

# A flourish of fluorine

**Herbert Roesky** relates how the small, highly electronegative fluorine atom unveiled the chemical reactivity of noble gases and found many practical applications. But it can also render organic compounds highly toxic or pollutants.

**F**luorine's name derives from fluorspar — or fluorite,  $\text{CaF}_2$  (pictured) — which in earlier times was used as a flux to facilitate smelting. As early as the seventeenth century, fluorspar was found to emit light when heated, and gave its name to the fluorescence phenomenon. In 1886, the French chemist Henri Moissan electrolysed a solution of  $\text{KHF}_2$  in anhydrous HF and obtained a gas that caused crystalline silicon to burst in flames. He immediately reported his results to the French Academy of Sciences with the following words: "One can indeed make various hypotheses on the nature of the liberated gas, the simplest would be that we are in the presence of fluorine". Moissan was to be awarded the Nobel Prize in Chemistry in 1906 for the discovery of 'le fluor'.

Fluorine chemistry developed rapidly during the Second World War, with American scientists working on the 'Manhattan project' to separate fissionable uranium-235 from uranium-238. Uranium is present in nature as three isotopes —  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$  (99.28%, 0.73% and 0.005% abundance, respectively) — but these have very similar properties and are therefore difficult to separate. It was the volatility of uranium hexafluoride that turned out to be the key discovery for their separation: the current gaseous diffusion and centrifuge processes to enrich uranium in  $^{235}\text{U}$ , which rely on a slight mass difference between the two isotopes, both use uranium hexafluoride. Ensuring that this technology does not proliferate is one of today's key political issues.

Although other syntheses have been shown — such as from  $\text{K}_2\text{MnF}_6$  and  $\text{SbF}_5$  — the preparation of elemental fluorine is still largely based on the pioneering work of Moissan. On an industrial scale, the main use of elemental fluorine is in the production of  $\text{UF}_6$  and  $\text{SF}_6$ , which is used as a dielectric medium in electric devices. A number of metal fluorides with unusually high oxidation states such as

$\text{AuF}_5$ ,  $\text{AgF}_3$ ,  $\text{NiF}_3$ ,  $\text{NiF}_4$  and  $\text{HgF}_4$  have also been synthesized in recent years, and are used as very strong oxidizing agents.

A milestone in chemistry was achieved through the use of fluorine: the discovery of the reactivity of noble gases — when xenon fluoride was prepared by Neil Bartlett in 1962 — which challenged the generally accepted view that noble gases were inert. This led to the preparation of an extended number of noble gas fluorides and their derivatives, as well as fluorides of krypton and radon.

Owing to its small atomic size and covalent behaviour, the substitution of hydrogen or oxygen by fluorine in organic molecules usually results in a large number of new compounds of an interesting nature, featuring very stable covalent carbon-fluorine bonds. The best-known example is the widespread use of Teflon (polytetrafluoroethylene) in non-stick cooking pans.

These stable carbon-fluorine bonds have also been used with enormous success in the design of pharmacologically active molecules. The lengths of the C-H and C-F bonds are not too dissimilar, but the stability of C-F and its powerful electron-withdrawing properties give rise to very desirable properties in drug design, and most organofluorines can be safely used without the risk of releasing toxic fluoride. For example, an aromatic ring fluorinated in its *para* position cannot be metabolized by enzymes in the body into poisonous epoxides. Currently, about 20% of pharmaceutical products, as well as 30% of agrochemical compounds, contain fluorine, and this proportion is rising.

Organofluorines can also be highly toxic, however — monofluoroacetic acid, for example, is lethal in humans at oral doses

of 2–8 mg kg<sup>-1</sup> through disruption of the citric acid cycle, which is important for the energy supply of the cells. Moreover, chlorofluorocarbons (CFCs) were extensively used in refrigerators and aerosols owing to their extreme kinetic stability in the atmosphere, but they proved to be catastrophic in the stratosphere, leading to depletion of the ozone layer.

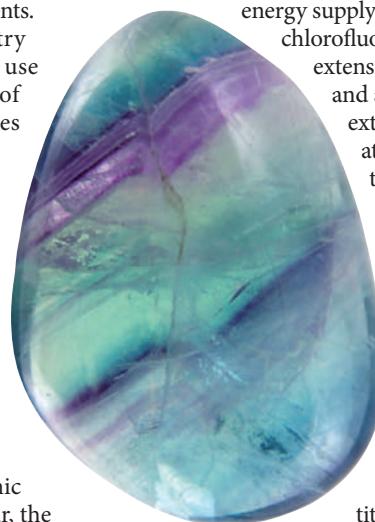
Recent developments in fluorine chemistry include the use of perfluorocarbons and hydrofluoroethers in liquid–liquid extraction separation, and catalysts containing fluorinated tags. Cyclopentadienyl titaniumtrifluoride ( $\text{Cp}^*\text{TiF}_3$ , where  $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) and its

derivatives are also very effective catalysts for the polymerization of styrene: the  $\text{Cp}^*\text{TiF}_3$  catalyst is about 50 times more active than its chlorinated counterpart, at a lower cocatalyst-to-catalyst ratio (300 versus 900 for the chlorinated system). For industrial uses, both the high activity and low cocatalyst-to-catalyst ratio allow tremendous cost reduction.

Finally, returning to fluorspar, compounds of the type  $\text{LCaF}$  (where L is a  $\beta$ -diketiminate ligand) have been prepared. In contrast to fluorspar, they are soluble in organic solvents and can be used as intermediates to cover surfaces with  $\text{CaF}_2$  — a coating that is transparent to visible light, and resistant to acids and bases.

Although fluorine compounds have a key role in electric cars, electronic devices, space technology and pharmaceuticals, they can also have disastrous effects, and scientists working in this field need to be very alert. □

**HERBERT W. ROESKY** is at the Institute of Inorganic Chemistry, University of Göttingen, Tammanstrasse 4, 37077 Göttingen, Germany. e-mail: hroesky@gwdg.de



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