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Solvent-free synthesis of new open-framework oxalate structures†

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An oxalic acid flux method has been developed to prepare new open-framework oxalate-based structures with hcb, 10^3, and dia topologies. It is also interesting that a new bifunctional organic ligand can be obtained from oxalate ligand and amine under the solvent-free conditions.

Metal–organic frameworks have been the focus of recent research interest because of their intriguing crystalline structures and potential applications in catalysis, gas storage, separation, non-linear optics, and sensing.[1] One of the key factors to tune their framework topologies is the judicious choice of different organic ligands as the cross-linkers.[2] As one of the simplest imaginable organic linkers, oxalic acid has strong ability to bind metals and exhibits diverse connection modes in the preparation of new framework structures.[3] The short metal···metal distance in metal oxalate frameworks may endow these compounds with interesting optical, electronic, and magnetic properties. In general, open-framework metal oxalates have been hydro/solvothermally synthesized in sealed autoclaves under autogenous pressure.[4]

Solvent-free approach for the synthesis of crystalline open-framework materials has shown several advantages over conventional hydro/solvothermal methods: low cost, simple process, reducing pollution and decreasing system pressure.[5] More importantly, it can avoid the influence of solvent on the final structure, indicating that some new open-framework structures with unprecedented topologies may be obtained by this unique approach.[6] Previously, we reported the synthesis of several new open-framework metal phosphites in a solvent-free flux of H_3PO_3.[7] Considering that oxalic acid has a low melting point of 101.5 °C, it is expected that the replacement of H_3PO_3 by oxalic acid under similar synthetic conditions will promote the growth of single crystals of open-framework metal oxalates. Herein, we report a solvent-free approach to the synthesis of four oxalate-based compounds, formulated as $(Hdpa)_4\cdot Zn_4(ox)_6\cdot 1.5H_2O$ (**1**), $(Hdpa)_2\cdot Co_2(ox)_3\cdot 2H_2O$ (**2**), $H_2dmpda\cdot Mn_2(H_2PO_4)_2(ox)_2\cdot H_2O$ (**3**), and $Zn(ox)(L1)\cdot 0.4H_2O$ (**4**), in a flux of oxalic acid without the addition of water as a solvent, where dpa = diisopropylamine, ox = oxalate, and dmpda = *N*,*N*-dimethyl-1,3-propanediamine.‡

Colorless block-like crystals of compound **1** were obtained by the reaction of $Zn(OAc)_2\cdot 2H_2O$, $H_2C_2O_4\cdot 2H_2O$ and dpa in a molar ratio of 2 : 1 : 2 at 150 °C for 9 d. The product was washed with distilled water and dried in air. The diffraction peaks on the experimental and simulated powder X-ray diffraction (XRD) patterns of the as-synthesized compound corresponded well in position, indicating the phase purity of the as-synthesized sample. Single-crystal structural analysis reveals that compound **1** has a three-dimensional framework constructed from zinc atoms and oxalate ligands. The zinc atoms each have an octahedrally coordinated geometry by bonding with six oxygen atoms from three oxalate ligands, and the oxalate ligands each bridge two zinc atoms in bisbidentate mode. The connectivity in such a way gives rise to an open-framework structure with intersecting multi-directional channels (Fig. 1a). The Zn–O bond lengths are in the range 2.055(4)–2.176(3) Å, and O–Zn–O bond angles are between 78.16(11)–173.83(14)°.

A striking structural feature of compound **1** is that it consists solely of extra-large 20-membered rings delimited by ten ZnO_6 octahedra and ten oxalate ligands. The pore size of the 20-ring window is about 6.8 × 15.4 Å, calculated from the distance between the framework oxygen atoms across the window. Viewed along the [100], [010], [001], [110], [101], and [011] directions, the structure displays multidirectional puckered 20-ring channels with

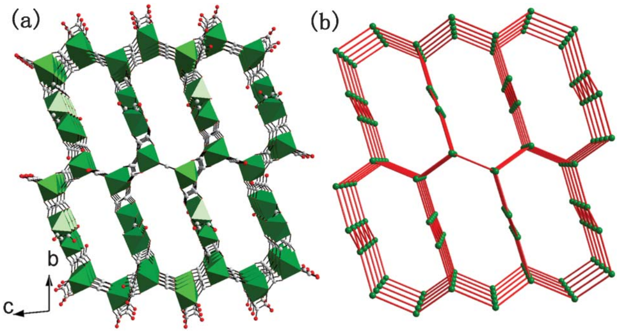

Fig. 1 (a) Perspective view of the structure of **1** along the [100] direction, showing the extra-large 20-ring channels delimited by ten ZnO_6 octahedra and ten oxalate ligands. (b) The compound has a novel 10^3 network by regarding Zn atoms as 3-connected nodes in the network. Color code: ZnO_6 octahedra, green; C, gray; O, red.

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different pore apertures. The protonated organic cations reside in the free voids and interact with framework oxygen atoms through extensive hydrogen bonds. The shortest N···O distances are in the range of 2.871(5)–2.960(6) Å. A void space analysis using the program PLATON indicates that these organic cations and water molecules occupy 66.3% of the unit cell volume.[8]

By regarding the zinc atoms as 3-connected nodes, the structure of **1** has a novel 10^3 topology (Fig. 1b). In metal oxalate structures, honeycomb layered network with 12-ring windows is often found. However, three-dimensional metal oxalates with 10^3 networks have been rarely reported. So far, only two examples are known: one is an iron oxalate $[Fe(2,2'\text{-bpy})_3][Fe_2(ox)_3]$ and its structural analogues with a chiral srs topology, and the other is a zinc oxalate $(C_3H_{10}N)_2{\cdot}[Zn_2(C_2O_4)_3]{\cdot}3H_2O$ with a ths topology.[9] Both of them are uniform nets with vertex symbols of $10^5.10^5.10^5$ (for srs net) and $10^2.10^4.10^4$ (for ths net). By careful analysis of the structure of **1**, it is found that there are two different vertex symbols in the structure: $10^2.10^2.10^4$ (for Zn1 and Zn4 sites) and $10.10^3.10^3$ (for Zn2 and Zn4 sites). As far as we know, such framework topology has been observed for the first time in the open-framework structures.

The use of $Co(OAc)_2{\cdot}2H_2O$ as the metal source under similar solvent-free conditions to compound **1** gave rise to red prism-like single crystals of **2**. The phase purity of this compound is confirmed by powder XRD analysis. Single-crystal XRD analysis reveals that compound **2** has a layered structure intercalated with monoprotonated dpa cations. The cobalt oxalate layer features circular 12-ring windows delimited by six CoO_6 octahedra and six oxalate ligands, as shown in Fig. 2a. The diameter of the 12-ring window is about 7.8 Å, calculated from the distance between the oxalate oxygen atoms across the window. By regarding the cobalt atoms as 3-connected nodes, the structure of **2** has a hcb topology (Fig. 2b). The cobalt oxalate layers are stacked along the [001] direction in an ABAB sequence. The organic cations are disordered within the interlayer region and balance the overall negative electrostatic charge of cobalt oxalate layers.

It is noteworthy that the solvent-free approach can be readily extended to prepare a new inorganic–organic hybrid-framework solid. The reaction of $Mn(H_2PO_4)_2{\cdot}2H_2O$, $H_2C_2O_4{\cdot}2H_2O$ and dmpda in a molar ratio of 2 : 3 : 2 at 150 °C for 7 d resulted in the formation of light-pink rod-like single crystals of **3**. The product was washed with distilled water and dried in air. The agreement between the experimental and simulated powder XRD patterns indicates the phase purity of as-synthesized compound. Single-crystal XRD analysis reveals that the structure of **3** consists of an anionic manganese phosphate–oxalate framework and diprotonated dmpda cations. The asymmetric unit contains 32 non-hydrogen atoms, of which 24 atoms belong to the host framework and 8 atoms to the guest species. Each manganese atom has an octahedral coordination sphere, bonded by four oxalate oxygen atoms and two phosphate oxygen atoms. Each phosphorous atom shares two oxygen atoms with adjacent manganese atoms, leaving two vertices occupied by terminal hydroxyl groups. The oxalate ligands each connect with two manganese atoms in bisbidentate mode. The Mn–O bond lengths are between 2.066(3)–2.215(2) Å, and the P–O bond lengths vary from 1.475(3) to 1.570(3) Å. The stoichiometry of $[Mn_2(H_2PO_4)_2(C_2O_4)_2]$ would create a net charge of −2, which is balanced by one diprotonated dmdpa cation.

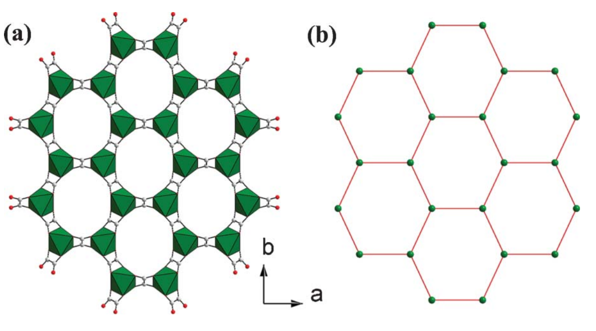

Fig. 2 (a) The layered structure of **2** with 12-ring windows delimited by six CoO_6 octahedra and six oxalate ligands. (b) The compound has a hcb topology by regarding Co atoms as 3-connected nodes in the network. Color code: CoO_6 octahedra, green; C, gray; O, red.

Different from compounds **1** and **2** containing only oxalate as its oxoanion, the structure of **3** has two different oxoanions: oxalate and phosphate. The connection between manganese atoms and oxalate ligands creates chain-like structures running along the [100] direction, as shown in Fig. 3a. The phosphate oxygen atoms complete the octahedral environment around manganese atom and the manganese oxalate chains are further linked by H_2PO_4 tetrahedra to result in a three-dimensional hybrid framework. Alternatively, the hybrid framework can be understood as manganese phosphate chains linked by oxalate ligands (Fig. 3b).

An instructive way to view the framework of **3** is in terms of a diamond structure, where the carbon positions are occupied by manganese atoms and C–C bonds are replaced by H_2PO_4 tetrahedra and oxalate groups (Fig. 2c and 2d). As expected, the structure contains only 12-ring windows delimited by six MnO_6 octahedra and six oxoanions. Two types of 12-ring windows have been found in the structure. Type I pore consists of six MnO6, four oxalate groups, and two H_2PO_4 tetrahedra. Type II consists of six MnO_6, two oxalate groups, and four H_2PO_4 tetrahedra.

Prior to this work, the synthesis of a hybrid framework compound $Mn_2(H_2PO_4)_2(C_2O_4)$ without employing any solvent molecules has been explored by Lightfoot and co-workers.[10] The three-dimensional structure of this compound can be understood as manganese phosphate layers pillared by oxalate ligands. A void space analysis employing PLATON indicates that this compound is a dense phase without solvent-accessible voids. In comparison,

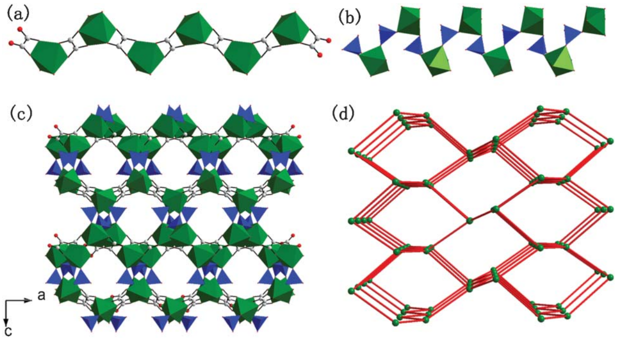

Fig. 3 (a) Manganese oxalate chain. (b) Manganese phosphate chain. (c) The framework structure of **3** viewed along the [010] direction. (d) Compound **3** has a diamond topology by regarding Mn atoms as 4-connected nodes in the network. Color code: MnO_6 octahedra, green; PO_4 tetrahedra, blue; C, gray; O, red.

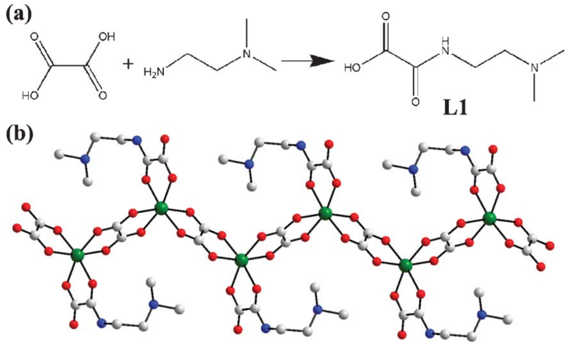

Fig. 4 (a) Representation of the *in situ* formation of L1 ligand in compound **4**. (b) The chain-like structure of compound **4**. Color code: Zn, green; C, gray; O, red, N, blue.

compound **3** has an open-framework structure with 12-ring channels. The organic cations and water molecules are accommodated in the free voids and they occupy 37.1% of the unit cell volume.

Also interesting is the *in situ* formation of a new organic ligand (L1) under solvent-free conditions from the reaction between oxalic acid and *N*,*N*-dimethylethylenediamine molecule (Fig. 4a). The L1 ligand plays a dual role in the chain-like structure of **4** (Fig. 4b). It acts as a terminal ligand to complete octahedral environment around zinc atom as well as a charge-balancing agent containing one monoprotonated amino group.

Thermogravimetric analysis indicated that compound **1** lost its crystalline water molecules in the temperature region 70–135 °C. The organic cations and oxalate groups began to decompose at a temperature higher than 220 °C. The total weight loss between 70–420 °C is 73.41%, which is in agreement with the value of 73.44% if the final product is assumed to be ZnO. For compound **3**, the total weight loss of 51.06% between 160–700 °C is caused by the loss of crystalline water molecules, the decomposition of organic cations and oxalate ligands, and the dehydration of H_2PO_4 groups. Assuming the final phase to be $MnPO_4$, the expected weight loss of 50.21% is in agreement with the observed value. The fluorescent spectra of compounds **1** and **3** were measured in the solid state at room temperature. Upon excitation at 248 nm, the two compounds gave a similar emission band with a peak maximum at 401 nm, which could be tentatively assigned to ligand-to-metal charge transfer.[11]

In summary, a solvent-free approach has been developed for the synthesis of new open-framework oxalate compounds with hcb, 10^3, and dia topologies. The *in situ* formation of an amide molecule from oxalic acid and amine demonstrates that this approach can be extended to the synthesis of new organic ligands. Given that a large number of amines can be used as the structure-directing agents in the synthetic system, new crystalline metal oxalates with novel framework topologies are expected to be produced. Further work on this subject is in progress.

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Notes and references

‡ Data collections were performed on an Oxford Xcalibur diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL program package.[12] Crystal data for **1**: $C_{36}H_{67}N_4O_{25.5}Zn_4$, $M = 1225.42$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.4178(3)$ Å, $b = 15.4572(6)$ Å, $c = 18.2451(9)$ Å, $\alpha = 95.399(4)^\circ$, $\beta = 91.352(4)^\circ$, $\gamma = 90.312(3)^\circ$, $V = 2643.39(19)$ Å^3, $Z = 2$, $Dc = 1.540$ g cm^{-3}, $\mu = 1.877$ mm^{-1}, 19 853 reflections measured, 9311 unique ($R_{int} = 0.0401$). Final wR_2 (all data) = 0.11619, final $R_1 = 0.0526$. Crystal data for **2**: $C_{18}H_{36}Co_2N_2O_{14}$, $M = 622.35$, orthorhombic, space group *Cmca* (no. 64), $a = 15.5337(4)$ Å, $b = 9.8251(3)$ Å, $c = 16.7644(5)$ Å, $V = 2558.59(13)$ Å^3, $Z = 4$, $Dc = 1.616$ g cm^{-3}, $\mu = 1.367$ mm^{-1}, 4788 reflections measured, 1169 unique ($R_{int} = 0.0276$). Final wR_2 (all data) = 0.1368, final $R_1 = 0.0417$. Crystal data for **3**: $C_9H_{22}Mn_2N_2O_{17}P_2$, $M = 602.11$, orthorhombic, space group *Pbca* (no. 61), $a = 9.6900(6)$ Å, $b = 14.4331(8)$ Å, $c = 29.8442(8)$ Å, $V = 4173.9(4)$ Å^3, $Z = 8$, $Dc = 1.916$ g cm^{-3}, $\mu = 1.451$ mm^{-1}, 15 127 reflections measured, 3680 unique ($R_{int} = 0.0367$). Final wR_2 (all data) = 0.0902, final $R_1 = 0.0382$. Crystal data for **4**: $C_8H_{12.8}N_2O_{7.4}Zn$, $M = 320.77$, monoclinic, space group *C*2/*c* (no. 15), $a = 13.884(3)$ Å, $b = 12.146(2)$ Å, $c = 16.327(3)$ Å, $\beta = 114.50(3)^\circ$, $V = 2505.3(9)$ Å^3, $Z = 8$, $Dc = 1.701$ g cm^{-3}, $\mu = 1.992$ mm^{-1}, 9114 reflections measured, 2197 unique ($R_{int} = 0.0368$). Final wR_2 (all data) = 0.1041, final $R_1 = 0.0362$.

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