

## PAPER

# A rare alb-4,8-Cmce metal–coordination network based on tetrazolate and phosphonate functionalized 1,3,5,7-tetraphenyladamantane†

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Symmetric tetrahedral ligands are prominent, but somewhat under-investigated building blocks for the generation of coordination polymeric networks. Coordination networks  $[\text{Mn}_5\text{Cl}_2(\text{L}^1)_2(\text{H}_2\text{O})_4(\text{DMF})_4]\cdot 3\text{H}_2\text{O}\cdot 7\text{DMF}$ , **1** and the  $[\text{La}_2(\text{H}_5\text{L}^2)_2(\text{H}_2\text{O})_6]$ , **2** are synthesized under mild solvothermal methods in DMF from the adamantane-based tetrahedral ligands, 1,3,5,7-tetrakis(4-phenyltetrazol-5-yl)adamantane ( $\text{H}_4\text{L}^1$ ), reported for the first time, and 1,3,5,7-tetrakis(4-phenylphosphonic acid)adamantane ( $\text{H}_8\text{L}^2$ ), respectively. Compounds **1** and **2** are based on completely different pentanuclear and binuclear secondary metal building units, respectively, and have different symmetries, but demonstrate an interesting coincidence of underlying topologies, which could be interpreted as a directing or 'imprinting' effect of the symmetry of the rigid tetrahedral ligands. Both structures represent examples of a rarely observed (4,8)-coordinated net. The  $\chi_{\text{MT}}$  product for **1** at room temperature is slightly lower than the expected for five Mn(II) ions with  $S = 5/2$  and  $g \approx 1.98$  and on lowering the temperature  $\chi_{\text{MT}}$  approaches the expected value for a single Mn(II) as a result of the antiferromagnetic coupling through the tetrazolate bridges.

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## Introduction

Metal–organic frameworks (MOFs) or three-dimensional porous coordination polymers (PCPs)<sup>1</sup> are the subject of continuous attention.<sup>2–7</sup> The reason for that is their porosity, the large inner surface areas, the tuneable pore sizes and the topologies,<sup>8</sup> which provides for versatile architectures<sup>9,10</sup> and potential applications.<sup>2,11–13</sup> Such applications include ion exchange, gas adsorption and storage of, in particular, hydrogen and methane,<sup>14–18</sup> water sorption for heat transformation,<sup>19</sup> gas<sup>20–22</sup> and liquid<sup>23</sup> separation processes, drug delivery,<sup>24,25</sup> sensor technology,<sup>26,27</sup> heterogeneous catalysis,<sup>28</sup> hosts for metal colloids or nanoparticles<sup>29,30</sup> or polymerization

reactions,<sup>31</sup> pollutant sequestration,<sup>32</sup> microelectronics,<sup>33</sup> luminescence,<sup>34</sup> non-linear optics<sup>35</sup> and magnetism.<sup>36</sup>

A fundamental problem in the synthesis of PCPs is to increase the porosity (surface area and/or pore size), while preserving the framework robustness. The designs of known rigid PCPs involves mostly the use of rigid bidentate or tridentate ligands. Prototypical ligands are linear benzene-1,4-dicarboxylate and trigonal-planar benzene-1,3,5-tricarboxylate together with their extended homologues.<sup>2,3,8,37</sup> These ligands act as organic spacers connecting metal ions or metal-containing secondary building units (SBUs) according to Robson's concept.<sup>38,39</sup> On the contrary, the use of rigid symmetric tetrahedral ligands, a next step in the series of rigid linear and trigonal-planar ligands, is much less pronounced. Two reasons could be given why: lesser synthetic accessibility and the close vicinity of the functional groups for small tetrahedral ligands, which leads to the formation of denser structures. A lesser utility of tetrahedral building blocks is sometimes assumed, because the most frequent diamondoid topology<sup>40</sup> is prone to interpenetration.<sup>41</sup> We believe that this reasoning is not generally applicable, since it does not take into account the benefits of the rigid symmetric tetrahedral building units in PCPs built up from non-tetrahedral metal SBUs, where the symmetric ligand may 'imprint' symmetry into the resultant structure. Analysis of such 'imprinting' is important for the development of new

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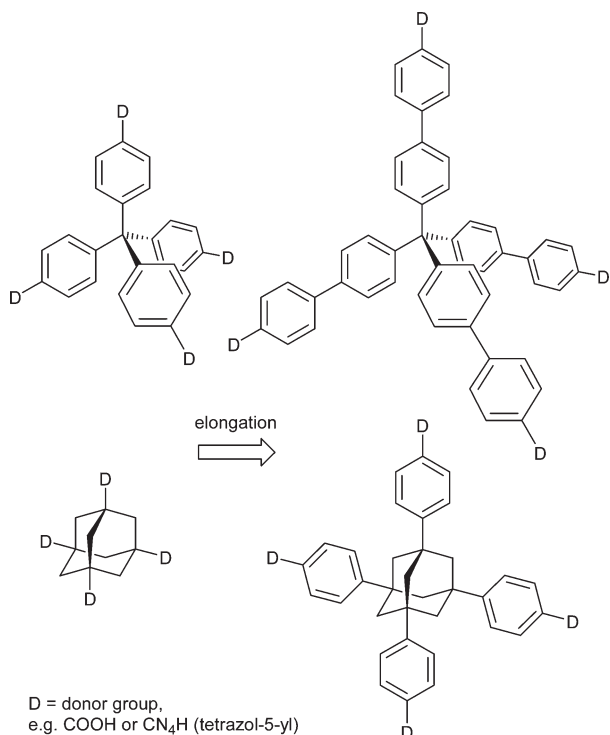
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† Electronic supplementary information (ESI) available: Synthesis of ligands, structural data and related information of **1** and **2**, topological analysis, TGA, PXRD. CCDC 910535 and 910536. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26819a

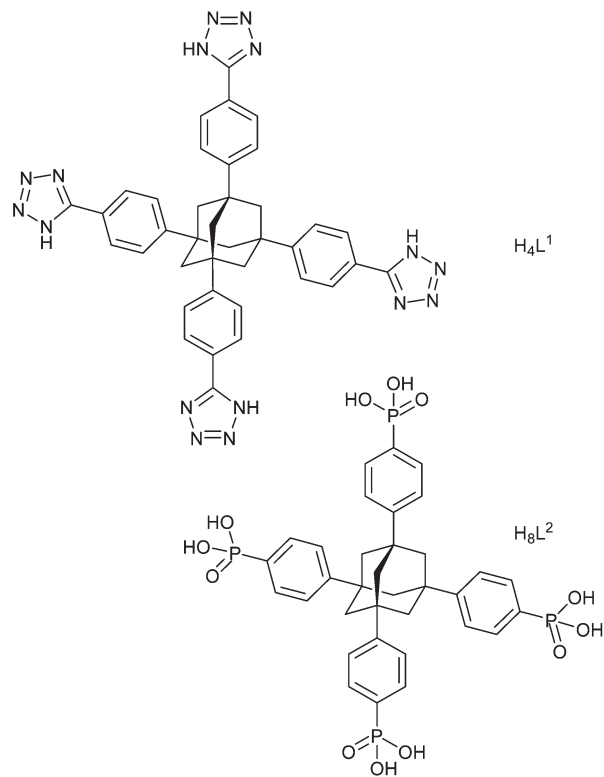
PCPs under conditions when predictions still remain uncertain.

The most important classes of scarce tetrahedral organic ligands are represented by tetraphenylmethane<sup>42–45</sup> and adamantane derivatives (Scheme 1).<sup>44,46,47</sup> Results with these perfect symmetrical ligands can be traced back to the first, most seminal PCP work.<sup>48</sup> Elongated tetrakis(4-biphenyl)-methane and 1,3,5,7-tetraphenyladamantane derivatives (Scheme 1) are even less used, but exactly these extended ligands are most interesting in the context of highly porous PCPs. About five PCPs were obtained with deprotonated 1,3,5,7-adamantane-tetraphen-4-yl tetracarboxylic,<sup>46</sup> tetraphosphonic,<sup>49,50</sup> or tetrasulfonic<sup>49,51</sup> acid, respectively. Very recent examples also include prospective PCPs based on the tetrakis(biphenyl)methane building block reflecting the gradually growing interest in the tetrahedral ligand class.<sup>45,52,53</sup>

Here we present two coordination polymers based on not yet reported 1,3,5,7-tetrakis(4-phenyltetrazol-5-yl)adamantane,  $H_4L^1$ , and scarcely investigated 1,3,5,7-tetrakis(4-phenylphosphonic acid)adamantane,  $H_8L^2$ ,<sup>50</sup> (Scheme 2) with the coincidence of the rare (4,8)-coordinated network topology. The results are discussed in the context of interest towards frameworks with high-connectivity and long internodal bridges for the generation of non-interpenetrated structures with large pores and elongated ligands. Comparison is made with the only known geometrical analogue of  $H_4L^1$ , the smaller tetrakis(4-phenyltetrazol-5-yl)methane ligand ( $H_4\text{tptm}$ ) (cf. Fig. 2).<sup>54</sup>



**Scheme 1** Tetrahedral linkers based on the methane and adamantane cores.



**Scheme 2** Tetrahedral linkers with the adamantane core used in this work.

## Experimental

All inorganic salts were of reagent grade and used without further purification. Dimethylformamide, DMF (VWR, ACS-grade) and MeOH (Acros, spectroscopic grade) were used as delivered. The syntheses of  $H_4L^1$  is described in the ESI.†  $H_8L^2$  was obtained as described in ref. 49 Details concerning the physical methods of investigation are given in the ESI.†

### Synthesis of $[Mn_5Cl_2(L^1)_2(H_2O)_4(DMF)_4] \cdot 3H_2O \cdot 7DMF$ , **1**

Anhydrous  $MnCl_2$  (398 mg, 3.16 mmol) and  $H_4L^1 \cdot 6.5H_2O$  (225 mg, 0.27 mmol), were dissolved in a mixture of DMF (22.5 mL) and MeOH (22.5 mL) inside a 50 mL glass vial sealed with a Teflon lined screw cap. The solution was heated for 8 days at 70 °C. Large spherical polycrystalline conglomerates of almost colorless crystals were deposited starting from the second day of heating. The supernatant, containing a minor amount of non-crystalline deposit, was decanted and the crystalline precipitate was quickly transferred into a Schlenk funnel with a frit for the subsequent washing and filtration operations under inert gas. Some remaining non-crystalline admixtures were separated by suspending the crystalline precipitate multiple times in a 1 : 1 mixture of DMF : MeOH and removing the supernatant with a Pasteur pipette followed by double rinsing of the deposit with the same solvent mixture and suction filtration. Subsequent overnight drying *in vacuo* ( $10^{-2}$  Torr) at r.t. yielded 312 mg (85% based on  $H_4L^1 \cdot 6.5H_2O$ ) of almost colorless crystalline product.

The product is slightly soluble in DMF, insoluble in non-polar organic solvents and is sensitive to moist air, which leads to a color change to dark brown after prolonged time. The compound is stable for at least one hour in air without significant visible deterioration. FT-IR (neat)  $\nu$ ,  $\text{cm}^{-1}$ : 3500–2900 (w, br), 2928 (w, sh), 2854 (w), 1645 (vs), 1496 (w), 1450 (m), 1418 (m), 1384(s, sh), 1253 (w), 1105 (m), 1060 (w), 1008 (m), 841 (m), 788 (w), 761 (s), 729(w), 678 (m), 662 (m).  $\text{C}_{109}\text{H}_{147}\text{Cl}_2\text{Mn}_5\text{N}_{43}\text{O}_{18}$  (2693.21, 1) calc. C 48.61, H 5.50, N 22.36; found C 48.72, H 5.61, N 22.31%.

### Synthesis of $[\text{La}_2(\text{H}_2\text{O})_6(\text{H}_5\text{L}^2)_2]\cdot\text{Solv}$ , 2

$\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  (17 mg, 39  $\mu\text{mol}$ ) of was dissolved in 50  $\mu\text{L}$  of water in a small test tube ( $d_{\text{in}} = 6$  mm). Methanol (2 mL) was layered over the aqueous solution, followed by a solution of 5.0 mg (6.5  $\mu\text{mol}$ ) of  $\text{H}_8\text{L}^2$  in 1 mL of MeOH. Within two days at r.t. small droplets of liquid precipitated on the wall of the tube and crystals were growing within the droplets during the next two weeks. The crystals were separated by centrifugation, washed with 0.5 mL of water and after final separation were dried in air. Yield: 1.6 mg (25% based on  $\text{H}_8\text{L}^2$ ) of colorless microcrystalline powder.

FT-IR (KBr)  $\nu$ ,  $\text{cm}^{-1}$ : 3410 (vs, br), 2926 (w), 2898 (w), 2851 (w), 1604 (s, sh), 1501 (w), 1445 (w), 1395 (m), 1360 (w), 1138 (vs), 1055 (vs), 1016 (m), 918 (m), 829 (m), 703 (m), 566 (s), 492 (m).

### X-ray crystallography

Single crystal X-ray diffraction experiments were performed on a Bruker APEX II QUAZAR system equipped with a multilayer mirror and an  $\text{I}\mu\text{S}$  Mo  $\text{K}\alpha$  source ( $\lambda = 0.71073$  Å).

Crystals of the as-synthesized form of **1** grew inherently as polycrystalline aggregates with some single-crystalline domains (Fig. S3 in ESI†). All attempts to separate a single crystal from the bulk material were unsuccessful and a two component non-merohedral twin was measured. The indexing of the two twin domains was done using the Reciprocal Lattice Viewer tool in APEX2.<sup>55</sup> All non-hydrogen atoms of the framework residue in **1** were refined anisotropically, except for disordered guest and coordinated solvent molecules. The high *R*-values of **1** can be traced to the disordered guest solvent molecules in the pores and are not due to twinning or data quality.

Small single crystals of **2** were found in the crystalline bulk material next to larger intergrown crystals (Fig. S5 in ESI†). It was possible to perform the measurement on a tiny  $0.03 \times 0.07 \times 0.08$  mm single crystal, which was only diffracting to a resolution of 0.87 Å. The low diffracting power originates from the crystal size, guest molecules in the MOF cavities and disorder in the crystal. A combination of weak high-angle data and pores in the crystal is typical for a lower-than-used-to X-ray data quality in MOF structures. All non-hydrogen atoms in **2** were refined using anisotropic displacement parameters including the guest molecules, *i.e.* water and MeOH. Due to diffuse packing of solvent molecules in combination with an average data resolution, not all solvent molecules could be located. SQUEEZE (PLATON)<sup>56</sup> could be used to decrease the *R*<sub>1</sub> to 7.12% but was not included for the reported structure as

some of the guest molecules are participating in the hydrogen bonded network.

Further details, including crystal data and structure refinement are given in the ESI.†

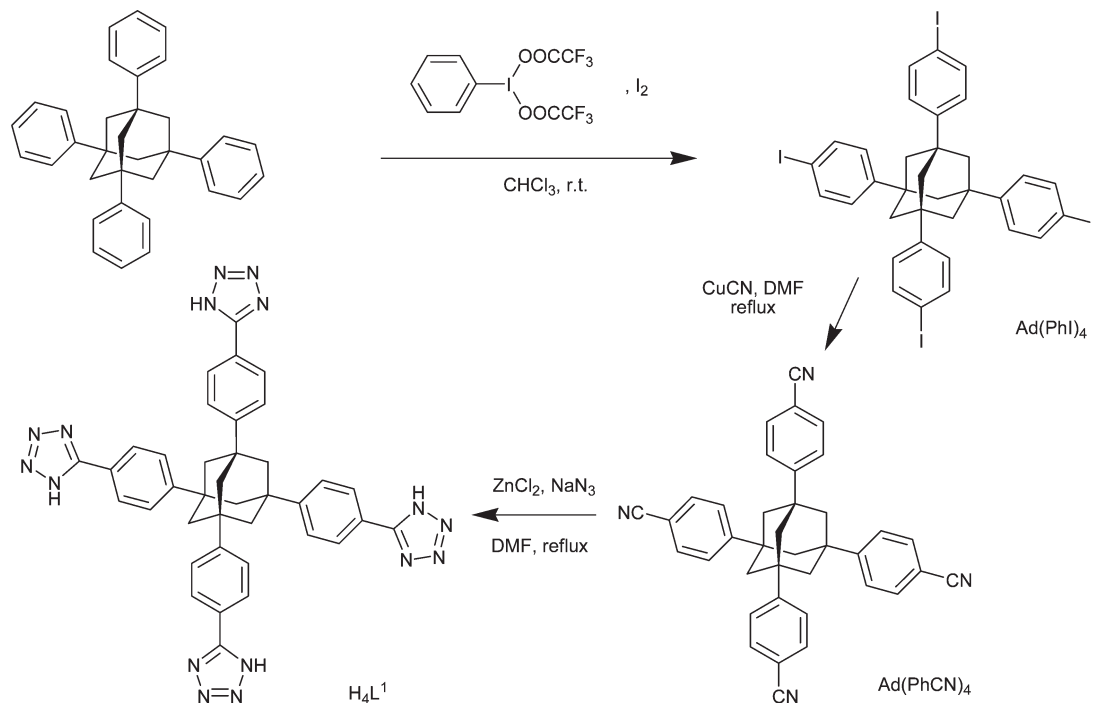
## Results and discussion

The synthesis of the  $\text{H}_4\text{L}^1$  ligand was performed starting from the known 1,3,5,7-tetrakis(4-iodophenyl)adamantane,  $\text{Ad}(\text{PhI})_4$ <sup>57</sup> in two steps: formation of the tetranitrile  $\text{Ad}(\text{PhCN})_4$  by the Rosenmund–von Braun reaction followed by a Huisgen 1,3-dipolar cycloaddition of azide to the nitrile catalyzed by anhydrous zinc chloride (Scheme 3, Fig. 1). This transformation sequence is composed of simple high-yielding steps, which leave room for further optimization. Thus, the affordable parent 1,3,5,7-tetraphenyladamantane compound<sup>58</sup> renders the class of *para*-substituted tetraphenyladamantane molecules as accessible building blocks for the construction of PCPs.

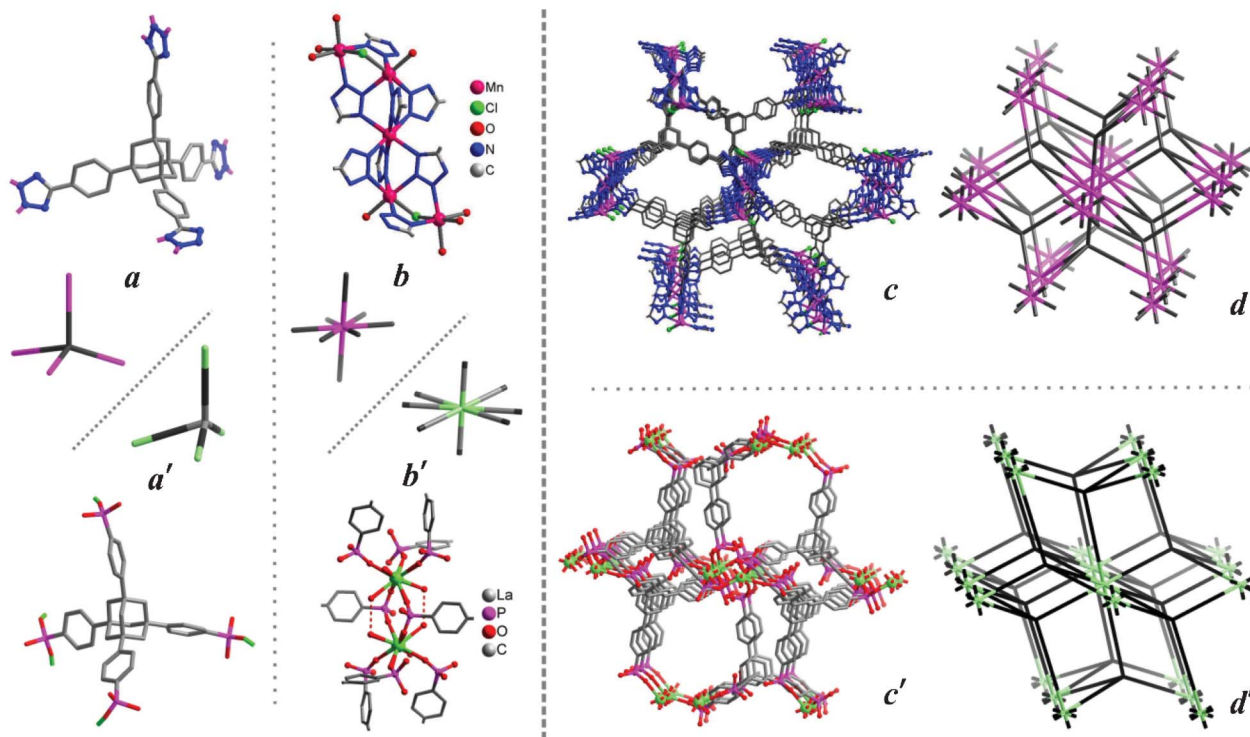
The reaction of  $\text{MnCl}_2$  with  $\text{H}_4\text{L}^1$  under standard mild solvothermal conditions<sup>59</sup> in DMF, typical for the preparation of a range of carboxylate and azolate complexes,<sup>8</sup> produced almost transparent crystals in a form of large spherical co-grown conglomerates. The product after washing and drying *in vacuo* at room temperature corresponded to the formula  $[\text{Mn}_5\text{Cl}_2(\text{L}^1)_2(\text{H}_2\text{O})_4(\text{DMF})_4]\cdot 3\text{H}_2\text{O}\cdot 7\text{DMF}$ , **1**. Crystallinity was preserved when **1** was protected from moist air as evidenced by the powder X-ray diffraction (PXRD) pattern (Fig. S19 in ESI†).

Single-crystal X-ray analysis on a small single crystal from the freshly prepared conglomerates of **1-as** (as synthesized) before washing and drying revealed a 3D framework-structure of formula  $\{\text{Mn}_5(\mu\text{-Cl})_2(\text{L}^1)_2(\text{H}_2\text{O})_4(\text{DMF})_4\}$  based on an extended pentanuclear manganese cluster, with a geometry close to linear (Fig. 1b). All three different manganese atom types of this centrosymmetric cluster, the terminal *fac*- $\{\text{MnClN}_2\text{O}_3\}$ , the middle  $\{\text{MnClN}_4\text{O}\}$  and the central  $\{\text{MnN}_6\}$  atom octahedrally coordinated. The octahedra are connected in a face-to-face fashion. Mn–N bond lengths are in the range of 2.22–2.40 Å and fit the expected Mn–N bond length range of 2.20–2.35 Å extracted from the CSD for Mn–N(azole/azolate) bonds (Fig. S9 and S10 in ESI†). Interestingly, **1** is only the third tetrazolate complex where the  $\{\text{MnN}_6\}$  coordination environment is observed besides the structures of imino-5,5'-ditetrazole<sup>60,61</sup> and  $\text{H}_4\text{ttpm}$  (Fig. 2).<sup>54</sup> However, the  $\{\text{MnN}_6\}$  arrangement is quite typical for other azolates, especially pyrazolates and imidazolates (52 occurrences found in CSD with typical Mn–N bond lengths in the 2.2–2.3 Å interval (Fig. S10, ESI†). The two known tetrazolate complexes with the  $\{\text{MnN}_6\}$  fragment have bond lengths within the range of 2.20–2.40 Å.

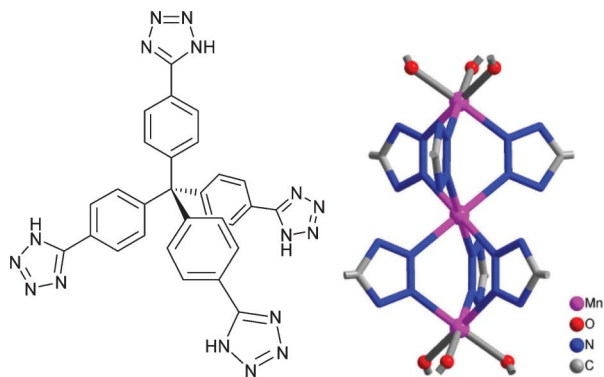
The above-mentioned complex of manganese with  $\text{H}_4\text{ttpm}$ ,  $[\text{Mn}_6(\text{ttpm})_3]\cdot 5\text{DMF}\cdot 3\text{H}_2\text{O}$ ,<sup>54</sup> where the ligand is metrically isomorphous with  $\text{H}_4\text{L}^1$ , is worth a comparison with **1**.  $[\text{Mn}_6(\text{ttpm})_3]\cdot 5\text{DMF}\cdot 3\text{H}_2\text{O}$  is based on a  $\{\text{Mn}_3(\text{tetrazolate})_6\}$  linear trinuclear cluster (Fig. 2), serving as a six-connected node in a framework with the (4,6) *garment* (**gar**) topology,<sup>62</sup> rare



**Scheme 3** Synthesis of the 1,3,5,7-tetrakis(4-phenyltetrazol-5-yl)adamantane,  $H_4L^1$  ligand.



**Fig. 1** The basic building blocks in  $[Mn_5Cl_2(L^1)_2(H_2O)_4(DMF)_4] \cdot xH_2O \cdot yDMF \cdot zH_2O$ , **1-as** (a-d, top), and  $[La_2(H_2O)_6(H_5L^2)_2] \cdot Solv$ , **2** (a'-d', bottom): the tetra-connected tetraphenyl-adamantane ligands ( $L^1$ ) $^{4-}$  (a) and ( $H_5L^2$ ) $^{3-}$  (a'), the octa-connected coordination clusters  $\{Mn_5Cl_2(H_2O)_4(DMF)_4\}$  (b) and  $\{La_2(H_2O)_6\}$  (b') with their bridging ligand coordination, sections of the complete frameworks (c, c') and the topological network representation (d, d').



**Fig. 2**  $H_4ttpm$  ligand and the trinuclear coordination-bonded cluster constituting the six-connected framework with a *garnet* topology in  $[Mn_6(ttpm)_3] \cdot 5DMF \cdot 3H_2O$ .<sup>54</sup>

for coordination polymers. The terminal  $\{MnN_3O_3\}$  and center  $\{MnN_6\}$  manganese atoms of the cluster have a similar coordination environment compared to **1**. Thus, scaling-up the ligand causes an expansion of the cluster from tri- to pentanuclear with preservation of its linear geometry, by the inclusion of a  $\{MnClN_4O\}$  fragment with a bridging chloride ion, which also substitutes one O-ligand at the terminal manganese atom. Such extension could, in principle, be continued by formation of linear  $2n + 1$  nuclear clusters with some adjustment in their connectivity by substitution of tetrazolate bridges with halido- or oxido-bridges. Interestingly, **1** is one of the first porous coordination polymers with a secondary building unit consisting of at least five manganese atoms in a row joined by azole/azolate bridges. Two other examples of coordination polymers are  $[Mn_2(BDT)Cl_2(DMF)_2] \cdot 1.5CH_3OH \cdot H_2O$ , BDT = benzene ditetrazolate,<sup>63</sup> a mixed ligand tetrazolate–triazolate polymer,<sup>64</sup> and eight molecular complexes with a metal chain equal or longer than five atoms.

The  $\{Mn_5(\mu-Cl)_2(H_2O)_4(DMF)_4\}$  cluster in **1** serves as an 8-connected node with a hexagonal-bipyramidal geometry, while the adamantane-based ligand gives rise to a tetrahedral node (Fig. 1b) thereby yielding the binodal (4,8)-connected underlying net  $\{4^5.6\}_2\{4^{10}.6^{14}.8^4\}$ .<sup>65</sup> To the best of our knowledge, there are only five recently published coordination polymers, namely of Co, Mg and Mn with the 5,5'-methylene-diisophthalate ligand,<sup>66,67</sup> of Zn with *m*-sulfonatophenylphosphonate and 4,4'-bipyridine ligands<sup>68</sup> and of Ce with the *N,N',N''*-tris(4-carboxylatephenyl)-1,3,5-benzenetricarboxamide ligand<sup>69</sup> which possess exactly the same underlying topology. The maximal space group symmetry of this net<sup>70</sup> is *Cmce* with hexagonal-bipyramidal vertices at 4a (site symmetry  $C_{2h}$ ) and tetrahedral vertices at 8f (site symmetry  $C_s$ ) Wyckoff positions (see ESI† for more details). Such unusual combination of coordination polyhedra (tetrahedron and hexagonal bipyramid) is a probable reason why the observed net was not included into the compilation of 'default' binodal nets for crystal design.<sup>71</sup> However, this net was generated by Blatov and Proserpio as a subnet of the (6,12)-coordinated **alb** net and could be given a name **alb**-4,8-Cmce as analyzed by the program package

TOPOS.<sup>72</sup> Group-subgroup relations show that with two symmetry-independent SBUs this net can be realized in orthorhombic space groups *Pbca* (the Mn compound in ref. 66), *Pbcn*, *Pccn*, *Pcca*, *Aea2*, *C222\_1* as well as in the two monoclinic space groups *P2\_1/c* and *C2/c*. The latter two symmetry groups are those of compound **1**, the cobalt, zinc and cerium compound in refs. 66, 68 and 69, respectively, and **2**.

The chance to observe the same network for the second time in a rather unrelated case could be viewed as a complete serendipity. Yet, it occurred during the screening of crystallization conditions aiming for the preparation of novel phosphonate complexes of lanthanides with another elongated tetrahedral ligand, the 1,3,5,7-tetrakis(4-phenylphosphonic acid)adamantane,  $H_8L$ .<sup>2,50</sup> Slow interdiffusion of an aqueous layer containing  $La(NO_3)_3 \cdot 6H_2O$  and a methanol ligand solution afforded a mingled deposit. The main constituent and optically the only crystalline phase of this deposit was  $[La_2(H_2O)_6(H_5L^2)_2] \cdot Solv, 2$ .

The structure of **2** is built upon binuclear  $\{La_2(H_2O)_4(\mu-Phos)_2(Phos)_3\}$  units (Phos =  $-PO(OH)O^-$  or  $-PO(OH)_2$ ), where the lanthanum ions are bridged by two Phos moieties and supported by two additional hydrogen bonds ( $O(H) \cdots O$  2.89 Å) between pairs of axially coordinated water molecules. The coordination environment of the eight-coordinated lanthanum ions is a slightly distorted tetragonal antiprism, a typical  $\{LnO_8\}$  configuration for lanthanides.

The absence of base during the crystallization ensured auto-acidification of the solution and, hence, slow crystallization in favorable reversible conditions. At the same time only a threefold deprotonation was achieved against the eightfold possible, yielding a quite open, but presumably not very stable framework, sustained only by two coordination-bonded bridges. A structural search for lanthanide (lanthanum included) complexes with phenylphosphonates revealed that exactly the same dinuclear unit is present in the structure of the coordination polymer  $[Nd_2(HL)(MeOH)_8] \cdot 3HCl \cdot H_4L \cdot 6H_2O$ ,  $H_4L = 2,2'-(O,O'$ -pentaethyleneglycol)-6,6'-(1,1'-binaphthyl)-diphosphonic acid<sup>73</sup> and in slightly distorted form in the molecular complex  $[La_2(HL)_2(H_2L)_2(H_2O)_8]$ ,  $H_3L = 3$ -carboxyphenylphosphonic acid. Taking into account the surprising scarcity of phenylphosphonate complexes with lanthanides (~18 examples), we conjecture the prevalence of such a motif in slightly acidic synthetic conditions (*i.e.*, if only a partial deprotonation of the phenylphosphonic acid is possible). In a more basic medium, at least in principle, the high coordination number of lanthanum would allow for the realization of a twelve-connected 'paddle-wheel'-like cluster node, possibly of higher stability. Such a high connectivity of a cluster node would probably exceed the reasonable nodal density for a still relatively short organic building block, but represent an interesting possibility for a further elongated ligand.

It is interesting to note that **2** is the first coordination polymer of a lanthanide with a truly multifunctional phenylphosphonate, *i.e.*, with more than two phosphonate moieties

in one ligand. We believe, that this points to an interesting, still undiscovered niche for designing lanthanide PCPs of high connectivity based on rigid phenylphosphonates. Not much is known on lanthanide with rigid phenylphosphonates with the exception of three compounds with long bifunctional phosphonates and a few other simpler compounds.<sup>73–75</sup> In contrast, non-rigid aliphatic phosphonates, *i.e.* characterized by the  $\{C_{alk}PO(OH)_2\}$  fragment, account for 273 polymeric structures reflecting the high interest fuelled by phosphonate chelators for lanthanide separation.<sup>76</sup>

Both complexes, **1** and **2** possess potentially open framework structures with maximal calculated porosity of 63% and 40% (VOID/SOLV procedures of PLATON<sup>56</sup> were performed on structural data with all the solvent molecules removed). As the manganese coordination polymer, **1**, sustained by *a priori* robust coordination-bonded clusters, was obtained phase-pure in significant quantities, it was tried to prepare it in a solvent-free form and determine the surface area experimentally. Unfortunately, both direct degassing and solvent exchange (methanol and dichloromethane were attempted) ended in framework collapse (all attempts at  $>120$  °C) or incomplete solvent exchange. The best sample, after exchange with methanol and degassing at 70 °C, demonstrated minor hydrogen sorption of about 0.45 wt% at 1 bar (Fig. S11 in ESI†), but complete lack of nitrogen sorption. The instability of framework **1** resembles that of the  $[Mn_6(tpm)_3] \cdot 5DMF \cdot 3H_2O$  compound,<sup>54</sup> where the preparation of the porous framework also failed. We believe that milder methods of solvent removal, *e.g.* supercritical CO<sub>2</sub> drying,<sup>77</sup> or freeze drying<sup>45</sup> could be more successful. A probable reason for instability of framework **1** may be hydrolytic cleavage of the Mn–N<sub>tetrazole</sub> and Mn–Cl bonds by minor rests of water at elevated temperatures causing fragmentation of clusters and structural collapse. However, further efforts were not invested since **1** is unstable in moist air (oxidation and/or hydrolysis with turning brown), which qualifies the material as non-promising for PCPs. The stability of **2** was not investigated in depth, but it slowly loses crystallinity in air, in accordance with the heavily hydrated and seemingly labile structure observed.

### Magnetic properties of **1**

The manganese complex **1** was subjected to magnetic measurements, also to assess the purity of the material (absence of higher valence states of manganese). The magnetic behavior is consistent with a Mn(II) linear pentanuclear complex exhibiting weak antiferromagnetic coupling mediated by the tetrazolate bridges.<sup>78–80</sup> Fig. 3 shows the temperature dependence of the  $\chi_M T$  product for compound **1**. At room temperature the  $\chi_M T$  product is slightly lower than the expected for five high-spin Mn(II) ions (observed  $20.90 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ; calculated  $\chi_M T = 5(N\beta^2 g^2 / 3kT) S(S+1) = 21.44 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ , with  $S = 5/2$  and  $g \approx 1.98$ ).<sup>81</sup> On lowering temperature,  $\chi_M T$  continuously decreases and tends to the value for a single Mn(II),  $4.30 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ , the limit value for antiferromagnetically coupled clusters with an odd number of Mn(II) ions.

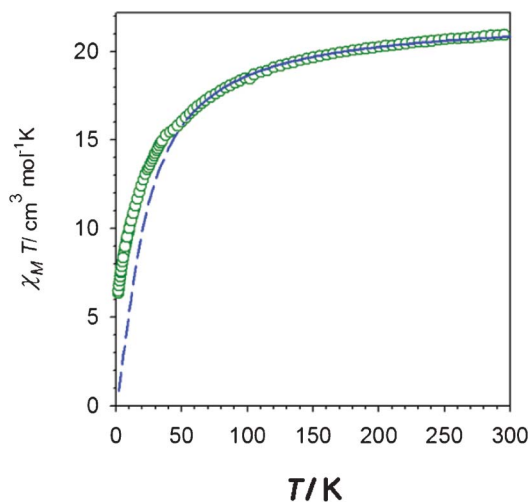
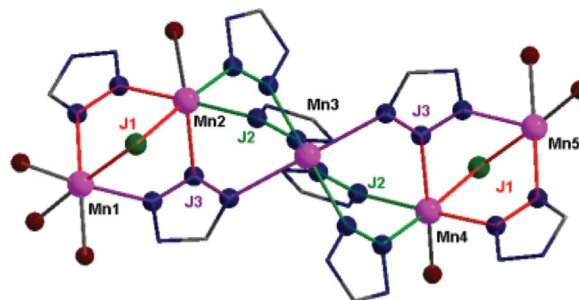


Fig. 3 Temperature dependence of the  $\chi_M T$  product for **1**. The line corresponds to the best fit to the Fisher equation for a regular chain of classical spins with  $S = 5/2$ .

As described above, the structure of compound **1** consists of extended pentanuclear clusters with geometry close to linear, in which chloride ions and tetrazolate ligands with  $\mu_2$ -1,2 and  $\mu_2$ -1,3 bridging modes connect the Mn(II) ions. A view of the cluster with the magnetic coupling arrangement is shown in Scheme 4.

The zero-field Hamiltonian for such a system is then  $H = -J_{12}(S_1 S_2) - J_{23}(S_2 S_3) - J_{34}(S_3 S_4) - J_{45}(S_4 S_5) - J_{13}(S_1 S_3) - J_{35}(S_3 S_5)$ .  $J_{12}$  and  $J_{45}$  involve a  $\mu_2$ -Cl and two  $\mu_2$ -1,2-tetrazolate bridges,  $J_{23}$  and  $J_{34}$  three  $\mu_2$ -1,2 tetrazolate bridges and  $J_{13}$  and  $J_{35}$  a  $\mu_2$ -1,3 one. As Mn(1) and Mn(2) are equivalent to Mn(5) and Mn(4), respectively, we can do  $J_1 = J_{12} = J_{45}$ ,  $J_2 = J_{23} = J_{34}$ , and  $J_3 = J_{13} = J_{35}$ , thus the spin Hamiltonian can be rewritten as  $H = -J_1(S_1 S_2 + S_4 S_5) - J_2(S_2 S_3 + S_3 S_4) - J_3(S_1 S_3 + S_3 S_5)$ . We have tried to analyze the magnetic susceptibility data with that Hamiltonian by means of the Magpack code.<sup>82</sup> However, we failed all our attempts probably because the multiplicity of the system is  $2(S+1)^5 = 6^5 = 7776$  which implies the program to diagonalize, and solve a matrix of  $7776 \times 7776$  for each  $(T, \chi_M T)$  experimental pair of values to calculate the three magnetic coupling constants and  $g$ , the Landé factor. In order to simplify somewhat the system we have made  $J_3 = 0$  (since



Scheme 4 Magnetic coupling exchange-pathways in **1**.

the coupling is very weak through this magnetic exchange-pathway),<sup>80,83</sup> also we made  $J = J_1 = J_2$  (since both magnetic exchange-pathways are similar), and reduced the experimental data set to 11, equally spaced in a logarithm scale from 2 to 300 K. However, the system worked for a week without convergence. Finally, we have analyzed the high temperature data ( $T > 50$  K) with the Fisher expression (based in the  $H = -J\sum_i S_i S_{i+1}$  Hamiltonian) for a regular chain of classical spins ( $S = 5/2$ ).<sup>79,84</sup> We took this decision since the other attempts failed, the cluster is rather large (pentanuclear), and in the high temperature region – when the magnetic correlation is small – the magnetic behavior of the cluster and that of the chain are expected to be very similar. Best fit parameters are  $g = 1.98$ ,  $J = -2.01 \text{ cm}^{-1}$  and  $R = 1.88 \times 10^{-5}$  ( $R$  is the agreement factor defined as  $\sum_i [(\chi_M T)_{\text{obs}(i)} - (\chi_M T)_{\text{calc}(i)}]^2 / \sum_i [(\chi_M T)_{\text{obs}(i)}]^2$ ). The value obtained for the magnetic coupling constant is an averaged value of  $J_1$ ,  $J_2$  and  $J_3$ . The theoretical plot reproduces very well the magnetic susceptibility data at temperatures above 50 K. However, the plot deviates at low temperatures since the low temperature limit of the  $\chi_M T$  product for an antiferromagnetic chain is zero (as a result of the cancellation of the spins), whereas the low temperature value for an antiferromagnetically coupled Mn(II) cluster with an odd number of Mn(II) ions is  $4.30 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ , that of a single Mn(II). The good value obtained for  $g$  and the reproducibility of the data at high temperatures support the purity of the sample and the oxidation state +2 for manganese. Additionally, the value of the magnetic coupling constant is not far from that found in other studies.<sup>78–80</sup>

## Conclusions

The occurrence of the rare alb-4,8-Cmce network topology in coordination polymers of quite different tetrahedral adamantane-based tetrazolate and phosphonate ligands reflects subtle relationships. We would interpret this finding of identical topologies as a ‘structure-directing role’ or ‘symmetry imprinting’ by the tetrahedral ligand towards adaptable metal secondary building units. It was demonstrated that manganese tetrazolate clusters, namely the  $\{\text{Mn}_3(\text{tetrazolate})_6\}$  versus  $\{\text{Mn}_5\text{Cl}_2(\text{tetrazolate})_8\}$  could ‘grow’ as the ligand is elongated. We are on the way to address the problem of symmetry ‘imprinting’ and elongation of tetrahedral ligands aiming for stable porous coordination frameworks with large pore sizes.

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