

News Item

Open and Shut Case for Anions

PHILIP C. H. MITCHELL

Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 2AD, U.K.

Chemists have long been fascinated by molecular structures with a central cavity which can encapsulate a molecule or ion. Such cavities are found in solids such as zeolites (Figure 1). Molecules such as crown ethers (Figure 2), and analogous natural products like the antibiotic valinomycin, are organic compounds with a particular ability to encapsulate electropositive cations (Na^+ , K^+ and so on) and render them soluble in organic solvents. Until very recently, purely inorganic analogues of the crown ethers had yet to be prepared. But now Achim Müller and colleagues in Germany report [1] a series of water-soluble vanadium oxides with encapsulated ions (chloride, bromide, iodide, carbonate). The compounds are easily made by heating vanadium pentoxide or a vanadate with a water solution of a hydrazinium (N_2H_5^+) salt and an anion. The work follows an earlier report from V.

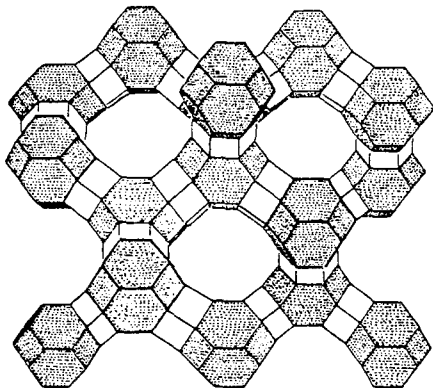


Fig. 1. A typical zeolite structure (faujasite) showing cavities which can accommodate guest molecules. Al and Si atoms are at the apices of the polyhedra and are linked by oxygen atoms (shown as lines) (from Ref. 7).

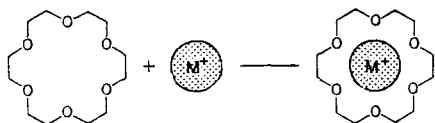


Fig. 2. A crown ether (18-crown-6) encapsulating a metal ion. The O-atoms are linked by $-\text{CH}_2-\text{CH}_2-$ units (from Ref. 8).

W. Day and colleagues [2] of the synthesis of a vanadium oxide inclusion complex, $[(\text{CH}_3\text{CN})\text{V}_{12}\text{O}_{32}]^{4-}$, which is soluble in acetonitrile. The new compounds are especially interesting because the encapsulated species are anions, whereas the guest species in most inclusion compounds are neutral molecules or cations.

In this branch of chemistry, a key idea is the structural match, in size and shape, of host and guest – leading to the property of selectivity. A zeolite with an appropriate channel and cavity size will admit a straight-chain hydrocarbon but exclude a bulkier branched-chain compound. Similarly, a particular crown ether, like the valinomycin antibiotic, may encapsulate and transport K^+ in preference to Na^+ because the cavity best accommodates the K^+ ion. The soluble vanadium oxides have a cavity size and charge which enables them to encapsulate halide and other anions.

Müller and colleagues' soluble vanadium oxides are hollow spheres built from linked VO_5 units (Figure 3). The spheres are hollow because of the propensity of vanadium (V), and more especially vanadium (IV) (formed by hydrazine reduction of vanadate), for fivefold coordination. In these VO_5 species, vanadium (IV) is at the centre of a square pyramid of oxygen atoms. With this structure, one of the six potential coordination sites (with octahedral symmetry) of vanadium is empty and remains so in the soluble oxide. The encapsulated anions are located symmetrically in the sphere's hollow centres.

The structure of the carbonate inclusion compound $(\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)\cdot\text{aq}])$ is especially fascinating (Figure 3). There are two equivalent positions within the hollow sphere which the triangular carbonate may occupy, the three carbonate oxygens interacting with one or other of two sets of three framework vanadium atoms. The vanadium oxide framework relaxes towards the carbonate ion, so that the final minimum-energy structure is a compromise between energy loss attributable to distortion of the oxide and energy gain due to the attraction of vanadium for carbonate. The six interacting vanadium atoms are displaced towards

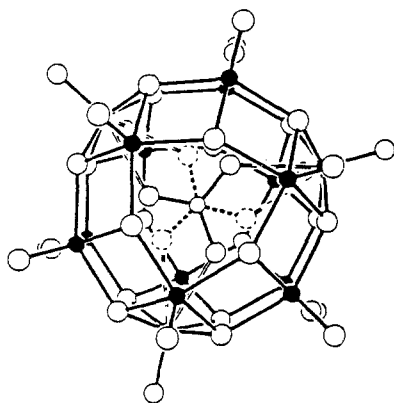


Fig. 3. Structure of Müller and colleagues' soluble vanadium-oxide/carbonate inclusion complex (from Ref. 1). Oxygen and carbon (of the central carbonate) are shown as open circles and vanadium as closed circles. Each sphere encapsulates only one carbonate; the broken lines represent the alternative, equivalent carbonate position. Oxygens of the carbonate are shown linked to framework vanadium atoms.

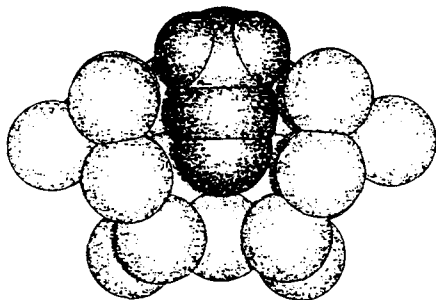


Fig. 4. A basket-shaped soluble vanadium oxide inclusion complex $[(\text{CH}_3\text{CN})\text{V}_{12}\text{O}_{32}]^{4-}$ (from Ref. 2). In this space-filling representation framework oxygens are shown as spheres surrounding the CH_3CN guest molecule. Note how the bulky CH_3 group (top) of the acetonitrile guest, which functions as the template molecule, projects from the basket preventing the completion of a vanadium oxide sphere.

the centre of the sphere – towards the carbonate – by about 19 picometres. The V—O (carbonate) distance is then about 230 pm, rather longer than a V—O single bond (200 pm). The guest–host interaction (which I prefer to describe as ion–dipole rather than covalent) thus causes the host to adjust to the guest. The structure is significant in the light of current computational studies of zeolites [3] (including our own work [4]) which indicate that a zeolite framework, for example ZSM-5, should relax to accommodate a guest molecule, such as methanol [3]. Müller and co-workers' new compounds, well characterized molecular analogues of zeolites, will probably provide a field day for solid-state computational chemists.

Without the captured anions, the spherical structures of the new oxide complexes would presumably not develop, so that evidently we have here examples of 'template' reactions: the guest species provides a template for the structure of the host. Such reactions are well known in coordination chemistry, in which a metal ion serves as a template for the organic synthesis: an example is copper phthalocyanine [5]. Analogously, in solid-state oxide chemistry, a template reaction is used to synthesize zeolitic aluminium phosphates [6]. Alumina, phosphoric acid and an amine (the template) are heated in water under pressure. The aluminium phosphate is built around the organic amine, the cavity size being determined by the size of the amine. To remove the organic amine and generate an empty cavity the aluminium phosphate amine must be heated to 600°C . What we do not yet know is whether it is possible to remove the captured anions from Müller and colleagues' oxides, creating an empty cavity while retaining the molecular structure.

Zeolites have important applications as molecular sieves and heterogeneous catalysts. Confined within the cavity, a molecule may encounter other molecules or be activated by interaction with the walls (a C—H bond of methanol, for example is stretched in ZSM-5 [3]). The cavity provides a reaction space rather as the active site of an enzyme does. Could the soluble vanadium oxides have analogous applications in homogenous solution chemistry? Vanadium oxides are known to be selective oxidation catalysts, and the new soluble vanadium oxides, like zeolites, provide a reaction space. With vanadium one also has the possibility of redox

chemistry involving the vanadium framework. What is crucial is that the reactant molecules or products should be able to pass in and out of the cavity: perhaps a porter is needed as well as a host.

From this point of view, Day's soluble vanadium oxide inclusion complexes [2] are especially attractive. The vanadium oxide structure builds around the acetonitrile template but is prevented from closing by the bulky methyl group. The vanadium oxide then forms a hemisphere or basket (Figure 4) in and out of which one can easily imagine molecules passing.

References

1. A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer, and J. Döring: *Angew. Chem. Int. Edn. Eng.* **29**, 926 (1990).
2. V. W. Day, W. G. Klemperer, and O. M. Yaghi: *J. Am. Chem. Soc.* **111**, 5959 (1989).
3. R. Vetrivel, C. R. A. Catlow, and E. A. Colbourn: *J. Phys. Chem.* **93**, 4594 (1989).
4. N. G. B. Drew, N. J. Jutson, P. C. H. Mitchell, and S. A. Wass: *Polyhedron* **8**, 1817 (1989).
5. C. A. Cotton, and G. Wilkinson: *Advanced Inorganic Chemistry* 5th edn, 344; 353 (Wiley, New York, 1988).
6. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen: *J. Am. Chem. Soc.* **104**, 1146 (1982).
7. A. F. Wells: *Structural Inorganic Chemistry* 4th edn, 830 (Oxford, 1975).
8. M. Hiraoka: *Crown Compounds*, 68 (Elsevier, Amsterdam, 1982).