

Vibrational spectroscopic studies of Guanidinium metal (M^{II}) sulphate hexahydrates [$M^{II} = \text{Co, Fe, Ni}$]

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Abstract

The Raman and FTIR spectra of $[\text{C}(\text{NH}_2)_3]_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (with $M = \text{Co, Fe, Ni}$) were recorded and analysed. The observed spectral bands are assigned in terms of vibrations of guanidinium ions, sulphate groups and water molecules. The analysis shows that the sulphate tetrahedra are distorted from their free state symmetry T_d to C_1 . This is attributed to the presence of hydrogen bonds from water molecules. The order of distortion of the metal oxygen octahedra influenced the distortion of the sulphate tetrahedra. The appearance of ν_1 – ν_3 modes of water molecules above 3300 cm^{-1} indicates the presence of weak hydrogen bonds.

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1. Introduction

The Guanidinium ion $[\text{C}(\text{NH}_2)_3]^+$, abbreviated as (Gu^+) has been of great importance to biochemists due to the fact that it is an important functional group present in the amino acid arginine as well as the basic constituent of many other biologically active molecules [1]. Gu^+ is a breakdown product of the purine family. Varieties of its derivatives are used in explosives and rocket propellant formulations [2]. Ferroelectric properties are also reported in certain guanidinium metallic sulphates [3]. Furthermore, Gu^+ -coordinated peroxo-complexes of transition metals are of considerable interest and can be used as molecular precursors for the deposition of multimetallic oxides of transition metals for which well-defined, water-soluble salts are very limited [4,5]. Despite the range of application, only a few vibrational spectroscopic studies regarding this family of compounds have been carried out [6–9]. Recently, Fleck et al. investigated the crystal

structure of several guanidinium metal sulphate hydrates [10]. In the present paper, we report the vibrational spectroscopic studies of guanidinium metal (M^{II}) sulphate hexahydrates ($M = \text{Co, Fe, Ni}$).

2. Experimental

The hexahydrated guanidinium bivalent metal sulphates with the chemical formula $[\text{C}(\text{NH}_2)_3]_2\text{M}^{II}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (with $M^{II} = \text{Co, Fe, Ni}$), abbreviated as GuCoS , GuFeS and GuNiS , respectively, were grown from aqueous solutions of equimolar mixtures of $[\text{C}(\text{NH}_2)_3]_2(\text{SO}_4)$ and M^{II}SO_4 ($M^{II} = \text{Co, Fe, Ni}$) at room temperature [10]. We also attempted to synthesise the respective guanidinium metal selenates, but without success — instead, only the single salt guanidinium hydrogen selenate could be obtained [11]. Crystals of the title compounds were grown by controlled evaporation over a period of several weeks. The crystals grown this way were rather large, some up to the size of over $0.5 \times 0.5 \times 1.5 \text{ cm}$. However, we did not attempt to use these crystals as seeds for the growth of larger single crystals (in order to examine physical properties), since they undergo plastic deformation even at very small mechanical

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Fig. 1. Single crystal of guanidinium Co^{II} sulphate hexahydrates (longest dimension 1.4 cm). Small detail: the crystals easily undergo plastic deformation and are therefore (unfortunately) unsuited for cutting or polishing.

stress. Thus, it is impossible to cut or polish the crystals to produce samples for optical or mechanical measurements. A photograph of one single crystal of GuCoS is shown in Fig. 1; a detailed view of one corner shows the deformation caused by removing another, only slightly intergrown crystal.

Raman spectra of the title compounds were recorded by using a Bruker RFS 100/S FT — Raman spectrometer in the region of $50\text{--}4000\text{ cm}^{-1}$. The IR spectra were recorded by using a Bruker IFS-66 v-FTIR spectrometer in the wave number region of $400\text{--}4000\text{ cm}^{-1}$, employing the KBr-pellet method.

3. Factor group analysis

The title compounds GuCoS , GuFeS and GuNiS all crystallise in the monoclinic crystal system (space group $P2_1/c$, $Z = 2$) [10]. The metal ions are situated at Ci sites, Gu^+ , sulphate and H_2O are occupying C_1 sites. The factor group analyses of these samples were carried out by the correlation method developed by Fateley et al. [12]. The total irreducible representation, excluding the acoustic modes, are distributed as

$$\Gamma_{291} = 72A_g + 72B_g + 74A_u + 73B_u.$$

4. Results and discussion

The structure of the title compounds can be described as a composition of $[\text{M}^{\text{II}}\text{O}_6]$ -octahedra with water molecules at the corners, and isolated sulphate tetrahedra that are connected via hydrogen bonds extending from the water molecules. In between, the Gu^+ -ions are located. This structure reminds of another type of similar compounds with the formula $\text{A}_2\text{M}(\text{H}_2\text{O})_6(\text{XO}_4)_2$ (A = monovalent cation, M = bivalent cation, X = hexavalent cation), popularly referred to as Tutton's salt ([13–15] and references therein). The spectral bands are assigned in terms of the vibrational frequencies of the building units SO_4^{2-} , Gu^+ and H_2O .

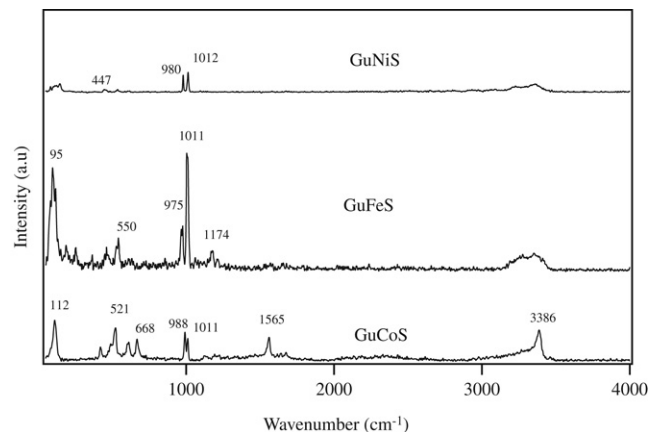


Fig. 2. Raman spectra of guanidinium M^{II} sulphate hexahydrates ($\text{M}^{\text{II}} = \text{Fe, Co, Ni}$) in the region $50\text{--}4000\text{ cm}^{-1}$.

4.1. Sulphate vibrations

In free state sulphate groups, the normal S–O-bond length is 1.47 \AA , the O–S–O-angle is about 109° , i.e. the ideal tetrahedral angle [5]. Usually, free sulphate groups with T_d symmetry have four fundamental vibrations, viz. $\nu_1(A_1)983$, $\nu_2(E)450$, $\nu_3(F_2)1105$ and $\nu_4(F_2)611\text{ cm}^{-1}$. All these modes are Raman active, whereas only ν_3 and ν_4 modes are IR active [16–20].

Generally, for crystals with structures similar to that of Tutton's salts, the non-degenerate symmetric stretching mode (ν_1) of sulphate anions is expected around 980 cm^{-1} as an intense band in the Raman spectra [19–21]. In the present study, the GuCoS compound has an intense band at 988 cm^{-1} in the Raman spectrum (Fig. 2) and a weak band at 980 cm^{-1} in the IR spectrum. The GuFeS has a strong band at 975 cm^{-1} : correspondingly, the IR spectrum has strong bands at 985 cm^{-1} . Similarly, there are intense bands at 979 in the Raman and a feeble band at 980 cm^{-1} in the IR spectrum of GuNiS . The doubly degenerate asymmetric stretching ν_2 modes of the sulphate groups are assigned in Table 1.

The asymmetric bending mode ν_4 can be observed in the Raman spectra as moderately strong bands at 607 and 668 cm^{-1} (GuCoS), the degeneracy being partially lifted. The IR spectrum shows three bands in the region at 587 , 617 and 652 cm^{-1} . In the Raman spectrum of GuFeS , there is a moderately strong band at 550 cm^{-1} , at a lower wave number region than its free ion value. However, in the IR spectrum the degeneracy of the mode is seen to be partially lifted and two bands are observed at 587 and 617 cm^{-1} . In GuNiS , a weak Raman band and a moderately intense IR-band is observed at 612 cm^{-1} . The other bands contributed by ν_3 mode of SO_4 tetrahedra are also assigned in Table 1.

As stated before, the sulphate tetrahedra and the $[\text{MO}_6]$ -octahedra are connected via hydrogen bonds only. In GuCoS , the metal oxygen coordination distances deviate slightly and range from $2.071(2)$ to $2.105(2)\text{ \AA}$, with the mean distance of 2.091 \AA and the difference between Co–O maximum and minimum is of the order of 0.034 \AA . Similarly, the Fe–O distance also varies from $2.100(2)$ to $2.130(2)\text{ \AA}$ with a mean

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