

## Neil Bartlett and the first noble-gas compound

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**Abstract** Neil Bartlett (1932–2008) was the first to produce non-transient amounts of a compound of a noble gas. By describing some of the circumstances of his seminal work we gain a glimpse into the process of his extraordinary experimental discovery. It happened in the spring of 1962 and was followed by an avalanche of other discoveries in noble-gas chemistry leading—over the years—to many new substances with the most interesting bonding properties and structures.

**Keywords** Neil Bartlett · Don Yost · Noble-gas compounds · Fluorine chemistry



Neil Bartlett

**Neil Bartlett** (at the 14th International Symposium on Fluorine Chemistry in Yokohama, Japan, 1994, photograph by I. Hargittai)

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In the June 1962 issue of *Proceedings of the Chemical Society* Neil Bartlett, then of the University of British Columbia, published one of the shortest—less than 250 words—seminal papers in science history announcing the discovery of a 1:1 compound between xenon and hexafluoroplatinate,  $\text{XePtF}_6$ , a mustard-yellow solid, whose formula could also be written as  $\text{Xe}^+[\text{PtF}_6]^-$  [1]. Bartlett first sent his report on  $\text{XePtF}_6$  to *Nature*, on April 2, 1962. It seemed to him that his manuscript might have been lost when he did not hear from the journal, so after a few weeks time, he withdrew his report. As he learned later *Nature* did acknowledge the receipt of his sending, but it mailed the acknowledgment by surface mail and it arrived in Vancouver only in June. By then Bartlett had sent off his note to the *Proceedings*, which was the forerunner of *Chemical Communications*. He was fully aware of the importance of bringing out the report about his discovery as quickly as possible. His manuscript arrived on May 4 at the *Proceedings*, was quickly accepted, and was printed in the next available issue, in June 1962 (Fig. 1).

Several ingredients came together for Bartlett's discovery in a fortunate way and it is of interest to discuss at least some of the circumstances of the discovery, because it is usually only the dry facts directly related to successful experiments that are described in the printed reports. The first interesting question is how the idea of trying to make a noble-gas compound came to Bartlett and how he came to the idea of trying the particular reaction between xenon and  $\text{PtF}_6$ . Here, our narrative is based on what Bartlett actually told me in an interview on May 11, 1999 [2]. The interview was followed up by e-mail messages. Bartlett was unequivocal in stating that nobody else suggested to him to try this particular reaction; it was his own idea (Bartlett N (June 13, 2000) Private communication by e-mail) (Figs. 2, 3, 4).

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For Irfan  
best kind regards  
& best wishes  
Neil Bartlett  
"May" 1999

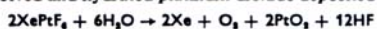
### Xenon Hexafluoroplatinate(v) $\text{Xe}^+[\text{PtF}_6]^-$

By NEIL BARTLETT

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A RECENT Communication<sup>1</sup> described the compound dioxygenyl hexafluoroplatinate(v),  $\text{O}_2^+\text{PtF}_6^-$ , which is formed when molecular oxygen is oxidised by platinum hexafluoride vapour. Since the first ionisation potential of molecular oxygen,<sup>2</sup> 12.2 eV, is comparable with that of xenon,<sup>3</sup> 12.13 eV, it appeared that xenon might also be oxidised by the hexafluoride.

Tensimetric titration of xenon (AIRCO "Reagent Grade") with platinum hexafluoride has proved the existence of a 1:1 compound,  $\text{XePtF}_6$ . This is an orange-yellow solid, which is insoluble in carbon tetrachloride, and has a negligible vapour pressure at room temperature. It sublimes in a vacuum when heated and the sublimate, when treated with water vapour, rapidly hydrolyses, xenon and oxygen being evolved and hydrated platinum dioxide deposited:



<sup>1</sup> Bartlett and Lohmann, *Proc. Chem. Soc.*, 1962, 115.

<sup>2</sup> Field and Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, 1957, pp. 114–116.

<sup>3</sup> Kapustinskii, *Quart. Rev.*, 1956, 10, 284.

The composition of the evolved gas was established by mass-spectrometric analysis.

Although inert-gas clathrates have been described, this compound is believed to be the first xenon charge-transfer compound which is stable at room temperatures. Lattice-energy calculations for the xenon compound, by means of Kapustinskii's equation,<sup>3</sup> give a value  $\sim 110$  kcal. mole<sup>-1</sup>, which is only 10 kcal. mole<sup>-1</sup> smaller than that calculated for the dioxygenyl compound. These values indicate that if the compounds are ionic the electron affinity of the platinum hexafluoride must have a minimum value of 170 kcal. mole<sup>-1</sup>.

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Fig. 1 The first report of a noble-gas compound in June 1962 with Bartlett's dedication to the author in 1999

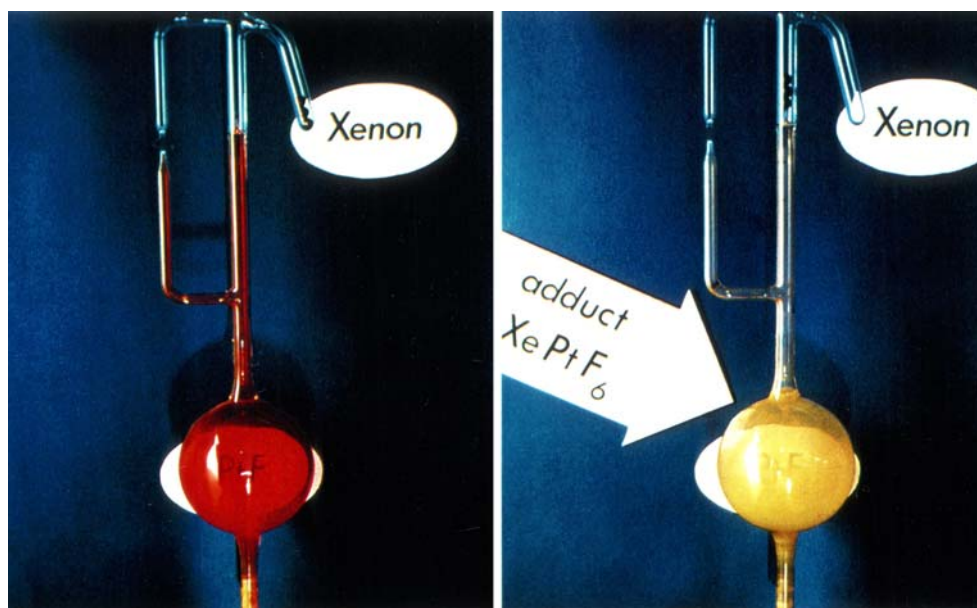


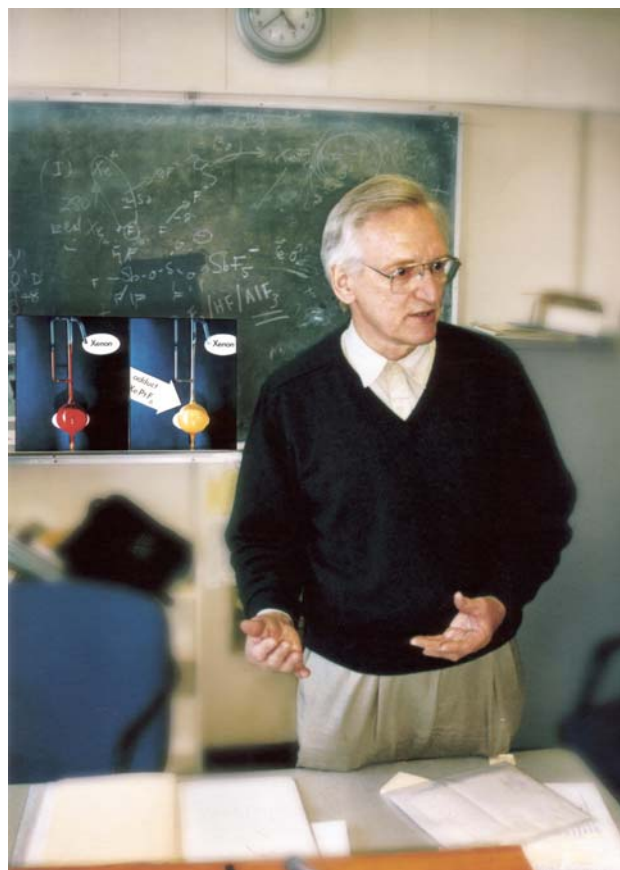
Fig. 2 The historic experiment producing the first noble-gas compound as it was recreated at the Lawrence Berkeley National Laboratory (courtesy of the late Neil Bartlett)



**Fig. 3** Neil Bartlett at the time of the production of the first noble-gas compound (courtesy of the late Neil Bartlett)

He did not start thinking about this until he had identified  $O_2PtF_6$ . Bernard Weinstock and his group at the Argonne National Laboratory had recently published their preparation of platinum hexafluoride. Bartlett did not find it easy to make his own  $PtF_6$ , which he needed for some other experiments; his trials, together with his student, Derek Lohman, however, led to an accidental preparation of a new substance of the composition of  $PtO_2F_6$  [3]. It took then a lot of experiments, thinking, and convincing doubting colleagues before Bartlett came to the conclusion that the substance could be looked at as being  $O_2^+PtF_6^-$ . When he finally convinced not only his peers but also himself of the correctness of this characterization, he realized that in  $PtF_6$  he possessed the most potent oxidizing agent ever discovered. This made him think about what might be even more difficult to oxidize than molecular oxygen.

It was another fortunate circumstance that at this time Bartlett was preparing for his undergraduate chemistry course, and studied the plot of ionization potential as a function of atomic number, which is a common illustration of periodicity. He noticed that the first ionization potential of molecular oxygen is comparable with the ionization potential of xenon. From this he concluded that it should be possible to oxidize xenon by platinum hexafluoride, just as it was possible to oxidize molecular oxygen. When he



**Fig. 4** Neil Bartlett in his laboratory at Berkeley on May 11, 1999, the day when he was closing it down (photograph courtesy of Magdolna Hargittai)

realized that the way to go was reacting xenon with  $PtF_6$ , he ordered some xenon. His means were limited and he had to restrict his order to 250 cc. of the noble gas. Although he already had two graduate students, they were inexperienced, and Bartlett had to do even the glassblowing for the apparatus he designed for the reaction.

The crucial experiment happened on March 23, 1962; it was a Friday, and the apparatus was brought together by 7 p.m. His two graduate students both had left at this hour as they lived in a student residency where dinner was served at 6:30 p.m. Bartlett was all alone in the lab. He broke the seal between  $PtF_6$  and xenon, and there was an immediate reaction. Bartlett desperately wanted to tell somebody—anybody—about it; he went out into the corridor, but there was not a soul in the whole building. So he went back to the lab and suddenly he was flooded with doubts, “Maybe xenon was impure, maybe there was some oxygen present, maybe I’m just fooling myself.” Both the urge to communicate about his experiment and the doubts seem to be typical in such moments of discovery.

Bartlett then sublimed the reaction product by heating it under vacuum, then condensed water onto it and collected



the evolving gas in one part of his apparatus. He then sealed this part of the apparatus and the next day he gave it to his mass spectrometrist colleague, David Frost. The mass spectrometric analyses during the next couple of days provided reassuring proof to Bartlett as to the composition of his product.

It is interesting that the world of chemistry appeared ready for Bartlett's discovery because within a couple of months a group of scientists at Argonne National Laboratory, Howard Claasen, Henry Selig, and John Malm reported the synthesis of the first binary xenon compound [4]. Then, before the end of 1962, the preparations of further noble-gas compounds were announced by Rudolf Hoppe and his group at the University of Münster, Germany [5], Jozef Slivnik and his group at the Jozef Stefan Nuclear Institute in Ljubljana (then Yugoslavia, now Slovenia) [6], and Paul Fields and his associates at the Argonne National Laboratory [7].

Word was also spreading fast about Bartlett's discovery even prior to its publication. Parallel to his initial submission to *Nature*, Bartlett informed four people whom he trusted about the manuscript; R. S. Nyholm at University College London, A. G. Sharpe and H. J. Emelius at Cambridge, UK, and R. D. Peacock at Imperial College, London (Bartlett N (June 13, 2000) Private communication by e-mail). Peacock later told Bartlett that he had shared this confidential information with others whom he trusted at a meeting of the Chemical Society. The news traveled fast. This was important for a later dispute that developed concerning the priority of the discovery of xenon tetrafluoride between the German group and the Argonne laboratory. Bartlett referred to this development as follows: "Certainly the Argonne discovery was a direct consequence of mine. I had after all strayed into their territory when I discovered the nature of  $O_2^+[PtF_6]^-$ . They were all set to repeat my experiment and to extend it to the other transition series hexafluorides. It was their experiments with xenon and  $RuF_6$ , which held the key (they recognized  $RuF_5$  among the products). Professor Hoppe has never acknowledged that his efforts were stimulated by my publication of  $XePtF_6$ , although he has acknowledged my priority (Bartlett N (June 13, 2000) Private communication by e-mail). In contrast with other priority disputes in connection with some of the follow-up discoveries, Bartlett's achievement has remained recognized as the pioneering one.

Bartlett was by far not the first who tried to prepare noble-gas compounds. The earliest attempts go back to the time of the isolation and identification of the noble gases and to Henri Moissan and William Ramsay at the end of the nineteenth century. The first noble gas discovered by Ramsay was argon and the discovery of fluorine by Moissan preceded it by 9 years only. When Ramsay observed the inertness of argon, he sent a sample to

Moissan who mixed it with fluorine and passed the reaction mixture through an electric discharge. He analyzed the effluent very carefully and could not detect any sign of any combination. He reported this observation to Ramsay and this early experiment had a strong impact in how chemists viewed the noble gases for a long time.

The most noteworthy of later attempts to prepare noble-gas compounds were by a professor at the Gates Chemical Laboratory of the California Institute of Technology, Don M. Yost, and his graduate student Albert L. Kaye in 1933 [8]. They acted upon Linus Pauling's suggestion and used a sample of xenon from Fredrick John Allen. Allen was Pauling's old chemistry teacher who was by then at Purdue University. Yost and Kaye's attempt did not succeed, but was found important enough to describe it in the *Journal of the American Chemical Society*. They concluded that "It cannot be said that definite evidence for compound formation was found." Even more significantly, they stated that "It does not follow, of course, that xenon fluoride is incapable of existing" [8].

According to Bartlett, it was unfortunate that Yost and Kaye used a quartz bulb for carrying out their reaction. When they passed an electric discharge through the bulb all they must have gotten was an attack on the walls of the quartz container. Bartlett supposed that they got silicon tetrafluoride in addition to oxygen liberated from the container material. Bartlett ascribed their main mistake to the fact that they did not take their reaction mixture out into the California sunlight [2].

Three decades later, after the discovery of the first noble-gas compounds, Yost summarized their efforts and the lessons that could be learned from them [9]. He described the rudimentary conditions of their experiments and noted that "only visionary scholars" could have dreamed of the conditions among which decades later similar experiments could be performed. He put it succinctly, "Fluorine chemistry was then carried out in the days of wooden ships and iron men." Yost did not in any way though belittle the significance of the achievements of the discoverers. On the contrary, he stated that "chemistry had reached a stationary state, during which no profoundly fundamental discoveries were reported or even deemed possible. ... This state of affairs has now been changed... So long as man shows any interest whatever in chemistry, the discovery of xenon and other noble-gas fluorides will not be forgotten." Further, Yost advanced his vision of the future: "One can envision a whole sombrero full of studies that can be made on noble-gas compounds and their derivatives, which will enrich our knowledge of nature and her laws." He also predicted that applications will come forward.

Incidentally, Bartlett used Pyrex glass in his experiments. In this connection, he learned important lessons from the Manhattan Project where the people involved in

making  $\text{UF}_6$  could work with fluorine more easily if they scrubbed the traces of HF out of their fluorine sample. This was possible to do by passing the fluorine over sodium fluoride, forming sodium bifluoride. The fluorine thus treated was much easier to contain in dry glass. Water content, on the other hand, would destroy the container regardless whether it was glass or quartz.

Actually, Bartlett considered it a great advantage for his experiment that he worked with glass and could always follow what was happening to his reaction mixture. In contrast, the Argonne people used metal lines and metal valves and they did not have the possibility to observe everything during the reaction. Bartlett stressed though that he had learned a lot from the Argonne work on platinum hexafluoride and he praised the beauty and sophistication of their work, especially their spectroscopy [2]. The Argonne group was also very strong in understanding the physics of the new compounds, including the Jahn–Teller features of their molecular structures [10].

On his part, Bartlett stayed in preparative inorganic chemistry throughout his career and produced exciting new substances that enriched our field enormously. When asked if there was ever a compound that he would have liked to prepare but never succeeded, he named gold hexafluoride. He said in 1999 as he was closing down his laboratory at the Berkeley campus, “Somebody else will now have to find the effective route to it. It should exist, if made at low temperature and kept cold” [2].

Neil Bartlett was a gracious man who could be happy at seeing other people succeeding as well. He could hardly contain his joy when he learned about the discovery of the new substance of HArF by a group of chemists in Helsinki [11]. He heard about it over the public radio at dinner time on August 24, 2000. The next day he sent an e-mail message to his fluorine chemist colleagues describing his ideas about what he supposed might have been the bonding properties of HArF. He also wrote to congratulate the group in Finland and subsequently “had an interesting and pleasant exchange of letters with them” (Bartlett N (January 11, 2001) Private communication by e-mail).

The molecular structures of noble-gas compounds have provided beautiful and instructive examples of various models of molecular geometry and chemical bonding. In particular, xenon hexafluoride provided an early proof for the validity and usefulness of the valence shell electron pair repulsion (VSEPR) model [12]. Its structure had been predicted to be regular octahedral on the basis of some rudimentary molecular orbital considerations. However, the valence shell of xenon contains a lone pair of electrons in addition to six bonding pairs in  $\text{XeF}_6$  and thus the shape of a distorted monocapped octahedron would be more consistent with the VSEPR model than a regular octahedral shape. Reliable experimental determinations then provided

evidence for the structure suggested by the VSEPR model. We have to add though that the last word has not been said about the molecular shape of xenon hexafluoride as there is no clear-cut decision between a regular octahedral shape and a distorted one. There are competing effects and the outcome of even the most sophisticated calculations depends on the extent these various effects are being taken into account.

Toward the end of his career as an experimentalist, Bartlett and his group at Berkeley returned to the topic of his original discovery and performed an extensive investigation concerning the nature of  $\text{XePtF}_6$  [13]. It is of interest to look at the authors’ list of this paper. Two of them were Bartlett’s associates at Berkeley. Then there was Narendra K. Jha who had been Bartlett’s doctoral student at UBC in the early 1960s and received his Ph.D. degree there in 1965, but by the time of this more recent paper he had long before left UBC. Nonetheless, he was assigned UBC affiliation, which is the more conspicuous since no other affiliation was given for him. In an almost romantic gesture, Bartlett added UBC to his own Berkeley affiliation.

In this review they used experimental results from the early 1960s and added new ones. They confirmed that when xenon was in large excess over platinum hexafluoride in the reaction mixture, the stoichiometry of the product approached 1:1. However, when the platinum hexafluoride exceeded the xenon, a different product formed, which was a sticky solid of deep red color. This product approached the composition of  $\text{Xe}(\text{PtF}_6)_2$ . This could correspond also to the product obtained when  $\text{XeF}_2$  and  $\text{PtF}_5$  were brought into interaction. This work, performed in 1999, investigated in great detail the nature and physical characterization of all possible products in related reactions. Here we note only that Bartlett never felt satisfied until he uncovered all possible angles of a problem. His new findings did not subtract anything from the significance of his original discovery, on the contrary, further enhanced the weight of his pioneering work. He gave a full account of his 40 years in fluorine chemistry as a chapter in a monograph in the year 2000 [14].

At this point it may be illuminating to have a few words about Neil Bartlett’s life and career [2]. He was born in 1932 in Newcastle-upon-Tyne, England. His parents started their married life at the time of the Great Depression and they ran a corner shop. His father had served in World War I and was severely gassed. The father died early and left his widow with three children, but she managed to cope, and encouraged her children to study. She was even very tolerant of Neil’s running chemical experiments at home accompanied with foul smells and frightening bangs. Neil and his brother augmented their pocket money by making and selling ice cream on weekends. Neil used the proceeds to buy chemicals and books.

Bartlett's maternal grandfather had the German-sounding name Vock, Friedrich Wilhelm Heinrich Johannes Vock in full, and he was from the small archipelago in the North Sea, Heligoland, which was British at the time. He migrated from Heligoland to Newcastle. When Queen Victoria and the German Kaiser exchanged Heligoland and Zanzibar in 1890, the grandfather became German. Bartlett's mother changed her name from Vock to Voak during World War I to make it sound more English.

Bartlett went to school in Newcastle and received his B.Sc. degree in 1954 and his Ph.D. degree in 1958, both from King's College, University of Durham, at Newcastle, which is today the University of Newcastle. In 1958, he moved to Vancouver, became a faculty member of the University of British Columbia, and stayed there until 1966. It was during this period that he discovered the first noble-gas compound.

Bartlett's stay at UBC was successful also for his rapid rise from lecturer to full professor in 5 years. On the other hand, he sensed some personal animosities—at least this is what he alluded to when looking back to this period in our conversation in 1999. In spite of his rapid advance in rank, he felt that UBC should have done better. At the same time, his contacts with the Argonne National Laboratory showed him the contrast in opportunities that he lacked in Vancouver. Then there was a laboratory accident on January 27, 1963, which somehow became associated with Vancouver in Bartlett's mind. He and one of his students were looking at an experiment and each was wearing a plastic visor. Although Bartlett had very good eyesight, the visor barred him from having a good look at the surface of the crystal that was being formed, so he put his visor up and so did his student. At that very moment the sample they were looking at blew up. They both were injured; Bartlett more heavily than the student. They were carted off to hospital where they stayed for over 4 weeks. Bartlett had some glass in his eye that kept bothering him for the next 27 years, and came out only in 1990.

There were other unfavorable conditions at UBC at the time, so when an attractive offer came from Princeton, he accepted. Eventually he realized that he felt more comfortable at UBC than at Princeton, at least in hindsight, that he preferred a smaller campus to a big one, and that he was a West Coast person rather than an East Coast one. When he had an invitation from Berkeley, he accepted it and moved to California in 1969. There he was Professor of Chemistry at the University and served also as Principal Investigator at the Lawrence Berkeley National Laboratory. When my wife and I visited him on May 11, 1999, he did not strike us as a happy person. The date was significant, because it was the day when he was closing down his laboratory for good.

Neil Bartlett was an internationally renowned scientist. Among many other distinctions, in 1973, he was elected Fellow of the Royal Society (London); he was a Foreign Associate of the National Academy of Sciences of the USA and of the French Academy of Sciences. In 1976, he received the Robert A. Welch Award in Chemistry. In 2006, the American Chemical Society and the Canadian Society for Chemistry honored him with an International Historical Chemical Landmark plaque on the wall of the building where his seminal discovery took place at UBC in 1962. It reads, both in English and in French.

### Neil Bartlett and reactive noble gases

In this building in 1962 Neil Bartlett demonstrated the first reaction of a noble gas. The noble gas family of elements—helium, neon, argon, krypton, xenon, and radon—had previously been regarded as inert. By combining xenon with a platinum fluoride, Bartlett created the first noble gas compound. This reaction began the field of noble gas chemistry, which became fundamental to the scientific understanding of the chemical bond. Noble gas compounds have helped create anti-tumor agents and have been used in lasers.

The first page of the first chapter in the Italian chemist turned famous writer Primo Levi's book, *The Periodic Table* says the following, "As late as 1962 a diligent chemist after long and ingenious efforts succeeded in forcing the Alien (xenon) to combine fleetingly with extremely avid and lively fluorine, and the feat seemed so extraordinary that he was given a Nobel prize" [15]. Bartlett never received the Nobel Prize, but this mark of distinction from Primo Levi reinforces the fact that the name Bartlett is immortalized as a result of his beautiful experiment in the annals of science.

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