

Using filter paper (Type VCWP, Millipore Corporation, Bedford, Mass., USA) impregnated with a 20% by weight solution of ligand (fig. 1) in p-nitroethylbenzene as the membrane in the cell assembly (see [8])

$\text{Ag;AgCl, 0.01M KCl} \parallel \text{membrane} \parallel \text{sample solution} \mid 0.1\text{M NH}_4\text{NO}_3 \mid \text{KCl(satd.), Hg}_2\text{Cl}_2;\text{Hg}$ (1)
and 0.1M aqueous solutions of the chlorides of the different cations, the selectivity sequence



is obtained. The comparison of this sequence with the one obtained analogously by impregnating the membrane with pure p-nitroethylbenzene:



clearly demonstrates the ligand's preference of Ca^{2+} over the other cations studied (see column 4 in table 1). Using equation (4) to describe the EMF of the cell (1), the selectivity constants $K_{\text{CaM}}^{\text{Pot}}$ given in table 1 are obtained through equation (5).

$$\text{EMF} = E_o + \frac{2.303 RT}{2F} \log(a_{\text{Ca}^{2+}} + K_{\text{CaM}}^{\text{Pot}} a_{\text{M}^{z+}}^{2/z}) \quad (4)$$

$$\log K_{\text{CaM}}^{\text{Pot}} = \frac{(\text{EMF}_2 - \text{EMF}_1)2F}{2.303 RT} - \log a^{(2/z)-1} \quad (5)$$

T : absolute temperature
R : gas constant
F : Faraday constant
EMF₁ : EMF of the cell assembly (1) with a 0.1M solution of calcium chloride as the sample
EMF₂ : EMF of the cell assembly (1) with a 0.1M solution of the interfering cation chloride as the sample

a : ion activities
z : charge of the interfering ion
E_o : temperature dependent constant

TABLE 1 Selectivity Constants $K_{\text{CaM}}^{\text{Pot}}$ (0.1M solutions)

Cation M	membrane with		effect of ligand on $K_{\text{CaM}}^{\text{Pot}}$ *)
	ligand(20% by weight in p-nitroethylbenzene)	p-nitroethylbenzene	
Ca^{2+}	1	1	1
Rb^+	$2 \cdot 10^{-1}$	$8 \cdot 10^6$	$2.5 \cdot 10^{-8}$
K^+	$9 \cdot 10^{-2}$	$6 \cdot 10^6$	$1.5 \cdot 10^{-8}$
Ba^{2+}	$8 \cdot 10^{-2}$	$1.3 \cdot 10^4$	$6.2 \cdot 10^{-6}$
Cs^+	$6 \cdot 10^{-2}$	$3 \cdot 10^6$	$2 \cdot 10^{-8}$
Sr^{2+}	10^{-2}	10	10^{-3}
Na^+	$7 \cdot 10^{-3}$	$1.2 \cdot 10^4$	$5.8 \cdot 10^{-7}$
Li^+	$3 \cdot 10^{-3}$	40	$7.5 \cdot 10^{-5}$
Mg^{2+}	$3 \cdot 10^{-5}$	$4 \cdot 10^{-2}$	$7.5 \cdot 10^{-4}$

*) Ratio of values in column 2 over those in column 3

The interaction of the ions with the ligand can be observed by NMR spectroscopy (see fig. 2 and table 2). Both in ^1H and ^{13}C resonance the groups showing the largest shifts due to complexation are those adjacent to the oxygen atoms suitable for coordination. In contrast to the cryptates [1], this ligand shows rapid exchange with alkali and alkaline earth metal

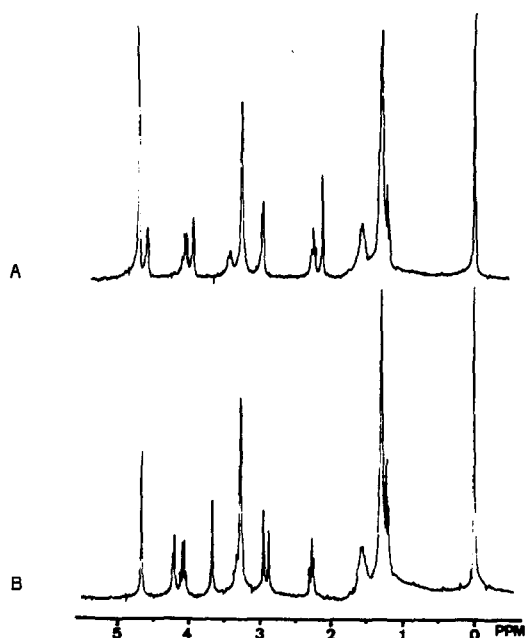


FIGURE 2. 270 MHz Proton Magnetic Resonance Spectra of the Ligand (see fig.1) Measured in Methanol- d_4 . A: ligand after addition of an excess of $\text{Ca}(\text{SCN})_2$. B: free ligand.

TABLE 2. ^1H and ^{13}C Chemical Shifts (ppm) of the Ligand (see fig.1) and its Complex with Ca^{2+} *)

Position (fig.1)	^1H (270 MHz)		^{13}C (22.63 MHz)	
	free ligand	complex (Ca^{2+})	free ligand	complex (Ca^{2+})
1	1.22	1.22	14.6	14.6
2	4.09/4.12	4.10/4.12	61.1	61.4
4			175.1	175.6
5	2.29	2.29	35.0	35.1
6	1.57	1.59	25.9	25.9
7-11	1.31	1.31	27.9-30.4	27.9-30.3
12	1.31	1.31	27.7	27.8
13	1.57	1.59	27.9-30.4	27.9-30.3
14	3.33	3.46	50.1	~49.5
16			171.1	172.3/172.0
17	4.24/4.25	4.64	70.4	70.6/69.9
19	3.70	4.00	71.5	70.8
N- CH_3	2.95/2.88	3.00/2.99	34.5/33.5	~34.5/~33.7

*) 270 MHz FT proton magnetic resonance spectra were run on a Bruker-Spectrospin HFX-270 spectrometer equipped with an FT unit, and the 22.63 MHz FT ^{13}C magnetic resonance spectra on a Bruker-Spectrospin HFX-10 spectrometer equipped with an FT unit B-SC-FFT-12. The chemical shifts are given in ppm relative to TMS in the solvent methanol.

cations*). Assuming rapid exchange, complex formation constants can be calculated from the chemical shifts of a given nucleus in the free ligand, in a nearly equimolar mixture of ligand and metal ion, and in the complex. Using the shift of the protons at C-17 the largest formation constant found for the cations studied is that obtained for Ca^{2+} , in agreement with sequence (2). Assuming a 1:1-type complex the formation constants in methanol are around 1000 and 10 for Ca^{2+} and K^+ respectively.

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*) The splitting of some signals (N-CH_3 ; H on C-17) is probably due to the hindered rotation around the -C-N-bond .

