Investigation of Host–Guest Interactions between Rubidium Salts and *N*-(Arylazoalkenoyl)azacoronands by Solid-State NMR Spectroscopy☆

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Received May 5, 1997

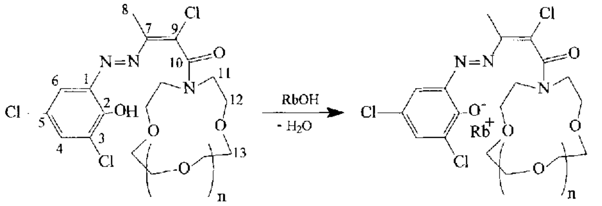
Keywords: *N*-(Arylazoalkenoyl)azacoronands / Rubidium salts / Host-guest interaction / ^{87}Rb MAS NMR spectroscopy / ^{13}C CPMAS NMR spectroscopy

Rubidium salts with *N*-(Arylazoalkenoyl)azacoronands (**2a–c**), were investigated using ^{87}Rb and ^{13}C solid-state NMR spectroscopy. From the NMR results it is concluded that there is a host–guest interaction. This suggests that the rubidium and ammonium ions, respectively, are incorporated into the cavity between the coronand and the chromophore.

The formation of non-covalent interactions between a host (e.g. a coronand) and a guest (e.g. a metal ion) is the basis of a supramolecular system, and on the basis of this principle it is possible to achieve recognition processes at molecular level whereby, in a similar fashion to biological receptors, smaller, spatially suitable molecules are incorporated.

Host-guest interactions in solution has already been subject of numerous studies using a variety of different methods[1][2][3][4][5]. For such studies in solids X-ray techniques are principally applied, e.g. the X-ray crystal structure analysis of dirubidium complexes of bis(anthracenediyl)cyclophanes[6].

The systems under investigation in our study were the *N*-(arylazoalkenoyl)azacoronand componds **1a**–**1c**[7], and the rubidium salts **2a**–**2c** derived from them[8]. As the crystal structure of the compound **1a**[7] shows, the angle between the plane of the chromophore and the plane of the azacrown is about 41°, thus forming a cavity which allows a guest molecule, of suitable size, to be incorporated.



1 **2**

1a / 2a: n=2 (1-Aza-15-crown-5)
1b / 2b: n=3 (1-Aza-18-crown-6)
1c / 2c: n=4 (1-Aza-21-crown-7)

Investigations of the salts **2a**–**2c** using X-ray powder diffraction techniques did not give definite evidence about the incorporation of the rubidium ion in the arylazobutenoate coronand system. Suitable crystals were not available in order to obtain a crystal structure, and the powder diffraction patterns did not show significant differences between **1** and **2**.

The subject of the present paper is the elucidation, by means of solid-state NMR spectroscopy, of the possiblity of incorporating the rubidium ion. Solid-state NMR spectroscopy allows the study of both the host molecule (^{13}C NMR) and, directly, the guest metal ion (^{87}Rb NMR). From changes in the values of the chemical shifts of the nuclei under investigation conclusions about the incorporation of the guest atom can be drawn. Moreover, rubidium (nuclear spin $I = 3/2$) posseses a quadrupole moment and can, therefore, be used as probe for the determination of the electric field gradient (EFG) at the nuclear site, and this can serve as an additional source of information.

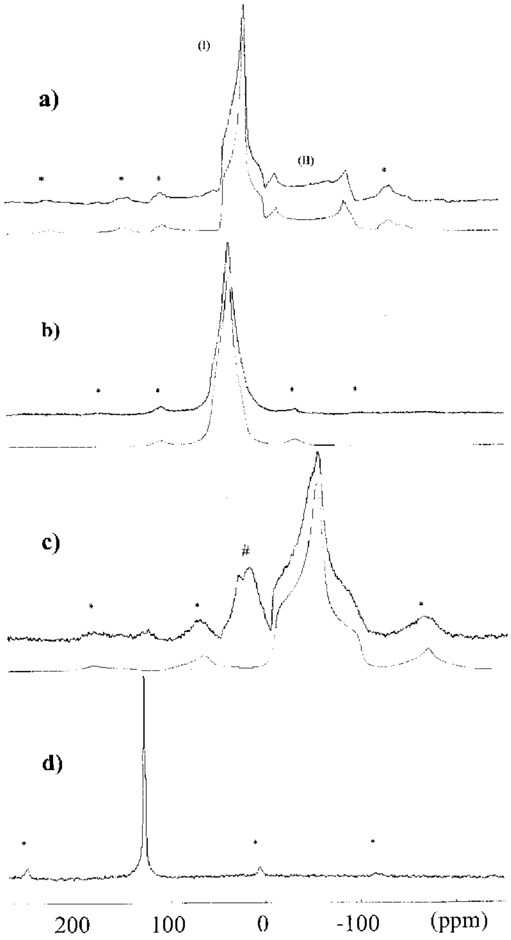
To answer the question of the possiblity of incorporation, in addition to the rubidium salts **2a**–**2c**, Rb_2SO_4, RbOH, and the rubidium salt of 2,4-dichlorophenol were also studied for comparison.

^{87}Rb MAS NMR Spectroscopy

Representative ^{87}Rb MAS NMR spectra of the azacoronand salts and test compounds are shown in Figure 1, together with the corresponding simulated theoretical powder patterns. The parameters obtained from the fitting procedure are presented in Table 1. It should be noted that, in the presence of the effects of quadrupole interaction, in second-order pertubation theory the actual chemical shift values cannot be derived from the peak maxima but only by a simulation of the (complicated) lineshape.

In Rb_2SO_4, which shows an orthorhombic (*Pnam*) crystal structure[9], the rubidium ions occupy two different sites (I and II). The results obtained are in good agreement with the published data of a detailed study by Fernandez et al.[10]. RbOH also gives a structured, broad, quadrupole powder pattern, which indicates a distinct electric field gradient at the rubidium sites. In addition to the pure ru-

Figure 1. Experimental and fitted ^{87}Rb MAS NMR spectra of a) Rb_2SO_4 (sites I and II), b) RbOH, c) Rb phenolate (# labels remaining RbOH of the starting material), and d) **2b**; stars denote spinning sidebands



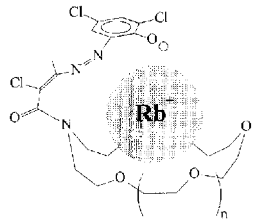
bidium hydroxide we also studied the rubidium salt of the dichlorphenol **3**, the anion of which corresponds to the anionic part of the complexes **2**. The spectrum in Figure 1c shows, in addition to the structured signal of the rubidium phenolate, a second peak (15% intensity) which we assign to the remaining RbOH of the starting material.

Table 1. ^{87}Rb MAS NMR results: chemical shift and NMR quadrupole coupling parameter

compound	quadrupole coupling constant [MHz][a]	η[b]	chemical shift
Rb_2SO_4 (I)	2.5	0.91	42.4[c]
Rb_2SO_4 (II)	5.2	0.11	15.8[c]
RbOH	2.2	0.9	46.6[c]
2a	< 0.5	–	126
2b	< 0.5	–	128
2c	< 0.5	–	128

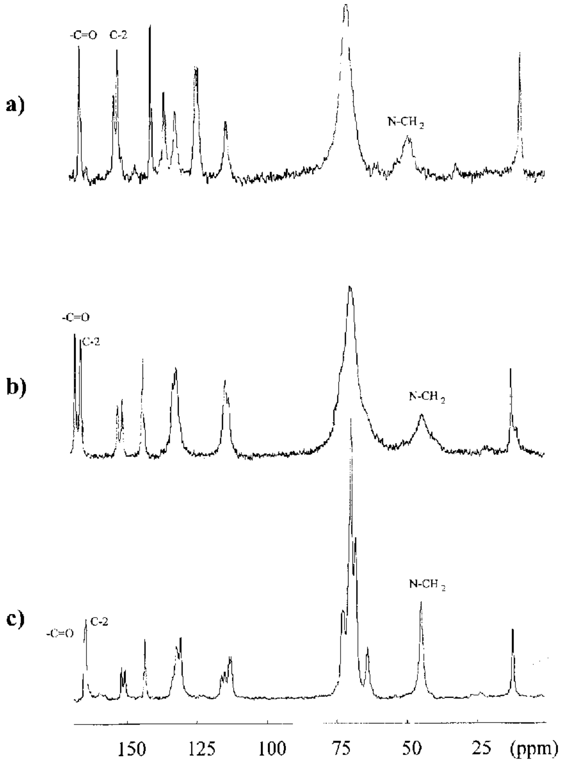
[a] Quadrupole coupling constant $Q_{cc} = e^2qQ/h^{-}$, where $eq = V_{zz}$ is the main component of the EFG tensor. – [b] Asymmetry parameter of the EFG tensor $\eta = (V_{xx} - V_{yy})/V_{zz}$ with $0 \leq \eta \leq 1$. – [c] Actual values derived from the simulated spectrum.

Figure 2. Proposed model of the rubidium incorporation of compounds **2**



The ^{87}Rb MAS NMR spectra which are of interest, those of the samples of the complexes **2**, clearly differ from those of the test compounds. As a representative example the spectrum of the compound **2b** is shown in Figure 1d. In all cases a sharp signal at $\delta = 128$ is observed; this differs in terms of both the chemical shift and the quadrupole interaction. Because of the unstructured lineshape, and its small width, a quadrupole coupling constant of only < 0.5 MHz was estimated. As a reason for this small EFG, and the striking low-field shift, we postulate the incorporation of the rubidium ion into the cavity between coronand and chromophore (see Figure 2). Obviously there is a high symmetry and, accordingly, a small electric field gradient at this site. This is supported by the fact that, for the compound **2a** (15-crown-5) which has the smallest crown, a line broadening of the NMR signal is observed, which we explain by the reduction in the volume of the cavity. The marked low-field shift can be attributed to the reduction of the magnetic shielding of the rubidium ion, as a result of the formation of a bond with partially covalent character.

Figure 3. ^{13}C CPMAS NMR spectra of a) **1b**, b) **2b**, and c) ammonium salt of **1b**



^{13}C CPMAS NMR Spectroscopy

The results of the ^{87}Rb MAS NMR studies are supported by ^{13}C CPMAS NMR measurements on the compounds **1a**−**1c** and **2a**−**2c**. Figure 3 shows representatively the spectra of **1b** and **2b**. In the salts **2a**−**2c** the chemical shifts of the individual C atoms (see Table 2) differ in comparison with those of the free host molecules **1**. However the changes are not as significant as in the case of the ^{87}Rb-NMR spectra. The changes of the C-2 atoms of the aromatic system are, as expected, due to the formation of phenolates, whereas the changes of the other aromatic C atoms cannot be so simply interpreted. Possibly they are caused by steric effects. Clear differences in the ^{13}C chemical shifts were, however, observed for the coronand system. Of particular note are the signals of the $N-CH_2$ groups of the ring system, which are shifted ca. 5 ppm towards high field.

Table 2. ^{13}C CPMAS NMR chemical shifts [in ppm] of **1** and **2**, and of **1** in CD_3CN solution for comparison

Assignment[a]	**1a**		**2a**	**1b**		**2b**	**1c**		**2c**
	CD_3CN	solid	solid	CD_3CN	solid	solid	CD_3CN	solid	solid
-C=O	164.7	164.2	163.8	166.3	165.4	165.1	166.3	165.7	166.7
=C-Cl	123.1	122.2	111.7	123.9	113.8	112.6	124.0	113.0	114.2
CH_3-C=	150.1	149.7	148.1	151.7	153.3	151.9	151.7	153.5	150.1
CH_3-C=	10.5	9.3	8.3	10.9	9.6	12.9	10.9	10.3	11.3
arom.C-1	137.4	137.4	140.3	137.7	140.4	143.2	139.4	140.3	143.5
arom.C-2	146.8	146.9	163.8	149.2	152.0	166.9	149.2	152.0	166.7
arom.C-3	124.2	124.2	113.4	125.3	123.7	113.8	125.3	123.6	114.2
arom.C-4(H)	132.7	134.2	129.3	133.5	132.0	131.5	133.6	133.6	131.2
arom.C-5	136.5	137.4	127.4	137.3	135.7	130.0	137.7	137.7	131.2
arom.C-6(H)	130.5	130.9	127.4	126.3	124.5	132.4	126.5	125.0	131.2
-N-CH2-	44.6 50.6	47.4 52.9	44.4 49.4	46.6 50.2	49.6 49.2	44.3	46.8 50.3	48.9 48.7	44.9 49.8
-O-CH2-	68.6 69.3 69.9 70.0 70.2 70.3 70.6 71.5	66.3 69.8 71.8	67.3(br) 73.6	69.2 69.8 70.7 70.8 70.9 70.9	71.3	69.8	69.5 70.1 70.9 71.1	70.0 71.6	70.9 73.6

[a] Using high-resolution APT spectra and increment analysis.

In accordance with the ^{87}Rb- and ^{13}C-NMR results we conclude that the rubidium ion is incorporated into the cavity between coronand and chromophore. This proposed model is illustrated in Figure 2. Investigations carried out with the corresponding ammonium salts of **1** showed analogous changes in the chemical shifts of the ^{13}C CPMAS NMR spectra (see Figure 3). This suggests that the ammonium ion, having a comparable ion radius to the rubidium ion, is also incorporated into the cavity.

This work was supported by the *Federal Ministry of Education, Science, Research, and Culture* (project No. 03C 3005). We are also grateful to the *Deutsche Forschungsgemeinschaft (DFG)* and the *Fonds der Chemischen Industrie* for financial support.

Experimental Section

NMR: The ^{87}Rb-NMR studies were carried out with a Varian Unity-plus 300. The solid-state spectra were recorded with the magic-angle spinning (MAS) technique using a Doty probe (5 mm) at 98.79 MHz. Spinning rates of 12.5 kHz were applied. Up to 20000 scans with a repetition time of 1 s were accumulated. As an external standard a 1 M $RbNO_3$ aqueous solution was used. − Spectral simulations were performed using a PC with an extended version of the program Winfit[11]. The simulation of the central transition and its spinning sidebands was carried out taking into consideration quadrupole effects in 2nd order perturbation theory. Effects of chemical shift anisotropy were not considered. − The solid-state ^{13}C-NMR spectra were recorded with cross polarization and magic angle spinning (CPMAS) techniques on a Bruker MSL 400 at 100.63 MHz. Spinning rates of 14 kHz (4 mm rotors) were applied. The corresponding high resolution spectra of the solutions were recorded with a Varian Unity-plus 300 spectrometer. The chemical shifts refer to TMS.

Rubidium Complexes: 1 mmol (509 mg of **1a**, 553 mg of **1b**, 598 mg of **1c**) of **1** dissolved in 10 ml of ethanol was added dropwise to a solution of 1 mmol (102 mg) of rubidium hydroxide in 20 ml of ethanol over a period of 5 min. After refluxing the mixture for 1 h, the solvent was evaporated in vacuo to dryness. The dark red residue was extracted with boiling toluene (3 × 10 ml) and dried in vacuo for 24 h.

2a: Yield 570 mg (96%); m.p. 98−101 °C. − MS (LSIMS); *m/z* (%): 596 (5) $[M^+ + H]$. − $C_{20}H_{25}Cl_3N_3O_6Rb$ (595.26): calcd. C 40.36, H 4.23, N 7.06; found C 39.95, H 4.01, N 6.85.

2b: Yield 608 mg (95%); m.p. 136−138 °C. − MS (LSIMS); *m/z* (%): 640 (100) $[M^+ + H]$. − $C_{22}H_{29}Cl_3N_3O_7Rb$ (639.02): calcd. C 41.30, H 4.43, N 6.60; found C 41.09, H 4.37, N 6.44.

2c: Yield 620 mg (91%); m.p. 123−125 °C. − MS (LSIMS); *m/z* (%): 684 (5) $[M^+ + H]$ − $C_{24}H_{33}Cl_3N_3O_8Rb$ (683.37): calcd. C 42.18, H 4.87, N 6.15; found C 42.50, H 5.05, N 6.02.

☆ Dedicated to Professor Dr. *Reiner Radeglia* on the occasion of his 60th birthday.

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