The first example of a functional pillared metal sulfonate network

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Barium 4,5-dihydroxybenzene-1,3-disulfonate, a pillared metal sulfonate network, possesses a microporous interlayer region through the use of a single type of 'bent' sulfonate group, and absorbs H_2S.

The design and synthesis of mixed inorganic–organic solids capable of including small molecules within void spaces in their structures, analogous to natural clays and zeolites,[1] has evolved into a diverse area of research.[2] A widely studied class of metal–organic networks, in this respect, has been the metal phosphonate salts of general formula $M^{n+}(O_3PR)_{n/2}$ where R is an aliphatic or aromatic organic group.[3] These systems often form two-dimensional structures where rigid O–M–O layers assemble, projecting the R groups between the layers. This alternating organic–inorganic layered topology can allow the intercalation of various small molecules between the layers, making these materials useful for chemical separations and/or catalytic applications.[4] However, since, typically, no void space exists between the layers prior to intercalation, an energy cost is associated with the act of separating the layers which can inhibit their usefulness. To overcome this limitation, the layers in these compounds can be 'pillared' to increase the void space between the layers and predispose the structure to guest inclusion. Pillaring is a strategy, first employed with clays and then with other layered materials, where counter ions, organic molecules, or polytopic ligands are used to 'prop' layers apart, resulting in greater porosity in addition to improved structural integrity.[5] Unfortunately, with prototypical metal phosphonate structures, the spacing between simple linear diphosphonate pillars (*e.g.* phenyl or biphenyl) is negligible, rendering the network ineffectual with regard to guest inclusion [Scheme 1(a)].[6] This adverse circumstance can be in part remedied by using mixed phosphonate or phosphate/phosphonate systems where the 'pillar' alternates with a smaller, non-pillaring phosphonate (*e.g.* methylphosphonate) or a phosphate group [Scheme 1(b)], thus generating porosity.[7] However, in addition to complicating the synthesis, this may result in a loss of structural regularity and a greater pore size distribution.[8]

Contrasting the metal phosphonate systems, our research is focused on using weaker metal–sulfonate ($M^{n+}(SO_3R)_n$) interactions to develop new layered and porous compounds.[9] This approach takes advantage of the flexible coordinative behavior of the SO_3^- group to obtain structures not attainable from the rigid O–M–O scaffolding of metal phosphonate networks. Of the relatively few structurally characterized $M_n(SO_3R)_n$ complexes which exist to date, all form layered networks.[9,10] Some of these can be classified as 'pillared' solids but they suffer from the aforementioned problem of virtually no space between adjacent R groups.[11] Even within these layered compounds, there exists substantial diversity with respect to the sulfonate coordination mode.[12] We, therefore, sought to exploit this flexible coordination by generating layered networks which would tolerate the incorporation of a 'bent' pillar. A bent pillar would not pack efficiently in the interlayer and, therefore, generate porosity [Scheme 1(c)] while offering a facile two-component synthesis. Herein, we report the structure, thermal analysis and sorption properties of barium 4,5-dihydroxy-benzene-1,3-disulfonate dihydrate, [Ba(**1**)(H_2O)]·H_2O. This compound represents the *first functional pillared metal sulfonate network*.[13] Significantly, interlayer void space is generated and the guests which occupy these sites may be removed while maintaining structural integrity.

[Ba(**1**)(H_2O)]·H_2O was metathesized from the commercially available Na_2[**1**]·H_2O by combining equimolar amounts of $BaCl_2$·$2H_2O$ and Na_2[**1**]·H_2O in minimal amounts of water. A white precipitate of [Ba(**1**)(H_2O)]·H_2O formed immediately,
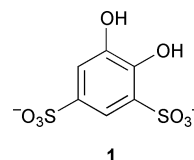
which was filtered off in 95% yield. Colorless, X-ray quality crystals were grown by diffusion of acetone vapor into a saturated aqueous solution of the complex.† The structure (Fig. 1) consists of infinite layers of sulfonate-bridged Ba^{2+} centers, in the *xy* plane, with **1** acting as a pillar to bridge adjacent layers through the two sulfonates. One SO_3 group coordinates to a layer in the $+z$ direction and other in the $-z$ direction, to give a *d*-spacing of 9.24(2) Å. The stability of the
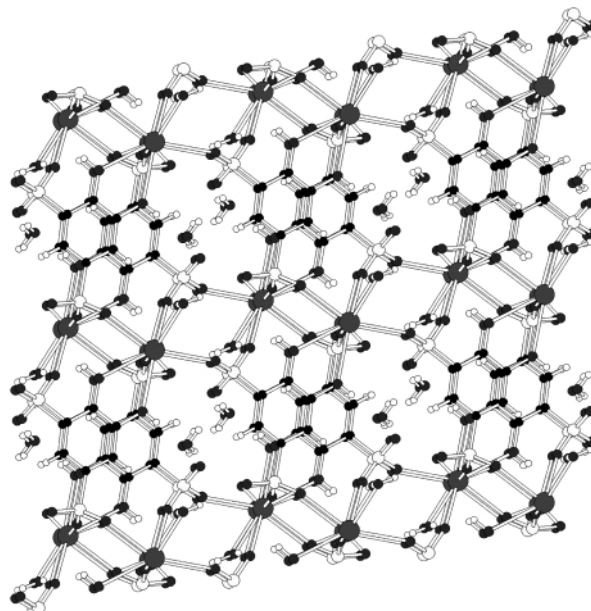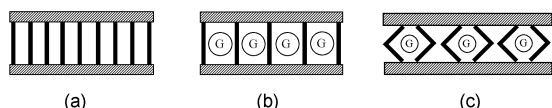

Fig. 1 View of the layered structure of [Ba(**1**)(H_2O)]·H_2O down the *a*-axis. Ba atoms: large circles, S atoms: medium, light grey circles, O atoms: small, dark grey circles, C atoms: small, black circles. Note the interlayer channels and the water molecules occupying them.

Scheme 1 Pillaring of layered networks showing (a) close packing of linear pillars with no void space; (b) alternating pillars and small R groups to generate porosity; (c) use of 'bent' pillars to create pores with a single type of R group.

pillars is augmented *via* the chelation of the catechol (4,5-diol) unit of **1** to a single Ba^{2+} center. The bent structure of **1**, with sulfonate groups oriented at 120°, opens up 16-membered rings in the interlayer between the pillars. The rings align along the *a*-axis to form channels which are filled with non-coordinated water molecules. The channels are approximately 4.0 Å in diameter. The construction of the layers is complex, with the one crystallographically unique Ba^{2+} ion being 9-coordinate and each molecule of **1**, in turn, coordinating to six different Ba^{2+} centers. The coordination of **1** is as follows. The catechol moiety of **1** chelates, in a doubly protonated form, to one barium center [Ba–O7 = 2.843(3), Ba–O8 = 2.791(3) Å]. The sulfonate group in the 3-position coordinates to two different Ba^{2+} centers, which are part of the same layer as the catechol-chelated Ba^{2+}, *via* a μ^2,η^2-mode [Ba–O5 = 2.750(3), Ba–O6 = 2.749(3) Å]. Sulfonates in the 1-position adopt a μ^3,η^3-coordination mode where all three Ba^{2+} ions are in the adjacent layer to those coordinating to the sulfonate in the 3-position. One of the Ba^{2+} centers is chelated by two of the sulfonate oxygen atoms resulting in four coordinating interactions in total [Ba–O1 = 2.737(3), 3.002(3), Ba–O2 = 2.875(3), Ba–O3 = 2.765(3) Å]. Each barium ion is 9-coordinate with an irregular geometry. The coordination sphere is comprised of six sulfonate oxygen atoms, from five different sulfonate groups, the two catechol oxygen atoms, and a water molecule [Ba–O9 = 2.751(3) Å] that projects into the interlayer.

The PXRD pattern and the elemental analysis of the bulk precipitate match those of the single crystal sample, indicating that these species have the same structure and composition. Thermal analysis revealed loss of included water at 110 °C and then gradual loss of the coordinated water to 420 °C at which point the sample decomposed.[14] Given that the aversion to employing sulfonates in the generation of extended materials has largely been due to their weaker coordinative tendencies, the stability of this network is quite remarkable. Importantly, the PXRD patterns of the dihydrate and the monohydrate showed that the framework remained intact after loss of the channel water molecules.[15] Removal of only the guest water molecules of [Ba(**1**)(H$_2$O)]·H$_2$O would leave empty channels, possibly with a topology imprinted by the water molecules. Therefore, based upon the structural similarity, the sorbent capabilities of the dehydrated framework with H$_2$S were examined. It was found that at 50 °C a mass increase of 7.5% was observed, corresponding to the uptake of 0.93 equivalents of H$_2$S with respect to the equivalent of expelled water.[16] Significantly, analogous experiments with methane and methanol revealed no mass increase, indicating selectivity for H$_2$S.

In conclusion, [Ba(**1**)(H$_2$O)]·H$_2$O represents the first example of a functional pillared metal sulfonate structure. The flexible coordination of the sulfonate group enables 'bent' pillars to be employed resulting in a microporous network in a system where only a single type of pillar is present. Despite relying on metal–sulfonate interactions in the pillars, the network is highly robust (> 400 °C). With regard to functionality, the guest water molecules can be removed and selectively replaced, almost quantitatively, by hydrogen sulfide.

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15 A comparison of the nine most intense peaks in the PXRD patterns of Ba[**1**]·2H$_2$O and of a sample dehydrated at 150 °C for two hours, to remove channel water molecules, shows a mean deviation of only 1.4%. Full details are given within the crystallographic material.

16 [Ba(**1**)(H$_2$O)]·H$_2$O was placed under a N$_2$ atmosphere, heated to 150 °C at 10 °C min^{-1}, then held at 150 °C for 10 min to remove the channel water. The sample was cooled to 50 °C and the purge gas changed to H$_2$S. The sample showed a mass gain of 7.5%. [Ba(**1**)(H$_2$O)] has a mass of 423 g mol^{-1}. In terms of molar equivalents, a 7.5% gain is therefore equivalent to 31.68 g mol^{-1} or 31.68/(34.06 g mol^{-1} H$_2$S) = 0.93 equivalents of H$_2$S.

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