CrystEngComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *CrystEngComm*, 2014, **16**, 148

Received 24th October 2013,
Accepted 31st October 2013

DOI: 10.1039/c3ce42162g

www.rsc.org/crystengcomm

A fluorite isoreticular series of porous framework complexes with tetrahedral ligands: new opportunities for azolate PCPs†

Ishtvan Boldog,*[ab] Konstantin Domasevitch,[a] Jana K. Maclaren,[c] Christian Heering,[b] Gamall Makhloufi[b] and Christoph Janiak*[b]

Three porous coordination polymers with a simplified formula of $[M_4(\mu_4\text{-Cl})L_2]\cdot n$Guest (M = Cu, Cd) based on two adamantane-derived tetrahedral tetrazolate ligands were synthesized. Along with one known representative, the row of compounds establishes a new isoreticular series with fluorite as the underlying net.

Porous coordination polymers[1] (PCPs or MOFs) are a dynamically developing field of research with a number of possible applications[2] including small molecule storage,[3] separation[4] and drug-delivery[5] as well as sensorics,[6] heterogeneous catalysis[7] and heat transformation.[8] Tunability of surface properties and record holding surface areas ($S_{BET} > 6000\ m^2\ g^{-1}$) of the potentially viable industrial materials are typically plagued by low chemical stability. Azolate PCPs (metal azolate frameworks),[9] particularly pyrazolates (or pyrazolides)[11,12,17–20] and imidazolates,[13] are known as one of the most robust materials, sometimes stable for prolonged time in boiling water (ZIF-8, 9, 10)[10] in comparison to deterioration of IRMOFs and most other carboxylate PCPs even in moist air under ambient conditions.[14] A number of recent strategies targeting construction of robust azolate frameworks involve various uses of small azolates, mixed functionality ligands and advanced methods of synthesis.[15]

There is a particular trend of increasing importance of particularly stable pyrazolate PCPs as evidenced by a number of contributions covered by a recent review.[9] Rapid progress is hampered by complications during growth of monocrystals, necessary for standard single crystal X-ray diffraction structure determination. This synthetic circumstance is slowly becoming less important with the spread of state-of-the-art powder X-ray diffraction structure determination, but the preparation of a single pure phase is not a straightforward task either.

An alternative to the tedious trial-and-error approach is the exploitation of an established isoreticular series that is characterized by consistent reproduction of the topology of the framework upon metrical scale-up of the organic building block. The concept of isoreticular frameworks contributed decisively to the status of carboxylate IRMOFs[16] as the most researched PCP class. Arguably of the highest practical significance[17] among azolate PCPs pertains to the recently established isoreticular series based on ditopic pyrazolates, namely the [M(L)] series (M = Zn, Co, H_2L = 4,4′-bipyrazole,[18] 3,3′,5,5′-tetramethyl-4,4′-bipyrazole[19] and 1,4-bis-(pyrazol-4-yl)-benzene),[20] and we perceive the direction of research targeting new robust azolate PCP series as crucial for the development of the area.

Our interest is focused on a isoreticular series based on tetrahedral ligands (*e.g.* based on tetraphenylmethane or adamantane platforms), a possibility which is still not developed fully even for the most researched carboxylate PCPs and is actively investigated.[21] Taking into account the low solubility of high-molecular weight tetratopic pyrazolate ligands and even more so the highly connected derived coordination polymers, we have chosen a model approach for investigating the structure formation principles for such ligands.

The approach implied the use of building blocks functionalized with tetrazole, a more convenient mimic group. Possessing four donor atoms, anionic tetrazolates could emulate pyrazolates and triazolates as the most typical exhibited denticity equal to two or three. Any tetrazolate structure according to this approach is viewed as a prototype,[9] which could be potentially reached with other azolates possessing an optimized number of donor atoms. Of course, such 'multi-target' mimicking is not strict, but it is rather a

[a] *Inorganic Chemistry Department, Taras Shevchenko National University of Kyiv, Vladimirskaya Street 64, Kyiv 01033, Ukraine. E-mail: ishtvan.boldog@gmail.com*
[b] *Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany*
[c] *Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstr. 21, D-79104, Freiburg i. Br., Germany*

† Electronic supplementary information (ESI) available: synthesis, crystallographic data and analytics, including additional discussion. CCDC 963507–963509. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce42162g

research directing tool, successfully used for targeting 1,2,3-triazolate analogues of tetrazolate prototypes, for example.[22]

Tetrazolate coordination polymers have an important advantage compared to their pyrazolate analogs in terms of their crystallization ability; that is, they have a higher chance of forming monocrystals. More acidic tetrazolate ligands have better solubilities, thus ensuring local 'reversibility' during the crystallization process that is necessary for successful crystal growth.

Two tetrahedral tetrazolate ligands were synthesized,†‡ namely the yet practically unexplored 1,3,5,7-tetrakis(tetrazol-5-yl) adamantane ($AdTtH_4$) and 1,3,5,7-tetrakis((tetrazol-5-yl)-phenyl) adamantane ($Ad(PhTtH)_4$). The two adamantane-based ligands, together with an already introduced tetrakis(tetrazol-5-yl) methane ($C(PhTtH)_4$) analogue,[23] represent a row of similar ligands with the latter being metrically in the middle (Fig. 1a).

The new ligands were subjected to complexation with various transition metals under a range of reasonable crystallization conditions. Entirely different products were obtained depending on the water content in the reaction medium. In the case of copper and cadmium, low temperature solvothermal conditions in dialkylamide-based solvent mixtures containing minute amounts of water yielded the compounds $\{[Cu_4(\mu_4\text{-}Cl)(Ad(Tt)_4)_2]_2Cu\}\cdot 9DMF$, **1**, $[Cu_4(\mu_4\text{-}Cl)(Ad(PhTt)_4)_2\cdot Cu_2Cl_3]\cdot 6DMA\cdot 2H_2O\cdot 4MeOH$, **2**, and $[Cd_4(\mu_4\text{-}Cl)(Ad(PhTt)_4)_2\cdot Cd_2Cl_3]\cdot Solv.$, **3** (Solv. = 4–6DMF·2H_2O·0–4MeOH with exact values dependent on method of synthesis).†,§

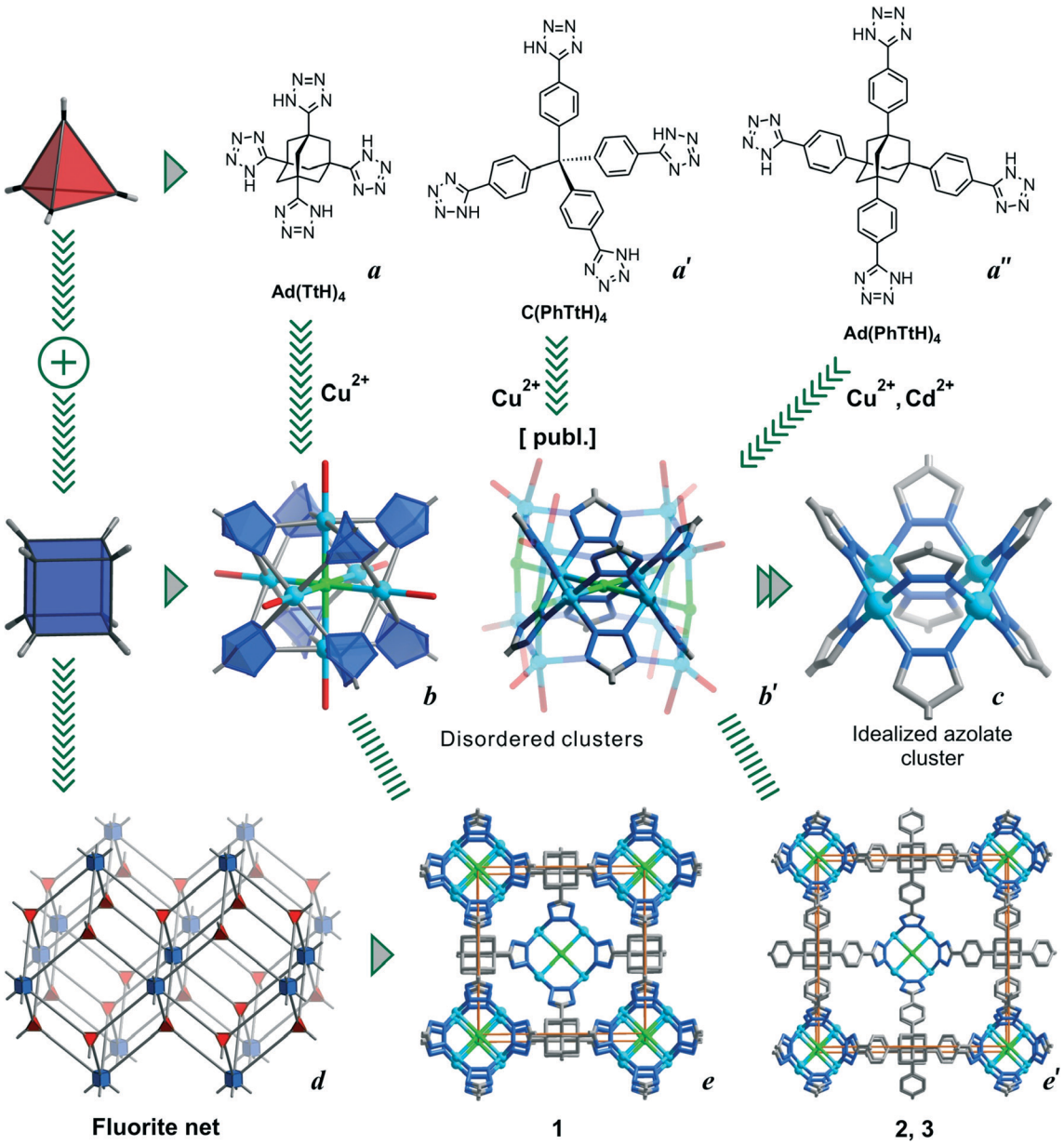

Fig. 1 Compounds **1**–**3** as representatives of the fluorite isoreticular series.

Compounds **1–3** together with the reported $[(Cu_4Cl)(C(PhTt)_4)_2]_2{\cdot}CuCl_2{\cdot}5DMF{\cdot}11H_2O$[23] establish an isoreticular PCP series with fluorite as the underlying net, **flu** (Fig. 1d). All compounds feature the same $\{[Cu_4(\mu_4\text{-Cl})L_2]\}$ 'core' framework with highly symmetric tetranuclear SBUs (Fig. 1b,b′) serving the role of 8-connected nodes. In its idealized form (Fig. 1c), eight bridging azolates join four metal atoms disposed in the corners of a square in a 'dual-crown' fashion. The observed realization of the cluster slightly varies in the row. In **1**, it is closest to the idealized prototype, though its simplicity is obscured by structural disorder: the cubic cluster adopts three mutually orthogonal orientations without change of connectivity. The isostructural **2** and **3** are based on extended clusters with involvement of additional 'external' metal ions, which are coordinated to N1/N4 atoms of the tetrazolate moieties, and involve additional chloride counteranions coordinated to the inner copper quartet. In this regard, the two latter compounds are similar to the already reported structure with the smaller $C(PhTtH)_4$ ligand, but interestingly, they contain a significantly larger amount of 'external' metal chloride, whose quantity is possibly variable, depending on the concentration of the metal salt during synthesis.

Chloride anions in the reaction medium play the role of a template and the use of other metal salts under the same conditions yielded poorly crystalline products. At the same time, the central μ_4-Cl and additional 'external' copper and chloride ions could in principle be removed by extraction, leaving the highly porous $[M_4L_2]$ framework.[23] Provided that the removal is complete, the porosity of **2** and **3** could reach 77% according to the structural data (vdW pore openings at ~10 Å). Remarkably, no interpenetration took place even at such significant scale-up of the ligand (aside from possible topological reasons, it could be explained by the high connectivity, disfavouring close disposition of the 8-connected nodes).

The stability and sorptive properties of **2** were tested in a series of experiments. Unfortunately, the extremely porous tetrazolate framework proved to be rather fragile and collapsed under mild degassing conditions. Best sorption results were obtained after partial degassing of a freshly prepared sample at 60 °C that demonstrated some hydrogen sorption at 0.46 wt% (1 bar, 77 K; Fig. S22†). The fragility of the framework of **2** was also confirmed by PXRD monitoring during attempted solvent exchange: the loss of crystallinity might have been sped up by removal of the 'external' copper chloride component. It corresponds well to the already decreased crystallinity reported for the previous member of the series.[23] Supercritical CO_2 drying may still allow collapse-free degassing, but the framework of **2** as the most porous member of the isoreticular series reaches the limit of conventional structural stability.

Nevertheless, the importance of the established isoreticular series for future research goes beyond the mere enumeration of representatives with significant structural stability. Most remarkable is the resilience of the ligand's metrics and the variability of the metal ion for the realization of the fluorite topology. The known Jahn–Teller distortion of the copper d^9- or malleability of the cadmium d^{10} coordination environment cannot ensure a firm structure directing principle. The results demonstrate that the self-assembly of the most symmetric 1 : 2 combination of cubic and tetrahedral building blocks is invariable under identical synthetic conditions. Concerning the possible pyrazolate analogue of the demonstrated isoreticular series, the $\{[Cu_4(pz)_8]\}$ cluster is described in the $[Cu_4(3\text{-phenylpyrazole})_8]$ molecular compound and recognized as an important potential synthon.[11] This cluster serves as a secondary building block in $[M_3(BTP)_2]$, (M = Ni, Co, Zn, Cu H_3BTP = 1,3,5-tris(1H-pyrazol-4-yl)-benzene), a row of robust isostructural PCPs with a sodalite underlying net.[24]

Thereby, the establishment of the isoreticular series of coordination polymers with tetrahedral tetrazolates sets out the targeted synthesis of possible Cu(II), Zn(II), Ni(II), Co(II), and Cd(II) pyrazolate analogues as a clear goal. The pyrazolate analogue-series should possess higher thermal and chemical stability due to higher covalency of coordination bonding and inertness of the pyrazole moiety. The corresponding research is underway.

Acknowledgements

The authors thank Dr. Holger Ott (Bruker AXS GmbH, Karlsruhe) and Dr. Alexandra Griffin (Agilent Technologies, Oxford) for helping with the crystallographic measurements. The work was supported by DFG grant Ja466/25-1. IB would like to express his sincere gratitude to the Alexander von Humboldt Foundation for the 1135450 STP fellowship grant.

Notes and references

‡ Compounds **1–3** were prepared by heating solutions of metal chlorides and ligands in DMF or DMA based solvent mixtures. For example, $[Cu_4(\mu_4\text{-Cl})(Ad(PhTt)_4)_2{\cdot}Cu_2Cl_3]{\cdot}6$ DMA$\cdot 2H_2O\cdot 4$MeOH, **2**, was obtained in a phase pure form as follows: a mixture of $CuCl_2{\cdot}2H_2O$ (460 mg, 2.7 mmol) and $Ad(PhTtH)_4{\cdot}6.5H_2O$ (160 mg, 0.193 mmol) in 32 ml of DMA and 8 ml MeOH was heated at 70 °C for 10 days. The flocky yellowish-green byproduct was separated by decantation using a 4 : 1 mixture of DMA–MeOH and the product was filtered, quickly washed with MeOH and dried for a short time at 5 Torr, r.t. Yield: 242 mg (48%).

§ Selected crystal data for **1–3**: $\{[Cu_4(\mu_4\text{-Cl})(Ad(Tt)_4)_2]_2Cu\}{\cdot}9$DMF, **1**: $C_{83}H_{111}Cl_2Cu_9N_{73}O_9$ FW = 2918.2, cubic, $Fm\bar{3}m$, a = 18.6421(19), V = 6478.6(11), Z = 2, 391 indep. refl. [R_{int} = 0.1051], 43 param., $R_1(I > 2\sigma)$ = 0.0629, wR_2(all data) = 0.1682. $[Cu_4(\mu_4\text{-Cl})(Ad(PhTt)_4)_2{\cdot}Cu_2Cl_3]{\cdot}6DMA\cdot 2H_2O\cdot 4$MeOH, **2**: $C_{76}H_{56}Cl_4Cu_6N_{32}{\cdot}$Solv., FW = 1940.57, tetragonal, $I4/mmm$, a = 18.9532(3), c = 31.3238(12), V = 11 252.3(5), Z = 2, 3259 indep. refl. [R_{int} = 0.1051], 121 param., $R_1(I > 2\sigma)$ = 0.0550, wR_2(all data) = 0.1673. $[Cd_4(\mu_4\text{-Cl})(Ad(PhTt)_4)_2{\cdot}Cd_2Cl_3]{\cdot}$Solv., **3**: $C_{76}H_{56}Cd_6Cl_4N_{32}{\cdot}$Solv., FW = 2233.73, tetragonal, $I4/mmm$, a = 19.7788(5), c = 31.6321(7), V = 12 374.5(5), 3094 indep. refl. [R_{int} = 0.0486], 111 param., $R_1(I > 2\sigma)$ = 0.0414, wR_2(all data) = 0.1228.

1 S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490; T. K. Maji and S. Kitagawa, *Pure Appl. Chem.*, 2007, **79**, 2155.

2 A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284.
3 R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966; X. A. Lin, N. R. Champness and M. Schröder, *Top. Curr. Chem.*, 2010, **293**, 35; M. Dinca and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766; M. Paik Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782.
4 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869; J.-R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
5 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.
6 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.
7 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; D. Farrusseng, S. Aguado and C. Pinel, *Angew. Chem., Int. Ed.*, 2009, **48**, 7502.
8 C. Janiak and S. K. Henninger, *Chimia*, 2013, **67**, 419.
9 J.-P. J. Zhang, Y.-B. Y. Zhang, J.-B. J. Lin and X.-M. X. Chen, *Chem. Rev.*, 2012, **112**, 1001.
10 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186.
11 M. A. Halcrow, *Dalton Trans.*, 2009, 2059.
12 M. Tonigold, Y. Lu, A. Mavrandonakis, S. Puls, R. Staudt, J. Maellmer, J. Sauer and D. Volkmer, *Chem.–Eur. J.*, 2011, **17**, 8671; N. Masciocchi, S. Galli, V. Colombo, A. Maspero, G. Palmisano, B. Seyyedi, C. Lamberti and S. Bordiga, *J. Am. Chem. Soc.*, 2010, **132**, 7902.
13 A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58; J. Zhang, T. Wu, C. Zhou, S. Chen, P. Feng and X. Bu, *Angew. Chem., Int. Ed.*, 2009, **48**, 2542.
14 J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 15834.
15 W. Ouellette, S. Jones and J. Zubieta, *CrystEngComm*, 2011, **13**, 4457; B. Xia, Z. Chen, Q. Zheng, H. Zheng, M. Deng, Y. Ling, L. Weng and Y. Zhou, *CrystEngComm*, 2013, **15**, 3484; Q. Shi, Z. Song, X. Kang, J. Dong and Y. Zhang, *CrystEngComm*, 2012, **14**, 8280; B. Seoane, J. M. Zamaro, C. Tellez and J. Coronas, *CrystEngComm*, 2012, **14**, 3103; R. Galvelis, B. Slater, A. K. Cheetham and C. Mellot-Draznieks, *CrystEngComm*, 2012, **14**, 374; Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, H. Su and Z. P. Lai, *CrystEngComm*, 2011, **13**, 6937.
16 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127.
17 V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.*, 2012, **134**, 12830.
18 C. Pettinari, A. Tăbăcaru, I. Boldog, K. V. Domasevitch, S. Galli and N. Masciocchi, *Inorg. Chem.*, 2012, **51**, 5235.
19 A. Tăbăcaru, C. Pettinari, I. Timokhin, F. Marchetti, F. Carrasco-Marín, F. J. Maldonado-Hódar, S. Galli and N. Masciocchi, *Cryst. Growth Des.*, 2013, **13**, 3087.
20 H. J. Choi, M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 7848.
21 L. Zhou, Y.-S. Xue, J. Zhang, H.-B. Du and X.-Z. You, *CrystEngComm*, 2013, **15**, 6199; Y. Zou, C. Y. Yu, Y. Y. Li and M. S. Lah, *CrystEngComm*, 2012, **14**, 7174; J. Guo, J. Yang, Y.-Y. Liu and J.-F. Ma, *CrystEngComm*, 2012, **14**, 6609.
22 A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784.
23 M. Dincă, A. Dailly and J. R. Long, *Chem.–Eur. J.*, 2008, **14**, 10280.
24 V. Colombo, S. Galli, H. J. Choi, G. D. Han, A. Maspero, G. Palmisano, N. Masciocchi and J. R. Long, *Chem. Sci.*, 2011, **2**, 1311.