

bonding interaction with two small atoms such as nitrogen<sup>3</sup> or oxygen — exactly as seen in the uranyl ion.

Uranyl ions are an extremely rare example of compounds in which the presence of non-valence, core electrons dictates the observed structure of a molecule. Such linear bonding interactions are not possible in transition-metal oxides because they do not possess valence *f* orbitals, and because the relativistic effects in transition metals aren't large enough to force any of their core orbitals to participate in bonding in a similar way. The key to Arnold and colleagues' discovery<sup>1</sup> is that they have found a way to disrupt the bonding interactions that stabilize U=O bonds so that the uranyl group can take part in an atypical reaction.

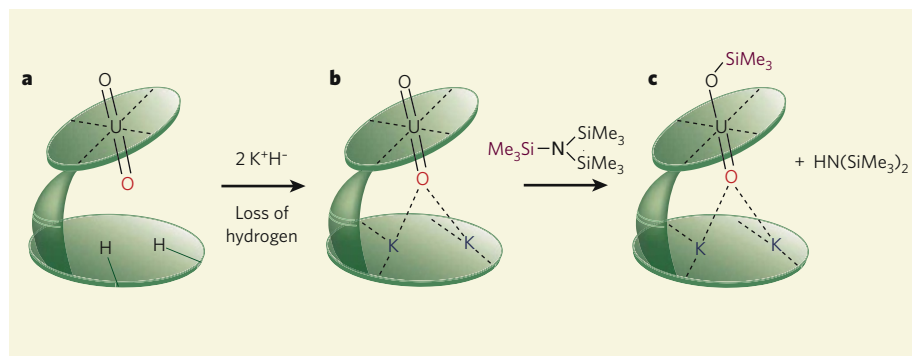
Arnold *et al.*<sup>1</sup> use a flexible ligand to simultaneously bind a uranyl ion and two potassium ions. The Pac-Man-like structure adopted by the ligand (Fig. 1) forces one of the uranyl oxygen atoms to donate electrons to the potassium ions. Under normal conditions<sup>4</sup>, interactions of this sort are not favourable; only the presence of the ligand scaffold makes it possible. The interaction with the potassium ions disrupts the characteristically strong U=O bonds, so that the uranium ion behaves as a strong oxidant<sup>5</sup>. The unbound oxygen atom is thus able to abstract a silicon-containing group from an organic substrate; the uranium atom accepts electrons (is reduced). Given the thermodynamic stability of the resulting silicon-oxygen bond, it is likely that the formation of such bonds also provides a substantial driving force for the observed reaction.

It is well documented<sup>6</sup> that the reactivity of transition-metal-oxide complexes can be tuned by changing ligands bound to the metal on the opposite side of the complex to an oxygen atom. Arnold and colleagues' process<sup>1</sup> is similar: the interaction of one of the oxygen atoms with metal ions affects the reactivity of the opposing oxygen atom. In this sense, the structure of the authors' ligand-ion

complex is similar to the active site of the enzyme cytochrome *c* oxidase, which converts oxygen molecules into water. Oxygen binds between two metal ions (one iron and one copper) in the enzyme active site, disrupting the bonding in the oxygen molecule and so facilitating a reduction reaction that cleaves the oxygen into two water molecules<sup>7</sup>.

You might think that any metal ion bound in the uranyl-ligand complex would be able to trigger Arnold and colleagues' reaction<sup>1</sup>, but this is not the case. Previous work<sup>8</sup> from the same group showed that several dipositive transition-metal ions — iron, manganese or cobalt — form bonding interactions to a uranyl oxygen atom when in complex with an appropriate ligand scaffold, but these complexes do not undergo the redox reaction observed for the potassium complex. This is puzzling, because potassium ions are not redox active, whereas the transition-metal ions are. Perhaps the greater size of potassium ions perturbs the U=O bond more than the smaller, transition-metal ions, thereby inducing the observed reaction. A crystal structure of the potassium-bound complex would help to clarify this, but it seems that the complex is not particularly stable, so its structure has not yet been determined. Further details of the reactivity and structures of the key compounds involved in Arnold and colleagues' reaction will undoubtedly be discovered as this intriguing chemistry is explored.

The authors' reported reaction<sup>1</sup> could perhaps be used as a strategy to manipulate uranyl ions in solution, but many questions must first be answered before its full potential can be realized. For example, can substrates other than silicon-containing compounds undergo reaction? Given that the current reaction is performed in an organic solvent, could this, or related chemistry, work in water, as would be needed for nuclear-fuel processing? And can this unusual reactivity be reproduced in oxide complexes of other, heavier actinide metals?



**Figure 1 | Uranyl-ion reaction induced by metal ions.** The oxygen atoms in uranyl ions ( $\text{UO}_2^{2+}$ ) are generally unreactive. **a**, Arnold *et al.*<sup>1</sup> show that uranyl ions bind to a rigid molecular scaffold (a ligand, shown schematically in green; dotted lines represent non-covalent binding interactions). **b**, The authors displace two hydrogen atoms in the uranyl-ligand complex with potassium (K, dark blue) ions. The potassium ions bind to the ligand close to one of the uranyl oxygen atoms (red), and so are forced to interact electronically with it. **c**, This interaction increases the reactivity of the remaining oxygen atom, which can remove a silicon-containing group ( $\text{SiMe}_3$ , purple, where Me represents a methyl group) from a substrate introduced into the reaction mixture. The uranium atom is simultaneously reduced.



## 50 YEARS AGO

"Team-work and discovery in science" — ... Dr. W. S. Kroll took issue with those who claim that the days of 'sealing wax-baling wire' science are over. The fight of the individual against the collectivity in which he lives is as old as humanity and it will never cease to exist. While Dr. Kroll granted that the team could not be avoided in development work, he challenged its justification in research ... He maintained that many laboratories in the United States are over-fond of gadgets and complicated equipment which often take more time to repair than to use. These instruments remove the investigator from his experiment ... We have to offer the recalcitrant lone-wolf research worker some asylum since he is now menaced with extinction. From *Nature* 18 January 1958.

## 100 YEARS AGO

"Public clocks and time distribution" — The interesting correspondence on "Lying Clocks" inaugurated by Sir John Cockburn in the *Times* has tended to degenerate into a display of advertisements by different firms interested in various systems of clock synchronisation ... [The] essential preliminary of the distribution of correct time signals is provided for by the Post Office authorities, working in cooperation with the Royal Observatory, Greenwich. The telegraphic service throughout the country is suspended for a few seconds, while the signal is sent through the trunk lines at 10 a.m. But, unfortunately, it is to be feared that the duty of forwarding this signal to the smaller towns is very carelessly and inefficiently performed ... If it were thoroughly well known that there did exist in every town and village an office where correct time could be had, even at some personal inconvenience, careful people would take the trouble to keep their clocks fairly accurate, and by so doing gradually educate the more indifferent to a higher standard.

From *Nature* 16 January 1908.

50 & 100 YEARS AGO