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Sulfonatocalixarene Counterion Exchange Binding Model in Action: Metal-Ion Catalysis Through Host-Guest Complexation

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p-Sulfonatocalixarene water soluble macrocyclic host receptors are known to form cooperative ternary complexes with complementary organic guest and metal cations. This property may be explored to enhance the interaction of weak nitrogen ligands with metal cations in a confined space showing some resemblance to metal-containing enzymes. However, the best of our knowledge, catalytic potential of this property remains unexplored. In this work the Ni^{2+} catalyzed hydrolysis of a picolinate ester (2,4-dinitrophenyl picolinate, **1**) was used as a model reaction to evaluate the effect of sulfonatocalixarene macrocycles in the kinetics of this reaction. The results show that the host molecules promote the reaction through simultaneous complexation of the metal cation and the substrate and, in the case of the larger calixarenes containing more basic phenol groups, substantially higher rate enhancements are observed owing to additional assistance provided by base/nucleophilic catalysis. However, due the ionic nature of these receptors auto-inhibition of the reaction is observed at higher concentrations due counterion (Na^+) binding that competes with the catalytically active Ni^{2+} -complexes.

1. Introduction

Catalysis through encapsulation of reactants in the nanosized cavities of synthetic host molecules is a topic that draw inspiration from Nature's enzymatic catalysts. The microscopic environment offered by the cavities of synthetic macrocyclic receptors displays several characteristics that are reminiscent of enzyme active sites and, therefore, can be exploited to accelerate and/or catalyze organic reactions. Substrate recognition, pre-orientation of reactants into reactive conformations, stabilization of intermediates/ transition states through non-covalent interactions or increase of effective concentrations are some of the features shared by enzymatic and supramolecular catalysts.[1–11] Another important strategy applied by enzymes builds on complexation-induced shifts of protolytic equilibria (i.e. pK_a shifts) to stabilize protonated/unprotonated reactive species under pH conditions where they usually are not observed. Similarly, both neutral and anionic synthetic receptors such cucurbiturils, *p*-sulfonatocalixarenes or metal-ligand coordinations cages are well-documented to provide extra stabilization to their positively charged guests through electrostatic interactions (ion-dipole, Coulombic, cation-π, etc) which often leads to higher selectivity towards positively charged species and consequently to complexation-induced upward pK_a shifts.[12–18] In fact, both the activation of substrates and/or the stabilization of intermediates through selective binding of the positively charged protonated species has been demonstrated to be an effective strategy for rate acceleration and catalysis of organic reactions through the formation of host-guest complexes.[19–24]

Conceptually equivalent to complexation-induced pK_a shifts, the amplification of metal ligand interactions between an organic guest/substrate and a metal cation brought together in close proximity through simultaneous encapsulation in a synthetic receptors holds great potential for catalytic applications.[11] This approach can be addressed through the functionalization of synthetic macrocyclic receptors with polydentate (often nitrogen-based) ligands for metal ion-binding[11] or by using macrocyclic receptors such as *p*-sulfonatocalix[n]arenes (SCn) or cucurbiturils which comprise binding pockets decorated with negatively charged or electronegative carbonyl groups, respectively, that in favorable conditions may accommodate the organic substrate and the metal cation in close proximity through the cooperative formation of heteroternary metal cation:substrate:receptor complexes.[25–29] In addition to their ability to form heteroternary complexes comprising a metal cation and an organic guests, SCn comprise phenols groups that offer the possibility of general base or nucleophilic participation in the catalyzed reaction. To test this hypothesis and evaluate for the first time the formation of heteroternary SCn complexes for catalysis, we selected the Ni^{2+} catalyzed hydrolysis of 2,4-dinitrophenyl picolinate (**1**) as model reaction (Scheme 1). The mechanism of this reaction was established by

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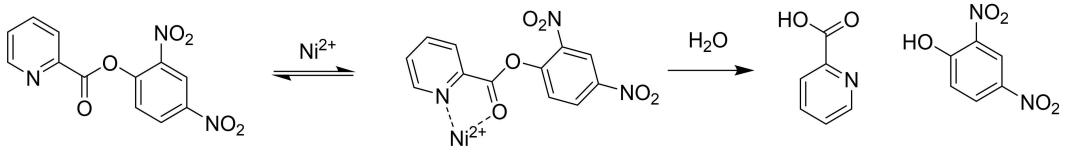
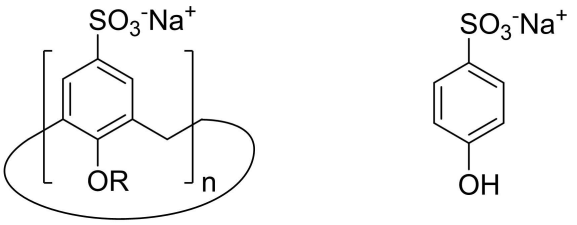


Scheme 1. Proposed mechanism for the Ni^{2+} catalyzed hydrolysis of 2,4-dinitrophenyl picolinate.

Fife and Przystas who found that both Ni^{2+} and Cu^{2+} activate the substrate, through a fast chelation equilibrium, followed by the rate-limiting attack of H_2O, ^{-}OH or acetate and formate buffers.[30]

2. Results and Discussion

The hydrolysis of **1** can be conveniently monitored by UV-Vis absorption spectroscopy at ca. 405 nm (maximum absorption of the 2,4-dinitrophenolate ion). At neutral pH and in the absence of buffers, the reaction proceeds slowly with a $t_{1/2} \approx 16$ hours. Firstly, the effect of different SCn (Scheme 2) and as well of the



HBS

SC4 n = 4 / R = H or Na^+
SC6 n = 6 / R = H or Na^+
SC8 n = 8 / R = H or Na^+
SC6HM n = 6 / R = CH_3

Scheme 2. Structures of the SCn used in this work along with their respective monomer HBS. Some hydroxyl protons are ionized at neutral pH.

parent monomer 4-hydroxybenzenesulfonate (HBS) on the observed rate constant (k_{obs}) for the hydrolysis of **1** was investigated at 25 °C. As can be observed both SC4 and SC6HM (see the Supporting Information) hardly affect the k_{obs} while on the other hand SC6, SC8 and HBS increase the rate of the 2,4-dinitrophenolate ion formation. However, while for HBS (see the Supporting Information) the k_{obs} values shows a linear dependence with its concentration, for the macrocyclic hosts SC6 and SC8 the plots show saturation profiles compatible with the formation of reactive host-guest complexes. The observed behavior can be assigned to the nucleophilic or base catalysis operated by the ionized phenol groups of these receptors. This agrees with the fact that both SC6HM that lacks ionizable phenol groups and SC4 for which the pK_a of the ionized phenol is very low ($pK_a = 3.3$) do not show appreciable catalytic effects.[31] On the other hand, SC6 and SC8 have more than one acidic phenol with pK_a values below 10, being the less acidic those with $pK_a = 4.9$ and $pK_a = 7.8$ for SC6 and SC8, respectively. This agrees with the higher rate enhancement observed for the larger calixarene.

Calixarenes, including SCn, may exist in different conformation owing to the rotation of the phenol units through the macrocyclic ring.[32] While SC4 is suggested to preferentially exist in a flexible cone conformation in solution, SC6 and SC8 are more flexible and their preferential conformation in aqueous solution cannot be elucidated.[33–35] The larger size and flexibility of these last receptors may also play a role in the observed catalytic effects enabling the approach of the hydroxyl groups to the substrate while for SC4 in the cone conformation these type of interactions are not feasible. Nevertheless, the structures of the complexes could not be experimentally investigated in the present work owing to the reactivity and low solubility of **1** in aqueous solution.

The kinetic data shown in Figure 1 for SC6 and SC8 can be fitted to a model [Eq. (1)] that considers the hydrolysis of free and complexed **1** with the respective rate constants being k_0 and k_1. Besides of the kinetic parameters, from data fitting to Equation (1) the apparent binding constant (K_{app}) for the formation of a host-guest complex between **1** and the SCn can also be obtained. However, it must be stressed that for the concentrations of SCn used here, SC6 and SC8 exist in solution as 1:1 and 1:2 sodium complexes and that different stoichiometric complexes containing **1**, SCn and Na^+ are likely to

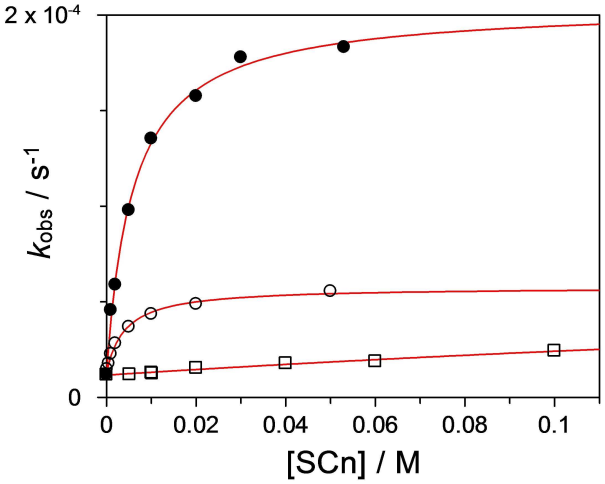


Figure 1. Observed rate constants (k_{obs}) for the hydrolysis of **1** in the presence of increasing concentrations SC4 (open squares), SC6 (open circles) and SC8 (closed circles). All experiments were carried out at 25 °C and at neutral pH conditions in the absence of buffers.

occur.[28,36–39] Therefore k_1 must be considered as an apparent rate constant that results from the sum of the rate constants of the different complexes averaged by their relative mole fraction.

$$k_{obs} = \frac{k_0 + k_1 K_{app}[SCn]}{1 + K_{app}[SCn]} \quad (1)$$

As can be observed from Table 1, reliable k_1 and K_{app} cannot be accurately obtained for SC4 either due to a very small catalytic effect or/and poor binding affinity of **1** towards this host. On the other hand, both SC6 and SC8 form host-guest complexes of moderate affinity with **1** (10^2 M^{-1} range), which is expected based on the lower affinity of these receptors for neutral aromatic species.[28,40,41] As already discussed above, the k_1 values seems to correlate with the pK_a of the ionizable phenols group of the SCn and thus the rate acceleration affect is higher for SC8.

Table 1. Rate and equilibrium constants for the hydrolysis of **1** in the presence of SCn at 25 °C.

	k_0 [s^{-1}]	k_1 [s^{-1}]	K_{app} [M^{-1}]
SC4[a]	$(1.2\pm0.2)\times10^{-5}$	–	–
SC6	$(1.3\pm0.2)\times10^{-5}$	$(5.8\pm1.0)\times10^{-5}$	237 ± 30
SC8	$(1.4\pm0.2)\times10^{-5}$	$(2.0\pm0.2)\times10^{-4}$	165 ± 20

[a] The small variation of the rate constants with the SC4 concentrations precluded a reliable fitting of data to Equation (1).

As previously mentioned, the hydrolysis of **1** is catalyzed by Lewis acids such as Ni^{2+} offering suitable conditions to test the catalytic potential of SCn through the formation of ternary complexes. When the k_{obs} for the hydrolysis of **1** is measured for different concentrations of Ni^{2+} (in the absence of SCn) a straight line is obtained in agreement with a low association constant ($K_{1:Ni2+}$) for the formation of the **1**: Ni^{2+} complex. According to the mechanism of Scheme 1 and assuming that the equilibrium reaction for the formation of the complex is much faster than the hydrolysis, it is straightforward to show that the k_{obs} is given by Equation (2) similar to Equation (1):

$$k_{obs} = \frac{k_0 + k_2 K_{1:Ni2+}[Ni^{2+}]}{1 + K_{1:Ni2+}[Ni^{2+}]} \quad (2)$$

When $K_{1:Ni2+}[Ni^{2+}] \ll 1$ (i.e. for small $K_{1:Ni2+}$), then Equation (2) is reduced to Equation (3) which can be experimentally confirmed by the straight line observed for k_{obs} vs [Ni^{2+}] plot. The slope of this plot gives a value for $k_2K_{1:Ni2+} = 0.019$ $s^{-1}.M^{-1}$ (see the Supporting Information).

$$k_{obs} = k_0 + k_2 K_{1:Ni2+}[Ni^{2+}] \quad (3)$$

Figure 2a shows the influence of SC4 on k_{obs} obtained at constant concentration of Ni^{2+} (0.01 M). As can be observed, the k_{obs} increases up to maximum at circa 0.01 M of SC4 and then the rate of the reaction starts to decrease as the concentration of the macrocycle is further increased. The rate acceleration can be ascribed to the higher affinity of SC4 towards the **1**: Ni^{2+} adduct forming a **1**: Ni^{2+}:SC4 ternary

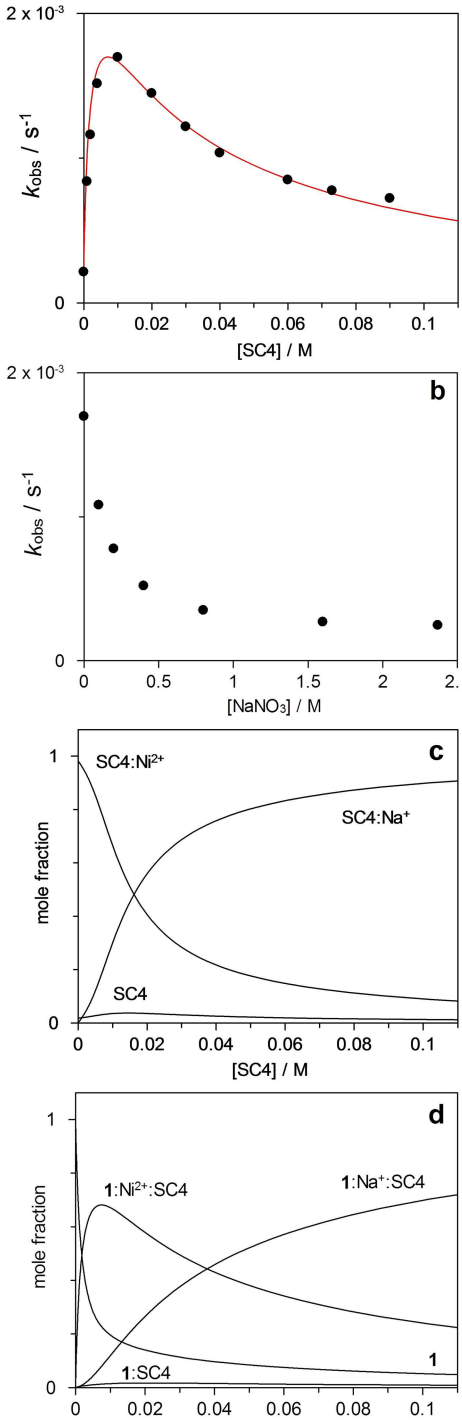
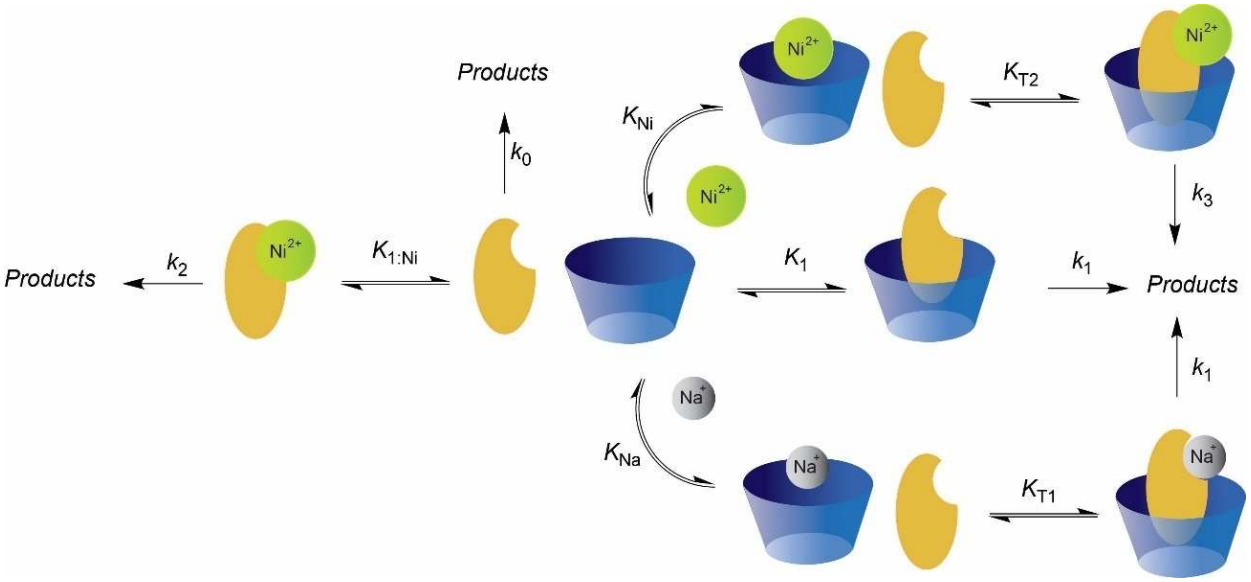


Figure 2. (**a**) Observed rate constants (k_{obs}) for the hydrolysis of **1** in the presence of increasing concentrations of SC4 in the presence of [Ni^{2+}] = 0.01 M. (**b**) Influence of NaNO3 on the k_{obs} for the hydrolysis of **1** in the presence of [Ni^{2+}] = 0.01 M and [SC4] = 0.01 M. (**c**) Mole fraction of SC4 species as a function of the SC4 concentration in the presence of [Ni^{2+}] = 0.01 M. (**d**) Mole fraction of **1** species as a function of the SC4 concentration in the presence of [Ni^{2+}] = 0.01 M. All experiments were carried out at 25 °C and at neutral pH conditions in the absence of buffers.



Scheme 3. Proposed mechanism for the complexation and hydrolysis of 1 with SC4 in the presence of Na^+ an Ni^{2+}.

Table 2. Rate and equilibrium constants (M^{-1}) for the hydrolysis of **1** in the presence of SCn and Ni^{2+} at 25 °C.

	K_1	K_{NiNa}	K_{T1}	K_{2T1}	K_{T2}	K_{2T2}	K_{T3}	k_3 [s^{-1}]
SC4	320 ± 60		150	–	612	–	–	$(2.4 \pm 0.4) \times 10^{-3}$
SC6	–	315 ± 60	< 500	< 10	< 1000	500 ± 100	400 ± 80	$(3.8 \pm 0.3) \times 10^{-3}$
SC8	–	1000 ± 200	–	180	< 1000	350 ± 75	350 ± 70	$(2.8 \pm 0.2) \times 10^{-2}$

complex which increases the effective concentration of the reactive species in solution and consequently its decomposition. At higher concentration the formation of the ternary complex between **1**, SC4, Na^+ counterions starts to predominate leading to a decrease in the observed rate constant. The proposed mechanism is presented in Scheme 3. As an approximation the rate constant (k_1) for the hydrolysis of the **1**: SC4 binary complex and for **1**: Na^+:SC4 ternary complex is considered to be the same. Based on the proposed mechanism, Equation (4) can be deduced to account for the observed rate constant for formation of 2,4-dinitrophenolate product. It is worth noting that the equilibrium concentrations of Na^+, Ni^{2+}, SC4 must be obtained through the resolution of the system of equations based on the mass balance and equilibrium expressions (see the Supporting Information).

As can be observed, the kinetic data in Figure 2a can be satisfactorily fitted with Equation (4) thus supporting the proposed mechanism. Owing to the high number of optimizable parameters, k_0 and $k_2K_{1:Ni}$ obtained above in independent experiments were fixed. Similarly, the values for $K_{Na} = 180\ M^{-1}$ and $K_{Ni} = 5560\ M^{-1}$ were known from previous works and also kept constant.[42] k_1 and K_1 that could not be obtained for SC4 from the kinetic experiments in the absence of Ni^{2+}, were estimated to be $k_1 \approx 2 \times 10^{-5}\ s^{-1}$ and $K_1 = 320\ M^{-1}$. The remaining kinetic and thermodynamic parameters were obtained from the fitting and are presented in Table 2. Noteworthy, the association constant for the binding of **1** towards SC4:Ni^{2+} ($K_{T2} = 610\ M^{-1}$) is almost two times higher than K_1 while the opposite effect is observed for the ternary complex with sodium cations ($K_{T2} = 150\ M^{-1}$) in agreement with positive and negative cooperativity phenomena already documented for the SC4 binding with other pyridine and azoalkanes guests in the presence of transitions and alkaline metal cations, respectively.[25,28] The cooperative formation of the ternary **1**: Ni^{2+}:SC4 complex can be proposed to be main responsible for the observed rate acceleration in the hydrolysis of **1**. Although the k_2 cannot be obtained independently, the observation of a linear dependence in the k_{obs} vs [Ni^{2+}] plot implies that $K_{1:Ni} \leq 1$ and therefore $k_2 \geq 0.019\ s^{-1}$. This observation implies that the rate constant for the hydrolysis of **1**: Ni^{2+} is lower for the ternary **1**: Ni^{2+}:SC4 complex ($k_3 = 2.5 \times 10^{-3}\ s^{-1}$) and therefore the SC4-induced rate enhancement must be attributed to an increase in the concentration of the metal-ligand complex promoted by the calixarene through the formation of the ternary complex. As a control experiment, the effect of $NaNO_3$ on the observed rate constants for the SC4 concentration where maximum rate acceleration was observed (0.01 M) was investigated (Figure 2b). As can be observed the k_{obs} decreases to the value observed in the absence of macrocycle in agreement with the displacement of Ni^{2+} from SC4 by Na^+ competitive binding.

With the binding constants determined, the speciation plots for SC4 and **1** species can be constructed (Figure 2c and 2d) showing that the mole fraction of the complex SC4: Ni^{2+} disappears to give SC4: Na^+ due counterion binding and the

preferential formation of the **1**: Ni^{2+}:SC4 at lower concentrations of SC4 and its disappearance at higher concentrations to give the **1**: Na^{+}:SC4 complex due to the increasing concentration of sodium counterions in solution.

$$k_{obs} = k_0 + k_2K_{1:Ni}[Ni^{2+}] + (K_{1:1} + K_{T1}K_{Na}[Na^{+}])k_1[SC4] + \frac{k_3K_{T2}K_{Ni}[Ni^{2+}][SC4]}{1 + K_{1:1}[SC4] + K_{T1}K_{Na}[Na^{+}][SC4] + K_{T2}K_{Ni}[Ni^{2+}][SC4]} \quad (4)$$

The Ni^{2+}-catalyzed hydrolysis of **1** was also investigated in presence of larger hosts SC6 and SC8. Figure 3 shows results obtained in these cases. Comparatively with SC4, the rate enhancement, at the maximum, is ca. 2-fold higher for SC6 and ca. 10-fold for SC8 demonstrating that the last one is much more efficient at promoting the Ni^{2+}-catalyzed hydrolysis of **1**. When compared with the results obtained in the absence of SC8, the rate is enhanced 85-fold with 10 mM of SC8. A similar mechanism to that proposed for SC4 in Scheme 3, can be proposed for SC6 and SC8 (see Scheme 4) but for these receptors the formation of 1:1 and 1:2 host:guest complexes with the metal cations and respective heteroternary complexes must be accounted for. Before analyzing the kinetic data presented in Figure 3, the binding constants for Ni^{2+} towards SC6 and SC8 were determined using the lucigenin displacement assay protocol previously stablished for other metal cations (see the Supporting Information).[38] This allowed the determination of the following binding constants $K_{Ni} = 1.6x10^5\ M^{-1}$, $K_{2Ni} = 2.4 \times 10^3\ M^{-1}$ for SC6 and $K_{Ni} = 1.5 \times 10^6\ M^{-1}$, $K_{2Ni} = 8.5 \times 10^3\ M^{-1}$ for SC8. The values are in agreement with an increase in the stability of the complexes as the charge of the host and guest increase, as expected for the formation of non-covalent species dominated by attractive coulombic interactions. In the same manner, the stability of the 1:2 SCn:Ni^{2+} complex shows negative cooperativity due to partial charge neutralization during the formation of the binary species.[38]

As can be observed from Scheme 4, the number of species that can be formed for SC6 and SC8 increase substantially with respect to SC4. This complex dynamic multistate system arises from the fact that these hosts can form 1:1, 1:2 and heteroternary complexes with the cations present in solution.[38] Then, the calixarene-metal complexes may bind **1** to form the respective ternary and quaternary complexes. In order to simplify the analysis of the kinetic data we neglected the potential formation of 1:2 host:guest complexes between SC6/8 and **1**. This approximation is based on the fact that in the experimental conditions the concentration of calixarene is usually higher than that of **1** and the binding constants for the formation these complexes are relatively small (see Table 1) which precludes the formation of 1:2 species at lower concentrations of host (unless their formation is highly cooperative but this is not expected on the basis of the stablished SCn binding properties). In a second approximation, it can be assumed that rate constants for the Ni^{2+} containing host-guest complexes are similar independently of their stoichiometry (k_3) and on the other hand, it is also assumed that SCn:**1** and as well the SCn:Na^{+}:**1**/SCn:2Na^{+}:**1** also show similar reactivity (k_1). In this way, the unknown parameters are k_3, K_1, K_{T1}, K_{2T1}, K_{T2}, K_{2T2}, K_{T3} and K_{NiNa}. The remaining parameters are introduced as constants using the values from Table 1 and Table S1 (see the

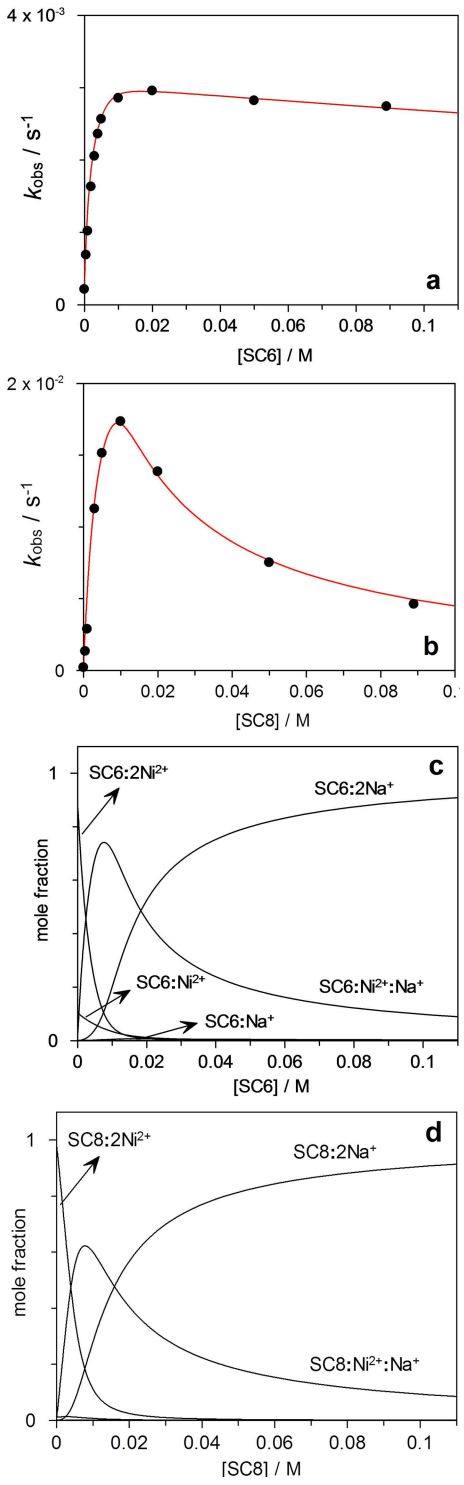
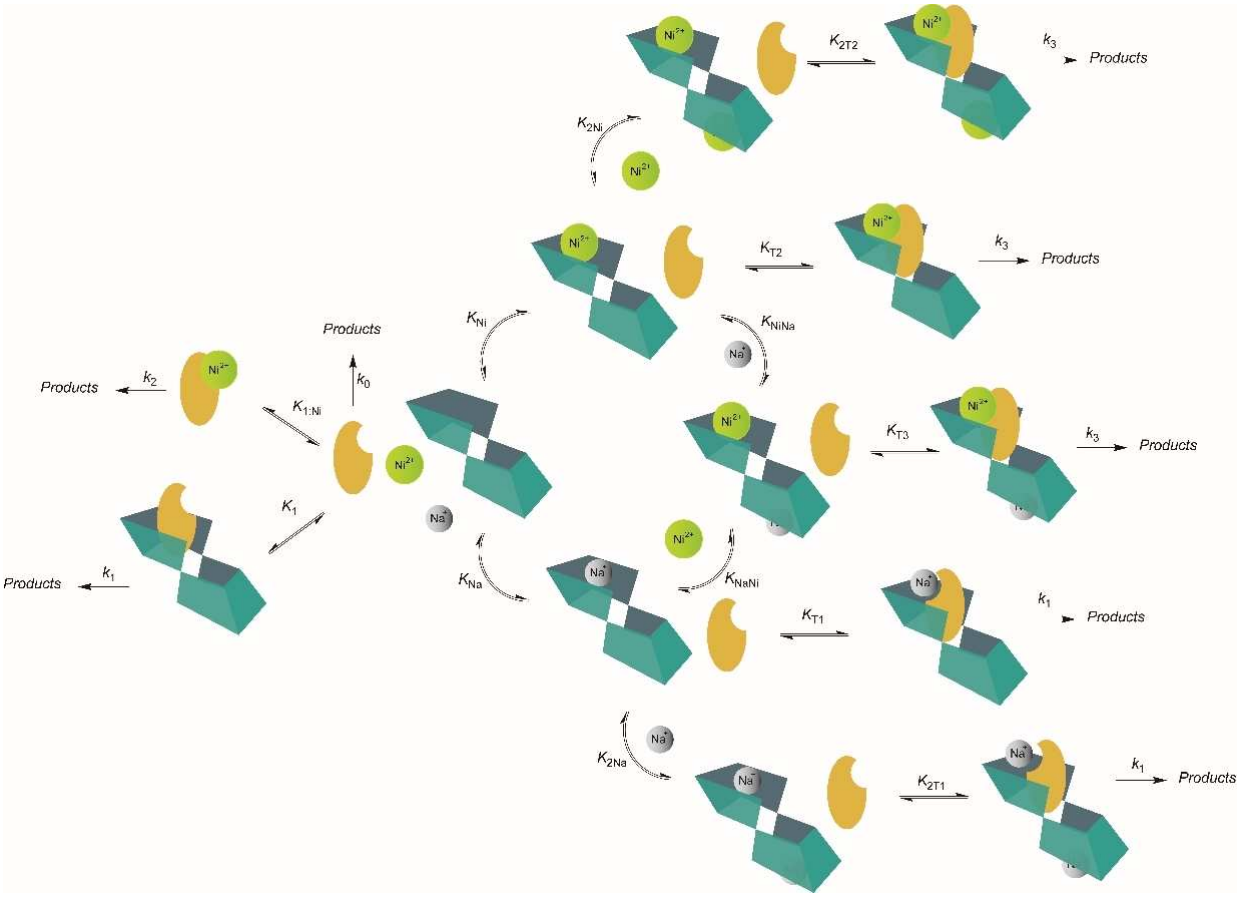


Figure 3. Observed rate constants (k_{obs}) for the hydrolysis of **1** in the presence [Ni^{2+}] = 0.01 M and increasing concentrations of (**a**) SC6 and (**b**) SC8. Mole fraction of SC6 (**c**) and SC8 (**d**) species as a function of the calixarene concentration in the presence of [Ni^{2+}] = 0.01 M. All experiments were carried out at 25 °C and at neutral pH conditions in the absence of buffers.



Scheme 4. Proposed mechanism for the complexation and hydrolysis of 1 with SC6 (or SC8) in the presence of Na^+ an Ni^{2+}.

Supporting Information). The observed rate constant is given by Equation (5) which is analogous to Equation (4) for SC4 where the equilibrium constants are related to the equilibria of Scheme 4. This Equation is then coupled the respective mass balance expressions and the systems can be numerically solver using the Newton-Raphson algorithm and the constants optimized. As can be observed from Figure 3 the theoretical model describes very well the experimental data. K_1 can be neglected as it does not contribute significantly to k_{obs} because the concentration of free SC6 or SC8 is very small under the experimental conditions, i.e., their complexes with metal cations predominate.[38] However, due to the large number of correlated parameters the binding and kinetics constants cannot be all accurately determined from the fitting. Nevertheless, some parameters can be estimated and the ones that included errors can be determined assuming the described approximations. As can be observed from speciation plots shown in figures 3c and 3d, the most abundant species are those for which the calixarene is occupied with 2 Na^+, 2 Ni^{2+} or 1 Na^+ and 1 Ni^{2+} and thus the binding constants for the association of **1** with these species can be determined and for the remaining ones only the upper limits can be estimated (Table 2). Owing to the more efficient charge neutralization of Ni^{2+}, K_{NiNa}, i.e., the binding constant for the formation of heteroternary complex $SCn:Ni^{2+}:Na^+$ was assumed to be equal to $K_{2Na}/2$. The constant is correlated with k_3 and therefore an underestimation of the first will lead to an overestimation of the last and *vice versa*. Based on these assumptions, the kinetic data of Figure 3 was successfully fitted using the combination of parameters shown in Table 2.

$$k_{obs} = k_0 + k_2 K_{1:Ni}[Ni^{2+}] + \frac{\left(K_1 + K_{T1}K_{Na}[Na^+] + K_{2T1}K_{Na}K_{2Na}[Na^+]^2\right)k_1[SCn]}{D} + \frac{\left(\begin{array}{l} K_{T2}K_{Ni}[Ni^{2+}] + K_{2T2}K_{Ni}K_{2Ni}[Ni^{2+}]^2 + \\ K_{T3}K_{Ni}K_{NiNa}[Ni^{2+}][Na^+] \end{array}\right)k_3[SCn]}{D} \quad (5)$$

With

$$D = 1 + K_1[SCn] + K_{T1}K_{Na}[Na^+][SCn] + K_{2T1}K_{Na}K_{2Na}[Na^+]^2[SCn] + K_{T2}K_{Ni}[Ni^{2+}][SCn] + K_{2T2}K_{Ni}K_{2Ni}[Ni^{2+}]^2[SCn] + K_{T3}K_{Ni}K_{NiNa}[Ni^{2+}][Na^+][SCn] \quad (6)$$

In the cases of SC6 and SC8 the rate acceleration is mainly due to the binding of **1** to $SCn:2Ni^{2+}$ and $SCn:Ni^{2+}:Na^{+}$ species which leads to an increase in the mole fraction of more reactive **1**: Ni^{2+}. Then, as for SC4, at concentrations above ca. 0.01 M of SC6 or SC8 the rate starts to decrease due to competitive binding of Na^{+} cations to the calixarene species. This is especially relevant in the cases of SC8 (and SC4) but for SC6 the decrease in k_{obs} is smoother due to inefficient binding of **1** to the SC6: $SCn:2Na^{+}$ species ($K_{2T1} < 10\ M^{-1}$). As for the hydrolysis of **1** in the absence of Ni^{2+}, the rate constant for the hydrolysis of **1** associated with Ni^{2+} and SCn (k_3) the values increase with more basic character of the ionizable phenol groups suggesting the participation of the phenolate in promoting the hydrolysis.

3. Conclusions

SCn were demonstrated to promote the Ni^{2+} catalyzed hydrolysis of **1** through higher-order complexes that promote the formation of reactive **1**- Ni^{2+} metal-ligands complexes in the confined environment provided by the macrocyclic receptor. The rate enhancement is mainly attributed to a thermodynamic effect, i.e. increase in the effective metal-ligand association constant for smaller hosts SC4 and SC6 while SC8 acts a multifunctional enzyme-mimetic catalyst that by one hand provide a microenvironment that brings together the substrate and the metal cation and on the other hand further promotes the reactions through participation of the weakly basic phenolate groups that assist the hydrolysis through base or nucleophilic catalysis. This reaction also served to test and demonstrate the SCn counterion exchange model and its application in the mechanistic interpretation of binding and catalysis involving multicomponent host-guest systems.

Experimental Section

Commercially available reagents were used as received. *p*-sulfonatocalixarenes and 2,4-dinitrophenyl picolinate were available from previous studies undertaken in our laboratory.[28,38,43] The kinetic experiments were triggered by injection of 30 μL of 5 mM stock solution of **1** in acetonitrile into a quartz cuvette containing 3 mL of an aqueous solution with all the remaining reactants. Hydrolysis reactions were followed by monitoring the UV/Vis absorbance of **1** at 405 nm at 25 °C. The absorbance-time data always fitted the first-order integrated rate equation.

Lucigenin fluorescence measurements were performed on a Varian-Cary Eclipse spectrofluorimeter at atmospheric pressure and ambient temperature (25 °C) using quartz cells of 1 cm path length. High purity Milli-Q water was used throughout the work. The excitation wavelength was selected at 368 nm, and in all cases changes in emission intensity were observed at 503 nm.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Binding Models · Calixarenes · Host-Guest Systems · Kinetics and Supramolecular Catalysis

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