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Chemical Preparation, Structural Investigation, and Thermal Behavior of a New Cyclohexaphosphate: $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$

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We describe the chemical preparation and crystal structure of zinc–cesium cyclohexaphosphate octahydrate: $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$. This new compound is monoclinic, $P2_1$, with the dimolecular unit cell $a = 11.895(9)$, $b = 12.663(7)$, $c = 8.079(8)$ Å, $\beta = 94.33(7)°$. This new type of noncentric atomic arrangement has a typical layer organization, built by corrugated layers of corner sharing ZnO_6 and P_6O_{18} entities, spreading perpendicular to the c direction. Cesium atoms are located in channels created by this network. One of the water molecules does not take part in the associated cation coordination polyhedra. The atomic arrangement was determined with a final R value of 0.035 for 4583 independent reflections. The thermal behavior has been investigated and interpreted by comparison with IR absorption spectroscopy, DTA, and DTG experiments. © 1994 Academic Press, Inc.

INTRODUCTION

Due to the lack of an appropriate starting material, the chemistry of cyclohexaphosphates has been slow to develop. Since the recent improvement by Schülke and Kayser (1) of the Griffith and Buxton process (2), convenient amounts of $Li_6P_6O_{18}$ can be easily prepared with an almost theoretical yield by thermal condensation of LiH_2PO_4. Following this discovery, a systematic investigation of the cyclohexaphosphate crystal chemistry was undertaken and today more than 60 members of this family are well characterized. The present state of the crystal chemistry of this family of phosphates has recently been reviewed (3). In the particular field of divalent–monovalent cation cyclohexaphosphates, more than 10 derivatives are presently known. Up to now, they have belonged to six different structure types, but all correspond to the general formula $M^{II}_2M^{I}_2P_6O_{18} \cdot xH_2O$. In the present study, we report chemical preparation and crystal structure of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$, the first divalent–monovalent cation cyclohexaphosphate containing cesium atoms.

EXPERIMENTAL

A. Chemical Preparation

The title compound was prepared in two steps. An aqueous solution of cyclohexaphosphoric acid was first prepared by passing a solution of $Li_6P_6O_{18}$ through an ion-exchange resin in its H-state (Amberlite IR-120). The lithium salt was prepared according to the process described by Schülke and Kayser (1) using purum p.a. Fluka chemicals. This solution was then neutralized by stoichiometric amounts of $ZnCO_3$ and Cs_2CO_3, both purum p.a. Fluka. Schematically, the reaction is

$$H_6P_6O_{18} + 2\,ZnCO_3 + Cs_2CO_3 \xrightarrow{5H_2O} Zn_2Cs_2P_6O_{18} \cdot 8H_2O + 3\,CO_2.$$

In order to avoid hydrolysis of the ring anion, the above reaction is performed at room temperature. The so-obtained solution is then slowly evaporated at room temperature until large rectangular prisms of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$ are formed. The title compound is stable for months under normal conditions of temperature and hygrometry.

B. Crystal Data

(*1*) *Unit-cell and space-group determination.* A preliminary single-crystal investigation was performed using the Weissenberg technique in order to determine symmetry and space group. Symmetry appeared to be monoclinic

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TABLE 1

Crystal Data and Experimental Parameters Used for the Intensity Data Collection; Strategy and Final Results of the Structure Determination

I. Crystal data	
Formula: $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$	Space group: $P2_1$
Crystal system: monoclinic	F_w = 1014.496
a = 11.896(9), b = 12.663(7), c = 8.079(8) Å, β = 94.33(7)°	V = 1213(3) Å^3 Z = 2
Refinement of unit cell parameters:	20 reflections (9.4 < θ < 10.9)
ρ_{cal} = 2.777 g cm^{-3}	$F(000)$ = 900
Linear absorption factor:	$\mu(AgK\alpha)$ = 28.857 cm^{-1}
Morphology: rectangular prism	Crystal size: 0.24 × 0.24 × 0.28 mm
II. Intensity measurement	
Temperature: 294 K	Wavelength: $AgK\alpha$ (0.5608 Å)
Diffractometer: Nonius CAD4	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Max. scan time: 65 sec	Theta range: 2–30°
Measurement area: $\pm h, k, l$	h_{max} = 20, k_{max} = 21, l_{max} = 14
Total background measuring time:	1/2 scan time
Total number of scanned reflections:	7779
Total number of independent reflections:	7411 (R_{int} = 0.02)
Two intensity and orientation reference reflections:	no variations
III. Structure determination	
Lorentz and polarization corrections:	No absorption correction
Program used: SDP (4)	Computer used: Micro-Vax II
Determination:	Direct methods with MULTAN (5)
Thermal displacement parameters:	anisotropic
Unique reflections included:	4583 with $I > 4\sigma(I)$
Weighting scheme: unitary	Refined parameters: 324
Residual Fourier density:	$-0.900 < \rho < 1.48\ e/Å^3$
Unweighted agreement factor R:	0.035
Weighted agreement factor R_w:	0.037
Esd: 1.482	Largest shift/error = 0.11
Drawings made with STRUPLO (6)	

and the only observed reflection condition ($0k0 = 2n$) corresponds to two possible space groups, $P2_1$ or $P2_1/m$. The structure determination will confirm the noncentrosymmetric $P2_1$ to be the proper one. The main crystallographic features of the title compound are given in Table 1.

(2) *Crystal structure.* The intensity data collection was performed using a CAD4 Enraf Nonius diffractometer. The experimental parameters used for this measurement, the strategy used for the structure determination, and its final results are gathered in Table 1.

C. Thermal Behavior

Thermal analysis was performed using a 2400 Setaram Analyser for ATG and a M5 Setaram Micro-ATD for DTA, both operating from room temperature up to 873 K at an average heating rate of 13 K/min.

D. Infrared Spectroscopy

Spectra were recorded in the range 4000–200 cm^{-1} with a Perkin–Elmer IR 983G spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

STRUCTURE DESCRIPTION

The present atomic arrangement is a typical layer organization. Slightly corrugated layers built by corner sharing P_6O_{18} ring anions and ZnO_6 octahedra are located in planes (a, b) separated by one period of the unit cell (8.079 Å). Inside such a layer, the ZnO_6 octahedra share five of their oxygen atoms with the adjacent P_6O_{18} rings. Figure 1, a projection of the atomic arrangement along the c direction, shows clearly the organization inside such a network. This ZnO_6–P_6O_{18} organization creates large channels in which the cesium atoms are located, all sited in planes $z = \frac{3}{8}$ and $\frac{5}{8}$. The cesium coordination polyhedra connect these layers along the c direction.

The phosphoric ring anion observed in the title compound has no internal symmetry and is so built by six independent PO_4 tetrahedra. In the present state of cyclohexaphosphate chemistry, recently reviewed by two of us (3), P_6O_{18} ring anions with no internal symmetry have been relatively rare, up to now only three examples have been reported (7–9). The main geometrical features of the present ring are reported in Table 3. The P–O–P and P–P–P angles range over the values commonly observed in this kind of ring, from 129.3 to 133.2° for P–O–P and from 85.89 to 116.48° for P–P–P. while the P–P distances

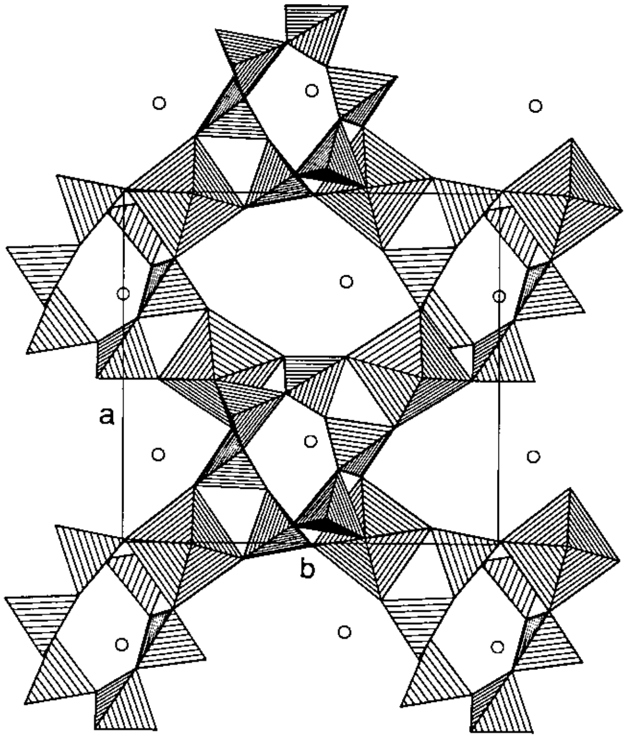

FIG. 1. Projection along the **c** direction of the atomic arrangement of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$. Empty circles represent cesium atoms. The water molecules have been omitted. P_6O_{18} ring anions and ZnO_6 octahedra are given in polyhedral representation.

TABLE 2
Final Atomic Coordinates and B_{eq} with their Esd in Parentheses
$B_{eq} = 4/3\ \Sigma_i\Sigma_j a_i b_j \beta_{ij}$

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}\ (\sigma)$
Cs(1)	0.29176(5)	0[a]	0.37857(6)	3.356(9)
Cs(2)	0.74770(5)	0.09353(5)	0.62544(7)	3.422(9)
Zn(1)	0.01246(5)	0.16499(5)	0.05182(8)	1.120(8)
Zn(2)	0.49842(5)	−0.24410(5)	0.11232(8)	1.254(8)
P(1)	0.9716(1)	0.4174(1)	0.0149(2)	0.97(2)
P(2)	0.7690(1)	0.2867(1)	−0.0129(2)	0.93(2)
P(3)	0.6141(1)	0.3121(1)	0.2476(2)	1.16(2)
P(4)	0.5249(1)	0.4999(1)	0.0775(2)	1.11(2)
P(5)	0.2717(1)	0.1283(1)	0.9374(2)	1.02(2)
P(6)	0.9193(1)	0.5604(1)	0.2839(2)	1.17(2)
O(L12)	0.8471(3)	0.3851(3)	0.9437(5)	1.27(6)
O(L16)	0.9505(4)	0.4507(3)	0.2004(5)	1.50(6)
O(E11)	−0.0074(3)	0.0075(3)	0.0832(5)	1.43(6)
O(E12)	0.0453(3)	0.3223(3)	0.0251(6)	1.55(6)
O(L23)	0.7330(3)	0.3201(4)	0.1668(5)	1.55(6)
O(E21)	0.3283(3)	0.7902(4)	0.1372(5)	1.42(6)
O(E22)	0.1623(3)	0.6899(3)	−0.0035(6)	1.58(6)
O(L34)	0.5718(4)	0.4328(3)	0.2370(5)	1.43(6)
O(E31)	0.3619(4)	0.7888(4)	0.5742(5)	1.93(7)
O(E32)	0.4643(3)	0.7429(3)	0.8565(5)	1.49(6)
O(L45)	0.6401(3)	0.5378(3)	0.0025(5)	1.32(6)
O(E41)	0.4659(3)	0.5935(4)	0.1406(6)	1.81(6)
O(E42)	0.5332(4)	0.9288(3)	0.0482(5)	1.63(6)
O(L56)	0.7880(3)	0.5747(4)	0.2280(5)	1.68(7)
O(E51)	0.3326(3)	0.2246(3)	0.8896(6)	1.75(7)
O(E52)	0.8099(3)	0.6363(3)	0.9337(5)	1.37(6)
O(E61)	0.9294(4)	0.5413(4)	0.4648(5)	2.07(8)
O(E62)	−0.0157(4)	0.6471(3)	0.2117(5)	1.59(6)
O(W1)	0.2480(4)	0.5078(6)	0.7573(7)	3.1(1)
O(W2)	0.5255(4)	0.7967(5)	0.3562(5)	2.54(9)
O(W3)	0.0044(6)	0.1842(4)	0.3024(6)	3.1(1)
O(W4)	0.2654(5)	0.3768(5)	0.1716(8)	3.2(1)
O(W5)	0.2805(6)	0.2543(7)	0.4670(9)	4.8(2)
O(W6)	0.5415(9)	0.0470(8)	0.366(1)	7.0(2)
O(W7)	0.083(1)	0.809(1)	0.451(1)	9.8(3)
O(W8)	0.882(2)	0.852(2)	0.362(3)	21.3(6)

[a] Fixed parameter.

ranging from 2.905 to 2.934 Å also correspond to generally measured values.

The coordination polyhedra of the two independent zinc atoms are slightly distorted octahedra built by five oxygen atoms and one water molecule. Within a range of 3.50 Å, the two cesium atoms have a ninefold coordination built by seven oxygen atoms and two water molecules for Cs(1) and five oxygen atoms and four water molecules for Cs(2).

Among the eight independent water molecules, the first seven are involved in associated cation polyhedra the last one is not, and its high thermal factor ($B_{eq} = 21.3$) reflects this situation. As in many similar cases, it is difficult to say if this high thermal factor must be attributed to a partly occupied crystallographic site or to an effective thermal motion.

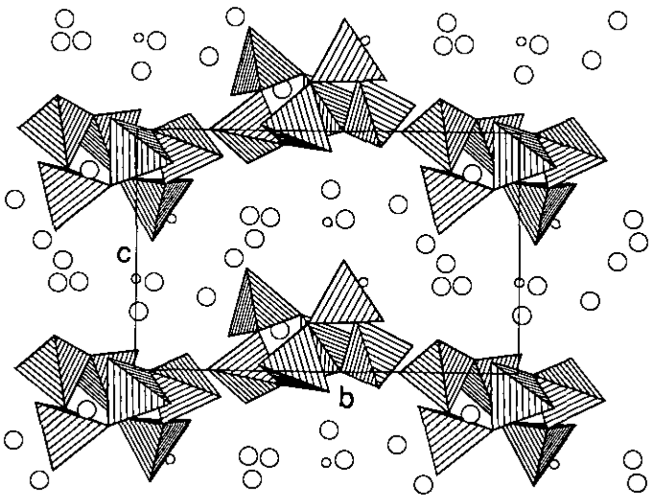

FIG. 2. Projection along the **a** direction of the atomic arrangement of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$. Only P_6O_{18} ring anions in polyhedral representation, water molecules (larger empty circles), and cesium atoms (smaller circles) are represented.

Figure 2, a projection along the **a** direction, is probably not the most suitable for the understanding of this arrangement, but has merit in that it reflects its layered organization.

Final atomic coordinates and B_{eq} for this atomic arrangement are gathered in Table 2.

THERMAL BEHAVIOR AND INFRARED SPECTROSCOPY

A. Thermal Behavior

The two curves corresponding to the DTA and TGA analysis in air atmosphere of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$ are given in Fig. 3. In order to interpret, as properly as possible, these two diagrams, we performed, in addition, an IR absorption study, which we report and discuss below.

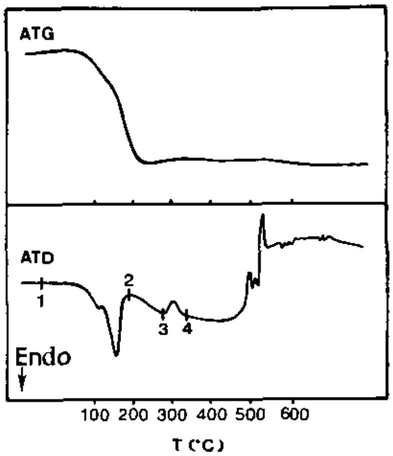

FIG. 3. DTA and DTG curves for $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$. The labels 1, 2, 3, and 4 refer to temperatures of heat treatment of the samples used in the IR examinations.

TABLE 3
Main Interatomic Distances (Å) and Bond Angles (°) in the Atomic Arrangement of $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$

		The P_6O_{18} Ring anion		
		The $P(1)O_4$ tetrahedron		
P(1)	O(L12)	O(L16)	O(E11)	O(E12)
O(L12)	1.600(4)	2.471(5)	2.480(5)	2.526(5)
O(L16)	101.3(2)	1.596(4)	2.544(6)	2.485(6)
O(E11)	107.7(2)	112.0(2)	1.471(4)	2.532(6)
O(E12)	109.7(2)	107.3(2)	117.6(2)	1.488(4)
		The $P(2)O_4$ tetrahedron		
P(2)	O(L12)	O(L23)	O(E21)	O(E22)
O(L12)	1.609(4)	2.480(6)	2.451(6)	2.522(5)
O(L23)	101.1(2)	1.603(4)	2.535(5)	2.504((6)
O(E21)	105.3(2)	111.0(2)	2.472(4)	2.539(6)
O(E22)	109.8(2)	108.9(2)	119.1(2)	1.473(4)
		The $P(3)O_4$ tetrahedron		
P(3)	O(L23)	O(L34)	O(E31)	O(E32)
O(L23)	1.607(4)	2.491(6)	2.487(6)	2.536(6)
O(L34)	101.6(2)	1.609(4)	2.466(6)	2.546(6)
O(E31)	107.5(2)	106.1(3)	1.475(4)	2.566(6)
O(E21)	109.8(2)	110.4(2)	119.8(3)	1.491(4)
		The $P(4)O_4$ tetrahedron		
P(4)	O(L34)	O(L45)	O(E41)	O(E42)
O(L34)	1.606(4)	2.502(6)	2.487(6)	2.533(6)
O(L45)	101.9(2)	1.614(4)	2.530(6)	2.488(6)
O(E41)	106.9(2)	109.2(2)	1.488(5)	2.585(6)
O(E42)	109.9(2)	106.6(2)	120.7(2)	1.487(4)
		The $P(5)O_4$ tetrahedron		
P(5)	O(L45)	O(L56)	O(E(51)	O(E52)
O(L45)	1.603(4)	2.475(5)	2.533(6)	2.475(6)
O(L56)	100.6(2)	1.613(4)	2.520(6)	2.536(6)
O(E51)	110.2(2)	108.8(2)	1.484(4)	2.558(6)
O(E52)	106.6(2)	109.9(2)	119.1(2)	1.482(4)
		The $P(6)O_4$ tetrahedron		
P(6)	O(L16)	O(L56)	O(E61)	O(E62)
O(L16)	1.601(4)	2.513(6)	2.455(6)	2.520(6)
O(L56)	103.4(2)	1.601(4)	2.481(6)	2.522(6)
O(E61)	105.8(2)	107.4(3)	1.477(4)	2.571(6)
O(E62)	109.3(2)	109.4(2)	120.3(3)	1.489(4)

P(1)–O(L12)–P(2)	130.8(2)	P(1)–P(2)	2.917(2)
P(2)–O(L23)–P(3)	131.2(3)	P(2)–P(3)	2.922(2)
P(3)–O(L34)–P(4)	129.3(3)	P(3)–P(4)	2.905(2)
P(4)–O(L45)–P(5)	130.8(3)	P(4)–P(5)	2.925(2)
P(5)–O(L56)–P(6)	129.6(3)	P(4)–P(6)	2.908(2)
P(6)–O(L61)–P(1)	133.2(3)	P(4)–P(1)	2.934(2)
P(1)–P(2)–P(3)	116.48(6)		
P(2)–P(3)–P(4)	88.69(5)		
P(3)–P(4)–P(5)	101.65(5)		
P(4)–P(5)–P(6)	114.76(6)		
P(5)–P(6)–P(1)	85.89(5)		
P(6)–P(1)–P(2)	100.66(5)		

	The ZnO_6 octahedra		
Zn(1)–O(E11)	2.026(4)	Zn(2)–O(E21)	2.094(4)
Zn(1)–O(E12)	2.044(4)	Zn(2)–O(E32)	2.081(4)
Zn(1)–O(E22)	2.109(4)	Zn(2)–O(E41)	2.108(4)
Zn(1)–O(E52)	2.138(4)	Zn(2)–O(E42)	2.295(4)
Zn(1)–O(E62)	2.144(4)	Zn(2)–O(E51)	2.050(4)
Zn(1)–O(W3)	2.049(4)	Zn(2)–O(W2)	2.038(4)

TABLE 3—*Continued*

	The CsO_9 polyhedra		
Cs(1)–O(L12)	3.308(4)	Cs(2)–O(E21)	3.312(4)
Cs(1)–O(E21)	3.344(4)	Cs(2)–O(E22)	3.383(4)
Cs(1)–O(L34)	3.449(4)	Cs(2)–O(E31)	3.175(5)
Cs(1)–O(E31)	3.184(5)	Cs(2)–O(E41)	3.284(4)
Cs(1)–O(L45)	3.280(4)	Cs(2)–O(E62)	3.419(4)
Cs(1)–O(E52)	3.214(4)	Cs(2)–O(W1)	3.281(6)
Cs(1)–O(E61)	3.053(5)	Cs(2)–O(W4)	3.207(6)
Cs(1)–O(W5)	3.304(9)	Cs(2)–O(W6)	3.15(1)
Cs(1)–O(W6)	3.04(1)	Cs(2)–O(W7)	3.47(1)

B. Infrared Spectroscopy

The investigated samples are labeled from 1 to 4. Sample 1 corresponds to $Zn_2Cs_2P_6O_{18} \cdot 8H_2O$ without any thermal treatment, while samples 2, 3, and 4 correspond to specimens previously heated from room temperature to, respectively, 473, 553, and 593 K and kept at these temperatures for about 5 min in air atmosphere.

The infrared absorption spectrum of the title compound (sample 1) is reported in Fig. 4. It exhibits:

—two broad bands at about 3422–3223 and another one at 1669 cm^{-1} corresponding to the water molecules of the arrangement; and

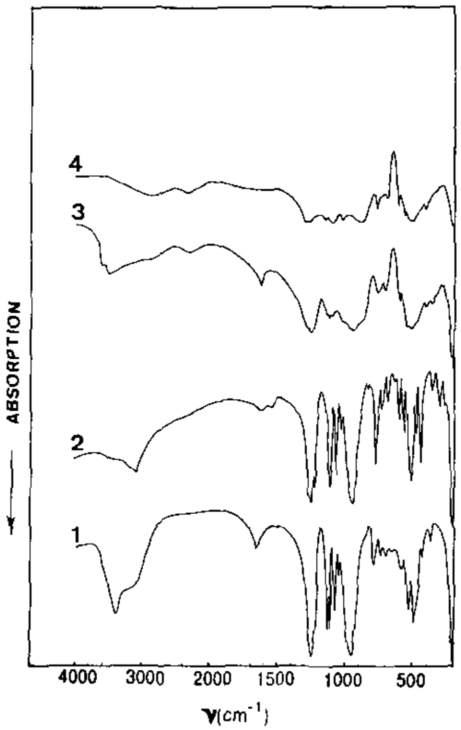

FIG. 4. IR spectra for the four specimens prepared according to the specifications reported in the IR investigation section.

—various valency–vibration bands, of which the positions, between 1300 and 600 cm^{-1}, and number are typical of a phosphoric ring anion (10). In this type of anion, the vibrations of the –O–P–O– groups take place at relatively high frequencies, $1200 < \nu_{as} < 1300$ cm^{-1} and $1050 < \nu_s < 1200$ cm^{-1}, and those corresponding to the P–O–P groups appear as a broad band ν_{as} around 980 cm^{-1} and a double ν_s between 800 and 700 cm^{-1}.

Figure 4 also shows the IR spectra of the samples labeled 2, 3, and 4 on the DTA curve (Fig. 3). The comparison shows that this phosphate undertakes at about 377 and 441 K two endothermic dehydrations, well confirmed by the weight losses observed on the TGA curve given in Fig. 3. This dehydration is not total, since the estimated weight loss from the DTG diagram corresponds to a departure of seven water molecules per formula unit and the IR absorption spectrum of sample 2, dehydrated at 473 K (Fig. 3), still exhibits specific absorption bands of water molecules and P_6O_{18} rings.

The thermal accidents observed at 555 and 580 K can probably be explained by a hydrolysis phenomenon, implying that a part of the residual water opens the ring anion and transforms it into a mixture of various condensed phosphates (oligo-, cyclo-, and polyphosphates) accompanied by a reorganization which increases, in this case, the content of high polyphosphates, the characteristic absorption bands of which are highest in the spectra IR 4. These types of processes have frequently been observed in condensed phosphate chemistry and recently by Watanabe *et al.* (11) in the domain of cyclooctaphosphates which, in different experimental conditions, decompose and essentially change into cyclotriphosphates.

The use of a part of the residual crystallization water in the hydrolysis phenomenon is justified by the last weight loss observed by DTG (Fig. 3), which clearly indicates the departure of less than one water molecule.

All these processes can explain the present, in the IR spectra of the samples 3 and 4, of two types of very characteristic absorption bands (Fig. 4):

—at 2900 and 2360 cm^{-1}, corresponding to P–OH (12), and

–at 1300 and 880 cm^{-1}, corresponding to linear phosphates (13).

At temperatures higher than 763 K, several additional phenomena are still observed, such as endo- and exothermic accidents on the DTA curve and a slight weight loss on the DTG curve. The complexity of the investigated evolution cannot justify an unambiguous interpretation of these last phenomena.

The interpretation of the thermal behavior should be complemented by an X-ray investigation to confirm by diffraction analysis the various steps suggested by the techniques used above, but in the case of condensed phosphates in which such a decyclization–reorganization occurs, intermediate amorphous phases corresponding to the reorganization steps are frequently observed and can range over a wide range of temperature. Through chromatographic analysis, the true nature of these amorphous phases has often been proved to be mainly constituted by a mixture of various oligophosphates. In addition, one must note that the $M^{II}(PO_3)_2$–$M^{I}PO_3$ phase equilibrium diagrams elaborated between the two corresponding polyphosphates are a fundamental tool for such investigations, mainly to clarify the last steps of the evolution. Unfortunately, in the case of the present study, the $Zn(PO_3)_2$–$CsPO_3$ phase equilibrium diagram has not yet been elaborated.

Additional materials. A list of thermal anisotropic displacement parameters and lists of observed and calculated structure factors can be obtained on request to the Tunisian authors.

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