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# An unprecedented 2-D rhombic molecular grid with a triangular cavity and a $V_4O_6$ cluster as the corner unit

**Ren-Gen Xiong,**[a] **Yong-Rong Xie,**[a] **Xiao-Zeng You** *[a] **and Chi-Ming Che**[b]

[a] *Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: xyz@netra.nju.edu.cn; Fax: 86 25 3317761 or 86 25 3314502*

[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

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**The reaction of $V_2O_5$ with isonicotinic acid (PYCOOH) affords a 2-D rhombic network, $V_4O_6(H_2O)_4(PYCOO)_4$ 1 with a triangular cavity and a $V_4O_6$ cluster as the corner unit.**

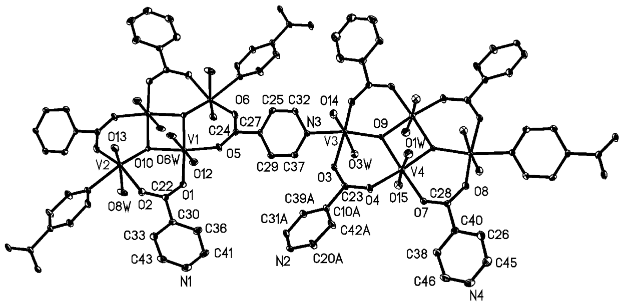

**Fig. 1** An asymmetric unit of **1** (thermal ellipsoids are drawn at the 30% probability level). Selected bond lengths (Å) and angles (°): V(1)–O(12) 1.591(4), V(1)–O(10) 1.931(3), V(1)–O(5) 2.056(4), V(1)–O(1) 2.059(4), V(1)–O(6W) 2.397(6), V(2)–O(13) 1.571(4), V(2)–O(8W) 2.198(5), V(2)–N(2B) 2.174(4), V(2)–O(2) 2.016(4), V(2)–O(10) 1.906(3), V(3)–O(14) 1.582(4), V(3)–O(9) 1.909(3), V(3)–O(3) 1.990(4), V(3)–N(3) 2.171(4), V(3)–O(3W) 2.266(5), V(4)–O(1W) 2.333(5), V(4)–O(15) 1.584(5), V(4)–O(4) 2.059(4), V(4)–O(7) 2.052(4), V(4)–O(9) 1.938(3); O(1)–V(1)–O(5) 82.07(15), O(1)–V(1)–O(10) 94.62(14), O(5)–V(1)–O(10) 159.37(17), O(12)–V(1)–O(6W) 173.5(2), O(12)–V(1)–O(10) 102.93(19), O(1)–V(1)–O(12) 94.44(18), O(5)–V(1)–O(12) 97.6(2), O(2)–V(2)–O(10) 94.94(16), O(13)–V(2)–O(10) 103.86(18), O(13)–V(2)–O(2) 96.0(2), O(13)–V(2)–O(8W) 169.84(19), O(2)–V(2)–N(2B) 84.00(16), N(3)–V(3)–O(3) 84.08(15), N(3)–V(3)–O(9) 161.95(17), O(3)–V(3)–O(9) 92.53(19), O(14)–V(3)–O(3) 98.02(19), O(14)–V(3)–O(9) 104.47(19), O(14)–V(3)–N(3) 93.56(19), O(14)–V(3)–O(3W) 171.58(19), O(4)–V(4)–O(7) 82.56(16), O(4)–V(4)–O(9) 91.76(15), O(7)–V(4)–O(9) 162.69(17), O(1W)–V(4)–O(15) 169.8(2), O(15)–V(4)–O(4) 95.7(2), O(15)–V(4)–O(7) 92.7(2), O(15)–V(4)–O(9) 104.16(19).

The search for molecular construction motifs, such as squares, rhomboids or metal-macrocycles has been largely driven by the desire to perform catalysis,[1] host–guest chemistry,[2] enantioselective separation,[3] non-linear optical material inclusions[4] and to prepare fluorescent molecular structures or sensors.[5,6] In comparison with rectangular assemblies there have been relatively few reports on triangular metallomacrocycles.[7] Furthermore, there are a lot of structural motifs such as squares, rectangles and honeycombs *etc.* formed through inter- or intra-molecular interactions involving hydrogen-bonding and π–π stacking interactions, other than coordinate covalent interactions.[8] This is especially true for complexes with rigid building blocks, a class of compounds that was very successfully employed for the construction of other shaped assemblies, such as squares, rectangles and honeycombs. A possible explanation, as suggested by Stang *et al.*, is the fact that the required 60° turning angle is quite uncommon in transition metal chemistry.[4] On the other hand, most such structures are based on mononuclear or multinuclear metal ions which act as corner units.[5,6] Motifs containing cluster units, as far as we are aware, are relatively rare.[9] Now, we have used a tridentate anion, $PYCOO^-$ (4-pyridinecarboxylic acid, PYCOOH) as the bridging ligand in a reaction with $V_2O_5$ under hydrothermal conditions to construct a novel two-dimensional, neutral rhombic grid with a $V_4O_6$ cluster as the corner unit, $V_4O_6(H_2O)_4(PYCOO)_4$ **1** in which each rhomb is bisected into two triangles by the diagonal of two $PYCOO^-$ ligands through π–π stacking interactions.

To the best of our knowledge, multi-dimensional coordination polymers with a triangular cavity and a cluster as the corner unit remain unknown although there are two unique examples of 2-D Cu–*N*,*N*′-(2-pyridyl)(4-pyridylmethyl)amine having a chiral triangular cavity and 3-D metal–4,4′-bipyridine (4,4′-bpy) molecular networks having triangular channels that are sustained by 4,4′-bpy spontaneously through both hydrogen-bonding and π–π stacking interactions.[10] Here we present the synthesis, crystal structure and magnetic properties of **1**.

Complex **1** was synthesized by hydrothermal reaction between $V_2O_5$ and PYCOOH.† The presence of the carboxylate group in **1** was confirmed by the very strong peaks at 1606, 1553, 1421 $cm^{-1}$, respectively, in the IR spectrum. A peak at 3423 $cm^{-1}$ indicates there may be coordinated water molecules persisting in **1**. This observation was further confirmed by thermogravimetric analysis (TGA) which was performed on the polycrystalline sample, indicating that one strikingly clean weight loss step occurred at 158 °C (8.11% loss), corresponding to the removal of four water molecules per formula unit (8.37% calculated). The dehydrated framework is stable between 177 and *ca.* 360 °C, decomposing beyond 360 °C. EPR results also show that the V atom oxidation state in **1** is +4.

The two-dimensional polymeric structure of **1** was revealed by a single crystal X-ray diffraction study.‡ The asymmetric unit contains two crystallographically unique $[VO(H_2O)]_2(O)$ units which share the same coordination modes around the V center in polymer **1** (see Fig. 1). Each V atom is six-coordinated and displays a slightly distorted octahedron in which two V atoms are bridged by a $\mu_3$-oxo and a μ-carboxylate of the isonicotinate. The remaining coordination position of the $\mu_3$-oxo group connects another V atom to form a $[(VO)_4(\mu_3\text{-}O)_2]$ tetranuclear cluster. Two apical positions around each V center are occupied by a terminal oxo and water molecule. It is interesting to note that the axial water molecule on the adjacent two V atoms has an opposite direction towards their defined plane [O(2)V(2)O(6B)N(2B)O(10) (0.0946 Å deviation from an ideal plane) for V(1); O(1)O(5)V(1)O(10)O(10B) (0.1001 Å) for V(2); N(3)O(8A)O(3)O(9)V(3) (0.0938 Å) for V(3); O(4)O(7)V(4)O(9)O(9A) (0.0962 Å) for V(4)]. Furthermore, there are two types of $PYCOO^-$ ligand, tridentate and bidentate. It is noteworthy that the two bidentate $PYCOO^-$ ligands bisect each rhombic net. Due to the diagonal of the rhomb in each net being longer than any sides of rhomb, two $PYCOO^-$

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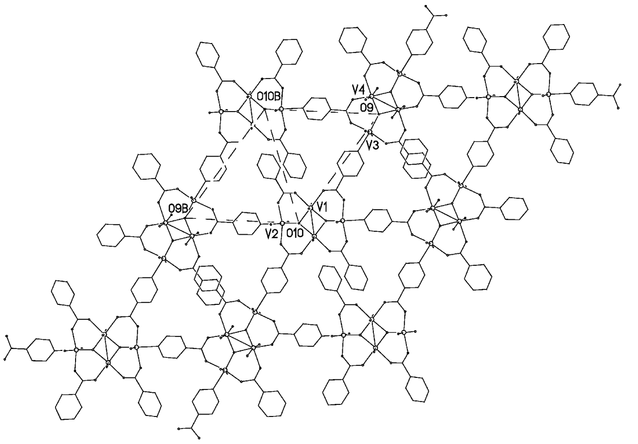

**Fig. 2** An extended 2-D network showing that there are two triangles [△O(9)O(10)O(10B) and △O(10)O(9B)O(10B)] in each rhomb of **1**.

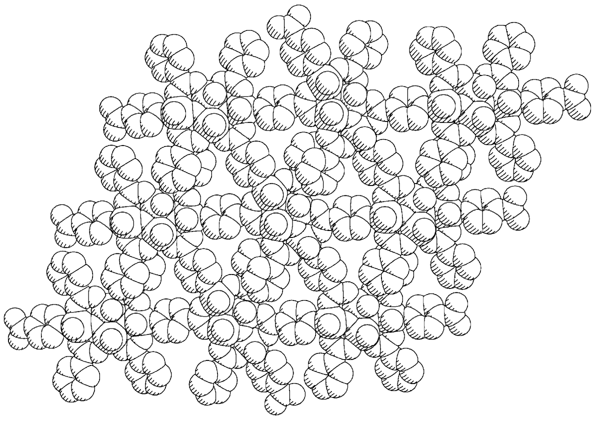

**Fig. 3** A space-filling representation of **1** clearly showing the formation of a triangular cavity.

ligands are needed to connect two V atoms on the end of a diagonal so that two PYCOO$^-$ ligands have to connect together by means of strong π–π stacking interactions of the pyridyl rings (about 3.28 Å) to form a diagonal. As a result, it can be considered that each rhomb net contains two triangles [△O(9)O(10)O(10B) and △O(10)O(9B)O(10B), as shown in Fig. 2] while each corner unit consists of a VO(V–V)OV tetranuclear cluster which is similar to that found in $\{([Me_2Sn(va)_{0.5}]_2O)_2{\cdot}2H_2O\}_n$ with an $Sn_4O_2$ cluster as the node[9c] (va = vanillic acid, 4-hydroxy-3-methoxybenzoic acid) but different from that found in $[(Zn_4O)(isophthalato)_3(4,4'\text{-bpy})_4]_n$ with a tetranuclear Zn core as the node.[9d] Thus, to the best of our knowledge, **1** represents the first example of a 2-D rhombic grid containing a triangular cavity and a tetranuclear cluster as the corner unit in the supramolecular motif. Moreover, each triangular area can be considered as being composed of O(9B)O(10)O(10B) with three different length sides of 11.317, 11.358 and 12.550 Å. Fig. 3 also clearly shows that there are two triangular cavities in each rhomb net of **1**. On the other hand, the two connecting $\mu_3$-oxo V atoms show a somewhat weak V–V interaction (2.829 Å). Clearly, the bond distance of V–O (terminal oxo) (1.591 Å) is much shorter than that of V–O-($\mu_3$-oxo) (1.931–1.933 Å). Thus, there is an order of V–O bond lengths in **1**, such that $V–O_{water}$ (2.397 Å) > $V–O_{carboxylate}$ (2.056–2.059 Å) > V–O-$\mu_3$ > $V–O_{terminal}$. There are no exceptional bond lengths found for C–N, C–O and V–O(water) in **1**.

The magnetic susceptibility data also support the V atom in **1** as being +4, with an average magnetic moment of 2.23 $\mu_B$ which is indicative of there being only one spin-electron in $V^{4+}$ ($4s^03d^1$). The effective magnetic moment per vanadium ion in **1** varies gradually from 2.23 $\mu_B$ at 300 K down to 2.11 $\mu_B$ at 78 K, indicative of a weak antiferromagnetic interaction between the metal ions (Curie–Weiss behavior, Curie temperature $\theta = -2.3$ K). This behavior is similar to that found in many V complexes.[11]

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## Notes and references

† Preparation of compound **1**: hydrothermal treatment of $V_2O_5$ (1 mmol) and isonicotinic acid (4 mmol) for three days at 130 °C afforded a brown prismatic crystalline product. The yield of **1** was 40% based on $V_2O_5$ (Found: C, 33.71; H, 2.71; N, 6.81. Calc.: C, 33.51; H, 2.81; N, 6.51%). IR (KBr, $cm^{-1}$): 3423w, 3000vw, 1606vs, 1553vs, 1421vs, 1234w, 1057w, 1027w, 962m, 858w, 769m, 675m, 577vw, 490w.

‡ Crystal data for **1**: $C_{24}H_{24}N_4O_{18}V_4$, triclinic, $P\bar{1}$ (no. 2), $a = 7.236(4)$, $b = 12.550(7)$, $c = 16.764(10)$ Å, $\alpha = 97.566(11)$, $\beta = 97.065$, $\gamma = 99.265(12)°$, $V = 1473.2(15)$ Å$^3$, $Z = 2$, $M = 860.23$, $D_c = 1.939$ Mg m$^{-3}$, $R_1 = 0.0548$, $wR_2 = 0.1652$ (5182 reflections), $T = 293$ K, $\mu = 1.324$ mm$^{-1}$, $S = 0.771$. CCDC reference number 155145. See http://www.rsc.org/suppdata/dt/b0/b010231h/ for crystallographic data in CIF or other electronic format.

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