The race for rutherfordium

Mitch André Garcia considers the disputed discovery of element 104 and takes a look at how the chemistry of this synthetic element is developing.

R utherfordium, the 104th element on the periodic table, was first synthesized artificially in the 1960s and was the subject of international controversy for decades. The dispute centred on who should get to name the new element. Historically, the discoverer of an element is afforded the right to name it, but when two groups have competing discovery claims this becomes complicated.

The first research group to claim discovery of element 104 was a team of scientists at Dubna (in what was the USSR) in 1964 (ref. 1). They observed an isotope that underwent spontaneous fission after bombarding their ²⁴²Pu target with a beam of ²²Ne ions. A second team of scientists at Berkeley in California — tried for years to replicate these experiments, but were unable to do so. Finally, in 1969, the team at Berkeley made element 104 with a different nuclear reaction; they used a target of 249Cf and a beam of ¹²C and ¹³C to produce ²⁵⁷Rf and ²⁵⁹Rf (ref. 2). Both of these isotopes of rutherfordium decay into nobelium by emitting α -particles. The characteristic decay energy and half-life of nobelium was also observed subsequent to the rutherfordium decays. Thus, the team at Berkeley was able to claim unambiguous detection of element 104 by following its chain of decays.

As the years went on neither group would give ground, and finally an international committee was assembled to determine which claims had more weight. The Transfermium Working Group (TWG) was put together by the International Union of Pure and Applied Physics (IUPAP) and its sister chemistry organization IUPAC. Although the TWG consisted of eminent scientists, none were heavy-element scientists or radiochemists.

In 1992 the TWG finally released its findings. The committee decided that both the Berkeley and Dubna groups should share the discovery claim for rutherfordium.

Sg

Bh

Db



One of the greatest achievements of Ernest Rutherford — for whom element 104 is named was the destruction of the plum-pudding model of the atomic nucleus.

This outcome was not what either research group wanted, but it was accepted with some protest. The name 'rutherfordium' was part of a broad set of compromises between both research groups that resulted in element 105 being named for Dubna and element 106 named for Glenn Seaborg. For more information about the controversial history of rutherfordium, see *The Transuranium People* by Darleane Hoffman, Albert Ghiorso and Glenn Seaborg³.

In 1970, Ghiorso and co-workers synthesized a new isotope of rutherfordium, ²⁶¹Rf (ref. 4). The half-life of this particular isotope is 69 s — which is relatively long in the context of transactinide elements - and so encouraged chemists to attempt the first liquid-phase studies of rutherfordium. At the time it was not known whether rutherfordium would behave like a group 4 metal or would follow the actinide series in its chemistry. In the same year, Robert Silva and colleagues⁵ in collaboration with Ghiorso's team eluted ²⁶¹Rf from a cation exchange resin in the presence of tetravalent zirconium and hafnium, and trivalent actinide tracers. The results of this experiment showed that 261Rf eluted with the

tetravalent hafnium and zirconium tracers and solidified its place as a group 4 metal.

Gas-phase chemistry studies of rutherfordium took advantage of the volatile properties of the group 4 metal chlorides. Anyone who has worked with hafnium(IV) chloride will no doubt remember the gag-inducing effect it has! Isothermal gas chromatography was performed with the chlorides of zirconium, hafnium and rutherfordium using a column of SiO₂ from set temperatures of 100 °C to 600 °C (ref. 6). The experiments measured the relative yields of products out of the column as a function of temperature, and then the adsorption enthalpies on SiO₂ from a Monte Carlo fit of their measurements were calculated. This was used as a yard stick for measuring volatility.

As expected for a heavier molecule, hafnium chloride was found to be less volatile than zirconium chloride (that is, a lower enthalpy of adsorption than zirconium chloride). However, the volatility of rutherfordium chloride was found to be nearly the same as zirconium chloride. This is a dramatic break from the trend that periodicity would predict. Presumably this is caused by some relativistic effect, but the exact mechanism that creates volatile salts of rutherfordium is still a mystery.

The future of rutherfordium chemistry will probably focus on devising chemical systems that help elucidate the role of relativistic effects in its chemistry, as well as the creation of new compound classes of rutherfordium, such as inorganic complexes and organometallics.

MITCH ANDRÉ GARCIA is at the University of California, Berkeley, in the Department of Chemistry, Berkeley, California 94720-1460, USA. e-mail: mitch@berkeley.edu

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Hs Mt Ds

Rg

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1d No