Electronic Supplementary Information

A Promising Hydrogen Peroxide Adduct of Ammonium Cyclopentazolate as Green Propellant Components

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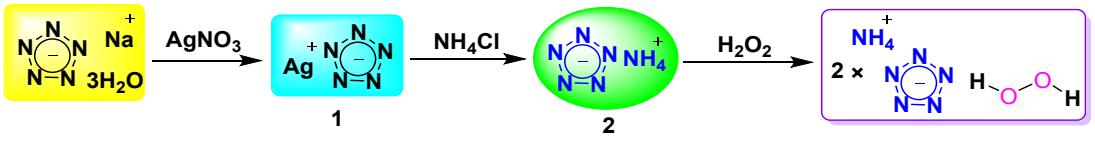
1 Experimental Procedures

***Caution*:** Although no unexpected explosions and hazards were encountered during this work, small scale and best safety practices (explosion-proof baffle, face shield and leather gloves) are strongly encouraged.

General Methods: All chemicals from commercial sources were reagent grade and used as received without further purification. The ^{1}H NMR spectra was performed on a 400 MHz (Bruker AVANCE 400) by using CD_3OD as solvent and locking solvent. IR spectra was recorded by a Thermo Nicolet AVATAR 6700 spectrum instrument with KBr sheets. Thermal property measurements were performed on a TG/DSC Mettler Toledo calorimeter equipped with an auto cool accessory at a scan rate of 5 ^oC min^{-1}. The heats of formation and detonation properties were calculated with the Gaussian 09 and EXPLO5 (version 6.02) software, respectively. Single crystal X-ray diffraction data were collected using an Oxford Xcalibur 3 diffractometer with Cu-Kα radiation (λ = 0.154184 Å).

Synthesis of $NH_4N_5{\cdot}½H_2O_2$. $[Na(H_2O)(N_5)]{\cdot}2H_2O$, AgN_5 and NH_4N_5 were prepared according to the published method.[1] NH_4N_5 (88 mg, 1.0 mmol) was added to a solution of hydrogen peroxide (30 wt%, 10 ml) to form a saturated solution and stirred at 25 °C for 6 hours. After slow solvent evaporation under room temperature (15-25 °C) for several days, the white-colored cuboid single crystals suitable for single crystal X-ray diffraction analysis were obtained. The yield of $NH_4N_5{\cdot}½H_2O_2$ is 50 wt%. $T_{d\ (onset)}$: 99.5 °C. ^{1}H NMR (CD_3OD): δ = 10.66 ppm for H_2O_2 peak; IR (KBr): $\tilde{\nu}$ = 1633, 1400, 1224 (s) cm^{-1}; elemental analysis calcd (%) for $NH_4N_5{\cdot}½H_2O_2$: H 4.76, N 79.92%; found: H 4.82, N 79.90%.



Scheme S1. Synthesis of $NH_4N_5{\cdot}½H_2O_2$.

2 Crystal Structure Data

Single crystal X-ray diffraction data was collected on an Oxford X calibur diffratometer with

Cu-Kα monochromated radiation (λ = 0.154184 Å) at 150 K. The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL program package.[2] All non-hydrogen atoms were refined anisotropoically. Relevant crystal data and refinement results are summarized in Table S1.

Table S1. Crystal data for $NH_4N_5{\cdot}½H_2O_2$ at different temperatures.

Empirical formula	N_6H_5O	N_6H_5O
Formula weight	105.10	105.10
Temperature/K	150	295
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$
a, Å	3.83966 (4)	3.9047 (8)
b, Å	13.19458 (13)	13.187 (9)
c, Å	9.19097 (9)	9.187 (3)
α, °	90	90
β, °	96.7349 (9)	96.30 (2)
γ, °	90	90
Volume, Å^3	462.426 (8)	470.2 (4)
Z	4	2
D_c, g/cm^3	1.510	1.485
μ / mm^{-1}	1.164	1.144
F(000)	220.0	220.0
Crystal size / mm^3	0.22 × 0.2 × 0.18	0.2 × 0.18 × 0.16
Radiation/ Å	Cu Kα (λ = 0.154184)	Cu Kα (λ = 0.154184)
2*θ* range for data collection [°]	11.79 to 154.494	11.788 to 155.394
Index ranges	-4 ≤h≤4, -16≤k≤16, -11≤l≤11	-4≤h≤2, -16≤k≤16, -11≤l≤11
Reflections collected	9425	6763
Independent reflections	975 [R_{int} = 0.0338, $R_θ$ = 0.0149]	973 [R_{int} = 0.0427, $R_θ$ = 0.0224]
Data / restraints / parameters	975 / 0 / 84	973 / 0 / 84
Goodness-of-fit on F^2	1.078	1.152
Final R indexes	R_1= 0.0309, wR_2 = 0.0806	R_1= 0.0364, wR_2 = 0.0833
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0827	R_1 = 0.0432, wR_2 = 0.0982
Largest diff. peak / hole / [e Å^{-3}]	0.17 / -0.32	0.17 / -0.32
CCDC number	1977776	1999931

Table S2. Selected bond distances for $NH_4N_5 \cdot ½H_2O_2$ at 150K.

parameter	bond length (Å)	parameter	bond length (Å)
O(1)-O(1)^{i}	1.4724 (13)	N(5)-N(1)	1.3180 (12)
N(2)-N(3)	1.3210 (11)	N(5)-N(4)	1.3201 (11)
N(2)-N(1)	1.3155 (11)	N(3)-N(4)	1.3172 (12)

Symmetry code: (i) 1-x, 1-y, 1-z.

Table S3. Selected bond angles for $NH_4N_5 \cdot ½H_2O_2$ at 150K.

parameter	bond angle (°)	parameter	bond angle (°)
N (1)-N(2)-N(3)	107.92(8)	N(2)-N(1)-N(5)	108.03 (8)
N(1)-N(5)-N(4)	108.16(8)	N(3)-N(4)-N(5)	107.72 (7)
N(4)-N(3)-N(2)	108.17(7)		

Table S4. Selected torsion angles for $NH_4N_5 \cdot ½H_2O_2$ at 150K.

parameter	bond angle (°)	parameter	bond angle (°)
N(2)-N(3)-N(4)-N(5)	0.06(10)	N(1)-N(5)-N(4)-N(3)	0.04 (10)
N(3)-N(2)-N(1)-N(5)	0.16(11)	N(4)-N(5)-N(1)-N(2)	-0.12 (11)
N(1)-N(2)-N(3)-N(4)	-0.13(10)		

Table S5. Selected hydrogen bonds for $NH_4N_5 \cdot ½H_2O_2$ at 150K.

parameter	bond length (Å)	parameter	bond length (Å)
O(1)-H(1)···N(1)	2.8113 (10)	N(6)-H(6) A···N(5)	2.9359 (11)
N(6)-H(6)B···N(2)	2.9622 (11)	N(6)-H(6)C···O(1)	2.8763 (10)
N(6)-H(6)D···N(3)	2.9757 (11)		

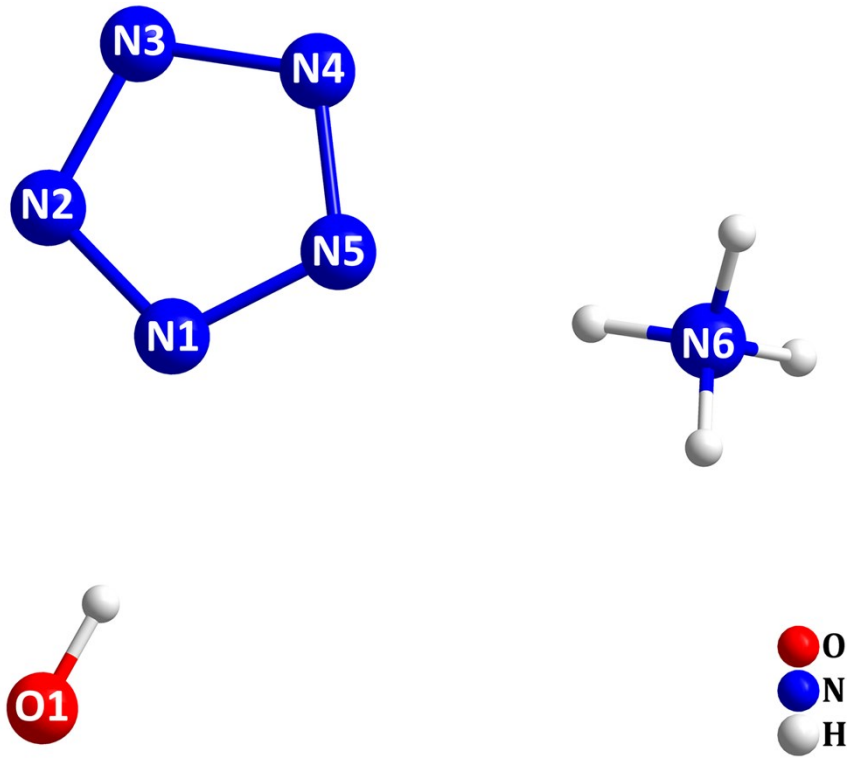


Fig. S1. The asymmetric unit of $NH_4N_5 \cdot ½H_2O_2$.

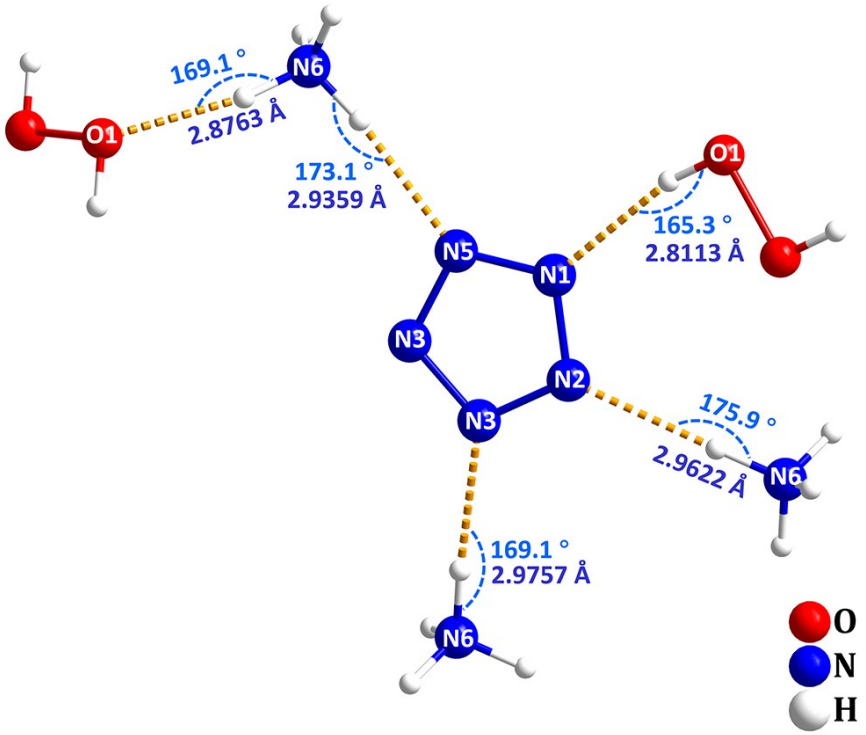


Fig. S2. Five types of hydrogen bonds in $NH_4N_5 \cdot ½H_2O_2$ at 150K.

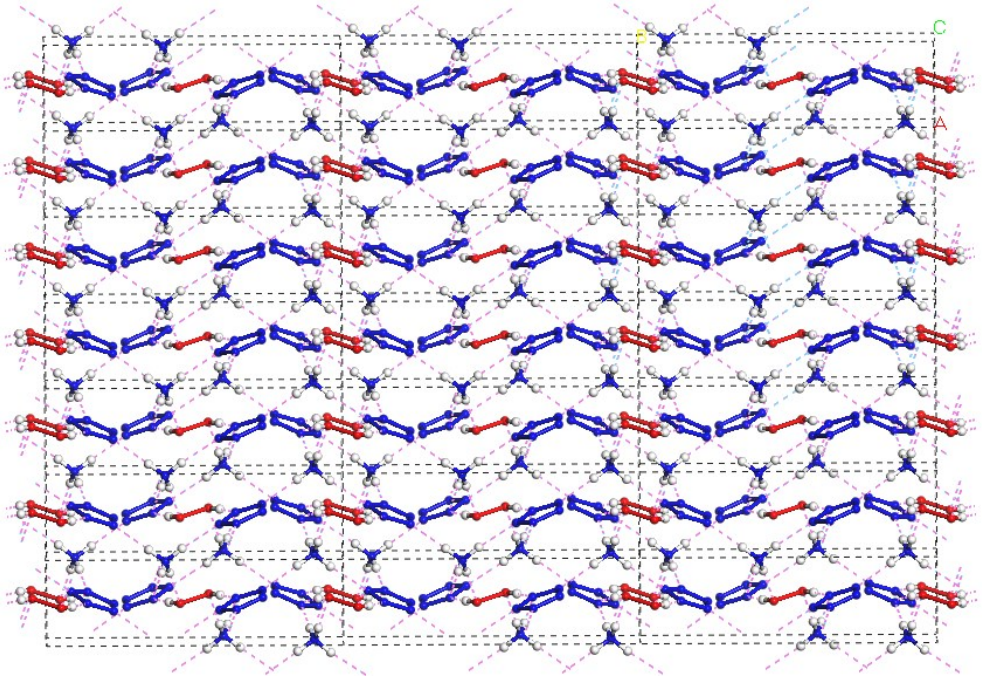


Fig. S3. The packing diagram of $NH_4N_5 \cdot ½H_2O_2$ viewed along the c axis.

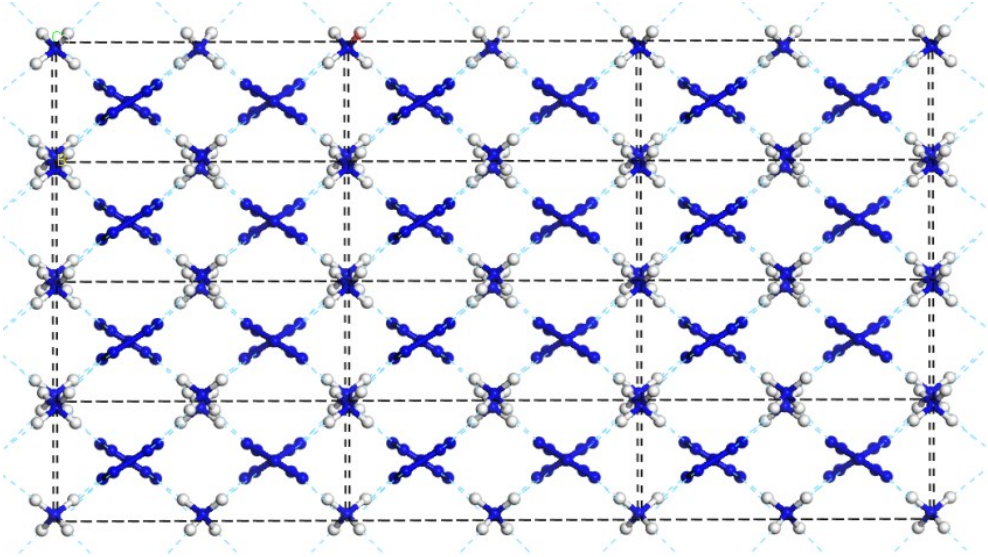


Fig. S4. The packing diagram of NH_4N_5 viewed along the c axis.

3 Computational methods

The heat of formation calculation: The theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of scripts.[3] There are two components (NH_4N_5 and hydrogen peroxide) in the molecule structure of $NH_4N_5 \cdot ½H_2O_2$. Herein, we consider it as a whole system to calculated the solid heat of formations (Δ_fH). The gas state heat of formation

of $NH_4N_5 \cdot ½H_2O_2$ was calculated by G4(MP2)_6x method. G4(MP2)_6x is a composite procedure with a lower cost but performance approaching that of G4. The solid-phase heat of formation can be calculated by the formula given in Equation (1):

$$\Delta H_f\,(\text{solid, 298 K}) = \Delta H_f\,(\text{gas, 298K}) - \Delta H_{sub} \qquad (1),$$

where ΔH_L is the heat of sublimation from gas-phase heat of formation. On the basis of the literature,[3] the heat of sublimation can be estimated with Trouton's rule according to Equation (2):

$$\Delta H_{sub} = 188/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1} \times \text{T} \qquad (2),$$

where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition.[4]

Table S6. The calculated enthalpies of $NH_4N_5 \cdot ½H_2O_2$.

Compd.	ΔH_f (gas, 298K) (kJ mol^{-1})	ΔH_{sub} (kJ mol^{-1})	ΔH_f (solid, 298K) (kJ mol^{-1}/kJ g^{-1})
$N_{12}H_{10}O_2$	527.72	70.03	457.69 / 2.178

4 Other Characterization Information

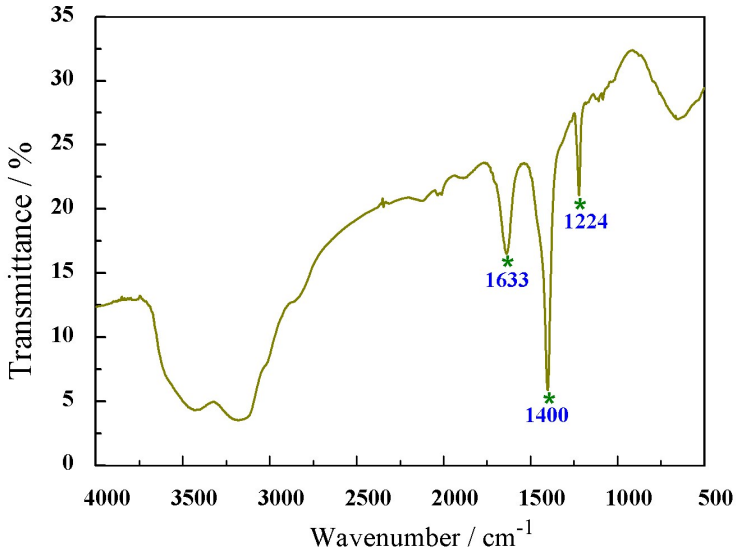


Fig. S5. Infrared spectra of $NH_4N_5 \cdot ½H_2O_2$, which indicates cyclo-N_5^- has an absorption peak in the IR band at 1224 cm^{-1}, which matches the reported vibrational peak at 1224 cm^{-1}.[5]

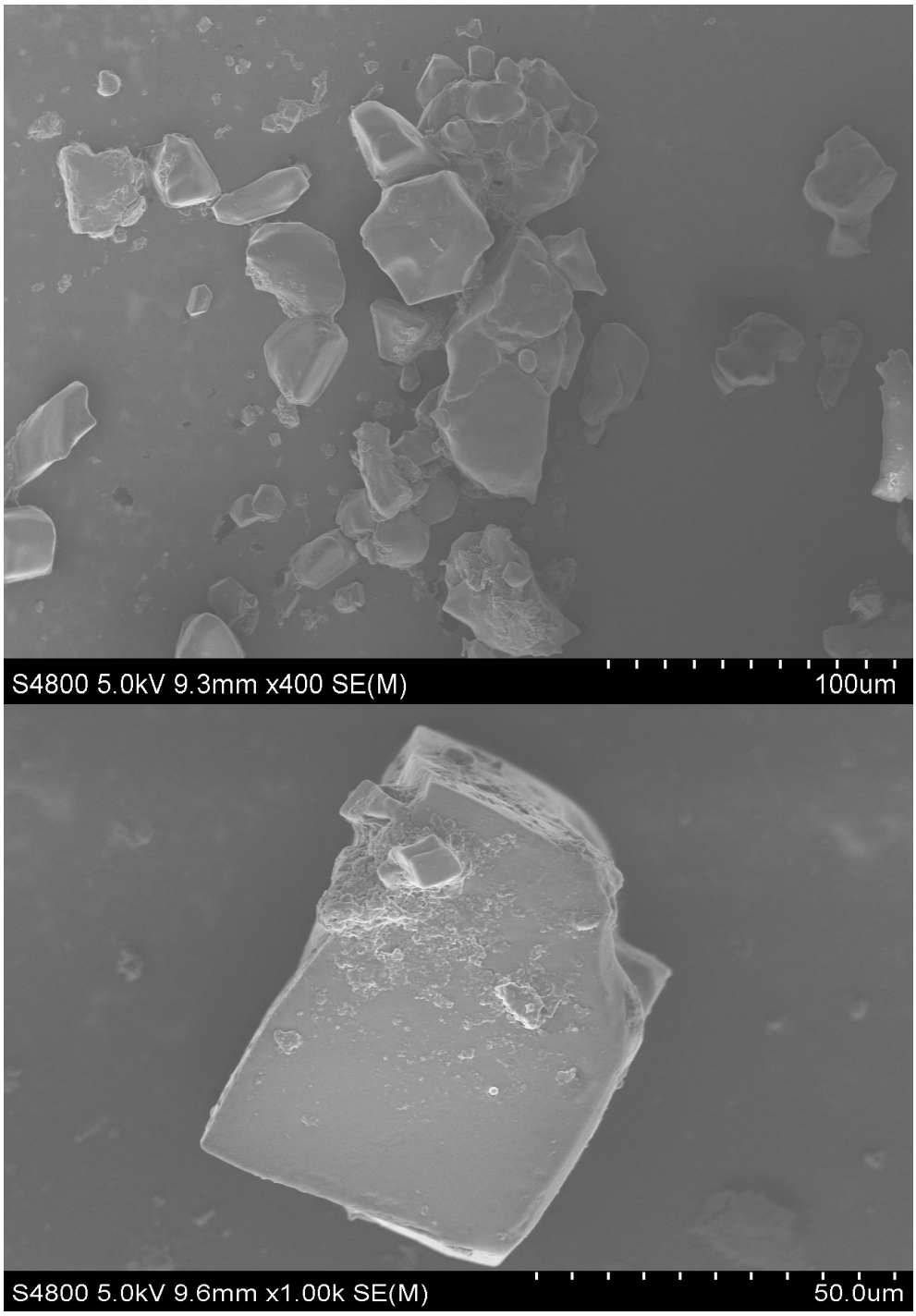


Fig. S6. SEM images of $NH_4N_5 \cdot ½H_2O_2$.

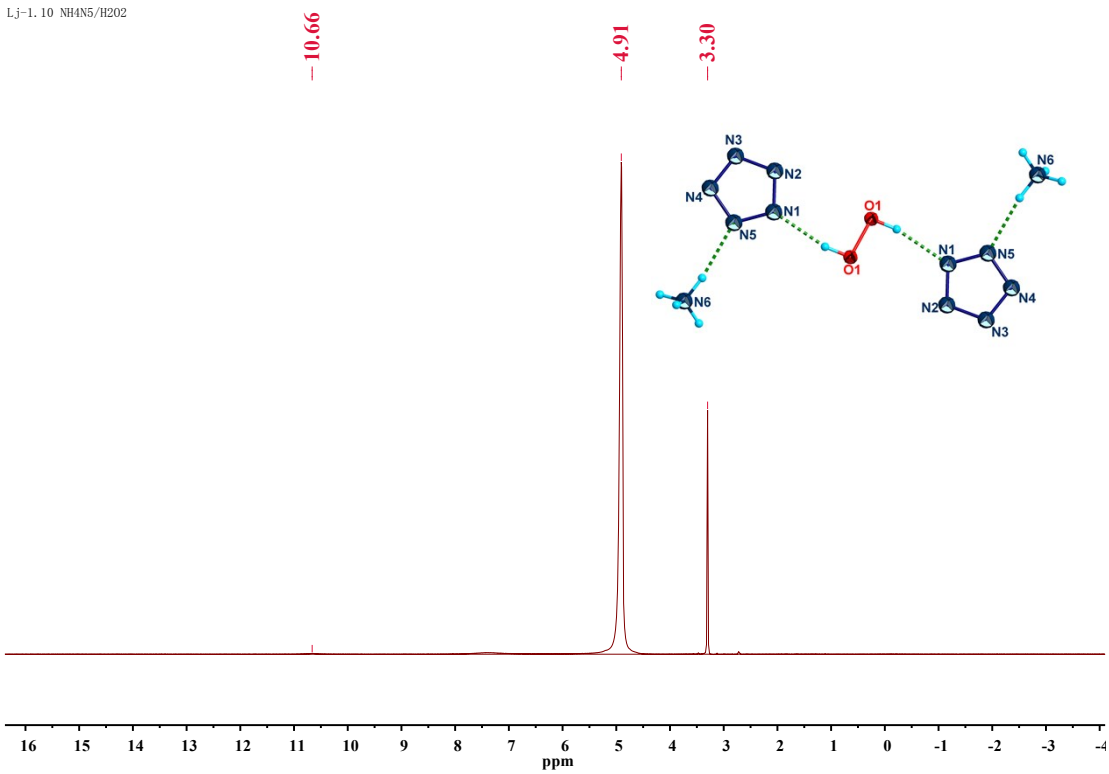


Fig. S7. ^{1}H NMR spectrum of $NH_4N_5{\cdot}½H_2O_2$ in CD_3OD.

Table S7. Selected parameters of $NH_4N_5{\cdot}½H_2O_2$ and NH_4N_5 in combustion chamber.

Products	$NH_4N_5{\cdot}½H_2O_2$	NH_4N_5
Heat of isobaric combustion (kJ/kg)	-4432.14	-3054.78
Total enthalpy of combustion products (kJ/kg)	2177.62	3055.18
Entropy of combustion products (kJ/K kg)	11.61	11.15
gaseous combustion temperature (**T_c**, K**)**	2673.9	1970.5
Mole number of gaseous products (mol/kg)	52.437	56.75
Total mole number of products (mol/kg)	52.437	56.75
Volume of gaseous products (L/kg)	1299.85	1406.77
Mass of gaseous products (g/kg)	999.9	999.9

Table S8. Combustion products composition of $NH_4N_5 \cdot ½H_2O_2$ in chamber.

Products	mol (%)	Formula weight (g mol^{-1})	Average formula weight (g mol^{-1})
N_2	54.4357	28	15.241996
H_2	27.0739	2	0.541478
H_2O	18.0901	18	3.256218
H	0.3353	1	0.003353
OH	0.0509	17	0.008653
NH_3	0.0077	17	0.001309
NO	0.0059	30	0.00177
O	0.0003	16	0.000048
O_2	0.0001	32	0.000032
N	0.0000	14	0
General average formula weight of Combustion products ($\overline{M}_1$)			19.05486

Table S9. Combustion products composition of NH_4N_5 in chamber.

Products	mol (%)	Formula weight	Average formula weight
N_2	60.0003	28	16.800084
H_2	39.9547	2	0.799094
NH_3	0.0345	17	0.005865
H	0.0105	1	0.000105
N	0.0000	14	0
General average formula Weight of Combustion Products ($\overline{M}_2$)			17.60515

Table S10. The values of $T_c / \overline{M}$ of $NH_4N_5 \cdot ½H_2O_2$ and NH_4N_5.

Products	$T_c / \overline{M}$
$NH_4N_5 \cdot ½H_2O_2$	140.3264
NH_4N_5	111.9275

5 References

[1] (a) Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang and M. Lu, *Nature,* 2017, **549**, 78-81; (b) Y. Xu, L. Tian, D. Li, P. Wang and M. Lu, *J. Mater. Chem. A,* 2019, **7**, 12468-12479.

[2] G. M. Sheldrick, *Acta. Crystallogr. Sect. A,* 2008, **64**, 112-122.

[3] (a) H. Gao, C. Ye, C. M. Piekarski and J. M. Shreeve, *J. Phys. Chem. C,* 2007, **111**, 10718-10731; (b) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013-5015.

[4] C. Yang, C. Zhang, Z. Zheng, C. Jiang, J. Luo, Y. Du, B. Hu, C. Sun and K. O. Christe, *J. Am. Chem. Soc.* 2018, **140**, 16488-16494.

[5] C. Zhang, C. Sun, B. Hu, C. Yu and M. Lu, *Science* 2017, **355**, 374-376.