CrystEngComm

This article can be cited before page numbers have been issued, to do this please use: M. Andruh, T. Mocanu, B. Niculina, L. Pop, S. Sova and I. Grosu, *CrystEngComm*, 2016, DOI: 10.1039/C6CE02146H.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/crystengcomm

View Article Online
DOI: 10.1039/C6CE02146H

COMMUNICATION

Coordination polymers constructed from tetrahedral shaped adamantane tectons†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

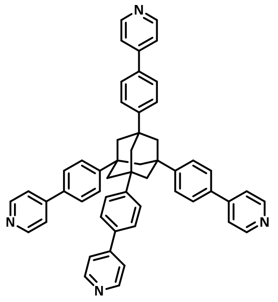
Teodora Mocanu,[a] Lidia Pop,[b] Niculina D. Hădade,[b] Sergiu Shova,[c] Ion Grosu,[b,*] and Marius Andruh[a,*]

Two rigid tetrahedral organic linkers derived from adamantane have been employed in constructing a 3-D, 4-fold interpenetrated framework featuring a PtS topology, $[CuL^1(H_2O)_2](BF_4)_2\cdot 8H_2O$ (1) (L^1= 1,3,5,7-tetrakis{4-(4-pyridyl)phenyl}adamantane), and a 2-fold interpenetrated grid–like coordination polymer, $[Mn(hfac)_2(L^2)_{0.5}]$ (2) (L^2= 1,3,5,7-tetrakis(4-cyano-phenyl)adamantane).

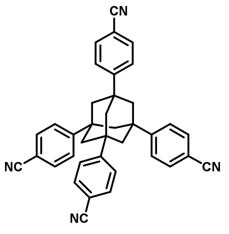
Tetrahedral divergent ligands played an important role in crystal engineering.[1] By developing the "node-and-spacer" approach, Robson has shown that coordination polymers featuring a diamond-like topology can be rationally obtained by combining two tectons: a metal ion with a preference for T_d coordination geometry, and an organic molecule with tetrahedrally-disposed coordination groups.[2] Several other basic inorganic structures are constructed from tetrahedral tectons (mainly metal ions): lonsdaleite (**lon**), quartz (**qtz**), $SrAl_2$ (**sra**) (tetrahedral nodes – uni- or binodal nets), PtS (**pts**) (a combination of tetrahedral and square planar nodes), Ge_3N_4 (tetrahedral and trigonal nodes in a 3:4 ratio), fluorite (**flu**) (tetrahedral and cubic centres) etc.[3] Even though a rich diversity of topologies can be envisioned, the number of coordination polymers described in the literature and relying upon tetrahedral spacers is quite low.[4] The network topologies are different from the diamondoid one when the metal ions have other stereochemical preferences.

The coordinating-prone units attached to tetrahedral skeletons (methane, silane or adamantane derivatives) can be anionic (carboxylate,[5] sulfonate,[6] phosphonate[7-9] groups), or neutral (pyridine,[10] triazole,[11] and tetrazole[8,12-13] fragments, cyano groups[2,14]). Tetra-substituted adamantane derivatives are useful tectons in generating robust porous structures showing high connectivity topologies.[6-8,12,14c] In spite of the fact that rigid organic tetrahedral tectons are encoded to orient the donor atoms towards the vertices of a regular tetrahedron, thus extending the molecular assembling into three dimensions, 2-D layered comprising organic ligands with T_d symmetry have also been described.[6a,14]

Herein, we report the crystal structures of two new coordination polymers constructed from copper(II) ions and $\{Mn^{II}(hfac)_2\}$ entities acting as nodes: $[CuL^1(H_2O)_2](BF_4)_2\cdot 8H_2O$ **1** and $[Mn(hfac)_2(L^2)_{0.5}]$ **2**, where L^1 and L^2 are tetrahedral spacers having four phenyl-pyridyl (L^1) or phenyl-cyano moieties (L^2) attached to an adamantane backbone (Scheme 1). The two assembling species have been chosen from the following reasons: Cu^{II} adopts various coordination numbers and geometries, but, only rarely tetrahedral; $\{Mn^{II}(hfac)_2\}$ has two positions available for the interaction with the spacer (either *cis* or *trans*). In the first case, Cu^{II}, the topology of the resulting coordination polymer cannot be easily predicted. In the second case, a 3-D coordination polymer is expected, if the donor atoms arising from the spacer occupy the *trans* positions at the manganese ion, and a 2-D coordination polymer, when the donor atoms from the spacer occupy the *cis* positions.



L^1



L^2

---

[a] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie no. 23, 020464, Bucharest, Romania
E-mail: mariusandruh@dnt.ro
[b] Centre of Supramolecular Organic and Organometallic Chemistry (CCSOOM), Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos, 400028, Cluj-Napoca, Romania
[c] "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, 700487 Iasi, Romania

†Electronic Supplementary Information (ESI) available: details of synthetic procedures, crystallographic data, figures of asymmetric units, spectral data, TGA curve and experimental and calculated powder diffraction patterns. CCDC 1508551 and 1508552. For ESI and X-ray crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6CE02146H

Scheme 1

The two adamantane derivatives, L^1 and L^2, have been already described in the literature.[15,8] In the case of tetrapyridyladamantane L^1 (Scheme S1), relevant improvements of the synthesis, compared to the method reported by Müller,[15] were elaborated. The employment of PdCl$_2$(dppf) instead of Pd(PPh$_3$)$_4$ lead to an increase of the yields from 27 to 41%, a reducing of the reaction time from 72 to 12 h, and an easier chromatographic separation of the target compound.‡

The reaction of L^1 with copper(II) tetrafluoroborate, in the presence of monoethanolamine, affords blue-green single crystals of [CuL^1(H$_2$O)$_2$](BF$_4$)$_2$·8H$_2$O **1**.‡ The investigation of the crystal structure§ of **1** reveals that each L^1 molecule connects four copper(II) ions (Figure 1) in a 3-D network (Figure 2). The copper ions display a distorted octahedral coordination geometry with four nitrogen atoms in the equatorial plane arising from four organic linker molecules (Cu1 – N1 = 2.026(8) Å) and two semi-coordinated water molecules in *trans* positions (Cu1 – O1W= 2.626(16) Å). The Cu···Cu distances are 18.130 Å (Cu1···Cu1^a, ^{a} = 1+*x*, 1+*y*, *z*), and 20.744 Å (Cu1···Cu1^b, ^{b} = 0.5+*x*, 2.5-*y*, 0.5+*z*). The 3-D cationic framework can be described as a binodal (4,4)-connected network with a platinum sulfide topology, where L^1 molecules play the role of tetrahedral sulfide nodes while the equatorial CuN$_4$ units replace platinum square planar centres. The analysis of the packing diagram shows the interpenetration of four independent 3-D nets of **1** (Figure 3). The structural changes of L^1, in comparison with the homolog derived from methane,[10b] are reflected in an increase of the interpenetration degree. To the best of our knowledge, this is the highest interpenetration degree encountered for molecular assemblies built from a rigid organic linker with T_d symmetry bearing pyridine moieties. The void space resulting upon interpenetration is filled by BF$_4^-$ anions and solvent molecules. Since the number of the water molecules could not be directly determined by the crystallographic measurements, we estimated the presence of eight water molecules per formula (ESI†) from the data obtained by elemental and thermogravimetric analyses. The diffuse reflectance electronic spectrum of **1** (Figure S3) shows a band at 604 nm, due to the hexacoordinated Cu^{II} ions.

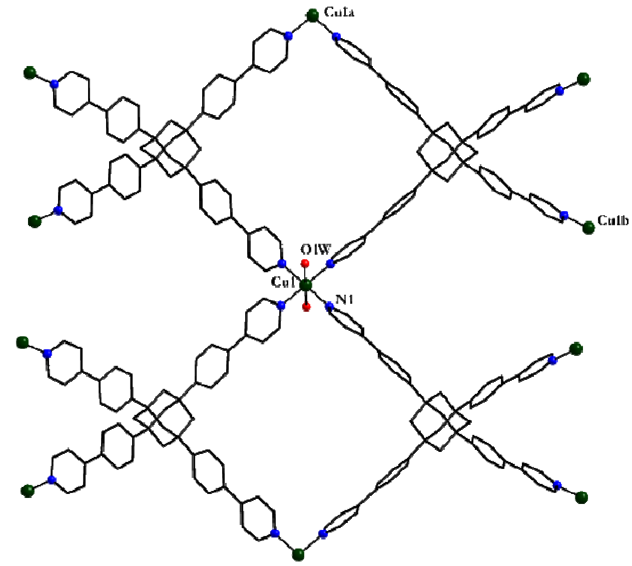


Figure 1. Perspective view of the coordination polymer in crystal **1** with atom numbering scheme.

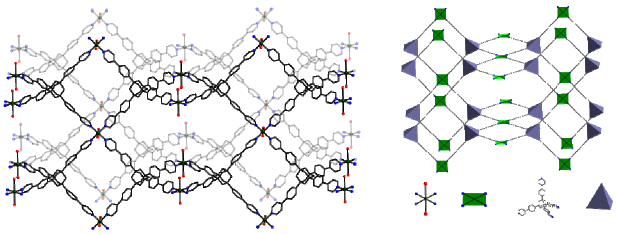


Figure 2. Perspective view of the 3-D coordination framework of **1** and the corresponding representation of platinum sulfide topology.

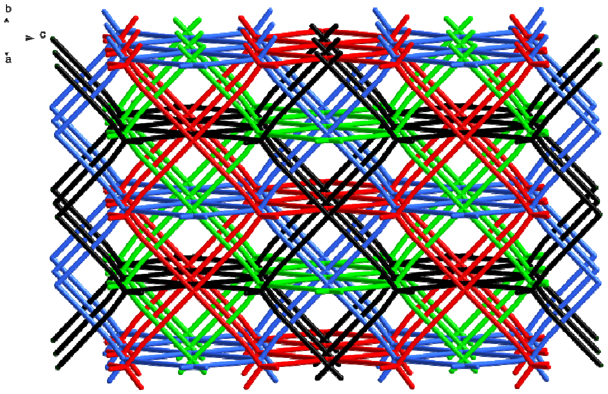


Figure 3. Crystal packing diagram in crystal **1**, showing the four-fold interpenetration.

Compound [Mn(hfac)$_2$(L^2)$_{0.5}$] **2** crystallizes in the tetragonal centrosymmetric I4$_1$/a space group.§ Taking into consideration the weak coordinating ability of nitrile containing molecules, we have employed a hexafluoroacetylacetonate metal complex, as the electron-withdrawing F atoms increase the Lewis acidity of the metal ion, thus favouring the coordination of the nitrile groups to the manganese ion, by replacing the weakly bounded aqua ligands. A neutral coordination structure is assembled by reacting [Mn(hfac)$_2$(H$_2$O)$_2$] with L^2 (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione).‡

The {Mn(hfac)$_2$} nodes are linked by L^2 molecules resulting in neutral (4,4)-connected grid-like layers. The Mn^{II} ions adopt a slightly distorted octahedral geometry with two chelating hfac$^-$ ligands (Mn – O1 = 2.128(4) Å, Mn – O2 = 2.154(5) Å) and two nitrogen ligand atoms disposed in *cis* positions (Mn – N1 = 2.239(7) Å) (Figure 4). Since L^2 acts as a 4-connecting knot, the low dimensionality of **2** can be ascribed exclusively to the *cis*-

View Article Online
DOI: 10.1039/C6CE02146H

arrangement of nitrogen donor atoms in {Mn(hfac)$_2$N$_2$} units, while a *trans* coordination of the nitrogen L^2 atoms to the metal centre would afford a 3-D net. In the case of honeycomb type layers[14b,c,] where the tetrahedral shaped ligand acts as 3-connecting node, the promotion into the third dimension is disrupted by the presence of solvent molecules or coordinating anions. The inherent chirality of the *cis*-isomer of the metal building blocks enables the formation of chains where two L^2 arms bridge metal centres of same octahedral delta (Δ) conformation and the other two arms bridge metal centres of lambda (Λ) conformation. Viewed along the *c* axis, the structure of **2** can be regarded as sets of zig-zag chains constructed, each one, by Mn^{II} nodes with the same chirality, and running perpendicular to each other. Layers with meshes of square cross section are thus formed (Figure 5). Two such layers interpenetrate (Figure. 6 a). Channels within the *ab* plane are formed (Figure 6 b).

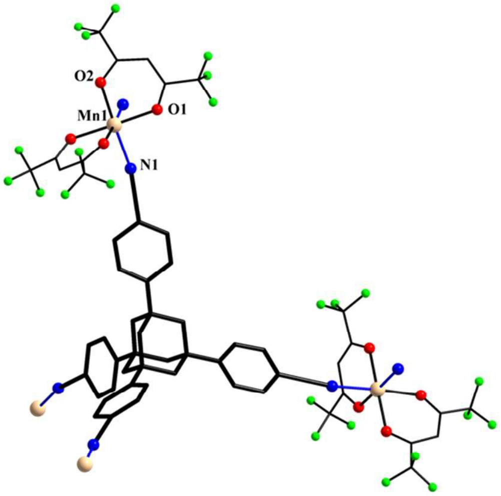


Figure 4. Fragment of crystal structure of **2** showing the interaction of the tetrahedral ligand L^2 with two {Mn(hfac)$_2$} units of opposite chirality.

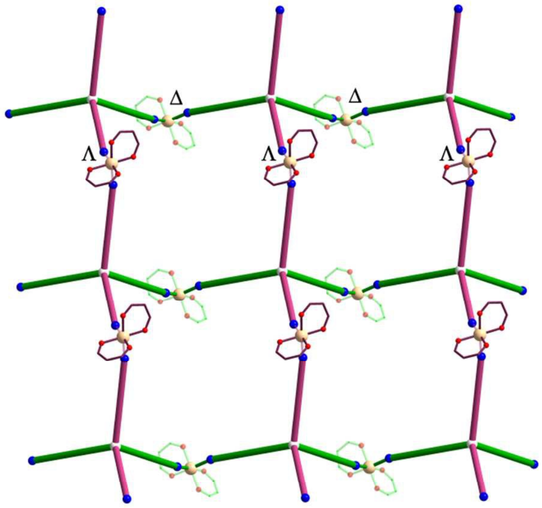


Figure 5. View of a layer in crystal **2** (See text: green – delta, violet – lambda configuration) (CF$_3$ groups were omitted for clarity).

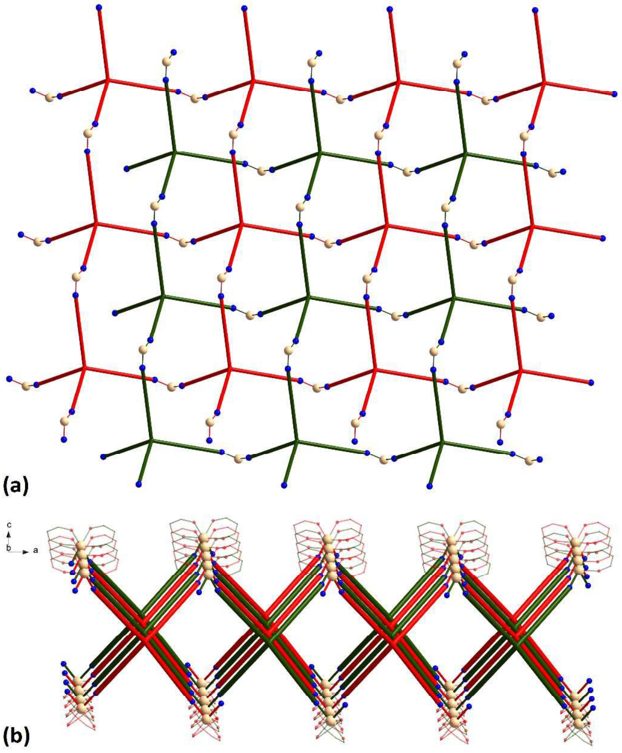


Figure 6. (a) Packing diagram of **2** showing the two-fold interpenetration of 2-D nets; (b) perspective view of channels.

In conclusion, two coordination polymers with different dimensionalities have been synthesized from rigid tetrahedral shaped tectons with adamantane scaffolds. We have emphasized the role played by the coordination preference of the metal centre, along with the organic linker's symmetry, in dictating the network topology. Compound **1** features a PtS-type topology of the network, with four interpenetrating nets. The low dimensionality of compound **2** arises from the employment of a neutral building block displaying a *cis*-conformation that limits the propagation into the third dimension. Studies to check the ability of the ligands to afford high connectivity networks with other metal ions are in progress.

Acknowledgement

This work was financially supported by UEFISCDI (Grant PNII-ID-PCCE-2011-2-0050) and by a grant of the Romanian National Authority for Scientific Research and Innovation, POCPOLIG, project nr. 67/08.09.

View Article Online
DOI: 10.1039/C6CE02146H

Notes and references

‡ Synthesis of L^1: To a 100 mL three-necked round-bottom flask equipped with a reflux condenser were added 4-pyridylboronic acid (0.258 g, 2.11 mmol), Pd(dppf)Cl_2 (0.043 g, 0.05 mmol), and Na_2CO_3 (0.452 g, 4.27 mmol) in dioxane/water (2.5:1 v/v, 35 mL) and the solution was flushed with argon for 20 min, after 1,3,5,7-tetrakis(4-iodophenyl)adamantane (0.25 g, 0.26 mmol) was added under argon atmosphere, and the reaction mixture was stirred at 80°C for 12 h. The solvent was evaporated, and the crude product was dissolved in chloroform and washed with water (2×50 mL) and satd. NH_4Cl solution (2×50 mL). The separated organic layer was dried over $MgSO_4$, filtered and concentrated under vacuum. After purification by column chromatography (silica gel, pentane/DCM/MeOH: 1.5:1:0.2, R_f= 0.45) the product was isolated as white solid (0.082 g, 41% yield). Tetrakis(*p*-cyanophenyl)adamantane L^2 was obtained (Scheme S2) in good yields (80%) starting from 1,3,5,7-tetrakis(*p*-iodophenyl)adamantane applying the procedure described in the literature.[8]

Synthesis of **1**: A methanol solution (4 mL) of $Cu(BF_4)_2{\cdot}6H_2O$ (0.0024 g, 0.007 mmol) was reacted with 0.0018 g (0.029 mmol) monoethanolamine in 4 mL methanol and the resulting mixture was left to slowly diffuse through an ethanol layer (5 mL) into 5 mL $CHCl_3$ of L^1 (0.0019 g, 0.0025 mmol). Blue green single crystals suitable for X-ray measurements appeared in two-three weeks. Yield (based on L^1): 0.0013 g, 46%. Selected IR data (KBr): 3315 (m), 3068 (w), 3033 (w), 2929 (w), 2897 (w), 2849 (w), 1664 (s), 1614 (vs), 1542 (m), 1493 (s), 1431(m), 1401 (w), 1356 (w), 1295 (w), 1236 (w), 1123 (s), 1073 (s), 1028 (s), 1007 (s), 1025 (m), 825 (w), 792 (s), 739 (w), 667 (w), 637 (w).

Synthesis of **2**: $[Mn(hfac)_2(H_2O)_2]$ H_2O (0.0038 g, 0.0072 mmol) was solubilized in 4 mL boiling n-heptane. Upon cooling to room temperature, 4 mL of CH_2Cl_2 were added and the solution was carefully layered on top of 2 mL CH_2Cl_2 solution of L^2 (0.002g, 0.0037 mmol) in a test tube. Yellow single crystals were formed in few days. Yield (based on L^2): 0.0015 g, 28%. Selected IR data (KBr): 3401 (m), 2939 (w), 2858 (w), 2262 (m), 2224 (m), 1647 (s), 1606(w), 1523 (w), 1493 (s), 1405 (w), 1369 (w), 1252 (s), 1196 (s), 1149 (vs), 1096 (w), 836 (w), 794 (w), 764 (w), 665(w).

§Crystal data for $\mathbf{[CuL^1(H_2O)_2](BF_4)_2{\cdot}8H_2O}$ **(1)**: $C_{54}H_{64}CuB_2F_8N_4O_{10}$, M = 1166.26, T = 293(2) K, tetragonal, space group *I*422, *a* = 12.8199(9), *c* = 32.617(4) Å, V = 5360.5(1) $Å^3$, D_c = 1.310 gcm^{-3}, μ = 1.218 mm^{-1}, Z = 4, Flack parameter = 0.42(7), reflections collected = 6049, independent reflection = 1932 [R_{int} = 0.0566]. Before SQUEEZE: *R* indices [$I > 2\sigma(I)$]: R_1 = 0.1033, wR_2 = 0.2671, *R* indices (all data): R_1 = 0.1507, wR_2 = 0.3199, GoF = 1.086 with $\Delta\rho_{min}/\Delta\rho_{max}$ = -0.244/1.258 $eÅ^{-3}$. After SQUEEZE: *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0750, wR_2 = 0.1876, *R* indices (all data): R_1 = 0.1138, wR_2 = 0.2237, GoF = 0.938 with $\Delta\rho_{min}/\Delta\rho_{max}$ = -0.216/0.939 $eÅ^{-3}$.

Crystal data for $[\mathbf{Mn(hfac)_2(L^2)_{0.5}}]$ **(2)**: $C_{29}H_{16}MnF_{12}N_2O_4$, M = 739.38, T = 293(2) K, tetragonal, space group $I4_1/a$, *a* = 11.645(5), *c* = 52.700(5) Å, V = 7146(6) $Å^3$, D_c = 1.374 gcm^{-3}, μ = 0.465 mm^{-1}, Z = 8, reflections collected = 32305, independent reflection = 3122 [R_{int} = 0.2541]. *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0604, wR_2 = 0.1342, *R* indices (all data): R_1 = 0.1674. wR_2 = 0.1807, GoF = 0.885 with $\Delta\rho_{min}/\Delta\rho_{max}$ = -0.249/0.534 $eÅ^{-3}$.

1 (a) R. Robson, *J. Chem. Soc., Dalton Trans*., 2000, 3735; (b) R. Robson, *Dalton Trans*., 2008, 5113; (c) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.,* 1995, **34**, 2311.

2 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc*., 1990, **112**, 1546.

3 S. R. Batten, S. M. Neville and D. R. Turner*, Coordination polymers: Design, analysis and applications*, Royal Society of Chemistry, Cambridge, 2008.

4 See, for example T. Muller and S. Bräse, *RSC Adv*., 2014, **4**, 6886 and references therein.

5 (a) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. Okeeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559; (b) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. Okeeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239; (c) M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z. U. Wang and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2014, **53**, 815; (d) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, *Angew. Chem. Int. Ed.*, 2004, **43**, 971; (e) L. Wen, P. Cheng and W. Lin, *Chem. Commun*., 2012, **48**, 2846; (f) L. Wen, P. Cheng and W. Lin, *Chem. Sci.*, 2012, **3**, 2288; (g) C. Tan, S. Yang, N. R.Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun*., 2011, **47**, 4487; (h) Y. E. Cheon and M. P. Suh, *Chem. Commun*., 2009, 2296; (i) L. Ma, A. Jin, Z. Xieand W. Lin, *Angew. Chem. Int. Ed.*, 2009, **48**, 9905; (j) M. Zhang, Y.-P. Chen and H.-C. Zhou, *CrystEngComm*, 2013, **15**, 9544; (k) R. P. Davies, R. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Cryst. Growth Des.*, 2010, **10**, 4571; (l) J. M. Gotthardt, K. F. White, B. F. Abrahams, C. Ritchie and C. Boskovic, *Cryst. Growth Des.*, 2012, **12**, 4425; (m) D. Liu,Z. Xie,L. Ma and W. Lin, *Inorg. Chem.*, 2010, **49**, 9107; (n) G. A. Senchyk, A. B. Lysenko, H. Krautscheid, E. B. Rusanov, A. N. Chernega, K. W. Krämer, S.-X. Liu, S. Decurtins and K. V. Domasevitch, *Inorg. Chem.*, 2013, **52**, 863.

6 (a) D. J. Hoffart, A. P. Côté and G. K. H. Shimizu, *Inorg. Chem.*, 2003, **42**, 8603; (b) D. J. Hoffart, S. A. Dalrymple and G. K. H. Shimizu, *Inorg. Chem*., 2005, **44**, 8868.

7 (a) J. M. Taylor, A. H. Mahmoudkhani and G. K. H. Shimizu, *Angew. Chem. Int. Ed.*, 2007, **46**, 795; (b) M. V. Vasylyev, E. J. Wachtel, R. Popovitz-Biro and R. Neumann, *Chem.Eur. J.*, 2006, **12**, 3507; (c) M. Vasylyev and R. Neumann, *Chem. Mater.*, 2006, **18**, 2781.

8 I. Boldog, K. V. Domasevitch, I. A. Baburin, H. Ott, B. Gil-Hernández, J. Sanchiz and C. Janiak, *CrystEngComm*, 2013, **15**, 1235.

9 A. Bulut, Y. Zorlu, E. Kirpi, A. Çetinkaya, M. Wörle, J. Beckmann and G. Yücesan, *Cryst. Growth Des.*, 2015, **15**, 5665.

10 (a) K. Matsumoto, M. Kannami, D. Inokuchi, H. Kurata, T. Kawase and M. Oda, *Org. Lett.*, 2007, **9**, 2903; (b) C. B. Caputo, V. N. Vukotic, N. M. Sirizzotti and S. J. Loeb, *Chem. Commun.*, 2011, **47**, 8545; (c) F. Geyer, F. Rominger, M. Vogtland and U. H. F. Bunz, *Cryst. Growth Des.*, 2015, **15**, 3539; (d) S. Shankar, R. Balgley, M. Lahav, S. R Cohen, R. Popovitz-Biro and M. E. van der Boom, *J. Am. Chem. Soc.*, 2015, **137**, 226; (e) X.-Y. Chen, H.-Y. Shi, R.-B. Huang, L.-S. Zheng and J. Tao, *Chem. Commun*., 2013, **49**, 10977; (f) X.-Y. Chen, R.-B. Huang, L.-S. Zheng and J. Tao, *Inorg. Chem.*, 2014, **53**, 5246.

11 (a) G. A. Senchyk, A. B. Lysenko, I. Boldog, E. B. Rusanov, A. N. Chernega, H. Krautscheid and K. V. Domasevitch, *Dalton Trans.*, 2012, **41**, 8675; (b) G. A. Senchyk, A. B. Lysenko, E. B. Rusanov, A. N. Chernega, J. Jezierska, K. V. Domasevitch and A. Ozarowski, *Eur. J. Inorg. Chem.*, 2012, 5802; (c) A. B. Lysenko, G. A. Senchyk, J. Lincke, D. Lässig, A. A. Fokin, E. D. Butova, P. R. Schreiner, H. Krautscheid and K. V. Domasevitch, *Dalton Trans.*, 2010, **39**, 4223.

12 (a) I. Boldog, K. V. Domasevitch, J. Sanchiz, P. Mayerd and C. Janiak, *Dalton Trans.*, 2014, **43**, 12590; (b) I. Boldog, K. Domasevitch, J. K. Maclaren, C. Heering, G. Makhloufi and C. Janiak, *CrystEngComm*, 2014, **16**, 148.

13 M. Dincă, A. Dailly and J. R. Long, *Chem. Eur. J.*, 2008, **14**, 10280.

14 (a) D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; (b) F.-Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36***,* 5090; (c) K. M. Patil,M. E. Dickinson,T.

View Article Online
DOI: 10.1039/C6CE02146H

Tremlett, S. C. Moratti and L. R. Hanton, *Cryst. Growth Des.*, 2016, **16**, 1038.
15 C. I. Schilling, O. Plietzsch, M. Nieger, T. Muller and S. Bräse, *Eur. J. Org. Chem.*, 2011, 1743.

View Article Online
DOI: 10.1039/C6CE02146H

Two coordination polymers with different dimensionalities have been constructed using rigid tetrahedral organic tectons derived from adamantane.