

# Following in the footsteps of Henri Moissan

## Unexpected discoveries ranging from $\text{NF}_4^+$ to the chemical synthesis of fluorine and polynitrogens

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**Résumé** En suivant les traces d'Henri Moissan : découvertes inédites depuis la synthèse chimique du fluor jusqu'aux cations  $\text{NF}_4^+$  et polynitrogénés

C'est en suivant la voie tracée par Henri Moissan que la synthèse du fluor par voie chimique a été découverte. Par ailleurs, dans le but de trouver des propulseurs de plus en plus puissants, toute une nouvelle chimie a été mise en place, conduisant à la découverte d'espèces extrêmement originales tels les cations fluorés  $\text{NF}_4^+$  et  $\text{ClF}_6^+$ , l'oxyfluorure de chlore  $\text{ClF}_3\text{O}_2$ , les anions  $\text{XeF}_5^-$  et  $\text{IF}_5^-$  en configuration pentagonale planaire et les cations polynitrogénés  $\text{N}_5^+$  et  $\text{C}(\text{N}_3)_3^+$ .

**Mots-clés** Moissan, synthèse chimique du fluor, propulseurs énergétiques, cations polynitrogénés, azotures, ion tétrafluoroammonium.

**Abstract** Following the fluorine isolation by Henri Moissan, this article gives the highlights of a new chemistry including the following areas: syntheses of the tetrafluoroammonium and hexafluorochlorine(VII) cations and of chlorine trifluoride-dioxide, the chemical synthesis of elemental fluorine, the synthesis of pentagonal-planar  $\text{AX}_5$  species, and polynitrogen and polyazide chemistry.

**Keywords** Moissan, chemical synthesis of fluorine, polynitrogen chemistry, tetrafluoroammonium cation, polyazides.

Henri Moissan was a true trailblazer. A learned watchmaker and pharmacist, working in plant physiology, he turned to inorganic chemistry, obtained his doctor's degree with a thesis on pyrophoric iron and iron oxides, then worked on nickel, manganese and chromium oxides and within two years he solved the most challenging inorganic chemistry problem of his generation, the synthesis and characterization of elemental fluorine. Using fluorine, he successfully synthesized many novel fluorides, but soon turned his attention to other great challenges, such as the preparation of synthetic diamonds, high temperature chemistry using an electric arc furnace, and metal hydride chemistry [1]. The versatility and legendary vision of his approaches are truly amazing and I cannot think of anyone who has inspired our own work in a similar way. In this brief review, some highlights of our own work are recounted. Although our work does not approach in any way the boldness and ingenuity of Moissan's discoveries, it nevertheless has repeatedly challenged existing views and dogmas.

### Syntheses from tetrafluoroammonium and hexafluorochloronium ions to chlorine trifluoride dioxide

During the late nineteen fifties and early nineteen sixties, extensive efforts were undertaken in the United States to discover novel and more powerful rocket propellants for the race to the moon. One promising candidate was the unknown tetrafluoroammonium cation,  $\text{NF}_4^+$ . However, the synthesis of this species presented formidable problems. First of all, theoreticians had predicted that this species should be too unstable to exist. Secondly, its parent molecule,  $\text{NF}_5$ , is nonexistent. Therefore, a synthesis was required

that involved the use of  $\text{NF}_3$  and the equivalent of an  $\text{F}^+$  cation which was also synthetically unavailable. These difficulties did not deter us, and in 1965 at Stauffer Chemical in Richmond, California, we discovered, using low-temperature glow-discharge, the  $\text{NF}_4^+$  cation [2]. It is noteworthy that the conditions were so well chosen that the experiment succeeded on the first attempt. In subsequent work at Rocketdyne, we prepared and characterized a large number of different  $\text{NF}_4^+$  salts and pioneered their use as solid propellant  $\text{NF}_3/\text{F}_2$  gas generators for chemical HF/DF lasers that are used in the antimissile defense system. We have developed the technology to prepare these exotic materials on a kilogram scale. With the syntheses of  $(\text{NF}_4^+)_2\text{NiF}_6^{2-}$  and  $\text{NF}_4^+\text{XeF}_7^-$ , we have achieved the ultimate goal of making salts that contain more usable fluorine per volume than liquid fluorine itself.

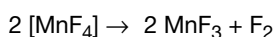
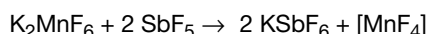
Another tall task was the synthesis of  $\text{ClF}_6^+$  because, as in the case of  $\text{NF}_4^+$ , the corresponding parent molecule,  $\text{ClF}_7$ , does not exist. Its successful synthesis was achieved by us at Rocketdyne in Canoga Park, California. Surprisingly, the approaches that had worked so well for  $\text{NF}_4^+$  were ineffective, and the powerful oxidizers  $\text{PtF}_6$  or  $\text{KrF}^+$  had to be used to oxidatively fluorinate  $\text{ClF}_5$  [3].

However, the most challenging synthesis in the halogen fluoride area was that of  $\text{ClF}_3\text{O}_2$ . It required the burning of 200 g of platinum wire in liquid fluorine to make  $\text{PtF}_6$ , reacting that at low-temperature with  $\text{FClO}_2$  to prepare small amounts of  $\text{ClO}_2\text{F}_2^+$  in erratic yields, and then running a series of chemical displacement and separation reactions to isolate about 3 mmol of the extremely reactive  $\text{ClF}_3\text{O}_2$ . The complete identification, characterization, and reaction chemistry of this compound was carried out with these 3 mmol [4]. Due to the great difficulty of this synthesis, no further work in this area has ever been reported since then.

## The chemical synthesis of elemental fluorine

Another notable achievement in preparative chemistry, without doubt, was the first chemical synthesis of elemental fluorine. It exemplified our willingness to challenge existing beliefs. For one and a half centuries, chemists had unsuccessfully attempted to synthesize elemental fluorine by purely chemical methods, and by 1986 every major textbook stated that Moissan's electrochemical synthesis was the only possible way to prepare fluorine. This, however, was no deterrent to attempt the chemical synthesis of fluorine. For the celebration of the Centenary of the discovery of fluorine by Moissan, which was held in 1986 in Paris, I successfully prepared in a three-day *tour de force* elemental fluorine by purely chemical means from starting materials which were known already in the days of Moissan.

The chemical synthesis of elemental fluorine was amazingly easy (see figure 1). It was based on the simple recognition that the anions of high oxidation states of transition metal fluorides are considerably more stable than their corresponding neutral parent molecules or cations and the rudimentary knowledge of the principle that stronger acids can displace weaker acids from their salts. It, therefore, required only the selection of a high oxidation state transition metal fluoride anion, such as  $[\text{MnF}_6]^{2-}$  which can be prepared in aqueous HF solution from manganese(+IV) oxide, and its displacement reaction with the stronger acid  $\text{SbF}_5$ , as shown by the following three equations:



Because the resulting  $\text{MnF}_4$  is thermodynamically unstable, it spontaneously decomposes to  $\text{MnF}_3$  and elemental fluorine. These results were presented in 1986 in Paris at the Centenary of the discovery of fluorine by Moissan and, thus, with exquisite timing a 150-year old dogma was shattered [5].

## Pentagonal-planar species

Another contribution from our group, which had a major impact on synthetic inorganic chemistry, was the development of a synthesis for truly anhydrous tetramethylammonium fluoride [6] that is often referred to in the literature as "naked fluoride" or "Christe reagent". It provided a source of highly soluble fluoride ion in combination with a chemically inert counter-ion and has led to a renaissance in high coordination number chemistry. It allowed the preparation and structural study of many new simple anions with coordination numbers greater than six. Typical examples for these types of ions from our group include  $[\text{IF}_5\text{O}]^{2-}$ , the first example of a pentagonal-bipyramidal  $\text{AX}_5\text{OE}$  species,  $[\text{TeF}_6\text{O}]^{2-}$ , the first example of a pentagonal-planar  $\text{AX}_5\text{XO}$  species,  $[\text{IF}_5\text{O}_2]^{2-}$ , the first example of a pentagonal-bipyramidal  $\text{AX}_5\text{O}_2$  species, and  $[\text{SbF}_7]^{2-}$  and  $[\text{BiF}_7]^{2-}$ , the first examples of hepta-coordinated pnictogens. With  $[\text{SbF}_7]^{2-}$  and  $[\text{BiF}_7]^{2-}$  [7], two highly stable and simple new compounds were prepared that previous investigators must have frequently encountered but missed, because of their preconceived convictions that octahedral  $\text{SbF}_6^-$  and  $\text{BiF}_6^-$  had already reached their maximum coordination numbers.

The synthesis of the  $\text{XeF}_5^-$  anion represents another landmark achievement [8]. It was the first pentagonal



Figure 1 - Experimental set-up used for the chemical synthesis of elemental fluorine.

planar  $\text{AX}_5$ -type compound (see figure 2) ever prepared, and as of today only two such compounds are known. The second one,  $[\text{IF}_5]^{2-}$ , has also been prepared by our group [9]. Interestingly, the  $\text{XeF}_5^-$  anion had previously been prepared by a Russian group but had not been recognized as such and was assigned incorrectly to an octahedral  $[\text{XeF}_6]^{2-}$  anion. As with  $[\text{SbF}_7]^{2-}$  and  $[\text{BiF}_7]^{2-}$ , thinking along conventional lines had prevented them from making an important new discovery.

## Lewis acidity scale

Our group has also made important contributions to general chemistry by the development of quantitative scales for oxidizer strengths [10] and Lewis acidities [11]. The quantitative Lewis acidity scale is a very important contribution to chemistry because until now no such scale existed. This scale is bound to become as important in Lewis acid chemistry as is the well accepted pH scale for Brønsted acids. It demonstrates the broad and systematic approach our group has taken when tackling difficult chemical problems.

## Polynitrogen and polyazide chemistry

Our recent interest has been concentrated on High Energy Density Materials (HEDM) and, in particular, on polynitrogen and polyazido chemistry. Our group has prepared

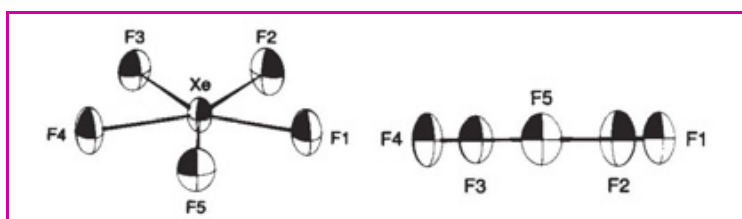


Figure 2 - Pentagonal-planar structure of the  $\text{XeF}_5^-$  anion, as determined by x-ray crystallography.

and characterized highly energetic salts, such as  $C(N_3)_3^+ClO_4^-$  and  $C(N_3)_3^+N(NO_2)_2^-$  [12], but clearly the most spectacular achievement was the synthesis of the  $N_5^+$  cation [13]. For more than 100 years, only one stable homonuclear polynitrogen species, the azide anion,  $N_3^-$ , had been known [14]. The synthesis of polynitrogen compounds is extremely challenging because of their high endothermicity and the resulting difficulties of handling these often very explosive materials. Surprisingly,  $N_5^+SbF_6^-$  is thermally stable up to 70 °C and can be prepared safely on a multi-gram scale. This discovery has received much public acclaim (see figure 3), even in daily newspapers, such as *The New York Times* and *The London Times*, and has been hailed by *Chemical & Engineering News* as “one of the top five achievements in chemistry in 1999”. The quote from Pamela Zurrer in *Chemical & Engineering News*, describing this work, very aptly characterized this work: “*The achievement strikes me as the essence of what chemists do, stripped about as bare as it can be: Chemists make interesting new stuff.*” Up to date, our group has synthesized and characterized a total of 13 different  $N_5^+$  salts, including spectacular compounds such as  $N_5^+P(N_3)_6^-$  and  $N_5^+B(N_3)_4^-$  [15].

Another spectacular polynitrogen species recently discovered by our group is the *cyclo*- $N_5^-$  anion [16] which has also received considerable publicity. This anion is isoelectronic with the cyclopentadienide anion and might lead to a completely inorganic counterpart to ferrocene chemistry.

During the past two years, our group has prepared and characterized a large number of exciting polyazido compounds, such as  $As(N_3)_3$ ,  $Sb(N_3)_3$ ,  $As(N_3)_5$ ,  $Sb(N_3)_5$ ,  $Sb(N_3)_6^-$ ,  $Te(N_3)_4$ ,  $Te(N_3)_5^-$ ,  $[Te(N_3)_6]^{2-}$ ,  $Ti(N_3)_4$ ,  $[Ti(N_3)_6]^{2-}$ ,  $Nb(N_3)_5$ ,  $Ta(N_3)_5$ ,  $Nb(N_3)_6^-$ ,  $Ta(N_3)_6^-$ ,  $Nb(N_3)_5 \cdot CH_3CN$ ,  $Ta(N_3)_5 \cdot CH_3CN$ ,  $Mo(N_3)_6$ ,  $W(N_3)_6$ ,  $Mo(N_3)_7^-$ ,  $W(N_3)_7^-$ ,  $NMn(N_3)_4^-$ ,  $NW(N_3)_4^-$ , and  $OW(N_3)_4$ . Most of these compounds are novel and constitute the first representatives of binary azides of their respective groups in the periodic system. They are extremely energetic and very difficult to handle and, therefore, represent the ultimate challenge to synthetic chemists.

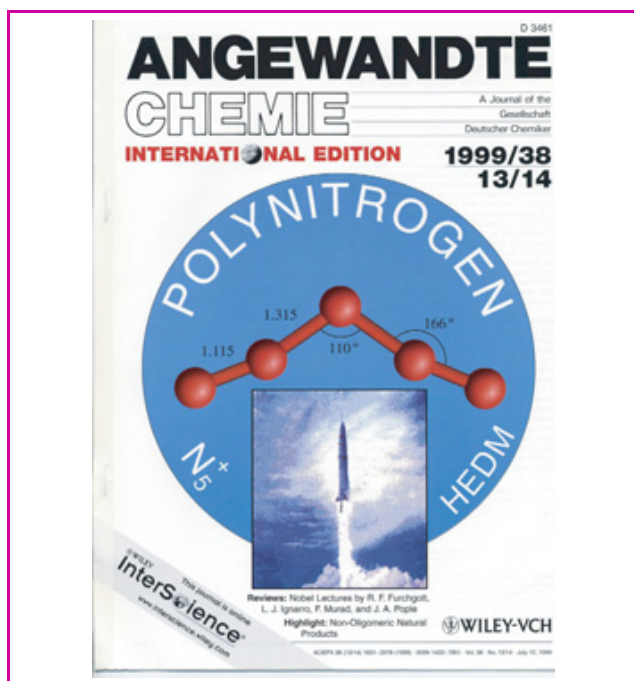


Figure 3 - Cover page from the *Angewandte Chemie* issue in which the  $N_5^+$  synthesis was published.

## Acknowledgments

In the limited space available here, I have been able to touch only upon a very small portion of our work and have selected only several areas which I thought might be of general interest to a broader audience and, also, are more closely related to the fields in which Henri Moissan has excelled. His work and example have been a great inspiration to all of us.

I am deeply indebted to my colleagues and collaborators whose names are given in the cited references. Without their help and devotion, this work could have never been accomplished. We are also grateful for financial support over the years from the Office of Naval Research, the Air Force Office of Scientific Research, the Army Research Office, the Defense Advanced Research Projects Agency, and the National Science Foundation.

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