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Synthesis, characterization and thermal behavior of tetrakis(melamine^{2+}) bis(melamine^{+}) pentakis(monohydrogenphosphate) tetrahydrate

Hakima Ait Youcef [a, *], Salah Chafaa [a], Rachida Doufnoune [b], Tahar Douadi [a]

[a] Laboratoire d'Electrochimie des Matériaux Moléculaires et des Complexes (LEMMC), Département de Génie des procédés, Faculté de Technologie, Université Ferhat Abbas, Sétif-1, 1900, Algeria
[b] Unité de Recherche sur les Matériaux Emergeants-Sétif-URMES, Equipe de Valorisation des Matériaux Polymériques, Université Ferhat Abbas, Sétif-1, Algeria

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ABSTRACT

A new organic–inorganic salt, tetrakis (2,4,6-triamino-1,3,5-triazin-1,3-diium) bis (2,4,6-triamino-1,3,5-triazin-1-ium) pentakis (monohydrogenphosphate) tetrahydrate, $4C_3H_8N_6^{+2}$. $2C_3H_7N_6^{+}$. $5HPO_4^{2-}$. $4H_2O$ was synthesized through the reaction of melamine and phosphoric acid in an acidic medium HCl/H_2O. It was then characterized by X-ray diffraction. The title compound crystallizes in monoclinic system with non-centrosymetric space group P 21 with lattice parameters $a = 11.3008$ Å, $b = 20.9798$ Å, $c = 12.2679$ Å, $\alpha = 90°$, $\beta = 117.236°$, $\gamma = 90°$, $Z = 2$ and $V = 2586.10$ (Å)^3. The UV–vis absorption spectrum UV–vis showed that the crystal has a good optical transmittance in the entire visible region with a lower cut off wavelength of 290 nm. The vibrational frequencies of various functional groups present in the crystal were identified by FT-IR analysis. The chemical structure of the compound was also confirmed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. TGA-DTA analysis revealed that the materials have a good thermal stability without any melting.

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1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) and its derivatives are widely used as industrial chemicals in the manufacture of dyes, plastics, fertilizers, textiles and its polymers play an important role in technological applications. If used in polymeric like epoxy resins, cellulose or flax fibers, melamine acts as a flame retardant [1–6]. The recent toxicological and pharmacological investigations explored nephrotoxicity, crystal formation in kidney and renal toxicity induced by melamine or its derivatives [7,8].

Melamine is an organic base which is able to form stable salts with most organic and inorganic acids. Many of these salts, such as those with boric acid, phosphoric acid, polyphosphoric acid, cyanuric acid, and sulfuric acid, are either commercial or have the potential to be viable as flame-retardant additives.

Several researchers have already studied the thermal behavior of melamine and its salts [9–12]. The presence of triazine ring in their structure gives improved hydrolytic and thermal stability [6]. Melamine and its salts are widely used in the formulation of fire retardant additive systems for polymeric materials [13–15]. Melamine also readily forms insoluble adducts with many organic and inorganic acids [16,17]. Thermal and flame retardation properties of melamine phosphate-modified epoxy resins were studied by Chen et al. [18]. As a continuation of these studies we synthesized a new complex of phosphonic acid with melamine as a crystal.

Melamine phosphates are considered to be attractive alternatives to halogen-containing flame-retardants because the latter release toxic and corrosive gases during combustion. The advantages of the flame-retardant characteristics of melamine phosphates materials are mainly attributed to an enhanced thermal stability [19,20], so an elucidation of their packing characteristics is particularly important.

Melamine is an interesting molecule in the field of crystal engineering [21–23] and supramolecular chemistry [24–30]. Crystals of melaminium salts exhibit interesting properties. Some melamine salts exhibit nonlinear optical behavior [31–33] like second harmonic generation (SHG). Melamine family crystals have over the years been subjected to extensive investigation by several

* Corresponding author.
E-mail address: hakimaaityoucef@yahoo.fr (H.A. Youcef).

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researchers for their nonlinear optical properties.

Crystals of melaminium selenate with non-centrosymmetric space group are optically active and generate the SHG [32]. High efficiency of SHG is observed in the crystals of double protonated melaminium bis(trichloroacetate) dihydrate [34]. Another non-centrosymmetric crystal of melaminium phosphate may also be used as a material for non-linear optics [35].

Many studies were performed to explain the behavior of melamine molecule in the solid state [36–42]. Generally, the solid state complexation of melamine with different organic and inorganic (mineral) acids has an interesting aspect. Particularly the hydrogen bonded system, which comprises most frequently the weak hydrogen bonds of N–H···O and O–H···O types [43–47].

Compounds containing partially protonated melaminium cations (M^{+}, M^{2+}) combined with different organic and inorganic counter ions have been reported. For the crystalline melamine and its organic or inorganic salts, most crystals contain only one melamine moiety, i.e. the neutral molecule, single or double protonated melaminium cations [25–33].

It is especially important to notice that X-ray experiments are not sufficiently sensitive to the presence of hydrogen participating in such intermolecular interactions as the precise localization of hydrogen bonds is difficult and even impossible sometimes (for very strong hydrogen bonds).

In this work, we have synthesized a new melaminium salt, namely: tetrakis (2,4,6-triamino-1,3,5-triazin-1,3-diium) bis (2,4,6-triamino-1,3,5-triazin-1-ium) pentakis (monohy-drogenphosphate) tetrahydrate, $4C_3H_8N_6^{+2}$. $2C_3H_7N_6^{+}$. $5HPO_4^{2-}$. $4H_2O$ (which will be referred to as 4 $M^{+2}2M^{+}5P$ $4H_2O$) as a crystal, and its structure has been determined by X-ray diffraction. To establish the chemical structure of $4M^{+2}2M^{+}5P$ $4H_2O$, FT-IR spectroscopy and NMR studies have also been carried out. The thermal decomposition behavior of the title compound has been studied by means of thermogravimetric analysis.

2. Experimental

2.1. Synthesis

$4M^{+2}2M^{+}5P4H_2O$ compound was synthesized by the chemical reaction of a commercially available melamine with phosphoric acid (Aldrich, purity: 99% and 85% respectively). These chemicals were used as supplied in a molar ratio of 1:6. To the hot aqueous solution of melamine, phosphoric acid solution was added slowly and the mixture was heated and kept at a minimum temperature of 80 °C under continuous stirring. Then a 10% solution of HCl was added drop-wise to the mixture reaction and stirred continuously to get the homogenous solution. The progress of the reaction was monitored by TLC analysis. After 4 h, a white precipitate was formed. The mixture was filtered and then allowed to cool, and the purity of the synthesized salt was further improved by a re-crystallization process. Tiny white crystals of the title compound were obtained after a period of time ranging from two to three weeks. The reaction scheme and the photograph of the grown crystal are shown in Fig. 1 and Fig. 2.

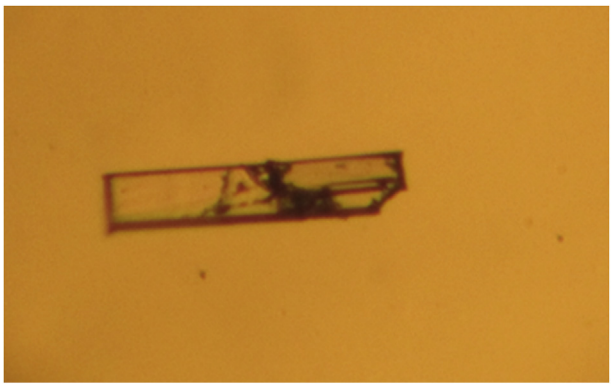

Fig. 2. Photograph of Melaminium pentakis(monohydrogenphosphate) tetrahydrate.

2.2. Characterization

The grown crystal of the title compound was subjected to single crystal XRD analysis using a Bruker AXS BV CCD diffractometer equipped with the graphite monochromator and using MoKα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by the SHELXS-97 direct methods and refined by the full-matrix least square method using the SHELXL-97 program [48]. Anisotropic thermal factors were determined for all non-hydrogen atoms. Unit cell refinement using all observed reflections and data reduction were performed using SAINT. All crystallographic parameters were deposited in the CCDC. The UV–Visible spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate was recorded between 200 and 800 nm using a Perkin Elmer Lambda 650 Spectrophotometer, the sample for this measurement was finely grounded and mixed with KBr. The FT-IR spectrum was recorded using Bruker FT-IR spectrometer in the region 4000–400 cm^{-1} at room temperature using the KBr pellet technique and each IR spectrum was acquired in 10 scans at 2 cm^{-1} resolution. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra of the title crystal were recorded using DMSO-d_6 as solvent on a Bruker Avance III 400 MHz spectrometer at room temperature. The thermal behavior of the crystal was determined by thermogravimetric analysis and differential thermal analysis using a Perkin Elmer TGA 4000 at a heating rate of 10 °C/min in a nitrogen atmosphere (50 ml/min) at the temperature range over 30–900 °C.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The single crystal XRD data of the title crystal indicates that it crystallizes in a monoclinic system with non-centrosymetric space group P 21 and Z = 2. The crystal structure parameters are a = 11.3008 Å, b = 20.9798 Å, c = 12.2679 Å, $\alpha = 90°$, $\beta = 117.236°$, $\gamma = 90°$. In accordance with the crystallographic data, during the complex formation, the acidic protons of phosphoric acid were transferred into the melamine molecules giving single protonated melaminium cations, and double protonated melaminium cations.

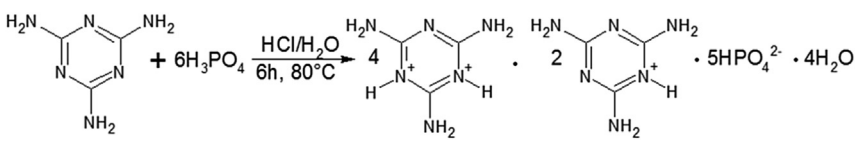

Fig. 1. Reaction scheme for the synthesis of Melaminium pentakis(monohydrogenphosphate) tetrahydrate.