ChemComm

Hydrothermal synthesis and crystal structures of two novel hybrid open-frameworks and a two-dimensional network based on tungsten(VI) oxides

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Received (in Cambridge, UK) 3rd July 2000, Accepted 13th September 2000
First published as an Advance Article on the web

Three new tungsten(VI) oxide hybrid materials, [$WO_3(pyz)_{0.5}$] (pyz = pyrazine) 1, [$WO_3(bpy)_{0.5}$] (bpy = 4,4′-bipyridyl) 2 and [$W_3O_{10}(enH_2)$] 3, have been hydrothermally synthesized: 1 and 2 exhibit covalent/coordination hybrid framework connectivities while the structure of 3 consists of novel layers comprised of distorted {WO_6} octahedra linked through edge- and corner-sharing interactions.

Crystal engineering of low-dimensional and porous materials is the main concern of many current research projects, owing to their potential applications in catalysis, sorption, separation and photochemistry.[1–6] Hydrothermal crystallization, in the presence of organic templating species, has been demonstrated to be a versatile technique for the synthesis of these kinds of materials.[4–6] Of significant importance is the ability of the organic molecules to influence profoundly the structure of synthesized products, and to direct their formation with particular structural and physical properties. The exquisite control over the detailed topology of the anionic framework that can be achieved by altering the steric and electronic properties of the template has been exploited to synthesize materials with an astonishingly diverse range of structural characteristics. In addition to silicon, aluminium and phosphorus,[6,7] a wide variety of other main group and transition metals such as Ga,[8] Mo,[9] V[10] and Fe[11] have been incorporated into the three-dimensional framework and two-dimensional network structures through hydrothermal synthesis in the presence of organic templating agents.

The chemistry of tungsten oxide clusters and their derivatives has been extensively studied owing to their unusual magnetic properties, potential medical uses derived from their antiviral and antibacterial activities, relevance in the design and development of new materials, proven roles in catalysis, and promise as catalysts for chemical transformations.[12] Although organic amines have been extensively used as templating or structure-directing agents in hydrothermal reactions, little work has been reported on their use in the hydrothermal synthesis of new tungsten oxides with the exception of [$H_3N(CH_2)_6NH_3]_4[W_{18}P_2O_{62}]\cdot H_2O$[13] and a few Keggin species.[14] Here, we report the hydrothermal synthesis and structural characterization of three novel tungsten(VI) oxide hybrid materials: [$WO_3(pyz)_{0.5}$] **1**, [$WO_3(bpy)_{0.5}$] **2** and [$W_3O_{10}(enH_2)$] **3**.

Compounds **1–3** were prepared from hydrothermal mixtures of $Na_2WO_4\cdot 2H_2O$, $MCl_2\cdot nH_2O$ (M = Cu, Zn), organoamines and H_2O, heated to 140–160 °C for 120–264 h.‡ Crystal structures were solved from the data collected using a Siemens P4 X-ray diffractometer.§ The IR spectra of **1–3** exhibited strong bands in the range 910–960 cm^{-1} attributed to ν(W=O). Thermogravimetric analysis indicated weight losses corresponding to the loss of ligands.¶

The structure of [$WO_3(pyz)_{0.5}$] **1** consists of layers of corner-sharing {WO_5N} octahedra parallel to the *ab*-plane linked through pyz molecules into a 3-D tungsten oxide/pyz framework [Fig. 1(a)]. The 3-D architecture of **1** can be described as an interwoven net of inorganic metal oxide layers and organic tethers. The tungsten oxide layers are stacked along the *c* axis in an ABAB… sequence. The connectivity between the tungsten oxide layers and pyz molecules results in one-dimensional rectangular channels along the *b* axis circumscribed by six {WO_5N} octahedra and two pyz molecules. The dimensions of the channels are *ca.* 7.7 × 5.2 Å. The coordination geometry at the W site is defined by one terminal oxo group, four bridging oxo groups and one pyz nitrogen donor with W–O bond lengths of 1.680(2), 4 × 1.8741(3) Å and W–N bond length of 2.440(3) Å. The significant lengthening in the W–N distance reflects the strong *trans* effects of the terminal oxo group.

Compound [$WO_3(bpy)_{0.5}$] **2** has a similar topology to compound **1**. As shown in Fig. 1(b), the structure of **2** consists of W/O/N layers, parallel to the *ab*-plane, of corner sharing {WO_5N} octahedra bridged through bpy ligands into a 3-D covalent/coordination hybrid framework. The connectivity between the tungsten oxide layers and bpy molecules results in one-dimensional rectangular channels along the [1 1 0] direction circumscribed by six {WO_5N} octahedra and two pyz molecules. The dimensions of the one-dimensional rectangular channels are *ca.* 11.9 × 5.2 Å. Each W site receives

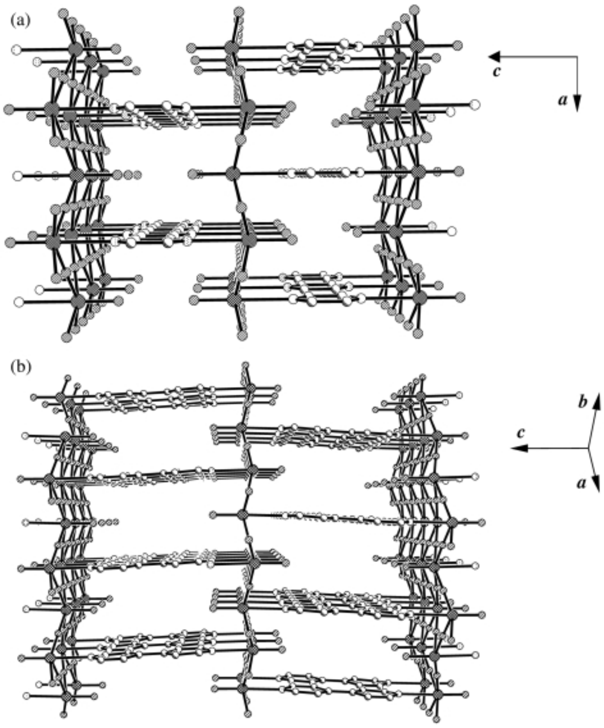

Fig. 1 (a) Crystal structure of [$WO_3(pyz)_{0.5}$] **1** viewed along the *b* axis. (b) Crystal structure of [$WO_3(bpy)_{0.5}$] **2** viewed along the [1 1 0] direction. Coordination of ligands (pyrazine or 4,4′-bipyridyl) to tungsten oxide layers results in a 3-D inorganic–organic framework with 1-D rectangular channels.

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DOI: 10.1039/b005303l

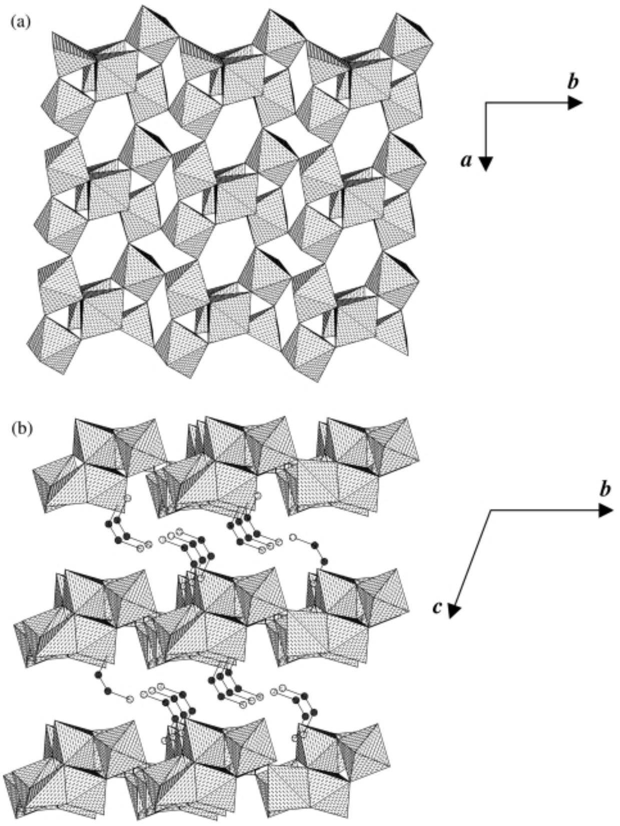

Fig. 2 (a) A polyhedral packing view of the $[W_3O_{10}]^{2-}$ layers of $[W_3O_{10}(enH_2)]$ **3** showing the puckered six-membered rings. (b) A polyhedral and ball-and-stick view of $[W_3O_{10}(enH_2)]$ **3.**

contributions from four bridging oxo groups, one terminal oxo group and one nitrogen donor with W–O bond lengths of 1.678(11), 2 × 1.8936(4), 1.851(13) and 1.897(12) Å, and W–N bond length of 2.409(14) Å.

The inorganic layers of compounds **1** and **2** are analogous to that of three-dimensional ReO_3-type WO_3 (r-WO_3).[15] However, the inorganic layers in r-WO_3 are connected through shared corners forming a three-dimensional structure whereas the tungsten oxide layers in compounds **1** and **2** are cross-linked by organodiamines through coordination bonds giving rise to their three-dimensional organic/inorganic hybrid structures. It is noteworthy that the synthesis conditions of compounds **1** and **2** differ from their molybdenum isostructures, $MoO_3(pyz)_{0.5}$ and $MoO_3(bpy)_{0.5}$.[16,17] It should also be noted that some carbon atoms in compounds **1** and **2** are disordered over two sites.

In contrast to the three-dimensional covalent/coordination hybrid frameworks of **1** and **2**, the structure of $[W_3O_{10}(enH_2)]$ **3** consists of $[W_3O_{10}]^{2-}$ layers [Fig. 2(a)], separated by interlamellar enH_2^{2+} cations [Fig. 2(b)]. The tungsten oxide layers contain infinite ribbons, two polyhedra thick, of edge- and corner-sharing $\{WO_6\}$ octehedra running parallel to the *b* axis. These infinite ribbons are connected by shared corners resulting in the layer structure of **3**. The $\{WO_6\}$ octohedra are distorted with W–O distances in the range 1.722(9)–2.307(7) Å. The layer structure of compound **3** exhibits a puckered six-membered ring circumscribed by six tungsten octahedra as shown in Fig. 2(a). Ethylenediamine cations are located between adjacent layers and are linked to the oxygen atoms of the tungstate units *via* hydrogen bonds.

It should be noted that the structure of anionic layer of compound **3** is quite different from that of $K_2W_3O_{10}$[18] although the tungstate anions in these two compounds have the same stoichiometry. The three-dimensional framework of $K_2W_3O_{10}$ consists of corner- and edge-sharing $\{WO_6\}$ octahedra. Moreover, the structures of known trimolybdates $[Mo_3O_{10}]^{2-}$ are composed of infinite chains of polymolybdate anions,[19,20] and the existence of a layered trimolybdate $[Mo_3O_{10}]^{2-}$ has not yet been reported. More interestingly, a one-dimensional example of compound **3** has also been isolated from hydrothermal media.[21]

The success in synthesizing compounds **1–3** provides innovative examples of the utility of the template-mediated hydrothermal method for the construction of versatile tungsten oxide hybrid solids. It further demonstrates the multifunctional roles of organoamines functioning as ligands bound to the tungsten oxide skeleton, as in compounds **1** and **2**, and as a simple counter ion in compound **3** in the cooperative assembly of organic/tungsten oxide hybrid materials. The current success opens up an exciting area of research in which the structural versatility of tungsten oxide materials can be evolved from the introduction of appropriate templates and optimization of reaction conditions.

Notes and references

‡ Hydrothermal reactions were carried out in sealed Teflon-lined stainless steel autoclave reactors. *Reaction conditions*: **1**: mol ratio $Na_2WO_4{\cdot}2H_2O : CuCl_2{\cdot}2H_2O : pyz : H_2O = 1.0:0.70:1.9:1096$, at 160 °C for 120 h; **2**: mol ratio $Na_2WO_4{\cdot}2H_2O : ZnCl_2 : bpy : H_2O = 1.0:0.2:0.6:539$, at 140 °C for 255 h; **3**: mol ratio $Na_2WO_4{\cdot}2H_2O : CuCl_2{\cdot}2H_2O : en : H_2O = 2.0:1.0:1.2:1110$, at 160 °C for 264 h.

§ *Crystal data*: $[WO_3(pyz)_{0.5}]$ **1**: $C_{0.25}H_{0.25}W_{0.125}N_{0.125}O_{0.375}$, $M_w = 33.959$, tetragonal, space group $I4/mmm$, $a = 5.2288(7)$, $c = 14.175(3)$ Å, $V = 387.55(10)$ Å^3, $Z = 32$, $D_c = 4.660$ g cm^{-3}, $\mu = 29.664$ mm^{-1}, $T = 296$ K, yellow plate, crystal size *ca.* 0.12 × 0.08 × 0.04 mm, $R_1/wR_2 = 0.0302/0.0802$ ($R_1/wR_2 = 0.0314/0.0805$ for all data). $[WO_3(bpy)_{0.5}]$ **2**: $C_5H_4W_1N_1O_3$, $M_w = 309.94$, orthorhombic, space group $Cmca$, $a = 7.4733(15)$, $b = 7.3927(15)$, $c = 22.570(4)$ Å, $V = 1246.9(4)$ Å^3, $Z = 16$, $D_c = 3.302$ g cm^{-3}, $\mu = 18.462$ mm^{-1}, $T = 296$ K, yellow plate, crystal size *ca.* 0.10 × 0.09 × 0.04 mm, $R_1/wR_2 = 0.0336/0.0776$ ($R_1/wR_2 = 0.0441/0.0809$ for all data). $[W_3O_{10}(enH_2)]$ **3**: $C_2H_{10}W_3N_2O_{10}$, $M_w = 773.67$, triclinic, space group $P\bar{1}$, $a = 7.343(2)$, $b = 7.373(3)$, $c = 9.889(3)$ Å, $\alpha = 93.99(2)$, $\beta = 109.714(16)$, $\gamma = 91.23(2)°$, $V = 502.2(3)$ Å^3, $Z = 2$, $D_c = 5.116$ g cm^{-3}, $\mu = 34.326$ mm^{-1}, $T = 296$ K, colorless plate, crystal size *ca.* 0.25 × 0.20 × 0.08 mm, $R_1/wR_2 = 0.0403/0.0970$ ($R_1/wR_2 = 0.0502/0.1021$ for all data).

CCDC 182/1777. See http://www.rsc.org/suppdata/cc/b0/b005303l/ for crystallographic files in .cif format.

¶ *TGA data*: weight loss for **1**: 14.35% (calc. 14.76%, 507–576 °C); **2**: 25.20% (calc. 25.24%, 498–572 °C); **3**: 8.08% (calc. 8.03%, 342–392 °C).

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