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INFORMATION ON THE COORDINATING SITES OF IONOPHORES OBTAINED BY CARBON-13 NMR RELAXATION TIME MEASUREMENTS

R. Buchi, E. Pretsch and W. Simon*
Department of Organic Chemistry
Swiss Federal Institute of Technology
Universitätsstrasse 16, 8006 Zurich,
Switzerland

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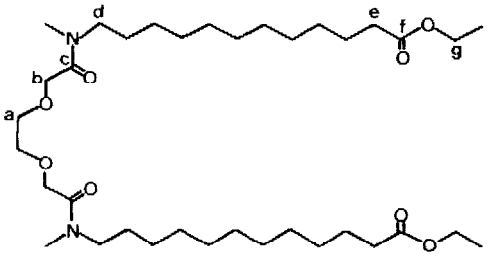
In contrast to most of the naturally occuring [1] and synthetic [2] neutral ionophores having a cyclic structure some non-cyclic ion carrier ligands [3] may form several kinds of complexes with the same cation [4] . It is therefore of particular interest to obtain information on the coordinating sites of such ligands in solution.

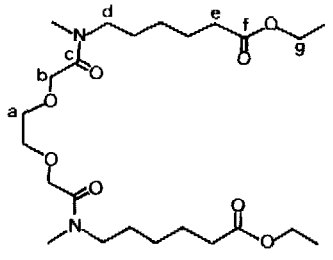
For the ^{13}C-^{1}H dipole-dipole relaxation the spin-lattice relaxation time T_1 is strongly influenced by the rotational mobility of a given carbon center [5]. The coordination to the metal ion may reduce both the overall reorientational motion and the internal mobility of carbon atoms in the vicinity of coordinating sites; the relaxation of more distant carbon atoms (e. g. in non-coordinating side chains) is generally governed by segmental motions [6] and should thus show only a minor dependence on the complexation.

Ligand I (see Figure 1) may form complexes with Ca^{2+}-ions of both 1:2 (metal:ligand) and 1:1 stoichiometry [4]. The relaxation times measured in chloroform for the free ligand L and the two types of complexes are compiled in Table 1. The formation of the 1:2 complex reduces the relaxation times of the carbons a to c by a factor of about 10 whereas the relaxation times of the carbons e to g are only minimally influenced. This behavior can be taken as an indication that under these conditions the ester carbonyl groups do not participate in the coordination (see also [4]). In contrast, in the 1:1 complex the relaxation times of the carbon atoms e to g are more strongly shortened by complexation; the acceleration of the relaxation rate of these carbons amounts only to a factor of about 2 to 3 as compared to a factor of 6 to 8 for the carbons a to c. The reason for

Figure 1: Structure of the ligands studied



Ligand I



Ligand II

this difference may lie in some freedom of internal motion of the chain despite the fact that both ester carbonyls are coordinated to the metal ion [4]. A reduction of the chain length from 11 to 5 methylene groups (ligand II, cf. Table 1) indeed leads to a ligand in which the coordination of the ester groups in the 1:1 complex causes a stronger acceleration of the relaxation rates of the carbons f to g relative to the corresponding carbons in ligand I.

It may be concluded that carbon-13 relaxation time measurements supply valuable information on the structure of complexes and may therefore be of help in designing molecules with ion selectivities superior to those obtained so far [7].

Table 1. Spin-Lattice Relaxation Times of Some Carbons of the Ligands I and II and their Complexes with $CaCl_2$

Carbon atom	Relaxation times T_1 [1] [sec] measured for ligand I			ligand II		
	free L	CaL_2 [2]	CaL [2]	free L	CaL_2 [2]	CaL [2]
a	0.6	0.04	0.09	0.7	0.11	0.11
b	0.5	0.04	0.09	0.5	0.11	0.11
c	10.1	1.2	1.2	10.1	2.0	1.8
d	0.4	3)	0.07	0.5	0.16	0.10
e	1.3	1.1	0.8	1.0	0.6	3)
f	32.2 [4]	23.0 [4]	11.2	35.3	14.5	6.7
g	3.7	3.1	1.8	3.4	2.5	1.2

1) Measured by the inversion recovery technique with a Bruker-Spectrospin HFX-90-B-SC-FFT-12 spectrometer. All standard deviations are less than 10% of the measured values. Nuclear Overhauser effect measurements indicate that the dipole-dipole relaxation mechanism dominates. Solvent: $CDCl_3$, concentrations: 0.1 M.

2) For the preparation of the ligands and complexes see [3,4].

3) Not measured because of overlapping of signals.

4) Prior to measurement dissolved oxygen was removed by bubbling argon through the sample solution for 1 hour.

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