

## 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).

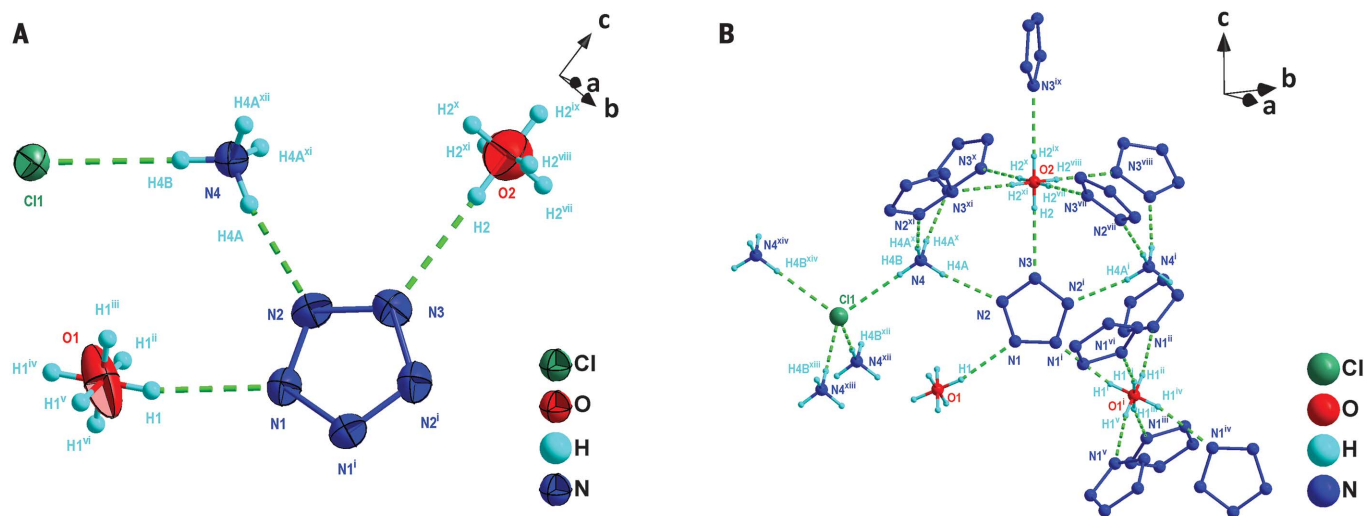
In our previous studies, we found that the formation of  $cyclo-N_5^-$  from arylpentazoles proceeded

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)<sub>2</sub>].

In our synthesis planning, Fe(Gly)<sub>2</sub> played a dual role as both a  $cyclo-N_5^-$  stabilizer and a *m*-CPBA mediator. When an aqueous solution of Fe(Gly)<sub>2</sub> (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

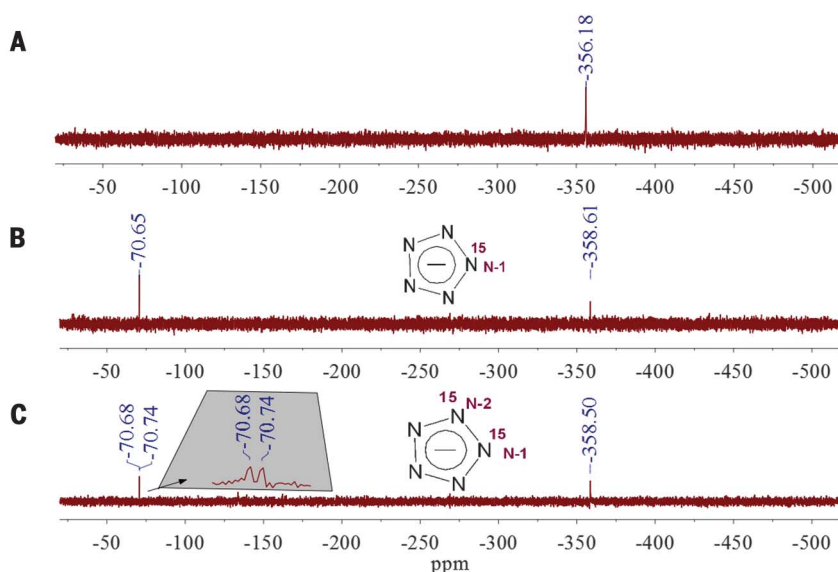
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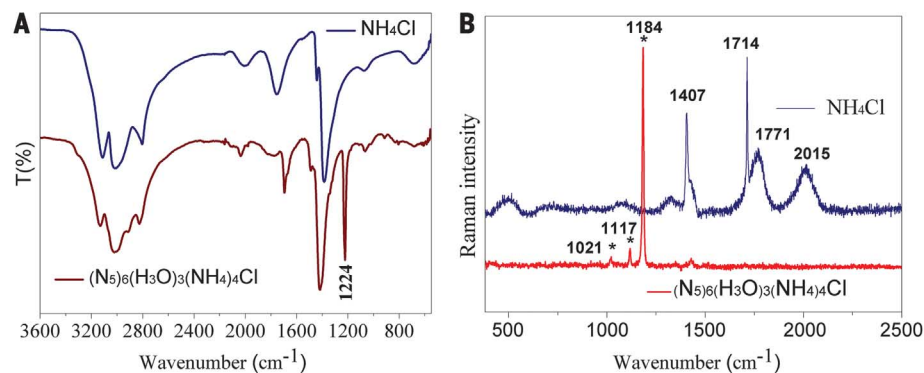


**Fig. 1. Crystallography.** (A) Ellipsoid plot of  $(N_5)_6(H_3O)_3(NH_4)_4Cl$  at the 50% probability level. The occupancies of  $H_3O^+$  (O1),  $H_3O^+$  (O2),  $Cl^-$ ,  $N_5^-$ , and  $NH_4^+$  are 1/12, 1/24, 1/24, 1/4, and 1/6, respectively. Symmetry codes: (i)  $1.75 - x, 1.75 - y, z$ ; (ii)  $1.5 - x, 0.25 + z, -0.25 + y$ ; (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)  $1.75 - z, 1.75 - x, y$ ; (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

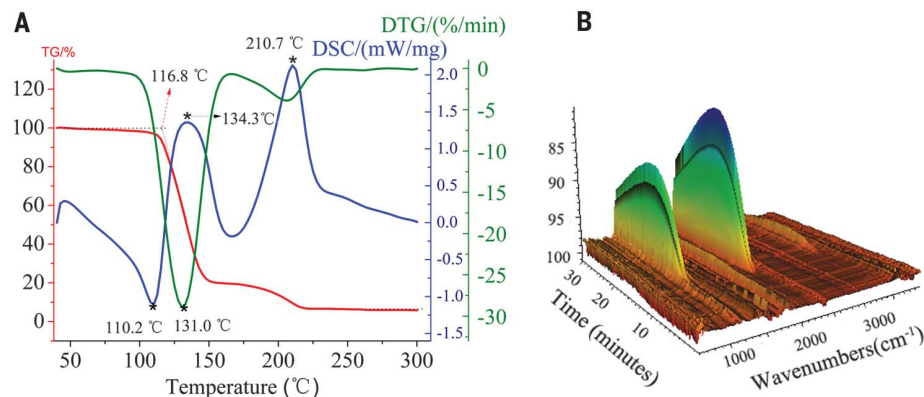
motifs in the crystal structure. Ellipsoids are plotted at the 50% probability level. Hydrogen bonds are indicated as green dotted lines. Symmetry codes: (i)  $1.75 - x, 1.75 - y, z$ ; (ii)  $1.5 - z, 0.25 + y, -0.25 + x$ ; (iii)  $1.75 - y, 0.5 + z, 1.25 - x$ ; (iv)  $0.25 + y, 0.25 + x, 1 - z$ ; (v)  $0.5 + z, 1.75 - x, 1.25 - y$ ; (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)  $x, 1.25 - y, 1.25 - z$ .



**Fig. 2. NMR spectra.** N-1 and N-2 represent the positions of the  $^{15}\text{N}$  labels. (A)  $^{15}\text{N}$  NMR spectrum of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ . (B)  $^{15}\text{N}$  NMR spectrum of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ , with labeled  $^{15}\text{N}$  atom at the N-1 position. (C)  $^{15}\text{N}$  NMR spectrum of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ , with labeled  $^{15}\text{N}$  atoms at the N-1 and N-2 positions.



**Fig. 3. Vibrational spectra.** (A) IR spectra of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  and  $\text{NH}_4\text{Cl}$ . (B) Raman spectra of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  and  $\text{NH}_4\text{Cl}$ .



**Fig. 4. Thermal analysis.** (A) TG-DSC-DTG curves of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  salt under nitrogen at 10 K/min. (B) IR spectra of gaseous products obtained from the thermal decomposition of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  under nitrogen.

isolated through silica gel column chromatography with an acceptable yield (19%) to give  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  as an air-stable white solid.

Primary structural confirmation came from single-crystal x-ray diffraction analysis. The pentazolates salt crystallized in the cubic space group  $Fd\bar{3}m$  with a cell volume of  $5801.0 \pm 0.5 \text{ \AA}^3$  (18). As seen in the ellipsoid plot of the pentazolates salt in Fig. 1A, the pentagonal  $\text{N}_5^-$  ring comprises five nitrogen atoms in a perfectly planar arrangement, as evident from the torsion angles ( $\text{N1}'\text{-N1-N2-N3}$ ,  $0^\circ$ ;  $\text{N1-N2-N3-N2}'$ ,  $0^\circ$ ). Each N atom offers a p-orbital electron to form a conjugated  $\pi_5$  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<sub>5</sub><sup>-</sup>* 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<sub>5</sub><sup>-</sup>* ( $D_{5h}$ , 1.327 Å) at the CCSD(T)/aug-cc-pVQZ level (23).

Relative to the unstable *cyclo-N<sub>5</sub><sup>-</sup>*, the  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  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 [ $\text{H}_3\text{O}^+$  (O1)], H4A ( $\text{NH}_4^+$ ), and H2 [ $\text{H}_3\text{O}^+$  (O2)] participate in hydrogen bonding with N1, N2, and N3 in *cyclo-N<sub>5</sub><sup>-</sup>*, 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  $10^\circ$ ) from linearity in their bond angles (O1-H1...N1,  $168^\circ$ ; N4-H4A...N2,  $171^\circ$ ; O2-H2...N3,  $180^\circ$ ) 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<sub>5</sub><sup>-</sup>*. The whole lattice is assumed to be a regular network, where the  $\text{H}_3\text{O}^+$  (O1),  $\text{NH}_4^+$ , and  $\text{H}_3\text{O}^+$  (O2) are considered nodes and the numerous hydrogen bonds represent node connections (figs. S18 and S19). In particular, the hydrogen atom H4B from the  $\text{NH}_4^+$  forms a hydrogen bond with neighboring  $\text{Cl}^-$  rather than with *cyclo-N<sub>5</sub><sup>-</sup>* (N4-H4B...Cl, 3.265 Å).

Chloride plays a critical role in stabilizing the pentazolates salt. After removal of  $\text{Cl}^-$  by precipitation with silver nitrate, the *cyclo-N<sub>5</sub><sup>-</sup>* decomposed quickly at ambient temperature (fig. S8). Similarly, the removal of  $\text{NH}_4^+$  from the pentazolates salt by treatment with Nessler's reagent (25) also resulted in the loss of its stability (fig. S9).

The pentazolates structure was also supported by  $^1\text{H}$  and  $^{15}\text{N}$  nuclear magnetic resonance (NMR) spectral data, measured in dimethyl sulfoxide ( $\text{DMSO}$ )- $d_6$  solvent with tetramethylsilane ( $^1\text{H}$ ) as an internal standard and  $\text{CH}_3\text{NO}_2$  ( $^{15}\text{N}$ ) as an external standard. Only one signal, at 7.17 ppm,

was observed in the  $^1\text{H}$  NMR spectrum (fig. S10), and the lone visible  $^{15}\text{N}$  signal resonated at  $-356.18$  ppm (Fig. 2A). Both signals were attributed to  $\text{NH}_4^+$ , with the  $^{15}\text{N}$  signal of *cyclo-N<sub>5</sub><sup>-</sup>* too weak to observe at natural abundance. We therefore synthesized an isotopolog with a  $^{15}\text{N}$  label at the N-1 pentazolate position (Fig. 2B), which exhibited an NMR resonance at  $-70.65$  ppm. For comparison, we also prepared a second isotopolog labeled at both N-1 and N-2 (Fig. 2C), which exhibited a strong singlet overlapped with neighboring sites in the  $^{15}\text{N}$  NMR spectrum.

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<sub>5</sub><sup>-</sup>* 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<sub>5</sub><sup>-</sup>* shows only one IR band at  $1224\text{ cm}^{-1}$  ( $E_1'$ ), which matches with its computed mode at  $1284\text{ cm}^{-1}$  (using the POL basis at the aug-cc-pVTZ geometry) (26). The Raman spectrum (785-nm excitation) shows bands at  $1184\text{ cm}^{-1}$  ( $A_1'$ ),  $1117\text{ cm}^{-1}$  ( $E_2'$ ), and  $1021\text{ cm}^{-1}$  ( $E_2''$ ), which are compatible with quantum chemical estimates for *cyclo-N<sub>5</sub><sup>-</sup>* at  $1222$ ,  $1124$ , and  $1059\text{ cm}^{-1}$  (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  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  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  $40^\circ$  to  $300^\circ\text{C}$  (Fig. 4A). The first weight loss step (about 81%) below  $168^\circ\text{C}$  could be related to the decomposition of *cyclo-N<sub>5</sub><sup>-</sup>*. A manual melting-point measurement confirmed that no melting was observed before the onset of decomposition at  $117^\circ\text{C}$ . In the mass spectra (fig. S12), changes of MS curves at 43 and 18 were observed along with the release of  $\text{N}_2$  in the first stage of decomposition of the pentazolate salt, which indicated the gener-

ation of  $\text{H}_2\text{O}$  and  $\text{HN}_3$  during the decomposition process. As found in the simultaneously recorded IR spectrum (Fig. 4B), the vibrational peaks at  $1136$ ,  $1169$ ,  $2118$ ,  $2154$ , and  $3317\text{ cm}^{-1}$  could be assigned to  $\text{HN}_3$  (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  $\text{HN}_3$  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  $160^\circ\text{C}$  and then cooling it to room temperature. The residues were subjected to Fourier transform IR analysis (fig. S14), which showed spectral features consistent with  $\text{NH}_4\text{N}_3$  (29). In addition, to our surprise, a crystal of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  in ethyl acetate stored at ambient temperature slowly decomposed into  $\text{NH}_4\text{N}_3$  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  $\text{NH}_4\text{N}_3$  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  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$  and was found to be surprisingly stable, with a decomposition onset temperature of  $117^\circ\text{C}$  in TG. It has potential as an ingredient in energetic polynitrogen compounds.

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#### SUPPLEMENTARY MATERIALS

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

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## Synthesis and characterization of the pentazolate anion *cyclo-N<sub>5</sub><sup>-</sup>* in (N<sub>5</sub>)<sub>6</sub>(H<sub>3</sub>O)<sub>3</sub>(NH<sub>4</sub>)<sub>4</sub>Cl

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### A salty route to an all-nitrogen ring

The flip side of the robust stability of N<sub>2</sub> 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.

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