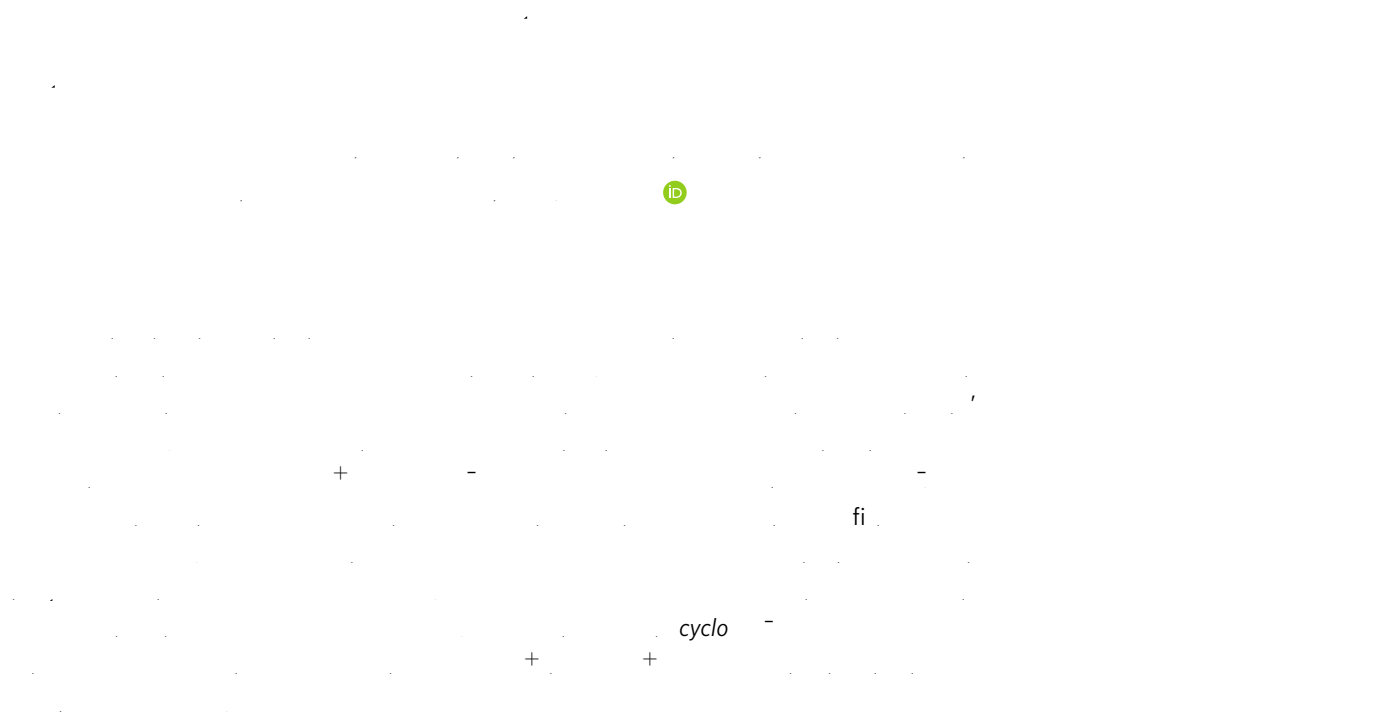


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The pentaolate anion, *cyclo-N₅⁻*, has recently been stabilized as $(N_5)_6(H_3O)_3(NH_4)_4Cl$ ¹ and $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$ ². This discovery has received much attention due to the potential applications of *cyclo-N₅⁻* in high-energy density materials (HEDMs) and as a starting material for the syntheses of inorganic ferrocene analogs. However, these *cyclo-N₅⁻* complexes contained non-energetic counter ions or groups to enhance their stability, thus impacting their energetic properties. The successful synthesis of an essentially naked *cyclo-N₅⁻* salt still has a huge challenge for the fascinating pentaole chemistry and related materials science.

HEDMs require both low sensitivity and high performance³. Polynitrogen compounds hold great promise due to their fast energy release and eco-friendly decomposition products⁴⁻⁷. Major advances in this area have been made during the past two decades, the two most remarkable new species discovered in this field are the pentaenium cation, N_5^+ ⁶⁻⁸ and the pentaolate anion, *cyclo-N₅⁻*⁹⁻¹². However, the reported N_5^+ and *cyclo-N₅⁻* complexes generally contain non-energetic counter ions or groups to enhance their stabilities. For example, SbF_6^- or SnF_6^{2-} are non-energetic counter ions in N_5^+ salts^{13,14}, and H_2O , Cl^- , NH_4^+ , and H_3O^+ are used to stabilize the *cyclo-N₅⁻* anion¹. These non-energetic components impact their energetic properties, such as heat of formation and detonation parameters. Therefore, it is important to reduce or eliminate these non-energetic components.

As part of our long-continued research, here, we report the synthesis of a water-stabilized *cyclo-N₅⁻* salt, $[Mg(H_2O)_6]^{2+}[(N_5)_2(H_2O)_4]^{2-}$, in which the non-energetic Cl^- of

$(N_5)_6(H_3O)_3(NH_4)_4Cl$ was removed. For the elimination of the water, a silver *cyclo-N₅⁻* complex (AgN_5) was precipitated by the addition of $AgNO_3$ to the $[Mg(H_2O)_6]^{2+}[(N_5)_2(H_2O)_4]^{2-}$ solution. By treatment with $NH_3 \cdot H_2O$, this AgN_5 complex was converted to a 3D-framework $[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$ salt, which was characterized by its crystal structure. The AgN_5 complex is stable up to 90 °C, is photolytically unstable decomposing to AgN_3 and N_2 , and Ag and N_2 are its only final decomposition products. The isolation of a silver *cyclo-N₅⁻* complex, devoid of stabilizing molecules and ions, such as H_2O , H_3O^+ , and NH_4^+ , constitutes a major advance in pentaole chemistry.

Results

Materials synthesis and structural design. The schematic in Fig. 1 illustrates the procedures for the syntheses of the AgN_5 and $[Ag(NH_3)_2]^+[Ag_3(N_5)_4]^-$. In view of previous research, our team have achieved a breakthrough in *cyclo-N₅⁻* chemistry involving the synthesis and characterization of the stable pentaolate salt, $(N_5)_6(H_3O)_3(NH_4)_4Cl$ ¹. We also demonstrated that a cobalt ion can effectively trap *cyclo-N₅⁻*, forming the stable compound $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$ ². As part of our continuing effort to prepare an essentially naked *cyclo-N₅⁻* salt, we first added magnesium nitrate to an aqueous solution of $(N_5)_6(H_3O)_3(NH_4)_4Cl$ at room temperature, resulting in the formation of a white crystalline precipitate of $[Mg(H_2O)_6]^{2+}[(N_5)_2(H_2O)_4]^{2-}$ (Fig. 2) in 85% yield based on the *cyclo-N₅⁻* content of $(N_5)_6(H_3O)_3(NH_4)_4Cl$. Subsequently, an aqueous solution of silver nitrate was added dropwise to the stirred $[Mg(H_2O)_6]^{2+}[(N_5)_2(H_2O)_4]^{2-}$ solution in methanol, resulting in the precipitation of the AgN_5 complex as a pale

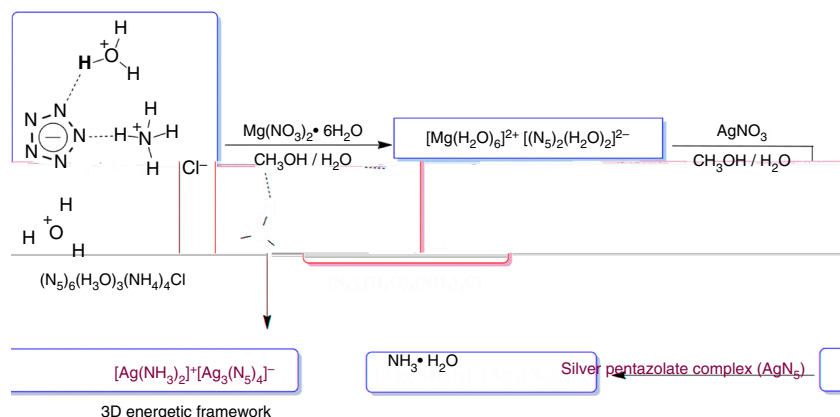


Fig. 1

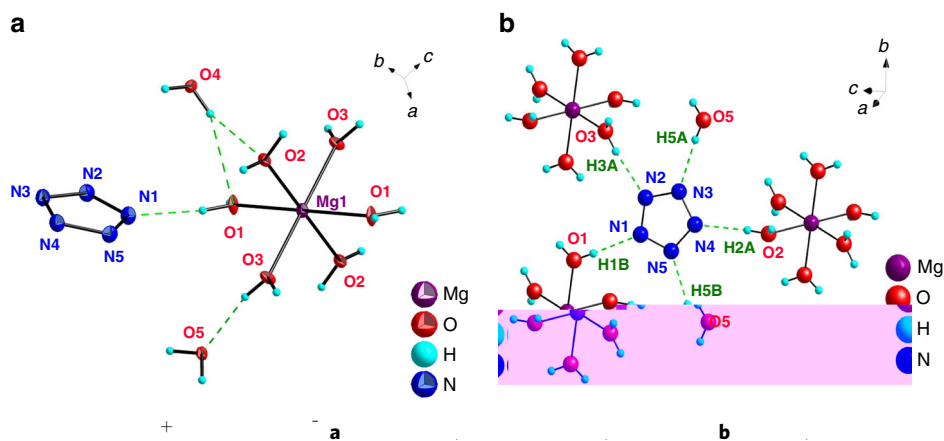


Fig. 2

white solid. However, the AgN_5 complex was light-sensitive and insoluble in all solvents tested. To further characterize this complex, we instantly treated it with 10 equiv. of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 wt %) at 0 °C, followed by warming to room temperature to liberate NH_3 and to provide colorless crystals of $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3\text{N}$

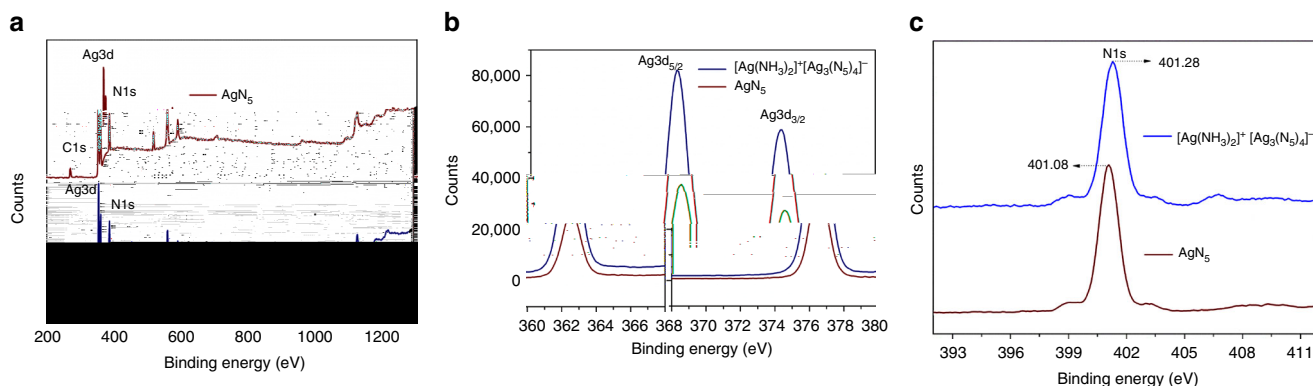


Fig. 4

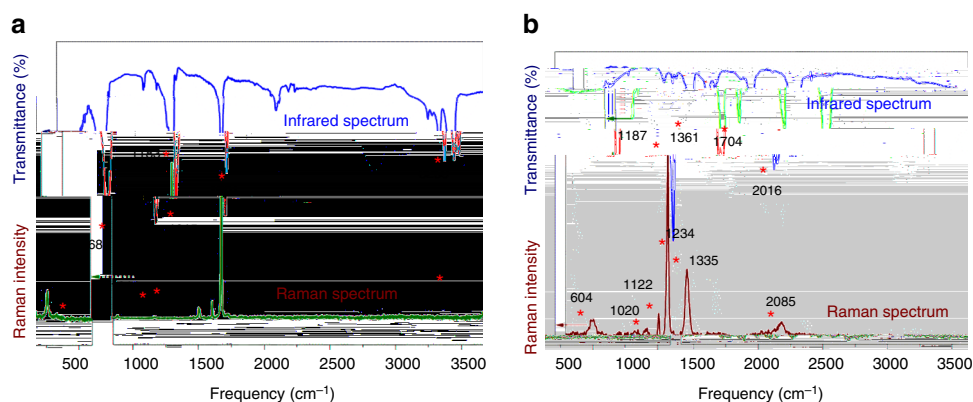


Fig. 5

Energetic metal-organic frameworks (energetic-MOFs) have recently received attention as insensitive HEDMs. The energetic-MOFs are constructed by metal ions and organic ligands, such as a *ides*, *fura ans*, *tria oles*, and *tetra oles*, via coordination bonds, which give one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) structures^{17–20}. Especially noteworthy is the fact that 3D frameworks usually possess more complicated connection modes than 1D and 2D frameworks, which could further enhance their structural stability²¹. As illustrated in Fig. 3c, the silver bridged penta olate anion in $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ can also be interpreted as a 3D energetic-framework, which is constructed from Ag1, Ag2 and *cyclo-N*₅⁻. The overall architecture of $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ is produced with tandem coordination bonding interactions between Ag⁺ and *cyclo-N*₅⁻. Continuous catenation in 3D directions is made possible by independent Ag⁺ centers as nodes, coordinatively bound to *cyclo-N*₅⁻ linkers. The propagation of both six-coordinated Ag1 and four-coordinated Ag2 to *cyclo-N*₅⁻ generates 3D polycatenated framework (Fig. 3f). Although Ag3 does not connect to the 3D framework, the coordinated $[\text{Ag}(\text{NH}_3)_2]^+$ is located right in the center of the voids of the crystal structure, and forms hydrogen bonds with the 3D-network (Fig. 3d), (N(11)-H(11A) N(2), 2.50 ; N(11)-H(11A) N(8), 2.31 ; N(11)-H(11B) N(5), 2.27 ; N(11)-H(11C) N(3), 2.69 ; N(11)-H(11C) N(10), 2.44). To better understand its structure, the 3D framework of $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ can be topologically defined as a 3,4,4,6-c net with long Schflfi symbol of $(4\cdot6^2)_2(4^2\cdot6^3\cdot8)_2(4^3\cdot6^3)_2(4^4\cdot6^2\cdot8^6\cdot10^3)$. As shown in

Supplementary Fig. 2, topological analysis indicates that the 3D framework of $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ can be abstracted as a binodal three- and four-connected net, each silver linker connects three or four *cyclo-N*₅⁻ anions, which corresponds better to the arrangement of atoms in the 3D framework structure. In addition, typical π - π stacking interactions are observed in $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ between the two off-center parallel *cyclo-N*₅⁻ rings (Fig. 3e), with centroid-centroid distances of 3.634(5) and 3.838(5) , respectively, which are consistent with previously reported π - π stacking distances between aromatic molecules²². The remarkable face-to-face π - π interactions are important contacts, similar to hydrogen bonding, enhancing the stability of the whole $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ structure. Attempts to determine the surface area and porosity of the 3D framework by Brunner-Emmet-Teller (BET) measurements were unsuccessful because of the inability to completely degas the samples due to their limited thermal stability and the small sample sizes used.

Physicochemical properties. The $[\text{Ag}(\text{NH}_3)_2]^+[\text{Ag}_3(\text{N}_5)_4]^-$ 3D framework was further investigated by X-ray photoelectron spectroscopy (XPS). Figure 4a shows the XPS wide scan spectrum, which exhibits N1s and Ag3d peaks only. Two peaks at 368.58 and 374.48 eV generated by photoelectrons emitted from the Ag3d core level, can be observed (Fig. 4b), which indicate the presence of only one type of oxidation state for silver that coordinates to the nitrogen atoms in *cyclo-N*₅⁻ and NH₃. Figure 4c

presents the high-resolution XPS results of N1s. Its binding energy at 401.28 eV is characteristic for the nitrogen atoms that form the *cyclo-N₅⁻* ring. These XPS spectra also demonstrate the similarity of the AgN₅ units in both compounds.

We further analyzed the structure of the AgN₅ complex and [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ by Raman and infrared spectroscopy. As can be seen from Fig. 5, the three typical *cyclo-N₅⁻* RA bands are present at about 1180 cm⁻¹ (A₁[']), 1120 cm⁻¹ (E₂[']) and 1020 cm⁻¹ (E₂[']) in both compounds, in excellent agreement with the frequencies observed for (N₅)₆(H₃O)₃(NH₄)₄Cl¹. For the NH₃ coordinated cation in [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ (Fig. 5a), two new characteristic bands are observed at 393 and 3266 cm⁻¹, which are due to the symmetric Ag-N₂ stretching mode of [NH₃-Ag-NH₃]⁺ and the NH₃ stretching modes, respectively^{23,24}. The infrared spectra of the two compounds show the characteristic absorption of the penta ole rings at ca. 1225 + 10 cm⁻¹ that is generally present in penta ole complexes. The assignments for the NH₃ bands in [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ are unequivocal, including the different N-H stretching vibrations in the region of 3000–3400 cm⁻¹, the symmetric deformation around 1601 cm⁻¹, and the rocking mode around 688 cm⁻¹. These absorptions of [Ag(NH₃)₂]⁺ in [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ agree with those of other diamine silver complexes, such as [Ag(NH₃)₂]NO₃ and [Ag(NH₃)₂]₂SO₄^{25,26}

[Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ residue exhibited the characteristic N₃⁻ peaks. An additional peak at 3320 cm⁻¹ was assigned to HN₃²⁹, suggesting the generation of HN₃ during the first stage of the decomposition, followed by its absorption on the surface of AgN₃. In the XRD analysis (Fig. 6h), the position and relative intensity of all diffraction peaks match well with those from a standard AgN₃ sample, further confirming the composition of the first-step residue as AgN₃. The XRD powder pattern of the decomposition residue (Fig. 6h) is distinct from that of the original pattern of the starting material before decomposition (Supplementary Fig. 7). One major difference between these complexes and the previously reported (N₅)₆(H₃O)₃(NH₄)₄Cl or Co(N₅)₂(H₂O)₄·4H₂O is that during the decomposition silver particles are produced along with complete release of N₂. The final thermal-decomposition residue from [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ was verified by optical microscopy as pure Ag, which has brilliant metallic luster and an irregular, faceted structure (Supplementary Fig. 8). We have further confirmed this result by using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) to characterize the morphology and determine the chemical phases. Figure 6a indicates that the Ag formed from the thermal-decomposition process consists of multiple nano-layers. Each nano-layer is formed by silver nanoparticles (Fig. 6b), which have small crystallites as evidenced by the XRD analysis. The corresponding intensities of all diffraction peaks are weak due to the relatively low degree of crystallinity (Fig. 6d). The EDX spectrum shows that Ag is the only element detected in the selected region (Fig. 6c). The EDX mappings (Figs. 6e–g) recorded in the whole SEM image indicate that the element on the surface is Ag. By contrast, nitrogen is not observed in the sample region, suggesting the absence of nitrides on the Ag surface. The structure of the AgN₅ complex was also studied in more detail. The XPS wide scan spectrum of the AgN₅ complex showed no significant changes compared to that of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻, indicating a similar chemical composition (except for hydrogen). The core-level spectra of N1s, and Ag3d are presented in the Fig. 4a. The only difference between the AgN₅ complex and [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ is that the N1s core levels are centered at 401.08 and 401.28 eV, respectively, which illustrates that the presence of different types of nitrogen groups in the AgN₅ complex has resulted in a slight shift. The IR and Raman spectra (Fig. 5b) show only the characteristic peaks of *cyclo*-N₅⁻ and AgN₃. To explain the formation of AgN₃, a sample of the AgN₅ complex was exposed to light for 24 h, and then the IR spectrum was re-recorded. It was found that the AgN₅ complex is extremely sensitive to light and completely decomposes to AgN₃, while the [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ salt is photolytically less sensitive due to the stabilization effect by the 3D framework. In combination with the structure of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ and the aforementioned data, it, therefore, can be concluded that the AgN₅ complex is composed of AgN₅ and AgN₃. This conclusion was further supported by elemental analysis. The total silver content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The found silver content in the AgN₅ complex was 62.3 wt%, intermediate between 60.7% (theoretical silver content in AgN₅) and 72% (theoretical silver content in AgN₃). The nitrogen content of another sample was also found to be intermediate between the theoretical values for AgN₅ and AgN₃. Furthermore, the thermal stability and decomposition behavior of the AgN₅ complex were also compared to those of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. As shown in Supplementary Fig. 9, the TG curve also shows two decomposition stages. The first stage involves loss of N₂ from AgN₅ at 120 °C to give AgN₃, and the second stage comprises the complete decomposition of AgN₃ at 337 °C to metallic Ag and N₂.

Discussion

Our results demonstrate the successful syntheses of a solvent-free silver *cyclo*-penta olate complex and [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. The complexes are stable up to 90 °C and only Ag and N₂ are observed as the final decomposition products. The original product from the [Mg(H₂O)₆]²⁺[(N₅)₂(H₂O)₄]²⁻/AgNO₃ reaction is AgN₅, which subsequently undergoes partial photolytical and/or thermal-decomposition to AgN₃. Although we could not obtain a crystal structure for AgN₅, the indirect evidence for its formation is convincing. The isolation of a *cyclo*-N₅⁻ metal complex, devoid of stabilizing molecules and ions, such as H₂O, H₃O⁺, and NH₄⁺, constitutes a major advance in *cyclo*-penta olate chemistry.

Methods

General information. Caution! Solid silver and penta olate are highly energetic and shock and friction sensitive. They should be handled only on a small scale with appropriate safety precautions, i.e., safety glasses, face shields, heavy leather gloves and jackets, and ear plugs.

Materials characterization. All reagents and solvents used were of analytical grade. (N₅)₆(H₃O)₃(NH₄)₄Cl was produced according to the methods described in the literature¹. Fourier-transform infrared spectra were recorded on a Thermo Nicolet IS10 instrument. Raman spectra were measured with a Renishaw (inVia) Raman spectrometer (785 nm excitation). TG-DSC-mass spectrometry (MS) measurements were performed on a Netzsch STA 409 PC/PG thermal analyzer at a heating rate of 5 K/min under argon atmosphere. X-ray photoelectron spectra (XPS) were carried out on a RBD upgraded PHI-5000C electron spectroscopy for chemical analysis (ESCA) system (Perkin Elmer) with Mg K α radiation (h ν = 1486.6 eV). The crystalline structure was characterized by X-ray powder diffraction (XRD) with a X-ray diffractometer (D8 advance), using a monochromated Cu target radiation source. The SEM mapping was observed under SEM (FEI Verios 460).

Synthesis of [Mg(H₂O)₆]²⁺[(N₅)₂(H₂O)₄]²⁻. A solution of Mg(NO₃)₂·6H₂O (0.79 g, 3.08 mmol) in a mixture of solvents (20 mL) of methanol and water (v/v, 1/1) was added to a methanol solution of (N₅)₆(H₃O)₃(NH₄)₄Cl (0.2 g, 0.34 mmol) and stirred at 20 °C for 8 h. The collected filtrate was evaporated under vacuum to furnish a residue. The targeted compound could be recrystallized from the mixture of acetone and methanol and dried in vacuum at room temperature for 4 h to afford the product with an 85% yield of [Mg(H₂O)₆]²⁺[(N₅)₂(H₂O)₄]²⁻ as an air-stable white solid.

Synthesis of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. An aqueous solution of silver nitrate (0.34 g, 1.91 mmol) was added dropwise to a solution of [Mg(H₂O)₆]²⁺[(N₅)₂(H₂O)₄]²⁻ (0.3 g, 0.87 mmol) in methanol while stirring at 20 °C for 30 min, producing the silver penta olate complex as a pale solid. It was quickly dissolved in 10 equiv. of NH₄OH and stirred at 0 °C for 20 min, followed by warming to room temperature to liberate NH₃, providing the target product, [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻, in 80% yield as an air-stable white solid.

Data availability. The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant data supporting the findings of this study are available on request. Structural data for [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ and [Mg(H₂O)₆]²⁺[(N₅)₂(H₂O)₄]²⁻ were deposited with the Inorganic Crystal Structure Database (ICSD) under deposition numbers CSD: 433114 and 433851, respectively.

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References

- Zhang, C., Sun, C. G., Hu, B. C., Yu, C. M. & Lu, M. Synthesis and characterization of the penta olate anion *cyclo*-N₅⁻ in (N₅)₆(H₃O)₃(NH₄)₄Cl. *Science* **355**, 374–376 (2017).
- Zhang, C. et al. A symmetric Co(N₅)₂(H₂O)₄·4H₂O high-nitrogen compound formed by cobalt (II) cation trapping of a *cyclo*-N₅⁻ anion. *Angew. Chem. Int. Ed.* **56**, 4512–4514 (2017).
- Klappe, T. M. & Sabat, C. M. Bistetraoles: Nitrogen-rich, high-performing, insensitive energetic compounds. *Chem. Mater.* **20**, 3629–3637 (2008).
- Nguyen, M. T. Polynitrogen compounds: I. Structure and stability of N₄ and N₅ systems. *Coord. Chem. Rev.* **244**, 93–113 (2003).

5. Eremets, M. I., Gavriluk, A. G., Trojan, I. A., Divenko, D. A. & Boehler, R. Single-bonded cubic form of nitrogen. *Nat. Mater.* **3**, 558–563 (2004).
6. Perera, S. A. & Bartlett, R. J. Coupled-cluster calculations of Raman intensities and their application to N_4 and N_5^- . *Chem. Phys. Lett.* **314**, 381–387 (1999).
7. Haiges, R. et al. Polyazide chemistry: The first binary group 6 azides, $Mo(N_3)_6$, $W(N_3)_6$, $[Mo(N_3)_7]^-$, and $[W(N_3)_7]^-$, and the $[NW(N_3)_4]^-$ and $[NMo(N_3)_4]^-$ ions. *Angew. Chem. Int. Ed.* **44**, 1860–1865 (2005).
8. Vij, A. et al. Polynitrogen chemistry. Synthesis, characterization, and crystal structure of surprisingly stable fluoroantimonate salts of N_5^+ . *J. Am. Chem. Soc.* **123**, 6308–6313 (2001).
9. Vij, A., Pavlovich, J. G., Wilson, W. W., Vij, V. & Christe, K. O. Experimental Detection of the pentazacyclopentadienide (pentazolate) anion, *cyclo-N5^-*. *Angew. Chem. Int. Ed.* **41**, 3051–3054 (2002).
10. Steele, B. A. & Oleynik, I. I. Pentazole and ammonium pentazolate: Crystalline hydro-nitrogens at high pressure. *J. Phys. Chem. A.* **121**, 1808–1813 (2017).
11. Banov, B. et al. Detection of *cyclo-N5^-* in THF solution. *Angew. Chem. Int. Ed.* **55**, 13233–13235 (2016).
12. Christe, K. O. Recent advances in the chemistry of N_5^+ , N_5^- and high-oxygen compounds. *Prop. Explos. Pyrotech.* **32**, 194–204 (2007).
13. Christe, K. O., Wilson, W. W., Sheehy, J. A. & Boatman, J. A. N_5^+ : A novel homoleptic polynitrogen ion as a high energy density material. *Angew. Chem. Int. Ed.* **38**, 2004–2009 (1999).
14. Haiges, R., Schneider, S., Schroer, T. & Christe, K. O. High-energy-density materials: Synthesis and characterization of $N_5^+[P(N_3)_6]^-$, $N_5^+[B(N_3)_4]^-$, $N_5^+[HF_2]^- \cdot nHF$, $N_5^+[BF_4]^-$, $N_5^+[PF_6]^-$, and $N_5^+[SO_3F]^-$. *Angew. Chem. Int. Ed.* **43**, 4919–4924 (2004).
15. Qu, X. N. et al. An Ag(I) energetic metal–organic framework assembled with the energetic combination of furan and tetraole: Synthesis, structure and energetic performance. *Dalton. Trans.* **45**, 6968–6973 (2016).
16. Borrajo-Calleja, G. M. et al. Synthesis of silver(I) and gold(I) complexes containing enantiopure pybox ligands. First assays on the silver(I)-catalyzed asymmetric addition of alkynes to imines. *Inorg. Chem.* **55**, 8794–8807 (2016).
17. Krawiec, M. et al. Hydronium copper(II)-tris(5-nitrotetraolate) trihydrate—a primary explosive. *Prop. Explos. Pyrotech.* **40**, 457–459 (2015).
18. Zhang, J. H., Dharavath, S., Mitchell, L. A., Parrish, D. A. & Shreeve, J. M. Energetic salts based on 3, 5-bis(dinitromethyl)-1, 2, 4-triazole monoanion and dianion: controllable preparation, characterization, and high performance. *J. Am. Chem. Soc.* **138**, 7500–7503 (2016).
19. McDonald, K. A., Seth, S. & Matger, A. J. Coordination polymers with high energy density: An emerging class of explosives. *Cryst. Growth Des.* **15**, 5963–5972 (2015).
20. Seth, S. & Matger, A. J. Coordination polymerization of 5, 5'-dinitro-2H, 2H'-3, 3'-bi-1, 2, 4-triazole leads to a dense explosive with high thermal stability. *Inorg. Chem.* **56**, 561–565 (2017).
21. Li, S. H. et al. 3D energetic metal-organic frameworks: Synthesis and properties of high energy materials. *Angew. Chem. Int. Ed.* **52**, 14031–14035 (2013).
22. Janiak, C. A critical account on π - π stacking in metal complexes with aromatic nitrogen-containing ligands. *J. Chem. Soc. Dalton. Trans.* **21**, 3885–3896 (2000).
23. Nilsson, K. B., Persson, I. & Kessler, V. G. Coordination chemistry of the solvated AgI and AuI ions in liquid and aqueous ammonia, trialkyl and triphenyl phosphite, and tri-n-butylphosphine solutions. *Inorg. Chem.* **45**, 6912–6921 (2006).
24. Ujike, T. & Tominaga, Y. Raman spectral analysis of liquid ammonia and aqueous solution of ammonia. *J. Raman Spectrosc.* **33**, 485–493 (2002).
25. Woidy, P. & Kraus, F. The diammine silver(I) acetate $[Ag(NH_3)_2]OAc$. *Z. Anorg. Allg. Chem.* **639**, 2643–2647 (2013).
26. Geddes, A. L. & Bottger, G. L. Infrared spectra of silver-ammine complexes. *Inorg. Chem.* **8**, 802–807 (1969).
27. Grocholl, L., Wang, J. J. & Gillan, E. G. Synthesis of sub-micron silver and silver sulfide particles via solvothermal silver azide decomposition. *Mater. Res. Bull.* **38**, 213–220 (2003).
28. Iqbal, Z., Prask, H. J. & Trevino, S. F. in *Energetic Materials* (eds Fair, H. D. & Walker, R. F.) 131–191 (Plenum Press, New York, 1977).
29. Dows, D. A. & Pimentel, G. C. Infrared spectra of gaseous and solid hydrazoic acid and deuterio-hydrazoic acid: The thermodynamic properties of HN_3 . *J. Chem. Phys.* **23**, 1258–1263 (1955).

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Author contributions

B.H. designed the scheme and conducted experiments. C.S., C.Z., C.J., C.Y., Y.D., Z.Z., and Y.Z. conducted the experiments. All the authors contributed to discussions of the results for the manuscript. C.S. and C.Z. wrote the manuscript. B.H., C.J., and Y.D. reviewed this manuscript. K.C. gave important suggestions on the paper and discussed the characterization of the silver pentazolate complex, he also revised this manuscript.

Additional information

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Competing interests: The authors declare no competing interests.

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