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HIGH-PRESSURE CHEMISTRY

Benzene-like N₆ hexazine rings

Sandra Ninet

The chemistry of polynitrogens has been enriched by a new isomer of N₆ through the synthesis, in a laser-heated diamond anvil cell, of a charged aromatic N₆⁴⁻ ring that is recoverable at ambient temperature under high pressure.

History shows that pressure is a powerful thermodynamical parameter for accessing new materials with unusual — and on occasions astonishing and/or sought-after — properties. Its industrial success started in 1913 with the synthesis of ammonia from N₂/H₂ mixtures, using pressures (P) of a few hundred bars to shift a chemical equilibrium following to the Le Chatelier's principle. Subsequently, in the 1950s, the design of large volume presses capable of generating several tens of kilobars allowed the formation of the first synthetic diamonds from the high-temperature compression of graphite¹. With recent advances in high-pressure technologies, pressures of several hundred GPa can now be routinely achieved, leading to compression energies comparable to those of chemical bonds (several eV) and therefore allowing access to new bonding schemes.

Among several emblematic examples, a spectacular illustration concerns the field of fundamental chemistry of N–N interactions. The strong N≡N triple bond (954 kJ/mol) is known to become unstable under high pressure and temperature (100 GPa, 2,000 K), inducing a polymerization of the N atoms to form a solid composed only of N–N single bonds adopting a cubic gauche structure². Now, writing in *Nature Chemistry*, Laniel and co-workers have shown that extreme pressure and temperatures conditions can also induce the formation of an aromatic N₆⁴⁻ cycle reminiscent of benzene, making a novel contribution to polynitrogen chemistry³.

Polynitrogen compounds in general are very promising high energy-density materials (HEDM), attractive for applications as propellants in space propulsion. Their strategic properties are directly related to the large dissociation energy difference between the N≡N triple bond and its double or single counterpart. This makes for an attractive route for chemical energy storage in polynitrogen compounds and an effective and clean release during their decomposition. However, although an impressive variety of architectures ranging from N₄ to N₁₂₀ with multiple isomers (such as chains, rings or buckyballs) have been predicted by calculations, the experimental synthesis of such stable polynitrogens has remained very challenging due to their low activation barrier towards decomposition.

Several processes have been intensively studied. Among them, high-pressure conditions have proven to be a fruitful route, as demonstrated in the N₆ system with the recent experimental observation of N₆²⁻ rings with either armchair⁴ or planar⁵ configurations. The present findings from Laniel and co-workers show that the charged aromatic version N₆⁴⁻, analogue of benzene, can also be synthesized. The presence of these aromatic N₆-rings has been detected in the complex structure of a new compound of stoichiometry K₉N₅₆, synthesized by direct reaction between potassium azide KN₃ and dinitrogen N₂ under high pressure (>40 GPa) and high temperature (T > 2,000 K) in laser-heating diamond anvil cell experiments. Notably, this compound was also recovered at ambient temperature under pressure.

The structure of the compound formed was solved and refined using single-crystal X-ray diffraction data collected on polycrystalline samples, by making use of fourth-generation synchrotrons (EBS-ESRF in particular) that produce highly focused and highly brilliant X-ray beam. This allowed the researchers to finely map the reactive zones in order to select suitable single crystals for analysis.

The reported unit cell contains no less than 520 atoms (see Fig. 1) and shows a very high unit-cell volume — the highest so far reported above 1 GPa (with $a = 5.2380(6)$ Å, $b = 34.560(3)$ Å and $c = 23.2050(19)$ Å, so that $V = 4,200.7(7)$ Å³ at 61 GPa). The refinement shows the presence of N₆ rings with planar geometry which co-exist, in minor proportion, with N₅ rings, N₂ molecules and potassium (4 N₆ rings, 56 N₅ rings, 72 N₂ dimers and 72 K per unit cell). By analysing the refined bond length and considering the charge conservation, the team suggested that the N₆ rings are charged with -4 electrons leading to a system composed of 10 π electrons as expected for standard aromatic compounds. DFT calculations were also performed that supported the structure proposed on the basis of experimental data, confirming the electronic delocalisation over the N₆ ring.

A metallic character was also predicted, compatible with the absence of intense Raman modes reported experimentally. Finally, the K₇₂[N₆]₄[N₅]₅₆[N₂]₇₂ was shown to be metastable upon decompression up to 32 GPa. All these results complement well the remarkable recent work by Alexander Goncharov and co-workers⁵, also reported in *Nature Chemistry*, which demonstrated the formation of an anti-aromatic planar N₆²⁻ ring from the self-reaction of NaK₃ under high pressure and temperature. On the heels of those findings, the present study shows that an initial excess of dinitrogen drastically modifies the reaction products, leading to new architectures of nitrogen atoms in an unusual ‘giant’ unit cell derived from experimental data made available to readers and experts in crystallography.

In addition to a breakthrough in the chemistry of N-rich compounds, this work adds to the mounting body of work that uses high-pressure synthesis as an efficient way to probe the existence of original compounds. Of course, the small sample volumes obtained in the diamond anvil cell syntheses (on the order of 10⁻⁵ mm³ for 100 GPa) and the extreme conditions required continue to hamper any practical applications. These studies are nevertheless crucial for fundamental sciences as they demonstrate the existence of stable exotic compounds and thus serve as a first step to design other synthetic processes to produce them under standard conditions, as it has been successfully shown in the case of diamond synthesis and, even more recently, for polynitrogen compounds⁶. Successes in high-pressure syntheses have been strongly correlated with technological developments. Now, as X-ray free electron lasers (XFEL) can generate ultrashort (of the order of femtosecond) and brilliant X-ray pulses with a repetition rate in the Hz to MHz range, they open again new perspectives through possible access to reaction pathways and kinetics even under extreme conditions, as recently shown for the pioneering high-pressure-XFEL syntheses in diamond anvil cell^{7,8}.

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Figure

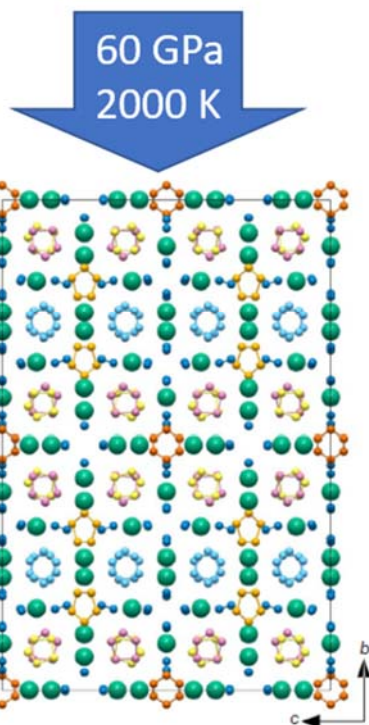


Figure 1; Schematic representation of the reaction between KN_3 and N_2 induced under high pressure and high temperature, and leading to the formation of the K_9N_{56} compound, which is recoverable at ambient temperature under high pressure. Bottom: the complex structure of K_9N_{56} . Colour code: green, K; orange, N atoms forming N_6 rings; blue, N atoms forming N_2 dimers; light orange, light blue, light pink and yellow, four crystallographically distinct N_5 rings stacked along the a axis.

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Competing interests

The author declares no competing interests.

