Packing high-energy together: binding the power of pentazolate and high-valence metals with strong bonds

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ABSTRACT: Stabilizing pentazolate anion in solid compounds is a challenging and important approach toward making environmentally friendly high energy density materials. Using a constrained crystal structure search method and rigorous bond analysis, we predicted the metastable structures of $Al(N_5)_3$ and $Mg(N_5)_2$. In contrast to common wisdom, our work demonstrates that metals, especially the multivalent metals such as Al and Mg, can stabilize pentazolate anions by forming strong metal-N bonds. Both compounds are metastable at ambient pressure and temperatures as high as 600 K. The multivalent metals not only stabilize the pentazolate anions but also greatly enhance the energy density. The decomposition of $Al(N_5)_3$ or $Mg(N_5)_2$ can release an energy of 4.61 kJ/g or 3.10 kJ/g, respectively, making them promising candidates as high energy density materials.

Keywords: High energetic density materials; Petazolate; High valence metals; Constrained structure search.

1. Introduction

Polynitrogens, such as pentazolate anion (*cyclo*-N_5^-), might pack an enormous amount of energy and release them while decomposing into products such as N_2 gas that is inert, non-toxic and has no green-house effect [1-3]. These superlative properties make them excellent candidates for high energy materials, such as future explosives and rocket propellants [3, 4]. The major challenge in this area is the lack of an effective method to synthesize the metastable polynitrogens at ambient conditions. Encouragingly, many metals (such as Na, Cs, Cu) are found to form stable pentazolates under high pressure [5-11], and among them, LiN_5 has been successfully recovered after releasing the high pressure after its synthesis [9]. This is because many metal ions are capable of forming strong bonds with N_5^- ligands.

Two major problems remain in the study of metal pentazolates. Firstly, adding metals or any other stabilizer agents might greatly reduce energy density. Indeed, in the recently synthesized pentazolate compounds $[Na(H_2O)(N_5)]\cdot 2H_2O$ and $(N_5)_6(H_3O)_3(NH_4)_4Cl$, although *cyclo*-$N_5^-$ is stabilized by forming hydrogen bonds with neighboring H_2O and NH_4^+ molecules [12-21], the presence of these molecules largely reduces the energy density. Secondly, the binding with metal ions, especially those capable of forming strong bonds with ligands, might reduce the aromaticity of *cyclo*-N_5^- and weakening the conjugated π bonds on the ring [21-23]. Furthermore, although several pentazolate compounds containing metals have been reported, the examples of metal pentazolates are still rare [5-11, 24-26]. There is a strong need for searching and studying new metal pentazolates, especially the structures and the properties of their metastable states under atmospheric pressure, which are still unknown.

In solving the above problems, we propose that high valence metals have an exceptional ability to lower the energy of *cyclo*-N_5^- rings. Using calculations based on density functional theory, we demonstrate that Al and Mg can form pentazolate compounds that can remain metastable up to 600 K. The bond analysis about bonding and antibonding interactions reveals that *cyclo*-N_5^- maintains its strong N-N bonding while binds with Al or Mg. Comparing with LiN_5, Al and Mg show much lower disturbance to the aromaticity of *cyclo*-N_5^-. Furthermore, the use of high valence metals can enhance the energy density instead of lowering it. While they decompose to stable M_3N_2 and nitrogen gas, the released energy of $Al(N_5)_3$ and $Mg(N_5)_2$ is up to 4.61 kJ/g and 3.10 kJ/g, respectively. As a matter of

fact, some metals such as Mg and Al are propellant materials and can release a great amount of energy while reacting with oxidants [27-30]. The released energy of $Al(N_5)_3$ and $Mg(N_5)_2$ is further improved to 6.72 kJ/g and 5.72 kJ/g while they decompose in the air or react with strong oxidants. Therefore, the results of high valance metal pentazolate compounds are inspiring for the exploration of metal pentazolates as clean HEDMs in the future.

2. Computational Details

The major challenge of this study is to predict the structures of the candidate compounds at atmospheric pressure. Although many metal pentazolates might be thermodynamically stable under high pressure, they become metastable and may undergo structural transformations upon the release of pressure. The metastable structures could be significantly different from their high-pressure structures. Our goal is to search the structure that is the lowest in energy among all metastable structures containing *cyclo*-N_5^- at 1 atm. This is not a straightforward task, since the search algorithms only work toward finding the global minimum although in some cases local minimum structures might also be found as byproducts. Here, we employ an approach in which the bond connectivity of N atoms in *cyclo*-N_5^- rings is restrained during the generation and evolution of the structures. The approach is applied to the Particle Swarm Optimization (PSO) algorithm as implemented in the CALYPSO code [31, 32]. Using this method, we searched the metastable structures of $Al(N_5)_3$ and $Mg(N_5)_2$ compounds with the lowest energy under atmospheric pressure, restricting all the N atoms in the form of *cyclo*-N_5^-. Up to 2800 stoichiometric structures of $[Mg(N_5)_2]_x$ and $[Al(N_5)_3]_x$ (x = 2−5) were generated, relaxed, and ranked based on their calculated energies. Among them, 30 low-energy structures were chosen for further geometry relaxations using finer parameters, and their energies were shown in Fig. S1. The energy of second stable structure is 0.09 eV and 0.11 eV per formula for $Mg(N_5)_2$ and $Al(N_5)_3$ higher than lowest one, the energy difference is enough to distinguish them as different structures in microcosmic world, and the large energy difference is caused by the strong Al-N (Mg-N) bond. In general, the stronger of chemical bond formed between atoms in structure, the more of total energy was influenced through altering its geometric morphology. Moreover, the other metastable structures presents similar bonding style but different space group and bond lengths. Therefore, the structures with the lowest energy could be identified for both compounds.

The geometry optimizations and electronic property calculations were carried out by the *Vienna ab initio* simulation *package* (VASP) [33, 34]. The single-electron wave function was expanded using a plane-wave basis set with an energy cutoff of 750 eV. The projector augmented wave (PAW) method [35] was used to describe the interactions between ions and electrons. The electron exchange and correlation were treated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [36]. Pseudopotentials are used to describe the ionic potentials, and $2p^6 3s^2$, $3s^2 3p^1$ and $2s^2 2p^3$ are treated as valence electrons for Mg, Al, and N atoms, respectively. The atomic positions and lattice constants were optimized using the conjugate gradient (CGs) scheme until the residual Hellmann–Feynman forces on each atom became less than 0.01 eV/Å, and the convergence criterion of electronic self-consistent energy was set to 1×10^{-5} eV. Brillouin zone (BZ) integrations were performed using a Monkhorst-Pack [37] k-point mesh with a resolution of $2\pi \times 0.01$ $Å^{-1}$. The *ab initio* molecular dynamics (MD) simulation were used to evaluate the stability for metastable structures. The simulations ran at finite temperature in the NVT ensemble with a large supercell containing about 100 atoms. The phonon calculations were carried out by using a finite displacement approach through the PHONOPY code [38, 39]. The high symmetry points in band structures of electrons and phonons were obtained from the online tool of seek-path [40].

3. Results and Discussion

3.1 Crystal structure and stability

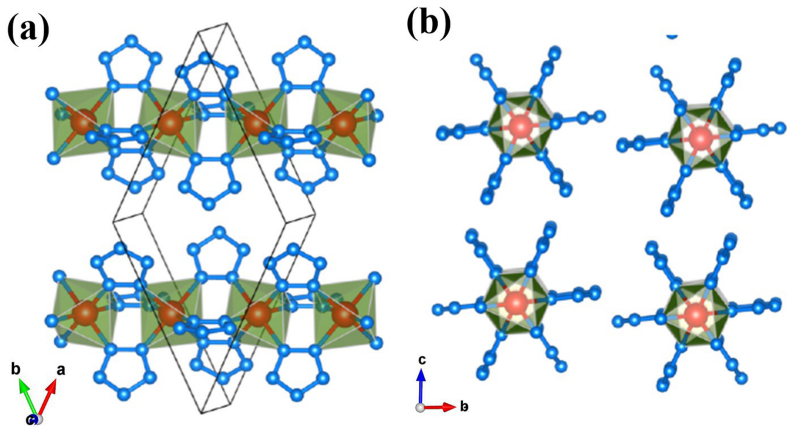

Fig. 1 (a) The most stable structure of $Al(N_5)_3$ at 0 GPa, composed with octahedral Al and η^2-N_5; (b) The same structure view along c axes.

The identified structures of $Al(N_5)_3$ and $Mg(N_5)_2$ are shown in Fig. 1 and Fig. S2, and their parameters and atomic positions are shown in Table S1. $Al(N_5)_3$ adopts a *C2/m* structure consisting of parallel $Al(N_5)_3$ chains, in which two N atoms on a *cyclo-*N_5^- ring bind with two neighboring Al atoms (bidentate η^2-N_5) and each Al atom binds with 6 different *cyclo-*N_5^- rings. In contrast to $Al(N_5)_3$, $Mg(N_5)_2$ forms a 3-dimensional extended solid with a space group of *Pbcn*, which is 0.18 eV per formula lower than recently reported *Fdd2* phase.[10] In this structure, three N atoms on each *cyclo-*N_5^- ring form bonds with three neighboring Mg atoms (tridentate η^3-N_5). The bond length of N-N and metal-N are marked in Fig. 4, the average length of N-N bonds in $Al(N_5)_3$ and $Mg(N_5)_2$ are 1.328 and 1.326 Å, respectively, which are very close to that in *P21/c*-LiN_5 (1.324 Å), $[Na(H_2O)(N_5)]\cdot 2H_2O$ (1.328 Å) and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$ (1.324 Å), indicating that *cyclo-*N_5^- rings are equally stabilized in $Al(N_5)_3$ and $Mg(N_5)_2$ as the reported pentazolate compounds.

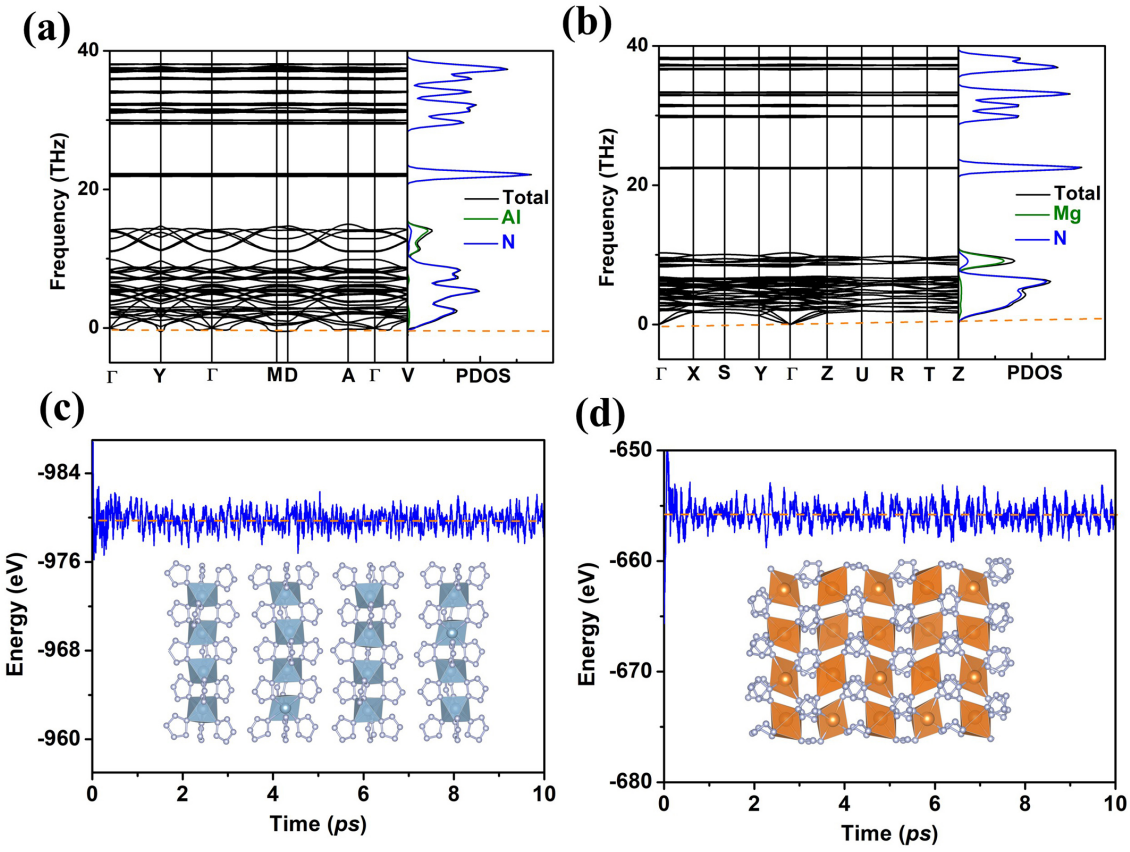

Fig. 2 Phonon dispersion curves for (a) $Al(N_5)_3$ and (b) $Mg(N_5)_2$; Images for the equilibrium structures at the end of 6 *ps* AIMD simulations and fluctuations of the total energies of (c) $Al(N_5)_3$

and (d) $Mg(N_5)_2$ at the temperature of 600 K. Images for the equilibrium structures at the end of 6 *ps* AIMD simulations are also presented in the figure.

To further evaluate the dynamic stability of $Al(N_5)_3$ and $Mg(N_5)_2$, we calculated their phonon spectra and show them in Fig. 2(a) and 2(b). There are no imaginary frequencies in the entire Brillouin zone at 1 atm, indicating both $Al(N_5)_3$ and $Mg(N_5)_2$ compounds are dynamically stable. The atomic motions are well separated in phonon PDOS. The high energy modes (> 22 THz) consist of N-N vibrations, the low energy modes (< 11 THz in $Al(N_5)_3$ and < 8 THz in $Mg(N_5)_2$) consist of the collective motions of *cyclo*-N_5^- ring, and the metal atom modes are right above the N_5- ring modes. There is almost no overlap between metal atom modes and N-N modes, which is due to the relatively weak binding between metal and N atoms as well as the large difference between their masses.

In order to use $Al(N_5)_3$ and $Mg(N_5)_2$ as high energy materials, they need to remain metastable under atmospheric pressure and room temperature. We performed *ab initio* molecular dynamics (AIMD) simulations for a supercell containing around 100 atoms. The simulations are carried out at a series of temperatures of 400 K, 600 K, 800 K and 1000 K with a time step of 2 *fs* for 5000 steps. As shown in Fig. 2(c) and 2(d), the energies and the structure features such as the distances between neighboring atoms remain similar to their original values after 10 *ps* of AIMD steps. Similar results are found for pair distributions and the statistically averaged distances of the closest Al-N (Mg-N), Al-Al (Mg-Mg) and N-N (Fig. S3). These results reveal that $Al(N_5)_3$ and $Mg(N_5)_2$ maintain their structural integrity at 600 K. At higher temperatures, the two compounds start to decompose as shown by the MD simulations (Fig. S4). It is interesting to notice the different decomposition paths between the metal pentazolate compounds and the arylpentazoles (ArN_5). In the latter case, the decomposition starts from the breaking of the N_5^- ring [41], whereas $Al(N_5)_3$ and $Mg(N_5)_2$ always starts from the breaking of metal-N bonds that will release the *cyclo*-N_5^- ring.

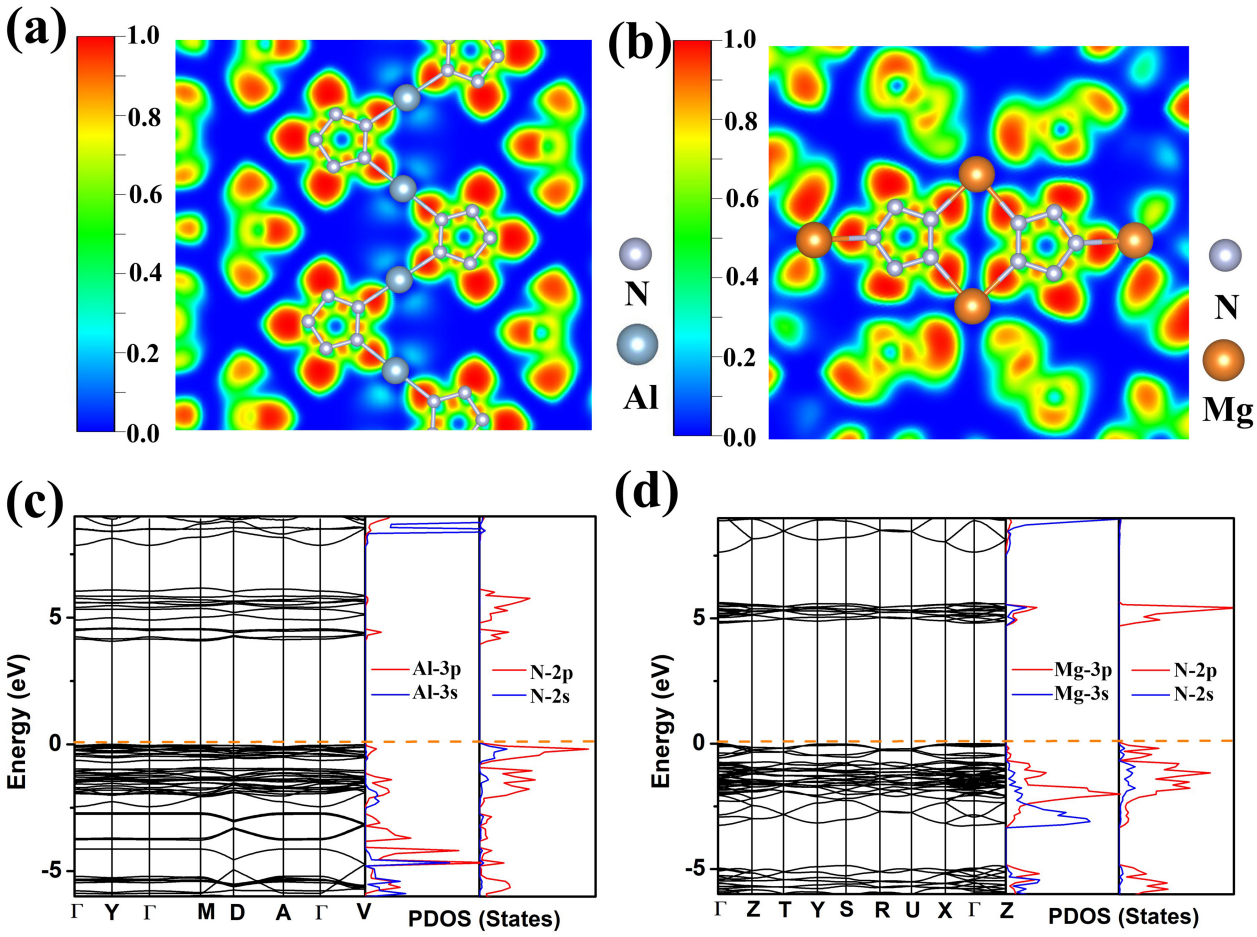

Fig. 3 The sectional view of ELF in a plane that shows both metals and *cyclo*-N_5^- in (a) $Al(N_5)_3$ and (b) $Mg(N_5)_2$; Electronic properties of (c) $Al(N_5)_3$ and (d) $Mg(N_5)_2$ at 0 GPa;

3.2 Electronic structures and bonding features

The mechanism that makes high valence metals good agents to stabilize pentazolate anions was further explored by electronic structure calculations and chemical bonds analysis. A series of electronic structure analysis for both $Al(N_5)_3$ and $Mg(N_5)_2$ compounds were used as evaluating method, including the electron localization function (ELF) calculations, band structure, the projected density of states (PDOS), the charge transfer in the framework of Bader's Quantum Theory of Atoms in Molecules (QTAIM) [42] and the Crystalline Orbital Hamiltonian Population (COHP) [43]. For comparisons, these properties were also calculated for LiN_5, $[Na(H_2O)(N_5)]\cdot 2H_2O$ and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$ compounds.[12] The ELF calculations reveal very strong covalent N-N bonds in the *cyclo*-N_5^- ring (Fig. 3(a) and 3(b)). However, it also indicates large covalent components for Al(Mg)-N bonds, although these bonds are mainly ionic. This point is confirmed by

the PDOS results that show clearly the overlap between Al (Mg) 3s and 3p states and N 2p states (Fig. 3(c) and 3(d)).

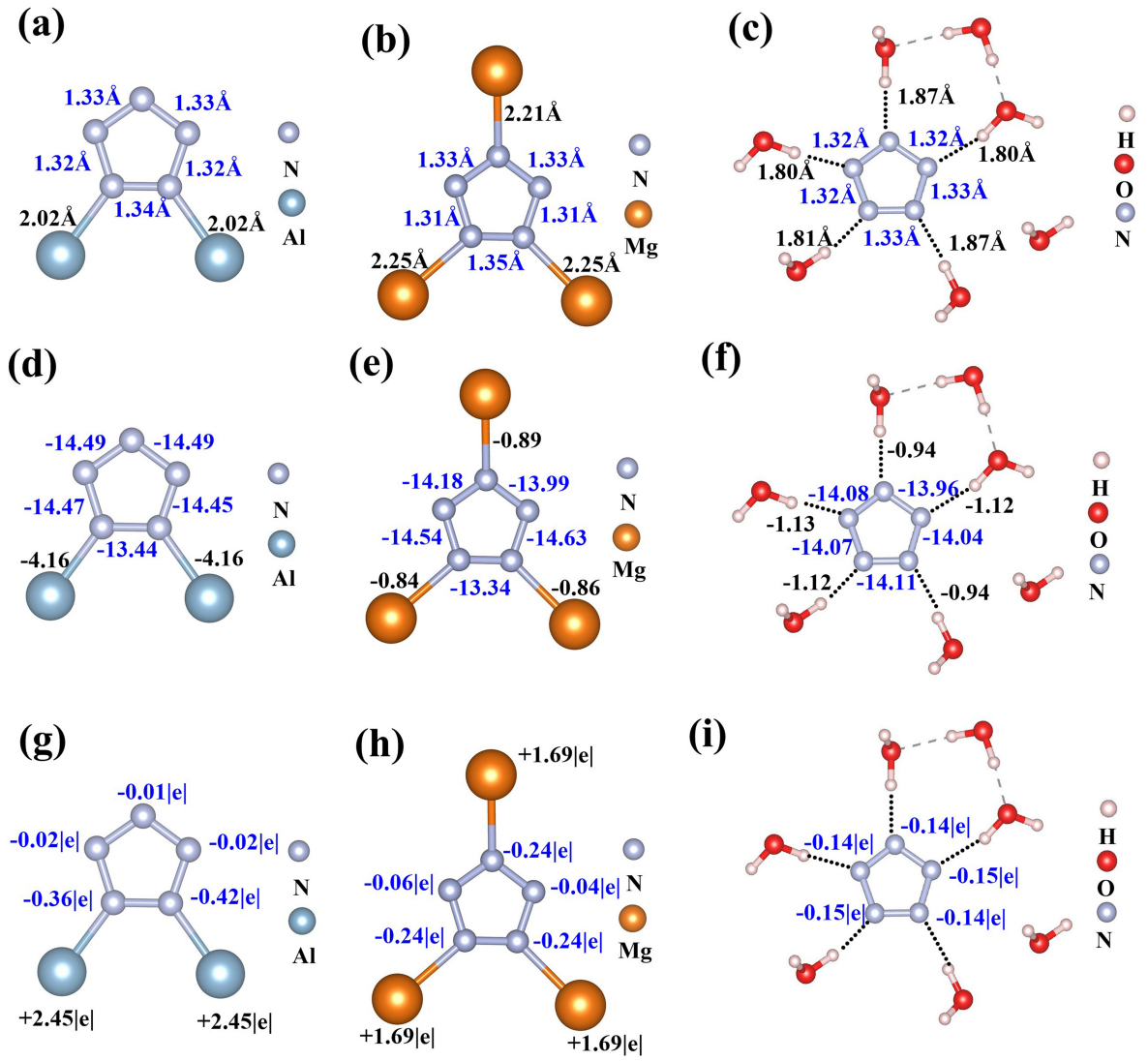

Fig. 4 the bond length information in (a) $Al(N_5)_3$, (b) $Mg(N_5)_2$ and (c) $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$; the ICOHP values are marked in the structure of (d)$Al(N_5)_3$, (e) $Mg(N_5)_2$ and (f) $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$; the atomic bader charge in (g) $Al(N_5)_3$, (h) $Mg(N_5)_2$ and (i) $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$.

The COHP results reveal that the binding with the metals especially the high valence metal (such as Al) does not weaken the N-N bonds on the *cyclo*-N_5^- ring. As a matter of fact, as shown in Fig. 4 and Fig. S5, the integrated COHP (ICOHP) values are the mxost significant for $Al(N_5)_3$ in comparison with other compounds such as $Mg(N_5)_2$, LiN_5, $[Na(H_2O)(N_5)]\cdot 2H_2O$ and $[Mg(H_2O)_6(N_5)_2]\cdot 4H_2O$. Correspondingly, the N-N bond lengths on the *cyclo*-N_5^- ring are comparable for all pentazolates. Among all the pentazolates, $Al(N_5)_3$ has the largest charge transfer

of 2.45 e from Al to neighboring *cyclo-*N_5^- rings. These charges are mainly localized on the N atoms bonded with Al.

Although this large charge transfer weakens the bond between the two N atoms bonded with Al atoms, the ICOHP values of other N-N bonds remain significant for $Al(N_5)_3$. Furthermore, COHP calculations also reveal a considerably strong Al-N (Mg-N) bond, as listed in Fig. S6. The ICOHP value of Al-N is as low as -4.16 that is much more significant than the value of -0.84 for Mg-N and any other metal-N bonds including the hydrogen bonds in $[Mg(H_2O)_6(N_5)_2] \cdot 4H_2O$ compound. Considering both the large ionic interactions and the strong covalent bonds between Al and neighboring N, the Al-N bond strength is exceedingly large comparing with metals with lower valence. As shown in the AIMD simulations, the strength of the metal-N bonds is the determining factor of the stability of pentazolates because the decomposition always starts from the breaking of the metal-N bonds.

3.3 High energy density

High valence metals can provide more electrons to the *cyclo-*N_5^- ring. Because fewer metal atoms are needed while forming stoichiometric pentazolates, it also exhibits less disturbance to the stability of the *cyclo-*N_5^- ring. Furthermore, the high valence metals themselves are often high energy materials, because they can release a great amount of energy while being oxidized. Depending on the surrounding, $Al(N_5)_3$ and $Mg(N_5)_2$ may have different pathways to decompose and release energy. If there is lack of air or O_2, they will decompose into N_2 and metal nitrides such as AlN for $Al(N_5)_3$ and Mg_3N_2 for $Mg(N_5)_2$. The energy releases are found to be 4.61 kJ/g and 3.10 kJ/g for the decomposition reactions of $Al(N_5)_3(s) \rightarrow AlN(s) + 7N_2(g)$ and $3Mg(N_5)_2(s) \rightarrow Mg_3N_2(s) + 14N_2(g)$, respectively.

While there is sufficient O_2 in the surrounding, the decomposition reactions of $Al(N_5)_3$ and MgN_{10} will produce N_2 and metal oxides, such as $4Al(N_5)_3(s) + 3O_2 \rightarrow 2Al_2O_3(s) + 30N_2(g)$ and $Mg(N_5)_2(s) + O_2 \rightarrow 2MgO(s) + 10N_2(g)$. The corresponding energy releases are 6.72 kJ/g and 5.72 kJ/g, respectively. Although these metals are already at high oxidation state, the reaction with stronger oxidants could still release a large quantity of energy, because the metal-O bonds are much stronger than that of metal-N_5 bonds. Therefore, the energy release of $Al(N_5)_3$ and $Mg(N_5)_2$ strongly depends on the surroundings, especially the presence of oxygen. These materials have the potential to be used in a large variety of cases that demand high energy density materials.

3.4 Possible synthetic routes

A major challenge of obtaining metastable pentazolate is to find a synthesis route. In the past, a major effort has been focused at breaking the C-N bond in arylpentazoles (ArN_5) [41]. Since the pentazolate salts are now available, they might be used directly to synthesize high valence metal pentazolates, such as $Al(N_5)_3$. Because the Al-N bonds are much stronger, this route is feasible if the correct precursors are chosen. Another possibility is to employ the high-pressure methods [8, 9]. Many metal pentazolates are shown to be stable (globally) under high enough pressure. Once the pressure is released, the pentazolate might be recovered. We calculated the enthalpy of the following reactions a*M_xN_y + b*N_2→ c*$M(N_5)_n$ by using the following formula:

$$H_f = \left[c * H_{M(N_5)_n} - a * H_{M_xN_y} - b * H_{N_2}\right]/(a)$$

in which enthalpy H is also obtained for the thermodynamically stable structures of certain compositions at each given pressure [44, 45]. The results indicate the formation enthalpy of $Mg(N_5)_2$ ($Al(N_5)_3$) will have a negative value when pressure increases to ~15 GPa (47 GPa) (Fig. S7a), which indicates $Mg(N_5)_2$ ($Al(N_5)_3$) are possible to form under this or higher pressure, and can be recovered as metastable compounds by releasing pressure to ambient conditions, similar as the case of LiN_5. In the process of releasing pressure to 1 atm, these compounds might be transparent, because of their large band gaps (Fig. S7b). This phenomenon can be directly measured in experiments.

4. Conclusion

In summary, our work shows that the high valence metals such as Al are the most effective agents to make controllable *cyclo*-N_5^- compounds at ambient conditions. They can provide more electrons to the *cyclo*-N_5^- ring and at the same time form strong metal-N bonds without significantly disturbing the N-N bond strength on the ring. The corresponding $Al(N_5)_3$ and $Mg(N_5)_2$ compounds show excellent metastability and can remain metastable up to 600 K at ambient conditions. Furthermore, the high valence metals may release a large quantity of energy while reacting with strong oxidants, making their pentazolates promising candidate high energy materials.

CRediT authorship contribution statement

M. M. and W. Y. designed the research and analyzed the results. W. Y. and L. Z. performed

calculations. X. L.,X. C. and Y. Z. involved in discussions. W. Y. and M. M. wrote the draft and all authors revised it.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/xxx.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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