

Structural and zeolitic features of a series of heterometallic supramolecular porous architectures based on tetrahedral $\{M(C_2O_4)_4\}^{4-}$ primary building units[†]

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The utilization of tetrahedral pre-formed coordination compounds $\{M(C_2O_4)_4\}^{4-}$ (M = Zr^{IV}, U^{IV}; C₂O₄²⁻ = oxalate) permitted the efficient construction of rare examples of heteronuclear supramolecular nano-porous architectures. A series of metal–organic coordination frameworks prepared by association of these building units with either Mn²⁺, Cd²⁺, or Mg²⁺ have been structurally characterized and are described. Their 3-D chemical scaffold is based on the primary tetrahedral building unit but their pore sizes and topologies could be varied through the M²⁺ metal ion involved in the assembling process, and the anionic tetrahedral moiety. These structures display channels with apertures up to 12 Å × 8 Å which are emptied of solvates at mild temperatures without affecting the chemical scaffold, the integrity of which is maintained up to 250–300 °C. A certain degree of flexibility of the coordination polymers upon guest release is suggested by the temperature dependence of the powder X-ray patterns and N₂ sorption experiments, but reversible and selective sorption of small molecules has been observed substantiating that these open-frameworks behave like sponges.

Introduction

A contemporary aspect of supramolecular chemistry aims at designing organizations with workable chemical, physical and/or structural properties according to the new perspectives these molecule-based materials open in material science. A promising approach to such functional materials involves coordination polymers. Given the diversity of geometries and electronic properties exhibited by the metal ions and the limitless number of organic ligands that can be envisaged, it is in principle possible to achieve supramolecular architectures with specifically tailored properties.^{1,2} This approach is currently intensively investigated for the preparation of micro-porous materials.³⁻⁷ Compared to traditional zeolites, coordination polymers offer the possibility of designing open frameworks exhibiting high porosities and large specific areas but also customized pore sizes, topologies, and chemical compositions. Several prototypical example of such porous architectures have been reported and were shown to be effective functional materials for catalysis,⁸ gas sorption and storage,9 or separation.10

The widely used route to form an open metal–organic framework consists of the direct assembly of a metal ion with a bridging ligand. The resulting network relies on the formation (during the association process) of the so-called secondary building units, or nodes, formed by the connection of the coordinating groups of the ligands to the metal ions. These nodes will determine the net topology and dimensionality of the coordination polymer.¹¹ An alternative route for the coordination compound able to assemble with a complementary module, typically a metal ion. Whereas this latter approach was shown to be very efficient for the preparation of several molecule-

† Electronic supplementary information (ESI) available: Thermogravimetric analysis for SPA-1, SPA-2, and EtOH@SPA-3, powder X-ray diffractogram at different temperatures for SPA-1 and SPA-3; positional coordinates, isotropic and anisotropic thermal parameters, ORTEP plot, bond lengths, and angles for all the reported structures. See http://dx.doi.org/10.1039/b503964a based materials like bimetallic magnets, for instance,¹²⁻¹⁴ it has seldom been envisaged for the construction of porous frameworks.¹⁵⁻²² We have considered a tetrafunctional synthon, $\{M(C_2O_4)_4\}^{4-}$, with tetrahedrally arranged oxalate linkers as a primary building unit.²³ Two evident benefits of this approach are *i*. to permit the pre-design and ideally-fix a node of the network by means of the linking capability and geometry of the molecular building block, and *ii*. to provide access to heterometallic open-frameworks through the assembling of this primary building unit with a second metal ion.

Herein we report that robust heterometallic 3D-coordination polymers with open frameworks are formed by association of tetrahedral building units $\{M(C_2O_4)_4\}^{4-}$ (M = Zr⁴⁺, U⁴⁺) with M²⁺ metal ions. A series of supramolecular nano-porous architectures (SPA) constructed with either Mn²⁺, Cd²⁺ or Mg²⁺ are described. They exhibit open frameworks which are easily emptied of solvates without collapsing, and become accessible for the sorption of small molecules.

Results and discussion

Synthesis and structural features

(a) $[K_2Mn{U(C_2O_4)_4} \cdot 9H_2O]$, SPA-1, and $[K_2Cd{U(C_2O_4)_4} \cdot 5H_2O] \cdot 4H_2O$, SPA-2. The reaction of $K_4U(C_2O_4)_4$ with either Mn^{2+} or Cd^{2+} in H_2O led respectively, to green $[K_2Mn{U(C_2O_4)_4} \cdot 9H_2O]$, SPA-1, and pink $[K_2Cd{U(C_2O_4)_4} \cdot 5H_2O]$; $4H_2O$, SPA-2. Since their X-ray structure analyses revealed that the two compounds exhibit the same network organization, we will describe here only the structure for the Cd derivative; SPA-1 is isostructural and has already been briefly communicated.²⁴ Well-shaped single crystals of $[K_2Cd{U(C_2O_4)_4} \cdot 5H_2O] \cdot 4H_2O$, SPA-2, suitable for X-ray diffraction analysis were grown by slow inter-diffusion of the reagent solutions. The crystal data for the compound are given in Table 1, an ORTEP plot with the atom numbering scheme, bond lengths and angles are provided as ESI.[†]

As a result of the reaction, each $\{U(C_2O_4)_4\}^{4-}$ building block is linked to four Cd^{II} ions by means of its oxalate ligands, as

Table 1 Crystal data for SPA-2, SPA-3, and SPA-4

	SPA-2	SPA-3	SPA-4 ^a
Empirical formula	$C_8H_{18}O_{25}K_2CdU$	$C_{14}H_{22}O_{39}K_2Mg_2U_2$	$C_8H_{10}O_{21}K_2MnZr$
Formula mass	942.8	1417.7	666.51
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	C2/m	$P2_1/n$
a/Å	11.473(1)	20.437(3)	14.699(2)
b/Å	8.968(1)	12.841(4)	12.630(2)
c/Å	11.524(1)	14.614(4)	11.819(1)
β/°	97.43(2)	94.52(3)	106.76(6)
V/Å ³	1175.8(2)	3823.2(6)	2100.8(8)
Ζ	2	4	4
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	2.663	2.424	2.107
F(000)	888	2568	1316
Crystal dimensions/mm	$0.08 \times 0.07 \times 0.06$	$0.34 \times 0.30 \times 0.20$	$0.21 \times 0.16 \times 0.07$
T/K	298	298	298
$\mu(Mo_{Ka})/mm^{-1}$	8.249	8.836	1.594
θ range/°	2.36-26.37	4.13-36.32	1.00-34.97
$2\theta_{\rm max}/^{\circ}$	52.7	72.6	72.6
Tot. no. of data collected	8688	22286	18238
No. of obsd data $[I \ge 2\sigma(I)]$	4662	6805	$6192 [I \ge 3\sigma(I)]$
$R_1, wR_2 [I \ge 2\sigma(I)]$	0.0160, 0.0449	0.0482, 0.1362	0.077, 0.242
R_1, wR_2 (all dat)	0.0171, 0.0642	0.0658, 0.1510	0.077, 0.242
Goodness-of-fit on F^2	1.207	1.047	1.093
No. of variables	335	276	317

^{*a*} The H_2O molecules located in the channels are highly disordered (see Experimental section) and could not all be positioned; moreover, the corresponding H atoms have not been included in the structure refinement but these have been considered for the formula, molecular mass, density, adsorption coefficients and *F*(000).



Fig. 1 View of the structure of the isostructural $[K_2Mn{U(C_2O_4)_4} \cdot 9H_2O]$,²⁴ **SPA-1**, and $[K_2Cd{U(C_2O_4)_4} \cdot 5H_2O] \cdot 4H_2O$ **SPA-2** (U⁴⁺ in blue, M²⁺ (Mn or Cd) in green, K⁺ in orange, the H₂O molecules are not shown). a) Detail of the {U(C_2O_4)_4-M} assembly; b) detail of the 24-atom ring superposition framing the channel aperture and location of the K⁺ cations; c) view of the porous architecture down the *b* axis showing the channels running through the structure. Selected bond lengths (Å): **SPA-1**: U–O(oxalate), 2.375(4)–2.456(4); U–O(water), 2.542(5); Mn–O, 2.283(4); U–Mn, 6.102(3)–6.193(3). **SPA-2**: U–O(oxalate), 2.384(4)–2.406(4); U–O(water), 2.554(5); Cd–O, 2.355(4)–2.452(4); U–Cd, 6.166(4)–6.252(4). K–O(oxalate), 2.797(5)–2.824(5), K–O(water), 2.856(4)–2.828(4). Further data can be found in the ESI.†

shown in Fig. 1. The coordination sphere of the Cd ions as well consists of four $Cd \leftarrow \{ \text{oxalate-U} \}$ linkages. Hence, every metal ion is connected four times by oxalate bridges to the other metal ion forming a three-dimensional framework with a diamond-like topology. The charge neutrality is provided by

two K⁺ cations. These are located in the chair-shaped hexagons generated by the interconnected tetrahedral units (Fig. 1b). Each K⁺ is positioned in the plane of the oxalate ligands and interacts with four O atoms of two {M(C₂O₄)} moieties. The K atoms thus complete the chemical scaffold forming the walls which delimit the channels running through the structure.

SPA-2 contains nine H₂O molecules. Five act as ligands, one for the U^{IV} center and two for each K⁺ ion, and the remaining four are located in the channels. These water molecules are easily released (*vide infra*) revealing an open framework. The main channels running through the structure develop along the *b* axis. Their apparent square opening of 6 Å × 6 Å results from the staggered superposition of the 24-atom rings formed by three interconnected {U–oxalate–Cd} fragments (Fig. 1). The effective porous architecture of **SPA-2** is clearly visible in Fig. 2 where the van der Waals volume of the chemical



Fig. 2 View of the framework of SPA-2 taking into account the van der Waals volume of the atoms (generated by Cerius 2). The blue surface corresponds to the walls of the porous volume. *Left*: projection in the *ac* plane. *Right* projection in the *ab* plane.



Fig. 3 View of the structure of $[K_2Mg_2\{U_2(C_2O_4)_7\}\cdot 2H_2O]\cdot 9H_2O$, **SPA-3** (U⁴⁺ blue, K⁺ orange, Mg²⁺ green, the H₂O molecules are not depicted). *Top*: Detail of the $\{U(C_2O_4)\}$ ladder organization and ladder interconnections framing the cavities. *Bottom*: View of the framework revealing the channels running through the structure along the *a* axis (*left*), *b* axis (*center*) and *c* axis (*right*). Selected bond lengths (Å): U–O(oxalate), 2.372(5)–2.553(4); Mg–O(oxalate), 2.799(9)–2.831(9); Mg–O(H₂O), 2.736(9); K–O(oxalate), 2.715(6)–2.912(7); U–U, 6.449(1)–6.392(1); further data can be found in the ESI.[†]

scaffold has been taken into account; the opening diameter of the channels is of *ca*. 3 Å. The volume accessible for a small molecule (H₂O) determined with Platon²⁵ is 347 Å³ per unit cell volume (1176 Å³) which represents 30% of void per unit volume for **SPA-2**. The same analysis has been performed for **SPA-1** revealing a potential porosity of 29% per unit volume (unit cell volume: 1151 Å³, potential free volume: 332 Å³).

(b) $[K_2Mg_2{U_2(C_2O_4)_7}\cdot 2H_2O]\cdot 9H_2O$, SPA-3. When $K_4U(C_2O_4)_4$ was reacted with Mg^{2+} in H_2O , green single crystals of SPA-3 with formula $[K_2Mg_2{U_2(C_2O_4)_7}\cdot 2H_2O]\cdot 9H_2O$ were obtained. The X-ray structure analysis revealed a 3D-coordination polymer with an association scheme of the building units different to that observed with Mn^{II} and Cd^{II} .²³ The crystal data for the compound are given in Table 1, an ORTEP plot with the atom numbering scheme, the bond lengths, and angles are provided as ESI.[†]

For **SPA-3**, the $\{U(C_2O_4)_4\}^{4-}$ units assemble by the mean of $\{U-\text{oxalate}-U\}$ linkages in a ladder type arrangement running along the *b* axis (Fig. 3) where each metal center displays five oxalate ligands in its coordination sphere but has lost formally half an oxalate. The 3-D framework results from the ladder interconnections realized by the coordination of the external oxalate ligands to the K and Mg ions. Views of the resulting scaffold revealing the porous nature of the structure are depicted in Fig. 3.

Channels are running through the structure in the three directions of space with apertures of 6 Å × 6 Å (along *a*), 12 Å × 8 Å (along *b*), and 5.5 Å × 5.5 Å (along *c*). Approximately 32% of the volume of the crystal remains available for small molecules (H₂O). ^{23,25} Taking into account the van der Waals volume of the atoms, the main channels along the *b* axis can be described as a diamond-shaped section with sides of *ca*. 5 Å and diagonals of 9 × 4 Å (Fig. 4).

 $[K_2Mn{Zr(C_2O_4)_4}\cdot8H_2O]$, SPA-4. We considered the possibility of replacing the U-based building unit by the related ${Zr(C_2O_4)_4}^{4-}$ complex. When the latter unit was reacted



Fig. 4 View of the framework of SPA-3 along the b axis taking into account the van der Waals volume of the atoms (generated by Cerius 2). The blue surface corresponds to the walls of the porous volume. (Reproduced from ref. 23.)

with Mn^{II} ions in H_2O [K₂Mn{Zr(C₂O₄)₄}·8H₂O], SPA-4, was obtained. Its composition was found to be similar to that of SPA-1 but with Zr instead of U; however, X-ray structure analysis for SPA-4 revealed a different network organization. The crystal data for SPA-4 are given in Table 1, an ORTEP plot with the atom numbering scheme, the bond lengths, and angles are provided as ESI.†

The most striking feature is found in the association of the ${Zr(C_2O_4)_4}$ units with the Mn^{II} ions. Indeed, the anticipated chelating interaction of the external oxygen atoms of the oxalate ligands is not observed. Instead a single oxygen atom is involved in the linkage of an oxalate to a Mn ion, in much the same fashion as for the coordination to the K cations. A view of the interactions of the K and Mn ions with a $\{Zr(C_2O_4)_4\}$ unit is shown in Fig. 5. Both the Mn and K ions are linked to up to four Zr units developing thus a 3D coordination polymer. The resulting framework can be seen as compact layers interconnected by bridging oxalate ligands. This scaffold frames channels running in one direction parallel to the layers (Fig. 5), their effective square shaped aperture is 5.5 Å \times 5.5 Å. The solvent accessible space in the crystal corresponds to 23% of the total volume,²⁵ which hosts eight H₂O molecules; four of them act as ligands for the Mn and K ions, the remaining four are solvates.



Fig. 5 View of the structure of $[K_2Mn{Zr(C_2O_4)_4}\cdot 8H_2O]$, **SPA-4**, with Zr^{4+} in blue, K^+ in orange, and Mn^{2+} in green, the H_2O molecules are not depicted. *Top:* Detail of the linkages between the Mn^{2+} and K^+ ions with the building unit ${Zr(C_2O_4)_4}^{+-}$. *Bottom:* View of the 3D framework revealing the channels running through the structure. Selected bond lengths (Å): Zr-O(oxalate), 2.163(3)–2.239(4); Mn–O(oxalate), 2.741(5)–2.972(4); K–O(oxalate), 2.664(4)–2.901(5); further data can be found in the ESI.†

The structural information gathered for this series of porous architectures shows that the utilization of the pre-formed tetrahedral coordination compound $\{M(C_2O_4)_4\}^{4-}$ spontaneously leads to 3D coordination polymers when associated with a Mn^{2+} , Mg^{2+} or Cd^{2+} metal ion. Attempts were made with other M^{2+} ions (*i.e.* Co, Ni, Cu, Zn, Pd) but they did not lead to crystalline solids suitable for structural characterization. Nevertheless, infrared spectroscopy and chemical analyses for these solids strongly suggest the formation of homometallic $\{M^{II}(C_2O_4)_{I_n}\}^{I_n}$ coordination polymers.

For SPA-1-4, the coordination network is based on the ability of the external atoms of the oxalates from the building unit to act as ligands for the other metal ions. The resulting structural features are, however, dependent on the engaged modules. The effect of the M2+ metal ions on the realized assemblage can be related to the different metal-ligand affinities and to the coordination sphere for this ion, like for instance Mn²⁺ and Mg²⁺ in SPA-1 and SPA-3. Conversely, ions with closely related characteristics will lead to isostructural networks, *i.e.* Mn²⁺ and Cd2+ in SPA-1 and SPA-2. The origin of the differences found when changing from $\{U(C_2O_4)_4\}^{4-}$ to its Zr counterpart, ${Zr(C_2O_4)_4}^{4-}$, is more subtle. As shown by SPA-1 and SPA-4, the networks developed by these building units with Mn²⁺ are different revealing different association schemes. Most likely, the origin is to be found in the ionic radii (0.80 Å for Zr^{IV} and 0.97 Å for U^{IV}) which govern the volume and flexibility of the ${M(C_2O_4)_4}^{4-}$ moieties. The geometrical data for ${U(C_2O_4)_4}^{4-}$ and $\{Zr(C_2O_4)_4\}^{4-}$ obtained from the structures described above reveal a distance between the central metal ion and the external oxygen atoms of the oxalate ligands ca. 0.2 Å longer for the U unit than for its Zr counter part (4.421-4.492 Å versus 4.228-4.269 Å). Moreover, the coordination sphere of the larger U ion is more flexible and may accommodate up to 10 atoms as shown by SPA-3. These features are already expressed in the solid state organizations of the $\{M(C_2O_4)_4\}^{4-}$ building units alone which consist of discrete complexes for the Zr moieties^{26,27} whereas the U units associate through oxalate bridges into 1-D coordination polymers.28

Thermogravimetric analyses (TGA) revealed that all H_2O molecules contained in the frameworks are released under mild conditions. The behavior for **SPA-3** (Fig. 6) is a typical example. First H_2O leaves the framework which leads to a mass decrease of 12% corresponding to the loss of 9 H_2O . This release is observed in the temperature range 30–120 °C and occurs in three steps suggesting different binding energies even for the lattice water. Above 120 °C and up to 250 °C the sample mass remains unchanged, in this temperature domain **SPA-3** is fully desolvated. Finally, for higher temperatures the compound decomposes. The characteristic temperatures for the end of solvent release and stability for each SPA are given in Table 2; the related TGA data are provided as ESI.[†] It can be noticed



Fig. 6 Themogravimetric analysis for SPA-3.

Table 2 Temperatures of dehydration ending and limit of thermal stability for SPA-1-4 deduced from TGA data^a

	Dehydration ending $T/^{\circ}C$	Upper thermal stability $T/^{\circ}C$
$\label{eq:constraint} \begin{array}{l} [K_2Mn\{U(C_2O_4)_4\}\cdot 9H_2O], \mbox{ SPA-1} \\ [K_2Cd\{U(C_2O_4)_4\}\cdot 9H_2O], \mbox{ SPA-2} \\ [K_2Mg_2\{U_2(C_2O_4)_7\}\cdot 11H_2O], \mbox{ SPA-3} \\ [K_2Mn\{Zr(C_2O_4)_4\}\cdot 8H_2O], \mbox{ SPA-4} \end{array}$	120 140 140 140	280 320 250

^a Measured under a N₂ stream, heating rate 1 °C min⁻¹. ^b Not determined.

that for **SPA-3** 9 H_2O are observed by TG whereas 11 are found by X-ray structure analysis. For all compounds reported here a decreased number of solvate molecules is found for the isolated solids both by TGA and chemical analysis as compared to their crystal structure data. This observation is in line with the fact that solvent release occurs at mild temperatures.

Further evidence for the persistence and stability of these frameworks upon solvent release was obtained from the X-ray powder diffractograms (XRPD) recorded at different temperatures. In Fig. 7 are depicted the XRPD for SPA-2 (from bottom to top) as synthesized at 25 °C, at 60 °C, at 120 °C, just after cooling back to 25 °C, and at the same temperature after 24 h in air. The diffractograms recorded at 60 and 120 °C show broader and weaker signals, revealing a loss of crystallinity upon solvent removal. Finally, when the evacuated sample was maintained in air for 24 h the initial X-ray pattern was recovered, indicating the re-adsorption of H₂O. The frameworks of SPA-1 and SPA-3 exhibit a related behavior (see ESI[†]). The dehydration-rehydration process for SPA-2 can also be followed by its color change from pink to green and back to pink. These supramolecular architectures thus belong to the third generation compounds of solvated solids, *i.e.* the sample recovers its initial crystalline phase after the desorption/adsorption process of its guest molecules.6,29



Fig. 7 X-Ray powder diffractograms recorded for compound SPA-2. From bottom to top: as synthesized at 25 °C, at 60 °C, at 120 °C, at 25 °C after H_2O release, after H_2O re-adsorption at 25 °C.

The evolutions of the XRPD patterns, especially the shifts of some of the diffraction peaks indicate that the crystal packing is modified by the H_2O release. However, the recovery of the initial diffractogram unambiguously confirms that the integrity of the framework, *i.e.* the metal–oxalate network connectivity, is not affected by solvent release. The evolution of the diffractogramm patterns during the desorption thus reveals a deformation of the network which can be related to a certain flexibility of the 3-D coordination polymer.^{30–33} The use of the rigid oxalate ligands was anticipated to avoid the collapse of the framework but the metal–ligand linkages remain flexible. Likely, the scaffold has a tendency to compensate the volume freed by the released solvent molecules. As a result, the effective porosity of the dehydrated solid might be reduced with respect to the potential porosity exhibited by the solvated structure.

In order to evaluate the surface area developed by the frameworks, adsorption isotherms of N_2 at 77 K were measured for **SPA-1** and **SPA-3**. For both compounds N_2 adsorption was observed for low relative pressures, therefore data were collected in the 0.05 to 0.2 *P*/*P*₀ range. From these data, Langmuir (and BET) surface areas were derived to be 25.4 (12.2) m² g⁻¹ and 34 (17.2) m² g⁻¹, respectively for **SPA-1** and **SPA-3**. These results suggest a very limited effective porosity for the desolvated frameworks which is in strong contrast with the potential porosity exhibited by the structures of the solvated architectures. The origin of the low effective porosity may be found in the flexibility

of the frameworks discussed above which compacts upon guest release and thus reduces the space freed by the solvates. It is worth noting here that the lower limit for N_2 sorption is a pore diameter of *ca*. 3.5 Å, therefore this adsorbate may not be best suited for the evaluation of microporosity in these compounds.

Despite the apparent small porosity, these frameworks exhibit reversible sorption properties. We have pointed out above that upon exposure to air, the evacuated frameworks recover their initial crystallographic phase, obviously they adsorb H_2O molecules. The H_2O uptake has been clearly established and quantified for **SPA-1** and **SPA-3** by recording the mass increase of a dehydrated powder (Fig. 8). Both the frameworks re-adsorb *ca.* 5 H_2O per formula unit. **SPA-3** was also found to adsorb small alcohol molecules (MeOH, EtOH) after dehydration and immersion in the corresponding anhydrous alcohol. In Fig. 9 is depicted the TGA of MeOH@**SPA-3** showing that



Fig. 8 Mass increase upon H_2O uptake for SPA-1 (*top*) and SPA-3 (*bottom*) in ambient conditions.



Fig. 9 Themogravimetric analysis for MeOH@SPA-3. The sample was heated from 20 to 115 °C and maintained at this temperature until the mass remained invariant before cooling it back to room temperature.

MeOH is gradually released upon heating. For EtOH@SPA-3 a related but slightly different release versus T behavior has been obtained (see ESI[†]). The XRPD showed these compounds to be rather amorphous. The sorption capacity per gram was roughly estimated from the TG data to be in the order of 1.2 and 0.93 mmol of alcohol, respectively MeOH and EtOH. These observations suggest that these coordination polymers behave as open solids provided that a chemical affinity exists between the potential guest molecules and the frameworks. In the reported examples when the external molecules have interaction capabilities (coordination, H-bonding), as is the case for H₂O or ROH, the network behaves like a sponge and soaks up these molecules but it stays sealed to molecules like N₂ which have no interactions with the scaffold.

Conclusion

The utilization of the tetrahedral pre-formed coordination compounds $\{M(C_2O_4)_4\}^{4-}$ permitted the efficient construction of rare examples of heteronuclear supramolecular nanoporous architectures. Their 3D chemical scaffold is based on the primary tetrahedral building unit but their pore sizes and topologies could be varied through the M²⁺ metal ion involved in the assembling process. It was found that the relative flexibility of the anionic tetrahedral moiety, in relation with its M^{IV} central ion (U *versus* Zr), may also influence the assembling scheme of the framework. These results further demonstrate that the use of a coordination compound as primary building unit is certainly a valuable and versatile approach for the construction of robust open frameworks. Moreover, this approach appears perfectly suited for the design of open frameworks with various compositions of metal ions.

A remarkable feature of the reported compounds is that whereas their effective porosity is strongly reduced upon dehydration they are still able to re-adsorb small molecules, and thus behave as porous solids. This reversible sorption process comes with a breathing framework which opens to accommodate guest molecules and compacts upon guest release. The chemical interactions between the guest molecules and the framework seems to be the key to these sorption properties. These observations point to the fact that the sorption potentiality of such flexible networks can not just be evaluated by the effective porosity exhibited by the evacuated solid.

The solvent release not only renders the pores accessible to other molecules but also liberates coordination sites on the metal ions. These may be regarded as Lewis acid centers and, consequently, these supramolecular porous architectures could be envisaged as catalysts. From this point of view, access to frameworks with given active centers (metal ions) becomes important and we currently develop our approach in this respect.

Experimental

The starting compounds $[K_4U(C_2O_4)_4]^{28}$ and $[K_4Zr(C_2O_4)_4]^{34}$ have been prepared according to described procedures. $UO_2(NO_3)_2$, $ZrOCl_2$, $K_2C_2O_4$ were purchased from usual commercial sources. All reagents were used as received.

CAUTION: Perchlorate salts are known to be potentially hazardous and must be used with care and always in small quantities. The ²³⁸U is an alpha emitter, the chemicals containing this metal ion must be handled with the required attention.

Synthesis

 $[K_2Mn{U(C_2O_4)}]$ -9H₂O, SPA-1. $K_4U(C_2O_4)_4$ was synthesized *in situ* from $U(C_2O_4)_2 \cdot 6H_2O$ (0.2 g, 0.4 mmol) and $K_2(C_2O_4) \cdot H_2O$ (0.15 g, 0.8 mmol) in H₂O (12 mL) at 80 °C. To the hot green solution, a solution of Mn(ClO₄)₂·6H₂O (0.15 g, 0.4 mmol) in H₂O (2 mL) was added. The reaction mixture was allowed to cool, and ethanol was slowly added without stirring yielding SPA-1 as a micro-crystalline light-green solid (0.27 g; 75%). The single-phase composition of the powder was checked by XRPD. Larger crystals were obtained when EtOH was allowed to mix by vapor diffusion with the H₂O solution. After 3 days green crystals of **SPA-1** (0.22 g; 62%) were collected and manually separated from the precipitated white manganese oxalate and light-green uranium oxalate. Anal. (%) Calcd. for $C_8O_{16}K_2MnU\cdot7H_2O$: C, 11.31; H, 1.66; K, 9.20; Mn, 6.47; U, 28.02 Found: C, 12.16; H, 1.62; K, 9.32; Mn, 6.58; U, 28.24. IR (KBr, cm⁻¹⁾: 3467 (s), 1654 (s), 1455 (m), 1440 (m), 1303 (m), 907 (w), 800 (m), 485 (m).

[K₂Cd{U(C₂O₄)}·5H₂O]·4H₂O, SPA-2. A solution of K₄U(C₂O₄)₄ was prepared from U(C₂O₄)₂·6H₂O (0.2 g, 0.4 mmol) and K₂(C₂O₄)·H₂O (0.15 g, 0.8 mmol) in H₂O (12 mL) at 80 °C. A solution of Cd(NO₃)₂·4H₂O (0.12 g, 0.4 mmol) in H₂O (5 mL) was dropwise added to this hot solution with slow stirring which yielded immediately a pink microcrystalline precipitate of SPA-2 (0.215 g; 68%). The single-phase composition of the powder was checked by XRPD. Larger single crystals of SPA-2 were obtained within 3 weeks by slow interdiffusion of the two aqueous solutions in an H-shaped tube (total volume 60 mL). These were washed with EtOH and dried in air (160 mg; 50%). Anal. (%) Calcd. for C₈H₁₈O₂₅CdK₂U: C, 10.19; H, 1.92; K, 8.29; Cd, 11.92; Found: C, 10.35; H, 1.92; K, 7.83; Cd, 11.47. IR (KBr, cm⁻¹⁾: 3482 (s), 1654 (s), 1458 (m), 1438 (m), 1303 (m), 907 (w), 800 (m), 486 (m).

[K₂Mg₂{U₂(C₂O₄)₇}·2H₂O]·9H₂O, SPA-3. K₄U(C₂O₄)₄ was synthesized *in situ* from U(C₂O₄)₂·6H₂O (0.2 g, 0.4 mmol) and K₂(C₂O₄)·H₂O (0.15 g, 0.8 mmol) in H₂O (12 mL) at 80 °C. To the hot green solution, a solution of Mg(ClO₄)₂·6H₂O (0.12 g, 0.4 mmol) in H₂O (2 mL) was added. The reaction mixture was allowed to cool, and ethanol was added by vapor diffusion. After 7 days green crystals (152 mg; 27%) were obtained that were manually separated from the precipitated white magnesium oxalate and light-green uranium oxalate. Anal. (%) Calcd. for C₁₄H₂₂O₃₉K₂Mg₂U₂: C, 11.87; H, 1.56; Mg, 3.43; U, 33.59 Found: C, 11.81; H, 1.36; Mg, 3.11; U, 34.01. IR (KBr, cm⁻¹⁾: 3397 (s), 1667 (s), 1633 (s), 1443 (m), 1372 (m), 1323 (m), 830 (m), 490 (m).

[K₂Mn{Zr(C₂O₄)₄}·8H₂O], SPA-4. An aqueous solution (10 mL) of K₄Zr(C₂O₄)₄·5H₂O (0.345 g, 0.5 mmol) was prepared and warmed to 80 °C. To the hot colorless solution Mn(ClO₄)₂·6H₂O (0.18 g, 0.5 mmol) in H₂O (3 mL) was added. The reaction mixture was allowed to cool, and ethanol was added by vapor diffusion. After 1 night colorless crystals (290 mg, 41%) were obtained. Anal. (%) Calcd. for C₈H₁₆O₂₄K₂MnZr: C, 13.34; H, 2.24; K,10.85; Mn, 7.62; Zr, 12.66 Found: C, 13.11; H, 2.04; K, 11.11; Mn, 7.41; Zr, 12.37 IR (KBr, cm⁻¹⁾: 3587 (s), 3491 (s), 1663 (s), 1457 (s), 1372 (m), 1337 (w), 1301 (m), 1122 (w), 917 (m), 808 (s).

Crystallographic studies

Single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer at 298 K (λ (Mo_{Ka}) = 0.71069 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values using SHELXL-97.³⁵ Crystal data are given in Table 1. For **SPA-4** the guest water molecules inside the channels were highly disordered in such a manner that they could not be readily resolved. No attempt was made to place the H atoms. The exact number of water molecules (eight) was deduced from chemical analysis.

CCDC reference numbers 246086, 266741 and 275039.

See http://dx.doi.org/10.1039/b503964a for crystallographic data in CIF or other electronic format.

The X-ray powder diffractograms for **SPA-1** and **SPA-3** were collected using a conventional (θ – 2θ) Phillips X-Pert diffractometer, with λ_{CuKa} , coupled to an Anton Parr oven. All data were collected in 5° < 2θ < 50° range, with 0.02 steps and 10 seconds of exposure. The compounds were heated at 1 °C min⁻¹.

The X-ray powder diffractograms for **SPA-2** were collected with a $(\theta - 2\theta)$ Panalytical X-Pert pro MPD diffractometer equipped with a X-celerator detector, using λ_{CoKa1} and λ_{CoKa2} with an Fe filter, coupled to an Anton Parr oven. Data were collected in 5° < $2\theta < 100^{\circ}$ range with 0.02 steps and 10 seconds of expositure. The compound was heated at 1 °C min⁻¹.

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