INFRARED AND RAMAN SPECTRA OF MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE (STRUVITE) AND ITS ISOMORPHOUS ANALOGUES

II. The O–H/N–H stretching region

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Abstract: The three investigated compounds – KMgPO₄·6H₂O (KMP), NH₄MgPO₄·6H₂O (NMP) and NH₄MgAsO₄·6H₂O (NMA) – are characterized by the existence, in their structure, of quite strong O⁻⁻O hydrogen bonds (of which some are among the shortest of this type ever found in crystalline hydrates, the O⁻⁻O distances being slightly above 260 pm). Reflecting the strength of the hydrogen bonds, a broad and structured feature extending from | 4000 down to | 2000 cm⁻¹ is found in the infrared spectra. Although not as rich in detail as the infrared spectra, the Raman ones are similar in appearance. Rather surprisingly, the spectral picture is not very different in the case of the two phosphate compounds (KMgPO₄·6H₂O and NH₄MgPO₄·6H₂O) although N–H stretching bands are expected in the same region of the spectrum of NMP. Thus, obviously, the intensity of the feature in the O–H/N–H stretching region is due mainly to modes of the water molecules whereas the NH₄ stretches contribute to a lesser degree to the shape and intensity. The comparison of the spectra in the O=D/N=D stretching region confirms this.

Key words: metal(I) magnesium phosphate hexahydrates; ammonium magnesium arsenate hexahydrate, infrared spectra, Raman spectra, potential protonic conductors.

1. INTRODUCTION

Ammonium magnesium phosphate hexahydrate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ (its mineralogical name is struvite and this name is also used to denote its synthetic analogue) is a biomineral present in human urinary and renal calculi [1] and is the compound that is precipitated in the course of the gravimetric determination of phosphates. Potassium magnesium phosphate hexahydrate, $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ (abbreviated as KMP$^1$) and ammonium magnesium arsenate hexahydrate (NMA or arsenstruvite), $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$ are isomorphous with struvite [2–6]. They all crystallize in the orthorhombic space group $Pmn2_1$ ($C_{2v}$) with $Z = 2$ [2–6]. All ions and two of the four crystallographically different types of water molecules occupy special positions with $C_s$ symmetry, while the H$_2$O molecules of the other two types are located at general positions. The pertinent portion of the crystal structure is shown in Fig. 1 which is produced using the neutron-diffraction data given in the paper by Ferraris, Fuess and Joswig [6]. In order to add to the clarity of the presentation, omitted are the univalent cations, the E atoms of the EO$_4^{3-}$ (E = P or As) anions and the oxygen atoms of these anions that are not involved in the hydrogen-bond network.

The H$_2$O molecules act as donors in hydrogen bonds that are among the shortest ones ever found in crystalline hydrates [7]. Thus, the O$_w$···O distances range from 263.0 to 269.5 pm in NMP (cf. Fig. 1), from 262.3 to 270.1 pm in KMP$^3$ and from 261.9 to 269.8 pm in NMA where the acceptors are, understandably, arsenate oxygens. For the H$_2$O molecules labelled O$_w$(1) there is an additional type of contact, this time with another water molecule, which corresponds to a weak hydrogen bond (the O$_w$···O$_w$ distances are 314.1 pm in struvite [6] (cf. Fig. 1), 314.2 pm in its potassium analogue [2] and 314.9 pm in the case of $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$ [3]. All O$_w$···O distances for the three studied compounds are listed in Table 1.

It should be noted that there is an important difference concerning the two H$_2$O molecules located on the mirror planes. Namely, the H1–O$_w$(1)–H2 molecules have all three atoms on the plane, whereas the mirror plane bisects the H3–O$_w$(2)–H3 molecules. As a consequence, the two hydrogen bonds formed by the molecules of the latter type are equivalent, whereas those of the former type of water molecules are not only non-equivalent but

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1 Ammonium magnesium phosphate hexahydrate will be abbreviated as NMP.

2 It should perhaps be noted that the crystal structure of struvite has been determined or refined on the basis of X-ray diffraction data by Whitaker and Jeffery [4] and by Abbona, Calleri and Ivaldi [5].

3 The acceptors, in both cases, are phosphate oxygens.