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Stabilization of the Pentazolate Anion in Three Anhydrous and Metal-Free Energetic Salts $(N_5^-)_2DABTT^{2+}$, $N_5^-GU^+$, and $N_5^-Oxahy^+$

Yuangang Xu, Qiuhan Lin, Pengcheng Wang,* and Ming Lu*

Abstract: According to previous reports, metal cations or water molecules are necessary for the stabilization of pentazolate anion (*cyclo*- N_5^-) at ambient temperature and pressure. Seeking a new existence way of N_5^- is a big challenge. In this work, three anhydrous, metal-free energetic salts based on *cyclo*- N_5^- 3,9-diamino-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[4,3-*e*:3',4'-*g*][1,2,4,5] tetrazepine-2,10-dium, *N*-carbamoylguanidinium, and oxalohydrazinium pentazolate were synthesized and isolated. All of the new salts were characterized by elemental analysis, IR spectroscopy, 1H , ^{13}C , and (in some cases) ^{15}N NMR spectroscopy, thermal analysis (TGA and DSC), and single-crystal X-ray diffraction. Computational studies associated with heats of formation and detonation performance were performed by using Gaussian 09 and Explo5 programs, respectively. The sensitivity of the salts towards impact and friction was determined, and overall the real N_5^- explosives show promising energetic properties.

The pentazolate anion *cyclo*- N_5^- has become a hot issue with board interest in the development of high-energy-density materials (HEDMs). Its high energy content is due to the large amount of energy released upon decomposition of single-bonded nitrogen in the condensed phase into triple-bonded N_2 molecules^[1]. Earliest, *cyclo*- N_5^- was discovered in aryl pentazole molecules in the late 1950s^[2]. After that, numerous attempts have been made to cleave the C-N bond of aryl pentazoles and isolate the *cyclo*- N_5^- anion or the pentazole (HN_5). The *cyclo*- N_5^- was first identified in the gas phase by Vij *et al.*^[3] in 2002 by cleaving the C-N bond in *p*-oxidophenyl pentazole. Then *cyclo*- N_5^- anion was detected by laser ionization of *p*-dimethylaminophenyl pentazole in 2003 by Östmark *et al.*^[4] and decomposition of the solid substituted phenylpentazole was also studied. For a long time, a variety of attempts to obtain *cyclo*- N_5^- anion in condensed phase by oxidative^[5], reductive^[6], and photocleavage^[7] methods had failed. It had attracted special attention in 2016 since Bazanov *et al.*^[8] found evidence for the formation of *cyclo*- N_5^- in tetrahydrofuran solution and direct detection showed this anion is stable under -40 °C. Afterwards, Steele *et al.*^[9] reported the first successful synthesis of *cyclo*- N_5^- in the solid phase cesium pentazolate salt (CsN_5), which is achieved by compressing and laser heating cesium azide (CsN_3) mixed with N_2 cryogenic liquid in a diamond anvil cell. Very recently, the ultimate goal of the stable presence of *cyclo*- N_5^- in the solid phase and ambient conditions was finally fulfilled by Zhang *et al.*^[10] in 2017. *Cyclo*- N_5^- was generated by oxidative cleavage of the C-N bond in 3,5-dimethyl-4-hydroxyphenylpentazole using *m*-chloroperbenzoic acid and ferrous bisglycinate and characterized by single-crystal X-ray crystallography as a

component of environmentally stable $(N_5)_6(H_3O)_3(NH_4)_4Cl$.

Metals are the key to achieving enhanced stability of *cyclo*- N_5^- in the solid phase. Much research was focused on finding suitable metallic cations, assembly of metals and *cyclo*- N_5^- , stability of metal- N_5 species and so on^[11]. Transition metal Mn, Fe, Co, and Zn cations^[12-14] were found can stabilize *cyclo*- N_5^- by coordination to form η^1 - σ -bonds. Alkali metal Na^[12] and Cs^[9] and alkaline-earth metal Mg^[12] cations can form ionic compounds with *cyclo*- N_5^- . In addition to CsN_5 , the synthesis of a series of metal- N_5^- hydrates $[Na(H_2O)(N_5)] \cdot 2H_2O$, $[M(H_2O)_4(N_5)_2] \cdot 4H_2O$ (M = Mn, Fe, Co, and Zn), and $[Mg(H_2O)_6(N_5)_2] \cdot 4H_2O$ (Figure 1) suggested that water plays a critical role in the stabilization of *cyclo*- N_5^- . For anhydrous CsN_5 , Cs transfers maximum negative charge to the N_5 rings to enable both aromaticity of the *cyclo*- N_5^- and ionic bonding between Cs cations and *cyclo*- N_5^- . While for the 3D metal-*cyclo*- N_5^- frameworks $[Na_6(N_5)_6(H_2O)_3]_n$ ^[14b] and MPF-1,^[14c] every *cyclo*- N_5^- ring was stabilized by five coordination bonds from five sodium cations.

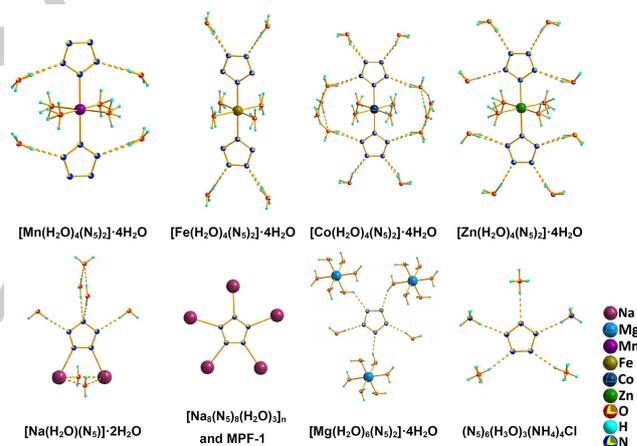
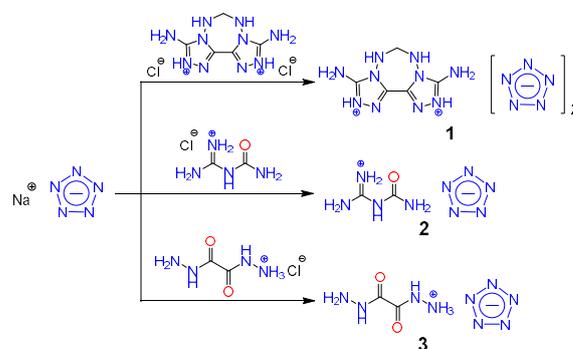


Figure 1. Reported *cyclo*- N_5^- -based compounds and their stable modes.



Scheme 1. Synthesis of anhydrous, metal-free energetic salts based on pentazolate anion.

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Until now, there are few stable non-metallic pentazolate salts at ambient conditions. Typical non-metallic ionic salt $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ stabilizes *cyclo*- N_5^- anion in the solid state by five hydrogen bonds from neighboring ammonium and hydronium cations.^[11a] However, the low density (1.34 g cm^{-3}) and non-energetic components (H_3O^+ , NH_4^+ , and Cl^-) make this material unable to meet the demands of HEDMs. With our continuing interest in exploring the fantastic chemistry of *cyclo*- N_5^- -based compounds, herein we report three anhydrous, metal-free energetic salts based on *cyclo*- N_5^- .

The synthesis of the new energetic salts is shown in Scheme 1. The raw material $[\text{Na}(\text{H}_2\text{O})(\text{N}_5)] \cdot 2\text{H}_2\text{O}$ was synthesized based on a previous report.^[12] The nitrogen-rich pentazolate salts, such as 3,9-diamino-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[4,3-*e*:3',4'-*g*][1,2,4,5]tetrazepine-2,10-dium (DABTT^{2+}), *N*-carbamoylguanidinium (GU^+), and oxalohydrazinium (Oxahy^+) pentazolate (**1-3**) can be obtained *via* metathesis reactions using sodium pentazolate $[\text{Na}(\text{H}_2\text{O})(\text{N}_5)] \cdot 2\text{H}_2\text{O}$ and the corresponding chlorides, respectively, can be considered, where the reaction is driven by the low solubility of sodium chloride.

The structures of **1-3** were confirmed by infrared (IR) spectroscopy, ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction. ^{15}N NMR spectrum of **2** was measured in dimethyl sulfoxide (DMSO)- D_6 with respect to CH_3NO_2 as an external standard. Nitrogen signals were assigned based on the literature^[15] and Giau NMR calculation with Gaussian 09^[16]. As shown in Figure 2, the nitrogen atoms of *cyclo*- N_5^- (N1) resonate at -5.95 ppm , consistent with the published data (-5.7 ppm)^[12]. Apart from the signal of the *cyclo*- N_5^- anion, the three kinds of hydrogen-attached nitrogen atoms have higher negative resonances. The N2 nitrogen atom (NH) resonates at the lowest field of all three at -269.19 ppm , whereas the two different kinds of NH_2 groups have very similar shifts at -291.28 ppm (N3) and -296.49 ppm (N4). In contrast to the spectrum of *N*-carbamoylguanidinium nitrate^[15], the signals for the cation (N2, N3, and N4) were shifted about 2 ppm to lower fields.

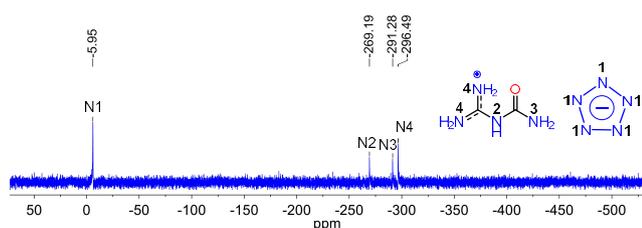


Figure 2. ^{15}N NMR spectrum of salt **2**.

Crystals of **1-3** were obtained by dissolving them in water, followed by slow volatilization at room temperature and determined at 173 K (Figure 3-5; for the crystallographic data and refinement details please see the Supporting Information). Salt **1** crystallizes in the monoclinic space group $\text{C}2/c$ with a density of 1.660 g cm^{-3} at 173 K and four molecules in the unit cell (Figure 3). The cation DABTT^{2+} exhibits a *trans* structure with the angle of 36.68° between two amino-triazole planes (Figure S14). The C3-N5 bond length of C-amino group is

$1.313(2) \text{ \AA}$, which is slightly shorter than three C-N bonds (C2-N2: $1.379(2) \text{ \AA}$; C3-N2: $1.3558(19) \text{ \AA}$; C3-N4: $1.334(2) \text{ \AA}$) and longer than one C-N bond (C2-N3: $1.291(2) \text{ \AA}$) of the triazole moiety. With the bond lengths of $1.291(2)$ to $1.385(2) \text{ \AA}$, the distances between the ring atoms of the triazole moiety lie between the length of formal C-N and N-N single and double bonds, which indicates the aromaticity of the ring system.^[17] The N-N bond lengths in *cyclo*- N_5^- anion are $1.302(2)$, $1.305(2)$, $1.311(2)$, $1.311(2)$, and $1.318(2) \text{ \AA}$; the average N-N bond distance (1.3096 \AA) is shorter than that of all the reported *cyclo*- N_5^- based crystals^[10,12-14] ($[\text{Na}(\text{H}_2\text{O})(\text{N}_5)] \cdot 2\text{H}_2\text{O}$: 1.316 \AA ; $[\text{Mg}(\text{H}_2\text{O})_6(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$: 1.316 \AA ; CsN_5 : 1.328 \AA (0 GPa); $[\text{Mn}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$: 1.320 \AA ; $[\text{Fe}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$: 1.329 \AA ; $[\text{Co}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$: 1.314 \AA ; $[\text{Zn}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$: 1.328 \AA ; and $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$: 1.315 \AA). Unlikely most compounds in Figure 1, *cyclo*- N_5^- in **1** lacks perfect planarity, with the largest torsion angle (N7-N10-N6-N9) of 0.52° which is smaller than that of $[\text{Mg}(\text{H}_2\text{O})_6(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ (0.85°). All hydrogenated atoms (C1, N1, N4, and N5) of the cations participate in hydrogen bonds act as donors, while all nitrogens (N6 to N10) of *cyclo*- N_5^- rings act as hydrogen-bond acceptors in **1** (Table S4, Figure S15).

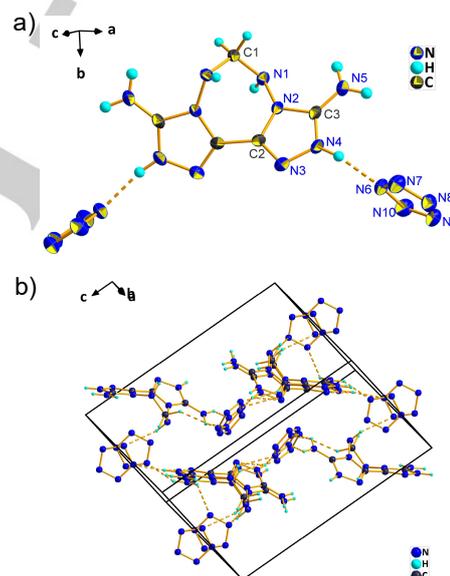


Figure 3. a) Single-crystal X-ray structure of salt **1** with thermal ellipsoids set at 50% probability. b) Unit cell of **1**. Dashed lines indicate strong hydrogen bonding.

Salt **2** crystallizes in the monoclinic $\text{P}2_1/c$ space group with four molecules in the unit cell. Its calculated density is 1.596 g cm^{-3} at 173 K, which is slightly lower than that of salt **1**. As shown in Figure 4a, the GU^+ together with *cyclo*- N_5^- anion are approximately in the plane, which can be seen from the torsion angle C1-C2-N5-N1 of 0.43° and N4-N1-N5-N2 of 0.2° . The C-N bond lengths and the N-C-N bond angles in the GU^+ are in the range of $1.313(2)$ - $1.356(2) \text{ \AA}$ and $113.20(14)$ - $126.22(16)^\circ$, respectively, which are typical values for the GU^+ cation.^[15] The N-N bond lengths in the *cyclo*- N_5^- are in the range of $1.299(2)$ - $1.335(2) \text{ \AA}$, with an average N-N bond distance of 1.318 \AA , which is similar to that of $[\text{Na}(\text{H}_2\text{O})(\text{N}_5)] \cdot 2\text{H}_2\text{O}$ (1.316 \AA),

$[\text{Mg}(\text{H}_2\text{O})_6(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ (1.316 Å), and $[\text{Mn}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ (1.320 Å). Since the amino groups in *N*-carbamoylguanidinium are excellent hydrogen-bonding donors, the discrete *cyclo-N*₅⁻ rings are linked into a stable 2D layer by the hydrogen-bonding interactions between cations and anions (Figure 4b and c). The face-to-face stacking of **2** (Figure 4b) shows that there are no significant interactions between adjacent layers.

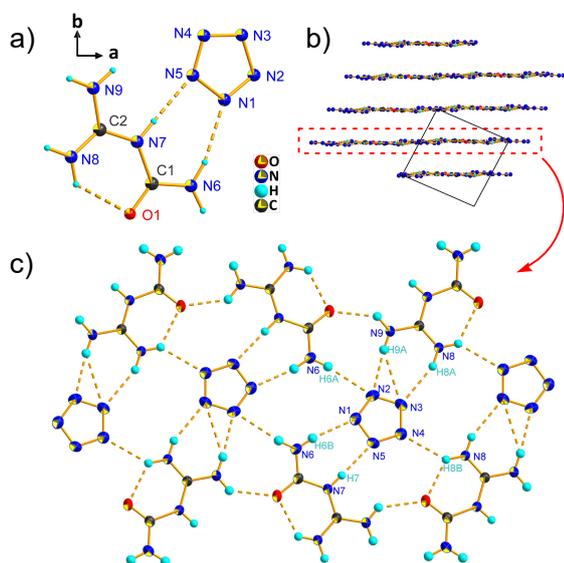


Figure 4. a) Single-crystal X-ray structure of salt **2** with thermal ellipsoids set at 50% probability. b) 3D structural layer network in **2**. c) 2D layered intermolecular interactions in the crystal structure of **2**. Dashed lines indicate strong hydrogen bonding.

Salt **3** crystallizes in the same space group (monoclinic $P2_1/c$) with **2** and eight molecules in the unit cell (Figure 5). Its crystal density (1.681 g cm⁻³ at 173 K) is higher than those of **1** and **2**. Two forms of *cyclo-N*₅⁻ can be found in **3**, with the N-N bond lengths in the range of 1.294(5)-1.339(5) Å and 1.301(5)-1.333(5) Å and the largest torsion angle N2-N1-N5-N4 of 0.64° and N10-N6-N7-N8 of 1.31°.

It is important to note that hydrogen bonds from nitrogen-rich cations instead of water molecules play a critical role in stabilizing *cyclo-N*₅⁻ anions in the crystals of **1-3**. Every *cyclo-N*₅⁻ ring participates in at least five hydrogen bonds (Figure 4c, S15, and S21). The lengths of the hydrogen bonds are shorter than the sum of the van der Waals radii ($r_w(\text{N}) + r_w(\text{N}) = 3.20$ Å), thus a strong hydrogen-bond network is formed (Table S4, S8, and S12).

To evaluate if salts **1-3** have potential as energetic materials, their densities, thermal stabilities, sensitivity properties as well as detonation performances were studied (Table 1). Salts **1-3** have higher densities than that of $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ ^[10]. Similar to most reported metal-N₅ complexes except $[\text{Co}(\text{H}_2\text{O})_4(\text{N}_5)_2] \cdot 4\text{H}_2\text{O}$ ^[12,13], the *cyclo-N*₅⁻ in **1-3** decomposed at 100, 110, and 95 °C, respectively (Figure S12, S13). To obtain a better understanding of the stabilities, the minimum Wiberg bond orders of the *cyclo-N*₅⁻ in **1-3** (1.3119, 1.366, and 1.0777) were calculated (Figure S24). Obviously, their theoretical stabilities

decrease in the sequence: **2** > **1** > **3**, which is consistent with the experimental data.

The heats of formation of **1-3** were calculated by using the Gaussian 09 (Revision A.02) suite of programs^[16]. *Cyclo-N*₅⁻ was found to have a heat of formation of 255.89 kJ mol⁻¹, in excellent agreement with the values of 249.37^[18], 254.6^[19], 260 ± 15^[20], 263.59^[21] kJ mol⁻¹ calculated at CCSD(T)/aug-cc-pVTZ, MP2(FU)/6-31G(d), CCSD(T)/6-311+G(3df), and RI-MP2-fc/TZVPP levels. As can be seen in Table 1, salts **1-3** exhibited positive heats of formation (203.4-1341.2 kJ mol⁻¹) and much larger than those of FOX-12 (guanyurea dinitramide, -355 kJ mol⁻¹) and RDX (1,3,5-trinitroperhydro-1,3,5-triazine, 80 kJ mol⁻¹).^[22] Among them, because of the presence of a fused tricyclic cation, **1** has the highest value of 1341.2 kJ mol⁻¹. The detonation performance of these salts were calculated using the Explo5 program (version 6.01)^[23]. The detonation velocity (*D*) and pressure (*P*) values were shown in Table 1. Salt **3** has the highest *D* (8320 m s⁻¹), which is comparable to FOX-12 and RDX. However, compared to RDX, the *P* of **3** is lower (27.1 GPa). Salt **1** and **2** have a moderate detonation performance (*D*: 7615 and 6920 m s⁻¹; *P*: 23.6 and 18.9 GPa) due to their high nitrogen but low oxygen contents and low densities. Therefore, further studies are expected to improve oxygen balance, increase packing coefficient, and heighten the density to a higher level for *cyclo-N*₅⁻ based energetic salts.

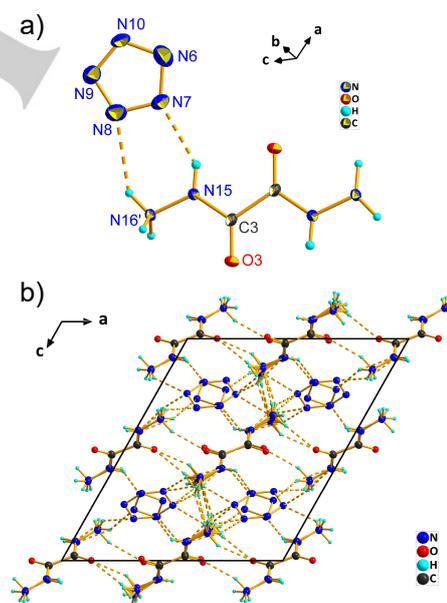


Figure 5. a) Single-crystal X-ray structure of salt **3** with thermal ellipsoids set at 50% probability. b) A view of the packing down the *b*-axis of the unit cell of **3**. Dashed lines indicate strong hydrogen bonding.

Their sensitivities toward friction and impact were tested using standard BAM techniques.^[24] For **2**, the impact sensitivity is 14 J, while the friction sensitivity is 160 N. More insensitive than the other two salts arises from the effect of the stable layer-by-layer stacking. Salt **1** is similar to RDX with respect to friction and less sensitive to impact than RDX. While salt **3** is found to be more sensitive than RDX.

Table 1. Physicochemical and energetic properties of **1-3** compared with FOX-12 and RDX.

	$d^{[a]}$ [g cm ⁻³]	$T_d^{[b]}$ [°C]	$\Delta H_f^{[c]}$ [kJ mol ⁻¹] / [kJ g ⁻¹]	$D^{[d]}$ [m s ⁻¹]	$P^{[e]}$ [GPa]	IS ^[f] [J]	FS ^[g] [N]	N ^[h] [%]	OB ^[i] [%]
1	1.660/1.629	100	1341.2/3.83	7615	23.6	10	120	79.98	-45.7
2	1.596/1.567	110	203.4/1.18	6920	18.9	14	160	72.81	-41.6
3	1.681/1.650	95	388.1/2.05	8320	27.1	6	80	66.65	-29.6
FOX-12 ^[ii]	1.75	201	-355.0/-1.70	8323	26.6	30	350	46.89	-3.8
RDX ^[ii]	1.80	205	80.0/0.36	8748	34.9	7	120	37.84	0

[a] Crystal density at 173 K. Values after slashes were recalculated from low-temperature X-ray densities ($d_{298K} = d_T / [1 + 1.5 \cdot 10^{-4} (298-T)]$). [b] Decomposition temperature from TGA (5 °C min⁻¹). [c] Calculated heat of formation in solid state. [d] Calculated detonation velocity. [e] Calculated detonation pressure. [f] Impact sensitivity. [g] Friction sensitivity. [h] Nitrogen content. [i] Oxygen balance (based on CO) for C_aH_bO_cN_d, $1600(c-a-b/2)/M_w$, M_w = molecular weight. [j] Ref. [22].

In summary, three new nitrogen-rich ionic derivatives (**1-3**) of pentazolate anion (*cyclo*-N₅⁻) were synthesized and fully characterized. These salts still have acceptable thermal stability (T_d : 95-110 °C) although the *cyclo*-N₅⁻ anions are no longer stabilized by metals and water molecules. All new salts show positive heats of formation, especially **1** has the highest value of 1341.2 kJ mol⁻¹. The oxalohydrazinium salt **3** has a detonation velocity of 8320 m s⁻¹ and a detonation pressure of 27.1 GPa, which is comparable to the nitrogen-rich salt FOX-12. This work highlights *cyclo*-N₅⁻ as a next generation energetic building block and may provide new inspiration for the design and synthesis of N₅-based HEDMs.

Acknowledgements

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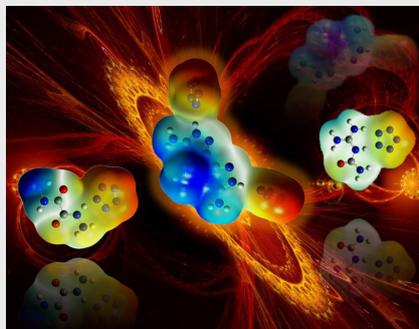
Keywords: pentazole • nitrogen • crystal structures • polynitrogen compounds • energetic materials

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Entry for the Table of Contents

COMMUNICATION

Three new nitrogen-rich ionic derivatives of pentazolate anion (*cyclo*-N₅⁻) 3,9-diamino-6,7-dihydro-5*H*-bis([1,2,4]triazolo)[4,3-*e*:3',4'-*g*][1,2,4,5]tetrazepine-2,10-dium, *N*-carbamoylguanidinium, and oxalohydrazinium pentazolate were synthesized and fully characterized. Single crystal X-ray structure analyses revealed the stabilization mechanism of the *cyclo*-N₅⁻ in anhydrous, metal-free solid phase. Their physicochemical and energetic properties have also been studied.



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Stabilization of the Pentazolate Anion in Three Anhydrous and Metal-Free Energetic Salts (N₅)₂DABTT²⁺, N₅⁻GU⁺, and N₅⁻Oxahy⁺