J. Mater. Environ. Sci. 6 (12) (2015) 3476-3482 *Tridane et al.*
ISSN : 2028-2508
CODEN: JMESCN

Chemical preparation, crystallographic characterization, vibrational study and thermal behavior of a new cyclotriphosphate $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ superphosphate fertilizer

M. Tridane[a,b] and S. Belaaouad[a]

[a] *Laboratoire de Chimie-Physique des Matériaux, Faculté des Sciences Ben M'sik, B. P. 7955. Casablanca. Maroc.*
[b]*Centre Régional des Métiers de l'Education et de la Formation du Grand Casablanca (CRMEF). Derb Ghallef - Bd. Bir Anzarane - Casablanca Anfa Maroc.*

Corresponding Author. E-mail : tridane.malika@gmail.com Tel : (+212600305453)

Abstract

A new cyclotriphosphate hexahydrate of manganese and ammonium, $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, was obtained as polycrystalline samples by the method of ion-exchange resin. Its crystallographic characterization, vibrational study and thermal behavior are given. $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ crystallizes in the monoclinic system, C2/m, with the following unit cell parameters : a = 13.178(3)Å, b = 11.030(2)Å, c = 9.965(2)Å, β = 126.76(2)° and Z = 2. The P_3O_9 ring of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ has a C_s symmetry . The intermediate products of dehydration of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ are $Mn_2P_4O_{12}$ and $Mn_2P_2O_7$. The total dehydration and calcination of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ lead to a cyclotetraphosphate, $Mn_2P_4O_{12}$. The thermal behavior of the title compound has been investigated and interpreted by IR absorption and X-ray diffraction experiments. $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, $Mn_2P_4O_{12}$ and $Mn_2P_2O_7$ have been found to have a wide range of applications and can be used as catalysts, ion exchangers, reactants in ionic conditions, intercalation reactions, superphosphate fertilizers and as inorganic pigments in ceramics.

Keywords: cyclotriphosphate, cyclotetraphosphate, superphosphate fertilizers, thermal behavior, vibrational study.

Introduction

Multivalent metal phosphates have a number of technologically useful properties [1]. However, this has posed the question of industrial manufacture of a number of condensed phosphates, being required in the form of single crystals or polycrystalline samples. Up to now, the only example of cyclotriphosphates with a general formula $MnM^I_4(P_3O_9)_2.nH_2O$ is given by the mixed manganese potassium cyclotriphosphate dihydrate : $MnK_4(P_3O_9)_2.2H_2O$ [2] and few studies were performed on the thermal behavior of cyclotriphosphates containing ammonium ion [3,4,5,6,7,8]. The present work describes the Chemical preparation, crystallographic characterization, vibrational study and thermal behavior of a new cyclotriphosphate, $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, by X-ray diffraction, infrared spectrometry, thermal analyses TGA and DTA.

2. Experimental

2.1. *X-ray diffraction*

Powder diffraction patterns were registered with a « SIEMENS » diffractometer using CuKλ radiation (λ = 1.5406Å).

2.2. *Infrared spectrometry*

Spectra were recorded in the range 4000-400 cm^{-1} with a « Perkin Elmer IR 983G » spectrophotometer, using samples dispersed in spectroscopically pure KBr pellets.

2.3. *Thermal behavior*

Thermal analyses TGA-DTA coupled were performed using the « multimodule 92 Setaram Analyzer » operating from room temperature up to 1400°C, in platinum crucible, at various heating rates from 1 to 15°C/min.

2.4. Preparation

Polycrystalline samples of the title compound, $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, were prepared by adding slowly dilute cyclotriphosphoric acid to an aqueous solution of manganese carbonate and ammonium carbonate with a stoichiometric ratio $NH_4/Mn = 4$, according to the following chemical reaction :

$$\mathbf{2H_3P_3O_9 + MnCO_3 + 2(NH_4)_2CO_3 \longrightarrow Mn(NH_4)_4(P_3O_9)_2.6H_2O + 3CO_2}$$

The so-obtained solution is then slowly evaporated at room temperature until polycrystalline samples of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ are obtained. The polycrystalline samples are stable in air for many months under normal conditions of temperature and hygrometry. The cyclotriphosphoric acid used in this reaction was prepared from an aqueous solution of $Na_3P_3O_9$ passed through an ion-exchange resin "Amberlite IR 120"[9]. $Na_3P_3O_9$ was obtained by thermal treatment of sodium dihydrogenomonophosphate, at 530°C for 5 hours in air according to :

$$\mathbf{3\ NaH_2PO_4 \longrightarrow Na_3P_3O_9 + 3\ H_2O}$$

3. Results and Discussion

3.1. Crystallographic Characterisation

$Mn(NH_4)_4(P_3O_9)_2.6H_2O$ is isotypic of four cyclotriphosphates : $ZnK_4(P_3O_9)_2.6H_2O$ [10], $CoRb_4(P_3O_9)_2.\ 6H_2O$ [11], $NiRb_4(P_3O_9)_2.\ 6H_2O$ [12] and $ZnRb_4(P_3O_9)_2.\ 6H_2O$ [2]. $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ crystallizes in the monoclinic system, C2/m, with the following unit cell parameters : a = 13.178(3)Å, b = 11.030(2)Å, c = 9.965(2)Å, β = 126.76(2)° and Z=2. The X-ray diffractogram of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ is reported in Figure 1 (table 1).

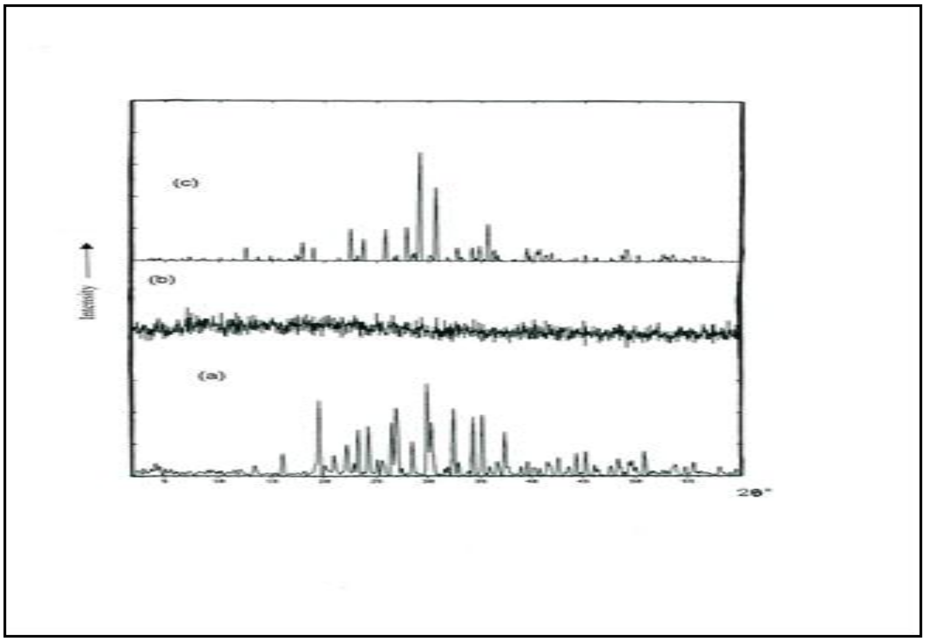

Figure 1: X-ray powder diffractograms of phosphates :(a)$Mn(NH_4)_4(P_3O_9)_2$ (b) amorphous phase and (c) $Mn_2P_4O_{12}$

Table 1: X-ray powder diffraction data for $Mn(NH_4)_4(P_3O_9)_2.6H_2O$

hkl	d_{cal}(Å)	d_{obs}(Å)	I/Imax	hkl	d_{cal}(Å)	d_{obs}(Å)	I/Imax
110	7.62	7.65	6	40-4	2.444	2.448	16
11-1	7.32	7.33	8	20-4	2.402	2.402	48
20-1	6.57	6.59	12	420	2.381	2.381	10
020	5.52	5.52	24	222	2.304	2.307	12
02-1	4.54	4.54	82	04-2	2.269	2.272	16
021	4.54	4.54	82	042	2.269	2.272	16
11-2	4.40	4.41	13	51-4	2.239	2.239	10
22-1	4.22	4.23	22	22-4	2.202	2.209	10
31-1	4.01	4.00	34	331	2.167	2.169	15
31-2	3.877	3.886	14	150	2.159	2.157	12
220	3.814	3.816	50	24-3	2.116	2.118	21
22-2	3.658	3.663	54	60-4	2.071	2.070	10
201	3.536	3.537	18	62-3	2.035	2.037	26
130	3.472	3.472	17	421	2.004	2.000	27
310	3.353	3.354	58	35-1	1.964	1.966	12
20-3	3.299	3.297	74	203	1.953	1.953	8
02-2	3.234	3.236	9	440	1.907	1.905	12
022	3.234	3.236	9	02-4	1.877	1.879	19
31-3	3.125	3.126	37	024	1.877	1.879	19
131	2.977	2.980	100	223	1.841	1.843	15
11-3	2.939	2.944	59	060	1.838	1.833	17
42-2	2.822	2.827	8	71-4	1.822	1.820	10
33-1	2.797	2.800	10	061	1.792	1.792	27
040	2.758	2.756	73	06-1	1.792	1.792	27
42-1	2.719	2.719	15	260	1.736	1.736	6
400	2.639	2.641	6	351	1.704	1.701	13
04-1	2.606	2.609	6	73-3	1.675	1.674	10
041	2.606	2.609	64	64-4	1.656	1.654	15
24-1	2.543	2.546	67	243	1.594	1.590	10
51-3	2.494	2.499	12	71-6	1.550	1.551	8

3.2. Vibrational Study

The IR absorption spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ is reported in Figure 2. It exhibits :

- five strong bands at 3540, 3220, 3050, 1661 and 1422 cm^{-1}. The band at 3540 cm^{-1} is attributed to the stretching vibration of the water molecules. The band at 3220 cm^{-1} is relative to the stretching vibration of both water molecules and ammonium ion [13]. The band at 3050 cm^{-1} is attributed to the stretching vibration of ammonium ion [13]. The band at 1661 cm^{-1}, which is due to the bending vibration, corresponds to both water molecules and ammonium ion [13]. The band at 1422 cm^{-1} represents the bending band of ammonium ion. This last band, that is usually located between 1500 and 1400 cm^{-1}, is never masked by the water molecules bands [13];
- Between 1300 and 600 cm^{-1}, the spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ (Figure 2; table 2) shows valency vibration bands characteristic of phosphates with ring anions [14,15,16]. Among these bands can be distinguished :

* the vibration bands of the (O-P-O) end groups at high frequencies : $1200 < \nu_{as} < 1300$ cm^{-1} and $1100 < \nu_s < 1200$ cm^{-1} ;

* the valency vibrations of the (P-O-P) ring groups represented by a wide band centered at about 1020-980 cm^{-1} which can be attributed to the ν_{as} (P-O-P) antisymmetric vibrations and by a strong band between 700 and 800 cm^{-1} which can be related to the ν_s (P-O-P) symmetric vibrations. The nature of the vibration corresponding to the different observed bands, in the spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, is given in Table 1.

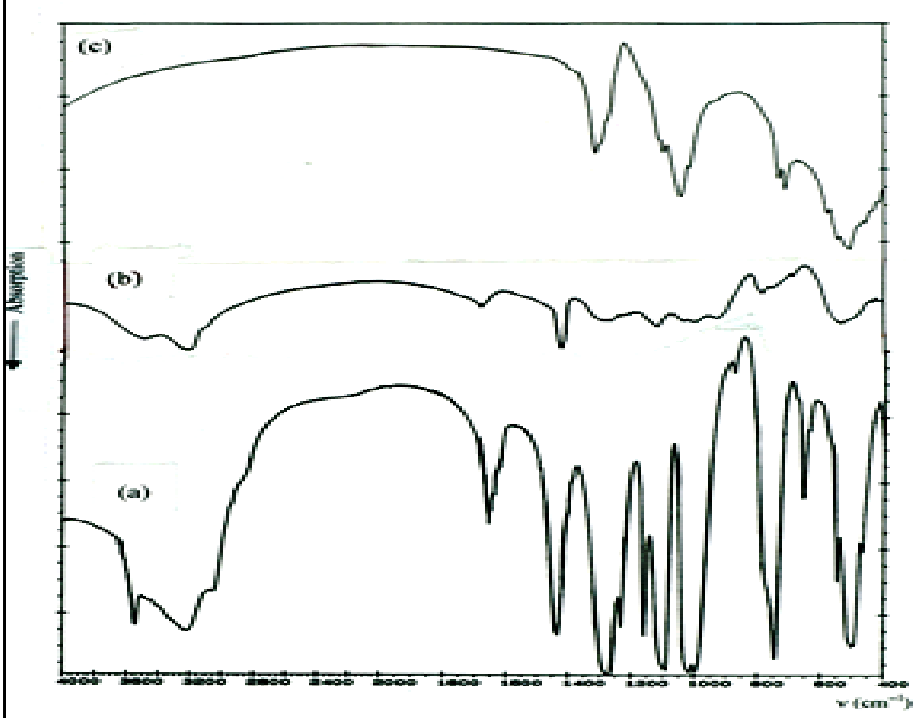

Figure 2. IR spectra of the phosphates : (a)$Mn(NH_4)_4(P_3O_9)_2.6H_2O$, (b) amorphous phase and (c) $Mn_2P_4O_{12}$

The IR absorption results agree also with those obtained by X-ray diffraction.

The IR spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ has been analysed on the basis of vibrational spectra of other cyclotriphosphates, $LnP_3O_9.3H_2O$ [14,16] (space group C^1_{3h}, Z = 2 [17]) and $M^IM^{II}P_3O_9$ benitoïte structure [18] (space group D^2_{3h}, Z = 2). In our case, the local P_3O_9 symmetry is m or C_s according to the crystallographic characterization, of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ isotypic of four cyclotriphosphates :

$ZnK_4(P_3O_9)_2.6H_2O$ [10], $CoRb_4(P_3O_9)_2$. $6H_2O$ [11], $NiRb_4(P_3O_9)_2$. $6H_2O$ [12] and $ZnRb_4(P_3O_9)_2$. $6H_2O$ [2], and yields to 30 normal modes active in IR and Raman, 17A′ and 13A″. Such modes are distributed betweenn valence and deformation modes as Γvalence = 7A′(IR, Ra) + 5A″(IR, Ra) and Γdeformation = 10A′(IR, Ra) + 8A″(IR, Ra). For the valence vibrations, nine vibrations are observed and the expected vibrations are twelve for a free P_3O_9 ring, as evidenced by the structural determination of $ZnK_4(P_3O_9)_2.6H_2O$ [10], $CoRb_4(P_3O_9)_2$. $6H_2O$ [11], $NiRb_4(P_3O_9)_2$. $6H_2O$ [12] and $ZnRb_4(P_3O_9)_2$. $6H_2O$ [2] isotypic of the title compound $Mn(NH_4)_4(P_3O_9)_2.6H_2O$. Therefore one can neglect the perturbations related to the presence of four rings and twelve water molecules inside the unit-cell. The correspondence between free P_3O_9 valence vibrations and different local symmetries is presented in table 3. The nine vibration frequencies are attributed to the four valence vibrations : υ_{as} PO_2, υ_s PO_2, υ_{as} POP and υ_s POP. Compared to C_{3h}, the higher number of frequencies is related to a degeneracy lifting of E′ and E″ modes and to an activity of A′ modes for a non-polar ring. The strong vibration band at 744 cm^{-1} can be considered as a signature of the P_3O_9 ring [16,19,20]. The other vibration bands at lower wavenumbers are attributed to the deformation modes δPOP, γPOP and δPO_2.

3.3. *Thermal Behavior*

The two curves corresponding to the TGA (TG-DTG) and DTA analyses in air atmosphere and at a heating rate 2°C/min of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ are given in Figure 3. The DTA curve (figure 3) exhibits six endothermic peaks.

- The peaks lying at 52°C, 124°C, 163°C and 277°C define three stages of dehydration in the temperature range 29-303°C. To each of these peaks corresponds a weight loss confirmed by a peak on the DTG curve representing the derivative of the TGA curve (figure 3). The whole weight loss accompanying the dehydration is evidenced in the TG curve and is equivalent to the departure of six water molecules per formula unit of cyclotriphosphate $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ (experimental and calculated weight percentage of the water content are 15.24% and 15.23% respectively).
- The peak observed at 417°C is due to the evolving of four moles of ammonia per formula unit of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ (experimental and calculated weight percentage of the ammonia content are the same 9.59%). To this endothermic peak situated at 417°C corresponds a weight loss, in the temperature range 303-783°C, confirmed by a peak on the DTG curve representing the derivative of the TGA curve (figure 3).
- The large peak at about 1100°C is due to the removal of water ($2H_2O$) and phosphorus oxide ($2P_2O_5$), well observed on the TG curve (figure 3) from 1018°C. The thermal behavior of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ was also studied in a step manner of temperature by X-ray diffraction and IR absorption between 20°C and 1000°C. $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ is stable until 70°C. The removal of the six water molecules of hydration of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$, observed in the temperature range 100-250°C, destroyed the crystalline network and brings to an intermediate amorphous phase which does not diffract the X-ray (Figure 1), nor exhibits the IR absorption bands characteristic of a cyclic phosphate (Figure 2) [14,15,16]. The bending band of NH_4^+, which is located in the domain 1500-1400 cm^{-1}, subsists in the IR spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ heated between 100°C and 250°C (Figure 2).

Table 2: Frequencies (cm^{-1}) of IR absorption bands for $Mn(NH_4)_4(P_3O_9)_2.6H_2O$

ν (cm^{-1})	I	vibration [13,14,15,16]
3540	VS	ν OH
3220	VS	ν OH + ν_d NH
3050	S	ν_s NH
1661	S	ν_δ HOH + δ_d HNH
1422	VS	δ_d HNH
1264	VS	ν_{as} PO_2
1222	S	
1159	S	ν_s PO_2
1089	VS	
1025	VS	ν_{as} POP
983	VS	
879	vs	
744	VS	ν_s POP
681	sh	
653	S	
589	sh	δ PO_2 + δ POP
554	m	+ γ POP
505	VS	
490	VS	
463	vs	

I : intensity, VS : very strong, S : strong, vs : very small, m : medium, sh : shoulder

The amorphous product is then the mixture MnO + P_2O_5 + $[NH_4PO_3]_\infty$ [21]. $[NH_4PO_3]_\infty$ under liberation of ammonia between 300°C and 350°C leads to the formation of $[HPO_3]_\infty$ [22]. In fact, the bending band of NH_4^+ observed between 1500 and 1400 cm^{-1}, doesn't appear in the IR spectrum of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ heated at 400°C (Figure 2c). From 350°C, the atomic rearrangement of MnO and P_2O_5 occurs and provokes the start of crystallization of cyclotetraphosphate, $Mn_2P_4O_{12}$ [23]. So, the product resulting from the decomposition of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ at 400°C is the mixture $Mn_2P_4O_{12}$ and $[HPO_3]_\infty$. At 500°C, $[HPO_3]_\infty$ is decomposed by evolving water ($2H_2O$) and phosphorus oxide ($2P_2O_5$) and the product resulting from the calcination of the title compound at this same temperature, 500°C, is $Mn_2P_4O_{12}$ pure [23] **(Figures 1 and 2)**. The latter result is confirmed by the chemical analyses and X-ray diffraction which prove the existence of $Mn_2P_4O_{12}$ pure. The final phase of the calcination of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ is the cyclotetraphosphate $Mn_2P_4O_{12}$ [23].

Table 3: Comparison of free P_3O_9 ring valence vibrations for C_{3h} , D_{3h} and C_s symmetries

$LnP_3O_9.3H_2O$ C_{3h} [14,16]			Molecular group D_{3h}			Free P_3O_9 C_s			Mode
Mode	Activity (IR,Ra)	observed (IR,Ra)	Mode	Activity (IR,Ra)		Mode	Activity (IR,Ra)	$Mn(NH_4)_4(P_3O_9)_2.6H_2O$ IR	
A″	(+,-)	(1286,-)	A''_2	(+,-)	→	A′	(+,+)	1264	$\upsilon_{as}PO_2$
E″	(-,+)	(-,1246)	E″	(-,+)	→	A′	(+,+)	1222	
					↘	A″	(+,+)		
A′	(-,+)	(-,1172)	A'_1	(-,+)	→	A′	(+,+)	1159	υ_sPO_2
E′	(+,+)	(1102,1104)	E′	(+,+)	→	A″	(+,+)	1089	
					↘	A′	(+,+)		
E′	(+,+)	(1037,1026)	E′	(+,+)	→	A″	(+,+)	1025	$\upsilon_{as}POP$
					↘	A′	(+,+)	983	
A′	(-,+)	(-,-)	A'_2	(-,-)	→	A″	(+,+)	879	
E′	(+,+)	(763,763)	E′	(+,+)	→	A″	(+,+)	744	υ_sPOP
					↘	A′	(+,+)		
A′	(-,+)	(-,656)	A'_1	(-,+)	→	A′	(+,+)	653	

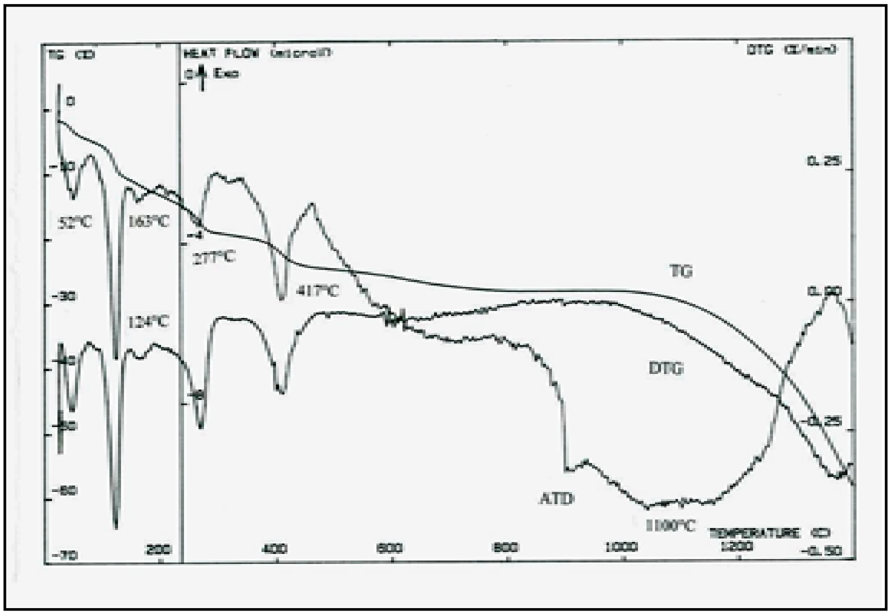

Figure 3: TGA and DTA curves of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ at rising temperature (2°C/min)

Conclusion

The present work concerns the preparation, crystallographic characterization and vibrational study of new ammonium manganese cyclotriphosphate hexahydrate $Mn(NH_4)_4(P_3O_9)_2.6H_2O$. The thermal evolution of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ has been followed by thermal analyses TGA and DTA, X-ray diffraction and infrared spectrometry. The total dehydration of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ leads at 500°C to the anhydrous form, cyclotetraphosphate $Mn_2P_4O_{12}$. It's the first time that the dehydration and the calcination of a cyclotriphosphate (P_3O_9) leads to a cyclotetraphosphate (P_4O_{12}). The title compound can be used as catalyst, ion exchanger, reactant in ionic conditions, intercalation reactions, superphosphate fertilizer and as inorganic pigment in ceramics.

References

1. Le Flem J., Eur. J. *Solid State Inorg. Chem*. 28 (1991) 3-8.
2. Averbuch-Pouchot M. T., Prisset J.-L. and Durif A., *Eur. J. Solid State Inorg. Chem*. 30 (1993) 71-81.
3. Tridane M., Kheireddine A., Fahim I., Moutaabbid H., Moutaabbid M., Tace EL. M., Charaf A., Radid M., Salhamen F., Benmokhtar S. *Verres, Céramiques & Composites* 4 (2015) 20-27.
4. Takenaka A., Motooka I. and Nariai H., *Bull. Chem. Soc. Jpn*. 60 (1987) 4299-4305.
5. Feldmann Von. W., *Z. anorg. allg. Chem*. 400-2 (1973) 97-102.
6. Belaaouad S., Sbai K. and Jouini A., *Solid State Sciences,* 2 (2000) 655-661.
7. Belaaouad S., Sbai K., Kenz A. and Pierrot M., *Mat. Res. Innovat*. 3, (2000) 352-359.
8. Tace EL. M., Charaf A., Fahim I., Moutaabbid M., Kheïreddine A., Ouaalla F-E., Tridane M., Sbai K., Radid M. and Belaaouad S., *Phosphorus, Sulfur, and Silicon and the Related Elements*. 186 (2011) 1501-1514.
9. Jouini A. and Durif A., *C. R. Acad. Sci.* 297 (1983) 573-575.
10. Seethanen D., Durif A. and Averbuch-Pouchot M. T., *Acta Crystallogr. B* 34 (1978) 14-17.
11. Belkhiria M. S., Dabbabi M. and Ben-Amara M., *Acta Crystallogr. C* 43 (1987) 2270-2272.
12. Jouini A., (1988) Thèse d'état, Faculté des Sciences de Tunis, Tunisie.
13. Sbai K., Atibi A., Charaf A., Radid M. and Jouini A., *Ann. Chim. Sci. Mat.,* 26(6) (2001) 45- 61.
14. Kheireddine A., Tridane M. and Belaaouad S., *Mediterr. J. Chem*., 2(4) (2013) 549-568.
15. Tace EL. M. , Charaf A., Fahim I., Moutaabbid M., Kheïreddine A., Ouaalla F-E. , Tridane M., Sbai K., Radid M. and Belaaouad S., *Phosphorus, Sulfur, and Silicon and the Related Elements.* 186 (7) (2011) 1501-1514.
16. Tarte P., Rulmont A., Sbai K. and Simonot-Grange M. H., *Spectrochim. Acta.* 43A-3 (1987) 337 -345.
17. Bagieu-Beucher M., Durif A., *Bull. Soc. Fr. Minér. Crist*. 94 (1971) 440-441.
18. Masse R., Grenier J. C., Averbuch-Pouchot M. T., Tranqui D. and Durif A., *Bull. Soc. Fr. Minér. Crist.* 90 (1967) 158-161.
19. Ignatev I. S., Lazarev A. N., *Dokl. Akad. Nauk. SSSR.* 191, (1970) 596-599 (pp. 218-221 of the English translation).
20. George B. L., Joe I. H., Aruldhas G., , *J. Raman Spectrosc*. 23 (1992) 417-419.
21. Shen C. Y., Stahlheber N. E. and Dyroff D. R., *J. Am. Chem. Soc.* 91 (1969) 62-67.
22. Hahn B., *J. Am., Chem. Soc*.73, (1951) 5091-5093.
23. Hinsch Th., Guse W. and Saalfeld H., J. Cryst. Growth. 79 (1986) 205-209.