Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 6 Issue 01, January-2017

Extraction and Complexation of Metal Cations with Methoxy Derivative of Octahomotetraoxacalix[4]arene

B. Mellah
Laboratory of Composite
Materials and Clay Minerals,
National Center of Researches in
Material Sciences,
Technopole Borj Cédria, Tunisia

N. Komatsu
Department of Chemistry,
Graduate School of Science,
Kyoto University, Sakyo-Ku, Japan

F. Arnaud-Neu
ECPM, University of Louis Pasteur,
Strasbourg, France

R. Abidi
Faculty of Sciences of Bizerte,
Bizerte, Tunisia

Abstract: **The ionophoric properties of a methoxy derivative of *p*-methyl octahomotetraoxacalix[4]arene have been investigated and evaluated by UV/vis spectrophotometer and ESI-MS. The studies have been followed towards metal cations in acetonitrile and have given the formation of mononuclear complexes. Some considerable selectivity has been detected mainly towards Cs^+, Ba^{2+}, Cu^{2+} and Hg^{2+}.**

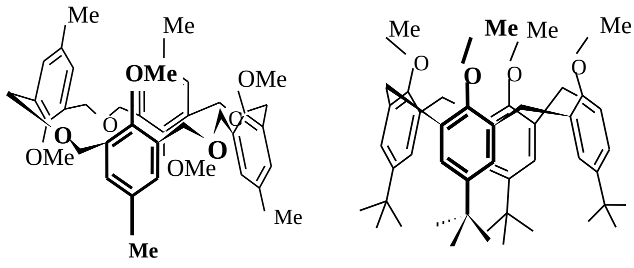
Keywords: ***Octahomotetraoxacalixarene, 1,2-alternate, selectivity, metal cations, extraction, complexation.***

I. INTRODUCTION

Calixarenes are macrocyclic receptors known by their molecular recognition properties [1-4]. They have been widely used in many fields, including selective extraction of metal ions [4-12].

The oxacalixarenes, a new family among calixarenes, are distinguished by the presence of one or more $-CH_2OCH_2-$ units in the ring instead of the methylene bridge. Therefore, the molecular size and flexibility are increased in comparison with their calixarenes homologous [13-15]. Although, few studies have been reported, possibly due to the low yield in their synthesis, our interests on oxacaliarenes have been focused on the preparation and the study of their binding properties towards metal cations [16-22]. In the present work, the complexation and extraction of metal cations by tetramethoxy *p*-methyl octahomotetraoxacalix[4]arene **1** have been studied. This ligand has been prepared by Komatsu and al. [23] The behavior of **1** towards metal cations have been discussed and compared to its homologous tetramethoxy *p*-*tert*-butylcalix[4]arene **2** (figure 1).

Each aromatic units in the oxacalix[4]arene derivative **1** is carrying a methoxy function in the norrow rim and methyl substituent in the widder rim [23]. Its conformation is 1,2-alternate in its solid state while in solution the conformation is varying due to the small size and weak hydrogen interactions between methyl substituent.



1

2

Figure 1: Structures of methoxy derivative of oxacalix[4]arene (**1**) and its homologous calix[4]arene (**2**).

This mobility has been shown by a conformational study followed by ^1H-NMR demonstrating a coalescence of signals [23]. However, in the case of the calixarene homologous **2**, its cone conformation is maintained. In the presence of Li^+ and Na^+, the cone conformation is kept and has been demonstrated by an NMR study in $CDCl_3/CD_3OD$ (4:1) [24]. While the addition of $KClO_4$ and $AgClO_4$ vary the cone conformation to partial and 1,3-alternat conformations, respectively. Both cations Ag^+ and K^+ were encapsulated within the cavity due to the interactions with one/two oxygen atoms and two aromatics rings units in front [24-25].

In the present work, two approaches have been used in order to quantify the interactions between different metal cations: the liquid-liquid extraction of picrates salts from water into dichloromethane at 20˚C, and the determination of the stœchiomety and stability constants of complexes. Both studies were spectrophotometrically followed. The complexation study was performed in acetonitrile and the spectra were recorded in the range of wavelength 250-300 nm. The acetonitrile was chosen for the solubility of **1** in it. For the extraction study, the molar absorptivities used as reported by Pedersen (λ_{max}=354 nm; ε=1.5 x 10^{-4} in water; and λ_{max} =378 nm; ε=1.8 x 10^{-4} in dichloromethane).

II. RESULTS AND DISCUSSION

A. *Extraction study*

The extraction of picrate salts by **1** was established according to the standard method of extraction described in literature [26]. The use of picrate salt is due to its high solubility in aqueous phase and insolubility in organic solvent, for that the transfer of picrate anions (A^-) ions from aqueous to organic phase is associated to the cation (M^+) coordination with the neutral extractant (L), initially dissolved in dichloromethane. The equilibrium of extraction processes of metal salts by extractant at the liquid/liquid interfaces has been clarified by Kudo [27] and Agnihotri [28]. The extraction equilibrium constant defines quantitatively the extraction efficiency of metal from aqueous to organic phase. It describes also the strength of the complex formed and the ability of making ion pair between complex-cation and picrate anion.

The two-phase equilibrium containing metal ion (M^+), picrate anion (A^-), and ligand (L) can be defined as:

$$M_{aq}^{+} + A_{aq}^{-} + L_{org} \overset{K_e}{\leftrightarrows} MLA_{org}$$

MLA_{org} defines complex. To calculate K_e, the distribution of all species present in both phases has to be considered and determined from the following equilibriums:

$$\begin{array}{ccc} MLA_{org} & \overset{K_d}{\leftrightarrows} & ML^{+}_{org} + A^{-}_{org} \\ L_{org} & \overset{P_e}{\leftrightarrows} & L_{aq} \\ M_{aq}^{+} + L_{aq} & \overset{K_s}{\leftrightarrows} & ML^{+}_{aq} \end{array}$$

From these equations, the final equation of K_e is defined as:

$$K_e = \frac{[1 + P_e + P_e K_s f(M_0 - A)][2A + K_d - (K_d^2 - 4K_d A)^{1/2}]}{2f[M_0 - A][A_0 - A][L_0 - A]}$$

Where P_e: partition coefficient of the ligand in water-dichloromethane
K_d: dissociation constant of MLA in the organic phase
K_s: stability constant of ML^+ in aqueous phase
f: single ion activity coefficient of the aqueous phase
A: concentration of picrate anion in organic phase
M_0, A_0 and L_0: initial concentrations of the metal ion, picrate and ligand, respectively.

The results are expressed as percent extraction (%E) of cations from water into dichloromethane. The percent extractions of cations are the average of at least three experiments and reported on table 1. As shown on table 1, the percentage of extraction range between 0 and 20.5% for alkali and alkaline-earth cations and from 0 to 14.1 for transition and heavy metal cations. These results are slightly higher for hard acids (alkali and alkaline-earth cations), according to the Pearson acid base concept [29]. Moreover, the highest values of (%E) are in favor of largest cations such as rubidium and cesium and it is owing to the large size of the aromatic ring of **1** (the distances between faced aromatic rings are 8.36 and 8.14 Å [23]). Furthermore, the flexibility of **1** is a considerable factor in the selectivity and efficiency in extraction as established by Talanova et al. [30]. They also reported that the picrate anions participate also in the extraction process due to both strong interactions between π-π stacking with aromatic ring and O…H interaction between picrate and oxacalixarene **1** [30].

Table 1: Percent extraction (%E) of metal cations from water into dichloromethane, at 20°C.

Cations	**Li^+**	**Na^+**	**K^+**	**Rb^+**	**Cs^+**	**Mg^{2+}**	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**
Ionic radius (Å)	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
%E [a] (1)	14.6	15.4	15.6	20.3	20.5	≤1	1.2	3.2	4.3
%E (2)[31]	<1	6.2	3.8	<1	<1	-	<1	-	<1
Cations	**Mn^{2+}**	**Co^{2+}**	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Hg^{2+}**	**Pb^{2+}**	**Ag^+**
Ionic radius (Å)	0.83	0.75	0.69	0.73	0.75	0.95	1.02	1.18	1.15
%E [a]	≤1	≤1	≤1	≤1	≤1	13.5	-	14.1	8.9

[a] Metal picrates values with uncertainties less than 1%.

The profiles of extraction of **1** and **2** are different. In fact, the extraction efficiency of **1** is proportional to the size of alkali metals. However, with ligand **2**, the extraction affinity is less important and insignificant for Li^+, Rb^+ and Cs^+ (%E≤1). The maximum value of (%E) found for ligand **2** is towards Na^+ (%E= 6.2). Thus, the presence of four bridges CH_2OCH_2 in ligand **1** confers it a larger hole able to encapsulate largest cations, unlike **2**. Similar behavior for **1** was found with alkaline-earth cations where the percentages of extraction increase with the size of cations. In the case of soft acids, the extraction affinity of transition metal cations is generally weak (%E ≤ 1) while in the case of heavy metal cations, cadmium and lead are more extracted by **1** (%E = 13.5 and 14.1 respectively). The soft base character of benzene units could explain the slightly increase of affinity towards cadmium, lead and silver.

B. *Complexation study*

The complexation of metal cations has been followed by spectrophotometry absorption UV in acetonitrile in the range of 250-300 nm, and has shown different spectral changes. The spectrum of free ligand exhibits a maximum of absorbance in 282 nm and a shoulder in 275 nm. Generally, the addition of metal cations leads to a decrease in absorbance. In some cases, an isobestic point appears (around 253 nm for Mn^{2+} and 260 for Hg^{2+}). Figure 2 illustrates the spectral changes corresponding to the complexation of lithium by **1**.

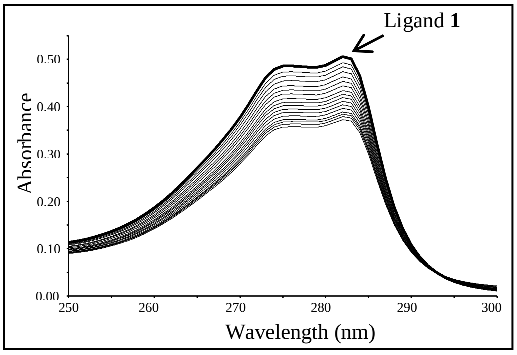


Figure 2: Spectrum UV of complexation of Li^+ by 1 in acetonitrile, θ = 25°C, I = 10^{-2} mol.L^{-1} (Et_4NClO_4), ($C_L = 1.07 \times 10^{-4}$ mol.L^{-1}, $0 \leq R \leq 16$).

The treatment of UV spectra by the digital program Letagrop-Spefo [32] has allowed the detection of stoichiometies M:L=1:1 of complexes formed with all cations. Their stability constants have been calculated and collected on table 2.

Table 2: Stability constants of complexes ML (log β_{11}) of metal complexes in acetonitrile, I=10^{-2} mol.L^{-1} (Et_4NClO_4 or Et_4NNO_3), at 25°C.

Cations	**Li^+**	**Na^+**	**K^+**	**Rb^+**	**Cs^+**	**Mg^{2+}**	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**
log $\beta_{11}{}^a$	3.8	3.9	3.5	2.9	4.1	3.3	3.9	2.7	4.4
Cations	**Mn^{2+}**	**Co^{2+}**	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Hg^{2+}**	**Pb^{2+}**	**Ag^+**
log $\beta_{11}{}^a$	3.6	4.0	4.1	5.5	2.5	3.5	5.7	4.4	3.43

^{a} Standard deviation σ_{n-1}on the mean of several experiments < 0.05.

The stability constants of mononuclear complexes formed with hard cations (alkali and alkaline-earth cations) shift between 2.7 and 4.4 logarithmic units. They are almost similar with cations having close sizes. In fact, the stability constants of small sized cations Na^+ and Ca^{2+} are around 3.9 logarithmic units while those with large size Cs^+ and Ba^{2+} are around 4.2 logarithmic units. Moreover, the stability constants increase twice, firstly for Na^+ and secondly for Cs^+. Same behavior was observed for alkaline-earth cations where the affinity increases for Ca^{2+} and Ba^{2+}. As comparison with its homologous **2**, only titrations of lithium and sodium cations were followed in acetonitrile and the complexes formed were also mononuclears. Unlike ligand **1**, the affinity of **2** decreases from Li^+ (log β_{11}= 5.0) to Na^+ (log β_{11}=3.9) [31].

As regards to stability, the complex $[Li.\mathbf{2}]^+$ is 17 times more stable than $[Li.\mathbf{1}]^+$, while complexes $[Na.\mathbf{2}]^+$ and $[Na.\mathbf{1}]^+$ are similar. Therefore, the affinity of **1** could be explained by both size and conformation effects. This ligand is larger in cavity, than ligand **2**, due to the presence of four CH_2-O-CH_2 oxa bridges. Its large size allows the easy inclusion of and encapsulation of larger cations. Moreover, its 1,2 alternate conformation increases the stability of the complex by O-donor interaction of a couple of methoxy substituents in both side: upper and lower rim.

Furthermore, this ligand **1** has shown considerable selectivities: towards Ba^{2+} ($S_{Ba^{2+}/Sr^{2+}}$ = 50) and towards Cs^+ (S_{Cs^+/Rb^+} = 16). In the case of ligand **2**, complexes ML were formed with alkaline-earth cations and no significant selectivity was detected due to the similarity in their stability constants (log β_{11}=3.1) [31].

The complexation of transition (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and heavy (Cd^{2+}, Hg^{2+}, Pb^{2+} and Ag^+) metal cations has shown the formation of ML species. Their stability constants shift between 2.5 and 5.5 logarithmic units for transition metals and from 3.4 and 5.7 logarithmic units for heavy metals. The stability sequence in the transition metal series follows the Irving-Williams rule[33], increasing from Mn^{2+} to Cu^{2+} and then decreasing for Zn^{2+}. This sequence highlights the selectivity of **1** towards Cu^{2+} ($S_{Cu^{2+}/Zn^{2+}}$= 9.1 × 10^2) (figure 3).

The complex $[Hg.\mathbf{1}]^{2+}$ is 200 times more stable than $[Ag.\mathbf{1}]^+$. While, complexes ML of Ag^+ and of Cd^{2+} have similar stabilities.

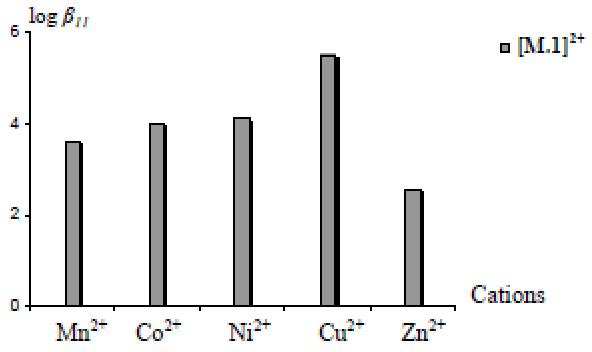


Figure 3: Profile of stability of complexes ML of transition metal cations with ligand **1**.

A further study of complexation has been followed by mass spectrometry ESI-MS in acetonitrile. The titration of **1** by Rb^+ within different ratio R=C_M/C_L equal to 1, 2,..,10 has confirmed the stoichiometry ML of complex. In addition, some signals appearing on the free ligand spectrum were assigned to complexes $[NH_4.\mathbf{1}]^+$, $[Na.\mathbf{1}]^+$ and $[K.\mathbf{1}]^+$, already present as impurities. The first addition of Rb^+ make out the appearance of a signal corresponding to the complex $[Rb.\mathbf{1}]^+$ at 741 m/z. This signal becomes major at the end of titration. A second signal, very weak, has appeared corresponding to the complex $[Rb_2.\mathbf{1}.(ClO_4)]^+$ with a proportion less than 2% compared to ML (figure 4).

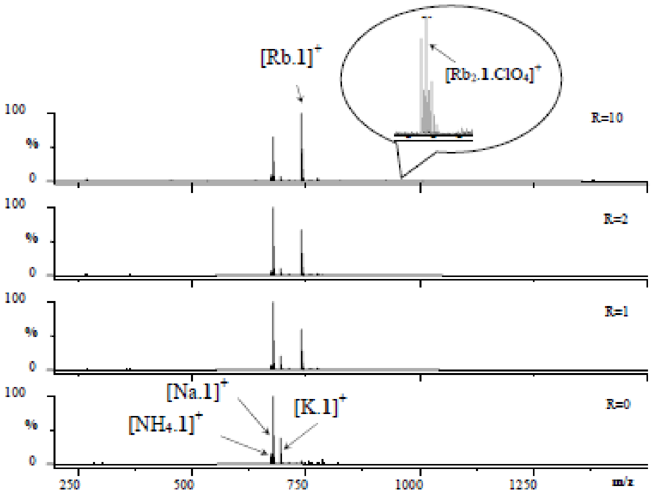


Figure 4: Spectrum ESI-MS relative to the complexation of Rb^+ by **1**, in acetonitrile, R =0, 1, 2, 10.

III. EXPERIMENTAL

A. *Synthesis of tetramethoxy octahomotetraoxacalix[4]arene 1 [23]*

The reductive homocoupling reaction of the arenedialdehyde (1 mmol) was carried out in the presence of Et_3SiH (2.2 equiv), CH_2Cl_2 (30 ml) and a catalytic amount of a Lewis acid Me_3SiOTf (5 mol%). The crude residue was separated by stepwise isolation by column chromatography on silica gel (1:3 or 1:2 ethyl acetate-hexane) followed by GPC. The mass of the macrocycle was determined by MALDI-TOF-MS spectra. The octahomotetraoxa-calix[4]arene **1** was obtained with a yield of 16%. The X-ray crystallographic analysis has revealed the 1,2-alternate conformations of the compound. The dihedral angles between each aromatic ring are of 23.3º and 83.2º, respectively, and the distances between faced aromatic rings are 8.36 and 8.14 Å [23].

B. *Extraction biphasic*

The determination of the percentages of extraction (%E) of picrate salts from water into dichloromethane has been followed as Pedersen method [26]. Two solutions were prepared: one aqueous (C= 2.5×10^{-4} mol.L^{-1}) of picrate salts and one of ligand (C= 2.5×10^{-4} mol.L^{-1}) in CH_2Cl_2. 5 ml of each solution are mixed and stirred during 30 min at 20.0°C (± 0.1). The mixture was then centrifuged to complete the phase separation before measurement. The percentage extraction (%E) was calculated from the following expression in which A_0 is the absorbance of the aqueous solution of a blank experiment without ligand **1** and A is the absorbance of the aqueous solution after separation: $\%E = (A_0 - A)\times100/A_0$.

C. *Stability constants*

The stability constant β_{xy} are the concentration ratio: $[M_xL_y^{xn+}]/([M^{n+}]^x[L]^y)$ (where M^{n+} = metal and L = ligand). They were calculated in acetonitrile (Riedel-deHaën, analytical reagent) by spectrophotometry of absorption UV at 25 °C. The ionic strength was maintained by 0.01 mol.L^{-1} of Et_4NClO_4 (Fluka, purum) or of Et_4NNO_3 (Acros) according to the literature. [21] The spectra have been recorded from 250 and 300 nm by a spectrophotometer Perkin Elmer Lambda 11. The results were treated by a digital program Letagrop-Spefo.[31] The metal salts were either perchlorates or nitrate: $LiClO_4$, $Ca(ClO_4)_2{\cdot}4H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$ and $Hg(NO_3)_2$ (Fluka, purum), $KClO_4$ and $Ba(ClO_4)_2$ (Prolabo), $NaClO_4$ and $RbClO_4$ (Sigma), $CsClO_4$ and $Sr(ClO_4)_2{\cdot}6H_2O$ (Alfa Aesar), $Zn(ClO_4)_2{\cdot}6H_2O$ and $Pb(ClO_4)_2$ (Johnson Matthey Alfa Products), $AgNO_3$ (Strem Chemicals), $Mg(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ (Merck). All these salts were dried under vacuum during at least 24 h before use. The concentrations of each metal solution (in the exception of alkali cations and Ag^+) have been found by complexometry in the presence of color indicator [34].

D. *ESI-MS*

Solutions of ligand and cations have been prepared in acetonitrile ($C_L\approx10^{-4}$ mol.L^{-1} and $C_M\approx10^{-3}$ mol.L^{-1}, respectively). They were then mixed according to different ration $R=C_M/C_L$ (0; 1; 2 and 10) and analyzed immediately by ESI-MS. The instrument was firstly calibrated by multi-protonated ions as myoglobin ion and the spectrum resolution was in the positive mode. The source was heated until 200 °C and the voltage of the outlet capillary (Taylor Cone) ranges between 60 and 160 V.

Samples were introduced into the spectrometer by a syringe, with a flow rate of 5 µl / min. The spectrogram was recorded between 100 and 3000 m/z. In our study, we systematically determined the charge state of each peak appearing on the spectrogram. To do this, the isotopic profile of these peaks has been established. Each molecule does not lead to a single species, but a set of species of different mass due to the statistical distribution of isotopes. Except in some cases, the distance between successive peaks isotope was a unit m/z. If this species is multi-charged, the charge will be given by the ratio r=1/d, where d is the distance between two peaks.

IV. CONCLUSION

The study of the ionophoric properties of a novel methoxy derivative of octahomotetraoxacalix[4]arene **1** towards metal cations has been followed via two approaches: complexation in homogenous solvent and biphasic extraction from water into dichloromethane. Both techniques have shown the high affinity of **1** towards large sized cations as Cs^+ and Ba^{2+}. This predisposition has been explained by both flexibility and large size of **1** owing to the presence of four CH_2-O-CH_2 oxa bridges. Moreover, the complexation study has shown the formation of ML species. All the complexes formed by **1** are generally more stables than those formed by its homologous calixarènes **2**. Some interesting selectivities have been found out mainly towards Cs^+, Ba^{2+}, Cu^{2+} and Hg^{2+}.

The study of the biphasic transfer of metal cations picrates shows that **1** exhibits weak extraction efficiency mainly towards transition metal cations. However, it is more effective with alkali and heavy metals.

REFERENCES

[1] C. D. Gutsche (1983), Acc. Chem. Res., 16, 161.

[2] C. D. Gutsche (1989), in «Calixarenes», J. F. Stoddart (Eds.), "Monographs in Supramolecular Chemistry", No.1, The Royal Society of Chemistry, Cambridge.

[3] J. Vicens, V. Böhmer (Eds.) (1991), in «Calixarenes: A Versatile Class of Macrocyclic Compounds», J. E. D. Davies Ed., Topics in Inclusion Science, vol. 3, Kluwer Academic Publishers, Dordrecht.

[4] Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens (Eds.) (2001), Kluwer Academic Publishers, Dordrecht.

[5] C. D. Gutsche (1989), Calixarenes, Royal Society of Chemistry, Cambridge, a) Pgs. 61-62. b) Pgs. 99-101.

[6] J. Vicens, Z. Asfari, J. Harrowfield (Eds.) (1995), Calixarenes 50th anniversary: Commemorative Issue, Kluwer Academic Publishers, Dordrecht.

[7] M. J. Schwing-Weill, F. Arnaud-Neu, M. A. McKervey (1992), J. Phys. Org. Chem., 5, 496.

[8] F. Arnaud-Neu, E. M. Collins, M. Deasy, G. Ferguson, S. J. Harris, B. Kaitner, A. J. Lough, M. A. McKervey, E. Marques, B. L. Ruhl, M. Schwing-Weill, E. M. Seward (1989), J. Am. Chem. Soc., 111, 8681.

[9] S. K. Chang, I. Cho (1986), J. Chem. Soc., Perkin Trans. I, 211.

[10] K. Ohto, E. Murakami, T. Shinihara, K. Shiratsuchi, K. Inoue, M. Iwasaki (1997), Anal. Chim. Acta., 341, 275.

[11] G. Ferguson, B. Kaitner, M. A. McKervey, E. M. Seward (1987), J. Chem. Soc., Chem. Commun., 584.

[12] F. Arnaud-Neu, D. Cremin, D. Cunningham, S. J. Harris, P. McArdle, M. A. McKervey, M. McManus, M. J. Schwing-Weill, K. Ziat (1991), J. Inc. Phenom. Molec. Recogn. Chem., 10, 329.

[13] C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan (1981), J. Am. Chem. Soc., 103, 3782.

[14] C. Bavoux, F. Vocanson, M. Perrin, R. Lamartine (1995), J. Incl. Phenom. Mol. Recogn. Chem., 22, 119.

[15] B. Dhawan, C. D. Gutsche (1983), J. Org. Chem., 48, 1536.

[16] P. M. Marcos, S. Félix, J. R. Ascenso, M. A. P. Segurado, P. Thuéry, B. Mellah, S. Michel, V. Hubscher-Bruder, F. Arnaud-Neu (2007), New Journal of Chemistry, 31, 2111.

[17] L. Baklouti, J. Vicens, B. Mellah, M. Mahouachi, A. Ben Othman, R. Abidi (2006), Organic Chemistry: An India Journal, 2, Issue 1-3.

[18] P. M. Marcos, B. Mellah, J. R. Ascenso, S. Michel, V. Hubscher-Bruder, F. Arnaud-Neu (2006), New Journal of Chemistry, 30, 1655.

[19] P. M. Marcos, S. Félix, J. R. Ascenso, M. A. P. Segurado, B. Mellah, R. Abidi, V. Hubscher-Bruder, F. Arnaud-Neu (2006), Supramol. Chem., 18 (2), 147-159.

[20] B. Mellah, R. Abidi, H. Herchbach, K. No, J. S. Kim, F. Arnaud, V. Hubscher (2010), Journal of Inclusion Phenomena and Macrocyclic Chemistry, 66, 153.

[21] B. Mellah, R. Abidi, K. No (2009), Journal of Inclusion Phenomena and Macrocyclic Chemistry, 22, 49.

[22] B. Mellah, L. Baklouti, R. Abidi, J. Vicens (2005), Letters in Org. Chem., 2, 590-594. 15.

[23] N. Komatsu, T. Chishiro (2001), J. Chem. Soc., Perkin Trans., 1, 1532.

[24] K. Iwamoto, A. Ikeda, K. Araki, T. Harada, S. Shinkai (1993), Tetrahedron, 49, 609.

[25] A. Ikeda, S. Shinkai (1997), Chem. Rev., 97, 1713.

[26] C. J. Pedersen (1967), J. Am. Chem. Soc., 89, 2495.

[27] Y. Kudo, T. Nakamori, C. Numako (2016), Hindawi Publishing Corporation Journal of Chemistry, in press.

[28] P. Agnihotri, B. Ganguly, E. Suresh, P. Parimal, P. K. Ghosh (2003), Ind. J. Chem., 42, 2439.

[29] R. G. Pearson (1963), J. Am. Chem. Soc., 85, 3533.

[30] G. G. Talanova, N. S. A. Elkarim, V. S. Hanes, R. E. Jr, H-S. Hwang, R. A. Bartsh, R. D. Rogers (1999), J. Am. Chem. Soc., 121, 11281.

[31] S. K. Chang, I. Cho (1986), J. Chem. Soc. Perkin Trans. I.

[32] G. Sillen, B. Warnqvist (1968), Ark. Kemi, 31, 377-390.

[33] H. Irving, R. J. P. Williams (1953), J. Chem. Soc., 3192.

[34] “Méthodes d’Analyse Complexométrique avec le Titriplex”, Merck, E., Ed. (1992); 3 Grafis: Darmstadt.