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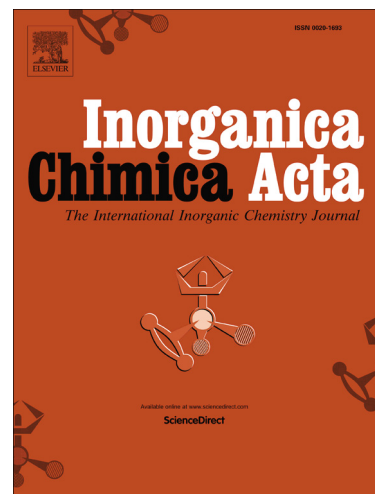
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Direct formation of $[\text{NH}_4]\text{N}_3$ from a pentazolate salt through single-crystal to single-crystal transformation

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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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ to the known $[\text{NH}_4]\text{N}_3$ 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.

Keywords: azide anion; characterization; crystal structure; pentazolate anion; transformation

1. Introduction

Polynitrogen ions (N_n , $n \geq 3$), 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 ($[\text{NH}_4]\text{N}_3$) 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 $[\text{NH}_4]\text{N}_3$ 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 $[\text{NH}_4]\text{N}_3$ [9, 10]. Furthermore, it has been predicted that $[\text{NH}_4]\text{N}_3$ can undergo a pressure-induced phase transition at 36 GPa to a hydronitrogen solid of $(\text{NH})_4$ [11, 12]. Although considerable studies have been carried out for $[\text{NH}_4]\text{N}_3$, many fundamental aspects of $[\text{NH}_4]\text{N}_3$ 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 $[\text{NH}_4]\text{NO}_3$ or between HN_3 and $[\text{NH}_4]\text{OH}$ [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 $[\text{NH}_4]\text{N}_3$ by other methods is available. Herein, a direct formation of $[\text{NH}_4]\text{N}_3$ via release of nitrogen molecules was found in the pentazolate salt, $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$.

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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$

The $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ 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 $-18\text{ }^{\circ}\text{C}$ for two weeks. After filtration, the solid crystals were washed with ethyl acetate and collected.

2.3 Preparation of crystal $[\text{NH}_4]\text{N}_3$

$[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ has a high level solubility in polar solvents, including water, methanol, and acetonitrile, while is insoluble in solvents such as ethyl acetate and tetrahydrofuran. Interestingly, after the crystals were suspended in a small quantity of ethyl acetate and placed at $30\text{ }^{\circ}\text{C}$, the $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ salt gradually transformed into crystals $[\text{NH}_4]\text{N}_3$ 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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ [15]. Although *cyclo*- N_5^- anion was prepared at low temperature by the rupture of the C–N bond in 3,5-dimethyl-4-hydroxyphenylpentazole (HPP) through treatment with m-chloroperbenzoic acid (m-CPBA) and ferrous bisglycinate $[\text{Fe}(\text{Gly})_2]$, the salt was proved to be stable up to $117\text{ }^{\circ}\text{C}$ through TGA analysis. Determined by single-crystal X-ray diffraction, the unit-cell of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ is built by the stacking of close-packed layers of the *cyclo*- N_5^- anion and NH_4^+ , H_3O^+ cations (Supporting Information, Figure S1). Interestingly, the block crystals of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ stored in ethyl acetate at $30\text{ }^{\circ}\text{C}$ slowly transformed into crystals of $[\text{NH}_4]\text{N}_3$ over the course of two months (Scheme 1 and Figure 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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ to $[\text{NH}_4]\text{N}_3$ [16]. As shown in Figure 2, $[\text{NH}_4]\text{N}_3$ crystallized in the orthorhombic space group $Pmna$ with a cell volume of $289.49(18)\text{ \AA}^3$. 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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$, the unit-cell volume decreases by 95%, owing to the release of nitrogen and water molecules involving the structure change. The azide groups $\text{N}(2)\text{-N}(3)\text{-N}(2)^{\text{ii}}$ and $\text{N}(4)\text{-N}(5)\text{-N}(4)^{\text{iii}}$ are aligned along a axis and parallel to the plane (010), respectively. These distances between nitrogens in $[\text{NH}_4]\text{N}_3$ (1.180 and 1.178 Å) are shorter than the normal $\text{N}=\text{N}$ double bond lengths ($\text{NH}=\text{NH}$, 1.252 Å) and longer than the bond length in free N_2 ($\text{N}=\text{N}$, 1.100 Å) [17, 18] indicating the partial double-bond character for the N-N bonds. The average N-N bond length in $[\text{NH}_4]\text{N}_3$ 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 well-founded estimate compared to cyclo-N_5^- . 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 $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$, hydrogen bonding plays a dominant role in strengthening the stability of cyclo-N_5^- . The hydrogen bonding in $[\text{NH}_4]\text{N}_3$ are shown in Figure 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 NH_4^+ cation and the negative termini of the N_3^- ions. Figure 3b indicates that each NH_4^+ cation is surrounded by four N_3^- 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 $8i$, which are capable of engaging in hydrogen bonding with N2 and N4 in N_3^- , respectively. By comparing the hydrogen bond $\text{N4-H4A}\cdots\text{N2}$ (2.912 Å) in $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ with the corresponding $\text{N1-H1A}\cdots\text{N2}$ (2.103 Å) and $\text{N1-H1B}\cdots\text{N4}$ (2.060 Å) in

$[\text{NH}_4]\text{N}_3$, a noticeable decrease, about 28 %, is found in the length of hydrogen bonds during crystal transformation from $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ to $[\text{NH}_4]\text{N}_3$. Generally, the strength of a hydrogen bond depends almost linearly on its length [20]; It can be seen that the observed N4-H4A \cdots N2 bond angle is 171° while the N1-H1A \cdots N2 and N1-H1B \cdots 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 $[\text{NH}_4]\text{N}_3$ crystal are indicative of stronger hydrogen bonds as compared to the hydrogen bond strength in $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$.

In order to observe the NMR spectrum changes of crystal transformation, we heated a batch of ^{15}N -labeled single crystal of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ at 40°C for 4 h under vacuum. The utilization of ^{15}N -labeled *cyclo-N₅⁻* ensured that the weak ^{15}N 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)- d_6 solvent and measured by ^{15}N nuclear magnetic resonance (NMR) with CH_3NO_2 (^{15}N) as an external standard. The results of chemical shift are shown in Figure 4. By comparison with $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$, 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 ^{15}N -labeled NaN_3 [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 $[\text{NH}_4]\text{N}_3$ crystal from the $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ crystal should be rather slow.

To study and monitor structure transformation on powder samples of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$, we also made an attempt to heat the solid $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ 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 figure 5, after complex $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ was heated at 40, 60, 80, 100, 120, 140 and 160 °C for 4 h, respectively. The signal for *cyclo*- N_5^- gradually became weak and eventually vanished but the signal at about 2100 cm^{-1} became increasingly prominent. Significant transformation of N_5^- occurred at 120 °C, and by comparison with the peaks, it could be deduced that the transformation process on powder samples of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ was at relatively slow speed, but could be facilitated via heating. In particular, it was worth mentioning that no melting process occurred even though $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ 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 $[\text{NH}_4]\text{N}_3$ phase. A low-frequency mode located at 638 cm^{-1} was assigned as a N_3^- 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 $3000\text{--}3200\text{ cm}^{-1}$, 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].

Conclusion

In conclusion, it is demonstrated that the $[\text{NH}_4]\text{N}_3$ crystal can be obtained from the pentazolate salt $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ via the irreversible 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^- .

Acknowledgements

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Figure Captions

Scheme 1. The decomposition product of the block crystals of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$.

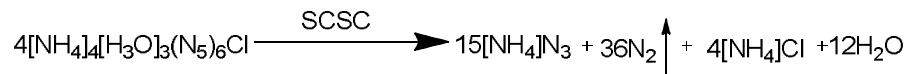
Figure 1. The route of single-crystal transformation and optical microscopic photographs of (a) one single crystal of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ and (b) one single crystal of $[\text{NH}_4]\text{N}_3$.

Figure 2. X-ray crystallographic structure. (a) Ellipsoid plot of $[\text{NH}_4]\text{N}_3$ 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 $[\text{NH}_4]\text{N}_3$ along [111]plane.

Figure 3. Schematic representation of the hydrogen-bonding in $[\text{NH}_4]\text{N}_3$. (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; (xiv) -0.5+x, 3-y, -0.5+z; (xv) 1-x, 3-y, -z; (b) a view of packing along c axis

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

Figure 5. IR spectra of solid $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ after heating at from 40 to 160 °C.



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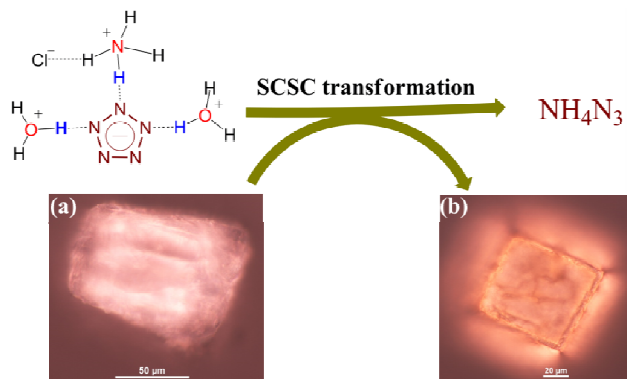


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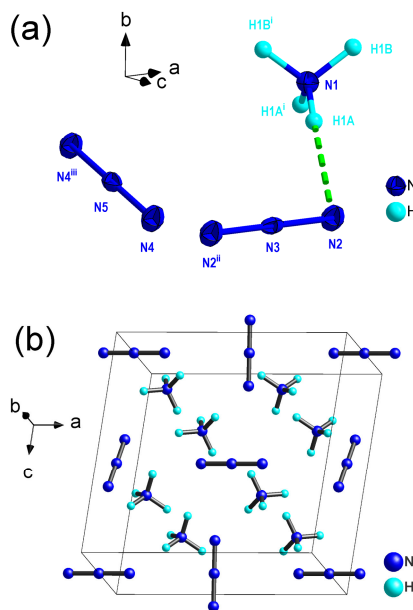


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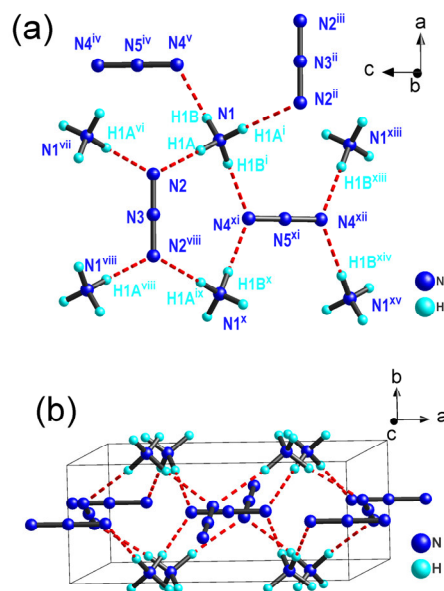


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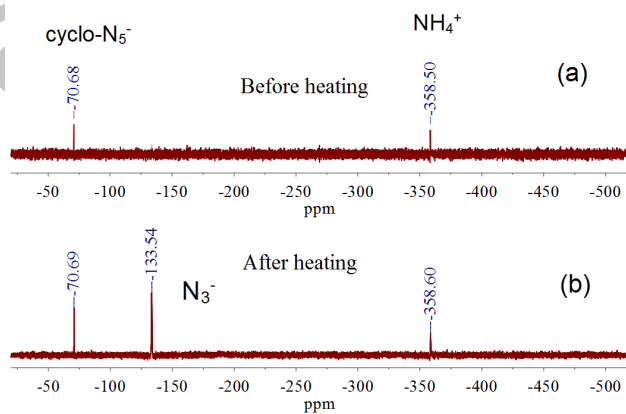


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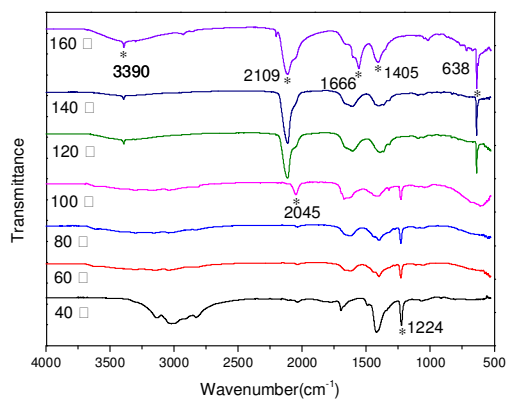


Figure 5. IR spectra of solid $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ after heating at from 40 to 160 °C.

We here describe an unprecedented example of single-crystal to single-crystal spontaneous transformation from a pentazolate salt $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ to a known $[\text{NH}_4]\text{N}_3$ via N_2 and H_2O release, which involves the cleavage of the N-N bonds and the change in space group. The transformation helps facilitate the understanding on the relationship of polynitrogen anions between the long-known N_3^- anion and the recently synthesized cyclo- N_5^- .

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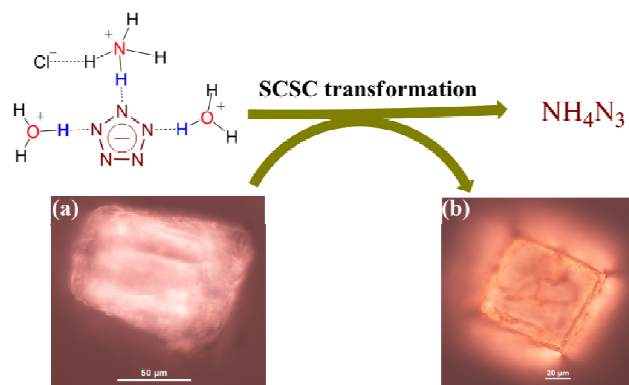


Figure: The route of single-crystal transformation and optical microscopic photographs of (a) one single crystal of $[\text{NH}_4]_4[\text{H}_3\text{O}]_3(\text{N}_5)_6\text{Cl}$ and (b) one single crystal of $[\text{NH}_4]\text{N}_3$.