

Short communication

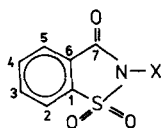
Metal-to-ligand bonding in some metal saccharinates: a ^{13}C NMR studyErich Kleinpeter^a, Dieter Ströhl^a, Gligor Jovanovski^b and Bojan Šoptrajanov^b^aSektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Weinbergweg 16, 4050 Halle (Saale) (Germany)^bInstitut za hemija, PMF, Univerzitet "Kiril i Metodij", Skopje (Yugoslavia)

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INTRODUCTION

The crystal structures of a number of solid saccharinates of various metals have been determined recently [1-6]. On the basis of the comparison of the observed metal-to-ligand distances with the sum of the van der Waals radii, the bonding in $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{sac})_2 \cdot 7\text{H}_2\text{O}$ and $\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$ was thought to be purely ionic [1,2], and that in $\text{Hg}(\text{sac})_2$ and $\text{Hg}(\text{sac})\text{Cl}$ [4,5] to be mostly covalent, whereas the M-N bonds in the series of saccharinates having the general formula $\text{M}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ (M=Mn, Fe(II), Co, Ni, Zn and Cd) [3] were considered to be of the intermediate type. Attempts were also made to find other structural features (interatomic bonds and/or angles) which could be correlated with the expected character of the metal-to-ligand bonds. It was found that, indeed, the C-C, C-N and C-S bond length and the interatomic angles within the five-membered ring (see Scheme 1) of the saccharinate ligands change rather regularly

Scheme 1



Compound	X	Crystal water
<u>1</u>	H	—
<u>2</u>	Hg(sac)	—
<u>3</u>	Cd(sac)	6 · H ₂ O
<u>4</u>	Zn(sac)	6 · H ₂ O
<u>5</u>	Pb(sac)	H ₂ O
<u>6</u>	Mg(sac)	7 · H ₂ O
<u>7</u>	Na ₃ (sac) ₂	2 · H ₂ O

on going from the purely ionic to the covalent saccharinates (or, for that matter, saccharin itself). It was further concluded that these changes are due to the redistribution of the electron density in the saccharinate anions.

The hydrates of several solid metal saccharinates have been studied by infrared spectroscopy as well but these studies were devoted to the bonding of the water molecules [7-9] and to the dependence of the C=O stretching frequencies on the participation (or absence of such) of the carbonyl oxygens in the coordination polyhedra of the metals [9,10]. The question of the character of the metal-to-saccharinate bonding was not considered in these studies.

To the best of our knowledge, no systematic study of metal saccharinates in solution has been carried out so far. It was thought, therefore, that a ^{13}C NMR spectroscopic study could shed some light on the problem of the metal-to-saccharinate bonding in these compounds (at least in DMSO solution) and could serve as an independent (albeit indirect) test of the validity of the conclusions drawn from the X-ray studies.

EXPERIMENTAL

The solid compounds were prepared and recrystallized as described elsewhere [1-6]. The preparation methods are essentially identical to those proposed by Defournel [11]. The ^{13}C NMR spectra of saccharin and the saccharinates of Hg, Cd, Zn, Pb, Mg and Na were measured in DMSO- d_6 solutions, using a BRUKER WP-200 NMR Spectrometer operating at 50.327 MHz. An attempt was made to record the spectra of the saccharinates of Mn, Fe, Co and Ni but, unfortunately, these compounds were found to be paramagnetic.

RESULTS AND DISCUSSIONS

The ^{13}C chemical shifts in the NMR spectra of the investigated compounds are collected in Table 1. The assignment of the signals from C-1, C-6 and C-

TABLE 1

^{13}C -chemical shifts δ (ppm) of saccharin **1** and some metal saccharinates **2-7** (DMSO- d_6 /TMS)

Compound	C-1	C-2-C-5 ^a				C-6	C-7	av ^b
1 sac	139.2	121.2	124.9	134.8	135.6	127.4	160.7	134.8
2 Hg(sac) ₂	142.3	120.8	124.5	134.1	134.8	128.9	163.8	135.6
3 Cd(sac) ₂ ·6H ₂ O	145.1	119.2	122.7	131.3	131.8	134.2	168.1	136.0
4 Zn(sac) ₂ ·6H ₂ O	144.5	119.7	123.2	132.2	132.5	133.4	167.8	136.2
5 Pb(sac) ₂ ·H ₂ O	145.0	119.3	122.6	131.4	131.8	134.4	168.5	136.1
6 Mg(sac) ₂ ·7H ₂ O	145.3	119.0	122.5	130.9	131.5	134.8	167.8	136.0
7 Na ₃ (sac) ₃ ·2H ₂ O	145.3	119.1	122.5	131.1	131.6	134.6	168.2	136.1

^aNot further assigned.

^bAverage chemical shift $\delta_{av} = \sum_{i=1}^n \delta_{ci}/n$.

7 was based on the characteristic chemical shift ranges and substituent induced shifts. The signals from C-2 to C-5 were treated together and were not assigned in detail.

The analysis of the data given in Table 1 shows, first of all, that the values of the average chemical shifts of all investigated compounds are rather close to each other, although significant shielding differences could be observed for the chemical shifts of individual carbon atoms. This indicates that the values of the chemical shifts are determined predominantly by the local π -electron density, whereas other effects (such as the electric field effects, etc.) could be neglected. It has to be noted, however, that in comparison with the δ_{av} values in compounds **3-5** (Scheme 1), the δ_{av} in $\text{Hg}(\text{sac})_2$ is somewhat lower and the corresponding value for saccharin itself is even lower. The two latter compounds are those in which covalent bonding is either beyond any doubt (saccharin [12,13]) or highly likely (mercury saccharinate).

As far as the individual chemical shifts are concerned, it is remarkable that the chemical shifts of C-1, C-6 and C-7 are downfield and those of C-3, C-4 and C-5 are upfield in the spectrum of $\text{Hg}(\text{sac})_2$ as compared with those in the spectra of the other metal saccharinates. The trend is even more pronounced if saccharin rather than $\text{Hg}(\text{sac})_2$ is taken into account.

The similarities between the spectra of saccharin and $\text{Hg}(\text{sac})_2$ may be taken as an indication that in the latter compound the metal-to-ligand bonding is essentially covalent in character. It is important to note that the spectra of the saccharinates of zinc and especially of cadmium (compounds **3** and **4**) are practically identical to those of the lead, magnesium or sodium salts (compounds **5**, **6** and **7**, respectively). Accordingly, the character of the M-N bonds in compounds **3** and **4** (at least in DMSO solution) should be considered to be essentially ionic. Still, the C-1 and C-6 shifts for $\text{Zn}(\text{sac})_2$ are the smallest and the C-2, C-3, C-4 and C-5 ones the largest among compounds **3-7**. The conclusions drawn are in accord with the results of the crystallographic studies [1-6] and the conductivity measurements of the compounds studied [14]:

No.	Compound	Relative conductivity of 0.01 molar solutions in dimethyl sulfoxide
4	$\text{Zn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$	1
5	$\text{Pb}(\text{sac})_2 \cdot \text{H}_2\text{O}$	0.89
3	$\text{Cd}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$	0.83
	$\text{Fe}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$	0.71
7	$\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$	0.60
	$\text{Co}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$	0.52
	$\text{ClHg}(\text{sac})$	0.03
2	$\text{Hg}(\text{sac})_2$	0.02
1	sac	0.09

Both the compounds 3–7 and two paramagnetic relatives (Fe, Co saccharinates) were found as mainly ionic species whereas the conductivity of saccharin and $\text{Hg}(\text{sac})_2$ is due to the covalent nature of the bond under discussion, remarkably low. Also the conductivity of $\text{Zn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ is the highest obtained as expected from the former NMR studies.

In conclusion, the application of ^{13}C NMR spectroscopy has proven to be a valuable tool for examining the character of the metal-to-saccharinate bonds in the studied compounds.

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