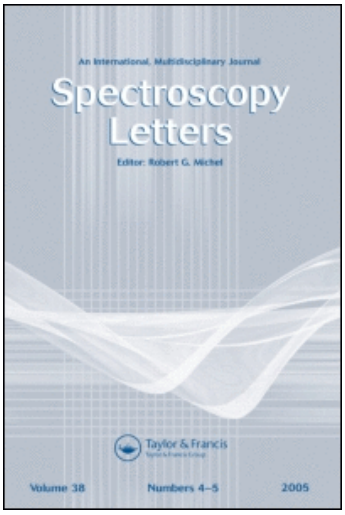

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FT Infrared Spectra of Binuclear Copper(II) Imidazole Saccharinato Complex: Correlation with the Structure

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FT INFRARED SPECTRA OF BINUCLEAR COPPER(II) IMIDAZOLE SACCHARINATO COMPLEX: CORRELATION WITH THE STRUCTURE

Key words: FT IR spectra, copper imidazole saccharinate, spectra-structure correlations

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ABSTRACT

The FT infrared spectra of the binuclear copper(II) complex with imidazole and saccharin and of its iminodeuterated analogue at room (RT) and liquid nitrogen temperature (LNT) are recorded. The bands that are mainly due to the NH, ND, CO, SO_2 and metal-ligand stretchings are assigned. The spectral characteristics are correlated with the available structural data and compared with the corresponding data for other saccharinates and imidazole complexes.

While the spectral appearance in the NH, ND and SO_2 regions is in agreement with the structural data, the carbonyl stretchings do not conform the pronounced difference between the lengths of the two structurally non-equivalent carbonyl groups found by earlier structural studies.

INTRODUCTION

Mainly due to the effectiveness of the compounds of saccharin (systematic name: 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide) in biological systems, an extensive research work has been done in this field during the last several decades. The structural and spectroscopic properties of saccharin as a ligand or an anion (or both) in the saccharinates of various metals are thus well known. Because of suspected pathological effects, however, metal-saccharinato compounds containing aromatic nitrogen bases as ligands have received certain scientific attention lately. In this sense, we have undertaken a systematic spectroscopic and structural research of saccharinato adducts with various mono- or polymembered ring bases. In the present communication, the results of the infrared study of copper(II) complex containing saccharin and *imidazole* are reported.

Up to now, the crystal structures of imidazole saccharinato complexes of Co(II)[1] and Ni(II)[2] of a general formula $[M(HIm)_4(H_2O)_2](sac)_2$ as well as the structures of the binuclear Cu(II)[3] and Cd(II)[4] complexes of a general formula $[M_2(HIm)_4(sac)_4]$ were reported (in what follows, the acronyms *HIm*, *py*, *bpy*, *Hsac* and *sac* denote imidazole, pyridine, 2,2'-bipyridine, saccharin and saccharinato ion or ligand, respectively). From the structural point of view, the last two compounds are rather interesting, each featuring two coordination modes (monodentate *N*-donating and bidentate bridging) of saccharinato ligands in its structure.

Except for the electronic absorption spectra[1,2,5], no other spectroscopic data about these compounds exist. In the present study, the RT and LNT infrared spectra of the copper(II) imidazole saccharinato complex in the 4000-500 cm^{-1} region as well as its RT spectrum in the 400-200 cm^{-1} region are recorded. Considering the previous infrared studies and the spectra-structural correlations in a series of saccharinates and imidazole complexes of various metals, an assignment of the characteristic bands is made. The spectral characteristics in the regions of NH, ND, CO, SO_2 and metal-ligand stretchings are discussed in sense of the available structural data.

EXPERIMENTAL

The compound was prepared by addition of warm aqueous solution of saccharin and imidazole to an aqueous solution of copper(II) acetate in stoichiometric amounts, during continuous stirring of the reaction mixture. Blue prismatic crystals were grown at RT after several days. No spectral change was observed after recrystallization from water. The results from the elemental (C, H, N) analysis corresponded to the given formula.[3]

The spectra were recorded with Perkin-Elmer System 2000 FT IR interferometer (middle infrared, resolution of 4 cm^{-1}; far infrared, resolution of 2 cm^{-1}). For the LNT spectra a Graseby Specac P/N 21525 variable temperature cell with KBr windows was employed. Solid samples in KBr pellets served to record the spectra in the 4000-500 cm^{-1} region, while Nujol mulled solid samples placed between polyethylene plates were used for the 400-200 cm^{-1} region. The program GRAMS/386[6] was used for band fitting.

Partially deuterated analogue of the complex was easily obtained by exposing a powdered protiated sample to D_2O vapors in an evacuated desiccator for several days.

RESULTS AND DISCUSSION

Spectral Data

The FT IR spectra of the copper(II) imidazole saccharinato complex recorded at RT and LNT in the 4000-500 cm^{-1} region are shown in Fig. 1.

Structural Data

Details about the structure of the copper(II) imidazole saccharinato complex {the full name of the compound is bis[μ-1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido-κN:κO]bis[1,2-benzisothiazol-3(2*H*)-one 1,1-dioxido-κN]-tetrakis(imidazole)dicopper(II)} can be found in the paper describing its crystal structure.[3] Thus, only brief data which are relevant for discussion of the spectra will be given below.

The structure of copper(II) imidazole saccharinate features a dimeric moiety, composed of two $Cu(HIm)_2(sac)_2$ units connected to each other by an inversion center. Both saccharinato ligands of the unit are coordinated to the metal atom through their nitrogen atoms. One of them, however, through its carbonyl oxygen, is also coordinated to the metal atom of the other unit in an amidato-bridging manner. Thus an eight-membered nearly planar ring is formed. Because of the symmetry center, only two structurally different saccharinato ligands as well as two non-equivalent imidazoles exist in the structure.

The characteristic coordination of the metal atom is a trigonal bipyramide. Two saccharinato nitrogen atoms (one of the saccharinato ligands being *N*-donating and the other one being bridging) and a carbonyl oxygen atom (originating from the bridging saccharinato ligand coordinated also to the neighboring Cu atom) form the equatorial plane. The apex positions are occupied by nitrogen atoms of two imidazole molecules.

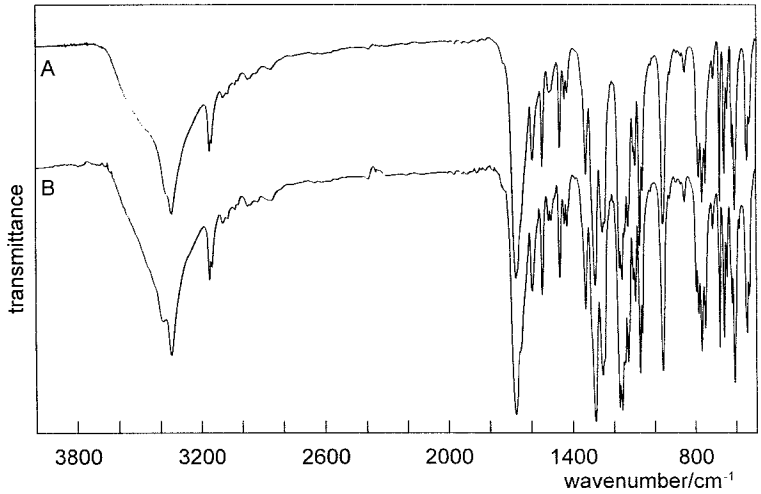

FIG. 1. The RT (A) and LNT (B) FT Infrared Spectra of $[Cu_2(HIm)_4(sac)_4]$ in the 4000-500 cm^{-1} Region.

Spectra-Structure Correlations

N-H/D stretching regions

Due to the deprotonation, the split ν(NH) band in the solid-state spectrum of saccharin, except for one so far known example[7], is absent in the spectra of the metal-saccharinato compounds. On the other hand, the series of overlapping ν(NH) and ν(CH) bands in the 3300-2100 cm^{-1} region of the solid-state spectrum of pure imidazole[8,9], besides the ν(CH) bands, is usually replaced by one or two fairly sharp and symmetric stretching bands of the imino group in the spectra of its metal complexes.[9,10] The bands appear in the broad spectral region from 3500 to 3100 cm^{-1}.

An asymmetric strong band at 3342 cm^{-1}, with two shoulders on its high-frequency side (at about 3470 and 3370 cm^{-1}), is present in the NH stretching region of the RT spectrum of the studied complex (Fig. 1). On

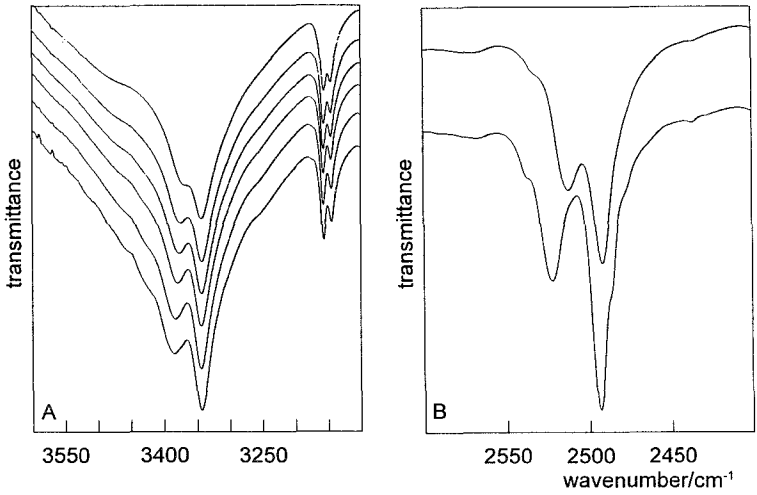

FIG. 2. Behavior of the Bands in the NH Stretching Region on Lowering the Temperature (the Temperature Lowers from the Uppermost to the Lowest Curve) (A). The ND Stretching Region of the RT (Upper Curve) and LNT (Lower Curve) in the Spectrum of Partially Deuterated $[Cu_2(HIm)_4(sac)_4]$ (B).

lowering the temperature, however, as shown in Figs. 1 and 2A, the shoulder at 3370 cm^{-1} separates in a clearly visible band. So, in fact, *two* rather strong and overlapped bands with maxima at 3383 and 3343 cm^{-1} (LNT) are present in the region where the ν(NH) modes are expected.

The appearance of the LNT spectrum in the ν(NH) region corresponds with the existence of *two* non-equivalent NH groups in the structure. According to the structural data[3], the two crystallographically non-equivalent imino groups differ in the strength of the hydrogen bonding. Namely, there are two intermolecular three-centered hydrogen bonds between the imidazole imino groups and saccharinato sulphonyl oxygen atoms. Considering the noticeably larger shift to higher frequencies of the higher-frequency band on

lowering the temperature (about 13 cm^{-1}) compared to the lower-frequency band (1 cm^{-1}) (Fig. 2A), it can be supposed that this band corresponds to the imino group involved in highly-bent hydrogen bonding.[3,11]

In order to confirm the assignment of the ν(NH) modes, the spectrum of an iminodeuterated analogue of the complex was also recorded. Namely, it has been shown that the imidazole imino groups undergo rapid H/D exchange[10], although the complete and selective deuteration of imidazole is known to be troublesome. The ν(ND) region in the spectrum of the deuteroimino analogue (deuteration of approximately 50 %) of the compound at RT and LNT is given in Fig. 2B. It is clearly shown that *two* distinct ν(ND) bands (2522 and 2493 cm^{-1}) appear in the LNT spectrum. Their temperature change behavior is similar to that of the corresponding ν(NH) bands (Fig. 2A).

Carbonyl stretching region

The appearance of this spectral region of saccharinates is usually complicated by presence of bands arising from the benzenoid stretching modes of the saccharinato ligand as well as by water bending bands in the case of solid hydrates.[12-14] Benzenoid stretching modes, however, are known to appear as sharper and somewhat less intense bands compared to the carbonyl stretching modes at frequencies below 1600 cm^{-1} [15,16], while the structural data for the studied compound[3] reveal that it is anhydrous. Additional weak combination band originating from the imidazole ring is also expected around 1665 cm^{-1}.[8] It is known, namely, that the bands belonging to the heterocyclic basic ligands, besides eventual minor shifts and splittings, do not undergo drastic changes upon complexation.[17]

A single, very strong and rather asymmetric band (with a maximum at 1674 cm^{-1}) appears in the carbonyl stretching region of the RT infrared

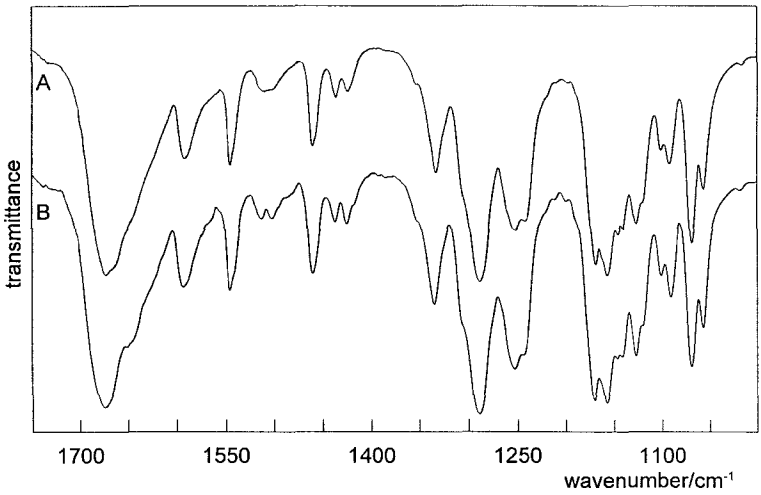

FIG. 3. The 1750-1000 cm^{-1} Region in the RT (A) and the LNT (B) Spectra of $[Cu_2(HIm)_4(sac)_4]$.

spectrum of the title compound, accompanied by at least two shoulders (at around 1664 and 1648 cm^{-1}) (Fig. 3). In the LNT spectrum, however, the shoulder at 1664 cm^{-1} (RT) is less pronounced and the asymmetric shape of the band is less preserved. Probably this shoulder originates from the above mentioned weak combination band of imidazole.[8] The shoulder at 1648 cm^{-1}, on the other hand, separates into a band at 1651 cm^{-1} (Fig. 3). If it is so, *two* bands, at 1674 and 1651 cm^{-1} (LNT), corresponding to the non-bridging and the bridging carbonyl group, respectively, can be assigned as ν(CO) modes. As seen in Fig. 4, the complex band in the 1700-1630 cm^{-1} region can be fitted well by three bands at 1675, 1665 and 1645 cm^{-1}, along with the above discussion.

The appearance of *two* carbonyl stretching bands in the LNT infrared spectrum is in agreement with the existence of *two* non-equivalent carbonyl

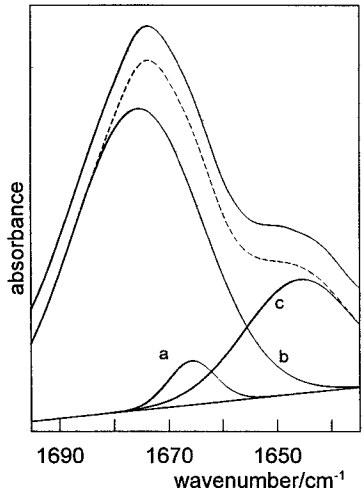

FIG. 4. The Original LNT (Full Line) and Reconstructed (Dashed Line) Spectrum of $[Cu_2(HIm)_4(sac)_4]$ in the Carbonyl Stretching Region (a,b and c are the Component Spectra).

groups in the structure.[3] The comparison of the spectroscopic and structural data concerning the carbonyl groups in various metal saccharinates (Table 1) is consistent with the ν(CO) assignment made. Namely, the ν(CO) frequency in the studied complex, in accordance with the shorter average C-O distance, is higher compared to the corresponding averaged ν(CO) frequencies of the saccharinates of Na and Mg that also feature coordination through a saccharinato carbonyl group. Furthermore, the C-O distance of the *bridging* CO group of the title compound seems quite normal being similar to the corresponding averaged values in the saccharinates of Mg and Na. The unexpectedly short C-O distance of the *non-bridging* CO group, on the other hand, gives raise to noticeably higher frequency of the ν(CO) band, comparable to that found in mercury(II) saccharinate, which features

TABLE 1

Basic Structural and Spectroscopic Data Concerning the Carbonyl Groups in Some Metal Saccharinates

Compound	No of co-ordinated CO groups	R(C-O)/pm	R(C-O)$_{av}$/pm	Frequency Data/cm^{-1}	
				ν(CO)	ν(CO)$_{av}$
Hg(sac)$_2$ Ref. 13, 32	0	118(2) 120(2) 122(2) 123(2)	121	1680 1705	1692
HgCl(sac) Ref. 13, 33	0	123(2)	123	1694	1694
Hg(bpy)(sac)$_2$ Ref. 34, 35	0	121.7(6) 123.3(6)	122.5	1615 1630	1622
Pb(sac)$_2$·H$_2$O Ref. 36, 37	0	120.4(15) 125.5(15)	122.9	1601 1610	1605
Mg(sac)$_2$ · 7H$_2$O Ref. 13, 21	1	124.0(3) 124.2(3)	124.1	1627 1660	1643
Na$_3$(sac)$_3$ · 2H$_2$O Ref. 13, 21	3	123.0(3) 124.1(4) 123.7(3)	123.6	1635	1635
Cu$_2$(HIm)$_4$(sac)$_4$ Structure: Ref. 3 Spectra: this work	1	110.3(6)* 122.3(5)	116.3	1674 1651	1662

* A discussion of this value is given in the text.

a fairly short C-O distance [118(2) pm] as well. The covalent character of the metal-saccharinato bonds in the latter case, however, should also be considered as one of the factors that increase the ν(CO) frequency.[13]

The considerably smaller intensity of the ν(CO) band corresponding to the bridging CO group compared to that prescribed to the non-bridging CO

group is another interesting feature. One of the reasons leading to this fact could be related to the presence of two different types of coordination of saccharinato ligand to the metal atom. It should be born in mind, however, that the correlation of the number of crystallographically independent carbonyl groups in the structure and the number of ν(CO) bands in the infrared spectrum is not always straightforward.[13]

Even so, it seems that the structural data concerning the carbonyl groups in the studied compound need some more attention. It is to be noticed that the lengths of the non-bridging and the bridging carbonyl group are *unexpectedly different* from each other [110.3(6) and 122.3(5) pm, respectively, as taken from the Table 2 in the Ref. 3). We could not find a reasonable explanation of the abnormally small length of the shorter C-O bond and neither was this discussed by the authors in the article reporting on the structure.[3] Namely, the lengths of the saccharinato carbonyl groups in the structural studies of all so far studied saccharinato compounds were estimated around (mostly longer than) 120 pm (for example, see the data presented in Table 1 and in the Refs. 1, 2, 4, 13). On the other hand, taking into account the frequency difference between the two bands assigned by this study as carbonyl stretching modes in the spectrum of the studied compound, it is even more hopeful to expect that there should not be such a drastic difference in the lengths of the two non-equivalent carbonyl groups. Therefore, having in sight the earlier structural data about the metal saccharinates as well as the spectral appearance of the carbonyl stretching region of the studied complex, we consider that either the present case is somewhat exceptional from what was previously found in a series of metal saccharinato compounds or, eventually, the value given for the length of the non-bridging carbonyl group [110.3(6) pm] might need further correction.

TABLE 2

Some Structural and Spectroscopic Data Concerning the Sulphonyl Groups in Saccharin and Some Metal Saccharinates

Compound	*R*(S-O)/pm	∠(OSO)/°	SO_2 Frequency Data/cm^{-1} *					
			ν_{as}	ν_s	Δ	Δ'	Δ''	ν_s/ν_a
Saccharin Ref. 14			1335	1180	155			0.884
Ref. 38	142.7(2) 142.8(2)	117.4(1)						
Ref. 39	142.9(4) 140.9(4)	117.7(1)						
Saccharinates								
Na Refs. 14, 18, 21	144.3(2) 145.0(2)	112.9(1)						
	144.6(2) 145.6(2)	113.9(1)	1260	1150	110	75	30	0.913
	144.5(2) 145.5(2)	114.0(1)						
Mg Refs. 14, 18, 21	144.5(2) 144.9(2)	114.4(1)	1265	1155	110	70	25	0.913
	142.2(2) 144.5(2)	114.4(1)						
Mn(II) Refs. 14, 20	143.7(2) 144.5(2)	116.1(1)	1288	1155	133	47	25	0.897
Studied compound [this work]			1288	1157	131	43	23	0.898
Ref. 3	142.0(4) 143.8(4)	113.3(3)						
	143.9(4) 144.5(4)	115.4(3)						

* The values in the last column are dimensionless. The symbols denote:
$\Delta = \tilde{\nu}(\nu_{as}) - \tilde{\nu}(\nu_s)$; $\Delta' = \tilde{\nu}[\nu_{as}(\text{Hsac})] - \tilde{\nu}[\nu_{as}(\text{M-sac})]$; $\Delta'' = \tilde{\nu}[\nu_s(\text{Hsac})] - \tilde{\nu}[\nu_s(\text{M-sac})]$.

The frequency of the carbonyl stretching band can be used to make certain predictions on the type of the metal-saccharin bonding.[12,13] As expected, the ν(CO) frequencies in the spectrum of the title compound are lower than the corresponding frequency in the spectrum of saccharin itself (1725 cm^{-1}).[14] The lowering of the ν(CO) mode frequency in the metal saccharinates compared to the corresponding mode in saccharin is found to be more pronounced in the ionic saccharinates than in the saccharinates where the metal-saccharin bonding is mainly of covalent type. The observed ν(CO) frequencies in the spectrum of the copper(II) imidazole saccharinato complex are lower compared to the frequency of the corresponding mode in the *covalently* bonded saccharinates of Hg(II) and ClHg(II), but higher than in the *ionic* saccharinates of Na, Mg and Pb(II) as well as in 2,2'-bipyridine saccharinato complex of Hg(II) (Table 1). According to this, it is to suppose that the character of the metal-saccharin bonding in the studied compound is of an *intermediate* type.

Sulphonyl stretching region

The assignment of the bands arising from the ν(SO_2) modes is usually complicated by the presence of other bands in this region.[18] Namely, according to the *ab initio* calculations for the saccharinato nitranion[19] as well as the results of normal coordinate treatment of phtalimide and the potassium salts of phtalimide and tetrachlorophtalimide[15,16], at least *five* to *six* bands originating from the saccharinato ligand are expected in the 1345-1100 cm^{-1} region. *Five* bands are found in this region in the infrared spectrum of imidazole, although only *two* bands are expected from the NCT results.[8]

The structural data for the studied complex[3] reveal that the sulphonyl groups participate in intermolecular hydrogen bonding, which could further

complicate the spectral appearance. The sulphonyl stretching bands are usually characterized by strong intensity and thus can be sometimes distinguished from the sharp benzenoid bands, as well as from the bands arising from the imidazole ring. The benzenoid bands, on the other hand, are found to be just slightly sensitive to temperature changes, which can be helpful in empirical assignments.

At least *ten* bands with appreciable intensity can be seen in the 1345-1100 cm^{-1} region of the LNT spectrum of the title compound (Fig. 3). The strongest one among them, with a maximum at 1288 cm^{-1}, could undoubtedly be assigned as *antisymmetric stretching mode* of the sulphonyl groups.

The assignment of the *symmetric stretching mode*, however, seems more complicated. Among several bands in the 1200-1100 cm^{-1} region, where the $\nu_s(SO_2)$ modes are expected, the most prominent bands at 1170 and 1157 cm^{-1} seem promising for this assignment (Fig. 3). Since both bands show similar temperature-change behavior, the empirical assignment of the band arising from the $\nu_s(SO_2)$ mode would be somewhat tentative. However, considering the earlier spectra-structure correlations in metal saccharinates[18] as well as the structural data for the Cu(II) imidazole saccharinato complex[3], it seems that the band at 1157 cm^{-1} would be a better choice to be assigned as $\nu_s(SO_2)$ mode. Namely, as shown in Table 2, the SO_2 structural parameters in copper(II) imidazole saccharinate are similar to the SO_2 parameters in the saccharinates of Mn(II), Na and Mg. It is to be noticed that the parameters of one of the SO_2 groups in the studied complex are similar to those of the SO_2 group in Mn(II) saccharinate.[20] At the same time, the frequencies of the $\nu(SO_2)$ modes in the spectra of both compounds are almost the same, which additionally confirms the assignment made.

In the saccharinate of sodium the three O-S-O angles differ slightly from each other (the maximum difference is 1,1 °).[21] Besides the presence of *three* structurally different O-S-O angles in the structure, only *one* pair of bands attributable to the sulphonyl stretchings is found in its spectrum. The difference between the values of the *two* structurally non-equivalent O-S-O angles in the studied complex (2,1 °) is close to the corresponding one found in sodium saccharinate. This implies that, in spite of the expectation of two pairs of SO_2 bands corresponding to the *two* structurally different sulphonyl groups, only *one* pair of bands might be, in fact, observed.

Otherwise, as it was found in the case of all previously studied saccharinates[18], due to the electron redistribution within the five-membered ring of the saccharinato ligand upon the deprotonation of the saccharin molecule, the frequencies of the sulphonyl stretching modes in the studied compound are lower compared to the corresponding frequencies in the spectrum of saccharin itself (Table 2).

Far infrared region

According to the NCT results, bands originating from the internal vibrational modes of imidazole are not expected in the 390-190 cm^{-1} region.[8] As our recent far-infrared study on a series of saccharinato compounds has shown[22], however, no bands originating from the internal modes of the saccharinate are expected to appear below 390 cm^{-1}.

The assignment of the stretching Cu-N(HIm) bands in the far infrared region was made considering the previous data for the metal-ligand stretching frequencies in a series of copper(II) complexes with various heterocyclic bases.[11,17,23-28] According to the metal isotope substitution results[23], the fairly strong band at 286 cm^{-1} in the spectrum of the distorted octahedral complex $Cu(HIm)_4Cl_2$ has been assigned to the ν[Cu-N(HIm)] mode, while

in the spectrum of polymeric octahedral $Cu(HIm)_2Cl_2$, the band at 306 cm^{-1} has been attributed to the corresponding mode. The bands at 307 and 286 cm^{-1} in the case of $[Cu(HIm)_4(ClO_4)_2]$ have been assigned as antisymmetric and symmetric Cu-N(HIm) stretching, respectively, but only one such band (at 290 cm^{-1}) was found for $[Cu(HIm)_4(NO_3)_2]$.[24] Some earlier studies[17] have shown that the ν(Cu-N) mode in the copper(II) complexes with nitrogen bases should appear as a strong band around 254 cm^{-1}. It is also known that this mode can sometimes be characterized by splitting due to the crystal field effect.[23]

Considering the above discussion, the strong band at 259 cm^{-1} in the RT spectrum of the title compound (Fig. 5) seems to be a good candidate to be assigned to the ν[Cu-N(HIm)] mode. One of the factors leading to the complex structure of the band might be the existence of different, albeit very similar Cu-N(HIm) distances [194.8(4) and 195.8(4) pm] in the structure. Because of its relatively high frequency, it seems unlikely for this band to be the result of lattice vibrational modes.

As it was already mentioned, the coordination polyhedron around the Cu atom can be described as a somewhat distorted trigonal bipyramide.[3] Namely, the equatorial Cu-N(sac) bonds [211.3(4) and 206.9(4) pm for the bridging and the non-bridging saccharinato ligand, respectively], as well as the Cu-O(sac) bond [226.6(3) pm], are noticeably longer than the Cu-N(HIm) bonds [194.8(4) and 195.8(4) pm], the latter being orientated towards the apexes of the coordination polyhedron. The difference in the basicity of the saccharinato ligand as compared to imidazole is surely one of the reasons leading to this fact. This might be taken as indication[17,24] that the bands originating from the ν[Cu-N(sac)] modes are to be expected at *lower* frequencies compared to the bands resulting from the Cu-N(HIm) stret-

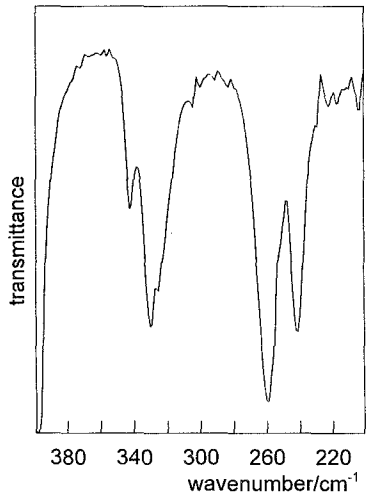

FIG. 5. The Far Infrared Region in the RT Spectrum of $[Cu_2(HIm)_4(sac)_4]$.

ching modes. Our detailed literature survey has shown, however, that data on ν[metal-N(sac)] assignments are rather scarce. It should be mentioned here that the ν[Zn-N(sac)] bands in $[Zn(py)_2(sac)_2]$ were expected lower than 224 cm^{-1}.[29]

According to the above description, it can be supposed that the asymmetric band around 240 cm^{-1} (Fig. 5) is in connection with the Cu-N(sac) stretching modes.

The ν(Cu-O) modes are expected to result in weaker bands and to appear at higher frequencies than the ν(Cu-N) modes[30], in regions where bands from the internal ligand modes are also expected. Although some of the bands around 330 cm^{-1} [31] in the spectrum of the title compound (Fig. 5) might include some ν[Cu-O(sac)] character, it is to be mentioned that all of the assignments in the far-infrared are tentative and a further study is needed in order to obtain more reliable results.

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REFERENCES

1. Li J., Zhang Y., Lin W., Liu S., Huang J., X-ray Crystal Structure and Electronic Spectrum of the Complex $[Co(C_3H_4N_2)_4(H_2O)_2](C_6H_4COSO_2N)_2$, *Polyhedron* 1992; **11**:419-422.
2. Zhang Y., Li J., Lin W., Liu S., Huang J., Synthesis, Crystal Structure and Spectral Studies of the Complex $[Ni(C_3H_4N_2)_4(H_2O)_2]\cdot(C_6H_4COSO_2N)_2$, *J. Cryst. Spec. Res.* 1992; **22**: 433-438.
3. Liu S., Huang J., Li J., Lin W., Structure of a Copper Complex Containing Saccharin and Imidazole: $[Cu_2(C_6H_4COSO_2N)_4(C_3H_4N_2)_4]$, *Acta Crystallogr.* 1991; C**47:** 41-43.
4. Li J., Ke Y., Wang Q., Wu X., Synthesis, Crystal and Molecular Structure of $Cd_2(sacch)_4(Im)_4$, *Cryst. Res. Technol.* 1997; **32**: 481-483.
5. Zhang Y., Li J., The Electronic Absorption Spectra of Binuclear Complexes, $[Cu(o\text{-}phen)(sal)]NO_3$ and $[Cu_2(sacch)_4(im)_4]$ crystal, *Spectrosc. Lett.* 1991; **24**:1395-1404.
6. GRAMS/386 for Microsoft Windows, Ver. 2.02, Galactic Industries Co., 1991-1993.
7. Ferrer E. G., Etcheverry S. B., Baran E. J., Darstellung und Eigenschaften von Vanadyl(IV)-Saccharinat, *Monatsh. Chem.* 1993; **124**: 355-366.
8. Cordes M., Walter L. J., Infrared and Raman Spectra of Heterocyclic Compounds-I The Infrared Studies and Normal Vibrations of Imidazole, *Spectrochim. Acta* 1968; A**24**: 237-252.
9. Davis J. W., Smith J., Imidazole Complexes with Cobalt(II) Salts, *J. Chem. Soc.* 1971; **A**: 317-324.
10. Hodgson B. J., Percy C. G., Thornton A. D., Band Assignments in the i.r. Spectrum of *cis,cis*-bis(glycinato)*cis*-bis(ilidazole)nickel(II) by Multiple Isotopic Labelling, *Spectrochim. Acta* 1979; A**35**: 949-952.
11. Knop O., Westerhause W., Falk M., Infrared Spectra of the Ammonium Ion in Crystals. Part VIII. Spectroscopic Criteria of Highly Bent Hydrogen Bonds, *Can. J. Chem.* 1980; **58**: 867-874.
12. Jovanovski G., Šoptrajanov B., Bonding of the Carbonyl Group in Metal Saccharinates: Correlation with the Infrared Spectra, *J. Mol. Struct.* 1988; **174**: 467-472.
13. Jovanovski G., Šoptrajanov B., Kamenar B., Spectra-Structure Correlations in Some Metal Saccharinates, *Bull. Chem. Technol. Macedonia* 1990; **8**: 47-66.

14. Jovanovski G., *Ph. D. Thesis*, University of Zagreb, 1981.

15. Hase I., The Infrared and Raman Spectra of Phtalimide, N-*d*-Phtalimide and Potassium Phtalimide, *J. Mol. Struct.* 1978; **48**: 33-42.

16. Hase I., The Infrared and Raman Spectra of Tetrachlorophtalic Anhydride, Tetrachlorophtalimide, N-*d*-Tetrachlorophtalimide and Potassium Tetrachlorophtalimide, *J. Mol. Struct.* 1979; **52**: 163-173.

17. Goldstein M., Monney F. E., Anderson A., Gebbie A. H., The Infrared Spectra and Structure of Complexes of Copper(II) Halides and Heterocyclic Bases, *Spectrochim. Acta*, **21** (1965) 105.

18. Jovanovski G., Tančeva S., Šoptrajanov B., The SO_2 Stretching Vibrations in Some Metal Saccharinates: Spectra-Structure Correlations, *Spectrosc. Lett.* 1995; **28**: 1095-1109.

19. Binev G., Stamboliyska A. B., Velcheva E. A., The Infrared Spectra and Structure of o-Sulfobenzoimide (Saccharin) and of Its Nitranion: An ab initio Force Field Treatment, *Spectrochim. Acta*, 1996; **A52**: 1135-1143.

20. Kamenar B., Jovanovski G., Manganese(II) Saccharinate Hexahydrate, $Mn(C_7H_4NO_3S)_2{\cdot}6H_2O$, and Isomorphism with the Analogous Fe, Co, Ni, Zn and Cd Complexes, *Cryst. Struct. Commun.* 1982; **11**: 257-261.

21. Jovanovski G., Kamenar B., Two Ionic Saccharinates: (1a) Sodium Saccharinate 2/3 Hydrate, $C_7H_4NO_3SNa{\cdot}2/3H_2O$ (1b) Magnesium Disaccharinate Heptahydrate, $(C_7H_4NO_3S)_2Mg{\cdot}7H_2O$, *Cryst. Struct. Commun.* 1982; **11**: 247-255.

22. Jovanovski G., Naumov P., Grupče O., Pejov Lj., to be published.

23. Cornilsen B. C., Nakamoto K., Metal Isotope Effect on Metal-Ligand Vibrations-XII. Imidazole Complexes with Co(II), Ni(II), Cu(II) and Zn(II), *J. Inorg. Nucl. Chem.* 1974; **36**: 2467-2471.

24. Hodgson B. J., Percy C. G., Thornton A. D., The Infrared Spectra of Imidazole Complexes of First Transition Series Metal(II) Nitrates and Perchlorates, *J. Mol. Struct.* 1980; **66**: 81-92.

25. Oglezneva T. M., Lavrenova L. G., IR Spectra of Valence Oscillations of Metal-Ligand Bonds in Metal Complexes with Tetrazoles, *Zh. Neorg. Khim.* 1985; **30**: 1473-1478.

26. Taylor E. C., Underhill A. E., Complexes of Cobalt(II) and Nickel(II) with Imidazole, *J. Chem. Soc.* 1969; **A**: 368-372.

27. Eilbeck W. J., Holmes F., Taylor C. E., Underhill A. E., Cobalt(II), Nickel(II), and Copper(II) Complexes of 2-Methylimidazole, *J. Chem. Soc.* 1968; **A**: 128-132.

28. Goodgame D. M. L., Goodgame M., Hayward P. J., Rayner-Canham G. W., Low-Energy Vibrational Spectra of Some Imidazole Complexes, *Inorg. Chem.* 1968; **7**: 2447-2451.

29. Quinzani O. V., Tarulli S., Piro O. E., Baran E. J., Castellano E. E., Crystal Structure, Vibrational Spectra and Thermal Analysis of Bis(saccharinato)bis(pyridine)zinc(II), *Z. Naturforsch.* 1997; **B52**: 183-187.

30. Nakagawa I., Shimanouchi T., Infrared Absorption Spectra of Aquo Complexes and the Nature of Coordination Bonds, *Spectrochim. Acta*, 1964; **20**: 429-439.

31. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed. New York: John Wiley, 1977.

32. Kamenar B., Jovanovski G., Grdenić D., Mercury(II) Saccharinate, $Hg(C_7H_4NO_3S)_2$, *Cryst. Struct. Commun.* 1982; **11**: 263-268.

33. Jovanovski G., Kamenar B., Ferguson G., Kaitner B., Structure of Chloromercury(II) Saccharinate, *Acta Crystallogr.* 1988; C**44**: 616-618.

34. Hergold-Brundić A., Kamenar B., Jovanovski G., Structure of the 1:1 Complex of Mercury(II) Saccharinate with 2,2'-Bipyridyl, *Acta Crystallogr.* 1989; C**45**: 556-558.

35. Grupče O., Jovanovski G., Mirčeski V., Spectra-Structure Correlations in 2,2'-Bipyridine Mercury(II) Saccharinate: Comparison with Mercury(II) Saccharinate and Chloromercury(II) Saccharinate, *Spetrosc. Lett.* 1994; **27**: 691-699.

36. Jovanovski G., Hergold-Brundić A., Kamenar B., Structure of Lead(II) Disaccharinate Monohydrate, *Acta Crystallogr.* 1988; C**44**: 63-66.

37. Tančeva S., Jovanovski G., Šoptrajanov B., Infrared Spectra of Protiated and Deuterated Lead(II) Saccharinate Monohydrate: Spectra-Structure Correlations, *Spectrosc. Lett.* 1992; **25**: 927-941.

38. Bart J. C. J., The Crystal and Molecular Structure of Saccharin (*o*-Sulphobenzoic Imide), *J. Chem. Soc.* 1968; B: 376-382.

39. Okaya Y., The Crystal Structure of Saccharin, *o*-Sulfobenzoimide, $C_6H_4CO.NH.SO_2$, an Artificial Sweetening, *Acta Crystallogr.* 1969; B**28**: 2257-2263.

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