

# Brief encounters with dubnium

Lars Öhrström tells of the fleeting, but still tangible, chemistry of dubnium, the heaviest of the group 5 elements.

Now you see me, now you don't, this might be a fitting exit line for a dubnium atom slipping through our hands as it decays by sending out an alpha particle. However, the chemist gets the last laugh, as it is this very vanishing act that makes the one-atom-at-a-time chemistry experiments on element 105, a heavier analogue of tantalum, feasible.

As one of the most hotly disputed elements during the transfermium name dispute, when the Cold War cast a dark shadow on science, dubnium initially went under many names. It was synthesized by groups in the Soviet Union and the United States in the late 1960s, starting in Dubna — the science city outside Moscow that was to eventually give its name to the element. There, scientists smashed  $^{243}\text{Am}$  with  $^{22}\text{Ne}$  producing a mixture of  $^{260}\text{Db}$  and  $^{261}\text{Db}$  ( $t_{1/2} = 1.5\text{--}1.8\text{ s}$ ) after the loss of five and four neutrons, respectively, and announced the discovery of nielsbohrium. Around the same time, their principal rivals from Berkeley used  $^{15}\text{N}$  to hit a  $^{249}\text{Cf}$  target and formed  $^{260}\text{Db}$ , proposing the name hahnium<sup>1</sup>. The dispute was eventually resolved<sup>2</sup> and the name dubnium was adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1997.

One often meets with the opinion that the transfermium elements are of limited use on account of their short lifetimes. On the contrary, take radiopharmaceuticals used in diagnostics for example. These must decay relatively quickly to provide an image for the physician in a timely manner. For this purpose, the  $^{99\text{m}}\text{Tc}$  isotope is routinely employed; it has a half-life of 6 hours, which is approximately four times shorter than that of  $^{268}\text{Db}$  — the longest-lived Db isotope known.

The real problem for dubnium use is its slow production rate. One atom of the most studied dubnium isotope,  $^{262}\text{Db}$  ( $t_{1/2} = 34\text{ s}$ ), can be prepared in less than 1 minute, whereas for the  $^{268}\text{Db}$  isotope — the final alpha-decay product from the synthesis of elements 113, 115 and 117 — we are talking



Legendary transuranium and transactinide scientists Georgy Flerov (1913–1990), Yuri Oganessian (1933–) and Glenn Seaborg (1912–1999) on the Volga River bank in Dubna, Russia. Photo reproduced with permission from the Joint Institute for Nuclear Research, Dubna.

about atoms per week. Thus with current technology, the chances of accumulating any meaningful amount of dubnium is nil.

So, we cannot expect to prepare dinuclear compounds characteristic of the group 5 elements, such as the analogues of the dimeric  $\text{Ta}_2\text{Cl}_{10}$ . Luckily, the gas-phase chemistry of  $\text{Ta}_2\text{Cl}_{10}$  is that of the pentacoordinated mononuclear complex. As a result  $\text{DbCl}_5$ ,  $\text{DbBr}_5$ , and also  $\text{DbOCl}_3$  — the latter of which is expected from the reaction with traces of oxygen in the carrier gas — have been inferred from one-atom-at-a-time experiments.

These techniques are becoming increasingly sophisticated such that investigation of dubnium's aqueous chemistry is now possible<sup>3</sup>. Both  $[\text{DbOCl}_4]^-$  and  $[\text{Db}(\text{OH})_2\text{Cl}_4]^-$ , and even complexes with the chelating  $\alpha$ -hydroxyisobutyric acid, have been suggested, based on where in the chain of chromatography, extraction and surface detection a characteristic Db alpha decay is observed. Crucial for these experiments is comparison with lighter analogues under the same circumstances. For example, radioactive isotopes of Hf and Ta, produced by neutron activation, were recently used to develop an extraction

system for the separation of dubnium from its group 4 neighbour rutherfordium<sup>4</sup>.

One has to be aware that a simple extrapolation from the properties of the lighter group members (Nb and Ta in this case) is not an adequate way of predicting the properties of the  $6d$  elements. As the nucleus gets heavier, relativistic effects come into play, so the experiments need to be complemented by advanced quantum chemistry. In this case, such calculations suggest an increased stability of the +5 oxidation state and an electron configuration of  $[\text{Rn}]5f^{14}6d^37s^2$ , concurrent with Db being the heaviest member of group 5 (ref. 1).

This intricate interplay between theory and experiment is of interest and importance not only to chemists, but also to nuclear physicists trying to establish the identity of new elements. When these decay into unknown isotopes, as for elements 113, 115 and 117 where many alpha-decay chains ended in  $^{268}\text{Db}$ , it is vital to establish the identity of these isotopes so that the back-calculation will give the right atomic number of the new element<sup>5</sup>.

So, in this borderland where chemistry meets physics, nothing should be taken for granted and one does well to remember that even after a new superheavy element has obtained its place in the periodic table, isotopes with higher stability may yet be discovered, as indeed was the case for dubnium. □

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