**in your element**

# Regarding ruthenium

From humble beginnings in Siberia, ruthenium has blossomed into an incredibly interesting and useful element. **Simon Higgins** looks at its role in past — and perhaps future — Nobel Prize-winning discoveries.

Given its position in the middle of the *d*-block of the periodic table, it is not surprising that ruthenium exemplifies many of the properties of the transition metals — such as forming complexes in a wide range of formal oxidation states (from VIII to –II). First described in 1844 by Karl Klaus, who isolated it from the insoluble residue left on dissolving crude Siberian platinum in *aqua regia*, it was named after Russia (Latin *Ruthenia*) — partly in tribute to Klaus's homeland and partly in recognition of the earlier efforts of Gottfried Osann who had suggested the existence of new elements in these residues, one of which he had named ruthenium.

Ruthenium is rare (it comprises roughly $10^{-7}$% of the Earth's crust). It is usually found together with its five fellow 'platinum group' metals (Os, Rh, Ir, Pd and Pt), but because of the much greater demand for rhodium and platinum, ruthenium is currently fairly inexpensive (£3.60/\$5.60 per gram). Industrially, it is used as a hardener, in alloys with platinum and palladium for applications in electrical switching gear. Moreover, titanium's resistance to corrosion can be greatly increased by alloying it with small amounts (<1%) of ruthenium.

A fascinating and sometimes an enigmatic element, the chemistry of ruthenium seems to hold nearly unique charisma in the eyes of its investigators. For example, in 1984 a magisterial book, *The Chemistry of Ruthenium* by Seddon and Seddon, offered complete critical coverage of the literature up to 1978; it would be difficult to envisage a similarly comprehensive update today!

Together with osmium and xenon, ruthenium exhibits the highest known formal oxidation state in the periodic table — VIII — in $RuO_4$. This volatile and toxic compound, which has an odour of ozone if one is foolhardy enough to sniff it, is soluble in $CCl_4$ and is a strong oxidant.

The compound usually used as a starting material in ruthenium chemistry, however, is 'hydrated ruthenium trichloride', an almost black, reflective solid that is obtained industrially by dissolving $RuO_4$ in aqueous HCl and evaporating to dryness. It is soluble in a wide range of solvents, is comparatively reactive, and — despite its name — mainly consists of oxo-bridged dimeric Ru(IV) chloro-complexes.

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A landmark in coordination chemistry was the 1965 report by Allen and Senoff of the first synthetic complexes of $N_2$, $[Ru(NH_3)_5(N_2)]X_2$ (X = anion). These were originally made by treatment of 'ruthenium trichloride hydrate' with hydrazine, and showed a weak band in their infrared spectra at around 2,100 cm$^{-1}$, owing to the N≡N stretch. Their discovery triggered a new field — synthetic nitrogen-fixation catalysis — which has produced much new chemistry and insight, but sadly, no lower-cost rival for the Haber–Bosch process so far.

Nowadays, ruthenium is at the forefront of several important areas of science. For example, the development of air- and moisture-tolerant homogeneous ruthenium catalysts for alkene metathesis has had a major impact in total synthesis and in materials chemistry, resulting in a share of the 2005 Nobel Prize in Chemistry for their pioneer, Bob Grubbs. Ruthenium complexes are also extensively employed in enantioselective hydrogenation reactions in organic synthesis (exemplified by the work of Ryoji Noyori, who was one of the winners of the 2001 Nobel Prize in Chemistry), and are now being investigated in chemotherapy.

Perhaps the most-studied ruthenium complex of recent times has been [Ru(2,2′-bipyridine)$_3$]$^{2+}$, sometimes called rubipy, and its derivatives. On irradiation with visible light, rubipy produces a long-lived photoexcited triplet, essentially [Ru$^{\mathrm{III}}$(2,2′-bipyridine)$_2$(2,2′-bipyridine$^{\bullet-}$)]$^{2+}$. The Ru(III) is a strong oxidant, whereas the 2,2′-bipyridine radical anion is a powerful reductant. It was pointed out in the mid-1970s that, in principle, this photoexcited state is capable of both oxidizing and reducing water, to $O_2$ and $H_2$ respectively, giving rise to much research. In practice, the system only works in the presence of a sacrificial reducing agent and a quencher, typically methyl viologen, and gives only $H_2$.

More recently, related complexes have been much studied as dyes in dye-sensitized solar cells, such as the Grätzel cell. Here, the dye is covalently attached to wide-bandgap semiconductor nanoparticles (usually $TiO_2$) that act as an anode, to which the photogenerated state transfers an electron. The resulting Ru(III) is reduced by iodide ions in a liquid electrolyte, and the iodine produced is itself re-reduced at a cathode. Such cells are proposed as potential low-cost rivals to silicon solar cells.

Over 150 years since ruthenium's discovery, its chemistry continues to provide fascinating new findings and potential technologies. No doubt its lure will continue to attract others to its study. ❐

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