Synthesis of AgN₅ and its extended 3D energetic framework

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The pentazolate anion, as a polynitrogen species, holds great promise as a high-energy density material for explosive or propulsion applications. Designing pentazole complexes that contain minimal non-energetic components is desirable in order to increase the material’s energy density. Here, we report a solvent-free pentazolate complex, AgN₅, and a 3D energetic-framework, [Ag(NH₃)₂⁺][Ag₃(N₅)₄⁻], constructed from silver and cyclo-N₅. The complexes are stable up to 90 °C and only Ag and N₂ are observed as the final decomposition products. Efforts to isolate pure AgN₅ were unsuccessful due to partial photolytical and/or thermal-decomposition to AgN₃. Convincing evidence for the formation of AgN₅ as the original reaction product is presented. The isolation of a cyclo-N₅⁻ complex, devoid of stabilizing molecules and ions, such as H₂O, H₃O⁺, and NH₄⁺, constitutes a major advance in pentazole chemistry.

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

HEDMs require both low sensitivity and high performance. Polynitrogen compounds hold great promise due to their fast energy release and eco-friendly decomposition products. Polynitrogen compounds hold great promise due to their fast energy release and eco-friendly decomposition products.

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 \( cyclo-N_5^- \) chemistry involving the synthesis and characterization of the stable pentazole salt, \((N_5)_6(H_2O)_3(NH_4)_4Cl\). We also demonstrated that a cobalt ion can effectively trap \( cyclo-N_5^- \), forming the stable compound \(Co(N_5)_2(H_2O)_4\) \(4H_2O\). As part of our continuing effort to prepare an essentially naked \( cyclo-N_5^- \) salt, we first added magnesium nitrate to an aqueous solution of \((N_5)_6(H_2O)_3(NH_4)_4Cl\) 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 \( cyclo-N_5^- \) content of \((N_5)_6(H_2O)_3(NH_4)_4Cl\). 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 yellow solid. Further treatment with \( NH_3 \cdot H_2O \) resulted in the precipitation of the AgN\(_5\) complex as a pale yellow solid.
white solid. However, the AgN₅ complex was light-sensitive and insoluble in all solvents tested. To further characterize this complex, we instantly treated it with 10 equiv. of NH₃·H₂O (25 wt %) at 0 °C, followed by warming to room temperature to liberate NH₃ and to provide colorless crystals of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ (Supplementary Fig. 1). This compound is thermally stable up to about 90 °C, where it starts to decompose with N₂ evolution to [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. The crystal structure of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ is unique and is of vital importance for the further construction of novel pentazolate complexes. As a consequence, we synthesized the AgN₅ complex and its 3D-framework complex, [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. The structure of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ was determined by single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic space group P2₁/c with a calculated density of 3.2 g/cm³ at 123 K (Supplementary Tables 2–6). The density value is the highest crystal density reported so far for any cyclo-N₅⁻ complex, and is largely due to the presence of four heavy silver atoms. As depicted in the Oak Ridge Thermal Ellipsoid plot (ORTEP) of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ (Fig. 3a), the asymmetrical unit contains half of an [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ molecule, which is composed of two Ag(I) cations (50% occupancy for Ag1 and Ag3, 100% occupancy for Ag2), two cyclo-N₅⁻ rings, and one coordinated NH₃ molecule. One cyclo-N₅⁻ ring is no longer perfectly planar, showing a small degree of distortion, as evident from the torsion angles of N(6)-N(7)-N(8)-N(9) being −0.3° and N(8)-N(9)-N(10)-N(6) being 0.2°. In contrast, the other cyclo-N₅⁻ ring resists distortion from planarity, causing a change in the N-N bond length (1.323–1.336 Å), which are slightly longer than the N-N bonds (1.318–1.320 Å) in Co(N₅)₂(H₂O)₄·4H₂O. Figure 3b shows the coordination environment of the Ag cations. There are three crystallographically independent Ag centers in the structure. Ag3 is bridging between two ammonia molecules in a linear configuration with relatively short Ag–N distances (2.110 Å; N(11)-Ag(3)-N(11), 180°). Ag2 is coordinated by four cyclo-N₅⁻ rings, where four N atoms (N1, N4, N6, N9) adopt a distorted tetrahedral configuration around Ag2, with intermediate Ag2–N distances ranging from 2.332 to 2.370 Å, whereas Ag1 is surrounded by three pairs of cyclo-N₅⁻ rings (N3, N7, and N10) adopting an octahedral geometry with two cyclo-N₅⁻ rings at the apical positions and four cyclo-N₅⁻ rings at the equatorial sites. The average Ag1–N distance of 2.519 Å is much longer than the reported values for triazolate complexes of Ag(I) (average 2.11 Å)¹⁶, and the longest bond in the structure, Ag1-N10 (2.669 Å), indicates that the interaction between Ag and cyclo-N₅⁻ is weak.

[Fig. 3 Crystal structure of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. a ORTEP plot of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ at the 50% probability level. b The coordinate diagram of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻. c Unit cell view along the b axis. d Schematic representation of the hydrogen-bonded motifs in the crystal structure: H-bonds are indicated as dotted lines. e π-π stacking interaction in the crystal structure (Cg1 and Cg2 were the centers of cyclo-N₅⁻). f The 3D framework of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻.]

Energetic metal-organic frameworks (energetic-MOFs) have recently received attention as insensitive HEDMs. The energetic-MOFs are constructed from metal ions and organic ligands, such as azides, furazans, triazoles, and tetrazoles, via coordination bonds, which give one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) structures.\(^\text{17-20}\) 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 stability.\(^\text{21}\) As illustrated in connection modes than 1D and 2D frameworks, which could

![Fig. 4 XPS spectra. a The wide scan spectra of \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\) and the AgN\(_5\) complex. b Core-level Ag3d XPS spectrum. c Core-level N1s XPS spectrum.](image)

**Fig. 5 Vibrational spectra. a Infrared and Raman spectra of solid \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\). b Infrared and Raman spectra of the solid AgN\(_5\) complex. The red asterisks stand for the position of peak value.**

Supplementary Fig. 2, topological analysis indicates that the 3D framework of \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\) 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 \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\) between the two off-center parallel cyclo-N\(_5\) rings (Fig. 3e), with centroid–centroid distances of 3.634(5) Å and 3.838(5) Å, respectively, which are consistent with previous π–π stacking distances between aromatic molecules.\(^\text{22}\) The remarkable face-to-face π–π interactions are important contacts, similar to hydrogen bonding, enhancing the stability of the whole \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\) 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 \([\text{Ag(NH}_3\text{)}_2]^+ [\text{Ag}_3\text{(N}_5\text{)}_4]^–\) 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 NH\(_3\). 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 (E'_2) in both compounds, in excellent agreement with the frequencies observed for (N₃)₆(H₂O)₆(NH₃)₆Cl⁻. 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-N ² stretching mode of the coordinated NH₃ and the NH₃ stretching modes, respectively.¹²,¹³ The infrared spectra of the two compounds show the characteristic absorption of the pentazole rings at ca. 1225 ± 10 cm⁻¹ that is generally present in pentazole 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 In the infrared spectrum of the AgN₅ complex one additional unassigned band is observed at 1704 cm⁻¹. In the vibrational spectra of the AgN₅ complex (Fig. 5b), bands due to N₅⁻ are observed at 2085, 1335, and 604 cm⁻¹ in the RA spectrum (Supplementary Fig. 3), and at 2016 and 1361 cm⁻¹ in the infrared (IR) spectrum which are due to N₅⁻ (ref. ²⁷). The fact that the vibrational spectra of the AgN₅ complex essentially show only bands due to N₅⁻ and N₃⁻ lends further support to our identification of this compound as a mixture of solvent-free AgN₅ and AgN₃. This conclusion is further supported by the crystal structure of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻, in which no evidence for solvate methanol or water molecules was found. Furthermore, the elemental analysis shows the carbon content in the sample of [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ to be lower than 0.5%. If some disordered small molecules, such as methanol, existed, they would result in the carbon content to be higher than 0.5%. In addition, no characteristic absorption bands of H₂O or CH₃OH were observed in the IR and RA spectra.

The minor slope in the TG curve before 100 °C in the Supplementary Fig. 4 can be attributed to the small sample size and some slight decomposition due to the light-sensitivity of the sample. It is also worth mentioning that there were no endothermic peaks in the differential scanning calorimetry (DSC) curve in the 50–90 °C temperature region, as would be expected for the evaporation of H₂O or CH₃OH. The thermal-decomposition behavior and the stability of Ag in the [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ were investigated by thermogravimetric differential scanning calorimetry (TG-DSC) under an argon atmosphere. [Ag(NH₃)₂]⁺[Ag₃(N₅)₄]⁻ showed a two-step rapid decomposition beginning at 90 °C with a mass loss of about 25% between 90 and 134 °C, followed by the loss of another approximately 25% between 134 and 320 °C (Supplementary Figs. 4 and 5). Using thermogravimetric analysis, coupled with mass spectroscopy (TG-Mass), a change of the MS curve at mass 17 (NH₃) was observed along with the release of N₂ in the first stage of the decomposition (Supplementary Fig. 6). The second step probably involves the decomposition of AgN₃ to give Ag and N₂.²⁸

To confirm the overall decomposition process, the decomposition residue from the first weight loss was investigated by slowly heating the complexes under argon to 100 °C and then cooling them back to room temperature, followed by IR and powder X-ray diffraction (XRD) analyses. The IR spectrum of the
[Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$] residue exhibited the characteristic N$_5^-$ peaks. An additional peak at 3320 cm$^{-1}$ was assigned to HN$_3$,$^{28}$ suggesting the generation of HN$_3$ during the first stage of the decomposition, followed by its absorption on the surface of AgN$_3$. In the XRD analysis (Fig. 6h), the position and relative intensity of all diffraction peaks match well with those from a standard AgN$_3$ sample, further confirming the composition of the first-step residue as AgN$_3$. 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 ($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2\mathrm{O}$ and Co($\mathrm{N}_5$)$\mathrm{H}_2\mathrm{O}_4$ is that during the decomposition silver particles are produced along with complete release of N$_2$. The final thermal-decomposition residue from [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{OH}$ 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 nitrates on the Ag surface. The structure of the AgN$_3$ complex was also studied in more detail. The XPS wide scan spectrum of the AgN$_3$ complex showed no significant changes compared to that of [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-$, indicating a similar chemical composition (except for hydrogen). The core-level spectra of N1s, Ag3d, and N1s are presented in the Fig. 4a. The only difference between the AgN$_3$ complex and [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-$ is that the N1s core levels are centered at 401.08 and 401.28 eV, respectively, which suggests the generation of HN$_3$ during the decomposition. The IR and Raman spectra (Fig. 5b) show only the characteristic peaks of cyclo-$\mathrm{N}_5$ and AgN$_3$. To explain the formation of AgN$_3$ while the [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-$ was discovered during the first stage of the decomposition, some relevant data supporting the authors’ claim. 

Discussion

Our results demonstrate the successful syntheses of a solvent-free silver cyclo-pentazolate complex and [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{OH}$. The complexes are stable up to 90 °C and only Ag and N$_2$ are observed as the final decomposition products. The original product from the [Mg(H$_2$O)$_6$]$^2$[($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2\mathrm{O}$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{OH}$ reaction is AgN$_3$, which subsequently undergoes partial photolytical and/or thermal-decomposition to AgN$_3$. Although we could not obtain a crystal structure for AgN$_3$, the indirect evidence for its formation is convincing. The isolation of a cyclo-$\mathrm{N}_5$ metal complex, devoid of stabilizing molecules and ions, such as H$_2$O, H$_3$O$^+$, and NH$_4^+$, constitutes a major advance in cyclo-pentazolate chemistry.

Methods

General information. Cautions! Solid silver azide and pentazolate are highly sensitive to 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. ($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2\mathrm{O}$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$ was produced according to the methods described in the literature,$^{6}$ and the corresponding IR and Raman data were deposited with the Inorganic Crystal Structure Database (ICSD) under deposition numbers CSD: 433114 and 433851, respectively. The IR and Raman spectra were measured 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 Netsch 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 Kα radiation (hv = 1486.6 eV). The crystalline structure was characterized by X-ray powder diffraction (XRD) with a X-ray diffractometer (D8 advance), using a monochromatized Cu Kα target radiation source. The SEM mapping was observed under SEM (FEI verios 460).

Synthesis of [Mg(H$_2$O)$_6$]$^2$[($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2\mathrm{O}$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$. A solution of Mg(NO$_3$)$_2$·6H$_2$O (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 ($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2\mathrm{O}$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$ (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(H$_2$O)$_6$]$^2$[($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2$O]$^+$ as an air-stable white solid.

Synthesis of [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$. An aqueous solution of silver nitrate (0.34 g, 1.91 mmol) was added dropwise to a solution of [Mg(H$_2$O)$_6$]$^2$[($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2$O]$^+$ (0.3 g, 0.87 mmol) in methanol while stirring at 20 °C for 30 min, producing the silver pentazolate complex as a pale solid. It was quickly dissolved in 10 equiv. of NH$_3$·H$_2$O and stirred at 0 °C for 20 min, followed by warming to room temperature to liberate NH$_3$, providing the target product, [Ag(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$; 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(NH$_3$)$_2$]$^+$[Ag$_3$(N$_5$)$_4$]$^-\text{Cl}$ and [Mg(H$_2$O)$_6$]$^2$[($\mathrm{N}_5\mathrm{H}_3$)$\mathrm{H}_2$O]$^+$ were deposited with the Inorganic Crystal Structure Database (ICSD) under deposition numbers CSD: 433114 and 433851, respectively.

Received: 13 September 2017 Accepted: 5 March 2018 Published online: 28 March 2018

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Acknowledgements

We are grateful for financial support provided through the Fundamental Research Funds for the Central Universities (No. 30917011101), University of Science and Technology Liaoning Fund for Young Talent (No. 601011506-8), and the Priority Academic Program Development of Jiangsu Higher Education Institutions. We also thank Huaping Bai (Analysis and Testing Center of Nanjing University of Science and Technology) for testing of the XRD spectra, Wanying Tang (Analysis and Testing Center of Nanjing University of Science and Technology) for testing of the IR spectra, Wenxiai Wei (Yangzhou University) for testing of the Raman spectra, Chuanqiang Zhou (Yangzhou University) for testing of the XPS spectra and Fengfeng Wang (Institute of Materia Medica, Chinese Academy of Medical Science & Peking Union Medical College) for his expert crystallographic analysis. Karl Christe gratefully acknowledges financial support from the Office of Naval Research.

Author contributions

B.H. designed the scheme and conducted experiments. C.S., C.Z., C.J., C.Y., 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

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-03678-y.

Competing interests: The authors declare no competing interests.

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