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Infrared and Raman spectra of magnesium ammonium phosphate hexahydrate (*struvite*) and its isomorphous analogues. VII: Spectra of protiated and partially deuterated hexagonal magnesium caesium phosphate hexahydrate

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ABSTRACT

The Fourier transform infrared and Raman spectra of the struvite analogue, hexagonal magnesium caesium phosphate hexahydrate, $MgCsPO_4 \cdot 6H_2O$ (*hP50*) and of its partially deuterated analogues were recorded from room temperature (RT) down to the boiling temperature of liquid nitrogen (LNT). The existence of strong hydrogen bonds between water molecules and $PO_4{}^{3-}$ ions is supported by the appearance of a broad band from 3600 to 2200 cm^{-1} in the O–H stretching region of the vibrational spectra. In the region of the OD stretching vibrations of isotopically isolated HDO molecules of the analogue with a small deuterium content (≈5% D), at least two bands (from the expected three) are observed in the difference LNT infrared spectrum. In the region of $\nu_3(PO_4)$ modes of the infrared spectra, a broad and asymmetric band (at around 1000 cm^{-1}) is found, while in the region of the $\nu_4(PO_4)$ bending vibration and of the external modes of the water molecules, several bands can be seen. The intense band at 945 cm^{-1} in the Raman spectra can with certainty be attributed to the $\nu_1(PO_4)$ mode. On the basis of a careful analysis of the RT and LNT spectra of the protiated compound, as well as those of its partially deuterated analogues, the asymmetric band at around 550 cm^{-1} could be assigned to the components of the $\nu_4(PO_4)$ mode, the bands between 470 and 430 cm^{-1} to the $\nu_2(PO_4)$ vibrations and the remaining ones as due to pure or coupled librational and translational modes of the water molecules. The external modes of the phosphate ions and those of the water molecules are mixed.

1. Introduction

The phosphates of some metals posses certain interesting non-linear optical, ferroelectric, antiferroelectric and magnetic properties, ionic conductivity, etc. These characteristics stimulate the preparation and study of various materials with potential conducting properties (for example, crystalline hydrates of metal phosphates in the structure of which strong hydrogen bonds are present) which is of special scientific and practical interest. Various methods have been employed for studying the structural features of such compounds, including vibrational (infrared and Raman) spectroscopy.

Such reasons have inspired us to investigate the structural features of the phosphate compounds using vibrational spectroscopy [1–7] with emphasis on the struvite-type compounds [8–13] to which the general formula $M^IM^{II}PO_4 \cdot 6H_2O$ ($M^I = NH_4$, K, Rb, Cs, Tl; M^{II} = Mg, Ni) can be ascribed. With the exception of the caesium analogue, all others crystallize in the orthorhombic system.

The infrared spectra of $MgM^IPO_4 \cdot 6H_2O$ ($M^I = NH_4$, K, Rb, Cs, Tl) recorded at room temperature (RT) have been studied by Banks et al. [14]. The RT Raman spectrum of struvite, $MgNH_4PO_4 \cdot 6H_2O$, has also been published previously [15,16]. The vibrational spectra of $MgKPO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot 6H_2O$, $MgNH_4AsO_4 \cdot 6H_2O$, $NiKPO_4 \cdot 6H_2O$, and $NiNH_4PO_4 \cdot 6H_2O$ have been studied in our laboratory as well, and interesting results have been obtained [8–13]. In order to clarify, as much as possible, some of the observed spectral characteristics, studying more compounds from the struvite series is of special importance.

In this work, the study of the Fourier transform infrared and Raman spectra of $MgCsPO_4 \cdot 6H_2O$ (*hP50*) (recorded at room temperature, RT and at the boiling temperature of liquid nitrogen, LNT) and those of the series of its deuterated analogues is carried out and is discussed in detail.

Depending on the method of preparation, $MgCsPO_4 \cdot 6H_2O$ crystallizes in the cubic system (*cF100*, space group F–43 m i.e. T_d^2) with $Z = 4$ [17,18] or in the hexagonal system (*hP50*, space group $P6_3mc$

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i.e. C_{6v}^4) with $Z = 2$ [19,20]. It should be pointed out here that the hexagonal $MgCsPO_4 \cdot 6H_2O$ is obtained at normal conditions whereas the cubic analogue is produced at a temperature of 280 °C and pressure of around 7 MPa. Thus, the compound under investigation is not, strictly speaking, *isomorphous* to struvite as is implied by the general title of the present series of papers.

The crystallographic data of $MgCsPO_4 \cdot 6H_2O$ (*hP50*) [19,20] indicate that the univalent cations, divalent cations and the PO_4^{3-} anions occupy special sites with C_{3v} symmetry, whereas the oxygen atoms of the two types of crystallographically different water molecules and two of the hydrogen atoms lay on sites with *m* symmetry, whereas the remaining hydrogen atoms occupy general positions. Thus the symmetry of one of the two types of water molecules is C_s (all atoms of these molecules are located on the mirror plane) and that of the other type may be taken as either C_{2v} (only the oxygen atoms of the water molecules of this type are found on the mirror plane, while the hydrogen atoms are located on general positions and are mirror images of one another) or as C_s (if only the symmetry of the site on which the oxygen atom is located). The water molecules form three O···O types of quite short hydrogen bonds (the acceptors are phosphate oxygens) with distances of 263.0, 264.3 and 267.2 pm [20]. A rather unique two-dimensional H-bond system exists in this very interesting structure with cyclohexane-like antidromic (6O + 6H) H-bonded rings (O4H3O1) connected perpendicularly to the asymmetric water molecules (H1O3H2), forming triple sets of tricyclic H-bond systems.

2. Experimental

The investigated compound was prepared with precipitation from aqueous solutions. The synthesis was performed in a small beaker by mixing 3 mL solution containing 0.1 g of caesium chloride and 0.2 g of magnesium chloride hexahydrate with 5 mL of a solution containing 0.25 g disodium hydrogenphosphate dodecahydrate. Before mixing, the solutions were cooled down to 4 °C and than the reaction system was kept at the same temperature for 48 hours. After this recrystallization time, the precipitate was separated with filtration under vacuum and dried at room temperature.

The spectra were recorded, from both pressed KBr disks and from mulls, at room and liquid-nitrogen temperature (RT and LNT, respectively). The infrared spectra were recorded using a Perkin-Elmer System 2000 infrared interferometer. The variable-temperature cell P/N 21525 (Graseby Specac) was used for the low-temperature measurements. The far infrared spectra were recorded in Nujol between polyethylene pellets. For obtaining a good signal-to-noise ratio, 64 scans were collected and averaged at LNT, whereas 32 scans appeared to be enough at RT. The resolution of the instrument was 4 cm^{-1}. GRAMS ANALYST 2000 [21] and GRAMS 32 [22] packages were used for spectra acquisition and management. The FT Raman spectra were recorded (with a resolution of 2 cm^{-1}) on a Brucker RFS 100 \ s FT Raman equipped with an Nd: YAG laser emitting at 1064 nm. For a good signal-to-noise ratio, 500 scans were accumulated and averaged. All Raman spectra were recorded under identical experimental conditions.

3. Results and discussion

The Fourier transform infrared and Raman spectra of $MgCsPO_4 \cdot 6H_2O$ (*hP50*)[1] recorded at RT and at LNT are given in Figs. 1 and 2. These spectra are similar to the ones obtained for other studied struvite-type compounds [8–13].

3.1. Internal vibrations of water molecules

As previously mentioned, two crystallographically different types of water molecules with effective symmetry C_s and C_{2v} (the oxygen atoms of both types are situated on sites with *m* symmetry) exist in the structure of title compound. The correlations diagrams (Table 1) imply that, in absence of correlation-field effects, from each distinct type of water molecules three infrared active and three Raman active internal modes are expected. Under the influence of the correlation field, each vibration is split into four components (two of them doubly degenerate). The components of the A_1 and E_1 symmetry type are infrared and Raman active, whereas those of the E_2 symmetry are only Raman active.

3.1.1. Stretching vibrations of the water molecules

As in the previously studied vibrational spectra of *orthorhombic* struvite-type compounds [8–13], one broad, structured and asymmetric band which is deuteration sensitive is observed in the O–H stretching region of the spectra of the *hexagonal* $MgCsPO_4 \cdot 6H_2O$ (Fig. 3). The feature is obviously a result of overlap of several bands contributing to the width and the asymmetric character of this band. The position of the centroid of the complex band is below 3000 cm^{-1} suggesting, in agreement with the structural data [20], the presence of strong hydrogen bonds in the structure.

Having in mind that one of the two types of water molecules possesses two equivalent protons and the other has two non-equivalent protons, three types of HDO molecules should be formed upon deuteration. Consequently, when the deuterium content is low (1–5% D), three bands are expected in the O-D streching region. In the low-temperature difference infrared spectrum of the slightly deuterated analogue (Fig. 4), three bands (at 2255, 2180 and 2090 cm^{-1}) are actually observed. The higher-frequency one can be attributed to the O–D stretching vibrations of the isotopically isolated O_w4-D3···O1 groupings[2] where the O_w4···O1 distance is reported [20] to be 267.2 pm, whereas the bands at 2180 and 2090 cm^{-1} should be attributed to the O–D stretchings of the H2O_w3–D1···O2 and H1–O_w3–D2···O1 groupings where the O_w3···O2 and O_w3···O1 distances are 264.3 and 263.0 pm, respectively [20].

3.1.2. Bending vibrations of the water molecules

The bending region of the water molecules is particularly interesting because of the band substructure and the relatively wide range (from around 1900 to 1350 cm^{-1}) in which bands appear (Fig. 5). The spectral pattern in this region is very similar to that observed for the other studied struvite-type compounds [8–13] differing only in the position of the centroid of the complex band. In the present case, namely, it seems to be at lower frequency than the value of the bending HOH vibration of gaseous water (1595 cm^{-1}). The conclusion is supported by the appearance of the band at 1540 cm^{-1} found in the spectrum of the highly deuterated analogue (top curve in Fig. 6) and believed to arise from the bending vibrations of the HOH molecules remaining in the sample.

3.2. External vibrations of the water molecules

Considering the existence of two crystallographically non-equivalent types of water molecules lying on sites with *m* symmetry in the structure of the studied compound, in absence of correlation-field effects six infrared active and six Raman active

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[1] In order to avoid the repetition of the rather involved '$MgCsPO_4 \cdot 6H_2O$ (*hP50*)' notation (where *hP50* is the Pearson notation specifying the hexagonal form of $MgCsPO_4 \cdot 6H_2O$), when the hexagonal modification is meant, it will be referred to as 'the title compound'.

[2] The labeling of the atoms is as in Ref. 20, only a subscript 'w' is added where needed to distinguish the water oxygens from the phosphate ones.