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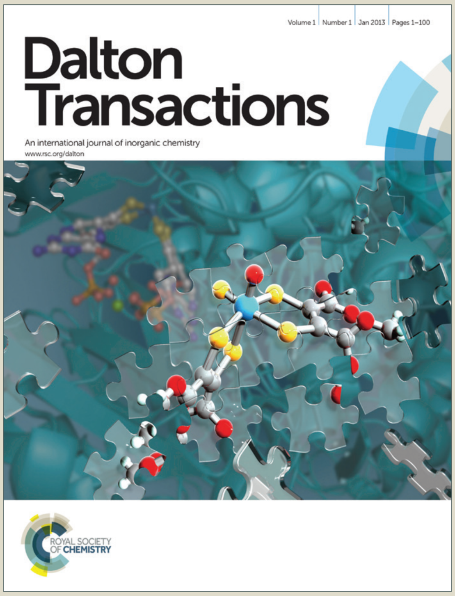

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Cite this: DOI: 10.1039/x0xx00000x

Layered V-B-O Polyoxometalate Nets Linked by Diethylenetriamine Complexes with Dangling Amine Groups

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Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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Two layered V-B-O contained polyoxometalate (POM) net structures, denoted as SUT-12 and SUT-13, are reported here. SUT-12 was synthesized by the boric acid flux method, and it represents the first 2D structure constructed from the V_6B_{20} vanadoborate cluster. SUT-13 was synthesized through the hydrothermal method and constructed from $V_{12}B_6P_{12}$ vanadium borophosphate clusters. In both structures, the vanadoborate or vanadium borophosphate clusters were linked through in-situ formed $Zn(DETA)_2$ or $Cu(DETA)_2$ complexes. Surprisingly, for all DETA molecules in the two metal complexes, there is one dangling amine group when it coordinated to the metal. The phenomena of the dangling amine group feature is abnormal and the $Cu(DETA)_2$ complexes in SUT-13 was taken as an example and studied by the density function theory (DFT) calculation in order to understand this unusual feature.

Diethylenetriamine (DETA) is a very important organic amine, which has been used as a template for the synthesis of many inorganic or organic-inorganic hybrid open framework materials. For instance, in the open framework germanate system, DETA can direct the formation of SU-16[1], FJ-17[2], SU-46[3], SU-22, SU-23[4], FJ-3[5], LMN[6]. In the zinc phosphate system, Chang et al.[7] performed the experiments showed that when varying the zinc source, temperature and solvents, DETA can direct the formation of various open framework zinc phosphate structures with different channel dimensionality and compositions. On the other hand, DETA can also be used as a coordination reagent, which can be coordinated to transition metals to form metal complexes. These metal complexes can also be worked as templates, like in FJ-1a[8], FJ-6[9], JU-85[10], UT-6, AlPO-5 and AlPO-34[11]. In few cases, the metal complexes can act as linkers to connect other structure building units to form open frameworks, and it is believed that the connectivity of the specific building units could be richer. A typical example is in FJ-14, Lin et al[12] used $Ni_2(DETA)_2$ as a linker to construct a 16-ring open framework nickel-zinc phosphate material.

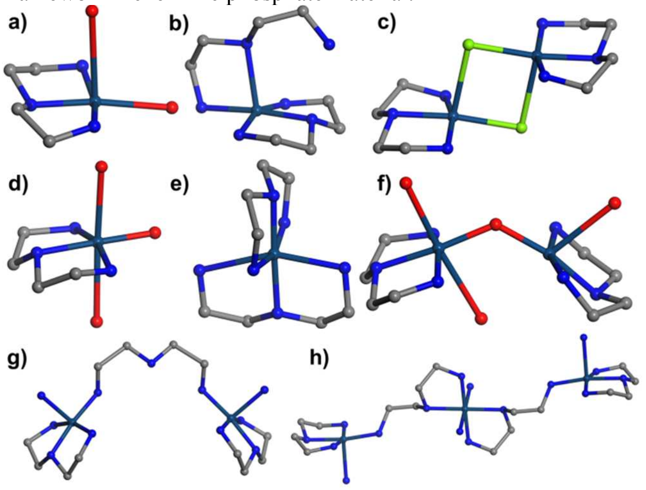

Fig. 1 Different configurations of Cu-DETA complexes. Colour scheme for different elements: red, oxygen; light green, chlorine; grey, carbon; blue, nitrogen; dark blue, copper. The hydrogen atoms are omitted for clarification.

The fruitful chemistry of DETA attracted a lot of attention and had been studied extensively from both experimental and modeling chemistry point of view during the past decades[13–15]. The attractive effect of DETA was also proved by the DETA contained structures recorded in the CCDC (Cambridge Crystallographic Data Centre) database, where there are more than 900 structures reported with DETA involved, either as templates, counter ions or coordination amines. The configuration of the DETA in metal complexes plays a crucial role in the connectivity of the resulted structures. As reported in the database, DETA can be coordinated to lots of metals from the main group till rare earth, such as Ba, In, Ga, In, Cu, Zn, Pt, Au, Ni, Co, La, Ce, Y, etc. With any specific metal, the stereochemistry of DETA in the metal complexes also varies in the solid state. Taking Cu-DETA complexes as an example, the copper can be coordinated

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Electronic Supplementary Information (ESI) available: Synthetic methods, characterization details, X-ray crystallographic files in CIF format, IR spectra, Powder X-ray patterns, and other structure figures. See DOI: 10.1039/c000000x/

in the square pyramid configuration with three nitrogen atoms from DETA coordinated to Cu as shown in Fig. 1a, 1b and 1c; DETA can also coordinate to copper with all three nitrogen atoms to form an octahedral configuration copper; in some cases, the DETA can be coordinated to two copper atoms as shown in Fig. 1g and 1h. But it is rare that the DETA molecules coordinated to the copper atoms with two nitrogen atoms leaving the last one nitrogen uncoordinated as shown in Fig. 1b. Actually, since the copper or zinc atoms can be coordinated with other atoms in a range of 4-6 coordination, it would be interesting to understand why it is so uncommon for the polyamines with one dangling amine group. And it is also expected that when the dangling amine group involved metal complexes are hybrid in the microporous materials, the resulted crystalline microporous materials may enhance their performance in applications such as CO_2 capture, heavy metal removal, because the amine group can form strong chemical bonds with CO_2 or heavy metal ions as discovered in other types of amine group modified materials like MOFs, mesoporous silica [16–18].

Vanadoborates or vanadium borophosphates are typical cluster-based compounds, which are composed of vanadium-oxo pyramid together with boron-oxo triangles/tetrahedra. Depending on different templates and synthesis conditions, the resulted vanadoborates and vanadium borophosphates can have several different types of clusters as the building units. In most of the vanadoborates, the clusters are closed as cage-like clusters, such as $V_{12}B_{16}$[19], $V_{12}B_{17}$, $V_{12}B_{18}$[20], $V_{10}B_{28}$[21], V_6B_{20}[22], as summarized in our previous paper[20,23], except the rare ring-like $V_{12}B_{32}$ cluster[24]. Compared to the cage-like clusters in vanadoborates, vanadium borophosphates are more likely to form ring-like clusters[25–28] although the sheet-like[29,30] and cage-like[31–33] clusters in vanadium borophosphates were also reported. They can form open 8-rings and 12-rings with various B:P:V ratios under different experimental conditions. With different types of rings, a lot of zero- and one-dimensional vanadium borophosphates have been reported. In a few cases, like in Cu-VBPO1 and Cu-VBPO2[28], the metal-organic complex such as $Cu(NH_2CH_2CH_2NH_2)_2$ worked as linkers to connect the 12-ring vanadium borophosphate clusters to form a 2D network. In Cu-VBPO1, all nitrogen atoms from ethylenediamine molecules are coordinated to the copper atoms, and the $Cu(NH_2CH_2CH_2NH_2)_2$ complex is disordered into two different positions. Here, we used boric acid flux and hydrothermal methods separately in different systems to synthesize one $Zn(DETA)_2$-linked layered vanadoborates and one $Cu(DETA)_2$-linked layered vanadium borophosphate, where all DETA molecules are coordinated to the metal ions with dangling amine groups exposed to the channel.

SUT-12 crystallized in the space group *P*-1, with a =11.865 Å, b = 13.231 Å, c =13.288 Å, α = 61.735˚, β = 79.118˚, γ = 65.680˚. The structure is constructed from V_6B_{20} clusters (Fig. 2a) linked by $Zn[NH(CH_2CH_2NH_2)_2]_2$ complexes (Fig. 2b). The V_6B_{20} cluster was discovered decades ago with four different 0D or 1D structures[22,34–36]. V_6B_{20} is composed of two raft-like polyborate ligands with the formula of $[B_{10}O_{16}H_3]$ layers sandwiching a V_6 ring. As stated in the literatures[22,36], this cluster can be obtained by both boric acid flux methods and hydrothermal synthesis. In SUT-12, the six V=O distances in the V_6B_{20} cluster range between 1.578 Å and 1.607 Å and the V-O distances in the basal of the square pyramid range from 1.935 Å to 1.959 Å. The valence calculation suggested a mixed valence of V^{4+} and V^{5+} in the six vanadium atoms with the average valence summation of 4.218. It was difficult to distinguish V^{4+} and V^{5+} for these six vanadium atoms due to the similar valence summations. The mixed valence of V in vanadoborates clusters is common and have been reported in a lot of types of vanadoborate clusters with different combination of VO_5 and BO_x (x=3 or 4) polyhedra[19–21,37,38]. Except SUT-12 in the synthesized product, there is also an impurity phase, VB-7 where isolated V_6B_{20} clusters are closely packed. The structure of VB-7 was determined by synchrotron radiation single crystal X-ray diffraction, and it crystallized in the space group C*2/c,* with the unit cell of a = 20.128 Å, b = 13.363 Å, c = 21.559 Å, β = 97.256˚.

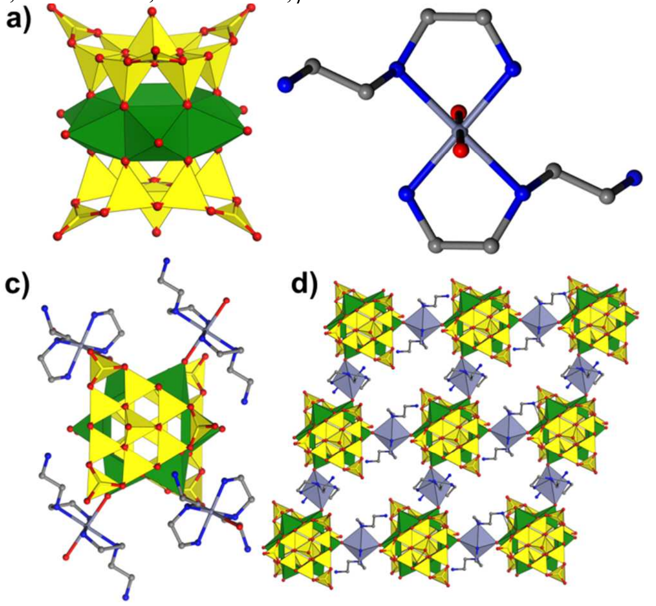

Fig. 2 The cluster and linker in SUT-12. a) V_6B_{20} cluster. b) $Zn(DETA)_2$ complex. c) V_6B_{20} cluster linked out through four zinc complexes. d) The 2D layered net in SUT-12. Colour scheme for different elements: red, oxygen; yellow, boron; grey, carbon; light grey, zinc; green, vanadium.

Previous reports showed that V_6B_{20} clusters were difficult to be connected into 2D or 3D structures although efforts have been taken[22]. Benefitted from the introducing of zinc and organic templates in our synthesis, the V_6B_{20} clusters was connected through four apical V1=O and V2=O bonds by $Zn[NH(CH_2CH_2NH_2)_2]_2$ complexes (Fig. 2c) to further form a tilted 2D square net as shown in Fig. 2d. As far as we know, this is the first 2D structure constructed from V_6B_{20} clusters. Moreover, in both diethylenetriamine molecules, the dangling side chain was observed, i.e. only two of the three nitrogen atoms in the diethylenetriamine ligand were coordinated to the zinc atom. This is further supported by IR spectrum that the original deformation and wagging oscillation of ν_d(NH) and $\nu_d(NH_2)$ of the amine groups at 1597 cm^{-1} and 1455 cm^{-1} (Fig. S1) were shifted and spitted into three peaks at 1607 cm^{-1}, 1520 cm^{-1} and 1476 cm^{-1} (Fig. S2).

Considering the similar coordination geometry of BO_4 and PO_4 polyhedra, it is worth introducing the PO_4 polyhedron into the vanadoborates. By including H_3PO_4 in the hydrothermal synthesis process, SUT-13 crystals were obtained. The obtained crystals of SUT-13 are dark blue and prism-like. Single-crystal X-ray diffraction shows that SUT-13 composes of $V_6B_6P_{12}O_{72}{}^{18-}$ ($V_{12}B_6P_{12}$) clusters (Fig. 3a) linked by $Cu(DETA)_2$ complexes (Fig.3b). The $V_{12}B_6P_{12}$ cluster in the -3 symmetry is constructed with six V_2O_8 dimers and six BP_2O_{10} trimmers located along the ring alternatively. V_2O_8 dimmers are formed by two edge-sharing square-pyramidal VO_5 polyhedra and the BP_2O_{10} units are constructed by two PO_4 tetrahedra and one BO_4 tetrahedron in a vertex-sharing mode. The $V_{12}B_6P_{12}$ cluster is further linked to six others by $Cu(DETA)_2$ complexes through V=O to form a 2D network as shown in Fig. 3c and 3d. In a single layer of SUT-13, two different types of 12-rings are formed: one is inside the

$V_{12}B_6P_{12}$ cluster while the other is between three $V_{12}B_6P_{12}$ clusters. The ring-like feature of the $V_{12}B_6P_{12}$ cluster different from the cage-like vanadoborate clusters, such as $V_{12}B_{16}$[19], $V_{12}B_{17}$, $V_{12}B_{18}$[20], $V_{10}B_{28}$[21], V_6B_{20}[22]. Considering the V_2O_8 dimmers as nodes, the BP_2O_{10} and $Cu(DETA)_2$ as edges, the single layer of SUT-13 can be topologically simplified as a graphene layer. The layers of SUT-13 stack along the *c*-axis following the *R*-lattice symmetry.

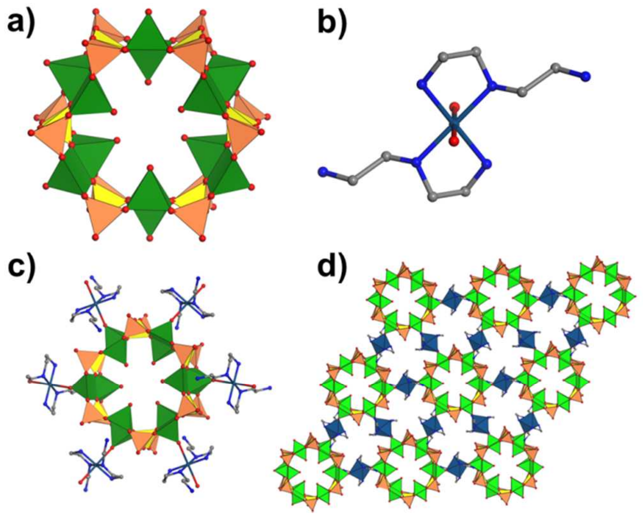

Fig. 3 The cluster and linker in SUT-13. a) A polyhedral view of the $V_{12}P_{12}B_6$ cluster; b) The ball and stick view of the linker $Cu(DETA)_2$; c) The cluster of SUT-13 with six $Cu(DETA)_2$ complexes surrounded; d) A singe 2D layer of SUT-13. Color scheme for different elements: red, oxygen; yellow, boron; dark yellow, phosphor; grey, carbon; blue, copper; green, vanadium.

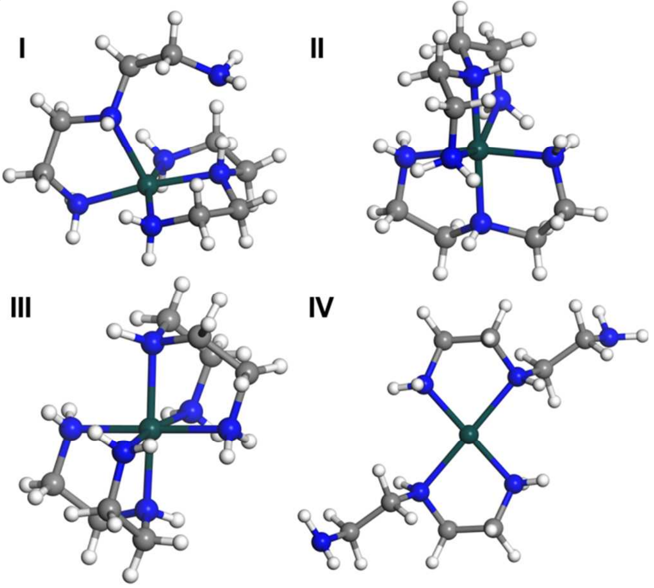

Fig.4 Different configurations of $Cu(DETA)_2$ complexes.

In SUT-12 and SUT-13, the dangling amine group feature is shown in the bridging complexes ($Zn(DETA)_2$ and $Cu(DETA)_2$), which are in a similar but uncommon configuration regarding to DETA molecules. In order to investigate the formation of this configuration, the first principle density functional theory (DFT) calculation was performed to determine the complexation energies of different configurations[39,40] using Cu as an example. The possible configurations of the mono $Cu(DETA)_2$ complexes found in the CCDC database including the one reported here in SUT-13 are shown in Fig.4. The calculated complexation energies of the different configurations in Fig. 4 are -432.713 kcal/mol for I,-430.651 kcal/mol for II, -423.290 kcal/mol for III and -420.510 kcal/mol for IV, respectively. These calculations indicate slightly lower stability for the complex configuration in SUT-13. Considering the oxygen atoms coordinated to the copper atoms and the $Cu(DETA)_2$ complexes, we also performed the DFT calculation on the water coordinated copper-DETA complexes with the exact configurations shown in Fig. S7. A high complexation energy was also found for the complex with corresponding configurations in SUT-13, which indicates the configuration of DETA in SUT-13 is difficult to be formed, explaining why the abnormal feature of the dangling amine group in the $Cu(DETA)_2$ complexes of SUT-13 is not reported before. A possible reason to explain the observation of the unusual configurations in SUT-12 and SUT-13 could be due to the formation of hydrogen bonds between the dangling NH_2 groups and the framework in these materials.

Based on two different synthesis methods, two different layered net structures was synthesized by using in-situ formed metal complexes to link the vanadoborate and vanadium borophosphate clusters, respectively. Interesting, all DETA molecules in the complexes of two structures shows rarely observed dangling amine groups. It is difficult to explain why the DETA molecules prefer to coordinating metal ions with dangling amine groups, but the DFT calculations suggest that the configuration in SUT-12 and SUT-13 are more energetic unfeasible compared to other reported configurations.

Acknowledgements: This project was supported by the Swedish Research Council (VR), the Swedish Governmental Agency for Innovation Systems (VINNOVA) through the Berzelii EXSELENT, the National Basic Research Program of China (2013CB933402). H.C. thanks the China Scholarship Council. Maoping Pu is acknowledged for his nice discussion regarding to the modelling. We thank Beamline I19 in Diamond light Source, UK for single crystal X-ray diffraction data collection.

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Table of Contents

Dangling amine groups were found in the diethylenetriamine (DETA) metal complexes, which worked as linkers in construction of two-dimensional V-B-O polyoxometalate.