REPORT

INORGANIC CHEMISTRY

Synthesis and characterization of the pentazolate anion *cyclo*-N_5^- in $(N_5)_6(H_3O)_3(NH_4)_4Cl$

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Pentazole (HN_5), an unstable molecular ring comprising five nitrogen atoms, has been of great interest to researchers for the better part of a century. We report the synthesis and characterization of the pentazolate anion stabilized in a $(N_5)_6(H_3O)_3(NH_4)_4Cl$ salt. The anion was generated by direct cleavage of the C–N bond in a multisubstituted arylpentazole using *m*-chloroperbenzoic acid and ferrous bisglycinate. The structure was confirmed by single-crystal x-ray diffraction analysis, which highlighted stabilization of the *cyclo*-N_5^- ring by chloride, ammonium, and hydronium. Thermal analysis indicated the stability of the salt below 117°C on the basis of thermogravimetry-measured onset decomposition temperature.

Pentazole (HN_5) and its anion (*cyclo*-N_5^-) have been identified as potential constituents of materials with high energy density, and accordingly they are candidates for possible applications in both military and civilian contexts (*1*–*3*). Generally, *cyclo*-N_5^- has been stabilized only at low temperature, through conjugation with an aromatic ring bearing a strong electron-donating group (*4*–*7*). In this conjugated structure, the C–N bond is much stronger than either the N–N single bond or N=N double bond (*8*). The selective cleavage of the C–N bond in arylpentazoles while keeping *cyclo*-N_5^- intact still presents a great challenge. Several elegant methodologies have been applied to this problem, including the use of electrospray negative-ion mass spectrometry for selective C–N bond cleavage or, more recently, radical anion to activate the C–N bond (*9*–*11*). However, to date, all attempts to prepare the solid form of *cyclo*-N_5^- via the cleavage of this C–N bond have proven unsuccessful (*12*–*16*).

In our previous studies, we found that the formation of *cyclo*-N_5^- from arylpentazoles proceeded more efficiently upon increasing the number of electron-donating groups at the meta/para-position of the aryl groups (*17*). We then considered adding a reagent to stabilize the *cyclo*-N_5^- immediately after cleavage of the aryl-pentazole bond. After hundreds of experiments targeting efficient C–N bond cleavage, we succeeded in isolating a stable salt, $(N_5)_6(H_3O)_3(NH_4)_4Cl$ (fig. S1), prepared 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 [$Fe(Gly)_2$].

In our synthesis planning, $Fe(Gly)_2$ played a dual role as both a *cyclo*-N_5^- stabilizer and a *m*-CPBA mediator. When an aqueous solution of $Fe(Gly)_2$ (2.5 equivalents) was added to a stirred solution of HPP (1 equivalent) in acetonitrile and methanol (v/v, 1/1) at −45°C, no chemical reaction occurred, which indicated that the ferrous complex was insensitive to HPP and unlikely to destroy the five-membered nitrogen ring in the HPP molecule. After adding *m*-CPBA (4 equivalents) in cold methanol, *cyclo*-N_5^- was readily detected in the solution by electrospray ionization (ESI) mass spectrometry: The intense negative ion peak could be observed at a mass/charge ratio *m/z* of 70.09 (figs. S2 to S7). Upon completion of the reaction, the insoluble materials were eliminated by filtration. The collected filtrate was evaporated under vacuum to furnish a dark-brown solid. The pure product could be

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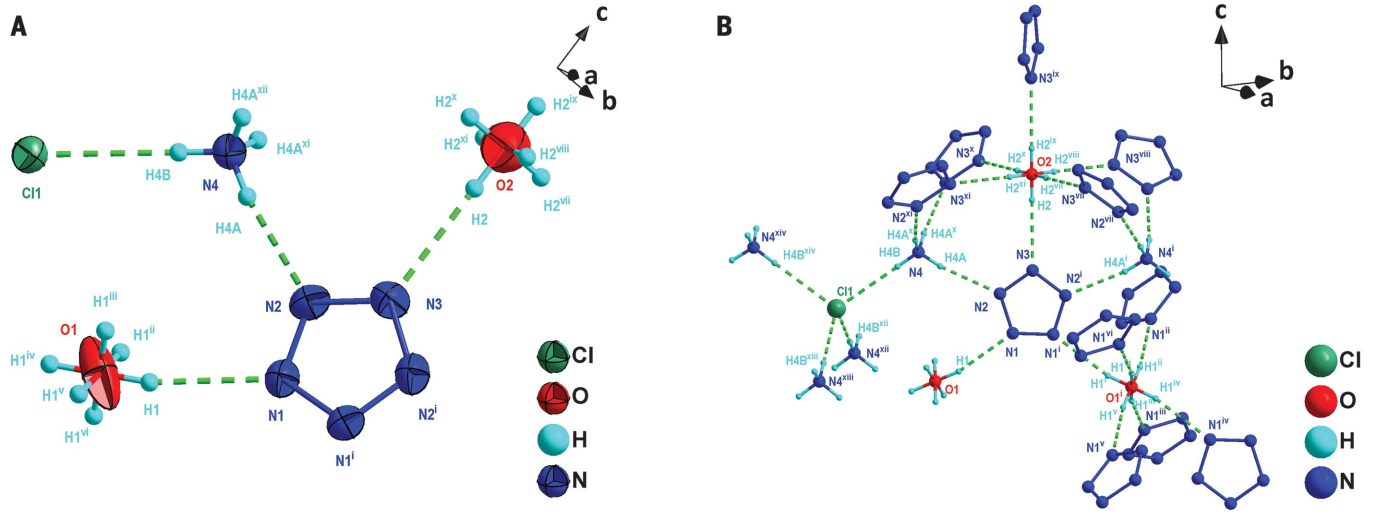

Fig. 1. Crystallography. (**A**) Ellipsoid plot of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ at the 50% probability level. The occupancies of H_3O^+ (O1), H_3O^+ (O2), Cl^-, N_5^-, and NH_4^+ are 1/12, 1/24, 1/24, 1/4, and 1/6, respectively. Symmetry codes: (i) 1.75 − *x*, 1.75 − *y*, *z*; (ii) 1.5 − *x*, 0.25 + *z*, −0.25 + *y*; (iii) 0.25 + *z*, 1.5 − *y*, −0.25 + *x*; (iv) 1.5 − *y*, 1.5 − *x*, 1 − *z*; (v) *y*, 1.25 − *z*, 1.25 − *x*; (vi) 1.25 − *z*, *x*, 1.25 − *y*; (vii) 1.75 − *y*, 1.75 − *z*, *x*; (viii) 1.75 − *z*, 1.75 − *x*, *y*; (ix) *x*, 1.75 − *y*, 1.75 − *z*; (x) *y*, *z*, *x*; (xi) *z*, *x*, *y*; (xii) *y*, *z*, *x*. (**B**) Schematic representation of the hydrogen-bonded motifs in the crystal structure. Ellipsoids are plotted at the 50% probability level. Hydrogen bonds are indicated as green dotted lines. Symmetry codes: (i) 1.75 − *x*, 1.75 − *y*, *z*; (ii) 1.5 − *z*, 0.25 + *y*, −0.25 + *x*; (iii) 1.75 − *y*, 0.5 + *z*, 1.25 − *x*; (iv) 0.25 + *y*, 0.25 + *x*, 1 − *z*; (v) 0.5 + *z*, 1.75 − *x*, 1.25 − *y*; (vi) 0.25 + *x*, 1.5 − *z*, −0.25 + *y*; (vii) 1.75 − *z*, 1.75 − *x*, *y*; (viii) 1.75 − *y*, 1.75 − *z*, *x*; (ix) *x*, 1.75 − *y*, 1.75 − *z*; (x) *z*, *x*, *y*; (xi) *y*, *z*, *x*; (xii) 1.25 − *x*, *y*, 1.25 − *z*; (xiii) *x*, 1.25 − *y*, 1.25 − *z*; (xiv) *x*, 1.25 − *y*, 1.25 − *z*.

isolated through silica gel column chromatography with an acceptable yield (19%) to give $(N_5)_6(H_3O)_3(NH_4)_4Cl$ as an air-stable white solid.

Primary structural confirmation came from single-crystal x-ray diffraction analysis. The pentazolate salt crystallized in the cubic space group *Fd-3m* with a cell volume of 5801.0 ± 0.5 Å^3 (*18*). As seen in the ellipsoid plot of the pentazolate salt in Fig. 1A, the pentagonal N_5^- ring comprises five nitrogen atoms in a perfectly planar arrangement, as evident from the torsion angles (N1′-N1-N2-N3, 0°; N1-N2-N3-N2′, 0°). Each N atom offers a p-orbital electron to form a conjugated π_5^6 bond together with another single electron, which in principle fulfills the geometric criterion of aromaticity. Relevant bond distances and angles are shown in tables S2 and S3. The N–N bond lengths in *cyclo*-N_5^- are 1.309 Å, 1.310 Å, 1.310 Å, 1.324 Å, and 1.324 Å; the average N–N bond distance (1.315 Å)—intermediate between N–N single bond lengths (hydrazine, 1.452 Å) (*19*) and N=N double bond lengths (*trans*-diamine, 1.252 Å) (*20*)—is slightly shorter than both the experimental N–N bond distance for 4-dimethylaminophenylpentazole (average 1.323 Å) (*21*, *22*) and the calculated distance for *cyclo*-N_5^- (D_{5h}, 1.327 Å) at the CCSD(T)/aug-cc-pVQZ level (*23*).

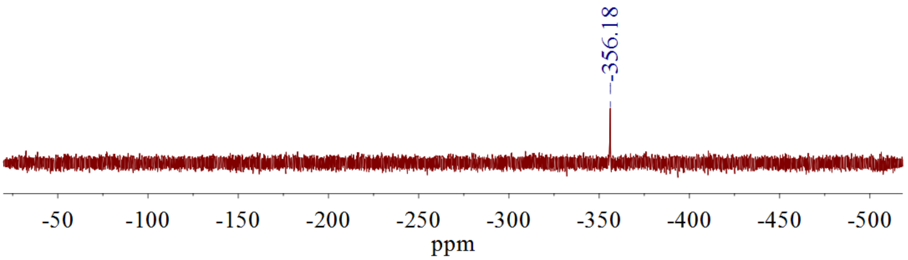

Fig. 2. ^{15}N NMR spectrum of $(N_5)_6(H_3O)_3(NH_4)_4Cl$.

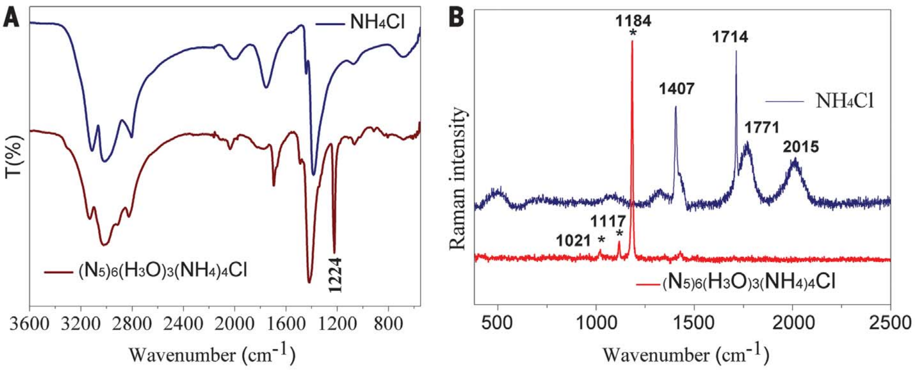

Fig. 3. Vibrational spectra. (**A**) IR spectra of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ and NH_4Cl. (**B**) Raman spectra of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ and NH_4Cl.

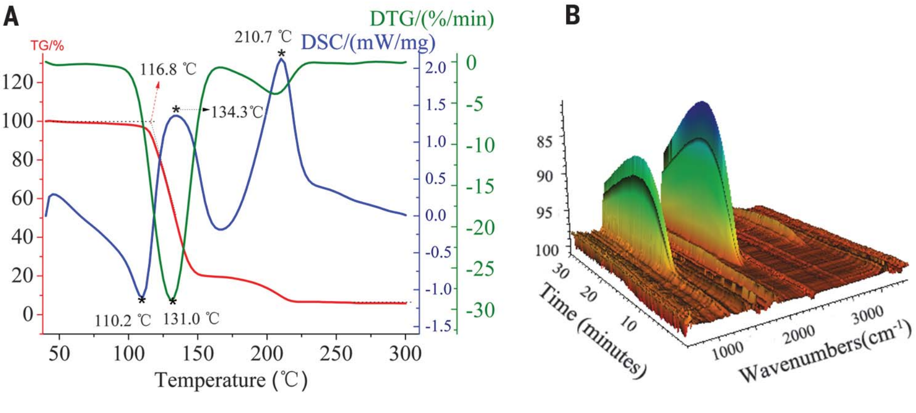

Fig. 4. Thermal analysis. (**A**) TG-DSC-DTG curves of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ salt under nitrogen at 10 K/min. (**B**) IR spectra of gaseous products obtained from the thermal decomposition of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ under nitrogen.

Relative to the unstable *cyclo*-N_5^-, the $(N_5)_6(H_3O)_3(NH_4)_4Cl$ salt exhibits excellent thermal stability, which can be attributed to the extensive hydrogen-bonding interactions between the cations and anions. As shown in Fig. 1B and table S4, the hydrogen atoms H1 [H_3O^+ (O1)], H4A (NH_4^+), and H2 [H_3O^+ (O2)] participate in hydrogen bonding with N1, N2, and N3 in *cyclo*-N_5^-, respectively (O1-H1···N1, 2.995 Å; N4-H4A···N2, 2.912 Å; O2-H2···N3, 3.090 Å). Generally, the strength of a hydrogen bond depends almost linearly on its length; the aforementioned lengths of the hydrogen bonds are almost the same, and the small deviations (almost 10°) from linearity in their bond angles (O1-H1···N1, 168°; N4-H4A···N2, 171°; O2-H2···N3, 180°) likely have a relatively minor effect (*24*); the hydrogen bonds are of similar strength and play an equally important role in tightly connecting the neighboring *cyclo*-N_5^-. The whole lattice is assumed to be a regular network, where the H_3O^+ (O1), NH_4^+, and H_3O^+ (O2) are considered nodes and the numerous hydrogen bonds represent node connections (figs. S18 and S19). In particular, the hydrogen atom H4B from the NH_4^+ forms a hydrogen bond with neighboring Cl^- rather than with *cyclo*-N_5^- (N4-H4B···Cl1, 3.265 Å).

Chloride plays a critical role in stabilizing the pentazolate salt. After removal of Cl^- by precipitation with silver nitrate, the *cyclo*-N_5^- precipitated quickly at ambient temperature (fig. S8). Similarly, the removal of NH_4^+ from the pentazolate salt by treatment with Nessler's reagent (*25*) also resulted in the loss of its stability (fig. S9).

The pentazolate structure was also supported by ^1H and ^{15}N nuclear magnetic resonance (NMR) spectral data, measured in dimethyl sulfoxide (DMSO)–d_6 solvent with tetramethylsilane (^1H) as an internal standard and CH_3NO_2 (^{15}N) as an external standard. Only one signal, at 7.17 ppm, was observed in the ^1H NMR spectrum (fig. S10), and the lone visible ^{15}N signal resonated at –356.18 ppm (Fig. 2). Both signals were attributed to NH_4^+, with the ^{15}N signal of *cyclo*-N_5^- too weak to observe at natural abundance.

We also acquired infrared (IR) and Raman vibrational spectra of the pentazolate salt (Fig. 3). In the context of D_{5h} symmetry, group theory analysis shows that the stretching modes of planar *cyclo*-N_5^- span $A_1' + E_1' + 2E_2' + E_2''$ irreducible representations (*3*). Only the E_1' mode is IR-active, whereas the A_1' and E_2' are Raman-active and E_2'' is neither IR-active nor Raman-active. Consistent with this analysis, *cyclo*-N_5^- shows only one IR band at 1224 cm^{-1} (E_1'), which matches with its computed mode at 1284 cm^{-1} (using the POL basis at the aug-cc-pVTZ geometry) (*26*). The Raman spectrum (785-nm excitation) shows bands at 1184 cm^{-1} (A_1'), 1117 cm^{-1} (E_2'), and 1021 cm^{-1} (E_2'), which are compatible with quantum chemical estimates for *cyclo*-N_5^- at 1222, 1124, and 1059 cm^{-1} (*3*).

To study the thermal stability and decomposition behavior of the pentazolate salt, we applied thermogravimetry–differential scanning calorimetry–derivative thermogravimetry–mass spectrometry–IR spectroscopy (TG-DSC-DTG-MS-IR) to $(N_5)_6(H_3O)_3(NH_4)_4Cl$ powder (Fig. 4). A corresponding decomposition path is proposed in fig. S11. The TG curve exhibits two distinct weight losses in the temperature range of 40° to 300°C (Fig. 4A). The first weight loss step (about 81%) below 168°C could be related to the decomposition of *cyclo*-N_5^-. A manual melting-point measurement confirmed that no melting was observed before the onset of decomposition at 117°C. In the mass spectra (fig. S12), changes of MS curves at 43 and 18 were observed along with the release of N_2 in the first stage of decomposition of the pentazolate salt, which indicated the generation of H_2O and HN_3 during the decomposition process. As found in the simultaneously recorded IR spectrum (Fig. 4B), the vibrational peaks at 1136, 1169, 2118, 2154, and 3317 cm^{-1} could be assigned to HN_3 (*27*, *28*), which is further evidence for its release. We also probed the decomposition process under an argon atmosphere using mass spectrometry with high sensitivity for selected ion monitoring, and generation of HN_3 was confirmed with the MS curve at 43 (fig. S13).

We confirmed the decomposed residue in the first weight loss by slowly heating the salt under nitrogen to 160°C and then cooling it to room temperature. The residues were subjected to Fourier transform IR analysis (fig. S14), which showed spectral features consistent with NH_4N_3 (*29*). In addition, to our surprise, a crystal of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ in ethyl acetate stored at ambient temperature slowly decomposed into NH_4N_3 crystals over the course of 6 months, as confirmed by x-ray diffraction (fig. S20). The second weight loss occurred at higher temperature and was relatively small (13%) compared with the first, which could be attributed fundamentally to the decomposition of NH_4N_3 and other residues.

Our results end the long search for a bulk synthesis of the pentazolate anion. It was characterized as a component in the unexpected structure $(N_5)_6(H_3O)_3(NH_4)_4Cl$ and was found to be surprisingly stable, with a decomposition onset temperature of 117°C in TG. It has potential as an ingredient in energetic polynitrogen compounds.

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ACKNOWLEDGMENTS

Supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions. We thank L. Yi [Analysis and Testing Center, Nanjing University of Science and Technology (NJUST)] for testing of NMR spectra; X. L. Bao (Shanghai Jiaotong University) for testing of crystal structure; F. F. Wang (Institute of Materia Medica, Chinese Academy of Medical Science, and Peking Union Medical College) for expert crystallographic analysis; and C. Jiang, H. W. Yang, L. D. Lu, and X. D. Wu (NJUST) for comments on the manuscript. Additional data are in the supplementary materials. Crystallographic parameters are available free of charge from FIZ Karlsruhe under reference CSD-431382.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/355/6323/374/suppl/DC1
Materials and Methods
Figs. S1 to S20
Tables S1 to S5
References (*30*–*34*)

18 June 2016; resubmitted 20 September 2016
Accepted 28 November 2016
10.1126/science.aah3840

Science

Synthesis and characterization of the pentazolate anion *cyclo*-N_5? in $(N_5)_6(H_3O)_3(NH_4)_4Cl$

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Science **355** (6323), 374-376.
DOI: 10.1126/science.aah3840originally published online January 26, 2017

A salty route to an all-nitrogen ring

The flip side of the robust stability of N_2 is the instability of any larger molecules composed exclusively of nitrogen. These molecules nonetheless remain enticing targets for explosive and propellant applications. Zhang *et al.* successfully prepared the pentazolate ion, a negatively charged ring of five nitrogens, by oxidative cleavage of a C−N bond in an aryl-substituted precursor (see the Perspective by Christe). The molecule was stabilized and isolated in the solid state as a hydrated ammonium chloride salt. Spectroscopic and crystallographic characterization confirmed the ring's planar geometry.

Science, this issue p. 374; see also p. 351

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