

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 $0.5 \times 0.5 \times 1.5\text{ cm}$. 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 .

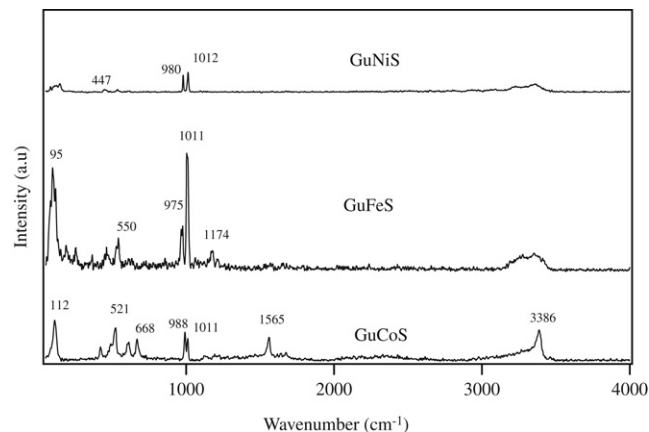


Fig. 2. Raman spectra of guanidinium M^{II} sulphate hexahydrates ($\text{M}^{\text{II}} = \text{Fe, Co, Ni}$) in the region $50\text{--}4000\text{ cm}^{-1}$.

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

Table 1
Spectral data (cm⁻¹)

[C(NH ₂) ₃] ₂ Co(SO ₄) ₂ · 6H ₂ O		[C(NH ₂) ₃] ₂ Fe(SO ₄) ₂ · 6H ₂ O		[C(NH ₂) ₃] ₂ Ni(SO ₄) ₂ · 6H ₂ O		Assignments
Raman	IR	Raman	IR	Raman	IR	
				79 w		Lattice modes
112 vs		95 vs		117 w		
		150 vvw		146 m		
		188 vvw				γ NH ₂
		255 vw				
		364 vvw				
415 m	406 w				405 vvw	ν ₂ SO ₄ ²⁻
	437 w		440 sh	447 w		
	457 w	459 vw	470 sh			
491 sh						
524 vvs	527 w		520 s	532 w	528 m	CN ₃ angle deformation (in-plane)
	543 sh					
	576 sh	550 ms				ν ₄ SO ₄ ²⁻
	587 sh		587 sh			
607 ms	617 m		617 s	613 vvw	612 ms	
668 ms	652 sh					
	740 w		740 vw			CN ₃ angle deformation (out of plane)
	767 w		877 s			
		860 vvw				
988 vvs	980 w	975 s	985 s	979 vs	980 w	ν ₁ SO ₄ ²⁻
1011 sh		1008 vvs	1002 s	1008 vvs		ν _S CN ₃
			1020 s			
1121 vw	1097 vs				1098 vs	ν ₃ SO ₄ ²⁻
1195 vw		1174 w	1131 vs		1120 sh	P NH ₂
			1219 s			
			1536 m			
1565 vs			1554 sh		1573 s	ν CN ₃ & δ NH ₂
	1573 w					
1642 vw					1630 sh	δ _S NH ₂ & ν ₂ H ₂ O
1676 vw	1661 s		1661 vs		1660 s	
2316 wbr (1982–2589)			3152 s		3173 m	
				3226 m	3260 m	ν _S NH ₂
	3210 m					
3265 sh	3260 m	3274 m				ν ₁ –ν ₃ H ₂ O
3340 sh						
3386 vs	3414 vs	3353 m		3361 ms		ν ₁ –ν ₃ H ₂ O
			3433 s		3403 s	
			3617 s			

vw — very weak; w — weak; wbr — weak broad, m — medium; vvw — very very weak; sh — shoulder; ms — moderately strong; vvs — very very strong, s — strong.

distance of 2.112 Å, the difference between the Fe–O maximum and minimum is of the order of 0.030 Å. In contrast, the NiO₆-octahedron is almost regular, the average Ni–O distance is 2.057 Å, the difference between the Ni–O maximum and minimum is of the order of 0.014 Å. The sulphate tetrahedra are not sharing common corners with octahedra but are connected to them by hydrogen bonds from all three water molecules [10]. As a result, the S–O bond lengths are affected by this

coordination. Thus, the O–S–O angle is lower than that of ideal tetrahedral angle, 109°, found in undistorted SO₄²⁻ groups [18]. Lifting of the degeneracies of the sulphate groups' ν₄ mode as well as the slight shifting of the stretching modes from the free ion values suggest that the angular distortion of the sulphate tetrahedra is greater than the bond distortion in GuCoS and GuFeS, which is in agreement with the above structural information and previously reported vibrational spectroscopic

studies of Tutton's salts [19–22]. The appearance of IR-inactive ν_1 and ν_2 modes in the IR spectra suggests the distortion of the tetrahedra from their free ion symmetry T_d to C_1 [22]. This is attributed to the presence of hydrogen bonds from water molecules.

4.2. Vibrations of the guanidinium ion

In the gas phase, the isolated Gu^+ ion has a perfect D_{3h} symmetry which is due to the “Y” — aromaticity of the isolated π -electron system. However, in the solid state the symmetry may be lowered to C_{3v} due to the non-planarity (i.e., the “pyramidisation”) of the amino groups. A further lowering of symmetry may occur as a result of hydrogen bonding towards other atoms such as oxygen atoms of water molecules. The vibrational modes can be assigned by taking the C–N-bonds as a group frequency (CN_3) and the N–H-bonds with another group frequency of NH_2 . Most of the vibrational bands contributed by the Gu^+ ions overlap with those of sulphate groups and water molecules. Consequently, an unambiguous assignment of these bands is limited. The calculated values of the CN_3 symmetric stretching vibrations are at 1041 cm^{-1} (A_1), 1695 cm^{-1} (E), the CN_3 angle deformation at 498 cm^{-1} , the in-plane skeleton deformation at 498 cm^{-1} (E) and the CN_3 out-of-plane angle deformation at 717 cm^{-1} (A). Usually, the frequencies of these vibrations are modified due to interatomic hydrogen bonding present in the crystalline system [8]. In the title compounds, however, the Gu^+ groups are situated parallel to the layers of $[\text{MO}_6]$ -octahedra and $[\text{SO}_4]$ -tetrahedra without any hydrogen bonds; as a result N–H vibrational frequencies are expected to be similar to that of free guanidinium ions [10,24]. The very strong band observed in the Raman spectra at 1011 cm^{-1} (GuCoS) and the highly intense bands at 1008 cm^{-1} in GuFeS and GuNiS are attributed to symmetric stretching vibrations of the CN_3 group of guanidinium ions as reported by Krishnan and Neelakantan [23]. The bands observed at 1661 cm^{-1} in the IR spectra are attributed to CN_3 asymmetric stretching mode, the broad spectral profile also has contributions from bending modes of H_2O and NH_2 deformations. Strong bands observed in Raman spectra at 3386 , 3353 and 3363 cm^{-1} in GuCoS, GuFeS and GuNiS, respectively, are attributed to the NH stretching and NH_2 asymmetric stretching vibrations [24]. Moderately intense IR bands at 3260 cm^{-1} in GuCoS and GuNiS can be assigned to the symmetric stretching mode of NH_2 . In the guanidinium group there are three C–N bonds. Multiple bands are expected for a CN_3 structure with varying bond length. In the present study, only one band is observed in the Raman spectrum of the title compounds, corresponding to this vibration as assigned previously at around 1011 cm^{-1} which indicates that the C–N bonds have nearly equal length [24].

4.3. H_2O Vibration

In the free water molecule (symmetry C_{2v}), there are three fundamental vibrational modes, namely ν_1 at 3652 , ν_2

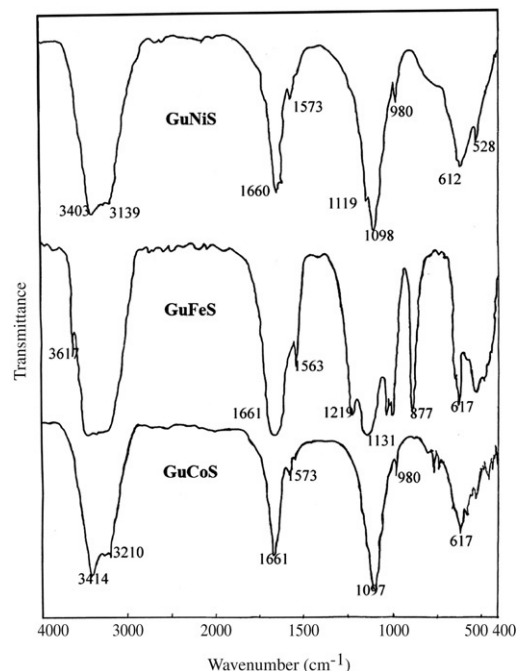


Fig. 3. FTIR spectra of guanidinium M^{II} sulphate hexahydrates ($\text{M}^{\text{II}} = \text{Fe, Co, Ni}$) in the region $400\text{--}4000\text{ cm}^{-1}$.

at 1595 and ν_3 at 3756 cm^{-1} . In the Raman spectrum of GuCoS, a strong band is observed at 3386 cm^{-1} , with a shoulder at 3340 cm^{-1} . In the IR spectrum, a broad band with moderate intensity extending from 3210 to 3414 with a peak at 3260 cm^{-1} is observed. In GuFeS, a broad band is found in the Raman spectrum; the band width extends from 3149 to 3462 cm^{-1} with a peak at 3274 cm^{-1} and a shoulder at 3353 cm^{-1} . In the IR spectrum, these bands are located at 3433 and 3618 cm^{-1} . GuNiS has a broad band in the IR spectrum extending from 3173 to 3403 cm^{-1} with a peak at 3260 cm^{-1} , in its Raman spectrum the broad band extends from 3173 to 3470 cm^{-1} , having an intense peak at 3361 cm^{-1} . These bands are assigned as $\nu_1\text{--}\nu_3$ modes of coordinated H_2O in the crystals under investigation [16,17,19,20,22,25]. The H_2O -bending mode can contribute a high intensity band in the IR spectrum in the 1650 cm^{-1} region Fig. 3. The appearance of the OH-stretching modes at lower wave number than those of the free state values and that of bending modes at higher wave numbers and broad nature of bands profile indicate the presence of hydrogen bonds in the crystal in agreement with the available crystal structural data [10,22,25]. The appearance of $\nu_1\text{--}\nu_3$ modes of water molecules above 3300 cm^{-1} indicates the presence of weakly bonded hydrogen bonds in the samples under investigation [22].

5. Conclusion

The lifting of degeneracies of the ν_4 mode of sulphate tetrahedra as well as the slight shifting of the stretching modes from free ion values suggest that the angular distortion of sulphate ion is greater than the bond distortion in GuCoS and GuFeS. The observed splitting of the ν_1 mode of the sulphate tetrahedra and the appearance of the IR-inactive ν_1 and ν_2

modes in the IR spectra further suggest the distortion of the sulphate tetrahedra from its ideal symmetry T_d to C_1 . This is attributed to the presence of hydrogen bonds through water molecules. The appearance of ν_1 – ν_3 modes of water molecules above 3300 cm^{-1} indicates the presence of weak hydrogen bonds in the samples under investigation.

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