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Spectrochimica Acta Part A 66 (2007) 1340–1346
SPECTROCHIMICA ACTA PART A
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Vibrational spectroscopic analysis of cytosine monohydrate and its copper(II) complex

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Received 9 April 2006; accepted 15 April 2006

Abstract

Single crystals of cytosine monohydrate and its copper(II) complex were grown by slow evaporation in an aqueous solution at room temperature. The solubility studies were carried out at different temperatures in deionized water. Cytosine monohydrate and the copper(II) complex of cytosine were characterized by recording IR, Raman and UV spectra. The various vibrational modes of the crystals have been classified using factor group and site group analysis. Vibrational assignments were proposed for both the systems based on the spectral investigations.

Keywords: Solubility; Factor group analysis; Vibrational analysis; Optical transmission

1. Introduction

The study of the larger bio-molecules such as DNA and proteins could well be accounted by examining the smaller functional groups of which they are composed. Cytosine is one of the pyrimidines found in the deoxyribonucleic acid that had been crystallized by many researchers [1–3] as it is one of the fundamental nucleic acid base leading to the synthesis of many nucleosides, nucleotides, etc. The cytosine molecules are hydrogen bonded in parallel ribbons and each water molecule is bonded to three cytosine's, two through the carbonyl oxygen's at 2.78 and 2.85 Å and one to the amino group at 2.97 Å. The hydrated pyrimidine complex revealed the role of water in DNA, as the hydration changes the A form of DNA to the B form [4]. Raman tool has been mainly used in the investigation of DNA conformations [5].

The metal complexes of nucleic acid bases and their derivatives have acquired much importance because of their biological activities such as antitumour, antimicrobial, etc. The present work also employs the 3d metal complex of cytosine to evaluate the differences between the complexed and uncomplexed cytosine monohydrate. The 3d metal perchlorate complexes with pyrimidine and purine bases has been widely studied due to their effective interaction of copper(II) ions with guanine–cytosine pairs of DNA, disrupting the hydrogen bonding which causes destabilization of the nucleic acid structure [6]. The interaction of metal ions with nucleic acid bases could be the reason for the modification of the properties of nucleic acids [7]. Several studies revealed the dependence of different metal binding sites of cytosine and various types of protonation on the structure of the metal complexes. Cytosine binds the metal atom through N3 site when unidentate, through N3, N4 or N3, O2 when bidentate [8–10].

The present study aims at covering the entire region of the Raman spectrum in order to get the complete phonon picture. Group theoretical method has been employed to obtain the internal and external modes of the fundamental lattice vibrations of the titled compounds. Vibrational assignments based on the IR and Raman spectral data elucidate the modes and those that are observed out of the predicted modes from theoretical considerations are assigned.

2. Experimental

2.1. Synthesis

Cytosine purchased from Lancaster Chemicals (UK) has been dissolved in deionized water and kept for the growth of cytosine

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doi:10.1016/j.saa.2006.04.046

Table 1
Influence of solvents and solvent mixtures on growth forms of cytosine monohydrate (A) and copper(II)–cytosine complex (B)

Solvent	Solubility g/100 ml		Habit		Visual quality	
	A	B	A	B	A	B
Water	7.3	4	Rectangular plates	Rectangular thick plates	Transparent colorless	Blue
Methanol	6.8	3.4	Small needles very small needles	Rectangular thin plates	Less transparent	Blue
Ethanol	6.4	3.1	Needles	Small plate like	Less transparent	Blue
Methanol + water (1:1)	7.1	3.8	Small needles	Rectangular thick plates	Transparent	Blue
Ethanol + water (1:1)	6.7	3.3		Rectangular thin plates	Transparent	Blue

monohydrate crystal. The copper(II) cytosine complex was synthesized according to the reaction:

$$Cu(ClO_4)_2{\cdot}6H_2O + 4(C_4H_5N_3O) \rightarrow Cu(C_4H_5N_3O)_4(ClO_4)_2{\cdot}2H_2O + 4H_2O$$

2.2. Solubility studies

Different solvents such as deionized water, methanol, ethanol, methanol–water 1:1 ratio and ethanol–water 1:1 ratio were tried for pure cytosine and the copper(II) complex of cytosine. Solubility in deionized water was found to be better than the mixtures and the as grown crystals were found to have better shape and transparency in deionized water. Previous literatures suggest that even with a little amount of water the probability of getting a monohydrate is very high for cytosine [3]. The solubility of the synthesized materials in various solvents and the parameters of the crystal habits are presented in Table 1.

The amount of cytosine and the copper(II) cytosine complex dissolved in 10 ml of water at 30 °C were estimated from the saturated solution. The experiment was repeated at different temperatures and the solubility of the two synthesized materials were investigated in deionized water and plotted in Fig. 1. Both the systems show a linear increase in the solute concentration with respect to temperature, however in the copper(II) cytosine complex the increase was found to be less when compared to the pure cytosine. The decrease in the solubility may be due to the reduction in pH which results in the formation of excess positive and negative ions.

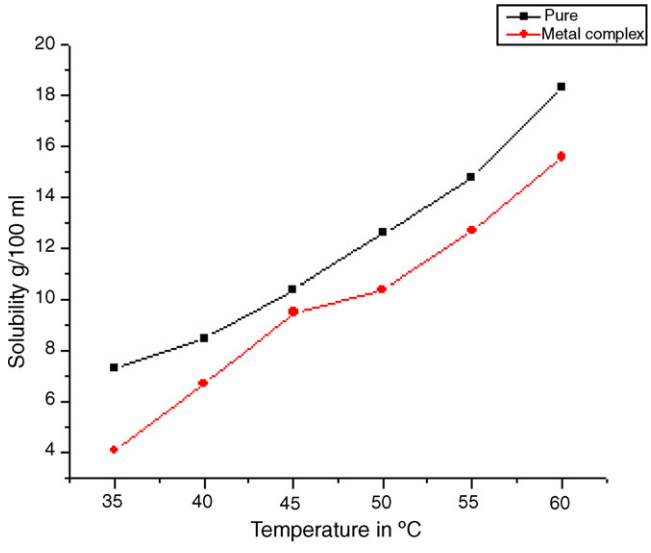

Fig. 1. Solubility curves of cytosine monohydrate and copper(II)–cytosine complex.

2.3. Crystal growth

Single crystals of cytosine and copper(II) cytosine complex were grown using water as solvent by slow evaporation technique. Single crystal of cytosine monohydrate was harvested in a week. The size of the crystals has improved after recrystallization and the size of the crystal was 10 mm × 2 mm × 0.3 mm as shown in Fig. 2(a). Cytosine and copper perchlorate were taken in the stoichiometry ratio 4:1 and dissolved in deionized water. The resulting mixture was well stirred using a magnetic stirrer, filtered and kept for slow evaporation. The synthesized salt was recrystallized a number of times in deionized water to

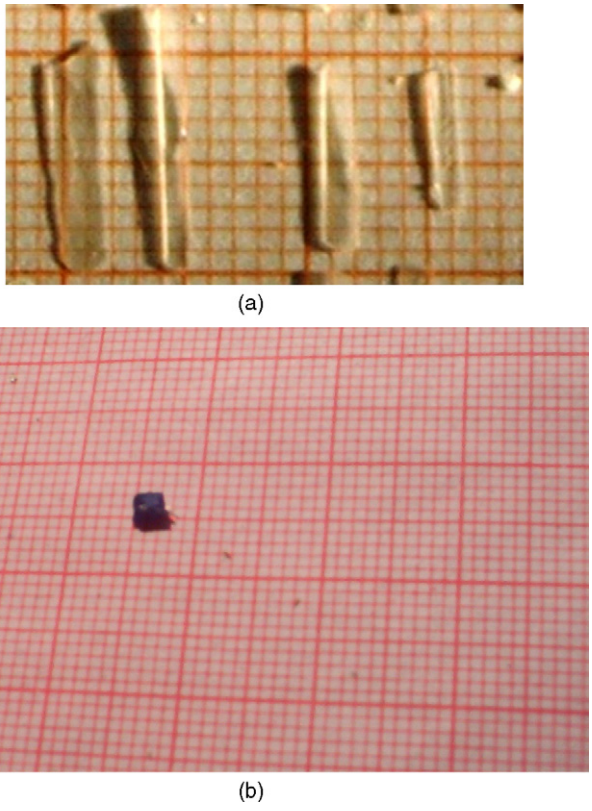

Fig. 2. (a) Water grown cytosine monohydrate crystal; (b) water grown copper(II)–cytosine complex crystal.

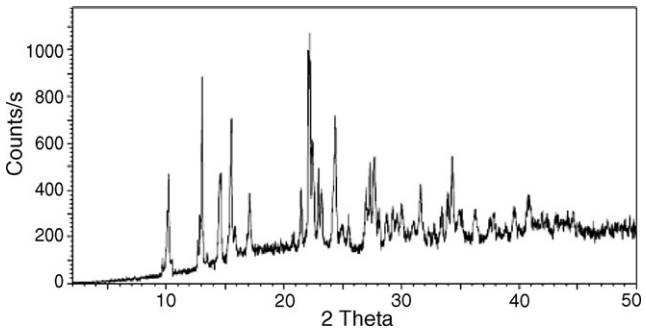

Fig. 3. Powder XRD of copper(II)–cytosine complex.

Table 2
Lattice parameters of cytosine monohydrate and copper(II) complex of cytosine

Parameters	Cytosine monohydrate[a]	Copper(II)–cytosine complex[b]	Copper(II)–cytosine complex[c]
Crystal symmetry	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/C$	P-1	P-1
Z	4	2	2
A (Å)	7.801	11.663	11.667
B (Å)	9.844	12.601	12.605
c (Å)	7.683	11.410	11.417
α (°)	90	112.63	112.71
β (°)	99.42	112.75	112.80
γ (°)	90	69.07	69.02
D	1.478	1.793	1.817
U (Å^3)	575.01	1383.9	1401.17

[a] Ref. [1].
[b] Ref. [13].
[c] Present work.

get good quality crystal of size 3 mm × 3 mm × 4 mm as shown in Fig. 2(b).

3. X-ray diffraction analysis

The copper(II) cytosine complex crystal was characterized by powder X-ray diffraction analysis to confirm its crystal structure. The Riche Seifert SH-37/80 diffractometer with the Cu Kα_1 radiation of 1.5406 Å (scanning speed of 0.5°/min) was used to record the X-ray diffraction pattern. The recorded X-ray spectrum is shown in Fig. 3. The lattice parameters derived from the diffraction pattern are found to be in agreement with the literature values and are presented in Table 2.

4. Factor group analysis

4.1. Cytosine monohydrate

The cytosine monohydrate belongs to monoclinic system and the unit cell contains four formula units. The space group of the crystal is C_{2h}–$P2_1/c$ [11]. The site symmetry is C_1. The unit cell contains 64 atoms giving rise to a total of 192 vibrational modes. These modes are classified according to the irreducible representations of the point group C_{2h}. The site correlation method of factor group analysis [12] was applied to classify the vibrational modes of cytosine monohydrate. The representation, Γ_{total}, of all the vibrations can be decomposed according to the irreducible representation of the point group C_{2h} as $[48A_g + 48A_u + 48B_g + 48B_u]$ among which are included the three acoustic modes corresponding to the block translations of the crystal Γ_{vib}, acoustic = $A_u + 2B_u$. The remaining 189 vibrations are optic modes. Group theoretical consideration shows that these 189 optical modes can be divided into 45 external modes (including rotational and translational lattice modes) and 144 internal modes. Among the 144 internal modes, the irreducible representation of cytosine molecule is $33A_g + 33A_u + 33B_g + 33B_u$ and the remaining 12 given by $3A_g + 3A_u + 3B_g + 3B_u$ correspond to water molecules. Total external vibrations specifically translations and rotations for both cytosine and water molecule are given by $12A_g + 12A_u + 12B_g + 12B_u$. Summary of the factor group analysis of cytosine monohydrate is given in Table 3.

4.2. Copper(II) cytosine complex

The copper(II) cytosine complex crystallizes in the triclinic system with P-1 space group [13]. The primitive cell consists of two molecules per unit cell comprising of 138 atoms, which are in general position. The representation corresponding to the total degrees of freedom is given by $\Gamma_N = 207A_g + 207A_u$ from where acoustic modes $\Gamma_T = 3A_u$ when removed gives a combination describing the optic modes $\Gamma_o = 207A_g + 204A_u$. Specification of the unit-cell modes can be performed as follows:

- translational lattice modes: $\Gamma_T = 27A_g + 27A_u$;
- rotational lattice modes: $\Gamma_B = 24A_g + 24A_u$;
- internal modes of the cytosine: $\Gamma_n = 132A_g + 132A_u$;

Table 3
Summary of the factor group analysis of cytosine monohydrate

Factor group C_{2h} species	4($C_4H_5N_3O$), C_1 sites		4(H_2O), C_1 sites		C_1 sites				Optical modes	Acoustic modes
	Internal modes	External modes	Internal modes	External modes	C	H	N	O		
A_g (R)	33	3T, 3R	3	3T, 3R	12	21	9	6	48	
B_g (R)	33	3T, 3R	3	3T, 3R	12	21	9	6	48	
A_u (IR)	33	3T, 3R	3	3T, 3R	12	21	9	6	47	1
B_u (IR)	33	3T, 3R	3	3T, 3R	12	21	9	6	46	2
	132	12T, 12R	12	12T, 12R	48	84	36	24	189	3

Table 4
Summary of the factor group analysis of copper(II)–cytosine complex

Factor group species C_i	$8(C_4H_5N_3O)$, C_1 sites		$4(H_2O)$, C_1 sites		$4(ClO_4^-)$, C_1 sites		Cu	General C_1 sites						Optical modes	Acoustic modes
	I	E	I	E	I	E		C	H	N	O	Cl	Cu		
A_g (R)	132	12T, 12R	6	6T, 6R	18	6T, 6R	3T	48	72	36	42	6	3	207	0
A_u (IR)	132	12T, 12R	6	6T, 6R	18	6T, 6R	3T	48	72	36	42	6	3	204	3
	264	24T, 24R	12	12T, 12R	36	12T, 12R	6T	96	144	72	84	12	6	411	3

I: internal modes; E: external modes.

- internal modes of the water molecule: $\Gamma_n = 6A_g + 6A_u$;
- internal modes of the perchlorate ion: $\Gamma_n = 18A_g + 18A_u$.

The summary of the factor group analysis of the complex system is given in Table 4.

5. Recording of spectra

FT-Raman spectra of the samples were recorded in the range 10–3600 cm^{-1} at room temperature using the BRUKER RFS 100/s Spectrophotometer which employs 1064 nm Nd–YAG laser excitation with 4 cm^{-1} resolution. The solid sample was taken in the sample holder and was subjected to laser irradiation. The orientation of the sample holder was adjusted to obtain maximum amplitude. The infrared spectra were recorded with a BRUKER IFS 66 V vacuum FT Spectrometer in the range 450–4000 cm^{-1} with a KBr pellet and extended to Far-IR in the range 100–600 cm^{-1} with CsI window.

6. Vibrational analysis

6.1. Spectrum and band assignments

The mid-IR, Far-IR and Raman spectra of cytosine monohydrate and copper(II) cytosine complex are presented in Figs. 4–6, respectively. Observed frequencies and their band assignments were listed in Table 5.

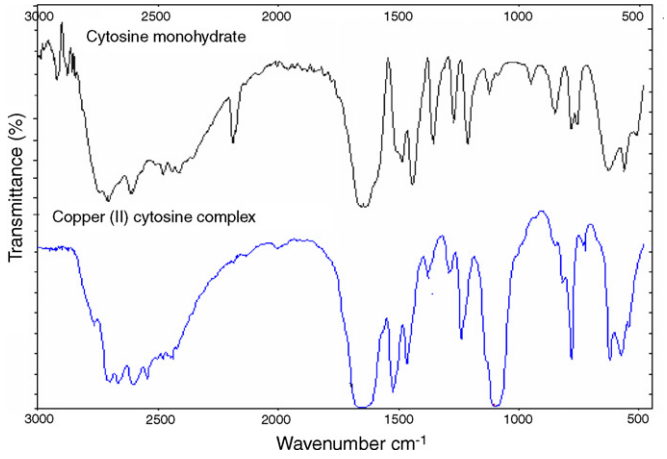

Fig. 4. FT-IR spectrum of cytosine monohydrate and copper(II)–cytosine complex.

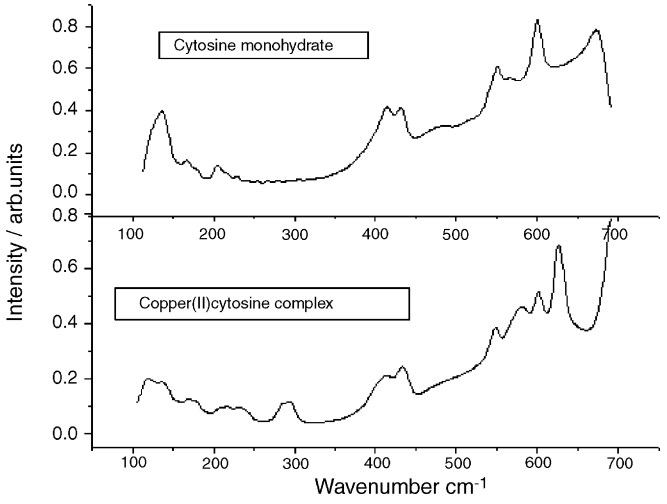

Fig. 5. Far-IR spectrum of cytosine monohydrate and copper(II)–cytosine complex.

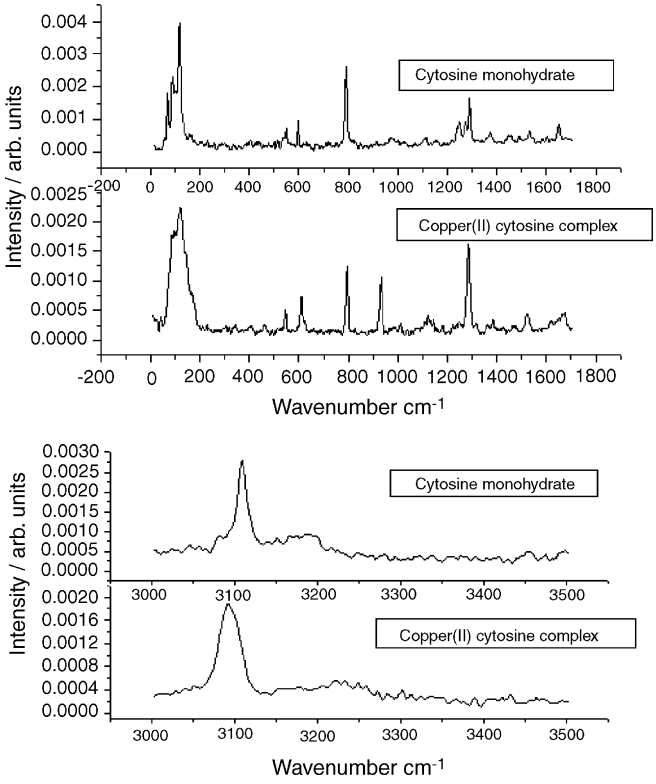

Fig. 6. FT-Raman spectra of cytosine monohydrate and copper(II)–cytosine complex.

Table 5
Assignment of various vibrational modes of cytosine monohydrate and copper(II)–cytosine complex

Cytosine monohydrate			Copper(II)–cytosine complex		
Wave number (cm^{-1})		Assignment	Wave number (cm−1)		Assignment
IR	Raman		IR	Raman	
	3453w	ν(OH)	3450m	3432w	ν(OH)
3439s		ν(OH)	3402s		$\nu(NH_2)$
3370s		$\nu_{as}(NH_2)$	3321s		$\nu_{as}(NH_2)$
3182s	3186m	$\nu_{as}(NH_2)$, ν(NH)	3215s	3221m	$\nu_{as}(NH_2)$, ν(NH)
3100m, sh	3110s	ν(CH)	3092s	3091m	ν(CH)
1664vs	1649ms	ν(C=O), ν(C=N), $\delta(NH_2)$		1674m	ν(C=O), ν(C=N), $\delta(NH_2)$
1615vs		ν(C=O), ν(C=N), $\delta(NH_2)$	1663vs	1663m	ν(C=O), ν(C=N), $\delta(NH_2)$
1540m, sh	1531m	ν(C=N), δ(NH), ν ring	1528s	1521m	ν(C=N), δ(NH), ν ring
1499ms	1489w	ν(C=N), δ(NH), ν ring	1469ms		ν(C–N), δ(NH), ν ring
1456s	1456w	ν(C=N), δ(NH), ν ring	1377w	1384w	ν(C–N), δ(CH)
	1446w	δ(CH)	1288w	1284s	ν ring, δ(CH)
1373m	1372w	ν(C–N), δ(CH)	1244m		δ(NH)
1289m	1289s	ν ring, δ(CH)		1121m	ν ring, $\rho(NH_2)$
	1276ms	δ(CH out-of phase)	1106vs	1108w	$\nu_3(ClO_4^-)$
1234m	1247ms	δ(NH)		932s	$\nu_1(ClO_4^-)$
1146w		ν ring, $\rho(NH_2)$			
977w	974w	ν ring, $\rho(NH_2)$	817w		
881mw		ν ring, $\rho(NH_2)$	787s	794s	ν ring, δ ring
814m		ν(NH)	735w		$\rho(H_2O)$
792m	790vs	ν ring, δ ring	629ms	610m	$\nu_4(ClO_4^-)$
664ms		NH_2 wagging	581ms		ν ring, δ ring
600ms	598s	ν ring, δ ring	555m	546m	NH_2 wagging
549m	549m	NH_2 wagging		461w	$\nu_2(ClO_4^-)$
497w		τ(NH)	433m		$\nu_{cytosine}$
430m		$\nu_{cytosine}$	413m		$\nu_{cytosine}$
413m		$\nu_{cytosine}$	291m		$\nu_{(Cu–cytosine)}$
204w		$\nu_{cytosine}$	232w		$\nu_{(Cu–cytosine)}$
166w			171w		
136m	120vs	Lattice	138m		
	88s	Lattice	118w	122vs	Lattice
	68s	Lattice		96s	Lattice
				88s	Lattice

6.2. Analysis of spectra

6.2.1. 3500–3100 cm^{-1} region

IR and Raman show the presence of water molecules in both ligand and its copper complex. The strong IR absorption peaks of cytosine monohydrate at 3439, 3370, 3181 cm^{-1} are shifted by 11–60 cm^{-1} in the complex and the intensity falls by 6–7%. The Raman spectra in the high frequency region support this evidence but the intensity of the peaks is very low. They are assigned to OH, NH_2 and CH stretching vibrations. The reason for the shift in the vibrational frequencies may be due to the difference in hydrogen bonding nature. In both ligand molecule and in the metal complex the hydrogen bonding is between the carbonyl oxygen and hydrogen of free amino group. In addition a H-bonding between perchlorate anion and N(1)H of cytosine strengthen the hydrogen bonding in the complex. The strength of the O–H–O hydrogen bonds can be obtained from the knowledge of the position and width of the O–H bands [14]. The O–H–O distances in cytosine monohydrate and in the copper(II) cytosine complex were around 2.80 and 2.45Å, respectively. An up shift of 11 cm^{-1} from 3439 cm^{-1} and the reduction in bond length in the case of the complex reveal the strong hydrogen bonding in the complex. The O–H vibrations are usually weak in Raman scattering [14] than its counter part IR suggest the precise assignment of OH bands in the region of study. Thus a comparison of the infrared and Raman spectra allows an additional check on the correctness of the assignment of characteristic group frequencies. An additional strong peak at 3108 cm^{-1} in Raman spectrum of the uncomplexed system and peak of medium intensity at 3220 cm^{-1} in Raman spectrum of the complexed system has been assigned to CH symmetric stretching.

6.2.2. 1700–1500 cm^{-1} region

The very strong absorption at 1663 $cm^{-1}$is retained as such but broad maxima with an increasing intensity is observed in the complex masking the absorption of the peak 1615 cm^{-1} in cytosine monohydrate. The band assigned to C=N and C=C which appears around 1540 cm^{-1} in the spectrum of the free ligand, is appreciably shifted with increased intensity of absorption in the complex in IR, whereas a shift and lesser intensity in Raman observations were noticed. This modification in the

intensity and shifts in the frequencies suggest the formation of the N(3)-bonded metal complex. Previous studies [15,16] suggest N3 as the possible site for protonation in cytosine molecule and also the preferred site for N(3) bonded metal complexes of cytosine.

6.2.3. 1500–600 cm^{-1} region

The band related to ν-ring and ν(C–N) single bonded (in plane deformations) stretching frequencies between1499 and 1373 cm^{-1} exhibits intensity changes and shifts in their frequency as a consequence of the new charge distribution in the cytosine ring. The bands shown between1288 and 600 cm^{-1} have been assigned to ring vibrations, bending vibrations and asymmetric stretching vibrations. The additional new lines in the complex are1106 and 629 cm^{-1} in IR and 1108, 932 and 611 cm^{-1} in Raman. The fact that the strong absorption at 1106 cm^{-1} in IR and weak absorption at 1108 cm^{-1} in Raman is characteristic of ClO_4^- anion [17,18] in the complex. Since ClO_4^- peak appears as a singlet without any splitting, it must be present as a single ionic entity. The other two lines in IR and Raman also correspond to the characteristic presence of ClO_4^- anion. The IR inactive peaks observed by Palaniandavar et al. at 470 and 920 cm^{-1} may be due to methanol–water solvent. The strong lines observed in IR were found to be weak in Raman and vice versa.

6.2.4. 600–50 cm^{-1} region

The region 500–200 cm^{-1} has been assigned to free ligand cytosine. A new line of weak intensity found in the complex at 461 cm^{-1} in Raman has assigned to ν_2 ClO_4^- [8] and it rarely co-ordinates with metal complexes in aqueous solution [19]. A few additional lines in the complex at 291, 232 and 212 cm^{-1} which have been assigned to $\nu_{(Cu–cytosine)}$ appear only in IR spectra [20]. The region 120–60 cm^{-1} contains few strong peaks in Raman, which may be due to the combinations of translational and librational motions of cytosines and translations of water molecules.

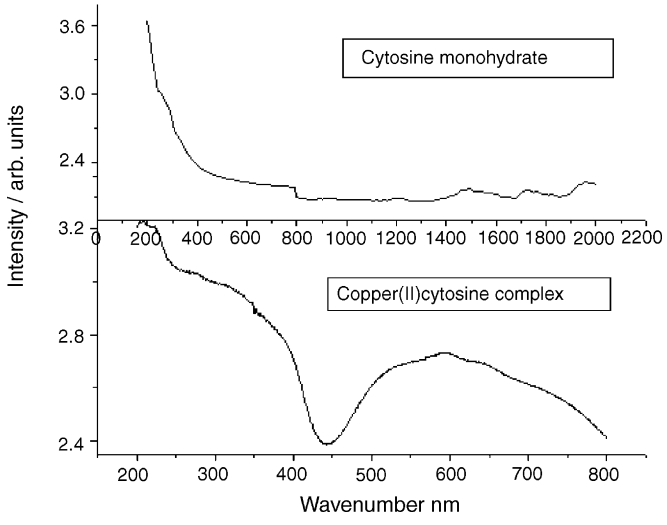

Fig. 7. Optical transmission spectrum of cytosine monohydrate and copper(II)–cytosine complex.

7. Optical transmission studies

The transmission spectrum of cytosine monohydrate and its copper(II)–cytosine complex was recorded using a Varian Cary 5E UV–vis–NIR spectrophotometer in the range 200–2000 nm with high resolution (Fig. 7). The useful transmission wavelength of cytosine monohydrate extends from 390 to 1400 nm and the lower cut-off being 390 nm. The absorbance in this region is nearly 2.2 units. In the copper(II) complex of cytosine, the lower cut off is at 440 nm with a characteristic absorption corresponding to blue light.

The large bump shown in Fig. 7 reveals the very narrow region of absorption or a strong and sharp absorption peak. This may be attributed to the strong bonding of copper to the cytosine ligand. So the region of optical transparency of the complex crystal has been drastically reduced when compared to the uncomplexed cytosine monohydrate.

8. Conclusion

Good quality single crystals of cytosine monohydrate and copper(II)–cytosine complex were grown in deionized water using slow evaporation technique. The growth rate and the yield were found to be better than the other alcohol solvents and their mixtures. The comparison of these two systems reveals the strong complexation ability of copper with cytosine. The change in the crystal structure of the complex may be due to the strong co-ordination of copper(II)–N(3) cytosine interaction and the complex hydrogen bonding between the cation and anion with the ligand cytosine.

The perchlorate anion does not have direct co-ordination with copper as it lies at a distance of 4 Å from the co-ordination plane [21], suggesting that they are held in lattice holes by coulombic forces and exhibit no indication of disorder. This has been confirmed by the very slight disorder in the tetrahedral geometry of the anion as revealed by the coincidence of the vibrational frequencies with their natural frequencies. The IR inactive ν_1 and ν_2 appear only in Raman also confirm the above evidence. The slight deviation may be due to the coordination of the anion with the ligand cytosine through hydrogen bonding. The uncomplexed cytosine monohydrte has transparency in the UV–visible region but transparency is reduced to a greater extent in the complex due to strong metal ligand interaction.

Acknowledgements

The authors are thankful to IISC, Bangalore, IIT Madras, Chennai, and IGCAR, Kalpakkam for making available their spectral facilities. One of the authors (S. Kalyanaraman) is indebted to the UGC, Government of India, New Delhi for the award of teacher fellowship under the Faculty Improvement Program and thankful to Dr. V. Umayorubagan for providing a platform for doing research at the Department of Chemistry, ST. Hindu College, Nagercoil, India.

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