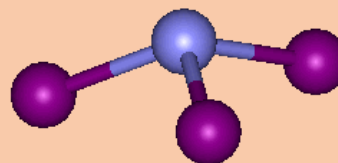


Nitrogen Triiodide

The well-known explosive crystals

Simon Cotton
Uppingham School, Rutland, UK



Nitrogen triiodide, NI₃

Molecule of the Month December 2001

Also available: [JSmol](#) versions.

Sounds like another boring covalent molecule

This one's explosive! When dry solid nitrogen triiodide is touched, even with a feather, it decomposes rather violently. Click on the images below to see an animation.



Before...



...After

Very impressive! The purple smoke is iodine vapour, I suppose?

Yes. In the animation, the shockwave from the first detonation sets off the second sample of NI₃.

Why is it so explosive?

The process $2 \text{NI}_3 (\text{s}) \rightarrow \text{N}_2 (\text{g}) + 3 \text{I}_2 (\text{s})$ is exothermic, so that $\text{N}_2 (\text{g}) + 3 \text{I}_2 (\text{s}) \rightarrow 2 \text{NI}_3 (\text{s})$ is endothermic. Endothermic compounds tend to be unstable.

Is that all?

Not at all, things are more complicated than they seem. Traditionally, nitrogen triiodide is made by reacting iodine with aqueous ammonia solution. That does not produce NI₃, an ammonia complex is obtained instead. This is either [NI₃.NH₃] or [NI₃.(NH₃)₃], and the ammonia cannot be removed from this.

So can pure NI₃ be made?

This wasn't achieved until 1990, when it was found that boron nitride reacted with iodine monofluoride in CFC₁₃ at -30°C.



What is pure NI₃ like?

It's a dark red solid that can be sublimed in a vacuum at -20°C. It decomposes at 0°C, sometimes explosively.

Can you make other nitrogen trihalides?

Yes, certainly, thanks to some brave and intrepid chemists. NCl₃ was the first of the family to be made in 1811, by Pierre L. Dulong, who later became Professor of Chemistry at the Ecole Polytechnique in Paris; he lost 3 fingers and an eye in studying it. He made it by the reaction of chlorine with slightly acidic NH₄Cl. The main route used commercially today is the electrolysis of slightly acidic

ammonium chloride; the NCl_3 is removed as fast it is formed using an air current. This air/ NCl_3 mixture is much more stable than pure NCl_3 and is commercially important. It is also formed in swimming pools when the chlorine gas used to disinfect the water reacts with nitrogen compounds found in urine, and can be a health risk to people like lifeguards who work continuously around the water. NCl_3 can be formed when chlorine reacts with nitrogen compounds in wastewater treatment plants. The particular danger associated with the formation of NCl_3 under these conditions is that a combination of its sensitive nature and low solubility in water leads to explosive droplets of NCl_3 .

Stable NF_3 was first made in 1928 by Otto Ruff, a German chemist (d.1939) who probably made more fluorides than anyone else, by electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride. Another route uses the reaction of ammonia with fluorine/nitrogen mixtures over a copper catalyst.



NBr_3 was originally synthesised in 1975 by the reaction of bis(trimethylsilyl)bromamine with ClBr at -78°C .

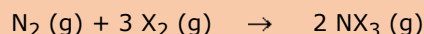


What are they like?

NF_3 is pretty unreactive at room temperature; it is not affected by water and only reacts with most metals on heating. NCl_3 is much more reactive; it is light-sensitive and, like all the other halides, apart from NF_3 , explosive. All these compounds are volatile, as expected for small covalent molecules.

Why is NF_3 stable but the others are unstable?

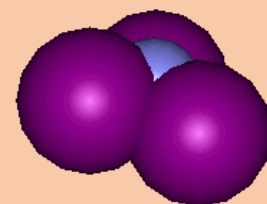
For all these compounds, it is possible to work out ΔH_f for the formation of NX_3 in the gas phase, using bond energies.



The process is not especially favourable owing to the difficulty in breaking the very strong N-N triple bond ($E(\text{N-N}) = 945 \text{ kJ mol}^{-1}$). Using values for the F-F and N-F bond energies of 159 and 278 kJ mol^{-1} , respectively, $\Delta H_f = -123 \text{ kJ mol}^{-1}$ (per mole of NF_3); similarly, for ammonia, using H-H and N-H bond energies of 436 and 390 kJ mol^{-1} , respectively, $\Delta H_f = -43 \text{ kJ mol}^{-1}$ (per mole of NH_3). In contrast, using I-I and N-I bond energies of 151 and 169 kJ mol^{-1} , respectively, ΔH_f per mole of $\text{NI}_3 = +192 \text{ kJ mol}^{-1}$.

One factor making NF_3 more stable than the other NX_3 is the very low F-F bond energy (159 kJ mol^{-1}).

This has been ascribed to repulsions between lone pairs on the two rather proximate fluorine atoms. Additionally, the N-F bond is also particularly strong, as would be expected for a linkage between two elements in the first short period. The other NX_3 molecules may be less stable than NF_3 owing to congestion round the small central nitrogen atom leading to non-bonded repulsive interactions between the halogens. This is particularly bad for large iodine atoms, as can be seen in the space-fill image of NI_3 , right.



What is their structure?

In all these compounds, the nitrogen atom has a complete "octet", with four outer-shell electron pairs; one of these is a non-bonding ("lone") pair. These arrange themselves as far apart as possible around the nitrogen atom in a roughly tetrahedral disposition, to minimise repulsions between the negative charge clouds.

However, because repulsions involving lone pairs are stronger than those involving just bond pairs, the X-N-X angles are a little under the regular tetrahedral angle of $109\frac{1}{2}^\circ$; thus the value for ammonia, NH_3 , is 107.5° . Because fluorine is much more electronegative than hydrogen, the bond pairs of electrons are attracted away from nitrogen, so that in NF_3 the bond angle is actually 102.3° . In contrast, the corresponding value for NCl_3 is 107.1° , although on electronegativity grounds it would be expected to be intermediate between the values for NF_3 and NH_3 . This may possibly be due to non-bonded Cl...Cl repulsions.



The molecules themselves have a trigonal (triangular) pyramid shape. They are, of course, polar. NF_3 has a small dipole moment (0.234D) in comparison with NH_3 (1.42D); an explanation for this is that the moment due to the nitrogen atom and its lone pair is in opposition to the moment associated with the three polar N-F bonds in NF_3 . NCl_3 also has a small dipole moment (0.6D).

They sound very exotic- do they actually have any uses?

NCl_3 is used as a dilute mixture in air to bleach and sterilise flour and as a fungicide for citrus fruits and melons. The semiconductor industry uses NF_3 as an etchant of thin films, also for cleaning up chemical vapour deposition chambers, both uses depending on the use of a plasma to produce fluorine from NF_3 . It is also used as an oxidizer of high energy fuels, for the preparation of tetrafluorohydrazine (another fuel), and for the fluorination of fluorocarbon olefins, whilst it has been studied as a high-energy oxidiser for HF-DF chemical lasers.

	NF ₃	NCl ₃	NBr ₃	NI ₃
First synthesised	1928	1811	1975	1990 (ammonia adduct 1813)
Description (at RT)	Colourless gas	Pale yellow oil	Deep red solid	Red-black crystals
m.p. (°C)	-208.5	-40	-	-
b.p. (°C)	-129	71	-	-
< X-N-X (°)	102.3	107.1	-	-
N-X (pm)	137	175.9	-	-
N-X bond energy (kJ mol⁻¹)	278	188	169	-
Dipole moment (D)	0.234	0.6	-	-
ΔH_f (kJ mol⁻¹)	-114	232	220 (est)	159 (est)

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