# Unusual Complexation Behavior of Metallomacrocycles Based on Isothiosemicarbazides with Respect to Alkali and Alkaline Earth Metal Ions: Novel 2:1 Associates

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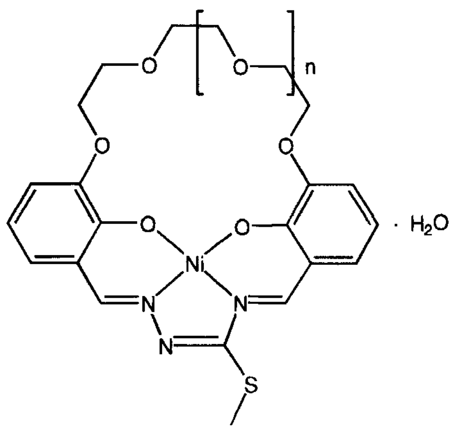
Received July 17, 1995

**Key Words:** Metallomacrocycles / Nickel complexes / Complexation reactions

The reactions between alkali and alkaline earth metal ions and nickel(II) macrocycles based on *S*-alkylated isothiosemicarbazides with different crown ether cavity size were studied in propylene carbonate by spectrophotometric and calorimetric titrations. Metallomacrocycles **1** and **2** exhibit normal behavior on 1:1 complexation with alkali- and alkaline earth metal ions and resemble in this respect 15C5 and 18C6, respectively. The most stable complexes are formed by these "ligands" when the diameter of the cation and the crown ether hole have approximately the same size. The most striking feature of the complexation processes studied is the formation of 1:2 metal-ligand associates even in the case of the smallest cations. These associates are very different from "normal" crown ether sandwich complexes. In reality, the particle formed is an associate between a 1:1 complex, in which the corresponding metal ion is well accommodated inside the ligand cavity, and a second metallomacrocyclic ligand. Their formation is disfavored by enthalpic contributions. A special kind of "switch" from these associates to normal sandwich complexes takes place in the case of **1**, when the cation diameter compared to hole size increases. The macrocycle **2** forms this kind of associates with all akali and alkaline earth ions.

The complexation of cations by crown ethers and other macrocycles in different solvents has been subject of numerous publications. These investigations were reviewed by Izatt et al.[1,2]. At the same time complexation properties of neutral metallomacrocycles with respect to metal ions were studied much less extensively[3]. One of the reasons is the lack of positive cooperativity in binding two metal ions. Quite recently, however, a positive cooperativity in the binding of 3d and alkali metals was reported[4]. Without the knowledge of the thermodynamic parameters, it is not possible to get an insight into the factors influencing the selectivity and the complexation behavior of such metallomacrocyclic receptors.

In this paper we report on the thermodynamics of alkali and alkaline earth metal ion complexation in a dipolar aprotic solvent, propylene carbonate, with metallomacrocycles **1** and **2**, differing in the number of oxygen donors and crown-ether cavity size.



**1**: n = 1
**2**: n = 2

## Results and Discussion

Interactions between metallomacrocycles **1** and **2** and alkali and alkaline earth metal ions were studied by spectrophotometric and calorimetric titrations. Examination of the electronic absorption spectra during titration indicated that the following complexation reactions proceed in solution:

$$M^{n+} + NiL \rightleftharpoons MNiL^{n+}$$
$$MNiL^{n+} + NiL \rightleftharpoons M(NiL)_2^{n+}$$

The stability constants $K_1$ and $K_2$ are given by:

$K_1 = [MNiL^{n+}]/[M^{n+}][NiL] \qquad K_2 = [M(NiL)_2^{n+}]/[MNiL^{n+}][NiL]$

The most illustrative curve, reflecting the presence of two

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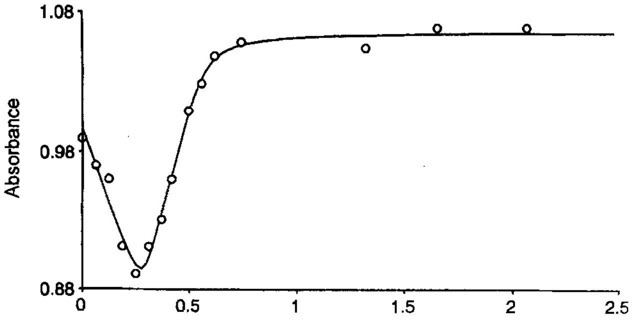
complex species (1:1 and 1:2) in solution is shown in Figure 1. The values of log*K*, $\Delta H$ and $T\Delta S$ for the complexation of alkali and alkaline earth metal ions by the two different (in size and number of oxygen donors) metallomacrocycles are summarized in Table 1.

Figure 1. Absorbance of solutions containing metallomacrocycle **1** ($c = 6.0 \cdot 10^{-5}$ M) with different concentrations of Ba(II) salt in propylene carbonate at 25°C



The data show that upon complexation of the 1:1 type the investigated metallomacrocycles **1** and **2** behave in an analogous manner to crown ethers[5,6].

The stability of the 1:1 species depends mainly on the fit of the metallomacrocycle cavity size to cation diameter. If the cavity and cation dimensions are comparable or equal, the ligands form very stable complexes. In this case optimal interactions between all the ligand donor atoms and the complexed cation are possible. Thus, the most stable 1:1 complexes are formed between macrocycle **1** and $Li^+$, $Na^+$, and $K^+$. The formation of these 1:1 complexes is accompanied by the highest values of the reaction enthalpies in comparison with the other alkali metal ions. Cations which are too big to fit into the cavity are not able to interact optimally with all donor atoms. In this case the complexed cation is located above the crown ether oxygen mean plane. As a result, a reduction in the values of the reaction enthalpies is expected, as can be seen for reaction of **1** with $Rb^+$ and $Cs^+$. The general trend of $\Delta H$ changes during complexation of **1** with alkali and alkaline earth metal ions is analogous to complexation of 15C5 with corresponding metal ions[5]. System **2** in this respect is very similar to 18C6 (except for $Li^+$)[6]. More insight into the reactions taking place in solution is possible for the complexation of $K^+$ and $Ba^{2+}$ since both cations are almost identical in size. This means that all other factors influencing the values of the entropic contributions are constant (e. g. deformation of the metallomacrocycle, changes in the number of particles during the reaction, except the differences in solvation of cations). The selectivity towards 1:1 complexation of **1** with $Ba^{2+}$ exceeds two orders of magnitude when compared with that for $K^+$. The difference of the $T\Delta S$ values of both cations at 25°C is as follows:

$$\Delta(T\Delta S) = T\Delta S_{Ba^{2+}} - T\Delta S_{K^+} = 25.7 \text{ kJ mol}^{-1}$$

The difference is connected, as was outlined above, only with differences in the solvation number of both cations. The entropy of fusion for propylene carbonate at 25°C was estimated to be 9.0 kJ mol$^{-1}$[7]. If we use this value an approximate estimation of the difference in the number of solvent molecules liberated during complex formation of both cations is possible:

$$\Delta(T\Delta S)/T\Delta S_{\text{fusion}} = 2.9$$

Table 1. Thermodynamic parameters for the complexation reactions of the metallomacrocycles **1** and **2** with alkali and alkaline earth metal ions in propylene carbonate (units in kJ·mol$^{-1}$)

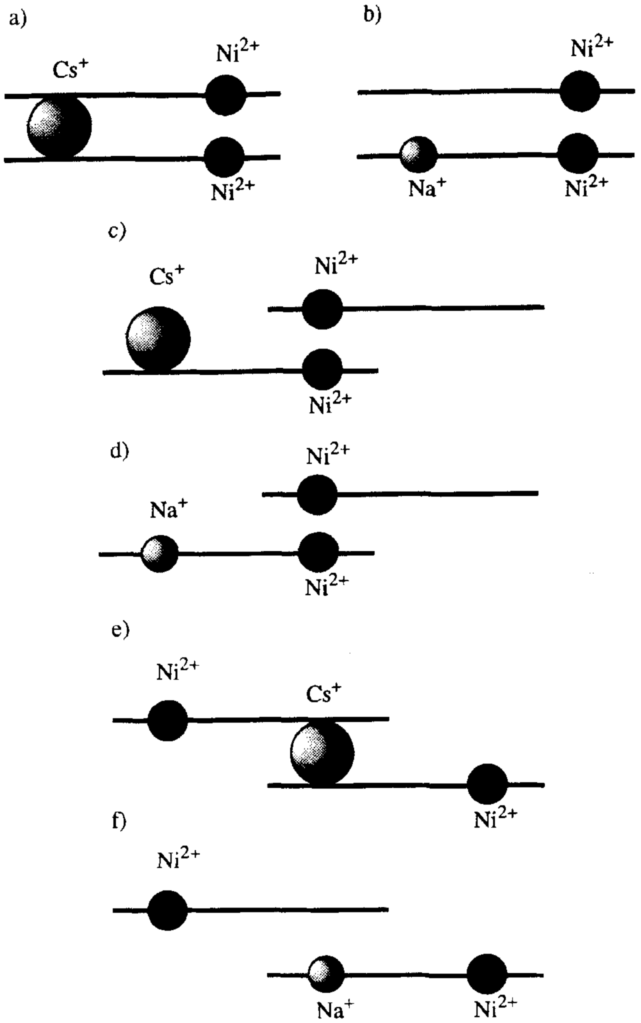
| Cation | Cation radius | Metallo-macro-cycle | Log $K_1$ | Log $K_2$ | - $\Sigma\Delta H_i$ | - $\Delta H_1$ | $T\Delta S_1$ | - $\Delta H_2$ | $T\Delta S_2$ |
|---|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 0.68 | 1 | > 5[a] | [b] | 15.3 ± 0.5 | 23.7 ± 0.2 | | - 8.5 ± 0.7 | |
| $Na^+$ | 0.97 | 1 | 8.20 ± 0.6 | 3.99 ± 0.4 | 23.3 ± 0.3 | 26.1 ± 0.4 | 20.5 ± 3.8 | - 2.8 ± 0.7 | 25.6 ± 3.0 |
| $K^+$ | 1.33 | 1 | 5.49 ± 0.4 | 7.49 ± 0.4 | 70.3 ± 0.6 | 26.7 ± 0.5 | 4.5 ± 1.8 | 43.6 ± 1.1 | - 1.0 ± 1.2 |
| $Rb^+$ | 1.47 | 1 | < 1 | 9.44 ± 0.3 | 74.4 ± 0.5 | 19.7 ± 0.3 | | 54.7 ± 0.8 | - 1.1 ± 0.9 |
| $Cs^+$ | 1.67 | 1 | < 2 | 8.75 ± 0.3 | 72.2 ± 0.8 | 13.0 ± 0.6 | | 59.2 ± 1.4 | - 9.5 ± 0.3 |
| $Mg^{++}$ | 0.66 | 1 | 2.63 ± 0.2[a] | [b] | 27.1 ± 0.3 | 21.7 ± 0.5 | - 6.8 ± 0.6 | 5.4 ± 0.8 | |
| $Ca^{++}$ | 0.99 | 1 | 5.88 ± 0.3 | 3.38 ± 0.3 | 31.8 ± 0.5 | 11.5 ± 0.4 | 21.9 ± 1.3 | 20.3 ± 0.9 | - 1.1 ± 0.8 |
| $Sr^{++}$ | 1.12 | 1 | 6.28 ± 0.4 | 3.05 ± 0.2 | 29.0 ± 0.4 | 14.0 ± 0.6 | 21.7 ± 1.7 | 15.0 ± 1.0 | 2.3 ± 0.2 |
| $Ba^{++}$ | 1.34 | 1 | 8.16 ± 0.3 | 6.12 ± 0.2 | 33.1 ± 0.6 | 16.1 ± 0.3 | 30.3 ± 1.4 | 17.0 ± 0.9 | 17.8 ± 0.3 |
| $Li^+$ | 0.68 | 2 | | | 19.5 ± 0.3 | 48.3 ± 0.6 | | - 28.8 ± 0.9 | |
| $Na^+$ | 0.97 | 2 | 7.19 ± 0.6 | < 4 | 7.2 ± 0.2 | 23.0 ± 0.8 | 17.9 ± 2.7 | - 15.8 ± 1.0 | |
| $K^+$ | 1.33 | 2 | | | 10.1 ± 0.4 | 38.5 ± 0.3 | | - 28.4 ± 0.7 | |
| $Rb^+$ | 1.47 | 2 | | | 10.2 ± 0.2 | 35.9 ± 0.8 | | - 25.7 ± 1.0 | |
| $Cs^+$ | 1.67 | 2 | | | 16.0 ± 0.1 | 32.4 ± 0.2 | | - 16.4 ± 0.3 | |
| $Mg^{++}$ | 0.66 | 2 | 3.91 ± 0.2[a] | [b] | 13.3 ± 0.3 | 18.6 ± 0.2 | 3.6 ± 1.0 | - 5.3 ± 0.5 | |
| $Ca^{++}$ | 0.99 | 2 | 5.18 ± 0.4 | 3.26 ± 0.2 | 18.4 ± 0.4 | 22.7 ± 3.0 | 6.7 ± 1.5 | - 4.3 ± 3.4 | 22.9 ± 4.5 |
| $Sr^{++}$ | 1.12 | 2 | 5.26 ± 0.4 | 3.52 ± 0.2 | 20.2 ± 1.3 | 28.0 ± 0.1 | 1.9 ± 2.1 | - 7.8 ± 1.4 | 27.8 ± 2.5 |
| $Ba^{++}$ | 1.34 | 2 | 5.42 ± 0.3 | 3.68 ± 0.2 | 24.6 ± 0.4 | 49.2 ± 0.3 | - 18.4 ± 1.4 | - 24.6 ± 0.7 | 45.5 ± 1.9 |

[a] According to calorimetric titration. – [b] Not determinable.

This number indicates that approximately 3 molecules of solvent are set free upon complexation of Ba$^{2+}$ compared with K$^{+}$. These findings are in accordance with the differences in the solvation number of Ba$^{2+}$ and K$^{+}$[8,9]. This is similar to the behavior of crown ethers upon formation of 1:1 complexes with alkali and alkaline earth metal ions.

The situation becomes more complex when considering 1:2 metal ligand complexes (Table 1). This is due to the fact that different types of such complexes are possible, as illustrated schematically in Figure 2. It needs to be pointed out that associates a), b), c), and d) imply $\pi-\pi$ interactions between the $\pi$ systems of the ligands, and not Ni-Ni interactions.

Figure 2. The possible kinds of 2:1 complexes and associates formed in solution between metallomacrocycles 1 and 2 and alkali and alkaline earth metal ions



It is not surprising that by increasing the metal ion size the tendency to form 1:2 complexes of the sandwich type with metallomacrocycle **1** increases as well. Thus, by the interaction of Rb$^{+}$ and Cs$^{+}$ with **1** stable 1:2 complexes (see Table 1) are formed, which is in accordance with the classical concept of "ion-cavity" size compatibility. The formation of this kind of complex is favored by enthalpic contributions. Schematically, this corresponds to the case illustrated in Figure 2a. In the case of Sr$^{2+}$ and Ba$^{2+}$ the enthalphies for the formation of 1:1 and 1:2 complexes are identical within experimental error. This means that the interactions of the second ligand with the complexed cation are not influenced by the first ligand.

It should be noted that already in the case of the 1:1 complex of **Ba(CF$_3$SO$_3$)$_2$** and **1** the alkaline earth metal ion is displaced from the mean plane of the polyether oxygen atoms by 0.601 Å, as revealed by X-ray diffraction[10].

The main peculiarity of the complexation process of the investigated "ligands" with alkali and alkaline earth metal ions is the formation of complexes (or associates) of the 2:1 type, even in the case of smallest cations, such as Li$^{+}$, Na$^{+}$, Mg$^{2+}$ (Table 1). *Such a behavior has not been observed previously in any other ligand system.* Ligand **2**, larger in size and number of donor atoms, forms such kinds of 2:1 associates with all alkali and alkaline earth ions. However, the second metallomacrocyclic ligand practically does not interact with a complexed cation accommodated inside the cavity of the first ligand, as indicated by the positive $\Delta H$ values. Figure 2b shows schematically one of the possible variants of such 2:1 associates. If we take into account the thermodynamic data given in Table 1, the formation of the other kinds of species presented in Figure 2 appears less probable, although at present this cannot be proven unambiguously. If the radii of the complexed cations are much larger than the cavity radii, the respective ligands of the 2:1 complexes are not expected to have any appreciable interactions. Thus, the ligands of the kind of species represented in Figure 2a are likely to rotate with formation of the type of species illustrated in Figure 2e, i. e., they are equally probable. The measured values of the reaction enthalpies for the formation of 1:1 and 2:1 complexes with ligand **1** and Sr$^{2+}$ and Ba$^{2+}$ support this interpretation. If the values of the reaction enthalpies for the formation of the 2:1 complexes are higher than the corresponding values for the formation of the 1:1 complexes as in the case of ligand **1** and K$^{+}$, then this may be caused by changes in the solvation of the cation due to the 2:1 complex formation or additional interactions between both ligands (Figure 2a). Therefore, the structure given in Figure 2c may be an intermediate because it is energetically less favored when compared with that shown in Figure 2a. Steric hindrance between the metallomacrocycles might be expected to favor the formation of sandwich species depicted in Figure 2e, as shown by Beer in other systems[11]. However, in view of the X-ray diffraction data of **1** which reveal $\pi-\pi$ stacking[10], such a possibility is less likely.

If the radii of the cations are small with respect to the cavity dimensions, the formation of associates as in Figure 2b can be supposed. The structure shown in Figure 2d may be an intermediate in the formation of associates shown in Figure 2b. On going from the structure shown in Figure 2d to that one in Figure 2b, some of the solvent molecules near the cation and around the ligands are set free, and the reaction is favored by entropy. The same is true with the possible structure shown in Figure 2d as an intermediate only in the formation of the associate given in Figure 2b. In Figure 2f no interactions between the small complexed cation and the second ligand are possible. Therefore this structure will not really exist.

It should be noted that in the absence of metal ions an association of the metallomacrocycles does not take place. This conclusion is supported by the fact that the Lambert-Beer law is fulfilled for solutions of **1** and **2** in propylene carbonate in the used range of concentrations. The presence of positively charged ions in solution reduces the repulsions between donor atoms of the corresponding metallomacrocycle molecules and in such a way contributes, perhaps, to the formation of 2:1 associates. In particular, the following argumentation seems plausible. From the entropic point of view, the 2:1 complexation in the case of both kinds of metallomacrocycles, and especially in the case of ligand **2** (with bigger size of crown ether cavity), is unfavorable. However, the loss of entropy arising from molecular association is compensated by the gain in entropy from the favorable $\pi-\pi$ interaction between conjugated di(salicylidene)isothiosemicarbazide parts of the molecules, a release of water, and releasing solvent molecules liberated upon desolvation of metallomacrocycles, forming corresponding dimeric units. Such $\pi-\pi$ interaction is thus likely. Indeed, an X-ray structural analysis of some closely related systems shows stacked structures[12,13]. The same situation is revealed in the case of **1**. According to the X-ray diffraction[10] the molecules **1** pack in pairs about centers of symmetry, with the coordination planes of the Ni atoms lying parallel to one another and separated by 3.4 Å. Note that this separation between the parallel moieties is considered to be optimal for $\pi-\pi$ interactions[14].

We were not able to obtain supportive evidence for $\pi-\pi$ interactions in solution by NOESY-NMR experiments. So the results presented above do not allow an unambiguous decision as to the nature of the 2:1 species. However, the thermodynamic data are compatible with the proposed structure of 2:1 associates (Figure 2b). Moreover, even in the most favorable circumstance of a suitable stacking geometry only weak interligand NOEs are to be expected.

Finally, we want to stress once more that the kind of dimeric associate formed depends mainly on the diameter of the cation. When the cation is small with respect to the hole size of the crown ether moiety of the metallomacrocycle, a novel 1:2 associate as shown in Figure 2b is assembled, in which there is no interaction between the metal ion of the 1:1 complex molecule and the second metallomacrocyclic ligand. If the cation is larger than the cavity size of metallomacrocycle, then a switch to the "normal" 1:2 sandwich complex (Figure 2a) takes place.

This work was supported by the *Deutsche Forschungsgemeinschaft* (Leibniz-Programm). V. B. A. thanks the *Alexander-von-Humboldt-Stiftung* for a research fellowship.

## Experimental

*Chemicals:* Complexes **1** and **2** were obtained in two steps from the corresponding nickel-barium complexes as described below. 3,3′-(3,6-Dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) and 3,3′-(3,6,9-trioxaundecane-1,11-diyldioxy)bis(2-hydroxybenzaldehyde) were obtained as described in ref.[12].

*5-(Methylthio)-13,16,19,22-tetraoxa-3,4,6-triazatricyclo[21.3.1.1$^{8,12}$]octacosa-1(27),2,4,6,8,10,12(28),23,25-nonaene-27,28-diolato(2−) $N^3$,$N^6$,$O^{27}$,$O^{28}$]nickelbarium(2+) Bis(trifluoromethanesulfonate)* **[NiBaL($CF_3SO_3$)$_2$]**: To a refluxing solution of $Ba(CF_3SO_3)_2$ (0.87 g, 2 mmol) in $CH_3OH$ (200 ml) were added dropwise a solution of 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) (0.78 g, 2 mmol) in THF (25 ml) and a solution of *S*-methylisothiosemicarbazide hydroiodide (0.47 g, 2 mmol) in $CH_3OH$ (25 ml) over a period of 4 h under inert gas. The resulting yellow-orange solution was heated at reflux for 15 min after which time a solution of $Ni(CH_3COO)_2 \cdot 4\,H_2O$ (0.50 g, 2 mmol) in $CH_3OH$ (25 ml) was added in one portion. Subsequently, the dark red solution was cooled to room temp., then concentrated to 75 ml and saturated with pentane (40 ml). The red product crystallized; it was filtered off and washed with $CH_3OH$/pentane (2:1). Yield 0.65 g (34%). – $C_{24}H_{23}BaF_6N_3NiO_{12}S_3$ (951.7): calcd. C 30.29, H 2.44, N 4.55; found C 30.33, H 2.51, N 4.55. – $^1H$ NMR ([D$_6$]DMSO): $\delta$ = 9.12 (s, 1H, CH=N$_{hydrazine}$), 8.89 (s, 1H, CH=N$_{thioamide}$), 7.9–6.9 (m, 6H, ArH), 4.28 (br. s, 4H, $ArOCH_2$), 3.99 (br. s, 4H, $OCH_2$), 3.88 (s, 4H, $OCH_2$), 2.79 (s, 3H, $SCH_3$). – MS, *m/z*: 802 [$M^+ - CF_3SO_3$].

*Synthesis of* **1**: A suspension of NiBaL($CF_3SO_3$)$_2$ (0.32 g) in $CHCl_3$ (40 ml) was stirred with a solution of guanidinium sulfate (1.0 g) in $H_2O$ (40 ml) for 2 h. The organic layer was separated, dried with $MgSO_4$ and concentrated. The product was precipitated with hexane. Yield: 0.10 g (50%). – $C_{22}H_{25}N_3NiO_7S$ (534.2): calcd. C 49.46, H 4.72, N 7.87; found C 49.05, H 4.34, N 7.99. – $^1H$ NMR ($CDCl_3$): $\delta$ = 8.09 (s, 1H, CH=N$_{hydrazine}$), 7.86 (s, 1H, CH=N$_{thioamide}$), 7.0–6.85 (m, 2H, ArH), 6.85–6.7 (m, 2H, ArH), 6.6–6.5 (m, 2H, ArH), 4.15–4.05 (m, 4H, $ArOCH_2$), 4.05–3.95 (m, 4H, $OCH_2$), 3.94 (s, 4H, $OCH_2$), 2.72 (s, 3H, $SCH_3$). – MS, *m/z*: 515 [$M^+ - 18$]. The structures proposed for NiBaL ($CF_3SO_3$)$_2$ and **1** are confirmed by X-ray diffraction studies[10].

*Complex* **2** was obtained in the same way as **1**. Yield 0.88 g (76%), m. p. 165–167°C. – $C_{24}H_{29}N_3NiO_8S$ (578.3): calcd. C 49.85, H 5.05, N 7.27; found 49.43, H 5.46, N 6.93. – $^1H$ NMR ($CDCl_3$): $\delta$ = 8.09 (s, 1H, CH=N$_{hydrazine}$), 7.87 (s, 1H, CH=N$_{thioamide}$), 7.0–6.8 (m, 4H, ArH), 6.6–6.5 (m, 2H, ArH), 4.2–4.0 (m, 8H, $OCH_2$), 3.9–3.75 (m, 4H, $OCH_2$), 3.75–3.6 (m, 4H, $OCH_2$), 2.70 (s, 3H, $SCH_3$), 2.11 (br. s, 3H, $H_2O$). – MS, *m/z*: 559 [$M^+ - 18$].

The *alkali metal tetraphenylborates* were prepared and purified according to literature procedures[15]. *Heptafluorobutyrates* were prepared by adding the solid alkaline earth hydroxides to a concentrated aqueous solution of heptafluorobutyric acid (Aldrich) until no further dissolution of the hydroxide could be observed. The residue was washed with dichloromethane and dried in vacuo. Dry propylene carbonate (Aldrich, max. 0.005% water) was used as solvent for spectrophotometric and calorimetric titrations. All other chemicals were reagent grade and were used without further purification.

NMR spectra were recorded in $CDCl_3$ with TMS as internal standard. Positive ion fast atom bombardment (FAB) mass spectra were obtained with *m*-nitrobenzyl alcohol as a matrix.

*Spectrophotometric Titrations:* A Varian Cary 5 spectrophotometer was used for spectrophotometric titration. Absorbance of the metallomacrocycles **1** and **2** ($c = 6.0 \cdot 10^{-5} - 7.0 \cdot 10^{-5}$ M) in propylene carbonate as a function of the concentration of metal salt added was measured at 305 nm ($Na^+$, $Rb^+$, $Ca^{2+}$, $Sr^{2+}$), 311 nm

($Ba^{2+}$), 395 nm ($K^+$, $Cs^+$) in the case of **1** and at 298, 302, 304 nm ($Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) in the case of **2** at 25°C. A matched pair of quartz cells with a path length $d = 1.000$ cm was used. Absorbance $A$ at a constant wavelength in the case of 1:2 metal-ligand complex formation is described by the following equation:

$$A = d(\varepsilon_{\mathrm{NiL}}[\mathrm{NiL}] + \varepsilon^{n+}_{\mathrm{MNiL}}[\mathrm{MNiL}^{n+}] + \varepsilon^{n+}_{\mathrm{M(NiL)_2}}[\mathrm{M(NiL)}_2^{n+}])$$

where $\varepsilon_{\mathrm{NiL}}$, $\varepsilon^{n+}_{\mathrm{MNiL}}$ and $\varepsilon^{n+}_{\mathrm{M(NiL)_2}}$ are the molar extinction coefficients and [NiL], [$\mathrm{MNiL}^{n+}$], and [$\mathrm{M(NiL)_2}^{n+}$] the molar concentrations of the "ligand" and the complexes formed. The unknown stability constants $K_1$ and $K_2$ and extinction coefficients $\varepsilon^{n+}_{\mathrm{MNiL}}$ and $\varepsilon^{n+}_{\mathrm{M(NiL)_2}}$ were calculated by least-square methods[16]. The molar extinction coefficients of the ligands used were calculated from independent measurements. The experimental points as obtained typically for the complexation of $Ba^{2+}$ by the metallomacrocycle **1** together with the fitted curve are shown in Figure 1.

*Calorimetric Measurements:* A Tronac model 450 precision calorimeter was employed to measure the reaction heats at 25°C. The titration and calibration procedures were similar to those described in the literature[17,18]. In particular, the titrations were performed by adding metallomacrocycle solutions of concentration 0.01 M at a constant rate to 40 ml of propylene carbonate containing an excess of the respective metal salt in order to provide the exclusive formation of 1:1 complexes. To determine $\Sigma\Delta H_i$ the titrations were performed by adding a metal salt solution of concentration 0.001 M to an excess of the corresponding metallomacrocycle in 40 ml of propylene carbonate. Each titration was repeated at least twice. The heats of dilution, determined in separate runs, were negligible in the concentration ranges of metallomacrocycles and metal salts used. The enthalpy changes for the systems were calculated by using the least-square program[17].

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