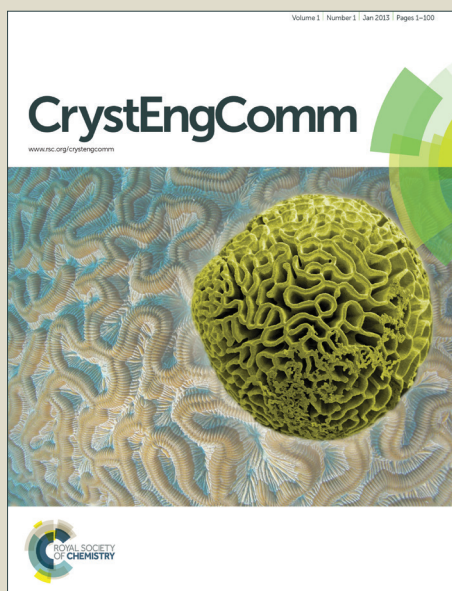


CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

A unique microporous copper-trimesate selenite with high selectivity for CO₂

Cite this: DOI: 10.1039/x0xx00000x

Giannis. S. Papaefstathiou,^a Kota S. Subrahmanyam,^b Gerasimos. S. Armatas,^c Christos. D. Malliakas,^b Mercouri. G. Kanatzidis^b and Manolis. J. Manos^{*c}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A copper-trimesate selenite compound is reported, which shows a robust 3-D porous structure with unprecedented structural characteristics and represents a unique example of a metal inorganic-organic framework with considerable permanent microporosity and selective CO₂ sorption property.

The synthesis and study of Metal Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs) have risen at the forefront of inorganic and materials science research.^{1,2} This is not surprising taking into account the exceptional properties of these compounds and potential applications in various fields including gas storage and separation, catalysis, sensing, drug delivery etc.^{1,2} Besides tuning the properties of existing MOFs, it is also of great importance to discover new compounds that may exhibit features not observed for the already reported materials.

A strategy that can afford MOFs with unseen structures and properties comprises the simultaneous use of polytopic organic ligands and inorganic anions with metal binding capability, such as SO₄²⁻, PO₄³⁻, SO₃²⁻, SeO₃²⁻, TeO₃²⁻, CO₃²⁻ etc.³ Such MOFs, which can be called Metal Inorganic Organic Frameworks (**MINOFs**), may show not only unique structural characteristics but also properties arising from the presence of the inorganic anionic ligands, making them a distinct class of metal organic framework materials. For example, it is well known that the incorporation of QO₃²⁻ (Q=S, Se, Te) anions often leads to non-centrosymmetric structures due to the lone pair of electrons of these ligands and many acentric compounds with these anions display interesting non-linear optical properties (e.g. Second Harmonic Generation, SHG).⁴ So far, MOFs containing bridging inorganic anionic groups in combination with organic polytopic ligands have been reported sporadically³ and in addition, the vast majority of such materials described in the literature are nonporous with very few exceptions.³¹

Herein we present the compound [Cu₄(btc)₂(SeO₃)(H₂O)₂].6H₂O (**MINOF-1**) (H₃btc=1,3,5-benzene-tricarboxylic acid), which exhibits a

robust 3-D open framework structure and also adopts a highly unusual structural topology as a result of the insertion of SeO₃²⁻ ligands into the copper trimesate net. Importantly, **MINOF-1** represents a unique example of a coordination polymer based on both organic and inorganic polytopic ligands that shows significant permanent microporosity and high CO₂ uptake and selectivity vs. CH₄.

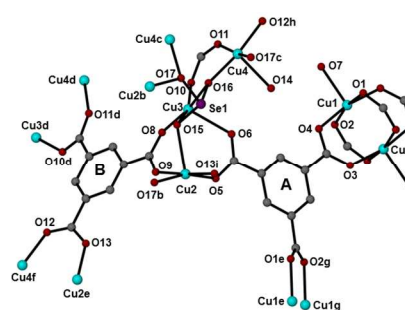


Figure 1. Representation of the connectivity of the Cu²⁺ ions, btc³⁻ ligands (**A** and **B**) and SeO₃²⁻ group in **MINOF-1**. The H atoms were omitted for clarity. Symmetry codes: a: 3/2-x, 1/2-y, 1-z; b: 1-x, -y, -z; c: 1-x, y, 1/2-z; d: x, 1-y, z-1/2; e: x, -y, z-1/2; f: x, y, z-1; g: 3/2-x, y-1/2, 1/2-z; h: x, y, 1+z; i: x, -y, 1/2+z.

Compound **MINOF-1** was isolated as plate-like crystals (Fig. S1, ESI) by a reaction of Cu(NO₃)₂·3H₂O, H₃btc and KSeCN in EtOH:H₂O (1:1) at 90 °C. The SeO₃²⁻ ligands are presumably formed *in situ* by the decomposition of SeCN⁻ under the hydrothermal conditions. Note that **MINOF-1** cannot be isolated by using SeO₃²⁻ instead of SeCN⁻; reactions in the presence of SeO₃²⁻ led to mixtures of [Cu₃(btc)₂(H₂O)₃] (**HKUST-1**)^{5a} and chalcogenite [Cu(SeO₃)₂(H₂O)₂].^{5b} Therefore, the slow transformation of SeCN⁻ to SeO₃²⁻ seems to be the key for the successful synthesis of the metal-organic selenite compound.

The compound crystallizes in the monoclinic space group C2/c.† There are four crystallographically unique Cu²⁺ in the structure, all adopting a square pyramidal coordination geometry (Fig. 1): Cu1 is coordinated with four carboxylic oxygen atoms (O1-O4) and one terminal water (O7) solvent, Cu2 and Cu3 are connected with three

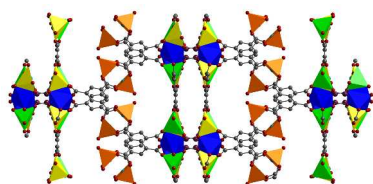


Figure 2. The 3-D framework of **MINOF-1** with polyhedral representation of the Cu^{2+} ions. Cu1, orange; Cu2, blue; Cu3, green; Cu4, yellow; Se, purple; O, red; C, grey. Guests and H atoms were omitted for clarity.

carboxylate oxygen atoms (O9, O5, O13; O8, O6, O10 respectively) and two oxygen atoms from SeO_3^{2-} groups (O15, O17; O15, O16 respectively), whereas Cu_4 is linked with two carboxylate (O11, O12) and two SeO_3^{2-} oxygen atoms (O16, O17) and one terminal water (O14) ligand. The structure is a 3-D framework, which is constructed by the combination of paddle-wheel $[\text{Cu}_2(\text{COO})_4]$ SBUs and a double Cu^{2+} - SeO_3^{2-} -btc³⁻ layer and exhibits large channels running along c-axis (Fig. 2). The dinuclear SBUs are formed by two symmetry-equivalent Cu1 and four trimesate anions (**A**), whereas the double layer is composed of a trinuclear unit $[\text{Cu}_3]$ comprising the Cu2, Cu3 and Cu4 ions, the μ_5 - SeO_3^{2-} ligands and trimesate anions of the second type (**B**) (Fig. 1 and 2). The underline topology of this framework is quite complex as evidenced from the high number of the different nodes (Fig. S2). Specifically, this 5-nodal network consists of an 8-connected node attributed to the $[\text{Cu}_3]$ subunits (Cu2, Cu3 and Cu4), two 3-connected nodes attributed to the SeO_3^{2-} anions and the trimesate anion **B** and two 4-connected nodes corresponding to the second trimesate anion **A** and the $[\text{Cu}_3]$ paddle wheel subunits respectively. The point symbol for this 3,3,4,4,8-connected network is $(4^{10}.6^{15}.8^3)_2(4^3)_2(4^4.6^2)_2(6^2.8^3.10)(6^2.8)_2$ and it is, as expected, unique so far. The structure of the MOF presented (**MINOF-1**) is special and unique for several reasons: a) **MINOF-1** adopts a unique and highly unusual structural type (see above), b) this MOF is a rare example of a coordination polymer combining SeO_3^{2-} and organic polytopic ligands (the known ones are very few examples of non-porous vanadium or lanthanide coordination polymers^{3i,k}) and c) the combination of the famous paddle wheel $[\text{Cu}_2(\text{COO})_4]$ SBUs and layers of Cu^{2+} ions connected with both inorganic and organic polytopic ligands in **MINOF-1** is unprecedented.

To investigate whether is possible to remove the lattice and coordinating solvents from the **MINOF-1** without collapse of the porous structure, high temperature (200 °C) crystallographic study has been performed on a single crystal of the compound. The results indicate that the structural integrity of the compound is retained upon the removal of the solvents and the dry material (**MINOF-1'**) crystallizes in the same space group as the pristine compound with slight changes in the cell parameters.[†] The underline network of **MINOF-1'** is quite similar to that of the pristine material, but there are some striking differences between the two structures. Thus, the connectivity of the $[\text{Cu}_3]$ subunits, the trimesate anion **B** and the SeO_3^{2-} within the double layer is exactly the same in both **MINOF-1** and **MINOF-1'** (Fig. S3). However, the removal of the coordinated water molecule (O14) from Cu_4 was accompanied by a flip of one carboxylate unit of the trimesate anion **A** which now bridges two $[\text{Cu}_3]$ subunits. This, in turn increases the connectivity of the $[\text{Cu}_3]$ nodes from 8 to 9 and the connectivity of the respective trimesate anion **A**

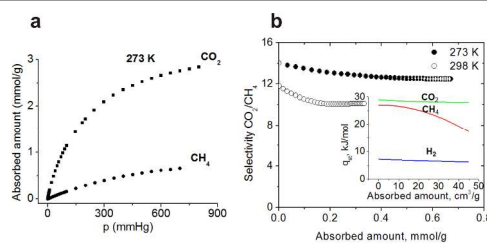


Figure 3. (a) The CO_2 and CH_4 adsorption isotherms at 273 K. (b) The CO_2/CH_4 selectivities for **MINOF-1'** predicted by applying IAST to the CO_2 and CH_4 single-component isotherms at 273 and 298 K. Inset: The isosteric heat of adsorption (q_{st}) for CO_2 , CH_4 and H_2 as a function of the loading amount.

from 3 to 4 (Fig. S4). Therefore, the resulting network is again 5-nodal but it is now $3_4,4_4,9$ -connected with point symbol $(4^{17}.6^{18}.8)_2(4^3.6^2.8)_2(4^3)_2(4^4.6^2)_2$, and it is, as expected unique (Fig. S5).

Nitrogen physisorption measurements recorded at 77 K for the activated sample (**MINOF-1'**) revealed a type-I isotherm, characteristic of a microporous material, as shown in Fig. S6. The apparent Langmuir surface area is $504 \text{ m}^2 \text{ g}^{-1}$ (BET $400 \text{ m}^2 \text{ g}^{-1}$) and the total pore volume is $0.21 \text{ cm}^3 \text{ g}^{-1}$ at $0.98 p/p_0$. Analysis of the N_2 adsorption data with the non-local density function theory (NLDFT) gives a pore size of ca. 6 \AA , which correlates well with the crystal structure of **MINOF-1'** (calculated pore size from PLATON⁶ ~ 6.1 \AA). To further investigate the gas sorption properties of **MINOF-1'**, gas adsorption isotherms were measured for H_2 , CO_2 and CH_4 at different temperatures. **MINOF-1'** showed a significant hydrogen uptake at 1 atm and 77 K (0.88 wt\%) and, even at 87 K (0.67 wt\%), which is higher than that for mesoporous MCM-41 silica (0.57 wt\%),^{7a} zeolite ZSM-5 (0.71 wt\%)^{7b} and ICP particles (0.56 – 0.69 wt\%)^{7c} and comparable to that of several microporous MOFs (0.8 – 1.2 wt\%).^{7d–g} The isosteric heat of H_2 adsorption (q_{st}), as calculated by fitting the adsorption data at 77 and 87 K to appropriate virial-type equations, is $\sim 7 \text{ kJ mol}^{-1}$ at zero coverage (Fig. 3b inset, Fig. S7), which is comparable to the corresponding values found for many MOFs promising for hydrogen storage.^{7g} More interestingly, **MINOF-1'** showed a remarkable ability to selectively absorb carbon dioxide from a gas mixture with methane at near ambient temperature. The CO_2 uptake at 1 bar and 273 K is 2.8 mmol g^{-1} (Fig. 3a), while at 298 K is 1.9 mmol g^{-1} . This adsorption capacity exceeds that of some famous MOFs such as MOF-5 and ZIF-100 (1.5 and 1.7 mmol/g respectively, at 273 K and 1 bar) and compares well with some of the best CO_2 sorbents.^{7h} The CH_4 uptake is 0.7 mmol g^{-1} (Fig. 3) and 0.25 mmol g^{-1} at 273 and 298 K, respectively. Analysis of the adsorption data using the ideal adsorption solution theory (IAST)⁷ⁱ (Fig. S8) reveals that the CO_2/CH_4 selectivity in **MINOF-1'** is ~ 14 at 273 K and ~ 12 at 298 K for a $\text{CO}_2:\text{CH}_4 = 50:50$ mixture, in the low-pressure limit (near zero coverage), see Fig. 3b. These CO_2/CH_4 selectivity values of **MINOF-1'** compare well with those for MOFs showing great promise for CO_2 separation.^{7h} The CO_2/CH_4 gas mixture separation in **MINOF-1'** may be attributed to the preferential adsorption of quadrupolar CO_2 by the coordinatively unsaturated Cu^{2+} sites (Lewis acids) of the metal-organic framework; such induced-dipole interactions are not favourable for nonpolar CH_4 molecules. As for the strength of these interactions, the isosteric heat of CO_2 and CH_4 adsorption, obtained by fitting the adsorption data at 263, 273 and

298 K to appropriate virial-type equations (Fig. S9), was found to be ~ 29 and ~ 27 kJ mol⁻¹ at the limit of zero coverage, respectively (Fig. 3b inset). Considering that the kinetic diameter of CO₂ and CH₄ molecules is ~ 3.3 Å and ~ 3.8 Å respectively, i.e. smaller than the pore size of MINOF-1' (ca. 6 Å), these results indicate preferential adsorption interactions between the surface functionalities of MINOF-1' and CO₂ molecules, thus supporting solubility separation of CO₂ over CH₄.

In conclusion, the amalgamation of copper-trimesate and copper-trimesate selenite moieties in MINOF-1 led to a structure with features unseen in MOFs chemistry. The new compound exhibits a highly robust open framework structure, which is retained upon the removal of guest and coordinating water solvents. Interestingly, the dehydration can be even achieved on a single crystal of the material heated at 200 °C. This single-crystal-to-single-crystal (SCSC) transformation is accompanied by a flip of a carboxylate unit which, in effect, led to a dehydrated material with different topological features. Remarkably, MINOF-1 displays considerable permanent microporosity, which has been rarely observed so far in coordination polymers combining both inorganic and organic polytopic ligands. The high CO₂ uptake and its selective adsorption over CH₄ at near ambient conditions as well as the significant isosteric heat of adsorption for H₂ are also important properties of MINOF-1. Furthermore, the synthetic approach presented in this paper provides a means for the discovery of many new porous MOFs with novel structural features and possibly unusual and interesting physical properties. Our research efforts are now focused towards this direction.

Acknowledgements

Financial support from the National Science Foundation (Grant DMR-1104965) is gratefully acknowledged (MGK).

Notes and references

^a Laboratory of Inorganic Chemistry, Chemistry Department, National and Kapodistrian University of Athens, 15771 Zografou, Greece

^b Chemistry Department, Northwestern University, Evanston, IL 60208, USA

^c Department of Materials Science and Technology, University of Crete, 71003 Heraklion, Greece

^d Chemistry Department, University of Ioannina, 45510 Ioannina, Greece Email: emanos@cc.uoi.gr

†Crystal data for MINOF-1: C₁₈H₂₂Cu₄O₂₃Se, *M* = 939.48, monoclinic, *C*2/c, *a* = 41.0363(18) Å, *b* = 12.1733(4) Å, *c* = 14.1609(5) Å, β = 100.869(3)°, *V* = 6947.1(5) Å³, *T* = 293(2) K, *Z* = 8, 17377 reflections measured, 6115 independent reflections (*R*_{int} = 0.0875). The final *R*₁ and *wR*(*F*²) values were 0.0639 (*I* > 2σ(*I*)) and 0.1371 (*I* > 2σ(*I*)) respectively; *GOF* = 1.093. Crystal data for MINOF-1': C₁₈H₆Cu₄O₁₅Se, *M* = 795.39, monoclinic, *C*2/c, *a* = 38.391(6) Å, *b* = 12.3697(11) Å, *c* = 14.1757(14) Å, β = 90.165(10)°, *V* = 6732(2) Å³, *T* = 473(2) K, *Z* = 8, 26274 reflections measured, 5938 independent reflections (*R*_{int} = 0.2794). The final *R*₁ and *wR*(*F*²) values were 0.1312 (*I* > 2σ(*I*)) and 0.2912 (*I* > 2σ(*I*)) respectively; *GOF* = 1.071.

†Electronic Supplementary Information (ESI) available: Experimental details, structural figures, sorption isotherms, SEM image, thermal

analysis, IR, and PXRD data (Fig. S10-S13). CCDC 968879 and 968880 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/c000000x/

- (a) M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (b) G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- (a) S. T. Zheng, T. Wu, J. A. Zhang, M. Chow, R. A. Nieto, P. Y. Feng and X. H. Bu, *Angew. Chem. Int. Ed.*, 2010, **49**, 5362; (b) D. X. Xue, A. J. Cairns, Y. Belmabkhout, L. Wojtas, Y. Liu, M. H. Alkordi and M. Eddaoudi, *J. Am. Chem. Soc.*, 2013, **135**, 7660; (c) R. E. Morris and P. S. Wheatley, *Angew. Chem. Int. Ed.*, 2008, **47**, 4966; (d) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695; (e) E. Neofotistou, C. D. Malliakas and P. N. Trikalitis, *Chem.-Eur. J.*, 2009, **15**, 4523; (f) L. Q. Ma, J. M. Falkowski, C. Abney and W. B. Lin, *Nat. Chem.*, 2010, **2**, 838; (g) Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887.
- (a) S. I. Swamy, J. Bacsá, J. T. A. Jones, K. C. Stylianou, A. Steiner, L. K. Ritchie, T. Hasell, J. A. Gould, A. Laybourn, Y. Z. Khimyak, D. J. Adams, M. J. Rosseinsky and A. I. Cooper, *J. Am. Chem. Soc.*, 2010, **132**, 12773; (b) Y.-C. Chang and S.-L. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 9848; (c) G. J. Halder, H. Park, R. J. Funk, K. W. Chapman, L. K. Engerer, U. Geiser and J. A. Schluter, *Cryst. Growth Des.*, 2009, **9**, 3609; (d) Y.-Y. Lin, Y.-B. Zhang, J.-P. Zhang and X.-M. Chen, *Cryst. Growth Des.*, 2008, **8**, 3673; (e) Z. Xu, Q. Wang, H. Li, W. Meng, Y. Han, H. Hou and Y. Fan, *Chem. Commun.*, 2012, **48**, 5736; (f) L. Carlucci, G. Ciani and D. M. Proserpio, *Chem. Commun.*, 2004, **40**, 380; (g) D.-T. Nguyen, E. Chew, Q. Zhang, A. Choi and X. Bu, *Inorg. Chem.*, 2006, **45**, 10722; (h) K. P. Rao and C. N. R. Rao, *Inorg. Chem.*, 2007, **46**, 2511; (i) X.-F. Guo, M. L. Feng, Z.-L. Xie, J.-R. Li and X.-Y. Huang, *Dalton. Trans.*, 2008, 3101; (k) Z. Dai, X. Chen, Z. Shi, D. Zhang, G. Li and S. Feng, *Inorg. Chem.*, 2003, **42**, 908; (l) J. Lincke, D. Laßig, M. Kobalz, J. Bergmann, M. Handke, J. Möllmer, M. Lange, C. Roth, A. Möller, R. Staudt and H. Krautscheid, *Inorg. Chem.*, 2012, **51**, 7579.
- P. S. Halasyamani and K. R. Poeppelmeier, *Chem. Mater.*, 1998, **10**, 2753.
- (a) S. S. -Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **238**, 1148; (b) T. Asai, R. Kiriya, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2395.
- A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- (a) M. G. Nijkamp, J. Raaymakers, A. J. van Dillen and K. P. de Jong, *Appl. Phys. A: Mater. Sci. Process.*, 2001, **72**, 619; (b) A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen and K. P. Lillerud, *J. Am. Chem. Soc.* 2005, **127**, 6361; (c) Y.-M. Jeon, G. S. Armatas, D. Kim, M. G. Kanatzidis and C. A. Mirkin, *Small*, 2009, **5**, 46; (d) B. Chen, S. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H. C. Zhou, *Inorg. Chem.* 2007, **46**, 1233; (e) J. L. Rowsell, A. R. Millward, K. S. Park and O. M. Yaghi, *J. Am. Chem. Soc.* 2004, **126**, 5666; (f) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* 2004, **306**, 1012; (g) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (h) -R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena and H.-C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791; (i) A. L. Myers, *Adsorption*, 2003, **9**, 9.

The incorporation of SeO_3^{2-} ligands into a copper-trimesate net results in a microporous metal organic framework with a highly unusual structural topology, which also shows high CO_2 uptake and selectivity vs. CH_4 .

