JOURNAL OF
Materials
CHEMISTRY

Synthesis of two new aluminophosphate based layered materials using Tet-A as a structure-directing agent

Paul S. Wheatley,[a] Christopher J. Love,[a] John J. Morrison,[a] Ian J. Shannon[b] and Russell E. Morris*[a]

[a]*School of Chemistry, University of St. Andrews, The Purdie Building, North Haugh, St. Andrews, Fife, UK KY16 9ST. E-mail: reml@st-andrews.ac.uk*
[b]*School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT*

Received 6th July 2001, Accepted 15th November 2001
First published as an Advance Article on the web 17th January 2002

A layered aluminofluorophosphate and a cobalt–aluminophosphate material have been prepared using the azamacrocycle *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Tet-A) as a structure-directing agent (SDA). Both were synthesised using hydrothermal techniques and their structures solved using microcrystal X-ray diffraction. The first material, [F, Tet-A]-AlPO-1, has the molecular formula $Al_{10}P_{10}O_{40}F_2C_{16}N_4H_{38}$ and crystallises in the orthorhombic space group $Pca2_1$. Its inorganic layered structure is related to the AlPO-41 (AFO) zeolite structure type. The second material, [Co, Tet-A]-AlPO-2, has the formula $Al_4(PO_4)_4(HPO_4)_2{\cdot}[Co(C_{16}N_4H_{36})]{\cdot}C_{16}N_4H_{38}{\cdot}2H_2O$ and crystallises in the triclinic space group $P\bar{1}$. This material contains a cobalt–Tet-A complex that is covalently bound to the inorganic framework and an uncoordinated Tet-A molecule that is hydrogen bonded to the framework.

Introduction

The synthesis of microporous materials is an area of immense interest. The use of organic amines to direct the structures of microporous materials is well known, and has led to a rich diversity of structural architecture. Surprisingly, until recently, macrocyclic polyamines had been relatively little studied as possible structure directing agents (SDAs). At first glance, they would seem to be ideal candidates for this sort of use, and have the added attractive feature that they can be regarded as functional molecules in their own right. This leads to the possibility of using the as-synthesised solid as an inorganic–organic hybrid rather than simply burning the SDA out of the framework to leave the porous material. The combination of inorganic and organic moieties leads to both novel structural architectures and unusual properties unique to the hybrids, and has been used to prepare materials with catalytic and optical properties.[1] Recently we reported the synthesis from fluoride media of cyclam–GaPO (formula $(GaPO_4)_2(OH)F_2{\cdot}Ga(C_{10}N_4H_{24})$),[2] a zeolite-related gallium phosphate material containing cyclam (**1**, Fig. 1) (1,4,8,11-tetraazacyclotetradecane). This is a new type of inorganic–organic hybrid consisting of layers of a gallophosphate framework linked by a gallium–cyclam complex to form a three-dimensional structure. We have subsequently reported further development of this structure by the substitution of transition metal ions for gallium in both the cyclam complex and the framework.[3] The incorporation of these ions could lead to interesting magnetic and catalytic properties and prove useful in future investigations of this family of materials. In particular, the controlled substitution of functional metals into the different regions of hybrid structures of this type could lead to multifunctional materials with properties that are vastly different to those available at the present time. Other similar materials where a macrocycle is incorporated into the framework have since been reported by Patarin[4,5] and Wright.[6]

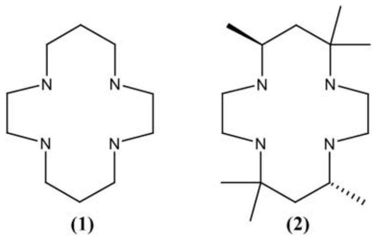
(1) **(2)**

Fig. 1 Cyclam (**1**) and Tet-A (**2**).

More usually, however, the structure directing agents are found occupying positions inside the cavities or interlamellar spaces of these type of materials. In order to encourage this type of behaviour, and to discourage the formation of the macrocycle complex, it is preferable to choose the framework metal ions so that they are too small to coordinate to the macrocycle easily, or to methylate the secondary nitrogen of the macrocycle. So when cyclam or a derivative of cyclam is used as a template for aluminium phosphates (AlPOs) the aluminium is not coordinated by the macrocycle because it is too small to do so effectively. This combined with the use of framework transition metal ions has led to the development of STA-6 and -7 by Wright *et al.*[7] In addition to these developments using cyclam derivatives, Férey has reported MIL-1,[8] a material containing a hexaaza macrocycle as the SDA and the incorporation of porphyrins into zeolites X and Y has been reported by Khan and Hriljac.[9] In this paper we report the synthesis and characterisation using microcrystal X-ray diffraction of two novel aluminophosphate materials using the macrocycle *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Tet-A) (**2**) as the structure directing agent. [F, Tet-A]-AlPO-1 consists of an aluminophosphate layered structure with Tet-A occluded between the layers. [Co, Tet-A]-AlPO-2, prepared in the presence of added Co^{2+}, ions has half the Tet-A molecules coordinated to the cobalt ions, and half as the free ligand in the structure. As far as we are aware, these two materials are the first aluminium phosphates to be prepared using this azamacrocycle and [Co, Tet-A]-AlPO-2 is the first material to contain a macrocycle both coordinating to a metal ion and uncoordinated. Both materials were characterised by microcrystal X-ray diffraction at a synchrotron source, thermogravimetric analysis and

DOI: 10.1039/b106005h

CHN elemental analysis. [F, Tet-A]-AlPO-1 was also characterised by solid state NMR and [Co, Tet-A]-AlPO-2 by EXAFS spectroscopy.

Experimental

Synthesis

Synthesis of *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Tet-A) was as described previously.[10]

[F, Tet-A]-AlPO-1, $Al_{10}P_{10}O_{40}F_2C_{16}N_4H_{38}$. 0.23 g of aluminium hydroxide (Aldrich) was dispersed into 10 ml of distilled water and 0.34 g of phosphoric acid (85 wt% in H_2O, Aldrich) and the mixture stirred until homogeneous. 0.04 g of hydrofluoric acid (48 wt% in H_2O, Aldrich) and 0.16 g of Tet-A were added to the mixture and stirred until it was homogeneous. Trimethylamine (45 wt% in H_2O, Aldrich) was added to adjust the initial pH to 4. This mixture was aged for 1 hour at 25 °C, transferred to a polytetrafluoroethylene lined acid digestion bomb (23 ml, Parr) and heated at 150 °C for 96 hours. The resultant crystalline product was recovered by sonication and filtration, washed with distilled water and acetone then dried in air. Elemental analysis calculated (%) for $Al_{10}P_{10}O_{40}F_2\cdot C_{16}N_4H_{38}$: C 12.45, H 2.48, N 3.63; found C 12.65, H 2.51, N 3.66.

[Co, Tet-A]-AlPO-2, $Al_4(PO_4)_4(HPO_4)_2.[Co(C_{16}N_4H_{36})].C_{16}N_4H_{38}.2H_2O$. 0.19 g of aluminium hydroxide (Aldrich) and 0.15 g of cobalt(II) acetate tetrahydrate (Aldrich) were dispersed in 10 ml of distilled water and 0.35 g of phosphoric acid (85 wt% in H_2O, Aldrich) and the mixture stirred until homogeneous. Then Tet-A was added so that the initial pH of the gel was approximately 7. This mixture was aged for 1 hour at 25 °C, transferred to a polytetrafluoroethylene lined acid digestion bomb (23 ml, Parr) and heated at 190 °C for 52 hours. The resultant crystalline product was recovered by filtration, washed with distilled water and acetone then dried in air. Elemental analysis calculated (%) for $Al_4(PO_4)_4(HPO_4)_2\cdot[Co(C_{16}N_4H_{36})]\cdot C_{16}N_4H_{38}\cdot 2H_2O$: C 28.56, H 5.99, N 8.33; found C 27.66, H 5.91, N 7.95.

Characterisation

Powder X-ray diffraction was carried out on a STOE STADIP diffractometer operating on monochromated Cu $K_{\alpha 1}$ radiation. Powder data were collected in Debye–Scherrer geometry using 0.5 mm quartz capillaries over 14 hours. Single-crystal X-ray diffraction was carried out with a Bruker AXS SMART CCD area-detector diffractometer on the high-flux single-crystal diffraction station 9.8 at CCLRC Daresbury Laboratory Synchrotron Radiation Source, Cheshire, UK. The wavelength of the radiation used was approximately 0.68 Å (exact wavelength for each experiment is given in the supplementary material).

Samples were examined by thermogravimetric analysis (TGA) using a TA Instruments SDT 2960 simultaneous DTA–TGA thermogravimetric analyser. Samples were heated in an alumina crucible at a rate of 10 °C min^{-1} to a maximum temperature of 1000 °C in a flowing atmosphere of oxygen (100 ml min^{-1}). Re-calcined aluminium oxide was used as the reference material.

The organic content of the samples were measured using a Carlo Erba CHN elemental analyser. MAS NMR experiments were carried out on [F, Tet-A]-AlPO-1 using the EPSRC Solid-State NMR Service (Durham) on a Varian Unityplus 300 MHz spectrometer. Chemical shifts are reported with respect to 1 M aqueous $AlCl_3$, TMS, $CFCl_3$, CH_3NO_2 and 85% H_3PO_4 for ^{27}Al, ^{13}C, ^{19}F, ^{15}N and ^{31}P respectively. ^{27}Al MAS NMR spectra were obtained using a spinning rate of 8.2 kHz, acquisition time of 6 ms and relaxation delay of 0.2 s. ^{13}C CP MAS NMR spectra were obtained using a spinning rate of 4.2 kHz, acquisition time of 20 ms, relaxation delay of 1 s and a contact time of 1 ms. ^{19}F MAS NMR spectra were obtained using a spinning rate of 14.7 kHz, acquisition time of 5 ms and relaxation delay of 20 s. ^{15}N CP MAS NMR spectra were obtained using a spinning rate of 4.3 kHz, acquisition time of 40 ms, relaxation delay of 2 s and contact time of 20 ms. ^{31}P MAS NMR spectra were obtained using a spin rate of 4 kHz, acquisition time of 20 ms and relaxation delay of 120 s.

EXAFS data were collected using station 8.1 at the Daresbury Synchrotron Radiation Source (energy 2 GeV, current typically 200 mA) operating in transmission mode. Wavelength selection was accomplished using a double crystal Si(111) monochromator set at 50% harmonic rejection. The Co K-edge position was determined using cobalt foil, while the [Co, Tet-A]AlPO-2 sample was mounted as a self supporting wafer. Data were processed with EXCALIB (raw data processing), EXBACK (background subtraction) and EXCURV98 (comparing theoretical and experimental EXAFS).[11] In fitting the data, curved wave theory was used and theoretical phase shifts were generated from within the EXCURV98 program. Statistical significance testing for the addition of each shell was applied using the method of Joyner.[12]

Magnetic susceptibility data were collected on a Johnson-Matthey magnetic susceptibility balance.

Results and discussion

The colourless crystals of [F, Tet-A]-AlPO-1 and the pale blue single crystals of [Co, Tet-A]-AlPO-2 recovered from the reaction mixtures were all too small for conventional laboratory X-ray diffraction experiments and so X-ray data were collected at station 9.8 of the Synchrotron Radiation Source at the Daresbury Laboratory, Cheshire, U.K. Data reduction was carried out using the Bruker AXS SAINT and SADABS packages.[13] Both structures were solved by direct methods (SHELXS-97)[14] and refined with full-matrix least-squares technique (SHELXL-97).[14] In both cases, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed. Details of data collection and refinement parameters are given in Table 1. Full details of the structure determinations are available electronically as Crystallographic Information Files. CCDC reference numbers 170520 and 161208. See http://www.rsc.org/suppdata/jm/b1/b106005h/ for crystallographic files in .cif or other electronic format.

Table 1 Crystal structure and refinement data

Sample title	[F, Tet-A]-AlPO-1	[Co, Tet-A]-AlPO-2
Chemical formula	$Al_{10}P_{10}O_{40}F_2C_{16}H_{38}N_4$	$Al_4(PO_4)_4(HPO_4)_2\cdot$ $[Co(C_{16}H_{36}N_4)]\cdot$ $C_{16}H_{38}N_4\cdot 2H_2O$
Crystal size/mm	0.06 × 0.03 × 0.02	0.05 × 0.03 × 0.02
Unit cell:		
a/Å	16.8349(3)	9.4614(8)
b/Å	9.6773(2)	11.7168(10)
c/Å	32.7691(6)	13.6647(12)
α/°	90	85.372(2)
β/°	90	75.818(2)
γ/°	90	89.362(2)
Cell volume/Å^3	5338.62(18)	1463.8(2)
Z	4	1
Symmetry, space group	Orthorhombic, $Pca2_1$	Triclinic, $P\bar{1}$
Unique reflections	14152	7315
Observed reflections	10471	6356
Parameters/restraints	530/683	349/31
wR (F^2 observed data)	0.2858	0.2397
R (F observed data)	0.1035	0.0878
S (F^2 all data)	1.028	1.09

The single crystals prepared using these methods are not of the highest quality, as can be seen by the rather high agreement factors. The crystals of [F, Tet-A]-AlPO-1 were of particularly poor quality: inspection through an optical polarising microscope revealed marked striations on all faces of the crystals. The poor quality of the crystals was reflected in the refinement of the structural model against the X-ray diffraction data. The refinement of anisotropic displacement parameters on the aluminium phosphate framework of [F, Tet-A]-AlPO-1 gave rise to elongated and oddly shaped thermal ellipsoids. However, there were a large number of crystallographically independent atoms in the aluminophosphate layers of this structure that are in almost identical chemical environments. This is confirmed by the ^{19}F, ^{31}P and ^{27}Al NMR experiments which show no resolution of the individual crystallographic fluorine, phosphorus or aluminium atoms, just a broad single resonance. This information allowed us to use similarity restraints (see SHELXS-97)[14] in the least-squares refinement. This improved the anisotropic displacement parameters of this structure somewhat, and the final inclusion of restraints on the anisotropic displacement parameters led to physically sensible values. The final bond lengths and angles are comparable with other aluminophosphate and organic species previously solved. In [F, Tet-A]-AlPO-1, the deepest hole was -1.42 e Å^{-3} with the highest residual electron density peak of 2.29 e Å^{-3} 0.71 Å from a phosphorus atom in the framework. Analysis of residuals showed that the refinement was in general well behaved and that there were no obvious systematic errors with the refinements. The refinement of [Co, Tet-A]-AlPO-2 proceeded with fewer problems and yielded a result consistent with other similar materials.[2] The deepest hole was -1.34 e Å^{-3} with the highest residual electron density peak of 2.36 e Å^{-3} 1.28 Å from a hydrogen atom of the Tet-A SDA. Examination of this peak showed it to be too close to other atoms to be refined as a chemically sensible atom.

The structure of [F, Tet-A]-AlPO-1 (see Fig. 2) contains phosphorus- and aluminium-centred tetrahedra, sharing corners to produce a layered structure closely related to AlPO-41 (AFO) zeolite structure type. The structure is related to AlPO-41 in that translation of the layers by 0.5 *a* and 0.5 *b*, followed by condensation in the *c*-direction directly reproduces the AFO framework. Thermal treatment of [F, Tet-A]-AlPO-1 was attempted to see if it could be transformed into AlPO-41. Unfortunately, most of the crystallinity was lost from the sample once the SDAs were removed, and there was no evidence for the AlPO-41 framework being formed. Fluoride is bonded to aluminium in the framework and extends out into the interlamellar space which the Tet-A SDA occupies. Tet-A forms strong hydrogen bonds to the framework oxygens and weak hydrogen bonds to the framework fluoride (see Table 2). From the acidic synthesis conditions and charge balancing considerations we would expect each Tet-A molecule to be diprotonated.

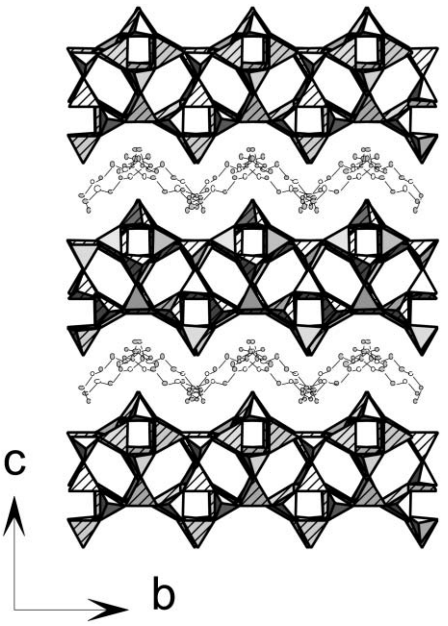

Fig. 2 Polyhedral view of [F, Tet-A]-AlPO-1 P-Centred tetrahedra are unhatched, Al-centred tetrahedra are hatched.

Table 2 Hydrogen bond geometry for [F, Tet-A]-AlPO-1

D–H···A	D–H Distance/Å	H···A Distance/Å	D···A Distance/Å	D–H···A Angle/°
N2–H2B···O30	0.9201	1.7550	2.656(12)	165.43
N3–H3A···F2	0.9202	2.4972	3.309(10)	147.28
N4–H4B···O39^{i}	0.9203	1.7202	2.611(14)	161.89
C2–H2B···F2^{ii}	0.9898	2.3759	3.351(11)	168.07
C7–H7A···F1^{iii}	0.9902	2.3479	3.232(12)	148.19

Symmetry operators; i $1 - x, 1 - y, -\frac{1}{2} + z$, ii $\frac{1}{2} + x, 1 - y, z$, iii $\frac{1}{2} - x, 1 + y, -\frac{1}{2} + z$.

The ^{19}F MAS NMR contains an intense peak at $\delta = -183.7$ ppm with a slight upfield shoulder (see Fig. 3). This confirms that fluoride is present in the structure and attempts to synthesise [F, Tet-A]-AlPO-1 without fluoride have failed. ^{13}C and ^{15}N MAS NMR ($\delta = -327.5$ and -319.2) confirms that the Tet-A SDA is still intact within the structure (see Fig. 4). The ^{27}Al chemical shift depends on its coordination state. For aluminophosphates the four coordination range is around 40 ppm.[15] Simulation of the quadrupolar bandshape with one aluminium species gives a reasonable fit with $\delta_{\mathrm{iso}} = 44.4$ ppm and $\eta = 0.15$ indicating that aluminium centres are tetrahedral. The ^{31}P chemical shift ($\delta = -27.8$ ppm) confirms that the phosphorus centres are also tetrahedral.[15] In both cases the crystallographically distinct sites could not be resolved into separate resonances in the experiments, indicating that the crystallographically distinct sites are in chemically similar environments agreeing with the structure refinement.

TGA analysis of [F, Tet-A]-AlPO-1 is also consistent with the X-ray diffraction structure. The first small mass loss observed was probably due to surface water while the major mass loss observed in the TGA of [F, Tet-A]-AlPO-1 (see Fig. 5) corresponds to one molecule of Tet-A per formula unit (Observed 21.18%, calculated 21.02%). The results of the CHN analysis were also consistent with the formula (calculated C 12.45, H 2.48, N 3.63; found C 12.65, H 2.51, N 3.66%).

The structure of [Co, Tet-A]-AlPO-2 consists of chains of aluminium and phosphorus centred tetrahedra running parallel to the crystallographic *a*-axis. The $[\mathrm{Al_2P_3O_{12}}]^{3-}$ chains are built

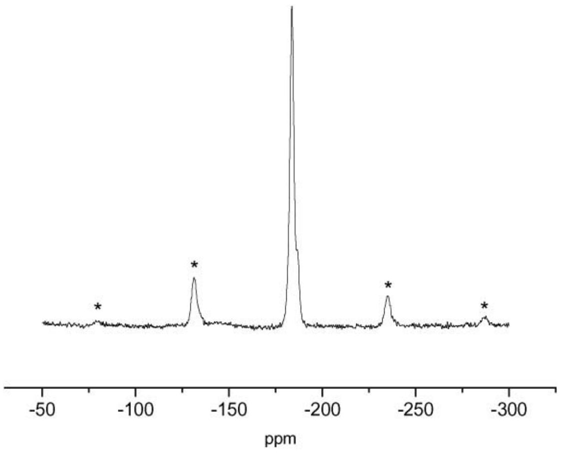

Fig. 3 ^{19}F MAS NMR of [F, Tet-A]-AlPO-1. Asterisks denote spinning sidebands.

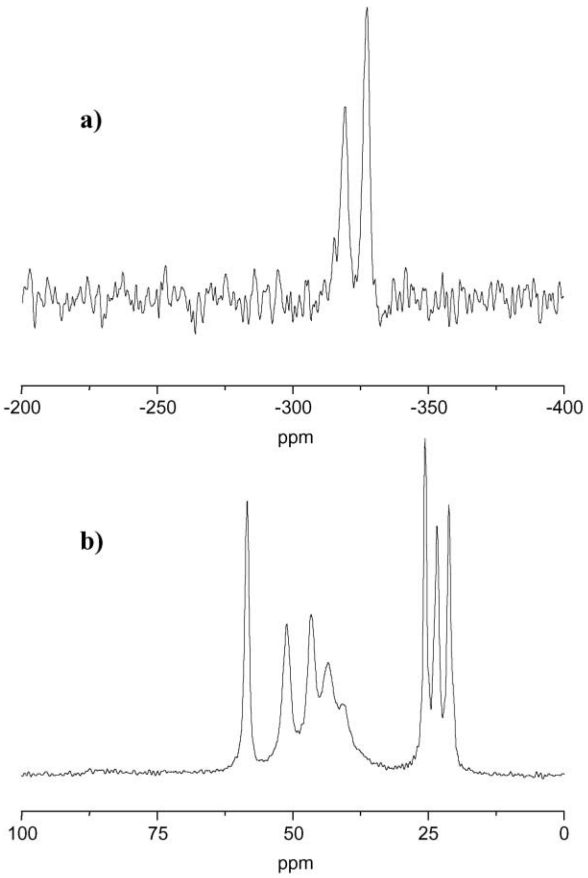

Fig. 4 ^{15}N (a) and ^{13}C (b) CP MAS NMR of [F, Tet-A]-AlPO-1.

up of edge-sharing four-membered rings arranged in the same manner as the chain found in the aluminophosphate Ir(chxn)$_3$-[$Al_2P_3O_{12}$]·$4H_2O$.[16] The chains are linked into layers by the cobalt ions, which lie on an inversion centre and are coordinated to half of the macrocycles (see Figs. 6 and 7) in a similar manner to that seen in a number of the other inorganic–organic hybrids described above.[2–5] The layers are parallel to the *ac*-plane of the unit cell. This is the first compound of this type to contain a coordinated macrocycle other than cyclam. The remaining Tet-A molecules (see Fig. 6) are occluded between the layers in a manner more akin to the normal templating arrangement seen in many layered and microporous aluminophosphates such as STA-6 and -7.[6] Although it is difficult to be absolutely certain of the location of the protons, which are needed to maintain charge balance in the structure, the uncoordinated Tet-A is most probably diprotonated. This is not unreasonable considering the conditions used in the synthesis of the material. One of the three hanging P–O bonds must then also be protonated, although from the diffraction data it is not clear which one.

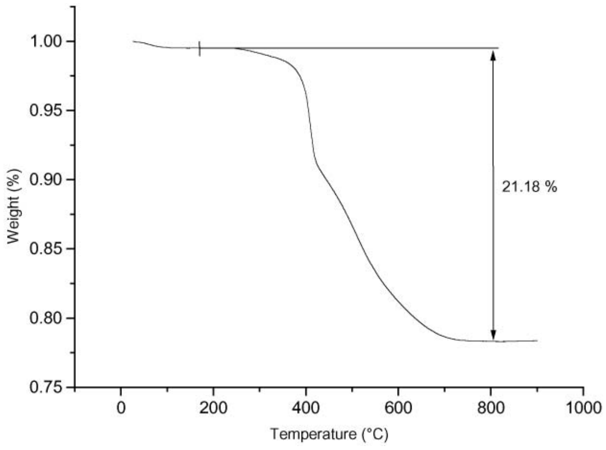

Fig. 5 TGA of [F, Tet-A]-AlPO-1.

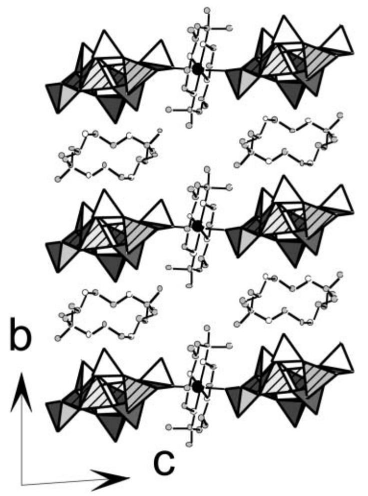

Fig. 6 View of [Co, Tet-A]-AlPO-2 down the crystallographic *a*-axis clearly showing the two types of Tet-A, one coordinated to the cobalt ion (dark sphere) and one uncoordinated. The P and Al centres are shown as hatched and unhatched polyhedra respectively.

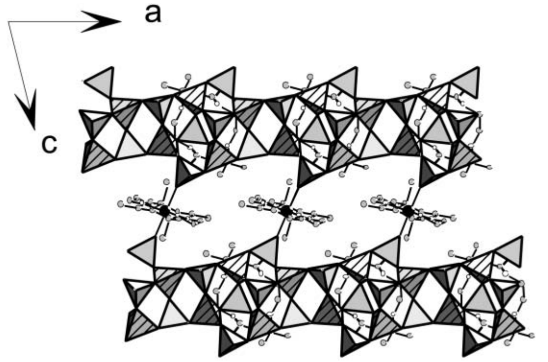

Fig. 7 View of [Co, Tet-A]-AlPO-2 parallel to the *b*-axis.

The uncoordinated Tet-A (contains N11 and N14) is strongly hydrogen bonded to the aluminophosphate chains. On the other hand the coordinated Tet-A (contains N1 and N4) forms no short hydrogen bonds to the aluminophosphate chain (see Table 3). This is in contrast to the aluminophosphates described previously where cyclam is coordinated in a similar fashion, but where hydrogen bonding from the coordinated cyclam to the aluminophosphate framework is important.[6] The molecule of water (oxygen O13) located in this structure acts as hydrogen bond donors to two framework oxygens (see Table 3).

TGA analysis of [Co, Tet-A]-AlPO-2 is also consistent with the X-ray diffraction structure (see Fig. 8). The first mass loss observed is due to two water molecules per formula unit and also some surface water (observed 3.66%, calculated 2.68%).

Table 3 Hydrogen bond geometry for [Co, Tet-A]-AlPO-2

D–H···A	D–H Distance/Å	H···A Distance/Å	D···A Distance/Å	D–H···A Angle/°
N11–H11A···O3^{i}	0.9199	1.7083	2.619(5)	169.95
N11–H11B···O11	0.9200	1.9407	2.847(5)	168.13
N14–H14A···O11	0.9200	1.9306	2.840(5)	169.45
N14–H14B···O7^{i}	0.9197	1.7858	2.672(5)	160.86
O13–H131···O7^{ii}	0.9637	1.8778	2.805(7)	160.44
O13–H132···O9^{iii}	0.9662	2.1689	3.098(6)	160.86

Symmetry operators; i $1-x,-y,-1-z$, ii $-1+x,1+y,z$, iii $1-x,1-y,1-z$.

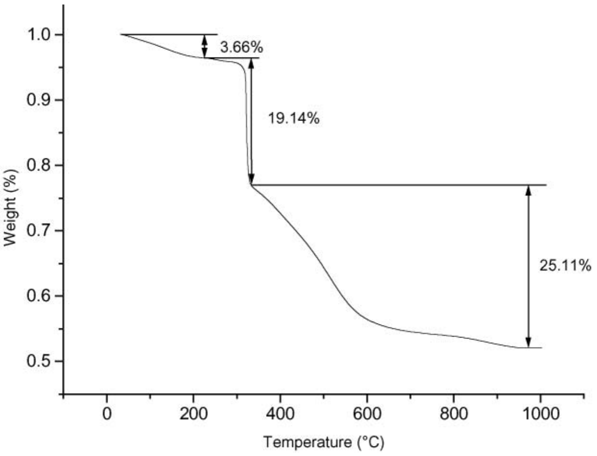

Fig. 8 TGA of [Co, Tet-A]-AlPO-2.

The next two mass losses are due to the uncoordinated and coordinated Tet-A molecules. The first observed mass loss (19.14%) is a little lower than the calculated (21.29%) for the uncoordinated Tet-A. The last observed mass loss (25.11%) is a little larger than the theoretical one (21.14%) for the coordinated Tet-A molecule. The results of the CHN analysis were also consistent with the formula mentioned above (calculated C 28.56, H 5.99, N 8.33; found C 27.66, H 5.91, N 7.95%). Magnetic susceptibility measurements yielded an effective magnetic moment of $\sim 4.7\ \mu_B$, which is consistent with cobalt(II) in high spin octahedral/pseudo octahedral coordination.

To confirm the coordination of the cobalt by the Tet-A molecule, EXAFS spectra were collected at the Co K absorption edge. Despite the slightly poor quality of the spectrum at values of k above 9 Å^{-1}(see Fig. 9) the final refinement (see Table 4) confirmed that the coordination around cobalt was indeed octahedral. The resultant four Co–N distances (2.09 Å) compared very well with those from the single crystal X-ray diffraction study (two at 2.092 (4) Å and two at 2.100 (5) Å), as did the distances to the axial oxygen atoms (2.09 Å from EXAFS, 2.073 (2) Å from diffraction). The eight closest carbon atoms from the macrocycle also fitted very well.

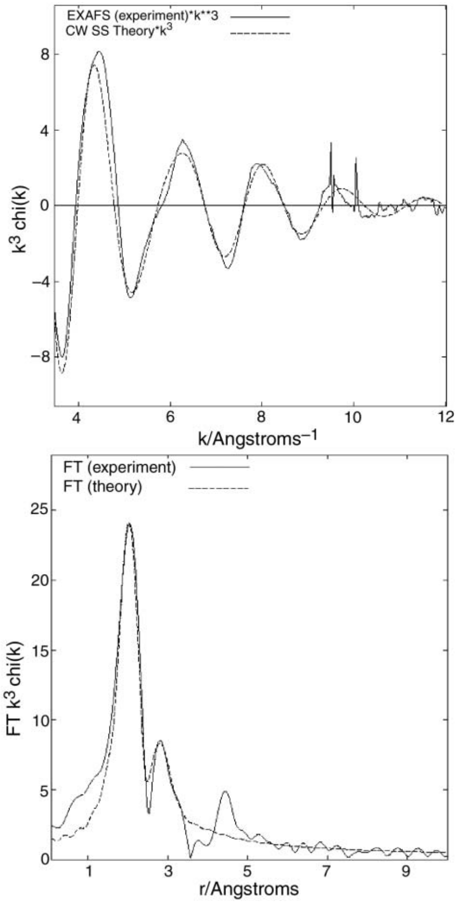

Fig. 9 Comparison of observed and calculated EXAFS data (top) and the associated Fourier transform (bottom).

Table 4 Summary of Co K edge EXAFS for [Co, Tet-A]-AlPO-2^a

	Co–N/Å	Co–O/Å	Co–C/Å	Co–C/Å
Refined distances (*ca.* ±[0.03] Å)	2.09	2.09	2.87	3.03
Occupation numbers (N)	4	2	4	4
Debye–Waller factors ($2\sigma^2$)	0.012	0.010	0.012	0.015

^{a}AFAC = 0.90; R(%) = 26.72

The presence of a macrocycle both coordinated and in its free ligand form in the same solid illustrates the different types of material that may be formed using these methods. Further experiments with macrocycles of different sizes and functionalisation, and to substitute other metals into both the macrocycle complex and the aluminophosphate regions of the structure, are under way in order to study the scope of these materials.

Conclusion

Two novel materials have been prepared, for the first time containing the methylated analogue of cyclam, Tet-A. The range of structures available, with the macrocycle either coordinated or uncoordinated to metal offers the prospect of preparing more functional materials using this approach.

Despite the relatively poor quality single crystal X-ray diffraction data from small, weakly scattering crystals the use of other techniques (EXAFS, NMR, TGA *etc.*) has confirmed the structures of the solids.

Acknowledgements

We thank the EPSRC for funding this research and for access to the Synchrotron Radiation Source at Daresbury. We also thank Dr David Apperley at the EPSRC Solid State NMR service at Durham. R.E.M. thanks the Royal Society for the provision of a University Research Fellowship.

References

1 (*a*) D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431; (*b*) G. Alberti, M. Casciola, U. Costantino and R. Vivani, *Adv. Mater.*, 1996, **8**, 291.
2 D. S. Wragg, G. B. Hix and R. E. Morris, *J. Am. Chem. Soc.*, 1998, **120**, 6822.
3 D. S. Wragg and R. E. Morris, *J. Mater. Chem.*, 2001, **11**, 513.
4 P. Reinert, J. Patarin and B. Marler, *Eur. J. Solid State Inorg. Chem.*, 1998, **35**, 389.
5 T. Wessels, L. B. McCusker, C. Baerlocher, P. Reinert and J. Patarin, *Microporous Mesoporous Mater.*, 1998, **23**, 67.
6 M. J. Maple, E. F. Philp, A. M. Z. Slawin, P. Lightfoot, P. A. Cox and P. A. Wright, *J. Mater. Chem.*, 2001, **11**, 98.
7 (*a*) P. A. Wright, M. J. Maple, A. M. Z. Slawin, V. Patinec, R. A. Aitken, S. Welsh and P. A. Cox, *J. Chem. Soc., Dalton Trans.*, 2000, 1243; (*b*) R. Garcia, E. F. Philp, A. M. Z. Slawin, P. A. Wright and P. Cox, *J. Mater. Chem.*, 2001, **11**, 1421.
8 F. Serpaggi, T. Loiseau, F. Taulelle and G. Férey, *Microporous Mesoporous Mater.*, 1998, **20**, 197.
9 T. A. Khan and J. A. Hriljac, *Inorg. Chim. Acta*, 1999, **294**, 179.
10 (*a*) R. W. Hay, G. A. Lawrance and N. F. Curtis, *J. Chem. Soc., Perkin Trans. 1*, 1975, 591; (*b*) A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1990, **112**, 2273.

11 N. Binsted, EXCURV98: CCLRC Daresbury Laboratory computer program, 1998.

12 R. W. Joyner, K. J. Martin and P. Meehan, *J. Phys. C*, 1987, **20**, 4005.

13 G. M. Sheldrick, SADABS, Program for scaling and correction of area detector data, University of Göttingen, 1997.

14 SHELXS-97 and SHELX-97, Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

15 T. Loiseau, C. Mellot-Draznieks, C. Sassoye, S. Girard, N. Guillou, C. Huguenard, F. Taulelle and G. Ferey, *J. Am. Chem. Soc.*, 2001, **123**, 9642.

16 D. J. Williams, J. S. Kruger, A. F. McLeroy, A. P. Wilkinson and J. C. Hanson, *Chem. Mater.*, 1999, **11**, 2241.