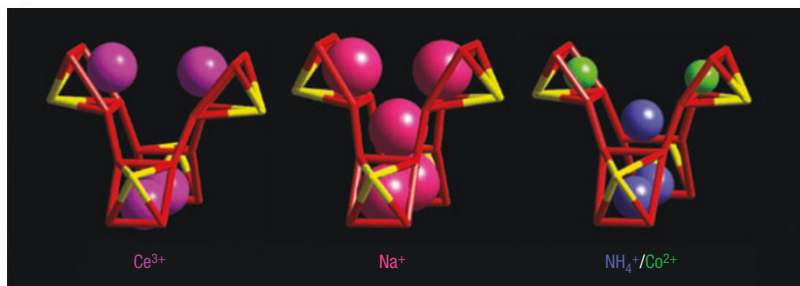


are occupied. Detailed conformational analysis of this structure coupled with quantitative evaluation of ion binding constants have identified a cooperative effect responsible for this unusual behaviour^{3,4}. The binding of Co^{2+} triggers some conformational changes that distort the two adjacent cation binding sites, such that Co^{2+} binding is inhibited at these sites, whereas the opposite site remains unaffected. This phenomenon is known as negative cooperativity. To make a parallel with biological chemistry, cation binding is regulated by the same type of allosteric effect — when a ligand binding to an enzyme produces a conformational change that affects its enzymatic activity — observed in regulatory enzymes composed of multiple subunits.

Given the presence of twenty equivalent cation binding sites in the $[\text{S}_{30}\text{Mo}_{132}\text{O}_{492}]^{72-}$ anion studied by Müller and co-workers, negative cooperativity and allosteric effects similar to those observed in the system of Leyrie and Hervé are likely to play a major role in the binding of cations to this new huge system. The sulphate groups lining the interior perimeter of the cation binding channels are not rigidly fixed to the polymolybdate framework. Instead, they are attached by flexible hinges such that cations bound to the sulphate groups in any one of the channels influence the conformation and hence the cation affinity of the three nearest-neighbour channels that have sulphate groups in common; this effect extends above and beyond any



electronic and electrostatic effects. Unfortunately, these conformational effects have not yet been observed by crystal structure analysis due to crystallographic disorder. But Müller and co-workers have nonetheless established a wide range of architectures based on the different binding modes of several cations that could serve as a platform for future technologies such as artificial cells and nanoscale ion chromatography.

References

1. Müller, A. *et al. Angew. Chem. Int. Edn* **42**, 5039–5044 (2003).
2. Müller, A. *et al. Angew. Chem. Int. Edn* **42**, 2085–2090 (2003).
3. Leyrie, M. & Hervé, G. *Nouv. J. Chim.* **2**, 223–237 (1978).
4. Robert, F., Leyrie, M., Hervé, G., Tézé, A. & Jeannin, Y. *Inorg. Chem.* **19**, 1746–1752 (1980).
5. Wassermann, K. & Pope, M. T. *Inorg. Chem.* **40**, 2763–2768 (2001).

Figure 2 Different binding for different cations. The behaviour of the $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ anion studied in the 1970s by Leyrie and Hervé^{4,5}. Oxygen and arsenic atoms are located at the intersections of line segments coloured red and yellow, respectively. Cations are represented by spheres.

MATERIAL WITNESS

Towards a materials ecology

The appointment of Michael Leavitt as head of the US Environmental Protection Agency will create some uncertainty about the future of the US environment. Favoured by George W. Bush, Leavitt stands accused of being soft on industry — the state of Utah, of which Leavitt was governor, has been brazenly violating the Clean Water Act.

But whether or not Leavitt succeeds in cleaning up American air and water, that is no longer really the key issue for industry's environmental impact. There is increasing recognition that the introduction and enforcement of pollution laws is only one facet of so-called industrial ecology, in which cleaner technologies are part of the broader matter of sustainability.

Valerie Thomas and Tom Graedel have attempted to set out an “intellectual agenda” for the materials-related aspects of sustainable consumption (*Environ. Sci. Technol.*, advance online publication <http://dx.doi.org/10.1021/es034475c>). They try to identify “tractable research questions for which good progress can be expected over a 1–2 decade time frame.”

Thomas and Graedel distinguish between ‘engineered’ systems, meaning in effect how industries operate, and ‘global’ systems, meaning industry's impact on worldwide environmental problems such as global warming, as well as the effects on human health and welfare, economics and resources. Green engineering has generally proceeded on a process-by-process basis, with some significant results: energy consumption in new refrigerators has dropped by two thirds over the past 25 years, for example. But Urmila Diwekar has now proposed a generic integrated framework for greener chemicals processing, which may help to reconcile the conflicting objectives that such designs tend to

pose (*Environ. Sci. Technol.*, advance online publication <http://dx.doi.org/10.1021/es0344617>).

Experience shows that cleaner technologies are not necessarily delivered simply by ample research funding — legislation, in the form of emissions restrictions, for example, can itself stimulate innovation by creating a market for pollution-reducing systems (M. R. Taylor *et al. Environ. Sci. Technol.* **37**, 4527–4534; 2003).

At the global level, Thomas and Graedel say that we need to start analysing ‘materials cycles’ along the same lines as natural biogeochemical cycles of elements such as carbon, nitrogen and phosphorus. Materials cycles would of course be more dependent on human activities. A knowledge of how materials flow between reservoirs such as soil, mines, landfills and human tissues would help identify those flows that are most damaging or profligate, and could make it easier to quantify, say, health impacts or life-cycle analyses. In the same bio-inspired spirit, we can regard the transfer of materials such as metals, plastics and paper between industries as ‘food webs’ that might be engineered for greater efficiency, and we can consider cities as organisms having ‘metabolisms’ with certain materials inputs and outputs.

Thomas suggests that one future aspect of materials recycling and reuse might be “product self-management”, whereby products themselves become responsible for their end-of-life fate through the use of bar codes or radio devices that advertise a product's availability for scavenging, salvage and resale (*Environ. Sci. Technol.*, advance online publication <http://dx.doi.org/10.1021/es0345120>) — creating what we might call smart trash.



Philip Ball