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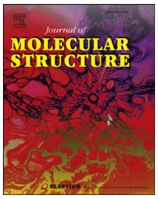

Synthesis and characterization of a new cyclohexaphosphate, $(C_6H_7ClN)_6P_6O_{18}\cdot 0.5(H_2O)$

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ABSTRACT

A new cyclohexaphosphate with the composition $(C_6H_7ClN)_6P_6O_{18}\cdot 0.5(H_2O)$ has been synthesized at room temperature in the presence of 4-chloroaniline as organic template and investigated by various physicochemical techniques. Its unit cell is triclinic P-1 with parameters $a = 9.0054(8)$, $b = 10.1053(9)$, $c = 16.4454(14)$ Å, $\alpha = 100.476(7)$, $\beta = 93.485(7)$, $\gamma = 115.407(9)$ °, Z = 2 and V = 1313.0(2)Å^3. The structure involves a network of inorganic parallel layers built up by $P_6O_{18}^{6-}$ ring anions, NH_3 groups and water molecules. Charge balance is achieved by the protonated amine which is trapped in the interlayer space and interacts with the organic framework through strong hydrogen bonding. The ^{13}C, ^{15}N and ^{31}P CP-MAS NMR spectra are in agreement with the X-ray structure. The vibrational absorption bands were identified by infrared spectroscopy. DFT calculations allowed the attribution of the NMR peaks.

1. Introduction

Since the preparation and identification of $Li_6P_6O_{18}\cdot 6H_2O$ [1], this salt has been used as starting material to prepare other cyclohexaphosphates. Organic phosphate materials have attracted considerable interest in recent years because of their structural diversity, stability and potential uses in various fields. Indeed, depending on the cation associated with the phosphate anion, such compounds could have interesting structures and properties potentially useful in nonlinear optics [2], heterogeneous catalysis [3], photochemical and photophysical processes [4], molecular sieves [5], and other areas that include electronic materials [6] and ceramic precursors [7].

In the present work, the results of X-ray structure analysis of a new cyclohexaphosphate, $(C_6H_7ClN)_6P_6O_{18}\cdot 0.5(H_2O)$, prepared by an ion-exchange resin, 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_2O, and the organic donor molecules. This hybrid material was also characterized by solid-state NMR and infrared spectroscopy.

2. Experimental

2.1. Chemical preparation

An acidic aqueous solution of $H_6P_6O_{18}$ (10 mL, 3.5 mmol) is immediately neutralized by the stoichiometric amount of 4-chloroaniline (21 mmol in 20 mL of ethanol) under continuous stirring until the solution exhibits a light yellowish aspect. Schematically the reaction can be written:

$$H_6P_6O_{18} + 6(C_6H_6ClN) \xrightarrow{H_2O} (C_6H_7ClN)_6P_6O_{18}\cdot 0.5\ H_2O$$

The entire molecular structure of the obtained cyclohexaphosphate is:

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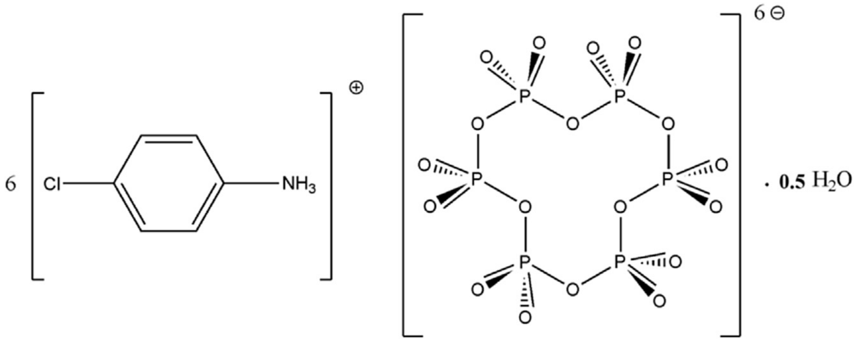

The resulting solution is then slowly evaporated at room temperature for several days to give large rectangular prisms of the title compound which are stable for months in normal conditions of temperature and humidity. The cyclohexaphosphoric acid used in this reaction was produced from an aqueous solution of $Li_6P_6O_{18}$ [1] passed through an ion exchange resin (Amberlite IR120).

2.2. X-ray single crystal structural analysis

A suitable crystal was selected and mounted on a Gemini kappa-geometry diffractometer (Agilent Technologies UK Ltd) equipped with an Atlas CCD detector and using the Mo radiation ($\lambda = 0.71073$ Å).

Intensities were collected at 100 K by means of the CrysalisPro software [8]. Reflection indexing, unit–cell parameters refinement, Lorentz-polarization correction, peak integration and background determination were carried out with the CrysalisPro software [8]. An analytical absorption correction was applied using the modeled faces of the crystal [9]. The resulting set of *hkl* was used for structure solution and refinement.

The structure was solved by direct methods with SIR97 [10] and the least-square refinement on F^2 was achieved with the CRYSTALS software [11].

All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 and N–H in the range 0.86–0.89 Å) and U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom, after which the positions were refined with riding constraints.

The drawings were made with Diamond [12]. The details of data collection, refinement and crystallographic data are summarized in Table 1.

2.3. NMR and IR measurements

The NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C, 30.30 MHz for ^{15}N and 121.51 MHz for ^{31}P with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C, ^{15}N and ^{31}P NMR chemical shifts are given relative to tetramethylsilane, neat nitromethane and 85 wt.% phosphoric acid, respectively (precision 0.5 ppm). For ^{13}C and ^{15}N, the spectra were recorded by use of cross polarization (CP) from protons (contact time 2 ms). Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons. For ^{31}P, the isotropic chemical shift values (δ_{iso}) of the three 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 the ^{31}P MAS-NMR spectrum was carried out by using the Bruker program WINFIT [13]. The intensities of the side

Table 1
Crystal data and experimental parameters used for the intensity data collection. Procedure and final results of the structure determination.

Empirical formula	$C_{36}H_{43}Cl_6N_6O_{18.5}P_6$
Formula weight [g mol^{-1}]	627.16
Crystal color, habit	yellow, block
Crystal temperature [K]	100
Crystal size [mm^3]	0.304 × 0.506 × 0.663
Radiation, wavelength [Å]	Mo*Kα*, 0.71073
Crystal system	triclinic
Space group	P-1
Unit-cell dimensions:	
a, *b*, *c* [Å]	9.0054(8), 10.1053(9),16.4454(14)
α, *β*, *γ* [°]	100.476(7), 93.485(7), 115.407(9)
Volume [Å^3]	1313.0(2)
Z	2
Density calc. [g cm^{-3}]	1.586
Reflections for cell determination	25
θ-range for cell determination [°]	8–10
Absorption coefficient μ [mm^{-1}]	0.586
F(000)	641
θ-Range for data collection [°]	3.011 to 29.538
Limiting indices	$-12 \le h \le 12$, $-13 \le k \le 13$, $-19 \le l \le 22$
Reflections collected/unique	23,373/6523 (*R*int = 0.041)
Refinement method	Full-matrix least-squares on F^2
Data, restrains, parameters (I > 2 σ)	5235, 0, 335
Goodness-of-fit on F^2	0.9805
R indices (all data, on F^2)	R = 0.0758, wR = 0.1125
$\Delta\rho$(min, max)[e Å^{-3}]	−1.62 and1.50