Poly[[hexaaquabis[μ_4-2-hydroxy-5-(4-sulfonatophenyldiazenyl)benzoato]-dibarium(II)] 4,4′-bipyridine solvate]

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The title compound, $\{[Ba_2(C_{13}H_8N_2O_6S)_2(H_2O)_6] \cdot C_{10}H_8N_2\}_n$, possesses a novel two-dimensional porous coordination network, in which each Ba^{II} ion is nine-coordinated by three carboxylate O atoms, two sulfonate O atoms and four water molecules in an irregular coordination environment. Hydrogen-bond interactions between coordinated water molecules and sulfonate/hydroxyl groups hold the network layers together and produce a three-dimensional supramolecular architecture.

Comment

The self-assemblies of metal–organic frameworks (MOFs) are of great interest owing to their fascinating structural topologies and potential applications in materials science (Moulton & Zaworotko, 2001; Leininger et al., 2000; Belanger et al., 1999; Eddaoudi et al., 2001; Evans & Lin, 2002). Accordingly, the judicious choice of organic building blocks with various assembly modes and unique functional properties is very significant in optimizing structural topology and desired functions (Cote & Shimizu, 2003; Makinen et al., 2001; Hix et al., 2001; Drumel, Janvier, Barboux et al., 1995; Drumel, Janvier, Deniaud & Bujoli, 1995). In recent years, azobenzene derivatives used as building blocks have attracted attention because the combination of these photofunctional molecules with transition metals (TMs) may result in interesting magnetic, optical and electronic properties (Otsuki et al., 2003; Nishihara, 2005). So far, most metal cations in the reported azo-based metal complexes are d-block TM ions, while such complexes with alkaline-earth metals (the s-block metals), especially barium-containing MOFs, are rare (Kennedy et al., 2001, 2004). Azo-based s-block metal complexes are of general interest to structural chemists, because they have more flexible configurations than azo-based TM complexes in forming MOFs, but the s-block complexes are still less common than the TM complexes in supramolecular chemistry and crystal engineering. In addition, the structures of these

compounds as colourants are of specific interest to the dye and pigment industries (Kennedy et al., 2004, and references therein). 5-(4-Sulfophenylazo)salicylic acid disodium salt (abbreviated as Na_2Sasa, see scheme), an azobenzene-containing building block that exhibits versatile coordination modes and can form directional hydrogen bonds based on the different binding abilities of the salicylate and sulfonate groups, may provide great opportunities for constructing functional molecular assemblies with interesting networks. However, the structures and properties of metal complexes with the Sasa ligand have been little explored so far. The Sasa ligand is used here for the first time to prepare a barium-based MOF, a two-dimensional coordination polymer with one-dimensional channels, $\{[Ba_2(Sasa)_2(H_2O)_6] \cdot Bpy\}_n$ (Bpy is 4,4′-bipyridine), (I), in which the salicylate group of Sasa coordinates to the Ba ions in a μ_3-η^2,η^1-bimetallic bridging–chelating mode. Such a coordination mode is not only rare for salicylate-based complexes but has also never been observed in the associated Ba-based MOFs.
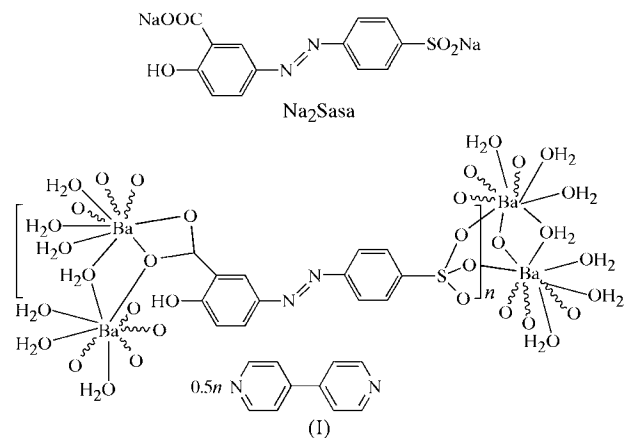
The asymmetric unit of the title compound is composed of one Ba^{II} ion, one Sasa anion, one-half of a Bpy molecule and three coordinated water molecules (Fig. 1). Atom Ba1 is nine-coordinated and has an irregular coordination environment containing three carboxylate O atoms (O1, O2 and O2^{ii}), two sulfonate O atoms (O4^{iii} and O6^i) from two Sasa ligands [Ba1—O = 2.7687 (19)–2.943 (2) Å; symmetry codes are as given in the caption to Fig. 1], and two bridging (O3W and O3W^{ii}) and two terminal (O1W and O2W) water molecules [Ba1—OW = 2.773 (2)–2.804 (2) Å]. Each Ba^{II} ion is bridged through water molecules to form a $\{Ba—O3W\}_n$ backbone chain running along the b axis. These backbone chains are further connected to each other by O atoms from the salicylate and sulfonate groups of the Sasa ligands, coordinated to two Ba^{II} ions in a μ_3-η^2,η^1-bimetallic bridging–chelating mode and a syn–syn bridging fashion, respectively, giving rise to a two-dimensional layer in the bc plane (Fig. 2a). Sulfonate atom O5 and the OH group of the Sasa ligand remain uncoordinated in the structure (see scheme). This layer is characteristic of a slab with a thickness of 8.27 Å (the length of the a axis), containing one-dimensional channels along the b axis (Fig. 2b), with an approximate free-pore diameter of 11.35 × 2.86 Å (the O3W···O3W and C13···C13 distances not including the van

metal-organic compounds

der Waals radii), in which Bpy molecules are situated. Calculations using *PLATON* (Spek, 2003) show that there are no residual solvent-accessible voids in the prototype unit, but 23.9% of the volume of the unit cell is available after removing the Bpy molecules. The slabs stack in . . . *AAA* . . . modes along the *a* axis. Hydrogen bonds (Table 1) between the coordinated water molecules and the O atoms of the SO_3^-/OH^- groups link adjacent slabs into a three-dimensional supramolecular framework (Fig. 2*b*). Like the structure-directing agents in porous materials (Liu *et al.*, 2007), the Bpy molecules as the guest are only located in the channels (Fig. 2*b*) and are in contact with the pore wall *via* strong hydrogen-bonding interactions [N3· · ·O3*W* = 2.712 (3) Å] and weak π–π interactions (the centroid–centroid distance is 3.825 Å, and the interplanar distance between the pyridyl

Figure 3
Part of the structure in the title complex, showing the hydrogen-bonding interactions between the pyridyl N atoms and bridging water molecules (dashed lines), as well as π–π interactions between the pyridyl rings and the aromatic rings of Sasa ligands (grey shadows).
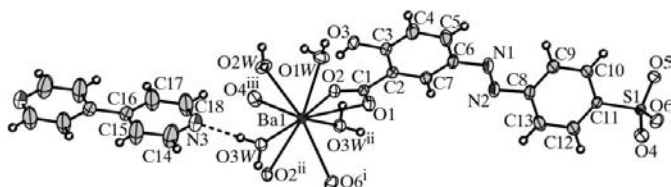

Figure 1
A view of the title complex, showing the atom-labelling scheme and the completed Ba^{II} coordination environment. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.]
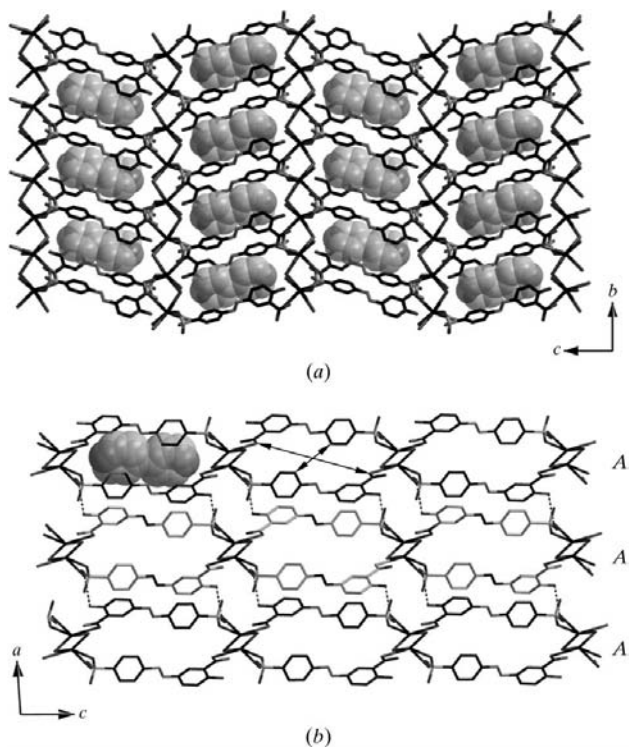
rings and the aromatic rings of the Sasa ligands is *ca* 3.70 Å, resulting in an offset angle of 14.5°; Fig. 3).

The framework collapsed when the Bpy molecules were removed from the channels at 628 K, perhaps because of the strong hydrogen-bonding interactions and π–π stacking interactions between the host and guest molecules. Attempts to replace Bpy with low boiling or/and low-conjugated N-heterocyclic molecules, such as pyridine and methyl-pyridine, are in progress. For the construction of porous MOFs, the frequent occurrence of interpenetration or uncontrollable interlayer stacking in staggered mode generally leads to no void space in the molecular packing structure, despite the fact that porous coordination networks can be obtained more easily. Such a two-dimensional slab–layer structure with one-dimensional channels is undoubtedly of great advantage in avoiding nonporous structures resulted from interpenetration or staggered stacking, and may shed some light on the design and construction of new porous materials. Until now, only a few simple complexes that include *s*-block metals and sulfonated azo anions have been reported, and these exhibit ion-pair, discrete, one-dimensional chain/ladder-like and two-dimensional structures (Kennedy *et al.*, 2001, 2004); the title compound is the first two-dimensional slab–layer compound with one-dimensional channels, and this type of structure is also rare in metal–organic coordination complexes.

Figure 2
(*a*) The structure of the two-dimensional porous layer extending along the *bc* plane and (*b*) a view of the one-dimensional channel propagating along the *b*-axis direction. The uncoordinated 4,4′-bipyridine molecules fill the channels. H atoms have been omitted for clarity.
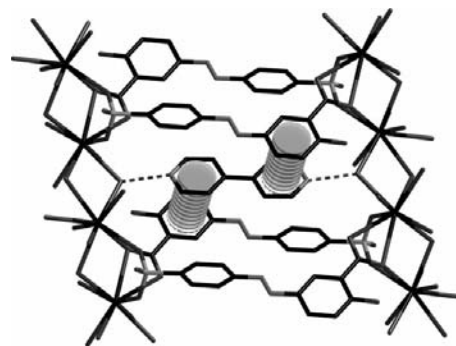
Experimental

A mixture of BaCl$_2$·2H$_2$O (0.244 g, 1.0 mmol), Na$_2$Sasa (0.366 g, 1.0 mmol) and Bpy (0.156 g, 1.0 mmol) in water (10 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 383 K for 2 d under autogenous pressure. After slow cooling of the reaction mixture to room temperature at a rate of 2 K h^{-1}, red block-shaped crystals suitable for X-ray diffraction analysis were obtained in high yield. Analysis calculated for C$_{36}$H$_{36}$Ba$_2$N$_6$O$_{18}$S$_2$: C 36.65, H 3.08, N 7.12%; found: C 36.57, H 3.03, N 7.03%. IR (KBr, cm^{-1}): 3499 (*s*), 1625 (*s*), 1595 (*s*), 1481 (*m*), 1463 (*m*), 1216 (*s*), 1174 (*s*), 1123 (*s*), 1034 (*s*), 1008 (*s*), 846 (*m*), 804 (*m*), 686 (*m*), 622 (*m*). Thermogravimetric analysis showed a continuous weight loss between 368 and 443 K, corresponding to the loss of all coordinated water molecules (found:

9.31%; calculated: 9.16%). A 12.93% weight loss between 453 and 628 K may be due to the volatilization of Bpy; the organic ligand then decomposes gradually until 878 K and, finally, the sample was converted to a mixture of BaO and $BaSO_4$.

Crystal data

$[Ba_2(C_{13}H_8N_2O_6S)_2(H_2O)_6]\cdot$
$C_{10}H_8N_2$
$M_r = 1179.51$
Monoclinic, $P2_1/c$
$a = 8.2706 (16)$ Å
$b = 8.3878 (16)$ Å
$c = 30.342 (6)$ Å

$\beta = 93.542 (2)°$
$V = 2100.8 (7)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.05$ mm^{-1}
$T = 293 (2)$ K
$0.38 \times 0.27 \times 0.18$ mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
  $T_{min} = 0.736$, $T_{max} = 1.000$
  (expected range = 0.509–0.692)

13373 measured reflections
4594 independent reflections
4420 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.061$
$S = 1.07$
4594 reflections
290 parameters

6 restraints
H-atoms parameters constrained
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3···O2	0.82	1.83	2.558 (3)	147
O1W—H1A···O5^i	0.85	2.07	2.871 (3)	158
O1W—H1B···O5^{ii}	0.85	1.97	2.798 (3)	166
O2W—H2A···O3^{iii}	0.85	2.12	2.960 (3)	173
O2W—H2B···O6^{iv}	0.85	2.06	2.900 (3)	172
O3W—H3A···N3	0.85	1.87	2.712 (3)	172
O3W—H3B···O3^v	0.85	2.21	2.977 (3)	151
O3W—H3B···O1W^{vi}	0.85	2.49	2.981 (3)	118

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x - 1, -y + 1, -z + 1$; (iii) $-x - 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (v) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (vi) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

H atoms attached to C atoms and the hydroxyl O atom were positioned geometrically and treated as riding, with C—H distances of 0.95 Å and an O—H distance of 0.82 Å, and with $U_{iso}(H)$ values of $1.2U_{eq}(C)$ or $1.5U_{eq}(O)$. H atoms of water molecules were located in difference Fourier maps and included in the subsequent refinement using restraints [O—H = 0.85 (1) Å and H···H = 1.39 (2) Å, with $U_{iso}(H) = 1.5U_{eq}(O)$].

Data collection: *CrystalClear* (Rigaku/MSC, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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