

Synthesis and Crystal Structure of $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$

Introduction

The first reaction leading to hypophosphoric acid was reported by Schiel [1] and the salt was characterized by Salzer [2]. Since 1960, few studies were performed on hypodiphosphate [3-5]. In this work we report the synthesis and the single-crystal structure of lithium dihydrogen hypodiphosphate dihydrate, $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$.

The new hypodiphosphate salt, $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$, was synthesized by soft chemistry reactions from aqueous solutions of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6 \text{H}_2\text{O}$ and lithium hydroxide. The compound crystallizes in the monoclinic space group $P2_1/n$ with two formula units per unit cell and $a = 6.144(1)$, $b = 5.155(1)$, $c = 12.106(3)$ Å, $\beta = 104.03(2)^\circ$ and $V = 372.0(1)$ Å³.

Experimental

Disodium dihydrogen hypodiphosphate dihydrate was prepared using the procedure reported by Leininger and Chulski [6]. A solution of dilithium dihydrogen hypodiphosphate was obtained by adding LiOH to a solution of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6 \text{H}_2\text{O}$ in 35 mL distilled water at 30°C. Slowly cooling at room temperature yielded block-shaped colorless crystals of the title compound within one week.

The FT-Raman and FT-IR/FIR spectra of the title compound have been recorded, especially with respect to the $[\text{H}_2\text{P}_2\text{O}_6]^{2-}$ group.

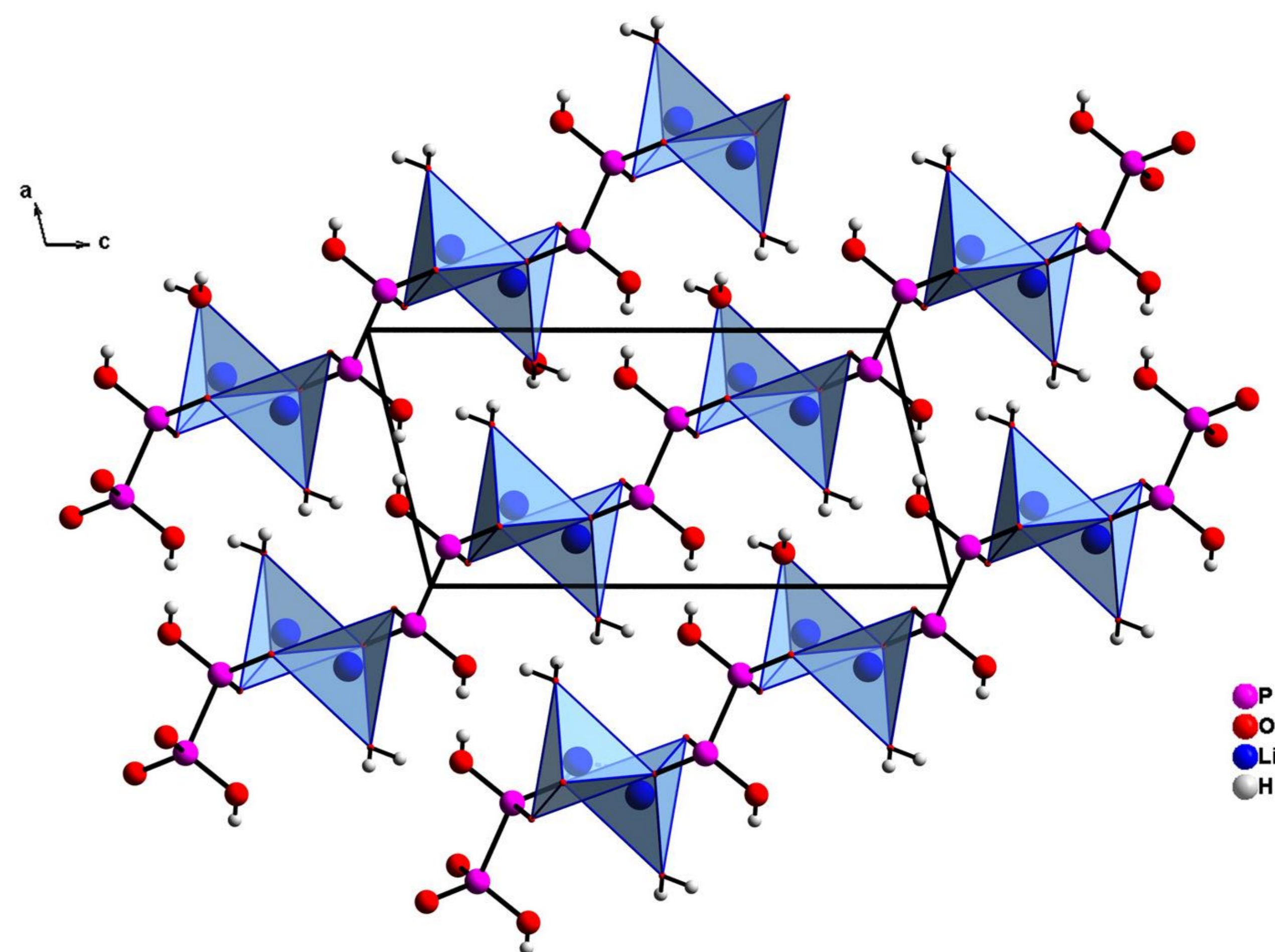


Fig. 1 Projection of the crystal structure of $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$ along [010].

Structure description

Dilithium dihydrogen hypodiphosphate dihydrate crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with two formula units per unit cell and cell parameters $a = 6.144(1)$ Å, $b = 5.155(1)$ Å, $c = 12.106(3)$ Å, $\beta = 104.03(2)^\circ$ and $V = 372.0(1)$ Å³ (Tab. 1 and Fig. 1)

The crystal structure of $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$ is characterized by discrete $[\text{H}_2\text{P}_2\text{O}_6]^{2-}$ anions in staggered conformation, tetrahedral $[\text{LiO}_4]$ and water molecules, held together by hydrogen bonds. The P – P distance amounts to 2.182 Å and the P – O bond lengths range from 1.502 to 1.546 Å, similar to those reported previously [3-5]. The $[\text{H}_2\text{P}_2\text{O}_6]^{2-}$ units are surrounded by $[\text{LiO}_4]$ groups and water molecules connected via hydrogen bonds, with O ... O distances from 2.449 to 3.159 Å and O – H ... O angles from 157.8 to 175.4° (Tab2). The lithium ions exhibit slight deviations from the ideal tetrahedral symmetry with P – O bond distances from 1.927 to 2.033 Å and O – P – O bond angles from 104.4 to 119.1° (Fig. 2).

The FT-Raman spectrum is presented in Fig. 3. The $[\text{H}_2\text{P}_2\text{O}_6]^{2-}$ ion exhibits D_{3d} symmetry. The spectral region below 600 cm^{-1} belongs to $[\text{H}_2\text{P}_2\text{O}_6]^{2-}$, in which the peak at 322 cm^{-1} is the mixed symmetric P – O and P – P stretching modes. The peak at 280 cm^{-1} belong to bendings. The lattice vibrations can be recognized below about 150 cm^{-1} .

Tab. 2 Selected bond lengths [Å] and angles [°] for the title compound.

$[\text{H}_2\text{P}_2\text{O}_6]^{2-}$ ion			
P – P ⁱ	2.182(1)	O1 – P – O2	115.8(1)
P – O1	1.502(2)	O1 – P – O3	109.9(1)
P – O2	1.528(2)	O2 – P – O3	109.6(1)
P – O3	1.546(2)	O1 – P – P	110.0(1)
H – O2	0.681(5)	O2 – P – P	104.7(1)
Li coordination			
Li – O1	1.927(5)	O1 – Li – O4	105.4(2)
Li – O4	1.954(5)	O1 – Li – O1 ⁱ	119.1(2)
Li – O1 ⁱ	1.965(5)	O1 – Li – O3 ⁱ	104.4(2)
Li – O3	2.033(5)	O3 – Li – O4	116.9(2)
Hydrogen bonds			
O3 – H3 – O3 ⁱⁱ	2.449(1)	∠ O3 – H3 – O3 ⁱⁱ	175.4(6)
O4 – Hb – O3	2.848(2)	∠ O4 – Hb – O3	159.4(6)
O4 – Ha – O3 ⁱⁱ	3.159(1)	∠ O4 – Ha – O3 ⁱⁱ	157.8(6)

Symmetry codes: i) $x, y - 1, z$; ii) $-x + 2, -y, -z + 1$.

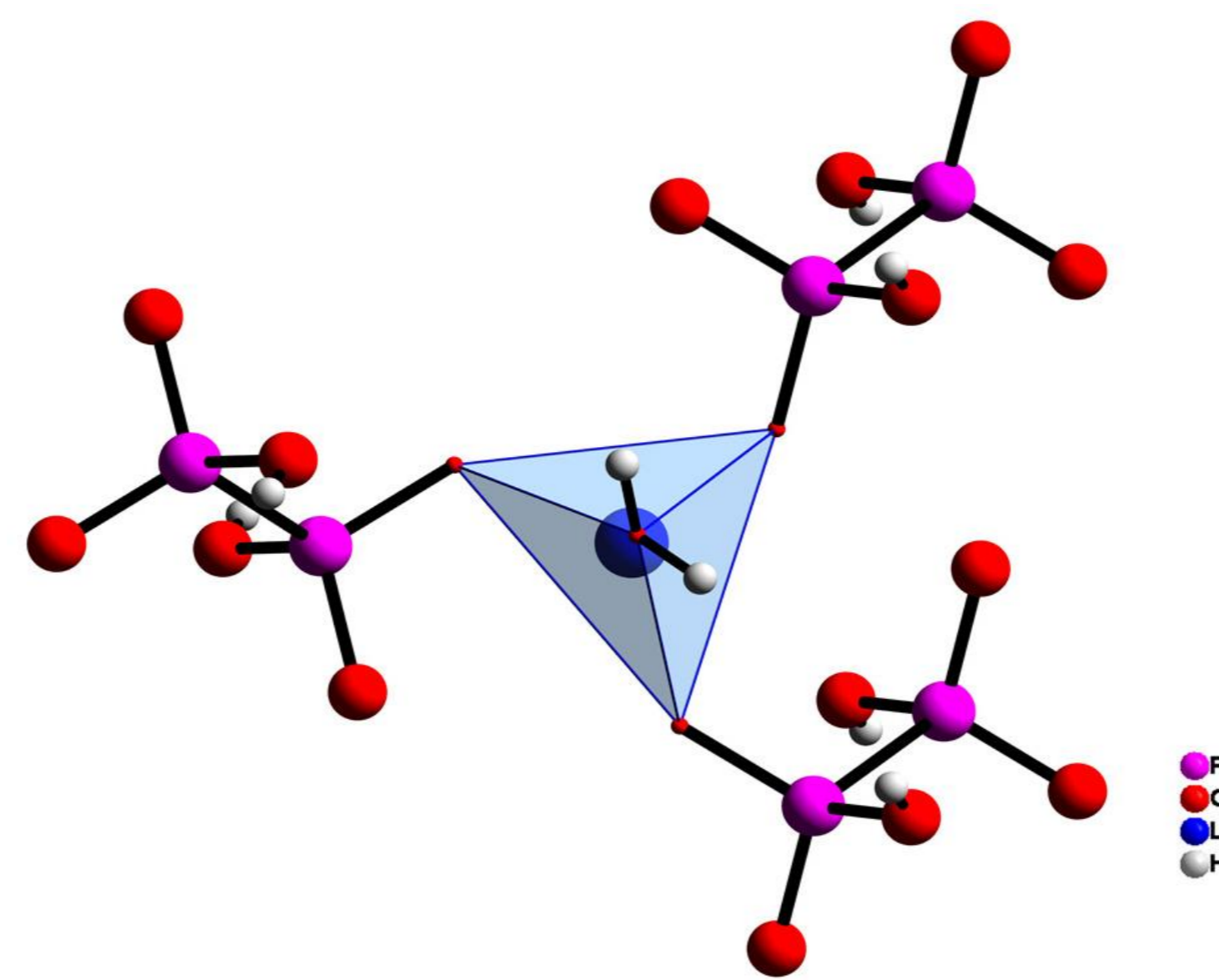


Fig. 2 Li coordination in $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$.

References

- [1] J. Schiel, *Ann. Chem. Pharm.* **109** (1859) 317.
- [2] T. Salzer, *Ann. Chem.* **187** (1877) 322.
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- [4] A. Wilson, H. McD. McGeachin, *Acta Cryst.* **17** (1964) 1352.
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- [6] E. Leininger, T. Chulski, *J. Amer. Chem. Soc.* **71** (1949) 2385.

Tab. 1 Crystallographic data and structure refinement parameter for $\text{Li}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2 \text{H}_2\text{O}$.

Crystal system	monoclinic
Space group / Z	$P2_1/n$
a [Å]	6.144 (1)
b [Å]	5.155(1)
c [Å]	12.106(3)
β [°]	104.03(2)
Volume [Å ³]	372.0(1)
D_{calc} [g · cm ⁻³]	1.874
Measurement device	STOE IPDS II
μ (MoK α) [mm ⁻¹]	0.711
$F(000)$	212
T [K]	223
Crystal size [mm ³]	0.29 x 0.28 x 0.26
$\Theta_{\text{min, max}}$ [°]	1.00 – 25.02
$h_{\text{min}}, h_{\text{max}}, k_{\text{min}}, k_{\text{max}}, l_{\text{min}}, l_{\text{max}}$	7, -6, 5, -5, -14, 14
Unique reflections	658
Data / parameters	658 / 67
Goodness-of-Fit	1.090
$R1$ [$>2\sigma(I)$]	0.0389
$wR2$ [$>2\sigma(I)$]	0.0913
$R1$ (all data)	0.0489
$wR2$ (all data)	0.0937
Largest diff. peak and hole [e Å ⁻³]	0.630 / -0.445

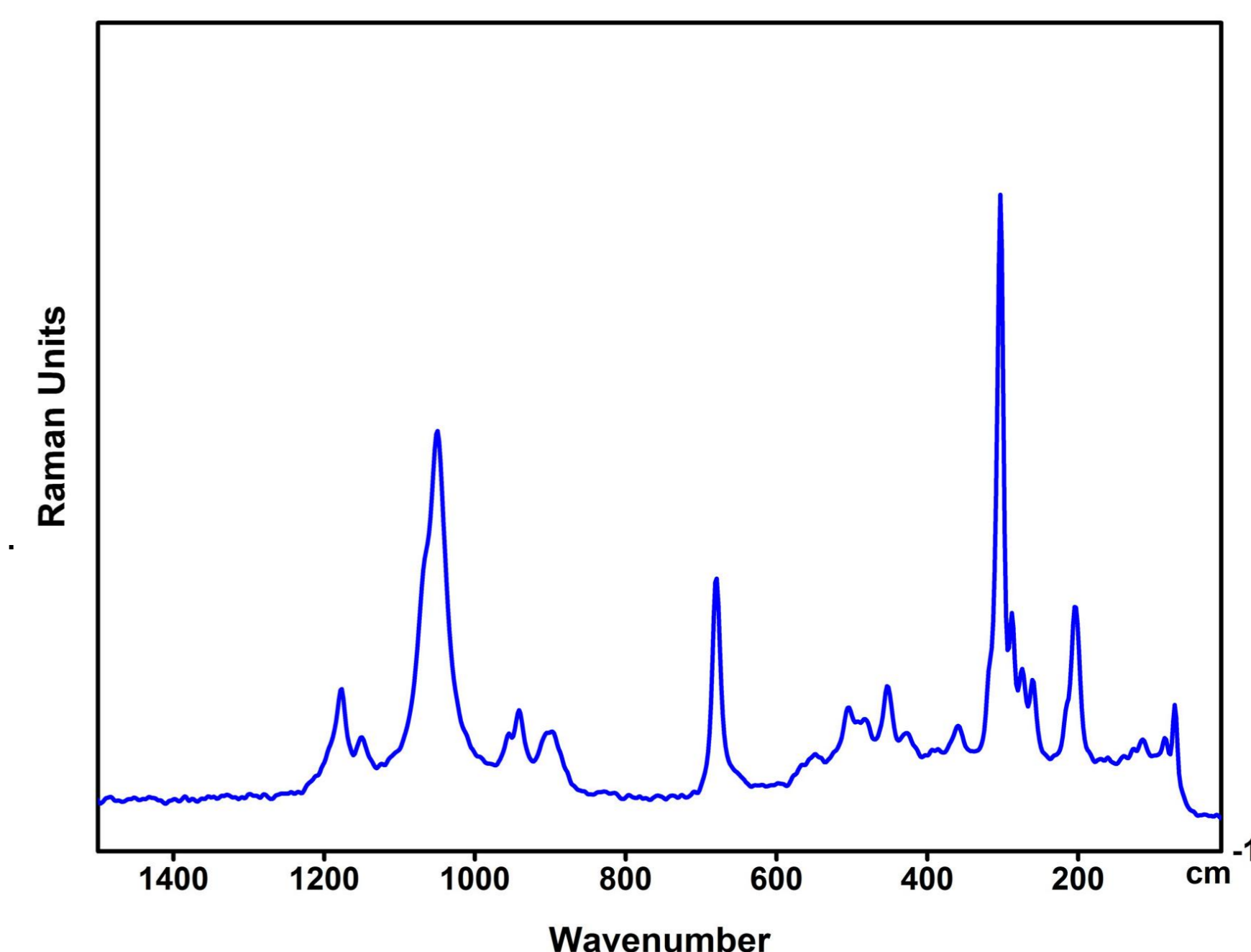


Fig. 3 FT-Raman spektrum ($\lambda_{\text{exc.}} = 1064$ nm) of title compound (Raman intensity in arbitrary units).