FULL PAPER

Strontium Methylphosphonate Trihydrate: An Example of a New Class of Host Materials for Intercalation Reactions – Synthesis, Structure and Intercalation Behavior

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A new compound with formula $SrCH_3PO_3 \cdot 3H_2O$ has been prepared, characterized by thermogravimetry, IR spectroscopy and powder X-ray diffraction, and its structure has been determined from single-crystal X-ray diffraction data. Strontium methylphosphonate trihydrate crystallizes in an orthorhombic system with space group *Pbca* (No. 61), $Z = 8$ and with lattice parameters $a = 7.8838(6)$, $b = 8.5173(5)$, $c = 21.5272(15)$ Å. Primary alcohols, amines, and 1,2-diols with straight carbon chains were intercalated into this strontium methylphosphonate compound. For all three types of intercalate, a linear dependence of the interlayer distance on the number of carbon atoms in the aliphatic chain of the guest was found. From these results, the arrangements of the guest molecules in the interlayer space of the host ($SrCH_3PO_3$) structure were deduced. The amine intercalates are unstable, and the guest species can be released from the host by washing the intercalate with an aprotic solvent. Conversely, the alcohol and diol intercalates are surprisingly stable. The reason for this stability may be due to the fact that the oxygen atom of an alcohol or diol species can replace the oxygen atom of the coordinated water molecule in the host. A successful attempt to intercalate polymeric species, namely poly(ethylene glycol), was made, which opens the way for the preparation of nanocomposites with this type of host material.

Introduction

Layered solids that are able to form intercalation compounds are used in sorption,[1] energy storage,[2] molecular recognition,[3] catalysis,[4] as nanocomposites with polymers,[5] and in pharmaceutical applications.[6] Due to these potential applications, new host materials are in increasing demand. Frequently used host materials include, among others, clays, layered double hydroxides, metal phosphates, oxides, and chalcogenides.[7] Metal phosphonates are also promising host materials owing to their structural variability.

Organophosphonates are known to form layered compounds with a wide range of metals. The most studied are zirconium phosphonates,[8] as they are the most stable ones. In addition to zirconium phosphonates, other layered metal phosphonates have been prepared, and intercalation reactions carried out by replacing water molecules coordinated to metal centers with different amines have been studied.[9] In the group of alkaline-earth metal phosphonates, several hydrogen phenylphosphonates with general formula $M(C_6H_5PO_3H)_2$ (M = Ca, Sr, Ba) have been described[10] and the intercalation of amines into calcium[11] and barium hydrogen phenylphosphonates[12] have been studied. The intercalation reactions were driven by acid–base interactions between the acidic phosphonate groups and the amine bases. Regarding the attempts to intercalate organic guests into lamellar methylphosphonates, a reaction of calcium hydrogen methylphosphonate monohydrate, $Ca(CH_3PO_3H)_2 \cdot H_2O$, with *n*-alkylmonoamines has been reported.[13] The change in the interlamellar distance was independent of the increase in the carbon chain length of the guest, and was also unaffected by an increase in the amine concentration. These results indicated that the base was probably only bonded to the surface of the lamellae.

Recently, we have prepared several new phenylphosphonates of calcium,[14] strontium[15] and barium[16] with general formula $MeC_6H_5PO_3 \cdot 2H_2O$ (Me = Ca, Sr, Ba) and investigated their intercalation reactions with amines and alcohols.[17] As these host materials do not contain acidic hydrogen atoms, the intercalation reaction is not due to

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acid–base interactions between the host and the guest (as it was the case of amine intercalation into the hydrogen phenylphosphonates mentioned above). In our case, the intercalation is most probably accomplished by a coordinative intercalation process as defined by Clearfield et al.,[9e,18] which is by interaction between the central metal atom of the host and a free electron pair present in the functional group of the guest. A more detailed investigation of this phenomenon is hindered by the impossibility of preparing these host materials in a crystalline form suitable for a single-crystal XRD analysis. Now, we have succeeded in the preparation of suitable crystals of a new host material related to $MeC_6H_5PO_3 \cdot 2H_2O$, namely, strontium methylphosphonate trihydrate, $SrCH_3PO_3 \cdot 3H_2O$. The structure of this material has been determined, and we have investigated its intercalation reactions. This study helped us to elucidate the way in which the guest species are anchored in the interlayer space of the host material. This phosphonate is able to intercalate quite a wide range of guest materials; the preparation and characterization of these intercalates are also described.

Results and Discussion

Structure of $SrCH_3PO_3 \cdot 3H_2O$

Compound $SrCH_3PO_3 \cdot 3H_2O$ crystallizes in an orthorhombic system with space group *Pbca* (No. 61) and its crystallographic parameters are given in Table 1. The stron-

Table 1. Crystallographic data and structure refinement parameters for $SrCH_3PO_3 \cdot 3H_2O$.

Empirical formula	CH_9O_6PSr
Formula mass	235.67 gmol^{-1}
Color; habit	Colorless; plates
Crystal size	$0.3 \times 0.3 \times 0.16$ mm
Crystal system	orthorhombic
Space group	*Pbca* (No. 61)
Cell parameters	$a = 7.8838(6)$ Å
	$b = 8.5173(5)$ Å
	$c = 21.5272(15)$ Å
Cell volume	1445.52(17) Å^3
Z	8
Calculated density	2.16567 gcm^{-3}
Absorption coefficient	7.649 mm^{-1}
$F(000)$	912
Temperature	150(1) K
Wavelength	0.71073 Å
θ range for data collection	1–27.5°
Index ranges	$-8 \leq h \leq 9, -10 \leq k \leq 10, -26 \leq l \leq 25$
Reflections collected	10837
Independent reflections	1475 [$1268 \geq 2\sigma(I)$]
Absorption correction	integration
Transmission	$T_{max} = 0.275, T_{min} = 0.124$
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	1475/0/89
Goodness-of-fit on F^2	1.161
Final R indices [$I > 2\sigma(I)$]	$R1^{[a]} = 0.0363, wR2^{[b]} = 0.0808$
R indices (all data)	$R1 = 0.0458, wR2 = 0.0856$
Extinction coefficient	0.0070(6)
Largest diff. peak/hole	0.740/–0.902

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 8.2077P]$ where $P = (F_o^2 + 2F_c^2)/3$.

tium ion is seven-coordinate and has a pentagonal-bipyramidal geometry, analogously to the coordination sphere found in $Ca(CH_3PO_3) \cdot H_2O$.[19] The coordination environment of the strontium and phosphorus atoms is shown in Figure 1 together with the numbering scheme for all atoms.
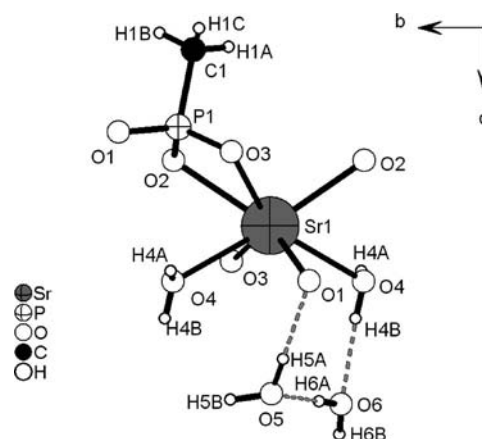

Figure 1. Atom labeling scheme for strontium methylphosphonate trihydrate with the hydrogen-bonding system for the water molecules indicated as dashed lines.

Five of the oxygen atoms (denoted O1, O2 and O3 in Figure 1) have bond lengths in the 2.447(3)–2.618(3) Å range and belong to phosphonate groups; the two remaining oxygen atoms (O4) have bond lengths of 2.705(3) and 2.717(3) Å and can be assigned to water molecules. The Sr–O distances (Table 2) are within the limits found for other phosphonates, for instance $Sr(HOOCC_6H_4PO_3)$[20] and $Sr(C_6H_5PO_3 H)_2$.[10b] The O2 and O3 oxygen atoms are of the μ_3-type, and each bridges two strontium ions as shown in Figure 2 that depicts the inorganic fragment of $SrCH_3PO_3 \cdot 3H_2O$.

Table 2. Selected bond lengths [Å] and angles [°] for $SrCH_3PO_3 \cdot 3H_2O$.[a]

Sr1–O3^i	2.447(3)	O3^i–Sr1–O1^{ii}	131.5(1)
Sr1–O1^{ii}	2.527(3)	O3^i–Sr1–O2^{iii}	122.25(10)
Sr1–O2^{iii}	2.558(3)	O3^i–Sr1–O3	134.21(13)
Sr1–O3	2.589(3)	O3^i–Sr1–O2	77.86(10)
Sr1–O2	2.618(3)	O3^i–Sr1–O4	75.0(1)
Sr1–O4	2.705(3)	O3^i–Sr1–O4^{iv}	84.33(10)
Sr1–O4^{iv}	2.717(3)	O3^i–Sr1–O1^{iii}	76.59(9)
P1–O3	1.513(3)	O3–P1–O1	113.91(18)
P1–O1	1.529(3)	O3–P1–O2	108.26(17)
P1–O2	1.533(3)	O1–P1–O2	109.32(18)
P1–C1	1.787(4)	O3–P1–C1	107.9(2)
O1–P1–C1	109.4(2)	Sr1–O4–Sr1^{iii}	103.59(11)
O2–P1–C1	107.9(2)		

[a] Symmetry operators: (i) 0.5 + *x*, *y*, 0.5 – *z*; (ii) 1 – *x*, –0.5 + *y*, 0.5 – *z*; (iii) 1.5 – *x*, –0.5 + *y*, *z*; (iv) 1.5 – *x*, 0.5 + *y*, *z*.

In addition, the phosphonate group chelates to the strontium ion through atoms O2 and O3 resulting in an O2–Sr–O3 angle of 56.5(1)°. The O1 oxygen atom is bonded to one Sr ion only. Thus, each phosphonate group connects four strontium atoms in a ($\kappa^1, \kappa^2, \kappa^2$)-$\mu_4$ coordination mode. The same type of bonding between phosphonate groups and metal ions was found in $Cd(CH_3PO_3) \cdot H_2O$[9a] and other di-
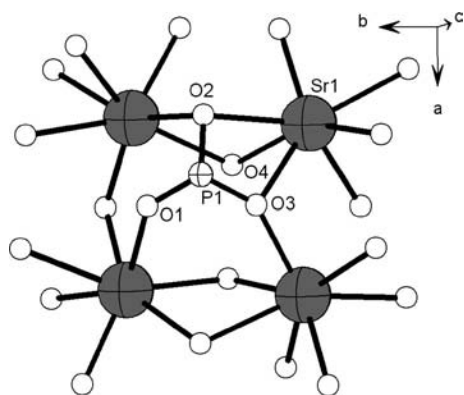
Figure 2. Bonding scheme for the phosphonate group. Methyl groups, interlayer water molecules and hydrogen atoms are omitted for clarity.

Figure 4. Stacking of the methylphosphonate layers as viewed along the b axis. Part of the hydrogen-bond system is shown as dashed lines.

valent metal alkyl- and arylphosphonates.[21] Unlike the Sr ion in $SrCH_3PO_3 \cdot 3H_2O$, the metal ions in these phosphonates are octahedrally six-fold coordinated by five oxygen atoms from phosphonate groups and one oxygen atom from a terminal water molecule. In $SrCH_3PO_3 \cdot 3H_2O$, the coordinated water molecule (O4 oxygen atom) bridges Sr atoms in the b direction. In this way, a layer composed of $Sr[(H_2O)\text{-}CH_3PO_3]$ neutral "slabs" is formed in the ab plane as shown in Figure 3.
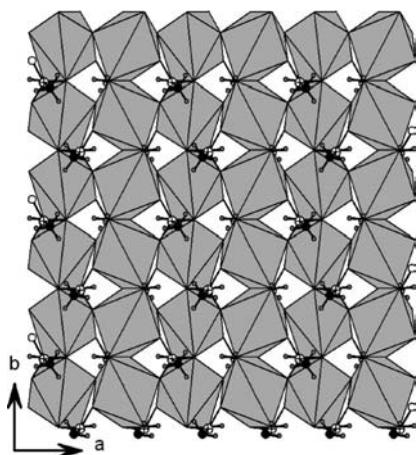

Figure 3. Strontium phosphonate layer as viewed along the c axis.

The methylphosphonate groups are placed in an alternating fashion above and below the plane of the layers. The layers are stacked in the c direction with another two water molecules residing in the interlayer space (Figure 4). As is obvious from this figure the methyl groups are not evenly placed, so that the layers form a kind of a corrugated structure.

The interlayer water molecules are hydrogen-bonded to each other, to the coordinated water molecules, and to the O1 phosphonate oxygen atoms. The hydrogen-bond system, shown in the left part of Figure 4 as dashed lines, provides the stacking interactions that hold the phosphonate layers together.
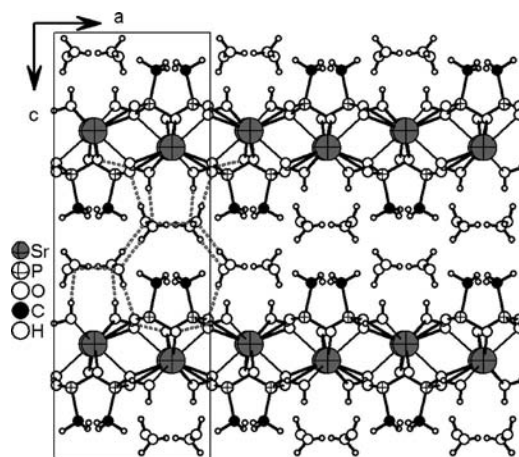
Strontium Methylphosphonate as a Host Material

Strontium methylphosphonate trihydrate for the intercalation reactions was precipitated from solution as a white powder that gave an XRD powder pattern that corresponded to that which was calculated for the structure determined from single-crystal XRD data.

The weight loss for $SrCH_3PO_3 \cdot 3H_2O$ that is observed upon heating of the material in air can be described schematically by the following three-step reaction:

$2\ SrCH_3PO_3 \cdot 3H_2O\ \rightarrow\ 2\ SrCH_3PO_3 \cdot H_2O\ \rightarrow\ 2\ SrCH_3PO_3\ \rightarrow\ Sr_2P_2O_7$

The corresponding thermogravimetric curve is shown in Figure 5a. The release of two molecules of water per formula unit corresponds to a theoretical weight decrease of 84.7% (found 84.8% at 145 °C), the calculated weight decrease to complete dehydration is 77.1% (release of the co-
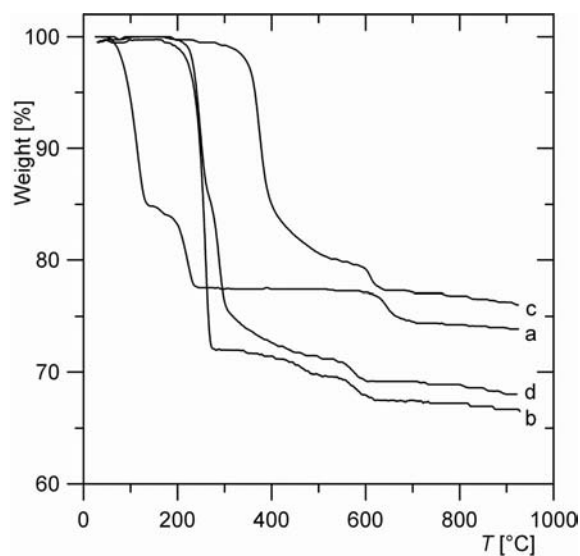

Figure 5. Thermogravimetric curves for $SrCH_3PO_3 \cdot 3H_2O$ (a), $SrCH_3PO_3 \cdot 1\text{-pentanol}$ (b), $SrCH_3PO_3 \cdot 1,5\text{-pentanediol}$ (c), and $SrCH_3PO_3 \cdot 1,2\text{-pentanediol}$ (d).

ordinated water molecules, found 77.5% at 250 °C), and the decomposition of the organic parts corresponds to a weight loss of 74.1% (found 73.9% at 920 °C). The product of heating $SrCH_3PO_3 \cdot 3H_2O$ to 950 °C is $Sr_2P_2O_7$, as confirmed by powder XRD analysis (PDF No. 24-1011).[22] The two molecules of water in the interlayer space are held very loosely as indicated by the low temperature of their release. The third water molecule is part of the layer structure, and therefore is lost at higher temperature than the water in the interlayer spaces.

The loss of water is also accompanied by a decrease in the basal spacing of the host layer structure. The powder pattern of methylphosphonate trihydrate was indexed from 71 lines in an orthorhombic system with the cell parameters given in Table 3, and with space group *Pbca* (No. 61). The basal spacing (10.8 Å) and the water content do not change when the crystals are left in an atmosphere with a relative humidity (RH) >9%. Strontium methylphosphonate monohydrate (basal spacing 8.50 Å) can be prepared either by heating of the trihydrate to 140 °C, as indicated by the thermogravimetric curve of $SrCH_3PO_3 \cdot 3H_2O$, or by storing it over P_2O_5 or KOH. The compound $SrCH_3PO_3 \cdot H_2O$ is monoclinic, with space group $P2_1/m$ (No. 11) and with cell parameters given in Table 3.

The change over time in the X-ray powder pattern of $SrCH_3PO_3 \cdot 3H_2O$ on heating of the compound to 50 °C is shown in Figure 6.

Apart from the peaks corresponding to the trihydrate and monohydrate in the XRD powder pattern, peaks corresponding to another transition phase were observed; this phase had a basal spacing of about 10.2 Å. This phase appears only in coexistence with the trihydrate and monohydrate; it cannot be isolated, and its water content cannot be determined. Anhydrous strontium methylphosphonate is formed by the thermal dehydration of the trihydrate at 300 °C, and its basal spacing is 8.0 Å. This compound is also monoclinic with the cell parameters given in Table 3. The total thickness of the $SrCH_3PO_3$ layers, as estimated from the structure of $SrCH_3PO_3 \cdot 3H_2O$, is >8 Å. Supposing that this thickness is retained in anhydrous $SrCH_3PO_3$, we can presume that the layers are wedged into each other through their methyl groups, and almost no space is left between the host layers. This prevents penetration of larger molecules into the interlayer space, and thus precludes the intercalation of organic guests into anhydrous strontium methylphosphonate.
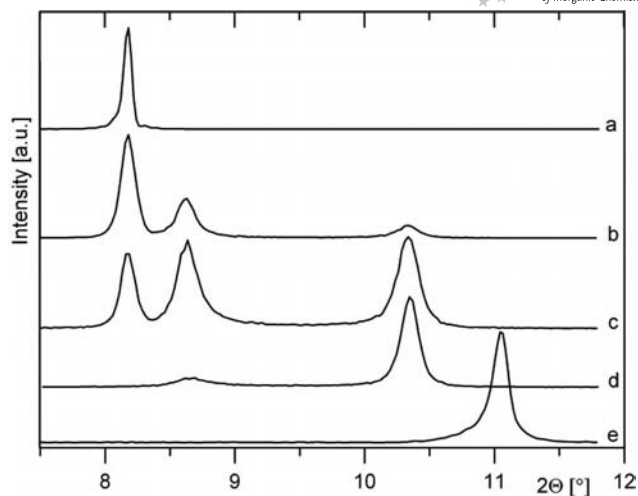

Figure 6. X-ray powder patterns of $SrCH_3PO_3 \cdot 3H_2O$ at room temperature (a), at 50 °C (b), heated to 50 °C for 15 min (c) and 30 min (d), dehydrated $SrCH_3PO_3$ prepared by heating $SrCH_3PO_3 \cdot 3H_2O$ to 300 °C (e).

Infrared Spectra of Strontium Methylphosphonates

The infrared spectra of $SrCH_3PO_3 \cdot 3H_2O$, $SrCH_3PO_3 \cdot H_2O$, $SrCH_3PO_3$, and $SrCH_3PO_3 \cdot 1$-pentanol are shown in Figure 7. The spectrum of strontium phenylphosphonate dihydrate ($SrC_6H_5PO_3 \cdot 2H_2O$), which is also shown in the figure, was discussed in detail in a previous paper.[15] The obtained data well support the results from the XRD and TGA analyses.

Characteristic vibration peaks corresponding to the methyl groups are observed in the spectra of the strontium methylphosphonates: CH stretching vibrations in the region around 2970 cm^{-1}, CH deformation vibrations at about 1443 cm^{-1}, and CH rocking vibration at 763 cm^{-1}. The last peak is situated at a relatively high position due to the restriction of this vibration in the interlayer structure. In all spectra we observed peaks corresponding to P–O stretching vibrations in the region 1200–900 cm^{-1}, and peaks corresponding to O–P–O bending vibrations in the region 600–410 cm^{-1} (Figure 7a, spectra 1, 2, and 3). The spectra of both strontium methylphosphonate hydrates, $SrCH_3PO_3 \cdot 3H_2O$ and $SrCH_3PO_3 \cdot H_2O$, are very similar. They differ from the spectrum of the dehydrated form, $SrCH_3PO_3$, by the presence of a sharp high-frequency peak at 3663 cm^{-1} (Figure 7b), which is most probably due to the vibrations

Table 3. Cell parameters for strontium methylphosphonates and their intercalates.

Sample	a [Å]	b [Å]	c [Å]	β [°][a]	M(n)[b]	F(n)[c]	n[d]
$SrCH_3PO_3 \cdot 3H_2O$	7.9113(6)	8.5357(5)	21.615(1)	90	71.3	137.5(0.0026, 56)	20
$SrCH_3PO_3 \cdot H_2O$	4.283(2)	7.797(2)	9.028(2)	109.710(5)	37.9	26.1(0.0059, 129)	20
$SrCH_3PO_3$	8.131(3)	6.966(2)	7.075(3)	100.22(3)	19.69	23.2(0.0127, 68)	20
$SrCH_3PO_3 \cdot C_5H_{11}OH$	7.929(4)	8.66(1)	15.07(2)	90	21.6	25.9(0.0123, 44)	14
$SrCH_3PO_3 \cdot 1,5\text{-}C_5H_{10}(OH)_2$	7.894(5)	8.591(7)	21.92(2)	90	8.8	10.2(0.0183, 75)	14
$SrCH_3PO_3 \cdot 1,2\text{-}C_5H_{10}(OH)_2$	7.920(4)	8.627(7)	29.07(2)	90	11.4	19.7(0.0125, 61)	15
$SrCH_3PO_3 \cdot 2$-cyclohexylethanol	18.444(6)	7.986(3)	8.644(3)	90	14.6	21.9(0.0125, 73)	20

[a] $\alpha = \gamma = 90°$. [b] Figure of merit according to ref.[26] [c] Figure of merit according to ref.[27] [d] Number of diffraction lines used for the determination of the cell parameters.
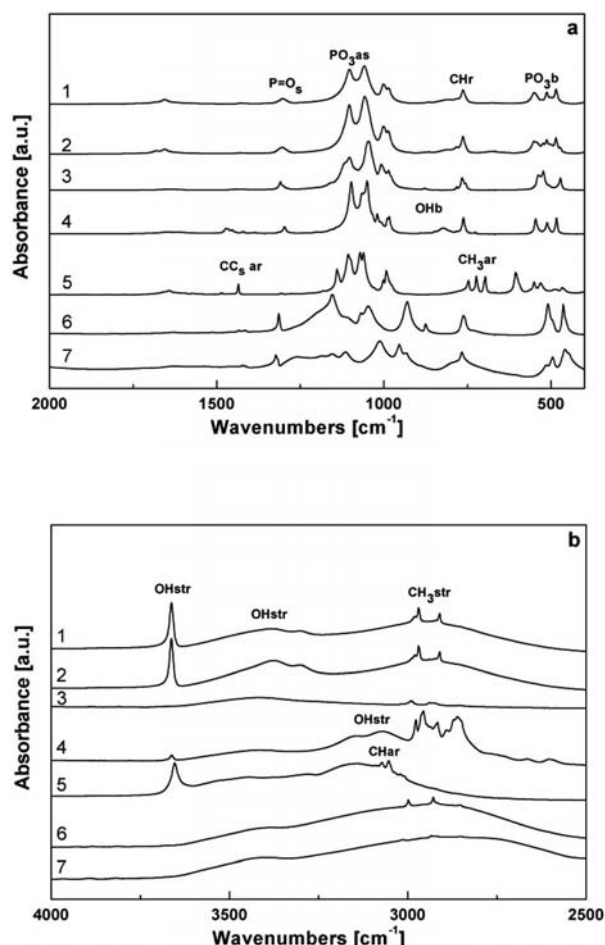
Figure 7. FTIR spectra of $SrCH_3PO_3 \cdot 3H_2O$ (1), $SrCH_3PO_3 \cdot H_2O$ (2), $SrCH_3PO_3$ (3), and $CH_3PO_3 \cdot 1$-pentanol (4). Spectra of $SrC_6H_5PO_3 \cdot 2H_2O$ (5), $Sr(CH_3PO_3H)_2$ (6) and of methylphosphonic acid, $CH_3PO_3H_2$ (7), are shown for comparison.

of water molecules coordinated to the metal atoms. This peak disappears after dehydration. A broad band with two maxima at 3374 and 3300 cm^{-1} in the spectra of the hydrates indicates the presence of coordinated water molecules in the inorganic structure (Figure 7b, spectrum 2). The broad band with a maximum at 3418 cm^{-1} in the spectrum of anhydrous $SrCH_3PO_3$ is most probably due to the vibrations of the adsorbed water. The spectrum of $SrCH_3PO_3$ differs from the spectra of the hydrates in the region where the stretching vibrations of the CH_3 groups occur. The two maxima are shifted from 2970 and 2910 cm^{-1} to 2990 and to a doublet at 2938/2925 cm^{-1}, respectively. The absence of water in $SrCH_3PO_3$ also causes an internal stress leading to a deformation of the phosphonate group, which results in some changes to the PO_3 stretching vibrations.[15]

The infrared spectra of all three strontium methylphosphonates exhibit several strong bands at 1103, 1057, and 1007 cm^{-1}, that can be assigned to asymmetric and symmetric PO_2 stretching vibrations, and the peaks at 986 cm^{-1} are assigned to an asymmetric stretching P–O$^-$ vibration[23] (Figure 7a). To help explain the presence of the bands at 1302 cm^{-1}, the spectra of hydrogen methylphosphonate $Sr(CH_3PO_3H)_2$ and methylphosphonic acid, $CH_3PO_3H_2$,

are included in Figure 7. In their spectra we observed well-developed bands corresponding to P=O stretching vibrations at about 1320 cm^{-1}, which is missing in the spectrum of $SrC_6H_5PO_3 \cdot 2H_2O$ due to the delocalization of the P=O double bond in the PO_3^{2-} groups. The presence of the small peaks in this region of the spectra for all three studied strontium methylphosphonates may be explained by the fact that the delocalization of the PO_3^{2-} group is less in methylphosphonate than in phenylphosphonate.

Intercalation

The ability of strontium methylphosphonate to intercalate organic neutral compounds was studied. The potential guest compounds were predominantly straight-chain amines and alcohols, namely primary monoamines and monoalcohols, 1,ω-alkanediols, and 1,2-alkanediols. A series of sharp basal reflections were observed in the powder XRD patterns for the intercalates from which basal spacings could be determined.

Intercalation of Amines

Aliphatic amines can be intercalated at room temperature, but the intercalates are very unstable; they lose their guest during washing with toluene or hexane, or during drying in an evacuated ampoule, therefore the guest content cannot be determined.

As shown in Figure 8, the basal spacing [taken as the d value of the (001) Bragg reflections] of the amine intercalates (increasing in chain length from 1-propylamine to 1-octylamine) increases linearly with the length of the carbon chain, n_C. Provided that all the alkyl chains are in an *anti* conformation, the basal spacing, c, changes with n_C according to the relation [Equation (1)]:

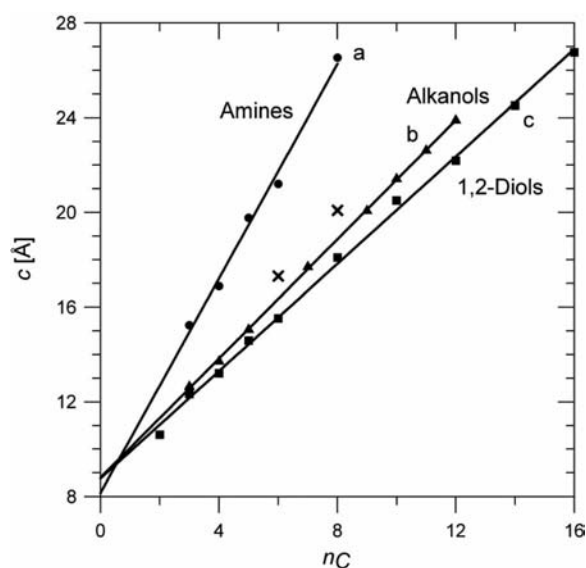$$\Delta c / \Delta n_C = 1.279 \cdot m \cdot \sin a \qquad (1)$$

Figure 8. Dependence of the basal spacing c on the number of carbon atoms in the chain of the guest species, n_C, for the intercalates of strontium methylphosphonates with amines (circles), n-alkanols (triangles and crosses) and 1,2-alkanediols (squares).

This equation has been described in our previous work,[24] where m is the number of the layers of guest molecules in the interlayer space of the host, and α is the inclination of the axis of the carbon chain of the guest molecule. The linear regression analysis of this dependence for the amine intercalates provides a value for the slope, $\Delta c/\Delta n_C$, that is equal to 2.26. This value is too high for the amine molecules to be arranged in the interlayer space as a monomolecular layer. Considering a bimolecular layer arrangement, $m = 2$, the angle α equals 62°. It means that the amine molecules are deposited in the interlayer space in two layers with the aliphatic chains inclined at an angle of 62° with respect to the planes of the host layers. The low value of c (8.16 Å) when $n_C = 0$, obtained from the regression line, suggests that the amine molecules are slightly interdigitated in these two layers.

Intercalation of Alcohols

Three types of alcohol were intercalated into strontium methylphosphonate: (i) 1-alkanols, (ii) 1,ω-alkanediols, and (iii) 1,2-alkanediols. For comparison with these three groups of intercalates, intercalates of alcohols with five carbon atoms in the chain (C_5 alcohols), namely, 1-pentanol, 1,5-pentanediol, and 1,2-pentanediol, are also discussed in detail herein. In contrast to the amines, the alcohol intercalates are generally stable under ambient conditions and can be easily isolated by removing excess guest by evaporation or by washing of the intercalate with toluene or hexane. On heating, the intercalates decompose in two steps, as shown in Figure 5b–d. In the first step, the intercalated alcohol is released, and in the second step, above 600 °C, the methylphosphonate decomposes. The product from heating of the methylphosphonate alcohol intercalates to 950 °C is $Sr_2P_2O_7$, as confirmed by powder XRD (PDF No. 24-1011).[22] It follows from the shape of the thermogravimetric curve that the alkanol intercalates do not contain water; this means that the water molecules, which are coordinated to the strontium atom in the host compound, are replaced by alkanol molecules in these intercalates. This may be the reason for the good stability of these intercalates. The thermogravimetric curves for the alkanol intercalates differ slightly in the 200–500 °C region depending on the type of the alkanol, as exemplified by the C_5 alcohols in Figure 5. The 1-alkanol intercalates release their guest in one simple step within the 200–300 °C range (Figure 5b), whereas 1,2-alkanediols are released in the same temperature range but in two close steps (Figure 5c). It can be speculated that in the case of the 1,2-diols the guest molecules are bonded to the host layers in two different ways, either by a primary or secondary OH group. Nevertheless, this theory could not be confirmed independently. The 1,5-pentanediol intercalate releases its guest molecules at temperatures >100 °C. The high stability of the 1,ω-diol intercalates can be explained by presuming that these guest molecules are anchored to both host layers, forming a kind of pillared structure. These pillared structures have been found for diols in-

tercalated in zirconium phosphate[25] and vanadyl phosphate.[24]

From the decrease in the weight observed for the first step in the TGA plots for the intercalates, the amount of intercalated alcohol (x) can be calculated. In Table 4 the observed weight losses and those calculated from the presumed alcohol contents are summarized. From this table it is obvious that the alcohol content of the intercalates decreases with increasing length of the alcohol's carbon chain. Probably, the longer chains prevent full intercalation of the alcohols into the interlayer space, and the products remain partially hydrated. In the case of 1,2-diols, only 1,2-ethanediol is fully intercalated into strontium methylphosphonate (see Table 4), and the formula of the intercalate is $SrCH_3PO_3\cdot HOCH_2CH_2OH$. Although 1,2-ethanediol can be considered as a diol with terminal OH groups (1,ω-diol), its amount in the intercalate ($x = 1.0$) indicates that this diol is not pillared and is bonded to one phosphonate layer through only one OH group.

Table 4. Composition of the $SrCH_3PO_3\cdot x$(alkanol) intercalates as calculated from their TGA data.

Alkanol	x	First weight loss (found/calcd.)	Second weight loss (found/calcd.)
Ethanol	1.00	20.0/20.23	3.0/3.08
Propanol	1.00	24.0/24.74	3.0/2.84
Pentanol	0.90	30.0/30.40	3.0/2.69
Hexanol	0.75	29.0/29.68	3.0/2.72
Undecanol	0.80	41.0/43.15	3.0/2.20
Dodecanol	0.72	42.5/42.49	2.0/2.22
1,2-Ethanediol	1.00	26.0/25.47	3.0/2.88
1,2-Pentanediol	0.72	29.0/29.22	3.0/2.73
1,2-Hexanediol	0.81	33.0/34.51	3.0/2.53

In comparison with 1,2-alkanediols, 1,ω-alkanediols intercalate poorly, and the intercalates that are formed are usually accompanied by strontium methylphosphonate monohydrate or anhydrous strontium methylphosphonate. Only the 1,5-pentanediol intercalate, containing half a pentanediol molecule per formula unit, was prepared in a pure form. The basal spacing of this intercalate is 10.93 Å, which is very similar to that of strontium methylphosphonate trihydrate (10.80 Å), but the thermal behavior of this intercalate is quite different from that of the host (see Figure 5c). The 1,5-pentanediol guest molecule is released in one step from about 300 °C to about 600 °C (weight decrease: found 20.5%, calcd. 20.9%), the remaining organic component of the methylphosphonate host decomposes above 600 °C (found 3.0%, calcd. 3.1%).

The lattice parameters for the C_5 alcohol intercalates are given in Table 3. It can be deduced from these values that the structure of the host layer is retained in the intercalates, because the values of the a and b lattice parameters are roughly the same as those for $SrCH_3PO_3\cdot 3H_2O$. As in the case of the amine intercalates, the basal spacing, c, for the 1-alkanol intercalates depends linearly on the number of carbon atoms in the alkyl chain of the guest, n_C (except in the case of the hexanol and octanol intercalates), and the slope of the regression line is 1.26 and the y intercept (the

value of c at $n_C = 0$) is 8.79 Å (Figure 8). The angle at which the straight carbon chains are tilted with respect to the planes of the host layers, calculated according to Equation (1), is 80° and the 1-alkanol molecules are deposited as a monolayer in the interlayer space of the host. A similar linear dependence was found for the 1,2-alkanediol intercalates for which the slope of the regression line is 1.13, and the y intercept is 8.77 Å, which provides a chain-tilting angle of 62°. Therefore, for this case the guest molecules are also presumed to reside in the interlayer space as a monolayer. Most probably the second hydroxy group is attracted to the host layers, and this causes the small chain-tilting angle.

The reason why the alcohol intercalates are more stable than the amine ones can be explained in the following way: In the structure of $SrCH_3PO_3 \cdot 3H_2O$ the bridging water molecule is coordinated to two Sr ions through its two free electron pairs; the position of this water molecule is most favorable for this coordination mode as indicated by the Sr–O4–Sr angle of 103.6° (where O4 is the oxygen atom of the coordinated water molecule; see Figures 1 and 2 and Table 2). We can presume that the position of this coordinated water molecule is also retained in $SrCH_3PO_3 \cdot H_2O$. The oxygen atom of the alcohol molecules in the intercalates can be expected to assume the same position, with the same coordination arrangement as seen in $SrCH_3PO_3 \cdot 3H_2O$ and $SrCH_3PO_3 \cdot H_2O$. This hypothesis is supported by the fact that the values of c when $n_C = 0$, calculated from linear dependence, are 8.79 Å and 8.77 Å for the 1-alkanol and 1,2-alkanediol intercalates, respectively. These values are very close to the basal spacing found for $SrCH_3PO_3 \cdot H_2O$ (8.50 Å). The stability of the intercalates is influenced by free electron pairs on a donor atom – oxygen and nitrogen atoms in alcohols and amines, respectively. Two electron pairs on an oxygen donor atom in $SrCH_3PO_3 \cdot H_2O$ are bonded strongly to two metal centers, whereas one electron pair on a nitrogen atom in an amine molecule should be bound more freely than in the case of the oxygen atom. The coordinated water molecule of the host structure can be replaced by the oxygen atom of the alcohol molecule, and therefore a relatively strong bond between the host layer and the guest is formed. Such bonding is suppressed in the case of intercalated amines, and the coordination of the amine molecules with the host is expected to be weaker.

The way in which the alcohol molecules are anchored to the host layers is also reflected in the change of the infrared spectrum of strontium methylphosphonate after the intercalation of 1-pentanol, especially in the region of the OH stretching vibrations (see Figure 7b, spectrum 4). The small sharp peak at 3662 cm^{-1} in the spectrum most probably corresponds to the residual water molecule coordinated to the metal atom. A broad band with maxima at 3421, 3141 and 3071 cm^{-1} corresponds to vibrations of the OH group. The presence of pentanol in the intercalate is also reflected by the occurrence of a peak at 1473 cm^{-1} in the spectrum that is associated with CH_2 scissoring vibrations, and by CH_3 umbrella vibrations at 1385 cm^{-1} (see Figure 7a, spectrum 4). Peaks corresponding to pentanol C–O stretching

vibrations are expected in the 1260–1000 cm^{-1} region of the intercalate spectrum, but are overlapped by various P–O vibrations. A small but relatively broad band at 822 cm^{-1} most probably corresponds to an OH group out-of-plane bending vibration.

In the case of cyclohexanol, an intercalate is formed with a basal spacing of 11.51 Å. The intercalate is less stable than the straight chain alkanol intercalates. A diffraction line associated with strontium methylphosphonate trihydrate appears in the powder XRD pattern of the intercalate when the sample is exposed to air with ambient humidity (RH ≈ 40%) for several hours. On heating, the intercalate shows one weight decrease in the 200–300 °C range. This loss corresponds to a formula of either $SrCH_3PO_3 \cdot 0.57C_6H_{11}OH$ or $SrCH_3PO_3 \cdot 0.5C_6H_{11}OH \cdot 0.5H_2O$. The small amount of cyclohexanol in the intercalate may be due to the large cross section of the molecule, which prevents full intercalation (one alcohol molecule per formula unit) unlike the situation that is typical for alcohols with straight carbon chains that is described above. The shape of the cyclohexanol molecules is also responsible for the low stability of the intercalate as the anchoring of cyclohexanol to the host layers is hindered by the steric requirements of the cyclohexyl groups, which are too bulky to be placed easily among the methyl groups of the host.

On the other hand, 2-cyclohexylethanol forms a stable intercalate with a basal spacing of 18.44 Å, which contains one alcohol molecule per formula unit. In this intercalate, the hydroxyethylene fragment is inserted into the voids between the host methyl groups in a way that is analogous to that of the straight-chain alcohols guests, so that the cyclohexyl part of the molecule is not influenced by steric hindrance from the methyl groups of the host.

Oxygen-containing oligomers and polymers, namely bis(ethylene glycol), tris(ethylene glycol) and poly(ethylene glycol), form stable intercalates when hydrothermally treated at 100 °C with $SrCH_3PO_3 \cdot 1$-pentanol.

The intercalate with bis(ethylene glycol) (DEG) has a basal spacing of 10.70 Å. The intercalate decomposes in two steps: The first step that is above 300 °C equates to a weight loss of about 22.5% and corresponds to the release of half a molecule of DEG (calcd. 22.6%), the second loss above 600 °C is caused by the decomposition of methylphosphonate (calcd. 3.0%, found 2.5%).

The intercalate with tris(ethylene glycol) (TEG) has a basal spacing of 13.72 Å. The intercalate decomposes in one step above 300 °C, the weight losses caused by the release of TEG and the decomposition of methylphosphonate cannot be distinguished. The total observed weight loss of 32% is in a good agreement with the theoretical value for $SrCH_3PO_3 \cdot 0.5TEG$ (calcd. 31.98%, which is the sum of 29.25% from the release of TEG and 2.73% from the decomposition of methylphosphonate).

The intercalate with commercial poly(ethylene glycol) (PEG 1000) that has a basal spacing of 9.70 Å decomposes in one step above 200 °C, and the weight losses caused by the release of PEG and the decomposition of methylphosphonate cannot be distinguished. A total weight loss of

24% corresponds to the formula $SrCH_3PO_3 \cdot 1.0(C_2H_4O)$ where C_2H_4O is a monomeric unit of PEG 1000.

The glycol/$SrCH_3PO_3$ ratios indicate different ways in which the glycol molecules are arranged in the interlayer space. The DEG and TEG guests are anchored like 1,ω-diols (glycol/$SrCH_3PO_3$ = 0.5, a value that is analogous to that found for 1,ω-diols), whereas PEG 1000 coordinates to the strontium ions through its ether oxygen atoms, and the PEG chains lie parallel to the host layers.

The dimethyl carbonate intercalate $SrCH_3PO_3 \cdot H_2O \cdot 0.5(CH_3CO_3CH_3)$ that has a basal spacing of 11.31 Å is not stable under ambient conditions: The guest is slowly released, and the diffraction line associated with strontium methylphosphonate trihydrate appears from the powder XRD pattern after about 1 h. Also, cyclohexanone can be intercalated into strontium methylphosphonate, but the intercalate that has a basal spacing of 13.74 Å was only prepared as a mixture with strontium methylphosphonate trihydrate and monohydrate; therefore, we were not able to determine its composition.

Conclusions

Strontium methylphosphonate represents a new layered material with a simple composition and a facile preparation. Using the method of a slow sorption of ethanol vapors into a saturated aqueous solution, we were able to prepare strontium methylphosphonate trihydrate crystals suitable for a crystal-structure determination. The strontium ions in this compound are heptacoordinated to the oxygen atoms of the phosphonate groups and the oxygen atoms of coordinated water molecules. An inorganic layer is thus formed, from which the methyl groups extend out. The interlayer space is filled with water molecules of crystallization, which can be easily released either by heating or by storing the trihydrate in a dry environment to form a monohydrate with formula $SrCH_3PO_3 \cdot H_2O$ and with a lower basal spacing. This monohydrate can be completely dehydrated by heating to >300 °C.

Layered $SrCH_3PO_3 \cdot 3H_2O$ can serve as a host material for the intercalation of organic compounds containing atoms with free electron pairs. We were able to intercalate amines and alcohols into this compound. As the structure of the host compound, strontium methylphosphonate, is known in this case, the positioning of the guest molecules in the interlayer space and the way in which the guest molecules are anchored to the host layers can be deduced. The driving force for this intercalation is the coordination of the nitrogen or oxygen atoms of the guest to the strontium ions of the host.

The ability to intercalate polymeric guests into strontium methylphosphonate, as proven by the intercalation of PEG 1000 into this material, suggests the possible use of this host material for the formation of polymeric nanocomposites. Also, other oxygen-containing guest species can be intercalated into $SrCH_3PO_3$, for example dimethyl carbonate.

To the best of our knowledge, this paper provides the first description of the coordinative intercalation of neutral organic guests into a strontium compound. Together with our previously published papers on the intercalation of guest species into calcium[17a] and barium[17b] phenylphosphonates, this is one of the first examples of coordinative intercalation into alkaline-earth metal phosphonates.

Experimental Section

General: All starting chemicals were obtained from commercial sources and were used without further purification.

Synthesis of Strontium Methylphosphonate Trihydrate ($SrCH_3PO_3 \cdot 3H_2O$): Strontium methylphosphonate trihydrate, $SrCH_3PO_3 \cdot 3H_2O$, was prepared according to a method analogous to that used for the preparation of strontium phenylphosphonate dihydrate.[15] A solution of concentrated ammonia was added to methylphosphonic acid (1.92 g, 2×10^{-2} mol) in water (50 mL) until pH = 9. A solution of $SrCl_2 \cdot 6H_2O$ (5.332 g, 2×10^{-2} mol) in water (25 mL) was added to the methylphosphonic acid solution at room temperature whilst stirring. A white precipitate appeared after about 10 min and was separated by filtration. Another part of product was precipitated from the filtrate by adding ethanol (75 mL). The combined precipitates were washed with a mixture of water and ethanol (1:1). The white product in a 4.48 g yield (95%) was dried in air at room temperature.

Crystallization of Strontium Methylphosphonate Trihydrate: Single crystals of $SrCH_3PO_3 \cdot 3H_2O$ were obtained by slow sorption of ethanol vapors into a saturated aqueous solution of the phosphonate prepared as described above. A beaker containing the phosphonate solution (25 mL) was placed into a dessicator together with a saturated solution of urea in ethanol in a separated open vessel. Colorless plate-like crystals of strontium methylphosphonate appeared after two weeks. The crystals were carefully removed from the mother solution and used for single-crystal XRD-ray measurements.

Intercalation Reactions: Aliphatic amines were intercalated by stirring a suspension of $SrCH_3PO_3 \cdot 3H_2O$ (0.1 g) in the corresponding amine (8 mL) at room temperature (in the case of ethylamine at 0 °C) for 2 d.

The alcohol intercalates were prepared by solvothermal treatment of a suspension of $SrCH_3PO_3 \cdot 3H_2O$ (0.1 g) in the corresponding alcohol (9 mL) in a Teflon-lined 23 mL Parr acid digestion bomb, which was heated under autogenous pressure at 130 °C for 16 h. The alkanol intercalates can also be prepared by heating the host compound, while suspended in the corresponding alcohol, in a microwave field in a way described previously,[24,25] except in the case of the propanol and butanol intercalates, which cannot be prepared, probably because the desired reaction temperature cannot be achieved due to low boiling points of these alcohols.

The intercalations of bis(ethylene glycol) (DEG), tris(ethylene glycol) (TEG) and poly(ethylene glycol) (PEG 1000) into strontium methylphosphonate were achieved by displacing pentanol from a previously prepared pentanol intercalate. A suspension of the pentanol intercalate was solvothermally treated in the corresponding guest (9 mL) at 100 °C for 20 h.

Dimethylcarbonate, cyclohexanol and 2-cyclohexylethanol were intercalated into strontium methylphosphonate by displacing pre-

viously intercalated butylamine. The excess liquid amine was removed from the 1-butylamine intercalate by filtration, and the wet solid intercalate was used for the subsequent displacement reactions. The 1-butylamine intercalate dispersed in dimethyl carbonate was heated at 90 °C for 3 h. A suspension of the 1-butylamine intercalate in cyclohexanol or 2-cyclohexylethanol was solvothermaly treated at 150 °C for 20 h.

Characterization: The X-ray data of a colorless crystal of $SrCH_3PO_3·3H_2O$ were obtained at 150 K with a Nonius Kappa CCD diffractometer, fitted with an Oxford Cryostream low-temperature device, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), in a φ- and χ-scan mode. Data reductions were performed with DENZO-SMN.[28] The absorption was corrected for by integration methods.[29] Structures were solved by direct methods (Sir92)[30] and refined by full-matrix least-squares techniques based on F^2 (SHELXL97).[31] Hydrogen atoms were mostly located from the difference Fourier maps. However, to ensure the uniformity of the crystal refinements, all hydrogen atoms were recalculated at idealized positions (riding model), and temperature factors $U_{iso}(H) = 1.2U_{eq}$ (pivot atom) were assigned, with 0.93 Å for C–H bonds of aromatic hydrogen atoms, and 0.82 Å for O–H bonds. CCDC-793319 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction data were obtained with a D8 Advance diffractometer (Bruker AXS, Germany) with Bragg–Brentano θ-θ geometry (40 kV, 40 mA) using Cu-K_α radiation with a secondary graphite monochromator. The diffraction angles were measured at room temperature from 2 to 37° (2θ) in 0.025° steps with a counting time of 2 s per step. Indexing of the powder pattern was carried out with a DICVOL91 computer program[32] embedded in the CRYSFIRE computer program package.[33] The space groups were determined by processing the data in the Checkcell program.[34]

The thermogravimetric analysis (TGA) was performed with a homemade apparatus constructed from a computer-controlled oven and a Sartorius BP210S balance. The thermogravimetric measurements were carried out in air between 30 and 960 °C at a heating rate of 5 °C min^{-1}.

Infrared spectra in the range of 400–4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution with a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer equipped with a DTGS TEC detector. Measurements of the powdered samples were performed ex situ in the transmission mode with KBr pellets. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path.

Acknowledgments

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