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COORDINATING SITES IN NON-CYCLIC NEUTRAL IONOPHORES DETERMINED BY Mn^{2+} INDUCED ^{13}C-SPIN-LATTICE RELAXATION

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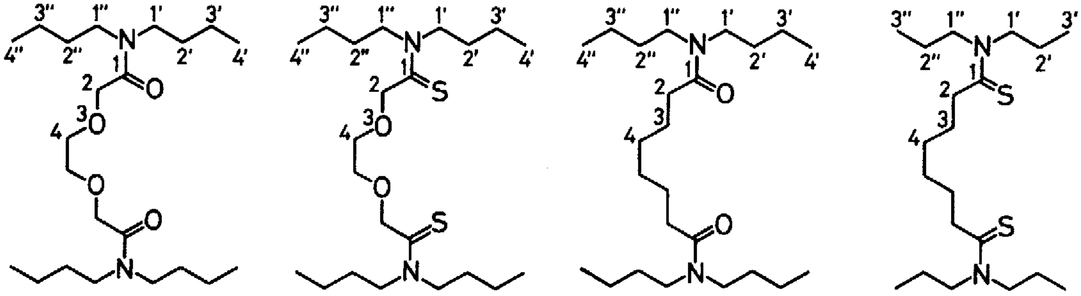
Abstract: ^{13}C-Spin-lattice relaxation times induced by Mn^{2+} were measured for some ionophores and interpreted in terms of the ion-ligand interaction and position of the metal ion relative to the carbon atoms.

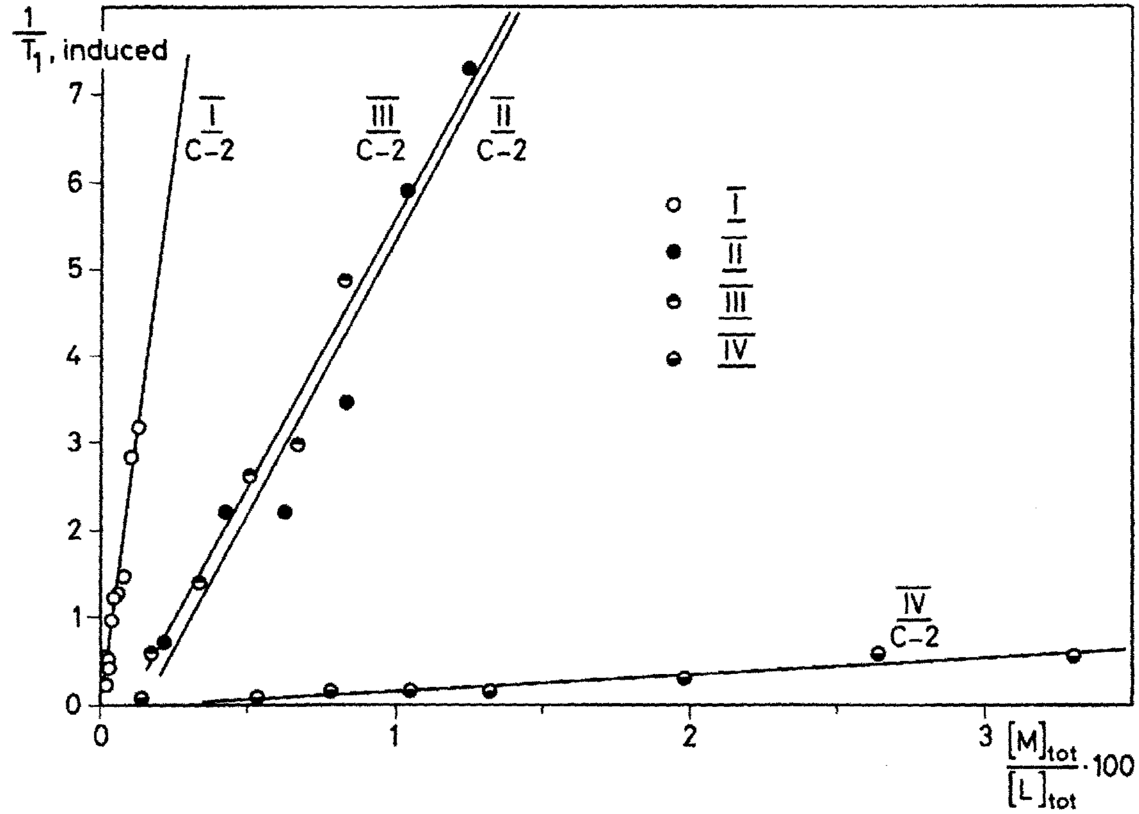
Spin-lattice relaxation time measurements are among the few techniques that yield information pertaining to the coordinating sites of cations with neutral complexing agents in solution [1,2,3]. Since Mn^{2+} is a transition metal ion with high A character [4], it is an interesting probe to sample potential binding sites for alkaline earth cations, especially Ca^{2+}. Here we report on the determination of such sites in a series of neutral, lipophilic non-cyclic complexing agents (see Figure 1), which are ionophores for alkaline earth (I) and B metal cations (II) respectively [5].

Figure 1. Structure of the ligands studied



I II III IV

Figure 2. Functions $\frac{1}{T_1}$,induced $[s^{-1}]$ vs. $([M]_{tot}/[L]_{tot}) \cdot 100$ for the carbon atoms C-2 of the ligands I-IV



deed, the effect of Mn^{2+} on T_1 in IV is similar for all carbon atoms, indicating that only a negligible fraction of Mn^{2+} is complexed by this compound (see Table 1).

The Mn^{2+}-induced spin-lattice relaxation-time changes T_1,induced (Eq.1) depend on the distance of the complexed ion from the individual carbon atoms (Eq.2).

$$\frac{1}{T_1}\text{, induced} = \frac{1}{T_1}\text{, observed} - \frac{1}{T_1}\text{, ligand} \qquad (1)$$

$$\frac{1}{T_1}\text{, induced} = \text{const} \cdot \tau_r \cdot \bar{n} \cdot \frac{[M]_{tot}}{[L]_{tot}} \cdot \frac{1}{r^6} \qquad (2)$$

τ_r : isotropic rotational correlation time
$\bar{n}$: mean number of coordinated ligand molecules per metal ion
$[M]_{tot}$,$[L]_{tot}$: concentration of Mn^{2+} respectively ligand
r : distance of the carbon atom from the metal ion
const : this term includes magnetic properties as well as complex formation constants

Eq.2 is valid under the following assumptions (see also [1,6]):

- fast exchange between free and complexed ligands
- negligible effect of free Mn^{2+} as well as of Mn^{2+} in other complexes on the relaxation rate of the species considered
- isotropic rotational motion
- small fraction of complexed ligand ($[L]_{tot} >> [M]_{tot}$)
- extreme narrowing ($\omega_I^2 \tau_r^2 << 1$, where ω_I is the Larmor frequency of the ^{13}C nucleus).

The Mn^{2+}-induced spin-lattice relaxation-time changes for carbon atom 2 in the complexing agents I to IV are presented in Figure 2. It becomes obvious that the thioamide group in IV does not interact strongly with Mn^{2+}. This is very much in contrast to the amide groups in III. An additional stabilization is obtained by introducing ether-oxygen atoms (ligand I). The replacement of the amide groups in I by the thioamide function reduces the interaction with Mn^{2+} (ligand II). These results suggest that Mn^{2+} interacts with the ether and amide oxygen atoms of the ligands discussed but hardly binds to thioamides.

These findings are consistent with the corresponding plots for the other carbon atoms. As expected, the atoms farther from the Mn^{2+} (e. g. C-2' and C-3' in I, II and III) undergo smaller changes in the spin-lattice relaxation times. In-

Table 1. Slopes of the linear regression of $\frac{1}{T_1}{}_{,\text{induced}}$ vs. $([M]_{tot}/[L]_{tot}) \cdot 100$ (see also Fig. 2) for the individual carbon atoms of the ligands I-IV

Carbon atom	Slope of the regression and its standard deviation			
	I	II	III	IV
1	21.0 ± 1.3	4.44 ± 0.58	a)	0.13 ± 0.01
2	25.1 ± 1.9	6.10 ± 0.76	6.24 ± 0.77	0.20 ± 0.02
3	-	-	3.95 ± 0.36	0.14 ± 0.02
4	21.3 ± 2.0	7.10 ± 0.82	2.29 ± 0.25	0.10 ± 0.03
1', 1"	8.03± 1.57	0.72 ± 0.26	2.52 ± 0.24	0.19 ± 0.03
2', 2"	4.37± 0.60	0.63 ± 0.16	1.46 ± 0.17	0.12 ± 0.02
3', 3"	2.96± 0.21	0.69 ± 0.19	0.94 ± 0.07	0.10 ± 0.01
4', 4"	1.32± 0.29	0.40 ± 0.04	0.80 ± 0.05	-

a) Not determined because of extensive line broadening.

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