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**SPECTRA-STRUCTURE CORRELATIONS IN 2,2'-BIPYRIDINE
MERCURY(II) SACCHARINATE: COMPARISON WITH
MERCURY(II) SACCHARINATE AND CHLOROMERCURY(II)
SACCHARINATE***

Key words: Mercury(II) saccharinates, bipyridine complex, infrared spectra,
spectra-structure correlations

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ABSTRACT

The infrared spectrum of 1:1 complex of mercury(II) saccharinate with 2,2'-bipyridine, $[\text{Hg}(\text{C}_7\text{H}_4\text{NO}_3\text{S})_2(\text{C}_{10}\text{H}_8\text{N}_2)]$, was studied in the CO and SO₂ stretching regions. The appearance of the spectrum in the region of the carbonyl stretching modes was correlated with the number of non-equivalent CO groups in the structure. The spectral and structural characteristics of the CO groups in the title compound were compared with the corresponding ones in the mercury(II) saccharinate and chloromercury(II) saccharinate. It was found that the frequency of the CO stretchings in the spectrum of $\text{Hg}(\text{bpy})(\text{sac})_2$ is significantly lower (1630 and 1615 cm⁻¹) than the frequency of the corresponding modes in the spectra of covalently bonded mercury(II) saccharinate (1705 and 1680 cm⁻¹) and chloromercury saccharinate (1694 cm⁻¹). An attempt was also made to assign the bands which are mainly due to the symmetric and the antisymmetric SO₂ stretching vibrations.

*Saccharin is 1,2-benzisothiazol-3(2H)-one 1,1-dioxide

INTRODUCTION

Working on the investigation of the ligation properties of saccharin in various metal saccharinates, we have studied the structural characteristics of three different complexes of saccharin with mercury¹⁻⁷: $\text{Hg}(\text{sac})_2$, $\text{ClHg}(\text{sac})$ and $\text{Hg}(\text{bpy})(\text{sac})_2$ (sac and bpy denoting – saccharin and bipyridine, respectively). It was found that the saccharinate N to Hg bonds of 214.1(4) and 212.0(4) pm in the title compound³ are longer than the corresponding bonds in the structure of mercury(II) saccharinate (203 – 206 pm)¹ and chloromercury(II) saccharinate (202.1 pm)². The elongation of the Hg–N bonds in the bipyridine complex has been attributed to the increase of the coordination number of Hg from *two* [in $\text{Hg}(\text{sac})_2$ and $\text{ClHg}(\text{sac})$] to *four* [in $\text{Hg}(\text{bpy})(\text{sac})_2$]^{1-3, 10}.

It was found, however, that the frequency of the CO stretching modes in the spectrum of $\text{Hg}(\text{bpy})(\text{sac})_2$ (1630 and 1615 cm^{-1}) is significantly *lower* than the frequency of the corresponding modes in the spectra of $\text{Hg}(\text{sac})_2$ (1705 and 1680 cm^{-1})⁴⁻⁶ and $\text{ClHg}(\text{sac})$ (1694 cm^{-1})⁴⁻⁶. Otherwise, the frequency of the stretching CO vibrations in the spectra of metal saccharinates is *lower* than in saccharin itself but the magnitude of the frequency lowering depends on the type of the metal-to-saccharin bond, the shifting being more pronounced on going from the purely covalent to the ionic saccharinates⁴⁻⁹.

The availability of structural data for saccharin^{11,12}, $\text{Hg}(\text{sac})_2$ ¹, $\text{ClHg}(\text{sac})$ ² and $\text{Hg}(\text{bpy})(\text{sac})_2$ ³ as well as of some spectroscopic data for saccharin⁶ and a series of metal saccharinates⁴⁻⁹ makes it possible to attempt to correlate the type of bonding and the frequencies of the CO stretching modes and thus test the probability that the frequency of the $\nu(\text{CO})$ mode in $\text{Hg}(\text{bpy})(\text{sac})_2$ is an indication of the existence of some ionic character along the Hg–N(saccharin) bond. It is the main subject of the present paper.

EXPERIMENTAL

The studied compound was prepared and recrystallized according to the method described by Hergold-Brundić *et al.*³. The infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer, using KBr pellets. The low-temperature infrared spectra were measured on a variable temperature cell

(RIIC VLT-2). For the conductivity measurements an Iskra type conductometer with standard conductometric cell was used.

RESULTS AND DISCUSSION

Spectral data

The low-temperature (LNT) infrared spectrum of 1:1 complex of mercury(II) saccharinate with 2,2'-bipyridine is shown in Fig. 1. Fig. 2 shows the room-temperature infrared spectra of saccharin, $\text{Hg}(\text{sac})_2$, $\text{ClHg}(\text{sac})$ and $\text{Hg}(\text{bpy})(\text{sac})_2$ in the regions of the stretching vibrations of CO and SO_2 groups belonging to the five-membered ring of saccharin itself or to saccharinate ligands in metal saccharinates.

Structural data

The more detailed data about the crystal structures of $\text{Hg}(\text{sac})_2$, $\text{ClHg}(\text{sac})$ and $\text{Hg}(\text{bpy})(\text{sac})_2$ as well as for saccharin itself are given in references 1–3, 11 and 12. Here, only the data concerning the type of bonding and the CO and SO_2 groups will be summed up.

Spectra-structure correlations

CO stretchings. The situation in the CO stretching region in the infrared spectra of metal saccharinates is, in general, complicated by the presence in the same spectral region of bands due to some of the vibrations of the six-membered aromatic ring and (in the case of the hydrates) of bands arising from the HOH bending vibrations^{4–6}. Fortunately, the title compound, $\text{Hg}(\text{bpy})(\text{sac})_2$, as well as the two other mercury saccharinates, $\text{Hg}(\text{sac})_2$ and $\text{ClHg}(\text{sac})$, are anhydrous, while the benzenoid stretching bands, nevertheless, appear *lower*^{13,14} (below 1600 cm^{-1}) and are sharper than the bands originating from the CO stretches.

Fig. 2 shows that the sharp bands around 1590 cm^{-1} in the spectra of saccharin, $\text{Hg}(\text{sac})_2$, $\text{ClHg}(\text{sac})$ and $\text{Hg}(\text{bpy})(\text{sac})_2$ have almost the same frequency and are undoubtedly due to at least one of the modes belonging to the benzenoid stretchings. It is therefore evident that the two bands above 1600

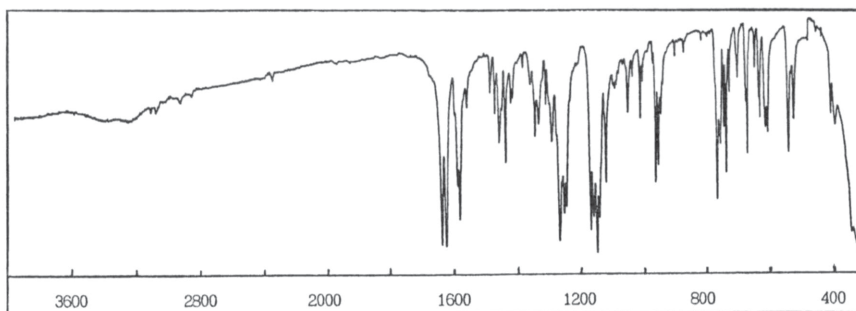


FIG. 1. Low-temperature (LNT) infrared spectrum of 1:1 complex of mercury(II) saccharinate with 2,2'-bipyridine, $\text{Hg}(\text{bpy})(\text{sac})_2$.

cm^{-1} in the spectrum of $\text{Hg}(\text{bpy})(\text{sac})_2$ (cf curve 4 in Fig. 2) originate from the CO stretching vibrations. Although the bond length difference between the *two* crystallographically independent C=O groups in the structure (121.7 and 123.3 pm)³ is small (1.6 pm), the appearance of *two* rather separated strong bands in the region of the CO stretching modes is in agreement with the structural data.

Fig 2 also shows that the frequency of both carbonyl stretching vibrations in the spectrum of *covalently* bonded $\text{Hg}(\text{bpy})(\text{sac})_2$ (1630 and 1615 cm^{-1}) is *lower* than the frequency of the corresponding mode in saccharin itself (1725 cm^{-1}) but, at least on the first sight, unexpectedly *lower* than in the other two also *covalently* bonded mercury saccharinates, $\text{Hg}(\text{sac})_2$ (1705 and 1680 cm^{-1}) and $\text{ClHg}(\text{sac})$ (1694 cm^{-1}). These shifts of the carbonyl stretches to lower frequencies are even *similar* to the previously observed values in the spectra of a series of *ionic* saccharinates^{4-6,8,9}. It could be a serious indication that the mercury-to-saccharin bond in $\text{Hg}(\text{bpy})(\text{sac})_2$ is partly *ionic* in character. This conclusion is in accordance with the results of the conductivity measurements of the studied compounds⁷, (see Table 2).

The existence of some extent of ionic character in the title compound is, to some extent, in agreement with the existence of longer Hg-N(saccharinato) distances (212.0 and 214.1 pm) in $\text{Hg}(\text{bpy})(\text{sac})_2$ compared to the distances of the corresponding bonds in $\text{Hg}(\text{sac})_2$ and $\text{ClHg}(\text{sac})$ [203 to 206 pm in $\text{Hg}(\text{sac})_2$ and 202.1 pm in $\text{ClHg}(\text{sac})$]. It should, however, be born in mind that the above

TABLE 1
Some Characteristic Data Concerning the Type of Bonding and the CO
and SO₂ Groups in Saccharin, Hg(sac)₂, ClHg(sac) and Hg(bpy)(sac)₂.

	C o m p o u n d			
	Saccharin	Hg(sac) ₂	ClHg(sac)	Hg(bpy)(sac) ₂
Number of non-equivalent CO and SO ₂ groups	1	4	1	2
<i>R</i> (C-O)/pm	122.0 ¹¹ 121.4 ¹²	122 123 120 118	123	121.7 123.3
<i>R</i> (S-O)/pm	142.7 ¹¹ 142.8 ¹¹ 140.9 ¹² 142.9 ¹²	144 144 142 143 141 142 142 143	142.6 143.3	144.5 143.2 143.2 143.4
∠ O-S-O ^o	117.4 ¹¹ 117.7 ¹²	116.7 117.2 118.7 111.8	117.2	115.9 116.2
Characteristic coordination of mercury atom		digonal	digonal	tetrahedral
<i>R</i> (Hg-N _{sac})/pm		204 205 203 206	202.1	214.1 212.0

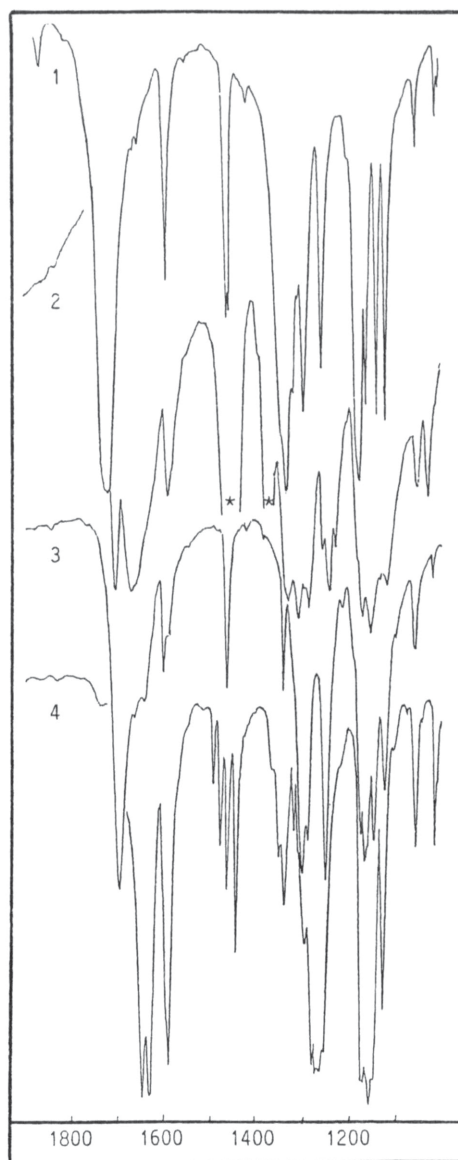


FIG. 2. Room-temperature (RT) infrared spectra of saccharin (1), Hg(sac)₂ (2), ClHg(sac) (3) and Hg(bpy)(sac)₂ (4) in the regions of the stretching vibrations of CO and SO₂ groups (the asterisks denote Nujol bands)

TABLE 2
*Relative Conductivity of Investigated Compounds
 in a Solution of Dimethyl Sulfoxide ($c = 0.01 \text{ mol} \cdot \text{dm}^{-3}$)*

No.	Compound	Relative conductivity
1.	saccharin	0.09
2.	Hg(sac) ₂	0.02
3.	HgCl(sac)	0.03
4.	Hg(bpy)(sac) ₂	0.23

mentioned elongation is mainly influenced by the increase of the coordination number of Hg from *two* [in Hg(sac)₂ and ClHg(sac)] to *four* [in Hg(bpy)(sac)₂]^{1-3,10}.

SO₂ stretchings. The strong bands due to the two SO₂ stretching vibrations are expected¹⁵⁻¹⁸ in the 1350-1100 cm⁻¹ region. It should be born in mind, however, that the bands originating from the two additional types of vibrations, in the same spectral region, are expected to appear. That is, the normal-coordinate analysis for phtalimide, potassium phtalimide and its tetrachloro analogue has shown that, at least *four*¹³ or possibly *six*¹⁴ bands should appear in the 1360-1130 cm⁻¹ region as a result of ring stretches. On the other hand, the spectrum of Hg(bpy)₂Cl₂ shows that *four* additional bands due to bipyridyl vibrations appear in the region from 1320 to 1160 cm⁻¹. All in all, about *ten to twelve* bands are expected in the 1360-1100 cm⁻¹ spectral region.

As mentioned above, the S-O distances in the two crystallographically different SO₂ groups in the structure of the title compound are very close to each other (144.5 and 143.2 pm in the first and 143.2 and 143.4 pm in the second SO₂ group), while the two O-S-O angles are almost the same (115.9 and 116.2 °). Judging from the above-mentioned very close similarity between the two SO₂ groups in the structure of Hg(bpy)(sac)₂ it seems reasonable to suppose that only one pair of bands due to antisymmetric and symmetric SO₂ vibrations should appear in the spectrum.

As seen in Fig. 2, (curve 4), *thirteen* bands of various intensity appear in the infrared spectrum of Hg(bpy)(sac)₂ in the region from 1360 to 1100 cm⁻¹ but *two* complex bands (each having *four* submaxima) dominate among them.

Their centroids are at about 1275 and 1160 cm^{-1} . There is no doubt that the band arising from the antisymmetric SO_2 stretching vibrations in the spectrum of the title compound is one of the constituents of the above-mentioned high-frequency complex band with a centroid at about 1275 cm^{-1} but it is difficult to say which one is due to the $\nu_{\text{as}}(\text{SO}_2)$ mode. The situation with the $\nu_{\text{s}}(\text{SO}_2)$ mode is the same.

In spite of the difficulties concerning the determination of the precise frequencies of the bands due to the $\nu_{\text{as}}(\text{SO}_2)$ and $\nu_{\text{s}}(\text{SO}_2)$ modes, it is evident that the frequency of the antisymmetric and symmetric SO_2 stretching bands in the title compound is *lower* than that of the corresponding bands in the spectrum of saccharin⁶, $\text{ClHg}(\text{sac})$ ^{6,9} and $\text{Hg}(\text{sac})_2$ ^{6,9} (see Fig. 2) and falls close to the region of the corresponding frequencies of the ionic saccharinates of Na ^{6,9}, Mg ^{6,9} and Mn ^{6,9}. Various factors, however, determine the frequency difference of the two SO_2 stretching modes⁹. Therefore, the position of the SO_2 bands cannot be used to make conclusions about the type of metal-to-ligand bonding.

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