

SPECTRA-STRUCTURE CORRELATIONS IN SOME METAL SACCHARINATES

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The structural data for a number of metal saccharinates (those of Na, Mg, Mn, Fe, Co, Ni, Zn, Cd and Hg) were correlated with the observed infrared frequencies of the C=O, O-H and O-D stretching vibrations of protiated and partially deuterated samples.

The correlation showed that irrespectively on whether or not the carbonyl oxygens participate in the coordination polyhedra of the metal atoms and/or take part in hydrogen bonding, the frequencies of the carbonyl stretching vibrations in the spectra of metal saccharinates are lower than in those of saccharin itself.

The values of the $O_{W...O}$ distances estimated on the basis of the spectroscopic data are in agreement with those experimentally found.

INTRODUCTION

The conclusions about the existence of contacts between the central metal atom and the ligand in various metal complexes are very often based on the behaviour of a single vibrational band in the spectrum. Since the carbonyl stretch is considered to be a rather good group vibration, its frequency is often used to make structural inferences. It is, namely, assumed that the participation of the carbonyl oxygen in bonding to the metal atoms or in hydrogen bonding (where it acts as a proton acceptor) would reduce the electron density along the C=O bond, decrease its order and, thus, lower the frequency of the carbonyl stretching vibration.

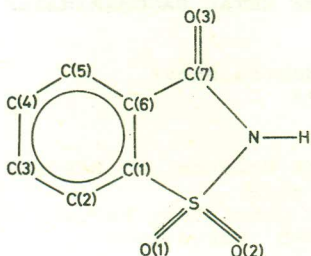


Fig. 1. Structural formula of saccharin

The availability [1, 2] of structural data for saccharin (Fig. 1) as well as for a series of its compounds with various metals (cf. [3] and references therein) makes it possible to attempt to correlate the type of bonding, on the one hand, and the frequencies of the C=O stretching bands, on the other, and thus test the reliability of the general belief that conclusions about the participation of the carbonyl oxygens in intermolecular interactions can indeed be drawn on the basis of the position of the C=O stretching bands in the vibrational (e.g. infrared) spectra.

Since the majority of the studied by us metal saccharinates were crystallohydrates, also correlated were the frequencies of the O-D stretching vibrations of the isotopically isolated HDO molecules with the crystallographically determined $O_w \dots O$ (and $O_w \dots N$) distances.

EXPERIMENTAL

The investigated compounds were prepared by standard methods. The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer. The X-ray data were collected on a Philips PW 1100 four-circle diffractometer. Standard crystallographic programs were used for structure determination and refinement.

RESULTS AND DISCUSSION

Bonding of the carbonyl group and correlations with the infrared C=O stretching frequencies

General considerations. - The assignment of the bands originating from the carbonyl stretching vibrations in saccharin and the studied metal saccharinates (the compounds of Na, Mg, Mn, Fe, Co, Ni, Zn, Cd and Hg were included in the study) was accompanied by some difficulties.

First of all, bands due to some of the vibrations localized mainly in the six-membered aromatic ring and, in the case of the crystallohydrates, to the water bending vibrations were present in the same spectral region. The benzenoid ring stretching bands, however, were usually found to be much sharper than those originating from carbonyl stretches whereas those arising from water bending vibrations were almost completely eliminated in the spectra of the highly deuterated samples.

The overlapping of bands attributable to the stretches of structurally non-equivalent carbonyl groups with close C=O bond lengths or the appearance, because of symmetry reasons, of more than one band (despite the fact that all C=O groups in the structure were equivalent) compounded the difficulties outlined previously. In the latter case an average of the observed frequencies was taken as a measure of the value of the force constant, whilst in the former the frequencies were estimated as closely as possible.

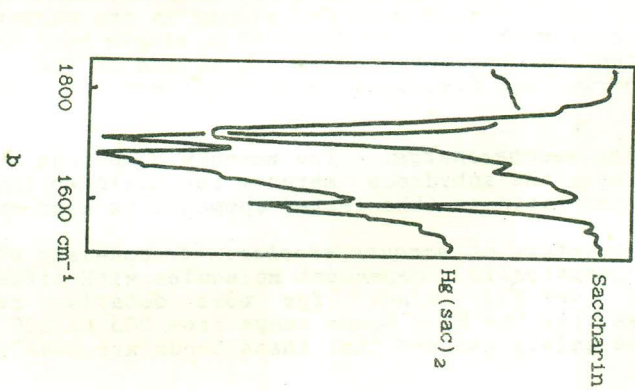
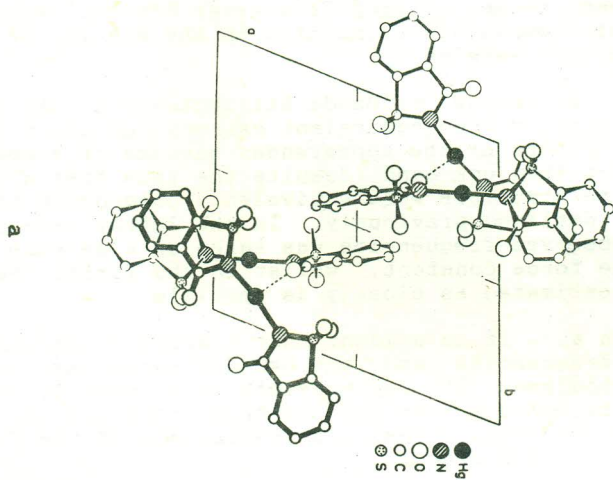
All in all, it is evident that a precise correlation between the frequencies and the C=O distances was not possible. Nevertheless, it was possible to attempt to correlate *the type of bonding*, on the one hand, and *the carbonyl stretching frequencies* (exact or estimated) of the C=O stretching bands, on the other.

Saccharin. - The carbonyl oxygens in the structure of saccharin are involved (as proton acceptors) in the formation of cyclic dimers which are held together by hydrogen bonds of the N...O type [1, 2] (the N...O distances are 279.4 pm according to Bart [1] and 279.6 pm according to Okaya [2], the values for the C=O bond lengths given in ref. 1 and ref. 2 being 122.0 and 121.4 pm, respectively). The existence of *only one type of C=O groups* in the structure is in agreement with the appearance of a *single* band in the region of the carbonyl stretching vibrations of the spectrum of saccharin, its frequency being 1725 cm^{-1} [3].

Mercury saccharinates. - Two mercury compounds were in fact studied: the anhydrous mercury saccharinate and chloromercury saccharinate (the latter compound is also anhydrous).

The structure of *mercury saccharinate* consists of two crystallographically independent molecules with different geometries (see Fig. 2a and, for more details, ref. 4). The values for the Hg-N bonds range from 203 to 206 pm and it can be safely assumed that these bonds are covalent. As for

$R(\text{CO})/\text{\AA}$: 122, 123, 120, 118



$\nu(\text{C}=\text{O})/\text{cm}^{-1}$: 1705, 1680

$\Delta\nu(\text{C}=\text{O})/\text{cm}^{-1}$: 20, 45

Fig. 2. The crystal structure (a) and the $\nu(\text{C}=\text{O})$ region in the LMF infrared spectrum (b) of $\text{Hg}(\text{sac})_2$

the carboxyl oxygens, one of the four non-equivalent ones - that labelled O(213) - comes rather close (259 pm) to a mercury atom and another one, labelled O(123), is also in contact with mercury but at a much longer distance (280 pm) (see Fig. 2a).

In spite of the existence of *four* crystallographically different CO groups in the structure, only *two* bands are found in the region of the stretching C=O vibrations of the infrared spectra. The frequencies of both bands are clearly *lower* than in the spectrum of saccharin (see Fig. 2b) although the differences in the frequencies are slight (20 and 45 cm^{-1}).

The existence of *one* type of CO group (with the C=O distance equal to 123 pm) in the covalent structure of *chloromercury saccharinate* [5] is paralleled by the appearance of *only one* carbonyl stretching band [3] whose frequency (1694 cm^{-1}) is 31 cm^{-1} lower than that of the corresponding band in the spectrum of the saccharin.

Manganese saccharinate hexahydrate and compounds isomorphous to it. - Although all C=O groups in the structure of manganese saccharinate hexahydrate are *equivalent* [6], in the spectrum of this compound (see Fig. 3b and, for more details, ref. 3) *two* carbonyl stretching bands are observed, at *much lower frequencies* (1620 and 1581 cm^{-1}) than in saccharin, the situation being analogous in the spectra of the Fe, Co, Ni, Zn and Cd compounds which are isomorphous to the manganese one (the splitting is symmetry based). The carbonyl oxygen does not participate in the coordination sphere of the central metal atom but acts as a proton acceptor of two protons from neighbouring water molecules (see Fig. 3a). The corresponding $\text{O}_w \dots \text{O}$ distances are 274.0 and 281.4 pm.

Magnesium saccharinate heptahydrate. - Only one of the two crystallographically non-equivalent carbonyl oxygens in the ionic structure of magnesium saccharinate heptahydrate, labelled O(23) in [7], participates (as a proton acceptor) in the formation of hydrogen bonds with two water molecules (the $\text{O}_w \dots \text{O}$ distances being 275.4 and 275.7 pm, respectively) but is not coordinated to magnesium. The other carbonyl oxygen is part of the coordination polyhedron around the magnesium atom. Despite the fact that the two carbonyl distances [C-O(13) and C-O(23)] are very close to each other (124.2 and 124.0 pm, respectively), in the infrared spectrum two *clearly separated bands* (at 1660 and 1627 cm^{-1} [3]) are found.

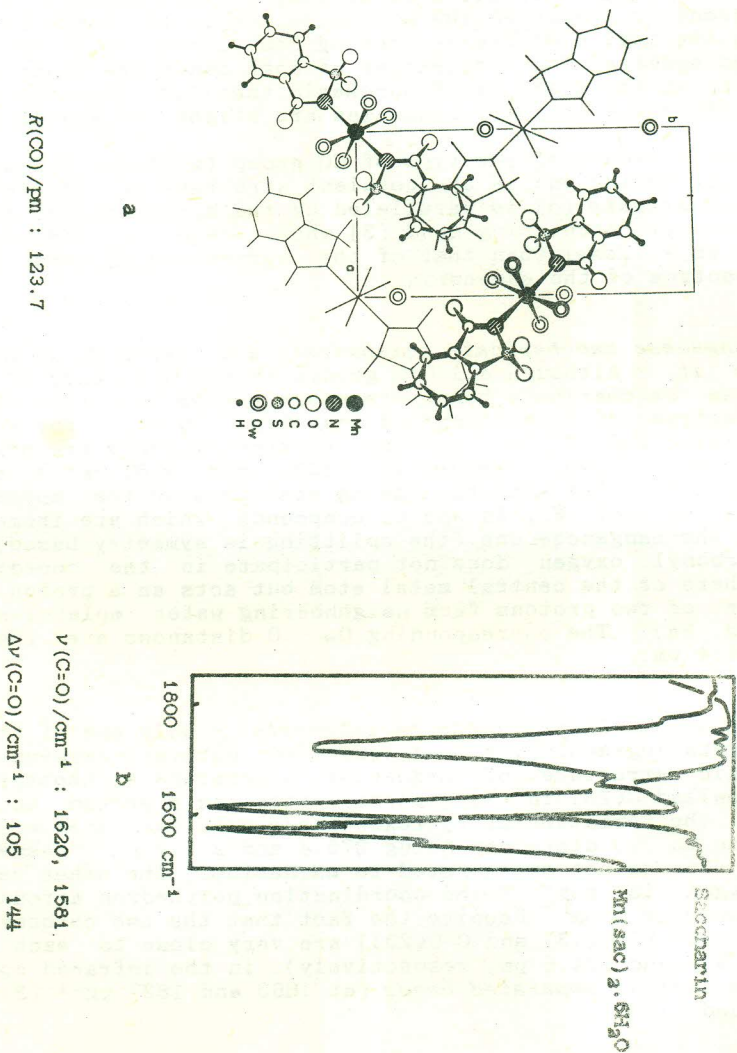


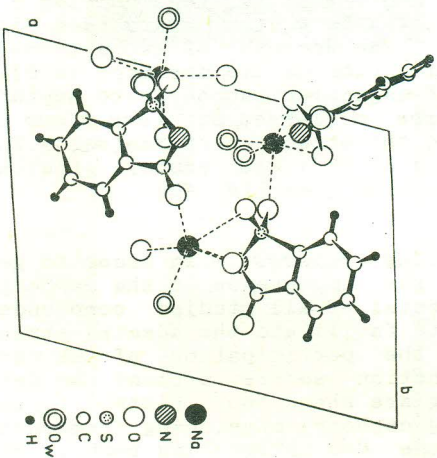
Fig. 3. The crystal structure (a) and the $\nu(\text{C}=\text{O})$ region in the LNT infrared spectrum (b) of $\text{Mn}(\text{sac})_2 \cdot 5\text{H}_2\text{O}$

Sodium saccharinate. - All oxygen atoms [they are labelled O(13), O(23) and O(33) in ref. 7] from the three crystallographically different carbonyl groups in the structure of ionic $\text{Na}(\text{sac}) \cdot 2\text{H}_2\text{O}$ (sac denotes a saccharinate ion) are coordinated to sodium atoms (see Fig. 4a). Of these, only O(33) is an acceptor of two protons from neighbouring water molecules (the $\text{O}_w \dots \text{O}$ distance is 274.6 pm). Contrary to the case of magnesium saccharinate heptahydrate, the existence of *three different but very close* C-O distances (see Fig. 4a) in the structure of $\text{Na}(\text{sac}) \cdot 2\text{H}_2\text{O}$ is manifested by appearance of *only one* carbonyl stretching band in the infrared spectrum (see Fig. 4b).

Concluding remarks. - In order to get a more complete picture, the appearance of the carbonyl stretching region in the spectra of all studied compounds is given in Fig. 5. In order to facilitate the spectra-structure correlations, data about the participation of the carbonyl oxygens in the coordination sphere around the metal and/or in hydrogen bonding are shown too. Listed, furthermore, are the corresponding carbonyl stretching frequencies (averaged when more than one C=O stretching band is present) as well as the values for the C=O bond lengths (again averaged in cases when more than one C=O group is present).

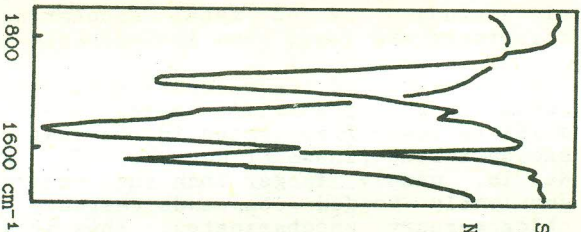
The analysis of the data has shown that :

1. Irrespectively on whether or not the carbonyl oxygens participate in the coordination sphere around the metal atoms and/or take part in hydrogen bonding, the frequency of the carbonyl stretching vibrations in the spectra of all studied by us metal saccharinates with known structures are *lower* than in saccharin itself.
2. The lowering of the carbonyl stretching vibrations depends on the *type of the metal-to-saccharin bond*. The shift to lower frequencies in the case of the ionic metal saccharinates (those of Mn, Fe, Co, Ni, Zn, Cd, Mg and Na) is, namely, larger than that observed in the case of covalently bonded compounds (mercury saccharinate and chloromercury saccharinate). Thus it is obvious that on passing from neutral saccharin to a saccharinate ion, a redistribution of the electron density (with its decrease within the carbonyl group) takes place. This electron density reduction along the carbonyl group is more expressed in the case of ionic metal saccharinates.



$R(\text{CO})/\text{pm} : 123.0, 124.1, 123.7$

a



Saccharin

$\text{Na}_3(\text{sac}) \cdot 2.2\text{H}_2\text{O}$

b

$\nu(\text{C}=\text{O})/\text{cm}^{-1} : 1635$

$\Delta\nu(\text{C}=\text{O})/\text{cm}^{-1} : 90$

Fig. 4. The crystal structure (a) and the $\nu(\text{C}=\text{O})$ region in the LNT infrared spectrum (b) of $\text{Na}_3(\text{sac}) \cdot 3.2\text{H}_2\text{O}$

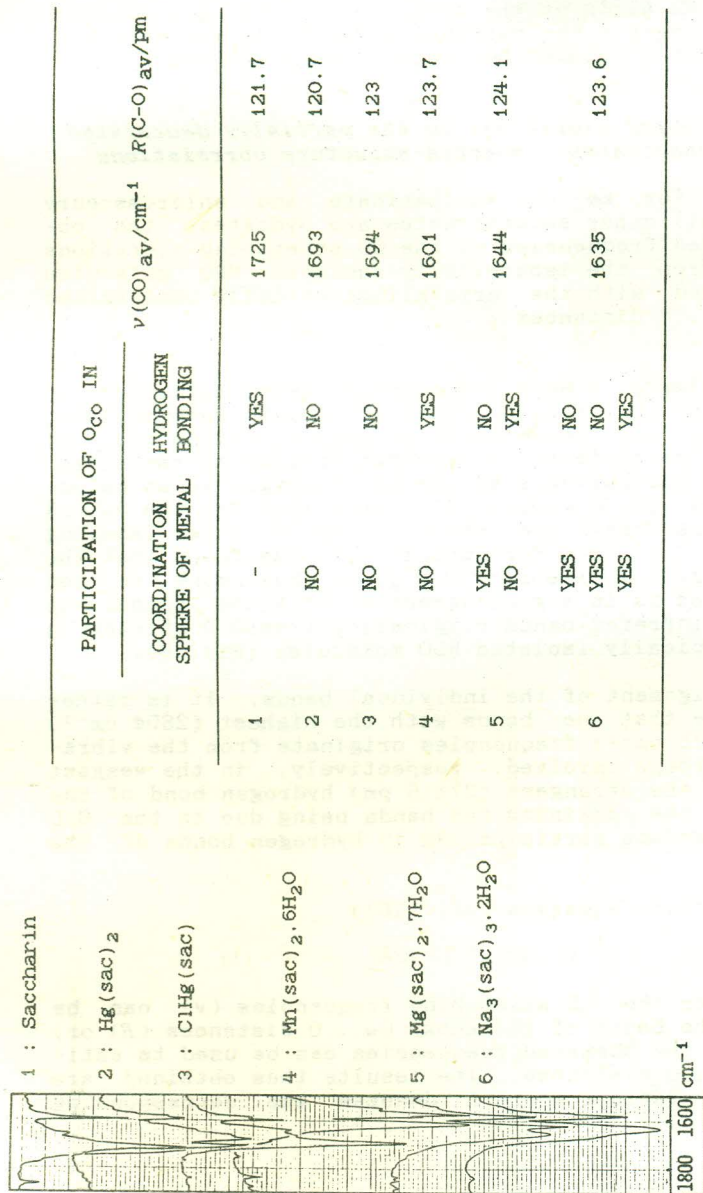


Fig. 5. The $\nu(\text{C=O})$ region in the LNT infrared spectra of the investigated compounds (additional data are given; see text)

3. It is not advisable to draw far-reaching conclusions concerning the manner of bonding of the atoms of a given group (in this case - the carbonyl oxygens in saccharinates) on the basis of the behaviour of a single vibrational band (here - the carbonyl stretch) in the spectrum. In fact, this is *known*, but very often *neglected*.

The O-D stretching vibrations in the partially deuterated metal saccharinates : spectra-structure correlations

Since except for mercury saccharinate and chloromercury saccharinate all other saccharinates are hydrates, the observed infrared frequencies of the OD stretching vibrations originating from the isotopically isolated HDO molecules were correlated with the crystallographically determined $O_w \dots O$ and $O_w \dots N$ distances.

Sodium saccharinate. - Both independent water molecules in the structure of the triclinic form of sodium saccharinate, $Na_3(sac)_3 \cdot 2H_2O$, are coordinated to sodium cations and, at the same time, participate in hydrogen bonding to the nitrogen atoms from saccharinate anions or to oxygen atoms belonging to the SO_2 and CO groups [7]. The values for the $O_w \dots N$ and $O_w \dots O$ distances are shown in Fig. 6 (the labeling scheme of ref. 7 is used throughout). It was found that the existence of *four independent O-H groups* belonging to the water molecules is in a good agreement with the appearance of *four* [8,9] infrared bands originating from O-D stretching modes of isotopically isolated HDO molecules (Fig. 6).

As for the assignment of the individual bands, it is rather safe to assume that the bands with the highest (2604 cm^{-1}) and lowest (2425 cm^{-1}) frequencies originate from the vibrations of O-D groups involved, respectively, in the weakest (290.8 pm) and the strongest (274.6 pm) hydrogen bond of the $O_w \dots O$ type, the remaining two bands being due to the O-D stretches of groups participating in hydrogen bonds of the $O_w \dots N$ type.

Using the following equation (cf. [10])

$$\nu/\text{cm}^{-1} = 2727 - 8.97 \cdot 10 \exp(-3.73 R/\text{\AA}) \quad (1)$$

the values for the O-D stretching frequencies (ν) can be estimated on the basis of the known $O_w \dots O$ distances (R) or, alternatively, the observed frequencies can be used to estimate the $O_w \dots O$ distances. The results thus obtained are summarized in Table I where A denotes the corresponding acceptor atom.

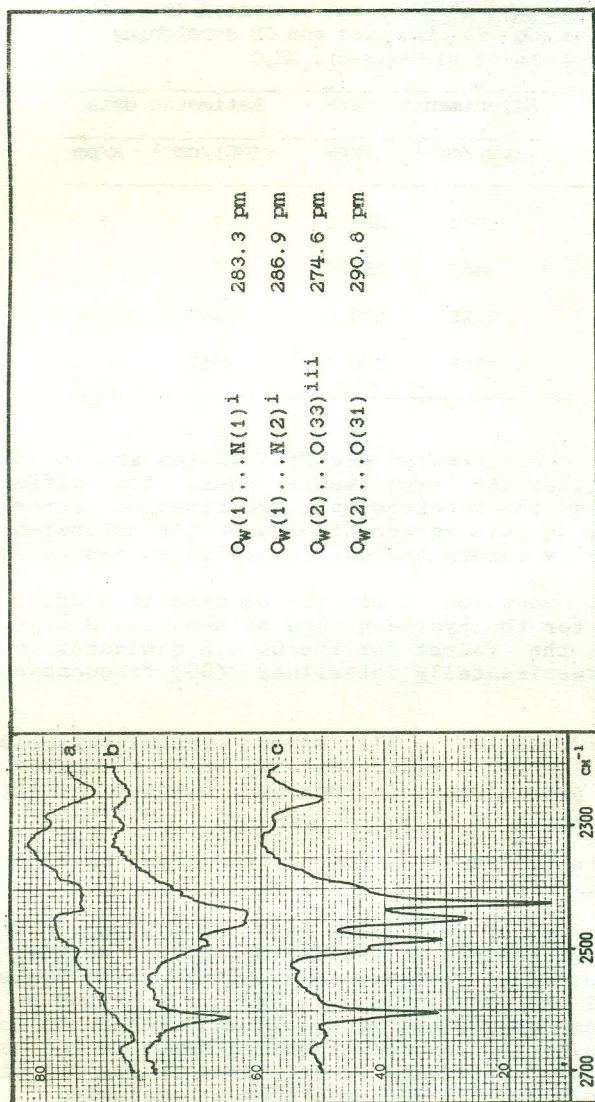


Fig. 6. The $O_w \dots A$ distances in the structure of $Na_3(sac)_3 \cdot 2H_2O$ and the $\nu(OD)$ region in the RT (b) and LMT (c) infrared spectra of partially deuterated $Na_3(sac)_3 \cdot 2H_2O$ (curve a : the spectrum of the protiated compound)

Table I. Experimental (ref. 7-9) and estimated (ref. 10) values for the $O_w \dots A$ distances and OD stretching frequencies in $Na_3(sac)_3 \cdot 2H_2O$

O_w	A	Experimental data		Estimated data	
		$\nu(OD)/cm^{-1}$	R/pm	$\nu(OD)/cm^{-1}$	R/pm
$O_w(1)$	N(1)	2448	283.3	?	?
$O_w(1)$	N(2)	2483	286.9	?	?
$O_w(2)$	O(33)	2425	274.6	2407	276.0
$O_w(2)$	O(31)	2604	290.8	2552	300.7

As can be seen, the estimated O-D frequencies are for 52 and 18 cm^{-1} higher than the experimental ones, the difference exceeding by far the spectroscopic experimental error. On the other hand, a fair agreement between the estimated and the experimentally determined $O_w \dots O$ distances was obtained.

Unfortunately, equation 1 can not be used to predict the $\nu(OD)$ values for the hydrogen bond of the $O_w \dots N$ type or, alternatively, the values for the $O_w \dots N$ distances on the basis of the experimentally determined $\nu(OD)$ frequencies.

Magnesium saccharinate. - All seven crystallographically non-equivalent water molecules in the structure of $Mg(sac)_2 \cdot 7H_2O$ participate in hydrogen bonding either to oxygen atoms (from CO or SO₂ groups) or to nitrogens from the saccharinate anions. The values for the $O_w \dots O$ and $O_w \dots N$ distances are shown in Fig. 7 (the labeling scheme is that of ref. 7).

The appearance [8] of only *seven* bands in the region of the OD stretching vibrations of the isotopically isolated HDO molecules (instead of *fourteen* as expected on the basis of the structural characteristics) is certainly caused by the existence of some very close $R(O_w \dots A)$ values and the consequent overlapping of the corresponding bands in the spectrum. The non-equal intensity of the bands in the O-D stretching region (cf. Fig. 7) supports such a conclusion.

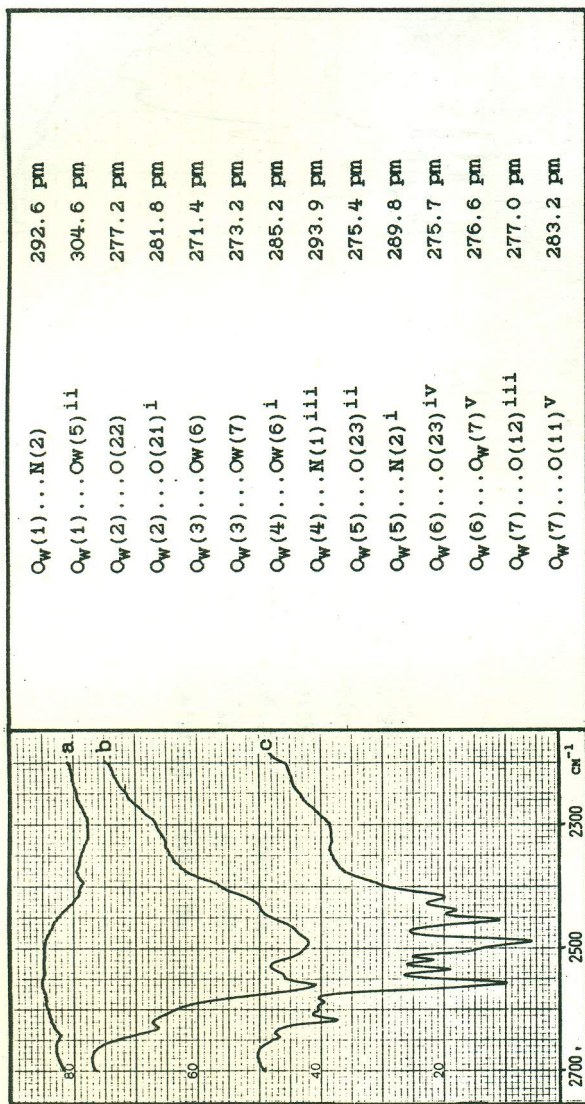


Fig. 7. The $O_W \dots N$ distances in the structure of $Mg(\text{sac})_2 \cdot 7H_2O$ and the $\nu(\text{OD})$ region in the FT (b) and LNT (c) infrared spectra of partially deuterated $Mg(\text{sac})_2 \cdot 7H_2O$ (curve a : the spectrum of the protiated compound)

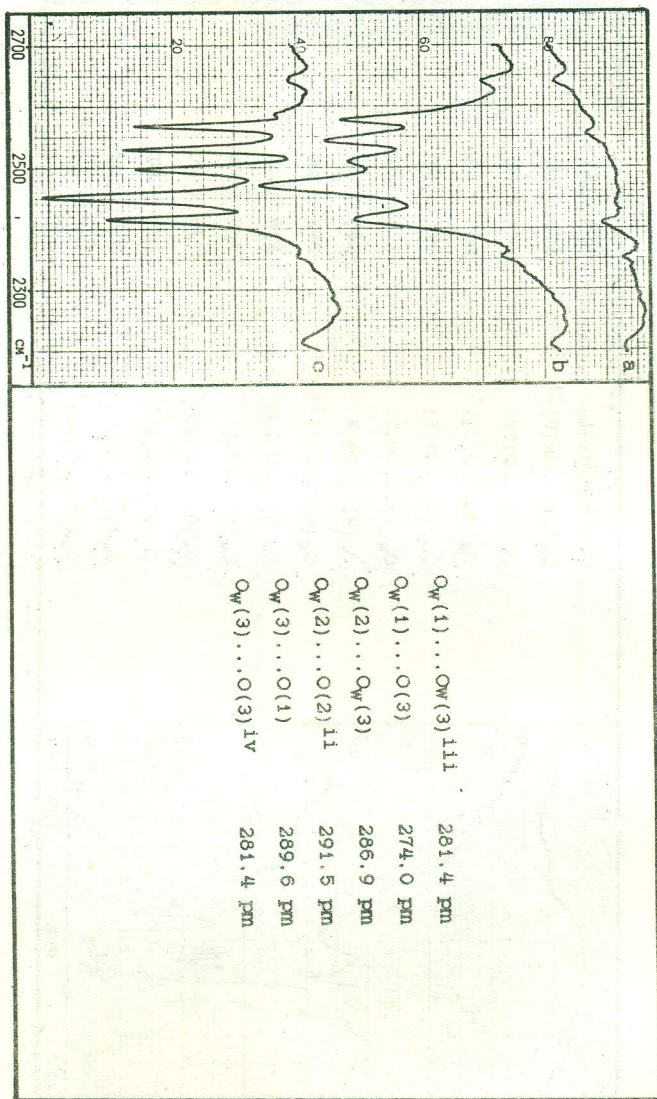


Fig. 8. The $\text{O}_w \dots \text{A}$ distances in the structure of $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ and the $\nu(\text{OD})$ region in the PR (b) and LNT (c) infrared spectra of partially deuterated $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ (curve a; the spectrum of the protiated compound).

Manganese saccharinate and its isomorphs. - Of the three crystallographically non-equivalent water molecules in the structure of $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ (as well as in its isomorphous analogues - the hexahydrates of the saccharinates of Fe, Co, Ni, 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 SO₂ groups [6]). The values for the $\text{O}_w \dots \text{O}$ distances in the structure of the manganese compound range from 274.0 to 291.5 pm, two of them being (see the table accompanying Fig. 8) practically identical (281.4 pm). This accidental coincidence of the structural parameters makes it possible to explain the existence [8,11] of five bands (instead of the expected six) in the OD stretching region of isotopically isolated HDO molecules (Fig. 8).

It is worth mentioning that the spectral picture in the region of the OH stretching vibrations of the isotopically isolated HDO molecules by DOD molecules is analogous (see Fig. 9).

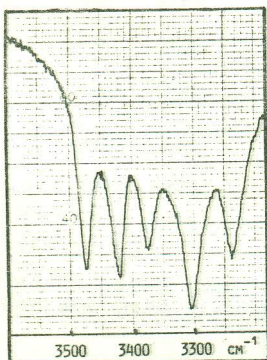


Fig. 9. The $\nu(\text{OH})$ region in the LNT infrared spectrum of partially deuterated $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$

Using equation 1 and the experimental values for the OD stretching frequencies or the $\text{O}_w \dots \text{O}$ distances, the $\nu(\text{OD})$ and $R(\text{O}_w \dots \text{O})$ values were estimated. The values are shown in Table II.

Generally speaking, in the case of the compounds isomorphous with $\text{Mn}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ a very similar spectral picture is observed in the OD stretching region of the spectra of samples containing isotopically isolated HDO molecules. There are, however, some frequency differences, especially in the region of the lowest-lying band (see Fig. 10 and refs. 8 and 11). In fact, in the spectrum of the cadmium compound the fifth band is only barely resolved at LNT (Fig. 10) but, as discussed in [8], appears very clearly at higher temperatures (Fig. 11).

Using equation 1, the values for the $\text{O}_w \dots \text{O}$ distances in the structure of the series of isomorphous saccharinates of the Fe, Co, Ni, Zn and Cd were estimated on the basis of the experimentally determined values for the OD stretching frequencies of isotopically isolated HDO molecules. The estima-

Table II. Experimental [6,8,11] and estimated [10] values for the $O_w...O$ distances, OD stretching frequencies and corresponding differences between the experimental and estimated values in $Mn(sac)_2 \cdot 6H_2O$

$R(O_w...O)/\text{pm}$			$\nu(OD)/\text{cm}^{-1}$		
Experimental	Estimated	ΔR	Experimental	Estimated	$\Delta \nu$
274.0	275.4	-1.4	2416	2404	+12
281.4	278.7	+2.7	2452	2476	-24
281.4	278.7	+2.7	2452	2476	-24
286.9	282.4	+4.5	2488	2521	-33
289.6	287.6	+2.0	2530	2548	-18
291.5	293.3	-1.8	2568	2557	+11

ted values, together with the corresponding experimentally found $R(O_w...O)$ and $\nu(OD)$ values for $Mn(sac)_2 \cdot 6H_2O$ are shown in Table III.

Concluding remarks. - The correlation of the spectral and structural data concerning the water molecules in the studied metal saccharinates has shown that :

1. The agreement between the number of crystallographically determined different $O_w...O$ distances in the structure, on the one hand, and the number of the bands originating from the OD stretching vibrations of the isotopically isolated HDO molecules in the infrared spectra, on the other, is good.
2. The existence (as in the case of the saccharinate of Mg) of a large number of bands in a relatively narrow spectral region makes the correlation difficult.
3. The agreement between the estimated and the experimentally determined OD stretching frequencies in some cases is rather poor, whereas a fair agreement between the estimated and the experimentally determined $O_w...O$ distances was obtained.

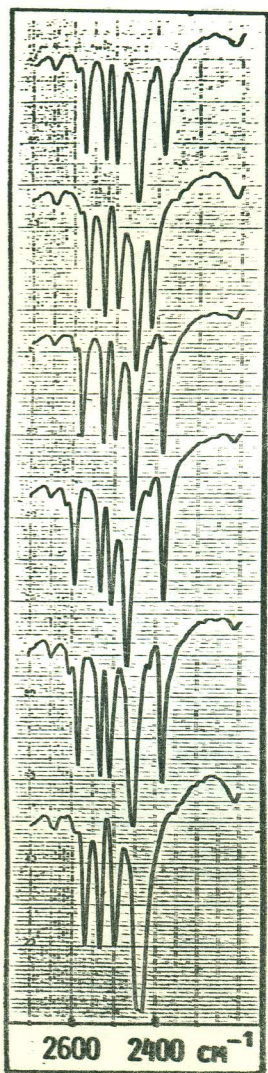


Fig. 10. The OD stretching region in the LNT infrared spectra of the $N(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ type compounds

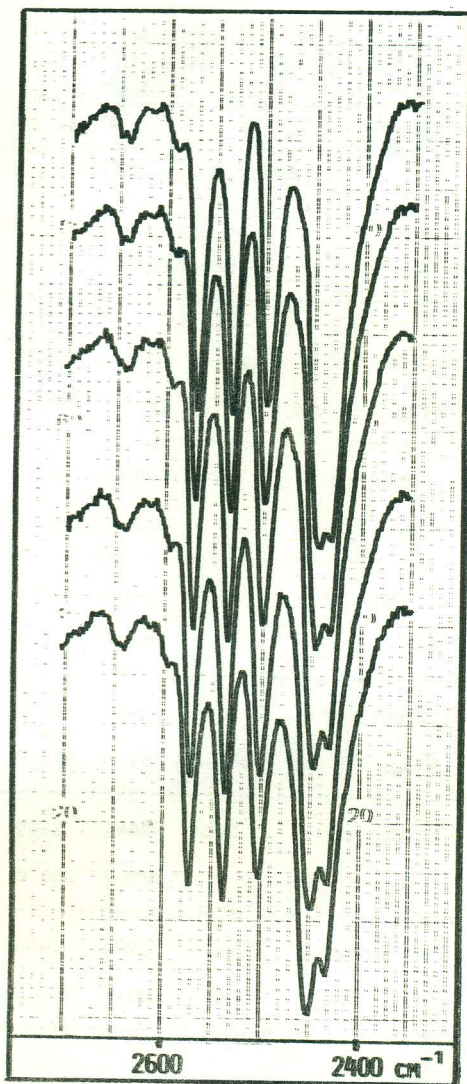


Fig. 11. Changes, on increasing the temperature, in the $\nu(\text{OD})$ region of partially deuterated $\text{Cd}(\text{sac})_2 \cdot 6\text{H}_2\text{O}$ (see text)

Table III. Estimated [10] $O_w...O$ distances in the isomorphous saccharinates of Fe, Co, Ni, Zn and Cd, compared with the experimentally [6, 8] determined values for $R(O_w...O)$ and $\nu(OD)$ in $Mn(sac)_2 \cdot 6H_2O$

M(II)		Water(1)		Water(2)		Water(3)	
Fe	$\nu(OD)/cm^{-1}$	2385	2450	2490	2573	2450	2527
	$R(O_w...O)/pm$	266.2	281.0	287.0	291.7	281.0	289.3
Co	$\nu(OD)/cm^{-1}$	2384	2457	2500	2579	2457	2528
	$R(O_w...O)/pm$	266.8	282.0	287.0	291.8	282.1	289.5
Ni	$\nu(OD)/cm^{-1}$	2381	2469	2507	2594	2469	2532
	$R(O_w...O)/pm$	265.3	283.7	287.8	292.2	283.7	289.8
Zn	$\nu(OD)/cm^{-1}$	2381	2454	2509	2583	2454	2531
	$R(O_w...O)/pm$	265.2	281.6	288.0	292.0	281.6	289.7
Cd	$\nu(OD)/cm^{-1}$	2431	2441	2499	2570	2441	2534
	$R(O_w...O)/pm$	277.2	279.2	287.0	291.6	279.2	289.9
Mn	$\nu(OD)/cm^{-1}$	2416	2452	2498	2568	2452	2529
	$R(O_w...O)/pm$	274.0	281.4	286.9	291.5	281.4	289.6

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ИЗВОД

СПЕКТАР-СТРУКТУРНИ КОРЕЛАЦИИ КАЈ НЕКОИ МЕТАЛНИ САХАРИНАТИ

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Структурните податоци за повеќе метални сахаринати (оние на Na, Mg, Mn, Fe, Co, Ni, Zn, Cd и Hg) се корелирани со набљудуваните фреквенции на валентните C-O, O-H и O-D вибрации во инфрацрвените спектри на протираните и делумно деутерирани обрасци.

Корелацијата покажа дека, без оглед на тоа дали кислородните атоми од карбонилните групи учествуваат или не учествуваат во координационите полиедри на металните атоми, односно дали земаат или не земаат учество во образување на водородни врски, фреквенциите на валентните C-O вибрации во спектрите на металните сахаринати се пониски од оние кај самиот сахарин.

Вредностите на $O_w \dots O$ растојанијата што се проценети врз основа на спектроскопските податоци се во согласност со оние што се најдени експериментално.