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Spectroscopic investigations on salicylate complex of creatinine (A bio molecule)

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ABSTRACT

The FT-infrared and FT-Raman spectra of creatininium salicylate crystal have been recorded and analysed at room temperature. The vibrational assignments of the observed wavenumbers are proposed on the basis of group theoretical analysis. The FT-IR and FT-Raman spectra are reported in the 4000–400 cm^{-1} region. There is extensive intermolecular hydrogen bonding in the crystal and this is responsible for the changes in the position and intensity of several bands. Vibrational assignments are given for all the observed bands. A pronounced change was observed in the N–H stretching frequencies of the NH_2 group. It is proposed that the amide NH_2 group influence by the intermolecular hydrogen bond in the complexes. The hydrogen bonding effect on the creatininium modes are analysed.

Keywords: Creatininium benzoate, Infrared spectrum, Raman spectrum, Factor group analysis, Graph-set motif, Hydrogen bonding

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INTRODUCTION

Creatinine anhydride, $C_4H_7N_3O$, a nitrogenous organic acid, which is found in muscle tissue and blood and normally excreted in the urine as a metabolic waste. Urinary excretion of creatinine is relatively constant from day to day, and reflects mainly the amount of muscle tissue in the body. Therefore the amounts of various components of urine are often expressed relative to creatinine. It is mainly filtered by the kidney, though a small amount is actively secreted. There is little-to-no tubular reabsorption of creatinine. If the filtering of the kidney is deficient, blood levels rise. As a result, creatinine blood levels may be used to calculate creatinine clearance (ClCr), which reflects the Glomerular Filtration Rate (GFR). The GFR is clinically important because it is a measurement of renal function. However, in cases of severe renal dysfunction, the creatinine clearance rate will be overestimated because the active secretion of creatinine will account for a larger fraction of the total creatinine cleared. Measurement of

creatinine levels in serum and determination of renal clearance of creatinine are widely used for laboratory diagnosis of renal and muscular function [1].

NMR spectroscopic studies and high-level theoretical calculations indicate that the amino tautomer of creatinine is more stable in aqueous solutions [2, 3]. On the other hand, in the gas phase, the imino tautomer is probably more stable [4], while in a sufficiently acidic medium, creatinine is protonated apparently at N3, forming the creatininium cation with strongly delocalized charge [5, 6]. Creatinine, being a natural metabolite of creatinine, is an important bioligand. The presence of several donor groups in its main tautomeric forms determines its strong coordination capacity. The complexation ability towards a number of metal ions: Ag(I), Hg(II), Cd(II), Zn(II), Co(II), Ni(II), Cu(II), Pt(II), Pd(II) was studied [7, 8, 9, 10, 11]. Similarly studies of organic – inorganic hybrid materials, including amino acids and various inorganic acids [12, 13, 14] have received a great deal of attention in recent years because of their electrical, magnetic and optical properties [15].

Hydrogen bonds in hybrid compounds are of interest because of their widespread biological occurrence. For example, hydrogen bonds between phosphate groups and histidine imidazole groups are involved in the active-site substrate – binding mechanism of ribonucleases [16] and in regulation of the oxygen affinity of deoxy hemoglobin by 2,3-diphosphoglycreate [17]. The crystal structures of creatinine with organic/ inorganic acid complexes reported are creatininium nitrate [18], creatininium benzoate [19], Creatininium dipicolinate monohydrate [20] etc. The complexes were studied to understand the hydrogen bonding of creatinine with other acids, hence the stability and reactivity of the complexes. Based on the above specifics, in the present investigation, creatinine was treated with the salicylic acid and the title compound was crystallized.

MATERIALS AND METHODS

Preparation

Crystals of creatininium salicylate were crystallized from an aqueous solution of creatinine and salicylic acid with a stoichiometric ratio of 1:1 at low temperature by slow evaporation. After 8 days, needle-shaped, transparent and colorless crystals of creatininium salicylate were obtained.

Single crystal XRD studies

Unit cell parameters and structure of creatininium salicylate crystal were determined from single-crystal X-ray diffraction data obtained with a Bruker SMART APEX CCD area detector diffractometer (graphite-monochromated, MoK_α = 0.71073 Å).

Unit cell dimensions	a = 7.6764(3) Å $\alpha = 90°$
	b = 12.4775(8) Å $\beta = 101.12(5)°$
	c = 12.4186(9) Å $\gamma = 90°$
Volume	V = 1167.3(4) Å^3

The above results are perfectly matches with the earlier results [21]. Hence, the crystalline phase is confirmed and the CIF of the creatinine salicylate is used for further calculations.

Vibrational spectroscopic measurements

Infrared spectral measurements were made with a Nexus 670 FTIR spectrometer with a resolution of ~1–2 cm^{-1} over the range 4000–400 cm^{-1}, the samples being mixed with KBr powder and pressed into discs under high pressure. The disc was used to obtain good spectra. Radiation of 1064 nm from the same Nexus 670 FT Raman spectrometer of Nd:YAG laser was used as the source of excitation. The laser power was maintained at 1.5 watts. The spectral range is in the range of the 3600 – 100 cm^{-1} for stokes lines and 2000 – 200 cm^{-1} in anti-stokes lines. The measured spectral lines had a resolution of 2–3 cm^{-1} in the same range of the wavenumber. Indium-Gallium Arsenide detector is used as a detector.

RESULTS AND DISCUSSION

Crystal structure and factor group analysis

The unit cell of the crystal is determined using Bruker SMART APEX CCD area-detector diffractometer. The unit cell has four formula units (Z = 4). The crystal structure and information about the hydrogen bonds were already reported in x-ray diffraction study [21]. The asymmetric unit contains one creatininium cation and one salicylate anion (Figure 1), crystallographic data are presented in Table 1. The H atom of the salicylic acid is migrated to the N site of the creatinine leading to the expected creatininium cation and salicylate anion. This is reflected in the spectrum from the wavenumbers of the functional groups, like amine and carboxyl groups.

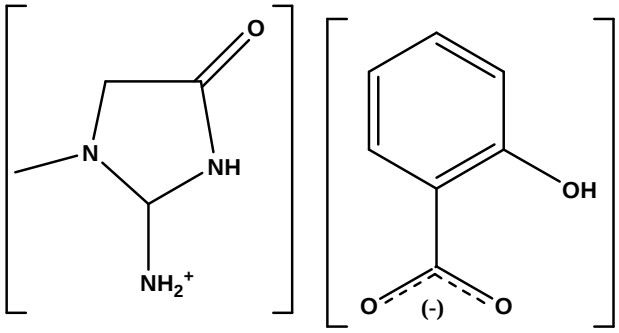

Figure 1. Scheme diagram of creatininium salicylate

Table 1. Crystallographic Data

Particulars	Creatininium salicylate
Molecular Formula	$C_4H_8N_3O^+.C_7H_5O_3^-$
Molecular weight	251.24
Unit cell dimensions	a = 7.6763(3) Å b = 12.4775(8) Å c = 12.4187(9) Å β = 101.12(5)°
Volume	1167.3(4)Å^3
Crystal system	monoclinic
Space group	$P2_1/n$
Z, Density	4, 1.431 Mgm^{-3}

Factor Group Analysis

Factor group analysis is a method used for determining symmetry of vibrations. The numbers of normal modes of the crystals creatininium salicylate were determined by group theory analysis using the correlation method based upon the symmetry of the molecules. The results obtained are presented in the Table 1. Factor group analysis using the standard correlation method was carried out [22, 23]. There are 369 vibrational modes excluding the three acoustic modes ($\Gamma_{\text{acoustic}} = A_u^{IR} + 2B_u^{IR}$). It is distributed as $\Gamma_{crystal} = 93A_g^{IR,R} + 93B_g^{IR,R} + 92A_u^{IR} + 91B_u^{IR}$. The A_g and B_g species are IR and Raman active. The other two vibrational species A_u and B_u are only Raman active. The molecular configuration of the title compound is show in Figure 2.

Table 1 Factor group analysis of creatininium salicylate $(C_4H_8N_3O)^+.(C_7H_5O_3)^-$; space group: $P2_1/n = C_{2h}$; z = 4

	Modes and degrees of freedom for each species		Site symmetry C_1	Factor group analysis C_{2h}
Creatininium $(C_4H_8N_3O)^+$	Vibrational	168	A	$42A_g+42B_g+42A_u+42B_u$
	Translational	12	A	$3A_g+3B_g+3A_u+3B_u$
	Libration	12	A	$3A_g+3B_g+3A_u+3B_u$
Salicylate $(C_7H_5O_3)^-$	Vibrational	156	A	$39A_g+39B_g+39A_u+39B_u$
	Translational	12	A	$3A_g+3B_g+3A_u+3B_u$
	Libration	12	A	$3A_g+3B_g+3A_u+3B_u$

$$\Gamma_{\text{vibrational}} = 81A_g^{IR,R} + 81B_g^{IR,R} + 81A_u^{IR} + 81B_u^{IR};\ \Gamma_{\text{translational}} = 6A_g^{IR,R} + 6B_g^{IR,R} + 6A_u^{IR} + 6B_u^{IR};$$

$$\Gamma_{\text{rotational}} = 6A_g^{IR,R} + 6B_g^{IR,R} + 6A_u^{IR} + 6B_u^{IR};$$

$$\Gamma_{crystal}^{total} = \Gamma_{(C_4H_8N_3O)^+} + \Gamma_{(C_7H_5O_3)^-} = 93A_g^{IR,R} + 93B_g^{IR,R} + 93A_u^{IR} + 93B_u^{IR};\ \Gamma_{\text{acoustic}} = A_u^{IR} + 2B_u^{IR};$$

$$\Gamma_{crystal} = \Gamma_{crystal}^{total} - \Gamma_{acoustic} = 93A_g^{IR,R} + 93B_g^{IR,R} + 92A_u^{IR} + 91B_u^{IR}$$

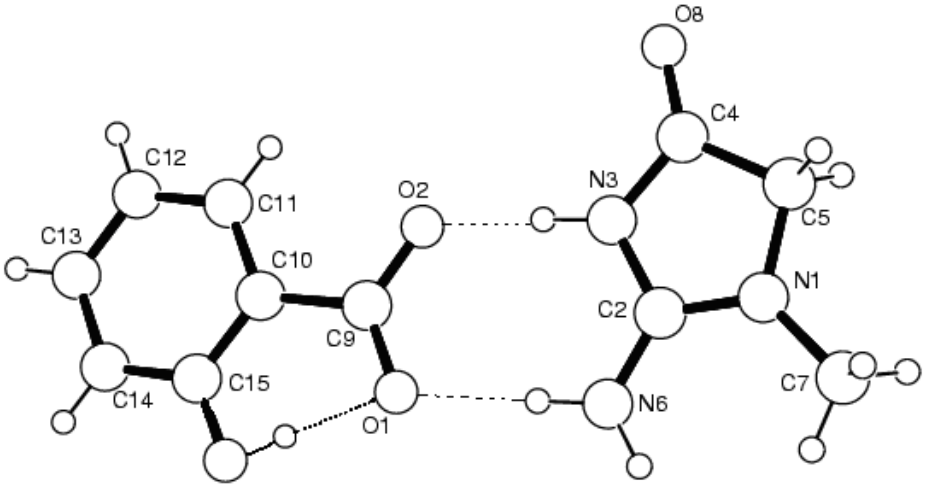

Figure 2 Structural view of creatininium salicylate which shows self associated S(6) motif and ring $R_2^2(8)$ motif

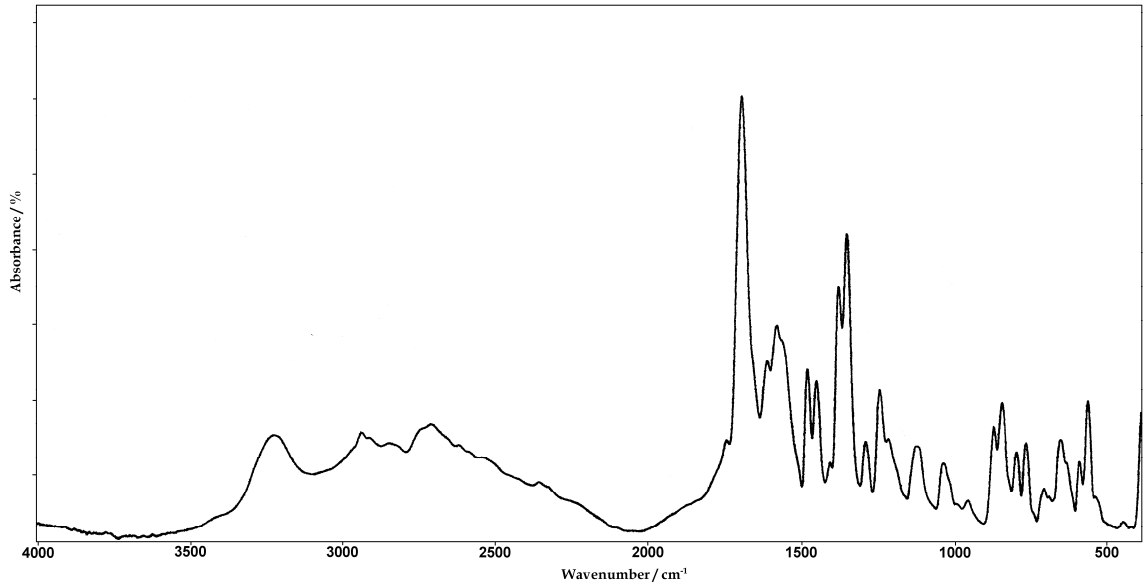

Figure 3 Infrared spectrum of creatininium salicylate

Vibrational Analysis

The normal modes of vibrations are classified into skeletal or fingerprint vibrations that involve many of the atoms to move the same extent and characteristic group vibrations, which involve only a small portion of the molecule. The crystal creatininium salcylate is identified with many functional groups like, NH_2, NH, CH_3, CH_2, C=O, C-N, COO-, C-O(H), O-C=O, C-C=O, C-C-O and O-C-O. In addition skeletal vibrations like C-C, C-C-C, C-C-N, C-N-C, N-C-N and C-C-C-C also exist in this compound. The characteristic wavenumbers of these groups are expected to change in their intensity and position according to their environment and the hydrogen bonding association in the

crystal packing. The crystal packing is stabilized through the classical N-H…O and O-H…O interactions and non-classical C-H…O interactions [21]. The asymmetric unit itself contains ring $R_2^2(8)$ motif [24]. These enriched hydrogen bonds are expected to change the position and intensity of the wavenumbers considerably. The observed infrared and Raman spectra are presented in Figures 3 and 4 respectively. The observed wavenumbers together with the proposed assignments are given in Table 2.

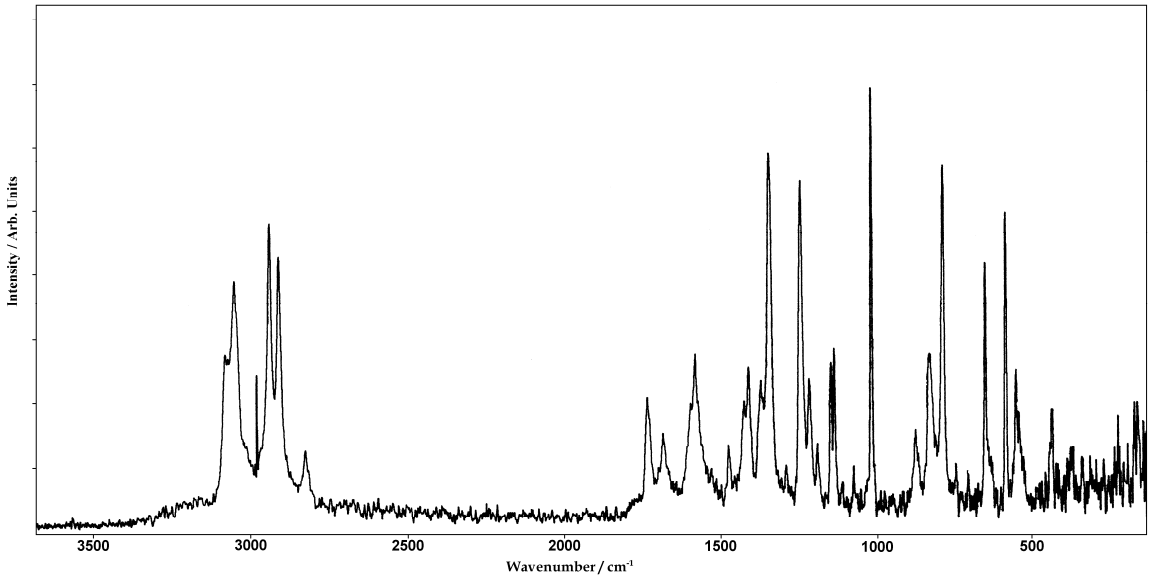

Figure 4 Raman spectrum of creatininium salicylate

Spectra of aromatic compounds in the infrared region, from 4000 to 800 cm^{-1} contain bands that are characteristic of the aromatic group. These bands are primarily associated with the motion of the benzene ring at the aromatic C-H bonds [25]. The high wave number region around 3500-1500 cm^{-1} consist the bands due to NH_2, CH_3, CH_2, C=O, COO^-, C-N, N-H and C-H stretching vibrations. The low wave number region around 1500-450 cm^{-1} contains bands due to deformation, twisting and rocking vibrations of the various groups. The skeletal vibrations are all coupled together and they occur in the region around 1150-500 cm^{-1}. The lattice vibrations occur below 400 cm^{-1}.

Vibration of Creatininium Cation

The structural investigation of the tile compound reveals the protonation on the N site of the creatinine molecule and its cationic nature. The asymmetric unit of the tile compound contains one creatininium cation and one salicylate anion (Fig. 2), with normal bond lengths and angles corresponding to those observed in similar structures [18, 21]. The expected proton transfer from salicylic acid to creatinine occurs at N3 of the imidazolyl ring. This result in an increase in the C2—N3 bond distance and a decrease of C2-N6 compared with the corresponding values found in the neutral creatinine molecule [26].

The creatininium cation is linked to anion through three two centered N-H…O and one two centered O-H…O hydrogen bonds. This strong and moderate hydrogen bonds lead to downshifting of the stretching mode of vibrations in high wave number region. The N-H asymmetric stretching frequency is observed in the 3060 cm^{-1} in the Raman spectrum which is superimpose of the bands due to the $-CH_3$, $-CH_2-$ and –OH stretching frequencies. The same is observed at 3123 cm^{-1} in the infrared spectrum as a broad medium band. As well, the amine group, NH_2, shows the bending vibrational wavenumbers in the regions of 1660-1610 cm^{-1}. The medium intensity band at 1619 cm^{-1} in infrared is assigned for asymmetric deformation mode.

The C-N asymmetric stretching modes of vibrations lie in the expected region. It is observed as a strong band in the infrared spectrum and a medium band in Raman spectrum at 1487 cm^{-1}. Normally, this band is observed along with the $-CH_2$ rocking frequency, the fundamental of which is observed near 700 cm^{-1}. The same case is repeated here

with the fundamental of rocking frequency is observed at 716 cm^{-1} as a weak band. The band at 1458 cm^{-1} in IR spectrum is overlapping of C-N stretching and CH_2 rocking frequencies.

Table 2. Observed vibrational ($\bar{\nu}$) bands for creatininium salicylate

Infrared $\bar{\nu}$ / cm^{-1}	Raman $\bar{\nu}$ / cm^{-1}	Assignment
3228 m		O-H & C-O(H) str.; N-H...O str.
	3123 m	NH_2 asym. str.
	3060 s	N-H asym. str. ; Aromatic C-H str.
	2989 s	CH_3 asym str.; (C)O-H str.
2944 m	2947 s	CH_3 sym str.
	2918 s	CH_2 asym str.
	2834 m	CH_2 sym str.
2718 m		C=O & O-H str. unconj.
	1745 m	C=O str.
1699 vs	1695 m	
1619 m		NH_2 asym def.
1587 s	1592 s	COO^- asym str.
1487 s	1487 m	C-N asym str.; CH_2 rock
1458 s		C-N asym str.; CH_2 rock
	1422 m	CH_3 asym def.
1384 s	1379 m	COO^- sym str.; CH_3 sym. def.
1357 vs	1357 vs	CH_3 sym def.; CH_2 wag; O-H i.p. def.
1298 w		C – OH i.p.def.
1251 m	1256 vs	CH_2 twist
	1228 m	CH def.
1204 sh	1202 m	CH i.p.def.
	1159 s	CH def
	1148 s	C – OH str.
1134 m		NH_2 rock
	1086 m	Phenol O-H & C-O Stretch
1045 w		C-C-N asym str.; CH_2 wag.
	1029 vs	C-N sym Str. ; CH_3 rock.
991 w		C-N sym str.; CH_3 rock
880 w	890 m	C – C – N sym str.
852 m	847 s	C – C str
806 w	802 vs	Aromatic C-H Bending; Benz.1,2-disub
775 m		Aromatic C-H Bending
	762 w	Aromatic C-H Bending
	723 w	Aromatic C-H Bending
716 w		CH_2 rock
661 m	668 m	COO^- sciss.
600 w	603 s	O-C=O i.p. def.
572 m	569 m	C-C=O def.
	561 m	COO^- wag
	476 w	COO^- rock; C-C=O i.p. def.
	456 m	COO^- rock
	442 w	COO^- rock
	434 w	C-C-C-C. i.ph. def.
	415 w	C-C-C-C. i.ph. def.
	407 w	C-C-C-C. o.ph. def.
	388 w	C-C-C-C. o.ph. def.
	361 w	
	334 w	
	314 w	
	291 w	
	256 w	Lattice vibration
	245 w	
	214 w	
	192 w	
	164 w	

The CH_3 asymmetric and symmetric stretching modes are expected to occur nearly at 2980 - 2890 cm^{-1}, respectively. In this compound, the presence of Raman line at 2989 cm^{-1} corresponds to asymmetric stretching vibration. The wavenumbers at 2944 cm^{-1} in infrared spectrum and 2947 cm^{-1} in Raman spectrum correspond to the CH_3 symmetric mode. Generally, the wavenumbers of the CH_2 vibrational modes depend on its immediate

environment. The stretching modes of the CH_2 group usually occur in the region 3100-2800 cm^{-1}. A medium intensity of Raman line at 2834 cm^{-1} is assigned to CH_2 symmetric stretching mode of vibration. The medium intensity Raman line at 1422 cm^{-1} is due to CH_3 asymmetric deformation [27,28]. A strong IR band at 1384 cm^{-1} and a medium band at 1379 cm^{-1} are assigned to CH_3 symmetric deformation and COO^- symmetric stretching modes of the vibrations. The spectral lines in the region of 1000-1100 cm^{-1} are due to C-N symmetric stretching vibrations. A very strong band at 1029 cm^{-1} is due to the rocking mode of the CH_3 group vibration coupled with the C-N symmetric stretching frequency. The same is observed at 991 cm^{-1} in the IR spectrum as a weak band.

There is one CH_3 group in the creatininium cation which is performing the deformation vibration. This deformation mode is observed at 1422 cm^{-1} in Raman spectrum as a medium intensity band. The bending frequencies like wagging, twisting and rocking modes of CH_2 vibrations have been greatly influenced in the spectra. Generally, the wagging modes of CH_2 groups are expected to spread out over a wide frequency region, viz., 1357-1170 cm^{-1}. Here, the CH_2 wagging mode is observed as at 1357 cm^{-1} in Raman spectrum. The rocking frequencies of the CH_2 group are observed at 1487 and 991 cm^{-1} in IR spectrum and a medium peak at 1487 cm^{-1} in Raman spectrum.

Vibration of Salicylate anion

The observed assignments of the salicylate anion are coinciding well with that of ethyl salicylate and methyl salicylate [29, 30]. The ionized carboxylic group gives rise to antisymmetric COO^- stretch at 1600-1570 cm^{-1} and symmetric COO^- stretch around 1400 cm^{-1}. In the present compound the strong intensity lines at 1587 cm^{-1} in the IR spectrum and 1592 cm^{-1} in Raman spectrum has been assigned to asymmetric stretching mode vibrations of ionized carboxylic group (COO^-). Strong band at 1384 cm^{-1} in IR spectrum and medium intensity band at 1379 cm^{-1} in Raman spectrum correspond to COO^- symmetric stretching mode of vibration. These bands are lower than the expected range owing to strong hydrogen bonding interactions which was revealed in the X-ray crystallographic data [21].

The rocking, wagging, scissoring in-plane and out-of-plane deformation modes of COO^- ionized carboxylic group are expected at 502, 577 and 665 cm^{-1}, respectively. For the title compound, the rocking modes are spread over 476, 456 and 442 cm^{-1} in Raman and the wagging mode appears at 572 cm^{-1} in IR spectrum and 561 cm^{-1} in Raman spectrum. The scissoring deformation mode is identified as medium intensity lines at 661 cm^{-1} in IR spectrum and 668 cm^{-1} in Raman spectrum.

The O-C=O in-plane deformation mode is observed as a strong intensity line at 603 cm^{-1} in Raman and a weak intensity peak at 600 cm^{-1}. A medium band at 572 cm^{-1} in IR and a strong band at 569 cm^{-1} in Raman is attributed to the same C-C-O deformation modes.

Normally, the absorption bands in the region 3600 - 3200 and 3100 - 2800 cm^{-1} are due to O-H and C-H stretching vibrational modes of phenol. The presence of O-H group and the O…H bond involved in the hydrogen bonding interactions give rise to a moderate intensity line at 3228 cm^{-1} in Raman in overtone with the water in the KBr pellet. The O-H in-plane deformation mode is observed at 1357 cm^{-1} in both the spectrum with the overlapping of $-CH_3$ and CH_2 deformational modes. This indicates the presence of salicylate ion. Aromatic C-H ring stretching is observed at 3060 cm^{-1} in Raman as overlapped with the N-H asymmetric stretching mode. The C-C-C-C in-phase deformation modes are observed as a weak intensity bands at 434 and 415 cm^{-1} in Raman spectrum. The out-of-phase deformation modes are observed as weak intensity peaks at 407 and 388 cm^{-1} in Raman spectrum.

Hydrogen Bonding

The N-H and NH_2 site of the creatininium cations are making strong hydrogen bonds with the carboxylate O atoms of the salicylate anions. Three intermolecular N-H…O and one intramolecular O-H…O hydrogen bonds are observed in the structure. Hence, the structure is observed to exhibits a three dimensional hydrogen-bonding pattern with three two-centered hydrogen bonds. The crystal has four salicylate anion groups in the unit cell and they help in stabilizing the crystal structure through hydrogen bonding. The bond lengths for strong, normal and weak hydrogen bonds are 2.4-2.7 Å, 2.7-2.9 Å, above 2.9 Å, respectively [31]. It will cause a downshifting of stretching mode of vibrations and up shifting of deformation modes.

This is reflected in the infrared spectrum of the compound, where the strong and broad band in the Raman spectrum, which is attributed to N-H asymmetric stretching. This is shifted down around 120 cm^{-1} from the expected free ion value. Normally, the linear distortion is much greater than the angular distortion leading to the linear distortion shift

as a high value, which is also observed in the present case. The stretching frequencies of O-H groups are lowered around 300 cm^{-1}, which is an essential proof for the existence of hydrogen bonds. Normally, the phenol OH group is observed around 3650-3600 cm^{-1} for free state. But, in hydrogen bonded OH groups, these stretching frequencies will be downshifted for few hundreds of wavenumbers and bending frequencies will be upshifted. The O-H bending frequency at 1086 cm^{-1} is observed to be upshifted nearly 136 cm^{-1}.

The IR spectra of the compound obtained in KBr, Nujol and Fluorolube generally show a strong broad absorption band around 3500 cm^{-1}. In the title compound also, a medium band at 3228 cm^{-1} is observed in the IR spectrum which is assigned to the water O-H stretching band. This is also downshifted due to the hydrogen bonding interaction.

CONCLUSION

The infrared and Raman vibrational modes of creatininium salicylate have been assigned. The title compound is confirmed from the x-ray unit cell determination. The migration of hydrogen from salicylic acid to the N site of the creatinine and the formation of the creatininium cation and salicylate anion is confirmed in x-ray structural preliminary investigation. The same is reiterated in the spectral investigations with the carboxylate and -NH fundamental frequencies. Further the skeletal vibrations are assigned to the corresponding group. The downshifting of several stretching wavenumbers together with increases in many of the deformation wavenumbers confirms the existence of extensive intermolecular hydrogen bonds.

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REFERENCES

[1] M. B. Madaras, R. P. Buck, *Anal. Chem.*, **1996**, 68, 3832.
[2] D. Kotsyubynskyy, S. Molchanov, A. Gryff-Keller, *Pol. J. Chem.*, **2004**, 78, 239.
[3] J. S. Craw, S. P. Greatbanks, I. H. Hillier, M. J. Harrison, N. A. Burton, *J. Chem. Phys.*, **1997**, 106, 6612.
[4] A. R. Butler, C. J. Glidewell, *J. Chem. Soc. Per. Trans.*, **1985**, 2, 1465.
[5] R. E. Reddick, G. L. Kenyon, *J. Am. Chem. Soc.*, **1987**, 109, 4380.
[6] A. Olofson, K. Yakushijin, D. A. Horne, *J. Org. Chem.*, **1998**, 63, 5787.
[7] A. J. Canty, M. Fyfe, B. M. Gatehouse, *Inorg. Chem.*, **1972**, 17, 1467.
[8] M. R. Udupa, B. Krebs, *Inorg. Chim. Acta*, **1979**, 33, 241.
[9] S. Muralidharan, K. S. Nagaraja, M. R. Udupa, *Transit Met Chem.*, **1984**, 9, 218.
[10] M. Miteva, P. R. Bontchev, K. Kabassanov, *Polyhedron*, **1985**, 4, 1159.
[11] P. R. Bontchev, M. Mitewa, G. Gesntcheva, J. Macicek, O. Angelova, V. I. Nefedov, Proc 11th Conf Coord Chem., **1987**, Smolenice, CSSR , 35.
[12] N. Benali-Cherif, L. Bendheif, K. Bouchouit, A. Cherouana, *Ann. Chim. Sci. Mater.*, **2004**, 29, 11
[13] K. Bouchouit, N. Benali-Cherif, L. Benguedouar, L. Bendheif, H. Merazig, *Acta Cryst.*, **2002**, E58, 1397.
[14] L. Bendheif, N. Benali-Cherif, L. Benguedouar, K. Bouchouit, H. Merazig, *Acta Cryst.*, **2003**, E59, 141.
[15] C. R. Kagan, D. S. B. Mitzi, C. D. Dimitrakopoulos, *Science*, **1999**, 286, 945.
[16] M. F. Richards, H. W. Wyckoff, W. D. Carison, N. M. Allewell, M. Lee, Y. Mitsui, *Cold Spring Harbor Symp Quant Biol.*, **1972**, 36, 25.
[17] M. F. Pesrutz, I. F. Ten Eyck, *Cold Spring Harbor Symp Quant Biol.*, **1972**, 36, 295.
[18] F. Berrah, H. Lamraoui, N. Benali-Cherif, *Acta Cryst.*, **2005**, E61, o210.
[19] S. A. Bahadur, S. Sivapragasam, R. S. Kannan, B. Sridhar, *Acta Cryst.*, **2007a**, E63, o1714.
[20] A. Moghimi, M. A. Sharif, H. Aghabozorg, *Acta Cryst.*, **2004**, E60, o1790.
[21] S. Goswami, S. Jana, A. Hazra, H. K. Fun, S. Anjum, A. Ur. Rahman, *Cryst. Eng. Comm.*, **2006**, **8**, 712-718.
[22] W. G. Fateley, F. R. Dollish, N. T. McDevitt, F. F. Bentley, Infrared and Raman Selection Rules for Molecular and Lattice Vibrations (Wiley, New York, **1972**).
[23] F. A. Cotton, Chemical Applications of Group Theory (2nd Ed., Wiley Eastern Limited, **1990**).
[24] J. Bernstein, R. E. Davis, L. Shimoni, N. L. Chang, *Angew Chem. Int. Ed. Engl.*, **1995**, 34, 1555.
[25] J. C. Hawkes, A. J. Neale, *Spectrochimica Acta*, **1960**, 16(6), 633.

[26] G. Smith, J. M. White, *Aust. J. Chem.*, **2001**, 54, 97.
[27] N. B. Colthup, L. H. Daly, S. E. Willely, Introduction to Infrared and Raman Spectroscopy (Academic Press, New York, **1990**).
[28] F. R. Dollish, W. G. Fateley, Characteristic Raman Frequencies of Organic-Compounds (Wiley, New York, **1973**).
[29] C. Yohannan Panicker, Hema Tresa Varghese, L. Ushakumary, Journal of Raman Spectroscopy, **2009**, 40, 2023.
[30] Hema Tresa Varghese, C. Yohannan Panicker, Daizy Philip, James R Mannekutla, S. R. Inamdar, Spectrochimica Acta Part A Molecular and Biomolecular Spectroscopy, **2007,** 66, 959.
[31] I. D. Brown, *Acta Crystallogr*., **1976**, A32, 24.