Studies of $N_{12}$and their metal-containing clusters

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Abstract – Polynitrogen molecules have been proposed and discussed as potential high energy-density materials for a number of years. The calculations for N_6 complexes performed have shown that outside molecular structures behind the bonding line there are some maxima of difference density, the latter causing the likely polynitrogen species (N_n, n>6) to be formed. As much as twelve likely N_{12} have been found by using the density functional theory method and exchange-correlation potential BHHLYP in a triple zeta valence basis. One of these can be appeared in azide crystals, whereas the other is intermediate for nitrogen fullerene. Besides, the two structures have been predicted having a C_5 symmetry axis. The former corresponds to C_{5h} symmetric form and the latter is of a deformed icosahedron. The evolution of the ordered nitrogen nets of 12 atoms has been studied. Stable clusters M_7N_{24} have been investigated.

For several years the prospects for polynitrogen molecules that are unknown experimentally as potential candidates for high energy density forms have been investigated [1,2]. The high energy content of polynitrogen species stems from the unusually strong triple bond in N_2 compared to the N-N single and double bonds. More specifically, the triple bond energy in N_2 is much more than three times the average N-N single bond energy or three- halves the average N-N double bond energy. Thus, the decomposition of any polynitrogen compound into N_2 will be accompanied by a large release of energy. Although chemists have long thought to synthesize stable polynitrogen compounds since the isolation of N_2 in 1772 and the discovery of the azide anion N_3^- in 1890, experimental studies are not successful enough. It was only in 1999 that another polynitrogen species could be synthesized in macroscopic quantities- the N_5^+ cation [3] for stable $N_5^+AsF_6^-$ and later one more $N_5^+Sb_2F_{11}^-$ was synthesized [4]. Some information about recent studies of metal azide decay product by mass-spectrometric methods can be found in [5]. So, when studying the composition and velocity motion of decay products of a lead azide and styphnate mixture by dynamical multicanal mass spectrometry technique after explosion initiated in electric field only N_2, N_3 and N_6 have been identified, the signal provokated by N_3 and N_6 arising earlier than that of N_2. This enables us to suppose the molecular nitrogen to be a secondary decay product of explosive decomposition which is formed after a mechanical structural failure of the samples investigated has started. Electric field decomposition of KN_3 and AgN_3 showed the decay product mass to be equal to 84 a.u. [6], it being identified as N_6. Polynitrogen species have been studied by a number of experimental techniques for a carbon nitride film [7]. There are some experimental and theoretical data for amorphous polymeric phases of high pressure and crystalline forms of polymeric nitrogen of chain-like [8] and layered structures [9].

A number of researchers have performed the extensive first-principle simulations for understanding electronic structure of polynitrogen compounds [10–14]. More accurate calculations have been made for N_n (n=4–10) [14], those for N_n (n>10) are presented in a lesser number of papers. Thus, the configurations of a low symmetric broken-chain type and the two bonded pentagons for N_{12} have been predicted [13] and high symmetric (dodecahedral) ones-for N_{20} [15]. In the paper given one tries to simulate as many N_{12} configurations as possible, both low symmetrical and high symmetrical ones [16].

We calculated N_6 structures earlier [16] and predicted that outside molecular complexes behind the bonding line there were some maxima of difference density. Therefore, we drew a conclusion that N_n (n>6) could be formed. To simulate the likely geometrical structures we used both the symmetries studied earlier and those obtained by converging N_6 compounds.

As a result, as much as 12 most symmetrical likely N_{12} have been predicted by means of quantum-chemical program Gamess [17] by using the density-functional theory method and exchange-correlation potential [18] in a triple zeta valence basis set presented in Fig. 1. The tables (1–3) show their stable geometries and total energies. Low-symmetry configurations *a* and *b* possess the lowest energy (see [13]). The *c* complex has a larger energy and it can be appeared in silver and potassium azides if there are cation vacancies in them. All configurations are located into alphabetical order as their total energy grows. It's of interest that *i* and *l* structures possess fivefold symmetry. However, they can be unstable since their energy is high enough.

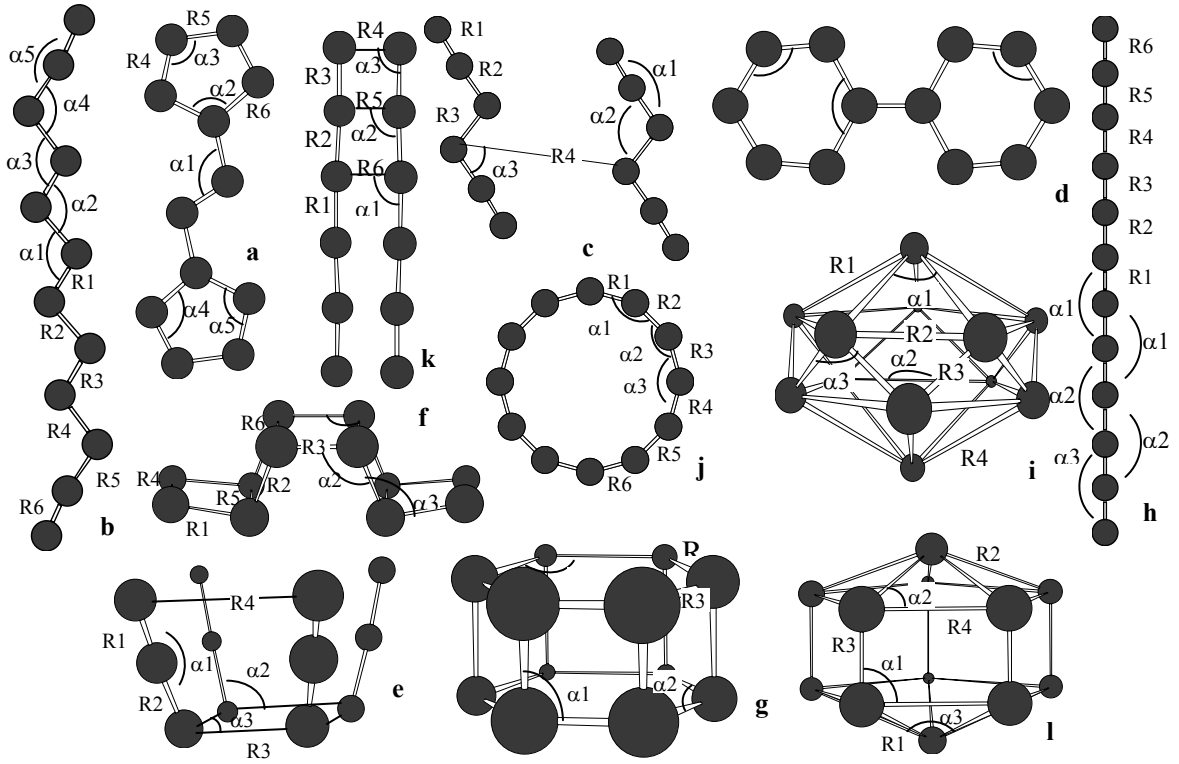


Fig. 1. The likely geometrical configurations for N_{12}

Table 1. Stable parameters and total energies for N_{12} *(a, b)*

N_{12} ***a***	*R1, Å*	*R2, Å*	*R3, Å*	*R4, Å*	*R5, Å*	*R6, Å*
	1.215	1.355	1.321	1.260	1.352	1.316
	α1	*α2*	*α3*	*α4*	*α5*	E_t, *a.e.*
	112.10	111.96	109.52	104.88	104.49	-656.50228
N_{12} ***b***	*R1, Å*	*R2, Å*	*R3, Å*	*R4, Å*	*R5, Å*	*R6, Å*
	1.223	1.388	1.226	1.363	1.253	1.381
	α1	*α2*	*α3*	*α4*	*α5*	E_t, *a.e.*
	108.20	107.16	109.94	108.74	172.02	-656.44848

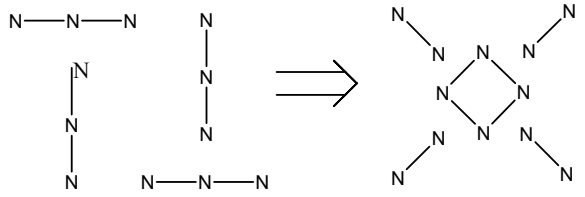
Table 2. Stable parameters and total energies for N_{12} *(c-g, i, l)*

	R1, Å	*R2, Å*	*R3, Å*	*R4, Å*	*α1*	*α2*	*α3*	E_t, *a.e.*
N_{12} ***c***	1.111	1.230	1.427	4.085	173.78º	108.89º	48.96º	-656.44057
N_{12} ***d***	1.270	1.379	1.256	1.312	124.40º	113.62º	124.87º	-656.30749
N_{12} ***e***	1.143	1.183	2.301	2.892	175.17º	98.97º	90.00º	-656.19323
N_{12} ***g***	1.475	1.471	1.471	1.471	90.00º	120.00º	120.00º	-655.92061
N_{12} ***i***	2.013	2.045	1.341	2.013	61.07º	99.39º	99.39º	-655.64534
N_{12}***l***	1.843	1.843	1.278	2.000	90.00º	57.13º	65.74º	-655.24237

Table 3. Stable parameters and total energies for N_{12} *(f, h, j, l)*

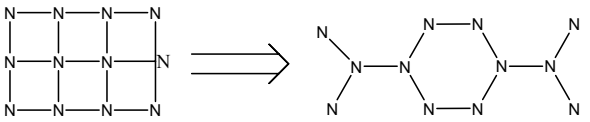
	R1, Å	*R2, Å*	*R3, Å*	*R4, Å*	*R5, Å*	*R6, Å*	*α1*	*α2*	*α3*	E_t, *a.e.*
N_{12}***f***	1.421	1.450	1.469	1.233	1.485	1.474	90.00º	112.41º	106.41º	-656.11763
N_{12}***h***	1.182	1.176	1.193	1.221	1.162	1.152	180.00º	180.00º	180.00º	-655.76618
N_{12}***j***	1.198	1.198	1.198	1.198	1.198	1.198	150.00º	150.00º	150.00º	-655.56204
N_{12}***k***	1.456	1.430	1.395	1.358	1.304	1.413	90.00º	92.19º	88.89º	-655.43010

The evolution of the ordered nitrogen nets has been studied. The most primitive square net containing about 12 atoms in gas phase is reconstructed as follows:



and then the structure breaks because of N_3 terminal group separation.

Another set is of interest since the similar atomic configuration takes place on a crystal surface in case an anionic layer forms it. One can see such a reconstruction as:



and then four N_2 groups are separated. Such decomposition may occur provided the metal vacancies are formed under a surface layer and anionic vacancies lie on the surface itself.

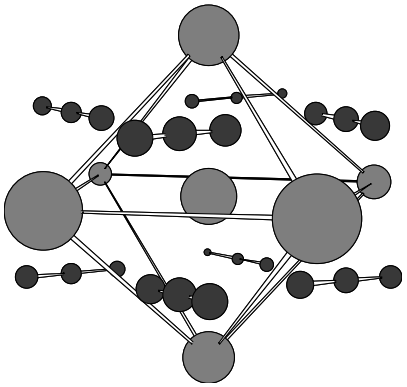


Fig. 2. Geometrical structure of $K_7(N_3)_8^-$

The metal atoms are sure to take part in crystalline azide decomposition. The process takes place by forming secondary clusters. In [16] clusters were studied consisting of T- oriented N_3 azide groups and metal atoms. The simplest stable cluster appeared to be M_2N_6 where metal atoms are located above and under the space of T –oriented azide groups. It is worth noting that the distance between metal atoms in a cluster turned out to be close enough to those of the corresponding atoms in a crystalline lattice. The main peculiarity of M_2N_6 is that nitrogen terminal atoms are nonequivalent, the latter may cause it to be dissociated; the likely reaction pathways have been discussed. We study various types of N_{12} given in Fig. 1 in a crystalline matrix and their interaction with metal atoms as well. On the other hand, of greater interest is the clusters whose geometry is close to the fragments of the corresponding crystals. It is clear that in this case the point symmetry of a crystallographic unit cell doesn't change greatly and the cluster charge is small enough. $K_7(N_3)^-_8$ presented in Fig. 2 meets all these requirements. The calculations performed by Hartree – Fock in a triple zeta valence basis showed that the similar cluster may exist separately in a gas phase. The distance between neighbouring azides is found to increase from 3.148 Å to 3.521 Å, and the angle between them changes from 90° for crystals to 96.74° for clusters. N-N bonding length for azide groups decreases from 1.174 Å to 1.160 Å. The distance between potassium atoms decreases as well, namely that between cationic layers and neighbouring atoms in a layer equals 3.547 Å and 4.322 Å, respectively. The total energy of the clusters involved E_t =–5501.20558 a.u.

The reaction pathways need to be studied.

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