



Spectroscopic properties of guanidinium zinc sulphate $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$ and *ab initio* calculations of $[\text{C}(\text{NH}_2)_3]_2$ and $\text{HC}(\text{NH}_2)_3$

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ABSTRACT

Raman and FTIR spectra of guanidinium zinc sulphate $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$ are recorded and the spectral bands assignment is carried out in terms of the fundamental modes of vibration of the guanidinium cations and sulphate anions. The analysis of the spectrum reveals distorted SO_4^{2-} tetrahedra with distinct S–O bonds. The distortion of the sulphate tetrahedra is attributed to Zn–O–S–O–Zn bridging in the structure as well as hydrogen bonding. The CN_3 group is planar which is expressed in the twofold symmetry along the C–N (1) vector. Spectral studies also reveal the presence of hydrogen bonds in the sample. The vibrational frequencies of $[\text{C}(\text{NH}_2)_3]_2$ and $\text{HC}(\text{NH}_2)_3$ are computed using Gaussian 03 with HF/6-31G* as basis set.

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1. Introduction

Guanidinium complexes are biologically important due to their presence as a functional group in amino acids [1–5]. Their physical properties are of considerable interest with regard to the variety of applications in the field of ferroelectricity, biotechnology, medicine, etc. Recently, our group has reported structural and spectral studies of hydrated transition metal guanidinium compounds [5–7]. Among the transition metal guanidinium complexes, the zinc compound is the only anhydrous guanidinium sulphate [6,8]. As part of our continuing interest on guanidinium compounds we have recorded Raman and infrared spectra of guanidinium zinc sulphate ($[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$). The ground state vibrational frequencies of guanidinium ions have been computed previously at the Hartree-Fock level with Gaussian 90 program [1]. In order to get more insight into the vibrational aspects of guanidinium, the *ab initio* computations of $[\text{C}(\text{NH}_2)_3]_2$ and $\text{HC}(\text{NH}_2)_3$ are also carried out by using Gaussian 03 [9].

2. Experimental

Guanidinium zinc sulphate $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$, abbreviated as GuZnS, was grown from an aqueous solution of guanidinium sulphate $[\text{C}(\text{NH}_2)_3]_2(\text{SO}_4)$ and zinc sulphate $[\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}]$ taken in stoichiometric proportion at room temperature by slow evaporation [6,8]. The Raman spectrum was recorded using a Bruker FRS 100/SFT Raman spectrometer in the region 50–4000 cm^{-1} . FTIR spectrum of the compound was recorded with a Bruker IFS 66v-FTIR spectrometer in the range 400–4000 cm^{-1} using KBr pellet method.

3. *Ab initio* computations of vibrational frequencies

The program used for the computation of vibrational frequencies was Gaussian 03 with HF/6-31G* as basis set [9]. The vibrational frequencies computed by this method contain systematic errors due to negligence of electron correlation. Thus a scaling factor of 0.8929 for HF/6-31G* basis set is employed. The assignment of the calculated frequencies of $[\text{C}(\text{NH}_2)_3]_2$ and $\text{HC}(\text{NH}_2)_3$ molecules is aided by the animation option of MOLEKEL program [10,11] for visual presentation of the vibrational modes. The optimized geometry of $[\text{C}(\text{NH}_2)_3]_2$ and $\text{HC}(\text{NH}_2)_3$ is shown in Figs. 1 and 2, respectively. The calculated values of the vibrational frequencies along with the spectral assignments are given in Tables 1 and 2. Geometrical parameters are also given as supplementary data (Tables 4 and 5).

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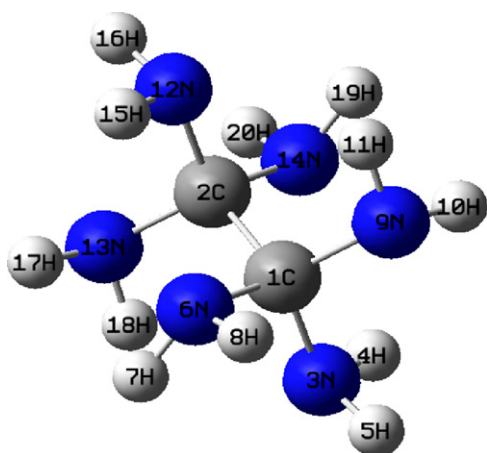


Fig. 1. The optimized geometry of $[\text{C}(\text{NH}_2)_3]_2$.

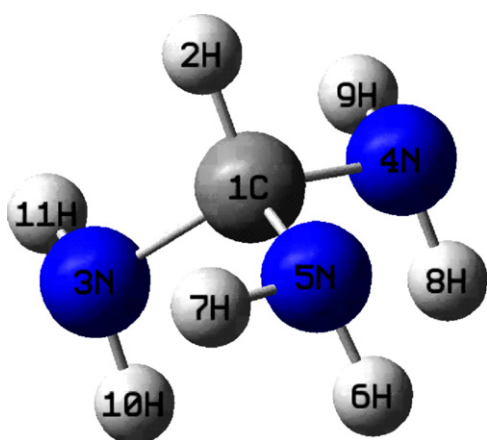


Fig. 2. The optimized geometry of $\text{HC}(\text{NH}_2)_3$.

4. Factor group analysis

The $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$ belongs to the body centered tetragonal crystal system with space group $I\bar{4}2d$ (D_{2d}^{12}) with $a = 9.515$ and $c = 14.351$ Å, with $Z = 4$, $Z^B = 2$ [6,8]. The factor group analysis of the title compound is carried out by the correlation method developed by Fateley et.al. [12]. The total irreducible representation excluding

Table 2

Vibrational frequencies (cm^{-1}) of $\text{HC}(\text{NH}_2)_3$ by *ab initio* computation and assignments.

ν calculated	Assignments
3316	$\nu_{\text{as}}\text{NH}_2$
3307	$\nu_{\text{as}}\text{NH}_2$
3300	$\nu_{\text{as}}\text{NH}_2$
3237	$\nu_{\text{s}}\text{NH}_2$
3232	$\nu_{\text{s}}\text{NH}_2$
3227	$\nu_{\text{s}}\text{NH}_2$
2878	νCH
1621	δNH_2
1599	δNH_2
1590	δNH_2
1413	$\delta\text{CH}, \text{NH}_2$ twist or rock
1382	NH_2 twist or rock
1332	NH_2 twist or rock
1168	$\nu_{\text{as}}\text{C}-\text{N}_3$
1131	$\nu_{\text{as}}\text{C}-\text{N}_3$
1065	NH_2 wagging
1011	NH_2 wagging
956	NH_2 wagging
925	γCH
875	NH_2 wagging
851	$\nu_{\text{s}}\text{C}-\text{N}_3$
530	Deform C–N
457	Deform C–N
431	Deform C–N
301	NH_2 torsion
260	NH_2 torsion
200	C–N ₃ torsion

the acoustic modes, is given below:

$$\Gamma_{183} = 31 A_1 + 31 A_2 + 31 B_1 + 30 B_2 + 30 E$$

5. Results and discussion

The structure of GuZnS consists of a three-dimensional framework of interconnected zinc and sulphate ions. The sulphate ions have tetrahedral coordination surrounding the cations of zinc, so that $\text{Zn}-\text{O}-\text{S}-\text{O}-\text{Zn}$ bridging occurs in the structure. The guanidinium ions are connected to the sulphate ions through hydrogen bonding [6,8]. The band assignment of the Raman and FTIR spectra of the title compound is done in terms of the fundamental modes of vibration of guanidinium ions (Gu^+) and the sulphate ions (SO_4^{-2}).

Table 1

Vibrational frequencies (cm^{-1}) of $[\text{C}(\text{NH}_2)_3]_2$ obtained by *ab initio* computation.

ν calculated	Assignments	ν calculated	Assignments	ν calculated	Assignments
124	Torsion CN_3	854	NH_2 wagging	1617	δNH_2
229	Torsion CN_3	888	NH_2 wagging	1622	δNH_2
263	Torsion CN_3	904	NH_2 wagging	1623	δNH_2
281	Torsion CN_3	919	NH_2 wagging	1633	δNH_2
283	Torsion CN_3	940	NH_2 wagging	1644	δNH_2
306	Torsion NH_2	944	NH_2 wagging	1647	δNH_2
340	Torsion NH_2	971	$\nu\text{C}-\text{N}$	3329	$\nu_{\text{s}}\text{NH}_2$
341	Torsion NH_2	992	$\nu\text{C}-\text{N}$	3330	$\nu_{\text{s}}\text{NH}_2$
365	Torsion NH_2	1016	$\nu\text{C}-\text{N}$	3335	$\nu_{\text{s}}\text{NH}_2$
380	Torsion NH_2	1044	$\nu\text{C}-\text{N}$	3336	$\nu_{\text{s}}\text{NH}_2$
385	Torsion NH_2	1049	$\nu\text{C}-\text{N}$	3340	$\nu_{\text{s}}\text{NH}_2$
410	Deform C–N	1103	$\nu\text{C}-\text{N}$	3341	$\nu_{\text{s}}\text{NH}_2$
446	Deform C–N	1253	NH_2 twist/rock	3409	$\nu_{\text{as}}\text{NH}_2$
469	Deform C–N	1273	NH_2 twist/rock	3410	$\nu_{\text{as}}\text{NH}_2$
538	Deform C–N	1297	NH_2 twist/rock	3414	$\nu_{\text{as}}\text{NH}_2$
557	Deform C–N	1324	NH_2 twist/rock	3415	$\nu_{\text{as}}\text{NH}_2$
568	Deform C–N	1334	NH_2 twist/rock	3417	$\nu_{\text{as}}\text{NH}_2$
694	$\nu\text{C}-\text{C}$	1388	NH_2 twist/rock	3418	$\nu_{\text{as}}\text{NH}_2$

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