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A sponge-like luminescent coordination framework *via* an *Aufbau* approach†

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Received (in Columbia, MO, USA) 10th May 2002, Accepted 5th July 2002
First published as an Advance Article on the web 1st August 2002

A luminescent mixed-metal coordination network with sponge-like sorption features is formed by stepwise assembly.

One of the primary rationales for a coordination chemistry approach to extended solid networks is the prospect of greater diversity both with respect to structure and function.[1] While not necessarily a corollary, in many cases, greater diversity translates to a loss of structural predictability as slight variations in synthetic conditions can yield new frameworks.[2] In our ongoing studies of the sulfonate group as a linker in coordination solids,[3–6] we sought to employ principles of hard/soft acid base theory to develop a step-wise, and hence more controllable, approach to extended coordination frameworks.[7] Another possible benefit to this *Aufbau* methodology would be that any properties of a discrete coordination compound formed initially could be more directly extended to an infinite network with retention of the desired features.

This work deals with $\{Ba_2(H_2O)_4[Eu\mathbf{L}_3(H_2O)_2](H_2O)_{5.44}Cl\}_\infty$ **1**, where **L** is 4,4′-disulfo-2,2′-bipyridine *N*,*N*′-dioxide. This framework incorporates a sulfonated luminescent Eu building block, cross-linked into a three-dimensional structure through alkaline earth/sulfonate interactions. While individual interactions between sulfonate oxygen atoms and metal ions are generally weaker, when employed cooperatively in a supramolecular manner, robust solids can and do result.[5] The observed trend in our work is that sulfonate-linked frameworks tend to be more coordinatively flexible than their phosphonate or carboxylate counterparts, but are ultimately stable.[4] The frameworks reported herein contains channels filled with water molecules as well as labile coordination sites on the metals surrounding the pore. The framework is cationic as Cl^- ions reside in small ‘grottos’ in the sides of the channels. Upon removal of the water, the structure contracts, but swells reversibly upon reintroduction of water. Framework **1** absorbs other molecules and preliminary studies show guest dependence of luminescence, a promising result for sensor applications.

$EuCl_3$ was complexed with $Na_2\mathbf{L}$,[8] in water to generate *in situ* $Na_3[Eu\mathbf{L}_3(H_2O)_2]$, **2**. Compound **2** presents six monoanionic sulfonate groups in a divergent fashion from a luminescent core. $[Ln(2,2'\text{-bipyridine } N,N'\text{-dioxide})_4]^{3+}$ species are known to exhibit room temperature luminescence,[9,10] so **1** was anticipated to have similar properties. Compound **2** was complexed with $BaCl_2$ in aqueous solution to form the complex, $Ba_2(H_2O)_4[Eu\mathbf{L}_3(H_2O)_2](H_2O)_{5.44}Cl$ **1**.[11] Single crystals were obtained *via* diffusion of acetone into an aqueous solution of **1**.‡

Compound **1** forms a three-dimensional framework consisting of $[Eu\mathbf{L}_3(H_2O)_2]^{3-}$ units cross-linked by Ba^{2+}–SO_3 interactions. In **1**, the asymmetric unit is comprised of one Eu^{3+} center, three molecules of **L**, two Ba^{2+} ions, one Cl^- ion, and three types of water molecules, that is, those bound to Ba, those bound to Eu, and those uncoordinated in the channels. The structure contains channels that run along the *c*-axis as shown in Fig. 1. The dimensions of these channels are approximately 12.49 Å high with a width of 9.84 Å as defined by the shortest *trans*-channel metal–metal distances. These values convert to ~8.5 × 5.8 Å when van der Waals radii are considered. This reference was chosen owing to the labile nature of the aquo ligands on both Ba and Eu centers which point directly into the channels. Uncoordinated water molecules, ~5.5 per Eu center as modeled crystallographically, occupy the channels. The shortest *trans*-channels distances between aquo ligands are 8.41 and 5.34 Å. The full coordination sphere of the Eu center is comprised of six oxygen atoms from the N-oxides of three molecules of **L**, and two aquo ligands. There is no coordination of sulfonate oxygen atoms to the Eu center.

The interactions between the SO_3 groups and the alkaline earth ions form a highly aggregated structure as one Ba center crosslinks four $[Eu\mathbf{L}_3(H_2O)_2]^{3-}$ building blocks and the other Ba center links five such units. Ba1 is nine-coordinate with an irregular coordination sphere composed of seven sulfonate oxygen atoms, from six different sulfonate groups, and two water molecules. These six sulfonate groups originate from six different molecules of **L** which in turn are associated with four different $[Eu\mathbf{L}_3(H_2O)_2]^{3-}$ units. The coordination environment about Ba2 is a distorted square antiprism of two water molecules and six sulfonate oxygen atoms. The six sulfonate oxygen atoms are again from six different sulfonate groups associated with six different molecules of **L**. In this case, the Ba^{2+} ions serve to bring together five $[Eu\mathbf{L}_3(H_2O)_2]^{3-}$ units. Extensive crosslinking in the framework is to be expected due to the 2 : 1 charge ratio between Ba and sulfonate ions, and also that sulfonate groups from the same molecule of **L** are not suitably disposed in space to chelate to a single Ba^{2+} ion.

An interesting feature of **1** is the inclusion of Cl^- ions. There exist smaller cavities off the sides of the water-filled channels,

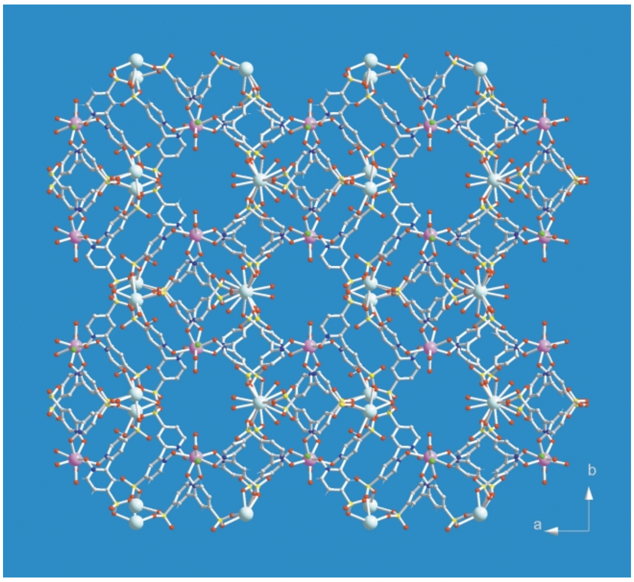

Fig. 1 Single crystal X-ray structure of **1** viewed down the *c*-axis. Eu, purple; Ba, large grey; O, red; N, blue; S, yellow; C, small grey. Note the channels with aquo ligands pointing into them.

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† Electronic supplementary information (ESI) available: characterisation data. See http://www.rsc.org/suppdata/cc/b2/b204573g/

DOI: 10.1039/b204573g

behind the Eu centers, where the Cl^- ions reside. Each Cl^- ion forms H-bonds to one Eu-bound water molecule (O1W···Cl1 3.129(8) Å) and the protons of four different α-carbons of pyridine rings (Cl···C 3.60(1)–3.85(1) Å, Cl···H–C 167.2(5)–177.8(5) °). Fig. 2 shows the location of these H-bonded 'grottos' relative to the channels in Fig. 1. In Fig. 2, the channels lie in a horizontal fashion adjacent to the rows of Ba^{2+} ions. A relative positioning of the channel can be envisioned by the placement of the aquo ligands on the Eu center.

We have previously described a sulfonate group as a 'ball of Velcro.'[4] This analogy describes the sulfonate's flexible ligating properties owing to the multiple weak metal–oxygen interactions. Correspondingly, **1** exhibits sponge-like sorption properties. Thermogravimetric analyses of **1** showed a steady mass loss to 105 °C corresponding to loss of both free and coordinated water molecules (13.29% obs., 13.42% calc.).[12] This sample is then stable to 320 °C. Powder X-ray diffraction after dehydration showed the solid to be amorphous.[13] Thus, upon loss of water, the structure of **1** collapses. This collapse is not total as surface area measurements revealed a small internal surface area (15.2 $m^2\ g^{-1}$).[14] Upon reintroduction of water vapor, the PXRD pattern remains amorphous. Based upon this data alone, it may be tempting to conclude that the framework has collapsed irreversibly. Notably, however, TGA data reveal that, in fact, **1** resorbs $>95\%$ of the lost solvent, a value requiring uptake of *both* coordinated and free H_2O. This sorption/desorption cycle can be repeated, again with $>95\%$ re-uptake of water relative to the first resorption. The fact that the solid does not completely revert to its nascent form with each cycle is sufficient to yield the observed amorphous PXRD pattern.

Compound **1** shows expected red luminescence (λ_{exc} = 464 nm, λ_{em} = 612 nm) of a Eu^{3+} coordination complex.[15–17] Preliminary studies show marked effects of solvent on the intensity of the hypersensitive $^5D_0$ to $^7F_2$ transition. There is a ~50% decrease in intensity of this peak in the absence of water and ~70% decrease in the presence of nitrobenzene.[18] More detailed study of luminescence dependence on both solvent and intra-channel anion will be reported in a full paper.

The present work concerns the formation of a sponge-like solid *via* a stepwise assembly. Significantly, the physicochemical properties of the discrete building block are extended to the infinite solid. This approach offers an added element of control in the ongoing study of tunable extended solids.

We thank Dr R. McDonald at the University of Alberta for single crystal X-ray data collection and Drs J. Ripmeester and G. Enright at the National Research Council of Canada for use of their PXRD. This work was funded by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

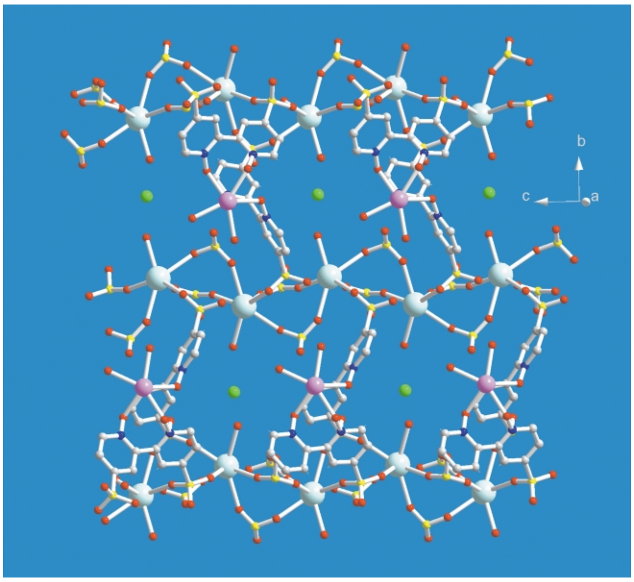

Fig. 2 Compound **1** viewed slightly off the *a*-axis. Green spheres indicate Cl^- ions that exist in H-bonded 'grottos'. For some ligands, only the sulfonate groups are shown.

Notes and references

‡ *Crystal data* for $\{Ba_2(H_2O)_4[Eu\mathbf{L}_3(H_2O)_2](H_2O)_{5.44}Cl\}_\infty$ **1**: $C_{30}H_{25.50}Ba_2ClEuN_6O_{34.50}S_6$, M = 1676.51, monoclinic, space group $P2_1/c$ (no. 14), a = 24.550(2), b = 23.026(2), c = 10.487(1) Å, β = 98.796(2), V = 5858.5(10) $Å^3$, Z = 4, D_c = 1.901 Mg m^{-3}, μ(Mo-Kα) = 2.743 mm^{-1}, crystal size 0.62 × 0.06 × 0.02 mm. Data were collected on a Bruker P4 diffractometer with a SMART 1000 CCD area detector using Mo-Kα radiation. A total of 26058 reflections ($1.22 < \theta < 26.42°$) were processed of which 11951 were unique and significant with $I_{net} > 2\sigma(I_{net})$. Structure solution, refinement and molecular graphics were carried out with the SHELXTL software package, release 5.1.[19] Final residuals for $I_{net} > 2\sigma(I_{net})$ were R_1 = 0.0636 and wR_2 = 0.1558 (GoF = 1.086) for 722 parameters. CCDC reference number 186040. See http://www.rsc.org/suppdata/cc/b2/b204573g/ for crystallographic data in CIF or other electronic format.

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13 PXRD were performed on a Scintag X2 powder X-ray diffractometer at the Steacie Institute for Molecular Sciences (NRCC).
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