

## Synthesis, Structure, and Physicochemical Studies of Hexakis(2,4-dimethylanilinium) Cyclohexaphosphate Hexahydrate

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Chemical preparation, crystal structure, thermal analysis, IR absorption, and NMR studies are given for a new organic cyclohexaphosphate, the hexakis(2,4-dimethylanilinium) cyclohexaphosphate hexahydrate ((2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O). This compound crystallizes in the monoclinic space group *P2<sub>1</sub>/n*, with cell parameters *a* = 10.914(4) Å, *b* = 11.198(3) Å, *c* = 25.670(2) Å, *β* = 95.05(4)°, *Z* = 2, and *V* = 3124(2) Å<sup>3</sup>. Its crystal structure is determined and refined to a final *R* = 0.054 for 4627 independent reflections. The atomic arrangement can be described as a layer organization built by P<sub>6</sub>O<sub>18</sub>-ring anions and H<sub>2</sub>O molecules. Between these layers are located the organic groups that form H-bonds with O-atoms of the P<sub>6</sub>O<sub>18</sub> rings and H<sub>2</sub>O molecules. Determination of the geometric characteristics of the H-bonds show the existence in this structure of four particularly strong H-bonding contacts (1.75, 1.76, 1.78, and 1.87 Å).

**1. Introduction.** – Since the preparation and the identification of Li<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O [1], this salt has been used as starting material to prepare other cyclohexaphosphates. Depending on the cation associated with the phosphate anion, such compounds could have interesting structures and properties potentially useful in various application fields (nonlinear optics [2], heterogeneous catalysis [3], photochemical and photo-physical processes [4], molecular sieves [5], and other areas that include electronic materials [6] and ceramic precursors [7]).

In the present work, the results of the X-ray structure analysis of a new organic cyclohexaphosphate, the hexakis(2,4-dimethylanilinium) cyclohexaphosphate hexahydrate ((2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O), are discussed with respect to the geometry and flexibility of the cyclohexaphosphate ring system and H-bonding interactions between the inorganic acceptor, the solvent H<sub>2</sub>O, and the organic donor molecules.

**2. Results and Discussion.** – 2.1. *Structure Description.* The crystal-structure determination shows that (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O crystallizes in the mono-

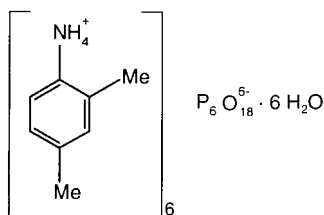


Table 1. Crystal Data and Structure Refinement of  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ 

Empirical formula	$\text{C}_{48}\text{H}_{84}\text{N}_6\text{O}_{24}\text{P}_6$	Reflections for cell determination	25
$M_r$	1315.06	$\tau$ Range for cell determination [ $^\circ$ ]	8–10
Crystal color, habit	colorless, prism	Absorption coefficient $\mu$ [ $\text{mm}^{-1}$ ]	0.138
Crystal temperature [K]	296	$F(000)$	1392
Crystal size [mm]	$0.35 \times 0.30 \times 0.30$	$\theta$ Range for data collection [ $^\circ$ ]	2 to 25
Radiation, wavelength [ $\text{\AA}$ ]	$\text{AgK}\alpha$ , 0.5608	Limiting indices	$-16 \leq h \leq 16, 0 \leq k \leq 16,$ $0 \leq l \leq 38$
Crystal system	monoclinic	Reflections collected/unique	11872/11656 ( $R_{\text{int}} = 0.032$ )
Space group	$P2_1/n$	Absorption correction	no absorption correction
Unit-cell dimensions:		Refinement method	full-matrix least-squares on $F$
$a$ [ $\text{\AA}$ ]	10.914(4)	Data, restraints, parameters	4627, 0, 379
$b$ [ $\text{\AA}$ ]	11.198(3)	( $I > 3\sigma$ )	
$c$ [ $\text{\AA}$ ]	25.670(2)	Goodness-of-fit on $F$	1.520
$\beta$ [ $^\circ$ ]	95.05(4)	Final $R$ indices	$R_1 = 0.054, wR_2 = 0.054$
Volume [ $\text{\AA}^3$ ]	3124(2)	$R$ indices (all data, on $F$ )	$wR_2 = 0.072, R_1 = 0.182$
$Z$	2	Extinction coefficient	0.0063043(5)
Density calc. [ $\text{g cm}^{-3}$ ]	1.398	$\Delta\rho$ (min, max) [ $\text{e \AA}^{-3}$ ]	– 0.340, 0.360

clinic system. Crystal data and structure-refinement results are summarized in *Table 1*. The compound has a structure that includes an organic cation (2,4-dimethylanilinium), an inorganic anion ( $\text{P}_6\text{O}_{18}^{6-}$ ), and solvent molecules ( $\text{H}_2\text{O}$ ). A perspective view of these entities is depicted in *Fig. 1*, while the complete atomic arrangement is shown in *Fig. 2*. This latter shows the organization of the different components into two entities. The first one includes the  $\text{P}_6\text{O}_{18}$  rings,  $\text{NH}_3$  groups, and  $\text{H}_2\text{O}$  molecules involved in H-bonds. The second one consists of the organic ring systems, which show no stacking interactions.

The inorganic entities form two parallel layers developed around the  $(a,b)$  planes at  $z = 0$  and  $z = 1/2$ . Between these layers, the organic groups are located such that H-bonds *via* their  $\text{NH}_3$  groups with  $\text{P}_6\text{O}_{18}$  rings and  $\text{H}_2\text{O}$  molecules can be established.

Inside such a layer, the cyclohexaphosphate ring is located around the inversion centers  $(0,0,1/2)$ ,  $(1/2,1/2,0)$  and is built up by three independent  $\text{PO}_4$  tetrahedra. This ring is distorted: the P–P–P angles vary between  $101.66(4)^\circ$  and  $113.29(5)^\circ$ . These angles, with an average of  $106.35(5)^\circ$ , show very large deviations from the ideal value of  $120^\circ$ , compared to other types of phosphate rings such as cyclotri- and cyclotetraphosphates, in which the P–P–P angles never depart significantly from their ideal values of  $60 \pm 2^\circ$  for cyclotriphosphates and  $90 \pm 4^\circ$  for cyclotetraphosphates. Cyclotri- and cyclotetraphosphates are much less flexible than the described cyclohexaphosphates which, in the ideal configuration, have a void in the center. According to the flexibility of the  $\text{PO}_4$  tetrahedra, an equilibrium between repulsion of the O-atoms and the attraction to H-bonding donor groups of the organic parts and the  $\text{H}_2\text{O}$  molecules can destroy the ideal geometry of the six P-atoms. This can also be demonstrated by comparing the distances of the symmetry-related P-atoms ( $\text{P}(1)–\text{P}(1') = 5.754 \text{ \AA}$ ,  $\text{P}(2)–\text{P}(2') = 5.627 \text{ \AA}$ , and  $\text{P}(3)–\text{P}(3') = 5.159 \text{ \AA}$ ), which exhibit a deviation varying between 0.127 and 0.596  $\text{\AA}$ . The presence of strong H-bonds such as  $\text{N–H} \cdots \text{O}$  (1.75, 1.76, 1.78, and 1.87  $\text{\AA}$ ) (*Table 2*) in the compound studied here is certainly one of the most-important distortion factors. Nevertheless, this distortion is comparatively less

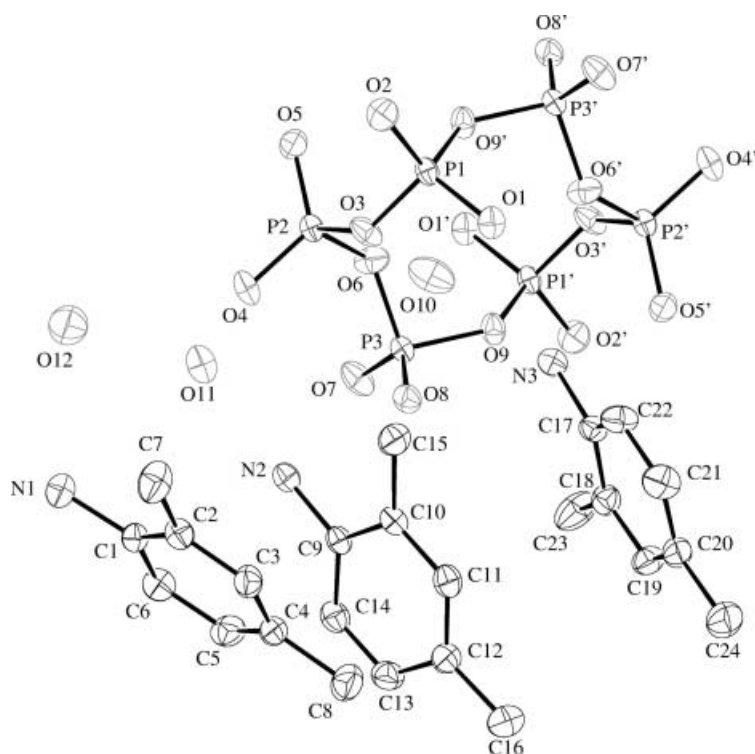


Fig. 1. ORTEP Plot of inorganic anion and independent organic cations of  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$  with atom numbering scheme and thermal ellipsoids at 35% of probability

important than that observed in  $\text{Cs}_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ , which shows the greatest distortion for the same angles ( $93.2\text{--}145.5^\circ$ ) [8].

The great flexibility of the  $\text{P}_6\text{O}_{18}$  ring probably explains the strong stability of cyclohexaphosphates in comparison with the smaller cycles such as  $\text{P}_3\text{O}_9$  and  $\text{P}_4\text{O}_{12}$ . In each  $\text{PO}_4$  tetrahedron coexist three different types of  $\text{O}\text{--P}\text{--O}$  angles. The  $\text{O(L)}\text{--P}\text{--O(L)}$  angles, corresponding to the largest  $\text{P}\text{--O}$  bonds, are always close to  $100^\circ$ . The  $\text{O(L)}\text{--P}\text{--O(E)}$  angles have values expected for a regular tetrahedron, while the  $\text{O(E)}\text{--P}\text{--O(E)}$  angles corresponding to the shortest  $\text{P}\text{--O}$  distances always have larger values, close to  $120^\circ$ , probably due to the mutual repulsion of the non-bridging O-atoms.

In this atomic arrangement, there are three independent organic groups. The number of these latter is equal to that of independent P-atoms in the  $\text{P}_6\text{O}_{18}$  ring having an internal symmetry  $P\text{-}1$ . This was already observed in another compound of the same type [9]. The organic molecules participate with  $\text{H}_2\text{O}$  molecules in the H-bonding scheme of  $\text{N}\text{--H}\cdots\text{O}$  and  $\text{O}\text{--H}\cdots\text{O}$  interactions (Table 2), which connect the different entities of the  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$  structure. This compound is a combination of a cation derived from a polarizable organic molecule (2,4-dimethylaniline) with an inorganic anion, cyclohexaphosphate, capable of forming strong H-

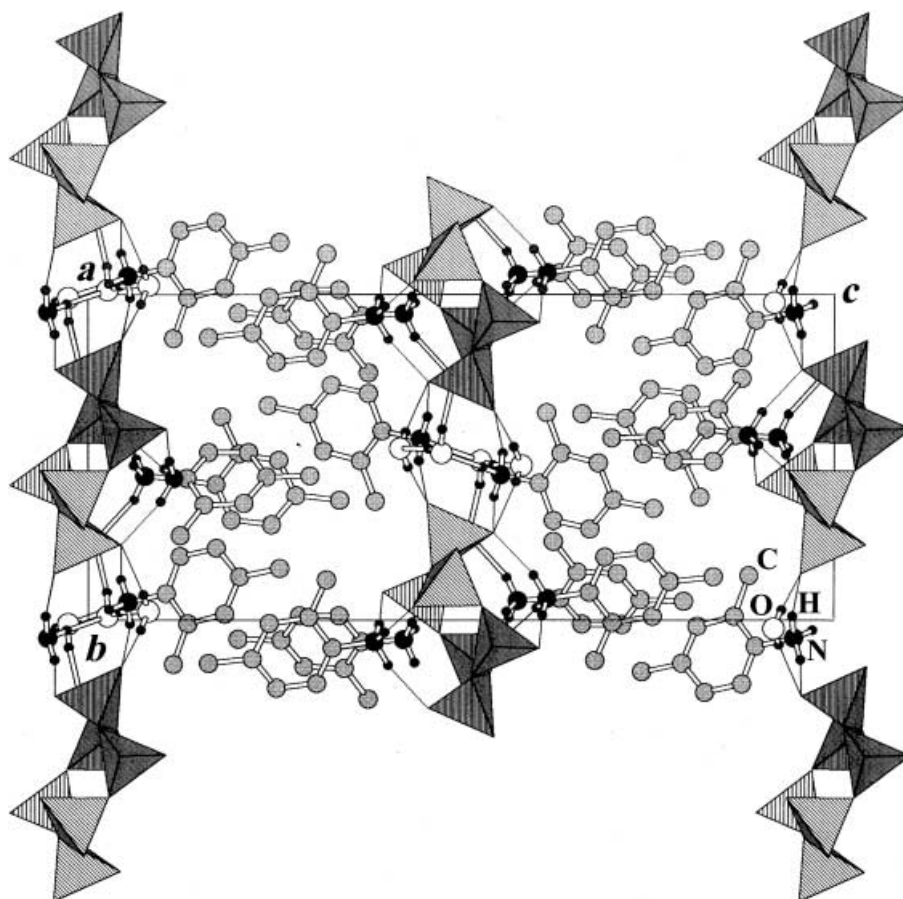


Fig. 2. Projection of the structure of  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ , along the *a* axis. The cyclohexaphosphate anion is given in a tetrahedral representation. The smaller black dots represent the H-atoms. The other atoms are indicated by their symbols. H-Bonds are indicated by solid and dotted lines.

bonded crystal structures. The bonding energy of the H-bonds is an important factor in the formation of interesting materials possessing nonlinear optical properties, notably those exhibiting second harmonic generation (SHG) [10][11] when they are non-centrosymmetric.

**2.2. NMR Results.** Cyclohexaphosphates are formed by tetrahedra sharing two corners with neighboring tetrahedra ( $Q^2$  units in *Lipmaa's* notation) [12], and two other ones interacting with cations. According to this, the isotopic chemical shift values  $\sigma_{\text{iso}}$  are higher than those corresponding to monophosphates (between  $-10$  and  $+5$  ppm) or diphosphates (between  $-10$  and  $-20$  ppm) of alkali and alkaline-earth cations [13–17]. Chemical-shift values of cyclohexaphosphates are similar to those obtained previously in polyphosphates, indicating that  $\sigma_{\text{iso}}$  values are mainly defined by tetrahedral condensation of phosphates.

Table 2. *H-Bond Scheme in (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O<sup>a</sup>)*

N(O)–H ... O	N(O)–H [Å]	N(O)–O [Å]	N(O)H ... O [Å]	N(O)–H ... O [°]
O(W1)–H(1W1) ... O(E11)	0.73	2.897(4)	2.17	170.4
O(W1)–H(2W1) ... O(E21)	0.90	2.895(4)	2.00	172.1
O(W2)–H(1W2) ... O(E12)	0.87	2.823(4)	1.99	159.5
O(W2)–H(2W2) ... O(E13)	0.83	2.761(4)	1.96	163.9
O(W3)–H(1W3) ... O(W1)	0.78	2.867(5)	2.10	168.1
O(W3)–H(2W3) ... O(W2)	0.95	2.882(4)	1.95	166.9
N(1)–H(1N1) ... O(E13)	0.93	2.953(4)	2.24	119.6
N(1)–H(2N1) ... O(W3)	0.96	2.737(5)	1.78	169.6
N(1)–H(3N1) ... O(E21)	0.98	2.861(4)	1.90	168.2
N(2)–H(1N2) ... O(E12)	0.99	2.735(4)	1.75	177.7
N(2)–H(2N2) ... O(E23)	1.03	2.739(4)	1.76	156.7
N(2)–H(3N2) ... O(W2)	0.89	2.822(4)	1.97	161.5
N(3)–H(1N3) ... O(E11)	0.98	2.938(4)	1.99	160.3
N(3)–H(2N3) ... O(E23)	0.89	2.851(4)	1.96	170.4
N(3)–H(3N3) ... O(E22)	0.90	2.761(4)	1.87	171.7

<sup>a</sup>) N(O) = N or O; W1, W2, W3 = H<sub>2</sub>O in three different positions; E11, E12, E13 = positions of the three O-atoms at P(1); E21, E22, E23 = positions of the three O-atoms at P(2).

The solid-state <sup>31</sup>P-NMR spectrum of the sample analyzed is formed by three components with their corresponding satellite spinning side bands spaced at equal intervals (*Fig. 3*). As the chemical environments of all P-atoms are similar in this cyclohexaphosphate, resolved components must correspond to different crystallographic sites occupied by P-atoms. On the other hand, distortions of the polyhedra are responsible for the observed chemical-shift anisotropies and for the detection of spinning-side-band patterns covering important regions of the <sup>31</sup>P-NMR spectra. Spectral regions occupied by these bands are proportional to tetrahedral distortions. Hence, NMR patterns could be used to monitor distortions. To analyze this point, the experimental envelopes were deconvoluted, determining for each component  $\sigma_{\text{iso}}$ ,  $\Delta\sigma$ , and  $\eta$  (*Table 3*).

Table 3. *Isotopic Chemical Shift ( $\sigma_{\text{iso}}$ ), Linewidth, Amplitude, Anisotropy ( $\Delta\sigma$ ) and Asymmetry ( $\eta$ ) Parameters of MAS-<sup>31</sup>P-NMR Components in the Cyclohexaphosphate (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>PO<sub>18</sub>·6 H<sub>2</sub>O*

$\sigma_{\text{iso}}$ [ppm]	Linewidth [ppm]	Amplitude	$\Delta\sigma$	$\eta$
–20.58	1.88	2049	–127.65	0.45
–23.96	3.08	1691	–132.75	0.40
–28.02	2.53	1479	–142.96	0.45

The cyclohexaphosphate group has a center of gravity that coincides with a crystallographic center of symmetry. This is deduced from the NMR analysis of the asymmetry parameter  $\eta$ , which is near 0.4, indicating that the local symmetry of the tetrahedra is lower. This agrees with the results obtained with other cyclohexaphosphates [18].

To analyze the distortions on PO<sub>4</sub> tetrahedra, dispersions on P–O distances and P–O–P angles were calculated from the X-ray-diffraction data reported for (2,4-

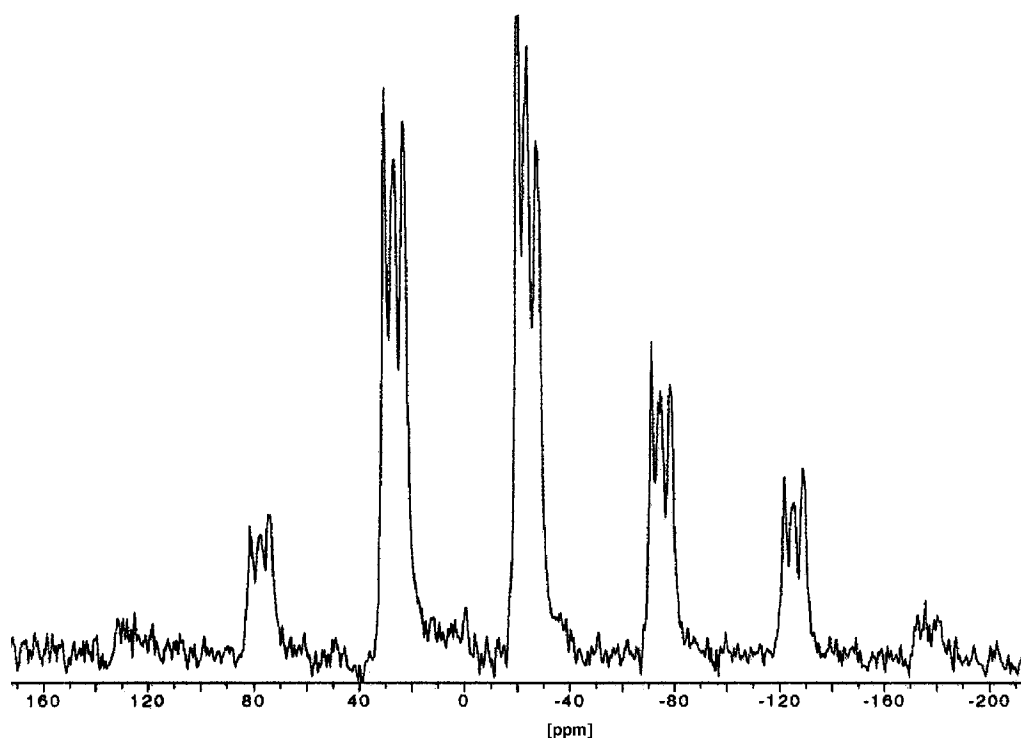


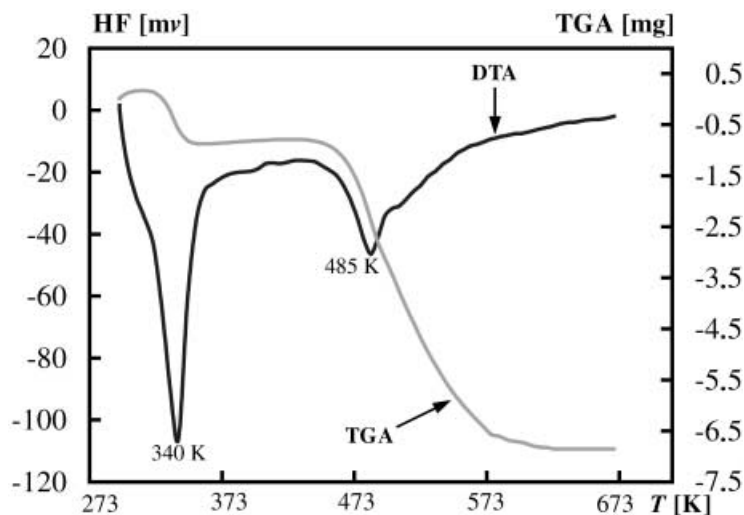
Fig. 3. Magic-angle-spinning (MAS)  $^{31}\text{P}$ -NMR Spectrum of  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18} \cdot 6 \text{H}_2\text{O}$

$\text{Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18} \cdot 6 \text{H}_2\text{O}$ . From the data, the average values of the distortion indices  $ID(\text{P}-\text{O})$  and  $ID(\text{O}-\text{P}-\text{O})$  were calculated [19]. Obtained  $ID(\text{P}-\text{O})$  and  $ID(\text{O}-\text{P}-\text{O})$  values are always near 0.04, showing that most tetrahedra display similar distortions (Table 4). According to this observation, deduced  $\Delta\sigma$  values are always near  $-135$  ppm, and  $\eta$  values are close to 0.5 as previously reported [18]. Therefore, anisotropies associated with tetrahedral distortions cannot be used to assign NMR components to different crystallographic sites. However,  $\sigma_{\text{iso}}$  values of NMR components change appreciably in this cyclohexaphosphate, indicating that factors other than tetrahedral condensation affect this parameter. Among structural factors invoked to explain differences in  $\sigma_{\text{iso}}$  values,  $\text{P}-\text{O}-\text{P}$  angles (geometric factor) are the most relevant. Thus the  $\text{P}-\text{O}-\text{P}$  angles defining the phosphate chain were considered. For that, the average of the two  $\text{P}-\text{O}-\text{P}$  angles defined by each P-atom with neighboring tetrahedra were taken into account (Table 4). The correlation between the chemical shift values  $\sigma_{\text{iso}}$  of NMR components and  $\text{P}-\text{O}-\text{P}$  angles of some cyclohexaphosphates has previously been described [18]. It has been shown that the chemical shift decreases when the  $\text{P}-\text{O}-\text{P}$  angle increases. Thus, we deduce the following assignments:  $\sigma_{\text{iso}}(\text{P}(1)) = -20.58$  ppm,  $\sigma_{\text{iso}}(\text{P}(2)) = -23.96$  ppm, and  $\sigma_{\text{iso}}(\text{P}(3)) = -28.02$  ppm.

Table 4. *Interatomic P–O Distances [Å], O–P–O Angles [°], Tetrahedral Distortion Indexes ID (P–O) and ID (O–P–O), and Mean <POP> Angles of the Cyclohexaphosphate (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O*

Tetrahedron	P–O (mean)	ID (P–O)	O–P–O (mean)	ID (O–P–O)	<P–O–P>
P(1)O <sub>4</sub>	1.539	0.039	89.37	0.035	108.8
P(2)O <sub>4</sub>	1.534	0.038	88.43	0.050	109.6
P(3)O <sub>4</sub>	1.535	0.041	89.05	0.041	117.2

2.3. *Thermal Analysis.* The two curves corresponding to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in open air are given in Fig. 4. The DTA curve shows that the cyclohexaphosphate undergoes two main endothermic phenomena. The first one is a dehydration which occurs at about 360 K and is accompanied by an obvious weight loss observed in the TGA curve. From this latter, we deduce a departure of six H<sub>2</sub>O molecules (H<sub>2</sub>O: exper. 8.81%, calc. 8.22%). This total dehydration leads to an intermediate amorphous material that does not diffract the X-rays and no longer exhibits the IR absorption bands characteristic of a cyclic phosphate. Around 485 K, the organic entities and the P<sub>6</sub>O<sub>18</sub> ring of this amorphous phase start to decompose over a wide temperature range. One obtains a viscous substance of polyphosphoric acid contaminated with a carbon black deposit. This is also confirmed by the significant weight loss observed in the TGA curve (exper. 60.01%, calc. 55.71%).

Fig. 4. *DTA and TGA Curves of (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sub>6</sub>P<sub>6</sub>O<sub>18</sub>·6 H<sub>2</sub>O, between room temperature and 623 K*

2.4. *IR Absorption Spectroscopy.* The IR absorption spectrum reported in Fig. 5 exhibits: 1) broad bands between 3500 and 2500 cm<sup>-1</sup> and 1650 and 1400 cm<sup>-1</sup> corresponding to the valency vibrations of the H<sub>2</sub>O molecules and (2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> cations of the compound; 2) various valency and bending vibrations whose number and positions, between 1300 and 600 cm<sup>-1</sup>, are both characteristic of a phosphate anion [20]. In these types of anions, the vibrations of the O–P–O groups appear at relatively high frequencies, *i.e.*, 1200 <  $\tilde{\nu}_{\text{as}}$  < 1300 cm<sup>-1</sup> and 1050 <  $\tilde{\nu}_{\text{as}}$  < 1200 cm<sup>-1</sup>, and those corre-

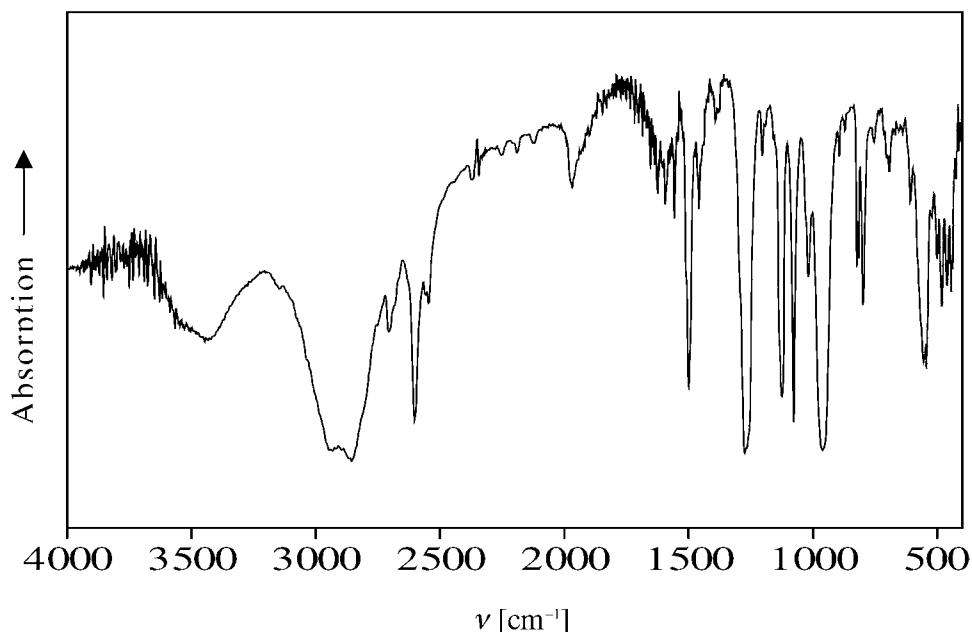


Fig. 5. IR Spectrum of  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$

sponding to the P–O–P groups constitute a broad band for  $\tilde{\nu}_{\text{as}}$  at ca.  $960\text{ cm}^{-1}$  and a doublet for  $\nu_{\text{as}}$  between  $800$  and  $700\text{ cm}^{-1}$ .

### 3. Experimental Part

1. *Synthesis.* Hexakis(2,4-dimethylanilinium) cyclohexaphosphate hexahydrate  $(2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_3)_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$  was prepared by an acid-base reaction. An aq. soln. of cyclohexaphosphoric acid ( $\text{H}_6\text{P}_6\text{O}_{18}$ ) was first obtained by passing a soln. of  $\text{Li}_6\text{P}_6\text{O}_{18}$  (prepared according to the procedure of *Schülke* and *Kayser* [1]) through an ion-exchange resin (*Amberlite IR 120*,  $\text{H}^+$  form). Dist. 2,4-dimethylaniline was added dropwise to the  $\text{H}_6\text{P}_6\text{O}_{18}$  soln. with continuous stirring until the soln. was light greenish. Slow evaporation at r.t. for several days led to transparent colorless thin single crystals, stable under normal conditions of temp. and humidity.

2. *Analyses.* 2.1. *X-Ray Diffraction.* The crystal structure of the title compound was determined with a single crystal. The intensity-data collection was performed with a *Mach3 Enraf-Nonius* diffractometer with  $\text{AgK}\alpha$  radiation ( $\lambda\ 0.5608\ \text{\AA}$ ). The experimental parameters used during the intensity measurements are summarized in *Table 1*. The structure was solved by direct methods and refined by the full-matrix least-squares method based on  $F$  with 'TexSan' software [21]. H-Atoms were located by difference *Fourier* syntheses but not refined. Their  $B_{\text{iso}}$  were fixed by the software at similar values of their adjacent N- or O-Atom equivalent isotropic parameters.

Crystallographic data (CIF) for the structure reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-203431. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

2.2. *Thermal Analysis.* Thermal analysis was performed with the multimodule *92-Setaram* analyzer operating from r.t. up to  $623\text{ K}$  at an average heating rate of  $5^\circ/\text{min}$ .

2.3. *NMR Spectroscopy.*  $^1\text{H}$ -Decoupled magic-angle-spinning (MAS)  $^{31}\text{P}$ -NMR spectrum: *Bruker DSX-300* solid-state high-resolution spectrometer; at r.t.,  $121.51\text{ kHz}$ , and  $7.05\text{ T}$ ;  $\Pi/2$  pulses of  $4.0\ \mu\text{s}$  duration with 10-s recycle times were sufficient to cause no changes in the relative peak intensities; cylindrical rotor with a spinning rate of  $5\text{ kHz}$ ;  $\sigma$  in ppm with respect to  $85\%$  aq.  $\text{H}_3\text{PO}_4$  soln. Isotopic chemical shift values ( $\sigma_{\text{iso}}$ ) of NMR



components were determined from the position of the side band that did not change in the spectra taken with different spinning rates.

The analysis of MAS-<sup>31</sup>P-NMR spectrum was carried out by using the *Bruker* program WINFIT [22]. The intensities of the side bands were computed by the method of *Herzfeld* and *Berger* [23]. Chemical-shift anisotropies ( $\Delta\sigma$ ) and the asymmetry parameter ( $\eta$ ) of NMR components were determined (*Table 4*).

2.4. *IR Spectroscopy*. IR Spectra: recording in the range 4000–400 cm<sup>-1</sup>; *Perkin-Elmer-FTIR* spectrophotometer; samples dispersed in spectroscopically pure KBr pellets.

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