

A highly porous interpenetrated MOF-5-type network based on bipyrazolate linkers†

Cite this: *CrystEngComm*, 2013, 15, 9352

Received 8th July 2013,
Accepted 14th August 2013

DOI: 10.1039/c3ce41339j

www.rsc.org/crystengcomm

A novel cobalt(II) metal organic framework containing two interpenetrated nets with the cubic *pcu-a* topology of MOF-5 has been synthesized and characterized. In spite of being interpenetrated, this material exhibits a highly accessible porous structure.

Metal organic frameworks (MOFs) are a class of synthetic porous materials that have drawn recent attention¹ due to the wide range of possible applications, spanning, *inter alia*, from gas storage² and purification³ to catalysis⁴ and drug delivery.⁵ The versatility of MOFs is strictly related to the variety of three-dimensional porous networks that can be derived from the different spatial constrictions originating from a wide selection of building blocks (*i.e.* metal fragments and organic linkers).⁶ As already realized, the higher the potential porosity of the network, the larger the probability to achieve *n*-fold interpenetrated structures, with concomitant lower accessibility of the pores.⁷ Despite this evidence, interpenetration is not always a drawback, as the induced spatial confinement may lead to stronger interactions and more pronounced selectivity toward specific guest molecules.⁸

The tetranuclear M_4O^{6+} node, found in the prototypic MOF-5 material (where $M = Zn$) reported by Yaghi and co-workers back in 1999,⁹ is a highly desirable secondary building unit (SBU), since it favours the formation of porous networks featuring predictable structural aspects.

As a matter of fact, in the vast majority of MOFs containing this SBU, each edge of the M_4O tetrahedra is capped by *exo*-bidentate polycarboxylate linkers.¹⁰ Recently, a number of species containing M_4O^{6+} clusters capped by nearly isosteric *exo*-bidentate bipyrazolate or pyrazolate/carboxylate moieties, imparting an enhanced framework stability, have been reported by the groups of Volkmer^{11,12} and Chen,¹³ as well as by us.¹⁴

In this context, we report herein on the synthesis, crystal structure, thermal and chemical behaviour, and textural properties of a two-fold interpenetrated Co-based MOF containing Co_4O^{6+} nodes connected by bipyrazolate linear linkers. The robust M–N(pyrazolate) coordination bonds, the occurrence of interpenetration¹⁵ and, possibly, the bulkiness of the methyl residues¹⁴ concomitantly contribute to the remarkable thermal stability observed. It is noteworthy that although Volkmer and co-workers demonstrated that a certain degree of interpenetration takes place in MFU-1,¹² to the best of our knowledge, this is the first report on a fully interpenetrated structural analogue of MOF-5 based exclusively on bipyrazolate linkers.

The reaction of $Co(AcO)_2$ and 4,4'-buta-1,3-diyne-1,4-diyl-bis(1-Boc-3,5-dimethyl-pyrazole) (Boc_2L) (Scheme 1) in DMF at 125 °C in a Teflon liner affords, after the slow release of the Boc protecting groups, a bright blue microcrystalline material of formulation $[Co_4O(L)_3] \cdot 8DMF \cdot 5H_2O$ ($Co_4O(L)_3$). $Co_4O(L)_3$ crystallizes in the cubic space group $I-43m$ ‡ with $a = 16.6103(7)$ Å and $V = 4582.8(5)$ Å³.§

Its 3-D porous framework is based on two interpenetrated networks of *pcu-a* topology, containing six-connected Co_4O^{6+} nodes reciprocally bridged by L^{2-} ligands (Fig. 1). Significantly, the two networks cross at the buta-1,3-diyne residues favoring, by their low steric hindrance, mutual interpenetration.

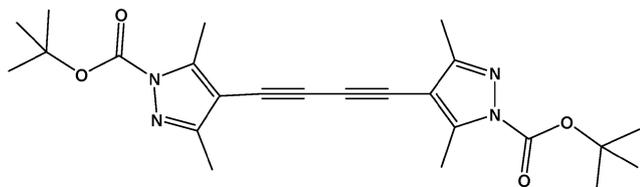
The structure of $Co_4O(L)_3$ is similar to that of the interpenetrated MOF-5,¹⁵ which possesses an interdigitated CaB_6 -type topology; moreover, $Co_4O(L)_3$ comprises octahedral $Co_4O(dmpz)_6$ nodes ($dmpz = 3,5$ -dimethylpyrazolate) analogous

^a Departamento de Química Inorgánica, Universidad de Granada, Av. Fuentenueva S/N, 18071 Granada, Spain. E-mail: elsa@ugr.es, jarn@ugr.es; Fax: +34 958 248526; Tel: +34 958 248093

^b Departamento de Química Orgánica, Universidad de Granada, Av. Fuentenueva S/N, 18071 Granada, Spain

^c Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, Via Valleggio 11, 22100 Como, Italy

† Electronic supplementary information (ESI) available: Detailed experimental methods, elemental analysis, thermal analysis and stability tests. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41339j



Scheme 1 4,4'-Buta-1,3-diyne-1,4-diylbis(1-Boc-3,5-dimethyl-pyrazole) (Boc_2L) used in the synthesis of the $\text{Co}_4\text{O}(\text{L})_3$ system.

to the discrete heteroleptic pyrazolate-bridged tetranuclear $\text{Co}(\text{II})$ clusters¹⁶ and which are also reminiscent of the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ archetypic secondary building units of MOF-5 (Fig. 2).

The occurrence of interpenetration significantly reduces the expected void volume, as well as the pore size and pore windows. Indeed, the latter, which for the non-interpenetrated structure would be more than 10 Å wide, in the interwoven net possess an opening of approximately 8.3 Å only (Fig. S2†). In spite of this, approximately 68% of the total volume is potentially accessible, a very high value for a doubly interpenetrated system, reasonably due to the appreciable length of the organic linkers and to the low steric demand of their but-1,3-diyne residues. As a matter of fact, $\text{Co}_4\text{O}(\text{L})_3$ is highly accessible for both N_2 and CO_2 gaseous probes (see below).

Notably, all the attempts carried out to increase the void volume by isolating the non-interpenetrated $\text{Co}_4\text{O}(\text{L})_3$ framework invariably failed. The use of templates (of various chemical nature and different concentrations, namely, DEF, benzene, naphthalene, and cyclohexane) as well as the modification of the reaction conditions (*i.e.* concentration and temperature, that in some cases resulted to be crucial in determining whether a framework presents interpenetration or not)¹⁷ unavoidably led either to the interpenetrated $\text{Co}_4\text{O}(\text{L})_3$ species or to amorphous solids.

Thermogravimetric analyses performed on $\text{Co}_4\text{O}(\text{L})_3$ in both air and nitrogen atmospheres have revealed very high

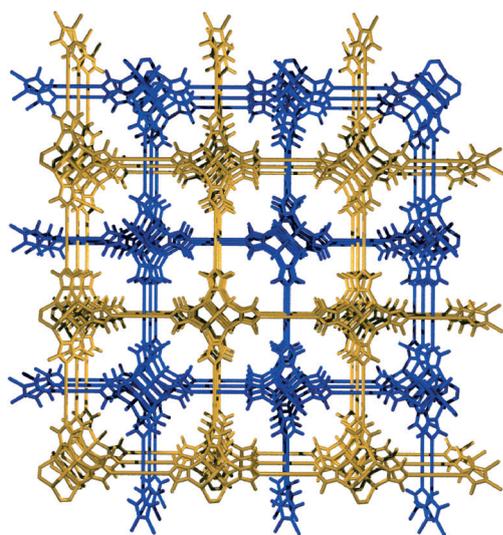


Fig. 1 Perspective view, down [001], of the doubly interpenetrated *pcu-a* networks found in the crystal structure of $\text{Co}_4\text{O}(\text{L})_3$. The two symmetry-related frameworks are depicted in blue and yellow for the sake of clarity.

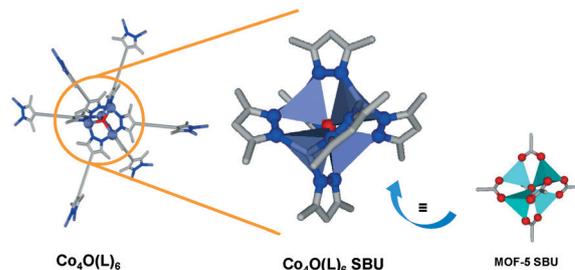


Fig. 2 View of the $\text{Co}_4\text{O}(\text{L})_6$ cluster (left), with magnification of its $\text{Co}_4\text{O}(\text{dmpz})_6$ core (centre), reminiscent of the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ SBU found in MOF-5 (right).

thermal robustness, with the decomposition beginning only at 360 °C (Fig. S3†). As witnessed by the perfect overlap between the two traces, the material proves to be neither oxidized by atmospheric oxygen nor damaged by ambient moisture, even if solvent guest molecules had already left the framework.

The freshly prepared material progressively loses solvent guest molecules in the 25–200 °C temperature range; the relative weight loss (39.5%) is in good agreement with the total amount of solvent calculated by means of elemental analysis data (5 H_2O molecules and 8 DMF molecules per formula unit corresponding to 41.2%, see ESI†). The fact that DMF leaves the network at temperatures higher than its boiling point should not be surprising, as it is indicative of the occurrence of a trapping phenomenon, kinetic in nature, determined by the size of the pore windows and requiring an extra input of energy. As proven by powder diffraction measurements, in which superstructure peaks breaking body-centered symmetry have never been observed, the degree of interpenetration, on changing from one batch to another, is always maintained. This is in agreement with the perfect overlap among the TG curves measured for different batches, for which the weight drop corresponding to the guest solvent molecules removal is constant. We attribute this occurrence to the rather ideal matching of the less hindered portion of the ligands, nicely fitting one next to each other as two perpendicular crankshafts do.

Chemical stability tests performed on $\text{Co}_4\text{O}(\text{L})_3$ (Fig. S4†) show that, after suspension in water, benzene and methanol at room temperature, the material invariably loses crystallinity, likely because the framework is severely damaged by the exchange of guest solvent molecules. In detail, when the solid is suspended in water at room temperature, amorphization starts after 4 h, although the distinctive features of the XRPD pattern of $\text{Co}_4\text{O}(\text{L})_3$ are still pronounced. The stability of $\text{Co}_4\text{O}(\text{L})_3$ is lower in MeOH at room temperature, since the material becomes almost completely amorphous just after 1 h of treatment. Differently, when the solid is stirred in dry benzene, not only amorphization but also a phase transformation is observed after 4 h, as confirmed by the appearance of a new peak at $2\theta = 12.1^\circ$.

The chemical stability tests highlight a modest hydrophobicity of the $\text{Co}_4\text{O}(\text{L})_3$ framework, which nevertheless shows a lower sensitivity to hydrolysis than those MOFs containing

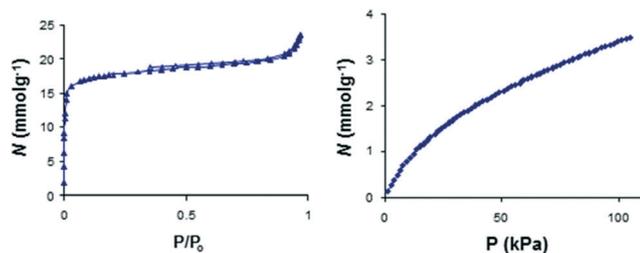


Fig. 3 (Left) N₂ (77 K) and (right) CO₂ (273 K) adsorption isotherms for Co₄O(L)₃. Empty symbols denote desorption.

the same M₄O⁶⁺ clusters but carboxylate ligands.¹⁸ Reasonably, as already demonstrated by us,¹⁴ the methyl groups on the L spacers play a very important role, protecting the metal clusters from the rapid damage that could be caused by water molecules. In this regard, it should be noted that all attempts to construct the same network with the analogous linker not possessing the methyl groups, namely, 4,4'-buta-1,3-diyne-1,4-diylbipyrazole, were fruitless.

The permanent porosity of Co₄O(L)₃ toward N₂ (77 K) and CO₂ (273 K) gas probes has been tested (Fig. 3) using solid samples activated under high vacuum at 200 °C, as suggested by the thermogravimetric analysis curve.

The nitrogen adsorption isotherm is of type I, as expected for a microporous solid, and the desorption branch perfectly matches the adsorption one. In spite of framework interpenetration, the BET and Langmuir specific surface areas of 1355 m² g⁻¹ and 1760 m² g⁻¹, respectively, are remarkably high. Likewise, the N₂ uptake approaches 20 mmol g⁻¹ at P/P₀ = 0.9, which corresponds to an accessible pore volume of 0.70 mL g⁻¹ (0.50 mL mL⁻¹), approaching the one calculated from the crystal structure. Worthy of note, the Langmuir specific surface area value obtained for Co₄O(L)₃ is significantly higher than those reported for the interpenetrated MOF-5 (1130 m² g⁻¹)¹⁵ and for SUMOF-2 (1167 m² g⁻¹),¹⁹ which contain carboxylate-based linkers in structures with similar SBUs and cell dimensions.

Finally, the CO₂ physisorption isotherm is also of type I. At CO₂ pressures of 100 kPa, the uptake of CO₂ for Co₄O(L)₃ at 273 K is 3.42 mmol g⁻¹. This value, although slightly lower than that of SUMOF-2 (4.26 mmol g⁻¹),¹⁷ is remarkably higher than that of the non-interpenetrated MOF-5 (1.50 mmol g⁻¹),²⁰ indicating that pore confinement increases with interpenetration and is responsible for the strong interactions with the quadrupolar CO₂ molecule.

Consequently, it can be concluded that, in spite of the interpenetrated nature of the framework of Co₄O(L)₃, *i*) high accessibility to small molecules is not prevented and *ii*) the extended surface granted by the two concomitant networks enhances the specific surface area.

Conclusion

In conclusion, we have synthesized the novel two-fold interpenetrated MOF Co₄O(L)₃ containing tetrahedral Co₄O⁶⁺

nodes analogous to those found in MOF-5, connected by bipyrazolate linear linkers with low steric demand. The unusual thermal robustness of Co₄O(L)₃ (if compared to the bicarboxylate archetypes) can be explained in terms of the fundamental role played by *i*) the purely N-donor bipyrazolate building blocks, *ii*) the methyl groups on the linkers, protecting the metal clusters, and *iii*) interpenetration, commonly considered an annoying feature. On the contrary, despite the occurrence of interpenetration, Co₄O(L)₃ shows a remarkable porosity, exceeding that of previously reported bicarboxylate-based frameworks with a closely related structure.

Acknowledgements

The authors are grateful for the generous support by the Spanish MCINN (project: CTQ2011-22787 and E. Q. P. FPI fellowship) and Junta de Andalucía (projects: P10-FQM-6050 and P09-FQM-4981).

Notes and references

‡ The similar agreement factors and residual plots in the final Rietveld refinements for a disordered *Im-3m* model and an ordered *I-43m* one suggest the presence of local (two-fold) disorder of the Co₄O tetrahedra and of the ligands, the orientations of which are spatially uncorrelated. The model here proposed, in *I-43m*, has the advantage of easier interpretation and graphical rendering.

§ Crystal data for Co₄O(L)₃, [Co₄O(C₁₄N₄H₁₂)₃](C₃H₇NO)₈(H₂O)₅, M_r = 1635.37; cubic, *I-43m*, *a* = 16.6103(7) Å, *V* = 4582.8(5) Å³, *Z* = 2, *F*(000) = 2508, μ(CuKα) = 60.8 cm⁻¹, ρ = 1.18 g cm⁻³, R_p = 0.006, R_{wp} = 0.012, R_{Bragg} = 0.831 for 4426 datapoints and 41 parameters. Please note that the very low figures of merit are due to the very pronounced background affected by the fluorescence of cobalt, which cannot be eliminated in our instrumental set-up.

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