Cu-PDC-bpa solid coordination frameworks (PDC=2,5-pyrindinedicarboxylate; bpa=1,2-DI(4-pyridil)ethane): 2D and 3D structural flexibility producing a 3-c herringbone array next to ideal

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A B S T R A C T

Combination of polycarboxylate anions and dipyridyl ligands is an effective strategy to produce solid coordination frameworks (SCF) which are crystalline materials based on connections between metal ions through organic ligands. In this context, this work is focused on two novel CuII-based SCFs exhibiting PDC (2,5-pyrindinedicarboxylate) and bpa (1,2-di(4-pyridil)ethane), being the first structures reported in literature containing both ligands. Chemical formula are [Cu2((PDC)2(bpa))2(H2O)2]·3H2O·DMF (1), and [Cu2(PDC)2(bpa)(H2O)]·7H2O (2), where DMF is dimethylformamide. Compounds 1 and 2 have been characterized by means of X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimetric (TG) analysis, differential thermal analysis (DTA) and dielectric measurements. The crystallographic analysis revealed that compounds 1 and 2 can be described as herringbone-type layers formed by helicoidal Cu-PDC-Cu chains connected through bpa ligands. Solvent molecules are crystallized between the layers, providing the inter-layer connections through hydrogen bonds. Differences between both compounds are attributable to the flexibility of bpa (in 2D) as well as to the 3D packing of the layers which is solvent dependent. This fact results in the fact that compound 2 is the most regular 3-c herringbone array reported so far. The structural dynamism of these networks is responsible for the crystalline to-amorphous to-crystalline (CAC) transformation from compound 1 to compound 2. Crystallochemical features for both compounds have also been studied and compared to similar 3-connected herringbone-arrays.

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1. Introduction

Solid coordination frameworks (SCF) [1–4] represent one of the most studied material-family during the last decade thanks to the variety of structures that can be formed by using metal complexes as synthons.

Porous SCFs, in particular, can exhibit large cavities and high surface areas, so they have opened a wide range of applications in fields like gas storage [5–7], gas separation [8–10], drug delivery [11–13], chemical sensing [14,15], heterogeneous catalysis [16–18], biomedical imaging [19] and many others [20,21]. Therefore, they are receiving increasing attention as they can display a wide range of interesting functional properties like dielectric [22–24] behavior and water sorption for heat transformation [25,26].

Furthermore, these materials can present flexible or soft porous networks, producing the third generation of porous coordination polymers [27], which are especially interesting as they can exhibit structural dynamism compared to the rigid MOFs (metal organic frameworks). This dynamic nature seems to be advantageous for the development of new materials, and can be provoked by the presence of external stimuli, as light, heat, guest removal, condensation, or reactions between the ligands. This property can be enhanced by means of flexible ligands, being able to accommodate...
structural changes upon the exchange of different solvents located as host molecules in the cavities of the guest framework.

On the other hand, the mobility of guest molecules in SCFs with interconnected channels can be expected to produce interesting dielectric response [28–30]. In this way, focus has also been directed to the possible appearance of electrical order or dielectric anomalies induced by order-disorder processes of polar and/or H-bonded guest molecules located in the channels of the host structures. Besides, phase transformations are of interest in this type of systems. Particularly, some crystalline-to-amorphous-to-crystalline (CAC) transformations in literature are outstanding [31,32].

Polycarboxylate spacers are some of the most used ligands to built this kind of networks, being the 2,5-pyridinedicarboxylic acid (PDC) our choice. This ligand is non-centrosymmetric, exhibits five potential donor atoms, and has been observed to produce up to twenty three coordination modes (we first reported four of them) [33–36]. The dimensionality of the crystalline structures is influenced, in most of the cases, by the use of a secondary organic ligand that usually acts as a structural spacer. In these sense, we have focused our work on combinations of PDC with dipyridyl ligands. More specifically, the work herein presented is devoted to the unexplored PDC-bpa combination (bpa = 1,2-di(4-pyridil) ethane). As observed in Scheme 1, where the Lewis structure for both ligands has been drawn, bpa can be found as two geometric isomers, anti and gauche [37,38].

Taking into account the above mentioned aspects, this work reports on two novel CuPDC-bpa compounds exhibiting 2D herringbone-arrays. The new solids are related to Cu-PDC-bpe compounds published by us elsewhere [39] where bpe is 1,2-di(4-pyridyl)ethane. In that article we first established the different nature of the 4-c and 3-c herringbone arrays, and did identify the structural features for the 3-c ones. The interest of the present work lies on the fact that, as previously said, it first explores the PDC-bpa combination. The change from bpe [39] to bpa (current work) results in flexible herringbone-type SCFs related by a phase transformation. On the other hand, the lack of reversibility for this transformation is coherent with the fact that one of the compounds is the closest one to ideal 3-c herringbone-type arrangement reported so far. This work also discusses on the 2D and 3D flexibility making this phase transformation possible. In this sense, dielectric measurements have been performed in order to discuss the role of guest molecule mobility in the transformation.

2. Experimental section

2.1. Materials and general methods

All solvents and chemicals were used as received from reliable commercial sources. The reactants, 2,5-pyridinedicarboxylic acid (H$_2$PDC), 1,2-di(4-pyridylethene), copper (II) nitrate hydrated 99%, triethylamine (Et$_3$N) and the solvent N,N-dimethylformamide (DMF) 99.8%, were purchased from Sigma-Aldrich Co. The nitric acid 65% (HNO$_3$) and ethanol (EtOH) 96% were purchased from Panreac.

The thermogravimetric analysis (TGA) was performed under air atmosphere on a SDT 2960Simultaneous DSC-TGA TA Instrument. Heating rate was RT–500 °C (5 °C min$^{-1}$). The IR spectra were obtained with a Jasco FT/IR-6100 spectrophotometer in the 400–4000 cm$^{-1}$ range with pressed KBr pellets. C, H and N elemental analyses were measured using a Euro EA 3000 Elemental analyzer.

The complex dielectric permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$) of these samples was measured as a function of frequency and temperature with a parallel-plate capacitor coupled to a Solartron 1260A Impedance/Gain-Phase Analyzer, capable of measuring in the frequency range of 10 μHz to 1 MHz. The capacitor was mounted in a Jains SVT200T cryostat refrigered with liquid nitrogen and with Lakeshore 332 incorporated to control the temperature from 100 K to 350 K.

As the obtained single crystals of 1 were not big enough to perform single crystal dielectric measurements, pellets made out of well-dried samples were measured instead. Such pellets with an area of approximately of 300 mm$^2$ and thickness of approximately 0.5 mm were prepared to fit into the capacitor, and silver paste was painted on their surfaces to ensure a good electrical contact with the electrodes.

All the dielectric measurements were carried out in a nitrogen atmosphere where several cycles of vacuum and nitrogen gas were performed to ensure that the sample environment was free of water.

2.2. Synthesis of compound 1

H$_2$PDC (40.4 mg, 0.25 mmol), bpa (46.3 mg, 0.25 mmol) and Cu(NO$_3$)$_2$.6H$_2$O (93.3 mg, 0.5 mmol) were dissolved in a solvent mixture of DMF/H$_2$O (10/10 mL) after stirring for 1 h at RT. The pH value was adjusted to 4.5 using Et$_3$N and HNO$_3$ (0.5 M). The resulting solution was sealed in a teflon-lined autoclave for microwaves (XP1500), heating at 140 °C during 45 min in order to improve the solubility of the reagents. Then, the solution was filtered and dropped in a glass crystallizing dish. After twelve hours, blue prismatic crystals were obtained. The sample was washed and dried with ethanol, collecting a crystal for X-ray diffraction experiment. The density was measured by the flotation method in a mixture of bromoform/cholorofom being 1.68(5) g cm$^{-3}$ (Found: C, 43.1(2); H, 3.95(2); N, 8.43(3). Calc. for C$_{29}$H$_{35}$Cu$_2$N$_5$O$_{14}$: C, 43.24; H, 4.35; N, 8.70. IR: vmax/cm$^{-1}$ 3424 (OH), 1656 and 1622 (aroC=C), 1281 (C–N), 1560 (asCOO), 1425, 1389 and 1352 (sCOO), 835, 768 and 693 (C–H) and 549–532 (Cu–N) (Fig. S1, ESIf)).

2.3. Synthesis of compound 2

H$_2$PDC (93.3 mg, 0.5 mmol), bpa (81.1 mg, 0.5 mmol) and Cu(NO$_3$)$_2$.2.5H$_2$O were dissolved in a solvent mixture of H$_2$O/EtOH (20/10 mL) after stirring for 1 h at 60 °C. The resulting solution was filtered and dropped in a glass crystallizing dish. After several days, blue prismatic crystals were obtained. The sample was washed with ethanol, collecting a crystal for X-ray diffraction experiment. The density was measured by the flotation method in a mixture of
2.4. Single-crystal X-ray diffraction

Prismatic single-crystals of compounds 1 and 2 with dimensions given in Table 1 were selected under polarizing microscope and mounted on MicroMounts. Single-crystal data were collected at 100 K on an Agilent Technologies Supernova single source diffractometer with Cu-Kα radiation (1.54184 Å) for compound 1 and Mo-Kα (0.71073 Å) radiation for compound 2. Details of crystal data and some features of the structures refinements are reported in Table 1, and selected bond length and angles are listed in Tables S1 and S2 (ESI).

Lattice constants were obtained by using a standard program belonging to the diffractometer software, confirming at the same time the good quality of the single-crystals. The Lorentz polarization and absorption corrections were made with the diffractometer software, taking into account the size and shape of the crystals [40]. The structures were solved by direct methods using SIR92 program [41], with the monoclinic P2₁ space group for compound 1, and the C2/c for compound 2, which allowed us to obtain the positions of the copper atoms, as well as the oxygen and nitrogen atoms and some of the carbon atoms of both PDC and bpa ligands of compounds 1 and 2. The refinement of the crystal structures was performed by full-matrix least-squares based on F²

Using the SHELXL-97 program [42], obtaining the remaining carbon atoms and allowing the allocation of the hydrogen atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms (Figs. S3 and S4, ESI). The hydrogen atoms belonging to the organic molecules were fixed geometrically and allowed the ride on their parent carbon atoms (C–H 0.93 Å), and were refined with common isotropic displacements. The position of the hydrogen atoms bonded to the coordinating water molecules of compounds 1 and 2, as well as the hydrogen atoms bonded to the crystalization water molecules of compound 1, were fixed using DFIX and DANG instructions in the refinement to adjust the O–H distance to 0.82 Å and the H–O–H angle to 12°, respectively. In compound 2, there is one crystallization molecule of water disordered in two parts, and another one is situated in a special position, being its occupancy of 0.5. The hydrogen atoms of these water molecules were not considered due to the lack of density in the residual density map. Attempts to solve the structure for 1 in P2₁/n were fruitless.

3. Results and discussion

3.1. Crystal structures

Crystal structures for compounds [Cu₂(PDC)₂(bpa)(H₂O)₂·3H₂O·DMF]⁵, and [Cu₂(PDC)₂(bpa)·(H₂O)₂·7H₂O] (2) are quite similar, so they will be described together. In fact, both compounds consist of 2D arrays of the 3–c herringbone-type (Fig. 1). We have recently reported on similar arrays for Cu–PDC–bpe systems (bpe = (1,2-di(4-pyridyl)ethene) [39] For both compounds, Cu atoms have square pyramidal coordination environment, being coordinated to two oxygen atoms and a nitrogen atom (from two different PDC ligands) and to a nitrogen atom belonging to a bpa ligand in the equatorial plane and to a water molecule on the apical position. (Figs. S3 and S4, ESI).

As observed in Fig. 1, herringbone arrays exhibit different angles and distances which will be discussed below. These differences are based on the distinct torsion angles for bpa in compounds 1 (10.15°) and 2 (5.55°). Both angles correspond to the anti conformation. On the other hand, PDC ligands linking Cu₁ and Cu₂ atoms in 1 are rotated in comparison to the PDC ligands linking equivalent Cu₁ atom in 2 (Fig. S5, ESI).

These herringbone layers are interconnected via hydrogen...
and 2.0366(2) Å (Tables S1 and S2, ESI†). Most significant bond distances and angles for compounds 1 and 2 are reported in Tables S5 and S6 (ESI†), respectively.

In summary, the same synthon (Cu–PDC–0.5bpa–H2O) produces herringbone arrays with quite different features. In fact, as observed in Fig. 1, the 2D array for 2 is closer to an ideal 3-c herringbone (where metal atoms should be coplanar). Thus, these differences influence on the stacking mode.

As observed in Fig. 3, packing of these layers takes place along the [010] direction. The diameter of the channels has been evaluated by means of the Voronoi–Dirichlet polyhedra, which were constructed through the Dirichlet program included in TOPOS [43] (Fig. S6, ESI†). The dimensions of these channels are 2.888 Å × 2.584 Å for 1, and 3.150 Å × 2.014 Å for 2. On the other hand, the interlayer distances are quite different for both compounds. Minimum and maximum intermetal distances are 7.858 Å and 11.479 Å for 1, and 6.366 Å and 7.155 Å for 2 (Fig. S7, ESI†). The fact that compound 2 is nearer the ideal 3-c herringbone array allows the planes to be closer.

Topological features for compounds 1 and 2 were analyzed by means of the TOPOS [46] software, revealing a hcb Shubnikov hexagonal plane net (Point symbol = 63 and vertex symbol = [6.6.6]), corresponding to the topology shown in Fig. S8, ESI†.

The distortion of coordination polyhedra was evaluated according to Avnir method [44,45] based on the continuous symmetry measures (CSM), by means of SHAPE program [46], and the results can be seen on Table 2. The projection of the as-calculated values on the distortion diagram can be seen in Fig. S9, ESI†. As observed for the three analyzed CuII ions, distortion is on a non-Berry pathway that converts the trigonal bypiramid into a square pyramid [47] (Spy) with a soft contribution of a vacant octahedron (VOC) distortion. In fact, for Cu1 and Cu2 in compound 1, the axial distances (Cu1–O2W = 2.2488(2) Å and Cu2–O1W = 2.2197(2) Å) are longer than the equatorial ones (going from 1.9340(2) Å to 2.0366(2) Å). Similarly, for compound 2, the axial distance Cu1–OSW is 2.259(2) Å, and the equatorial ones go from 1.9737(2) Å to 1.999(2) Å.

3.2. Herringbone mapping

As said before, we elsewhere reported a mapping of the herringbone-type structures identifying two types of arrays depending on the number of connections for each metal ion: this is, 4-connected (4-c) or 3-connected (3-c). Furthermore, we identified the structural parameters defining the 3-c herringbone arrays, correlating angles and distances (Scheme 2) [39,48–56].

Representative values for compounds 1 and 2 are shown in Table 3. Representation of these values can be seen in Fig. 4. As observed, compound 1 lies on the typical zone around a1 = a3 ≈ 60° and a2 ≈ 75°. On the other hand, as far as we are concerned, values for 2 indicate that this compound is the closest one to an ideal 3-c herringbone reported so far (ideality referred to angles). Obviously, the fact that a1 + a2 + a3 for 2 is 332.50° (this is, close to 360° which is the value corresponding to coplanarity) is in accordance with the later. For compound 1, a1 + a2 + a3 = 280.15°. This is an habitual value for similar arrays.

3.3. Thermogravimetry

In order to study the thermal stability of compounds 1 and 2, thermogravimetric (TG) analysis was performed.
Compound 1 shows two-stages of mass loss (Fig. S10, ESI†). The first of them, starting at RT and finishing at about 245 °C, has been assigned to the removal of the crystallization and coordination molecules of water and DMF (20.1% calc. and 18.32% exp.). The second one (63.35% calc. and 61.38% exp.) is an abrupt mass loss, and corresponds to the removal of both organic ligands occurring between 245 °C and 340 °C. The residue has been identified by X-ray powder diffraction as CuO [57].

The TG analysis of compound 2 shows a weight loss of 17.1% from RT to 100 °C (Fig. S11, ESI†), attributed to the crystallization and coordination molecules of water (18.5% calc.).

Table 2
Geometrical distortions of the trigonal bypiramid (TBPY) and Berry square pyramid (SPY), calculated using SHAPE software.

<table>
<thead>
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<th>Compounds</th>
<th>Pentacoordinate</th>
<th>S(TBPY)</th>
<th>S(SPY)</th>
</tr>
</thead>
<tbody>
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<td>Compound 1</td>
<td>Cu(1)</td>
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</tr>
<tr>
<td></td>
<td>Cu(2)</td>
<td>5.47</td>
<td>1.08</td>
</tr>
<tr>
<td>Compound 2</td>
<td>Cu(1)</td>
<td>4.40</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 3
Structural parameters for compounds 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>Compound 1</th>
<th>Compound 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₁ (°)</td>
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<td>162.19</td>
</tr>
<tr>
<td>a₂ (°)</td>
<td>68.03</td>
<td>95.46</td>
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<tr>
<td>a₃ (°)</td>
<td>75.64</td>
<td>74.85</td>
</tr>
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<td>dₐ (Å)</td>
<td>7.25</td>
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</tr>
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<td>dₘ (Å)</td>
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<td>13.33</td>
</tr>
<tr>
<td>dₙ (Å)</td>
<td>12.11</td>
<td>13.09</td>
</tr>
<tr>
<td>a₁ - a₃ (°)</td>
<td>60.84</td>
<td>87.34</td>
</tr>
</tbody>
</table>

Fig. 2. 3D supramolecular framework for (left) compound 1 and (right) compound 2. Crystallization molecules of water are shown in red, and DMF molecules in violet. Zoomed images at the bottom show the hydrogen bonds as dashed lines (all hydrogen atoms are omitted). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Packing for (left) compound 1 and (right) compound 2, showing the A-A-A and A-B-A disposition of the layers, respectively. Crystallization molecules of water are shown in red, and DMF molecules in violet (all hydrogen atoms are omitted for clarity). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Representation of the a₂ parameter vs. the a₁-a₃ parameter for the herringbone arrays found in literature. Compounds 1 (purple) and 2 (red) are marked by filled symbols. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Compound 1 shows two-stages of mass loss (Fig. S10, ESI†). The first of them, starting at RT and finishing at about 245 °C, has been assigned to the removal of the crystallization and coordination molecules of water and DMF (20.1% calc. and 18.32% exp.). The second one (63.35% calc. and 61.38% exp.) is an abrupt mass loss, and corresponds to the removal of both organic ligands occurring between 245 °C and 340 °C. The residue has been identified by X-ray powder diffraction as CuO [57].

The TG analysis of compound 2 shows a weight loss of 17.1% from RT to 100 °C (Fig. S11, ESI†), attributed to the crystallization and coordination molecules of water (18.5% calc.). The curve shows...
Dielectric properties are interesting for various technological applications. In fact, outstanding materials exhibiting colossal dielectric constants (CDC), like some metal oxides, have been reported elsewhere [61–64]. Concerning this topic, there has been a fruitful debate about intrinsic and apparent colossal dielectric constants. In this sense, we elsewhere reported on some nanoporous SCFs (also known as metal-organic frameworks) exhibiting apparent CDCs [65] in which the dielectric behavior is attributed to an order-disorder process of the guest molecules allocated in the cavities of the framework. Additionally, this effect is enhanced by the activation of extrinsic interfacial polarization effects associated with the diffusion of numerous guest molecules through the channels and the formation of a concomitant electrical double layer.

Compounds 1 and 2 are also SCFs but the cavities occupied by solvent molecules are much smaller (2.888 Å × 2.584 Å for 1, and 3.150 Å × 2.014 Å for 2). Therefore, mobility of the guest molecules is expected to be lower than required for CDC. However, even if there is a reduced mobility, dielectric measurements could provide useful information associated to the CAC transformation from 1 to 2, as it involves the removal of DMF molecules and the entrance of water into the cavities of the framework.

Thus, Fig. 6 shows the temperature dependence of the real part of the complex dielectric permittivity \(\varepsilon'_i\) (the so-called dielectric constant) of pressed pellets of 1. The obtained results show the following interesting features; (i) this compound displays an almost constant \(\varepsilon'_i\) (about 4–4.5) in the low-temperature regime below 225 K; (ii) above that temperature the dielectric constant increases with temperature, and the rise is more pronounced above 300 K, reaching a maximim value \(\varepsilon'_{\text{max}} \sim 14\) at 350 K (iii) the increasing of the dielectric constant with temperature depends on the frequency of the ac electric field and agrees well with the common dielectric law [30] Similar values of the dielectric constant have been reported elsewhere for other 2D SFCs [22,23,66].

The dielectric response exhibited by compound 1 can be directly attributed to the presence of dipolar guest molecules inside the cavities of the framework and to their concomitant orientational polarizability. In view of the obtained results, at low temperatures the guest molecules exhibit very reduced thermal motion. Nevertheless, their degree of freedom markedly increases with temperature, resulting in a higher polarizability close to room temperature, and thus in a higher dielectric constant. On the other
hand, the absence of any dielectric anomalies excludes the presence of cooperative order-disorder processes of the dipolar guest molecules located in the structure within the temperature range studied.

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4. Conclusions

The same synthon (Cu–PDC–0.5bpa–H₂O) produces two different 3-c herringbone arrays thanks to the torsion flexibility of bpa ligand. Additionally, these planes get 3D packed according to distinct modes that are solvent dependent since the interlayer connections are based on hydrogen bonds. Therefore, 2D and 3D flexibility has been observed for the compounds herein studied. The role of the guest molecules has been determined, and a CAC technical support is gratefully acknowledged. SGilker (UPV/EHU) technical support is gratefully acknowledged. F. Llanó-Tomé thanks the “Ministerio de Ciencia e Innovación” for a fellowship (BES-2011-045781).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2015.06.039.

References


