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Host–Guest Systems

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Intercalation of Organic Molecules into Vanadium(IV) Benzenedicarboxylate: Adsorbate Structure and Selective Absorption of Organosulfur Compounds**

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The capacity and selectivity of nanoporous materials in the absorption and separation of molecular mixtures depend on specific interactions between the host frameworks and removable guest species, and in some cases the degree to which the structure of the host lattice can relax as the molecular species are intercalated. The classical zeolite frameworks are relatively rigid and exhibit little deformation upon loading and unloading of various guest species.[1] On the other hand, intercalation into layered structures leads to expansion of the interlayer separation because of the very weak interlayer bonding and can lead to complete exfoliation of the layers.[2]

Flexibility without loss of crystallinity is expected for structures containing rigid building blocks linked by relatively deformable hingelike units. Examples of framework flexibility have been found in a number of metal–organic frameworks (MOFs).[3] Among them, a group of compounds first reported by Férey and co-workers,[4] based on chains of *trans* corner-sharing octahedra $\{MO_6\}$ (M = V,[4] Cr,[5] Al,[6] Fe,[7] and In[8]) cross-linked by 1,4-benzenedicarboxylate (bdc) upon removal or absorption of guest species, show remarkable framework flexibility. The first member of the group $[\{V(OH)(bdc)\}(H_2bdc)_x]$[4] loses the guest acid on heating in

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air, and at the same time the framework V^{3+} ions are oxidized to V^{4+} without changing the topology of the framework.

Sorption studies of these MOFs have focused on H_2 adsorption,[9] but some studies of the absorption of CO_2[10] and CH_4[11] have been reported. Of particular relevance to this study is the report by Férey and co-workers on the adsorption of CH_4 and CO_2 by [M(OH)(bdc)] (M = Cr, Al) and [V(O)(bdc)].[11a] The V^{IV} phase [V(O)(bdc)] shows some differences in the absorption isotherms relative to the trivalent compounds, but the amounts of CO_2 adsorbed above 10 bar are comparable. The relatively weak enthalpy of adsorption suggested that [V(O)(bdc)] has no specific adsorption sites for CO_2.[11a]

Herein, we report the synthesis of single crystals of $[V(O)(bdc)](H_2bdc)_{0.71}$ (**1**) directly. After removal of the guest acid molecules by heating **1** in air, we show that the [V(O)(bdc)] structure is sufficiently flexible to undergo single-crystal-to-single-crystal transformations upon absorption of aniline, thiophene, and acetone from the liquid phase, thus enabling the details of the guest structure, framework–guest interactions, and framework deformations to be determined from single-crystal X-ray diffraction data. Furthermore, we have observed rapid and highly selective gas-phase absorption of thiophene from methane by [V(O)(bdc)], a process relevant to natural-gas clean-up. This application and others of MOFs have been described in a recent review.[12]

The octahedral chain in the structure of $[V(O)(bdc)](H_2bdc)_{0.71}$ (**1**) contains a -V=O–V=O- backbone with alternating short and long V–O apical bonds of the $\{VO_6\}$ octahedra. The equatorial corners of the $\{VO_6\}$ octahedra are shared with the bdc ligands that cross-link the octahedral chains to form 1D rhombshaped tunnels, which are each filled by two columns of guest H_2bdc. Assuming that the H_2bdc molecules in each column are linked by hydrogen bonds similar to those in $[In(OH)(bdc)]\cdot(H_2bdc)_{0.75}$[8] and that a H_2bdc molecule has a length of 9.6 Å, a theoretical number of 0.71 guest H_2bdc molecules per vanadium atom can be derived from the lattice constants. This guest-acid content is confirmed by chemical analysis and structure refinements.[13] The columns of the guest H_2bdc molecules in different tunnels are found randomly disordered over positions shifted relative to each other along the tunnel axis in steps of approximately 1.4 Å. Thermal removal of the guest H_2bdc led to crystals of [V(O)(bdc)] (**2**) suitable for single-crystal X-ray measurement.[14] Our determination of the structure of **2** is in agreement with that reported earlier by Férey and co-workers.[4]

Although the structures of **2** and [M(OH)(bdc)] (M = Al^{3+}, Cr^{3+}, and V^{3+}) have the same topology and belong to the same space group, *Pnma*, they show important differences in local symmetry. In the latter structure, the metal atom is located at an inversion center, whereas the symmetry mirror planes are perpendicular to the octahedral chain and pass through the centers of the bdc ligands. The inversion symmetry center in **2** is shifted to the center of the bdc ligand because the V^{4+} ion is displaced from the center of a $\{VO_6\}$ octahedron to form a V–O double bond. The mirror plane is parallel to the octahedral chain and runs through the -V=O–V=O- backbone. This symmetry difference between the frameworks naturally leads to different space-group symmetries of the corresponding compounds intercalated by the guest H_2bdc molecules.

The $[M(OH)(bdc)](H_2bdc)_x$ phases have the same space-group symmetry as [M(OH)(bdc)], with the guest H_2bdc molecules in neighboring tunnels oriented perpendicular to each other. The same arrangement of the guest molecules is found in **1**, probably because this pattern allows all columns of guest H_2bdc molecules to have favorable π–π interactions with the framework bdc molecules. This arrangement of the guest H_2bdc molecules is not compatible, however, with the symmetry of **2**. The space-group symmetry of **1** is lowered to the non-centrosymmetric $P2_12_12_1$, which was confirmed by structure refinements and by second harmonic generation (SHG) measurements. The SHG efficiency measured on a powder sample of **1** is comparable to that of quartz.

Upon immersion in liquid aniline, thiophene, and acetone, the crystals of **2** transformed into the intercalation compounds [V(O)(bdc)](aniline) (**3**), $[V(O)(bdc)](thiophene)_{0.91}$ (**4**), and [V(O)(bdc)](acetone) (**5**), respectively, without losing their single-crystallinity. Part of each structure, drawn to emphasize the guest-molecule orientations, is shown in Figure 1. The aniline molecule (ca. 7.5 Å long) is much shorter than H_2bdc but still longer than the period (6.8 Å) of the [V(O)(bdc)] framework along the tunnel axis. The

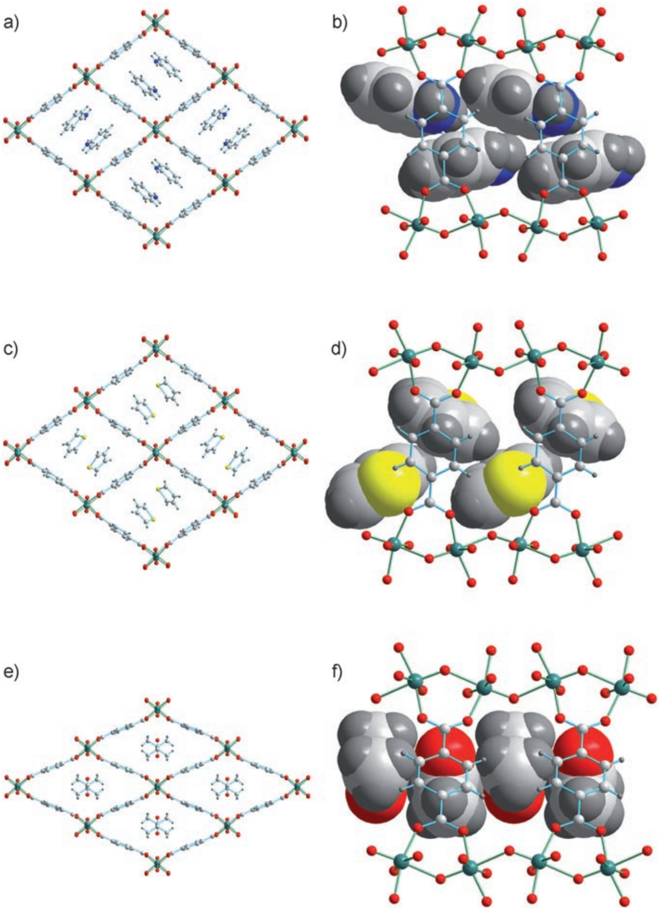

Figure 1. The structures of a,b) [V(O)(bdc)](aniline) (**3**); c,d) $[V(O)(bdc)](thiophene)_{0.91}$ (**4**); and e,f) [V(O)(bdc)](acetone) (**5**). b), d), f) Guest molecules in space-filling representation.

intercalated aniline molecules in **3** form angles of ± 17° to the tunnel axis, which can be considered as a compromise between adapting to the framework period, maximizing packing efficiency, and facilitating π–π interactions with the framework bdc ligands. The shortest distance between the benzene-ring center of aniline and the carbon atoms of the bdc benzene ring is 3.507(1) Å, and the distance between their benzene-ring centers is 4.43(1) Å, which indicates a π–π interaction with substantial ring–ring offset.[15] The π–π interactions are complemented by weak C–H···π and N–H···π interactions between the aniline molecules and the bdc ligands. The packing of thiophene molecules in **4** is similar to aniline in **3**, but the angles between the thiophene molecules and the tunnel axis are changed to ± 26°, probably as a result of the smaller molecular size. A clear C–H···π interaction between the thiophene molecules and the framework bdc molecule seems to play a major rule in dictating the thiophene orientation.[16] The occupancy of the thiophene position was refined to 0.91(1) in agreement with the absorption measurements (see below). Similar to **1**, the guest-molecule packing in **3** and **4**, which results from the weak interactions between the guest molecules and the host framework, is not compatible with the space-group symmetry of [V(O)(bdc)]. The centrosymmetric space group *Pnma* of [V(O)(bdc)] changes to the chiral space group $P2_12_12_1$ upon loading of the guest aniline or thiophene molecules.

Unlike the aniline and thiophene molecules that form two columns in each tunnel, the acetone molecules in **5** are stacked into one column along the tunnel axis with an antiparallel packing pattern. The intermolecular C=O···C=O distances 3.506(1)–3.510(1) Å within the column indicate weak dipolar carbonyl–carbonyl interactions between the acetone molecules, which probably dictate the packing pattern.[17] The [V(O)(bdc)] tunnel is too small to host two columns of the antiparallel-packed acetone molecules. With only one column of acetone molecules in each tunnel, the framework deforms so that the rhombshaped tunnel section flattens substantially. The flattening not only improves packing efficiency of the whole structure but also facilitates dipolar interactions between the carbonyl group of acetone and the carboxylate groups of the framework bdc ligands (C=O···CO_2: 3.267(1) Å). The packing of the acetone molecules is compatible with the symmetry of the [V(O)(bdc)] framework; therefore, **5** has the same space-group symmetry as **2**.

Upon intercalation of the guest molecules, the tunnel openings in [V(O)(bdc)] systematically shrink because of the interactions between the guest molecules and the host framework. This behavior is illustrated by the ratio of the two diagonals of the tunnel section, which changes from 13.99:16.06 (0.87) in **2** to 13.03:16.85 (0.77) in **3**, 12.62:17.09 (0.74) in **4**, 12.42:17.17 (0.72) in **1**, and 10.21:18.41 (0.55) in **5**. For comparison, the shrinkage on going from [Al(OH)(bdc)]·H_2bdc to [Al(OH)(bdc)]·H_2O is even larger 7.61:19.51 (0.39). The deformations are realized mainly through changes of the torsion angle V–O=C–C, which is the most flexible component of the framework. The packing density calculated for the guest-molecule column of **5** is 122.2 Å^3 per acetone molecule, which is almost identical to that of liquid acetone. In contrast, the guest-packing densities calculated for **3** and **4** are both approximately 21 % lower than the corresponding liquid densities of the guest molecules, assuming a full occupancy, probably because the oriented interactions between the guest molecules and the framework bdc ligands also dictate the stoichiometry of the intercalated compounds.

Thiophene is also absorbed by [V(O)(bdc)] directly from the gas phase (Figure 2). Single crystals of [V(O)(bdc)]-$(H_2bdc)_{0.71}$ were heated on a thermobalance in flowing air to 350 °C to remove the H_2bdc guest molecules. After cooling to room temperature, the gas stream was switched to a 5 % CH_4/He stream. The data in Figure 2 show that methane is not absorbed under these conditions. The gas stream was switched to a 5 % CH_4/He stream saturated with thiophene at ambient temperature and 1 atm (10 kPa at 20 °C). Rapid absorption occurs on exposure to methane/thiophene/He corresponding to the uptake of 0.88 molecules of thiophene per [V(O)(bdc)], in agreement with the liquid-phase uptake. The inset in Figure 2 shows that the uptake kinetics are fast. Similar results were obtained for the uptake of dimethyl sulfide and thiophene at 1 kPa (see Table 1).

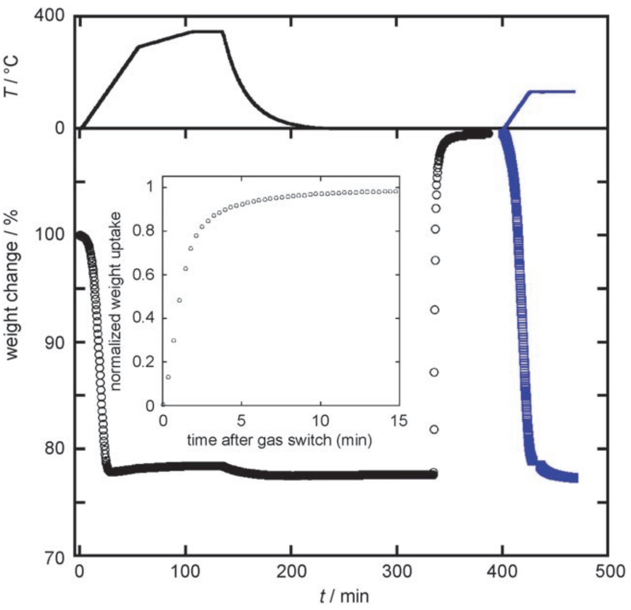

Figure 2. Thiophene uptake by [V(O)(bdc)] from methane saturated with thiophene at ambient temperature. The temperature profile is shown in the top panel and the corresponding weight change in the bottom panel. The inset shows an expanded view of the thiophene uptake kinetics. The data in blue show a second experiment in which a sample saturated with thiophene at ambient temperature is heated to 150 °C.

Table 1: Gas-phase adsorption by [V(O)(bdc)].

Formula	Δwt %	Molecules [f.u.][a]	*P* [kPa][b]
$(CH_3)_2S$	+34.0	1.12	66.9
C_4H_4S	+31.9	0.88	10.0
C_4H_4S	+23.4	0.65	1.0

[a] Formula unit. [b] Partial pressure.

The reversibility of thiophene uptake was investigated thermogravimetrically and by X-ray diffraction studies. A sample was saturated with thiophene on a thermobalance following the procedure described above. When the sample reached constant weight at ambient temperature, the temperature was raised to 150 °C. Thiophene desorbed and the sample weight returned to its initial value (blue data points in Figure 2). An X-ray powder pattern of the final sample indicated complete retention of crystallinity. A single crystal of [V(O)(bdc)](thiophene) was heated to 200 °C for 30 min to remove the thiophene. The results show that the structure reverts to space group *Pnma*, and the complete absence of any electron density in the channels indicates complete desorption of thiophene. The lattice parameters are $a = 6.813(2)$, $b = 16.248(4)$, and $c = 13.749(3)$ Å, which indicate a 1 % smaller cell volume than **2** and suggest that annealing at over 200 °C is necessary to allow the framework to completely relax.

The structural details of the four intercalated compounds presented herein, and the selective and reversible removal of sulfur-containing molecules from methane, show the importance of noncovalent oriented weak interactions in the packing of organic molecules within channels of a specific metal–organic framework. Such interactions, although relatively weak, can readily cause remarkable deformation and symmetry changes in the framework, thus pointing to effective ways of manipulating known materials or designing new materials with targeted properties through intercalation chemistry.

Experimental Section

$[V(O)(bdc)](H_2bdc)_{0.71}$ (**1**) was synthesized by hydrothermal reaction from a mixture of VO_2, HCl, H_2bdc, and H_2O (molar ratio = 1:2:0.5:77). The mixture was heated at 220 °C in a sealed teflon vessel for 3 days. By using vacuum filtration and drying in air, red-brown prisms of **1** were recovered as a major phase together with dark-green impurities, which were readily removed by washing with methanol. For the absorption measurements, red prism crystals of **1** were heated in air to 350 °C at a rate of 3 °C min^{-1} to form [V(O)(bdc)] (**2**). Intercalation experiments were carried out by immersing crystals of **2** in liquid aniline, thiophene, and acetone. For gas-phase absorption, crystals of **1** were heated on a thermobalance to 350 °C in air to remove H_2bdc. The sample was maintained at constant temperature for 30 min and then cooled to 28 °C. When the weight was constant at 28 °C, the air flow was switched to 5 % CH_4/He. After the weight became constant, the flow of 5 % CH_4/He was passed through a bubbler containing liquid $(CH_3)_2S$. After a short time, the weight of [V(O)(bdc)] increased dramatically.

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[13] **1**: Elemental analysis (%) calcd for $[V(O)(bdc)](H_2bdc)_{0.71}$: V 14.6, C 47.08, H 2.37; found: 14.8; C 47.10, H 2.68; crystal data: space group $P2_12_12_1$, $a = 6.8094(3)$, $b = 12.4220(6)$, $c = 17.1733(8)$ Å, $V = 1452.6(1)$ Å^3, $Z = 4$, $T = 223$ K, $d_{calcd} = 1.593$ g cm^{-3}; single-crystal data were collected on a Siemens SMART/CCD diffractometer (14526 reflections total, 3498 unique, $R_{int} = 0.0478$); the structure was solved and refined with the SHELXTL software package; final refinements converged at $R1 = 0.0394$ for all 3498 reflections and 188 parameters.

[14] Thermogravimetric analyses of **1** carried out in air at 3 °C min^{-1} showed two weight-loss events. The first between 320 and 400 °C corresponds to the loss of the guest H_2bdc. The second between 440 and 480 °C corresponds to the loss of framework bdc. A sample heated at 390 °C for 10 h was confirmed to be identical to MIL-47 by IR spectroscopy (disappearance of the band at ca. 1700 cm^{-1} characteristic of free $-C{=}O$ species) and single-crystal X-ray diffraction ([V(O)(bdc)] (**2**): space group *Pnma*, $a = 6.8249(8)$, $b = 16.073(2)$, $c = 13.995(2)$, $T = 293$ K, $d_{calcd} =$

1.000 g cm^{-3}, $R1 = 0.0443$ for all 1904 unique reflections and 67 parameters). After immersing the [V(O)(bdc)] crystals in the corresponding guest liquid in air at room temperature for approximately 1 h, a suitable crystal for each intercalation phase was selected and sealed in a capillary together with the guest liquid in air and mounted on a Siemens SMART/CCD diffractometer for X-ray data collection. **3**: space group $P2_12_12_1$, $a = 6.785(1)$, $b = 13.031(2)$, $c = 16.851(2)$ Å, $V = 1489.8(4)$ Å^3, $Z = 4$, $T = 223$ K, $d_{calcd} = 1.445$ g cm^{-3}. 12940 reflections total, 3511 unique, $R_{int} = 0.0698$; $R1 = 0.0394$ for all 3511 unique reflections and 180 parameters. **4**: space group $P2_12_12_1$, $a = 6.786(1)$, $b = 12.618(2)$, $c = 17.086(3)$ Å, $V = 1463.0(4)$ Å^3, $Z = 4$, $T = 223$ K, $d_{calcd} = 1.503$ g cm^{-3}; 8691 reflections total, 3368 unique, $R_{int} = 0.0641$; $R1 = 0.0695$ for all 3368 unique reflections and 174 parameters. **5**: space group $Pnma$, $a = 6.796(3)$, $b = 18.410(8)$, $c = 10.214(4)$ Å, $V = 1278.0(9)$ Å^3, $Z = 4$, $T = 223$ K, $d_{calc} = 1.431$ g cm^{-3}; 7544 reflections total, 1006 unique, $R_{int} = 0.2022$; $R1 = 0.134$ for all 1006 unique reflections and 43 parameters. The crystal quality of **5** is comparatively poor probably because of the large unit-cell changes during intercalation. CCDC 619387–619391 (**1**–**5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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