A mesoporous hydrogen-bonded organic–inorganic framework bearing the isopolymolybdate $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$†‡

Reinaldo Atencio,* Alexander Briceño and Xacvier Galindo

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The mesoporous H-bonded organic–inorganic hybrid material is built up from the assembly of the isopolymolybdate $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ and H_2bipy^{2+}, which displays large interconnected cavities and exhibits a reversible water sorption behaviour while maintaining its striking crystal integrity.

Research on assemblies of hybrid materials based on the exploitation of the synergism between inorganic and organic moieties has attracted much attention owing to the possibility of developing new materials with an augmented functionality with regard to the individual components.[1] An important example of such solid materials is the family of the polyoxometalates[2] (POMs), which combines structural and electronic diversity with a wide range of useful applications, *e.g.*, adsorption,[3] catalysis,[4] medicine[5] and materials science.[6] A fascinating and challenging aspect of the POMs lies in the rational synthesis of large clusters and the exploration of their utilization as supramolecular nanometer models.[7] Conventionally, polymolybdates are isolated from self-assembly processes controlled by oxidation–reduction reactions and/or from condensation-polymerisation of Mo^{VI} entities at pH lower than 3.[3,8] In particular, as the existence and stability of the macroisopolyanion $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ in solution at pH ~ 1 have been documented,[9] its structure–property relationship remains largely unexplored and only one crystal structure has been reported so far,[9b,c] whereas another two containing reduced species of $\{Mo\}_{36}$ are known.[7g,9e] In this report, the possibility of isolating new crystalline solids bearing this $\{Mo\}_{36}$ moiety as a counterpart of a hybrid material is demonstrated by the synthesis and structural characterization of the open framework $\{[Mo_{36}O_{112}(OH_2)_{16}](H_2bipy)_4\}\cdot 28H_2O$ (**1**) which exhibits a reversible sorption behaviour for water molecules.

Compound **1** was prepared§ from an acidified sodium molybdate solution (pH ~ 1) and using 4,4′-bipyridine (bipy) as the organic component. The asymmetric unit of the crystal structure¶ contains a fragment '$[Mo_{18}O_{56}(OH_2)_8]^{4-}$' (Fig. 1a), two cations H_2bipy^{2+} and fourteen water molecules of crystallization. The $\{Mo\}_{18}$ unit is constructed from the combination of sixteen $\{MoO_6\}$ pseudo-octahedra and two $\{MoO_7\}$ distorted pentagonal bipyramids. Based on the kind of coordinated oxygen atoms, the coordination environment around the Mo may be classified into six types of polyhedra: one $\{Mo(\mu\text{-}O_6)\}$ (see Mo9), two $\{(O{=})Mo(\mu\text{-}O_4)(OH_2)\}$ (Mo13 and Mo16), four $\{(O{=})_2Mo(\mu\text{-}O_3)(OH_2)\}$ (Mo3, Mo6, Mo7 and Mo11), four $\{(O{=})Mo(\mu\text{-}O_5)\}$ (Mo4, Mo5, Mo14 and Mo15), two $\{(O{=})_2Mo(\mu\text{-}O_4)\}$ and two $\{Mo_2(\mu\text{-}O_8)(\mu\text{-}OH_2)\}$ octahedra that edges share (see Mo1–Mo2 and Mo17–Mo18). The self-assembly from two $\{Mo\}_{18}$ moieties, *via* sharing the Mo12–O35–$Mo7^i$ and Mo12–O35–$Mo13^i$ corners ($i = -x, -y, -z$), leads to the final pseudo-spherical $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ anion, which shows a large internal cavity of approximately 0.7 × 0.5 nm (Fig. 1b). This moiety is similar to those previously observed in the crystal structure of $K_8[Mo_{36}O_{112}(OH_2)_{16}]\cdot 36H_2O$.[9b,c]

The crystal structure consists of an open framework built up from the H-bonded assembly of centrosymmetric $\{Mo\}_{36}$ and H_2bipy^{2+}. The cation–anion interaction occurs through an extensive hydrogen bonding including N–H···O [range N···O = 2.77(3)–3.15(3) Å] and C–H···O [range C···O = 3.10(3)–3.39(3) Å]. The crystal packing appears to be dominated by the shape and the nanometric size of the cluster in such a way that the H_2bipy^{2+} are settled in the cavities left by the anions (Fig. 2).

This disposition yields a framework with large, roughly rectangular channels along the *b*-axis (*ca.* 1.9 × 0.5 nm; Fig. 2) located just above and below each cluster, allowing the interconnection of the channels and the internal cavities of the anion. Thus, the resulting solvent-accessible space in the crystal structure corresponds to 21.50% (1755.6 $Å^3$ per unit cell) of the total volume (8120 $Å^3$),[10] which hosts twenty-eight crystallization water molecules. The remaining solvent-accessible voids, after considering the guest molecules, is 50 $Å^3$. An intricate set of hydrogen bonds between crystallization and coordination water molecules and oxo groups on the oxide surface clusters O–H···O

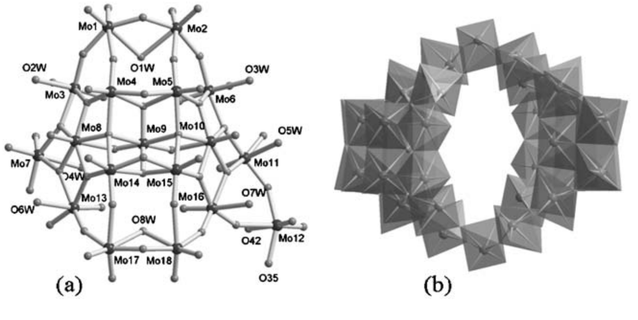

Fig. 1 (a) Fragment '$[Mo_{18}O_{56}(OH_2)_8]^{4-}$' found in the asymmetric unit of **1**. (b) Isopolymolybdate $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ showing the internal cavity. Range of distance: $Mo{=}O_{(t)}$: 1.654(9)–1.742(10) Å; $Mo\text{–}O_{(\mu 2)}$: 1.715(9)–2.349(9) Å; $Mo\text{–}O_{(\mu 3)}$: 1.735(10)–2.300(9) Å, $Mo\text{–}O_{(\mu 4)}$: 2.067(8)–2.384(9) Å, $Mo\text{–}Owater_{(t)}$: 2.335(10)–2.469(10) Å, $Mo\text{–}Owater_{(\mu 2)}$: 2.394(10)–2.470(9) Å. Bond angles for *cis* oxo ligands in the range 67.1(3)–108.8(4)°.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b413825b/

‡ Dedicated to Dr Gabriel Chuchani, on the occasion of his 80th birthday.

*ratencio@ivic.ve

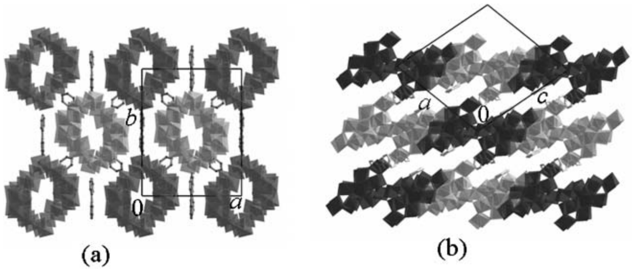

Fig. 2 (a) View of the crystal structure of **1** along *c*-axis. (b) View along the *b*-axis showing the nano-channels where water molecules (omitted) are hosted.

[range O···O = 2.52(3)–2.83(4) Å] helps to sustain the three-dimensional network.

The crystallization water molecules are poorly ordered. Most of them were found partially disordered at least in two sets of positions. This kind of disorder appears to be common in arrangements based on giant polyoxomolybdates which show a very low stability with a tendency towards facile loss of the water molecules. This feature makes difficult the exact determination of the amount of molecules in such arrays.[7] In some cases, spectacular solid-state transformations of discrete Mo-clusters lead to 1- and 2-D polymers, favoured by fast dehydration processes of crystallization water molecules at room temperature without loss of the crystalline integrity.[7b,d] The presence of large channels occupied by guest molecules found in **1**, prompted us to evaluate its water sorption properties through the combination of thermal analysis and X-ray powder diffraction (XRPD) experiments. The TG analysis agrees well with the crystallographic determination; the curve shows a first step of weight loss (30–340 °C) attributed to the dehydration of the material (crystallization and coordinated water molecules) (found: 11.81%; calc.: 11.88%). A second weight loss (330–480 °C) is assigned to the decomposition of the organic counterion (found: 10.25%; calc.: 9.49%). Interestingly, the main features of the XRPD pattern (Fig. 3) of a sample heated at 100 °C during 1 h compare well with those of the fresh sample; in spite of the anticipated partial intensity loss, the positions of the most intense peaks appear to be only slightly shifted to lower 2θ-angles, probably due to a contraction of the crystal structure. This result suggests that the H-bonded network maintains, at least partially, its structural integrity during the desorption process.

After the dehydration process, the same sample was exposed to moist ambient conditions during 6 h, and a new pattern recorded, showing no marked change in the peak positions relative to the patterns either of the dehydrated sample or the fresh sample. However, the increase of the peak intensities as well as the reappearance of some peaks at lower 2θ-angle, suggests that the network appears to recover the crystallinity that could have been affected during the dehydration process. Additional TG analysis indicated that a fresh sample heated to 100 °C undergoes a weight loss of 8.12% (Calc. 7. 56% for 28 water molecules). When this sample was exposed overnight to room atmosphere, it readily readsorbed water molecules. A new TG analysis demonstrated that the amount of water readsorbed overnight corresponds to the amount lost during the heating. The same sample may undergo several subsequent dehydration and rehydration cycles without suffering important weight changes. A remarkable feature of this material is the reversible changes of colour during such processes; from colourless to light blue up to light green during dehydration and *vice versa*. All these observations are consistent with a reversible water desorption–readsorption process. Finally, to confirm the permanent porosity of **1** after dehydration, a N_2 physisorption experiment was carried out. An analysis by a DFT method shows the typical pore size distribution of a mesoporous material (20–500 Å). To the best of our knowledge, this is a very uncommon desorption–readsorption behaviour of an H-bonded inorganic–organic hybrid material involving a polyoxometalate. Only recently, the self-assembly of a discrete biimidazole Ni-complex[11] was achieved which yielded a robust H-bonded network that interestingly maintains its striking integrity after a reversible water sorption process. Further studies to demonstrate the use of $\{Mo\}_{36}$ as a building block to obtain new porous materials from the modular assembly with different organic moieties are in progress.

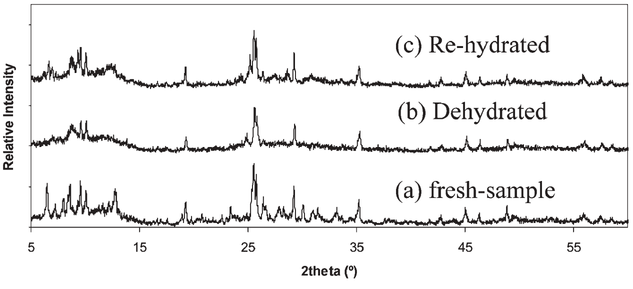

Fig. 3 XRPD of **1**: (a) fresh sample, (b) sample heated to 100 °C during 1 h, and (c) rehydrated sample.

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Reinaldo Atencio,* Alexander Briceño and Xacvier Galindo
Laboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas, 1020-A, Venezuela. E-mail: ratencio@ivic.ve; Fax: +58 212 5041350; Tel: +58 212 5041609

Notes and references

§ Compound $\{[Mo_{36}O_{112}(OH_2)_{16}](H_2bipy)_4\}\cdot 28H_2O$ (**1**) was prepared by dissolving $Na_2MoO_4\cdot 2H_2O$ (1.18 g, 4.88 mmol) in 50 mL of distilled water and adjusting the pH to ~1 with concentrated HCl. The resultant solution was stored during 24 h at 25 °C. Bipy (0.10 g, 0.64 mmol) was dissolved in 50 mL of water and added dropwise to the Mo-solution. White crystalline solid of **1** was immediately formed. Anal. calcd. (%) for $C_{40}H_{128}Mo_{36}N_8O_{156}$: C, 7.20; H, 1.93; N, 1.68; found (%): C, 8.60; H, 1.99; N, 1.89. IR (KBr, cm^{-1}): 3600–3200 (N^+–H), 1634–1620 and 1490 (C=C and C=N), 952–885, 852 (Mo=O, Mo–O–Mo).

¶ Crystal data for **1**: $C_{40}H_{128}Mo_{36}N_8O_{156}$, M = 6671.204, monoclinic, space group $P2_1/n$, a = 18.756 (4), b = 22.961 (7), c = 19.810 (5) Å, β = 106.87 (1)°, U = 8164 (3) Å^3, Z = 2, T = 293(2) K, μ = 2.786 mm^{-1}, D_c = 2.693 g cm^{-3}, 14887 refl. measured, 9329 with $I > 2\sigma(I)$, $R1$ = 0.059, R_W = 0.1432. Data reduction and refinement were carried out with teXsan and SHELXTL-PLUS, respectively.[12] CCDC 249299. See http://www.rsc.org/suppdata/cc/b4/b413825b/ for crystallographic data in .cif or other electronic format.

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