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Kasprzaka 44/52, 01-224 Warsaw, Poland tel.: +48 22 3432000 fax: +48 22 3433333 ichf@ichf.edu.pl www.ichf.edu.pl

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Going against the grain – nitrogen turns out to be hypersociable!

> *Nitrogen is everywhere: even in the air there is four times as much of it as oxygen. However, it is reluctant to form chemical bonds, especially with more than four atoms. Chemists from Warsaw predict, however, that contrary to the rules of typical chemistry, in appropriately selected conditions there may be a nitrogen that nobody has ever seen: one capable of forming up to six chemical bonds.*

Nobody expected this. Computer simulations suggest that nitrogen, a very well-known element, with a reputation for being reluctant to react could, at a high enough pressure, break the chemical rules and become extremely gregarious: a single atom would then be able to form even six chemical bonds. This surprising discovery has been made by researchers at the Institute of Physical Chemistry of the Polish Academy of Sciences (IPC PAS) in Warsaw and the New Technology Centre at the University of Warsaw (CeNT UW), funded by grants from the Polish National Science Centre.

Chemists have long known that nitrogen may occasionally have a valency of five, which means that it is potentially able to form bonds with five other atoms. Another element with similar properties is phosphorus, which is adjacent to nitrogen in the periodic table.

“Nitrogen, however, behaves differently to phosphorus: in practice, it forms five bonds with at most four other atoms, and more usually with three, as in the popular nitric acid HNO_3. We decided to investigate, using the computer, the possibility of obtaining a compound in which pentavalent nitrogen would combine with five neighbours by covalent interactions – chemical bonds. We analyzed thousands of crystal structures of nitrogen compounds with fluorine arising at high pressures. We were hoping to see some structures containing nitrogen pentafluoride NF_5 particles. We were completely unprepared for the fact that in one of the crystals we ran into ions with the formula NF_6^- in which the nitrogen atom bonds with as many as six fluorine atoms,” says Dr. Patryk Zaleski-Ejgierd (IPC PAS).

Dr Dominik Kurzydlowski (CeNT UW), co-author of the publication in the journal *Scientific Reports*, explains the essence of the discovery as follows: “Two electrons are typically required for the formation of a single covalent bond. The problem with nitrogen lies in the fact that when creating various compounds it ‘trades’ electrons so as to always be surrounded by eight of them. This constrains the total number of atoms bonded to nitrogen to no more than four. We were the first to find a stable crystal in which nitrogen breaks the octet rule, i.e. the requirement to possess exactly eight electrons, and forms bonds involving a total of up to twelve electrons.”

Compounds in which an element breaks the octet rule octet are called hypervalent. Many elements can form hypervalent compounds, including phosphorus, sulphur and various metals. This phenomenon is advantageous because it significantly widens the number of possible compounds the element can form. For example, if it were not for hypervalency, sulphur would not form sulphuric acid and phosphorus could not be one of the building blocks of DNA.

The calculations and simulations associated with the search for hypervalent nitrogen were carried out at the IPC PAS using density functional theory, that is, the method normally used in solid state calculations. However, the discovery's authors used one of the more advanced embodiments of this theory, the hybrid functional. It makes it possible to describe chemical bonds very accurately, but it takes much longer to perform the calculations.

“The compounds we tested, as well as the conditions under which these compounds were formed, were very exotic. The accuracy of the calculations was therefore our absolute priority which is why we decided to use the hybrid functional for the calculations,” says Dr. Kurzydlowski and stresses that carrying out the simulation within a reasonable timeframe was made possible thanks to cooperation with the Interdisciplinary Centre for Mathematical and Computational Modelling, University of Warsaw.

A thorough analysis of the results of computer simulation allowed the researchers to identify the unique crystal structure that with an increase in pressure at some point automatically ionizes in a very particular way. A reorganization takes place during which the molecular crystal, originally formed of a mixture of gases NF_3 and F_2, transforms into a complex ionic crystal constructed of NF_4^-, NF_2^+ and... NF_6^- ions. (It should be mentioned here that despite the exotic name, ionic crystals are common in nature. They include many minerals, among others popular rock salt, whose crystal structure is formed of sodium cations Na^+ and chloride anions Cl^-).

The pressure required for the synthesis of crystals containing NF_6^- amounts to 400-500 thousand atmospheres which is within the reach of current experimental techniques. Simulations suggest that after formation the crystals would remain metastable even at much lower pressures. Does that also mean under normal atmospheric pressure?

“I wouldn't bet too much money on that, but it cannot be completely ruled out that one day you will simply be able to pick up the crystals we predict with unique NF_6^- ions. If they do turn out to be so stable, who knows, perhaps it will be possible to find some interesting applications for them?” wonders Dr. Zaleski-Ejgierd.

However, taking a crystal with NF_6^- ions into your hand would probably not be a very good idea. Nitrogen trifluoride is already a strong oxidizing agent that must be stored in steel cylinders. A crystal of nitrogen pentafluoride mixed with NF_6^- would be an even stronger oxidant and we can assume that even the construction of a container allowing for its safe storage could cause engineers considerable difficulties.

The Institute of Physical Chemistry of the Polish Academy of Sciences (http://www.ichf.edu.pl/) was established in 1955 as one of the first chemical institutes of the PAS. The Institute's scientific profile is strongly related to the newest global trends in the development of physical chemistry and chemical physics. Scientific research is conducted in nine scientific departments. CHEMIPAN R&D Laboratories, operating as part of the Institute, implement, produce and commercialise specialist chemicals to be used, in particular, in agriculture and pharmaceutical industry. The Institute publishes approximately 200 original research papers annually.

CONTACTS:

Dr. **Patryk Zaleski-Ejgierd**
Institute of Physical Chemistry of the Polish Academy of Sciences
tel. +48 22 3433355
email: pzaleski@ichf.edu.pl

SCIENTIFIC PAPERS:

"Hexacoordinated nitrogen(V) stabilized by high pressure"; D. Kurzydłowski, P. Zaleski-Ejgierd;
Scientific Reports 6, 36049 (2016); DOI: 10.1038/srep36049

LINKS:

http://www.ichf.edu.pl/
The website of the Institute of Physical Chemistry of the Polish Academy of Sciences.

http://www.ichf.edu.pl/press/
Press releases of the Institute of Physical Chemistry of the Polish Academy of Sciences.

IMAGES:

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Nitrogen is able to form even six chemical bonds, reveal computer simulations from the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw. (Source: IPC PAS, Grzegorz Krzyżewski)