SHORT PAPER

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Infrared and Raman spectra of bis(melaminium) sulfate dihydrate[†]

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Room temperature powder infrared and Raman measurements for the new melaminium salt, bis(2,4,6-triamino-1,3,5-triazin-1-ium) sulfate dihydrate, $2C_3H_7N_6^+\cdot SO_4^{2-}\cdot 2H_2O$, in the crystalline state, were carried out. The vibrational spectra in the region of internal vibrations of the ions corroborate recent X-ray data of Janczak *et al*. Some spectral features of this new crystal are referred to those of other crystalline melaminium salts.

Keywords: melamine, sulfate, hydrogen bond, infrared, Raman, structure-spectra correlation

Along with the dimer of cyanamide, the trimer, melamine (2,4,6-triamino-1,3,5-triazine), is of interest in crystal engineering[1] and supramolecular chemistry[2]. For a better understanding of the vibrational behaviour of the melamine molecule, the characterization of bis(melaminium) sulfate dihydrate with the help of infrared and Raman techniques was undertaken.

The salts of sulfuric acid are interesting because some of them exhibit nonlinear optical properties, namely second harmonic generation. This phenomenon was already observed (and its efficiency determined) for the powder sample of $K_4LiH_3(SO_4)_4$[3] using the Kurtz-Perry method as described in ref. 4. It is equal to 1.2 in relation to quartz. Temperature-dependent second harmonic generation in the $^6LiRbSO_4$ and $^7LiRbSO_4$, crystals, also containing SO_4^{2-} anions, has been reported.[5] Structural and vibrational studies of crystals comprising similar organic or inorganic parts can be useful in elucidation of the role of these molecular units in the generation of second harmonic light. It seemed therefore to be worthwhile to characterize the title crystal by second harmonic preliminary powder measurements.

A few papers assigning the internal vibrations of the melamine molecule have already been published.[6-12] The fundamental frequency assignments for melamine and melamine-d_6 were performed almost 50 years ago in the classical paper of Jones and Orville-Thomas.[7] Some of the aforementioned work was devoted to the band assignment for melamine and hexa(methoxymethyl)melamine.[8] A few of the fundamentals were assigned in the paper of Meier *et al.*[9] They also presented the form of some of the normal modes of methylol melamines.

The crystal structure of bis(melaminium) sulfate dihydrate was determined at room temperature quite recently.[13] According to data presented there, the title crystal comprises mono-protonated melaminium (1+) residues, sulfate (2-) anions, and water molecules. Generally, the solid state complexation of melamine with different organic and inorganic (mineral) acids has an interesting aspect concerning the hydrogen bond system formed. Such a system comprises most frequently the N-H···O and O-H···O types.[13-22] This phenomenon is a feature of self-organization processes, widely reported in the literature.

Experimental

Preparation. The starting compounds, melamine (Aldrich, 99 %) and sulfuric acid (Aldrich, 95–98 %) were used as supplied and prepared in the ratio of 1:3. The dissolved acid was added dropwise to a hot solution of melamine. After the solution was cooled to room temperature it remained clear. The solution was purified with the aid of active charcoal. The solution slowly evaporated over the course of a few days until colourless transparent crystals appeared.

Spectroscopic measurements. The vibrational measurements were carried out at room temperature. Infrared spectra were taken with a Bruker IFS-88 spectrometer in the region 4000–80 cm^{-1}. Resolution was set to 2 cm^{-1}, and the signal/noise ratio was established by 32 scans, weak apodisation. Powder Fourier transform Raman (FTRaman) spectra were taken with an FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. A Nd^{3+}:YAG air-cooled diode pumped laser of power *ca* 200mW was used as an exciting source. The incident laser excitation is 1064 nm. The scattered light was collected at the angle of 180° in the region 3600–80 cm^{-1}, resolution 2 cm^{-1}, 256 scans. Due to the poor detector response, the Raman counterparts of the infrared bands located above 3200 cm^{-1} are not observed in the spectrum presented in Fig. 2.

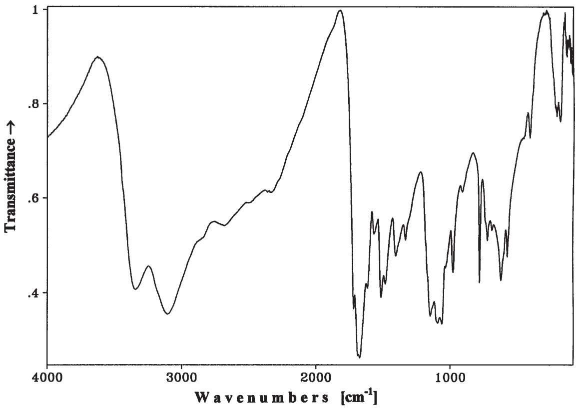

Fig.1 Room temperature powder FTIR spectrum of bis (melaminium) sulfate dihydrate crystal.

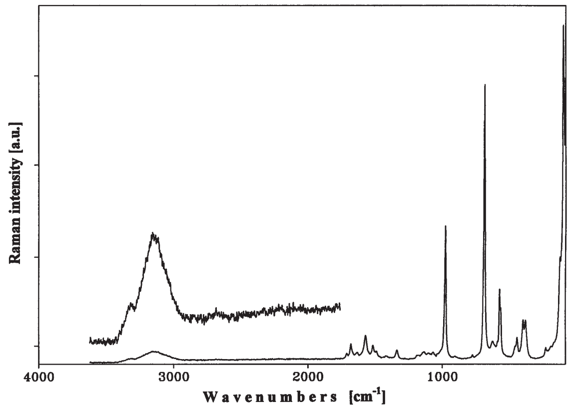

Fig. 2 Room temperature powder FTRaman spectrum of bis(melaminium) sulfate dihydrate crystal.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

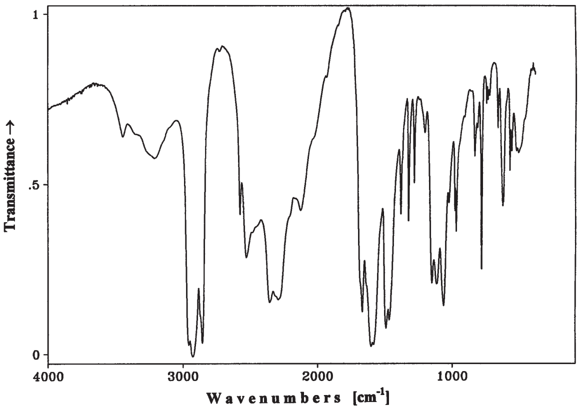

Fig. 3 Room temperature powder FTIR spectrum of deuteriated bis(melaminium) sulfate dihydrate crystal.

The polycrystalline powders were obtained by grinding in an agate mortar with a pestle. The sample, suspension in oil, was placed between KBr windows. The powder infrared spectrum was taken both in Nujol and Fluorolube to eliminate bands originating from the oils. The deuterated analogue was obtained by recrystallization from D_2O.

The measured spectra are shown in Figs 1–3. The wavenumbers of the bands and their relative intensities are given in Table 1.

Discussion; band assignments

The bands observed in the measured region 4000–380 cm^{-1} arise from the vibrations of protons in the hydrogen bonds, the internal vibrations of the sulfate anions and melaminium cations, and from the vibrations of water molecules. The bands below 200 cm^{-1} in the Raman spectrum arise from the lattice vibrations of the crystal.

The vibrations of melaminium residues. Generally, an attempt is made to give the most precise and current assignment. In some cases, however, the earlier assignments, or, for comparison, the earlier together with a more recent proposal, are presented.

The very weak (vw) Raman band at 978 cm^{-1} originating from triazine ring N in-phase radial type of vibration is an excellent Raman group frequency. This vibration does not couple with the substituent groups and can be found in the 969–992 cm^{-1} region.[11] Such a band is present in the FTRaman spectra of all other melamine complexes obtained by the author. Bands are present in melaminium acrylate at 981 cm^{-1} (vw), melaminium butyrate at 982 cm^{-1} (vw), melaminium glutarate at 977 cm^{-1} (w), melaminium arsenate at 978 cm^{-1} (vw), melaminium phthalate at 984 cm^{-1} (vw), melaminium glycolate at 985 cm^{-1} (vw), and in melaminium perchlorate at 982 cm^{-1} (w). However, in the case of the crystal at present studied a strong band from the symmetric stretching vibration of the SO_4^{2-} ion coincides with, and obscures, the melamine ring band.

The most intense band in the FTRaman spectrum is that at 688 cm^{-1}. This is very characteristic for all melamine complexes, and originates from the symmetric vibrations of the sym-triazine ring. The location of this band was analysed in several crystalline melaminium salts.[23] It was observed that the complexation of melamine causes, in all cases, an increase in the frequency of analysed vibration compared to the value for melamine crystal. It is supposed that, due to the number of intense ionic and donor-acceptor types of interaction with its environment, the triazine ring becomes more rigid.

Unfortunately, for some melamine bands the precise assignment remains an open question.

The vibrations of sulfate anions. For an isolated SO_4 group with T_d symmetry there are four normal modes: $\nu_3(F_2)$ = 1150 cm^{-1} (asym stretch), $\nu_1(A_1)$ = 983 cm^{-1} (sym stretch), $\nu_4(F_2)$ = 611 cm^{-1} (asym def) and $\nu_2(E)$ = 450 cm^{-1} (sym def). No band is observed at about 890 cm^{-1} (S-O_H stretch, ν_3'). It corroborates the SO_4^{2-} form of sulfate anion with slightly distorted tetrahedral geometry and almost equal S-O distances (1.45, 1.46, 1.48 and 1.48 Å).[13] Due to lowering of the symmetry from an ideal configuration and the crystal field effect, the splitting can be observed for the doubly degenerate ν_2 mode and for the triply degenerate ν_3 and ν_4 modes. These bands were detected and their assignments are given in Table 1.

Table 1 Vibrational spectra of melaminium sulfate dihydrate

IR	FTRaman	IR deuterated	Tentative assignment
3440ssh		3443m	H_2O stretch
3345vsb	3329vw	3344wb	N–H···N, N–H···O and O–H···O stretch, 2.91–3.12 Å
		3247m	
		3212m	
3099vsb	3144vwb	3153msh	N–H···N, N–H···O and O–H···O stretch, 2.81–2.91 Å
		3099wsh	
2850sb			N–H···O and O-H···O stretch, 2.71–2.80 Å
2680mb	2687vw		Combination tone: NH_2 asym stretch - side chain out-of-plane C–N bend[7]
		2576m	D_2O stretch (3436/2576 = 1.33)
		2530s	N–D···N, N–D···O and O–D···O stretch, 2.91–3.12 Å (3345/2530 = 1.32)
2497m			
		2482s	
		2454s	
		2355vs	N–D···N, N–D···O and O–D···O stretch, 2.81–2.91 Å (3100/2355 = 1.32)
2332m			
		2307vs	
		2291vs	N–D···O and O–D···O stretch, 2.71–2.80 Å (2850/2291 = 1.24)
		2205m	Combination tone: ND_2 asym stretch - side chain out-of-plane C-N bend, (2680/2205 = 1.22)
		2123m	
		2028w	
		1931vw	
		1844vw	
1718vs	1712vw	1710wsh	NH_2 bend
1687vs	1681vw	1681s	Ring stretch
1683vs			NH_2 bend
1670vs		1666vs	Ring stretch
		1635s	
1613s	1633vw		H_2O bend
		1600vs	Ring stretch (lowered due to deuteration)
		1581vs	Ring stretch (lowered due to deuteration)
1567m	1570vw		Side-chain asym C-N stretch[7]; ring: quadrant stretch[8]; NCN bend + ring def and NH_2 sciss
1514m	1515vw		Skeletal mode of the six-membered ring

Table 1 *Continued*

IR	FTRaman	IR deuterated	Tentative assignment
1481s	1492vw	1490vs	Skeletal mode of the six-membered ring
1405m	1416vw		N–H···N, N–H···O and O–H···O in-plane bend, (2.91–3.12 Å)
1381msh			
1332m	1339vw		Ring: semi-circle stretch[11]
		1322vs	ND_2 bend (1718/1322 = 1.30)
1311mb			O–H···O in-plane bend
	1281vw		Ring: semi-circle stretch + exogenous C–N contract[8]
		1279m	ND_2 bend (1683/1279 = 1.32)
		1244w	
		1221wsh	
		1201w	D_2O in-plane bend (1613/1201 = 1.34)
1182msh	1189vw		O–H···O in-plane bend, 2.74 Å
1166ssh			N–H···O in-plane bend, 2.71 Å
1146vs	1135vw	1149s	$\nu_3SO_4^{2-}$
1090vs	1105vw	1114s	$\nu_3SO_4^{2-}$
		1071vssh	
1058vs	1066vw		$\nu_3SO_4^{2-}$
1037s			Ring breath[7]
		1023m	N–D···N, N–D···O and O–D···O in-plane bend, (2.91–3.12 Å), 1405/1023 = 1.37
981ssh			
977s	978s	978m	$\nu_1SO_4^{2-}$
		968s	
		945msh	
910w	908vw	907w	Ring breath
		860w	
		832m	
		824wsh	
		811w	
		791w	
779s	778vw	781s	Side-chain out-of-plane C-N bend[7]; ring-sextant out-of-plane bend[11]
		745w	
737m		734w	Ring def. (out-of-plane), and N–H···O out-of-plane bend, 2.71 Å
721m			Ring bend[7] and O–H···O out-of-plane bend, 2.74 Å
689m	688vs		Symmetric ring breath
		659w	
		652w	
		632msh	
620mb	626vw		H_2O lib
619s		622m	$\nu_4SO_4^{2-}$
603m	589vw	598w	$\nu_4SO_4^{2-}$ and H_2O twist
571m	573w	570m	$\nu_4SO_4^{2-}$
563m	564w	556	Ring bend[7]
		522m	
		506mb	D_2O lib, (620/506 = 1.26)
455wb	457vw	460w	Combination tone: NH_2 bend - NH_2 rock[7]
	443vw		$\nu_2SO_4^{2-}$
407w	398w		$\nu_2SO_4^{2-}$
384vwsh	379w		Ring: quadrant out-of-plane[11]
207w	227vw		Side-chain out-of-plane bend
179w	187vw		Lattice vibration
	165vw		Lattice vibration
127vw	120m		Lattice vibration
	98vs		Lattice vibration

s – strong; w – weak; v – very; sh – shoulder; b – broad; m – medium; stretch – stretching; bend – bending; rock – rocking; twist – twisting; lib – libration; breath – breathing; asym – asymmetric; sym – symmetric; sciss-scissoring

In the infrared spectra of the sulfates containing SO_4^{2-} anions[24-26] one can notice very strong bands at about 1200 cm^{-1}, which unambiguously originate from asymmetric stretching vibrations. Thus the very strong bands observed in the infrared spectrum of the title compound at 1146 cm^{-1} (with a shoulder at 1166 cm^{-1}), 1090 and 1058 cm^{-1} are assigned to these vibrations. In the $K_4LiH_3(SO_4)_4$ crystal similar bands are observed in the infrared spectrum at 1227 and 1176 cm^{-1}.[23] For $Rb_4LiH_3(SO_4)_4$ they are observed at 1227 and 1198 cm^{-1}.[27]

Similarly, a strong band at 978 cm^{-1} originates from symmetric stretching SO_4 group vibration. Analogous bands are observed at 1026, 1015 and 1002 cm^{-1} in a crystalline complex of L-lysine with sulfuric acid,[23] as well as at 1051 and 1052 cm^{-1} for $K_4LiH_3(SO_4)_4$ and $Rb_4LiH_3(SO_4)_4$, respectively.

The proposed assignments for bending type vibrations of the sulfate groups are given in Table 1.

The vibrations of water molecules. In the title crystal, water molecules, together with sulfate anions, are engaged in establishment of the three-dimensional network formed by chains of melaminium residues. Multiple donor-acceptor hydrogen-bond interactions are driving forces in this self-organization process.

The four water molecules in the elementary unit cell of the title crystal are involved as donors in hydrogen bonds with SO_4^{2-} groups and as acceptors in hydrogen bonds with the melaminium residues.[13] These hydrogen bonds are relatively weak, with lengths of 2.737, 2.798, 3.028 and 2.776, 2.859, 3.039 Å, respectively. The water molecules are connected together by hydrogen bonds with length 2.887Å.

The infrared bands corresponding to stretching vibrations of the water molecules are masked by intense and broad absorption originating from the vibrations of weak hydrogen bonds. Their Raman counterparts were not visible due to the insufficient sensitivity of the detector above 3200 cm^{-1}.

The bands corresponding to in-plane deformation type of vibrations were found at 1620 cm^{-1} (IR, s) and at 1633 cm^{-1} (Raman, vw).

The medium infrared band located at 603 cm^{-1} with very weak Raman counterpart at 589 cm^{-1} were assigned to twisting vibrations of the water molecules. A similar infrared band is observed at 607 cm^{-1} with broad and medium intensity in the case of the melaminium bis(4-hydroxybenzenesulfonate) dihydrate crystal.[15, 23]

The hydrogen bonds vibrations. According to Janczak and Perpetuo[13] there are three types of hydrogen bonds in the crystal under study. They are O-H···O type with lengths 2.74, 2.80, 2.89 and 3.03 Å. Ten bonds of N-H···O type cover the ranges of 2.71-2.78 and 2.86-3.07 Å. The lengths of the weakest N-H···N type are in the region of 2.92-3.07 Å. Moreover, the hydrogen atoms of the water molecules are involved in O-H···O hydrogen bonds of length 2.887 Å.

Due to interactions of melaminium cations with sulfate anions and water molecules *via* the hydrogen bridges, in the case of bis(melaminium) sulfate dihydrate there are no pairs of N-H bonds close to each other and with almost the same length. There are 14 N–H bonds with the lengths within the range of 0.83–0.89 Å.[13] Hydrogen bonds, in which all hydrogen atoms of the above-mentioned N–H bonds are engaged, cover the range of 2.71–3.12 Å.

There are therefore no conditions for strong coupling between particular N–H oscillators of NH_2 groups, as in the case of the melamine crystal.[28] Such coupling results in two sharp bands at 3468 and 3418 cm^{-1} (3469 and 3419 cm^{-1}) in infrared (Raman) spectra of the melamine crystal, corresponding to the asymmetric stretching vibrations of the NH_2 groups (ν_aNH_2). On the other hand, the ν_sNH_2 vibration gives the very strong and broad infrared band at 3329 cm^{-1}, with its very weak and broad Raman counterpart at the same position.

In the case of the title crystal, almost every N–H bond would be to some extent independent, having the transition dipole moments parallel to the N–H vectors. They can be collected into groups according their lengths. On this basis, a tentative assignment of the bands in the region 4000–1600 cm^{-1} is proposed in Table 1. It should be noted that the isotopic ratio for the band observed at 2850 cm^{-1} is 1.24. It seems that the shorter hydrogen bonds vibrate more anharmonically. A similar situation is observed in the case of melaminium citrate.[23]

System of weak hydrogen bonds of N–H···X type, X = N, O, Cl, Br, *etc*., is a characteristic feature for all melaminium salts. The position of the infrared bands originating from asymmetric stretching type of vibrations of such a bonds were analysed in several crystalline complexes of melamine.[23,29]

For the title crystal, the assignment for bands originating from in-plane and out-of-plane bending vibrations of hydrogen bonds are given in Table 1.

Lattice vibrations. The greatest differences between the Raman spectra of melamine and the studied melaminium salt crystals are observed in the range of lattice vibrations, *i.e.* for the wavenumbers lower than 200 cm^{-1}. Instead of seven Raman bands – among of them four very strong – in melamine, only one very strong band at 98 cm^{-1} is present in bis(melaminium) sulfate dihydrate. Additionally, a medium band at 120 cm^{-1} and two very weak bands at 165 and 187 cm^{-1} are observed.

Conclusion

Most infrared and Raman bands corresponding to theoretical literature data were assigned. Generally, the vibrational spectra support structural data recently published.

Weak N–H···X bonds, X = N, O are manifest in the vibrational spectra as perturbed amino group vibrations of the melaminium mono-protonated cations. In the case of bis(melaminium) sulfate dihydrate the bending modes were localised at 1670–1720 cm^{-1}.

An important role in the self-assembly process of the melamine salts is played by weak self-association through hydrogen bonds (2.71–3.12 Å). A combination of this type of interaction link together the melaminium cations, water molecules and sulfate anions, forming a three-dimensional network. The water molecule can be considered as a glue element in the crystal structure stabilised by a set of intermolecular hydrogen bonds involving both N–H···O and O–H···O types.

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