

# Toward the Rational Design of Open-Framework Materials

Anthony K. Cheetham and C.N.R. Rao

**A**s we were preparing this article by Anthony K. Cheetham and C.N.R. Rao for publication, reports of the tsunami resulting from the 9.0 earthquake in the Indian Ocean last December grabbed our hearts. Immediately we thought of our many friends and colleagues around the world.

We were glad to hear that those we knew and their families were safe, but our view is small and the stories are many. Among those who escaped to safety was C.N.R. Rao, who had been vacationing with his family in Sri Lanka. They were riding a boat on a river close to Galle in southwest Sri Lanka when the tsunami struck. They managed to find their way to shore and caught a bus out of town, leaving behind their damaged hotel and tragic memories.

This news reaching the Materials Research Society headquarters reminded us in a very personal way that the scientific community is not only a group of scientists doing their jobs, but also a world community of people. This article by Cheetham and Rao is itself a testimony of that view. It is our first publication of an article based on the IUMRS Sōmiya Award, an international award recognizing materials research collaboration across at least two continents. In Cheetham and Rao's article and the accompanying sidebar, we see both the independence of science from borders as well as the bonds that form out of the unique backdrops of our lives.

Perhaps materials science itself will find defenses to such natural disasters as tsunamis—through resilient low-cost building materials, sensing and warning systems, materials to assist in water purification, and understanding the behavior of the earth itself. At this poignant time, we send our concern and good wishes to all of the people affected by this tsunami, and we look for ways that science and scientists can improve circumstances around the world through our inter-continental reach.

—Eds.

## Abstract

In spite of the enormous level of interest in open-framework materials (materials with porous channel structures, such as zeolites), the mechanisms by which they are formed are in many cases poorly understood. As a consequence, our ability to design reaction conditions that might lead to the formation of particular crystal architectures is quite limited. This article discusses the state of the art in this area, with particular emphasis on our joint work that was recently recognized by the 2004 Sōmiya Award from the International Union of Materials Research Societies (IUMRS) and presented at the 2004 Materials Research Society Spring Meeting/IUMRS 9th International Conference on Electronic Materials.

**Keywords:** adsorption, catalytic materials, hydrothermal conditions, open-framework materials, structure, zeolites.

## Introduction

There has been an explosion of interest in open-framework materials during the last 15 years, driven largely by the potential of these porous-structure materials for applications in catalysis, separations, and other areas. Work in the 1990s focused heavily in the area of phosphates and showed that open-framework materials were not restricted to aluminosilicates, zeolites, and aluminum phosphates but could be synthesized with virtually any metal phosphate.<sup>1</sup> It was also shown that open-framework materials could be made with other chemistries such as binary oxides, halides, sulfides, and sulfates. Since the mid-1990s, there has also been considerable emphasis on hybrid inorganic-organic materials, especially in the context of metal carboxylate frameworks.<sup>2</sup> For example, coordination polymer systems based upon well-defined metal cluster units connected by rigid, bifunctional organic linkers have been particularly well studied and are certainly amenable to rational design.<sup>3</sup> Progress in the use of phosphates and some of these other chemistries, however, has relied more on serendipity and intuition rather than de-

sign. This short overview examines the status of this area, emphasizing the progress that has been made toward the directed synthesis of open-framework materials. It focuses in particular on our joint work, which was recently recognized by the 2004 Sōmiya Award from the International Union of Materials Research Societies. (See the sidebar that accompanies this article for more on this research collaboration.)

## Metal Phosphates

The open-framework aluminum phosphates were discovered by Flanigen and co-workers in 1982,<sup>4</sup> and a huge range of aluminum-based materials is now known. As with zeolite synthesis, extensive use is made of organic templates or structure-directing agents around which the inorganic framework is constructed, and the materials are normally sufficiently stable for the templates to be removed without collapsing the structure. In many but not all cases, there is a clear relationship between the framework architecture and the shape and size of the template molecule,<sup>5</sup> and this has led to the possibility of using computer

modeling to predict the ideal template molecule for the synthesis of a particular target framework.<sup>6</sup>

Open-framework phosphates of many other metals have now been synthesized, often using organic templates, but many of these frameworks cannot be rendered nanoporous by calcination due to their relatively poor kinetic stability. There are some important exceptions, however, including the nickel phosphates<sup>7</sup> and tin (II) phosphates,<sup>8</sup> both of which can exhibit reversible adsorption and desorption behavior.<sup>9,10</sup>

The tin systems are particularly interesting because they represent the first family of basic rather than acidic open-framework materials. Figure 1 shows an example of a

chiral three-dimensional (3D) framework in which the lone pairs on the Sn(II) ions are pointing into the channels.<sup>11</sup> Furthermore, a thorough study of tin phosphates showed for the first time in such systems that there exists a whole family of materials with different dimensionalities, each made from simple organic templates but with structures ranging from simple mononuclear  $\text{Sn}(\text{PO}_4)(\text{HPO}_4)^{3-}$  units,<sup>12</sup> through chains,<sup>13</sup> sheets,<sup>14</sup> and 3D<sup>11</sup> open-framework materials. This confirms that open-framework inorganic phosphates can exist in the full range of dimensionalities that are found in naturally occurring metal silicates. At the time of the work in the late 1990s, however, it was by no means clear

what factors might be used during synthesis to control the dimensionality of such a material.

Another finding that emerged from our work was the discovery that the organic template and the phosphate could be delivered in different ways during synthesis. For example, the use of amine phosphates leads to a rich variety of products;<sup>15</sup> organophosphate esters<sup>16,17</sup> and organophosphorus amides<sup>18</sup> were also explored with a number of metals.

### Oxalates, Carboxylates, and Other Hybrid Materials

The use of dicarboxylate linkers has featured prominently in the fashionable field

## A Hybrid of Cultures Channels into Collaborative Research in Materials Chemistry

The University of California at Santa Barbara (UCSB) occupies 989 acres of the California coast about 100 miles northwest of Los Angeles. The campus includes its own lagoon. With an enrollment of 19,799 students in the 2004–2005 academic year (94% of them in-state students, 5% from other states in the U.S., and 1% from outside the country) a prestigious faculty, and a library holding 2.6 million volumes, UCSB is not only one of the country's top academic universities, it has also been named "America's Hottest College for Surf and Ski."<sup>\*</sup> This is the campus where **Anthony K. Cheetham** directed the Materials Research Laboratory (MRL) from 1992 to 2004 and now heads the new International Center for Materials Research (ICMR).

**C.N.R. Rao** envisioned and founded the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), established in 1989 by India's Department of Science and Technology. The year commemorates the 100th anniversary of the birth of Jawaharlal Nehru, India's first prime

minister. The center's main campus resides on a 22-acre plot donated by the state government of Karnataka. The location is in the rural area of Jakkur on the Bangalore–Hyderabad highway, about 11 km from the Indian Institute of Science (IISc) in Bangalore. While India is considered to be a developing nation, Bangalore stands out as India's "Silicon Valley." Before the city's industrial and information technology booms, it was also known as "The Garden City," for its many local parks blooming with pink cassias, golden acacias, and jacarandas. On the drive to JNCASR, visitors pass by farms and herds of goats along the road and then enter the lush campus with its state-of-the-art research facilities.

From the midst of these two cultures a world apart, Rao and Cheetham discovered a common interest in the synthesis and characterization of novel materials. Their collaboration, spanning almost 30 years, has led to seminal publications in emerging areas of materials chemistry such as magnetic, nanoscale, and open-framework materials. In the past 10 years alone, they have published 40 joint papers.

Outside of their laboratories, Rao and Cheetham have provided a conduit for

other scientists to forge their own intercontinental collaborations. They jointly organized two workshops on advanced materials for developing countries (2001 in Trieste, Italy, and 2002 in Santiago, Chile), in concert with the Third World Academy of Sciences (TWAS) and the International Center for Theoretical Physics (ICTP). They are planning a third workshop, to be held in South Africa in the summer of 2005. Rao is the president of TWAS and Cheetham is an associate fellow.

Closer to home, Cheetham and Rao gathered 15 materials faculty members from UCSB for a workshop in Bangalore in 1998, and they brought about 30 materials scientists from the United States to India in the fall of 2004 through funding from the U.S. National Science Foundation.

The next step, Cheetham says, is to obtain funds for a graduate student exchange program. In large countries such as the United States and India, he notes, materials researchers rarely travel beyond their own national borders. Looking back at the demographics of students attending UCSB, for example, 94% of them have not even left their home state!

Cheetham is well versed on the benefits of collaborative research across diverse cultures, given his academic appointments at Christ Church in Oxford and the Royal Institution in London, his position as a distinguished fellow in JNCASR, and his activity as a member of the advisory board at HTE GmbH, Max-Planck-Institut für Festkörperforschung in Stuttgart, and the Center for Advanced Interdisciplinary Research in Materials Science at the Universidad de Chile in Santiago. As director of the MRL and now the ICMR at UCSB, he has led his students and postdoctoral

<sup>\*</sup>Newsweek/Kaplan "America's Hottest Colleges" Guide for 2005.

of hybrid inorganic–organic materials. Rigid linkers, such as 1,4-benzene dicarboxylate (terephthalate), have been used to design an extensive variety of coordination polymers, as mentioned earlier,<sup>3</sup> while flexible linkers, such as succinate and glutarate, have led to the creation of a wide range of less predictable structures. Oxalic acid represents the simplest case of a dicarboxylic acid, and a number of open-framework oxalates with organic template molecules have been reported in recent years.<sup>2</sup> Sn(II) again provided an excellent starting point for our joint work on oxalates, leading to the formation of a number of materials with unusual structures and various dimensionalities;<sup>19,20</sup> reactions with zinc also proved fruitful.<sup>21</sup>

In a variation on the oxalate theme, we also used squarate, which yielded a remarkable cobalt compound with a sodalite-like structure,<sup>22</sup> as well as a family of amine-templated squarates.<sup>23</sup>

Work on hybrids involving flexible carboxylates has been pursued in both of our laboratories. Unlike the coordination polymers, many of these materials can have extended metal–oxygen–metal (M–O–M) arrays that can give rise to better thermal stability as well as interesting electronic and magnetic properties. As with other open-framework materials, 1-, 2- and 3D systems are possible (both with respect to overall connectivity, as well as to M–O–M connectivity), and these have been realized with

a variety of metals and organic acids. Nickel succinate, which forms a remarkable 3D Ni–O–Ni open-framework structure (Figure 2),<sup>24</sup> belongs to a large, emerging class of similar materials that includes cadmium malonate.<sup>25</sup> In addition to the metal dicarboxylates, a large number of closely related hybrid materials have been reported, including both diphosphonates and carboxyphosphonates. Our joint work on the carboxyethylphosphonates of Pb(II) provides a typical example.<sup>26</sup>

### Building Open Frameworks with New Primary Building Units

Most of the inorganic open-framework materials have silicate, phosphate, and

associates into new territories, not only scientifically, but geographically.

“Working in another country is different,” he says. “Just the day-by-day, how people function, how they think, is different from what we’re accustomed to. Researchers get charged up, which leads to new ideas.” This is why he values international collaborations for his home institution: It’s a mechanism for developing good science.

The United States began the postdoctorate program, and other countries learned the value of it, Cheetham says. Now that technology has made international collaborations easier, Cheetham wants to implement this practice of cross-cultural collaboration earlier in the career of a scientist, starting at the graduate school level. Even though technology such as the Internet has enabled communication among collaborators across borders, Cheetham and Rao agree that building personal relationships make collaborations prosper.

Both scientists agree that their collaboration has revolutionized their individual research missions. They visit each other’s institutions annually to sustain their partnership. Rao is distinguished visiting professor in the MRL at UCSB. He holds 33 honorary doctorates from various universities around the world, and he is president of the Asia–Pacific Academy of Materials and a member of the International Science Advisory Board of UNESCO, the International Council for Chemistry of IUPAC/UNESCO, and the Executive Board of the Science Institutes Group at Princeton University. As director of IISc from 1984 to 1994 (covering the time JNCASR was being built until it became operational in 1994), and as founder-

president and now Linus Pauling Research Professor and honorary president of JNCASR, Rao continues to be in a position to influence and fund international collaborations among his researchers. He is now the chair of the Advisory Board of the ICMR, which places a special emphasis on research in Third World countries. With a history of establishing research

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centers in Bangalore, where he sponsored visiting fellows, Rao broadened his scope to encompass postdoctoral associates and PhD degree candidates, all for the purpose of strengthening the research studies.

Rao and Cheetham met in 1973 at Oxford, where Cheetham had just been appointed to the faculty and worked in the Chemical Crystallography Laboratory. Rao arrived as the Commonwealth Visiting Professor. They published their first joint paper in 1976 on the crystal structure of niobium dioxide. Over the next decade, they met at various Gordon Conferences and other scientific gatherings. In December 1985, they again met, this time in India. The Indian National Science Academy sponsored the Golden Jubilee, for which Rao chaired the solid-state

chemistry program; he invited many scientists, including Cheetham. When Cheetham became director of the MRL at UCSB in 1992, he wanted distinguished visitors to serve as ambassadors to the center; in 1995, he invited Rao. In the decade since, their collaboration has gathered considerable momentum. As director of the ICMR, Cheetham continues to obtain government grants to fund research and cover the visits of Rao and his students. Likewise, Rao has international visits built into the budget of his laboratory.

Last year, the International Union of Materials Research Societies (IUMRS) honored the joint work of Rao and Cheetham with the 2004 Somya Award. The award recognizes the achievement of a team of researchers that has collaborated across two or more continents during the past decade whose work is not only of the highest quality and well recognized by the international materials community, but that has also had a demonstrated major impact on technology or society. Cheetham and Rao received the award during a ceremony in San Francisco at the 2004 Materials Research Society Spring Meeting/IUMRS 9th International Conference on Electronic Materials.

The IUMRS Awards Committee said that the collaboration between Rao and Cheetham has had far-reaching consequences in the synthesis and characterization of a variety of novel materials and has scaled new heights in terms of the ability to design solids of predetermined structure with predicted properties. It also marks an extraordinary accomplishment in international collaboration in materials research with few parallels, a scientific partnership that has transcended cultural and national boundaries.



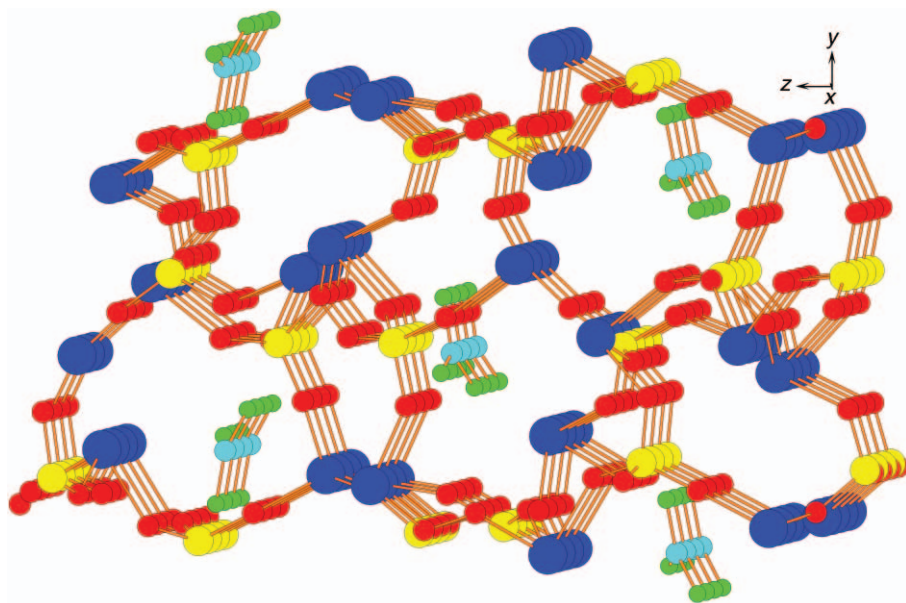


Figure 1. Schematic illustration of the structure of a chiral, three-dimensional Sn(II) phosphate open-framework structure, templated with guanidinium cations. Tin atoms are shown in dark blue, oxygen in red, phosphorus in yellow, nitrogen in green, and carbon in light blue. The lone pairs of the tin atoms protrude into the cavity, reducing the space available for sorbate molecules.

carboxylate anions as the primary building blocks. It is now becoming recognized, however, that open-framework materials can indeed be built that make use of other anions as the primary building units. Thus, 1-, 2- and 3D structures of amine-

templated open-framework materials with sulfate,<sup>27</sup> selenite,<sup>28</sup> and selenate<sup>29</sup> ions have been reported recently. In Figures 3 and 4, we show the 3D structures of an open-framework rare-earth sulfate<sup>27</sup> and a selenate,<sup>29</sup> respectively. In synthesizing these

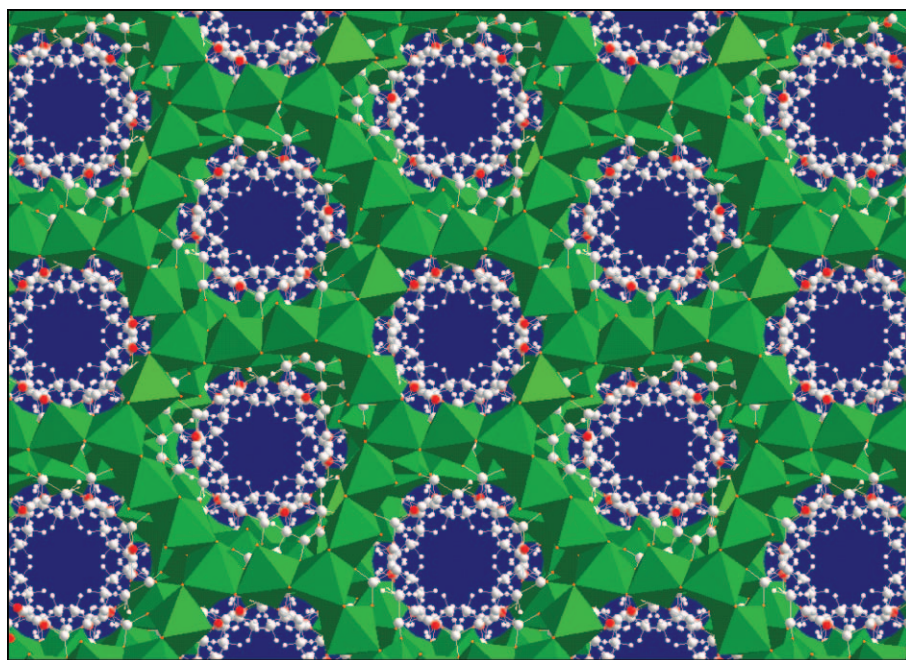


Figure 2. The three-dimensional Ni–O–Ni network of nickel succinate, showing cavities lined with the hydrophobic methylene groups of the succinate ions.

structures, some interesting chemistry is also revealed. For example, sulfates are stable under both basic and acidic conditions, but selenates cannot be prepared in basic media due to the unfavorable oxidation potential of Se(VI). We had to employ acidic conditions to prepare the compound in Figure 4. It is likely that novel open architectures employing combinations of different anions and metal ions will be synthesized in the future.

### Building-Up Process

One of the important aspects of inorganic-framework materials pertains to their mode of formation. An idea that is gaining credence is that secondary building units (SBUs) formed by the primary units (metal–oxygen polyhedra and anions) assemble in some way to give rise to the complex architectures.

Typical of the SBUs is the four-membered ring formed by two metal–oxygen polyhedra and two anionic tetrahedra, which is found in the full range of dimensionalities (Figure 5). There is also reason to believe that structures with progressive increases in dimensionality are formed under hydrothermal conditions.<sup>30</sup> Accordingly, 1D chain and ladder structures of metal phosphates are found to transform under relatively mild conditions to 2D and 3D structures. Two-dimensional layered structures similarly transform to 3D structures. Interestingly, acid degradation of 3D structures gives rise to lower-dimension structures.<sup>31</sup>

A particularly noteworthy finding is that 0D zinc phosphates, which are molecular systems, transform to chain-like and sodalite-related structures under mild conditions (Figure 6).<sup>32</sup> The 0D metal phosphates, comprising four-membered rings, are the SBUs in several metal phosphate families. That such transformations are not limited to open-framework metal phosphates alone is shown by our finding that metal squarates transform to the sodalite structure on heating.<sup>22</sup> The commonality between the squarates and the zinc phosphates is the four-membered ring motif.

We are gradually beginning to understand the factors that control the dimensionality of such structures. In a recent study on cobalt succinates,<sup>33</sup> we were able to obtain five different phases from a single reaction mixture of Co(OH)<sub>2</sub> and succinic acid heated under hydrothermal conditions at five different temperatures (60°C, 100°C, 150°C, 180°C, and 250°C). The resulting phases reveal an increase in dimensionality and framework density with increasing temperature, suggesting that the reactions proceed under thermodynamic control with the progressive elimination of water as the temperature is raised. We are currently



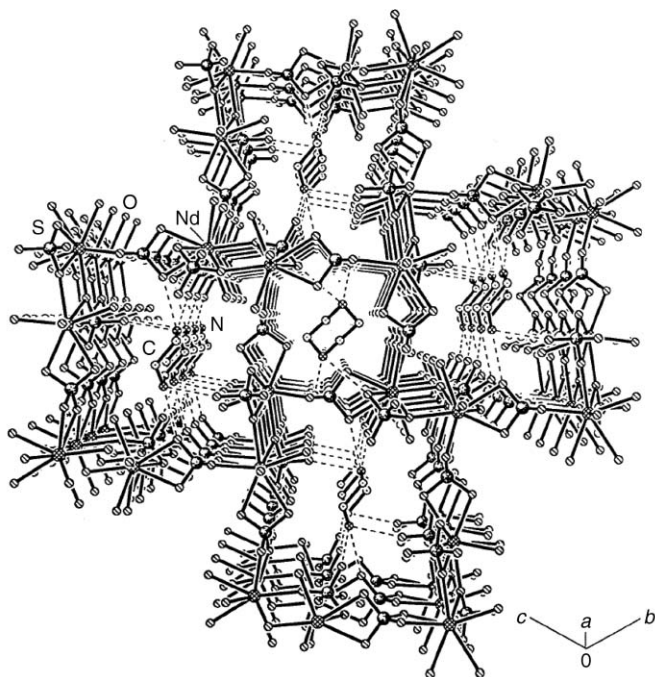


Figure 3. The three-dimensional framework structure of a rare-earth sulfate,  $[C_4N_2H_{12}][Nd_2(SO_4)_4(H_2O)_2]$ . Protonated piperazine molecules reside in the 8- and 12-membered channels running along the *a* axis.

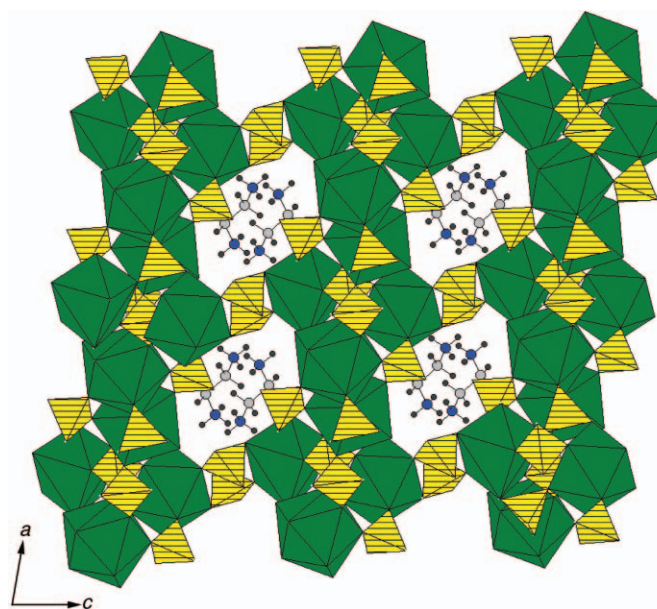


Figure 4. Polyhedral view of the framework structures of a three-dimensional lanthanum selenate,  $[C_2N_2H_{10}][La_2(SeO_4)_4(H_2O)_3] \cdot H_2O$ , with 12-membered channels along the *b* axis.

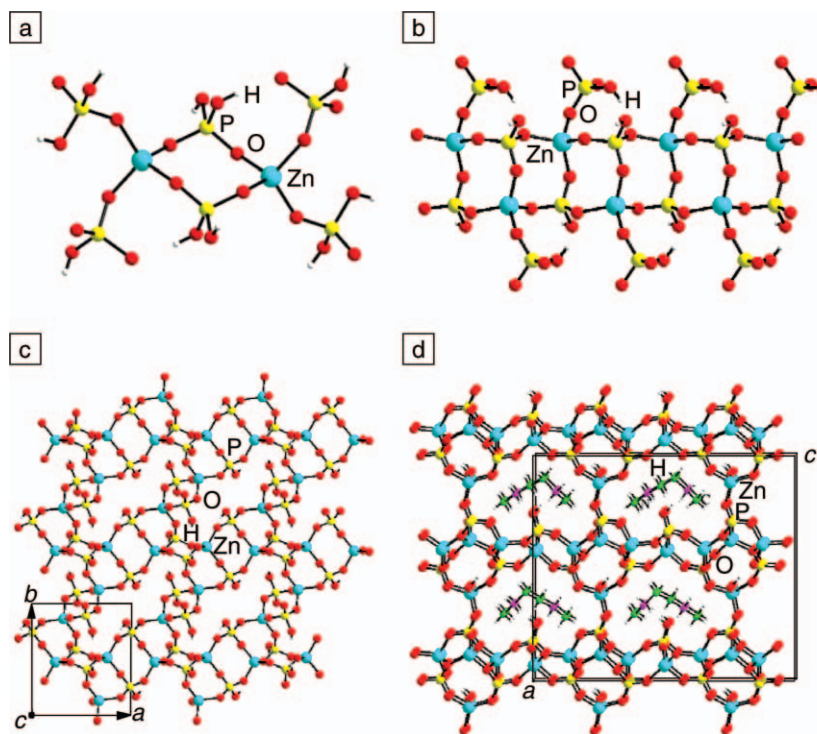


Figure 5. The four-membered ring, containing two metal polyhedra sharing vertices with two phosphate tetrahedra, is a common secondary building unit in metal phosphates. Here, it is shown in a family of zinc phosphates: (a) zero-dimensional, (b) one-dimensional ladder, (c) two-dimensional sheet, and (d) three-dimensional network.

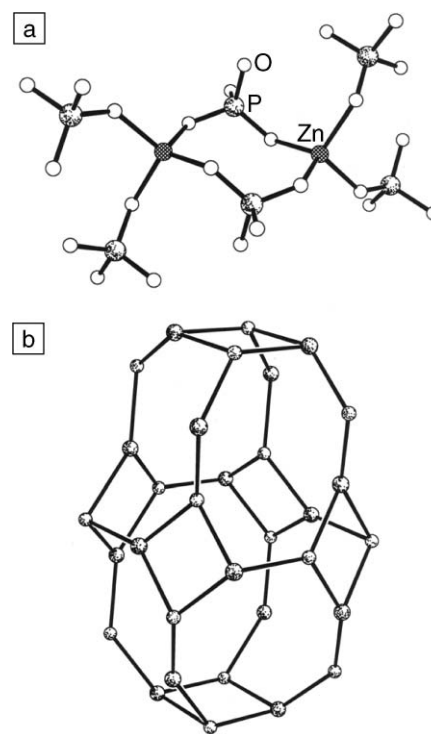


Figure 6. (a) The four-membered ring zinc phosphate,  $[N(CH_3)_4][Zn(H_2PO_4)_3]$ , and (b) the expanded sodalite structure with  $4^68^8$  cage formed on heating the four-membered ring under mild conditions.<sup>32</sup>

exploring this system in even greater detail using high-throughput experimentation methods in Munich.<sup>34</sup> It would appear that the formation of many other framework materials also occurs through a building-up process accompanying an increase in dimensionality. Thus, a hierarchy of metal oxalates of different dimensionalities has been isolated.<sup>35</sup> It would be of interest to explore whether simple metal oxalate complexes, which are coordination compounds, could give rise to chain, layer, and 3D structures on heating.

In terms of predicting the possible structures that can be formed from well-known SBUs, there has been considerable progress, particularly by the Versailles group, using simulated annealing methods.<sup>36</sup> For example, this approach has been used to predict hypothetical 3D frameworks of silicates and aluminum and gallium phosphates based upon the automated assembly of double-four rings.<sup>37</sup> This approach is now being extended to hybrid coordination polymers.

## Concluding Remarks

The area of open-framework materials will undoubtedly prosper in the next few years with the emergence of new architectures and design principles making use of a variety of primary and secondary building units. Another important direction in this area is likely to be the generation of new materials by making use of transformations from molecular systems.<sup>38</sup> In the context of inorganic-organic hybrid materials, compounds with unusual combinations of properties conferred by the inorganic and organic components may come to the fore. Alkali halide-incorporated metal oxalates are good examples of such materials.<sup>39</sup> Finally, since hybrid materials are by no means limited to systems based upon M-O bonds, hybrid porous solids based upon other chemistries, such as organo-sulfur and organo-nitrogen ligands,<sup>40</sup> are interesting areas that are likely to flourish.

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**Anthony K. Cheetham**, FRS, is professor of materials and chemistry and director of the new International Center for Materials Research ([www.icmr.ucsb.edu](http://www.icmr.ucsb.edu)) at the University of California, Santa Barbara.

Cheetham can be reached by e-mail at [cheetham@mrl.ucsb.edu](mailto:cheetham@mrl.ucsb.edu).



**C.N.R. Rao**, FRS, is the Linus Pauling Professor and honorary president of the Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore, India.

Rao can be reached by e-mail at [cnrrao@jncasr.ac.in](mailto:cnrrao@jncasr.ac.in).

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