

Supramolecular Open-Framework of a Bipyridinium-Carboxylate Based Copper Complex with High and Reversible Water Uptake

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Abstract. The rigid zwitterionic ligand 1,1'-bis(4-carboxylatphenyl)-(4,4'-bipyridinium) (*pc1*) and copper(II) ions give rise to a linear complex [Cu(*pc1*)₂(H₂O)₄]²⁺, which self assembles in a pseudo tetragonal supramolecular arrangement leading to the supramolecular openframework [Cu(*pc1*)₂(H₂O)₄](Cl)₂·8H₂O exhibiting an open structure including water molecules and chlorides in pores. The dehydration of this material occurs at relatively low temperature (70 °C) and results in structure modification accompanied by shrinking of the crystals. Characterization of the obtained material by FT-IR spectroscopy re-

Introduction

Bipyridinium-carboxylate units have emerged as an interesting class of ligands in coordination chemistry, particularly in the field of Coordination Polymers (CPs) or Porous CPs (PCPs). On one hand, these ligands are based on the cationic redox-active bipyridinium moiety (also called viologen)^[1] which has strong abilities to interact with electron donors, and on the other hand, they include units anchoring to the bipyridinium cores, which bear carboxylate groups able to bind metal ions. Bipyridinium units (V²⁺) are known to undergo a reversible one-electron reduction, which is accompanied with a color change as well as V^{•+} radicals are created due to the different absorption domains of V^{2+} (UV) and $V^{\bullet+}$ (visible).^[1-4] In the solid state, the color change process, which can be activated by light or by heating, results from an electron transfer from electron donors such as chlorides^[5-8] or caboxylates,^[9-18] towards the electron acceptor bipyridinium units. Thus, the bipyridinium-carboxylate ligands appeared as very suitable to achieve photo-[9-18] and/or thermochromic[16-18] materials be-

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veals appearance of coordinated carboxylates groups, which may indicate the formation of coordination polymer after dehydration. Water adsorption (maximum uptake 0.23 g H₂O per g) on dehydrated material allows to restore the initial structure. A large hysteresis in water adsorption-desorption isotherm is characteristic of a significant modification of the structure during the hydration-dehydration cycle which is in line with the structural transition determined from thermodiffractometry and FT-IR spectroscopy.

cause of the presence of both the electron donor and acceptor parts on the same molecular unit. In the corresponding crystal structures, the molecular organization is mainly driven by the electrostatic interactions between bipyridinium cations and carboxylate anions. As a consequence, dense packing structures are often obtained while interesting photo- or thermochromic properties of related materials are observed.

In this context, the use of such ligands in the field of Porous Coordination polymers (PCPs) remains a great challenge. However, the interest of incorporating such linkers in PCPs is double. Because of their cationic nature, they can have a similar role than metal open sites for efficiency H_2 or CO_2 uptake, and because of their electron-deficient character, they can strongly interact with polar and/or electron-rich guest molecules for chemical sensor or gas storage applications.^[16,17,19–24] These materials are mainly based on zwitterionic bipyridinium carboxylate ligands, metal ions, and an anionic bipyridinium carbolylate linker.^[16] However the use of rigid linkers instead of flexible ones extensively adopted in the field of photochromic materials seems to be the better strategy to achieve porous compounds.^[17,19–24]

Another important class of porous compounds, porous supramolecular networks (PSN), has recently attracted considerable attention.^[25–32] While in PCPs the building units are bonded covalently, the framework of PSN is based on intermolecular interactions such as hydrogen bonds or π ··· π interactions. Despite their lower strength these interactions afforded many PSNs with high thermal stability and permanent porosity. Inclusion of bipyridinium-based units in PSN would represent thus an interesting alternative way to combine porosity and redox properties. However, in contrast to PCP the PSN

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containing viologen units are very scarce. To the best of our knowledge only two PSN phases containing such units have been reported to date.^[33,34]

In this context, we report on an original supramolecular open-framework material based on $[Cu(pcI)_2(H_2O)_4]^{2+}$ complexes (pcl = 1,1'-bis(4-carboxylatphenyl)-(4,4'-bipyridinium)) and its water adsorption properties. We show that the rigid zwitterionic pcl ligand affords linear Cu complexes, which interact through $CO_2^{-\cdots}H(H_2O)$ -molecules-linked-to-copper-ions) hydrogen bonding, leading to an open structure containing in pores two chloride ions and eight water molecules per formula unit. Interestingly, this materials based on hydrophilic Cu²⁺ and bipyridinium units has a quite high water capacity of 0.23 g per g, whereas the release of water occurs at moderate temperature (60 °C).

Results and Discussion

Structure Description

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The asymmetric unit of the monoclinic structure of $[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$ includes one copper dication located on a symmetry center and one *pc1* molecule, which further form a centrosymmetric linear complex $[Cu(pc1)_2(H_2O)_4]^{2+}$ (Figure 1a). Around Cu²⁺, the carboxylate



groups are monodentate while four water molecules complete the copper coordination sphere leading to a Jan-Teller type (4+2) coordination with 4 short bond lengths $[2 \times d(Cu-O1$ carboxylate) = 1.968(2) Å and $2 \times d(Cu-O5-water)$ = 1.952(2) Å] and two longer bond lengths $[2 \times d(Cu-O6-water)]$ = 2.525(2) Å] (Figure 2a). These linear complexes self-assemble through hydrogen bonding involving the free carboxylate groups and the water molecules linked to copper ions [(O5) H···O4: d = 2.637(3) Å, Figure 2a]), leading to an open 2D supramolecular network (Figure 1a). The overall structure results from the stacking of these layers (Figure S1, Supporting Information). When viewed along the *a* direction (Figure 1b), a pseudo-tetragonal molecular arrangement appears with channels running along the *a* axis, incorporating a great quantity of water molecules, 8 per copper ion as well as 2 chlorides which counterbalance the dicationic charge of the complexes (Figure 1b). The void volume of this open structure has been estimated by considering only the chloride ions in pores (water molecules of pores removed): the squeeze routine of Platon leads to a free volume of 538 Å³ per unit cell, corresponding to a porosity of 20.5% (see Figure S2 for space filling and void modelling representations). It must be noted that only half of the water molecules present in channels have been located thanks to the X-ray analysis. They correspond to those close to the walls of the framework which interact quite strongly through hydrogen bonding with either the water molecules linked to copper ions or the pcl ligands. The other water molecules in the center of channels are certainly disordered, which doesn't allow their location.



Figure 1. Structure of $[Cu(pc1)_2(H_2O)_4](Cl)_2\cdot 8H_2O$: (a) partial view showing the layered supramolecular assembly of $[Cu(pc1)_2(H_2O)_4]^{2+}$ complexes (one is underlined by a rectangle) held together by hydrogen bonding involving the free carboxylate group and water molecules linked to copper ion (dashed lines); (b) general view of the structure showing the channels running along the *a* axis, including chloride ions and water molecules.

Figure 2. Details of the crystal structure of $[Cu(pc1)_2(H_2O)_4](Cl)_2(H_2O)_4](Cl)_2(H_2O)_4](Cl)_2(H_2O)_4(Cl)_2(H_2O)_4(H_2O)_$

Details of the structure showing weak interactions between complexes and free water molecules and chlorides are depicted in Figure 2, which first shows the environment of a copper polyhedron viewed along the Cu-O6_{apical} bond direction. We clearly see the important role of water molecules (O5) of the CuO₄ equatorial plane that interact with one free oxygen atom of the carboxylate group bound to Cu^{2+} [(O5)H···O2: d =2.652(3) Å], and, as already mentioned, with one oxygen atom of a free carboxylate group. Finally, the anionic charge borne by this free carboxylate is also stabilized by a quite strong hydrogen bonding with a free H₂O (O8) molecule [(O8)H···O4: d = 2.769(3) Å] which itself also interacts both with the apical water molecule [(O8)H···Cl: d = 2.822(4) Å] and the free chloride anion [(O5)H···O2: d = 3.243(3) Å]. Of great importance to explain the properties of the redox active bipyridinium based materials is the surrounding of the viologen core. Figure 2b shows the main weak interactions involving the bipyridinium unit in [Cu(pc1)₂(H₂O)₄](Cl)₂•8H₂O.

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It is first important to remind the asymmetrical situation of this symmetrical pcl ligand, as on one side a carboxylate group binds the copper ion, while on the other side, the carboxylate group is free. Thus, this last carboxylate group has certainly an intramolecular electron donor effect towards the close pyridinium cycle explaining that only two side contacts of (C)H···O(water molecules, O6 and O8) type between the pyridinium cycle and its neighbors are counted (Figure 2b). In contrast, the other pyridinium cycle is stabilized through several acceptor-donor side and face interactions. On one hand the side contacts occurs between hydrogen atoms borne by the C atoms in α position of N⁺ and either Cl [(C)H···Cl: d =2.755(3) Å] or O atoms of water molecules. On the other hand, face contacts involve a phenyl ring of a neighboring molecule, and a water molecule which interact with the electron deficient N⁺ site through its electron donor oxygen atom [Figure 2b, $N2 \cdot \cdot \cdot O5(H_2) = 3.360(2) \text{ Å}].$

Thermal Behavior and Water Adsorption Properties

The thermogravimetric analysis of [Cu(pc1)₂(H₂O)₄](Cl)₂. 8H₂O shows that a first weight loss of 19.48% is observed at moderate temperature (from 60 °C to 70 °C, Figure 3). This value quite well corresponds to the departure 12 water molecules per formula unit (calcd. 19.31%), indicating that all water molecules, the free ones and those linked to copper ions are removed in one step. The compound further decomposes over 250 °C. When single crystals of the initial hydrated complex are heated, it is worth noting that crystals keep their transparency while they become darker and smaller (Figure 3). Unfortunately, a loss of crystallinity occurs during the transformation leading to diffraction images with very broad peaks. If a (same) unit cell of the dehydrated crystal could be found for several tested crystals, however, the quality of the data collections did not allow solving the crystal structure with a satisfying result. It appears that the unit cell volume of the hydrated phase is 33% bigger than the one of the dehydrated phase $[V_{\text{dehydrated}} = 3940(5) \text{ Å}^3 = 2 \times 1970 \text{ Å}^3, a = 37.79(2) \text{ Å},$ b = 14.42(2) Å, c = 7.231(2) Å, $a = 90^{\circ}$, $\beta = 90.49(4)^{\circ}$, $\gamma = 90^{\circ}$ vs. $V_{\text{hydrated}} = 2619 \text{ Å}^3$), in good accordance with the observed contraction of crystals upon dehydration. In account of the crystal packing observed for $[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$, we can anticipate that the water molecules, which were coordinated to copper ions were replaced by the initial free carboxylate groups and/or chlorides ions in the dehydrated phase.



Figure 3. TGA analysis of a crystallized sample of [Cu(pc1)₂(H₂O)₄](Cl)₂·8H₂O indicating the weight loss of all water molecules around 65 °C, and photos of one crystal before and after heating, as well as after re-hydration during a few minutes in a saturated water atmosphere.

Our assumption about coordination of carboxylate groups to Cu²⁺ after dehydration is supported by the evolution of FTIR spectrum of $[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$ after dehydration (Figure 4). Comparison of the spectra recorded before and after dehydration with those of other carboxylate-based MOFs^[35,36] allowed us to identify the symmetric (v_s) and asymmetric (v_{as}) bands of the carboxylate groups of pcl ligands. Position of these bands and particularly their splitting were shown to be sensitive to the coordination mode of the carboxylates.^[37] In our case the analysis is hampered by the fact that in both solids the bands are broadened due to the presence of carboxylates in different coordination. Despite this fact, a clear shift of the bands maximums and corresponding increase of the splitting $\Delta v = v_{as} - v_s$ (from 183 to 206 cm⁻¹) are observed after dehydration (Figure 4). Such increase is characteristic of the transformation of ionic COO⁻ to a monodentate one.^[34] It shows



Figure 4. FT-IR spectra of hydrated [Cu(pc1)₂(H₂O)₄](Cl)₂·8H₂O (blue) and after dehydration at 90 °C (red).

thus that the fraction of the monodentate carboxylates in $[Cu(pc1)_2(H_2O)_4](Cl)_2\cdot 8H_2O$ increases upon dehydration. This is in favor of the formation of bonds between COO⁻ and Cu²⁺ during this process.

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We performed EPR measurement on both hydrated and dehydrated phases in order to know if bipyridinium radicals were present in samples, particularly in the colored dehydrated phase. In fact, it was known in such materials that an electron transfer from electron donor units such as chlorides or carboxylates to the bipyridinium core could occur upon irradiation or heating, leading to colored radical based materials.^[2,16–18] Here, no signal has been detected, meaning that the dark color of the dehydrated sample is certainly due to a direct chargetransfer band relatively to a more efficient donor-acceptor interaction.

The dehydration process was followed by thermodiffractometry (Figure 5). In good accordance with the starting temperature of water removal observed in TGA, we can observe a change in the diffraction peak positions as soon as 60 °C leading to a pattern with several new broad peaks. This result first confirms a loss of sample crystallinity through the transition while positions of peaks are in good accordance with the unit cell found from the single-crystal diffraction study of dehydrated crystals. The re-hydration of crystals can be fast upon exposure to water, particularly in a saturated water atmosphere: in a few minutes the crystals of the dehydrated phase break under the effect of re-hydration as a result of the increasing of crystal volume (+33%, Figure 3). The XRPD pattern of the rehydrated sample exhibit lines well corresponding to the initial hydrated compound, showing that the transformation is reversible with the recovering of the initial crystal structure (Figure 5).



Figure 5. XRPD patterns of a crystallized sample of $[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$ at different temperature and after re-hydration, as well as theoretical XRPD ("theo-as" = theoretical of the assynthesized compound, "theo-d" = theoretical of dehydrated phase), showing the phase transformation upon dehydration and the reversibility of the process.

The adsorption-desorption isotherm of water in fully dehydrated compound ($Cu(pc1)_2Cl_2$) is presented in Figure 6a. We must first notice that the water uptake is high for this compound and that the reached value [0.230 g(H₂O) per g] is very close to the expected one if the initial hydrated phase is recovered [0.233 g(H₂O) per g for 12 H₂O per Cu]. It is worth noting that this water content is considerably higher than the amounts reported for other PSN (0.1–0.15 g per g).^[30,31,38–43] The maximum uptake observed for Cu(*pc1*)₂Cl₂ is thus comparable with the capacity of 3A molecular sieves (0.22 g per g).^[44] The affinity of our solid to water is however much weaker than that of molecular sieves in which the adsorption of water at 25 °C occurs at much lower pressure (*P*/*P*₀ < 0.001).^[44]



Figure 6. (a) Adsorption-desorption isotherm of water at 25 °C in fully dehydrated $(Cu(pcI)_2Cl_2)$ leading to $[Cu(pcI)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$; (b) water uptake of the material at P/P₀ = 0.8 in successive adsorption-desorption cycles.

In addition to higher uptake the interaction between water and Cu(*pc1*)₂Cl₂ shows two distinctive features in comparison with other PSN. First of them is a very steep increase of adsorbed amount and second one is a large hysteresis between the adsorption and desorption branches (Figure 6a). No such features have previously been reported for other PSN in which the increase is rather gradual (see, for example the isotherms in references ^[30,42]). A steep increase and large hysteresis are characteristic of a gate opening phenomenon during adsorption.^[45,46] In our case the gate opening (corresponding to the step in water uptake) occurs after adsorption of 0.034 $g(H_2O)$ per g (Figure 6a), which corresponds to 1.7 water molecules per Cu. This number is close to 2 molecules per Cu needed to replace carboxylates coordinated to Cu. Given this observation and the results of FTIR we suggest that the opening of the pores occurs at this point since the first water molecules replace the carboxylates moieties of *pc1* in the environment of Cu atoms. This process allows to depolymerize the structure formed upon dehydration and to restore the initial supramolecular network. Besides 4 H_2O molecules bound to Cu ions, the presence of open pores in this framework allows accommodation of additional 8 H_2O molecules per Cu atom. The gate opening phenomenon during water adsorption in $[Cu(pc1)_2Cl_2]$ is thus in line with the structural transition determined from the temperature-dependent XRPD (see Figure 5). It is important to note that despite strong structural changes occurring in hydration-dehydration cycle and partial loss of crystallinity the material is fully recyclable (Figure 6b): its maximum water up-take remains constant in successive adsorption-desorption cycles.

Conclusions

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We report formation of novel viologen-containing supramolecular open-framework $[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$ [pc1 = 1, 1'-bis(4-carboxylatphenyl)-(4, 4'-bipyridinium)]. The structure is based on a pseudo tetragonal supramolecular arrangement of [Cu(pc1)₂(H₂O)₄]²⁺ complex ions. It is shown that upon dehydration the compound undergoes structural transition leading to significant shrinking of the unit cell. Evolution of FT-IR spectra of the solid allows emitting the hypothesis that during dehydration the carboxylates of pcl ligands become coordinated to Cu atoms. The process was found to be reversible: exposure of the dehydrated phase to water vapor results in depolymerization and formation of the initial supramolecular network, the water uptake reaching 0.23 g per g. Moreover, the adsorption - desorption cycles of water on $[Cu(pc1)_2Cl_2]$ can be repeated many times without any loss of capacity.

Experimental Section

Synthesis and Characterizations: All starting materials were of analytical grade and obtained from commercial sources without further purifications. Ligand 4,4'-bis(carboxyphenyl)-bipyridinium dichloride dihydrate (H2pc1Cl2·2H2O) was synthesized according to literature (Supporting Information). Thermogravimetric analyses were performed with a TGA-2050 TA Instruments Systems from room temperature to 1000 °C with a heating rate of 10 K·min⁻¹ in a nitrogen flow. The synthesis of [Cu(pc1)2(H2O)4](Cl)2·8H2O was carried out as follows: a mixture of H₂pc1Cl₂·2H₂O (50.6 mg, 0.1 mmol), CuCl₂·2H₂O (51.1 mg, 0.3 mmol), DMF (0.5 mL), methanol (1 mL), and H₂O (2 mL) was heated at 100 °C for 48 h in a 25 mL teflonlined stainless steel autoclave. After the mixture was slowly cooled down to room temperature at a rate of 2 K·h-1, crystals of [Cu(pc1)₂(H₂O)₄](Cl)₂·8H₂O and a very small amount of black powder, assigned to CuO, are obtained. The sample was washed with ethanol and air-dried. [Cu(pc1)2(H2O)4](Cl)2·8H2O (1) 72% yield based H₂PC1Cl₂·2H₂O. The elemental analysis (calcd. for on [Cu(pc1)₂(H₂O)₄](Cl)₂·8H₂O (1143.41): C 50.42; H 4.94; N 4.90%; found C, 49.25; H, 4.54; N, 4.76%) indicates that the analyzed elements are under-measured out, confirming the presence of CuO as an impurity. The purity of the hybrid compound is estimated to 98-99%.

X-ray Diffraction: X-ray Powder Diffraction measurements were carried out with a D8 Bruker diffractometer using Cu- $K\alpha_{1,2}$ radiation, equipped with a linear Vantec super speed detector and a TTK450 chamber. The X-ray Powder diffraction (XRPD) patterns of

[Cu(pc1)₂(H₂O)₄](Cl)₂•8H₂O showed that all the observed reflections can be indexed in the unit cell parameters obtained from single-crystal X-ray diffraction experiment (Supporting Information). X-ray diffraction data of selected single crystal were collected with a Bruker-Nonius KAPPA-CDD diffractometer equipped with a graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). A summary of crystallographic data and refinement results is listed in Table 1. The structure was solved and refined using the Shelx197 package. Positions and agitation parameters were refined by full-matrix least-squares routines against F^2 . All hydrogen atoms were treated with a riding model. Two independent water molecules were localized in pores (8 per unit cell). The squeeze routine of Platon was used to model the remaining electronic density in pores, giving 74 electrons per unit cell, which quite well corresponds to 8 water molecules (theoretical : 80 electrons), also in accordance with the TGA and adsorption measurements. Finally, refinements of positions and anisotropic displacement parameters of all non-hydrogen atoms lead to $R_1 = 0.049$. A more complete summary of crystallographic data for [Cu(pc1)₂(H₂O)₄](Cl)₂·8H₂O is given in the Supporting Information)

Table 1. Crystallographic data for [Cu(*pc1*)₂(H₂O)₄](Cl)₂•8H₂O.

	$[Cu(pc1)_2(H_2O)_4](Cl)_2 \cdot 8H_2O$
Crystal system	monoclinic
Space group	$P2_1/n$
a /Å	10.444(1)
a /Å	16.554(1)
a /Å	15.556(2)
a /°	90
βΙ°	103.16(1)
y /°	90
Volume /Å ³	2618.8(4)
$\rho_{\rm calcd}$ /mg·m ⁻³	1.439
2θ max	27.90
Temperature /K	293
Refl. collected [unique with $I > 2\sigma(I)$]	4318
Data (parameters)	330
$R_1 [I > 2\sigma(I)] [wR_2 \text{ (all data)}]$	0.049 / 0.149

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1483080 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Adsorption Measurements: Adsorption-desorption isotherms of water on $[Cu(pc1)_2(H_2O)_4](Cl)_2\cdot 8H_2O$ were measured at 298 K with a home-built McBain-type thermobalance. Before measurements the samples (ca. 10 mg) were outgassed at 453 K under vacuum (10⁻⁶ hPa) overnight. The detailed description of the experimental procedure can be found elsewhere.^[17] The estimated experimental error on the adsorbed amount was about 1 mg per g. The accuracy of the pressure measurement was 1% and the temperature was maintained within 1 K. To characterize the reversibility of water adsorption several successive cycles were done at 25 °C, in which the material was exposed to water at $P/P_0 = 0.8$ (25.2 hPa) and degassed under vacuum.

Supporting Information (see footnote on the first page of this article): Synthesis of the ligands, crystal data, powder X-ray diffraction patterns, and IR spectra.

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Supramolecular Open-Framework of a Bipyridinium-Carboxylate Based Copper Complex with High and Reversible Water Uptake

