BONDING OF THE CARBONYL GROUP IN METAL SACCHARINATES : CORRELATION WITH THE INFRARED SPECTRA

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Irrespectively on whether or not the carbonyl oxygens participate in some kind of intermolecular interaction (being part of the coordination polyhedra of the metal atoms and/or taking part in hydrogen bonding), the frequency of the carbonyl stretching vibrations in a number of metal saccharinates with known structues (Na, Mg, Mn, Fe, Co, Ni, Zn, Cd and Hg compounds were studied) are lower than in saccharine itself, apparently mainly as a result of the redistribution of the electron density which takes place on going from neutral saccharine to a saccharinate ion.

Since the carbonyl stretch is considered to be a good group vibration, its frequency is often used to make structural inferences. It is, for example, assumed that the participation in hydrogen bonding (where the carbonyl oxygen acts as a proton acceptor) would decrease the electron density of the C=O bond, decrease its order and, thus, lower the frequency. The participation of the carbonyl oxygen in bonding to the metal atoms should also alter the carbonyl stretching frequency.

The availability of structural data for saccharine [1,2] as well as for a number of metal saccharinates (those of Na, Mg, Mn, Fe, Co, Ni, Zn, Cd, Hg and Cu) [3–13] and for saccharine [4,5] 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 (admittedly, on a rather limited sample) the validity of the general belief that conclusions about the participation of the carbonyl oxygens in some kind of intermolecular bonding can be made on the basis of the comparison of the C=O stretching frequencies.

EXPERIMENTAL

The sodium salt (NaS) with a formula $Na_3(sac)_3 \cdot 2H_2O$ (hereafter sac denotes a saccharinate ion) was prepared according to the method described by Defournel [14] from warm aqueous solution of saccharine and sodium carbonate and recrystallized from ethanol (the recrystallization from water gives a

higher hydrate). The heptahydrate of the magnesium salt (de-
noted, for short, MgS) was prepared and recrystallized ana-
logously.

The hexahydrate of Mn(sac)$_2$ (MnS) was also prepared accor-
ding to Defournel [14] who, however, believed to have obtai-
ned a tetrahydrate (the isomorphous compounds of Fe, Co, Ni,
Zn and Cd are prepared in the same way — by slow evaporation
of stoichiometric mixtures of aqueous solutions of the chlo-
rides or sulfates of the metals and of sodium saccharinate).

Mercury(II) saccharinate (HgS) was prepared, apparently for
the first time, by one of us [13] by reacting aqueous solu-
tions of mercury acetate and sodium saccharinate. In fact,
our repeated attempts to prepre Hg(sac)$_2$ employing the ori-
ginal method of Defournel [14] systematically yielded a pro-
duct which was shown [6,13] to be chloromercury(II) saccha-
rinate, ClHg(sac) (ClHgS).

The hydrated saccharinates were deuterated by repeated re-
crystallization from D$_2$O or, in the case of the sodium com-
pound, from ethanol–D$_2$O mixtures.

The infrared spectra were recorded, from KBr pellets, on a
Perkin–Elmer 580 infrared spectrophotometer (in the case of
the mercury compounds Nujol mulls were used).

STRUCTURAL DATA

The details about the crystal structures of saccharine and
of the saccharinates of sodium, magnesium, manganese and
mercury which are given in refs. 1–6 will not be repeated
here. Instead, only the data pertaining the C=O groups and
their immediate environment will be briefly summed up.

The structure of saccharine is made up of molecules which
are held together by rather strong hydrogen bonds, thus
forming cyclic dimers. The carbonyl oxygens play the role of
proton acceptors, the N...O distance being 279.4 pm accor-
ding to Bart [1] and 279.6 pm according to Okaya [2]. The
values given in ref. 1 and ref. 2 for the length of the C=O
bond are 122.0 and 121.4 pm, those for the C-N distance are
137.5 and 136.9 pm whereas for the C-C-N angle the values
are 109.8 and 109.6 degrees respectively.

In the structure of Na$_2$(sac)$_x$.2H$_2$O there are three distinct
oxygen atoms, labelled O(13), O(23) and O(33) in ref. 3. Of
these, only O(33) acts as a proton acceptor (the donor being

one of the water molecule) in a hydrogen bond 274.6 pm long.
All three carbonyl oxygens are part of the coordination
polyhedra around the sodium atoms. The C-O distances are
123.0, 124.1 and 123.7 pm, whereas the corresponding C-N
distances and C-N-C angles have values of 135.4, 134.6 and
135.7 pm and 113.0, 113.7 and 113.5° respectively.

Of the two crystallographically non-equivalent carbonyl oxy-
gens in the structure of Mg(sac)$_2$.7H$_2$O, again only one, la-
belled O(23) in [3], is a proton acceptor and is involved in
hydrogen bonding with two neighbouring water molecules (the
O$_w$...O distances being 275.4 and 275.7 pm respectively) but
is not coordinated to magnesium. The other carbonyl oxygen,
on the other hand, enters the coordination polyhedron of
magnesium. The C-O(13) and C-O(23) distances are 124.2 and
124.0 pm respectively, the lengths of the corresponding C-N
bonds are 134.0 and 135.3 pm while the values of the two in-
cluded C-C-N angles have values of 114.2 and 113.8 degrees
respectively.

Only one type of carbonyl oxygen exists in the structure of
Mn(sac)$_2$.6H$_2$O [4], the C-O and C-N distances being 123.7 and
136.0 pm respectively and the C-C-N angle having a value of
113.2°. The carbonyl oxygen is an acceptor of two protons
from neighbouring water molecules (the O$_w$...O distances are
274.0 and 281.4 pm respectively).

In mercury saccharinate [5], none of the four non-equiva-
lent carbonyl oxygens could be hydrogen bonded since the
compound is anhydrous and no proton donor is present. The
four C-O distances are 122, 123, 120 and 118 pm, the C-N
bonds are 138, 137, 142 and 138 pm long and the correspon-
ding C-C-N angles have values of 112.4, 112.5, 109.9 and
108.3 degrees. One of the carbonyl oxygens, labelled O(213),
makes a rather short contact with a mercury atom (the dis-
tance of 259 pm is significantly shorter than the sum of the
van der Waals radii for Hg and O). Another carbonyl oxygen
is also in contact (much longer, however) with mercury (the
Hg-O distance is 280 pm).

A relatively short (275 pm) Hg...O contact is present in the
structure of chloromercury saccharinate [6] as well. The
single carbonyl oxygen is 123 pm away from its carbon, the
C-N bond is 145 pm long and the C-C-N angle has a value of
112°. If these values (as well as those for mercury saccha-
rinate) are to be compared with the previously given ones,
it should be born in mind that the standard deviations for
the mercury saccharinates are appreciably larger than for
the rest of the studied compounds. A general trend is, ne-

vertheless, apparent. In these two saccharinates (as well as in saccharine itself) the C=O bonds are shorter than in the ionic saccharinates, while the C-N bonds are longer. It should also be noted that in the ionic saccharinates the C-C-N angles are larger than in saccharine or in the two mercury saccharinates.

INFRARED DATA AND CORRELATIONS WITH THE STRUCTURES

The location of the carbonyl stretching bands in saccharine and the studied saccharinates is not always easy because of the presence, in the same spectral region, of bands due to some of the vibrations localized mainly in the six-membered aromatic ring and, in the case of the crystallohydrates, of bands originating from the water bending vibrations. These latter bands can be eliminated almost completely by recording the spectra of highly deuterated compounds (cf. Fig. 1) and the benzenoid ring stretching bands were usually sharper than those which are believed to arise from carbonyl stretches. Even so, the number of bands attributable to C=O stretching vibrations did not always correspond to the number of nonequivalent carbonyl groups. Thus, in the spectrum of the manganese compounds (and, in fact, in the spectra of the whole series of isomorphous compounds) because of symmetry reasons two carbonyl bands are found (Fig. 2), despite the fact that all C=O groups in the structure are equivalent.
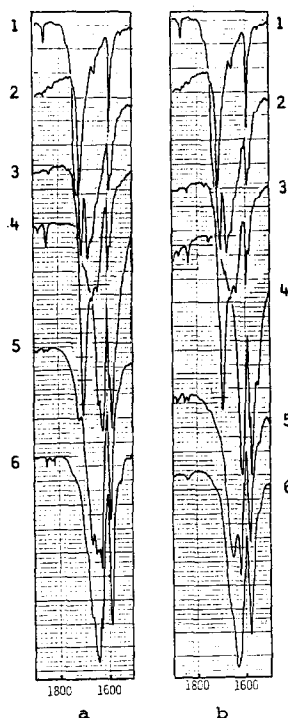
A precise correlation between the frequencies and C=O distances (or other relevant structural parameters) is not possible. Thus, in all compounds of the isomorphous series of hexahydrates of metal(II) saccharinates the frequencies of the carbonyl stretching bands are nearly the same, despite the fact that there is significant variation of the reported C=O bond lengths.

Fig. 1. The C=O stretching region in the IR spectra of : 1 - Hsac, 2 - HgS, 3 - ClHgS, 4 - MnS, 5 - MgS and 6 - NaS (a - protiated and b - deuterated compounds)

Nevertheless, it is clear that the carbonyl frequency is highest (1725 cm^{-1}) in the spectra of saccharine itself and slightly but clearly lower (close to 1700 cm^{-1}) in those of the two mercury
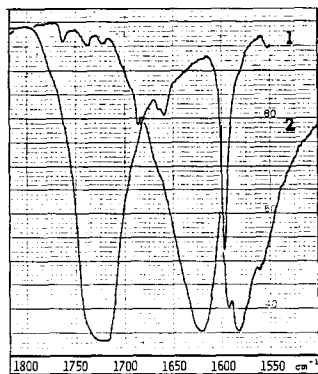
Fig. 2. The C=O stret-
ching region in the IR
spectra of saccharin
(1) and of MnS (2)

compounds. In the case of the io-
nic saccharinates (the Na, Mg and
Mn salts) the carbonyl stretching
bands are observed at much lower
frequencies (below 1660 cm^{-1}). It
should be noted that in mercury
saccharinate no band is found
above 1705 cm^{-1}, despite the fact
that two of the carbonyl oxygens
do not participate in any kind of
interaction and that the Hg...O
interaction of the third such
oxygen with mercury must be con-
sidered as weak.

On the other hand, as already po-
inted out, in all ionic compunds
the C—O distances are signifi-
cantly longer and the C-N bonds shorter than in saccharine
or in the two mercury sacharinate compounds. It thus seems
rather obvious that, on passing from neutral saccharine to a
saccharinate ion, a redistribution of the electron density
takes place. The free charge is apparently acting towards
the increase of the order of the bonds within the five-mem-
bered ring which, in turn, leads to a reduced electron den-
sity in the carbonyl group. In the mercury compounds the
effect is, naturally, present to a much lesser degree since
the metal-to-nitrogen bonds should, by all means, be consi-
dered as covalent.

The major factor determining the position of the carbonyl
stretching band(s) is, clearly, the whole bonding situation
within the saccharinate moiety rather than the additional
interactions (hydrogen bonding included) in which the carbo-
nyl oxygens take part (they too have, certainly, some ef-
fect, but it must be rather marginal). While all these
things could have been expected, the general conclusion of
the whole work is that one should not make far-reaching con-
clusions about the manner of bonding, especially intermole-
cular, of the atoms of a given group (in our case the carbo-
nyl oxygens in saccharinates) on the basis of the behaviour
of a single vibrational band (here — the carboxyl stretch)
alone. This is, to be sure, known, but often neglected.

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