International Journal Of

Recent Scientific Research

ISSN: 0976-3031

Volume: 6(12) December -2015

CHEMICAL PREPARATION, CRYSTAL STRUCTURE, IR STUDY AND THERMAL BEHAVIOR OF NEW BARIUM AND CESIUM CYCLOTRIPHOSPHATE DIHYDRATE $BaCsP_3O_9.2H_2O$ CRYSTAL

Belhabra M, Kheireddine A, Moutaabbid H, Benoit Baptiste, Lamsatfi R, Fahim I, Tridane M, Moutaabbid M and Belaaouad S

THE OFFICIAL PUBLICATION OF
INTERNATIONAL JOURNAL OF RECENT SCIENTIFIC RESEARCH (IJRSR)
http://www.recentscientific.com/ recentscientific@gmail.com

ISSN: 0976-3031

Available Online at http://www.recentscientific.com

International Journal of Recent Scientific Research
Vol. 6, Issue, 12, pp. 7832-7836, December, 2015

International Journal of Recent Scientific Research

RESEARCH ARTICLE

CHEMICAL PREPARATION, CRYSTAL STRUCTURE, IR STUDY AND THERMAL BEHAVIOR OF NEW BARIUM AND CESIUM CYCLOTRIPHOSPHATE DIHYDRATE $BaCsP_3O_9.2H_2O$ CRYSTAL

Belhabra M [*1], Kheireddine A[2], Moutaabbid H[3], Benoit Baptiste[4], Lamsatfi R[5], Fahim I[6], Tridane M[7], Moutaabbid M[8] and Belaaouad S[9]

[1,2,5,6,7,9] Laboratories De Chimie Physique Des Matériaux, Faculté Des Sciences Ben M'sik, Casablanca, Morocco
[3,4]Institut De Minéralogie Et De Physique Des Milieux Condensés, Université Pierre Et Marie Curie, 4 Place Jussieu, 75005 Paris, France
[8]Centre Régional Des Métiers D'enseignement ET De Formation Casablanca Anfa, Bd Bir Anzarane Casablanca. Maroc

ARTICLE INFO

Article History:

Received 05thSeptember, 2015
Received in revised form 08th October, 2015
Accepted 10th November, 2015
Published online 28st December, 2015

Key words:

Crystal structure, TG, barium cesium, cyclo- triphosphate, infrared spectroscopy.

ABSTRACT

Chemical preparation and crystal structure are reported for a new barium cesium cyclotriphosphate dihyd rate $BaCsP_3O_9.2H_2O$. This salt crystallizes in the monoclinic system, space group $P2_1/n$ a=7.6992(2) Å b=12.3237(3) Å c=11.8023(3) Å, β= 101.181° (3). The crystal structure was refined down to R_1=0.0401, R_2=0.0378 for 2213 unique reflections with I>2σ (I). The $BaCsP_3O_9.2H_2O$ structure can be described as; the phosphoric ring anions are interconnected by BaO_8 dodecahedra. The two oxygen of the water molecules in the present arrangement participate in the coordination spheres of the associated barium and cesium cations. The ther mogravimetric analysis shows that the removal of these two water molecules occurs in two stages between 105 and 600°C. The vibrational study by IR absorption spectroscopy of the title compound reveals the presence of three bands and confirm the existence of non-equivalent positions of water molecules in the structure.

INTRODUCTION

During a systematic investigation of cyclophosphates types $BaCsP_3O_9.xH_2O$, $BaCs_4(P_3O_9)_2.xH_2O$, $BaCs_2P_4O_{12}.2H_2O$, $Ba_3Cs_2(P_4O_{12})_2.2H_2O$, a new form $BaCsP_3O_9.2H_2O$ was obtained,. Barium and cesium cyclotriphosphate dihydrate, $BaCsP_3O_9.2H_2O$, was prepared for the first time by using Boulle's process [1] by R. Masse [2], who described it as a monohydrate and who reported a brief report of the single crystal XRD data.

In the present work, we report the chemical preparation, crystalline structure, thermo gravimetric analysis and infrared study of this new crystal barium and cesium cyclotriphosphate dihydrate, $BaCsP_3O_9.2H_2O$.

Experimental

Chemical Preparation

Single crystals of $BaCsP_3O_9.2H_2O$ were prepared by slowly adding dilute cyclotriphosphoric acid, $H_3P_3O_9$,to an aqueous solution of barium carbonate, $BaCO_3$, and cesium carbonate, Cs_2CO_3, with a stoichiometric ratio Ba/Cs = 1, according to the following chemical reaction:

$$H_3P_3O_9+BaCO_3+1/2Cs_2CO_3+1/2H_2O \longrightarrow BaCsP_3O_9.\ 2H_2O +3/2CO_2$$

The solution was then slowly evaporated at room temperature until single crystals of $BaCsP_3O_9.2H_2O$ were obtained. The cyclotriphosphoric acid, $H_3P_3O_9$, used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$ passed through an ion-exchange resin"Amberlite IR 120" [3]. $Na_3P_3O_9$ was obtained by thermal treatment of sodium dihydrogeno

*Corresponding author: **Belhabra M**
Laboratories De Chimie Physique Des Matériaux, Faculté Des Sciences Ben M'sik, Casablanca, Morocco

monophosphate, NaH_2PO_4, at 530 °C for 5 h in air, according to the following chemical reaction:

$$3NaH_2PO_4 \longrightarrow Na_3P_3O_9+3H_2O.$$

Xrd, Crystal Data, Intensity Data Collection and Structure

X-ray Single crystal structure determination of $BaCsP_3O_9.2H_2O$ was performed by using an Oxford Xcalibur S diffractometer at room temperature. 8 samples were mounted on a 4 circle diffractometer (50kV, 50mA) equipped with a Mo Kα radiation source (λ = 0.71073 Å). Data reduction, cell refinement, space group determination and scaling were performed using Crys AlisPro software [4]. An analytical absorption correction was applied using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid [5].

The main crystal data, the parameters used for intensity data collection and the reliability factor are summarized in (Table 1). The crystal structure was carried out with a direct method by using the SHELXS-97 program [6] implemented in Olex2 program [7] which permitted to locate all atoms. The hydrogen atoms were geometrically fixed with isotropic thermal parameters in idealized positions using HFIX option. Barium and cesium were located after subsequent cycles of refinement and difference-Fourier syntheses by using SHELXL-97[8].

The hydrogen atoms were localized by geometry. After some refinement cycles, using anisotropic thermal factors for the non-hydrogen atoms and isotropic thermal factors for the hydrogen ones, which positions were not refined, the final R value is 0.0401 for 1782 reflections with $I > 2\sigma(I)$. The final atomic coordinates are given in (Table 2). Main geometrical features, bond distances and angles are reported in (Table 3).

Powder X-ray diffraction data of $BaCs_4(PO_3)_6$ were recorded on a Panalytical MPD Pro in a Bragg-Brentano configuration with Cu (Kα) radiation (λ = 1.54056), The experimental 2θ range was 10–90° with a step size of 0.0668451° and a counting time of 10 s per step. The program of graphic tool for powder diffraction named Win PLOTR (Version 2012) was used to determine the observed diffraction peak positions for the four compounds.

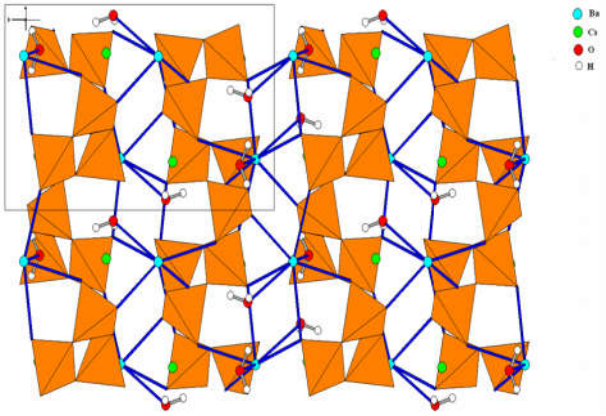

Figure 1 Projection along the c axis of the atomic arrangement in $BaCsP_3O_9.2H_2O$.

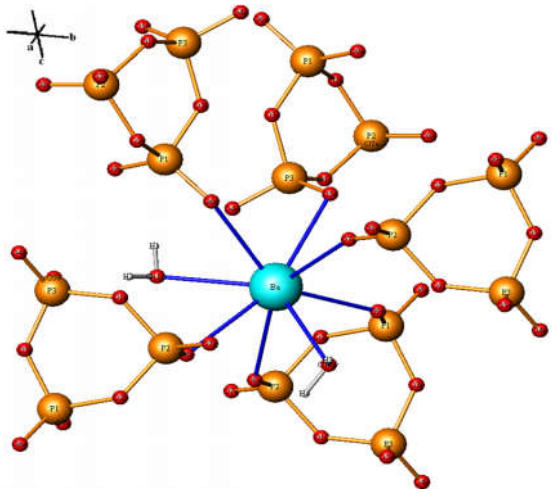

Figure 2 The coordination of the barium atom in in $BaCsP_3O_9.2H_2O$.

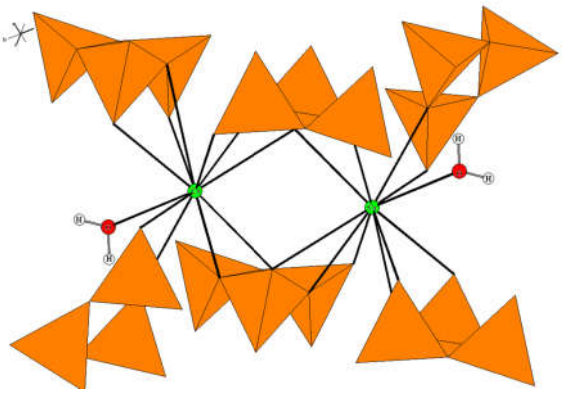

Figure 3 The coordination of the cesium atom in $BaCsP_3O_9.2H_2O$.

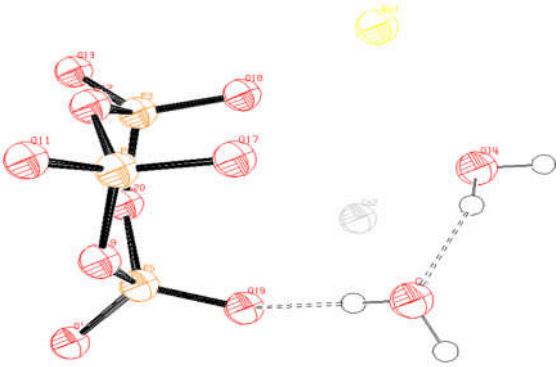

Figure 4 ORTEP representation of $BaCsP_3O_9.2H_2O$ (H-bonds are represented by dashed lines). Thermal ellipsoids are scaled to enclose 50% probability.

Fourier-Transform Infrared spectroscopy

Magna Nicolet 560 spectrometer (resolution 1 cm^{-1}, 200 scans) and Omnic software were used to characterize the stretching and bending bands between 400 and 4000cm^{-1}.

Thermal behavior. Non isothermal study of $BaCsP_3O_9.2H_2O$

Thermogravimetry analysis was conducted using a TGA Q500 V20.13 Build 39, thermobalance (sensitivity 0.1µg), in platinum crucible and in argon atmosphere. Sample weight was 10.0690 mg and the heating rate was 10 °C.min^{-1}.

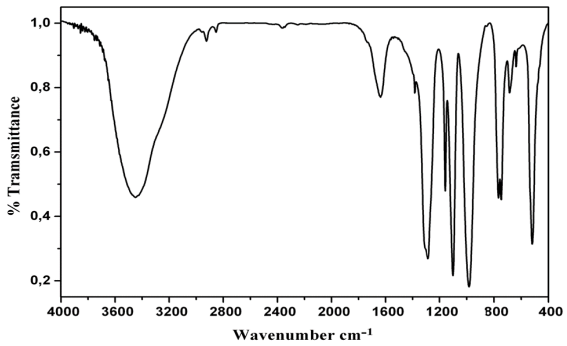

Figure 5 FT-IR spectrum of barium and cesium cyclotriphosphate dihydrate $BaCsP_3O_9.2H_2O$ crystal.

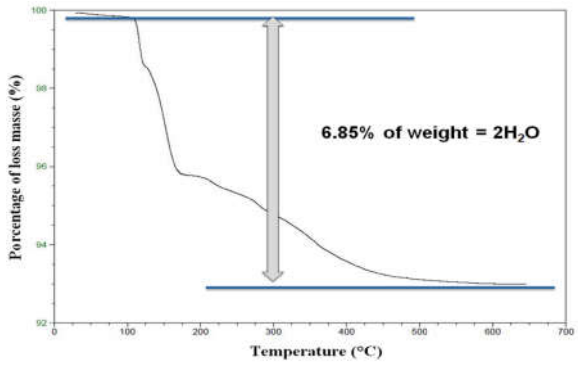

Figure 6 TG curves of $BaCsP_3O_9.2H_2O$ at rising temperature (10°C. min^{-1}).

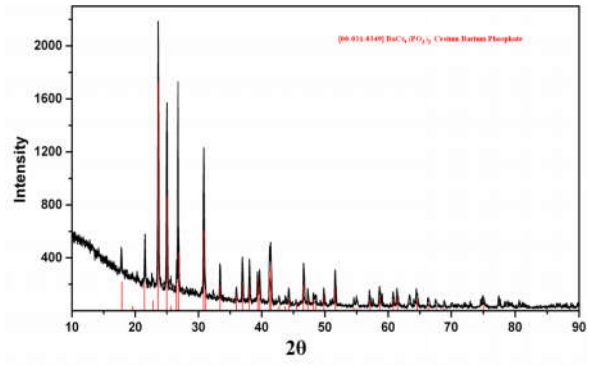

Figure 7 X-ray powder diffraction patterns for long chain polyphosphate of barium and cesium $BaCs_6(PO_3)_6$.

RESULTS AND DISCUSSION

Structure analysis

The final atomic positions and anisotropic thermal parameters for the non-hydrogen atoms in the $BaCsP_3O_9.2H_2O$ structure is given respectively in (Tables 2 and 3). A projection of the $BaCsP_3O_9.2H_2O$ atomic arrangement along the c axis is given in (Fig 1). It shows that all the components of the atomic arrangements are located around the 2 axis as to form arrays delimiting large channels parallel to the c direction**.**

The phosphoric group

The phosphoric ring anion observed in the present arrangement has no internal symmetry and is, so, built up by three non-equivalent PO_4 tetrahedra. The main geometrical features in this entity are reported in (Table 4). The P–P distances as well as the P–O–P and the P–P–P angles are in good accordance with previous investigations in cyclotriphosphates *[9]* containing ring anions without any internal symmetry.

Table 1 Crystal data and experimental parameters for the X-ray intensity data collection for $BaCsP_3O_9.2H_2O$.

Crystal data	
Formula/formula weight	BaCs $H_4O_{11}P_3$ /543.20g.mol^{-1}
Crystal system	Monoclinic
Space group/Z	*P* $2_1/n$ /4
parameters	*a*= 7.6992(2) Å *b*= 12.3237(3) Å *c*= 11.8023(3) Å, *β*= 101.18(3)°
Volume	*V*= 1098.57(5)Å^3
Calculated density (g/cm^3)	3.284
Absorption coefficient μ (mm^{-1})	7.362
F(0 0 0)	992.0
Size/color	(0.3296 × 0.1602 × 0.0957 mm^3)/colorless
Intensity measurement	
Diffractometer	Oxford Xcalibur S
Monochromator	Graphite
Wavelength (Mo Kα)	λ= 0.71073 Å
Temperature	293(2)
Theta range	3.50°/ 27.59°
h, k, l range	-10/10, -16/16, -15/15
Reflections collected	9176
Number of independent reflections	2448
Structure determination	
Unique reflections included (I > 2σI)	SHELXL-97
Programs used	147
Number of refined parameters	1.113
Goodness-of-fit on F2	0.0401/ 0.0378
R (anisotropic)/Rw (anisotropic)	0.170(15)
Extinction coefficient	R_1 = 0.0285, wR_2 = 0.0611
Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.0638
Final R indexes [all data]	0.78/-1.40
Largest diff. peak/hole / e Å^{-3}	

Table 2 Final atomic coordinates and U equivalent temperature factors for $BaCsP_3O_9.2H_2O$.

Atoms	X	Y	Z	U_{eq}
Ba	0.24946(3)	0.06963(2)	0.37463(2)	0.01486(9)
Cs	1.23531(4)	0.37670(3)	0.60501(3)	0.02500(10)
P(1)	0.49653(15)	0.33939(9)	0.34729(10)	0.0135(2)
P(2)	0.75498(15)	0.17362(10)	0.42595(10)	0.0140(2)
P(3)	0.72984(16)	0.35936(10)	0.57392(11)	0.0185(3)
O(1i)	0.8311(4)	0.2619(3)	0.5238(3)	0.0194(7)
O(2i)	0.6424(4)	0.2510(2)	0.3278(2)	0.0159(7)
O(3i)	0.6022(4)	0.4024(2)	0.4588(3)	0.0178(7)
O(4e)	0.8606(5)	0.4456(3)	0.6136(4)	0.0393(10)
O(5e)	0.6256(5)	0.3191(3)	0.6572(3)	0.0312(9)
O(6e)	0.4740(4)	0.4168(2)	0.2497(3)	0.0212(7)
O(7e)	0.9053(4)	0.1308(3)	0.3805(3)	0.0223(8)
O(8e)	0.6306(4)	0.0994(3)	0.4691(3)	0.0201(7)
O(9e)	0.3428(4)	0.2843(3)	0.3783(3)	0.0205(7)
O(10w)	0.2195(4)	0.1274(3)	0.5953(3)	0.0233(8)
O(11w)	0.5532(5)	0.0975(3)	0.7172(3)	0.0315(9)
H(1)	0.5738	0.0941	0.7926	0.047
H(2)	0.5846	0.1617	0.6363	0.047
H(3)	0.1274	0.1017	0.6242	0.035
H(4)	0.3191	0.0980	0.6366	0.035

i : Internal ; e : external ; w: water

Barium and cesium arrangement in the Structure

The barium atom, located on the twofold axis, is coordinated by two water molecules and six oxygen atoms (Fig 2), forming an almost regular dodecahedron. The Ba–O distances are spread between 2.298(6) and 2.349(6) Å. Each BaO_8 dodecahedra shares six oxygen atoms with two anionic rings belonging to two phosphoric layers, thus providing the cohesion between these layers. BaO_8 dodecahedra do not share

any edge or corner and form layers alternating with P_3O_9 ones. The shortest Ba-Ba distance is found to be 4.70731Å. The Cesium atom occupies a general position and is coordinated to ten external oxygen atoms and one water molecule (Fig 3). The Cs–O distances spread between 3.0278(2) and 3.5982(9).The water group, its environment, established by strong hydrogen bonds, is depicted in (Fig 4) as an ORTEP representation [10].

Table 3 Anisotropic thermal parameters (Å^2) for $BaCsP_3O_9.2H_2O$

Atom	U11(s)	U22	U33	U23	U13	U12
Ba	0.01483(15)	0.01281(16)	0.01595(15)	0.00044(10)	0.00056(11)	-0.00029(10)
Cs	0.02411(18)	0.0258(2)	0.02600(18)	0.00406(13)	0.00715(14)	0.00042(13)
P(1)	0.0146(6)	0.0132(6)	0.0122(5)	0.0016(4)	0.0015(5)	0.0020(5)
P(2)	0.0150(6)	0.0130(6)	0.0134(5)	0.0004(5)	0.0016(5)	0.0028(5)
P(3)	0.0171(6)	0.0193(7)	0.0171(6)	-0.0062(5)	-0.0015(5)	0.0022(5)
O(1i)	0.0173(16)	0.0172(17)	0.0207(17)	-0.0054(14)	-0.0035(14)	0.0032(14)
O(2i)	0.0195(17)	0.0166(17)	0.0113(15)	0.0007(13)	0.0023(13)	0.0071(14)
O(3i)	0.0192(17)	0.0140(17)	0.0176(17)	-0.0035(13)	-0.0026(14)	0.0027(14)
O(4e)	0.025(2)	0.027(2)	0.058(3)	-0.0226(19)	-0.0086(19)	-0.0009(17)
O(5e)	0.037(2)	0.037(2)	0.0201(18)	0.0038(16)	0.0079(17)	0.0101(18)
O(6e)	0.0241(18)	0.0194(17)	0.0210(18)	0.0080(14)	0.0067(15)	0.0069(15)
O(7e)	0.0173(17)	0.0245(19)	0.0247(18)	-0.0051(15)	0.0031(15)	0.0064(14)
O(8e)	0.0201(17)	0.0147(17)	0.0253(18)	0.0064(14)	0.0042(15)	0.0009(14)
O(9e)	0.0177(17)	0.0185(18)	0.0255(18)	0.0026(14)	0.0050(15)	-0.0004(14)
O(10w)	0.0190(17)	0.027(2)	0.0236(18)	-0.0012(15)	0.0043(15)	0.0010(15)
O(11w)	0.030(2)	0.034(2)	0.028(2)	-0.0008(17)	-0.0009(18)	-0.0001(18)

i : Internal ; e : external ; w: water

Table 4 Main interatomic distances (A°) and bond angles (°) in the P_3O_9 ring.

Tetrahedron around P(1)				
P(1)	O(2i)	O(3i)	O(6e)	O(9e)
O(2i)	1.6127(5)	100.7(9)	107.7(1)	109.8(7)
O(3i)	2.4805(3)	1.6067(6)	106.8(7)	108.8(6)
O(6e)	2.4984(3)	2.4802(1)	1.4796(3)	120.8(4)
O(9e)	2.5253(9)	2.5047(5)	2.5661(1)	1.4709(8)
Tetrahedron around P(2)				
P(2)	O(1i)	O(2i)	P(2)	O(1i)
O(1i)	1.6119(2)	100.6(7)	107.5(8)	109.8(3)
O(2i)	2.4852(7)	1.6165(2)	107.5(7)	108.5(1)
O(7e)	2.4843(1)	2.4879(6)	1.4650(7)	120.7(8)
O(8e)	2.5345(1)	2.5176(5)	2.5639(8)	1.4839(6)
Tetrahedron around P(3)				
P(3)	(O1i)	(O3i)	(O4e)	(O5e)
O(1i)	1.6059(7)	101.3(4)	107.7(7)	111.1(4)
O(3i)	2.4835(6)	1.6047(7)	107.3(7)	110.6(9)
O(4e)	2.4913(1)	2.48389	1.4763(3)	117.2(4)
O(5e)	2.5387(2)	2.5309(4)	2.5159(1)	1.4704(7)
P(1)-P2)		2.8772(2)	P(2)–O(1i)-P(3)	129.3(1)
P(1)-P3)		2.9288(6)	P(1)–O(2i)–P(3)	131.5(6)
P(2)-P3)		2.9082(6)	P(1)–O(3i)-P(2)	125.9(9)
P(2)-P(1)-P(3)		60.1(1)		
P(1)-P(2)-P(3)		60.8(2)		
P(1)-P(3)-P(2)		59.0(6)		

Infrared spectroscopy

Crystals were grounded in a mortar with KBr powder in a ratio 2/200 and pelleted in a press (8 tons, 30 s). Then they were stored at 95°C for one day to get dried before use.The IR spectrum of $BaCsP_3O_9.2H_2O$ illustrated in (Fig 5) reveals the presence of three band-s due to water molecules in the domain 4000–1600 cm^{-1}. This confirm the existence of non-equivalent positions of water molecules in the $BaCsP_3O_9.2H_2O$ atomic arrangement: 3449 cm^{-1} attributed to O–H valence vibration, around 3270 cm^{-1} to hydrogen bonds and 1637 cm^{-1} to δHOH deformation. The valence vibration bands related to the P_3O_9 cycles are expected in the domain 1400–650 cm^{-1} *[11]*, as well as possible bands due to interactions between P_3O_9 cycles and water molecules and also of water vibration modes. The vibration modes of the phosphate anions usually occur in the 1400–650 cm^{-1} area *[12]*. The two IR bands observed at 1384 and 1286 cm^{-1} can be attributed to the $\nu_{as}(PO_2)$ stretching vibration (Table 5). The shouldered band at 1157 cm^{-1} and the doublet observed at 1100 and 983 cm^{-1} can be assigned to $\nu_s(PO_2)$ and ν_{as}(POP), respectively. The most characteristic feature of the (P_3O_9) ring anions is the occurrence of a strong intensity band near 767 cm^{-1} in addition to 747cm^{-1} due to the ν_s(POP) stretching vibration. The weak peak appearing at 685 cm^{-1} can be assigned to ν_s (POP)*[13]*, The broad band's observed at 519 cm^{-1} and the weak peak at 637 cm^{-1}can be due to the deformation vibrations of the anionic group. In the spectral domain 650-400 cm^{-1}, the spectrum of $BaCsP_3O_9.2H_2O$ (Fig 5) shows bending vibration bands characteristic of phosphates with ring anions.

Table 5 Frequencies (cm^{-1}) of IR absorption bands for $BaCsP_3O_9.2H_2O$.

ν (cm^{-1})	Vibration
3449	ν OH
1637	δ HOH
1637	
1384	ν_{as} OPO^-
1286	
1157	ν_s OPO^-
1100	
983	ν_{as} POP
767	ν_s POP
747	
685	δ OPO^-
637	+
519	ρ OPO^-

Thermal Analysis

The curve corresponding to the TG analyses in air atmosphere and at a heating rate 10°C.min^{-1} of $BaCsP_3O_9.2H_2O$ are given in (Fig 6). The dehydration of the cyclotriphosphate of barium and cesium dihydrate $BaCsP_3O_9.2H_2O$ happens in two steps in two temperature ranges 105 – 180 °C, and 180 – 580°C (Fig 6). In the thermogravimetric (TG) curve, the first stage between 95 and 180°C corresponds to the elimination of 1.14 water molecules; the second stage from 180 to 580°C is due to the

elimination of 0.86water molecules. The final product of total thermal dehydrataion of $BaCsP_3O_9.2H_2O$ is the long chain polyphosphate of barium and cesium $BaCs_6(PO_3)_6$ (Fig 7) [2].

CONCLUSION

Crystals of the title compound, $BaCsP_3O_9.2H_2O$, have been synthesized using the method of ion exchange resin. The structure of $BaCsP_3O_9.2H_2O$ can be described as the phosphoric ring anion with no internal symmetry and is, built up by three non-equivalent PO_4 tetrahedra; the barium atom is coordinated by two water molecules and six oxygen atoms, forming an almost regular dodecahedron. The Cesium atom occupies a general position and is coordinated to ten external oxygen atoms and one water molecule and the water group, its environment, established by strong hydrogen bonds. The thermo gravimetric analysis has confirmed the existence of two water molecules as proven by the crystalline structure. The infra red spectrum of $BaCsP_3O_9.2H_2O$ exhibits the IR bands characteristic of $P_3O_9^{3-}$.

References

1. Kheireddine, M. Tridane and S. Belaaouad, Powder. Diffr. 27(1), 32 (March 2012).
2. R. Masse and M.T. Averbuch-Pouchot, Mat. Res. Bull. 12, 13 (1977).
3. Jouini and A. Durif, C. R. Acad. Sci. Paris 297 II, 573 (1983).
4. Oxford Diffraction, CrysAlis PRO CCD and CrysAlis PRO RED, Oxford Diffraction Ltd, Yarnton, England 2009.
5. R. C. Clark, and J. S. Reid, Acta Crystallogr. A, 887 (1995).
6. G. M. Sheldrick, SHELX-97, University of Gottingen, Federal Republic of Germany, 1997.
7. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, *J. Appl*. Crystallogr., 42, 339 (2009).
8. G. M. Sheldrick, Acta Cryst., A64, 112 (2008).
9. Durif, Crystal Chemistry of Condensed, Springer Science+ Business Media New York, 1995.
10. L. J. Farrugia, J. Appl. Cryst. 45, 849 (2012).
11. M.H.Simonot-Grange, *J. Solid State Chem*. 46(1), 76 (1983).
12. P.Tarte, A.Rulmont, K. Sbai and M.H. Simonot-Grange, Spectrochim. Acta 43A,337 (1987).
13. El. M. Tace, A. Charaf, I. Fahim, M. Moutaabbid, A. Kheïreddine, F.-E. Ouaalla, M. Tridane, K. Sbai, M. Radid and S. Belaaouad, Phos.sul. sili. rel. ele.; 186(7), 1501(01/2011).

How to cite this article:
Belhabra M.,Chemical Preparation, Crystal Structure, Ir Study And Thermal Behavior of New Barium And Cesium Cyclotriphosphate Dihydrate Bacsp3o9.2h2o Crystal. *International Journal of Recent Scientific Research Vol. 6, Issue, 12, pp. 7832-7836, December, 2015*

****

ISSN 0976-3031