



# Synthesis and characterization of a new family of alkylammonium–chromium phosphates with worm-like morphology



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## ABSTRACT

A series of layered alkylammonium–chromium phosphates, formulated as  $[C_nH_{2n+1}NH_3]Cr(OH)PO_4$  ( $n=2-6$ ), has been synthesized under hydrothermal conditions. The interlayer spacing, increasing linearly with the increase of alkyl-chain length from 13.61 Å ( $n=2$ ) to 21.20 Å ( $n=6$ ), is occupied by a double sheet of packed amine molecules with a tilt angle of ca. 51° respect to the inorganic sheet. The powders are constituted by circular plates (diameter = 0.5–3 μm, thickness = ~50 nm) with central holes when  $n=4-6$ , stacked in axial direction showing worm-like morphologies. The presence of holes, and some corrugated and zig-zag fashions observed on the edge of thin circular plates are the most probable ways for the reduction of the steric tensions between organic and inorganic portions in these hybrid materials. The thermal and thermo-oxidative stability of selected compounds have been studied, including the determination of activation energy data for the decomposition processes.

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## 1. Introduction

Open-framework metal phosphates constitute an important and versatile class of compounds which have been extensively studied over many decades, in particular layered metal phosphates, because of their many potential applications in the fields of ion-exchange, intercalation, catalysis, ion conduction, and adsorption or separation [1–4]. The wide choice of metals and the large variety of organic amines to be used as structural directing agents or templates suggests the possibility of tailored the structures for specific functions. Recently, investigations of *n*-alkylamine intercalated in layered transitions metal phosphates have yielded exciting structural diversity and controlled morphologies [5–7]. The incorporation of transition elements to the organically templated open-framework phosphates systems is particularly attractive due to the possibility of the variation in the coordination environment of metal ions, as well as, the possibility of observing interesting properties (potential applications in catalysis and separation processes, in addition to the rational design of new materials with properties for particular requirements). Although many such compounds have been prepared using amines as structural directing agents by hydrothermal methods [5,6], to the best of our knowledge, there are few prior reports concerning

amine-intercalated layered chromium(III) phosphates [7–9]. In this work, we present the hydrothermal synthesis and the thermal behaviour of a novel series of alkylammonium–chromium phosphates with worm-like morphologies.

## 2. Material and methods

### 2.1. Synthesis and characterization

The hydrothermal synthesis of alkylammonium–chromium phosphates were carried out in a stainless steel (100 mL) Teflon-line vessel under autogenous pressure. 1 M aqueous solutions of  $CrCl_3$  and  $H_3PO_4$  85% were used as the initial sources of chromium and phosphorous, respectively. The synthetic procedure included the mixing of  $CrCl_3$  and  $H_3PO_4$  solutions with a P:Cr molar ratio of 10:1; then the corresponding amount of pure amine  $C_nH_{2n+1}NH_2$  ( $n=2-6$ ) is added with a *n*-alkylamine:P molar ratio of 1:1. The reaction mixture (total volume 40 mL) was sealed and heated at 180 °C for 7 days. The obtained solid was filtered off, washed with an excess of distilled water and dried at room temperature. Microanalytical data (C, H and N) were obtained with an elemental model Vario MACRO elemental analyzer. The phosphorous and chromium contents were determined with a SpectraSpectrometer DCP-AEC after dissolving a weighted amount of sample in HF(aq). The elemental analysis results for the all synthesized compounds

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**Table 1**  
Analytical data for  $[C_nH_{2n+1}NH_3]Cr(OH)PO_4$  ( $n=2-6$ ) compounds.

n	Calculated					Experimental				
	%C	%N	%H	%P	%Cr	%C	%N	%H	%P	%Cr
2	11.42	6.66	4.28	14.76	24.76	12.8	7.3	4.9	14.9	24.9
3	16.07	6.25	4.91	13.83	23.21	15.8	6.0	5.2	14.1	23.8
4	20.16	5.88	5.46	13.02	21.84	21.2	6.0	5.9	13.5	22.1
5	23.80	5.55	5.95	12.30	20.63	23.7	5.1	5.6	12.8	20.9
6	27.06	5.26	6.39	11.65	19.54	27.0	5.2	6.2	11.2	19.0

are presented in Table 1. A good agreement between the experimental and calculated values is observed in all cases.

The infrared spectrum was collected at room temperature using FT-IR Bruker Tensor-27 spectrometer from KBr pellets over the range  $4000-400\text{ cm}^{-1}$  by averaging 15 scans at a maximum resolution of  $4\text{ cm}^{-1}$ . The powder X-ray diffraction pattern was recorded on X'pert Panalytical diffractometer with Cu-K $\alpha$  radiation ( $\lambda=1.5418\text{ \AA}$ ). The sample was gently ground in an agate mortar in order to minimize the preferred orientation. Micrographs and X-ray microanalysis (SEM/EDX) were recorded with a JEOL JSM-6100 electron microscope operating at 20 kV coupled with an INCA Energy-200 energy dispersive X-ray microanalysis system (EDX) with Oxford PentaFET ultrathin window detector. The TEM studies were performed on a JEOL JEM-2100F field emission transmission electron microscope operated at an accelerating voltage of 200 kV and equipped with an ultra-high resolution pole-piece that provided a point-resolution better than 0.19 nm. Fine powder of the sample was dispersed in ethanol, sonified and sprayed on a carbon coated copper grid, and then allowed to air-dry. Finally, SOLARUS 950 was used before observation.

## 2.2. Thermal analysis

A Mettler-Toledo equipment (TGA/SDTA851<sup>e</sup> and DSC822<sup>e</sup>) were used for the thermal analyses in both nitrogen and oxygen dynamic atmosphere (50 mL/min) at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . In TG test, a Pfeiffer Vacuum ThermoStar<sup>TM</sup> GSD301T mass spectrometer was used to determine the evacuated vapours. The masses  $m/z$  15 ( $\text{NH}_3$ ), 18 ( $\text{H}_2\text{O}$ ), 44 ( $\text{CO}_2$ ), 46 ( $\text{NO}_2$ ), 87 ( $\text{C}_5\text{H}_{11}\text{NH}_2$ ) and 101 ( $\text{C}_6\text{H}_{13}\text{NH}_2$ ) were tested by using a detector C-SEM, operating at 1200 V, with a time constant of 0.5 s.

The kinetics of conversion in solids are usually described by Eq. (1), where  $f(\alpha)$  is the reaction model,  $\alpha$  is the extent of conversion, which is determined experimentally as a fraction of the total mass loss in the process,  $k(T)$  is the Arrhenius rate constant,  $T$  is the temperature, and  $t$  is the time. Then, the rate of a solid-state reaction can be generally described by Eq. (2), where  $A$  is the pre-exponential factor,  $E$  the activation energy, and  $R$  the gas constant. The above rate expression can be considered as a function of temperature getting Eq. (3), where  $\beta$  is the heating rate. It is well known that the ambiguity of the kinetic triplet ( $E, A, f(\alpha)$ ) creates difficulties for predicting the behaviour of compounds over the range of experimental temperatures. This ambiguity can be overcome by using model-free isoconversional methods which allow estimating the activation energy as a function of  $\alpha$ , without the need to specify neither the reaction model nor the pre-exponential factor. The basic assumption of these methods is that the reaction rate for a constant extent of conversion,  $\alpha$ , depends only on temperature [10–13]. Constant  $E$  values can be expected in the case of single state decomposition while in a multistep process  $E$  varies with  $\alpha$  due to changes in the relative contributions of each single step to the overall reaction rate. The KAS method [14,15]

uses Coats–Redfern [16] approximation of the temperature integral that leads to Eq. (4). The integral form of the model function  $f(\alpha)$  is given by  $g(\alpha)$ . Thus, for  $\alpha=\text{const.}$ , a plot of  $\ln(\beta/T^2)$  versus  $1/T$ , obtained from thermal curves recorded at several heating rates, is a straight line whose slope allows evaluation of the activation energy. Three different heating rates were used in this study ( $\beta=5, 10, \text{ and } 20\text{ }^\circ\text{C}/\text{min}$ ).

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

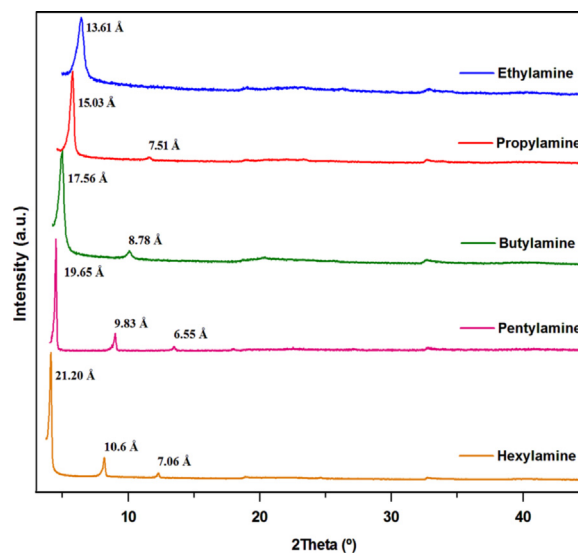
$$d\alpha/dt = A \exp(-E/RT)f(\alpha) \quad (2)$$

$$d\alpha/dT = (A/\beta)\exp(-E/RT)f(\alpha) \quad (3)$$

$$\ln(\beta/T^2) = \ln(AR/Eg(\alpha)) - (E/RT) \quad (4)$$

## 3. Results and discussion

First of all, it is important to mention that the hypothetical compound with methylamine  $[\text{CH}_3\text{NH}_3]\text{Cr}(\text{OH})\text{PO}_4$  was not obtained. Such behaviour is already known when the methylamine is used in the liquid phase synthesis or by exposing the solid to the methylamine vapour. In the case of liquid phase synthesis, the particles of the desired compound do not crystallize, whereas *via* vapour interaction, it leads to the complete amorphization of the compounds. For example, in the case of the liquid phase synthesis, the intercalation of  $\gamma\text{-Ti}(\text{H}_2\text{PO}_4)(\text{PO}_4) \cdot 2\text{H}_2\text{O}$  with methylamine in



**Fig. 1.** Powder X-ray diffraction patterns of  $[C_nH_{2n+1}NH_3]Cr(OH)PO_4$  ( $n=2-6$ ) compounds.

**Table 2**

Interlayer distance ( $d$ , in  $\text{\AA}$ ) for  $[C_nH_{2n+1}NH_3]Cr(OH)PO_4$  ( $n=2-6$ ) compounds obtained from PXRD data, and associated free area ( $A_F$ , in  $\text{\AA}^2$  per H-atom) at each acid centre on the basal plane assuming that the packing parameter is 1.

Intercalated amine	n	d	$A_F$
Ethylamine	2	13.61	24.60
<i>n</i> -Propylamine	3	15.03	25.58
<i>n</i> -Butylamine	4	17.56	23.40
<i>n</i> -Pentylamine	5	19.65	23.24
<i>n</i> -Hexylamine	6	21.20	24.20

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