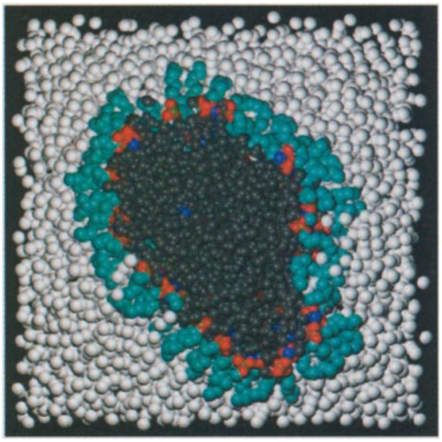

**Beyond the sphere.** Computer simulation of a reverse micelle ($w_0 = 10$) formed from a novel double-chained phosphate surfactant in $CO_2$. The system includes 1616 water molecules, 160 surfactant molecules, 160 counterions, and 6991 $CO_2$ molecules in a cubic box. Unlike the micelle in the first figure, this micelle is not restricted to a spherical shape. However, as in the other model, a large fraction (~90%) of the counterions are in contact with the interface. A big challenge of this simulation is to determine how many surfactant molecules are necessary for a given $w_0$ ratio.

For example, Salaniwal *et al.* (*13, 14*) have followed the molecular motions leading to the formation of reverse micelles from ternary mixtures of water, nonpolar molecules or $CO_2$, and surfactant.

In contrast, Faeder and Ladanyi (*11, 12*) use a model for an isolated reverse micelle and focus on the structure and dynamics of the micellar interior. The nonpolar phase is treated as a dielectric continuum, and surfactant head groups are confined to a spherical interface (see the first figure). The authors found reasonable agreement with IR spectroscopy measurements of solvation dynamics in reverse micelles.

Senapati *et al.* (*15*) have developed a third model that explicitly includes molecular components of the solution while focusing on the molecular properties of the reverse micellar interior. Molecular interactions drive the formation of the reverse micelles, leading to a range of shapes (see the second figure). A major advantage of molecular simulations over experiments is the ability to visualize the system and explore it layer by layer.

The advent of new experimental tools and faster computers promises to divulge more details about water in nanoscopic volumes. Starting with these simplified reverse micellar systems, we can begin to understand how differently water behaves when it is confined in biological cavities and how these pools affect biological function. As our understanding advances, we should be able to capitalize on the unusual properties of water in these confined spaces for applications such as the controlled formation of nanoparticles or the "fixing" of broken proteins.

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PERSPECTIVES: SOLID STATE CHEMISTRY

# Porous Materials with a Difference

**Mark M. Turnbull and Christopher P. Landee**

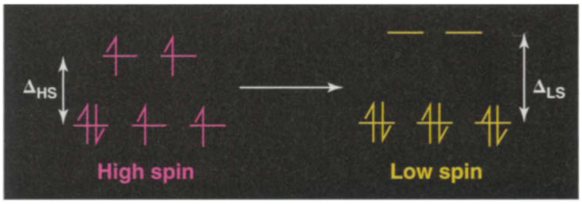
The design and preparation of porous molecular solids has been pursued for decades, inspired by the success of natural and synthetic zeolites in catalysis (*1*). Modern porous materials include metal oxides and salts (*2*), metal-organic coordination polymers (*3, 4*), and organic networks (*5*). They have been used in separation (*6*), ion-exchange (*7*), and sensor applications (*8*). The introduction of compounds with specific magnetic, optical, or electrical properties into such microporous solids should yield materials with unique responses to the adsorption of small molecules, interaction with radiation, or temperature changes.

On page 1762 of this issue, Halder *et al.* (*9*) report the synthesis and properties of a microporous material with such unusual properties. The symmetry, pore size, and thermal behavior of the material depend on the presence of small molecules (low molecular weight alcohols) in the lattice. Such complexes are referred to as host-guest complexes, where the lattice provides the "host" and the small, sorbed molecules are the "guests."

The most striking feature of the material is the change in the magnetic and optical properties that occurs when the guest molecules are gained or lost. In a process known as "spin crossover," some of the iron(II) atoms change their electronic configuration. This phenomenon can occur in octahedral metal complexes (with six ligands bound to the central metal ion) in which the metal ions contain four to seven electrons in their *d*-orbitals. The *d*-electron orbitals in a transition metal ion complex are split into different energy levels depending on the geometry of the complex. In the octahedral geometry, the splitting of the orbitals gives a pattern of two higher energy and three lower energy levels (see the figure).

These orbitals are usually occupied by the highest energy electrons in the compound, with a maximum of two electrons per orbital. Depending on the relative size of the orbital splitting energy (Δ) and the electron pairing energy (*P*, the energy introduced by the repulsion of two electrons in the same orbital), the compound can exist in the high-spin state ($\Delta < P$) or the low-spin state ($\Delta > P$). The most important difference between the two states is the number of unpaired electrons.

When Δ and *P* are of similar energy, the



**Spin crossover in an iron(II) complex.** Horizontal lines represent electron energy levels (orbitals); up and down arrows denote the electrons in these orbitals. Δ is the energy difference between the high- and low-energy orbitals. The ratio of Δ to the pairing energy, *P*, determines whether the complex is high spin or low spin.

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compound may undergo a spin crossover from one state to the other. The energy match between $\Delta$ and $P$ can be achieved through a careful choice of ligands. The crossover may then be induced by several factors, such as temperature, pressure, or exposure to light. It is accompanied by a change in the optical and magnetic properties of the material (*10*). In the case of iron(II), the high-spin state is generally strongly colored and paramagnetic, whereas the low-spin state is generally pale yellow to colorless and diamagnetic. Several metal ions will undergo spin crossover behavior, but most known examples contain iron(II).

The fine control between $\Delta$ and $P$ required for spin crossover is exhibited in the new complex of Halder *et al.* (*9*) in an unusual way. When the guest alcohol molecules are present in the lattice, roughly half of the iron atoms in the lattice undergo a spin crossover at low temperature. But when the guest molecules are removed, no spin crossover is observed, even though the guest alcohol molecules are not bound to any of the iron(II) atoms. One explanation is that hydrogen bonds between the alcohol guests and other ligands on the iron atoms are responsible for the change. A second possibility is the change induced in the lattice by the presence or loss of the guests.

It is not unusual for a host lattice to collapse upon loss of guest molecules. This collapse often leads to the irreversible destruction of the host lattice (*11*). In some systems, the cavities and pores are durable and do not change substantially in the absence of guest molecules (*12*). In unusual cases, the cavity may collapse to give an amorphous material and then regain crystallinity upon reintroduction of the guest (*13*), or crystallinity may be retained upon guest loss, but with a significant decrease in the cell volume (*14*).

The material of Halder *et al.* (*9*) is unusual in that the loss of guest molecules causes a substantial rearrangement of the lattice, with the crystals expanding in volume by 6%, even though the volume of the pores relative to the total volume of the crystal drops from 12% to 2%. Yet the sample remains crystalline throughout the transition. Crystallinity is retained even when the guest molecules are reabsorbed and the original structure regenerated. The material is composed of two interpenetrating lattices, and it may be the ability of these two lattices to slip past each other that provides the flexibility needed to allow such drastic changes without shattering the crystals.

Recent work has shown that the field of crystal engineering is entering a new age. Exciting results such as those of Halder *et al.* (*9*) demonstrate the versatility of solid-state structures and the ability of metal-organic structures to incorporate functionality that will allow for exciting magnetic, electrical, and optical properties. These advances will expand the uses of porous materials far beyond the well-developed catalytic systems.

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**PERSPECTIVES: OCEANOGRAPHY**

# Oceanic Salt Switch

**Ed Boyle**

On page 1769 of this issue, Adkins *et al.* (*1*) report data constraining the salinity (and density) of ocean deep waters during the last glacial period. In contrast to today's ocean, they find that at the last glacial maximum, the saltiest waters formed in the Southern Ocean. Global ocean circulation must thus differ substantially between glacial and warm (interglacial) periods.

Knowledge of the salinity is important for understanding glacial circulation because the deep sea is filled with the densest waters formed at high latitudes. Whether the deep circulation is properly described as a density-driven "thermohaline circulation" or whether it should really be understood as a wind- and tide-driven "meridional overturning circulation" has been the subject of a recent Perspective (*2*). It is clear, however, that density gradients in the deep sea are a key characteristic of ocean circulation patterns and that the deep sea today is filled by the densest waters whose density was established at high latitudes (*3*).

In the modern ocean, the densest deep waters are found in the Mediterranean Sea. This water is not very cold, but it is very salty. Mixing near the Gibraltar Sill greatly reduces the density of this water as it enters the open Atlantic, and it therefore does not sink to great depths.

The densest waters filling the open ocean form in the Antarctic (Antarctic Bottom Water, AABW). These waters are extremely cold but less salty than the ocean average (see the table). The second densest water in the ocean is formed at several sites in the high-latitude North Atlantic and its adjacent seas (North Atlantic Deep Water, NADW). These waters are not as cold as the AABW but are more salty (due to an excess of evaporation over precipitation in the Atlantic Basin and its adjacent seas).

The NADW is only slightly less dense than the AABW despite a substantially warmer temperature. Both appear to form at approximately equal rates when integrated over the whole ocean overturning time (~1000 years) (*4*). In the Pacific Ocean, no deep water forms in the northern high latitudes, and deep waters are thus a mixture of Atlantic and Antarctic waters, slightly freshened by mixing with low-salinity water from intermediate depths.

It has been clear for some time that the deep ocean was much colder at the last glacial maximum (LGM) than it is today (*5–8*). In contrast to today's deep sea, the temperature gradients in the deep sea appear to have been subtle at the LGM. It has also been evident that in the glacial North Atlantic, nutrient-depleted northern source waters were found at shallower depths than today, and the deepest north Atlantic basin they fill today was instead occupied by nutrient-rich water from the Southern Ocean (*9*, *10*).

Adkins *et al.* now demonstrate that the saltiest water in the glacial deep ocean was found in the Southern Ocean, a dramatic change from modern conditions, where the saltiest deep-ocean water derives from the North Atlantic. This conclusion derives from data on the chlorinity (total concentration of silver-titratable halides) of pore waters in marine sediments sampled by the Ocean Drilling Program (ODP).

During the last glacial period, massive continental glaciers covered northern North America and Fennoscandia. The Antarctic ice sheet was also thicker than it is today. These glaciers and ice sheets stored so much water that the sea level was

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