at 3390 cm⁻¹ was assigned as the N=N=N symmetric stretch and N=N=N bending, which is in excellent agreement with the previous study [27].

4. Conclusion

In conclusion, it is demonstrated that the $[NH_4]N_3$ crystal can be obtained from the pentazolate salt $[NH_4]_4[H_3O]_3(N_5)_6Cl$ via the inreversible single-crystal-to-single-crystal transformation, which is different from the general metathesis reactions. This surprising finding would further advance our understanding on the relationship of polynitrogen anions between the long-known stable polynitrogen anion N_3^- and the recently synthesized cyclo- N_5^- .

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ica.2018.02.001.

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