Polyoxoanions are inorganic oxide clusters. Having an excess of oxygen atoms, they typically bear a high negative charge. One of their key characteristics is a strong affinity for metal ions. Certain polyoxoanions can selectively trap divalent cations such as Ca\(^{2+}\) in the presence of monovalent cations such as Na\(^{+}\). These water-soluble anions can be potentially useful in any applications (and there are many) involving cation binding and exchange. A typical example is in the detergents industry, where polyphosphates are used as ‘builders’ to prevent the reaction of soap molecules with Ca\(^{2+}\), and therefore avoid the formation of insoluble scum.

Given the importance of cation binding in chemical processes, considerable effort has been devoted to the study of more complex polyoxoanions where more subtle effects might be achieved. Writing in Angewandte Chemie International Edition, Müller and co-workers\(^1\) show the exquisite structural variety of complexes that can be obtained by varying the size, shape, charge and hydration state of the cations bound to a polyoxoanion structure spanning three nanometres.

The systems studied by Müller and co-workers are hydrated salts of the polysulphatomolybdate anion \([S_{30}Mo_{132}O_{492}]^{72–}\). This anion has a highly symmetric spherical structure forming a porous round cage with channels providing access to the inside of the cage. (shown in Fig. 1\(^2\)). These channels are lined with sulphate groups that serve as metal ion binding sites. Planar organic cations, such as protonated urea, are too large to fit inside these channels, but small inorganic cations can enter and occupy binding sites, their binding mode determined by their size, charge and degree of hydration. As shown at the bottom of Fig. 1, once these cations find their place in the binding site, their presence alters the channel size and shape, and in principle, they offer a mechanism for controlling the flow of traffic entering and leaving the cage.

The potential implications of this effect are best appreciated through comparison with a simpler example — the arsenitotungstate ion \([As_4W_{40}O_{140}]^{28–}\), discovered by Leyrie and Hervé in the 1970s\(^3\). This polyoxoanion has an annular structure, with a central cation binding site surrounded by four equivalent binding sites arranged on its interior surface\(^4\). In this arrangement, a large central cavity similar to a very distorted cube of eight oxygen atoms is formed, whereas each of the four smaller binding sites has square pyramidal geometry defined by four basal oxygen atoms and an apical arsenic atom, as shown in Fig. 2. All four binding sites maintain fairly symmetric configurations in the Na\(^{+}\) salt, where all five cation sites are occupied by Na\(^{+}\) cations, and in the Ce\(^{3+}\) salt, where the four peripheral sites are occupied by Ce\(^{3+}\) cations but the central site is not\(^5\). A far different situation prevails in the presence of small transition metal ions, which form stronger and shorter metal–oxygen bonds. For example, the anion of Leyrie and Hervé will accommodate at most two Co\(^{2+}\) ions and the remaining binding sites will be occupied by ammonium cations. The Co\(^{2+}\) ions will occupy two of the peripheral binding sites at opposite locations (see Fig. 2), avoiding the alternative configuration in which adjacent sites...
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\(^{1,2}\). 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 \([S_{30}Mo_{132}O_{492}]^{72–}\) 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

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/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, landfill 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/es0346129) — creating what we might call smart trash.