Dedicated to Professor Ivan Petrov on the occasion of his 80th birthday

VIBRATIONAL STUDY AND SPECTRA-STRUCTURE CORRELATIONS IN MERCURY(II) CHLOROSACCHARINATE

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The vibrational spectra (infrared and Raman) of mercury(II) chlorosaccharinate in the 4000–380 cm^{-1} region (for infrared) and 1800–30 cm^{-1}) region (for Raman) are studied. The spectral assignments are based on the literature data for the *ab initio* calculations on the free deprotonated saccharinato species as well as the experimental data for the previously studied metal saccharinates. Special attention is paid to the CO and SO$_2$ stretching regions. Spectral characteristics of the studied compound are compared with the corresponding ones in the mercury(II) saccharinate and di-µ-chloro-bis[saccharinatopyridinemercury(II)]. The appearance of the spectra in the region of the carbonyl and sulfonyl stretching modes is correlated with the number of non-equivalent CO and SO$_2$ groups in the structure. It is found that the existence of only one type of CO and SO$_2$ groups in the structure is followed by the appearance of a single $\nu(CO)$ band as well as of only one pair of $\nu(SO_2)$ bands (antisymmetric and symmetric) in the infrared and Raman spectra. The small degree of the frequency lowering of the $\nu(CO)$, $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes in the spectrum of the studied compound compared to the corresponding modes in saccharin agrees well with the previously determined covalent character of the mercury-to-saccharin bonding in mercury(II) chlorosaccharinate.

Key words: mercury(II) chlorosaccharinate; FTIR spectrum; Raman spectrum; spectra-structure correlations

INTRODUCTION

Saccharin (*o*-sulfobenzimide) contains three functional groups (carbonyl, imino and sulfonyl) which are connected to each other in a five-membered ring condensed to a benzene ring. Its deprotonated form shows pronounced ability for complexation with various metals serving as a versatile polyfunctional ligand. It can be incorporated as an ion or a ligand, and often both as non-coordinated and coordinated saccharinato species in the same structure. The type of metal-to-saccharinato bonding in the saccharinates is found to extend from ionic to purely covalent. Acting as a ligand, however, deprotonated saccharin coordinates mostly through the nitrogen atom.

Working on the investigation of the coordination properties of saccharin in various metal saccharinates, in addition to other compounds, we have studied the structural characteristics of mercury(II) saccharinate [1] and mercury(II) chlorosaccharinate [2]. The study has shown that covalent type of mercury-to-saccharin bonding (through nitrogen atom) exists in both structures. However, contrary to mercury(II) saccharinate, where *four* crystallographically different saccharinato ligands are present in the structure, only *one* type of deprotonated saccharinato species is found in the mercury(II) chlorosaccharinate structure [2].

The compound is a convenient model for the detailed analysis of its vibrational (infrared and Raman) spectra as well as for correlation of the frequencies and the number of bands in the corresponding spectra with the crystallographic data. Comparisons were also made to the reported *ab initio* force field treatment for saccharin and its nitranion [3].

EXPERIMENTAL

The title compound is synthesized by addition of HgCL₂ water solution to a warm water solution of saccharin. White prismatic polycrystalline precipitate is obtained almost immediately. In order to obtain single crystals, precrystallization was performed from water or ethanol. More details of the procedure are given in [1].

The FT infrared spectrum in the 4000–380 cm⁻¹ frequency range is recorded with a System 2000 interferometer (Perkin-Elmer). Either 32 background and 64 sample or 128 background and 256 sample spectra at resolution from 1 to 4 cm⁻¹ were averaged. Since some differences were observed between the

spectra recorded in KBr and paraffin oil in the region of the ν(OH) and δ(HOH) modes, and consequently in the region of the CO stretches, the 4000–1500 cm⁻¹ spectral region was recorded in Nujol emulsion. The region from 1500 to 380 cm⁻¹ was obtained from KBr pellet. Solution spectra were not recorded because the compound was not soluble in available solvents, convenient for this technique.

The Raman spectrum of the powder sample, in the 1800–30 cm⁻¹ region, is recorded on a Renishaw 2000 instrument equipped with a Leica microscope, using a 514 nm argon-ion or a 780 nm diode lasers.

DESCRIPTION OF THE STRUCTURE

Crystal structure determination of the studied compound, in details, has already been published [2]. Here, only the basic characteristics will be mentioned: The title compound crystallizes in orthorhombic system, space group $Pca2_1$, with parameters of the unit cell: $a = 20.530(5)$, $b = 4.767(2)$, $c = 9.467(2)$ Å, $V = 926.5(8)$ Å³, $Z = 4$. The structure is built up of individual $C_7H_4ClHgNO_3S$ molecules. The mercury atom has a digonal characteristic coordination being bonded to the saccharinate N atom and Cl atom. The Hg–Cl and Hg–N bond lengths are 2.263(3) and 2.021(8) Å, respectively. The above mentioned Hg–Cl distance is significantly shorter compared to the corresponding values for the Hg–Cl distances [2.533(2) and 2.715(2) Å] found in di-μ-chloro-bis[saccharinatopyridinemercury(II)] [4] where two monomeric chloropyridinemercury(II) saccharinate moieties are joined, forming a tetrahedral arrangement around the mercury

atom. Similarly, the Hg–N bond length in the title compound [2.021(8) Å], where the Hg atom has a digonal characteristic coordination, is shorter compared to the Hg–Nsac* bond length [2.106(7) Å] in the above mentioned di-μ-chloro bridged complex [4] with a tetrahedrally coordinated mercury atom. The influence of the coordination pattern of the mercury atom on the Hg–N distance is clearly seen in the case of structures of the studied mercury(II) chlorosaccharinate [2], on the one hand, and mercury(II) saccharinate [1], on the other. Namely, the digonal characteristic coordination of the mercury atom in both compounds is followed by the presence of rather similar Hg–N distances in their structures [[2.021(8) Å for the former and 2.03(1) to 2.06(1) Å for the latter compound]. The Cl–Hg–N angle in the studied compound deviates only slightly from linearity [177.6(3) °].

RESULTS AND DISCUSSION

The FT IR spectrum of the studied compound in the 4000-1500 cm⁻¹ region recorded in the Nujol emulsion is shown in Fig. 1, whereas the spectral region from 1500 to 380 cm⁻¹ obtained from the KBr pellet is given in Fig. 2. The Raman spectrum is shown in Fig. 3. The corresponding vibrational assignments for the deprotonated saccharinato moieties in the 1800–50 cm⁻¹ region are given in Table 1.

General considerations

The assignment of the bands in the vibrational spectra of the studied compound was made consid-

ering the earlier HF/3-21G(d) results for the free deprotonated saccharin species and the experimental values for its DMSO solution [3] as well as the available literature data for the earlier empirical assignments of the spectra of various saccharinato complexes and salts [5–14]. Although one should be cautious when direct comparison between the spectrum of the molecular species and the corresponding deprotonated saccharin entities are made, having in mind that the phenylene ring of saccharin is the relatively less affected part by the depro-

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*Sac stands for deprotonated saccharin.

tonation compared to the sulfocarboximide moiety [3], the benzenoid Raman active modes in the saccharin spectrum as well as in the spectra of previously studied $[Fe(H_2O)_4(sac)_2 \cdot 2H_2O$ [8] and a series of alkali saccharinates [13] should be recognized in the spectra of the studied compound. Consequently, the intense Raman bands at 1015 and 702 cm^{-1} (Fig. 3) could undoubtedly assigned as in-plane and out-of-plane bending modes of the saccharinato benzene ring, respectively.
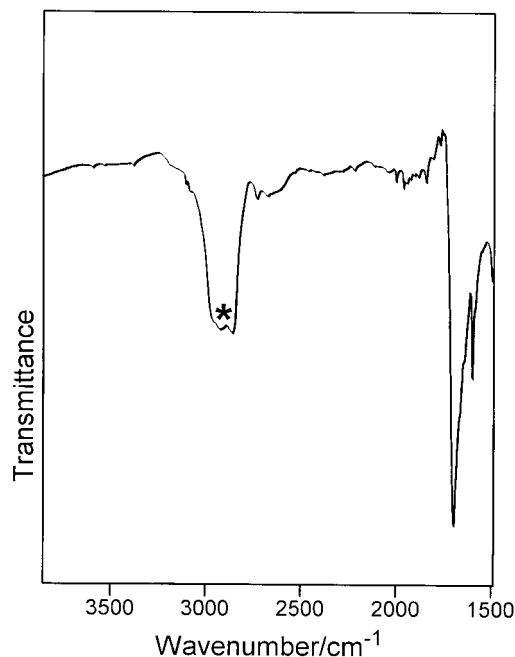

Fig. 1. The FT IR spectrum of the studied compound in the 4000–1500 cm^{-1} region recorded in the Nujol emulsion. The band originating from Nujol is denoted by an asterisk
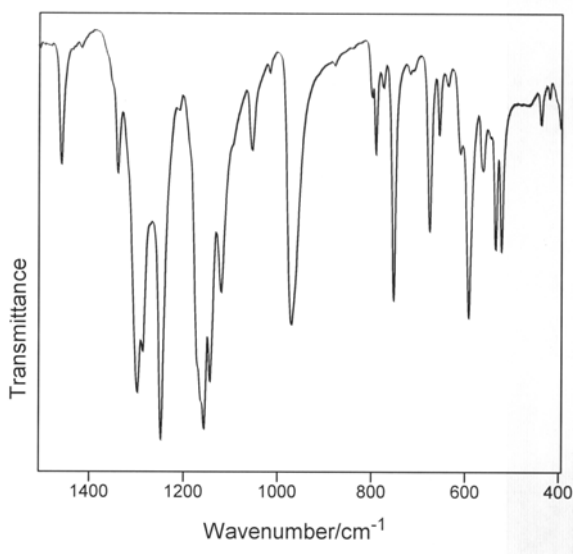

Fig. 2. The FT IR spectrum of the studied compound in the 1500–380 cm^{-1} region obtained from the KBr pellet
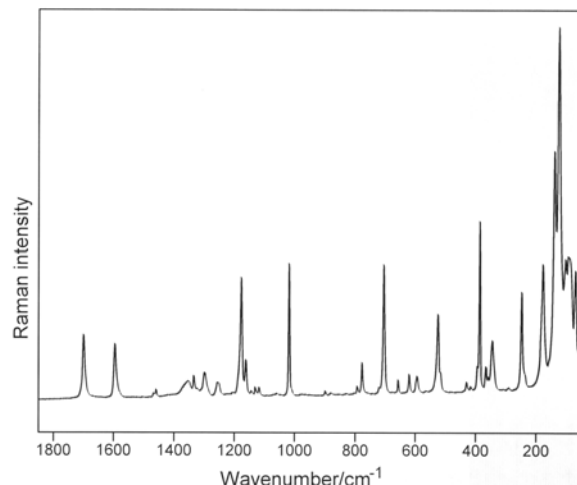
Fig. 3. The Raman spectrum of the studied compound in the 1800–30 cm^{-1} region

Another worth mentioning point is the coupling of the stretching CN mode with different vibrations of the groups within the five-membered saccharinato ring. According to the theoretical (*ab initio* force field) and experimental (solvent DMSO) infrared data for the saccharin molecule, the $\nu(CN)$ vibration contributes (about 40 %) to the $\delta(HNS)$ mode theoretically expected at 1361 cm^{-1} and experimentally registered at 1383 cm^{-1} [3]. In the case of the deprotonated saccharin, however, the *ab initio* force field calculations and experimental measurements have shown that, in addition to the $\nu(CO)$ mode (theoretically expected at 1700 cm^{-1} and experimentally registered at 1638 cm^{-1}), the $\nu(CN)$ vibration contributes to the $\nu(PhC)$ and $\delta(CSN)$ modes expected at 1201 cm^{-1} and recorded at 1220 cm^{-1} [3]. Although the calculated gasphase spectra are not directly comparable with those in the condensed phase, the theoretical predictions can point out certain trends in the latter. Having this in mind, it might be supposed that the $\nu(CN)$ mode contributes to the band at 1161 cm^{-1} (in infrared) and at 1160 cm^{-1} (in Raman) spectrum being coupled with ring modes (see Figs. 2 and 3 and Table 1). With the presence of the CN group in the five-membered saccharinato ring is also connected the strong infrared band at 968 cm^{-1}, which is attributed to the $\nu_{as}(CNS)$ mode [14]. It should be mentioned, however, that the corresponding mode in the Raman spectrum has not been registered.

T a b l e 1.

Assignment[*] of the experimental frequencies in the infrared and Raman spectra of mercury(II) chlorosaccharinate in the 1800–50 cm^{-1} region.

| No. | Experimental[a] | | Ab initio [3] | | Approximate assignment |
	Infrared	Raman	A[b]		
1	1694 vs	1699 m	1700	495.6	$\nu(CO)+\nu(CN)$[c]
2	1658 sh				Second order vibr.
4	1636 sh				Second order vibr.
5	1595 m	1594 m	1596	17.7	$\nu(CC)+\delta(CCC)$
6	1585 m		1584	13.8	$\nu(CC)+\delta(CCC)$
7		1465 vw	1468	4.5	$\delta(HCC)+\nu(CC)$
8	1458 m	1457 vw	1459	13.2	$\delta(HCC)+\nu(CC)$
9		1353 w			
10	1337 m	1333 w			$\delta(HCC)+\nu(CC)$
11	1296 vs	1296 w	1289	297.6	$\nu_{as}(SO_2)$
12	1285 s		1285	9.5	$\delta(HCC)+\delta(SCC)+\nu(CC)$
13	1245 vs	1251 w	1246	46.2	$\delta(HCC)+\nu(CC)$
14	1208 vw				
15	1167 s				
16	1161 s	1160 w	1201	450.3	$\nu(CN)+\nu(PhC+\delta(CSN)$
17	1155 vs	1175 s	1160	349.4	$\nu_s(SO_2)+\delta(CSN)+\nu(CC)$
18	1141 s	1139 vw	1135	2.4	$\nu(CC)+\delta(HCC)$
19		1127 vw	1127	0.6	$\nu(CC)+\delta(SCC)+\delta(HCC)$
20	1118 s	1114 vw	1117	40.9	$\delta(CCC)+\delta(HCC)$
21	1053 m	1054 vw			$\nu(CS)$
22	1015 w	1015 s			$\delta(CCC)$
23	968 vs				$\nu_{as}(CNS)$
24	876 vw	895 vw			
25	796 w				
26	788 m	788 vw			$\delta(CO)$
27	773 w	774 w			$\delta(CH)$
28	750 s				
29	715 vw	715 vw			
30	707 vw	702 s			$\delta(CCC)$
31	674 s				$\delta(CCC)$
32	654 w	654 w			
33	635 w				
34	607 w	616 w			
35	589 s	590 w			$\delta(OSO)$
36	560 m				
37	542 vw				

No.	Experimental[a]		Ab initio [3]	Approximate assignment
	Infrared	Raman	A^{b}	
38	532 s			δ(CCC)
39	520 s	521 m		δ(CCC)
40		513 sh		
42	436 w	425 vw		
43	416 vw	412 vw		
44	390 m	389 w		ρ(SO$_2$)
45		384 s		
46		363 w		
47		353 vw		
48		341 m		
49		244 s		ν(HgCl)
50		173 s		lattice vibration
51		135 vs		ν[HgN(sac)]
52		119 vvs		ν[HgN(sac)]
53		97 s		lattice vibration
54		84 s		lattice vibration
55		64 s		lattice vibration

* Based on the literature theoretical infrared data for the deprotonated saccharin as well as the literature data for the earlier empirical assignments of the spectra of various saccharinato complexes and salts.

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

[b] IR intensities (in km mol^{-1}) for saccharin anion.

[c] Vibrational modes: ν, stretching; δ, bending (all kinds of); ρ, rocking; subscripts: as, antisymmetric; s, symmetric.

According to Quanzini *et al*. [14], the stretching Zn–N(sac) vibration in the infrared spectrum of $[Zn(py)_2(sac)_2]^*$ is expected to appear lower than 224 cm^{-1}. Jubert et al. [8], however, assigned the band at 402 cm^{-1} in the Raman spectrum of $[Fe(H_2O)_4(sac)_2]\cdot2H_2O$ to the stretching Fe–N(sac) mode. Having in mind the mass of the mercury atom, the Hg–N(sac) stretching vibration in the spectrum of the studied compound should not be expected higher than 200 cm^{-1}. This expectation is in agreement with the published results for the ν(Hg–N) mode in HgCl$_2$Py$_2$ [15].

With four molecules in the unit cell, 21 lattice vibrations are expected in the Raman spectrum bellow 200 cm^{-1}. As seen from Fig. 3, there are *four* medium strong (at 173, 97, 84 and 64 cm^{-1}) and *two* very strong bands (at 135 and 119 cm^{-1}). At this point, the tentative assignment could consider one of the most prominent bands at 135/119 cm^{-1} as stretching Hg–N(sac) modes [15]. The

three lowest frequency bands at 97, 84 and 64 cm^{-1} most probably belong to lattice vibrations.

The spectral appearance in the low-frequency region is also influenced by the presence of bands appearing as a result of stretching Hg–Cl vibrations. According to Adams [15], the ν(Hg-Cl) mode in the gaseous HgCl$_2$ and HgClBr appears at 360 and 335 cm^{-1}, respectively, whereas its frequency in the HgClPy$_2$ is shifted to 292 cm^{-1}. It is evidently that the mass increasing of the second ligand [Mr(Cl) < Mr(Br) < Mr(Py)] is followed by the decreasing of the frequency of the ν(Hg-Cl) mode. Consequently, it seams reasonable the band at 244 cm^{-1} in the Raman spectrum of the studied compound to be prescribed to the stretching Hg–Cl mode (Fig. 3).

CO stretchings

A more detailed analysis of the carbonyl stretching vibrations in various metal saccharinates is published in papers [6, 11–13, 16]. It is shown that carbonyl stretchings in the spectra of metal

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* py – denotes pyridine

saccharinates appear as very strong bands in the 1700–1600 cm⁻¹ region. The frequencies are lower than the $\nu(CO)$ mode in the solid-state infrared spectrum of the saccharin itself [6, 9, 16]. The lowering depends on the type of the metal-saccharinato ligand/ion bonding and ranges from about 30 cm⁻¹ in the covalent saccharinates [6, 9, 11, 13, 16] to about 100 cm⁻¹ in purely ionic saccharinates [6, 11, 12, 16, 17].

The single strong band present in the infrared spectrum at 1694 cm⁻¹ (Fig. 1 and Table 1) as well as the single medium strong band in the Raman spectrum of the studied compound at 1699 cm⁻¹ (Fig. 3 and Table 1) can be undoubtedly attributed to the $\nu(CO)$ modes. The additional two shoulders present at 1658 and 1636 cm⁻¹ in the infrared spectrum, which are absent in the Raman spectrum, are too high to be prescribed to the benzenoid stretchings and probably arise as a result of second-order vibrations.

Although it is shown that the correlation between the number of the $\nu(CO)$ bands in the spectrum and the number of the structurally different carbonyl groups in saccharinates is not always possible [11], the appearance of the single $\nu(CO)$ band in the Raman and infrared spectrum of the studied compound agrees well with the presence of only one crystallographic type of carbonyl groups in its structure [2].

The small lowering ($\Delta\nu = 31$) of the infrared active out-of phase carbonyl stretching mode from 1725 cm⁻¹ (in the spectrum of saccharin) [12] down to 1694 cm⁻¹ in the spectrum of mercury(II) chlorosaccharinate, corresponds well with the previously determined covalent character of the mercury-to-saccharin bonding in the title compound [2]. Similar observation is made in the case of the covalently bonded mercury(II) saccharinate [1, 11] and di-μ-chloro-bis[saccharinatopyridinemercury(II)] [4]. Namely, the CO stretches in the infrared spectra of the above mentioned compounds are registered at 1705 and 1680 cm⁻¹ for the former [9], and at 1686 cm⁻¹ for the lather compound [4]. It confirms the earlier assumptions [11] that the frequency of the $\nu(CO)$ mode or its averaged values is related to the type of metal-to-N(sac) bonding and enables to distinguish between the covalent and ionic metal saccharinates. No significant frequency difference ($\Delta\nu = 2$), however, is observed in the case of the Raman active in-phase $\nu(CO)$ mode registered in the spectrum of saccharin at 1697 cm⁻¹ [12] compared to the corresponding mode at 1699 cm⁻¹ in the spectrum of the studied compound.

SO₂ vibrations

The detailed theoretical and empirical analysis of the SO₂ stretching vibrations in the compounds containing SO₂ groups (including the sulfonyl group belonging to the saccharinato five-membered ring in metal saccharinates), has shown that the SO₂ group could be considered as a characteristic group vibration [3, 10, 11, 18, 19]. In the spectra of the metal saccharinates, however, additional five bands originating from ring vibrations of the saccharinato ligand are expected [3] in the region (1335–1130 cm⁻¹) where the antisymmetric, $\nu_{as}(SO_2)$, and symmetric, $\nu_s(SO_2)$, sulfonyl stretching vibrations are supposed to appear or are experimentally registered. The benzenoid ring vibrations, however, are very often (but not always) found to be much sharper (less intense) compared to those arising from the sulfonyl stretches.

Three strong bands in the infrared (at 1296, 1285 and 1245 cm⁻¹) and *four* weak bands in the Raman spectrum (at 1333, 1320, 1296 and 1251 cm⁻¹) of the studied compound have been registered in the $\nu_{as}(SO_2)$ region (see Figs. 2 and 3 and Table 1). Having in mind the results of the theoretical analysis [3], as well as the results of the empirical analysis of the series of metal saccharinates [10], the bands at 1296 cm⁻¹ (in infrared) and at 1296 cm⁻¹ (in the Raman) spectrum are attributed to the antisymmetric SO₂ stretches. (The frequency disagreement between the previously published by us data concerning the $\nu(SO_2)$ modes and those mentioned in the present work is due to the change of the type of instrument.)

Among the *four* bands in the infrared spectrum (at 1167, 1161, 1155 and 1141 cm⁻¹) and *two* bands in the Raman spectrum (at 1175 and 1160 cm⁻¹) of the title compound in the region where the symmetric SO₂ stretching vibration is expected, the strongest band at 1155 cm⁻¹ in the infrared spectrum and also the more intense band in the Raman spectrum at 1175 cm⁻¹ are assigned as $\nu_s(SO_2)$ mode (see Table 1). Expectedly, the antisymmetric and the symmetric sulfonyl stretching vibrations are manifested by the appearance of the weak (1296 cm⁻¹) and the strong (1175 cm⁻¹) band in the Raman spectrum, respectively (Fig. 3).

The additional argument, why the strong infrared band at 1245 cm⁻¹ has not been considered as a serious candidate to be attributed to the $\nu_{as}(SO_2)$ should be mentioned here. Namely, the detailed analysis of the SO₂ stretches in metal saccharinates [10, 11] has shown that the $\nu(SO_2)$ fre-

quency is dependent on the O–S–O angle values rather than on the type of the metal-to-saccharinato type of bonding or on the S–O distances. An appropriate model for this effect is the structure of lead(II) saccharinate monohydrate where two crystallographically different SO_2 groups with O-S-O angles 111.8 and 120.4° exist [20]. The corresponding registered $\Delta = \tilde{\nu}\,[\nu_{as}(SO_2)] - \tilde{\nu}\,[\nu_s(SO_2)]$ values for the two pairs of $\nu(SO_2)$ bands in the infrared spectrum of lead(II) saccharinate monohydrate are 88 and 166, respectively [10, 17]. Consequently, the $\Delta = 90$ for the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes in the infrared spectrum of the title compound [supposing that the band at 1245 cm^{-1} should be attributed to the $\nu_{as}(SO_2)$ mode] does not correspond with the experimentally determined O–S–O angle (117.2 $^{\circ}$).

The above discussion is confirmed by the similarity between the already discussed frequencies of the $\nu_{as}(SO_2)$ (1296 cm^{-1}) and $\nu_s(SO_2)$ (1155 cm^{-1}) modes in the infrared spectrum of the studied compound and the frequencies of the corresponding modes in the spectrum of the previously studied di-μ-chloro-bis[saccharinatopyridine-mercury(II)] [1310 cm^{-1} for the $\nu_{as}(SO_2)$ mode, and 1174 cm^{-1} for the $\nu_s(SO_2)$ mode]. The correspond-ing O-S-O angles are also similar and amount 117.2° for the former, and 115.8° for the later compound.

Having all this in mind, it might be concluded that the presence of a single pair of $\nu(SO_2)$ bands in the infrared spectrum of mercury(II) chlorosaccharinate is a consequence of the existence of only one type of SO_2 groups in its structure [2].

In addition to the SO_2 stretchings, the bands arising from the $\delta(SO_2)$ as well as $\rho(SO_2)$, $\omega(SO_2)$ and $\tau(SO_2)$ modes are expected in the vibrational spectra of compounds containing SO_2 groups in the region below 600 cm^{-1}. According to Quinzani *et al.* [14], the strong band at 589 cm^{-1} (infrared) and the weak one at 590 cm^{-1} (Raman) are attributed to the $\delta(OSO)$ mode, whereas the bands at 390 cm^{-1} (infrared) and 389 cm^{-1} (Raman) could be prescribed to the $\rho(SO_2)$ mode. The assignment of the remaining $\omega(SO_2)$ and $\tau(SO_2)$ modes is not straightforward.

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Р е з и м е

ВИБРАЦИОНА СТУДИЈА И СПЕКТАР-СТРУКТУРНИ КОРЕЛАЦИИ КАЈ ЖИВА(II) ХЛОРСАХАРИНАТ

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Клучни зборови: жива(II) хлорсахаринат; инфрацрвен спектар; рамански спектар; спектар-структурни корелации

Изучувани се вибрационите (инфрацрвени и рамански) спектри на жива(II) хлорсахаринат во подрачјето 4000–380 cm^{-1} (за инфрацрвена) и 1800–30 cm^{-1} (за раманска) спектроскопија. Асигнацијата е направена врз основа на литературните податоци од *ab initio* пресметките за слободни депротонирани сахаринатни единки, како и експерименталните податоци за претходно изучуваните метални сахаринати. Посебно внимание е посветено на подрачјата на валентните CO и CO_2 вибрации. Спектралните карактеристики на изучуваното соединение се споредени со оние на соодветниот жива(II) сахаринат и ди-μ-хлоро-бис[сахаринато-пиридинжива(II). Изгледот на спектрите во подрачјето на валентните карбонилни и сулфонилни модови е корелиран со бројот на нееквивалентни CO и CO_2 групи во структурата. Најдено е дека постоењето на само еден тип на CO и CO_2 групи во структурата е проследено со појава на една ν(CO) лента, односно на еден пар на ν(CO_2) ленти (антисиметрична и симетрична) во инфрацрвениот и раманскиот спектар. Малото фреквентно снижување на модовите ν(CO), $ν_{ac}(CO_2)$ и $ν_c(CO_2)$ во инфрацрвениот спектар на изучуваното соединение, споредено со соодветните модови во спектарот на сахарин, е во согласност со претходно определениот ковалентен карактер на врската жива-сахарин во жива(II) хлорсахаринатот.