Глигор Јовановски

Acta Chim. Slov. **1997**, *44*(2), pp. 197-211

INFRARED INVESTIGATION OF $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ - A PSEUDO JAHN-TELLER COMPLEX

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ABSTRACT

The infrared properties of the dihydrate of tetraaquabis(saccharinato-*N*) copper(II), a compound characterized by a typical inherent instability of the pseudo Jahn-Teller type, were studied. The FTIR spectra of the protiated compound and of its deuterated analogues with varying deuterium content were recorded at room and liquid nitrogen temperature. The OH and OD, as well as the C=O and SO_2 stretching regions were compared to the corresponding regions in the IR spectra of the other members of the isomorphous series. The hydrogen bonding properties in this compound were discussed. The applicability of the previously derived correlation equation of the $\tilde{\nu} = f(R)$ type, where $\tilde{\nu}$ is the wavenumber of the ν(OD) vibrations from the isotopically isolated HDO molecules and R is the corresponding crystallographically determined $O_w \cdots O$ distance was tested for this compound. New regression analyses were performed, including the present data.

Keywords: Jahn-Teller instabillity; metal(II) saccharinates hexahydrates; tetraaquabis(saccharinato-*N*) copper(II); FTIR spectra, isomorphism.

INTRODUCTION

The dihydrate of tetraaquabis(saccharinato-*N*) copper(II) is a member of the isomorphous series of dihydrates of tetraaquabis(saccharinato-*N*) complexes of divalent metals (Fe, Ni, Co, Cd, Zn, Cu, V, Cr). As a consequence of the widespread usage of saccharin as a non-caloric sweetener and as a brightener in electroplating as well as its ability to form complexes[1] with various biologically significant metal ions, these compounds have been intensively studied in recent years, both experimentally [1-10] and theoretically [11]. The members of the series crystallize in the monoclinic $P2_1/c$ space group, with two formula units in the unit cell [6,7,10]. The coordination sphere of the central metal atom consists of two N atoms belonging to saccharinate anions and four water oxygen atoms, while two water oxygens do not participate in the coordination sphere. The metal atoms are located on the crystallographic inversion center and are characterized by distorted octahedral geometry, the distortion being the most pronounced in the case of the copper, vanadium and chromium compounds. The last three compounds contain metal ions with electronic configuration which is responsible for the static distortions of the Jahn-Teller type [12], or, rather, to the inherent *pseudo* Jahn-Teller instability [12] which is due to the lower symmetry of the metal coordination sphere. Such an instability, which results in particular static distortions, is responsible for several structural and spectroscopic characteristics of the copper compound. Thus, the copper compound is characterized by the most pronounced differences of the unit cell parameters, compared to the corresponding values in the structures remaining members of the series [7]. Also, the hydrogen bonding network in the copper compound is significantly different from that in the structures of the other members of the isomorphous series.

EXPERIMENTAL

The studied compound was obtained by gradually adding an equimolar quantity of copper(II) acetate to a warm aqueous solution of saccharin, and also by adding cop-

[1] With presumed potential biological effectiveness.

per(II) sulfate to the aqueous solution of sodium saccharinate. Recrystallization was performed from water. There were no differences between the infrared spectra of the compounds synthesized by these two ways. The samples deuterated to various degrees were obtained from appropriate H_2O/D_2O mixtures. The deuterates with a higher deuterium content were obtained in inert (argon) atmosphere.

The infrared spectra were recorded on a Perkin-Elmer FTIR system 2000. A variable temperature cell (Graseby Specac) was used for the liquid nitrogen temperature (LNT) measurements.

The infrared spectra of the protiated samples were recorded both in KBr pellets and in Nujol and Fluorolube mulls, while those of the deuterated samples with higher deuterium content were recorded only in Nujol and Fluorolube mulls. The spectra recorded by various techniques showed that the important spectral regions for this study were not affected by the particular technique employed.

RESULTS AND DISCUSSION

The infrared spectra of the dihydrate of tetraaquabis(saccharinato-*N*) copper(II) recorded at room (a) and liquid nitrogen temperature (b) are shown in Fig. 1. The regions of the OH and OD stretching vibrations in the spectra of the protiated and deuterated samples are presented in Fig. 2 and Fig. 3, respectively. The region of the C=O stretching vibrations in the spectra of the protiated and deuterated samples is presented in Fig. 4, whereas the region of the SO_2 stretching vibrations in the protiated sample is given in Fig. 5.

The regions of the O–H and O–D stretching vibrations

As it has already been briefly reported [13,14], the complex feature in the O–H stretching region in the spectra of the studied compound is much broader than that in the corresponding region of the spectra of the other members of the series. Furthermore, the existence of several well separated bands in this region is obvious even in the spectra recorded at room temperature (see Fig. 1). This can be easily understood in terms of the inherent instability of the pseudo-Jahn-Teller type that causes static distortions and af-

fects the organization of the hydrogen bonding network in this compound which is characterized by the existence of hydrogen bonds with a variety of strengths. Some of them are weaker, while others are much stronger than the hydrogen bonds in the other compounds in the series. the stronger hydrogen bonds being responsible for the appearance of the low-frequency bands in the O–H stretching region. The assignment of these low-frequency bands is accompanied with some difficulties arising from the presence of the C–H stretching bands in the region about 3100 cm^{-1}. However, this problem is easily avoidable, on the basis of the behavior of the bands upon deuteration. As is obvious from the spectra of the deuterated samples with various deuterium content shown on Fig. 2, the position of the bands appearing at 3099 and 3077 cm^{-1} are unaffected by the deuteration and their intensity, relative to the other bands in this region, increases with the increase of the deuterium content. It follows that they are undoubtedly due to the aromatic C–H stretching vibrations.

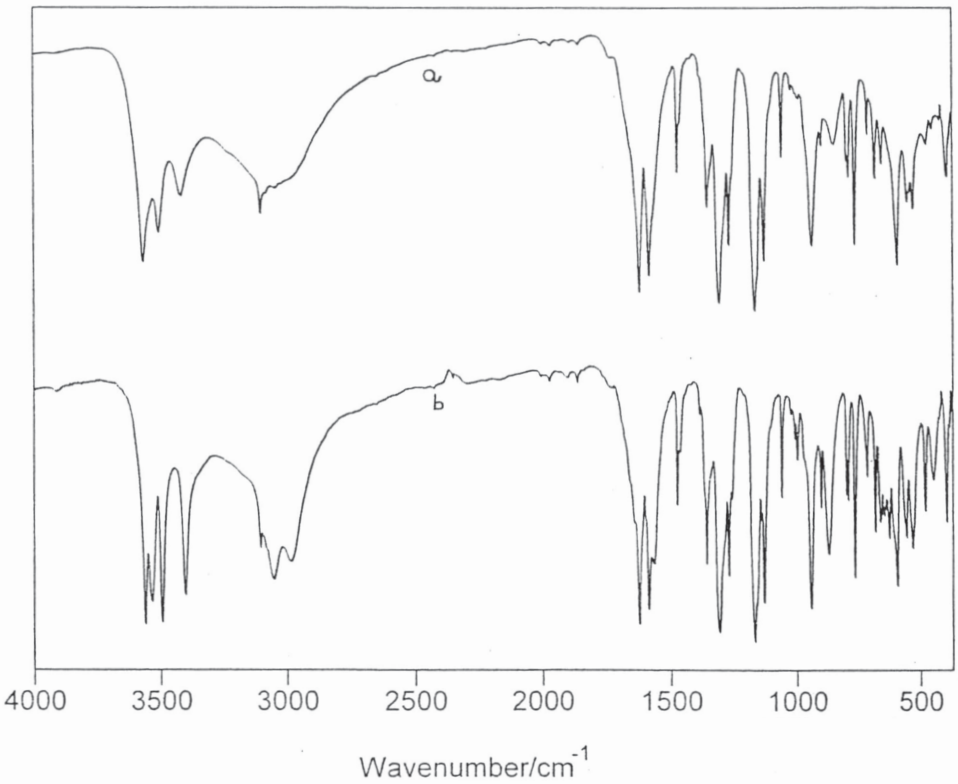

Fig. 1. RT (a) and LNT (b) FTIR spectra of he dihydrate of tetraaquabis(saccharinato-*N*) copper(II).

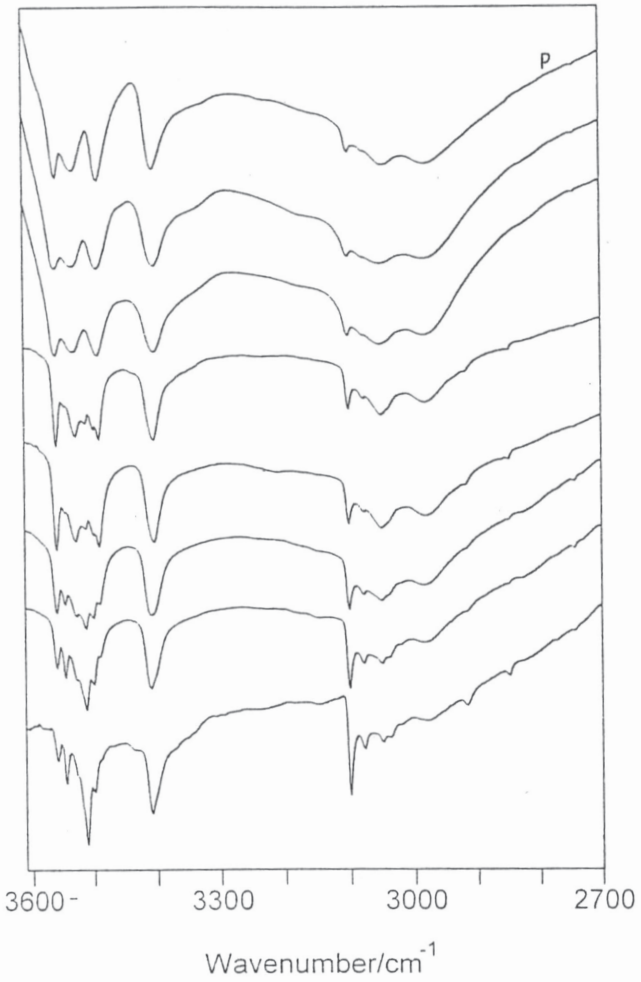

Fig. 2. The O–H stretching region in the LNT FTIR spectra of samples with various deuterium content; p-protiated sample. The deuterium content increases from the uppermost curve downwards.

The splitting of the bands in the region of O–H stretching vibrations into two groups is noticeable, the higher-frequency group appearing from about 3558 to 3400 cm^{-1} and the lower-frequency one appearing from 3050 to 2982 cm^{-1}. The picture is repeated for the O–D stretching region. The existence of two groups of well separated, even at room temperature, bands is also noticeable, in the infrared spectra of the highly deuterated samples. The higher frequency bands have frequencies from about

2643 to 2505 cm^{-1}, while the group of lower frequency bands appears from about 2292 to 2237 cm^{-1} (see Fig. 3).

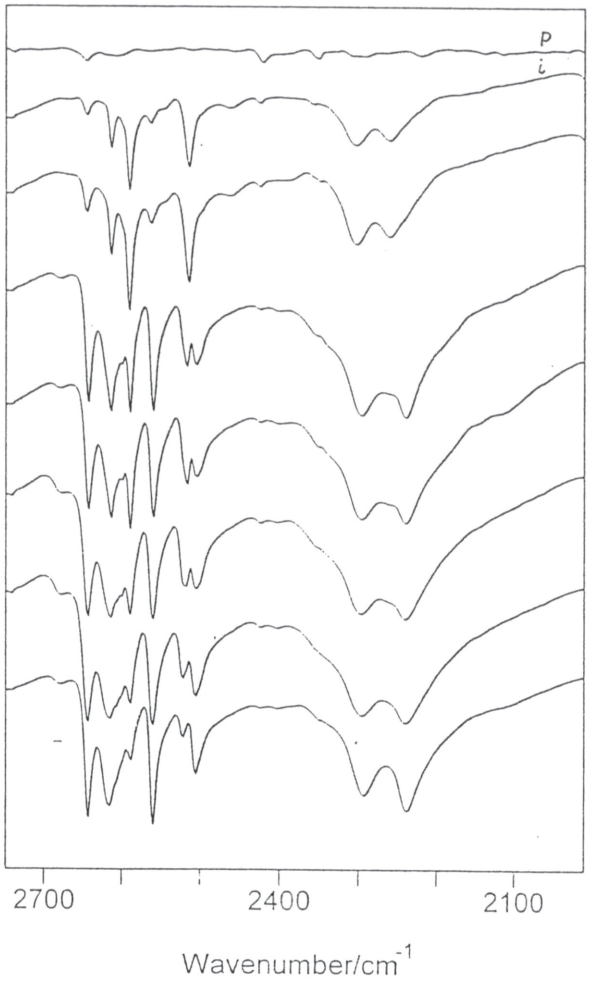

Fig. 3. The O–D stretching region in the LNT FTIR spectra of samples with various deuterium content; p-protiated sample; i-sample containing isotopically isolated O–D oscillators. The deuterium contents increases from the uppermost curve downwards

As seen from Fig. 3, five bands originating from isotopically isolated O–D oscillators appear in the O–D stretching region in the spectra of samples with very low deuterium content, rather than six expected from three crystallographically

non-equivalent water molecules in the structure. It should be noted that an analogous spectral behavior was found in the case of the other members of this series, and was explained in terms of an accidental degeneracy [5,10]. Such an explanation is also valid in the case of the investigated copper compound. However, the splitting into two groups of bands also exists in the region of O–D stretching vibrations in the samples with very low deuterium content, the higher frequency one consisting of three, and the lower one of two well separated bands.

Spectra-structure correlations

The observed values for the wavenumbers of the O–D stretching vibrations originating from the isotopically isolated HDO molecules for the members of the isomorphous series (except for the copper compound) have been correlated with the crystallographically determined values of the $O_w\cdots O$ distances [5,13,14]. A correlation equation of the following type:

$$R/\mathrm{pm} = a + b\ \ln(\Delta\tilde{\nu}/\mathrm{cm}^{-1})$$

was used, where $\Delta\tilde{\nu}$ is the difference between the OD stretching frequency of gaseous HDO (2727 cm^{-1}) and that observed in the crystal and R is the crystallographically determined $O_w\cdots O$ distance. The values for the coefficients a and b, obtained on the basis of the least squares criterion, were 447.128 and -29.754 respectively, the correlation coefficient being -0.9406. A higher value for the correlation coefficient could not be expected, since three different kinds of proton-acceptors (carbonyl oxygens, oxygens from the SO_2 groups and oxygens from the water molecules) exist in the structure. The calculated (according to this correlation equation), and the experimentally observed values for the wavenumbers of the O–D stretching vibrations originating from isotopically isolated HDO molecules in the dihydrate of tetraaquabis(saccharinato-*N*) copper(II) are compared in Table 1.

Table 1. The observed ($\tilde{\nu}_{obs}$). the calculated ($\tilde{\nu}_{calc}$) (by the previously derived correlation equation) values of the ν(O–D) vibrations. and the absolute values of their differences.

R/pm	$\tilde{\nu}_{calc.}$/cm^{-1}	$\tilde{\nu}_{obs.}$/cm^{-1}	$\lvert\Delta\tilde{\nu}\rvert = \lvert(\tilde{\nu}_{calc.} - \tilde{\nu}_{obs.})\rvert$/cm^{-1}
260.4	2195	2261	66
269.7	2338	2306	32
281.0	2461	2513	52
289.8	2529	2589	60
295.2	2562	2589	27
310.0	2627	2613	14

When the spectroscopically observed data for this compound were included in the correlation. (using a model equation of the same type), the values for the coefficients *a* and *b*. obtained on the basis of the least squares criterion. were 449.953 and -30.362 respectively. while the correlation coefficient dropped to -0.9384. The somewhat lower value of the correlation coefficient is perhaps related to the instability induced distortion of the structure of the copper compound [13].

The calculated (on the basis of the new correlation equation) values for the O–D stretching vibrations[2] and the experimentally observed ones for the all members of the series are presented in Table 2. The experimentally determined O···O distances were also compared with the corresponding values obtained using the new correlation equation. The results are summarized in Table 3.

[2] From the isotopically isolated HDO molecules

Table 2. Comparison of the experimentally obtained ($\tilde{\nu}_0$) and calculated by the correlation equation ($\tilde{\nu}_c$) values for the wavenumbers of ν(OD) modes ($\Delta\tilde{\nu}=\tilde{\nu}_0-\tilde{\nu}_c$).

M	$\tilde{\nu}_0$/cm^{-1}	$\tilde{\nu}_c$/cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1}
Zn	2381.00	2366.54	14.46
	2454.00	2477.74	-23.74
	2509.00	2525.11	-16.11
	2583.00	2561.86	21.14
	2454.00	2490.53	-36.53
	2531.00	2539.84	-8.84
Cd	2431.00	2412.07	18.93
	2441.00	2464.25	-23.25
	2441.00	2465.98	-24.98
	2499.00	2504.88	-5.88
	2534.00	2539.22	-5.22
	2570.00	2541.07	28.93
Mn	2416.00	2398.29	17.71
	2452.00	2469.39	-17.39
	2498.00	2512.08	-14.08
	2568.00	2542.29	25.71
	2452.00	2469.39	-17.39
	2529.00	2530.36	-1.36
Fe	2450.00	2427.25	22.75
	2385.00	2379.37	5.63
	2499.00	2521.08	-22.08
	2573.00	2553.50	19.50
	2450.00	2476.09	-26.09
	2527.00	2533.57	-6.57
Co	2457.00	2480.19	-23.19
	2384.00	2362.96	21.04
	2500.00	2514.89	-14.89
	2579.00	2564.56	14.44
	2457.00	2490.53	-33.53
	2528.00	2537.98	-9.98
Ni	2469.00	2495.92	-26.92
	2381.00	2347.03	33.97
	2507.00	2521.76	-14.76
	2594.00	2579.84	14.16
	2469.00	2505.61	-36.61
	2532.00	2543.50	-11.5
Cu	2261.00	2212.55	48.45
	2306.00	2348.28	-42.28
	2513.00	2465.98	47.02
	2589.00	2531.65	57.35
	2589.00	2563.48	25.52
	2613.00	2626.57	-13.57

Table 3. Comparison of the experimentally obtained (Ro) and calculated by the correlation equation (Rc) values for the O_W...O distances ($\Delta R = R_o - R_c$).

M	R_o/pm	R_c/pm	ΔR/pm
Zn	271.200	272.443	-1.243
	282.400	279.638	2.762
	288.800	286.469	2.331
	294.900	299.059	-4.159
	284.000	279.638	4.362
	291.100	289.699	1.401
Cd	275.300	277.182	-1.882
	280.800	278.226	2.574
	281.000	278.226	2.774
	285.900	285.107	0.793
	291.000	290.167	0.833
	291.300	296.435	-5.135
Mn	274.000	275.681	-1.681
	281.400	279.416	1.984
	286.900	284.974	1.926
	291.500	296.051	-4.551
	281.400	279.416	1.984
	289.600	289.390	0.210
Fe	276.800	279.196	-2.396
	272.300	272.796	-0.496
	288.200	285.107	3.093
	293.400	297.021	-3.621
	282.200	279.196	3.004
	290.100	289.085	1.015
Co	282.700	279.974	2.726
	270.900	272.708	-1.808
	287.300	285.240	2.060
	295.400	298.227	-2.827
	284.000	279.974	4.026
	290.800	289.237	1.563
Ni	284.700	281.354	3.346
	269.600	272.443	-2.843
	288.300	286.191	2.109
	298.400	301.472	-3.072
	286.000	281.354	4.646
	291.700	289.854	1.846
Cu	284.700	263.403	21.297
	269.600	266.486	3.114
	288.300	287.031	1.269
	298.400	300.352	-1.952
	286.000	300.352	-14.352
	291.700	306.152	-14.452

The region of the C=O stretching vibrations

As is well known, the assignment of the band(s) due to the C=O stretching vibrations in the infrared spectra of metal saccharinates is not always easy [3,4], mainly because of the following reasons. First, the appearance of several bands due to the benzenoid ring stretching vibrations is expected in the same spectral region and, in the case of crystallohydrates, bands due to the HOH bending vibrations are also expected there. The latter problem is easily solvable by recording spectra of the highly deuterated samples, since one simply "eliminates" the HOH bendings from the C=O stretching region. On the other hand, the bands originating from the stretching vibrations of the benzenoid ring are usually much sharper than those originating from the carbonyl group stretchings.

The previous investigations [3,4,5] of a number of metal saccharinates have shown that irrespective on whether the oxygen atom from the carbonyl group participates in the metal coordination sphere or in hydrogen bonding or not, the bands due to the carbonyl stretchings appear at lower frequencies than the corresponding ones in the spectrum of saccharin itself, the shift being dependent mainly on the degree of the ionic character of the metal-ligand bond.

The region of the C=O stretchings in the infrared spectra of copper saccharinate samples with various deuterium content is shown in Fig. 4. The spectra clearly indicate that the two bands appearing at 1619.5 and 1582.5 cm^{-1} should be attributed to C=O stretchings. Since only one crystallographic type of carbonyl group was found to exist in the structure of this compound, the appearance of two bands can be explained as being due to the symmetry reasons (symmetry-induced splitting) [3], as is also the case with the other members of the isomorphous series.

The region of the SO_2 stretching vibrations

The assignment of the bands originating from the sulphonyl stretching vibrations in these compounds is also accompanied by some difficulties, mainly because of the presence of bands originating from the stretching vibrations of the benzenoid ring in the same spectral region. As the normal-coordinate analysis for phtalimide and some related compounds [2] has shown, at least four or five bands due to the benzenoid ring stretch

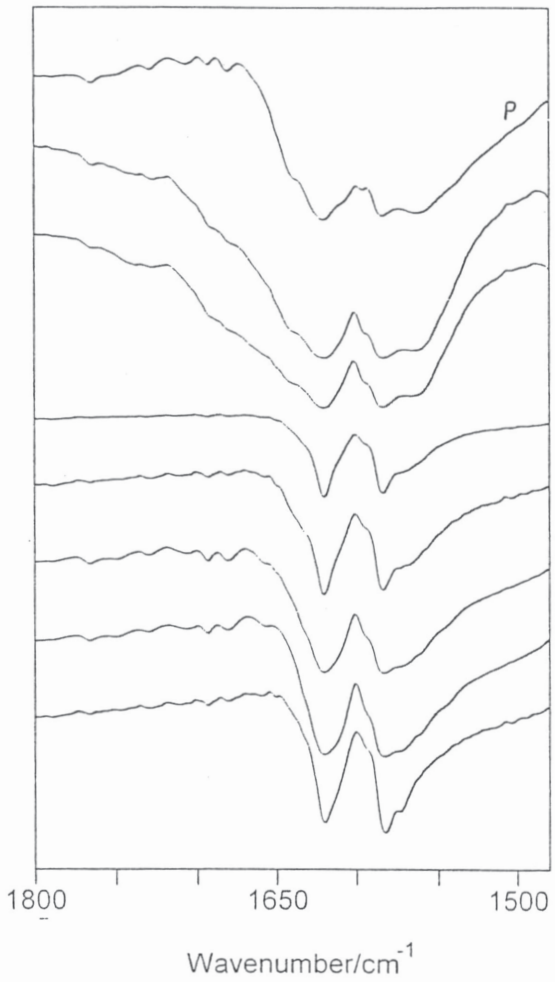

Fig. 4. The C=O stretching region in the LNT FTIR spectra of samples with various deuterium content: p-protiated sample. The deuterium content increases from the uppermost curve downwards

ings are expected to appear in the region from 1375 cm^{-1} to 1130 cm^{-1}. However, as it has already been mentioned, these bands are usually much sharper than those originating from the SO_2 stretchings. The normal-coordinate analysis for dimethyl sulphone and dimethyl sulphone-d_6, as well as the previously reported [2] model calculations for the N–S(O2)–C fragment of the saccharin anions, have shown that the SO_2 stretching modes can be considered as rather good group vibrations.

The spectral region where bands due to the sulphonyl stretching vibrations are expected to appear in the spectrum of the copper saccharinate is shown in Fig. 5. The

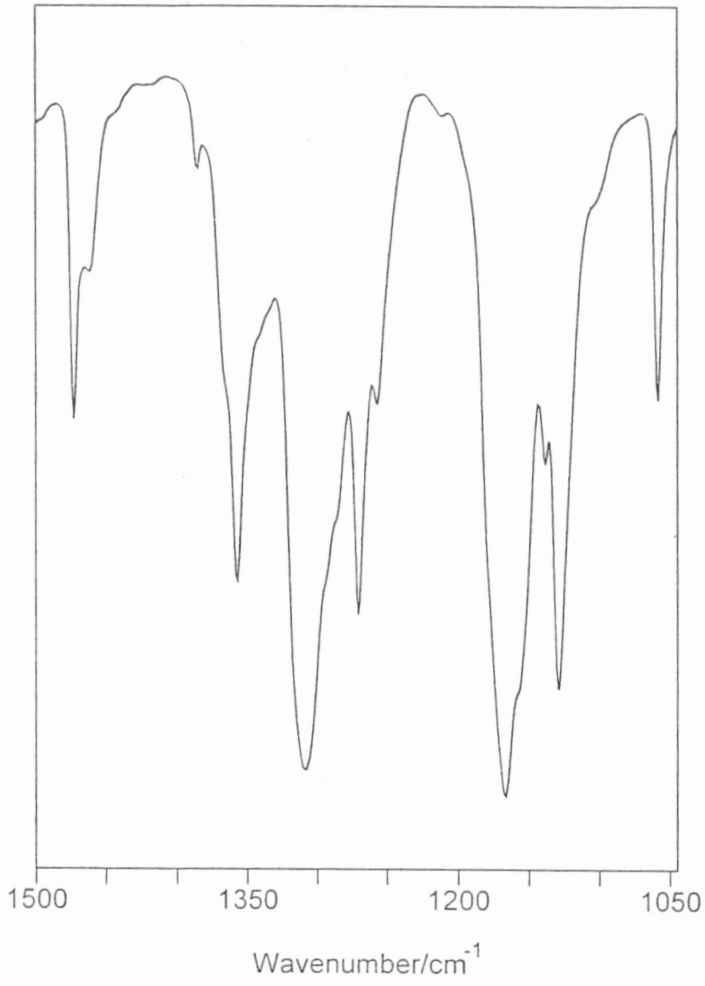

Fig. 5. The SO_2 stretching region in the LNT FTIR spectra of the protiated compound.

appearance of the band in this region is very similar to that in the corresponding region of the infrared spectra of the other members of the series. On the basis of what has been said, the two most intense bands, those at 1307.7 and 1164.4 cm^{-1}, were attributed to the antisymmetric and symmetric SO_2 stretchings, respectively. The existence of only two bands originating from sulphonyl stretchings in this region is consistent with the crystallographic equivalence of all sulphonyl groups in the structure of the copper compound (as well as in the structure of the other members of the isomorphous series). As it

has been shown [2], irrespective on either the character of the metal-saccharin bond (ionic, covalent, intermediate type), or on whether or not the sulphonyl oxygens participate in the coordination of the metal or in the hydrogen bonding, the frequencies of the SO_2 stretchings in metal saccharinates are lower than in saccharin, the frequency of the antisymmetric mode being more sensitive to the rearrangement of the electronic density due to the structural changes. The presented observations are consistent with these general trends.

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Povzetek. Dihidrat tetraakvabis(saharinato-*N*) bakra(II) smo raziskovali z infrardečo spektroskopijo. Pri sobni temperaturi in pri temperaturi tekočega dušika smo posneli FTIR spektre spojin z različno vsebnostjo devterija. Primerjali smo področja vibracij OH, OD, C=O in SO_2 z ustreznimi področji v IR spektrih spojin izomorfne serije. Opisali smo lastnosti vodikovih vezi v naslovni spojini. Preverili smo uporabnost prej izpeljane zveze vrste $\tilde{\nu} = f(R)$, kjer je $\tilde{\nu}$ valovno število ν(OD) vibracij, ki pripadajo izotopsko izoliranim HDO molekulam in R je kristalografsko določena razdalje $O_w \ldots O$. Opravili smo nove regresijske analize z vključenimi novimi podatki.
Ključne besede: Jahn-Tellerjeva nestabilnost; kovinski(II) saharinati heksahidrati; tetraakvabis-(saharinato-*N*) baker(II); FTIR spektri, izomorfizem.

Prejeto:
18. 4. 1997
Received: