Dalton Transactions

COMMUNICATION

An unprecedented high nuclearity catecholato-based Ti(IV)-architecture bearing labile pyridine ligands†

Cite this: DOI: 10.1039/c3dt53424c

Q1 Received 5th December 2013,
Accepted 13th December 2013

Q2 DOI: 10.1039/c3dt53424c

www.rsc.org/dalton

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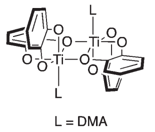
We describe the synthesis and characterisation of a robust S_4-symmetry titanium-based architecture bearing catecholato and pyridine ligands. This neutral complex formulated as $[Ti_{10}O_{12}(cat)_8(py)_8]$ displays a tetrahedral inorganic core decorated by catecholato ligands with unusual coordination modes. In solution, the pyridine ligands are labile as attested by DOSY studies at variable temperature. The light absorption property in the visible domain (λ_{max} = 411 nm, ε = 10 800) was also characterised for the complex.

In the field of materials science, crystalline coordination polymers (CPs) or metal–organic frameworks (MOFs) are of crucial importance owing to their high potentialities in separation,[1] gas storage,[2] drug delivery,[3] catalysis,[4] or magnetism.[5] Mainly, two synthetic routes have been explored to produce these crystalline materials. Usually, CPs are prepared under solvo- or hydrothermal conditions by reacting organic linkers with metallic salts. In contrast to this direct approach, an alternative synthetic route has recently emerged involving a sequential self-assembly approach (SSA). The SSA concerns first the preparation of self-assembled systems that are, in a second step, self-assembled with organic connectors.[6] These self-assembled systems are coordination networks,[7] polymetallic architectures[8] or metal–organic polyhedra (MOPs).[9] In order to realize a step-by-step synthesis of CPs from discrete inorganic complexes, several requirements must be met: first, the architectures should be characterized by well-defined geometries, high symmetries and excellent robustness. Second, the precursors should preferably be neutral entities in order to generate porous networks without the presence of counter-ions. Finally, labile ligands should decorate the edges of the structures to permit the formation of predictable structures through ligand substitution.

In our effort to generate titanium(IV)-MOFs that absorb light in the visible domain through a multistep approach, we report herein the straightforward synthesis, structural characterisation and behaviour in solution of a S_4-symmetry titanium(IV)-based architecture formulated as $[Ti_{10}O_{12}(cat)_8(py)_8]$ (cat = catecholato, py = pyridine).

$[Ti_{10}O_{12}(cat)_8(py)_8]$ was synthesized according to eqn (1) by reacting the readily available $[Ti_2(cat)_4(DMA)_2]$‡ (DMA = dimethylacetamide) complex in hot pyridine (100 °C).[10] After 48 hours of reaction, dark red crystals began to appear in the medium. After one week, the crystals were collected in 53% yield. This yield is highly reproducible if the pyridine used as a solvent contains only traces of water. The reaction was repeated by introducing an increasing excess of water in the medium; in this case the $[Ti_{10}O_{12}(cat)_8(py)_8]$ crystals were isolated in very poor yields (see ESI†). Q4



$$5[Ti_2(cat)_4(DMA)_2] + 12H_2O + 8py \rightarrow [Ti_{10}O_{12}(cat)_8(py)_8] + 12catH_2 + 10DMA \qquad (1)$$

Crystal structure determination indicates the formation of a nano-sized S_4 symmetry architecture constructed around a tetrahedral inorganic core composed of ten titanium centres (see Fig. 1) that co-crystallised with six pyridine molecules.

In this structure, two types of the rarely observed coordination mode for the catecholato ligand are noticed.[11] The purple coloured catecholato ligand in Fig. 1 concerns the four ligands adopting a singly bridging chelate μ_2-(*O*,*O*′,*O*′) mode, whereas the singly bridging μ_2-(*O*,*O*′) mode involves the four catecholato ligands coloured in orange. Concerning the metrical description of the complex the Ti_1–N_2 and Ti_2–N_1 bonds are found to measure 2.2262 Å and 2.2288 Å respectively. These bonds are much longer in comparison with no bridging

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Q3 †Electronic supplementary information (ESI) available. CCDC 953666. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53424c

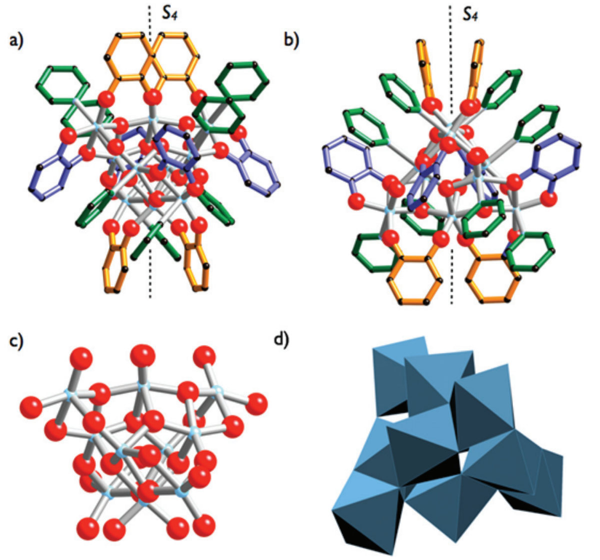

Fig. 1 Molecular structure of $[Ti_{10}O_{12}(cat)_8(py)_8]$. (a) View evidencing the S_4-symmetry of the complex. The two inequivalent cathecolato ligands are differently coloured (in orange and light purple). The pyridine ligands are coloured in green. The titanium atoms and the oxygen atoms are in blue and red respectively. The hydrogens are omitted for clarity. (b) View along the *x*-axis. (c) View of the inorganic core of the structure where only the Ti–O bonds are represented. This inorganic core is composed of ten titanium atoms, eight μ_3-oxo bridges (two inequivalent μ_3-oxo bridges are present), and four μ_2-oxo bridges, while the other oxygen atoms belong to the catecholato ligands. (d) Polyhedral model of the tetrahedral inorganic core of the complex.

$Ti–O_{(catecholato)}$ bonds (average length = 1.8666 ± 0.0050 Å) as is usually observed in other titanium complexes.[12] According to the continuous shape measures (CShM) concept,[13] the titanium atoms are located in six-fold distorted octahedral environments. For the two Ti_3 atoms that lie along the S_4-symmetry axis, their coordination polyhedron is close to the perfect octahedral geometry in comparison with the coordination polyhedra of Ti_1 and Ti_2 (Ti_1(CShM) = 2.016; Ti_2(CShM) = 1.430; Ti_3(CShM) = 1.321). The percentage of residual TiO_2 determined by thermogravimetric analysis, the determination of N, C, H percentage and the X-ray powder diffraction analysis allow us to undoubtedly conclude that the selected single crystal used for the structure resolution was not a synthetic artefact (see ESI†).

The behaviour in solution of the $[Ti_{10}O_{12}(cat)_8(py)_8]$ complex was evaluated by NMR techniques. The ^{1}H NMR spectrum of $[Ti_{10}O_{12}(cat)_8(py)_8]\cdot(py)_6$ crystals dissolved in CD_2Cl_2 reveals the presence of two sets of signals. The three large signals at δ = 8.40, 7.53 and 7.10 ppm are attributed to pyridine highlighting an exchange process for these molecules. This dynamic behaviour is probably linked to the exchange between the pyridine ligands and free pyridine in solution. A second set of rather complex well-defined signals corresponding to the resonance of catecholato protons are observed (see ESI†). The analysis of the ^{13}C NMR spectrum is much more straightforward since four signals with chemical shifts typical to $Ti–OC_{(catecholato)}$ are observed (δ = 159.10, 157.24, 155.53, 153.66 ppm) (see ESI†). This ^{13}C NMR signature is in full accord with a S_4-symmetry compound bearing two inequivalent catecholato ligands as determined in the solid-state for $[Ti_{10}O_{12}(cat)_8(py)_8]$.

A clear and unambiguous explanation of the $[Ti_{10}O_{12}(cat)_8(py)_8]$ behaviour in solution was obtained from DOSY (Diffusion Ordered Spectroscopy) measurements at two temperatures. Fig. 2a and b show the DOSY maps of the $[Ti_{10}O_{12}(cat)_8(py)_8]\cdot(py)_6$ crystals in CD_2Cl_2 at 298 K and 223 K. At room temperature, the DOSY experiment clearly suggests the decoordination of all the pyridine ligands as their diffusion (D = 1930 μm^2 s^{-1}) is very different from the one evaluated for the complex (D = 660 μm^2 s^{-1}). Furthermore, the hydrodynamic radius for the complex in solution calculated according to the Stokes–Einstein equation (R_h = 7.2 ± 0.7 Å) is in good accord with a theoretical one evaluated from a virtual $[Ti_{10}O_{12}(cat)_8]$ complex using a standard set of van der Waals radii of R_h =

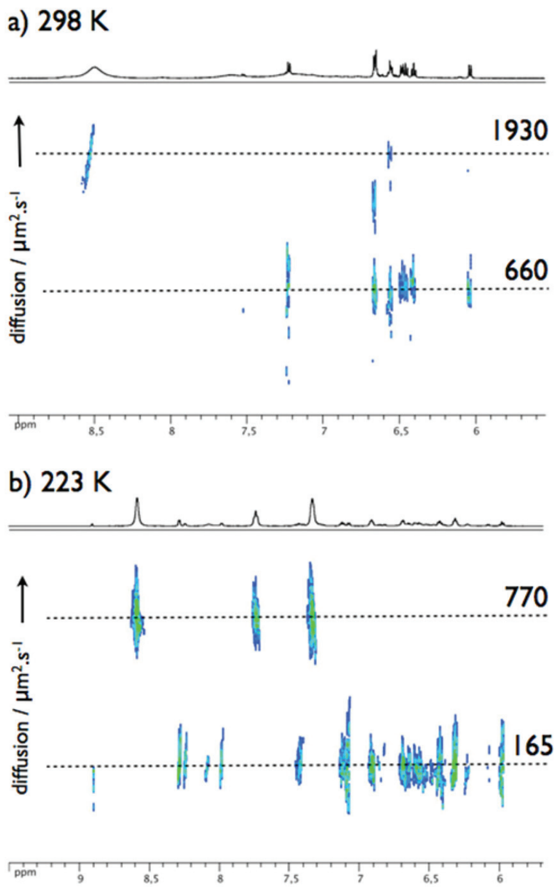

Fig. 2 (a) ^{1}H NMR DOSY spectrum of $[Ti_{10}O_{12}(cat)_8(py)_8]\cdot(py)_6$ and ^{1}H NMR spectrum in CD_2Cl_2 (600 MHz) at 298 K (aromatic region). Two signals are observed, one attributed to pyridine molecules (D = 1930 μm^2 s^{-1}) and the other related to the complex where the pyridine ligands are decoordinated. (b) ^{1}H NMR DOSY spectrum and ^{1}H NMR spectrum of $[Ti_{10}O_{12}(cat)_8(py)_8]\cdot(py)_6$ in CD_2Cl_2 (600 MHz) at 223 K. This DOSY map attests to the presence in solution of the titanium complex coordinated by the pyridine (D = 165 μm^2 s^{-1}) and free pyridine molecules (D = 770 μm^2 s^{-1}).

8.1 ± 0.5 Å.[14] At low temperature, the ^1H NMR spectrum has changed drastically. At 223 K, sharp signals are predominant and resonances closely related to free pyridine in CD_2Cl_2 are found (δ = 8.53, 7.69, 7.28 ppm). Moreover, the presence of signals attributed to coordinated pyridine is noticed. Concerning the DOSY analysis at 223 K, a single complex diffuses in solution for which a hydrodynamic radius of R_h = 10 ± 1 Å is calculated. In this case, this experimental value is in the same range as the calculated one determined from the $[Ti_{10}O_{12}(cat)_8(py)_8]$ structure (R_h = 8.75 ± 0.5 Å). Having proved no alteration for the $[Ti_{10}O_{12}(cat)_8(py)_8]$ complex upon dissolution and the lability of the pyridine ligands, the question of the $[Ti_{10}O_{12}(cat)_8(py)_8]$ stability in solution was tackled. In CD_2Cl_2 or $CDCl_3$ (not dried solvent), no modification of the spectrum of $[Ti_{10}O_{12}(cat)_8(py)_8]$ was noticed after several days. Even upon addition of D_2O (10 μml) in the $CDCl_3$ solution of the complex, no structural alteration of $[Ti_{10}O_{12}(cat)_8(py)_8]$ was noticed. Interestingly, this stability in solution contrasts strongly with the usual behaviour of titanium-based polynuclear aggregates.

It is noteworthy that in deuterated DMSO the stability of the complex is rather moderate. Although in this solvent the complex is undamaged for a period of four hours, after one week no signal attributed to the initial molecule was observed.

A remarkable feature of the $[Ti_{10}O_{12}(cat)_8(py)_8]$ complex is its deep red colour, a rarely observed attribute for Ti^{IV}-based complexes.[15] Whereas catechol and pyridine are known to absorb only in the UV-domain, the $[Ti_{10}O_{12}(cat)_8(py)_8]$ complex absorbs at a lower energy band (λ_{max} = 411 nm, ε = 10 800) (see ESI†). This band is responsible for the red colour of the complex that may be attributed to charge transfers between the lone pair of oxygen atoms and the empty 3d-orbitals of the Ti^{IV} ions.

Preliminary ligand substitution studies with 4-phenylpyridine and 4,4′-bipyridine are encouraging. By reacting $[Ti_{10}O_{12}(cat)_8(py)_8]$ with a slight excess of 4-phenylpyridine (Phpy) in chloroform, a complete substitution of the pyridyl ligands is observed for the final product isolated by precipitation with diethylether. The ^1H and ^{13}C NMR analysis attests to the S_4-symmetry of this new complex (Fig. 8 in ESI†). Microanalysis is also in good agreement with a complex formulated as $[Ti_{10}O_{12}(cat)_8(Phpy)_8]$. When 4,4′-bipyridine reacts with $[Ti_{10}O_{12}(cat)_8(py)_8]$ a dark red precipitate insoluble in common organic medium is instantaneously obtained. By addition of pyridine onto this recovered solid, the initial $[Ti_{10}O_{12}(cat)_8(py)_8]$ complex is quantitatively reformed.

In conclusion, we have reported the synthesis and characterisation of an original stable S_4-symmetry titanium-based architecture that incorporates both catecholato and labile pyridine ligands. Now, we envisaged reacting the $[Ti_{10}O_{12}(cat)_8(py)_8]$ with polypyridyl ligands to generate Ti–O based CPs absorbing visible rather than ultra-violet light.[16]

This work was done at Université de Strasbourg with public funds allocated by CNRS and the French government. We thank Nathalie Kyritsakas for recording single-crystal X-ray data and crystal structure determination.

Notes and references

‡ The reaction was conducted under air. In a 10 mm O.D. glass tube was suspended $[Ti_2(cat)_4(DMA)_2]$ (100 mg, 0.14 mmol) in pyridine (7.5 ml). The tube was sealed under vacuum and heated at 100 °C for one week. Back to room temperature, small dark red crystals were isolated by filtration and dried under reduced pressure to afford $[Ti_{10}O_{12}(cat)_8(py)_8]$ (53%). ^1H NMR (500 MHz, CD_2Cl_2): 8.42 (Pyr-H, broad s), 7.54 (Pyr-H, broad s), 7.18 (Cat-H, dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 4 H), 7.12 (Pyr-H, broad s), 6.60 (Cat-H, complex, 8 H), 6.50 (Cat-H, complex, 4 H), 6.39 (Cat-H, complex, 12 H), 5.98 (Cat-H, dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 4 H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): 159.1 (C–O catecholato), 157.2 (C–O catecholato), 155.5 (C–O catecholato), 153.7 (C–O catecholato), 148.9 (C–H (2,6) pyridine), 136.5 (C–H (4) pyridine), 123.7 (C–H (3,5) pyridine), 120.7 (C–H catecholato), 120.0 (C–H catecholato), 119.9 (C–H catecholato), 119.7 (C–H catecholato), 119.4 (C–H catecholato), 117.5 (C–H catecholato), 115.0 (C–H catecholato), 112.1 (C–H catecholato) ppm. IR: 1604, 1475, 1442, 1437, 1291, 1254, 1212, 1149, 1102, 1069, 1040, 1012, 905, 880, 820, 770, 742, 696, 669, 649, 624, 602 cm^{-1}. Anal. calcd for $C_{88}H_{72}N_8O_{28}Ti_{10}$, $2C_5H_5N$ (M_W 2326.02): C 50.59; H 3.55; N 6.02. Found C 50.60; H 3.76; N 6.21. X-ray data: empirical formula: $C_{118}H_{102}N_{14}O_{28}Ti_{10}$ ($C_{88}H_{72}N_8O_{28}Ti_{10}$, $6(C_5H_5N)$); formula mass: 2643.14; crystal system: tetragonal; space group: $I\bar{4}$; unit cell dimensions: a = 18.8962(3) Å, b = 18.8962(3) Å, c = 16.0089(6) Å; V = 5716.2(2) $Å^3$; Z = 2; density (calcd): 1.536 mg m^{-3}; crystal size: 0.09 × 0.08 × 0.07 mm^3; θ range for data collection: 2.16–29.08°; reflections collected: 39 869; independent reflections: 7313 [$R(int)$ = 0.0417]; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 7313/0/385; goodness-of-fit on F^2: 1.035; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0388, wR_2 = 0.0646; R indices (all data): R_1 = 0.0638, wR_2 = 0.0670. CCDC: 953666.

1 E. D. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606; J.-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; J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477; K. Kim, M. Banerjee, M. Yoon and S. Das, *Top. Curr. Chem.*, 2010, **293**, 115.

2 L. J. Murray, M. Dincă and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; A. U. Czaja, N. Trukhan and U. Müller, *Chem. Soc. Rev.*, 2009, **38**, 1284; D. Yuan, D. Zhao, D. Sun and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357; S. Ma and H.-C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 11734; D. Sun, S. Ma, Y. Ke, D. J. Collins and H.-C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 3896; N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127.

3 K. M. L. Taylor-Pashow, J. Della Rocca, Z. G. Xie, S. Tran and W. B. Lin, *J. Am. Chem. Soc.*, 2009, **131**, 14261; A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson and R. E. Morris, *J. Am. Chem. Soc.*, 2008, **130**, 10440; P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774.

4 T. Uemura, N. Yanai and S. Kitagawa, *Chem. Soc. Rev.*, 2009, **38**, 1228; L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248; J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. B. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450; F. Schrôder, D. Esken, M. Cokoja, M. W. E. van den Berg, O. I. Lebedev, G. van Tendeloo, B. Walaszek, G. Buntkowsky, H. H. Limbach, B. Chaudret and R. A. Fischer, *J. Am. Chem. Soc.*, 2008, **130**, 6119; Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo,

J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem., Int. Ed.*, 2008, **47**, 4144; M. H. Alkordi, Y. L. Liu, R. W. Larsen, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 12639.

5 M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353; L. M. C. Beltran and J. R. Long, *Acc. Chem. Res.*, 2005, **38**, 325; J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortes, L. Lezama and T. Rojo, *Coord. Chem. Rev.*, 1999, **195**, 1027; X. Y. Wang, Z. M. Wang and S. Gao, *Chem. Commun.*, 2008, 281.

6 B. J. Burnett and W. Choe, *Dalton Trans.*, 2012, **41**, 3889–3889.

7 T. Kitaura, F. Iwahori, R. Matsuda, S. Kitagawa, Y. Kubota, M. Takata and T. C. Kobayashi, *Inorg. Chem.*, 2004, **43**, 6522; Z. Chen, S. Xiang, D. Zhao and B. Chen, *Cryst. Growth Des.*, 2009, **9**, 5293; J. Sun, Y. Zhou, Q. Fang, Z. Chen, L. Weng, G. Zhu, S. Qiu and D. Zhao, *Inorg. Chem.*, 2006, **45**, 8677.

8 X.-L. Wang, C. Qin, S.-X. Wu, K.-Z. Shao, Y.-Q. Lan, S. Wang, D.-X. Zhu, Z.-M. Su and E.-B. Wang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5291–5295; Y.-L. Bai, J. Tao, R.-B. Huang and L.-S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 5344–5347.

9 A. Schoedel, A. J. Cairns, Y. Belmabkhout, L. Wojtas, M. Mohamed, Z. Zhang, D. M. Proserpio, M. Eddaoudi and M. Zaworotko, *Angew. Chem., Int. Ed.*, 2013, **52**, 2902–2905; U. Stoeck, S. Krause, V. Bon, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841–10843; J.-R. Li and H.-C. Zhou, *Nat. Chem.*, 2010, **2**, 893–898; J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400–1417; A. J. Cairns, J. A. Perman, L. Wojtas, V. C. Kravtsov, M. H. Alkordi, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2008, **130**, 1560–1561; J.-R. Li, D. J. Timmons and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6368–6369.

10 For the synthesis of $[Ti_2(cat)_4(DMA)_2]$ see: C. Chaumont, E. Huen, C. Huguenard, P. Mobian and M. Henry, *Polyhedron*, 2013, **57**, 70–76 or ESI. †

11 K. Gigant, A. Rammal and M. Henry, *J. Am. Chem. Soc.*, 2001, **123**, 11632–11637.

12 D. M. Weekes, N. Baradel, N. Kyritsakas, P. Mobian and M. Henry, *Eur. J. Inorg. Chem.*, 2012, **34**, 5701.

13 D. Casanova, M. Llunell, P. Alemany and S. Alavarez, *Chem.–Eur. J.*, 2005, **11**, 1479; H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1992, **114**, 7843; M. Pinsky and D. Avnir, *Inorg. Chem.*, 1998, **37**, 5575.

14 Average between a maximum value corresponding to the longest distance from the barycentre of the molecule and a minimum value $R_{\min} = (3V/4\pi)^{1/3}$ derived from the molecular volume (estimated according toA. Gavezotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220–5225). van der Waals radii used: H = 1.2 Å, C = 1.7 Å, O = 1.52 Å, N = 1.55 Å (seeA. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451) and Ti = 1.45 Å (assumed). The theoretical R_h value of the virtual $[Ti_{10}O_{12}(cat)_8]$ complex was calculated from the structure of $[Ti_{10}O_{12}(cat)_8(py)_8]$ by removing the py ligands of the structure.

15 H. Senouci, B. Millet, C. Volkringer, C. Huguenard, F. Taulelle and M. Henry, *C. R. Chim.*, 2010, **13**, 69–96; J. B. Benedict and P. Coppens, *J. Am. Chem. Soc.*, 2010, **132**, 2938–2944.

16 M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 10857; C. H. Hendon, D. Tiana, M. Fontecave, C. Sanchez, L. D'arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks and A. Walsh, *J. Am. Chem. Soc.*, 2013, **135**, 10942–10945.