Low temperature synthesis of ionic phosphates in dimethyl sulfoxide†

Martin Mangstl,a Vinicius R. Celinski,a Sebastian Johansson,a Johannes Weber,a Feng Anb and Jörn Schmedt auf der Günne*a

A new synthesis route for phosphates in an organic solvent at low temperatures is presented. The synthesis was done by dispersing a nitrate salt and phosphorus pentoxide in dimethyl sulfoxide. The synthesis can be performed under water-free conditions and yielded several organic and inorganic phosphates.

Crystal structure solution of bistetramethylammonium hydrogencyclotriphosphate, \([\text{N(CH}_3\text{)}_4]^+\text{HP}_3\text{O}_9\text{w}\), was achieved by combining information gained from powder X-ray diffraction, liquid NMR and solid state (2D) NMR.

The molecular structure of rubidium cyclotetraphosphate, Rb₄P₄O₁₂, was determined using liquid state NMR and solid state (2D) NMR spectroscopy.

Introduction

Phosphates are commonly used as flame retardant additives,¹⁻³ heterogeneous catalysts in organic synthesis,⁴ non-linear optic materials,⁵ luminescent materials,⁶⁻⁸ cathode materials for rechargeable batteries⁹⁻¹¹ and ion conductors.¹²⁻¹⁵ The targeted materials often require anhydrous experimental conditions to ensure water exclusion from synthesis.

There are several synthesis routes for obtaining phosphates as reported by Durif.¹⁶ The most common routes in aqueous solution are the Boullé’s process,¹⁷ ion-exchange techniques,¹⁸ crystallization in H₂O¹⁹ and gel diffusion techniques.²⁰ Functional materials based on nanoscale phosphates can be prepared via polyol-mediated synthesis.²¹,²² The most usual synthesis routes at high temperatures are hydrothermal syntheses,²³,²⁴ flux methods²⁵ and solid state reactions (calcination).²⁶ Thermal methods can often be supported by mechanochemical activation.²⁷⁻²⁹ To the best of our knowledge no synthesis routes for ionic phosphates are known which combine low temperature, non-aqueous solutions and P₄O₁₀ as a starting material.

The presented synthesis is based on the idea that the nitrate salt M(NO₃)ₓ (M⁺ being an organic or inorganic cation, x is 1 or 2 for mono- or divalent cations, respectively) can be thought of as the source for “M₂O” which subsequently reacts with P₄O₁₀ in dimethyl sulfoxide (DMSO). This hypothesis is corroborated by the observation of brown gases (nitrogen oxides) and the finding that polyphosphates are produced (vide infra).

Formally, the total reaction can be described by the following equation:

\[
\frac{4}{x} \text{M(NO}_3\text{)}_x + \text{P}_4\text{O}_{10} \xrightarrow{\Delta, \text{DMSO}} \text{M}_2\text{P}_4\text{O}_{12} + 4\text{NO}_2 + \text{O}_2
\]

In this contribution we provide evidence for the feasibility of this approach by characterization of reaction products of different nitrates with a combination of NMR and diffraction techniques.

Experimental

All solid educts were stored inside a glove box (MBräun, Garching, Germany) filled with dry argon. Every synthesis step was done under argon atmosphere using air-free techniques. In general we used for the described synthesis approach temperatures spanning a range from 58 °C to 135 °C and reaction times from 12 to 72 hours. An explanation for the long reaction times are the small solvent products of reagents and products in DMSO.

For synthesis of bistetramethylammonium (TMA) hydrogencyclotriphosphate 2.5 mmol (354.8 mg) phosphorus pentoxide (Riedel de Haën, 99%) and 5.0 mmol (680.8 mg) TMA nitrate (Alfa Aesar, 98%) were mixed. Subsequently 10 mL dimethyl sulfoxide (DMSO, Sigma Aldrich, anhydrous, >99.9%) was added dropwise under ice cooling. Cooling helps to reduce the product spectrum. We observed a wider product spectrum without cooling possibly due to decomposition reactions of DMSO. After reaching room temperature the suspension was heated to 58 °C for twelve hours. The obtained product was...
precipitated and washed five times with acetonitrile (Sigma Aldrich, 99.9%). A colourless phase pure powder was obtained.

For synthesis of rubidium cyclotetraphosphate 0.58 mmol (165.0 mg) phosphorus pentoxide (Riedel de Haën, 99%) and 2.32 mmol (342.1 mg) rubidium nitrate (Alfa Aesar, 99%) were mixed. Subsequently 2.5 mL dimethyl sulfoxide (Sigma Aldrich, anhydrous, >99.9%) was added dropwise under ice cooling. After reaching room temperature the suspension was heated to 135 °C for 72 hours. The obtained product was washed three times with acetonitrile (Sigma Aldrich, 99.9%). A colourless powder was obtained.

**Solid-state NMR spectroscopy**

For all measurements the 1H resonance of 1% Si(CH3)4 in CDCl3 served as an external secondary reference using the δ values for 13C, 15N and 31P as reported by the IUPAC.30

The 1H and 31P solid-state NMR spectra were measured on a Bruker Avance II-200 spectrometer operating at the frequencies of 200.18 and 81.03 MHz, respectively (magnetic field strength Ω0 = 4.7 T). Magic angle sample spinning (MAS) was carried out with a commercial 2.5 mm double resonance MAS probe.

The 31P{1H} MAS spectrum of (TMA)2HP3O9 was obtained at a sample spinning frequency of 6 kHz with a repetition delay of 128 s. Proton decoupling was implemented using continuous wave (CW) decoupling with a nutation frequency of 100 kHz. The 31P–31P 2D double-quantum (DQ) single-quantum (SQ) correlation MAS-NMR spectrum was obtained at a sample spinning frequency of 6 kHz with a repetition delay of 20 s using a transient adapted PostC7 sequence31,32 with a conversion period of 1.3 ms and rotor-synchronized data sampling of the indirect dimension. It accumulated 64 transients/FID. Proton decoupling was implemented using CW decoupling with a nutation frequency of 120 kHz.

Furthermore 1H, 13C, 15N and 31P solid-state MAS NMR spectra were recorded at ambient temperature on a Bruker Avance III spectrometer with an 11.7 T magnet, operating at the frequencies of 500.25, 125.79, 50.71 and 202.51 MHz, respectively. For 1H and 31P measurements magic angle sample spinning was carried out with a commercial 2.5 mm and for 13C and 15N with a commercial 4 mm double resonance MAS probe. The 31P{1H} MAS spectrum of Rb4P4O12 was obtained at a sample spinning frequency of 25 kHz with a repetition delay of 1200 s. Proton decoupling was implemented using CW decoupling with a nutation frequency of 100 kHz. The 31P{1H} MAS spectrum of Rb4P4O12 was obtained at a sample spinning frequency of 25 kHz with a repetition delay of 20 s using a transient adapted PostC7 sequence31,32 with a conversion period of 1.3 ms and rotor-synchronized data sampling of the indirect dimension. It accumulated 64 transients/FID. Proton decoupling was implemented using CW decoupling with a nutation frequency of 120 kHz.

**Powder X-ray diffraction**

The powder X-ray diffraction pattern of (TMA)2HP3O9 was recorded at 298 K on a STOE Stadi P powder diffractometer (STOE, Darmstadt, Germany) in Debye–Scherrer geometry (capillary inner diameter: 0.48 mm) by using Ge(111)-monochromated CuKα1 radiation (154.0596 pm) and a position-sensitive detector. Extraction of the peak positions and pattern indexing and Rietveld refinement were carried out by using the TOPAS package.39 Indexing by using the SVD method yielded an orthorhombic unit cell with parameters a = 10.506, b = 10.986 and c = 30.339 Å.

Structure solution was done with parallel tempering by using the FOX40 program. The molecules were restrained in different ways: cyclic phosphate units with the flexibility model “automatic from restraints, strict” and TMA units with the flexibility model “rigid bodies”. The molecules chosen reflect the prior knowledge due to the NMR experiments. Rietveld refinement of the final structure model was realized by applying the fundamental parameter approach implemented in TOPAS (direct convolution of source emission profiles, axial instrument contributions, crystallite size and micro-strain effects).41 For the TMA cation the bond lengths42 of C–H were constrained to 0.96 Å and N–C–H angles to 108.4° (average value of a TMA salt via neutron diffraction analysis given in ref. 43). The position of H97 was constrained to the center of the straight line between O7 and O9 from a neighbouring cyclotriphosphate unit. This is consistent with the presence of a strong (linear) hydrogen bond.44 The crystallographic data and further details of the data collection are given in Table 2. The positional and displacement parameters are shown in Table 3. The experimental powder diffraction pattern, the
difference profile of Rietveld refinement and peak positions are shown in Fig. 1.

Results and discussion

All products that we were able to trace by NMR so far, are related to \( P_4O_{10} \) by selectively breaking P–O–P bonds, thus only mono-, di-, tri-, cyclotri- and tetraphosphate were present but no higher polyphosphates. If \( H_2O \) is used as reagent, different hydrogenphosphates can be synthesized, for example \((TMA)_2HP_3O_9\) (see below). We note in passing that the mixture of the solvent dimethyl sulfoxide and \( P_4O_{10} \) is known in organic chemistry as “Onodera reagent” as a soft reagent for oxidizing alcohols which involves the formation of esters. In this contribution we analyzed the products starting from TMA nitrate and rubidium nitrate following the described recipe. All products that we were able to trace by NMR so far, are related to \( P_4O_{10} \) by selectively breaking P–O–P bonds, thus only mono-, di-, tri-, cyclotri- and tetraphosphate were present but no higher polyphosphates. If \( H_2O \) is used as reagent, different hydrogenphosphates can be synthesized, for example \((TMA)_2HP_3O_9\) (see below). We note in passing that the mixture of the solvent dimethyl sulfoxide and \( P_4O_{10} \) is known in organic chemistry as “Onodera reagent” as a soft reagent for oxidizing alcohols which involves the formation of esters. In this contribution we analyzed the products starting from TMA nitrate and rubidium nitrate following the described recipe.

\textbf{Bistetramethylammonium hydrogencyclotriphosphate}

To unambiguously identify the structure of \((TMA)_2HP_3O_9\), we characterized it by X-ray diffraction and NMR spectroscopy. The X-ray diffraction data were recorded from a powdered sample in a sealed glass capillary because suitable single crystals could not be obtained, despite several tries under different conditions. The structure solution had to respect constraints obtained from 1D and 2D NMR experiments, namely a limitation to three crystallographic orbits for the P atoms within the same cyclotriphosphate group (see NMR section below) which allow the definition of an asymmetric unit made of molecular units. This turns the structure solution into a simple task, despite the likely positional disorder in the tetramethylammonium ions. After indexing and a LeBail fit, all of the likely space groups are subjected to a “multiple world simulation” within the FOX program. P atoms on special positions are not to be expected because of 3 crystallographic P atoms in a single cyclotriphosphate anion evident through 31P 2D NMR spectroscopy (see below). Repeatedly, the same solution in the space group \( Pcab \) was found after parallel tempering of the 7 best space groups. The second best solution \( (Pca_{21}) \) has an about 8 times bigger cost function than the solution in \( Pcab \). The solution is in full agreement with the observed 31P, 1H, 13C and 15N NMR spectra.

All observed reflections were indexed on the basis of orthorhombic unit cell parameters \( a = 10.5057, b = 10.9861, c = 30.3397 \) \( \text{\AA} \) and according to that \((TMA)_2HP_3O_9\) turned out to be the only crystalline phase. A Rietveld refinement was performed in space group \( Pcab \) with a structure model that contained three phosphorus, nine oxygen, two nitrogen and eight carbon atoms in the asymmetric unit. Due to the low scattering power of hydrogen its positions are difficult to determine by X-ray diffraction. Therefore the hydrogen positions were constrained based on neutron diffraction analysis data of a TMA salt. Additional information about the hydrogen atoms are presented in the NMR section.

For the NMR study \((TMA)_2HP_3O_9\) was completely dissolved in \( D_2O \) to measure a 31P liquid NMR spectrum, where a single signal with a chemical shift of \(-20.91 \text{ ppm}\) can be observed. This is in agreement with the spectrum of a cyclotriphosphate.

The quantitative \( ^1H \) MAS NMR spectrum (Fig. 2) features a peak at 3.1 ppm that can be assigned to the TMA and a peak at 15.3 ppm that is typical for a strong hydrogen bond between oxygen atoms of cyclotriphosphate units. The signal intensity ratio of 24 : 1 is in agreement with the chemical formula \((TMA)_2HP_3O_9\) determined from X-ray diffraction.

The \( ^31P\{^1H\} \) MAS NMR spectrum of \((TMA)_2HP_3O_9\) (Fig. 3) displays signals of three different crystallographic orbits of phosphorus atoms at \(-20.7, -24.5 \) and \(-26.5 \text{ ppm}\). Note that no signal is visible at \( \delta = -45.9 \text{ ppm} \), which indicates that \( P_4O_{10} \) reacts quantitatively.

The homonuclear \( ^31P \) MAS single-quantum (SQ) double-quantum (DQ) correlation spectrum (Fig. 4) proves that these three signals belong to one crystalline phase due to the correlation peaks between them. Furthermore this correlation pattern is consistent with that of a cyclotriphosphate.

The heteronuclear \( ^2D\{^1H\} \) MAS correlation spectrum of \((TMA)_2HP_3O_9\) (Fig. 5) indicates spatial proximity between phosphorus and hydrogen atoms. A correlation peak can only be

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** Observed (black line) powder diffraction pattern of \((TMA)_2HP_3O_9\) \((CuK\alpha, 154.06 \text{ pm})\) as well as the difference profile (blue line) of the Rietveld refinement. Peak positions are marked by vertical red lines.

![Fig. 2](https://example.com/fig2.png)  
**Fig. 2** \(^1H\) MAS NMR spectrum of \((TMA)_2HP_3O_9\) measured at a sample spinning frequency of 25 kHz. The peak at 3.1 ppm can be assigned to the TMA cation and the peak at 15.3 ppm is typical for a strong hydrogen bond.
observed in the case of close $^{31}$P–$^1$H vicinity. As there are correlation peaks between the $^1$H signal at 3.1 ppm and all three $^{31}$P signals we conclude that every phosphorus site of the cyclotriphosphate is close to a TMA molecule. In contrast the $^1$H signal at 15.3 ppm correlates only with the two $^{31}$P peaks at $-24.5$ and $-26.5$ ppm. This denotes that these two phosphorus sites are closer to the strong hydrogen bond than the third one. A higher correlation signal intensity can be observed for the peak at $-24.5$ ppm than for the one at $-26.5$ ppm, which indicates that the hydrogen atom in the H-bond is located closer to the P atom with the chemical shift of $-24.5$ ppm. Thereby the nearest P–H distances are: P1–H97 = 2.3767, P1–H232 = 3.1455, P2–H142 = 2.9717, P2–H131 = 3.2154, P2–H111 = 3.2513, P2–H122 = 3.3473, P3–H97 = 2.5364, P3–H242 = 3.3110, P3–H111 = 3.3656 Å.

The crystal structure of (TMA)$_2$HP$_3$O$_9$ (Fig. 6) can be described by a chainlike arrangement of cyclophosphate units (orange polyhedra) which are linked by strong hydrogen bonds. The gaps are filled by the TMA cations indicated by the blue polyhedra. The empirical formula of (TMA)$_2$HP$_3$O$_9$ was clearly determined by structure solution and solid-state NMR study.

**Rubidium cyclotetraphosphate and orthophosphate**

An example of an inorganic phosphate will be presented by discussing the case of the hitherto unknown phase of Rb$_4$P$_4$O$_{12}$.
The existence of this cyclotetraphosphate was confirmed using liquid and solid state NMR only, because the phase of Rb₄P₄O₁₂ turned out to be X-ray amorphous. Rubidium cyclotetraphosphate occurred in mixtures with crystals of monoclinic RbH₂PO₄ and an unknown phosphorus-free crystalline side-phase. A detailed discussion of the side-phases and the amorphous character of Rb₄P₄O₁₂ can be found in the ESI† together with additional experimental evidence. The term Qⁿ here refers to phosphate groups classified by the number of bridging oxygen atoms n.

To this end the sample was completely dissolved in water. The liquid-state ³¹P NMR spectrum shows a single peak in Q₂ range with 81% and a single peak in the Q₀ range with 16% of the total peak area.⁴⁹ The rest (<3%) was distributed onto small peaks in the Q₁ and Q₂ range and is neglected in the following. This observation is consistent with a single phase or phase mixture consisting of cyclic phosphates and orthophosphate anions only.

The solid state NMR spectrum agrees with the quantitative liquid state NMR analysis: the ³¹P(¹H) MAS NMR spectrum (Fig. 7) displays peaks 1 at –20.6 and 2 at –21.7 ppm indicating the presence of two different phosphorus environments in the Q₂ regime. Peaks 3 at –2.6, 4 at –9.8 and 5 at –23.5 ppm can be assigned to monoclinic RbH₂PO₄⁵⁰ and small unknown impurities, respectively. Note the absence of the P₄O₁₀ peak (δ = –45.9 ppm) which indicates that the reaction of the reagent P₄O₁₀ was again quantitative.

The homonuclear ³¹P–³¹P MAS SQ-DQ correlation spectrum (Fig. 8) proves that peaks 1 and 2 belong to one phase due to the correlation peaks between them. The correlation pattern and shift range are consistent with the presence of a cyclotetraphosphate but not to a cyclotriphosphate because of the connectivity and peak areas of the Q₂ peaks. Catena phosphates can be excluded due to the absence of Q₁ signals.

Furthermore the absence of correlation peaks between Q₂ and Q₀ peaks means that the sample is a heterogeneous mixture of rubidium orthophosphate and rubidium cyclotetraphosphate.

The corresponding heteronuclear 2D ³¹P(¹H) MAS correlation spectrum (Fig. 9) indicates spatial proximity between phosphorus and hydrogen atoms in monoclinic RbH₂PO₄.

A correlation peak can only be observed in the case of ³¹P–¹H vicinity. Absence of correlation peaks for the ³¹P peaks 1 and 2, suggests that the synthesized cyclotetraphosphate is hydrogen-free, in contrast to the observed correlation peaks for ³¹P peak 3. This hypothesis was tested with the help of heteronuclear recoupling experiments.

Fig. 10 shows ³¹P(¹H) C-REDOR curves of the deconvoluted peaks 1 (circles), 2 (crosses) and 3 (squares). This experiment is much more sensitive to ³¹P–¹H proximities than cross-
polarization and is used to determine heteronuclear dipole–dipole coupling constants, which are closely related to internuclear distances. In agreement with the conclusions gained from the heteronuclear $^{31}$P{${}^1$H} MAS NMR spectrum (Fig. 9), peak 3 shows a dephased curve, due to hydrogen’s vicinity. As expected, the deconvoluted curves from peaks 1 and 2 display almost no dephasing. We estimate that less than one percent of the Rb+-cations is replaced with H+-cations (Fig. 10). These findings allow us to unambiguously establish the molecular structure and composition of the previously unknown phase Rb$_4$P$_4$O$_{12}$, which proves that the synthesis via nitrate decomposition in DMSO works also with inorganic cations (Table 1).

### Conclusion

The presented novel synthesis route gives access to unknown crystalline ionic phosphates at low temperatures. The usage of anhydrous solvents allows controlling the amount of water incorporated into the crystal structures. We foresee an impact of this route onto the synthesis of organic (temperature sensitive) phosphates and onto the synthesis of water-free phosphates which are necessary for many battery materials. Furthermore the soft reaction conditions may open a new way to porous phosphates which can’t be synthesized from the melt.

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### Notes and references


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49 Integrating the five peaks which can be observed in the 31P liquid NMR spectrum dissolved in D2O results in the following values: one peak at 0.84 ppm (Q1) with a peak area of 1.75 a.u. (15.96%), two peaks at –9.7 and –9.89 ppm (Q4) with a combined peak area of 0.32 a.u. (2.91%), one peak at –20.79 ppm (Q2) with a peak area of 0.11 a.u. (1%) and one peak at –21.55 ppm (Q3) with a peak area of 8.78 a.u. (80.1%).