

catalysts may not be acting homogeneously. Instead they are actually being oxidized, decomposing to form a layer of catalytically active iridium oxide, which, as they previously reported for compound **1** (Fig. 1b), can actually be seen as it appears on the electrode surface¹⁰. Whether a catalyst is acting homogeneously or heterogeneously can be very difficult to discern using conventional techniques, and spotting a thin film by eye is obviously not the most accurate of techniques. To better understand the catalytic species at work, and ultimately to improve their activity, it is critical to understand exactly how they work. Brudvig, Crabtree and colleagues have now faced up to this problem by removing the ambiguity between homogeneous and heterogeneous catalysis. They have been able to distinguish between molecular homogeneous water oxidation catalysis and heterogeneous film catalysis.

In their experiments they used an electrochemical quartz crystal nanobalance (EQCN) technique to observe whether or not catalytic species remain stable under catalytic conditions or decompose to form heterogeneous catalysts deposited on the electrode surface. They first followed the electrodeposition of iridium oxide by

decomposition of compound **1** in real time during electrochemical oxidation. The EQCN is able to measure very small changes in the mass of an electrode (on the order of nanograms) by correlating them with the changes that they cause to the oscillating frequency of an attached quartz crystal. As mentioned above, iridium oxide layer deposition is eventually visible to the naked eye on decomposition of compound **1** (ref. 10), but with this technique Brudvig, Crabtree and colleagues were able to measure the deposition of as little as 750 ng of iridium oxide (over four cyclic voltammetry sweeps). They combined these results with electrochemical measurements to estimate the percentage of active metal centres in the surface layer as being between ~5% and 10%.

The same experiments were then carried out for compound **3** but with a markedly different outcome. Rotating ring-disk electrochemical measurements combined with oxygen measurements using a Clark electrode showed that compound **3** was catalytically active for water oxidation but, using the EQCN, no change in the mass of the electrode was detected. In contrast to compound **1**, compound **3** was confirmed to be a truly molecular homogeneous catalyst.

There are several important contributions to the evolving story of water oxidation here. First, Brudvig, Crabtree and colleagues offer up a new type of molecular catalyst for water oxidation. Second, they illustrate a new approach to water oxidation electrocatalysis based on thin-film transition-metal-oxide coatings like the cobalt oxide films described by Nocera and co-workers¹¹. Finally, they describe a logical technique by which the activity of iridium molecules can be analysed to delineate between homogeneous and heterogeneous catalysis. □

Thomas J. Meyer is in the Department of Chemistry at the University of North Carolina, Chapel Hill, North Carolina 27599-3290, USA.
e-mail: tjmeyer@unc.edu

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IONOTHERMAL SYNTHESIS

A new spin on frustration

Solid-state science and technology in the twentieth century was defined by the transistor and the integrated circuit. Will the quest for a quantum spin liquid, which is inspired by theoretical and experimental advances, spawn the information technology of tomorrow?

Kenneth R. Poeppelmeier and Masaki Azuma

Synthetic chemistry is the core of chemistry, its essence, because it provides the indispensable molecules and materials that shape our world. Synthesis must come first, whether it is exploratory, targeted or, as is more often the case, some combination of both. The quest for a quantum spin liquid is inspired by theory and driven by the discovery of suitable new materials and lattice topologies¹. When antiferromagnetic materials are based on a triangular lattice — such as a kagome lattice (Fig. 1) — geometric frustration often results: in a triangle, each ion cannot be antiparallel to the other two. For a perfect system, this frustration would result in the ground state being inherently highly degenerate. Such correlated but fluid states are expected to

offer unusual physical phenomena that could enable future technologies¹.

Now, writing in *Nature Chemistry*, Philip Lightfoot and co-workers² report an ionothermal synthesis of a new quantum-spin-liquid candidate, $[\text{NH}_4]_2[\text{C}_7\text{H}_{14}\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$, which contains a frustrated magnetic spin-1/2 kagome network of $d^1 \text{V}^{4+}$ ions (Fig. 1). If this compound really is free from any distortion, it is the first realization of a perfect $S = 1/2$ kagome antiferromagnet.

Ionic liquids are by their nature binary — that is, made from cations and anions. The choice of these ionic species determines the properties of the solvent. Lightfoot and colleagues discovered that the specific solvent properties of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, or (EMIN-NTf₂), can be used to control the reduction

of metallic species and stabilize a particular oxidation state or combination of oxidation states that are otherwise difficult to access. Most V^{4+} compounds, for example, form low-dimensional compounds and clusters rather than the desired two-dimensional structures where spin frustration can be expected.

As shown in Fig. 1, the compound exhibits not one isolated kagome layer but two adjacent kagome layers linked by an octahedral $d^2 \text{V}^{3+}$ cation coordinated by fluoride anions. These double-pillared layers, which also contain charge-balancing ammonium cations, are separated by the large quinuclidinium cations, which act to isolate the magnetic $[\text{V}_7\text{O}_6\text{F}_{18}]^{3-}$ oxyfluoride layers. The compound exhibits a high degree of magnetic frustration with significant antiferromagnetic interactions, but no long-

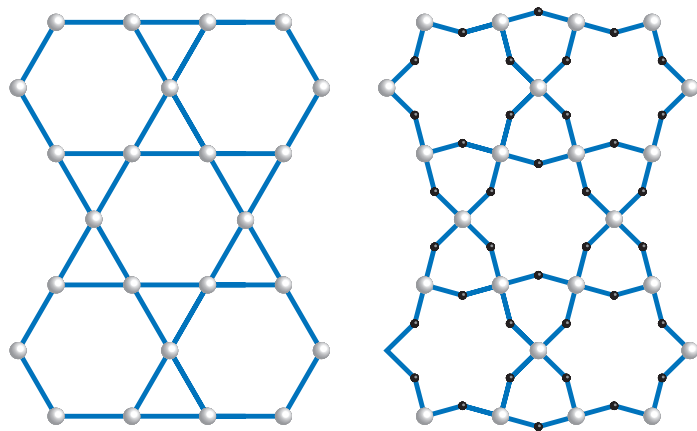


Figure 1 | The arrangement of certain metal ions in a kagome lattice can cause magnetic frustration. Left: ideal representation of a kagome network. Right: schematic representation of $[\text{NH}_4]_2[\text{C}_7\text{H}_4\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$, which contains a frustrated magnetic $S=1/2$ kagome network of $d^9\text{V}^{4+}$ ions. Fluoride ions are black spheres; $\text{V}^{\text{IV}}\text{OF}$ groups are white spheres. Figure reproduced from ref. 2.

range magnetic order or spin-freezing above 2 K. The absence of symmetry lowering and magnetic ordering at low temperature must be confirmed.

All liquids solidify at low temperature, and spin systems are no exception; they either order or freeze (into a spin glass) at low temperature. In one-dimensional systems such as Haldane, spin-Peierls and ladder compounds, the spin system avoids long-range ordering by forming singlet pairs³. A spin-liquid ground state is also expected for geometrically frustrated magnets with, for example, triangular, kagome or pyrochlore topologies⁴. Such a liquid state is indeed found in NiGa_2S_4 , an $S=1$ triangular system, and attracts much attention⁵. Kagome systems are studied intensively, as the degree

of frustration is greater compared with triangular systems⁶. Several candidates are known, but there has been no realization of a perfect $S=1/2$ kagome compound. The recent report of 'perfect kagome' herbertsmithite ($d^9\text{Cu}^{2+}$, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$) was striking, but with a 10% anti-site disorder between the magnetic copper ions and non-magnetic zinc ions^{7–11}. Volborthite^{12,13} ($\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2\cdot 2\text{H}_2\text{O}$) and vesignieite¹⁴ ($\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$) are also good candidates, but these are subject to anisotropic intra-kagome interactions because of structural deformations (symmetry lowering). A new QSL candidate is $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$, which shows no trace of long-range ordering down to 0.4 K. This $d^3\text{Mn}^{4+}$ $S=3/2$ case, which was prepared by a hydrothermal method, adopts a honeycomb

lattice. A honeycomb lattice is not frustrated when only the nearest interaction is considered, but $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ does not show long-range ordering, probably owing to the next-nearest-neighbour interactions^{15,16}.

The discovery of new frustrated magnets continues to excite, and at the same time challenge, the solid-state community. The partly exploratory, partly planned ionothermal synthesis reported by Lightfoot and co-workers reminds us that new phases not found in the natural world of minerals can be made and, more importantly, that the physics associated with them remains to be discovered. □

Kenneth R. Poeppelmeier is in the Department of Chemistry at Northwestern University, Evanston, Illinois 60208-3113, USA. Masaki Azuma is in the Materials and Structures Laboratory at Tokyo Institute of Technology, Yokohama 226-8503, Japan. e-mail: krp@northwestern.edu; mazuma@msl.titech.ac.jp

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PROTEIN NMR SPECTROSCOPY

Spinning into focus

Transient sedimentation of proteins inside a solid-state NMR rotor under fast magic-angle spinning offers a promising solution to the challenge of determining the structures of high-molecular-weight proteins with atomic resolution. This opens new opportunities for structural analysis of large macromolecules and macromolecular assemblies.

Tatyana Polenova

Spectacular discoveries made in the field of structural biology in the past two decades have brought insights into the architecture of numerous proteins, nucleic acids and biomolecular complexes. Structural studies of large biomacromolecules and molecular machinery, however, remain a challenge. Solution NMR spectroscopy is one of the primary techniques for the

determination of atomic-resolution protein structures¹. Although a powerful method with the ability to yield much information, solution NMR is restricted to soluble and relatively small proteins. Proteins above 60 kDa are usually not amenable to full structural characterization due to the inherent dependence of resonance line widths on molecular weight, with molecular-

tumbling-induced relaxation resulting in resonances that are broadened beyond detection in large molecules.

Solid-state NMR spectroscopy has recently emerged as an alternative method for atomic-resolution structure determination of proteins. To attain narrow peaks in the solid-state NMR spectra of proteins, the magic-angle spinning (MAS)