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CHEMICAL PREPARATION, THERMAL BEHAVIOR, KINETIC, IR STUDIES OF $CdK_4(P_3O_9)_2.2H_2O$, CRYSTALLOGRAPHIC DATA OF A NEW CYCLOTRIPHOSPHATE $CdK_4(P_3O_9)_2$ NEW FERTILIZER TYPE KP

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ABSTRACT

Chemical preparation, thermal behavior and IR studies are given for the cyclotriphosphate $CdK_4(P_3O_9)_2.2H_2O$ and its anhydrous form $CdK_4(P_3O_9)_2$. $CdK_4(P_3O_9)_2.2H_2O$, isotypic to $MnK_4(P_3O_9)_2.2H_2O$, is triclinic P-1 with the following unit-cell dimensions: a = 9.235(4)Å, b = 7.599(3)Å, c = 7.148(1)Å, α = 96.38(2)°, β = 103.90(5)°, γ = 102.06(3)° and Z = 1. The total dehydration of $CdK_4(P_3O_9)_2.2H_2O$, between 350°C and 420°C, leads to its anhydrous form $CdK_4(P_3O_9)_2$. $CdK_4(P_3O_9)_2$ is a new cyclotriphosphate crystallizing in the rhombohedral system, space group $P\text{-}3_1c$, Z = 2 with the following unit-cell dimensions: a = b = 7.337(3)Å and c = 19.920(1)Å. $CdK_4(P_3O_9)_2$ is stable until its melting point at 431°C. The thermal behavior of $CdK_4(P_3O_9)_2.2H_2O$ has been investigated and interpreted by comparison with IR absorption spectrometry and X-ray diffraction experiments. Two different methods Ozawa and KAS have been selected in studying the kinetics of thermal behavior of the title compound.

INTRODUCTION

During a systematic investigation of cyclotriphosphates of monovalent cations M^I ($M^I = Na^+, K^+, Ag^+$ and NH_4^+), manganese and cadmium, a new form of the potassium and cadmium salt $CdK_4(P_3O_9)_2$ has been obtained. Three cyclotriphosphates $MnNa_4(P_3O_9)_2.4H_2O$*[1,2,3]*, $Mn(NH_4)_4(P_3O_9)_2.6H_2O$*[3]*, $MnK_4(P_3O_9)_2.2H_2O$ and $MnAg_4(P_3O_9)_2.6H_2O$*[4, 5]* have already been prepared and characterized. The present work reports the chemical preparation, thermal behavior, IR studies of $CdK_4(P_3O_9)_2.2H_2O$ and its anhydrous form $CdK_4(P_3O_9)_2$ and crystallographic data of $CdK_4(P_3O_9)_2$. The kinetic of thermal dehydration of $CdK_4(P_3O_9)_2.2H_2O$ was studied using thermal analyses TGA-DTA coupled by two different methods. In this work, the kinetic and thermodynamic parameters for the dehydration process of $CdK_4(P_3O_9)_2.2H_2O$ are reported for the first time. It is to be noticed that $CdK_4(P_3O_9)_2.2H_2O$ and $CdK_4(P_3O_9)_2$ are binary fertilizers type PK and can be used in the production of fertilizers. $CdK_4(P_3O_9)_2.2H_2O$ and $CdK_4(P_3O_9)_2$ are stable under the normal conditions of temperature and pressure.

Experimental

Chemical Preparation

Polycrystalline samples of the title compound were prepared by slowly adding dilute cyclotriphosphoric acid to an aqueous solution of manganese carbonate and potassium carbonate with a stoichiometric ratio K/Mn = 4, according to the following chemical reaction**:**

$$2H_3P_3O_9 + CdCO_3 + 2K_2CO_3 \longrightarrow CdK_4(P_3O_9)_2.2H_2O + 3CO_2 + 1H_2O$$

The solution obtained was then slowly evaporated at room temperature until polycrystalline samples of $CdK_4(P_3O_9)_2.2H_2O$ were obtained. 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"*[6]*. $Na_3P_3O_9$ was obtained by thermal*[7]* treatment of sodium

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dihydrogenomonophosphate, at 530°C for 5 hours in air according to:

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

The weight loss performed by slowly heating up to a temperature of 200°C, confirms the compound as a dihydrate, $CdK_4(P_3O_9)_2.2H_2O$.

$CdK_4(P_3O_9)_2$ was obtained by total dehydration of $CdK_4(P_3O_9)_2.2H_2O$*[3, 8, 9]* under atmospheric pressure, between 350 and 420°C. With a further increase in temperature, $CdK_4(P_3O_9)_2$ melts at 431°C.

Both cyclotriphosphates, $CdK_4(P_3O_9)_2.2H_2O$ and its anhydrous form $CdK_4(P_3O_9)_2$, described in the present work are stable for years in normal conditions of temperature and humidity.

$CdK_4(P_3O_9)_2.2H_2O$ and $CdK_4(P_3O_9)_2$ have been studied through different techniques with the experimental conditions described below.

XRD, Crystal data, intensity data collection and structure

X-ray diffraction. Powder diffraction patterns were registered with a SIEMENS diffractometer type D 5000 using CuKα1 radiation (λ = 1.5406Å).

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.

Thermal behavior. Thermal analyses TGA-DTA coupled were performed using the multimodule 92 Setaram Analyzer operating from room temperature up to 1400°C, in a platinum crucible, at various heating rates from 1 to 15°C/min. The differential scanning calorimetry (DSC) was performed with a Setaram DSC 92 apparatus.

Crystallographic characterization

Crystal Data. $CdK_4(P_3O_9)_2.2H_2O$ is isotypic to $MnK_4(P_3O_9)_2.2H_2O$ whose atomic arrangement was determined by M. T. Averbuch-Pouchot*[10]*. $CdK_4(P_3O_9)_2.2H_2O$*[8]* is triclinic P-1 with the following unit-cell dimensions : a = 9.235(4)Å, b = 7.599(3)Å, c = 7.148(1)Å, α = 96.38(2)°, β = 103.90(5)°, γ = 102.06(3)° and Z = 1.

$CdK_4(P_3O_9)_2$ is isotypic to a series of five cyclotriphosphates corresponding to the general formula $M^{II}Tl_4(P_3O_9)_2$ (M^{II} = Mg^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+})*[11]*, of $MnTl_4(P_3O_9)_2$*[8]* , of $MnCa_2(P_3O_9)_2$*[12,13,14]* and also of $MnK_4(P_3O_9)_2$ studied in our laboratory. It is worth noting that $CdK_4(P_3O_9)_2.2H_2O$*[8,9]* has never been studied except its crystallographic characterization.

$CdK_4(P_3O_9)_2$ crystallizes in the rhombohedral system, space group P-3_1c, Z = 2 with the following unit-cell dimensions: a = b = 7.337(3)Å and c = 19.920(1)Å. The X-ray diffractogram of $CdK_4(P_3O_9)_2$ is reported in **Figure 1**. Indexing of the X-ray diffraction pattern of $CdK_4(P_3O_9)_2$ is reported in **Table 1**.

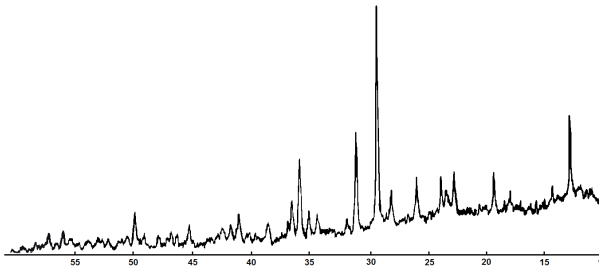

Figure 1 X-ray powder diffractograms of the phosphate $CdK_4(P_3O_9)_2.2H_2O$.

Table 1 Powder diffraction data of $CdK_4(P_3O_9)_2$

hkl	d_{cal}(Å)	d_{obs}(Å)	100I/I_0	hkl	d_{cal}(Å)	d_{obs}(Å)	100I/I_0
-	-	8.17	26	013	4.62	4.57	32
-	-	7.48	27	014	3.933	3.912	32
-	-	6.94	56	-	-	3.798	26
010	6.40	6.44	23	110	3.700	3.713	32
011	6.10	6.18	27	111	3.634	3.625	17
-	-	5.66	21	112	3.465	3.434	31
012	5.40	5.48	20	006	3.331	3.332	18
-	-	5.22	21	021	3.164	3.186	26
004	5.00	4.95	26	114	2.978	3.036	100
-	-	4.80	21	023	2.887	2.876	50

Theta range: 6-30°, Step size: 0.02°(2θ), Counting time : 30s

Infrared study

The IR absorption spectrum of $CdK_4(P_3O_9)_2.2H_2O$ is reported in **Figure 2a** and shows in the domain, 4000-3000 cm^{-1}, characteristic of the valence vibration bands (ν O-H), a large and strong band at 3450 cm^{-1} due to hydrogen bonds*[15]*. The domain, 1700-1600 cm^{-1}, characteristic of the bending vibration bands of water (δ HOH), shows one hand at 1630 cm^{-1} suggesting the existence of one type of water molecules in accordance with the crystalline structure of $CdK_4(P_3O_9)_2.2H_2O$, resolved on the basis of its isotypic compound $MnK_4(P_3O_9)_2.2H_2O$.

The range 1400-650 cm^{-1}, characteristic of the valence vibration bands of the cycle*[16,17]*, as well as possible bands due to interactons between P_3O_9 cycles and water molecules and also water vibration modes will be examined on the basis, of the crystalline structure of $CdK_4(P_3O_9)_2.2H_2O$ isotypic to $MnK_4(P_3O_9)_2.2H_2O$, and of our results of the 30 normal calculated frequencies of the P_3O_9 ring with high symmetry D_{3h}, of the frequency shifts during theoretical and successive isotopic substitutions of the equivalent atoms ^{31}P-^{33}P, $^{16}O_i$-$^{18}O_i$ and $^{16}O_e$-$^{18}O_e$, of the three equivalent atoms (3P,3O_i and 6O_e) belonging to the $P_3Oi_3Oe_6$ ring (D_{3h}). $CdK_4(P_3O_9)_2.2H_2O$ crystallizes in the triclinic system, space group P-1 (Ci), with a unit-cell containing two cycles P_3O_9 (one cycle is deduced from the other by the center of symmetry) with no local symmetry C_1. The reduced representation of the internal modes of the isolated ring P_3O_9 with D_{3h} symmetry is:

$\Gamma_{int} = 4A'_1(-,Ra) + 2A'_2(-,-) + 6E'(IR,Ra) + A''_1(-,-) + 3A''_2(IR,-) + 4E''(-,Ra)$.

The cycle P_3O_9 is built, theoretically, by three external (PO_2) groups and the P_3Oi_3 ring. Theoretical group analysis leads, for the valence vibration bands (the only ones which we consider here) to $\Gamma PO_2 = A'_1(-,Ra) + A''_2(IR,-) + E'(IR,Ra) + E''(-,Ra)$ and $\Gamma P_3Oi_3 = A'_1(-,Ra) + A'_2(-,-) + 2E'(IR,Ra)$. Theoretical

group analysis predicts six valence vibration bands for the PO_2 groups, six valence vibration bands for the P_3Oi_3 ring and 18 bending vibration bands for the P_3O_9 ring, Γbending = $2A'_1$(,Ra) + A'_2(-,-) + $A"_1$(-,-) + $2A"_2$ (IR,-) + 3E´(IR, Ra) + 3E"(-,Ra). These thirty fundamental frequencies of the cycle, D_{3h}, were calculated, by the MNDO method*[28]*, and their attribution was made by using successive isotopic substitutions ^{16}Oi-^{18}Oi, ^{31}P-^{33}P and ^{16}Oe-^{18}Oe (**Table 2**). From the isotopic effects (Δν), the contribution of each group of atoms, POiP and/or PO_2, to each calculated normal frequency was determinated. With this intention, we supposed that the pure movements of the POiP groups must leave the external oxygen atoms, Oe, fixed and those due to 100% of internal groups, Oi, fixed. By means of this assumption, the percentage of participation of each group was determinated (**Table 2**). The IR spectrum of CdK_4 $(P_3O_9)_2.2H_2O$ shows, in plus, 7, valence fundamental frequencies (in the range 1400-650 cm^{-1}). This number is less than, 12, predicted as well as for the isolated cycle with symmetry C_1 and for the crystalline unit-cell with group factor Ci in $CdK_4(P_3O_9)_2.2H_2O$ containing two P_3O_9 cycles, Γ_{val} =12Au(IR,-) + 12Ag(-,Ra). In fact, during the passage from the isolated cycle, with summetry C_1, to the crystalline unit-cell, each mode A of the site group is resolved into Au(IR,-) + Ag(-,Ra). It seems that the vibrationnal couplings between the two P_3O_9 cycles of the unit-cell, are absent or very weak, and don't disturb the IR spectrum of the title compound and don't allow the increasing of the IR frequencies to compare with those predicted for an isolated cycle with symmetry C_1.

We notice that the calculated frequencies values for the D_{3h} symmetry, are similar to those observed in the IR spectrum of $CdK_4(P_3O_9)_2.2H_2O$. On the basis of our results of calculations, using the MNDO method *[28]*, the fundamental frequencies of the $P_3O_9^{3-}$ cycle with high symmetry D_{3h} and the correlation group D_{3h} – group with low symmetry C_1, the attribution of the valence frequencies of the cycle, is proposed in **table 3**.

The crystalline structure of $MgTl_4$ $(P_3O_9)_2$*[11]*, proposed for CdK_4 $(P_3O_9)_2$ new phase, is described in the space group P-3_1c (D_{3d}^2) with two formula units (Z = 2) per unit-cell. The crystalline unit-cell contains four cycles occupying sites with local symmetry C_3. During the passage from the symmetry D_{3h} to the C_3 symmetry of the cycle, supposed isolated, of CdK_4 $(P_3O_9)_2$, the simple normal modes A´1, A´2, $A"_1$ and $A"_2$, Of the symmetry D_{3h}, are resolved each one into the mode A, of the symmetry C_3, and the doubly degenerate E´ and E" modes are resolved into the mode E of the symmetry C_3. For this reason, 7 IR bands are predicted, in the range of valence vibrations, for the isolated cycle with symmetry C_3 which has four vibration frequencies with simple modes A and four modes E. The experimental IR spectrum of $CdK_4(P_3O_9)_2$ **(Figure 2b)** shows, in the domain 1400-650 cm^{-1}, 7 IR fundamental bands. This number of six bands is less than that predicted for an isolated cycle with symmetry C_3. When we pass from the isolated cycle with symmetry C_3 to the crystalline unit-cell of CdK_4 $(P_3O_9)_2$ containing 4 cycles in interaction between them, the four IR bands with modes E, of the C_3 symmetry, should appear in the shape of a doublet of frequencies with modes Eu of the group factor D_{3d}.

Table2 IR frequencies and displacements (Δυ in cm^{-1}) calculated for the D_{3h} symmetry and for the substitutions of the internal oxygen atoms (Oi), of the external oxygen atoms (Oe) by the isotope ^{18}O and of the phosphorus atoms by the isotope ^{33}P and percentage of participation of the POP and PO_2 groups

$^{31}P_3{}^{16}O_9{}^{3-}$	$^{31}P_3{}^{18}Oi_3{}^{16}Oe_6{}^{3-}$		$^{33}P_3{}^{16}O_9{}^{3-}$		$^{31}P_3{}^{16}Oi_3{}^{18}Oe_6{}^{3-}$		% of
ν(cm^{-1})	ν(cm^{-1})	Δν(cm^{-1})	ν(cm^{-1})	Δν(cm^{-1})	ν(cm^{-1})	Δν(cm^{-1})	Participation
1288.39	1287.80	0.59	1269.56	18.83	1249.94	38.45	$\nu_{as}PO_2$ [99]
1272.42	1272.03	0.39	1254.33	18.09	1233.29	39.13	$\nu_{as}PO_2$ [100]
1272.42	1272.03	0.39	1254.33	18.09	1233.29	39.13	
1225.23	1179.02	46.20	1215.36	9.87	1223.90	1.32	ν_{as}POP [98] + $\upsilon_s PO_2$ [2]
1225.23	1179.02	46.20	1215.36	9.87	1223.90	1.32	
1169.25	1168.86	0.39	1156.27	12.98	1127.60	41.65	$\upsilon_s PO_2$ [100]
1108.62	1098.55	10.07	1102.24	6.38	1062.88	45.74	ν_{as}POP [18] + $\upsilon_s PO_2$ [82]
1108.62	1098.55	10.07	1102.24	6.38	1062.88	45.74	
1059.41	1010.98	48.43	1053.00	6.41	1058.95	0.46	υ_{as} POP [100]
780.72	768.35	12.36	765.35	15.37	775.94	4.78	υ_sPOP [73] + δPO_2 [27]
780.72	768.35	12.36	765.35	15.37	775.94	4.78	
671.06	659.43	11.64	663.25	7.82	660.26	10.81	υ_sPOP [52] + δPO_2 [48]
559.30	537.04	22.26	555.32	3.98	552.99	6.31	δPOP (δcycle) [78] + δPO_2 [22]
511.49	496.11	15.38	509.22	2.27	501.42	10.07	γPOP [60] + $\gamma_R PO_2$ [40]
436.79	433.11	3.68	432.47	4.32	422.93	13.86	δPOP [21] + δPO_2 [79]
436.79	433.11	3.68	432.47	4.32	422.93	13.86	
420.11	417.43	2.68	416.98	3.13	411.08	9.03	$\gamma_w PO_2$ [78]
418.64	406.27	12.37	416.98	1.66	410.11	8.52	γPOP [59] + $\gamma_T PO_2$ [41]
418.64	406.27	12.37	413.15	5.49	410.11	8.52	
302.05	301.64	0.41	301.40	0.64	289.37	12.68	δPO_2 [98]
298.72	292.60	6.12	298.18	0.54	289.37	9.35	δPOP[40] + $\gamma_W PO_2$ [60]
298.72	292.60	6.12	298.18	0.54	285.93	12.79	
280.98	279.09	1.89	279.07	1.91	269.75	11.23	γPOP [14] + $\gamma_T PO_2$ [86]
280.98	279.09	1.89	279.07	1.91	269.75	11.23	
256.58	253.04	3.55	255.07	1.51	246.51	10.07	δPOP [26] + γ_W PO_2 [74]
256.58	253.04	3.55	255.07	1.51	246.51	10.07	
214.09	214.06	0.03	214.06	0.03	201.82	12.28	$\gamma_T PO_2$ [100]
49.31	48.52	0.79	49.29	0.02	47.21	2.10	γPOP [27] + $\gamma_R PO_2$ [73]
35.02	34.37	0.65	35.02	0.00	33.59	1.43	γPOP [33] + $\gamma_R PO_2$ [67]
35.02	34.37	0.65	35.02	0.00	33.59	1.43	

ν_{as} : asymmetric stretching; ν_s : symmetric stretching; δ : bending; γ : out of plane P_3Oi_3;
γ_w : wagging ($\gamma \perp PO_2$); γ_R : rocking (γ // PO_2); γ_T : twisting; Oi : internal oxygen atom of the ring and Oe: external oxygen atom of the ring

Table 3 comparison of valence vibratory modes of the cycle, free with moleculary group D_{3h} (υ calculated), with site symmetry C_1 and of the two cycles of the unit-cell in interaction between them in $CdK_4(P_3O_9)_2.2H_2O$

Moleculary group D_{3h}					Site symmetry C_1		Group factor C_i	
ν_{cal} (cm^{-1})	I (Km/mol)	vibration	Mode	Activity	Mode	Activity	Mode Activity	$CdK_4(P_3O_9)_2.2H_2O$
1288	4264	$\upsilon_{as}PO_2$	A''$_2$	(IR , -)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	
1272	0	$\upsilon_{as}PO_2$	E''	(-, Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	1284 (VS)
1272	0				A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	
1225	7713	$\upsilon_{as}POP$	E'	(IR,Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	
1225	7714				A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	
1169	0	υ_sPO_2	A'$_1$	(-, Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	1150 (m)
1108	452	υ_sPO_2	E'	(IR,Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	
1108	451				A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	1095 (VS)
1059	0	$\upsilon_{as}POP$	A'$_2$	(- , -)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	1000 (VS)
781	1415	υ_sPOP	E'	(IR,Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	858 (sh)
781	1414				A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	771(S) 747 (S)
671	0	υ_sPOP	A'$_1$	(-, Ra)	A	(IR,Ra)	Ag (-,Ra) Au (IR,-)	684 (m)

VS: very strong S: Strong m: medium sh: shoulder

Table 4 Attribution of the observed valence IR frequencies (cm^{-1}) of the P_3O_9 ring (C_3) in $CdK_4(P_3O_9)_2.2H_2O$ (I) and $CdK_4(P_3O_9)_2$ (II)

S. G.			Δν (cm^{-1})			(I)	(II)	
C_3 vcal (cm^{-1})	I/Imax	Mode (IR, Ra)	^{16}Oi-^{18}Oi	^{31}P-^{33}P	^{16}Oe-^{18}Oe	IR		Main Movement
1288.39	55.20	A (+,+)	0.59	18.83	38.45			$\nu_{as}PO_2$
1272.42	0.01	E (+,+)	0.39	18.09	39.13	1284	1280	$\nu_{as}PO_2$
1272.42	0.01		0.39	18.09	39.13			
1225.23	100.00	E (+,+)	46.20	9.87	1.32			$\nu_{as}POP$
1225.23	100.00		46.20	9.87	1.32			
1169.25	0.00	A (+,+)	0.39	12.98	41.65			ν_sPO_2
						1150	1158	
1108.62	5.81	E (+,+)	10.07	6.38	45.74	1095	1095	ν_sPO_2
1108.62	5.81		10.07	6.38	45.74			
1059.41	0.00	A (+,+)	48.43	6.41	0.46	1000 858sh	1009 874sh	ν_{as} POP combination
780.72	18.34	E (+,+)	12.36	15.37	4.78	771	787	ν_s POP
780.72	18.34		12.36	15.37	4.78	747	748	
671.06	0.01	A (+,+)	11.64	7.82	10.67	684	684	ν_s POP

Δν (cm^{-1}) : effect of the isotopic substitution; Δν (cm^{-1}) : difference between the calculated Value of the frequency before and after the substitution; S. G. : site group.

This situation is due to the correlation group C_3 – group factor D_{3d} resolving the mode A, of C_3, into modes A_{1g}(-, Ra) + A_{2g}(-,-) + A_{1u}(-,-) + A_{2u}(IR, Ra), of the group D_{3d}, and the mode E into 2Eg(-,Ra) + 2Eu(IR,-).

We notice that the calculated frequencies values of the D_{3h} symmetry are similar to those observed in the IR spectra of $CdK_4(P_3O_9)_2.2H_2O$ and its anhydrous form $CdK_4(P_3O_9)_2$. On the basis of our results of calculations of the normal frequencies of the $P_3O_9^{3-}$ cycle with high symmetry D_{3h} and the

correlations group D_{3h} – groups with low symmetries C_3 and C_1, the assignment of the valence frequencies of the cycle, is given in **table 4**.

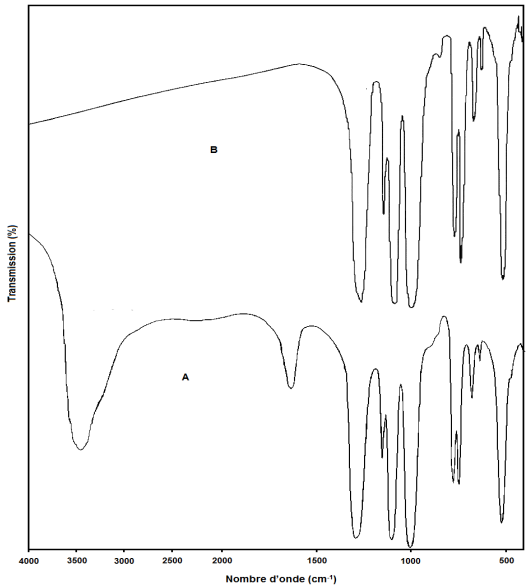

Figure 2 IR spectra of the phosphates: (a) $CdK_4(P_3O_9)_2.2H_2O$ and (b) $CdK_4(P_3O_9)_2$

Thermal Behavior

The two curves corresponding to the TGA and DTA analyses in air atmosphere and at a heating rate 3°C/min of $CdK_4(P_3O_9)_2.2H_2O$ are shown in Figure 3. The loss of water of dehydration on the TG curve (**Figure 3**) takes place in three steps between 50°C and 350°C corresponding to 4.62% weight loss instead of 4.63% for the theoretical one assuming $2H_2O$ in the formula.

The dehydration of the cyclotriphosphate dihydrate of cadmium and potassium $CdK_4(P_3O_9)_2.2H_2O$ happens in three steps in three temperature ranges 50 – 135°C, 135 – 215°C and 215 – 350°C **(Figure 3)**. In the thermogravimetric (TG) curve **(Figure 3)**, the first stage between 50 and 135°C attributed to the elimination of 1.1 water molecules corresponding to 2.54 weight loss, the second stage from 135 to 215°C is due to the elimination of 0.6 water molecule corresponding to 1.39 weight loss and the third stage 215 – 350°C attributed to the elimination of 0.3 water molecule corresponding to 0.69 weight loss.

The thermal analysis curve (DTA in **Figure 3**) shows that the cyclotriphosphate $CdK_4(P_3O_9)_2.2H_2O$ undertakes at 68°C and 217°C two endothermic peaks and one exothermic peak at 213°C. The first endothermic peak at 68°C is due to the dehydration (departure of $1H_2O$) of the title compound, $CdK_4(P_3O_9)_2.2H_2O$, well confirmed by the weight loss observed on the TG curve (**Figure 3**) between 50°C and 135°C. The second endothermic peak at 217°C is due to the dehydration (departure of $1H_2O$) of the title compound, $CdK_4(P_3O_9)_2.2H_2O$, well confirmed by the weight loss observed on the TG curve (**Figure 3**) between 135°C and 350°C. The only exothermic peak at 213°C on the DTA curve (**Figure 3**) is due to the crystallization of the anhydrous cyclotriphosphate $CdK_4(P_3O_9)_2$ well characterized by X-ray diffraction (**Figure 1**) and infrared spectrometry (**Figure 2b**).

The thermal behavior of $CdK_4(P_3O_9)_2.2H_2O$ was also studied in a step manner of temperature by X-ray diffraction and IR absorption experiments between 20°C and 431°C. $CdK_4(P_3O_9)_2.2H_2O$ is stable until 50°C. The removal of the two water molecules of hydration of $CdK_4(P_3O_9)_2.2H_2O$, observed in the temperature range 50-350°C, neither destroys the crystalline network nor yields to an intermediate amorphous phase but leads to the crystallization of a new ring phosphate (**Figure 1**) which exhibits the IR absorption bands characteristic of a cyclic phosphate*[16-27]* (**Figure 2b**). The water characteristic vibrations have disappeared after the complete dehydration at 350°C (**Figure 2b**). The product of the total dehydration of $CdK_4(P_3O_9)_2.2H_2O$ between 350 and 420°C is a new anhydrous cyclotriphosphate $CdK_4(P_3O_9)_2$ characterized in the present study. In fact, the only exothermic peak observed on the DTA curve (**Figure 3**) at 213°C corresponds to the crystallization of $CdK_4(P_3O_9)_2$. With further increase in temperature, $CdK_4(P_3O_9)_2$ remains stable and melts at 431°C.

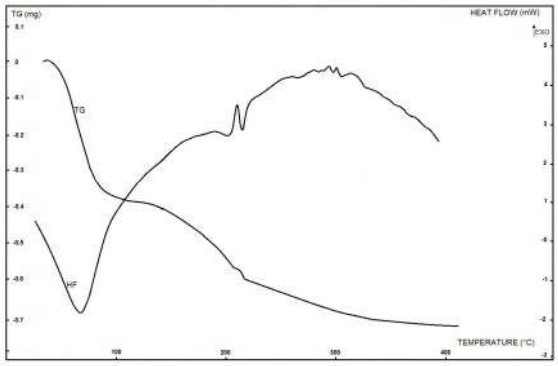

Figure 3 TGA and DTA curves of CdK4 (P3O9)2.2H2O at rising temperature (3°C/min)

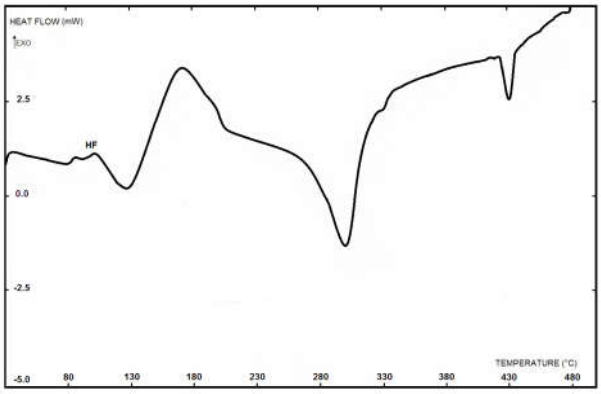

Figure 4 DSC curve of CdK4 (P3O9)2.2H2O at rising temperature (3°C/in)

The curves of differential scanning calorimetry (DSC) at different rising temperatures (3 and 10°C/min) of $CdK_4(P_3O_9)_2.2H_2O$, represented by the **Figures 4 and 5**, show one exothermic peak at 174°C for 3°C/min (184°C for 10°C/min) and three endothermic peaks at 129°C, 302°C and 431°C for 3°C/min (138°C, 326°C and 443°C for 10°C/min) **(Figures 4 and 5)**. The first two endothermic peaks correspond to the dehydration of $CdK_4(P_3O_9)_2.2H_2O$ and are then due to the departure of water molecules (peaks at 129°C ($1H_2O$) and 302°C ($1H_2O$) for 3°C/min; 138°C ($1H_2O$) and 326°C ($1H_2O$) for 10°C/min). The exothermic peaks at 174°C for 3°C/min and 184°C for 10°C/min are due to the crystallization of the

anhydrous form of the title compound, $CdK_4(P_3O_9)_2$, well characterized by X-ray diffraction (**Figure 1**) and infrared spectrometry (**Figure 2b**). The crystallization of $CdK_4(P_3O_9)_2$ was also observed on the DTA curve at 3°C/min by an exothermic peak at 213°C (**Figure 3**). The endothermic peaks at 431°C for 3°C/min and 443°C for 10°C/min are due to the melting of $CdK_4(P_3O_9)_2$. The values of the enthalpy variations of all the peaks, observed in the differential scanning calorimetry (DSC) curves at different rising temperatures (3 and 10°C/min) of $CdK_4(P_3O_9)_2.2H_2O$, are gathered in the **Table 5.**

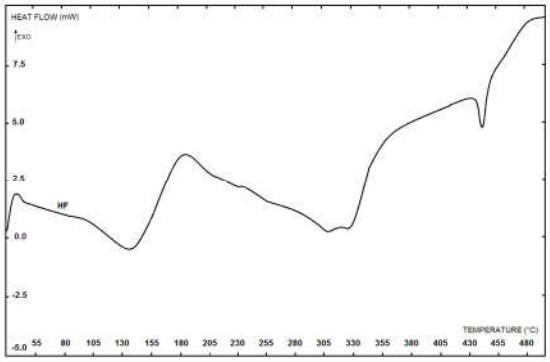

Figure 5 DSC curve of $CdK_4(P_3O_9)_2.2H_2O$ at rising temperature (10°C/min)

Table 5 Enthalpy variations of all the peaks observed in the differential scanning calorimetry (DSC) curves at different rising temperatures (3 and 10°C/min) of $CdK_4(P_3O_9)_2.2H_2O$

	3°C/min		10°C/min	
Peaks	T(°C)	ΔH (kcal.mol^{-1})	T(°C)	ΔH (kcal.mol^{-1})
First peak Removal of water ($1H_2O$)	129	7.54	138	6.68
Second peak Crystallization of $CdK_4(P_3O_9)_2$	174	-7.72	184	-6.81
Third peak Removal of water ($1H_2O$)	302	20.10	326	19.49
Fourth peak Melt of $CdK_4(P_3O_9)_2$	431	1.49 ΔS = 2.08 cal. K^{-1}. mol^{-1}	443	1.28 ΔS = 1.82 cal. K^{-1}. mol^{-1}

Estimation of the thermodynamic functions

Various equations of kinetic analyses are known such as Kissinger's method*[29]*, Kissinger-Akahira-Sunose (KAS) *[30]*, Ozawa*[31]*, Coats-Redfern*[32]* and Van Krevelen *et al. [33]* methods. Especially, the Ozawa and KAS equations were well described and widely used in the literature, therefore, these methods are selected in studying the kinetics of thermal dehydration of the title compound. So, water loss kinetic parameters were evaluated using the Kissinger-Akahira-Sunose (KAS) *[30]* and Ozawa*[31]* methods, from the curves $\ln(v/T^2_m) = f(1/T_m)$ and $\ln(v) = f(1/T_m)$ (**Figures 6 and 7**), where v is the heating rate and T_m the sample temperature at the thermal effect maximum. The characteristic temperatures at maximum dehydration rates, Tm in °C, at different heating rates from the DTA curves of $CdK_4(P_3O_9)_2.2H_2O$ are gathered in **table 6**.

Table 6 Characteristic temperatures at maximum dehydration rates, T_m in K, at different heating rates from the DTA curves of $CdK_4(P_3O_9)_2.2H_2O$

Heating rate *v*	3°C/min	5°C /min	10°C /min	15°C /min
First peak $1H_2O$	68	75	81	88
second peak $1H_2O$	217	225	230	238

From these temperatures and according to the Kissinger-Akahira-Sunose (KAS) *[30]* and Ozawa*[31]* methods, the apparent activation energies of dehydration were calculated for the cyclotriphosphate $CdK_4(P_3O_9)_2.2H_2O$. For the Kissinger-Akahira-Sunose (KAS) *[30]* method, the slope of the resulting straight line of the curve: $\ln(v/T^2_m) = f(1/T_m)$ (**Figure 6**), equals to : $-E_a/R$, allows the apparent activation energy to be calculated (**table 7**). Concerning the Ozawa*[31]* method, the slope of the resulting straight line on the curve : $\ln(v) = f(1/T_m)$ (**Figure 7**), equals to -1.0516E/R, allows also the apparent activation energy to be calculated by this second way (**table 7**). The equations used for the two methods are the following:

$$Ln\left(\frac{v}{T^2_m}\right) = Ln\left(\frac{AR}{E}\right) - \left(\frac{E}{R}\right)\left(\frac{1}{T_m}\right) \quad \text{for KAS } [30] \quad (1)$$

$$Ln(v) = Ln\left(\frac{AR}{1.0516E}\right) - 1.0516\left(\frac{E}{R}\right)\left(\frac{1}{T_m}\right) \quad \text{for OZAWA } [31] \quad (2)$$

The pre-exponential factor or Arrhenius constant (A) can be calculated from both KAS*[30]* and Ozawa*[31]* methods. The related thermodynamic functions can be calculated by using the activated complex theory (transition state) of Eyring *[34-36]*. The following general equation can be written *[36]*:

$$A = \left(\frac{e\chi\, k_B T_m}{h}\right) exp\left(\frac{\Delta S^*}{R}\right) \quad (3)$$

where e is the Neper number (e = 2.7183), χ is the transition factor, which is unity for the monomolecular reaction, k_B is the Boltzmann constant ($k_B = 1.3806 \times 10^{-23}$ J K^{-1}), h is Plank's constant ($h = 6.6261 \times 10^{-34}$ J s), T_m is the peak temperature of the DTA curve, R is the gas constant (R = 8.314 J K^{-1} mol^{-1}) and ΔS^* is the entropy change of transition state complex or entropy of activation. Thus, the entropy of activation may be calculated as follows:

$$\Delta S^* = RLn\frac{Ah}{e\chi\, k_B T_m} \quad (4)$$

The enthalpy change of transition state complex or heat of activation (ΔH^*) and Gibbs free energy of activation (ΔG^*) of decomposition were calculated according to Eqs. (5) and (6), respectively:

$$\Delta H^* = E^* \quad R\,T_m \quad (5)$$

$$\Delta G^* = \Delta H^* \quad T_m \Delta S^* \quad (6)$$

Where, E^* is the activation energy E_a of both KAS*[30]* and Ozawa*[31]* methods. The values of the activation energy are gathered in **Table 7**. Thermodynamic functions were calculated from Eqs. (4), (5) and (6) and summarized in **Table 8**. The negative values of ΔS^* from two methods for the dehydration step reveals that the activated state is less disordered compared to the initial state. These ΔS^* values suggest a large number of degrees of freedom due to rotation which may be interpreted as

a « slow » stage[36-38]in this step. The positive values of ΔG^* at all studied methods are due to the fact that, the dehydration processes are not spontaneous. The positivity of ΔG^* is controlled by a small activation entropy and a large positive activation enthalpy according to the Eq. 6. The endothermic peaks in DTA data agree well with the positive sign of the activation enthalpy (ΔH^*). The estimated thermodynamic functions ΔS^* and ΔG^* (**Table 8**) from two methods are different to some extent due to the different pre-exponential factor of about 10^7. While ΔH^* (**Table 8**) exhibits an independent behavior on the pre-exponential factor as seen from exhibiting nearly the same value.

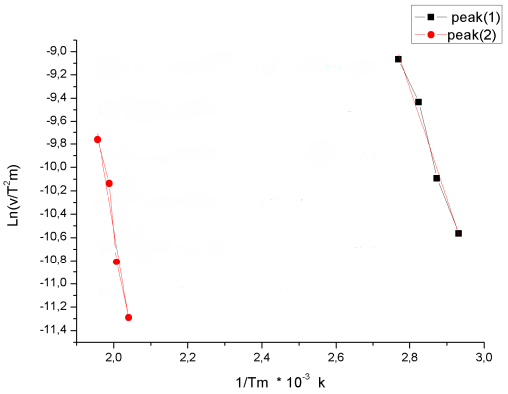

Figure 6 Ln (v/Tm^2) = f(1/Tm) for $CdK_4(P_3O_9)_2.2H_2O$

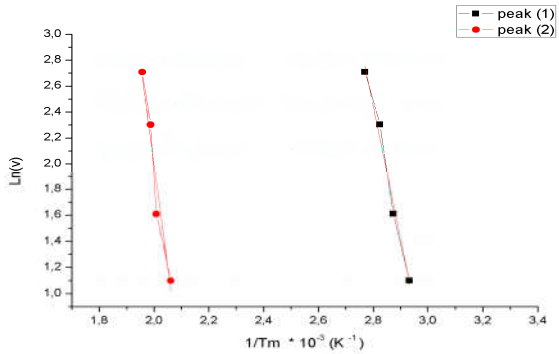

Figure 7 Ln (v) = f(1/Tm) for $CdK_4(P_3O_9)_2.2H_2O$

Table 7 Activation energy values E_a, pre-exponential factor (A) and correlation coefficient (r^2) calculated by ozawa and KAS methods for the dehydration of $CdK_4(P_3O_9)_2.2H_2O$ under atmospheric pressure

	Ozawa Method			KAS Method		
	E_a / kJ. mol^{-1}	r^2	A / min^{-1}	E_a / kJ. mol^{-1}	r^2	A / min^{-1}
First peak $1H_2O$	81.157	0.979	2.210×10^{12}	79.605	0.976	3.8109×10^{11}
Second peak $1H_2O$	124.664	0.943	1.291×10^{13}	122.832	0.953	2.9336×10^{12}

Table 8 Values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for dehydration step of $CdK_4(P_3O_9)_2.2H_2O$ calculated according to ozawa and KAS equations

	$CdK_4(P_3O_9)_2.2H_2O$					
Model	Ozawa method			KAS method		
	ΔS^* (J. K^{-1}.mol^{-1})	ΔH^* (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})	ΔS^* (J. K^{-1}.mol^{-1})	ΔH^* (kJ.mol^{-1})	ΔG^* (kJ.mol^{-1})
First peak $1H_2O$	-18.4964	78.156	84.833	-33.1106	76.604	88.557
Second peak $1H_2O$	-6.70611	120.415	123.842	-19.0310	118.584	128.309

CONCLUSION

The present work concerns the thermal behavior of $CdK_4(P_3O_9)_2.2H_2O$. This study allows us the identification and the characterization of a new phase $CdK_4(P_3O_9)_2$. The later is the final product of dehydration of $CdK_4(P_3O_9)_2.2H_2O$. This anhydrous phase is stable until its melting point at 431°C. According to the known crystalline structure of $CdK_4(P_3O_9)_2.2H_2O$, isotypic to $MnK_4(P_3O_9)_2.2H_2O$, whose water molecules are of constitution and of one type remove the solid in three kinetic steps with an activation energy of dehydration calculated by Ozawa and KAS methods. The passage from the dihydrated phase, $CdK_4(P_3O_9)_2.2H_2O$, to the anhydrous one, $CdK_4(P_3O_9)_2$, occurs with no amorphous phase and with no breaking of the cycle $P_3O_9^{3-}$ and is accompanied with an enthalpy variation measured of 56.32 kJ. mol^{-1} in the differential scanning calorimetry DSC. Two different methods Ozawa and KAS have been selected in studying the kinetics of thermal behavior of the title compound. In fact, in this work, the kenitecs and thermodynamic parameters for the dehydration process of $CdK_4(P_3O_9)_2.2H_2O$ have been calculated and reported for the first time. Finally, we have examinated and interpreted the IR spectra of the title compound and its anhydrous form $CdK_4(P_3O_9)_2$ in the light of the crystalline structures of their isotypic compounds respectively, of our results of calculations of the IR fundamental frequencies of the cycle $P_3O_9^{3-}$ with high symmetry D_{3h} and the successive isotopic substitutions of the equivalent atoms ^{31}P-^{33}P, $^{16}O_i$-$^{18}O_i$ and $^{16}O_e$-$^{18}O_e$, of the three equivalent atoms (3P, $3O_i$ and $6O_e$) belonging to the $P_3Oi_3Oe_6$ ring. The thermal behavior of $CdK_4(P_3O_9)_2.2H_2O$ can be summarized by the following schema:

$$CdK_4(P_3O_9)_2.2H_2O \xrightarrow{50\text{-}350^\circ C} CdK_4(P_3O_9)_2 + 2H_2O \xrightarrow{431^\circ C} \text{Melt of } CdK_4(P_3O_9)_2$$

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