

## Metal Saccharinates and Their Complexes with N-donor Ligands\*

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Received October 12, 1999; revised November 29, 1999; accepted May 15, 2000

The structural data for metal saccharinates and metal complexes including saccharin and various coordinated mono- (imidazole, pyridine) or polycyclic N-donor ligands (2,2'-bipyridine, 1,10-phenanthroline) were retrieved from the Cambridge Structural Database and analyzed. The influence of the nature of the metal ion and of the type of the metal-to-ligand bonding on the saccharinato geometry was examined. The structural data obtained by X-ray diffraction were correlated with the IR spectral features in the regions of the characteristic  $\nu(\text{CO})$  and  $\nu(\text{SO}_2)$  modes originating from the saccharinato ligands/ions as well as with the vibrations related to the  $\nu(\text{OH})$  and  $\nu(\text{OD})$  modes (in the case of crystallohydrates).

*Key words:* Cambridge Structural Database, ligation properties, metal saccharinates, N-donor ligands, saccharin, spectra, structures.

### INTRODUCTION

Saccharin (Figure 1) was discovered by Remsen and Fahlberg<sup>1</sup> in 1879. In *Chemical Abstracts*, besides the conventional name, saccharin appears as 1,2-benzisothiazole-3(2H)-one 1,1-dioxide. Saccharin is about 500 times sweeter than sugar. Its water soluble sodium salt therefore is widely used as artificial sweetener for diabetics as well as an additive in dietetic prod-

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\* Based upon the plenary lecture presented at the 8<sup>th</sup> Croatian-Slovenian Crystallographic Meeting, Rovinj, Croatia, June 17–19, 1999.

ucts. Saccharin, its derivatives and some metal saccharinates are found to be enzymatic inhibitors<sup>2</sup> and are also used as food additives and electroplating brighteners. The chemical properties and especially the physiological and biochemical activity of saccharin and its compounds have been intensively investigated mainly because of its suspected cancerogenic nature. In particular, since it has been shown that it causes cancer in rats,<sup>3</sup> saccharin joined the list of human potential cancer-causing substances in USA. After a long discussion, in 1997 saccharin was left on the list of potential human carcinogens.<sup>4</sup>

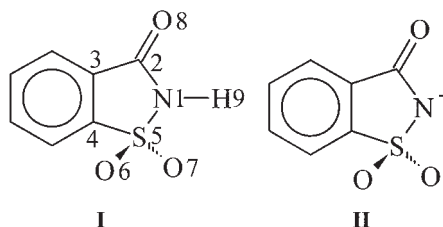


Figure 1. Saccharin (I) and saccharinato anion (II) formulae with the labeling scheme.

However, the wide commercial use of saccharin seems to have suppressed the suspicion of its potential harmful properties. So, the sale of food containing saccharin in USA, Canada and many other countries is allowed but with the following warning label: »Use of this product may be hazardous to your health. This product contains saccharin, which has been determined to cause cancer in laboratory animals«. Therefore, maybe it is about time to think of saccharin as a »sweetener that leaves a bitter aftertaste«

Saccharin contains three functional groups (carbonyl, imino and sulfonyl) connected to each other in a five-membered ring which is condensed to a relatively stiff benzene ring, Figure 1. Its deprotonated species shows pronounced ability for complexation. Namely, saccharin can serve as a versatile polyfunctional ligand being included as:

- i) an ion;
- ii) a ligand coordinated through
  - the nitrogen atom,
  - the carbonyl oxygen atom,
  - the sulfonyl oxygen atom,
  - the nitrogen atom and the carbonyl oxygen atom;
- iii) a neutral molecule;
- iv) several of the above modes in the same compound.

In order to establish the ligation properties of saccharin we have synthesized a series of metal saccharinates and studied their structural and spectroscopic characteristics using X-ray diffraction and IR spectroscopy. Research was broadened by including the metal complexes of saccharin with various mono- (imidazole, pyridine) or polycyclic N-donor bases (2,2'-bipyridine, 1,10-phenantroline) coordinated to the metal atom.\* Results obtained by other authors are also included in this analysis.

In order to obtain information on the geometry of deprotonated saccharin in the solid state we carried out a survey of the Cambridge Structural Database (CSD) for crystal structures of saccharinates.<sup>5</sup> In addition, we performed geometry optimizations of free saccharin molecule and free deprotonated saccharin using several semiempirical and *ab initio* methods.<sup>5</sup> The April 1999 version of CSD was searched for structures that contain unsubstituted saccharin (molecular or deprotonated).

In order to avoid any erroneous data, wherever possible, the extracted values of the relevant structural parameters were compared with the corresponding published data. Incomplete, incorrect data and data with  $R > 0.070$  were omitted from the analysis. In case of different data sets for the same compound, only the most accurate one was used.

Finally, 45 hits for saccharinates and 2 hits for saccharin were retrieved. Data for one structure published in the meantime (ammonium saccharinate) as well as 4 structures recently determined by us were added as well. Altogether, data sets for 50 saccharinates and 2 data sets for saccharin were used corresponding to a total of 70 deprotonated saccharin species considered. The detailed data for the compounds used in the survey of the Cambridge Structural Database can be found in Table 1 of Ref. 5.

## THEORETICAL STUDY

Calculations were performed with the Gaussian94 series of computer programs.<sup>6</sup> The geometries of isolated saccharin molecule and the corresponding anion were optimized with the AM1 and PM3 semiempirical methods. The resulting structures were used as starting points for further full geometry optimization at the Hartree-Fock level, using the basis set 6-31(d).

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\* The following abbreviations are used in the text: H(sac) – for saccharin; sac – for saccharinato ligand/ion; HIm – for imidazole; py – for pyridine; bpy – for 2,2'-bipyridine; phen – for phenantroline.

The saccharin molecule can be easily converted into the corresponding nitranion (Figure 1). As shown on Table 4 of Ref. 5, where the estimated partial charges for each atom of the five-membered ring of saccharin and saccharinato anion obtained from Mulliken population density analysis are given, various computational models provide different values.<sup>5</sup> Therefore, the absolute values of the charges predicted by this and the similar schemes should not be considered too literally. It might be beneficial, however, to employ them for comparison purposes. The analysis of these data shows that, on deprotonation, all oxygen atoms and the nitrogen atom, gain some negative charge and this is also likely for the positively charged C(2) and S(5) atoms, while the charges on C(3) and C(4) are only slightly changed. The deprotonation, therefore, is followed by redistribution of the negative charge over the residue, the largest portion being retained within the C(O)NSO<sub>2</sub> moiety.

The nitrogen atom is found to be more negatively charged than the carbonyl oxygen atom (O(8)). This might have implications on its coordination mode preferences in the solid state. It is notable that the sulfonyl oxygens are attached to substantially more positive center (the sulfur atom) compared to the carbonyl oxygen atom, bonded to C(2).

Besides the influence of the solid-state factors on the geometry of the parent molecule and the corresponding anion, the calculated redistribution of the negative charge upon deprotonation of saccharin results in following geometrical changes<sup>5</sup> (see Table 5 of Ref. 5):

- lengthening of the C–O and S–O bonds;
- shortening of the C–N bond and especially of the S–N bond;
- decrease of the O–S–O and S–N–C angles;
- increase of the C–S–N angle.

Also worth mentioning is that the angles around the S atom tend towards the ideal tetrahedral value of 109.5° upon deprotonation.

## THEORY *vs.* EXPERIMENT

The selected statistical and theoretical structural parameters of saccharin and its anion are given in Table I.

As seen from Table I, the average C–O distance (1.231 Å) is significantly shorter than the mean value (1.315 Å) between the standard double (1.205 Å) and single (1.425 Å) amide C–O bonds,<sup>7</sup> while the average value of the C–N bond length (1.361 Å) is very close to the mean value (1.353 Å) of amide C=N<sup>+</sup> (1.235 Å) and C–N (1.475 Å) bonds.<sup>7</sup>

TABLE I  
Selected statistical and theoretical structural parameters of saccharin and deprotonated saccharin

	Distances/Å				Angles/°		
	C–O	C–N	S–N	S–O	O–S–O	S–N–C	C–S–N
(Sac) <sub>av</sub>	1.217	1.372	1.663	1.428	117.5	115.05	92.45
(CSD) <sub>av</sub>	1.231	1.361	1.630	1.437	115.77	111.72	96.34
(this work) <sup>a</sup>	(23)	(25)	(20)	(10)	(1.71)	(1.24)	(1.08)
Diff. (CSD) <sup>b</sup>	0.014	−0.011	−0.033	0.009	−1.73	−3.33	3.89
Min (CSD)	0.103	1.304	1.592	1.411	111.75	109.79	92.23
Max (CSD)	1.278	1.456	1.670	1.470	109.79	117.70	98.0
	Distortion/% <sup>c</sup>						
CSD	1.1	−0.8	−2.0	0.6	−1.5	−2.9	4.2
AMI	1.5	−2.3	0.6	0.7	−4.6	−3.8	3.6
PM3	1.2	−3.1	−2.9	3.9	−4.5	−1.7	3.6
HF/3-21G(d)	1.7	−3.1	−4.4	1.1	−2.5	−1.9	4.8
HF/6-31++G(d,p)	2.1	−3.0	−4.0	1.3	−3.0	−3.5	5.8
MP2/6-31G(d)	1.8	−8.5	−4.7	1.2	−3.2	−4.2	7.2

<sup>a</sup> Standard deviations are given in parentheses.

<sup>b</sup> Obtained by subtraction of the mean saccharin values from the corresponding average CSD values of deprotonated saccharinato species.

<sup>c</sup> With respect to the saccharin values.

In order to inspect (at least qualitatively) whether the geometrical differences in the saccharinato five-membered ring between saccharin and deprotonated saccharin are primarily owing to intrinsic structural effects or are mainly influenced by the crystal packing factors, we compared the difference between the experimental average geometries of saccharin and deprotonated saccharin, on the one hand, and the corresponding theoretically predicted values (from their optimized gas-phase structures),<sup>5</sup> on the other (Table I).

The calculated changes qualitatively conform with the ones based on the CSD survey. It is, therefore, to believe that the differences between the geometry of saccharin in the solid state and its deprotonated form are predominantly caused by the redistribution of the nitranionic charge.

The influence of the crystal packing forces, however, should not be neglected. Namely, the predicted relative changes of the C–O and S–O bond lengths are larger than the averaged observed values. This implies that the perturbation of the structural parameters in the solid state from the corre-

sponding values in the gas phase (due to action of the crystal forces) is more pronounced in neutral saccharin than in deprotonated saccharin.

## EXPERIMENTAL STUDY

### *Structural Correlations*

#### *The »External« Ring Geometry (Carbonyl and Sulfonyl Groups)*

The above discussed electron redistribution in the five-membered ring of nitranion should be reflected on the lengths of the neighboring C–O and S–O bonds. Along with the expectations, the correlation of C–O and C–N bond lengths ( $r = 0.731$ ) shows that the lengthening of the C–N bond, shortens the adjacent C–O group, Figure 2.

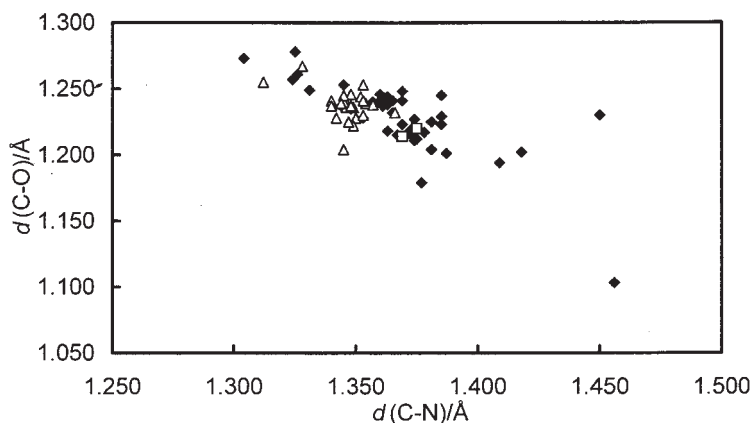


Figure 2. Plot of C–O vs. C–N distances in the metal saccharinates and saccharin (△ – ionic, ◆ – covalent, □ – saccharin).

An extreme case of the shortest C–N bond (1.304 Å)\* and very long C–O bond (1.273(4) Å) refers to one of the tin complexes where the geometry around the Sn is trigonal bipyramidal with O-ligands axial.<sup>8</sup> The saccharinato ligand in this compound is covalently bonded to the triphenylstannyl cation *via* its carbonyl oxygen. This lowers the electron density along the C–O bond, which receives some single bond character. On the other hand, the formal order of the adjacent C–N bond increases.

\* The standard deviation was not given in the original paper.

Contrary, the saccharinato ligand in chloromercury(II) saccharinate<sup>9</sup> is covalently bonded to the mercury(II) atom which is digonally coordinated by one Cl and one saccharinato N atom. The electron density along the C–N bond thus is reduced (1.45(2) Å) but apparently the effect is not transferred to the C–O bond (1.23(2) Å).

The most distorted saccharinato species is one of the two structurally non-equivalent saccharinato ligands in the binuclear complex [Cu<sub>2</sub>(HIm)<sub>4</sub>(N-sac)<sub>2</sub>(μ-N,O-sac)<sub>2</sub>] where the C–O distance (1.103(6) Å) of the non-coordinated CO group is the shortest while the C–N distance (1.456(6) Å) is the longest in the saccharinates<sup>10</sup> studied thus far. In our recent vibrational study<sup>11</sup> we could not find evidence that this anomaly is adequately reflected in the vibrational spectra of the complex: the corresponding C–O stretching mode in the IR spectrum of this compound (1675 cm<sup>-1</sup>) appears 50 cm<sup>-1</sup> lower than the ν(CO) mode in saccharin where the C–O distance is much longer (1.214(5) Å).<sup>12</sup>

The correlation between the S–N lengths and the mean S–O distances is much worse ( $r = 0.400$ ).<sup>5</sup> The O–S–O angle, on the other hand, exponentially increases ( $r = 0.789$ ) with the enlargement of the S–N distance.<sup>5</sup> Exclusion of the five worst fitting points gives  $r = 0.866$ .

The enlargement of the C–S–N angle lowers the O–S–O angle ( $r = 0.659$ ), both angles inclining towards the tetrahedral value (109.5°), Figure 3. Bending of the O–S–O angle of more than about 115°, however, does not yield values for the C–S–N greater than 98°, which seems to be the upper limit for this parameter in the studied cyclic system.<sup>5</sup>

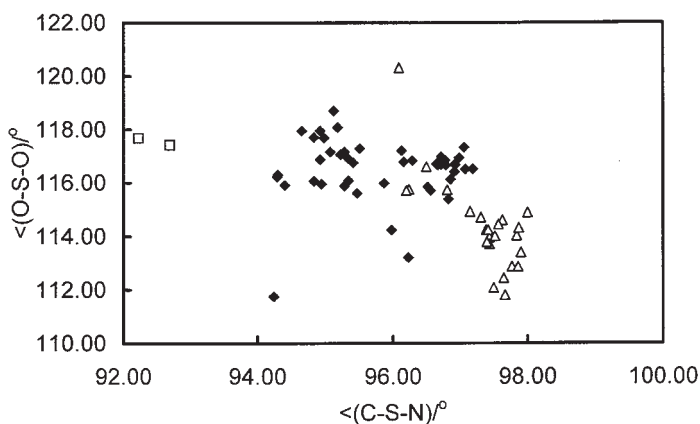


Figure 3. Plot of O–S–O angles vs. C–S–N angles in the metal saccharinates and saccharin (Δ – ionic, ◆ – covalent, □ – saccharin).

*The »Internal« Ring Geometry*

The structural data concerning the internal distortions of the five-membered ring were treated according to the two-dimensional approach of Dieterich *et al.*<sup>13</sup> This type of diagrams are plots of bond length differences *vs.* bond angle differences. In the present study four coordinates were used

$$\Delta d(\text{CC}) = 100[d(\text{C2-C3}) - d(\text{C3-C4})]$$

$$\Delta\alpha(\text{CC}) = 10[\angle(\text{C3-C2-N1}) - \angle(\text{C2-C3-C4})]$$

to describe the geometry of the C-C-C part of the ring, as well as

$$\Delta d(\text{SN}) = 100[d(\text{C4-S5}) - d(\text{C2-N1})]$$

$$\Delta\alpha(\text{SN}) = \angle(\text{S5-N1-C2}) - \angle(\text{C4-S5-N1})$$

for the distortions located primarily in the S-N fragment.

The deformations in the C-C-C part (Figure 4) show that data concentrate around the point  $\Delta\alpha(\text{CC}) = 30$  and  $\Delta d(\text{CC}) = 12$  and are more scattered to the negative side of  $\Delta\alpha(\text{CC})$ . The greatest distortion from the average geometry is found in the cases of digonally coordinated  $\text{HgCl}(\text{sac})^9$  and  $\text{Hg}(\text{sac})_2^{14}$  and tetrahedrally coordinated  $\text{Hg}(\text{bpy})(\text{sac})_2^{15}$  and  $[\text{HgCl}(\text{py})(\text{sac})]_2^{16}$  as well as in tetracoordinated  $\text{Cu}(\text{sac})(\text{R-py})^{17}$  or effectively pentacoordinated copper(II) saccharinates  $[\text{Cu}_2(\text{HIm})_4(\text{sac})_4]^{10}$ ,  $[\text{Cu}(\text{sac})(\text{bpy})_2] \text{sac} \cdot 3\text{H}_2\text{O}^{18}$  and  $[\text{Cu}(\text{sac})(\text{bpy})_2] \text{sac} \cdot 2\text{H}_2\text{O}^{19}$ . This indicates that the metal ion and the type of the bonding might influence the geometry of the deprotonated saccharin.

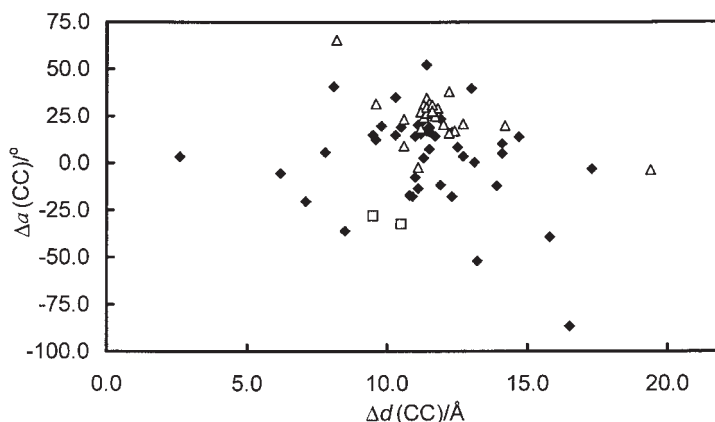


Figure 4. Dieterich *et al.* plot for the CCC(O) part of the saccharinato five-membered ring ( $\Delta$  – ionic,  $\blacklozenge$  – covalent,  $\square$  – saccharin).



The plot for the SN fragment (Figure 5) illustrates that mercury(II) saccharinates  $\text{HgCl}(\text{sac})^9$  and  $\text{Hg}(\text{sac})_2^{14}$  and copper(II) saccharinates  $[\text{Cu}_2(\text{HIm})_4(\text{sac})_4]^{10}$  and  $\text{Cu}(\text{sac})(\text{R-py})^{17}$  show some scatter towards lower  $\Delta d(\text{SN})$  and higher  $\Delta\alpha(\text{SN})$ .

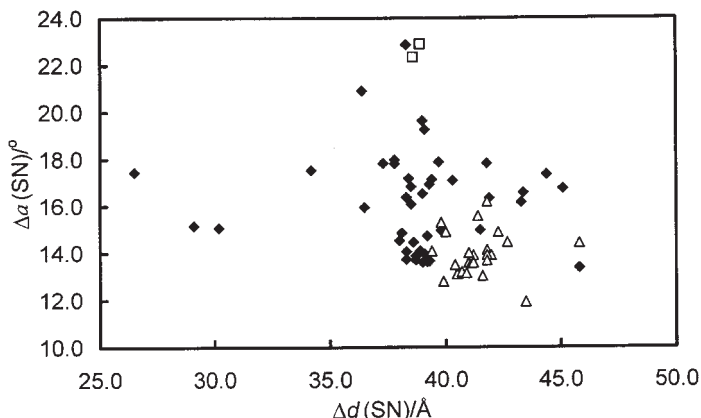


Figure 5. Dieterich *et al.* plot for the  $\text{CS}(\text{O}_2)\text{N}$  part of the saccharinato five-membered ring ( $\Delta$  – ionic,  $\blacklozenge$  – covalent,  $\square$  – saccharin).

Very distorted structures in the sense of high  $\Delta d(\text{SN})$  values are observed in  $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ ,<sup>20</sup> triphenylstannylsaccharinato complex<sup>8</sup> and two binuclear Cr(II) complexes<sup>21,22</sup> with formulae  $\text{Cr}_2(\text{sac})_4 \cdot 2\text{THF}^{21}$  and  $[\text{Cr}_2(\text{sac})_4(\text{py})_2] \cdot 2\text{py}^{22}$  that comprise amidato-like bridging saccharinato ligands *via* the N atom and carbonyl O atom.

#### *The Influence of the Metal Ion*

The existence of a series of eight isomorphous metal(II) saccharinate hexahydrates (metal(II) = V, Cr, Mn, Fe, Co, Ni, Cu, Zn) is useful for investigating some systematic trends in the geometry of the saccharinato ligand. As pointed out by Cotton *et al.*,<sup>23</sup> this octahedral structure is rather flexible and tolerates considerable structural changes without being collapsed and, at the same time, being suitable for structural studies.

The isomorphous series has already been used to study the Jahn-Teller distortion in the Cu and the Cr compounds.<sup>23,24</sup> Namely, the  $d^4$  and  $d^9$  configuration of Cr and Cu, respectively, cause contraction of four metal–ligand bonds and elongation of two metal–ligand bonds, the distortion around the metal ion being twice as large in the copper complex (see Figure 2 in Ref. 23). These trends are confirmed by the change in the length of the metal–

ligand (M–N and M–O) bonds and the unit cell volumes discussed in several occasions by Cotton *et al.*<sup>23,24</sup>

The variation (reduction) of the ionic size (corresponding to CN = 6)<sup>25</sup>

Metal(II)	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
Ionic size /Å	0.79	0.80	<b>0.83</b>	<b>0.78</b>	<b>0.74</b>	<b>0.69</b>	0.73	0.74	0.95

and the accompanying contraction of the M–N and M–O<sub>w</sub> distances in the series of the Mn(II), Fe(II), Co(II) and Ni(II) compounds leads to elongation of the C–N and C–O bonds, while V(II) and Zn(II) compounds show positive and negative shifts, respectively,<sup>5</sup> Figure 6. This trend is expected from the crystal field theory.<sup>25</sup> Conversely, the mean S–O distances are not significantly influenced by the type of the metal atom. Furthermore, the O–S–O angles are enlarged while the S–N–C angles show the opposite trend on going from Mn to Ni.<sup>5</sup>

It is a rather fundamental question, whether the changes in the geometry of the CNS fragment are a function of the electronic nature of the bonding (*i.e.* degree of covalency), on the bond distance, or both. Such problem, however, can not be investigated within the given isomorphous series, since the two variables are not independent of each other.

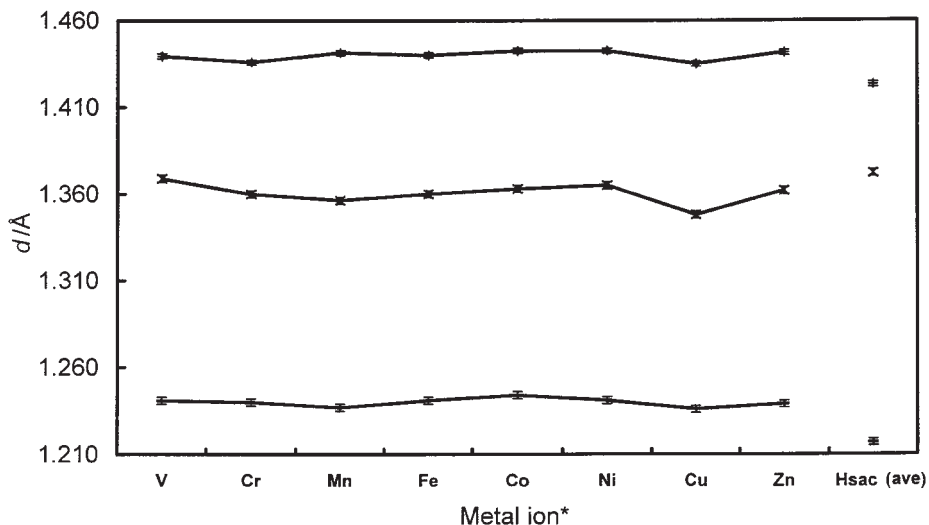


Figure 6. The C–O (lower line), C–N (middle line) and averaged S–O (upper line) distances of the isomorphous metal(II) saccharinates hexahydrates; (\*) the points on the right are the respective values for saccharin, averaged from two independent sets of data.

*The Influence of the Type of the Metal–Saccharinato Bonding*

The structural analysis has confirmed that deprotonated saccharin shows extraordinary versatility in the type of bonding in its metal compounds. 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 saccharinato ligand, furthermore, can be coordinated to the metal atom through the nitrogen atom, carbonyl oxygen or sulfonyl oxygens, but it can also serve as a bidentate amidato-like bridging agent, as it is the case with the structure of  $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ ,<sup>20</sup> Figure 7. The structure consists of  $\text{Pb}^{2+}$  cations, saccharinato anions and water molecules. Each  $\text{Pb}^{2+}$  ion is irregularly eight coordinated by six oxygen atoms and two nitrogen atoms. The carbonyl oxygen atom from one of the crystallographically independent saccharinato ions is coordinated to two  $\text{Pb}^{2+}$  ions, while the carbonyl oxygen atom from the other saccharinato ion is coordinated only to one  $\text{Pb}^{2+}$  ion (Figure 7).

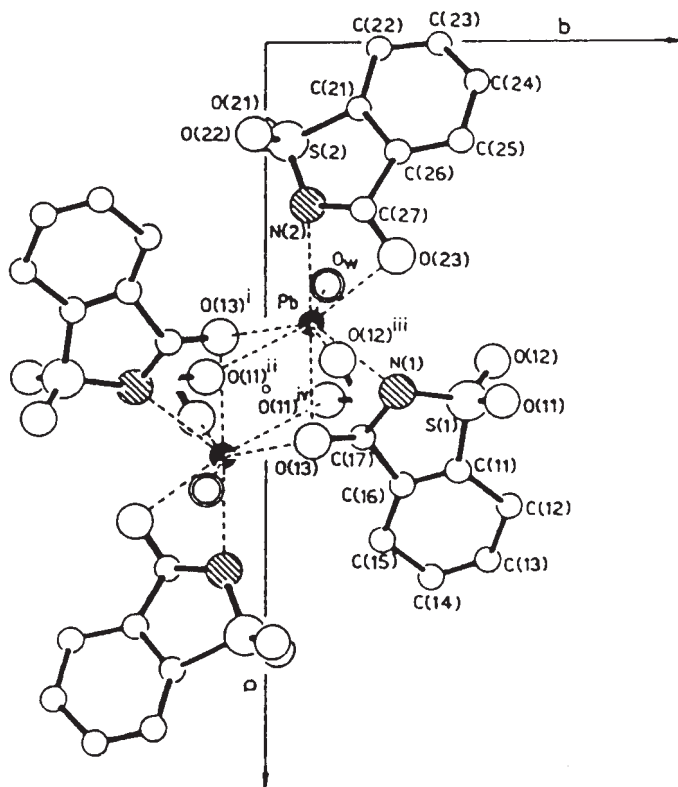


Figure 7. View on the structure of  $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ .

Two more structures of complexes  $[M(H_2O)_4(py)_2](sac)_2 \cdot 4H_2O$  ( $M = Co$  or  $Ni$ ) (Figure 8) and  $[HgCl(py)(sac)]_2$ <sup>16</sup> (see Fig. 1 in Ref. 16) illustrate the versatility in type of bonding of saccharin with various metals. The structure of former complex consists of  $[M(H_2O)_4(py)_2]^{2+}$  cations, non-coordinated saccharinato anions and also non-coordinated water molecules. The metal atom ( $Co$  or  $Ni$ ) lies on the inversion center and is octahedrally coordinated by four water oxygens and two pyridine nitrogen atoms. The mercury atom in the structure of the latter complex is surrounded with two chlorine atoms as well as one pyridine and one saccharinato nitrogen atom, forming a distorted tetrahedral arrangement. Two tetrahedra share one edge, consisting of two bridging chlorine atoms.

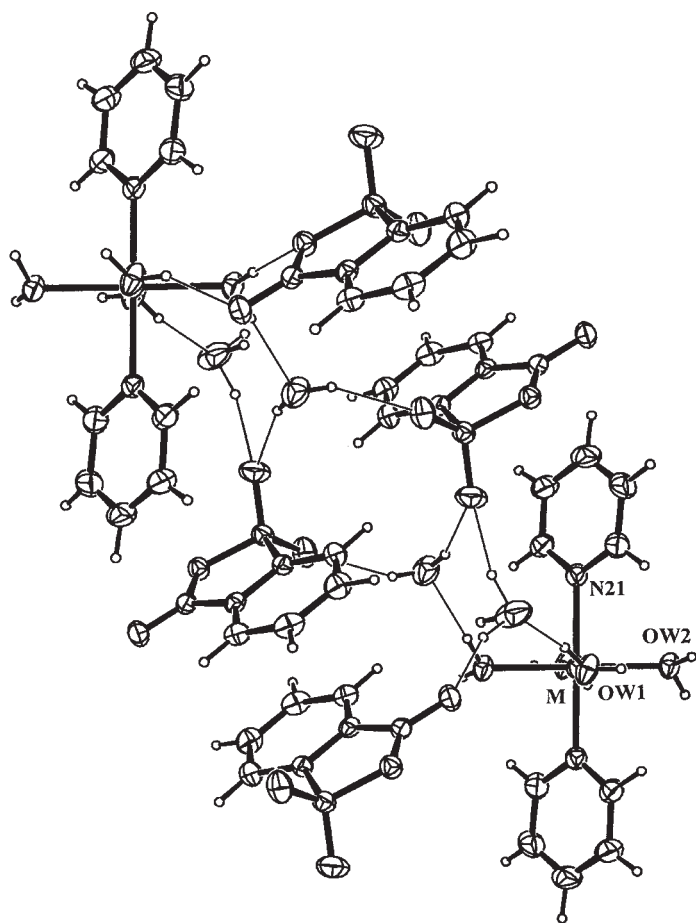


Figure 8. View on the structures of  $[M(H_2O)_4(py)_2]^{2+} \cdot 2sac^- \cdot 4H_2O$  ( $M = Co$  or  $Ni$ ).

Spectroscopic evidence was reported<sup>27</sup> in 1993 which suggested that the saccharinate of oxovanadium(II) includes saccharin molecules in its structure. We have recently synthesized Rb saccharinate and Cs saccharinate<sup>28</sup> that comprise neutral saccharin molecules as well, Figure 9. Their crystal structures have been also solved and will be published elsewhere.

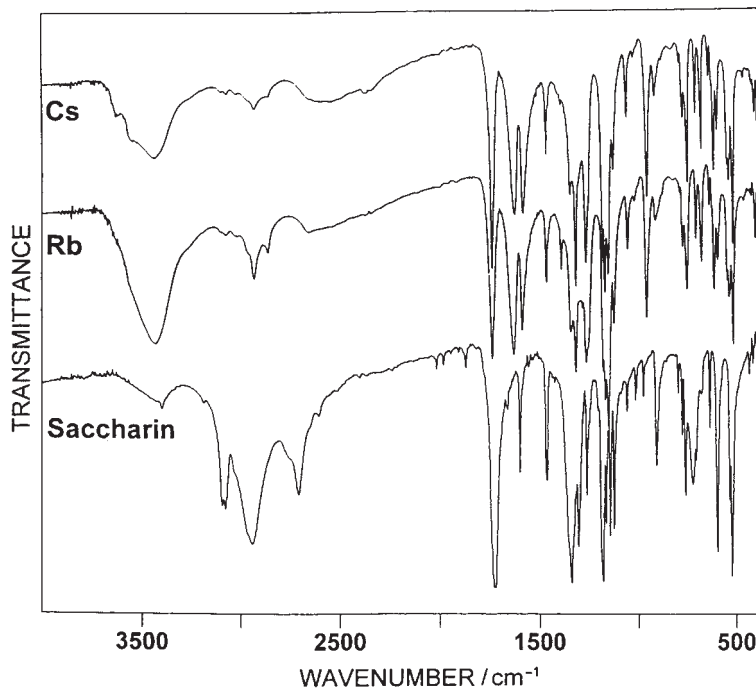


Figure 9. Infrared spectra of saccharin, Rb saccharinate and Cs saccharinate that comprise neutral saccharin molecules.

The analysis of structural characteristics of all saccharinates<sup>5</sup> has shown that from 70 deprotonated saccharin species, 46 are coordinated while 24 are non-coordinated. Acting as a ligand, however, deprotonated saccharin coordinates mostly through the nitrogen atom (34 cases from 46). Otherwise, the carboximido side seems to be slightly preferred for coordination over the sulfimido part. This might be mostly influenced by the greater partial negative charge on carbonyl than on sulfonyl oxygen atoms, estimated by most of the theoretical methods we used.

As it was shown above, the charge distribution within the saccharinato C(O)NSO<sub>2</sub> fragment notably influences its geometry. It is natural to expect,

therefore, that the type of metal–saccharinato bonding will be reflected on the geometry of the deprotonated saccharin as well.

On the other hand, the type of metal–saccharinato bonding in the saccharinates estimated from the comparison of sum of the van der Waals radii with respective determined metal–saccharinato distances is found to extend from ionic to purely covalent.

The general differences in the geometry among saccharinato ligands, saccharinato ions and molecular saccharin can be summarized as it follows:

– the changes of the geometry of the saccharinato five-membered ring on going from covalent to ionic saccharinates resemble those that accompany the conversion of saccharin molecule into a nitranion. This is quite understandable given that the N–H bond in the molecular saccharin is a covalent one;

– the saccharin molecule represents an extreme case of distortion considering the SN part of the ring being limiting geometry for the internal angle at the sulfur atom and for the correlation between the O–S–O angles and the S–N distances;

– the geometry of the saccharinato ions in the solid state tends to be more uniform than that of the covalently bonded (to the metal atom) saccharinato ligands. This finding confirms that besides the other structural effects (*e.g.*, the hydrogen bonding), coordination plays significant role for the geometry of the deprotonated saccharin;

– the C–O distances in the ionic saccharinates are in the 1.22–1.26 Å interval. The C–N distance is roughly restricted to the values within the 1.34–1.36 Å range. The covalent saccharinates, on the other hand, comprise much wider intervals for the C–O and C–N distances. On going from covalent to ionic saccharinates, the C–N bond shortens, while the C–O bond tends to be lengthened;

– the S–N bonds in the covalent saccharinates are usually longer than those in the ionic saccharinates. On passing from covalently bonded saccharinato ligands to ionic saccharinato species, averaged S–O distances tend to be greater. This is accompanied with bending of the O–S–O angle and enlargement of the C–S–N angle.

### *Spectra–Structure Correlations*

Precise assignment of the vibrational bands due to the saccharin itself, as a rather complex molecule, is complicated. In presence of other species in the system it is almost impossible. This, however, is not needed: the presence of bands due to the characteristic vibrations of the CO and SO<sub>2</sub> sac-

charinato groups as well as of  $\text{H}_2\text{O}$  molecules in the hydrated saccharinates can give valuable structural information.

### Water Stretches

The water (OH and OD) stretchings in the hydrated metal saccharinates have been continuously studied using isotopic dilution technique as a tool (at temperatures down to the liquid-nitrogen boiling temperature (LNT)). Here a few examples of spectra-structural correlations will be given.

Consistent with the presence of a single type of  $C_{2v}$  water molecules<sup>29</sup> in the structure of monoaquabis(pyridine)bis(saccharinato)copper(II),  $[\text{Cu}(\text{H}_2\text{O})(\text{py})_2(\text{sac})_2]$ , only one  $\nu(\text{OH})$  band ( $3418\text{ cm}^{-1}$  at LNT) as well as one  $\nu(\text{OD})$  band ( $2531\text{ cm}^{-1}$ ) appears in the LNT difference spectrum of the slightly deuterated analogue of the complex (Figure 10).

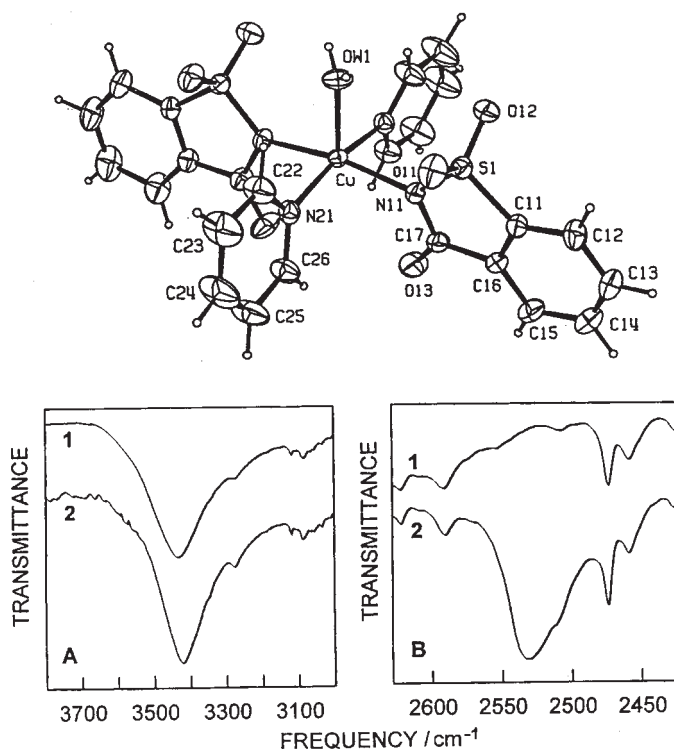


Figure 10. View on the structure of  $[\text{Cu}(\text{H}_2\text{O})(\text{py})_2(\text{sac})_2]$  (top) and its IR spectra in the  $\nu(\text{OH})$  and  $\nu(\text{OD})$  region: A1 refers to the OH stretches of the protiated sample at RT; A2 refers to the OH stretches of the protiated sample at LNT; B1 refers to the protiated sample at LNT; B2 refers to the OD stretches of the partially deuterated sample at LNT.

The spectral picture of lead(II) saccharinate monohydrate,  $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ , in the region of the  $\nu(\text{OH})$  stretchings of the highly deuterated samples as well as in the  $\nu(\text{OD})$  stretching region of the partially deuterated analogues<sup>30</sup> agrees well with the existence of only one type of water molecules in the structure (Figure 7);<sup>20</sup> the presence of asymmetric type of hydrogen-bonded water molecules in the structure is demonstrated by the appearance of two bands<sup>30</sup> in both above-mentioned spectral regions.

Of the three crystallographically non-equivalent water molecules in the structure of manganese(II) saccharinate hexahydrate,<sup>31</sup>  $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ , (as well as in the isomorphous analogues of V, Cr, Fe, Co, Ni, Cu, Zn and Cd), two are coordinated to the central metal atom and, at the same time, participate in hydrogen bonding with the non-coordinated water molecules or with oxygen atoms from the CO and  $\text{SO}_2$  groups. The  $\text{O}\cdots\text{O}_w$  distances range from 2.740(2) to 2.915(1) Å, two of them being practically identical (2.814(1) Å), (Figure 11). This accidental coincidence of the structural parameters makes it possible to explain the existence of five (instead of the expected six) bands in the OD stretching region of isotopically isolated HOD molecules<sup>32</sup> (Figure 11). It is worth mentioning that the spectral picture in the region of the OH stretchings of the isotopically isolated HOD molecules by DOD molecules is analogous (Figure 11).

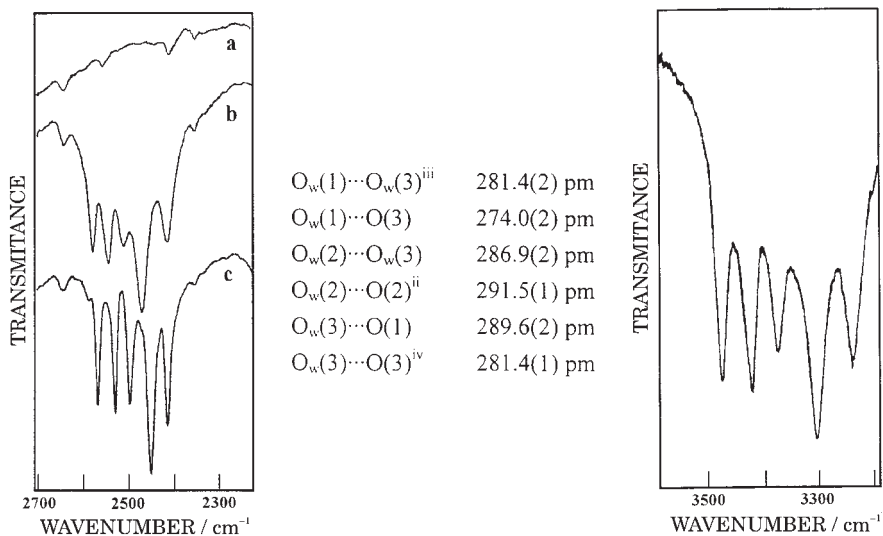


Figure 11. The  $\nu(\text{OD})$  region in the RT (b) and LNT (c) infrared spectra of partially deuterated  $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$  (curve a: the spectrum of the protiated compound) (left); the  $\text{O}_w\cdots\text{O}$  distances (middle); the  $\nu(\text{OH})$  region in the LNT infrared spectrum of highly deuterated  $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$  (right).



The copper compound, although a member of the above mentioned isomorphous series, is structurally somewhat different,<sup>33</sup> being characterized by an inherent pseudo Jahn-Teller instability. As a consequence, the hydrogen bonding in this compound is slightly different compared to that in the other members of the series. It is manifested by the appearance of spectral differences in the region of OH and OD stretching vibrations. The complex feature in the  $\nu(\text{OH})$  region of the copper compound is much broader compared to that of the other compounds.<sup>34</sup> Thus, it can be concluded that some of the hydrogen bonds in the copper compound are much stronger, while some are much weaker than those in the structures of the other members of the series. Similarly, the existence, in the  $\nu(\text{OD})$  region of the isotopically isolated HOD molecules, of two groups of bands<sup>34</sup> (Figure 12) can be considered as a further spectroscopic evidence for the existence of much stronger as well as also much weaker hydrogen bonds in the copper compound compared to the other members of the isomorphous series.

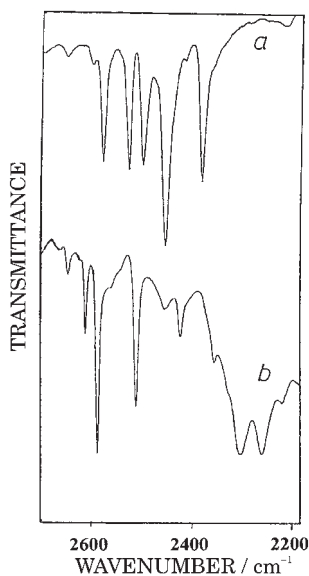


Figure 12. LNT infrared spectra of the Co (a) and Cu (b) saccharinates hexahydrates in the  $\nu(\text{OD})$  region of the partially deuterated samples.

### Carbonyl Stretchings

As it was already mentioned, the stretching vibrations of the carbonyl as well as of the sulfonyl group can be considered as a characteristic group vibrations being manifested by the appearance of very strong bands in the infrared spectrum of the corresponding compound. Therefore, they are often used to make structural inferences (in the cases when the crystal structure is not known) or to correlate the spectroscopic data with those obtained by crystal structure determination.

A few characteristic examples of correlation between the crystallographic and spectroscopic data will be mentioned for the C=O stretches. One of them is the manganese(II) saccharinate hexahydrate<sup>31</sup> and its isomorphous analogues of V,<sup>23</sup> Cr,<sup>24</sup> Fe,<sup>33</sup> Co,<sup>33</sup> Ni,<sup>33</sup> Cu,<sup>33</sup> Zn<sup>24,35</sup> and Cd.<sup>35</sup> Although all CO groups in the structure of this complex are equivalent (1.237(2) Å), two carbonyl stretching bands appear in its spectrum<sup>32</sup> at much lower frequencies (1620 and 1581 cm<sup>-1</sup>) than in saccharin (1725 cm<sup>-1</sup>). The spectral picture in the isomorphous compounds is analogous. The appearance of two bands can be explained as being due to the symmetry constraints (symmetry induced splitting).

Contrary to the case of manganese(II) saccharinate hexahydrate, the existence of three crystallographically different carbonyl groups (with very close C–O distances: 1.230(3), 1.241(4) and 1.237(3) Å) in the structure of triclinic form of trissodium trissaccharinate dihydrate,<sup>36</sup> Na<sub>3</sub>(sac)<sub>3</sub> · 2H<sub>2</sub>O, is manifested by appearance of only one (1635 cm<sup>-1</sup>) carbonyl stretching band\* in its infrared spectrum.<sup>32</sup> Its frequency is 90 cm<sup>-1</sup> lower than the corresponding made in the spectrum of saccharin.

Conversely, in spite of presence of four crystallographically different carbonyl groups (1.22(2), 1.23(2), 1.20(2) and 1.18(2) Å) in the covalent structure of mercury(II) saccharinate,<sup>14</sup> only two bands (1705 and 1680 cm<sup>-1</sup>) are found in its spectrum in the region of the carbonyl stretchings.<sup>32</sup> The frequencies of both bands are lower than in the spectrum of saccharin, although the differences are slight (20 and 45 cm<sup>-1</sup>).

Nevertheless, there are cases when the crystallographic and the spectroscopic data concerning the CO groups correlate with each other. This is the case, for example, with the covalent structure of chloromercury saccharinate<sup>9</sup> where the existence of only one type of CO groups in the structure (1.23(2) Å) is followed by the appearance of a single  $\nu(\text{CO})$  band in its infrared spectrum<sup>32</sup> (Figure 13), whose frequency is 31 cm<sup>-1</sup> lower than that of the corresponding band in the spectrum of saccharin.

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\* The band below 1600 cm<sup>-1</sup> is due to the benzenoid stretching mode of the saccharinato ion.

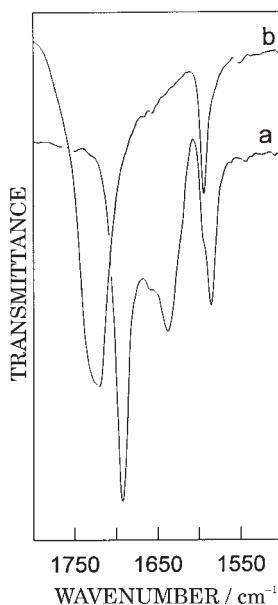


Figure 13. The  $\nu(\text{CO})$  region in the infrared spectrum of  $\text{HgCl}(\text{sac})$  (a) and saccharin (b).

The analysis of the carbonyl stretchings in the spectra of all studied metal saccharinates has shown that:

- irrespective of the participation in hydrogen bonding or/and in the coordination of the carbonyl group(s) around the metal atom, the  $\nu(\text{CO})$  mode in the spectra of saccharinates is always lower than the corresponding mode in saccharin itself;

- the degree of lowering depends on the character of the metal–saccharinato bonding, being more pronounced in the ionic than in the covalent saccharinates (see Table II);

- the number of the IR bands due to the  $\nu(\text{CO})$  modes does not always correlate with the number of the crystallographically non-equivalent CO groups in the structure (see Table II). Consequently, it is not possible to draw far-reaching structural conclusions on the basis of the behavior of the single vibrational band in the spectrum. In fact, this is well known, but very often neglected.

### *Sulfonyl Stretches*

As for the carbonyl groups, some characteristic examples of correlation between the spectroscopic and crystallographic data concerning the sulfonyl groups in various metal saccharinates will be also given here.

TABLE II

The number of non-equivalent CO groups in the structure *vs.* the number of  $\nu(\text{CO})$  bands and their frequency values in the IR spectra of saccharin and some metal saccharinates

Coumpoud	Number of non-equivalent CO groups	Number of $\nu(\text{CO})$ bands	$\nu(\text{CO})$ frequency / $\text{cm}^{-1}$
Saccharin	1	1	1725
HgCl(sac)	1	1	1694
[HgCl(py)(sac)] <sub>2</sub>	1	1	1686
Mg(sac) <sub>2</sub> · 7H <sub>2</sub> O	2	2	(16644) <sub>av</sub>
Na <sub>3</sub> (sac) <sub>3</sub> · 2H <sub>2</sub> O	3	1	1635
Hg(sac) <sub>2</sub>	4	2	(1693) <sub>av</sub>
M(sac) <sub>2</sub> · 6H <sub>2</sub> O (M = Fe, Co, Ni, Zn, Cd, Mn)	1	2	(1601) <sub>av</sub>
[Cu(H <sub>2</sub> O) (py) <sub>2</sub> (sac) <sub>2</sub> ]	1	2	(1663) <sub>av</sub>

The analysis of the SO<sub>2</sub> stretching region in the infrared spectrum of saccharin has shown that the presence of one type of SO<sub>2</sub> groups in its structure<sup>12,37</sup> is followed by appearance of two bands<sup>38</sup> due to the antisymmetric (1335  $\text{cm}^{-1}$ ) and symmetric stretching modes (1180  $\text{cm}^{-1}$ ), (Figure 14). Similarly, the presence of only one pair of SO<sub>2</sub> stretching bands<sup>38</sup> in the spectra of Mn(sac)<sub>2</sub> · 6H<sub>2</sub>O and HgCl(sac) is in consistence with the existence of only one type of SO<sub>2</sub> groups in their structures, Table III.

On the other hand, despite the presence of three crystallographically different SO<sub>2</sub> groups in Na<sub>3</sub>(sac)<sub>3</sub> · 2H<sub>2</sub>O<sup>36</sup> as well as of two non-equivalent SO<sub>2</sub> groups in Mg(sac)<sub>2</sub> · 7H<sub>2</sub>O,<sup>36</sup> only one pair of bands due to  $\nu_{\text{as}}(\text{SO}_2)$  and  $\nu_{\text{s}}(\text{SO}_2)$  modes is present in the infrared spectrum of each salt,<sup>38</sup> Table III.

The presence, however, of four different SO<sub>2</sub> groups in the structure of Hg(sac)<sub>2</sub><sup>14</sup> as well as of two non-equivalent SO<sub>2</sub> groups in the structure of Pb(sac)<sub>2</sub> · H<sub>2</sub>O<sup>20</sup> is followed by appearance of two pairs of SO<sub>2</sub> stretching bands in their infrared spectra,<sup>38</sup> Table III.

The above spectral behavior is consistent with crystallographic data for the metal saccharinates studied.<sup>38</sup> The SO<sub>2</sub> groups in the structures of the saccharinates of Mn(II)<sup>31</sup> and its isomorphous analogues as well as in the chloromercury compound<sup>9</sup> are equivalent while the values of the structurally different O–S–O angles in Na<sub>3</sub>(sac)<sub>3</sub> · 2H<sub>2</sub>O<sup>36</sup> and Mg(sac)<sub>2</sub> · 7H<sub>2</sub>O<sup>36</sup> are very close to each other. Conversely, two rather different values for the

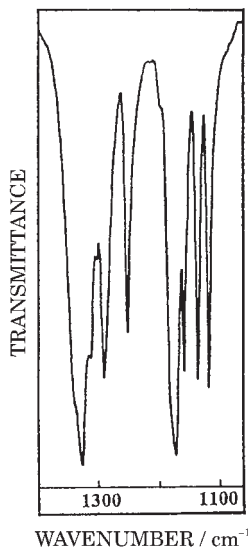


Figure 14. Infrared spectrum of saccharin in the  $\text{SO}_2$  stretching region.

O–S–O angles are present in the structure of  $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ ,<sup>20</sup> and similarly, the O–S–O angles present in the structure of  $\text{Hg}(\text{sac})_2$ <sup>14</sup> can be classified into two different groups. It is evident from the presented data that  $\nu_{\text{as}}(\text{SO}_2)$  and  $\nu_{\text{s}}(\text{SO}_2)$  frequencies in the spectra of the metal saccharinates studied are considerably influenced by the values of the O–S–O angles in the respective structures.

The detailed IR spectral study of metal saccharinates in the  $\text{SO}_2$  stretching region has shown that:

- the  $\nu(\text{SO}_2)$  modes in the spectra of saccharinates are always lower than the corresponding modes in the spectrum of saccharin itself;
- the antisymmetric stretching is more sensitive to structural changes than the symmetric one;
- the  $\nu(\text{SO}_2)$  modes are not indicative for the type of the metal–saccharinato bonds;
- it is possible to correlate the number of  $\nu(\text{SO}_2)$  bands with the number of structurally different sulfonyl groups;
- the  $\nu(\text{SO}_2)$  frequency is dependent on the O–S–O angle values rather than on the S–O distances.

TABLE III

The SO<sub>2</sub> geometry and frequencies in the IR spectra  
of saccharin and some metal saccharinates

Compound	$R(S-O)/\text{pm}$	$\angle(OSO) / ^\circ$	SO <sub>2</sub> frequency data/cm <sup>-1</sup> <sup>a</sup>																	
			$\nu_{\text{as}}$	$\nu_{\text{s}}$	$\Delta$	$\Delta'$	$\Delta''$	$\nu_{\text{s}}/\nu_{\text{as}}$												
Saccharin	142.7(2)	117.4(1)	1335	1180	155			0.884												
	142.8(2)																			
	142.9(4)	117.7(1)																		
	140.9(4)																			
Mn(II)	143.7(2)	116.1(1)	1288	1155	133	47	25	0.897												
	144.5(2)																			
ClHg(II)	142.6(9)	117.2(6)	1300	1163	137	35	17	0.895												
	143.3(10)																			
Na	144.3(2)	112.9(1)	1260	1150	110	75	30	0.913												
	145.0(2)																			
	144.6(2)	113.9(1)																		
	145.6(2)																			
	144.5(2)	114.0(1)																		
	145.5(2)																			
Mg	144.5(2)	114.4(1)	1265	1155	110	70	25	0.913												
	144.9(2)																			
	142.2(2)	114.4(1)																		
	144.5(2)																			
Hg(II)	143.5(15)	116.7(9)	1310	1155	155	25	25	0.882												
	144.3(20)																			
	142.2(16)	117.2(8)																		
	143.1(18)																			
	141.2(23)	118.7(11)							1286	1173	113	49	7	0.912						
	141.8(19)																			
	142.2(17)	111.8(9)																		
	143.4(13)																			
Pb(II)	143.9(9)	111.8(6)	1255	1167	88	80	13	0.930												
	143.3(9)																			
	146.3(19)	120.4(10)													1308	1142	166	27	38	0.873
	142.9(22)																			

<sup>a</sup> $\Delta = \nu_{\text{as}} - \nu_{\text{s}}$ ;  $\Delta' = \nu_{\text{as}}[\text{H}(\text{sac})] - \nu_{\text{as}}[\text{M-sac}]$ ;  $\Delta'' = \nu_{\text{s}}[\text{H}(\text{sac})] - \nu_{\text{s}}[\text{M-sac}]$ .

*Usefulness of Spectra-Structure Correlations*

As it was already shown above, in the cases when the crystal structure of the studied compound is known, the structural data can be used to make the empirical assignment of, at least, the most prominent bands in the infrared spectrum and, at the same time, to correlate the number of the bands due to the vibrations of the characteristic groups with the number of the corresponding crystallographically non-equivalent groups in the structure.

In the case when the crystal structure is unknown, the spectroscopic data can be used to predict some of the structural characteristics of the studied compound. Here, an example of use of spectroscopic data for making some structural inferences will be given. In an attempt, namely, to obtain some information about the character of the metal-to-ligand bonding in silver saccharinate, its infrared spectrum was studied.<sup>39</sup> It was shown that the silver-to-saccharin bond in silver saccharinate appears to be mainly ionic in character. This prediction was later confirmed by crystal structure determination.<sup>40</sup>

Another interesting example concerning the usefulness of spectra-structural correlations is the hydrate of sodium saccharinate. The sodium salt of saccharin is a well-known commercial product which is offered for sale (by various catalogues) as saccharin sodium salt dihydrate,  $C_7H_4NNaO_3S \cdot 2H_2O$ . Our spectroscopic and structural study, however, has shown that, in fact, two forms of sodium saccharinate exist. One of them is triclinic form (recrystallized from ethanol),  $Na(sac) \cdot 2/3H_2O$ ,<sup>36</sup> while the other one is monoclinic (recrystallized from  $H_2O$ ),<sup>41</sup>  $Na(sac) \cdot xH_2O$ . Since the crystal structure determination of the monoclinic form is in progress, the exact number of water molecules is still unknown. The analysis of the  $\nu(OD)$  region of the isotopically isolated HOD molecules, however, has unequivocally shown that the number of crystallographically non-equivalent water molecules in the monoclinic form of sodium saccharinate is much larger than two,<sup>41</sup> Figure 15. No one of the above two forms of sodium saccharinate corresponds to the chemical formula of the commercial sodium salt of saccharin,  $C_7H_4NNaO_3S \cdot 2H_2O$ , offered for sale.

The spectral appearance sometimes can be used in recognizing erroneous structural data. As an example, the results of the detailed comparison of the crystal structures of bis(2,2'-bipyridyl)saccharinato-*N*copper(II) saccharinate dihydrate<sup>15</sup> and bis(2,2'-bipyridine)saccharinato-*N*copper(II) saccharinate trihydrate<sup>42</sup> could be mentioned. The comparison of the structural data has shown that the subject of both papers is likely to be same compound and that the reported water content in the trihydrate is in error.<sup>43</sup> The thermal analysis, moreover, has inevitably confirmed such assumptions.<sup>43</sup>

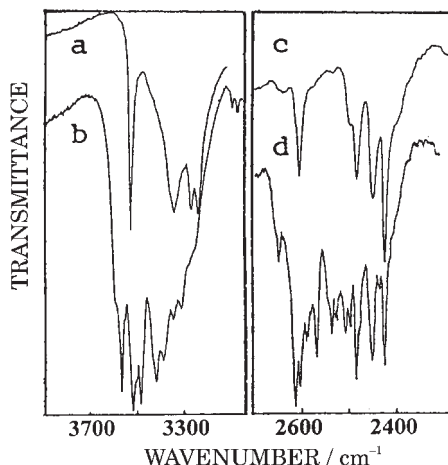


Figure 15. The O–H (a, b) and O–D (c, d) stretching region in the LNT infrared spectra of sodium saccharinate recrystallized from ethanol (a, c) and water (b, d).

*Acknowledgements.* – Special thanks are due to P. Naumov for critical reading of the manuscript and for the technical support. The author is also grateful to the referee for the very constructive suggestions regarding the improvement of the final version of the manuscript. The financial support by the Ministry of Science of the Republic of Macedonia and the Ministry of Science and Technology of the Republic of Croatia is highly appreciated.

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## SAŽETAK

### Metalni saharinati i njihovi kompleksi s N-donorskim ligandima

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U *Cambridge Structural Database* nađeni su i analizirani strukturni podaci za metalne saharinate i za metalne komplekse koji sadrže saharin i različite koordinirane mono- (imidazol, piridin) i policikličke N-donorske ligande (2,2'-bipiridin, 1,10-fenatrolin). Istraživan je utjecaj prirode metalnog iona i tipa veze metal–ligand na geometriju saharinata.

Strukturni podatci dobiveni difrakcijom X-zraka korelirani su sa značajkama spektara u područjima karakterističnih modova  $\nu(\text{CO})$  i  $\nu(\text{SO}_2)$  koji potječu od saharinata i također s vibracijama povezanim s  $\nu(\text{OH})$  i  $\nu(\text{OD})$  modovima (u slučaju kristalnih hidrata).