

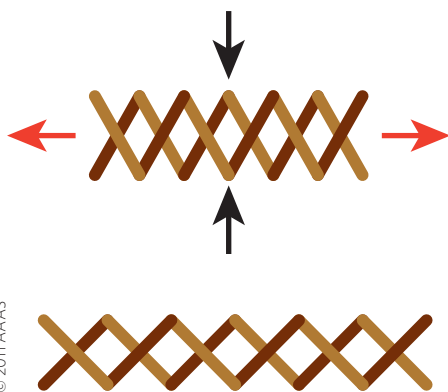
reaction outcome, because some reactions are sensitive to the precise stoichiometry of reagents. Linking the infrared signal from an intermediate to the pumping rate of the next reagent neatly gets around the problem.

The new method was applied in two different synthetic sequences. In the first — a pyrazole formation — an intermediate ynone was reacted with a hydrazine, with the process requiring only three equivalents of the toxic hydrazine reagent rather than the 5–10 the manually controlled procedure would use. In the second — a Roush crotylation — a reactive aldehyde intermediate that is too unstable to be stored was immediately reacted so that no manual handling was required.

MATERIALS CHEMISTRY

Under pressure

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When materials are cooled or put under pressure, most of them shrink. A few, however, respond by expanding under these conditions, normally only in one of the three dimensions. Now, Dominic Fortes and colleagues have discovered that a water–methanol system expands along one axis when under pressure and when cooled. Water–methanol systems, although relatively simple, have interesting properties especially when under pressure. For example, they can form clathrate cages that hinder flow in gas pipelines. The water–methanol system is also studied for its relevance to reactions in the interstellar medium and comets. Single crystals of methanol monohydrate are hard to form, however, so Fortes and colleagues examined the system using neutron powder diffraction.

The structure can be described as made up of weakly bonded sheets stacked along the *b* axis. The sheets themselves being formed of hydrogen-bonded chains that run along the *c* axis. When heated, the unit cell expands almost six times more than ice does — to an extent more typical of a liquid than a solid.

This would be even larger too, but for the *a* axis actually contracting slightly. After discovering this, the team expected that under pressure the structure would collapse along the *b* axis because the sheets are so weakly bonded together.

Up to 500 MPa, however, they found no evidence of a change to another phase. Instead, the crystal is remarkably compressible — especially in the *b* direction — but the *a* axis expands under pressure. On looking closely at the crystal structure, Fortes and co-workers discovered that the water–water chains act like a scissor jack or section of trellis and extend in response to pressure.

TUNGSTEN REACTIVITY

An unexpected move

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Combining functional groups can significantly alter their reactivities — for example, a ketene ($C=C=O$) is more reactive than either an alkene or a ketone. John Berry and co-workers from the University of Wisconsin have now shown that, in a similar manner, a complex featuring adjacent tungsten–tungsten and tungsten–oxygen multiple bonds undergoes an unanticipated reversible four-electron redox process.

A quadruply bonded ditungsten complex $\{W_2\}^{4+}$ was oxidized first to its $\{W_2\}^{6+}$ counterpart, then to the terminal oxo species $\{W_2O\}^{6+}$, which is stabilized by four tridentate ligands bridging the two tungsten centres. Characterization by a variety of techniques revealed that the $\{W_2O\}^{6+}$ core features a $W \equiv O$ triple bond, and is diamagnetic with two $W(IV)$ centres.

Although the strength of the $W(IV) \equiv O$ bond means that mononuclear $W(IV) \equiv O$ groups are typically inert towards oxygen-atom-transfer reactions, the researchers observed that the dinuclear $\{W_2O\}^{6+}$ moiety reacted with a phosphine. A simple oxygen transfer from the $\{W_2O\}^{6+}$ unit to the phosphine was expected, which would be accompanied by a two-electron reduction to form $\{W_2\}^{6+}$. But rather than a phosphine oxide, a phosphonium cation was formed and the oxygen atom was transferred to the acetonitrile solvent. The process is a four-electron reduction, recovering the initial quadruply bonded $\{W_2\}^{4+}$ complex.

Berry and colleagues suggest a two-step mechanism for the four-electron reduction, in which an electron transfer — the rate-limiting step — first occurs from the phosphine to the terminal oxo complex $\{W_2O\}^{6+}$. The resulting ditungsten oxo complex $\{W_2O\}^{4+}$ and phosphinyl radical then further react to give the $\{W_2\}^{4+}$ species and phosphonium cation, respectively.

blogroll

Less reductionism

A statistical look at the chemistry job market and nailing down the indefinable differences between chemistry and physics.

LabMonkey4Hire is a recent addition to the chemical blogosphere, with an aim to dissect and discuss the chemistry job market in the UK. LabMonkey freely admits to being “heavily inspired” by ChemJobber, who does the same in the USA. As well as weekly surveys of job sites, LabMonkey has offered some interesting posts, including a three-part series looking at ‘What do chemistry graduates do?’ (<http://go.nature.com/S47aTn>). Data from the Higher Education Statistics Agency in 2006–2009 reveals that as many graduates go into further study or training as enter employment (39%). But that hasn’t always been the case: more detail (<http://go.nature.com/zISY11>) reveals that the number entering employment dropped from 45% over the four years, while the proportion taking a higher degree rose from 26% to 30%. Most worrying of all, the levels ‘believed to be unemployed’ went from 6% to 9%, and those working as ‘retail, catering, waiting or bar staff’ shot up to 13%.

Curious Wavefunction, meanwhile, continues to fight on chemistry’s behalf, revisiting ‘The difference between chemistry and physics’ (<http://go.nature.com/sVeUD3>) with inspiration from Roald Hoffmann’s book *The Same and Not the Same*. Wavefunction uses the example of the carbonyl functional group, “a workhorse of chemistry”. Physics would explain its use in nucleophilic addition by a reduction to electrostatics, but chemists consider the angle of the attack, steric effects, reactivity and stereochemistry. So a completely reductionist approach fails, not because there is no connection between chemistry knowledge and the underlying physics, but “because the physics-based explanations tend to be useless at the level of chemistry”.

And finally...Azmanam on the ChemistryBlog showed off his Wolfram Alpha “reagent table widget” (<http://go.nature.com/M1WRfm>) that tells you useful physical properties of your favourite reagents.