

Crystal Structure and Characterization of CsH₅(AsO₄)₂: A New Cesium Pentahydrogen Arsenate, and Comparison with CsH₅(PO₄)₂ and RbH₅(AsO₄)₂

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Chemical preparation and X-ray single-crystal, vibrational, and calorimetric studies of CsH₅(AsO₄)₂ are described. The new compound crystallizes in the monoclinic system *P2₁/c* with cell parameters $a = 10.983(1) \text{ \AA}$, $b = 7.943(1) \text{ \AA}$, $c = 9.844(1) \text{ \AA}$, $\beta = 96.15(1)^\circ$, $V = 853.82(6) \text{ \AA}^3$, $Z = 4$, and $\rho_{\text{cal}} = 3.235 \text{ g cm}^{-3}$. The refinement of data leads to $R_1 = 0.0396$ and $WR_2 = 0.0809$ for 2377 observed reflections ($I > 2\sigma(I)$) refined with 122 parameters. The structure is different from RbH₅(AsO₄)₂ (orthorhombic) and similar to CsH₅(PO₄)₂ (monoclinic). The atomic arrangement can be described as layered organization of isolated arsenate tetrahedra; interleaved cesium cations ensure the cohesion of the structure. As in all atomic arrangements, we can observe the formation of an infinite network of anions connected by strong H bonds (2.436(4)–2.597(5) \AA). The hydrogen atoms were located from difference maps and the short contact (2.436(4) \AA), which is not astride any symmetry element, is of the type O–H...O asymmetrical. The Raman and infrared spectra of CsH₅(AsO₄)₂ recorded at room temperature in the frequency ranges 10–1000 cm⁻¹ and 250–4000 cm⁻¹, respectively, confirm the presence of two independent AsO₄³⁻ groups in the crystal. An assignment of all the bands is given. Differential scanning calorimetry shows that the title compound does not exhibit any phase transition in the range 123–473 K. © 2001 Academic Press

Key Words: crystal structure; hydrogen-bonding; Raman; infrared; DSC.

1. INTRODUCTION

Following our first investigation concerning the synthesis and the crystal structure of RbH₅(AsO₄)₂ compound (1), CsH₅(AsO₄)₂ (CPA) is considered to be the second alkali pentahydrogen arsenate, which is synthesized to enrich the family of compounds with general formula MH₅(XO₄)₂ ($M = \text{Rb, Cs, K, NH}_4$; $X = \text{P, As}$). Many pentahydrogen phosphates are presently known and a systematic survey of

their main crystallographic data has been reported (2–7). However, to our knowledge, no structural studies, except for RbH₅(AsO₄)₂, of the corresponding pentahydrogen arsenates salts have been conducted. In a previous paper, we reported that the crystal structure of RbH₅(AsO₄)₂ at room temperature is orthorhombic and belongs to the *Pbca* space group, with cell constants $a = 7.940(1) \text{ \AA}$, $b = 9.821(1) \text{ \AA}$, and $c = 20.424(1) \text{ \AA}$, eight molecules per unit cell (1), and is not isomorphous to RbH₅(PO₄)₂ (monoclinic with *C2/c* space group) (5). Recently, studies of new hydrogen-bonded systems have been of continuing interest due to the structural and physical properties of these compounds which are, today, oriented and supported by two main observations. The first is related to the dynamics of protons in solids which show ferroelectric or antiferroelectric order and proton spin glasses in the low-temperature phases (8–10). The second is devoted to the fast-ion transport which is usually observed in the high-temperature phases, leading to a high protonic conductivity in a superprotonic state. Pentahydrogen phosphates of alkali metals, at room temperature, are found mainly in two different space groups with monoclinic structures. KH₅(PO₄)₂ and CsH₅(PO₄)₂ belong to space group *P2₁/c*, whereas RbH₅(PO₄)₂, NH₄H₅(PO₄)₂, and TIH₅(PO₄)₂ belong to space group *C2/c*. The formation of strong hydrogen bonds is typical of the compounds with general formula MH₅(PO₄)₂. Very short O...O separation distances in the O–H...O hydrogen bonds are found in their structures [2.422(3) \AA ($M = \text{K}$), 2.431(5) \AA ($M = \text{TI}$), 2.426(3) \AA ($M = \text{Cs}$), and 2.452(3) \AA ($M = \text{Rb}$)]. A similar situation was discovered by us in RbH₅(AsO₄)₂ (2.432(6) \AA), making it possible to interpret these compounds as acido bis(dihydrogen phosphate)s or -(dihydrogen arsenate)s of univalent elements: $M[\text{H}(\text{H}_2\text{XO}_4)_2]$, where $X = \text{P}$ and As . In view of the considerable interest in hydrogen bonding in crystalline materials, our work has focused on synthesizing new cesium pentahydrogen arsenate, CsH₅(AsO₄)₂. An X-ray crystal structure of this material has been carried out as part of a research program on acidic arsenates and

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phosphates which often show short hydrogen bonds. This structural study is accompanied by infrared and Raman measurements and a brief summary of the calorimetric results will be given.

2. EXPERIMENTAL DETAILS

2.1. Chemical Preparation and Characterization of $\text{CsH}_5(\text{AsO}_4)_2$

Crystals of the title compound are produced from an aqueous stoichiometric solution of cesium carbonate, Cs_2CO_3 , and orthoarsenic acid, H_3AsO_4 , by the following reaction:



The resulting solution is kept under ambient conditions and was evaporated slowly to dryness. The powder obtained was then dissolved in warm water and allowed to evaporate slowly. A few days later, colorless, transparent, and prismatic single crystals with a size of about $0.30 \times 0.20 \times 0.20 \text{ mm}^3$ of CPA crystallize. Several recrystallizations were necessary to obtain single crystals suitable for X-ray study. It is noted that the compound is stable in air and its formula is determined by chemical analysis and confirmed by refinement of the crystal structure. Infrared absorption spectra of suspensions of crystalline powders in KBr were recorded on a Perkin-Elmer FT-IR 420 spectrophotometer in the range $250\text{--}4000 \text{ cm}^{-1}$. Raman spectra of polycrystalline samples sealed in glass tubes were obtained employing an RTI Dilor instrument using the 514.5 nm line of a Spectra-Physics argon ion laser. Differential scanning calorimetry (DSC) has been performed on a DSC Mettler T A 4000 between 123 and 473 K.

2.2. X-Ray Diffraction and Data Collection

Intensities of the diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer, using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters optimized by least-squares refinement were calculated and refined using indexation of the collected intensities. The raw intensity data were corrected for Lorentz and polarizing effects before refinement of the structure. No absorption correction was applied. Atomic scattering factors were taken from the International Tables for X-ray Crystallography (11); 3378 reflections were collected in the whole Ewald sphere for $1 < \theta < 33.73^\circ$, of which 2377 reflections had an intensity of $I > 2\sigma(I)$. Direct methods for structure resolution were used. The structure was successfully developed in the centrosymmetric space

TABLE 1
Summary of Crystal Data, Intensity Measurements, and Refinement Parameters for $\text{CsH}_5(\text{AsO}_4)_2$

I. Crystal Data	
Formula	$\text{CsH}_5(\text{AsO}_4)_2$
Formula Weight (g/mol)	415.79
System: monoclinic	Space group: $P2_1/c$
$a = 10.983(1)$	$Z = 4$
$b = 7.943(1)$	$\beta = 96.15(1)^\circ$
$c = 9.844(1) \text{ \AA}$	$V = 853.82(6) \text{ \AA}^3$
$\rho_{\text{cal}} = 3.235 \text{ g cm}^{-3}$	$F(000) = 760$
Linear absorption factor	$\mu(\text{MoK}\alpha) = 12.032 \text{ mm}^{-1}$
Morphology: prismatic	Habit: colorless
Crystal size	$0.30 \times 0.20 \times 0.20 \text{ mm}^3$
II. Intensity Measurements	
Temperature: 293(2) K	Wavelength: $\text{MoK}\alpha$ (0.71073 \AA)
Diffractometer	Enraf-Nonius Kappa CCD
Monochromator: graphite plate	Scan mode: $\omega\text{-}\theta$
Theta range	$1.00\text{--}33.73^\circ$
Measurement area, $+h, +k, l$	$h_{\text{max}} = 17, k_{\text{max}} = 12, l_{\text{max}} = 15$
Total reflections	3378
III. Structure Determination	
Lorentz and polarization corrections	No absorption correction
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Thermal displacement parameters	Isotropic for H atoms, anisotropic for non-H
Unique reflections included	2377 with $I > 2\sigma(I)$
Refined parameters: 122	Residual Fourier density: $-1.240 < \rho < 1.001 \text{ e. \AA}^{-3}$
Unweighted agreement factor ^a	$R_1 = 0.0396$ Weighted agreement factor ^a $wR_2 = 0.0809$

^a R values are defined as

$$R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|} \text{ and } wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{w^{-1} = [\sigma^2(F_o^2) + (0.0442P)^2 + 2.4726P]} \text{ and } P = (F_o^2 + 2F_c^2)/3.$$

group $P2_1/c$. Cesium atom positions were located using SHELXS-97 (12) whereas As and O atom positions were deduced from difference Fourier maps during the refinement of the structure with an adapted version of the SHELXL-97 program (13). There are four formula units in the unit cell and all the atoms are in general positions. The H atoms were located through difference maps with the aid of calculated bond distances and angles. The five acidic hydrogen atoms required in a unit cell by the chemical formula appear also in a general positions. The least-squares refinement, including isotropic hydrogen atoms, leads to the final reliability factors $R_1 = 0.0396$ and $wR_2 = 0.0809$, obtained by fitting 122 parameters. The final difference Fourier map had maximum and minimum peaks of 1 and -1.24 e/\AA^3 , respectively. Details of the data collection and structural analysis are presented in Table 1.

3. RESULTS AND DISCUSSION

3.1. Structure of $\text{CsH}_5(\text{AsO}_4)_2$

The structure of CPA is built up from discrete arsenate groups connected by $\text{O-H}\cdots\text{O}$ hydrogen bonds and through the electrostatic actions of the Cs^+ cations. A projection of the crystal structure of CPA on the ac plane is depicted in Fig. 1. It consists of AsO_4 tetrahedra which develop as chains including $\text{As}(1)\text{O}_4$ alternating with $\text{As}(2)\text{O}_4$ along the $[001]$ direction, at approximately $x = 0$ ($\text{As}(1)\text{O}_4$) and $x = \frac{1}{2}$ ($\text{As}(2)\text{O}_4$). It can be regarded also as being made of a zigzag sheets along $[100]$ at approximately

$z = \frac{1}{4}$ and $z = \frac{3}{4}$. In this structure, the cationic layers (Cs) are located between these sheets; interaction between oxygen and cesium atoms ensures the cohesion of the structure. The room-temperature crystal structure of CPA was found to be similar to that of $\text{CsH}_5(\text{PO}_4)_2$ (3). The analogy between the packing of these structures is significant as regards the atomic arrangement, the degree of distortion of the corresponding AsO_4/PO_4 tetrahedra, and the intertetrahedral hydrogen bonding (five hydrogen bonds). The overall structure of the two compounds can be described as a sequence of isolated AsO_4/PO_4 tetrahedra alternating with the cesium atoms in the c direction (Fig. 1). In the two structures, the AsO_4/PO_4 groups are connected by $\text{O-H}\cdots\text{O}$ hydrogen

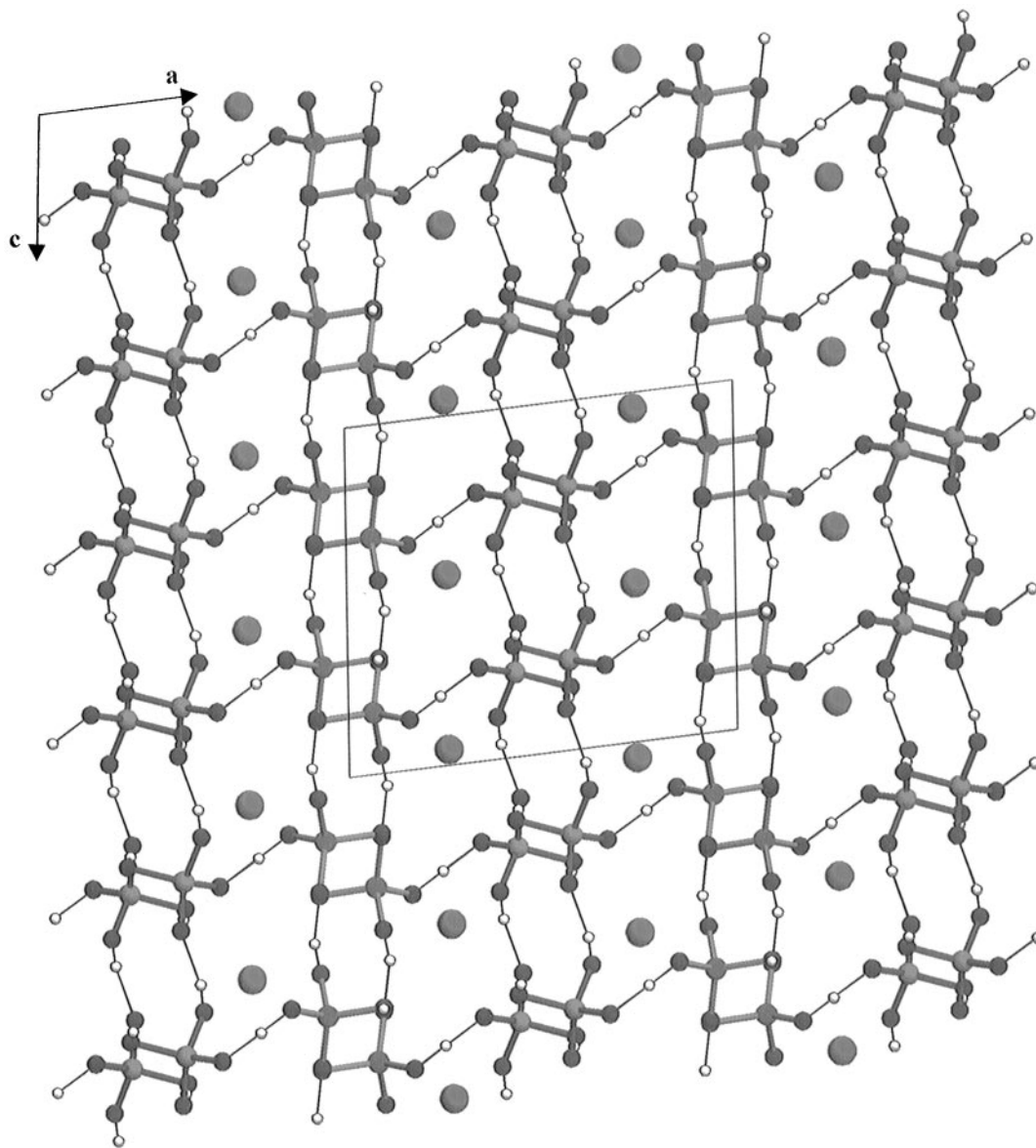


FIG. 1. Projection of the structure of $\text{CsH}_5(\text{AsO}_4)_2$ along $[010]$. The large circles represent cesium atoms, and the small circles represent hydrogen atoms. Arsenic anions are represented by tetrahedra. Hydrogen bonds are indicated by solid lines.

TABLE 2
Atomic Distances (Å) and Angles (°)

a. Arsenic Groups	
As(1)O ₄ Tetrahedron	
As(1)–O(11) = <u>1.651(3)</u>	O(11)–As(1)–O(12) = <u>114.41(16)</u>
As(1)–O(12) = 1.667(3)	O(11)–As(1)–O(13) = 105.73(17)
As(1)–O(13) = 1.697(3)	O(12)–As(1)–O(13) = 113.07(19)
As(1)–O(14) = <u>1.710(3)</u>	O(11)–As(1)–O(14) = 112.18(18)
	O(12)–As(1)–O(14) = 106.26(17)
	O(13)–As(1)–O(14) = <u>104.89(18)</u>
As(2)O ₄ Tetrahedron	
As(2)–O(21) = <u>1.657(3)</u>	O(21)–As(2)–O(22) = <u>113.34(16)</u>
As(2)–O(22) = 1.667(3)	O(21)–As(2)–O(23) = 106.73(15)
As(2)–O(23) = <u>1.707(3)</u>	O(22)–As(2)–O(23) = 111.41(16)
As(2)–O(24) = 1.706(3)	O(21)–As(2)–O(24) = 109.27(17)
	O(22)–As(2)–O(24) = 109.23(16)
	O(23)–As(2)–O(24) = <u>106.61(16)</u>
b. Hydrogen Bonds	
O(12)–H(12) = <u>1.044(12)</u>	O(22) ⋯ H(12) = <u>1.397(19)</u>
O(13)–H(13) = 0.846(22)	O(11) ^a ⋯ H(13) = 1.711(31)
O(14)–H(14) = <u>0.832(48)</u>	O(11) ^b ⋯ H(14) = <u>1.765(63)</u>
O(23)–H(23) = 0.909(39)	O(21) ^a ⋯ H(23) = 1.714(11)
O(24)–H(24) = 0.865(31)	O(21) ^c ⋯ H(24) = 1.730(47)
O(12) ⋯ O(22) = <u>2.436(4)</u>	O(12)–H(12) ⋯ O(22) = 171.45(5)
O(13) ⋯ O(11) ^a = 2.537(9)	O(13)–H(13) ⋯ O(11) ^a = 164.58(5)
O(14) ⋯ O(11) ^b = 2.597(1)	O(14)–H(14) ⋯ O(11) ^b = 176.17(5)
O(23) ⋯ O(21) ^a = 2.572(5)	O(23)–H(23) ⋯ O(21) ^a = <u>156.19(6)</u>
O(24) ⋯ O(21) ^c = 2.592(6)	O(24)–H(24) ⋯ O(21) ^c = 174.33(5)
c. Cesium Coordination	
Cs	
O(12) ^d = <u>3.130(3)</u>	O(23) = 3.281(3)
O(24) ^e = <u>3.175(3)</u>	O(14) ^f = 3.425(4)
O(22) ^a = 3.197(3)	O(24) ^h = 3.469(3)
O(14) ^f = 3.256(3)	O(21) ^h = 3.628(4)
O(13) = 3.270(3)	O(22) ⁱ = <u>3.679(3)</u>

Symmetry code: ^a $x, -y + \frac{1}{2}, z + \frac{1}{2}$; ^b $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; ^c $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; ^d $x, y + 1, z$; ^e $-x + 1, -y + 1, -z + 1$; ^f $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; ^g $-x, -y + 1, -z + 1$; ^h $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; ⁱ $x, y + 1, z$.

bonds in such a way, and in the two cases give rise to two-dimensional layers. The same results are obtained in RbH₅(AsO₄)₂, although this compound is not isostructural with CsH₅(AsO₄)₂. In the structure of CPA, we note the presence of two types of AsO₄ tetrahedra differing in their distortion. The main interatomic distances and bond angles for the two independent tetrahedra are given in Table 2. As can be seen, the AsO₄ coordination tetrahedron is not very symmetrical. Indeed, the As–O distance in As(1)O₄ tetrahedra ranges from 1.651(3) to 1.710(3) Å and angles O–As(1)–O are between 104.89(18) and 114.41(16)°, whereas in As(2)O₄ tetrahedra, the minimum and the maximum As–O distances are 1.667(3) and 1.706(3) Å, and the O–As(2)–O angles range from 106.61(16) to 113.34(16)°, indicating that the shape of As(1)O₄ is slightly distorted from that of As(2)O₄, but both are distorted (Table 2). It is

interesting to note that the introduction of the hydrogen atoms into the refinement of the crystal structure apparently lengthened the As–O bond distances; such an effect may be quite general and may cause the distortion of the corresponding AsO₄ tetrahedra. It is well known that As–OH distances are in general longer than As–O distances, and that As–OH distances decrease as the strength of the hydrogen bond O–H ⋯ O increases (14, 15). It is possible to use differences in bond lengths to identify with which O in the O ⋯ O bond the proton is more highly associated. So, the localization of the hydrogen atoms based on the As–O bond distances and indications in the difference electron maps is in good agreement with the hydrogen bond net which can be deduced from the short intermolecular O ⋯ O distances. Four of the eight As–O bond distances in CPA are significantly longer than the others (Table 2). The corresponding oxygen atoms, O(14), O(13), O(24), and O(23), can therefore be considered to belong to hydroxyl groups. The shortest As–O distances concern oxygen atoms O(11) and O(21), which are not involved in any O–H bond.

The bond distances As(1)–O(12) (1.667(3) Å) and As(2)–O(22) (1.667(3) Å) appear to be intermediate between the two precedent As–O distances. Furthermore, equal As(1)–O(12) and As(2)–O(22) lengths suggest that the two oxygen atoms O(12) and O(22) participate rather equally in the formation of hydrogen bonds. However, the hydrogen atom H(12) is not midway between the two oxygens, but lies closer to O(12) [O(12)–H(12) = 1.04(12) Å] than to O(22). The hydrogen atom H(12) links As(1)O₄ and As(2)O₄ tetrahedra by a short hydrogen bridge O(12)–H(12) ⋯ O(22) (2.436(4) Å) to form a kind of dimeric unit [H(H₂AsO₄)₂][−], called acido bis(dihydrogen arsenate)s, which are present in all the MH₅(PO₄)₂ structure studies, where M = K, Rb, Cs, and Tl. In RbH₅(AsO₄)₂ (1), analogous dimeric units are also formed by a short O–H ⋯ O bridge of 2.432(6) Å. From the results reported above, we can note that two oxygen atoms of each As(2)O₄ group are directly bonded to two hydrogen atoms in such a way as to form [H₂As(2)O₄][−] anions, and three oxygen atoms of each As(1)O₄ group are bonded to three hydrogen atoms to form H₃As(1)O₄ molecules, linked to the first anionic groups by the hydrogen atom H(12) to form H₂O₃As(1)OH(12)OAs(2)O₃H₂[−] entities. Distortions of AsO₄ tetrahedra are also evidenced by O–As–O angles. The O–As–O angles (Table 2) increase with a decrease of the average value of the two corresponding As–O distances. As shown in Fig. 2, the coordination sphere of cesium cations is determined by 10 oxygen atom neighbors, located at a Cs–O interaction distance varying from 3.130(3) to 3.679(3) Å with an average of 3.351(3) Å. These values are slightly shorter than that found in CsH₅(PO₄)₂, where the corresponding Cs–O interaction distances range from 3.172(3) to 3.793(3) Å with an average of 3.417(3) Å. The CsO₁₀ polyhedron is distorted as shown by the Cs–O bond lengths (Table 2).

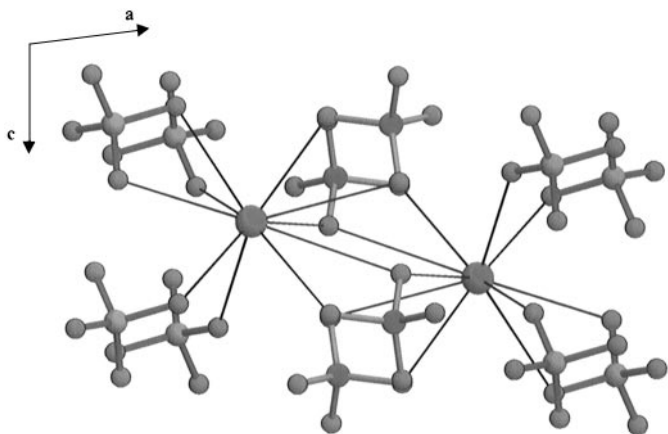


FIG. 2. Local coordination of cesium cations, with the same key for atoms as in Fig. 1.

3.2. The Hydrogen Bonding

A projection view of the title compound indicating the hydrogen bonding in CPA on the (010) plane is depicted in Fig. 1. Among the main geometrical features of the hydrogen bond network, reported in Table 2, it must be noted that all hydrogen atoms participate in the formation of hydrogen bonding. The hydrogen bonds were recognized from appropriate $\text{O} \cdots \text{O}$ distances of adjacent AsO_4 groups. The distances $\text{O} \cdots \text{H}$ vary from 1.397(19) to 1.765(63) Å and the

$\text{O}-\text{H} \cdots \text{O}$ angles have values between 156.19(6) and 176.17(5)°. The hydrogen bonds involving H atoms in AsO_4 groups are classical with $\text{O} \cdots \text{O}$ distances ranging from 2.537(9) to 2.597(1) Å with an average of 2.574 Å. These bonds are strong (16–18) and connect the arsenic entities in infinite chains running parallel to the [0 0 1] direction (Fig. 1), while those connecting these chains along the a axis correspond to a much shorter distance (2.436(4) Å), which is slightly longer than that found in $\text{CsH}_5(\text{PO}_4)_2$ (2.426(3) Å) and comparable to those in $\text{RbH}_5(\text{AsO}_4)_2$ and $\text{TlH}_5(\text{PO}_4)_2$, where the corresponding $\text{O} \cdots \text{O}$ distances are equal to 2.432(6) and 2.431(5) Å, respectively.

We note also that the high-resolution neutron diffraction study of $\text{KH}_5(\text{PO}_4)_2$ (Philippot *et al.*, 1972) (6) revealed in the case of this short contact an unsymmetric $\text{O}-\text{H} \cdots \text{O}$ bond, which is rare when the hydrogen bond is strong (Hamilton and Ibers, 1968) (19). The short $\text{O} \cdots \text{O}$ distance, which is not astride any symmetry element in this material, may be considered to be of the type $\text{O}-\text{H} \cdots \text{O}$ asymmetric. Room-temperature neutron diffraction appears to be very useful for understanding the nature of the short $\text{O}-\text{H} \cdots \text{O}$ bond.

4. CHARACTERIZATION

Infrared and Raman spectra of CPA at room temperature are shown in Figs. 3 and 4, respectively. The proposed assignment of the different bands (Table 3) was carried out

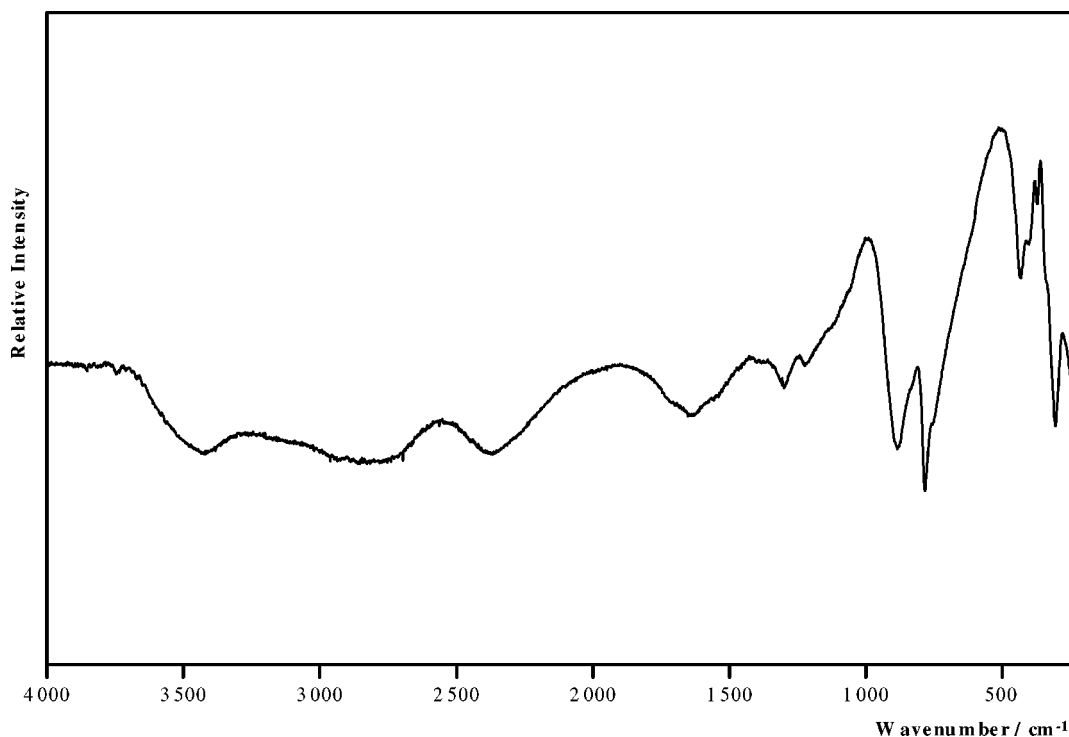


FIG. 3. IR spectrum at room temperature of $\text{CsH}_5(\text{AsO}_4)_2$ in the frequency range 250–4000 cm^{-1} .

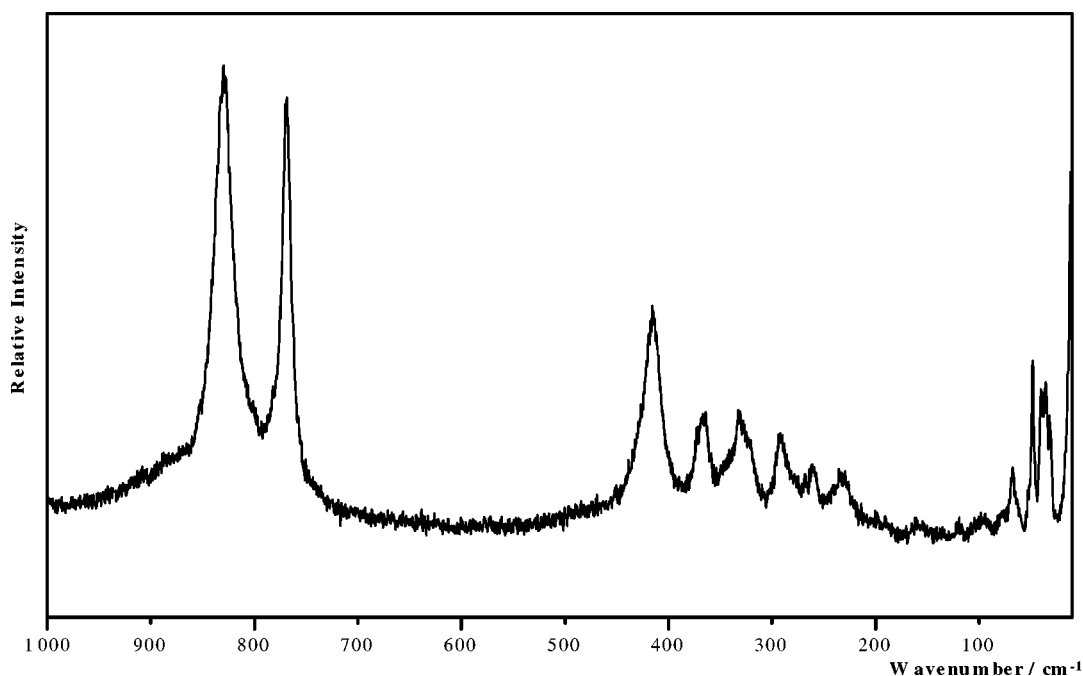


FIG. 4. Raman spectrum at 298 K of $\text{CsH}_5(\text{AsO}_4)_2$ in the frequency range 10–1000 cm^{-1} .

using data for similar arsenate compounds (20–22). The IR and Raman spectra of CPA that we obtained consist of a number of distinct and well-separated groups of bands, and can be divided into three frequency regions: 10–250 cm^{-1} , lattice mode; 250–1200 cm^{-1} , AsO_4 internal modes; and 1200–3700 cm^{-1} , high-frequency hydrogen modes (20–23). The bands below 125 cm^{-1} in Raman spectra are due to external modes which contain the translations of Cs^+ (24) and lattice vibrations of AsO_4^{3-} anions (25). On the other hand, the very weak lines between 125 and 200 cm^{-1} in Raman spectra probably correspond to the motion of $\text{O}-\text{H}\cdots\text{O}$ hydrogen stretching ($\nu_{\text{O}\cdots\text{O}}$) and bending ($\delta_{\text{O}\cdots\text{O}}$) of the infinite chains (H_2AsO_4^-)_n (9). We distinguish the $\nu_1(\text{AsO}_4)$ by the intense Raman band at about 767 cm^{-1} , and by the shoulder and the intense infrared bands near 760 and 782 cm^{-1} , respectively. Yet the ν_1 vibration is not degenerated ($\nu_1(a_1)$), which is why this weak splitting is not to the crystal field, but to the coexistence of two H_2AsO_4^- and H_3AsO_4 constituting the dimer $(\text{H}_2\text{AsO}_4\text{HAsO}_4\text{H}_2)^-$ (26, 27). By analogy with $M_3\text{H}(\text{SO}_4)_2$ ($M = \text{Na}, \text{K}, \text{Rb}, \text{and } \text{NH}_4$) (28, 29), the band with high frequency is attributed to the $\text{H}_2\text{As}(2)\text{O}_4^-$ group ($\nu_1(\text{H}_2\text{As}(2)\text{O}_4^-)$), whereas the one with low frequency is correlated to the $\text{H}_3\text{As}(1)\text{O}_4$ group ($\nu_1(\text{H}_3\text{As}(1)\text{O}_4)$). This constitutes spectroscopic evidence of a noncentrosymmetric dimer (28). This result is in agreement with X-ray data as regards the short intertetrahedral hydrogen bonding, which can be considered of the type $\text{O}-\text{H}\cdots\text{O}$ asymmetrical, implying the order of the acidic proton into this short

contact (2.436(4) Å). The $\nu_3(\text{AsO}_4)$ mode is assigned to the broad infrared band observed at 887 cm^{-1} , which is expected to be the most intense and broad band in the Raman spectrum at 830 cm^{-1} . The broad peaks observed in the region 235–425 cm^{-1} are associated with ν_4 and ν_2 of AsO_4^{3-} tetrahedra ($\nu_4 > \nu_2$). The two weak bands near 1212 and 1299 cm^{-1} in IR can be assigned to the $\delta(\text{As}-\text{O}-\text{H})$ bending vibration. The very weak peak around 1399 cm^{-1} in IR spectra is tentatively attributed to the hydrogen bending modes in the plane ($\delta(\text{OH})$). Other information which can be obtained from the vibrational spectra concerns the strength and the type of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, which remain practically the same in the strongly hydrogen-bonded crystals such as KH_2PO_4 , NaH_2PO_4 , CsHSO_4 , and CsH_2PO_4 (30–33). The corresponding OH stretching vibration gives rise to characteristic broad triobands of ABC type, associated with strongly hydrogen-bonded systems. The broad lines at 2760, 2360, and 1631 cm^{-1} in IR spectra can be assigned respectively to the ABC bonds of OH stretching vibrations of both the short and the long hydrogen bonds in CPA compound. The broadness of the ABC bands is not due to structural disorder of any kind, but is an intrinsic property of a strong hydrogen bond associated with vibrational anharmonicity of the OH group and the particular shapes of the $\text{O}-\text{H}\cdots\text{O}$ potential curves in the fundamental and excited states (34).

A typical result of the calorimetric study on single crystals of CPA is presented in Fig. 5, which shows the diagram obtained for freshly prepared samples heated between 123

TABLE 3
Infrared and Raman Frequencies of CPA

IR	I ^a	Raman	I ^a	Assignment
—		25	sh	Lattice vibrations of Cs^+ and AsO_4^{3-}
—		39	s	
—		42	s	
—		65	s	
—		75	mb	
—		100	vw	} $\delta_{\text{O}\cdots\text{O}}$
—		125	vw	
—		170	vw	} $\nu_{\text{O}\cdots\text{O}}$
—		200	vw	
—		235	wb	} $\nu_2(\text{AsO}_4)$
—		265	w	
306	s	290	mb	
—		335	mb	} $\nu_4(\text{AsO}_4)$
384	w	370	mb	
398	sh	415	sb	
434	s	—	—	} $\nu_1(\text{AsO}_4)$
760	sh	767	vs	
782	vs	—	—	} $\nu_3(\text{AsO}_4)$
887	sb	830	vsb	
1212	w	—	—	} $\delta(\text{As-O-H})$
1299	b	—	—	
1399	vw	—	—	$\delta(\text{OH})$
1631	vb	—	—	} $\nu(\text{OH})$
2360	vb	—	—	
2760	vb	—	—	
3402	b	—	—	$\nu(\text{OH})$ of free H_2O of KBr

^aRelative intensities: sh, shoulder; w, weak; vw, very weak; wb, weak broad; m, medium; mb, medium broad; b, broad; vb, very broad; s, strong; vs, very strong; sb, strong broad; vsb, very strong broad.

to 473 K. One endothermic peak has been observed at 427 K. This peak corresponds to the melting point of the product which occurs with an enthalpy change $\Delta H = 106 \text{ J g}^{-1}$. It is noted that the melting point was confirmed by using a Electrothermal 9200 micro-melting point apparatus. From this result, we can conclude that CPA, like $\text{RbH}_5(\text{AsO}_4)_2$ compound, does not exhibit any phase transitions. It is well known that compounds with short $\text{O-H}\cdots\text{O}$ hydrogen bonds are frequently ferroelectric or antiferroelectric in their low-temperature phase, and may exhibit superionic behavior in their high-temperature phase (35). The compounds belonging to the large family of KDP with general formula MX_2AO_4 ($M = \text{Cs, Rb, K, NH}_4$; $X = \text{H, D}$; and $A = \text{P, As}$) constitute a good example of materials with short hydrogen bridges. The H bonds in these materials are in a range where the proton would be disordered between two equilibrium sites in a double-minimum potential via a symmetrical hydrogen bridge. These disordered hydrogen bonds are of particular interest in relation to the structural phase transitions in these compounds. Despite this comparison, and because our material does not exhibit any phase transition, we can conclude that

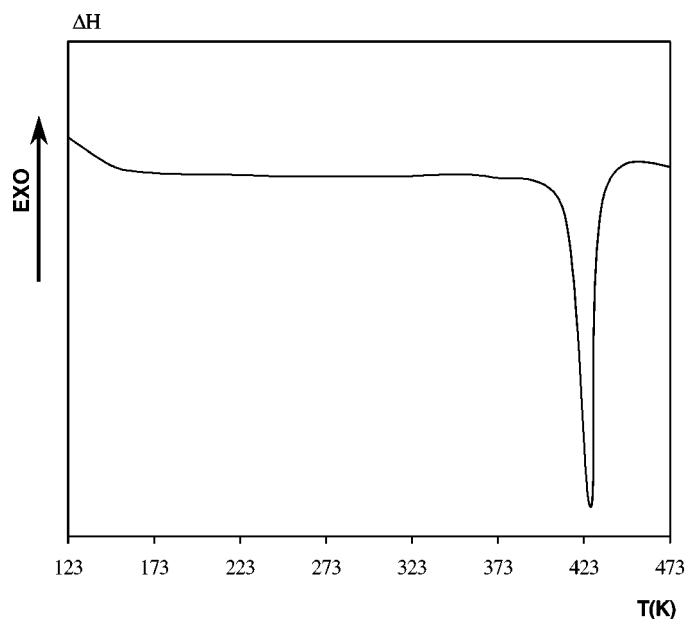


FIG. 5. DSC heating curve of $\text{CsH}_5(\text{AsO}_4)_2$ between 123 and 473 K. The heating rate is 5 K/min.

the acidic proton belonging to the short hydrogen bond ($2.436(4) \text{ \AA}$) in CPA is not disordered, and all the hydrogen bonds in this compound are asymmetric. This confirms our past work on $\text{RbH}_5(\text{AsO}_4)_2$.

5. CONCLUSION

This study demonstrates the synthesis and characterization of a new cesium pentahydrogen arsenate. The structural studies carried out have shown that the substitution of rubidium cation in $\text{RbH}_5(\text{AsO}_4)_2$ by the cesium cation in $\text{CsH}_5(\text{AsO}_4)_2$ changes the space group from $Pbca$ to $P2_1/c$, whereas the substitution of a phosphate group in $\text{CsH}_5(\text{PO}_4)_2$ by the arsenic group in $\text{CsH}_5(\text{AsO}_4)_2$ conserves the same space group $P2_1/c$. The structure of $\text{CsH}_5(\text{AsO}_4)_2$ is characterized by infinite chains built up by the hydrogen bonding joining the arsenic tetrahedra, which develop approximately parallel to the $[001]$ and $[100]$ directions. Cesium cations are inserted between these chains, to ensure the cohesion of the structure. Vibrational spectra of the title compound show clearly resolved strong bands in the AsO_4 tetrahedra and OH stretching vibrations, confirming the presence of two independent AsO_4 groups and strong hydrogen bonds in the crystal. $\text{CsH}_5(\text{AsO}_4)_2$ has been of interest mainly because it contains a short asymmetric hydrogen bond ($2.436(4) \text{ \AA}$). DSC measurements show no evidence of any phase transition in CPA crystals, which supports that the hydrogen atoms in the $\text{O-H}\cdots\text{O}$ bonds are ordered. Further investigations concerning new

compounds of this series, such as $\text{KH}_5(\text{AsO}_4)_2$, $\text{NH}_4\text{H}_5(\text{AsO}_4)_2$, and $\text{TiH}_5(\text{AsO}_4)_2$, are currently investigated and under discussion. The corresponding papers will be published later.

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