Synthesis and characterization of the pentazolate anion \( \text{cyclo-N}_5^- \) in \((\text{N}_5)6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}\)

Chong Zhang,1* Chenguo Sun,2* Bingcheng Hu,† Chuanning Yu,1 Ming Lu1†

Pentazole (HN₃), 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 pentazole anion stabilized in a \((\text{N}_6\text{H})_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}\) 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 \( \text{cyclo-N}_5^- \) 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 (HN₃) and its anion (\( \text{cyclo-N}_5^- \)) 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, \( \text{cyclo-N}_5^- \) 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 \( \text{cyclo-N}_5^- \) 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 \( \text{cyclo-N}_5^- \) via the cleavage of this C–N bond have proven unsuccessful (12–16).

In our previous studies, we found that the formation of \( \text{cyclo-N}_5^- \) 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 \( \text{cyclo-N}_5^- \) 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, \((\text{N}_6\text{H})_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}\) (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 \( \text{cyclo-N}_5^- \) 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, \( \text{cyclo-N}_5^- \) was readily detected in the solution by electrospray ionization 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

Fig. 1. Crystallography. (A) Ellipsoid plot of \((\text{N}_6\text{H})_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}\) at the 50% probability level. The occupancies of H₂O⁺ (O1), H₂O⁻ (O2), Cl⁻, N₆⁻, and NH₄⁺ 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 – y, x; (ix) x, 1.75 – y, 1.75 – z; (x) y, x, z; (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) 1.75 – 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) 0.25 + z, 1.75 – y, 1.25 – z; (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$_3$O)$_3$(NH$_4$)$_4$Cl 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-$3$m 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 p$_5^6$ 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–Nbond 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).

Relative to the unstable cyclo-N$_5^-$, the (N$_5$)$_6$(H$_3$O)$_3$(NH$_4$)$_4$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 [H3O$^+$ (O1)], H4A (NH$_4^+$), and H2 [H3O$^+$ (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$_2$O$^+$ (O1), NH$_4^+$, and H$_2$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 NH$_4^+$ forms a hydrogen bond with neighboring Cl$^-$ rather than with cyclo-N$_5^-$ (N4-H4A···Cl, 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$_5^-$ decomposed 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 $^1$H and $^{15}$N nuclear magnetic resonance (NMR) spectral data, measured in dimethyl sulfoxide (DMSO)–d$_6$ solvent with tetramethylsilane ($^1$H) as an internal standard and CH$_3$NO$_2$ ($^{15}$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 \( ^15N \) signal resonated at \(-356.18 \) ppm (fig. 2A). Both signals were attributed to \( NH_4^+ \), with the \( ^15N \) signal of cyclo-N\(_5\)-\( ^{-} \) too weak to observe at natural abundance. We therefore synthesized an isotopolog with a \( ^15N \) 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 \( ^15N \) 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\(_5\)-\( ^{-} \) 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\(^{-1} \) (\( E_1' \)), 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\(_3\)O\(_3\))(NH\(_4\))\(_4\)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° to 300°C (fig. 4A). The first weight loss (about 81%) below 168°C could be related to the decomposition of cyclo-N\(_5\)-\( ^{-} \). A manual melt-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\(_2\)O and HN\(_3\) during the decomposition process. As found in the simultaneously recorded IR spectrum (fig. 4B), the vibrational peaks at 1136, 1109, 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. S12).

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\(_4\)N\(_3\) (29). In addition, to our surprise, a crystal of (N\(_5\))\(_6\)(H\(_3\)O\(_3\))(NH\(_4\))\(_4\)Cl in ethyl acetate stored at ambient temperature slowly decomposed into NH\(_3\)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 NH\(_3\)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 synthesis of the pentazolate anion. It was characterized as a component in the unexpected synthesis of the pentazolate anion. It was characterized as a component in the unexpected synthesis of the pentazolate anion. It was characterized as a component in the unexpected synthesis of the pentazolate anion. It was characterized as a component in the unexpected synthesis of the pentazolate anion.

REFERENCES AND NOTES
18. See supplementary materials.

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SUPPLEMENTARY MATERIALS
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Synthesis and characterization of the pentazolate anion cyclo-N₅⁻ in (N₅)₆(H₃O)₃(NH₄)₄Cl
Chong Zhang, Chengguo Sun, Bingcheng Hu, Chuanming Yu and Ming Lu

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A salty route to an all-nitrogen ring

The flip side of the robust stability of N₂ 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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