



# Growth, spectroscopy properties and DFT based PCM calculations of guanidinium chlorochromate

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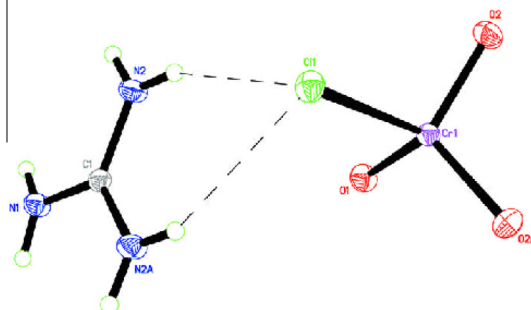
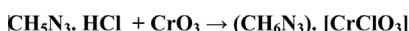
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## HIGHLIGHTS

- GCC is a nonlinear optical crystal, grown in large sizes from aqueous solutions.
- To study the vibration aspects of guanidine, the PCM computation is done.
- Absence of absorption in the visible region is useful for SHG applications.
- GCC crystal has wide optical band gap of 4.84 eV.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nonlinear optical single crystals of guanidinium chlorochromate [GCC] are grown by slow evaporation solution growth technique using water as the solvent. Purity of crystals is increased by the method of recrystallization. The solubility of the material is measured at various temperatures in de-ionized water. The grown crystals are characterized by single crystal XRD for obtaining unit cell parameters. The presence of functional groups and modes of vibrations are identified by FT-IR spectroscopy. The chemical structure of crystal is established by FT-NMR techniques. The UV–vis–NIR spectrum of GCC shows less absorption and good transmittance in the entire visible region enabling its use in optical application. Also, the Kurtz powder second harmonic generation test shows that the compound is a potential material for optical second harmonic generation. The theoretical vibration frequency of  $\text{HC}(\text{NH}_2)_3$  and  $[\text{C}(\text{NH}_2)_3]_2$  are analyzed in different solvent media.

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## Introduction

Materials with quadratic nonlinear optical (NLO) properties are currently attracting considerable interest. Organic materials are of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an

opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [1–3]. Also, organic nonlinear optical materials are attracting a great deal of attention, as they have large optical susceptibilities and inherent ultra-fast response times [4–6]. However, crystals of this kind of materials have certain inherent limitations, such as increased optical absorption, narrow transparency window and poor mechanical and thermal stability [7]. To overcome these problems, strategies of synthesizing organic–inorganic hybrid compounds has been proposed, which lead to the discovery of a new class of materials, namely the organometallic compounds. Organometallic

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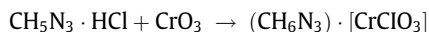
coordination compounds as NLO materials has attracted much more attention for their considerable high NLO coefficients, stable physico-chemical properties and better mechanical intension contrast to organic materials where polarizable inorganic molecules are stoichiometrically bound within an organic host [8].

In the field of nonlinear optical crystal growth, guanidinium complexes are playing a vital role. They are present as functional groups in aminoacids [9–11] and their physical properties are so important that they have a variety of applications in the field of ferroelectricity, biotechnology, medicine [12], etc. Guanidine is a strong Lewis base and the guanidinium cation may be easily anchored onto numerous inorganic and organic anions and polyanions, largely because of the presence of six potential donor sites for hydrogen-bonding interactions. Recently many structural and spectral studies of hydrated transition metal guanidinium compounds have been reported [13–15]. With our continuing interest on guanidinium compounds, we report here the growth of an organometallic crystal guanidinium chlorochromate, which is grown by slow evaporation method and the compound is characterized by single crystal and powder X-ray diffractogram (XRD) analysis, Fourier Transform infrared (FTIR) spectra, FT-NMR studies, UV–vis–NIR spectrum and second harmonic generation (SHG) studies. Polarizable continuum model [16,17] with water, methanol and benzene as solvents have been used for assessing the influence of the solvents and in vibration frequencies on the electronic structure of the investigated compound.

## Experimental studies

### Material synthesis and crystal growth

The GCC is synthesized from guanidinium hydrochloride and chromium trioxide that are taken in equimolar ratio. The calculated amounts of reactants are thoroughly dissolved in double distilled water and stirred continuously for 6 h using magnetic stirrer. The saturated solution is recrystallized several times to yield the purified material. Transparent GCC seed crystals are grown in a period of 2 weeks. The GCC crystal, produced from guanidinium hydrochloride and chromium trioxide is represented in the following reaction:



After careful selection of the seed crystal, it is immersed into the mother solution using nylon thread to encourage its growth into a bulk form. Good optical quality guanidinium chlorochromate single crystal of dimension  $27 \times 20 \times 30 \text{ mm}^3$  is harvested after a period of 1 month. The photograph of grown single crystal of GCC is shown in Fig. 1.



Fig. 1. Grown crystals of GCC.

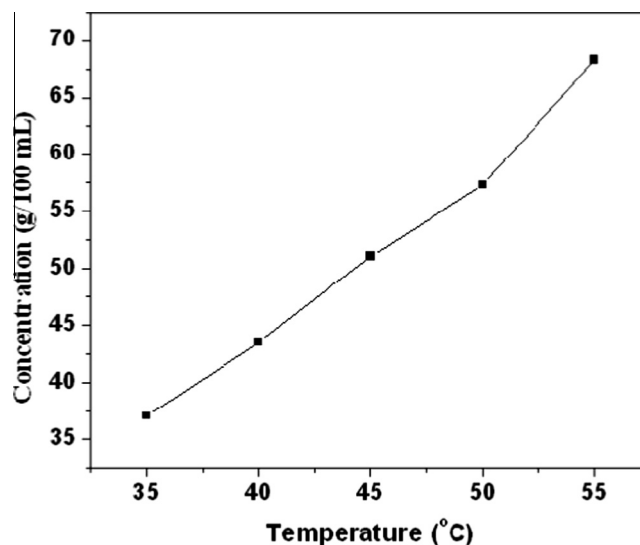


Fig. 2. Solubility of GCC in water.

### Solubility

The solubility of GCC in water was determined as a function of temperature in the range of 35–55 °C at the temperature interval of 5 °C. To determine the equilibrium concentration, the solution GCC was prepared using double distilled water as the solvent. The solution was maintained at a constant temperature and continuously stirred using a magnetic stirrer to ensure homogeneous concentration throughout the volume of the solution. On reaching the saturation, the content of the solution was analyzed gravimetrically [18] and this process was repeated for every temperature. The solubility curve is shown in Fig. 2. The solubility increases linearly with increase of temperature indicating the feasibility of growing this material either by slow cooling or slow evaporation methods.

### Characterization studies

The grown crystal is subjected to the following structural, spectral and optical studies. The single crystal XRD data of the grown GCC crystal is obtained using Enraf Nonius-CAD4 X-ray diffractometer. X-ray powder pattern of the crystal is recorded on a RICH SEIFERT powder X-ray diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The sample is scanned for  $2\theta$  range of 10–70 °C at a scan rate of 1 °/min. Morphology of the grown crystal is identified by the single crystal X-ray diffraction studies (Bruker kappa APEX11). The FT-IR spectrum of GCC is recorded using the FTIR spectrometer (BRUKE66V) in the region  $4000\text{--}400 \text{ cm}^{-1}$  by KBr pellet technique. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the GCC are recorded with a JEOL-GSX400 NMR spectrometer operated at 400 MHz with deuterated water ( $\text{D}_2\text{O}$ ) as solvent. The UV–vis spectrum of GCC crystal is recorded in the range 200 and 2000 nm using Perkin–Elmer 35 spectrophotometer. Kurtz and Perry powder method is employed to determine the SHG efficiency of GCC crystal.

## Results and discussion

### X-ray diffraction analysis

Unit cell parameters of the grown GCC crystal are obtained using the single crystal X-ray diffraction. It is observed that the title compound crystallizes in orthorhombic system with lattice parameters  $a = 6.11 \text{ \AA}$ ,  $b = 7.54 \text{ \AA}$ ,  $c = 14.89 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  and the volume of the material is found to be  $V = 685 (\text{\AA})^3$ . The obtained

lattice parameter values are in good agreement with the reported literature values [19]. The lattice parameters obtained from single crystal XRD are used for indexing and the powder XRD pattern of the grown crystals is shown in Fig. 3. The sharp peaks observed indicate the good crystallinity of the sample. From the morphology of GCC crystal it is observed that the growth rate of the crystal along the *a*- and *b*-axes is much larger than that along the *c*-axis. As depicted in Fig. 4, the morphology of GCC crystal is a polyhedron with four well-developed faces.

#### FTIR spectral analysis

Infrared spectra are an important record, which provide more information about the structure of a compound. In this technique almost all functional groups in a molecule absorb IR radiation characteristically within definite range of frequency [20]. IR spectra contain a number of bands at specific wave numbers. The aim of the vibrational analysis is to decide which of the vibrational modes in the molecule give rise to each of the observed bands at specific wave numbers in the FTIR spectra. The functional groups present in the molecule were identified and a satisfactory vibrational band assignment has been made for the fundamental modes of vibration by observing the position, shape and intensity of the bands. Vibrational frequencies of similar compounds like metformin [21,22], 5-aminoindole [23] have been taken into consideration for the assignment of fundamental vibrations of guanidinium chlorochromate. The range, 4000–400  $\text{cm}^{-1}$  is of prime importance for the study of an organic and metal organic compound by spectral analysis [24]. The FTIR spectrum of GCC is shown in Fig. 5.

#### Vibrational band assignment

##### N–H vibrations

The N–H stretching of C=N–H group occurs in the region 3500–3100  $\text{cm}^{-1}$ . Usually the frequency of this vibration is decreased in the presence of hydrogen bond [25]. The medium intensity bands at 3458, 3400, 3339, 3267, and 3192  $\text{cm}^{-1}$  have been assigned to N–H asymmetric and symmetric stretching vibrations, respectively.

##### C–N vibrations

Guanidines absorb strongly at 1685–1580  $\text{cm}^{-1}$  due to C=N stretching vibrations [21]. Therefore guanidinium chlorochromate has strong absorption band at 1645  $\text{cm}^{-1}$ . It has been reported that C–N stretching of aliphatic amine compounds is generally weak and occurs in the region 1220–1020  $\text{cm}^{-1}$  [26]. The weak intensity band in the FTIR spectrum at 1143  $\text{cm}^{-1}$  has been assigned to C–N

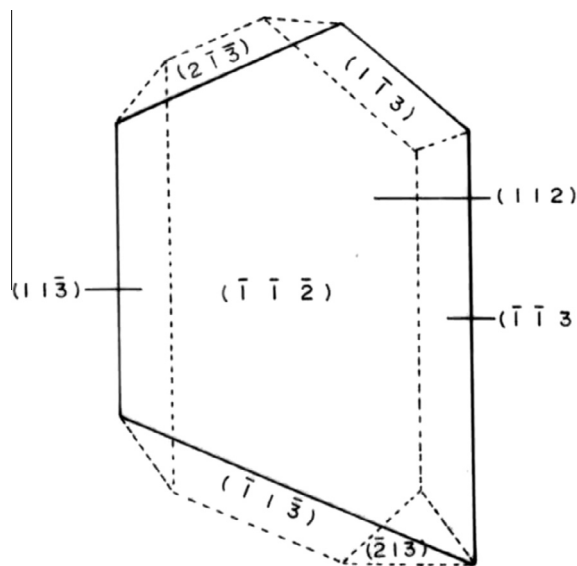


Fig. 4. Morphology of GCC.

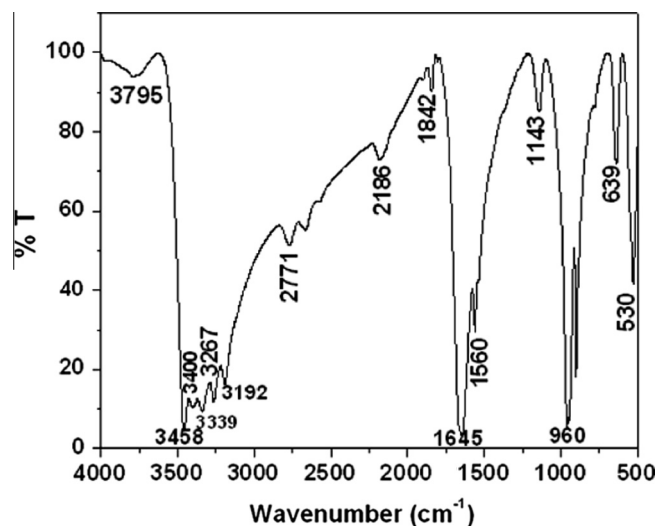


Fig. 5. FTIR spectrum of GCC.

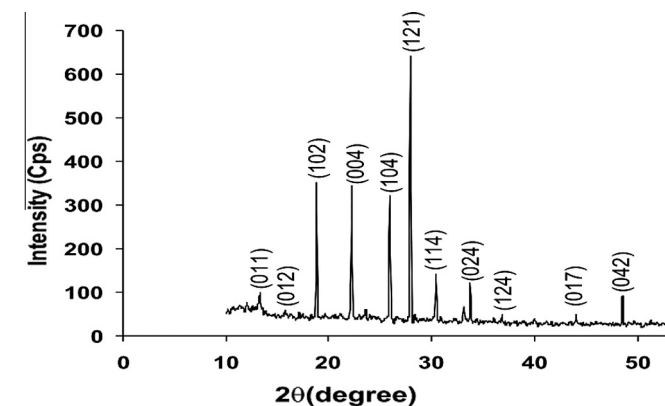


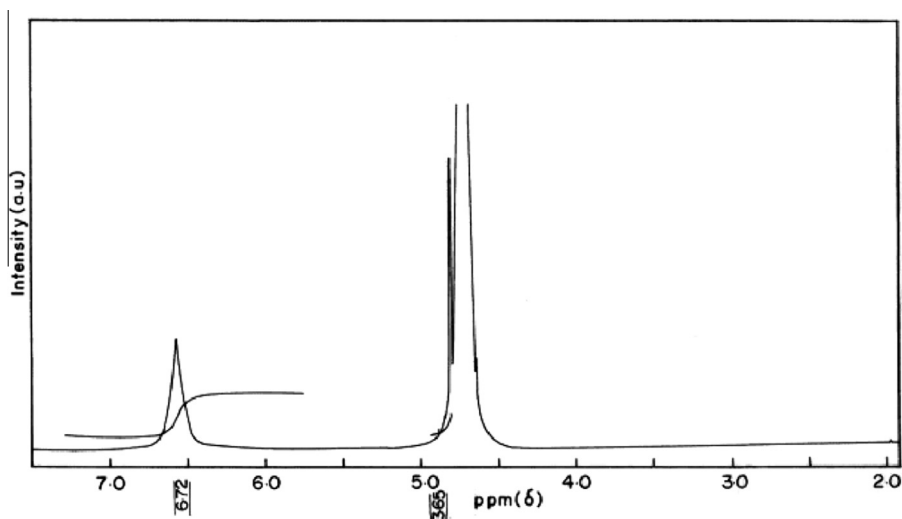
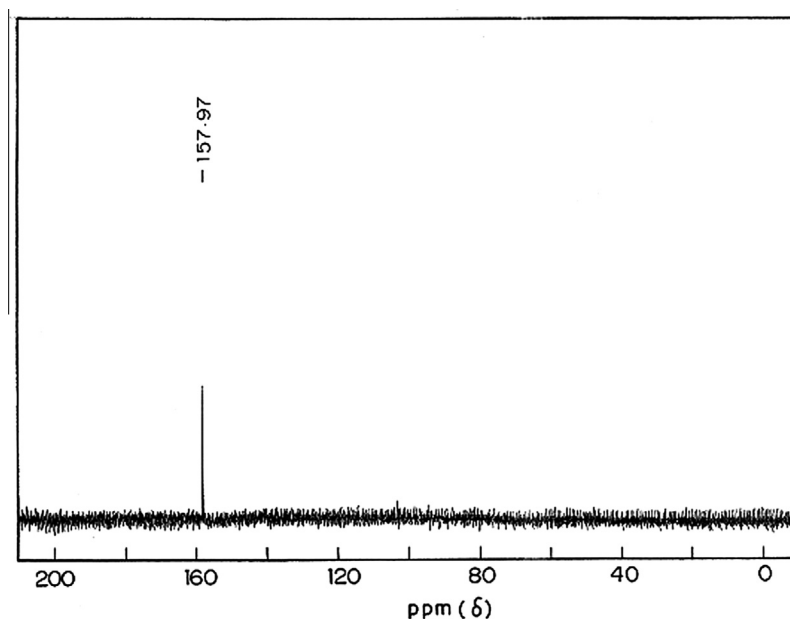
Fig. 3. Powder X-ray diffraction spectrum of GCC.

Table 1

Vibrational band assignment of GCC crystal.

Frequency ( $\text{cm}^{-1}$ )	Assignment
3458 m	$\nu_{\text{as}}\text{N-H}$
3400 m	$\nu_{\text{as}}\text{N-H}$
3339 m	$\nu_{\text{as}}\text{N-H}$
3267 m	$\nu_{\text{s}}\text{N-H}$
3192 w	$\nu_{\text{s}}\text{N-H}$
2771 w	$\nu\text{OH}$
2186 w	$\nu\text{OH}$
1645 s	$\nu\text{C=N}$
1560 vs	$\delta\text{NH}_2$
1143 w	$\nu\text{C-N}$
960 s	$\nu\text{Cr-O}$
947 s	$\nu\text{Cr-O}$
639 m	$\nu\text{Cr-O}$
530 m	$\nu\text{Cr-O}$

stretching vibration. The format peak arises due to nitrogen electron pair delocalization over carbon.

Fig. 6.  $^1\text{H}$  NMR spectrum of GCC.Fig. 7.  $^{13}\text{C}$  NMR spectrum of GCC.

#### O—H vibrations

Intermolecular hydrogen bonding between the donor and the acceptor molecules is the root cause for the NLO property of the materials [27]. The bands arising from O—H stretching of hydrogen bond vibrations [28] are noticed at  $2771$  and  $2186\text{ cm}^{-1}$ . These fine structures are due to intermolecular hydrogen bonding of each guanidinium hydrogen with neighboring hydrogens.

#### $\text{NH}_2$ vibrations

The band at  $1560\text{ cm}^{-1}$  has been assigned for  $\text{NH}_2$  in-plane deformation vibrations [22], which is normally observed between  $1590$  and  $1530\text{ cm}^{-1}$ .

#### Cr—O vibrations

Vibrations involving metal–ligand stretching and bending modes generally appear in the low-frequency region. This is due to the weak nature of the metal–ligand bond and due to the relatively heavy mass of the metal [29]. The metal–ligand vibrations

may couple with other low frequency vibrations in the metal complex. In general, the M—O stretching vibration gives a more intense and broad band than M—N stretching vibration. This may be attributed to the larger dipole moment change occurring with the M—O bond. Thus the peaks appearing below  $1000\text{ cm}^{-1}$  are assigned to Cr—O stretching vibration. The experimental vibrational frequencies of GCC are presented in Table 1.

#### FTNMR studies

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral analyses are the two important modern analytical technique used for the confirmation of molecular structure. The  $^1\text{H}$  NMR spectrum of GCC is shown in Fig. 6. From the proton NMR spectrum the peak at  $6.574\text{ ppm}$  is assigned to guanidinium hydrogen, as there is only one peak for which all the hydrogen atoms are equivalent with respect to electron shielding. The intense peak at  $3.65\text{ ppm}$  is due to  $\text{D}_2\text{O}$ .

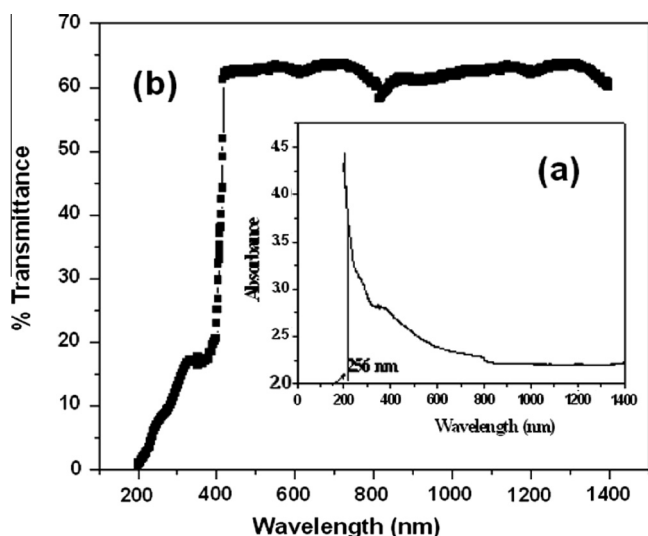


Fig. 8. (a) UV-vis-NIR absorption spectrum of GCC. (b) Optical transmission spectrum of GCC crystal.

Table 2

Electrostatic interaction and induced dipole moment.

Solvents	HC(NH <sub>2</sub> ) <sub>3</sub>			[C(NH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	
	Dielectric constant ( $\epsilon$ )	Electrostatic constant ( $\epsilon$ )	Induced dipole moment	Electrostatic interaction	Induced dipole moment
Water	78.35	−9.68	2.06	−14.91	3.74
Methanol	32.63	−9.66	2.05	−14.59	3.72
Benzene	2.27	−5.23	1.88	−7.80	3.31

The <sup>13</sup>C NMR spectrum is shown in Fig. 7. The characteristic absorption peaks of <sup>13</sup>C NMR spectra of GCC is explained as follows. The peak at 157.97 ppm is assigned to guanidinium carbon. As the spectrum does not carry any other peaks the crystal must be free of any impurities.

#### UV-vis-NIR spectral analysis

The UV-vis-NIR transmission and absorption studies are carried out for the grown crystal and the resultant spectra are shown in

Fig. 8a and b. From the absorption spectrum shown in Fig. 8a, it is evident that there is an absorption peak with UV cut off wavelength of 256 nm. It is also evident from this spectrum that there is no remarkable absorption observed above 256 nm till 1400 nm. The convincing proof for this result is obtained from transmission spectrum shown in Fig. 8b. The percentage of transmission of about 60% is attributed to better quality of the grown GCC crystal. As this crystal exhibits wide transmission range, it can be used for optical applications including the second harmonic generation of Nd: YAG laser of fundamental wavelength  $\lambda = 1064$  nm. It is clearly evident that the lower cut off wavelength lies near 256 nm. This low absorption throughout the entire visible region is one of the most essential parameter for frequency doubling process using diode and solid-state laser [30]. From the fundamental absorption at 256 nm the band gap energy of the material is calculated using the formula,  $E_g = (1.24/\lambda)$  eV, where  $\lambda$ -fundamental absorption wavelength (0.256  $\mu$ m). The band gap energy of the material is found to be 4.84 eV. This indicates that GCC is a high-energy band gap material.

#### Second harmonic generation study

Kurtz and Perry [31] second harmonic generation efficiency of the crystalline material is determined using Q switched Nd: YAG laser beam of  $\lambda = 1064$  nm. Pulse duration of 10 ns and frequency repetition of 10 Hz is passed through the powder sample. The SHG behavior is confirmed from the output of the laser beam which has bright green emission ( $\lambda = 532$  nm) from the powder sample. The second harmonic signal of 13 mV is obtained for an input energy of 31 mJ/pulse, while the standard KDP crystal gives a SHG signal of 28 mV for the same input energy. It is clear that the SHG efficiency of GCC is about 50% of that of KDP crystal.

#### DFT based PCM analysis

Solvation analysis is done in wide range of solvents. Computation has been performed both in the gas phase and in the solvent medium of its dielectric constants using Polarized Continuum Model (PCM) by with DFT using B3LYP basis set to interpret the solvent effect on the behavior of the solute molecules. The computer program GAMESS is used for this purpose. Solvation effect is an essential component of solution chemistry and it is very useful in pharmaceutical industry for heterocyclic organic compounds. The free energy of solvation effects are frequently dominated by electrostatic interaction. The electrostatic contribution to the free

Table 3

Vibrational frequencies of HC(NH<sub>2</sub>)<sub>3</sub>.

	Calculated frequency			Assignments
	Water ( $\epsilon$ ) = 78.35	Methanol ( $\epsilon$ ) = 32.63	Benzene ( $\epsilon$ ) = 2.27	
3316	3815	3698	3812	$\nu$ NH <sub>2</sub>
3307	3809	3692	3808	$\nu$ NH <sub>2</sub>
3300	3807	3687	3807	$\nu$ NH <sub>2</sub>
3237	3698	–	3695	$\nu$ NH <sub>2</sub>
3232	3692	–	3691	$\nu$ NH <sub>2</sub>
3227	3687	–	3686	$\nu$ NH <sub>2</sub>
2878	3003	3003	3006	$\nu$ CH
1621	1668	1668	1670	$\delta$ NH <sub>2</sub>
1599	1661	1660	1663	$\delta$ NH <sub>2</sub>
1590	1654	1654	1669	$\delta$ NH <sub>2</sub>
1413	1408	–	1459	CH, $\rho$ NH <sub>2</sub> or $\rho$ NH <sub>2</sub>
1382	1354	1353	1353	$\rho$ NH <sub>2</sub> or $\rho$ NH <sub>2</sub>
1332	1220	1219	1218	$\rho$ NH <sub>2</sub> or $\rho$ NH <sub>2</sub>
1168	1172	1172	1173	C–N <sub>3</sub>
1065	1031	1031	1030	$\omega$ NH <sub>2</sub>
1011	–	–	1004	$\omega$ NH <sub>2</sub>
925	902	902	901	$\delta$ CH
530	497	497	490	$\delta$ C–N



**Table 4**  
Vibrational frequencies of  $[\text{C}(\text{NH}_2)_3]_2$ .

	Calculated frequency			Assignments
	Water ( $\epsilon$ ) = 78.35	Methanol ( $\epsilon$ ) = 32.63	Benzene ( $\epsilon$ ) = 2.27	
3418	3698	3699	3693	$\nu\text{NH}_2$
3417	3692	3692	3691	$\nu\text{NH}_2$
3415	3689	3689	3683	$\nu\text{NH}_2$
3410	3678	3678	3678	$\nu\text{NH}_2$
3409	3672	3672	–	$\nu\text{NH}_2$
1647	1673	1673	1686	$\delta\text{NH}_2$
1644	1651	1652	1664	$\delta\text{NH}_2$
1633	1646	1646	1656	$\delta\text{NH}_2$
1623	1631	1632	1645	$\delta\text{NH}_2$
1622	1605	1606	1631	$\delta\text{NH}_2$
1617	1587	1588	1622	$\delta\text{NH}_2$
1388	1339	1368	1380	$\rho\text{NH}_2$ or $\rho\text{NH}_2$
1334	1325	1340	1335	$\rho\text{NH}_2$ or $\rho\text{NH}_2$
1297	1284	1285	1297	$\rho\text{NH}_2$ or $\rho\text{NH}_2$
1273	1236	1237	1247	$\rho\text{NH}_2$ or $\rho\text{NH}_2$
1253	1224	1225	1247	$\rho\text{NH}_2$ or $\rho\text{NH}_2$
1049	1047	1048	1057	$\nu\text{C}-\text{N}$
1044	1010	1011	1019	$\nu\text{C}-\text{N}$
1016	1000	1001	1011	$\nu\text{C}-\text{N}$
992	982	983	985	$\nu\text{C}-\text{N}$
971	972	973	–	$\nu\text{C}-\text{N}$
944	–	936	943	$\omega\text{NH}_2$
854	794	794	793	$\omega\text{NH}_2$
694	691	690	686	$\text{C}-\text{C}$
568	562	562	556	$\delta\text{C}-\text{N}$
557	551	551	552	$\delta\text{C}-\text{N}$
538	540	538	537	$\delta\text{C}-\text{N}$
469	534	534	512	$\delta\text{C}-\text{N}$
446	500	500	468	$\delta\text{C}-\text{N}$
410	432	432	422	$\delta\text{C}-\text{N}$
385	404	403	400	tors $\text{NH}_2$
380	397	397	398	tors $\text{NH}_2$
365	357	357	361	tors $\text{NH}_2$
341	341	341	341	tors $\text{NH}_2$
306	–	–	306	tors $\text{NH}_2$
263	234	234	236	tors $\text{CN}_3$
229	224	225	229	tors $\text{CN}_3$
124	117	117	118	tors $\text{CN}_3$

m: Medium, s: strong, vs: very strong, w: weak,  $\nu$ : stretching,  $\omega$ : wagging,  $\delta$ : bending or in-plane deformation,  $\rho$ : rocking,  $\tau$ : twisting, tors: torsional,  $\nu_{\text{as}}$ : asymmetric stretching,  $\nu_{\text{s}}$ : symmetric stretching.

energy of solvation depends partly on the dielectric constant of the solvent. This is supported by the data obtained in the present calculations. It is found that the dielectric constant increases and the electrostatic contribution to the free energy of solvation of both the molecules also increase. The same trend is observed in the induced dipole moment also and it is shown in Table 2. Selected frequencies of  $\text{HC}(\text{NH}_2)_3$  and  $[\text{C}(\text{NH}_2)_3]_2$  are listed and compared with the real frequencies of these compounds. From Tables 3 and 4, we observed that the frequencies in the polar solvents are always higher than that of the nonpolar solvents. In the case of  $\text{NH}_2$  stretching frequency shows an upward shift of nearly  $250\text{ cm}^{-1}$ . The amide band ( $\text{C}-\text{N}$ ) and  $\text{NH}_2$  wagging are almost the same. The selected frequencies of  $\text{NH}_2$  twist and rock shows the downward shift of  $15\text{--}30\text{ cm}^{-1}$ .

## Conclusion

Single crystals of GCC have been synthesized and grown by slow solvent evaporation technique. The solubility curve indicates moderate solubility of GCC in water with a positive solubility temperature gradient. The X-ray diffraction analysis has been carried out to find unit cell parameters and crystallinity of the grown crystal. The spectroscopic analyses confirm the functional group of the grown guanidinium chlorochromate crystal. The low optical absorption in the entire visible and near infrared region and low

cut-off wavelength, facilitates it to be a potential material for NLO application. The SHG test confirms that the crystal is 0.464 times that of KDP. Relative dipole moments of the guanidinium compounds have been investigated in detail by PCM calculation for both molecules. We have found that the imaginary frequency as obtained by both the molecules in solvent media provides considerable shift with that of real frequencies.

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