

Synthesis, Crystal Structure, and Vibrational Spectra of Ca₄P₆O₁₉ (Trömelite) – a *catena*-Hexaphosphate

Henning A. Höppe*

Freiburg, Albert-Ludwigs-Universität, Institut für Anorganische und Analytische Chemie

Professor Rüdiger Kniep zum 60. Geburtstag gewidmet

Abstract. The *catena*-hexaphosphate Ca₄P₆O₁₉ (Trömelite) was obtained by the reaction of calcium oxide with H₃PO₃ in a tube furnace at a temperature of 900 °C and crystallizes triclinic (space group $P\bar{1}$, $Z = 2$, $a = 685.70(9)$ pm, $b = 915.47(12)$ pm, $c = 1282.25(17)$ pm, $\alpha = 109.602(10)^\circ$, $\beta = 99.778(10)^\circ$, $\gamma = 91.917(10)^\circ$, $V = 743.70(17) \cdot 10^6$ pm³). According to the powder diffraction data of Ca₄P₆O₁₉ a Rietveld refinement of the lattice

constants was performed; this confirmed the single-crystal data. Trömelite contains chains of six condensed corner-sharing PO₄ tetrahedra with the Ca atoms in the voids of the resulting structure. IR and Raman data of Trömelite are also presented.

Keywords: Structure elucidation; Calcium; Phosphate; Catena structures; Vibrational spectroscopy

1 Introduction

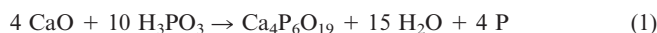
The large majority of hexaphosphates contain *cyclo*-hexaphosphate anions P₆O₁₈⁶⁻ [1]. *Catena*-phosphates comprising finite molecular anions, especially of larger chain length, occur rather rarely. The longest molecular *catena*-phosphates so far for which a crystal structure is reported are CsM₂P₅O₁₆ ($M = \text{V, Fe}$) [2] and Na₃Mg₂P₅O₁₆ [3]. In this contribution the crystal structure of a *catena*-hexaphosphate, namely Ca₄P₆O₁₉ (Trömelite), is presented. Trömelite is of considerable interest in prosthetic applications in medicine [4] and was reported for the first time by Hill et al. in 1944 as an incongruently melting phase during investigations on the phase diagram of CaO–P₂O₅ [5, 6]. Ohashi and van Wazer supposed Trömelite to be a pentaphosphate [7] but further chromatography experiments by Thilo et al. established that the title compound is a hexaphosphate of the likely composition Ca₄P₆O₁₉ [8]. They suggested a triclinic unit cell ($a = 940$ pm, $b = 1339$ pm, $c = 707$ pm, $\alpha = 109.5^\circ$, $\beta = 87.9^\circ$, $\gamma = 108.9^\circ$) based on X-ray powder diffraction data and X-ray film methods applied to a single-crystal. Apparently, a structure solution based on powder diffraction data of this compound was difficult and not successful. So far, the crystal structures of almost all adjacent phases in the phase diagram (e. g. β -Ca(PO₃)₂, α -Ca₂P₂O₇ and β -Ca₂P₂O₇)

were determined [9–11], now Trömelite could be determined as well.

2 Experimental

2.1 Synthesis

The synthesis of Ca₄P₆O₁₉ was performed in a tube furnace according to Eq. (1).



Under argon a mixture of 63 mg (1.1 mmol) calcium oxide (Merck, pure) and 209 mg (2.55 mmol) phosphorous acid (Riedel-de Haën, 98 %) was transferred into an alumina boat. The latter was then heated under a nitrogen flow to 770 K with a rate of 180 K h⁻¹. After 24 h no further condensation of water was detected and the boat containing 204 mg of a brown–red intermediate product ($\Delta m_{\text{exp}} = -25\%$, $\Delta m(15 \text{ H}_2\text{O})_{\text{theoret}} = -26\%$) was reground and 100 mg of this mixture were subsequently heated to 1170 K with a rate of 180 K h⁻¹ and maintained at this temperature for another 48 h until no further condensation of red phosphorus occurred. Then the mixture was cooled to room temperature with a rate of 60 K h⁻¹ and yielded Ca₄P₆O₁₉ with a small impurity of Ca(PO₃)₂. The formed red phosphorus evaporated off the reaction mixture and condensed at the inner surface of the silica tube ($\Delta m_{\text{exp}} = -16\%$, $\Delta m(4 \text{ P})_{\text{theoret}} = -16\%$). Finally, 84 mg (0.264 mmol, yield based on pure Trömelite: 96 %) of Ca₄P₆O₁₉ were obtained as a coarsely crystalline, colourless and non-hygroscopic powder.

2.2 Vibrational spectroscopy

An FTIR spectrum was obtained at room temperature by using a Bruker IFS 66v/S spectrometer. The samples were thoroughly mixed with dried KBr (approx. 2 mg sample, 300 mg KBr). Raman spectra were recorded by a Bruker FRA 106/S module with an Nd–YAG laser ($\lambda = 1064$ nm) scanning a range from 400 to 4000 cm⁻¹.

* Dr. H. A. Höppe
Institut für Anorganische und Analytische Chemie
Albert-Ludwigs-Universität Freiburg,
Albertstraße 21
D-79104 Freiburg, Germany
Fax: +49-(0)761-203-6012
E-Mail: henning.hoeppe@ac.uni-freiburg.de

Supporting information for this article is available on the WWW under <http://www.wiley-vch.de/home/zaac> or from the author

Table 1 Crystallographic data of Ca₄P₆O₁₉ (e.s.d.s. in parentheses)

Crystal Data		
Ca ₄ P ₆ O ₁₉		F(000) = 644
<i>M</i> = 650.14 g/mol		$\rho_{\text{X-ray}} = 2.903 \text{ g cm}^{-3}$
triclinic		Mo-K α -radiation
space group <i>P</i> $\bar{1}$ (no. 2)		$\lambda = 71.073 \text{ pm}$
<i>a</i> = 685.70(9) pm	$\alpha = 109.602(10)^\circ$	$\mu = 2.22 \text{ mm}^{-1}$
<i>b</i> = 915.47(12) pm	$\beta = 99.778(10)^\circ$	<i>T</i> = 293(2) K
<i>c</i> = 1282.25(17) pm	$\gamma = 91.917(10)^\circ$	crystal shape: block
<i>V</i> = 743.70(17) · 10 ⁶ pm ³		0.08 × 0.11 × 0.13 mm ³
<i>Z</i> = 2		colourless
Data Collection		
Stoe IPDS-II		<i>h</i> = -9 → 9
absorption correction: numerical		<i>k</i> = -12 → 12
<i>T</i> _{min} = 0.7602; <i>T</i> _{max} = 0.8513		<i>l</i> = -18 → 17
<i>R</i> _{int} = 0.1057		4325 independent reflections
2 θ _{max} = 60.0°		2243 observed reflections ($F_o^2 \geq 2 \sigma(F_o^2)$)
Refinement		
refinement on <i>F</i> ²		program used to refine structure: SHELXL-97 [15]
<i>R</i> 1 = 0.0567		$w^{-1} = \sigma^2 F_o^2 +$
(<i>xP</i>) ² + <i>yP</i> ; <i>P</i> = (<i>F</i> _o) ² + 2		<i>F</i> _c) ² /3
<i>wR</i> 2 = 0.0885		weighting scheme (<i>x/y</i>) 0.0139 / 0
Goof = 0.890		
9274 measured reflections		min. residual electron density: -0.757 eÅ ⁻³
263 parameters		max. residual electron density: 0.744 eÅ ⁻³
Powder Diffraction (Rietveld refinement of the lattice parameters)		program used to refine lattice parameters: GSAS [16, 17]
Ca ₄ P ₆ O ₁₉		
Mo-K α -radiation		<i>wR</i> _p = 0.033
<i>a</i> = 687.36(3) pm	$\alpha = 109.520(3)^\circ$	<i>R</i> _p = 0.026
<i>b</i> = 917.20(3) pm	$\beta = 99.828(3)^\circ$	<i>R</i> _F ² = 0.042
<i>c</i> = 1284.8(4) pm	$\gamma = 91.930(3)^\circ$	<i>R</i> _F = 0.024
		$\chi^2 = 1.103$
18 profile parameters		4361 reflections ($2\theta_{\text{max}} = 60.0^\circ$)

3 Results and Discussion

3.1 Synthesis

According to the phase diagram of the system CaO–P₂O₅ [5, 6], Trömelite is an incongruently melting compound and was originally obtained as an almost pure, micro-crystalline powder by annealing a stoichiometric mixture of CaO and P₂O₅ at 966 °C [8]. Even though Thilo et al. obtained single-crystals they did not solve the crystal structure. In this contribution phosphorous acid was used instead of P₂O₅ which apparently provides an environment that enhances the formation of single-crystals suitable for an X-ray based structure determination. A single-phase product could not be obtained, though, and small quantities of calcium metaphosphate, β–Ca(PO₃)₂ [9], are formed additionally. This problem was reported previously [8, 12]. The pyrolysis of sodium and calcium phosphonates, namely CaH₂(HPO₃)₂ · H₂O, was reported by Zobel et al. [13, 14] and the successful synthesis of Trömelite corresponds well with the results presented therein.

3.2 Crystal Structure Determination

X-ray diffraction data of the title compound Ca₄P₆O₁₉ were collected on a Stoe IPDS 2 diffractometer using Mo-K α radiation. A suitable single-crystal was enclosed in a Lindemann tube sealed under argon atmosphere. The diffraction data were corrected for

an intensity decay (8 %) and for absorption by applying a numerical correction based on an optimised crystal shape by the program X-Shape (Stoe & Cie., Darmstadt, Germany). According to the triclinic crystal system the space groups *P*1 and *P* $\bar{1}$ were taken into account. The structure solution and refinement was finally performed in the centrosymmetric space group *P* $\bar{1}$ (no. 2).

The crystal structure of Ca₄P₆O₁₉ was solved by direct methods using SHELXTL [15] and refined with anisotropic displacement parameters for all atoms. The relevant crystallographic data and further details of the X-ray data collection are summarized in Table 1. Table 2 shows the positional and displacement parameters for all atoms. In Table 3 selected interatomic distances and angles are listed. Furthermore all reflections detected by X-ray powder diffraction (Stoe Stadi P) of Ca₄P₆O₁₉ have been indexed and their observed intensities are in good agreement with the calculated diffraction pattern based on the single-crystal data and with the powder diffraction pattern published by Thilo et al. Additionally, the experimentally by Thilo et al. [8] determined density of Trömelite ($\rho = 2.85 \text{ g cm}^{-3}$) is in good agreement with $\rho_{\text{X-ray}} = 2.903 \text{ g cm}^{-3}$. A Rietveld refinement of the lattice parameters (Table 1) has been performed with the program GSAS [16, 17]. The powder diffraction pattern is available as electronic supporting information.

3.3 Crystal Structure

Ca₄P₆O₁₉ crystallizes in a new structure type and contains discrete non-condensed chains of six corner-sharing PO₄ tetrahedra forming a P₆O₁₉⁸⁻ anion (Fig. 1). The cations

Table 2 Atomic coordinates and anisotropic displacement parameters / 10^{-4} pm² for Ca₄P₆O₁₉ (e.s.d.s. in parentheses); all atoms are on Wyckoff position 2a; c. n. = coordination number

atom ^[c.n.]	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	U _{eq}
Ca(1) ^[7]	-0.0264(2)	-0.18177(15)	0.85240(11)	0.0082(5)	0.0123(5)	0.0103(6)	0.0057(4)	0.0013(4)	0.0016(4)	0.0099(3)
Ca(2) ^[7]	0.3542(2)	-0.13142(13)	0.12103(10)	0.0119(5)	0.0087(5)	0.0108(6)	0.0031(4)	0.0001(5)	0.0015(4)	0.0108(3)
Ca(3) ^[8]	0.8071(2)	-0.00683(14)	0.36628(11)	0.0129(5)	0.0120(6)	0.0090(6)	0.0048(4)	0.0016(4)	-0.0007(4)	0.0111(3)
Ca(4) ^[7]	-0.0984(2)	-0.65052(13)	0.66637(10)	0.0092(5)	0.0123(5)	0.0108(6)	0.0061(4)	0.0020(4)	0.0023(4)	0.0102(2)
P(1) ^[4]	0.2715(2)	0.0527(2)	0.37487(13)	0.0094(7)	0.0085(6)	0.0064(7)	0.0023(5)	0.0013(5)	0.0001(5)	0.0082(3)
P(2) ^[4]	0.6267(2)	-0.3307(2)	0.41718(12)	0.0075(6)	0.0091(6)	0.0075(7)	-0.0001(5)	0.0016(5)	0.0004(5)	0.0088(3)
P(3) ^[4]	0.7948(2)	0.3703(2)	0.37913(13)	0.0091(6)	0.0081(6)	0.0077(6)	0.0039(5)	0.0021(5)	0.0008(5)	0.0079(3)
P(4) ^[4]	0.5364(2)	0.2399(2)	0.15149(12)	0.0082(6)	0.0095(6)	0.0081(7)	0.0032(5)	0.0014(5)	0.0006(5)	0.0086(3)
P(5) ^[4]	-0.2884(2)	-0.4601(2)	0.90641(13)	0.0103(7)	0.0082(7)	0.0099(7)	0.0018(5)	0.0021(6)	-0.0003(5)	0.0098(3)
P(6) ^[4]	0.8740(2)	-0.1881(2)	0.11919(12)	0.0095(7)	0.0086(7)	0.0062(7)	0.0036(5)	0.0007(5)	-0.0019(5)	0.0080(3)
O(1) ^[2]	0.6137(7)	-0.2157(5)	0.5364(4)	0.016(2)	0.013(2)	0.014(2)	0.000(2)	0.011(2)	-0.001(2)	0.0146(9)
O(2) ^[2]	0.7076(7)	-0.4778(4)	0.4474(3)	0.021(2)	0.011(2)	0.012(2)	0.004(2)	0.007(2)	0.002(2)	0.0142(9)
O(3) ^[2]	0.6133(6)	0.2714(5)	0.2817(3)	0.014(2)	0.024(2)	0.008(2)	0.004(2)	-0.001(2)	-0.007(2)	0.0162(9)
O(4) ^[2]	0.4914(6)	0.4052(5)	0.1454(4)	0.013(2)	0.009(2)	0.029(3)	0.003(2)	0.002(2)	0.002(2)	0.0181(10)
O(5) ^[2]	-0.2471(7)	-0.3481(5)	0.0314(4)	0.027(2)	0.019(2)	0.011(2)	0.000(2)	0.005(2)	-0.014(2)	0.0206(11)
O(11) ^[1]	0.4355(6)	-0.0262(5)	0.3197(4)	0.015(2)	0.012(2)	0.011(2)	0.006(2)	0.005(2)	0.002(2)	0.0119(9)
O(12) ^[1]	0.1098(6)	0.0955(5)	0.2987(4)	0.015(2)	0.016(2)	0.011(2)	0.009(2)	0.000(2)	0.002(2)	0.0134(9)
O(13) ^[1]	0.1788(6)	-0.0325(5)	0.4410(4)	0.013(2)	0.011(2)	0.010(2)	0.002(2)	0.001(2)	-0.000(2)	0.0118(9)
O(21) ^[1]	0.4249(6)	-0.3773(5)	0.3504(4)	0.011(2)	0.019(2)	0.012(2)	0.002(2)	-0.002(2)	0.001(2)	0.0152(9)
O(22) ^[1]	0.7803(6)	-0.2673(5)	0.3702(4)	0.011(2)	0.017(2)	0.012(2)	0.006(2)	0.006(2)	0.004(2)	0.0121(9)
O(31) ^[1]	0.8407(6)	0.2778(5)	0.4544(4)	0.015(2)	0.009(2)	0.013(2)	0.006(2)	0.002(2)	0.001(2)	0.0122(9)
O(32) ^[1]	0.9516(6)	0.4091(5)	0.3231(4)	0.012(2)	0.010(2)	0.015(2)	0.006(2)	0.002(2)	0.001(2)	0.0120(9)
O(41) ^[1]	0.6935(6)	0.1869(5)	0.0843(4)	0.012(2)	0.019(2)	0.007(2)	0.004(2)	0.001(2)	-0.001(2)	0.0128(9)
O(42) ^[1]	0.3519(6)	0.1316(5)	0.1219(4)	0.009(2)	0.015(2)	0.010(2)	0.005(2)	-0.004(2)	-0.003(2)	0.0122(9)
O(51) ^[1]	-0.3407(7)	-0.6177(5)	0.9042(4)	0.019(2)	0.012(2)	0.021(2)	0.007(2)	0.000(2)	0.003(2)	0.0175(9)
O(52) ^[1]	-0.1297(7)	-0.4306(5)	0.8476(4)	0.015(2)	0.012(2)	0.015(2)	0.003(2)	0.005(2)	0.001(2)	0.0142(9)
O(61) ^[1]	0.0042(7)	-0.2304(5)	0.2082(4)	0.022(2)	0.015(2)	0.014(2)	0.008(2)	-0.004(2)	0.001(2)	0.0171(10)
O(62) ^[1]	0.7144(6)	-0.0880(5)	0.1645(4)	0.013(2)	0.018(2)	0.015(2)	0.008(2)	0.006(2)	0.007(2)	0.0142(9)
O(63) ^[1]	0.9974(6)	-0.1170(5)	0.0558(4)	0.012(2)	0.014(2)	0.009(2)	0.006(2)	0.000(2)	-0.002(2)	0.0116(9)

Table 3 Selected interatomic distances / pm and angles / ° for Ca₄P₆O₁₉ (e.s.d.s. in parentheses)

Ca(1) – O ^[1]	229.7(5) – 264.2(4)	7 distances
Ca(2) – O ^[1]	220.5(4) – 247.0(5)	6 distances
Ca(3) – O ^[1]	304.6(5)	7 distances
Ca(4) – O ^[1]	240.2(5) – 263.9(5)	6 distances
P1, P6 – O ^[1]	290.8(5)	
P1, P6 – O ^[2]	224.4(4) – 256.1(4)	
P2 – P5 – O ^[1]	275.2(4)	
P2 – P5 – O ^[2]	149.1(5) – 153.3(5)	
P2 – P5 – O ^[2]	161.2(4), 161.8(4)	
O ^{term} – P – O ^{br}	146.3(4) – 149.3(4)	
O ^{term} – P – O ^{term}	155.7(4) – 161.2(5)	
O ^{br} – P – O ^{br}	102.5(3) – 112.3(3)	
P – O ^[2] – P	109.5(3) – 120.4(3)	
	101.1(3) – 105.2(3)	
	129.5(3) – 144.5(3)	

are situated in the voids (Fig. 2) of the resulting structure. The conformation of the P₆O₁₉⁸⁻ anion is very similar to the infinite chains in Ca(PO₃)₂ [9]. In Trömelite all inner PO₄ tetrahedra are *cis*-connected to the neighbouring ones. This also holds for the structures of Ca(PO₃)₂ and CsMP₅O₁₆ (M = V, Fe), but not for Mg₂Na₃P₅O₁₆ where the anion has a V-shape.

The bond lengths between P and terminal O^[1] atoms ranging from 146.3(4) to 153.3(5) pm (average 149.5 pm) are significantly shorter than the bond lengths between P and the bridging O^[2] atoms (155.7(4) – 161.8(4) pm, average 159.1 pm). They agree very well with typical bond lengths inside phosphate chains in *catena*-pentaphosphates [2, 9, 18]. The O–P–O angles are in average (109.3°), close to the tetrahedral angle. As observed previously in *catena*-phosphates [2, 9], the angles O^{br} – P – O^{br} (br = bridging)

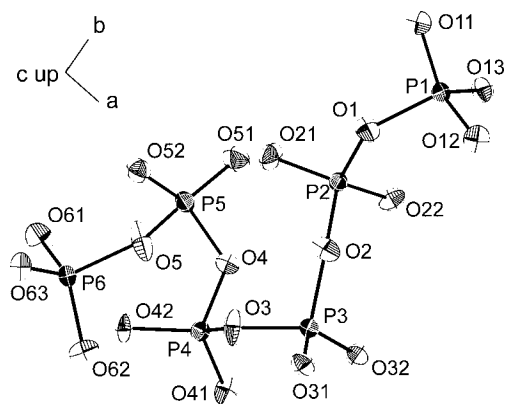


Fig. 1 View of the *catena*-hexaphosphate anion in Ca₄P₆O₁₉ approximately along [111] (P: dark gray, O: white), the displacement ellipsoids represent 75 % probability.

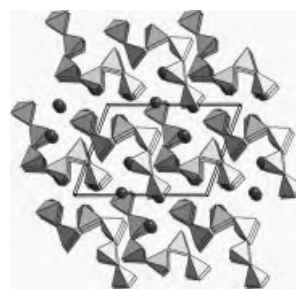


Fig. 2 Perspective view of the crystal structure of Ca₄P₆O₁₉ along [100] (PO₄ tetrahedra are shown as closed polyhedra, Ca: dark gray spheres, O: white spheres).

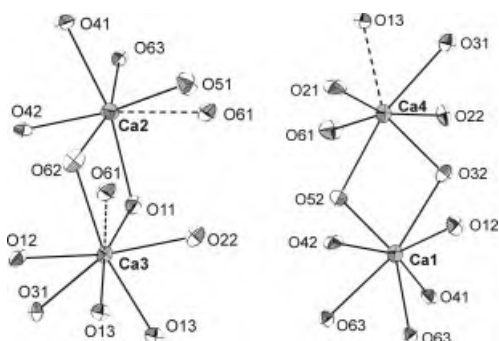


Fig. 3 Representation of the Ca environments in $\text{Ca}_4\text{P}_6\text{O}_{19}$ (Ca: gray, O: white), the displacement ellipsoids represent 75 % probability.

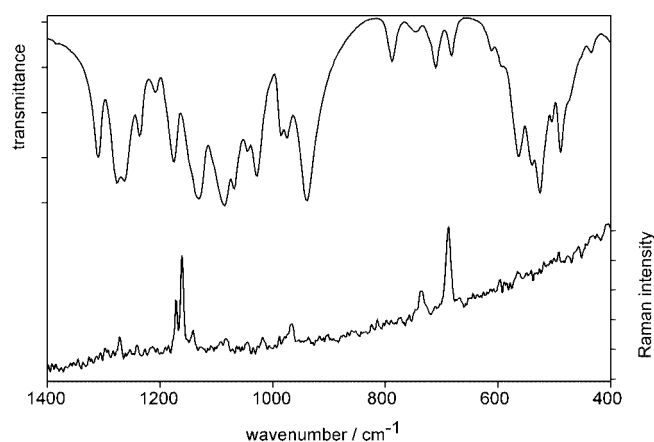


Fig. 4 Infrared and Raman vibrational spectra of $\text{Ca}_4\text{P}_6\text{O}_{19}$.

are significantly smaller compared with the angles $\text{O}^{\text{term}} - \text{P} - \text{O}^{\text{term}}$ (term = terminal) presumably due to a partial double-bond character of the $\text{P} - \text{O}^{\text{term}}$ bonds.

All four crystallographically independent Ca^{2+} ions are coordinated by terminal oxygen atoms $\text{O}^{\text{[1]}}$ only, the distances $\text{Ca}-\text{O}$ vary between 220.5(4) and 304.6(5) pm with an average value of 247.3 pm in good agreement with the sum of ionic radii of 248 pm [19]. The coordination polyhedra are fairly irregular (Fig. 3) in which the coordination number of Ca1 is seven, of Ca2 and Ca4 6+1 and of Ca3 7+1. The $\text{Ca}-\text{O}$ polyhedra form condensed layers approximately perpendicular [001] in which the polyhedra share common edges. These layers are linked by common vertices to form a condensed three-dimensional framework and the hexaphosphate anions are positioned between these layers.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-414341 ($\text{Ca}_4\text{P}_6\text{O}_{19}$), the name of the author, and citation of this publication.

3.4 Vibrational Spectroscopy

Figure 4 shows the vibrational spectra of the title compound $\text{Ca}_4\text{P}_6\text{O}_{19}$. Normally the IR spectra of *catena*-phosphates are not significantly different from those of *meta*-phosphates [20]. In $\text{Ca}_4\text{P}_6\text{O}_{19}$, the therein reported characteristic frequencies of *catena*-phosphates like the $\nu_{\text{as}}(\text{PO}_2)$ are detected between 1200 and 1310 cm^{-1} , the very intense $\nu_{\text{as}}(\text{POP})$ at 940 cm^{-1} and $\nu_{\text{as}}(\text{PO}_3)$ ranging from 1025 up to 1180 cm^{-1} . Additionally, the Raman spectra of $\text{Ca}_4\text{P}_6\text{O}_{19}$ show strong vibrations in the region around 1161 ($\nu_s(\text{PO}_3)$), at 738 and 688 cm^{-1} ($\nu_s(\text{POP})$). Thus the herein presented vibrational data are in good agreement with the expected values.

4 Conclusions

In this contribution the single-crystal structure determination of Trömelite, $\text{Ca}_4\text{P}_6\text{O}_{19}$, containing non-condensed *catena*-hexaphosphate anions is presented. The size of the triclinic unit cell determined by Thilo et al. in 1964 [8] is similar to that determined from the single-crystal X-ray diffraction data collection reported in this work. Due to the modified synthesis using phosphorous acid instead of calcium phosphates(V) single-crystals of a quality suitable for an X-ray diffraction data collection were obtained. The measured vibrational spectra of $\text{Ca}_4\text{P}_6\text{O}_{19}$ correspond well with the expected values for *catena*-phosphates [20]. All these results thus confirm that the compound known as Trömelite is indeed $\text{Ca}_4\text{P}_6\text{O}_{19}$ with the crystal structure described in this publication.

Acknowledgments. The author thanks Mrs. A. Becherer, Albert-Ludwigs-Universität Freiburg, for recording the vibrational spectra and Prof. H. Hillebrecht, Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, for valuable discussions and generous support.

References

- [1] M. T. Averbuch-Pouchot, A. Durif, *Eur. J. Solid State Inorg. Chem.* **1991**, 28, 9–22.
- [2] B. Klinkert, M. Jansen, *Z. Anorg. Allg. Chem.* **1988**, 567, 87–94.
- [3] Yu. I. Smolin, Yu. F. Shepelev, A. I. Domanskii, J. Majling, *Kristallografiya* **1978**, 23, 1264–1266.
- [4] Kyushu Refractories Co., Ltd. (A. Watanabe, Y. Takeuchi, S. Kihara, Y. Imada), JP 62019173 (July 19, 1985) [*C. A.* **1987**, 106, 182715z].
- [5] W. L. Hill, G. T. Faust, D. S. Reynolds, *Amer. J. Sci.* **1944**, 242, 457–477.
- [6] W. L. Hill, G. T. Faust, D. S. Reynolds, *Amer. J. Sci.* **1944**, 242, 542–562.
- [7] S. Ohashi, J. R. van Wazer, *J. Am. Chem. Soc.* **1959**, 81, 830–832.
- [8] W. Wiecker, A.-R. Grimmer, E. Thilo, *Z. Anorg. Allg. Chem.* **1964**, 330, 78–90.
- [9] M. Schneider, K. H. Jost, P. Leibnitz, *Z. Anorg. Allg. Chem.* **1985**, 527, 99–104.

- [10] C. Calvo, *Inorg. Chem.* **1968**, *7*, 1345–1351.
- [11] S. Boudin, A. Grandin, M. M. Borel, A. Leclaire, B. Raveau, *Acta Crystallogr. C* **1993**, *49*, 2062–2064.
- [12] D. R. Gard, *Phosphorus Sulfur Silicon Relat. Elem.* **1993**, *76*, 231–234.
- [13] D. Zobel, N. Ba, *Z. Chem.* **1969**, *9*, 433.
- [14] D. Zobel, N. Ba, *Z. Chem.* **1970**, *10*, 154, 197.
- [15] G. M. Sheldrick, *SHELXTL, V 5.10 Crystallographic System*, Bruker AXS Analytical X-ray Instruments Inc., Madison, 1997.
- [16] R. B. von Dreele, A. C. Larson, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2000.
- [17] B. H. Toby, EXPGUI, a graphical user interface for GSAS, *J. Appl. Cryst.* **2001**, *34*, 210.
- [18] W. H. Baur, *Acta Crystallogr.* **1974**, *B30*, 1195–1215.
- [19] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr.* **1969**, *B25*, 925.
- [20] A. Rulmont, R. Cahay, M. Liegeois-Duyckaerts, P. Tarte, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 207–219.