Accepted Manuscript

A HKUST-1 MOF inclusion compound with in-situ reduced copper(I) as $[Cu(NCCH_3)_4]^+$ cation complex in the octahedral A-type pore

Anas Tahli, Reda F.M. Elshaarawy, Ümit Köc, Anna Christin Kautz, Christoph Janiak

PII:	S0277-5387(16)30273-X
DOI:	http://dx.doi.org/10.1016/j.poly.2016.06.039
Reference:	POLY 12080
To appear in:	Polyhedron
Received Date:	17 February 2016
Accepted Date:	22 June 2016



Please cite this article as: A. Tahli, R.F.M. Elshaarawy, U. Köc, A.C. Kautz, C. Janiak, A HKUST-1 MOF inclusion compound with in-situ reduced copper(I) as [Cu(NCCH₃)₄]⁺ cation complex in the octahedral A-type pore, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.06.039

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A HKUST-1 MOF inclusion compound with in-situ reduced copper(I) as [Cu(NCCH₃)₄]⁺ cation complex in the octahedral A-type pore

Anas Tahli,^{a,b} Reda F. M. Elshaarawy,^{a,c} Ümit Köc,^a Anna Christin Kautz,^a Christoph Janiak^{a,}*

^a Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany. Email: <u>janiak@hhu.de</u>

^b Faculty of Science, Al-Furat University, Deir Ezzor, Syria

^c Faculty of Science, Suez University, Suez, Egypt

Graphical Abstract for

A HKUST-1 MOF inclusion compound with in-situ reduced copper(I) as $[Cu(NCCH_3)_4]^+$ cation complex in the octahedral A-type pore



The first HKUST-1 inclusion derivative with a defined guest in the octahedral A-type pores.

Rock

2

Abstract

Hydrothermal reaction of racemic 1,2-bis(1,2,4-triazol-4-yl)propane (*rac*-btrip) and benzene-1,3,5-tricarboxylic acid (H₃btc) with copper(II) acetate in an aqueous triethylamine and acetonitrile mixture afforded blue-green cuboctahedral crystals of the MOF inclusion compound 3D-{[Cu(NCCH₃)₄][Cu₃(μ_6 -btc)₂]₂(O₂CCH₃) (H₂O,CH₃CN)_x(btrip)_{1.5}}_n, **1.** This MOF is isostructural with the prototypical MOF HKUST-1 (Cu₃(btc)₂, Cu-btc) and the first HKUST-1 derivative which accommodates a defined guest, namely the cationic tetra(acetonitrile)copper(I) complex [Cu(NCCH₃)₄]⁺ in the A-type octahedral pores of the 3D HKUST-1 framework. In-situ reduction of Cu(II) to Cu(I) in the course of the hydrothermal synthesis is afforded by the sacrificial btrip ligand which is not incorporated as a linker but as a template molecule into the cuboctahedral B- and C-type pores according to ¹H NMR digestion analysis. N₂ adsorption isotherm for activated HKUST-1 inclusion compound **1** gave a BET surface area of 576 m²/g.

Keywords: Metal-organic framework, MOF; HKUST-1; inclusion compound; in-situ reduction; mixed-valence

1 Introduction

Porous coordination polymers (PCPs) also called metal-organic frameworks (MOFs) are intensively investigated due to their potential applications, such as gas storage [1], separation processes [2], catalysis [3], conductivity [4] and reversible water sorption for heat transformation [5]. Reaction conditions such as solvents, temperature, pH, the type of bridging ligands, the counter anions of metal salts can influence the still difficult to predict resulting structure of PCPs. Coordination polymers based on mixed-linkers [6] may allow for a fine-tuning of MOF properties and can show additional characteristics such as crystal-to-crystal transformations [7], short and long-range magnetic ordering [8], luminescence [9] etc.[10].

The combination of neutral nitrogen donor ligands with anionic carboxylate ligands are frequent choices for the synthesis of mixed-ligand networks [10]. The linker properties of 1,2-bis(1,2,4-triazol-4-yl)ethane (abbreviated as btre, Scheme 1) have recently been intensely studied in mixed-linker MOFs [7-11,12] and single-linker networks [13]. Herein, we report an attempt to construct mixed-linker networks by use of a chiral variant of btre, namely racemic 1,2-bis(1,2,4-triazol-4-yl)propane, *rac*-btrip (Scheme 1) in combination with benzene-1,3,5-tricarboxylate, btc^{3–}. The hydrothermal reaction yielded, however, an inclusion compound of

the well-know, prototypical MOF HKUST-1 ($Cu_3(btc)_2$, Cu-btc) [14] which is one of the most studied MOFs, because of easy formation [15], high porosity and known properties associated with this compound [16]. Here, we obtained HKUST-1 with the molecular cationic complex [$Cu(NCCH_3)_4$]⁺ as guest in the pores.

90



Scheme 1. 1,2-Bis(1,2,4-triazol-4-yl)alkane linkers.

2 Experimental section

2.1 Materials and instruments

Reagents and solvents were obtained from commercial sources and used without further purification. A programmable oven type UFP 400 from Memmert GmbH was used for solvo-/hydrothermal synthesis. The reactions were carried out in DURAN[®] culture glass tubes with PTFE-faced sealing wad, diameter 12 mm, height 100 mm and DIN thread 14 GL, which were closed with red PBT screw cap (Fig. S1, Supp. Info.), suitable for hydro-/solvothermal synthesis for coordination polymer synthesis up to 150 °C instead of an autoclave. The contents only come into contact with the glass and PTFE seal. The light microscopy images were observed with a Leica MS5 binocular eyepiece with transmitted light and polarization filter. The images of isolated crystals were taken with a Nikon COOLPIX 4500 digital camera through a special ocular connection. Infrared spectra were recorded with a Bruker Optik TENSOR 37 spectrophotometer using a Diamond ATR (Attenuated Total Reflection) unit from 4000 to 500 cm⁻¹. The following abbreviations were used to classify spectral bands: br (broad), sh (shoulder), very weak (vw), w (weak), m (medium), s (strong) and vs (very strong). The ¹H NMR spectra were recorded either on a Bruker Advance DRX 300 MHz NMR spectrometer with calibration against the residual protonated solvent signal D_2O (4.79) ppm). Thermogravimetric analysis was carried out in a simultaneous thermoanalysis apparatus TG 209 F3 from NETZSCH GmbH under flowing nitrogen gas 30 mL/min with a heating rate 10 °C min⁻¹ in the temperature range from 30 °C to 600 °C using Al crucible.

Powder X-ray diffraction patterns were measured at ambient temperature using a Bruker D2 PHASER in the Bragg-Brentano configuration with Cu-K α radiation ($\lambda = 1.54184$ Å), nickel filter and stationary flat panel sample holder in the range $2\theta = 5-50^{\circ}$ (step size 0.02° in 2θ). Simulated powder patterns were based on single-crystal data and calculated using the STOE

Win^{XPOW} software package [17] or Mercury v. 3.3 software [18]. The as-synthesized samples were dried in vacuum for *ca*. 2 hours at 40 °C before PXRD measurement.

Nitrogen sorption measurement was carried out with a Quantachrome Autosorb NOVA 4000e automated gas sorption system. Before the gas adsorption, the sample was washed in water twice over night, dried and loaded into glass tubes capped with septa. The weighed tubes were attached to the corresponding degassing port of the sorption analyzer, degassed under vacuum for 3 h at 200 °C, weighed again and then transferred to the analysis port of the sorption analyzer. BET surface areas were calculated from the nitrogen physisorption isotherms. The DFT calculations for the pore size distribution curves were made using the Nova Win 11.03 software employing the "N₂ at 77 K, slit pore, NL-DFT equilibrium" model [19]. Theoretical porosity calculations for the potential solvent volume in the solvent-depleted single-crystal X-ray structures are carried out with PLATON calc void/solv [20].

2.2 Synthesis of 1,2-bis(1,2,4-triazol-4-yl)propane, *rac*-btrip

Racemic 1,2-bis(1,2,4-triazol-4-yl)propane (*rac*-btrip) was synthesized by the reaction of *rac*-1,2-diaminopropane with *N*,*N*'-dimethylformamide azine using *p*-toluene sulfonic acid monohydrate as a catalyst in toluene under extra dry conditions at 120-130 °C [21,22,23]. *N*,*N*'-Dimethylformamide azine was synthesized from thionyl chloride, SOCl₂, *N*,*N*'-dimethylformamide, DMF, and hydrazine monohydrate, N_2H_4 ·H₂O following a literature procedure [21].

2.3 Synthesis of 3D-{[Cu(NCCH₃)₄][Cu₃(μ₆-btc)₂]₂(O₂CCH₃) (H₂O,CH₃CN)_x(btrip)_{1.5}}_n, 1

A solution of 16 mg (0.080 mmol) of copper acetate, $Cu(OAc)_2 \cdot H_2O$ in 0.5 mL of acetonitrile and 0.5 mL of water and a solution of 14 mg (0.080 mmol) of *rac*-btrip in 0.5 mL water were mixed in a glass tube for about 3-5 minutes. A portion of 8.4 mg (0.040 mmol) of H₃btc in 0.75 mL of Et₃N/H₂O solution (0.16 mol/L, 3eq to H₃btc) was dissolved using an ultrasonic bath and heating at 45-50 °C. As H₃btc was deprotonated by the basic amine medium it dissolved. Without the presence of base, H₃btc did not dissolve under the above temperature conditions in water. The resulting solution was combined with the previous mixture and shaken again for *ca*. 5 minutes in a DURAN glass tube, which was pressure sealed and then placed in a programmable furnace. The sample was heated to 125°C during 3 h, held at that temperature for 48 h, then cooled at a rate 5 or 10°C/h to ambient temperature. The resulting

blue-green single crystals of cuboctahedral shape (Fig. 1, Fig. S2 in Supp. Info.) were separated from some amorphous precipitate by decantation and washed with water. The reaction was repeated several times and found to be reproducible. The crystals are insoluble in water, ethanol or methanol. Yield 16 mg, 0.01 mmol, 90 % based on Cu(OAc)₂, quantitative based on H₃btc. FT-IR (ATR, cm⁻¹): 3109 (w, v, C-H), 1646 (s, v_{asym} C=O), 1612 (w, v_{sym} C=O), 1240 (s, v_{asym} C-O), 1190 (s, v_{sym} C-O), 871 (w, γ C-H), 758, 726 (s, γ , 1,3,5-trisubstituted benzene ring of btc). Copper acetate could also be replaced by 18 mg (0.080 mmol) of Cu(NO₃)₂·2.5H₂O to yield crystals which gave an identical powder X-ray diffraction pattern after activation (Fig. S3a in Supp. Info). The phase purity and representative nature of the single crystals for **1** were confirmed by the comparison of the measured and simulated PXRD patterns (Fig. S3b in Supp. Info). Some deviations between the simulated and measured PXRD are, however, expected as the simulated diffractogram cannot account for the electron density contributions in the pores which was squeezed out by PLATON (see below).



Fig. 1. Cuboctahedal single crystals of 1 (see Fig. S2 in Supp. Info for further photographs).

2.4 Crystallographic data collection and refinement.

Suitable single crystals (Fig. 1 and S2, Supp. Info) were carefully selected under a polarizing microscope and mounted in oil in a glass loop. *Data collection:* Bruker AXS Kappa APEX II CCD area-detector diffractometer with multilayer-mirror monochromator, Mo-K α radiation ($\lambda = 0.71073$ Å) from microfocus source, double-pass method with ϕ - and ω -scans. Data collection with APEX II [24], cell refinement and data reduction with SAINT [25], empirical absorption correction with SADABS [26]. *Structure analysis and refinement:* The structure was solved by direct methods, SHELXS-97, refinement was carried out by full-matrix least squares on F^2 using the SHELXL-97 software suite [27]. All non-hydrogen positions were

found and refined with anisotropic temperature factors. Hydrogen atoms on the aromatic rings and the carbon atoms were placed geometrically at calculated positions with an appropriate riding model (AFIX 43 for aromatic CH and AFIX 137 for CH₃) and an isotropic temperature factor of $U_{iso}(H) = 1.2 U_{ea}(CH)$ and 1.5 $U_{ea}(CH_3)$. The unit cell contains solvent or other guest molecules, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON [20]. A total of 1131 electrons were recovered in the unit cell void volume of 8925 $Å^3$ which corresponds to ~141 electrons per $C_{46.76}H_{24}Cu_7N_4O_{30}$ formula unit (Z = 8). The axial ligand on the Cu1 atom of the {Cu₂} node is either an aqua ligand, an acetonitrile ligand or a partially occupied acetate ligand. For the one $[Cu(NCCH_3)_4]^+$ guest per neutral $Cu_6(btc)_4$ equivalent one anionic charge is needed. This anion can be an acetate ligand which is then distributed over the six Cu1 atoms in the formula unit. The occupancy of the C6 atom of the assumed carboxylate group was refined to 0.11503 which is higher than required for a 1/6 occupancy on each Cu1 atom with its occupation factor of 0.25 due to the special position (0.25 : 6 = 0.04167). Hence, this C6 atom can also be part of an acetonitrile group, which then would require the O2 atom to be a nitrogen atom (cf. Fig. 2). The CH₃ group and the second O atom of the acetate group were too diffuse to be satisfactorily localized. Hence, their electron densities have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. Graphics were drawn with DIAMOND (Version 3.2) [28]. Details of the X-ray crystal data structure determination are provided in the Table 1. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. 1451953).

Empirical formula	$C_{46.76}H_{24}Cu_7N_4O_{30}$
Formula weight	1566.48
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	F m -3 m
Unit cell dimensions	a = 26.446(3) Å
Volume	18496(4) Å ³
Ζ	8
Density (calculated)	1.125 g/m^{-3}
Absorption coefficient μ	1.638 mm^{-1}

Table 1.	Crystal data	and structure	refinement	for 1 .
----------	--------------	---------------	------------	----------------

F(000)	6204
Crystal size	$0.10 \ge 0.10 \ge 0.10 = 0.10 = 0.10$
θ range for data collection	2.55 to 23.89°.
<i>h</i> , <i>k</i> , <i>l</i> Index ranges	-29,30, -30,30, -28,30
Reflections collected	24718
Independent reflections	780 [R(int) = 0.0648]
Completeness to $\theta = 23.89^{\circ}$	99.4%
Max. and min. transmission	0.8534 and 0.8534
Data / restraints / parameters	780 / 0 / 51
Final R indices [<i>I</i> >2sigma(<i>I</i>)] ^a	R1 = 0.0333, wR2 = 0.1048
R indices (all data) ^a	R1 = 0.0353, wR2 = 0.1059
Goodness-of-fit on $F^{2 b}$	1.473
Largest diff. peak and hole	0.255 and $-0.771 \text{ e} \text{ Å}^{-3}$
$a D = \left[\sum \left(\left\ E \right\ \right) / \sum \left\ E \right\ \right) / \sum \left\ E \right\ \right] : \dots D = \left[\sum \left(\left\ E \right\ \right) / \sum \left\ E \right\ \right] : \dots D$	$[\mu(E^2 - E^2)^2] / \sum [\mu(E^2)^2] \frac{b}{2} C c c dross of fit - b$

^a $R_1 = [\Sigma(||F_o| - ||F_c||)/\Sigma ||F_o||]; wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}.$ - ^b Goodness-of-fit = $[\Sigma [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}.$

3 Results and discussion

Blue-green crystals of 1 (Fig. 1 and Fig. S1, Supp. Info) were obtained from the hydrothermal reaction of copper(II) acetate monohydrate in the presence of rac-btrip and H₃btc/Et₃N in a water-acetonitrile solvent. Coordination frameworks constructed by metal ions and benzenetricarboxylic acid, H₃btc are extremely dependent on the deprotonation degree of H₃btc [29]. From the acid constants of H₃btc ($pKa_1 = 2.12$, $pKa_2 = 3.89$, $pKa_3 = 5.20$) [30], the deprotonation H₃btc can be achieved by triethylamine, Et₃N as base. From single-crystal Xray diffraction analysis the composition of 1 is determined as the 3D-network of HKUST-1, namely $[Cu_2(btc)_3]$ with $[Cu(NCCH_3)_4]^+$ cations as guests in the octahedral (A-type) voids to yield a solvent-guest-squeezed formula of $3D-\{[Cu(NCCH_3)_4][Cu_3(\mu_6-btc)_2]_2(O_2CCH_3)\}_n$ tetra(acetonitrile)copper(I)-catena{acetatobis(benzenetricaboxylato)tricuprate(II)} named (Fig. 2). It is known that Cu^{2+} ions can be reduced in-situ to Cu^+ by N-, O-, S-containing 4,4⁻-bipyridine, ligands, such as btre [13], pyridine-4-thiol, quinoxaline, pyridinedicarboxylate and others under hydrothermal conditions [31,32,33]. Also, under hydro(solvo)thermal conditions the simultaneous redox and self-assembly reaction of Cu^{2+} with organo-nitrogen species was observed where the organo-nitrogen species behave not

only as ligands but also as reducing agents towards Cu(II). This reduction then results in a decomposition of part of the organo-nitrogen species [13,34,35,36].





the ambiguous axial ligands on Cu1 have been omitted for clarity; in (c) hydrogen atoms were also omitted. Selected distances and angles are given in Table 2.

Compound **1** crystallizes in the cubic crystal system with the centrosymmetric space group *F* m-3m and eight formula units per unit cell. The asymmetric unit consists of a copper atom (Cu1, occupation factor 0.25) coordinated by a third of a btc ligand and an axial ligand plus a second copper atom (Cu2, occupation factor 0.04167) with one acetonitrile ligand (Fig. 2a). The Cu-btc framework in compound **1** is isostructural with the compound 3D-[Cu₃(μ_6 -btc)₂(H₂O)₃]_n, better known as HKUST-1 or Cu-btc reported by Williams et al. [14]. Therefore, we refrain here from a detailed description of the Cu-btc network.

Table 2. Selected distances (Å) and angles (°) in 1.

Cu1-O1	1.9685(16)	O1-Cu1-O1 ⁱⁱ	88.51(11)
Cu1-O2	2.142(5)	O1-Cu1-O1 ⁱⁱⁱ	167.35(10)
$Cu1\cdots Cu1^i$	2.6733(10)	O1-Cu1-O1 ^{iv}	90.10(11)
O1-C1	1.260(2)	O1-Cu1-O2	96.33(5)
C1-C2	1.502(4)	O1-Cu1-Cu1 ⁱ	83.67(5)
C2-C3	1.390(2)	O2-Cu1-Cu1 ⁱ	180.00(13)
Cu2-N	2.009(11)	C1-O1-Cu1	123.51(18)
N-C4	1.096(13)	N-Cu2-N ⁱ	109.5
C4-C5	1.442(16)	C4-N-Cu2	180(1)
		N-C4-C5	180(2)

Symmetry transformations: i = 0.5-x, y, 0.5-z; ii = z, y, x; iii = z, -y, x; iv = x, -y, z.

The tritopic btc linker, positioned on the crystallographic C₃ axes, coordinates six Cu atoms at its three carboxylate groups. Each Cu₂ paddlewheel unit (Fig. 2a) connects with four different btc ligands, that leads to the formation an open extended porous 3D-framework (Fig. 2c). The centers of six Cu₂-handles form the vertices of a super-octahedron (pore A) with four of the eight triangular faces covered by four btc ligands. This octahedral pore A accommodates the molecular complex cation $[Cu(CH_3CN)_4]^+$ (Fig. 2b). The acetonitrile ligands from $[Cu(CH_3CN)_4]^+$ point through the remaining four uncovered super-octahedral faces. The distances between the Cu₂ centroids along the octahedral vertex is 9.35 Å and opposite Cu₂ centroids around octahedral pore are 13.22 Å apart. For charge-neutrality to the $[Cu(CH_3CN)_4]^+$ cation an anion is needed. Most likely this comes from an axial acetato ligand

coordinated to one of the Cu₂ atoms of the paddlewheel SBU. The axial ligands on the Cu₁ atoms of the {Cu₂} node are either an aqua ligand, an acetonitrile ligand or a partially occupied acetate ligand. From this inherent disorder, only the directly bound atom to Cu could be found and refined. Thus, the 3D network is of composition 3D-{[Cu(NCCH₃)₄][Cu₃(μ_{6} -btc)₂]₂(O₂CCH₃) (H₂O,CH₃CN)_x]_n, tetra(acetonitrile)copper(I)-catena{acetatobis(benzene-tricaboxylato)tricuprate(II)} hydrate or acetonitrile solvate.

In the FT-IR spectrum (ATR) of compound **1** (Figure S4, Supp. Info.) the absence of the characteristic band of protonated carboxyl group (COOH) of H_3 btc proves, that the carboxylate groups are completely deprotonated [37]. A band at 642 cm⁻¹ is attributed to the triazole ring of the *rac*-btrip ligand in the cuboctahedral pores.

The ¹H NMR spectrum of compound **1** (obtained by complete dissolution of **1** in NaOD/D₂O) shows the signals for both the btc and the *rac*-btrip ligands in a 2.7 : 1 ratio (based on the three aryl protons and the methyl group of *rac*-btrip with also 3 H atoms) (Fig. S5a in Supp. Info). The framework should not and does not have to stay intact for the NMR solution study. The role of the NMR spectrum was solely to derive at the btc to btrip ligand ratio. In order to bring the framework into solution it has to be broken apart ("digestive dissolution"). Thus, the ¹H NMR analysis of **1** suggests that the *rac*-btrip molecules are located in the channels of the framework as non-coordinated guest molecules. Their high disorder made these *rac*-btrip molecules unobservable by X-ray single-crystal structure analysis.

The option "SQUEEZE" in PLATON [20] was used to remove diffuse contributions to the overall scattering without specific atom positions and gave about 141 electrons per $\{[Cu(NCCH_3)_4][Cu_3(\mu_6-btc)_2]_2\}$ formula unit. A btrip molecule of formula $C_7H_{10}N_6$ (178.20 g/mol) has 94 electrons, so that about 1.5 btrip ligands fit to 141 electrons. A ratio of 4 btc ligands to 1.5 btrip ligands would match with the NMR ratio of 2.7 : 1. Hence, a more complete formula of **1** would correspond to $3D-\{[Cu(CH_3CN)_4][Cu_3(\mu_6-btc)_2]_2(O_2CCH_3)\cdot(H_2O,CH_3CN)_x(btrip)_{1.5}\}_n$.

Isomorphous compounds of HKUST-1 with paddle-wheel SBUs and triangular btc ligands have been reported with copper, iron, molybdenum, chromium, nickel and zinc [38]. HKUST-1 structures have been reported with guest molecules or ions in the cuboctahedral pores B or C (Fig. S6 in Supp. Info.). These HKUST-1 derivatives were synthesized with different Keggin polyoxometalates (POMs) such as $[HPW_{12}O_{40}]^{2-}$, $[H_2SiW_{12}O_{40}]^{2-}$, $[H_2GeW_{12}O_{40}]^{2-}$, $[H_2SiMo_{12}O_{40}]^{2-}$, $[HPMo_{12}O_{40}]^{2-}$ and $[HAsMo_{12}O_{40}]^{2-}$ [39], or such as $[SiMo_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$, $[PMo_6W_6O_{40}]^{4-}$ [40], $[PMo_{11}VO_{40}]^{4-}$ $[PMo_{10}V_2O_{40}]^{5-}$ and $[PMo_9V_3O_{40}]^{6-}$ (Figures S7-S11, Supp. Info.) [41]. The HKUST-1 frameworks can encapsulate

metalloporphyrins B, Fe(III) Mn(III) in pores including or tetrakis(4sulphonatophenyl)porphyrin and Zn(II) tetrakis(4-methylpyridyl)porphyrin such that the porphyrin encapsulated HKUST-1 materials demonstrate crystallographically resolved porphyrin macrocycles in cavities reminiscent of heme pockets, while the remaining cavities allow small molecules to reach the active site for catalysis, much like channels in heme proteins (Figure S12, Supp. Info.) [42]. Metal complexes of meso-tetra(N-methyl-4pyridyl)porphine (TMPyP²⁺) cation such as [Fe(III)TMPyP]Cl₅, [Co(II)TMPyP]Cl₄, $[Mn(III)TMPyP]Cl_5$, $[M(II)TMPyP]^{4+}$ (M = Ni, Mg, Zn) can be encapsulated in pores B (Figure S13, Supp. Info.) [43]. Hence, to the best of our knowledge compound 1 appears to be the first HKUST-1 derivative which occupies a defined guest species in its small octahedral A-type pores.

3.1 Thermal analysis

Thermogravimetric analysis (TGA) was carried out in the temperature range 30-600°C following a pre-drying procedure of 2 h at 40 °C in vacuum of the sample during which the CH₃CN ligands of the $[Cu(NCCH_3)_4]^+$ cation were most likely lost already. Up to ~200 °C a mass loss of 20.6% is observed for **1**. The loss of 1.5 eq. of btrip would account for a 17% weight loss. In addition some axial aqua ligands on Cu1 may be lost as well. The de-solvated and guest-depleted 3D-network is thermally stable up to ~280 °C when the 3D-network begins to decompose in one weight-loss step on further heating (obs. 44.05%). The final residual mass of black precipitate is mostly assigned to CuO (obs. 34.84%) (Figure S14, Supp. Info.).

3.2 N₂ sorption study

The potential permanent porosity was studied by nitrogen gas sorption measurements. The porosity and BET surface area was evaluated from a N₂ adsorption isotherm at 77 K. For activation the sample was heated at 200 °C under vacuum for 3 h. The N₂ isotherm in Figure 3 can largely be classified as a composite of Type I and II with an H4 hysteresis loop. The more pronounces uptake at low P/P₀ is associated with the filling of micropores. The Type II part at high P/P₀ is given by the physisorption on non- to macroporous adsorbents. H4 loops are often found with aggregated crystals of microporous zeolites, mesoporous zeolites and micro-mesoporous carbons [44]. The Brunauer–Emmett–Teller (BET) surface area for **1** is calculated as 576 m²/g [45] (Langmuir surface area 676 m²/g), its total pore volume $V_P = 0.34$ cm³/g at P/P₀ = 0.95. The surface areas for HKUST-1, synthesized in DMF is 1507 m²/g, $V_P =$

 $0.75 \text{ cm}^3/\text{g}$ [46]. The derived pore widths for 1 are distributed around 18 and from 27-38 Å and beyond (pores of widths between 2 nm and 50 nm are mesopores). We ascribe the smaller surface area and pore volume of 1 to the filling of the A-type pores with the Cu(I) cation. The btrip ligand in the cuboctahedral B- and C-type pores is probably lost upon activation at 200 °C (as also suggested by TGA, see above) due to decomposition. This triazole ring decomposition is likely accompanied by gas evolution which ruptures parts of the Cu-btc frameworks leading to cracks and meso- to macroporous voids. At the same time experimental PXRD patterns measured before and after N₂ adsorption show that crystallinity is retained upon activation (Figure S2, Supp. Info.). Hence, we suggest that the larger crystals are shattered into smaller aggregated crystallites upon activation. This would be in line with the H4 hysteresis loop which has been found, e.g., for aggregated crystals or microporous zeolites [44].



Fig. 3. Nitrogen adsorption-desorption isotherms (left) at 77 K of **1**, and the derived pore-size distribution (right).

4 Conclusion

When H₃btc and *rac*-btrip were tried to combine with copper(II) salts in the presence of triethylamine as deprotonating base under hydrothermal conditions, the successfully crystallized product **1** had only the btc linker in the 3D network of $\{[Cu(NCCH_3)_4][Cu_3(\mu_6-btc)_2]_2(O_2CCH_3)\}_n$. The network part of $\{[Cu_3(\mu_6-btc)_2]_2\}_n$ is isostructural with the prototypical microporous MOF HKUST-1 3D- $[Cu_3(\mu_6-btc)_2(H_2O)_3]_n$, also named Cu-btc. The molecular complex cation $[Cu(NCCH_3)_4]^+$ is the first defined guest which occupies the A-type octahedral cages of the HKUST-1 network. The commonly occupied cuboctahedral B- and C-type pores contain the btrip ligand which was found by ¹H NMR after dissolution of the washed crystalline product in a 2.7 : 1 (= 4 : 1.5) btc : btrip molar ratio. Together with some

additional water and acetonitrile solvent molecules the overall formula for **1** would then come out to $3D-\{[Cu(NCCH_3)_4][Cu_3(\mu_6-btc)_2]_2(O_2CCH_3) (H_2O,CH_3CN)_x(btrip)_{1.5}\}_n$.

5 Appendix A. Supplementary data

CCDC 1451953 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

6 Acknowledgement

AT sincerely thanks the Al-Furat University and the Ministry of Higher Education in Syria for the financial support (scholarship) during his study in Germany (language course, Master and PhD degree). This work was funded by BMBF project OptiMat 03SF0492C.

7 References

[1] (a) L.J. Murray, M. Dincă, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294. (b) S.S. Han, J.L.
Mendoza-Cortés, W.A. Goddard III, Chem. Soc. Rev. 38 (2009) 1460. (c) J. Sculley, D. Yuan, H.-C.
Zhou, Energy Environ. Sci. 4 (2011) 2721. (d) Y. He, W. Zhou, G. Qian, B. Chen, Chem. Soc. Rev. 43 (2014) 5657.

[2] (a) H. Wu, Q. Gong, D.H. Olson, J. Li, Chem. Rev. 112 (2012) 836. (b) N. Nijem, H. Wu, P. Canepa, A. Marti, K.J. Balkus Jr., T. Thonhauser, J. Li, Y.J. Chabal, J. Am. Chem. Soc., 134 (2012) 15201. (c) K. Li, D.H. Olson, J. Li, Trends Inorg. Chem. 12 (2010) 13. (d) J.-R. Li, J. Sculley, H.-C. Zhou, Chem. Rev. 112 (2012) 869.

[3] (a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, Chem. Soc. Rev. 43 (2014) 6011. (b) M.
Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 112 (2012) 1196. (c) J.-Y. Lee, O.K. Farha, J. Roberts,
K.A. Scheidt, S.-B.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450. (d) D. Farrusseng, S.
Aguado, C. Pinel, Angew. Chem. Int. Ed. 48 (2009) 7502.

[4] (a) S. Horike, D. Umeyama, S. Kitagawa, Acc. Chem. Res. 46 (2013) 2376. (b) G. Givaja, P. Amo-Ochoa, C.J. Gómez-García, F. Zamora, Chem. Soc. Rev. 41 (2012) 115.

[5] (a) D. Fröhlich, S.K. Henninger, C. Janiak, Dalton Trans. 43 (2014) 15300. (b) F. Jeremias, D.
Fröhlich, C. Janiak, S.K. Henninger, New J. Chem. 38 (2014) 1846. (c) F. Jeremias, D. Fröhlich, C.
Janiak, S.K. Henninger, RSC Adv. 4 (2014) 24073. (d) C. Janiak, S. K. Henninger, Chimia 67 (2013) 419. (e) M. Wickenheisser, F. Jeremias, S.K. Henninger, C. Janiak, Inorg. Chim. Acta 407 (2013) 145.

(f) F. Jeremias, V. Lozan, S.K. Henninger, C. Janiak, Dalton Trans. 42 (2013) 15967. (g) A. Khutia, H.U. Rammelberg, T. Schmidt, S. Henninger, C. Janiak, Chem. Mater. 25 (2013) 790. (h) S.K. Henninger, F. Jeremias, H. Kummer, C. Janiak, Eur. J. Inorg. Chem. 2012 (2012) 2625. (i) F. Jeremias, A. Khutia, S.K. Henninger, C. Janiak, J. Mater. Chem. 22 (2012) 10148. (j) J. Ehrenmann, S.K. Henninger, C. Janiak, Eur. J. Inorg. Chem. 2011 (2011) 471. (k) S.K. Henninger, H.A. Habib, C. Janiak, J. Am. Chem. Soc. 131 (2009) 2776.

[6] (a) H. Erer, Polyhedron 102 (2015) 201. (b) S.-F. Zhang, F. Xiong, Z. He, Y. Liang, J.-R. Xue, L.-H. Jing, D.-B. Qin, Polyhedron 102 (2015) 401. (c) G.G. Sezer, O.Z. Yesilel, M. Arici, H. Erer, Polyhedron 102 (2015) 514. (d) D.K. Maity, B. Bhattacharya, A. Halder, A. Das, D. Ghoshal, Polyhedron 102 (2015) 634.

[7] H.A. Habib, J. Sanchiz, C. Janiak, Dalton Trans. (2008) 1734.

[8] H.A. Habib, J. Sanchiz, C. Janiak, Inorg. Chim. Acta 362 (2009) 2452.

[9] (a) W. Sun, J. Liu, H. Liu, Z. Liu, Polyhedron 109 (2016) 1. (b) H.A. Habib, A. Hoffmann, H.A.
Höppe, C. Janiak, Dalton Trans. (2009) 1742. (c) Y.-J. Mu, X.-L. Ma, B. Han, G.-F. Qin, Y.-Y. Niu,
H.-X. Lu, Polyhedron 67 (2014) 44. (d) L.-N. Zhang, X.-L. Sun, C.-X. Du, H.-W. Hou, Polyhedron 72 (2014) 90. (e) A.J. Calahorro, G. Zaragoza, A. Salinas-Castillo, J.M. Seco, A. Rodríguez-Diéguez,
Polyhedron 80 (2014) 228. (f) B.-B. Shi, S.-F. Liu, L. Guo, X.-Q. Li, G. Li, Polyhedron 83 (2014) 77.

[10] Z. Yin, Y.-L. Zhou, M.-H. Zeng, M. Kurmoo, Dalton Trans. 44 (2015) 5258.

[11] (a) J.-G. Ding, X. Zhu, Y.-F. Cui, N. Liang, P.-P. Sun, Q. Chen, B.-L. Li, H.-Y. Li,
CrystEngComm 16 (2014) 1632. (b) Y.-X. Zhang, J. Yang, W.-Q. Kan, J.-F. Ma, CrystEngComm 14 (2012) 6004. (c) G.A. Senchyk, V.O. Bukhan'ko, A.B. Lysenko, H. Krautscheid, E.B. Rusanov, A.N. Chernega, M. Karbowiak, K.V. Domasevitch, Inorg. Chem. 51 (2012) 8025. (d) A.B. Lysenko, G.A. Senchyk, J. Lincke, D. Lässig, A.A. Fokin, E.D. Butova, P.R. Schreiner, H. Krautscheid, K.V. Domasevitch, Dalton Trans. 39 (2010) 4223. (e) L. Yi, X. Yang, T. Lu, P. Cheng, Cryst. Growth Des. 5 (2005) 1215.

[12] H.A. Habib, C. Janiak, Acta Cryst. E64 (2008) o1199.

[13] H.A. Habib, A. Hoffmann, H.A. Höppe, G. Steinfeld, C. Janiak, Inorg. Chem. 48 (2009) 2166.

[14] S.S.-Y. Chui, S.M.-F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148.

[15] (a) Q.M. Wang, D. Shen, M. Bülow, M.L. Lau, S. Deng, F.R. Fitch, N.O. Lemcoff, J. Semanscin, Micropor. Mesopor. Mater. 55 (2002) 217. (b) K. Schlichte, T. Kratzke, S. Kaskel, Micropor. Mesopor. Mater. 73 (2004) 81.

[16] (a) N.C. Jeong, B. Samanta, C.Y. Lee, O.K. Farha, J.T. Hupp, J. Am. Chem. Soc. 134 (2012) 51.
(b) A.Ö. Yazaydin, A.I. Benin, S.A. Faheem, P. Jakubczak, J.J. Low, R.R. Willis, R.Q. Snurr, Chem. Mater. 21 (2009) 1425. (c) F. Jeremias, S.K. Henninger, C. Janiak, Chem. Commun. 48 (2012) 9708.

[17] STOE WinXPOW Version 1.10; STOE and Cie GmbH, Darmstadt, Germany, 2002.

[18] Mercury - Program for Crystal Structure Visualisation, Exploration and Analysis, The Cambridge Crystallographic Data Centre (CCDC), Version 3.3.1.

[19] (a) L.D. Gelb, K.E. Gubbins, R. Radhakrishnan, M. Sliwinska-Bartkowiak, Rep. Prog. Phys. 62 (1999) 1573. (b) P.I. Ravikovitch, A. Vishnyakov, R. Russo, A.V. Neimark, Langmuir 16 (2000) 2311.

[20] (a) A.L. Spek, Acta Crystallogr. D 65 (2009) 148. (b) A.L. Spek, J. Appl. Crystallogr. 36 (2003)
7. (c) A.L. Speck, PLATON - A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2008; Windows implementation: L.J. Farrugia, University of Glasgow, Scotland, Version 40608 (2008).

[21] (a) R.K. Bartlett, I.R. Humphrey, J. Chem. Soc. C (1967) 1664. (b) A.D. Naik, J. Marchand-Brynaert, Y. Garcia, Synthesis 1 (2008) 149.

[22] A. Tahli, J.K. Maclaren, I. Boldog, C. Janiak, Inorg. Chim. Acta 374 (2011) 506.

[23] D. Lässig, J. Lincke, H. Krautscheid, Tetrahedron Letters 51 (2010) 653.

[24] APEXII: Data collection program for the APEXII CCD area-detector system, Bruker Analytical X-ray Systems, Madison, Wisconsin, USA 2010.

[25] SAINT: Data Reduction and Frame Integration Program for the CCD Area-Detector System. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, 1997.

[26] G.M. Sheldrick, Program SADABS: Area-detector absorption correction, University of Göttingen, Germany, 1996.

[27] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.

[28] Diamond (Version 3.2k) for Windows, Crystal and Molecular Structure Visualization, Crystal Impact-K. Brandenburg and H. Putz GBr, Bonn, Germany 2009-2015.

[29] (a) W. Zheng, X. Liu, J. Guo, L. Wu, D. Liao, Inorg. Chim. Acta 357 (2004) 1571. (b) J.-C. Dai,
X.-T. Wu, Z.-Y. Fu, C.-P. cui, S.-M. Hu, W.-X. Du, L.-M. Wu, H.-H. Zhang, R.-Q. Sun, Inorg. Chem.
41 (2002) 1391.

[30] Y.-B. Yao, T. Xie, Y.-M. Gao, Handbook of Physical Chemistry, Shanghai Science and Technology Publication of China, Shanghai, 1985.

[31] (a) S. Jana, S. Chattopadhyay, Polyhedron 81 (2014) 298. (b) O.M. Yaghi, H. Li, J. Am. Chem. Soc. 117 (1995) 10401.

[32] (a) G. Prakash, M. Nirmala, R. Ramachandran, P. Viswanathamurthi, J.G. Malecki, J. Sanmartin,
Polyhedron 89 (2015) 62. (b) C.-D. Wu, C.-Z. Lu, H.-H. Zhuang, J.-S. Huang, Inorg. Chem. 41 (2002)
5636.

[33] J.Y. Lu, A.M. Babb, Inorg. Chem. 41 (2002) 1339.

[34] J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin, Y.-H. Wen, J. Am. Chem. Soc. 126 (2004) 7796.

[35] Y. Kang, Y.-G. Yao, Y.-Y. Qin, J. Zhang, Y.-B. Chen, Z.-J. Li, Y.-H. Wen, J.-K. Cheng, R.-F. Hu, Chem. Commun. (2004) 1046.

[36] Y.-H. Wen, J.-K. Cheng, J. Zhang, Z.-J. Li, Y. Kang, Y.-G. Yao, Inorg. Chem. Commun. 7 (2004) 1120.

[37] (a) L.J. Bellamy, The Infrared Spectra of Comples Molecules, Wiley, New York, 1958. (b) C.A.
Téllez S, E. Hollauer, M.A. Mondragon, V.M. Castaño, Spectrochimica Acta Part A: Molecular and
Biomolecular Spectroscopy 57 (2001) 993. (c) F. Billes, H. Endrédi, G. Keresztury, J. Mol. Struc.:
Theochem 530 (2000) 183. (d) D. Bougeard, N.Le Calvé, B. Saint Roch, A. Novak, J. Chem. Phys. 64 (1976) 5152. (e) W.-Q. Kan, J. Yang, Y.-Y. Liu, J.-F. Ma, Polyhedron 30 (2011) 2106.

[38] (a) (Fe2+/Fe3+) L. Xie, S. Liu, C. Gao, R. Cao, J. Cao, C. Sun, Z. Su, Inorg. Chem. 46 (2007)
7782. (b) (Cr3+) L.J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C.M. Brown, J.R. Long, J. Am. Chem. Soc. 132 (2010) 7856. (c) (Ni2+) P. Maniam, N. Stock, Inorg. Chem. 50 (2011) 5085. (d) (Zn2+) B. Moulton, J. Lu, R. Hajndl, S. Hariharan, M.J. Zaworotko, Angew. Chem. Int. Ed. 41 (2002) 2821.

[39] (a) C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, J. Am. Chem. Soc. 131
(2009) 1883. (b) F.-J. Ma, S.-X. Liu, D.-D. Liang, G.-J. Ren, F. Wei, Y.-G. Chen, Z.-M. Su, J. Solid
State Chem. 184 (2011) 3034.

[40] L. Yang, H. Naruke, T. Yamase, Inorg. Chem. Commun. 6 (2003) 1020.

[41] H. Yang, J. Li, L. Wang, W. Dai, Y. Lv, S. Gao, Catalysis Commun. 35 (2013) 101.

[42] R.W. Larsen, J. Miksovska, R.L. Musselman, L. Wojtas, J. Phys. Chem. A. 115 (2011) 11519.

[43] Z. Zhang, L. Zhang, L. Wojtas, M. Eddaoudi, M.J. Zaworotko, J. Am. Chem. Soc. 134 (2012)928.

[44] (a) M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol,K.S.W. Sing, Pure Appl. Chem. 87 (2015) 1051. (b) K.S.W. Sing, D.H. Everett, R.A.W. Haul, L.Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.

[45] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982.

[46] J.L.C. Rowsell, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 1304.