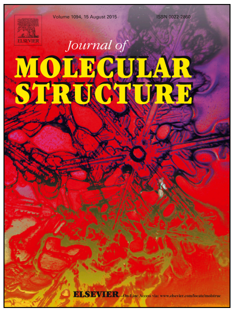

Synthesis, characterization and thermal behavior of tetrakis(melamine^{2+}) bis(melamine^{+}) pentakis(monohydrogenphosphate) tetrahydrate

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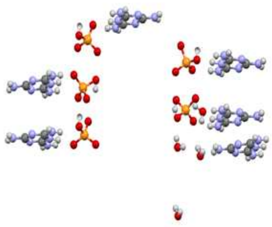

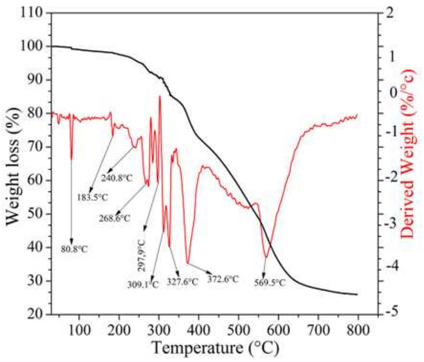
Weight loss (%)
Derived Weight (%/°c)
Temperature (°C)
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100
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100
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500
600
700
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80.8°C
183.5°C
240.8°C
268.6°C
297.9°C
309.1°C
327.6°C
372.6°C
569.5°C

Synthesis, Characterization and Thermal Behavior of Tetrakis(Melamine^{2+}) Bis(Melamine^{+}) Pentakis(monohydrogenphosphate) Tetrahydrate

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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=11.3008Å, b = 20.9798 Å, c=12.2679 Å, α=90°, β=117.236°, γ=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.

Keywords: Melamine; phosphoric acid; X-ray crystallography; FT-IR; FT-NMR; Thermal analysis (TGA & DTA).

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 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 (monohydrogenphosphate) tetrahydrate, $4C_3H_8N_6^{+2}$. $2C_3H_7N_6^{+}$. $5HPO_4^{2-}$. $4H_2O$ (which will be referred to as $4M^{+2}2M^{+}5P\ 4H_2O$) 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 hours, 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.

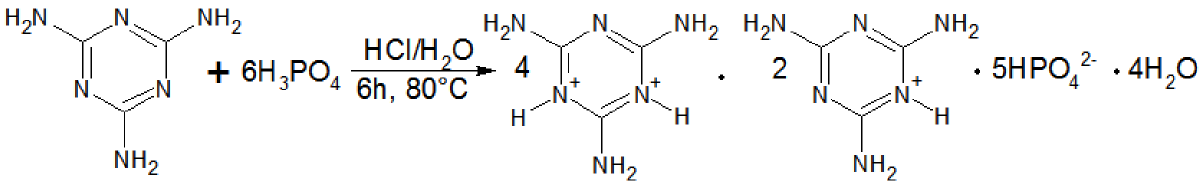

Fig. 1. Reaction scheme for the synthesis of Melaminium pentakis(monohydrogenphosphate) tetrahydrate.

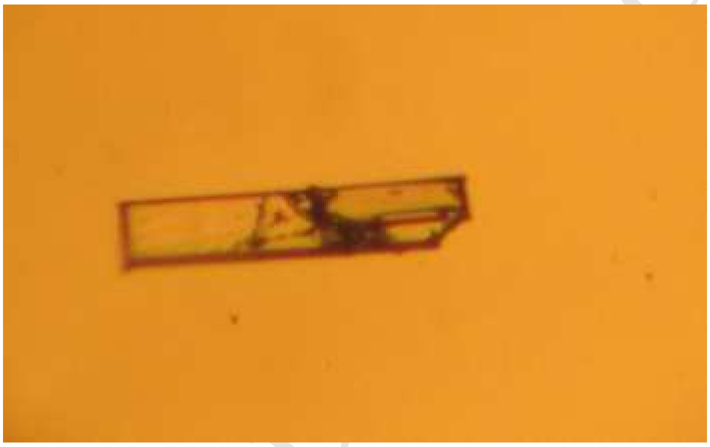

Fig. 2. Photograph of Melaminium pentakis(monohydrogenphosphate) tetrahydrate.

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 200–800 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 thermo gravimetric 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, α = 90°, β = 117.236°, γ = 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. The unit cell structure of melaminium penta monohydrogenephosphate tetrahydrate is shown in Fig. 3. The asymmetric unit contains two formal molecules which consist of two single protonated melaminium cations, four double protonated melaminium cations, five monohydrogen phosphate anions and four molecules of water. The crystal data and structure refinement details are given in Table 1. The detailed fractional atomic coordinates and equivalent isotopic displacement parameters were deposited in CCDC with the number 981733.

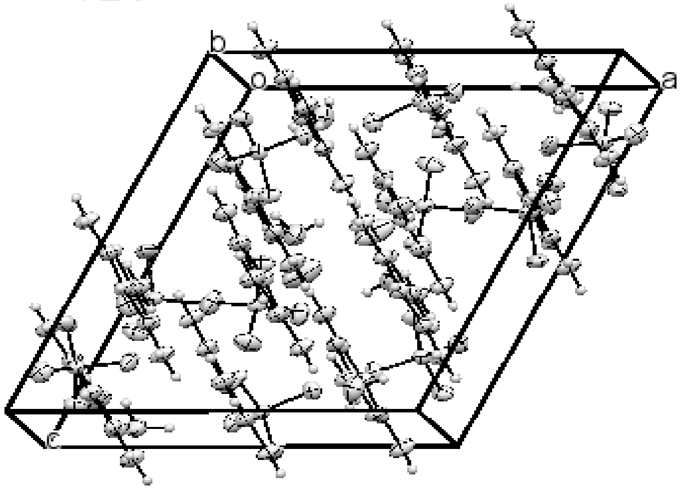

Fig. 3. Packing of the molecules in elementary unit cell.

It is to be noted that, compounds containing partially protonated melaminium cations (M^+ and M^{2+}) combined with different organic and inorganic counter-ions are widely reported [25-28,49-55]. In studies of the crystalline melamine and its organic or inorganic salts, most crystals contain only one melamine form, i.e. the neutral molecule combined with single or double_protonated melaminium cations [30,56,57]. In this paper we describe the structure of single protonated (M^+) and double protonated (M^{2+}) crystal.

3.2 Optical absorption analysis

Efficient nonlinear optical crystals have an optical transparency and lower cutoff wavelength between 200 and 300 nm [58]. The absorption spectrum of $4M^{+2}2M^{+}5P4H_2O$ crystal is shown in **Fig. 4**.

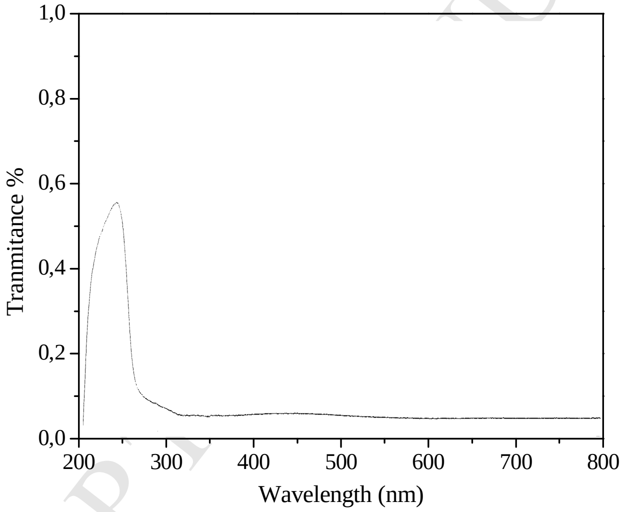

Fig. 4.UV–Vis spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

The lower cut off wavelength of $4M^{+2}2M^{+}5P4H_2O$ crystal was found to be at 290 nm. There is a strong absorption at 245 nm due to nitrogen-containing aromatic systems or an electronic excitation in this region [59,60]. In general, the absorption peaks of benzene appear mainly around 200 nm, also and require greater energy than that required for π-π^* transition and hence its absorption shows the blue end of the spectrum [60]. It is seen from the absorption spectrum that the absorption is minimum between 260 and 800 nm and the lower cut off wavelength is 290 nm which is sufficient for laser frequency doubling and other related opto-electronic applications in the ultra violet and visible region.

3.3 FT-IR analysis

The functional groups present in the synthesized compounds can be easily identified using The Infrared spectroscopy. The recorded FT-IR spectrum of $4M^{+2}2M^{+}5P4H_2O$ crystal is presented in Fig. 5.

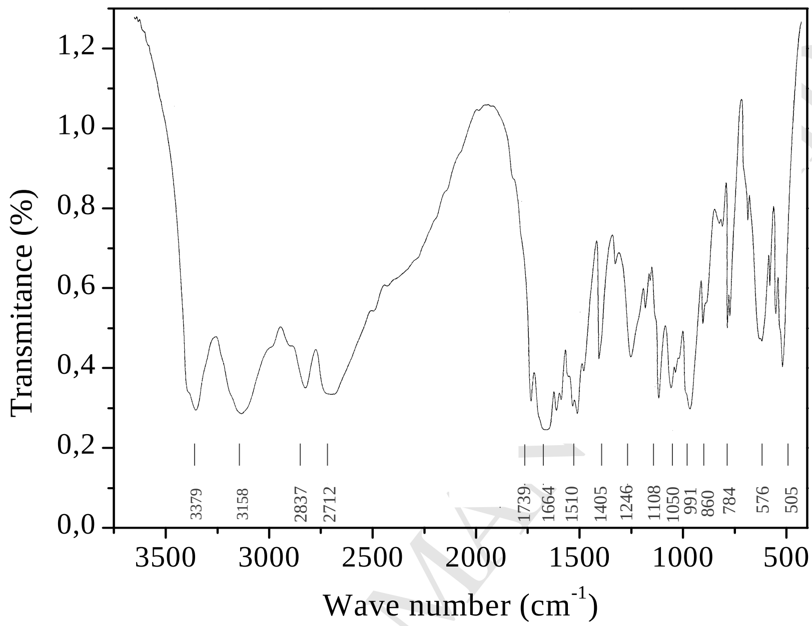

Fig. 5. FTIR spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

The characteristic frequency of the functional groups present in the title crystal were assigned and are presented in Table 2. The bands observed in the measured region arise from internal vibrations of melaminium cations, monohydrogenphosphate anions and water molecules. Melaminium residues often form hydrogen bonds of N–H···N and N–H···O types. The NH_2 groups interact with the acid residue through weak N–H···O hydrogen bonds. The band observed at 3420 cm^{-1} in the infrared spectrum is due to the OH stretching of water molecules [61]. The strong and broad band observed at 3379 cm$^{–1}$ is ascribed to NH_2 symmetric stretching vibrations, while the broad band at 3158 cm^{-1} is attributed to N–H···O and N–H···N stretching. The two IR broad bands at 2837 cm$^{–1}$and 2712 cm$^{–1}$ are assigned to NH_2 asymmetric stretching [36] and P–OH stretching of the hydrogen bonded to the PO4 units[62]. The medium band at 2354 cm^{-1} is due to the vibrations of the hydrogen bond formed by water molecules [63,64]. The sharp and broad infrared bands at 1739 cm^{-1} and 1664 cm^{-1} are assigned to NH_2 bending [36]. The bands at 1510 cm^{-1} and 576 cm^{-1} are attributed to the side chain asymmetric C–N stretching and in plane C–N bending vibration

[36]. The medium strong band at 1405 cm^{-1} is due to the semi-circle stretching vibrations mechanically coupled with exogenous C–N contract and NH bending vibration [40,41]. The medium sharp bands at 1246 cm^{-1}, 1108 cm^{-1} and 860 cm^{-1} are ascribed to the stretching vibration of P=O, P–O and P–O(H) bonds respectively. These three frequencies indicated the presence of an $(HPO_4)^{-2}$ entity in the structure of the compound [65]. The band at 1050 cm^{-1} was assigned to triazine ring breathing [36,39], while the band at 991 cm^{-1} was attributed to triazine ring N, in-plane radial type of vibration [40,41]. This band appeared for all melamine complexes. The medium strong band at 784 cm^{-1} is due to ring-sextant out of plane bending vibration [36].

3.4 FT-NMR analysis

The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra are presented in Fig. 6, Fig. 7 and Fig. 8 respectively.

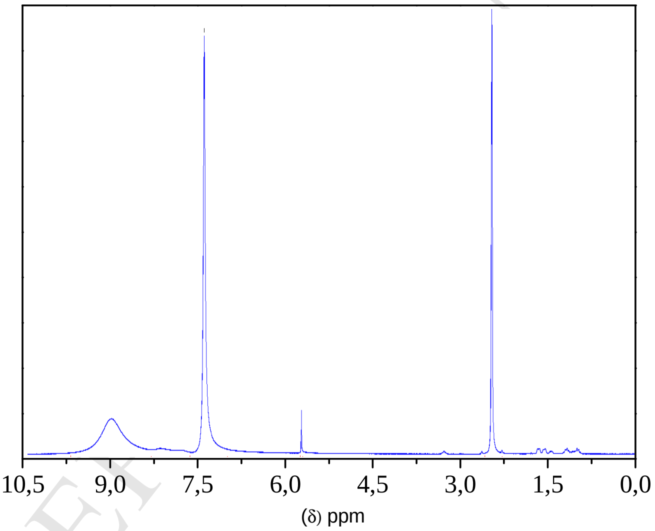

Fig. 6. ^{1}H NMR spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

In the ^{1}H NMR spectrum of melamine in DMSO-d$_6$, all the NH_2 groups give a single signal at 6.20 ppm. This peak was shifted to 7.409 ppm in the present case and this could be due to the addition of phosphoric acid [66]. A broad signal appears at 8.985 ppm and can be attributed to NH proton of the ring. The broadening of the signal may be due to the involvement of protons in hydrogen bonding with the monohydrogenphosphate oxygen P=O. The peak at 2.5 ppm is due to residual protons of deuterated DMSO-d$_6$. The chemical shift of the proton in –OH and NH_2 groups depends upon the temperature, solvent, concentration and the neighboring groups. The (phosphoric) –OH proton gives a singlet at 5.752 ppm.

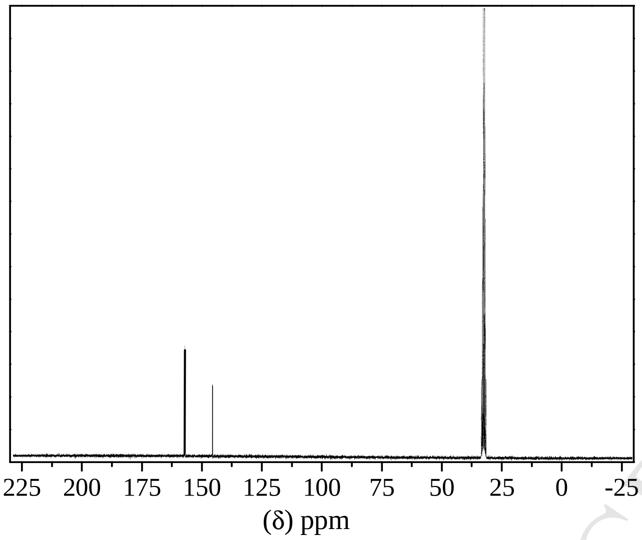

Fig. 7. ^{13}C NMR spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

The ^{13}C NMR spectrum shows that, the signals at 146.655 and 157.452 ppm are due to carbon atoms of melamine^{+} and melamine^{2+} molecules with the same environment respectively. A septet of signals observed around 40 ppm is due to the DMSO-d$_6$ solvent.

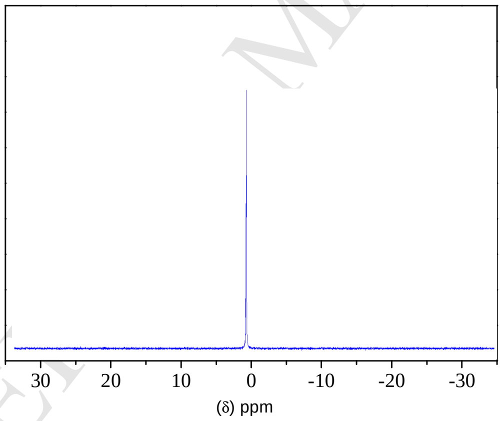

Fig. 8. ^{31}P NMR spectrum of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

The ^{31}P NMR spectrum contains only one single signal at 0.020 ppm and is due to the proton in the OH group attached to the phosphorus atom of monohydrogenphosphate. As no other peaks are observed, it is clear that the compound has been successfully synthesized and this suggests that it is a pure material.

3.5 Thermal analysis

The TGA and DTA traces of 4M^{+2}2M^{+}5P4H$_2$O are shown in Fig. 9. These thermograms were recorded to evaluate the thermal stability of the salts.

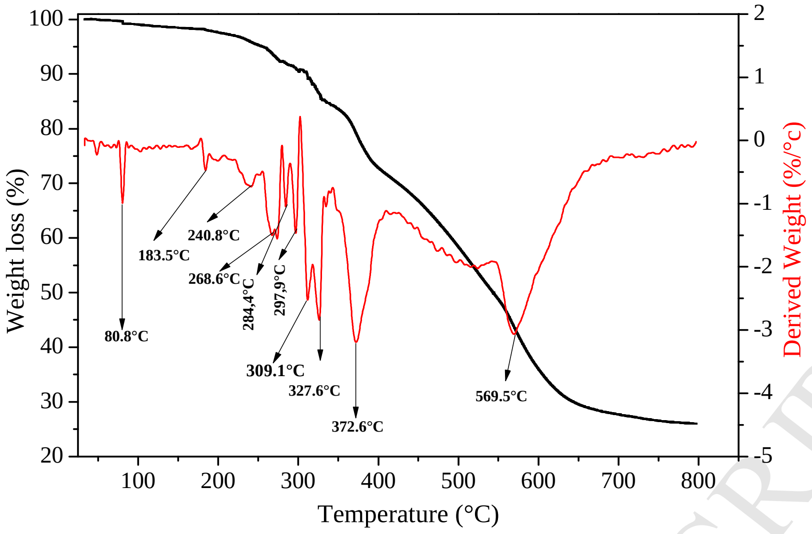

Fig. 9. TGA-DTA thermograms of melaminium pentakis(monohydrogenphosphate) tetrahydrate.

These thermograms show that the decomposition of the title compound takes place through four stages involving dehydration and decomposition. The first weight loss_region is due to anhydrous salt formation. Moreover, the first stage of decomposition takes place in the temperature range from 78.3 °C to 85.71 °C with a small weight loss of 0.45 % suggesting that hydrated water of $4M^{+2}2M^{+}5P4H_2O$ is eliminated from the structure of the compound. The corresponding DTA peak occurs at 80.8 1°C. The second and third stages of the decomposition takes place in the temperature ranges from 223.15 °C to 289.73 °C and from 290.1 °C to 405.93 °C with a significant weight loss of 5.31 % and 19.53 % accompanied by an elimination of melaminium^{+} and melaminium^{2+} cations. These stages are evidenced by seven exothermic peaks. These corresponding DTA peaks appear at 240.8, 268.6, 284.4, 297.9, 309.1, 327.6 and 372.6 °C. The last stage of decomposition which takes place in the temperature range from 405.93 °C to 643.52 °C with a significant weight loss of 42.10 % accompanied by a DTA peak at 569.5 °C is due to the elimination of monohydrogenphosphate anions with a final residue of 25 %.

The DTA thermogram shows an exothermic peak at about 183.5 °C which is the phase transition where the four water molecules are eliminated in this stage.

4. Conclusion

A new compound melaminium phosphate $4M^{+2}2M^{+}5P4H_2O$ was synthesized using melamine as the starting material. The single crystal obtained by a re-crystallization process in water at room temperature and its structure was investigated by means of the single crystal X-ray diffraction method. It has a white color and belongs to a non-centrosymmetric system P 21 with a prism geometry. The optical transmission analysis showed that the grown crystals were optically transparent and the lower cut off wavelength is 290 nm. The FT-IR spectrum clearly indicated the presence of functional groups in the complex. Several stretching and deformation modes confirmed the presence of extensive intermolecular hydrogen bonding in the crystal. FT-NMR spectrum analysis confirmed the molecular structure of the compound. TGA-DTA results indicated that $4M^{+2}2M^{+}5P4H_2O$ has a better thermal stability which makes it suitable for thermal applications. Moreover these complexes are very promising light emitting materials due to their good thermal stability. Further research has to be carried out and can be extended to several industrial and research applications.

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Figures captions:

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

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

Fig. 3. Packing of the molecules in elementary unit cell.

Fig. 4. UV–Vis spectrum of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Fig. 5. FTIR spectrum of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Fig. 6. ^{1}H NMR spectrum of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Fig. 7. ^{13}C NMR spectrum of melaminium pentakis (monohydrogenphosphate) tetrahydrate

Fig. 8. P NMR spectrum of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Fig. 9. TGA-DTA thermograms of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Tables captions:

Table 1

Crystallographic data and structure refinement parameters of melaminium pentakis (monohydrogenphosphate) tetrahydrate

Table 2

Vibration band assignment of melaminium pentakis (monohydrogenphosphate) tetrahydrate

Table 1

Crystallographic data and structure refinement parameters of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

Empirical formula	$4C_3H_8N_6^{+2}.2C_3H_7N_6^{+}.5HPO_4^{2-}.4H_2O$
Formula weight (g/mol)	1318.79
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.3008 (10)
b (Å)	20.9798 (2)
c (Å)	12.2679 (10)
α (°)	90
β (°)	117.2360 (10)
γ (°)	90
Temperature (K)	293 (2)
V (Å3)	2586.10 (4)
Z	2
λ $M_0K\alpha$ (Å)	0.71073
D_{calc} (Mg /m)	1.629
μ (mm^{-1})	0.291
F(000)	1338
Crystal size (mm^3)	0.1 x 0.1 x 0.1
Crystal colour/habit	White/ prism
θ Range (°)	5.12–27.50
hkl ranges	-14/14, -27/26, -15/15
Absorpt. correct. (T_{min}; T_{max})	0.971/0.971
Reflections collected/unique	11513/11513[R_{int}=0.0000]
Completeness to $2\theta = 27.50$	99.0%
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	11513/1/768
Goodness-of-fit on F^2	1.014
Final R indices[I>2σ(I)]	R_1= 0.0314, wR_2 = 0.0838
R indices (all data)	R_1= 0.0301, wR_2 = 0.0825
Largest difference peak and hole (*e*/Å3)	+0.387, -0.343
Independent reflections	6030

Table 2

Vibration band assignment of melaminium pentakis (monohydrogenphosphate) tetrahydrate.

FT-IR (Wave number cm^{-1})	Assignments	References
3420	O–H stretching of water	[61]
3379	NH_2 symmetric stretching	[36]
3220	O–H···O stretch	
3158	N–H···O and N–H···N stretching	
3020	O–H···O and N–H···O asymmetric stretching	
2837	Combination tone: NH_2 asymmetric stretch-side chain out of plane C–N bend	[36]
2712	P–OH stretching	[62]
2500	O–H···O stretch	
2430	O–H···O stretch, with water molecule	
2340	Vibrations of hydrogen bonds formed by water molecules	[63,64]
1739	NH_2 bending type of vibration	[36]
1680	H_2O in plane bend	[63]
1664	NH_2 bending	[36]
1620	Ring: quadrant stretching; NCN bend + ring deformation	[40] [39]
1584	H_2O in plane bend	[63]
1538	Side-chain asymmetric C–N stretching	[36]
1510	Side-chain asymmetric C–N stretching	[36]
1490	N–H deformation vibration	
1405	Ring: semi-circle stretching + exogenous C–N contract	[40,41]
1333	Ring: semi-circle stretch	[41]
1246	P=O stretching	[65]
1150	NH_2 rocking	[36]
1108	P–O asymmetric stretching	[66]
1050	Triazine ring vibration breath	[36]
1021	P–O symmetric stretching	[66]
991	Triazine ring N,in phase radial type of vibration	[38,41]
958	P–O–H deformation vibration	[66]
860	P–O(H) stretching of HPO_4	
901	O–H of water in plane bending	
784	Ring sextant out of plane bending	[36]
772	Ring bend out of plane bending	[39,44]
691	Symmetric type triazine ring	[39]
612	Ring bending	
576	C–N bending vibration	[36]
544	Side-chain in plane C–N bend	[36]
505	H_2O wagging	

HIGHLIGHTS

- A new Tetrakis(M^{2+})Bis(M^{+})Pentakis(hydrogenphosphate)Tetrahydrate was synthesised.
- The title compound was characterized by SXRD,UV-vis, FTIR, NMR and TGA-DTA studies.
- It crystallizes in monoclinic crystal system and the space group is P 21.
- The protonation of triazine caused dramatic changes in the frequencies of the ring.
- The new material has more thermal stability up to 200 °c.