Cu(II) bifunctional (N,O,O') coordination polymer: a case study for complex *ab-initio* crystal structure determination from PXRD data

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Abstract

The synthesis of a novel Cu(II) bifunctional (*N,O,O'*) coordination polymer, the Cu(PzHP) compound, has been carried out by coupling Cu(II) salts and the newly synthesized **H₂(PzHP)** organic linker (**H₂(PzHP)** = 1-[4-(1*H*)-pyrazolyl]-2-methyl-3-hydroxy-4(1*H*)-pyridinone). Despite to the numerous attempts done for the growth of suitable single crystals and to the synthetic trials carried out to ameliorate the crystallinity of the **Cu(PzHP)** coordination polymer, its diffraction pattern was always characterized by a discouraging, *less-than-ideal*, crystallinity. Notwithstanding the extended disorder, leading to an higher than required space group symmetry, we succeeded in the description of its relevant structural features by following an unconventional route to *ab-initio* structure solution. In this process consideration on the coordination ability of the ligand and on the space group symmetry have been taken into account to 'manually' achieve the initial structural model, highlighting that, in some cases, it is still possible to ascertain by PXRD the crystal structure of a material that shows *challenging*, broad, PXRD pattern.

Introduction

In coordination chemistry, the last two decades have observed a blooming of the research on the class of porous metal-organic frameworks (MOFs) structures,[1] with the aim of finding new solutions for highly relevant environmental problems, such as CO_2 capture and storage,[2-3] but also to technological aspects of modern materials science.[4] As MOFs are composed by metal ions connected through polytopic organic ligands, the possible combinations of these two components are almost infinite, and the limit to the discovery and potential applications of new structures is just upon the human imagination, as brilliantly stated by Feréy.[5] It is indeed true that the number of deposited structures of MOFs in the CSD is continuously increasing during the years.[1,6]

The organic ligands used as bridges between the metal centers possess a key role in the formation of structures with different topologies, if the metal ions show relatively fixed coordination geometries. Since the first times, *O*-based, and mostly, carboxylate-based linkers, have been widely explored for the synthesis of new materials and it is now well established that they works well in the formation of porous MOFs with almost predictable topologies. Azolate-based ligands have also been investigated with success revealing that they can give rise to a variety of structures possessing interesting properties and, on top, a relatively high structural stability.[7,8]

If one focuses his attention to the formation of structures with very high chemical and thermal stabilities, it has been widely demonstrated that the employment of strong metal-ligand bonds is the way to this goal.[9] Indeed, Zr-carboxylate MOFs are one of the most thermally stable materials yet synthesized[7] and, within metal-azolate frameworks, pyrazolate-based ones can led to highly thermally- and even chemically- stable MOFs.[10,11]

In the search of the best compromise between high stability and good reactivity of the MOF,[12] an idea that is coming out in the last years is to combine the versatility of *O*-based linkers with the robustness of *N*-based ones, with the design and synthesis of bifunctional organic linkers. While the idea of using two different type of ligands in a MOF has been widely investigated,[13] to the best of our knowledge only few researchers have explored to date the synthesis of MOFs from bifunctional ligands with both *O*-donor and azolate N-donor groups on the same organic skeleton.[14-16] Particularly, within azolates, the use of pyrazolate/*O*-donors bifunctional linkers is still limited in the literature.[17-21] This fact could be ascribed to difficulties in preparing these linkers in a fast, inexpensive and high-yield manner[22] and, above all, to the fact that pyrazolate-based linkers with low solubility often precipitates in the form of polycrystalline MOFs powders, preventing the researcher to grow suitable single crystals for routinely XRD structural analysis. However, when polycrystalline powders are available, *state-of-the-art* Powder X-Ray Diffraction (PXRD) methods comes to our hand and permits the description of the mayor structural features and the rationalization of the material properties by exploiting *ab-initio* structural analysis.[23]

Based on our knowledge on the synthesis and characterization of pyrazolate- and carboxylate/pyrazolate-based MOFs,[11,17,24-27] we have now synthesized a new mixed-site organic linker incorporating both *N*-pyrazolate and a (*O,O'*)-3,4-dihydroxypyridinonate (HP), related to maltol, as donor groups: the **H₂(PzHP)** ligand **4** (Scheme 1, **H₂(PzHP)**= 1-[4-(1*H*) -pyrazolyl]-2-methyl-3-hydroxy-4(1*H*)-pyridinone). This linker has been designed taking advantage of the presence of either a pyrazole ring (that assures high robustness of the MOFs) or an HP subunit, with well-known propensity to 5-membered metal chelate formation.[28] In the following, we describe the characterization of this newly organic ligand herein with its crystal structure, retrieved by conventional *ab-initio* structural analysis from PXRD data, collected from crystalline powders of the sample. Moreover, with the idea of searching for new MOFs structures, we coupled this ligand with Cu(II) metal ions and we obtained a novel Cu(II) coordination polymer, **Cu(PzHP)**, possessing an interesting hexagonal

structure with Cu(II) helix motif. The challenging diffraction profile of the **Cu(PzHP)**, characterized by few and relatively broad peaks and *less-than-ideal* crystallinity, required a rather new approach to structure solution by applying *state-of-the-art* structural powder diffraction techniques, which have now definitely increased the armamentarium at disposition of structural chemists, well beyond the traditional methods of qualitative and quantitative analyses.[29] In this contribution, we would like to confirm the utility of powder diffraction methods on dealing with low-crystalline materials hiding the intrinsic blurring of laboratory-scale instrumentation.

Experimental

Materials and Methods

All the solvents and the reagents were obtained from commercial suppliers and used as received. Elemental analyses were obtained with a Perkin Elmer CHN Analyzer 2400 Series II. IR spectra were acquired in Nujol mulls by means of a Shimadzu FT-IR Prestige 21 instrument over the range 4000–600 cm^{-1}. Thermogravimetric analyses and differential scanning calorimetry were performed simultaneously with a Netzsch STA 409 instrument under N_2, from 30 °C up to 900 °C, increasing the temperature with a rate of 5 °C min^{-1}. 3-O-benzylmaltol (**2**) was prepared according to the method of Gaeta *et al*.[30] 4-amino-1H-pyrazole (**1**) was obtained according to literature.[31]

Synthesis and characterization of the H$_2$(PzHP) ligand and its intermediates

Synthesis of 1-[4-(1H)-pyrazolyl]-2-methyl-3-(benzyloxy)-4(1H)-pyridinone 3. 4-amino-1H-pyrazole (830 mg, 10.0 mmol) was added to a solution of 3-O-benzylmaltol **2** (2.10 g, 9.72 mmol) in 50% aq EtOH (10 mL) followed by a catalytic amount of 2N NaOH (0.1 mL, 0.02 mmol), charged in a 25-mL Teflon-lined stainless steel vessel and heated at 160°C for 45 h. The solvent was then evaporated under vacuum. Later on, water (40 mL) and ethyl acetate (20 mL) were added to the obtained solid. The mixture was stirred for 2 h and filtered off. The obtained solid was dried under vacuum affording the title compound as a pure, white powder. Yield: 52 %. Anal. Calcd. for $C_{16}H_{15}O_2N_3$ (Mw= 281.32 g/mol): C,68.07; H,5.71; N,14.88. Found: C,67.59; H,5.40; N,14.88. IR (KBr, cm^{-1}): 3114 (br); 3064 (m); 2885 (br); 2825 (br); 1614 (s); 1543 (s); 1507 (s) cm^{-1}. ^{1}H-NMR (DMSO-d$_6$, 298.2 K): 1.95 (3H, s); 5.05 (2H, s); 6.20 (2H, d, J:7.52 Hz); 7.54 (2H, d, J:7.52 Hz); 7.36 (5H, m); 13.25 (1H, s, br). ^{13}C-NMR (DMSO-d$_6$, 298.2 K): 14.34 (CH$_3$); 72.46 (CH$_2$); 111.38 (CH); 141.46 (CH); 128.70 (CH); 124.57 (C); 138.21 (C); 141.95 (C); 145.55 (C)

Synthesis of 1-[4-(1H) -pyrazolyl]-2-methyl-3-(hydroxy)-4(1H)-pyridinone, H$_2$(PzHP), 4. A mixture of 1-[4-(1H)-pyrazolyl]-2-methyl-3-(benzyloxy)-4(1H)-pyridinone **3** (400 mg, 1.42 mmol) in AcOH (10 mL) and 10% Pd/C (30 mg) was placed in a 50-mL stainless steel autoclave and flushed with H_2. The autoclave was pressurized to 400 kPa and set aside for 4 h at room temperature. The mixture was filtered through a small Celite pad, rinsed with CH$_2$Cl$_2$ (2 x 10

mL). The combined filtrates were evaporated to dryness, heated at 100°C under vacuum (130 mPa) for 5 h to furnish **4** as a straw yellow solid (54% yield). Calcd. for $C_9H_9N_3O_2$ (Mw=191.07 g/mol) C, 53.19; H, 5.20; N, 20.55. Found: C, 53.43; H, 4.93; N, 19.22. IR (nujol): 3169 (br); 3221 (br); 2925 (br); 1635 (s); 1556 (s); 1496 (s); 1402 (m); 1234 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 298.2 K): 2.03 (3H, s); 6.17 (1H, AB syst, ^3J 7.3 Hz, H-5); 7.51 (1H, AB syst, ^3J 7.3 Hz, H-6); 7.93 (2H, s, H-pz). ^{13}C-NMR (DMSO-d_6, 298.2 K): 13.6 (CH_3); 111.38 (CH); 124.72 (C); 130.13 (C); 139.75 (CH); 145.45 (C); 170.14 (C). DSC/TGA: 275 °C (dec). UV-Vis: λ_{max}288 nm (ε 19000 $mol^{-1}cm^{-1}$)(MeOH)

Synthesis and characterization of Cu(PzHP)

To a 25-mL Teflon-lined stainless steel vessel was added ligand **4** (200 mg, 1.04 mmol) and $Cu(OAc)_2 \cdot H_2O$ (208 mg, 1.04 mmol) in 28% NH_4OH (8 mL). The autoclave was sealed, heated at 120°C and allowed to dwell under autogenous pressure at that temperature for 24 h. The system was then allowed to slowly cool to room temperature at a rate of 10°C/h, the blue-green precipitate was collected by filtration, washed with H_2O and dried under vacuum (130 mPa) at room temperature for 4 h (81% yield). Anal. Calc. for $C_9H_7N_3O_2Cu$ (Mw = 252.72 g/mol): C, 42.77; H, 2.79; N, 16.63. Found: C, 42.70; H, 2.06; N, 17.06. IR (Nujol): 3360 (br), 1596 (s), 1538 (w), 1475 (s), 1348 (s), 1305 (w), 1029 (m), 883(w), 850(w), 811(w), 730(m), 654(s) cm^{-1}.

Crystal structure determination by ab-initio PXRD methods

Gently ground powders of **H₂(PzHP)** and **Cu(PzHP)** compounds were deposited in the, 2 mm deep, hollow of a zero background plate (a properly misoriented quartz monocrystal). Diffraction experiments were performed using Cu-K$_\alpha$ radiation (λ = 1.5418 Å) on a vertical-scan Bruker AXS D8 Advance diffractometer in θ:θ mode, equipped with a Goebel Mirror and a linear Position Sensitive Detector (PSD), with the following optics: primary and secondary Soller slits, 2.3° and 2.5°, respectively; divergence slit, 0.1°; receiving slit, 2.82°. Generator setting: 40 kV, 40 mA. Temperature: room temperature. The nominal resolution for the present set-up is 0.08° 2θ (FWHM of the α_1 component) for the LaB_6 peak at about 21.3° (2θ). The accurate diffraction patterns at RT of **H₂(PzHP)** and **Cu(PzHP)** compounds were acquired in the 8–90° 2θ range, with Δ2θ = 0.02° and exposure time 5 s/step. The structural process is here described in detail for both samples.

H₂(PzHP): a standard peak search below 30° was followed by indexing through the singular value decomposition method,[32] implemented in TOPAS-R,[33] which led to a monoclinic cell of approximate dimensions: a = 6.46 Å , b = 12.81 Å, c = 10.84Å, β = 80.36 and V = 885.63 Å³ (GoF(20) = 15.91). Systematic absences led to individuate $P2_1/c$ as the most probable space group. Prior to structure solution, a Le Bail refinement was carried out (a = 6.4844 Å , b = 12.8123 Å, c = 10.829 Å and β = 80.4427; R_{wp} 10.676, Figure S1) in order to determine the background, cell and profile parameters to be used in the subsequent simulated annealing runs. A preliminary structural model was determined *ab initio* by the simulated annealing approach implemented in TOPAS-R. A rigid body was used to describe the **H₂PzHP** ligand.[34] A torsion angle around the N3-C1 bond, connecting the pyrazolate to the HP fragments, was let to refine.

Cu(PzHP): the same indexing procedure followed for **H₂(PzHP)** led to a hexagonal cell (chiral SG P6₁) of approximate dimensions: a = 10.15 Å, c = 17.26 Å and V = 1540.2 Å³ (GoF(20) = 27.2). The Le Bail refinement, in $P6_1$, afforded an R_{wp} of 5.54, well describing all, inherently quite broad, peaks (Figure S2). See main text for the detailed procedure followed in order to solve the crystal structure of the **Cu(PzHP)** polymer.

The peak shapes of both samples were described with the fundamental parameters approach[35] and with the aid of spherical harmonics. The background was modelled by a Chebyshev polynomial function. The thermal effect was simulated by using a single isotropic parameter for the metal ion, augmented by 2.0 Å² for lighter atoms. The final Rietveld refinement plots are supplied in Figure 1a and 1b for **H₂PzHP** and **CuPzHP**, respectively. Crystal data are reported in Table 1. Fractional atomic coordinates are provided with the Supporting Information as CIF file. Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No 1542711-1542713. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uks or http://www.ccdc.cam.ac.uk).

Thermodiffractometry

Variable-temperature X-ray powder diffraction (VT-XRPD) experiments were performed on **Cu(PzHP)**. The experiment was carried out in air coupling a custom-made sample heater,

assembled by Officina Elettrotecnica di Tenno, Ponte Arche, Italy, to the instrumental set-up described above. Powdered microcrystalline samples of the two species were ground in an agate mortar and were deposited in the hollow of on a quartz zero-background plate framed by an aluminium skeleton. The data were acquired within a sensible, low-angle 2θ range (9-30°), heating the samples in situ in the temperature range 30-300 °C, with steps of 20 °C. Le Bail parametric refinements on the data measured in the range 30-260 °C (*i.e.* before a significant loss of crystallinity was observed) allowed describing the behaviour of the unit cell parameters as a function of the temperature. The VT diffractograms and the results of the parametric data treatments are depicted in Figure 3. *When comparing TGA and VTXRPD results, the reader must be aware that the thermocouple of the VT-XRPD set-up is not in direct contact with the sample, this determining a slight difference in the temperature at which the same event is detected by the two techniques. The TGA temperatures have to be considered as more reliable.*

Results and discussion

With the aim of testing the ability of the **H₂(PzHP)** organic linker in the formation of porous metal-organic frameworks, we coupled it with Cu(II) ions, in basic conditions, and we isolated a blue-green polycrystalline powder. The numerous synthetic attempts carried out to ameliorate the crystallinity of this sample resulted in similarly poor batches. Moreover, attempts done for obtaining suitable single crystals for XRD analysis always failed out. It should be noted that, in any case in which it is feasible, single crystal X-ray diffraction has to be considered the structural approach of choice. However, those type of coordination compounds, that are built up by strong ligand-to-metal bonds, as this **Cu(PzHP)** specie, tend to precipitate as insoluble, polycrystalline powders because of the irreversible and quick formation of crystals, where growth and dissolution rates are not in equilibrium, as occurs during the formation of single crystals. As a consequence, the structural aspect of these specimens have to be derived by X-ray powder diffraction methods, that are nowadays definitely reaching their maturity.[36] However, there are very complex cases in which some compound show discouraging diffraction patterns, characterized by poor crystallinity, with few, broad, peaks possessing widths at half maximum as large as 0.3-0.4° (2θ). In these cases, even standard PXRD methods fails in the solution process and the relevant structural features have to be retrieved by coupling other chemical/topological or experimental observations.[37]

In this contribution we would like to highlight that, in some cases, it is still possible to describe the crystal structure of a coordination polymer that shows a challenging, low-quality, PXRD pattern. Here, we describe the remarkable result obtained for the description of the **Cu(PzHP)** coordination polymer by following the alternative strategy that is thoroughly discussed in the *rather unconventional* experimental section of this paper.

Synthesis of the organic linker and of Cu(PzHP) coordination polymer.

The synthetic approach to the ligand, highlighted in Scheme 1, was based on the ability of pyranones to react with ammonia and primary amines, to give pyridinones. In this *O,N*-exchange reaction , 4-pyranone acts as a vinylogous lactam undergoing nucleophilic attack by amines at C(2) in a Michael fashion, followed by ring opening and subsequent dehydrative cyclization to yield the pyridinone. In principle, the required ligand **4, H₂(PzHP)**, should be

attainable conveniently by heating the corresponding 4-pyranone (*i.e.*, maltol, a readily available commercial compound) with 1.5 equiv of 4-amino-1*H*-pyrazole under reaction conditions similar to those outlined by Fassihi *et al.*[38] However, despite considerable experimentation, all attempts have been to no avail. We surmised that the failure stemmed from the presence of unprotected enol OH in 1. To overcome this hurdle, we switched to *O*-benzyl derivative 2 as the starting material and optimized the reaction conditions to make *O,N*-exchange reaction.[39] Gratifyingly, when 2 and 4-amino-1*H*-pyrazole were reacted in EtOH-H_2O (1:1) in the presence of NaOH (cat.) in a sealed pressure tube at 160°C, all starting material had reacted after 45 h to give 3. Finally, catalytic hydrogenolysis of the *O*-benzyl function in 3 went uneventfully to deliver 4 in 31% overall (unoptimized) yield in 3 steps. We have than tried to crystallize the ligand for a detailed characterization of its crystal structure, however, as already observed by us in the past with poly-pyrazolate linkers,[22] any attempt of crystallization was thwarted by sudden precipitation. The sample, recovered as microcrystalline powder, is in fact highly insoluble in most organic solvents, requiring solid-state techniques for their complete analytical characterization (*vide infra*). **Cu(PzHP)** coordination polymer was obtained (81% yield) by hydrothermal synthesis carried out in solution of 4 and Cu(OAc)$_2$ in 28% aq. NH_4OH solution at 120°C for 24 h. HPs are reported to have pK_{a2} values in the range 9 to 10 in water, thus assuring the solubility of ligand **H$_2$(PzHP)** in the above reaction environment under the corresponding autogenous pressure. Any attempt to obtain single crystals or polycrystalline powders with a high degree of crystallinity was unsuccessful.

 IR spectra of ligand **H$_2$(PzHP)** exhibited bands at 3221 and 3169 cm^{-1}, respectively, assigned to v(OH) and v(NH) which disappears from complex **Cu(PzHP)** as an indicative of OH and NH deprotonation. Instead, in the complex, the band at 1596 cm^{-1} assigned to v (C=O) is shifted by 40 cm^{-1} in comparison with **H$_2$(PzHP)**, suggesting that the ligand is coordinated to the metal through *O*, *O'* and *N*. Finally, the spectra of **Cu(PzHP)** exhibited a broad band around 3400cm^{-1} ,v(H_2O), which is assigned to water molecules associated with the complex.

Details on the Unconventional Structure Solution process of Cu(PzHP)

Indexing and Le Bail refinement (see experimental section) of the **Cu(PzHP)** data clearly led to a hexagonal cell (chiral SG *P*6$_1$) of volume of 1540.2 Å^3. This cell volume (and symmetry) considerations, suggested the presence of six Cu(PzHP) formula unit per unit cell. However,

preliminary *ab initio* simulated annealing runs, in $P6_1$, using a flexible rigid body of the ligand (as described in the experimental section for **H$_2$(PzHP)**) and a Cu(II) ions, both in general position, were unsuccessful. This behaviour being possibly related to the inherent 'low quality' of the powder pattern, which has only a few broad peaks, *i.e.* to the presence of some extended disorder leading to a rising of the average symmetry.

In order to postpone the problem of dealing with a highly disordered ligand, we attempted to determine the position of the Cu(II) cation alone working either in the reciprocal space (using EXPO2014)[40] and in the real space (using TOPAS-R simulated annealing procedures). The two approaches conveyed a substantially similar location for the unique Cu(II) cation which, being close to a 6_1 screw-axis, defines a 6_1 helix with a very small radius (*ca.* 1.4 Å).

Unfortunately, further simulated annealing runs, allowing for a freely roto-translating ligand about the fixed Cu(II) cation, were unsuccessful and we decided to build a few trial structures, in $P6_1$, to be used as starting point for Rietveld refinements which are much more stable, and drivable, than Simulated Annealing runs.

Considering the congruence of the length of a Cu *exo*-N-coordinated PzHP moiety (HPPzCu) with that of the *a* (and *b*) axis, we supposed that the PzHP ligands are substantially aligned to the *a* (and *b*) axis, thus interconnecting adjacent helices. Accordingly, a flexible (about the N3a-C1a bond) HPPzCu rigid body was manually driven to have *i*) the Cu atom in the previously determined position (that is a general position); *ii*) the pyrazolate moiety bridging an adjacent Cu of the same helix; and *iii*) the HP moiety (HP = (*O,O'*)-3,4-dihydroxypyridinonate) chelating a Cu of an adjacent helix.

The subsequent Rietveld refinement reached a promising R_{wp} of 10.44 (Figure S3).

On the basis of the above coordination geometry it was clear that the HP unit can chelate the copper in the neighbouring helix either slightly above or slightly below the position pointed by the carbonyl, depending on the location of the hydroxyl group (which can stay above or below due to the free rotation about the N3a-C1a bond). This fact leads to conditional disorder either along *c* (*i.e.* within the helices) and in the *ab* plane (*i.e.* between the helices) which can be modelled either by increasing the symmetry of the space group to $P6_122$ (that gives rise to a better convergence with R_{wp} of 9.519 and R_{Bragg} = 3.71, see Figure S4) and the symmetry of the rigid body. To construct a new 'symmetric' rigid body, HP'Pz, we have added a methyl and a hydroxyl group and halved the occupancies of all atoms (actually the occupancies of the hydroxyl and the methyl groups, namely O2a, O3a, C9a and

C10a, are further halved to 0.25). When this new rigid body, HP'Pz, is used in our model, the Rietveld refinement converges to an even better convergence (R_{wp} = 9.060 and R_{Bragg} = 3.14, Figure S5) and more reasonable bond lengths and angles to reach our final structural model for the **Cu(PzHP)** coordination polymer. It should be noted that the Rietveld refinements done by either fixing the Cu atom and/or the rigid body on the C2 axis (Wykhoff positions *b* and *a*, respectively, in $P6_122$) always gave rise to worse convergences and unreliable bond lengths and angles, in agreement with our disordered model.

Crystallographic features of H_2(PzHP) and Cu(PzHP).

The **H_2(PzHP)** ligand (Figure 2) crystallizes in the monoclinic $P2_1/c$ space group. The asymmetric unit contains an full molecule of the ligand that lies in general position, indeed, a unit cell is composed by four ligands connected each other's by hydrogen bonds contacts. The crystal structure of the ligand (Figure 2) possesses supramolecular features recalling those of other pyrazolate-based ligands.[22] Indeed, as suggested by the broad IR bands centered in the range 3200 and 3160 cm^{-1}, also the crystal structure of **H_2(PzHP)** feature an extensive network of hydrogen bond interactions (Figure 2a). However, in this case, the presence of the HP unit generates further HB contacts: the typical HB dimers of carboxylate derivatives is observed and two HP units of two different ligands are arranged face-to face, but slightly staggered, with =O···H-O contacts. The =O group, moreover, bifurcates with a second HB with the N-H group (Figure 2b). Such a network is reasonably responsible for the very low solubility of this ligand in most organic solvents and for its difficulty in growing as single crystals.

The overall packing of the **Cu(PzHP)** polymers is depicted in Figure 3a and 3b that report the coordination environment at the Cu(II) ion. In Figure 3c, the tight helix of metal ions running along the *c* axis can be appreciated. On the whole, the crystal structure features a 3-D motif possessing very small cavities occupied by the methyl groups of the HP moiety. These channels have such a small dimension that they cannot accommodate any host, giving rise to a rigid, non-porous structure (see thermal behaviour).

More in detail, each metal center has distorted square pyramid coordination geometry, being penta-coordinated to two nitrogen and three oxygen atoms. Here, the carbonylic oxygen of the HP (O1a), which bridges two nearby copper centers and generates the 6_1 helices running along *c*, is found both in the apical and in one basal positions (see Figure 3b

and 3c). At variance, the deprotonated oxdrilic oxygen (O2a) is found on the other basal potision. The 3-D network of the framework is also built up by the typical exo-bidentate coordination mode of the pyrazole ring that also contributes to the formation of the metal chains. A further pictorial description of the disordered model in the $P6_122$ space group can be found in the Supporting Information as Figure S7.

Thermal Behaviour

The thermal characterization of **Cu(PzHP)** was performed by means of TGA/DSC simultaneous analysis (STA, Figure S8) and variable-temperature powder X-ray diffraction experiments (VT-PXRD, Figure 4). The thermogravimetric analysis revealed that the compound undergoes a very poor mass loss before 70 °C, which has been interpreted as the loss of moisture from the sample. The framework does not lose any other weight until decomposition, that starts at about 320 °C (T_{peak} = 370 °C)

VT-XRPD experiments substantiated the thermal robustness of **Cu(PzHP)** even in air. The loss of crystallinity and decomposition of the framework start at ca. 300 °C.

To substantiate the visual results of the thermodiffraction experiments, a Le Bail parametric treatment of the VT-XRPD data has been performed (Figure S9). The data of the unit cell parameters (a, c axis and cell volume) have been normalized to the room temperature parameters (30 °C) and highlight a substantially rigid behaviour of the framework. While the *a* axis is the less affected along the spanned temperature range, the *c* axis shows a very small contraction with a consequent smaller unit cell volume.

Conclusions

With the aim of obtaining thermally robust and chemically stable porous metal-organic frameworks we have designed a new bifuncitional organic linker based on the connection between a pyrazole and a HP unit. This ligand has been coupled with Cu(II) metal ions giving rise to a **Cu(PzHP) c**oordination polymer possessing a very discouraging diffraction pattern, characterized by less-than-ideal crystallinity. The extended disorder leading to an higher than required space group symmetry and, perhaps, some paracenstalline broadening of the peaks required a trial and error approach to structure solution in which consideration on the

coordination ability of the ligand and of the space group symmetry have been taken into account to achieve the final correct structural model.

This work can be anticipated in the direction of coupling this mixed-site ligand with different transition-metal ions, aiming at the formation of bi-metals species featuring soft and hard metal ions on binding the two different site of the linker. The resulting materials are expected to be chemically and thermally stable, thanks to the strength of the metal-pyrazolate bond.

Acknowledgements
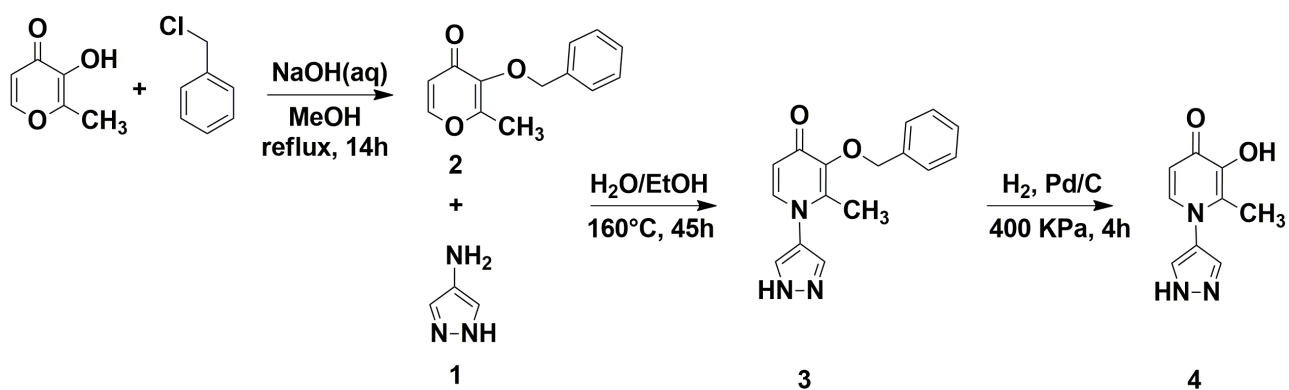
Scheme 1. Synthetic route to **H₂(PzHP)** ligand.

	H$_2$(PzHP)	Cu(PzHP)
Crystal System	Monoclinic	Hexagonal
Space Group	$P2_1/c$	$P6_122$
Fw (g mol^{-1})	191.07	252.72
a (Å)	6.4765(5)	10.1563(11)
b (Å)	12.7974(10)	-
c (Å)	10.8193(9)	17.3073(28)
Beta	80.4315(4)	-
Volume (Å^3)	884.25(1)	1546.08(43)
Z'	1	1
ρ_{calc} (g cm^3)	1.42	1.58
μ(Cu-K$_\alpha$) cm^{-1}	8.82	28.73
2θ range (°)	10–105	8–90
Data	4751	4100
R$_p$	0.092	0.066
R$_{wp}$	0.132	0.090
R$_{Bragg}$	7.46	2.81
Gof	6.682	7.691

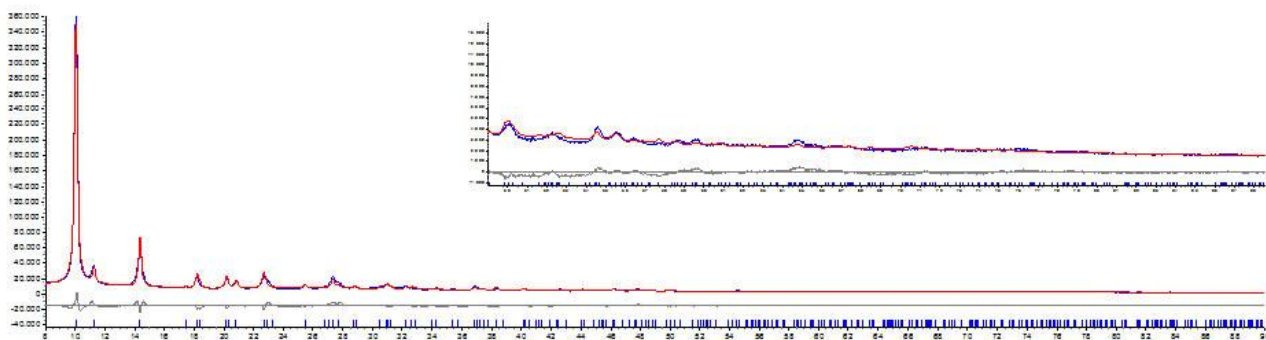**Table 1.** Crystal data for **H$_2$(PzHP)** and **Cu(PzHP)**
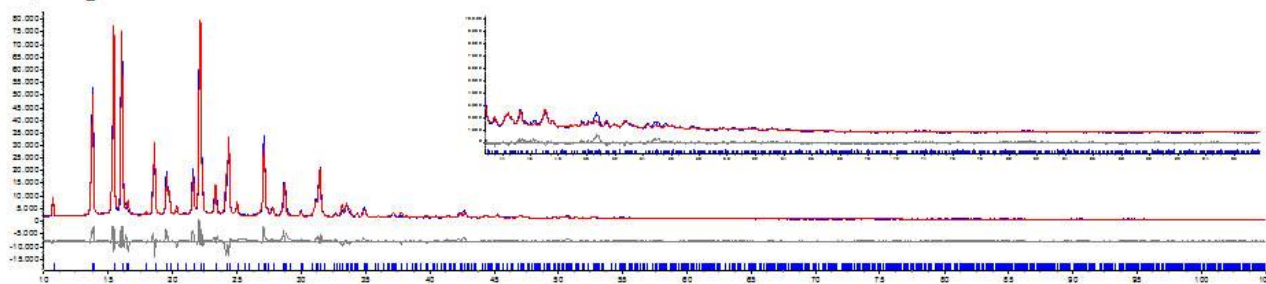
Figure 1. a) Rietveld Refinement plot for **H₂(PzHP)** ligand R_p and R_{wp} = 0.092 and 0.132; R_{Bragg} = 7.46; b) Rietveld Refinement plot for **Cu(PzHP)**. R_p and R_{wp} = 0.066 and 0.090; R_{Bragg} = 2.81
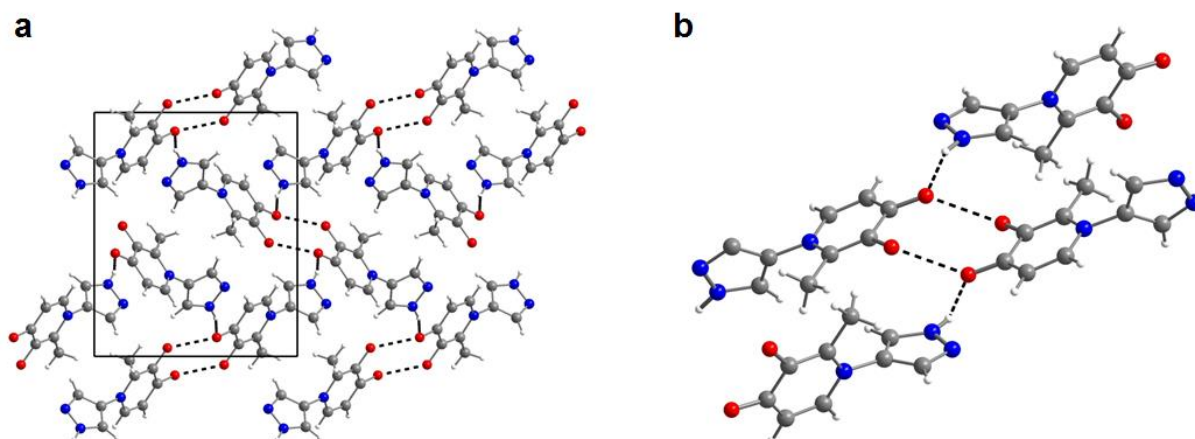
Figure 2. a) Representation of the crystal structure of the H_2(PzHP) ligand, highlighting the extended HB network. b) Detail of the HB connections: face-to-face $=O\cdots HO$ and $N-H\cdots O=$ HBs. Blue, nitrogen; grey, carbon; white, hydrogen. OH hydrogen atoms are omitted for clarity.
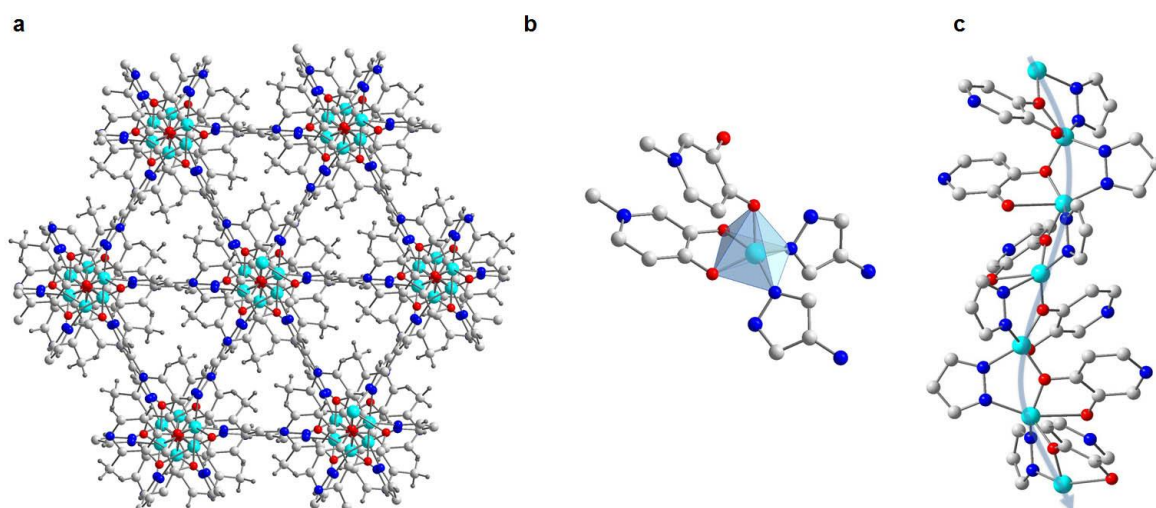

Figure 3. a) Representation of the three-dimensional network of the Cu(PzHP) coordination polymer viewed along the crystallographic c axis. b) Detail of the distorted square-pyramid geometry at the Cu(II) metal ions. c) Depiction of the Cu(II) tight helix running along the crystal.
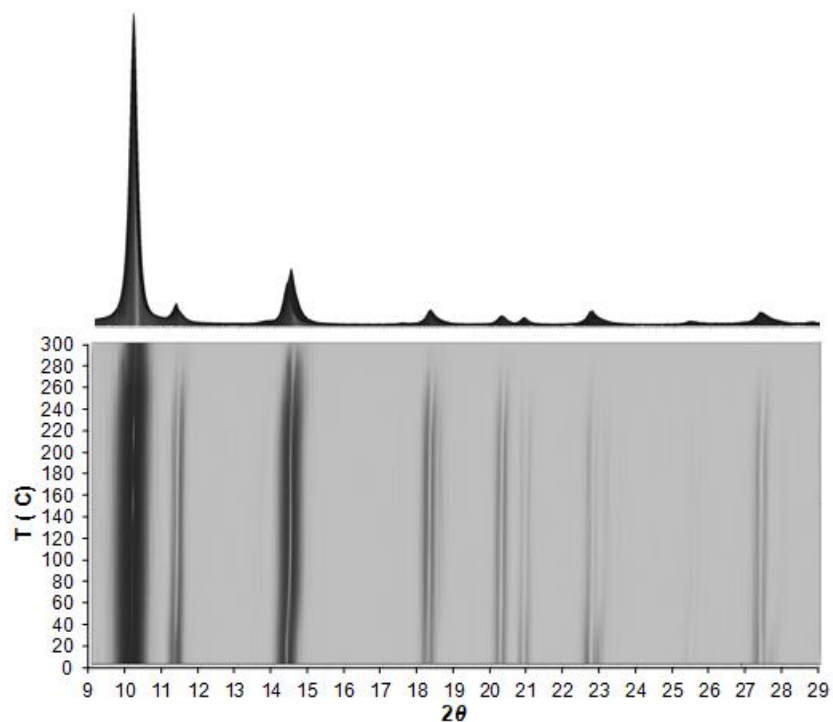
Figure 4. Variable Temperature Powder X-ray Diffraction Analysis plot for **Cu(PzHP)**. Lower: top-down view of the two dimensional plot; horizontal axis 2θ (°); vertical axis T (°C) Black lines represents peaks positions. Upper: front-space view of the peak positions.

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