Synthesis, Crystal Structure, Vibrational Study and DFT Computation of Barium Dihydrogenomonophosphate Ba(H₂PO₄)₂

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Abstract: The single crystal of barium dihydrogenomonophosphate, Ba(H₂PO₄)₂ was prepared by the direct method. This compound exists in two forms: one orthorhombic, the other triclinic. In this work, we are interested in the triclinic form from the vibrational and crystalline side too. X-ray crystallography showed that this compound crystallizes in the triclinic centrosymmetric with space group P-1 (Z=2) with a = 6.9917(5)Å, b = 7.1929(5)Å, c = 7.9667(9)Å, α = 104.517(8)°, β = 95.918(7)° and γ = 109.459(6). The structure was solved from 3444 independent reflections with R = 0.0198 with wR= 0.0633. The bands observed in the infrared and Raman spectra of Ba(H₂PO₄)₂ are assigned based on the literature results and the theoretical group analyses carried out in the group of factors Ci. The optimal molecular geometry, harmonic vibrational frequencies, infrared intensities, and Raman scattering activities were calculated using density functional theory (DFT/B3LYP) methods with the LanL2DZ basis set. The HOMO-LUMO properties and geometries of this compound have been determined and discussed. The computational structural parameters are generally in agreement with the experimental investigations. The theoretical infrared and Raman spectra for the title compound have been constructed.

Keywords: crystal structures; X-ray diffraction; Raman; Infrared; DFT; barium dihydrogenomonophosphate.

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1. Introduction

The title compound belongs to a family of Dihydrogenophosphate with the general formula MH₂PO₄ (M = K, Rb, Cs, NH₄, Tl). The sample presents some physical and chemical properties of interesting materials for potential applications, such as chemical sensors, ionic conductors, catalysts, and adsorbents [1-8]. This compound has been synthesized and studied...
by single-crystal X-ray diffraction analysis, infrared and Raman vibrational. This compound crystallizes in the triclinic system with the space group P-1.

The compound, Ba(H₂PO₄)₂, is isostructural with Sr(H₂PO₄)₂[1]. The single crystal dihydrogenomonophosphate of barium. This compound exists in two forms: one orthorhombic [2], the other triclinic. In this work, we are interested in the triclinic form from the vibrational and crystalline sides too. The present paper reports the synthesis, the crystal structure determination of the title compound by X-ray diffraction at room temperature, and the experimental and computational vibrational studies of a phosphate, which is characterized by the existence of Ba²⁺ and H₂PO₄⁻. The three-dimensional structure can be considered as consisting of independent [PO₄] tetrahedra. Two vertices of each tetrahedron [PO₄]³⁻ are connected to two H atoms to form phosphate [H₂PO₄]⁻ anions arranged to delimit large deformed cavities occupied by barium-cations. The Hydrogen atoms were positioned in idealized positions and included in the final cycles of refinement. We have obtained the best structural refinement with a final value of R= 0.0198 with wR= 0.0633.

2. Materials and Methods

2.1. Materials.

Orthophosphoric acid H₃PO₄ (85%) and strontium carbonate, BaCO₃ (98%), supplied by Merck, were used to prepare the single crystal of Barium dihydrogenomonophosphate, Ba(H₂PO₄)₂.

2.2. Crystal growth.

Single crystals of barium dihydrogen phosphate Ba(H₂PO₄)₂, was prepared by slowly adding 0.98 g (10 mmol) dilute H₃PO₄ (85%), neutralized with stoichiometric amounts of 0.20 g (2 mmol) Barium carbonate, BaCO₃ (98%). The so-obtained solution was then slowly evaporated at room temperature. Clear and good quality single crystals of parallelepiped shape were then recovered for an X-ray diffraction study.

2.3. X-ray diffraction and data collection.

XRD analyses were performed on Ba(H₂PO₄)₂ using a single-crystal X-ray diffractometer (RigakuXtaLAB Synergy-S) operating in Debye Scherrer geometry using Cu-Kα radiation and equipped with a HyPix–6000 HE area detector [9].

2.4. Infrared spectroscopy.

The infrared spectrum was recorded from 400-4000 cm⁻¹ with a Bruker tensor-27 FTIR spectrometer, using samples dispersed in spectroscopically pure KBr pellets (about 1% by mass of compound).

2.5. Raman spectroscopy.

The Raman spectrum was recorded from 100-3500 cm⁻¹ with a Raman dispersive microscope DXR2 (Thermo scientific). Excitation was accomplished with the 633 nm line of an argon-ion laser. Incident power was approximately 6Mw at the source and 10% of that at the sample.
3. Results and Discussion

3.1. Structure of Ba(H₂PO₄)₂ crystal.

X-ray diffraction of the Ba(H₂PO₄)₂ crystal showed that this compound crystallized in the triclinic system with P-1. The crystallographic data collection and the structure refinement are presented in Table 1.

The hydrogen atoms were placed in idealized positions and included in the final refinement cycles; we also got the best structural refinement, we found the final value of R, R= 0.0198, wR= 0.0633. Refined atomic positions and isotropic thermal factors are given in Table 2. The anisotropic thermal factors are given in Table 3. The interatomic distances(Å) and angles are presented in Table 4.

Table 1. Crystal structure data for Ba(H₂PO₄)₂.

| Formula | Ba(H₂PO₄)₂ |
|---------|------------|
| Formula weight (g/mol) | 331.31 |
| Temperature (k) | 100(10) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| a (Å) | 6.9917(5) |
| b (Å) | 7.1929(5) |
| c (Å) | 7.9667(9) |
| α (°) | 104.517(8) |
| β (°) | 95.918(7) |
| γ (°) | 109.459(6) |
| Volume (Å³) | 357.98(6) |
| Z | 2 |
| Calculated density (g/cm³) | 3.074 |
| Crystal size (mm) | 0.076 x 0.087 x 0.125 |
| Color | Colorless |
| Diffractometer | RigakuXtaLAB Synergy-S |
| F(000) | 308 |
| Absorption coefficient (mm⁻¹) | 5.996 |
| 2θ Range (°) | 5–61 |
| Index ranges | -9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11 |
| Reflections collected | 3444 |
| Unique data | 3444 [Rint= 2.26] |
| Data/restraints/parameters | 3444/3/116 |
| Goodness of fit on F² | 1.098 |
| Final R factors (I > 2σ(I)) | R1= 0.0198, wR2= 0.0633 |
| Final R factors (all data) | R1= 0.0199, wR2= 0.0634 |
| Extinction coefficient | 0.024(2) |
| Largest residual peak / hole (e Å⁻³) | 0.826 and -0.701 |
The crystal structure of barium dihydrogenomonophosphate, Ba(H₂PO₄)₂, consists of one barium Ba²⁺ cation and two phosphates [H₂PO₄⁻] anions (Figure 1). The various polyhedral views along [1 0 0], [0 1 0], and [0 0 1] directions of Ba(H₂PO₄)₂ crystal are represented in figures 2, 3, and 4, respectively. The barium dihydrogenomonophosphate Ba(H₂PO₄)₂ structure is a monophosphate whose two independent tetrahedral PO₄ have mean P-O distances of 1.54 Å.
They derive around the barium atom, a neighborhood of nine oxygen atoms (Figure 1). This triclinic variety is not structurally related to the orthorhombic variety. On the other hand, there are great structural analogies with Ca(H₂AsO₄)₂ [10]. We can expect a distribution of hydrogen atoms similar to that established in Ca(H₂AsO₄)₂.

Figure 1. Tridimensional view of Ba(H₂PO₄)₂ structure.

Figure 2. Polyhedral view down [1 0 0] direction of Ba(H₂PO₄)₂.

Figure 3. Polyhedral view down [0 1 0] direction of Ba(H₂PO₄)₂.
This probably involves hydrogen atoms on centers of symmetry in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ et $\frac{1}{2}, \frac{3}{2}, 0$. By comparing the study carried out on Ca(H$_2$AsO$_4$)$_2$, one can predict the important role played by the hydrogen bond in the cohesion of the tetrahedra between them in this compound.

The P(003)O4 groups are attached to the top and bottom of the P(002)O4 sheet by the O(008)-H(008)….O(006) and O(004)-H(004)....O(00A) hydrogen bonds. The phosphate sheets are held together by Ba$^{2+}$, which makes six of its nine coordination bonds with P(002)O4 O atoms. It was observed that the shortest distances, oxygen-oxygen, between two tetrahedral, are O(5)-O(5) and O(A)-O(A), 2.481(6), and 2.447(6), respectively (Table 4).

![Figure 4](image.png)

**Figure 4.** Polyhedral view down [0 0 1] of the structure of Ba(H$_2$PO$_4$)$_2$.

3.2. **Computational calculations results.**

3.2.1. X-ray and DFT comparative study.

The crystallographic data of our sample Ba(H$_2$PO$_4$)$_2$ allows us to validate the B3LYP / LanL2DZ method for the structural crystallization of the compound’s molecular geometry.

![Figure 5](image.png)

**Figure 5.** (a) Optimized molecular structure of Ba(H$_2$PO$_4$)$_2$ using DFT B3LYP/LanL2DZ calculation (b) Molecular structure of Ba(H$_2$PO$_4$)$_2$ as an ORTEP plot; displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as balls with an arbitrary radius.
Figure 5a and 5b show us the asymmetric unit of Ba(H$_2$PO$_4$)$_2$ by the ORTEP presentation and the DFT optimized geometry of Ba(H$_2$PO$_4$)$_2$, respectively. The structure optimization zero-point energy of the title compound in B3LYP/LanL2DZ is -642.5367 Hartree(-17484.3242 eV).

The optimized bond length, bond angles and dihedral angles of the title compound with the experimental values and the relative error values, expressed by the difference between the DFT values and some experimental data, are shown in Table 5.

Some experimental values were found to be slightly smaller than the optimized DFT bond lengths and bond angles, so the experimental results belong to molecules in the solid state, while the theoretical calculations belong to molecules isolated in the gaseous phase.

A comparison of the calculated geometrical parameters of the isolated ions and Ba(H$_2$PO$_4$)$_2$ containing the O–H-----O hydrogen bond provides information about the changes that occur upon the non-covalent bonding network and the crystal packing effect.

Table 5. Selected geometric parameters as determined by X-ray crystallography for Ba(H$_2$PO$_4$)$_2$, compared to that obtained by the theoretical calculation using DFT B3LYP/LanL2DZ, with relative error values.

| Ba(H$_2$PO$_4$)$_2$ | X-ray    | DFT    | Relative error % |
|--------------------|----------|--------|-----------------|
| Bond lengths (Å)   |          |        |                 |
| O006-P003          | 1.512    | 1.622  | -7              |
| O005-P003          | 1.527    | 1.621  | -6              |
| O007-P003          | 1.573    | 1.709  | -9              |
| O004-A-P003        | 1.526    | 1.692  | -11             |
| O00B-P002          | 1.496    | 1.620  | -8              |
| O008-P002          | 1.585    | 1.709  | -8              |
| O004-P002          | 1.571    | 1.692  | -8              |
| O009-P002          | 1.494    | 1.622  | -9              |
| O006-Ba01          | 2.926    | 2.734  | 7               |
| O009-Ba01          | 2.758    | 2.739  | 1               |
| O007-H007          | 0.720    | 0.976  | -36             |
| O00A-H00A          | 1.224    | 0.979  | 20              |
| O008-H008          | 0.74     | 0.9764 | -32             |
| O004-H004          | 0.74     | 0.9789 | -32             |
| Bond angles (°)    |          |        |                 |
| O005-P3-0006       | 113.08   | 106.868| 5               |
| O007-P3-0006       | 110.66   | 114.452| -3              |
| O005-P3-000A       | 112.33   | 112.415| 0               |
| O005-P3-0007       | 104.37   | 114.762| -10             |
| O006-P3-000A       | 108.69   | 112.567| -4              |
| O006-A-0007        | 107.52   | 95.708 | 11              |
| O009-P2-0004       | 103.04   | 112.926| -10             |
| O009-P2-000B       | 120.20   | 106.882| 11              |
| O009-P2-0008       | 110.22   | 114.076| -3              |
| O004-P2-000B       | 111.50   | 111.962| 0               |
| O004-P2-0008       | 108.40   | 95.708 | 12              |
| O008-P2-0008       | 103.19   | 115.164| -12             |
| P2-O004-H004       | 115.00   | 119.629| -4              |
| P2-O008-H008       | 115.00   | 116.286| -1              |
| P3-O007-H007       | 113.00   | 119.692| -6              |
| P3-O00A-H00A       | 121.10   | 116.237| 4               |
| P3-O006-Ba01       | 126.62   | 97.899 | 23              |
| P2-O009-Ba01       | 127.34   | 97.657 | 23              |

Consequently, the geometric characteristics that we have obtained from the isolated molecules could be used as references to follow the changes which occur during the interactions of the O–H-----O hydrogen bonds in Ba(H$_2$PO$_4$)$_2$. As Table 5 shows, the calculated bond lengths are slightly shorter than those of the isolated molecules.

The relative error is found to be important for some bond lengths [O00A-H00A, 20%], [O004–H004, 32%], [O008–H008,32%], [O007–H007, 36%], which are those involved in hydrogen bonding. The relative error is found to be important for some bond lengths [O00A-
H00A, 20%], [O004–H004, 32%], [O008–H008, 32%], [O007–H007, 36%], which are those involved in hydrogen bonding’s O007—H007•••O006 and O008—H008•••O006.

Concerning the angles, an important error between experimental and theoretical data is observed for P2–O009–Ba(01) (23%) and P2–O006–Ba(01) (23%), since the Sr1 ion is observed between O009 and O006 as a bridging atom, that links the P(2)O4 and P(3)O4 groups. Generally, the B3LYP/LanL2DZ calculations could be considered reliable. It simulates the crystal structure and the bond length order in the title compound. The X-ray measurement’s structural information is in good agreement with those obtained from DFT calculations.

3.2.2. Frontier molecular orbitals analysis.

The HOMO–LUMO energy gap of Ba(H2PO4)2 was calculated at the B3LYP/6-31G(d) level. Table 6 shows the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO). To visualize the molecular orbitals and to examine the charge, we performed the HOMO-LUMO analysis. Therefore to understand how molecules interact with other species, the two parameters mentioned are imperative (Figure 6). On the one hand, the outermost orbital containing electron, which tends to release electrons, is the highest occupied molecular orbital HOMO. On the other hand, the free space to accept electrons is the lowest unoccupied molecular orbital LUMO. The charge transfer interactions within the molecule can be explained by the HOMO-LUMO energy gap [11,12].

| Parameters | Ba DFT/ B3LYP/LanL2DZ | DFT/ B3LYP/LanL2DZ |
|------------|-------------------------|---------------------|
| Total energy (eV) | -17484.32417 | -7.53293 |
| EHOMO (eV) | -1.69853 | 7.53293 |
| ELUMO (eV) | 1.69853 | 5.8344 |
| Ionization potential I (eV) | 2.0556 | |
| Electron affinity, A | 5.8344 | |
| Egap =ΔEHOMO-LUMO (eV) | 2.0556 | |
| Dipolar moment (Debye) | 1127 |

**Table 6.** HOMO-LUMO Energy values calculated by DFT/B3LYP/LanL2DZ.

**Figure 6.** HOMO, LUMO orbitals and their corresponding energies calculated at the DFT/B3LYP/LanL2DZ for Ba(H2PO4)2.

The positive phase is represented in red and the negative phase is represented in green. The frontier molecular orbital energies, EHOMO and ELUMO, are -7.533 eV and -1.698 eV, respectively. Our system can be of low reactivity and of good stability because the DFT difference (B3LYP / LanL2DZ) calculated [E_{gap} = E_{LUMO} - E_{HOMO} = 5.834 eV] is considered to
be a relatively large bandgap [13]. We find that the energy gap is large, the molecule is not highly polarizable and has a low chemical reactivity. The ionization energy of a molecule is equal to the orbital’s energy from which the electron is ejected [14]. So, the ionization energy (IE) may be defined through the DFT method as the negative of the HOMO energy \[\text{IE} = -\text{E}_{\text{HOMO}} = 7.5329 \text{ eV}\].

3.3. Vibrational analysis.

3.3.1. \([\text{H}_2\text{PO}_4]\)^– vibrational mode.

The free \([\text{PO}_4]^{3–}\) tetrahedron is known to have tetrahedral symmetry \(T_d\) symmetry. Therefore, it has four normal modes of vibration, with \(A_1(v_1), E(v_2)\) and \(F_2(v_3 \text{ and } v_4)\) symmetries, with average wavenumbers of 938, 420, 1017 and 567 cm\(^{-1}\), respectively. All those symmetries were Raman active, except for \(v_3\) and \(v_4\), which were IR active [15-17]. The spectroscopic characteristics of the \([\text{HPO}_4]^{2–}\) ion (\(C_{3v}\) symmetry when is free) could be inferred from the free \([\text{PO}_4]^{3–}\) tetrahedron. The two stretching modes, \(v_1\) and \(v_3\), led to a quasi-symmetrical \(v_\text{s}(\text{PO}_2)\) stretching mode at 976 cm\(^{-1}\), another \(v_\text{s}(\text{P-OH})\) stretching mode around 884 cm\(^{-1}\), and a quasi-degenerated \(v_\text{a}(\text{PO}_2)\) state at about 1087 cm\(^{-1}\) (Figure6).

The fixation of two hydrogens on two oxygens (P-OH bonds) of the \([\text{PO}_4]^{3–}\) group reduces the ideal symmetry \(T_d\) to \(C_{2v}\), which is considered as an ideal point group symmetry of the \([\text{H}_2\text{PO}_4]\)^– group.

Based on structural data (P-1 space group) of \(\text{Ba(H}_2\text{PO}_4)_2\), there are observed at the site symmetry \(C_1\) and are considered isolated groups. Therefore, we can enumerate the group’s vibrational modes \([\text{H}_2\text{PO}_4]\) by applying the site group method. But, first, the determination of the vibrational modes in \(C_{2v}\) symmetry of the point group of \([\text{H}_2\text{PO}_4]\)^– gives 15 internal vibrations active in IR and Raman, except for the \(A_2\) modes, which are only active in Raman.

\[\Gamma_{\text{vib}}(\text{H}_2\text{PO}_4^–) = 6A_1\ (\text{IR, Ra}) + 4B_1\ (\text{IR, Ra}) + 2A_2\ (\text{Ra}) + 3B_2\ (\text{IR, Ra})\]

In fact, the correlations between the molecular group \(T_d\) of \([\text{PO}_4]^{3–}\) and the molecular group \(C_{2v}\) show the following effects (Table7): the vibrations \(v_1(A_1)\) and \(v_2(E)\) active in Raman in \(T_d\) symmetry become in \(C_{2v}\) group \(A_1\) active in IR and Raman, and \(A_1, A_2\); this latter mode is only Raman active in \(C_{2v}\). The vibrations \(v_3(T_1)\) and \(v_4(T_2)\) active in IR and Raman in \(T_d\) remain active in IR and Raman, with splitting into three components \((A_1, B_1, B_2)\). Theoretically, the appearance of certain modes under a single band and the lifting of the degeneracy for others can be explained by the analysis made in group \(C_{2v}\).

Considering the intra-ionic coupling for the \(\text{PO}_4\) stretching vibrations due to two longer P–OH and two shorter P–O bonds, the four stretching modes \(3v_\text{s}(\text{P–O})\ (A_1+\text{B}_1+\text{B}_2)\) and \(v_\text{s}(\text{P–O})\ (A_1)\) mentioned in Table7 may be regarded as \(v_\text{s}(\text{POH}), v_\text{a}(\text{POH}), v_\text{s}(\text{PO}_2)\) and \(v_\text{a}(\text{PO}_2)\) [17].

In addition, six vibrations involving OH motions are characteristic for \(\text{H}_2\text{PO}_4^–\): stretching O-H \([v(\text{OH})]\), in-plane bending POH \([\delta(\text{P–OH})]\) and out-of-plane bending POH \([\gamma(\text{P–OH})]\) for each OH bond may be added to the nine internal \(\text{PO}_4\) vibrations, which gives in total 15 fundamentals for \([\text{H}_2\text{PO}_4]^–\) [18]. The vibration distribution of \([\text{H}_2\text{PO}_4]^–\) in the factor group \(C_i\) is obtained by performing correlations between the \(C_{2v}\) molecular group of \([\text{H}_2\text{PO}_4]^–\) and the \(C_1\) site group which it occupies in the crystal and correlations between the site group and the group factor \(C_i\) corresponding to the space group P-1. The results obtained are given
in Table 8, we deduce the 30 vibrational modes representation Γ\text{vib} of the [H₂PO₄⁻]⁻ ion in the crystal.

\[ Γ\text{vib} (H₂PO₄⁻) = 15 \text{Ag(Ra)} + 15 \text{Au(IR)} \]

Table 8 shows that all vibrational modes of [H₂PO₄⁻]⁻ in group molecular C₂ᵥ are theoretically Raman and infrared active in the group factor. Due to the presence of the center of symmetry in the crystal (P-1), the Raman active modes of symmetry Ag are not active in infrared where the activity corresponds to Au symmetry and vice versa [19].

### Table 7. Internal vibration correlation diagram of the PO₄ group in [H₂PO₄⁻]⁻.

| Vibration   | Modes | Molecular group of [PO₄]²⁻ Td | Modes | Vibration |
|-------------|-------|-------------------------------|-------|-----------|
| vas(P-O)    | (v3)  | T₂ (Ra, IR)                   | B₁(Ra, IR) | vas (P-O) |
| vs(P-O)     | (v1)  | A₁ (Ra)                       | A₁(Ra, IR) | vs(P-O)   |
| δas(O-P-O)  | (v4)  | T₂ (Ra, IR)                   | B₁(Ra, IR) | pr (PO₂)  |
| δs(O-P-O)   | (v2)  | E (Ra)                        | A₁(Ra, IR) | δ (POPO)  |

### Table 8. Correlation diagram of [H₂PO₄⁻]⁻ group in the crystal Ba(H₂PO₄)₂.

| Molecular group: C₂ᵥ | Site group: C1 | Factor group: Ci |
|----------------------|----------------|------------------|
| 6A₁(Ra, IR)          | 15A(Ra, IR)    | 15 Ag (Ra)       |
| 4B₁(Ra, IR)          |                |                  |
| 2A₂ (Ra)             |                |                  |
| 3B₂(Ra, IR)          |                |                  |

#### 3.3.2. Infrared and Raman spectra.

The infrared and Raman spectra of Ba(H₂PO₄)₂ recorded at room temperature are shown in Figures 7 and 8, respectively, which exhibits one distinct region between 400-1300 cm⁻¹, corresponding to the internal vibrational modes of phosphate [H₂PO₄⁻]⁻ ion. Based on the theoretical analysis, all the bands observed in the infrared spectrum are considered with the symmetry Au of the factor group Ci, whereas those observed in the Raman spectrum are taken as Ag symmetry (Table 9). Comparing the spectral data obtained for the dihydrogen phosphate in the Refs [18-20]. We can interpret the bands due to [H₂PO₄⁻]⁻ ion. The vibrations corresponding to in-plane bending δ(P-OH) and to out-of-plane bending γ(P-OH) modes of phosphate [H₂PO₄⁻]⁻ ion are characteristic for acidic phosphates since they are absent in normal phosphates. It is to note that the in-plane and out-of-plane bending vibrations occur in the region 1350-1200 cm⁻¹ and 950-750 cm⁻¹ respectively [21, 22].

For the title compound, the strong band at 1218 cm⁻¹ can be assigned to the active Infrared in-plane modes δ(P-OH). The components stretching v₃(vasP-OH) and v₁(vsP-OH), vibrations of the [H₂PO₄⁻]⁻ may be the features observed as strong and medium absorptions bands at 976 cm⁻¹ and 884 cm⁻¹ in the IR spectrum(Figure 7). The shoulder band at 733 cm⁻¹ may be assigned to the out-of-plane bending γ(P-OH). This is observed in the Raman spectrum as weak bands at 741 cm⁻¹ (Figure 8).

The asymmetric bending v₄(δasO–P–O) of the phosphate [H₂PO₄⁻]⁻ anion appeared as medium and strong Infrared bands at 547 cm⁻¹ and 507 cm⁻¹, respectively. The Infrared medium
band observed at 432 cm\(^{-1}\) is assigned to the symmetric stretching modes \(\nu_2(\delta_s O-P-O)\) [23-29].

![Figure 7. IR spectrum of Ba(H\(_2\)PO\(_4\))\(_2\).](image)

![Figure 8. Raman spectrum of Ba(H\(_2\)PO\(_4\))\(_2\).](image)

![Figure 9. The infrared spectrum of Ba(H\(_2\)PO\(_4\))\(_2\) calculated by the DFT B3LYP/LanL2DZ method.](image)

![Figure 10. The Raman activity spectrum of Ba(H\(_2\)PO\(_4\))\(_2\) calculated by the DFT B3LYP/LanL2DZ method.](image)

4. Conclusions

Barium dihydrogenomonophosphate, Ba(H\(_2\)PO\(_4\))\(_2\) has been prepared by the direct method. Ba(H\(_2\)PO\(_4\))\(_2\) is isostructural with barium dihydrogenomonophosphate, Sr(H\(_2\)PO\(_4\))\(_2\), and crystallizes in the triclinic system with space group P-1 (Z=2).
Table 9. Experimental and calculated values of the vibration wavenumbers (cm\(^{-1}\)) for Ba(H\(_2\)PO\(_4\))\(_2\).

| Bands \(\nu\) (cm\(^{-1}\)) | Assignments |
|-----------------------------|-------------|
| IR (Au) Experimental Figure 7 | IR (Au) DFT Figure 9 | Raman (Ag) Experimental Figure 8 | Raman (Ag) DFT Figure 10 |
| 1218 | - | - | - | \(\delta(\text{P-OH})\) |
| 1127 | - | - | - | \(\nu_3(\nu_4\text{PO}_2)\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 1087 | 1066 | 1052 | 1069 | \(\nu_1(\nu_4\text{PO}_2)\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 976 | 909 | 990 | 979 | \(\nu_1(\nu_3\text{PO}_4^2)\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 983 | 951 | - | 912 | \(\nu_3(\nu_4\text{P-OH})\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 884 | - | 895 | - | \(\nu_1(\nu_3\text{P-OH})\) of [H\(_2\)PO\(_4\)]\(^-\)/\(\gamma(\text{P-OH})\) |
| 850 | - | 870 | - | \(\nu_1(\nu_3\text{P-OH})\) of [H\(_2\)PO\(_4\)]\(^-\)/\(\gamma(\text{P-OH})\) |
| 733 | 767 | 741 | 768 | \(\gamma(\text{P-OH})\) |
| 698 | - | 700 | - | \(\nu_4(\delta\text{O-P-O})\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 547 | - | 555 | - | \(\nu_4(\delta\text{O-P-O})\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 507 | - | 511 | - | \(\nu_4(\delta\text{O-P-O})\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 432 | 441 | 437 | 449 | \(\nu_4(\delta\text{O-P-O})\) of [H\(_2\)PO\(_4\)]\(^-\) |
| 420 | - | - | - | \(\nu_4(\delta\text{O-P-O})\) of [H\(_2\)PO\(_4\)]\(^-\) |

The title compound is studied by single-crystal X-ray diffraction analysis, infrared and Raman vibrational. The molecular geometry, harmonic vibrational frequencies, infrared intensities and Raman scattering activities were calculated by using the density functional theory (DFT/B3LYP) methods with the LanL2DZ basis set. The bands observed in the infrared and Raman spectra of Ba(H\(_2\)PO\(_4\))\(_2\) are assigned as a function of the results obtained in the literature and the theoretical group analyses carried out in the factor group \(\text{Ci}\). The three-dimensional structure can be considered as consisting of independent [PO\(_4\)] tetrahedra. Two vertices of each tetrahedron [PO\(_4\)]\(^3-\) are connected to two H atoms to form phosphate [H\(_2\)PO\(_4\)]\(^-\) anions arranged to delimit large deformed cavities occupied by barium-cations. The hydrogen atoms were positioned in idealized positions and included in the final cycles of refinement. The HOMO-LUMO properties have been studied and discussed. The theoretical results have been found to agree with the experimental results.

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Conflicts of Interest

The authors declare no conflict of interest.

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