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A novel polycatenated double-layered hybrid organic–inorganic material constructed from $[Zn_2(tp)(4,4'\text{-bpy})]_n^{2n+}$ layers and $V_4O_{12}^{4-}$ pillars

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A novel double-layered hybrid organic–inorganic material $[Zn_2(tp)(4,4'\text{-bpy})V_2O_6]$ has been prepared hydrothermally and X-ray crystallographic analysis shows that it has a three-dimensional network constructed from polycatenated tetravanadate-pillared double-layered sheets.

In addition to intriguing electronic, magnetic, and optical properties, their robustness and stability have made inorganic frameworks highly attractive in the search for new materials.[1] Meanwhile organic and co-ordination compounds built upon molecular building-blocks hold great promise for processability, flexibility, structural diversity, and geometrical control of properties such as the size, shape, and symmetry.[2] Incorporation of inorganic and organic counterparts into a single structure may generate a hybrid composite that enhances or combines the useful properties of the two.[3] One subclass of organic–inorganic hybrid materials is characterised by vanadium oxides or polyanionic clusters covalently co-ordinated to transition metal complexes or fragments. Though many organic–inorganic vanadium oxides containing complexes with discrete cluster-like and polymeric structures have been prepared, the organic ligands in most of these complexes are limited to organoamine ligands.[4] To our knowledge, organic–inorganic materials containing dicarboxylate ligands and vanadium oxides are rare,[5a,b] no complex containing mixed organoamine and dicarboxylate ligands has been reported. This may be attributed to the incorporation of dicarboxylate into the system giving rise to more negative charges and making the charge balance more difficult. Recently, we and others have successfully prepared some co-ordination polymers constructed from zinc cluster cores in the presence of both neutral and anionic carboxylate ligands.[6] This fact encouraged us to prepare $[Zn_2(tp)(4,4'\text{-bpy})V_2O_6]$ (**1**) (tp = terephthalate, 4,4′-bpy = 4,4′-bipyridine), which is a tetravanadate-pillared double-layered hybrid organic–inorganic material.

A mixture of NH_4VO_3 (0.117 g), $Zn(MeCO_2)_2\cdot H_2O$ (0.220 g), tp (0.166 g), NaOH (0.080 g), 4,4′-bpy (0.158 g) and water (10 ml) in a mole ratio 1 : 1 : 1 : 2 : 1 : 550 was stirred for 20 min in air, then transferred and sealed in a 23 ml Teflon-lined stainless steel container, which was heated to 180 °C and held at that temperature for 7 days. Pale-yellow block crystals of **1** were recovered as a single phase in 60% yield based on vanadium. Complex **1** is insoluble in water and common organic solvents. The elemental analysis and IR spectra † confirmed the formula of **1**. The thermogravimetric analysis (TGA) performed on polycrystalline samples indicated **1** is thermally stable up to 410 °C under dinitrogen, in accord with the fact that organic–inorganic hybrid products are usually stable.

Single-crystal X-ray analysis ‡ has revealed that **1** consists of tetravanadate-pillared double-layered sheets constructed from polymeric cationic $[Zn_2(tp)(4,4'\text{-bpy})]_n^{2n+}$ layers and tetravanadate $V_4O_{12}^{4-}$ molecular pillars. There are two zinc atoms and two vanadium atoms crystallographically independent in an asymmetrical unit, as shown in Fig. 1. The two zinc atoms have very similar co-ordination environments and each is co-ordinated in a tetrahedral geometry by one 4,4′-bpy nitrogen atom, one $V_4O_{12}^{4-}$ oxygen atom and two oxygen atoms from two tp ligands. The average Zn–O and Zn–N bond lengths are 1.95 and 2.03 Å, respectively, which are close to typical Zn–O and Zn–N distances.[7] The tp ligand acting in a bis-bidentate mode, as found in [Zn(tp)(4,4′-bpy)] and other related complexes,[7,8] bridges four zinc atoms. The $V_4O_{12}^{4-}$ cluster in the μ_4 mode, as reported in $[\{Co(3,3'\text{-bpy})_2\}_2V_4O_{12}]$ **2** and $[H_2pn][Mn(C_2O_4)(V_4O_{12})]$ **3** (pn = propane-1,3-diamine),[5b,c] is co-ordinated to four zinc atoms *via* four terminal oxygen atoms. However, the distances between a pair of adjacent M atoms [M = Zn(II), Co(II) or Mn(II)] at one side of the $V_4O_{12}^{4-}$ cluster in the three compounds are significantly different owing to the different steric conformation of the $V_4O_{12}^{4-}$ clusters. The much shorter Zn · · · Zn distance (3.26 Å) in **1** compared to the corresponding M · · · M distances in both **2** and **3** may also be attributed to the additional consolidation of the two zinc atoms by a bridging μ-carboxylate from tp. The V–O–V angles of 124.7(2) and 151.2(3)° are close to those of $[\{Zn(phen)\}_2V_4O_{12}]$, indicating that the $V_4O_{12}^{4-}$ cluster is in a chair-like configuration.[4b]

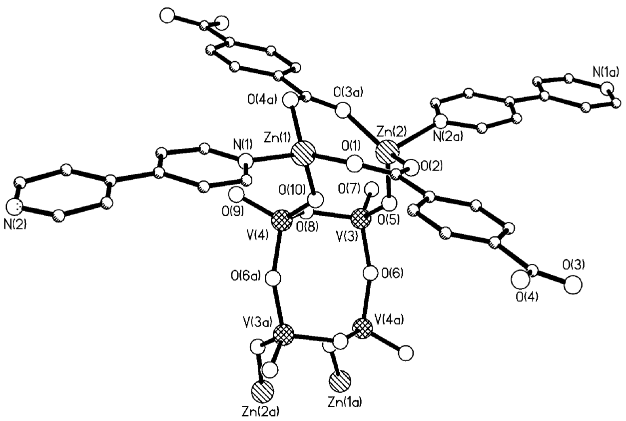


Fig. 1 The co-ordination environments of the zinc and vanadium atoms in **1**. Selected bond distances (Å) and bond angles (°): Zn(1)–O 1.950(3)–1.966(3), Zn(2)–O 1.955(3)–1.964(3), Zn(1)–N(1) 2.005(4), Zn(2)–N(2a) 2.071(4), V(3)–O 1.611(3)–1.818(3), V(4)–O 1.608(3)–1.800(3); O–Zn(1)–O 101.2(1)–129.2(2), O–Zn(2)–O 110.5(2)–132.5(2), O–V(3)–O 106.6(2)–111.0(2), O–V(4)–O 108.8(2)–110.5(2). Symmetry codes: (*a*) *x*, *y*, *z*; (*b*) −*x*, −*y*, −*z*.

It is interesting that the mixed organic tp and 4,4′-bpy bridges interlink the zinc dimers to generate a cationic rectangular grid $[Zn_2(tp)(4,4'\text{-bpy})]_n^{2n+}$, as shown in Fig. 2. Each pair of such cationic layers are then pillared face-to-face

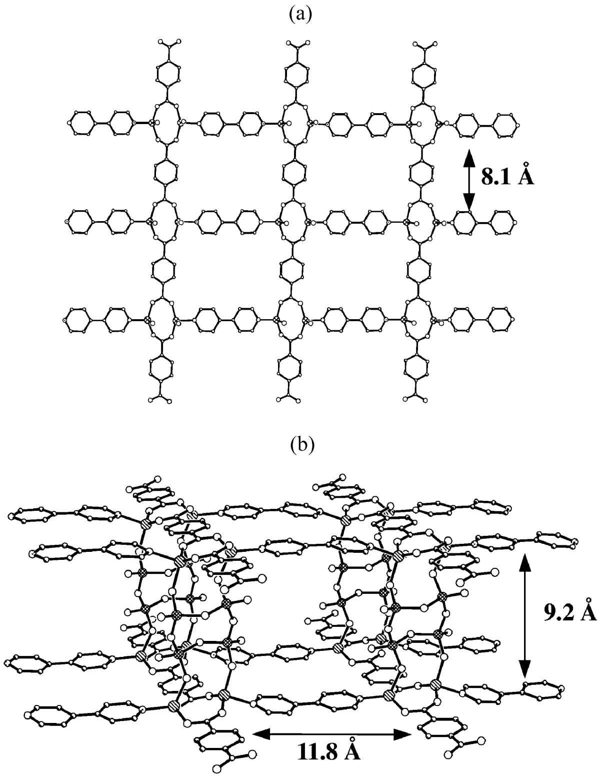
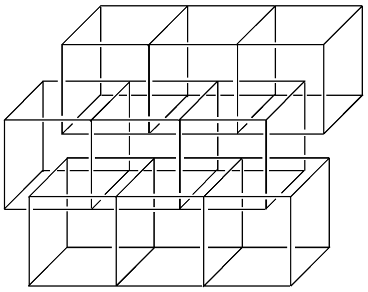


Fig. 2 Perspective view of the two-dimensional $[Zn_2(tp)(4,4'\text{-bpy})]_n^{2n+}$ cationic monolayer (a) and neutral double layer (b) in **1**.

by the $V_4O_{12}^{4-}$ clusters as a third kind of bridge, and form a pillared double-layered sheet; the two cationic layers are aligned in a slightly offset fashion due to the chair-like configuration of the $V_4O_{12}^{4-}$ pillars. Among the hybrid organic–inorganic materials, complex **1** represents the first example containing mixed organic ligands and the $V_4O_{12}^{4-}$ species as molecular pillars. Due to the negative charges on the $V_4O_{12}^{4-}$ species, the incorporation of dicarboxylate ligands into the system is very difficult, and the presence of 4,4′-bpy ligands and zinc atoms provides the possibility of charge compensation, resulting in the formation of the hybrid organic–inorganic material **1**.

Within the pillared double-layered sheet, there are three directional channels of sizes *ca.* 11.8 × 8.1, 11.8 × 9.2 and 9.2 × 8.1 Å, respectively. More interestingly, the pillared double-layered sheets of **1** are polycatenated, and extended into a three-dimensional structure, as shown in Scheme 1. Each double-layered sheet is bicatenated in a parallel fashion by two other double-layered sheets that pass through the channels of the first sheet. As far as we know, no pillared double-layered sheets extended into a three-dimensional structure *via* polycatenation have been documented.



Scheme 1 Schematic representation of the polycatenation in **1**.

In summary, we have prepared the first hybrid organic–inorganic material containing vanadium oxides and mixed ligands, which shows an interesting double-layer structure and polycatenation. The preparation of **1** further emphasises that the organic–inorganic hybrid products may increase or combine the useful properties of the constituent organic and inorganic components. The thermal stability of **1** up to 410 °C is unattainable for common organic components and the double-layered sheets with interlayer pillars are also difficult to construct using only inorganic building units. The successful design and synthesis of **1** containing mixed organoamine and dicarboxylate ligands may suggest a new route to the synthesis of novel hybrid organic–inorganic materials.

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Notes and references

† Anal. calc. for $C_{18}H_{12}N_2O_{10}V_2Zn_2$ **1**: C, 33.31; H, 1.86; N, 4.32%. Found: C, 32.96; H, 1.97; N, 4.53%. IR (KBr, cm^{-1}) for **1**: 3421m, 3009w, 1592s, 1541m, 1416s, 1388s, 1217m, 1071m, 972s, 915s, 887s, 839s, 743s, 645m, 560s.

‡ Crystal data for **1**: $C_{18}H_{12}N_2O_{10}V_2Zn_2$, $M_r = 648.92$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.537(6)$, $b = 10.760(6)$, $c = 11.272(8)$ Å, $\alpha = 80.66(1)$, $\beta = 63.27(2)$, $\gamma = 63.86(1)°$, $V = 1023.7(11)$ Å^3, $Z = 2$, $D_c = 1.860$ g cm^{-3}, $\mu = 3.263$ cm^{-1}. Data collection ($2 \le \theta \le 30°$) was performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS-97)[9] and refined using a full-matrix least-squares technique (SHELXL-97),[10] giving a final $R1$ value of 0.0473 for 308 parameters and 3759 unique reflections with $I \ge 2\sigma(I)$ and $wR2$ of 0.1316 for all 4916 reflections. CCDC reference number 155435. See http://www.rsc.org/suppdata/dt/b1/b100067p/ for crystallographic data in CIF or other electronic format.

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