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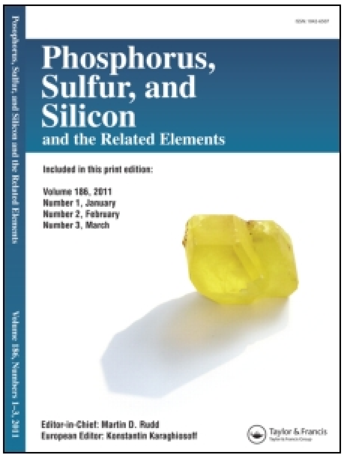

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis, Structure, and Physicochemical Studies of Hexakis (5-Chloro-2,4-dimethoxyanilinium)cyclohexaphosphate Tetrahydrate

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SYNTHESIS, STRUCTURE, AND PHYSICOCHEMICAL STUDIES OF HEXAKIS (5-CHLORO-2,4-DIMETHOXYANILINIUM) CYCLOHEXAPHOSPHATE TETRAHYDRATE

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The physicochemical properties of a new organic cyclohexaphosphate, [5-Cl-2,4-$(OCH_3)_2C_6H_2$-$NH_3]_6P_6O_{18}\cdot 4H_2O$, are discussed on the basis of an X-ray crystal structure investigation. This compound crystallizes in the monoclinic space group C2/c, with cell parameters a = 37.987(7) Å, b = 13.125(4) Å, c = 14.331(5) Å, β = 98.21(3)°, Z = 4, V = 7072(3) $Å^3$. Its crystal structure is determined and refined to a final R = 0.058 for 5223 independent reflections. The atomic arrangement can be described as a layer organization built up by P_6O_{18} ring anions and water molecules. Between these layers, the organic groups are located that form hydrogen bonds with oxygen atoms of P_6O_{18} rings and water molecules. Intermolecular π–π stacking interactions between two neighboring organic cation rings help to establish the crystal packing. Solid ^{31}P MAS-NMR spectroscopy is in agreement with X-ray structure. Ab initio calculations allow the attribution of the three phosphorus signals to the independent crystallographic sites. This compound is also characterized by thermal analysis and IR spectroscopy.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Crystal structure; cyclohexaphosphate; IR spectroscopy; nuclear magnetic resonance; thermal analysis; X-ray diffraction

INTRODUCTION

Hybrid materials with organic and inorganic components continue to be a focus area in solid state chemistry and materials sciences due to their potential applications in various fields, such as nonlinear optics,[1] heterogeneous catalysis,[2] photochemical and photophysical processes,[3] molecular sieves,[4] and other areas that include electronic materials[5] and ceramic precursors.[6]

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In the present article, the results of the X-ray structure analysis of a new organic cyclohexaphosphate, the hexakis(5-chloro-2,4-dimethoxyanilinium)cyclohexaphosphate tetrahydrate, are discussed with respect to the geometry and flexibility of the cyclohexaphosphate ring system and H-bonding interactions between the inorganic acceptor, the H_2O solvent, and the organic donor molecules.

RESULTS AND DISCUSSION

Structure Description

The crystal structure determination shows that the title compound crystallizes in the monoclinic system. Crystal data and structure refinement results are summarized in Table S1 (available online in the Supplemental Materials).

The chemical composition of the title compound includes three fundamental entities, the $P_6O_{18}^{6-}$ ring anions, the organic cations, and the water molecules. A perspective view of these entities is depicted in Figure 1, while the complete atomic arrangement is shown in Figure S1 (Supplemental Materials). This latter figure shows that the crystal structure

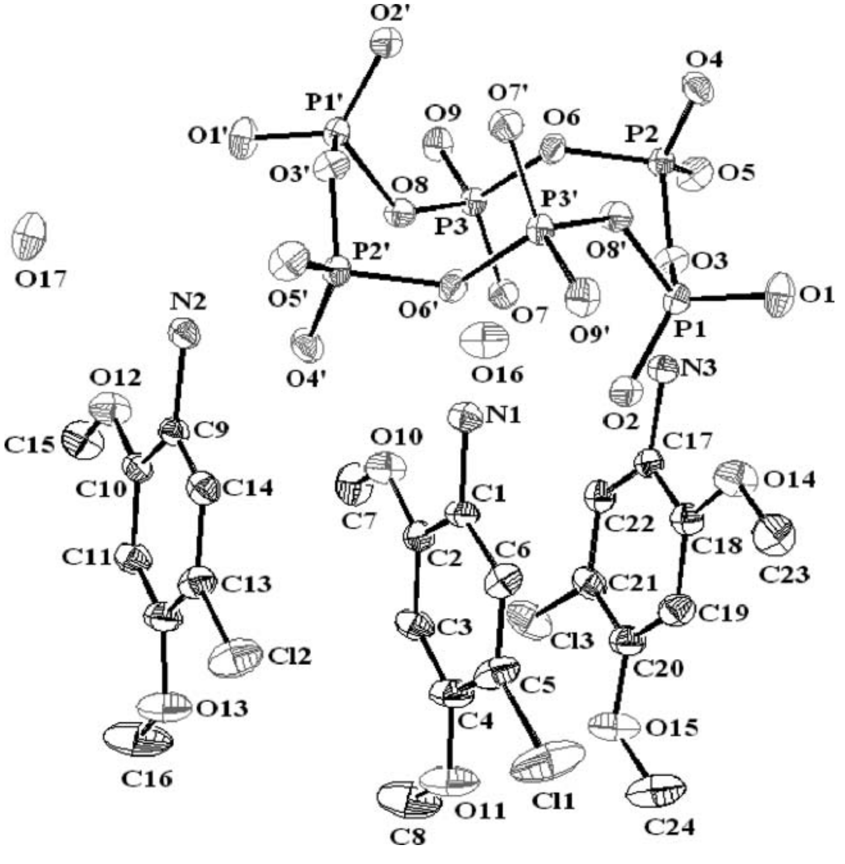

Figure 1 ORTEP plot of cyclohexaphosphoric anion and the independent organic cations of [5-Cl 2,4-$(OMe)_2C_6H_2{-}NH_3]_6P_6O_{18}.4H_2O$.

of $[5\text{-Cl-}2,4\text{-(OMe)}_2C_6H_2\text{-}NH_3]_6P_6O_{18}\cdot 4H_2O$ can be described as inorganic layers of cyclohexaphosphate anions, water molecules, and ammonium groups parallel to *bc*-planes at $x = 1/4$ and $x = 3/4$. Between these layers, the organic entities are located where they form H-bonds via their NH_3 groups with P_6O_{18} and water molecules. (Table S1).

Inside each inorganic layer, the P_6O_{18} rings are located around the inversion centers (1/4,1/4,0), (3/4,3/4,1/2) and are built up by three independent PO_4 tetrahedra (Figure S2). The P—P—P angles of 97.19(4)°, 104.51(4)°, and 111.94(4)° show that the phosphate rings are significantly distorted from the ideal value of 120°. It should be noted that these large deviations are commonly observed in cyclohexaphosphates with a ring of low symmetry as in the title compound. Nevertheless, this distortion is comparatively less important than that observed in $Cs_6P_6O_{18}\cdot 6H_2O$, which shows the greatest distortion for the same value (93.2–145.5°).[7] The great flexibility of the P_6O_{18} rings can probably explain the pronounced stability of cyclohexaphosphates compared with their smaller rings analogues. In spite of this distortion, examination of the main geometric features of the PO_4 tetrahedra (P—O distances and P—O—P or O—P—O angles, as well as P—P distances) shows that they are in accordance with values generally observed in condensed phosphate anions.[8]

Three independent organic cations coexist in this atomic arrangement located between anionic layers compensating their negative charge. An examination of the organic entity geometry shows that the atoms C1, C2, . . . , and C6 of the first organic cation ring, the atoms C9, C10, . . . , and C14 of the second one and the atoms C17, C18, . . . , and C22 of the third one have a good co-planarity. The carbon atoms of each ring form a conjugated plane with average deviations of 0.0086, 0.0098, and 0.0066 Å for the three rings, respectively. Moreover, these organic cation rings display an almost coplanar configuration with a dihedral angle of 5.58° between the first and second ring, of 3.95° between the second and the third one, and of 8.42° between the first and the third one. Figure S2 (Supplemental Materials) shows the way in which two adjacent cation rings run parallel and stack each other. The nearest centroid–centroid distance is between the first and the third ring. This value is equal to 3.689 Å, less than 3.8 Å, the maximum value accepted for π–π stacking interactions.[9] The values of the N—C, C—C distances and N—C—C, C—C—C angles range from 1.347 Å to 1.465 Å and 115.5° to 124.3°, respectively. These values show no significant difference deviation from those obtained in other organic cyclohexaphosphates.[10,11]

In this structure, the water molecules play a very important role in the cohesion of the various groups. They participate with organic groups through N—H . . . O and O—H . . . O hydrogen bonds in the cohesion with inorganic layers (Table S2, Supplemental Materials). The different interactions (hydrogen bonds, Van der waals, and electrostatic interactions) between organic cations and phosphate anions form a stable three-dimensional network.

NMR Results

The ^{31}P solid state NMR spectrum of the sample analyzed is formed by three components, at −18.1, −21.0, and −25.5 ppm (Figure 2a) with their corresponding satellite spinning side bands spaced at equal interval (Figure 2b). These chemical shift values are similar to those obtained previously in cyclohexaphosphate.[12]

As the chemical environment of all P atoms is similar in this cyclohexaphosphate, resolved components must correspond to different crystallographic sites occupied by phosphorus. However, 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 ^{31}P NMR spectra. Spectral regions occupied by these bands are proportional

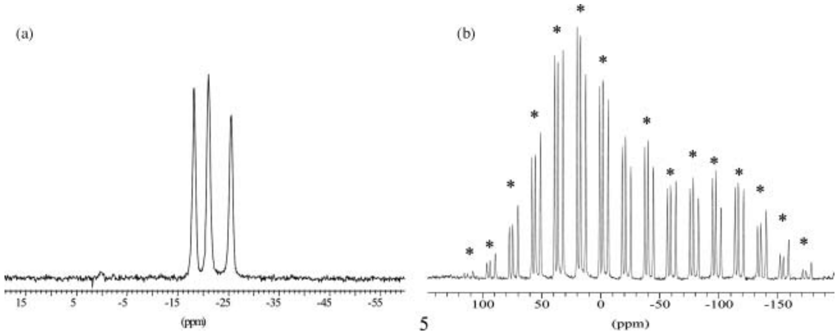

Figure 2 Isotropic band (a) and ^{31}P MAS-NMR spectrum (b) of crystalline [5-Cl 2,4-$(OMe)_2C_6H_2$-$NH_3]_6P_6O_{18}.4H_2O$. *Spinning sidebands.

to tetrahedral distortions. Hence, NMR patterns could be used to monitor distortions. In order to analyze this point, the experimental envelopes were deconvoluted, determining for each component σ_{iso}, $\Delta\sigma$, and η (Table S2, Supplemental Materials).

In order to analyze the distortions on PO_4 tetrahedra, dispersions on PO distances and POP angles have been calculated from XRD data reported in this compound. From this data, the average values of the distortion indices ID(PO) and ID (OPO) were calculated.[13] Obtained ID(PO) and ID(OPO) values are always near 0.04, showing that most tetrahedra display similar distortions (Table S3, Supplemental Materials). Moreover, 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 η, which is equal to 0.45 for the three crystallogaphically independent phosphorus atoms, indicating that the local symmetry of the tetrahedra is lower. This agrees with the results obtained with other cyclohexaphosphates.[14]

The attribution of NMR components to the phosphorus atoms P1, P2, and P3 was done by using ab initio calculations. For this purpose, the chemical shifts of three phosphorus atoms P1, P2, and P3 were calculated: $\delta_{\rm iso}(\rm P1) = 391.61$ ppm; $\delta_{\rm iso}(\rm P2) = 389.56$ ppm; and $\delta_{\rm iso}(\rm P3) = 394.52$ ppm. $\delta_{\rm iso}$ is the absolute chemical shift. As relative chemical shift, such as those experimentally measured, correspond to the difference, $\delta_{\rm exp} = \delta_{\rm ref} - \delta_{\rm iso}$, we can conclude from these theoretical calculations that P2 should be the less shielded. This allows us to propose the following assignments: $\delta_{\rm exp}(\rm P1) = -21.0$ ppm; $\delta_{\rm exp}(\rm P2) = -18.1$ ppm; and $\delta_{\rm exp}(\rm P3) = -25.5$ ppm.

Thermal Analysis

The two curves corresponding to DTA and TGA analysis in the open air are given in Figure S3 (Supplemental Materials). The DTA curve shows that the cyclohexaphosphate undergoes a succession of thermal phenomena. The first two endothermic peaks occur at about 408 and 414 K and correspond to the complete dehydration of the compound. They are accompanied by an obvious weight loss observed on the TGA curve. From this latter, we deduce a departure of four water molecules (water: exper. 4.8%, calc. 4.3%). This total dehydration gives rise 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. This amorphous product undergoes a decomposition of the [5-Cl-2,4-$(OMe)_2C_6H_2-NH_3$]

group in a wide temperature range (160–500°C). This is also confirmed by the significant weight loss observed on the TGA curve (exper. 68%, calc. 67.44%).

IR Absorption Spectroscopy

The infrared absorption spectrum reported in Figure S4 (Supplemental Materials) exhibits broad bands between 3500 and 2500 cm^{-1} and 1650 and 1400 cm^{-1} corresponding to the valency vibrations of the water molecules and $[5\text{-Cl-}2,4\text{-}(OMe)_2C_6H_2NH_3]^+$ cations of the compound, and also various valency and bending vibrations whose number and positions, between 1300 and 600 cm^{-1}, are both characteristic of a phosphoric anion.[15] In these types of anions, the vibrations of the O-P-O groups appear at relatively high frequencies $1200 < \nu_{as} < 1300\ cm^{-1}$ and $1050 < \nu_{as} < 1200\ cm^{-1}$, and those corresponding to the P-O-P groups constitute a broad band ν_{as} at about 960 cm^{-1} and a doublet ν_{as} between 800 and 700 cm^{-1}.

EXPERIMENTAL

Chemical Preparation

The title compound, $[5\text{-Cl-}2,4\text{-}(OCH_3)_2C_6H_2{-}NH_3]_6P_6O_{18}\cdot 4H_2O$, was synthesized by neutralization of an acidic aqueous solution(10 mL) of $H_6P_6O_{18}$ (3.5 mmol) with an ethanolic solution (2.8 mL) of amine (21 mmol). The cyclohexaphosphoric acid used was obtained by passing a solution of $Li_6P_6O_{18}$ (prepared according to the process described by Schülke and Kayser[16]) through an ion-exchange resin (amberlite IR 120) in its H-State. The resulting solution was allowed to evaporate slowly at room temperature for several days to give colorless single crystals with suitable dimensions, which are stable under normal conditions of temperature and humidity (3.9 g, 67% yield).

The title compound has been studied by various physico-chemical methods: X-ray diffraction, solid state NMR spectroscopy, infrared spectroscopy, and thermal analysis.

X-Ray Diffraction

The crystal structure of the title compound was determined on a single crystal. The intensity data collection was performed with a Mach3 Enraf-Nonius diffractometer using MoKα radiation ($\lambda = 0.7107$Å). The experimental parameters used during the intensity measurements are summarized in Table I. The structure was solved by direct methods and refined by the full matrix least-squares method based on F with TexSan software.[17] H atoms were located by difference Fourier syntheses, but they are not refined.

Crystallographic data (CIF) for the structure reported in this article have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-711482 Copies of the data can be obtained, free of charge, upon application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: int. code +44(1223)336-033; E-mail deposit@ccdc.cam.ac.uk).

Physical Measurements

NMR Spectroscopy. Proton decoupled ^{31}P MAS-NMR spectrum was recorded with a Bruker DSX-300 solid state high-resolution spectrometer operating at 121.51 MHz

Table I Crystal data, experimental parameters used for the intensity data collection, strategy, and final results of the structure determination

Empirical formula	$C_{48}H_{74}Cl_6N_6O_{34}P_6$
Mr	1677.66
Crystal color, habit	Brown, losangic
Crystal temperature [K]	296
Crystal size [mm]	0.50 × 0.50 × 0.20
Radiation, wavelength [Å]	*MoKα*, 0.7107
Crystal system	Monoclinic
Space group	*C2/c*
Unit-cell dimensions:	
a [Å]	37.987(7)
b [Å]	13.125(4)
c [Å]	14.331(5)
β [°]	98.21(3)
Volume [$Å^3$]	7072(3)
Z	4
Density calc.[g cm^{-3}]	1.542
Reflections for cell determination	25
τ Range for cell determination [°]	8–10
Absorption coefficient μ [mm^{-1}]	0.468
F(000)	3392
θ Range for data collection [°]	2 to 28
Limiting indices	$-50 \leq h \leq 50, 0 \leq k \leq 17, -5 \leq l \leq 18$
Reflections collected/unique	12625/8890 (*R*int = 0.032)
Absorption correction	No absorption correction
Refinement method	Full-matrix least-squares on *F*
Data, restrains, parameters (I > 2 σ)	5323, 0, 451
Goodness-of-fit on *F*	1.479
Final *R* indices	$R_1 = 0.057$, $wR_2 = 0.058$
R indices (all data, on *F*)	$wR_2 = 0.072$, $R_1 = 0.182$
Extinction coefficient	0.0063043(5)
$\Delta\rho$ (min, max) [e $Å^{-3}$]	−0.44 and 0.48

with a magnetic field strength of 7.05 T. Π/2 pulses of 4.0 μs duration with 10-sec recycle times were sufficient to cause no changes in the relative peak intensities. A cylindrical rotor with a spinning rate of 5 kHz was used. Isotopic chemical shift values (σ_{iso}) of NMR components were determined from the position of the side band that does not change in spectra taken with different spinning rates. All measurements were carried out at room temperature. The ^{31}P chemical shifts are given with respect to 85% H_3PO_4 aqueous solution.

The analysis of MAS-NMR spectrum was carried out by using the Bruker program WINFIT.[18]. The intensities of the side bands were computed by the Herzfeld and Berger's method.[19] Chemical shift anisotropies $(\Delta\sigma)$ and the asymmetry parameter $(\eta))$ of the three NMR components are listed (Table S2).

Thermal Behavior. Thermal Analysis was performed using the multimodule 92 Setaram analyzer operating from room temperature up to 623 K at an average heating rate of 5°C·min^{-1}.

Infrared Spectroscopy. IR spectra were recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer FTIR spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

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