NOTIZEN

^{1}H and ^{13}C NMR Spectroscopic Evidence for the Complexation of Potassium Cations by Cyclohexanedioxydiacetamides

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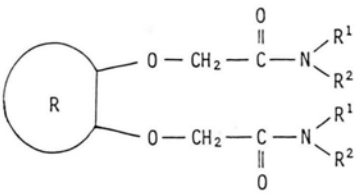
The complexation of cyclohexanedioxydiacetamides by K^+ cations may be studied by ^{1}H and ^{13}C NMR spectroscopy.

Neutral compounds featuring ether and amide groups (I, II) are potential chelating ligands for group IIA cations [1–3]. Recently we have studied the binding modes of ligands I by using ^{1}H and ^{13}C NMR spectroscopy and found that the ether and the carbonyl oxygens act as chelating centers [4]. We now report ^{1}H and ^{13}C NMR spectroscopic evidence for the complexation of potassium cations by compounds II. So far such a complexation has neither been observed by direct UV titration nor by picrate extraction methods [3].



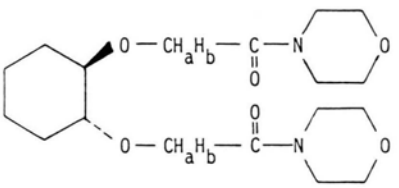
(I) R =

(II) R =

R_1; R_2 = alkyl group

Analogous to the ionophors I the *trans*-cyclohexanedioxydiacetamides II are able to coordinate Ca^{2+} and K^+ cations to form preferably 2:1 complexes. Upon complexation the ^{1}H NMR spectra change typically: in the ^{1}H NMR spectrum of free *trans*-cyclohexanedioxydiacetic acid morpholinoamide (in acetone-d_6, at room temperature) the methylene protons H_a and H_b appear as a singlet at δ 4.27 ppm. The addition of K^+ cations at room temperature results in a shift to lower field and a splitting of the former singlet into an AB pattern (Fig. 1).

ligand



[ligand]/[K^+]	T[°C]	$\delta(CH_2)$ [ppm]	$J(H_aH_b)$ [Hz]	Δy [Hz]
1/ 0	−50	4.27	13.9	4.0
1/ 0.33	25	4.31	13.6	0.5
1/ 0.5	25	4.33	13.7	0.8
1/ 1	25	4.36	13.9	1.1
1/ 5	25	4.45	14.5	2.2
1/10	25	4.48	14.6	2.1
1/20	25	4.50	15.0	2.2

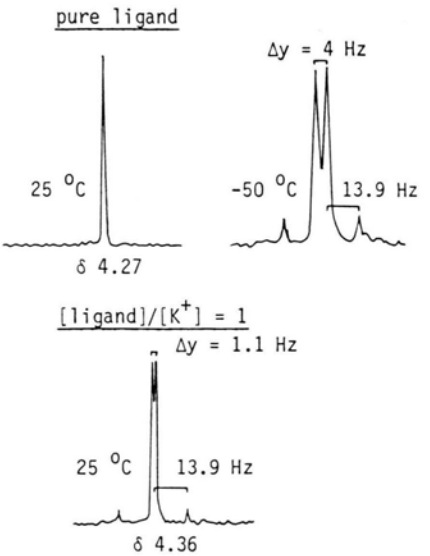


Fig. 1. ^{1}H NMR signals of the methylene protons H_a and H_b of 1,2-cyclohexanedioxydiacetic acid morpholinoamide and its K^+ complex in acetone-d_6.

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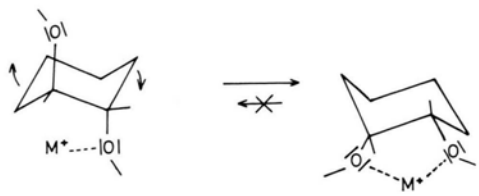
A downfield shift is expected upon complexation [4, 5]. An AB pattern for H_a and H_b should be observed even in the free ligand because the neighbouring cyclohexane ring renders these hydrogens diastereotopic. However, the appearance of an AB pattern at room temperature indicates a conformation change upon complexation. Studies with molecular models show that the chelate complexation locks the cyclohexane ring in the equatorial conformation that is already favored in the free ionophor (*ca.* 99%).

This interpretation is confirmed by the fact that the splitting of the methylene protons H_a and H_b cannot be observed upon complexation of I.



trans diaxial trans diequatorial

The complexation of II by K^+ cations can also be confirmed by ^{13}C NMR spectroscopy. The three carbon atoms that are directly bonded to the two oxygen atoms of a side chain are shifted to lower field ($\Delta\delta \approx$ 3 ppm) while the signals of all the other carbons remain nearly unchanged. Independent of the ratio $[II]/[K^+]$ we only observe one species in the ^1H and ^{13}C NMR spectra. This is indicative of a fast exchange mechanism between free K^+ cations and K^+/II-complexes. It is well documented that the NMR spectrum of a complex is dependent on the lifetime of the individual metal-ligand bonds [6].

The complexation of ligands of the type II with monovalent cations has been observed for the first time. Our studies have shown that NMR spectroscopy is a valuable tool for the determination of coordination modes of neutral ionophors, and for gaining information about intramolecular processes in ionophor-cation complexes.

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