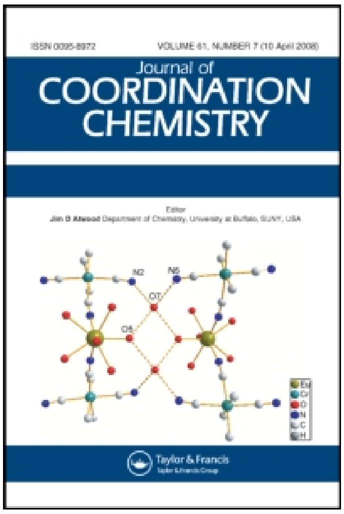

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Synthesis and crystal structure of a neutral open framework cobalt(II) phosphate $Co_6(PO_4)_4 \cdot 7H_2O$ with a channel structure

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Using tri-ethyl phosphate as a phosphate source, the hydrothermal reaction of cobalt(II) oxalate di-hydrate, zinc oxide and 1,8 di-amino octane at 200°C gave purple crystals of $Co_6(PO_4)_4 \cdot 7H_2O$ (**1**), along with a mixture of open-framework zinc–cobalt phosphates Co–Zn–HPO_4, and $Co_3(HPO_4)_2(2OH)$. Compound **1**, has been characterized by thermal analysis, FTIR and single crystal X-ray diffraction. The single crystal structure of $Co_6(PO_4)_4 \cdot 7H_2O$ reveals cobalt in four, five and six-fold coordination with linkages through the bridging water molecules and the oxygen atoms of the phosphate in the subunits. Four subunits are connected together through the oxygen atoms (PO_4), to form the three dimensional open framework structure, with a 20-member ring channel that hosts two uncoordinated water molecules. Thermal removal of the water molecules occurs between 400–600°C, with the collapse of the structure above 600°C.

Keywords: Cobalt phosphate; Zeotype; Open framework; Hydrothermal

1. Introduction

Widespread research on microporous transition metal phosphates, with open-framework structures is due in part to their potential applications as heterogeneous catalysts, sorbent materials, and ion exchangers [1–3]. Among the vast family of open-framework transition metal phosphates, the zincophosphates [4], iron phosphates [5], vanadium phosphates [6] and cobalt phosphates [7] constitute an important class of compounds. The cobalt phosphates are of particular interest, since cobalt can easily exhibit tetrahedral, in addition to five and six fold coordination leading to a large variety of structure types. For example, $Co_2(OH)PO_4$ and $NaCo_3(PO_4)(HPO_4)_2$ are structural analogues of the natural minerals *adamite* and *alluaudite*, respectively [8, 9], and several micro-porous cobalt phosphates with the formula $MCoPO_4$ (M = Na, K, Rb, Cs and NH_4^+) adopt the structure of known *zeolite* types [10–13], or new *zeolite*

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related Co–P–O frameworks [14–16]. In all of these structures, an organic amine, or mono cation are usually used as structure directing agent, and are always part of the open framework structure. Open framework cobalt phosphates without such a directing cation are generally difficult to prepare using conventional hydrothermal processes [17–18], and isolation of a neutral open framework cobalt phosphate is very rare.

Here, we report the hydrothermal synthesis, and characterization of a new cobalt phosphate framework possessing a 20-membered ring channel with novel structural features resembling those of *zeolites*.

2. Experimental

2.1. *Materials and methods*

All starting materials were purchased from Aldrich Chemical Company (USA) and used as received. The Fourier Transform FTIR spectrum was recorded within the 400–4000 cm^{-1} region on an IR 200 Thermo Nicolet spectrometer using KBr pellets. Elemental Analysis (Co, P) was carried out at the Cornell Center for Materials Research (CCMR), at the Optical and Microscope Facility. The EDS detector was made by Thermo-Noran using a Vantage system that includes standardless EDS software for processing the spectra to obtain the quantitative elemental analysis. The electron beam conditions were 15 kV and several *nanoamps*. The takeoff angle is always 40 degrees. The total of the standardless analysis is always 100% due to normalization. The thermo-gravimetric analysis and differential scanning calorimetry were carried out on a TA instrument at a temperature range of 30–800°C.

2.2. *Hydrothermal synthesis of the $Co_6(PO_4)_4 \cdot 7H_2O$*

$Co_6(PO_4)_4 \cdot 7H_2O$ (**1**) was synthesized using hydrothermal technique. In a typical synthesis, zinc oxide (0.24 g, 2.97 mmol), cobalt(II) oxalate dihydrate (0.6 g, 4.76 mmol), triethyl phosphate (0.6 g, 3.29 mmol), and 1,8-diaminooctane (0.6 g, 4.16 mmol) were added to 10 mL of doubly distilled water in a Teflon container inserted in a stainless steel vessel and heated at 200°C for ten days. The reaction produced a mixture of purple crystals, **1**, bluish-green crystals identified as Co–Zn–HPO_4, and a few red colored crystals which were identified as layered $Co_3(OH)_2(HPO_4)_2$ of known structure [19, 20]. The crystals were manually separated using magnifying glasses. The yield of **1** is about 0.18 g, 26%, based on the amount of starting cobalt(II). The energy dispersive X-ray analysis of **1** gave the Co : P atom ratio of approximately 3 : 2 in support of the composition.

2.3. *Determination of the crystal structure of 1*

A suitable single crystal with dimension $0.30 \times 0.20 \times 0.04\ mm^3$ was subjected to X-ray diffraction studies on a SMART Apex diffractometer using monochromatic Mo-Kα radiation with omega scan technique [21]. Using Saint+ [22] 19357 reflections were collected with 4851 independent reflections ($R(\mathrm{int}) = 0.0286$). The structure was solved

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$Co_6H_{14}O_{23}P_4$
Formula weight	863.58
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	8.2621(5)
b	12.9929(7)
c	17.1466(10)
α	90
β	101.4610(10)
γ	90
Volume (Å^3)	1803.96(18)
Z	4
Density (calculated) (Mg m^{-3})	3.165
Absorption coefficient (mm^{-1})	5.866
$F(000)$	1680
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.04$
Crystal shape, color	Plate, purple
θ range for data collection (°)	1.98–29.13
Limiting indices	$-11 \leq h \leq 11$, $-17 \leq k \leq 17$, $-23 \leq l \leq 23$
Reflections collected	19357
Independent reflections	4851 (R(int) = 0.0286)
Max. and min. transmission	0.791 and 0.363
Data/restraints/parameters	4851/35/340
Goodness-of-fit on F^2	1.179
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0427$, $wR_2 = 0.0995$
R indices (all data)	$R_1 = 0.0446$, $wR_2 = 0.1009$
Largest diff. peak and hole (e Å^{-3})	2.211 and −1.149

by direct method and refined by full-matrix least-squares on F^2, using SHELXTL version 6.14 [23]. The crystallographic data are given in table 1 and selected bond lengths and angles are listed in table 2. For the refinement of hydrogen atom positions, the initial positions were based either on the residual electron density (Q peaks) or (for those that could not be localized in the difference density Fourier map) on geometric and hydrogen bonding considerations. All hydrogen atoms were isotropically refined with a displacement parameter 1.5 that of the adjacent oxygen atom. The O–H distances were restrained to be 0.9 Å within a standard deviation of 0.02, and the H $\cdots$ H distances were restrained to be the same for all water molecules (within a standard deviation of 0.01). Atomic positional parameters, full tables of bond lengths and angles, and anisotropic temperature factors are available in CIF format, Fachinformationszentrum Karlsruhe (FIZ), reference number CSD 416823.

3. Results and discussion

3.1. *Structure description*

The asymmetric unit of **1** contains six crystallographically distinct cobalt and four phosphate groups. The structure consists of a network of vertex-linked CoO_6 octahedra [Co(1), Co(2), Co(3), Co(4)], trigonal bipyramidal subunits CoO_5 [Co(6)], and

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–O(15)#1	2.020(3)	Co(1)–O(11)#2	2.025(3)
Co(1)–O(5)	2.056(3)	Co(1)–O(1)	2.112(3)
Co(1)–O(17)	2.156(3)	Co(1)–O(20)#2	2.237(3)
Co(2)–O(9)	2.011(3)	Co(2)–O(13)	2.050(3)
Co(2)–O(1)	2.071(3)	Co(2)–O(5)	2.116(3)
Co(2)–O(19)	2.158(3)	Co(2)–O(18)	2.212(3)
Co(3)–O(4)#3	2.060(3)	Co(3)–O(7)	2.067(3)
Co(3)–O(17)#4	2.105(3)	Co(3)–O(13)	2.116(3)
Co(3)–O(12)#3	2.126(3)	Co(3)–O(18)	2.154(3)
Co(4)–O(7)#4	2.068(3)	Co(4)–O(4)#5	2.078(3)
Co(4)–O(14)	2.096(3)	Co(4)–O(19)	2.101(3)
Co(4)–O(11)	2.107(3)	Co(4)–O(20)	2.148(3)
Co(5)–O(16)#6	1.949(3)	Co(5)–O(10)	1.959(3)
Co(5)–O(8)#6	1.988(3)	Co(5)–O(12)#7	1.999(3)
Co(6)–O(2)#5	1.978(3)	Co(6)–O(8)#6	1.987(3)
Co(6)–O(14)	2.008(3)	Co(6)–O(21)	2.101(4)
Co(6)–O(10)	2.272(3)	P(1)–O(2)	1.536(3)
O(15)#1–Co(1)–O(11)#2	109.43(11)	O(15)#1–Co(1)–O(5)	87.05(11)
O(11)#2–Co(1)–O(5)	163.52(11)	O(15)#1–Co(1)–O(1)	88.39(11)
O(11)#2–Co(1)–O(1)	94.95(10)	O(5)–Co(1)–O(1)	85.24(10)
O(15)#1–Co(1)–O(17)	94.01(11)	O(11)#2–Co(1)–O(17)	86.42(11)
O(5)–Co(1)–O(17)	92.59(10)	O(13)–Co(2)–O(1)	160.55(11)
O(9)–Co(2)–O(5)	87.92(11)	O(13)–Co(2)–O(5)	93.54(11)
O(1)–Co(2)–O(5)	84.75(10)	O(9)–Co(2)–O(19)	94.55(11)
O(13)–Co(2)–O(19)	89.67(11)	O(1)–Co(2)–O(19)	90.99(10)
O(5)–Co(2)–O(19)	175.09(11)	O(9)–Co(2)–O(18)	170.92(11)
O(4)#3–Co(3)–O(17)#4	91.21(11)	O(7)–Co(3)–O(17)#4	169.50(11)
O(4)#3–Co(3)–O(13)	171.90(11)	O(7)–Co(3)–O(13)	97.48(11)
O(17)#4–Co(3)–O(13)	92.30(11)	O(7)#4–Co(4)–O(14)	101.97(11)
O(4)#5–Co(4)–O(14)	90.69(10)	O(7)#4–Co(4)–O(19)	92.72(10)
O(4)#5–Co(4)–O(19)	170.78(11)	O(14)–Co(4)–O(19)	92.64(11)
O(16)#6–Co(5)–O(12)#7	101.39(12)	O(10)–Co(5)–O(12)#7	127.78(12)
O(8)#6–Co(5)–O(12)#7	112.20(11)	O(2)#5–Co(6)–O(8)#6	110.06(12)

Symmetry transformations used to generate equivalent atoms: #1:$-x+3/2$, $y+1/2$, $-z+1/2$; #2: $-x+1/2$, $y+1/2$, $-z+1/2$; #3: $x+1$, y, z; #4: $-x+3/2$, $y-1/2$, $-z+1/2$; #5: $-x+1/2$, $y-1/2$, $-z+1/2$; #6: $-x+1$, $-y+1$, $-z$; #7: $-x$, $-y+1$, $-z$; #8: $x-1$, y, z.

tetrahedral CoO$_4$ moieties [Co(5)] that are interconnected by four PO$_4$ tetrahedra, and bridging water molecules. The Co–O distances in the octahedral geometry range from 2.011 to 2.237(3) Å. In the trigonal bipyramidal moieties, the Co–O distances range from 1.987(3) to 2.272(3) Å, while in the cobalt tetrahedral environment, the Co–O distances range from 1.949(3) to 1.999(3) Å. The P–O distances are in the range of 1.515(3)–1.558(3) Å, as expected. In the asymmetric unit shown in figure 1, the connectivity of cobalt and phosphorus in **1** is very unusual. P(3) is linked to Co(6), Co(4), and Co(2) through three of its oxygen atoms, P(4) is connected to Co(2) and Co(3) via one oxygen (triply bridging) and to Co(4) via a different oxygen, P(1) is connected to Co(1) and Co(2) via one bridging oxygen, and P(2) is connected to Co(1) and Co(2) via a bridging oxygen. All these linkages then form the secondary building units. The cobalt atoms Co(1), Co(2), Co(3) and Co(4) exhibit severely distorted octahedral geometries, and Co(5) occupies a distorted tetrahedral site. The environment of Co(6) can best be described as a distorted trigonal bipyramid, with the oxygen atoms labeled O(2A), O(8A) and O(14) occupying the trigonal plane and the atoms O(21) and O(10) occupying the axial positions, with an O(21)–Co(6)–O(10) angle of 166.42°.

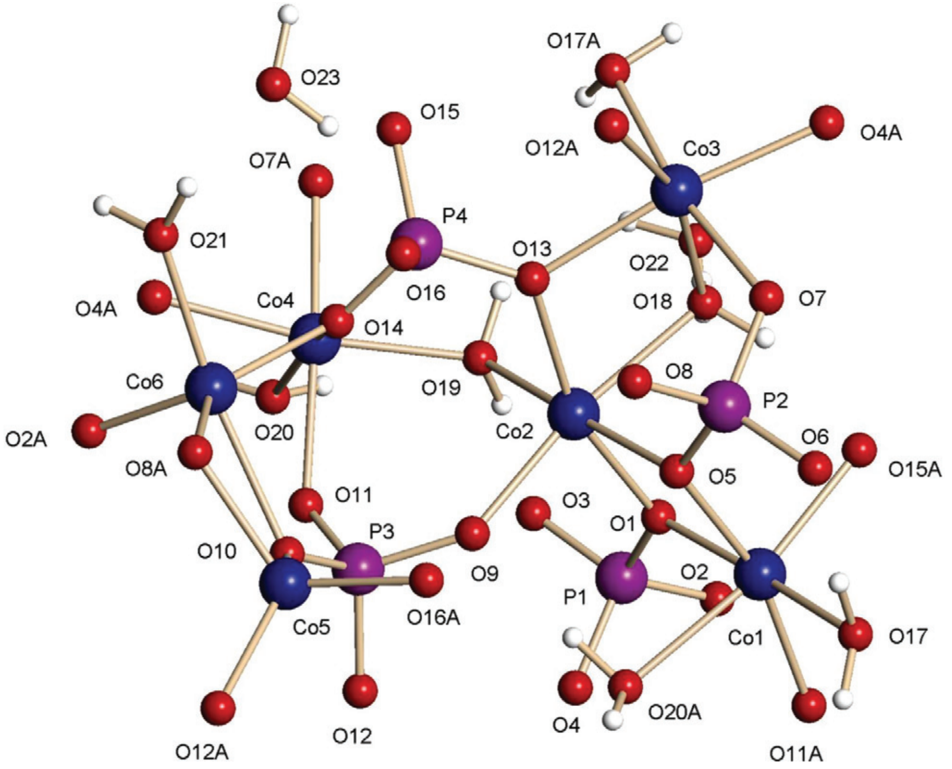

Figure 1. Asymmetric unit of **1** at 100 K.

The secondary building units are connected together by double and triply bridging oxygen atoms of the phosphate tetrahedra and by bridging water molecules to form the 20-member ring channel (MRC) in the unit cell. The view of this unit cell and the 20 MRC is shown in figure 2(a) and a polyhedral drawing is shown in figure 2(b).

3.2. *Spectral and thermal analysis*

The semi quantitative elemental analysis using EDS of **1** confirmed the atom ratio of cobalt to phosphorus as 3 : 2, which is in good agreement with the crystal structure formula $Co_6(PO_4)_4 \cdot 7H_2O$. The IR spectrum, figure 3, exhibits rather sharp bands at 3424 and 1631 cm^{-1}, which can be attributed to the strong O–H bonds of the bridging and free water molecules [24]. The peaks at 1103, 1021, 953(s) and 600–590 cm^{-1}(s) are attributed to the O–P–O and P–O vibrations.

The FTIR spectrum clearly confirms the absence of any organic template molecule (figure 3). The thermo-gravimetric analysis of **1** in the temperature range 30 to 800°C (figure 4) shows a two step weight loss. The first step that translates to less than 1% weight loss started at 100°C and continuously drops to 400°C. This weight loss may be associated with partial loss of the water molecules trapped in the channel, which also corresponds to an endothermic peak in the DSC at about the same temperature (400°C). The second weight loss commenced at about 400°C as a continuous drop,

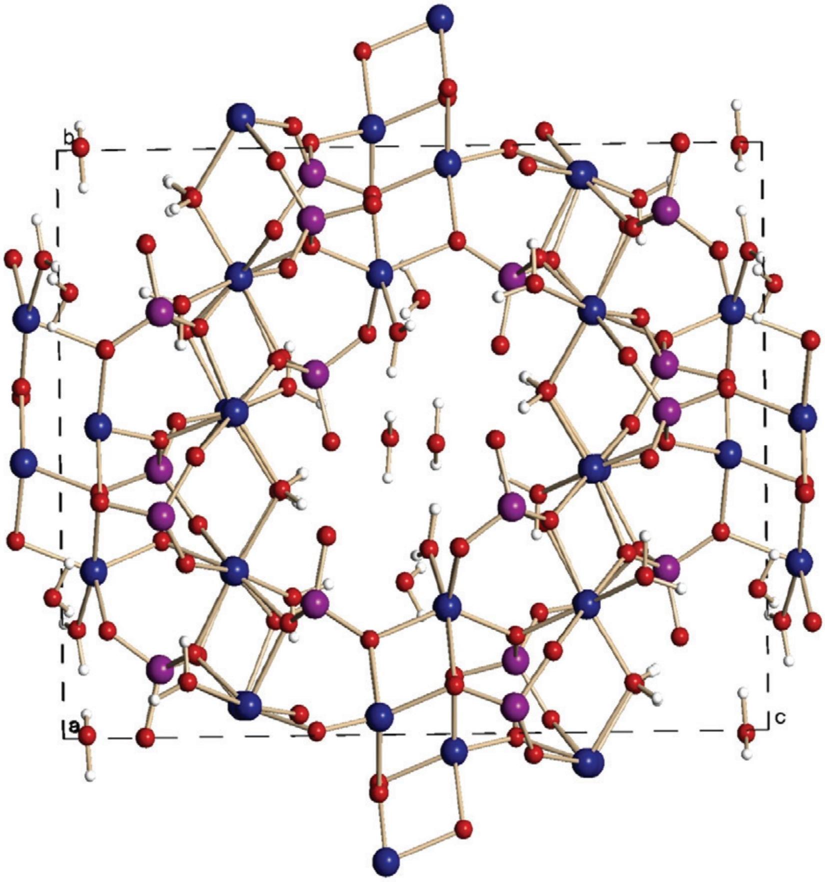

Figure 2a. Structure of **1** viewed along a-axis.

followed by a sharp drop at about 600°C that translates to about 3.4% weight loss. Associated with this sharp drop is an exothermic peak at 546°C and an endothermic peak at about 580°C.

This weight loss at about 600°C, with the associated endothermic and exothermic heat flow, is likely due to total loss of the occluded water, leading to the collapse of the open framework structure. The FTIR sample of the re-hydrated residue supports a completely different structure, especially with the absence of previously observed peaks in the finger print region of the FTIR (1102 cm^{-1}). The total weight loss observed from thermo-gravimetric analysis (4.38%) is lower than the theoretical value of 14.7% one would expect for complete loss of water molecules (5 coordinated H_2O and 2 free H_2O). The complete release of the two water molecules occupying the channel would produce a weight loss of about 4.2%, which is consistent with the observed weight loss after heating the sample to 600°C. At this temperature, there appears to be no loss of the bridging water molecules in the structure. In the thermo-gravimetric analysis on a framework cobalt phosphate structure, $Na_2Co_3(OH)(PO_4)_2 \cdot 0.25H_2O$ reported by Bontchev *et al.*, the occluded water molecules were only released between 400–600°C, and the observed weight loss of 2.02 compared well with the calculated

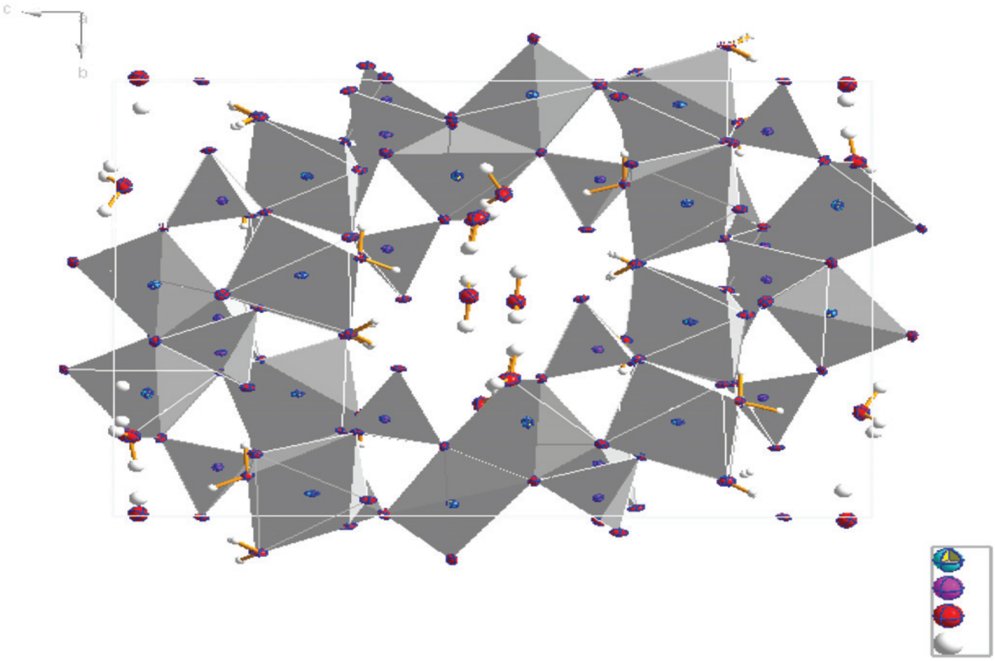

Figure 2b. Polyhedral view of **1**.

value of 1.93% [24]. For **1** the FTIR supports the presence of the OH stretching vibration at 3450 cm^{-1} from the coordinated water. This is expected for coordinated water molecules. However, the IR region below 1600 cm^{-1} shows a change in the material, possibly a collapse of the open framework. The removal of the uncoordinated water molecules would not create large "solvent accessible voids", i.e. using the Platon software [25], the voids created are smaller than the 40 Å^3 assumed for a usual water molecule which implies that the two H_2O molecules are tightly hydrogen bonded. A total collapse of the structure at a temperature above 600°C and a rearrangement to form a new cobalt–phosphate species are indicated by the exothermic peak in the DSC at 548°C and the endothermic peak at about 600°C (figure 5). While this latter step may involve the formation of some other bridging *aqua* species as confirmed by FTIR, the less than 0.1% weight loss does not allow us to associate this to any significant weight change. An isotopic substitution experiment using D_2O did not produce a significant change in the –OH stretching vibrations.

All attempts to synthesize this cobalt phosphate phase using ethylene diamine as the organic template always produced only two different cobalt–zinc phosphate phases: One cobalt–zinc phosphate phase with a 16MR channel, and the other cobalt–zinc phosphate phase resembles the mineral *adamite*.

4. Conclusion

In conclusion, we have synthesized and characterized a novel open framework cobalt phosphate structure, where the structure is based on four, five and six-coordinate cobalt

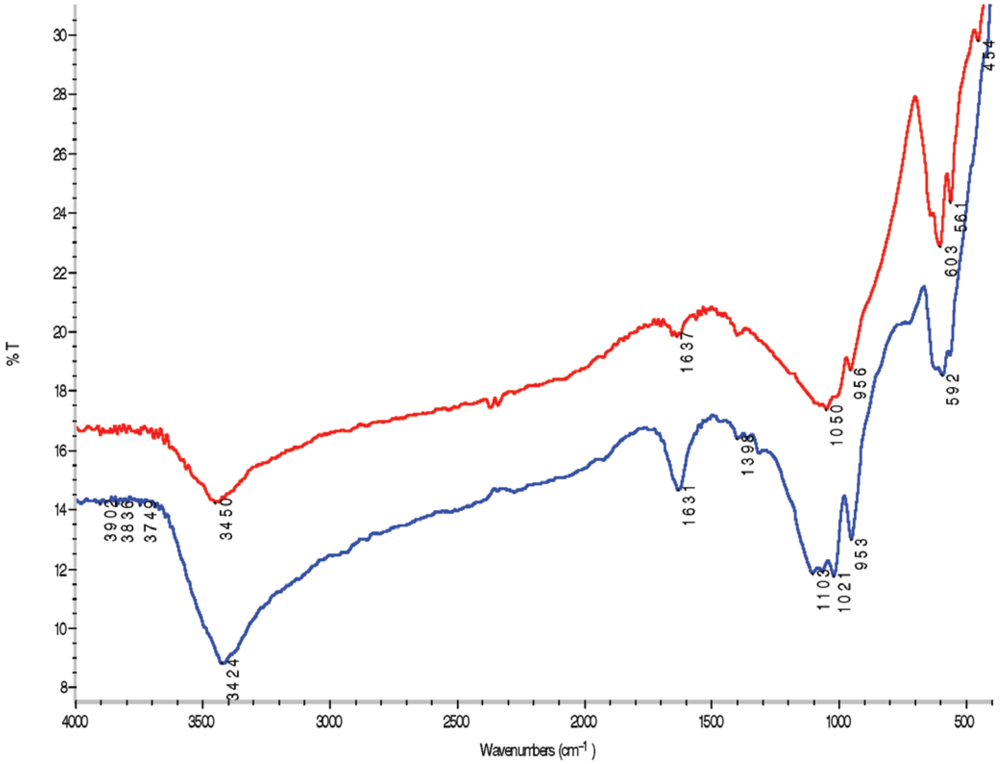

Figure 3. FTIR IR in KBr of (1) before (blue) and after (red) TGA and rehydration in water. The slight differences in the finger print region is indicative of structural differences between the original crystals and the compound formed after rehydration.

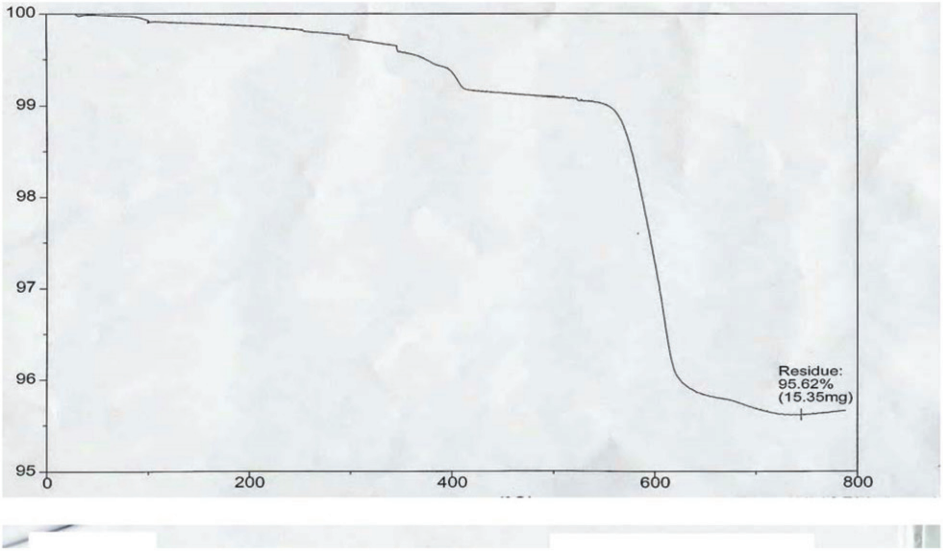

Figure 4. Thermo-graphimetric analysis.

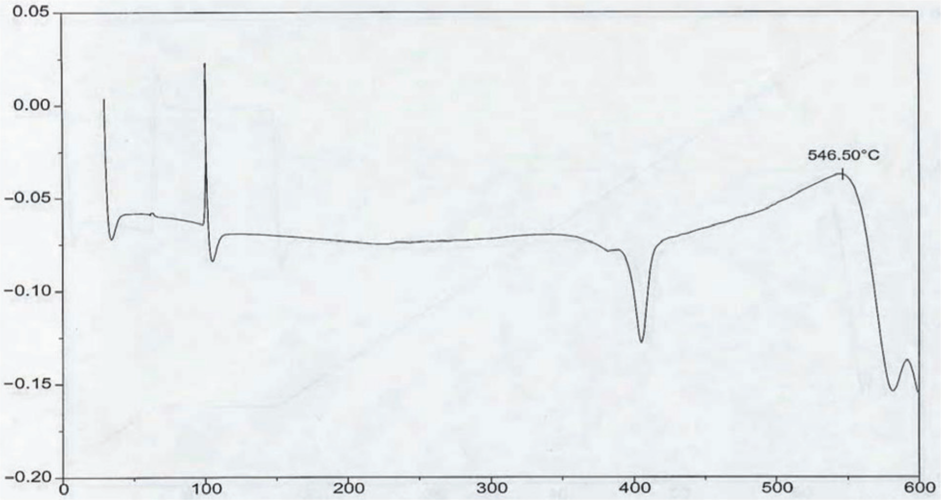

Figure 5. Differential scanning calorimetry.

with bridging water and oxygen from phosphate. The compound shows high thermal stability and may exhibit interesting catalytic properties based on its large 20 MRC and *zeolite* like features. Such investigation is currently underway in our laboratory.

Supplementary material

Detailed X-ray crystallographic data on **1**, has been been deposited with Fachinformationszentrum Karlsruhe (FIZ), Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary materials reference number CSD 416823, and can be obtained by contacting the CCDC/FIZ (quoting the article details and the corresponding SUP number).

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