Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Calorimetric Investigation of the Complexation of Didodecylcalix[4]arene-crown-6 with Alkali Metal and Ammonium Cations in Acetonitrile

John D. Lamb; Erik G. Nelson[a]; Dusten M. Macdonald[a]; Tatiana G. Levitskaia[b]
[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT [b] Oak Ridge National Laboratory, Bethel Valley Rd., Oak Ridge, TN

To cite this Article Lamb, John D. , Nelson, Erik G. , Macdonald, Dusten M. and Levitskaia, Tatiana G.(2001) 'Calorimetric Investigation of the Complexation of Didodecylcalix[4]arene-crown-6 with Alkali Metal and Ammonium Cations in Acetonitrile', Supramolecular Chemistry, 13: 2, 349 — 355

To link to this Article: DOI: 10.1080/10610270108027489

URL: http://dx.doi.org/10.1080/10610270108027489

SUPRAMOLECULAR CHEMISTRY, Vol. 13, pp. 349-355
Reprints available directly from the publisher
Photocopying permitted by license only

Calorimetric Investigation of the Complexation of Didodecylcalix[4]arene-crown-6 with Alkali Metal and Ammonium Cations in Acetonitrile

JOHN D. LAMB[a,*], ERIK G. NELSON[a], DUSTEN M. MACDONALD[a]
and TATIANA G. LEVITSKAIA[b]

[a]*Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84601;* [b]*Oak Ridge National Laboratory, Bethel Valley Rd., P.O. Box 2008, Building 4500 South, Mail Stop 6119, Oak Ridge, TN 37831*

(Received 24 May 2000)

The Cs^+ selectivity of some calix-crown ligands makes them excellent candidates for use in separation systems such as liquid membranes. Separation performance can be understood and predicted from thermodynamic data for cation complexation. We have therefore determined the log K, ΔH and ΔS for the interaction of Na^+, K^+, Rb^+, Cs^+ and NH_4^+ with didodecyl-calix[4]arene-crown-6 in acetonitrile at 25°C by titration calorimetry. The ligand is strongly selective for Cs^+, and the selectivity trend results entirely from the enthalpy contribution, with entropy effects opposing the trend. These results are discussed in light of some corresponding data obtained by other researchers with similar ligands.

Keywords: Calorimetry; Calixarene; Crown; Metal ion complexation; Cesium separation

INTRODUCTION

Storage and disposal of liquid radioactive waste is a major concern in the United States and other industrialized countries. Involved is the accumulated waste from weapons manufacturing and power generation over the past sixty years. Much of this waste has simply been put into large storage tanks for lack of safe, economical, or politically viable methods of disposal. The DOE site at Hanford, Washington alone contains 204,000 cubic meters of liquid radioactive waste in 177 underground storage tanks [1]. This kind of storage is not a good permanent solution. Over the years many of these tanks have sprung leaks. Recent soil tests near one of the tanks found ^{137}Cs from leakage at the 130-foot level [2].

One way to dispose of radioactive waste that is most promising is to vitrify the waste into a glass mixture. However, this is an extremely costly process at about $1M per canister. Since radioactive species in the tanks account for about 0.01% by mass of the waste, removal and concentration of these species holds the promise of greatly simplifying and lowering the cost of waste disposal [3,4]. For these reasons, ^{137}Cs, a prevalent radionuclide in nuclear waste, is desirable for removal.

---

*Corresponding author. e-mail: john_lamb@byu.edu

One promising separation method for metal cations involves use of polymer inclusion membranes (PIM)s. In PIMs, a polymer matrix supports a hydrophobic liquid plasticizer in which a macrocyclic cation carrier may be dissolved. For separation purposes, the PIM is placed between the aqueous sample and an aqueous receiving solution, and the carrier in the membrane selectively transports target species to the receiving phase. We have recently shown that PIM selectivity and permeability can be accurately predicted using thermodynamic data for ligand-metal complexation (ΔH, ΔG, ΔS and K in homogeneous solution) [5].

The ligand studied in this work, didodecylcalix[4]arene-crown-6 (12C4C6), was chosen because ligands of this type have been shown to complex cesium with a high degree of selectivity [6]. The hydrophobicity lent to this ligand by the two dodecyl substituents makes it a good candidate for use as a PIM carrier.

RESULTS AND DISCUSSION

The results of the calorimetric determination of ΔH, ΔS, ΔG and log K for 12C4C6 complexation reactions in acetonitrile are presented in Table I, column 1. The selectivity sequence of this ligand under these conditions is $Na^+ < K^+ < Rb^+ \sim NH_4^+ < Cs^+$. This is assuming that the log K for Na^+ is very small, in keeping with the fact that so little heat was produced with this cation that log K could not be measured. It is instructive to examine this trend as a function of the ionic radius of the cation. Approximations of ionic radii for these cations include $Na^+ \sim 102$ pm, $K^+ \sim 138$ pm, $Rb^+ \sim 149$ pm, $NH_4^+ \sim 151$ pm and $Cs^+ \sim 170$ pm [7]. From the data in Table I, it can be seen that for all ligands studied, K increases with increasing ionic radius of the complexed cation, reaching a peak for Cs^+. In a simple view, this trend towards increasingly stable complexes in the order $Na^+ < K^+ < Rb^+ \sim NH_4^+ < Cs^+$ arises because the space available in the crown-ether loop of calix[4]arene-crown-6 derivatives is just about the right size to fit the Cs^+ ion [8]. Other ions which fit more loosely in the cavity do not associate as favorably with the oxygen atoms of the crown-ether chain, or with the calixarene aryl groups. This explanation is supported by the observation that $-\Delta H$ values describing complex formation for a given ligand increase in the order $Na^+ < K^+ < Rb^+ \sim NH_4^+ < Cs^+$. The high degree of similarity between results for NH_4^+ and Rb^+ implies that the NH_4^+ is bound by electrostatic forces, with little participation of hydrogen bonding.

$T\Delta S$ values for 12C4C6 complexation follow the opposite trend as $-\Delta H$ values, becoming less positive as the ionic radius of the cation increases. This trend is observed because the smaller cations are more strongly desolvated upon complex formation, and also because they allow the crown-ether loop more conformational flexibility [8]. Thus, the selectivity of 12C4C6 for Cs^+ over the other cations is enthalpically driven and entropically opposed.

The site of complexation of the Cs^+ ion inside the cavity of 12C4C6 can be directly related to the Cs^+ binding site determined by X-ray crystallography for a similar mono-calix-crown derivative. Casnati *et al.* have shown that in such ligands the cation is located in a position so that it interacts most strongly with the crown-ether oxygen atoms near the calix ring, and with the π-electron density of the neighboring aromatic rings [6]. Evidence for the participation of the calixarene's aromatic groups in complex formation has been derived from x-ray crystal data, and from confirmatory ^1H NMR studies in solution [9]. Some groups still dispute the role of cation-π interaction as an important factor in calix-crown Cs^+ selectivity [10,11], but the preponderance of evidence seems to favor the view that the aromatic groups which are situated near the crown-ether loop play an important role in complex formation and selectivity. In bis-calix-crown derivatives a similar binding site is expected [8].

TABLE I Thermodynamic data for calix-crown complexation

	12C4C6[a]	C4C6C6[b]	BC4C6C6[b]	NC4C6C6[b]	C4C6C6[c]
log K Na^+	[d]	1.97 ± 0.08	1.5 ± 0.2	1.4 ± 0.2	1.52 ± 0.07
log K K^+	4.77 ± 0.05	4.12 ± 0.08	4.32 ± 0.05	4.2 ± 0.3	4.1 ± 0.1
log K Rb^+	5.4 ± 0.2	4.41 ± 0.04	4.39 ± 0.04	4.4 ± 0.1	4.3 ± 0.1
log K Cs^+	6.19 ± 0.02	4. 9 ± 0.1	4.9 ± 0.2	4.9 ± 0.2	4.8 ± 0.3
log K NH_4^+	5.4 ± 0.1	–	–	–	–
$-\Delta H/kJ\ mol^{-1}$ Na^+	[d]	[d]	[d]	[d]	[d]
$-\Delta H/kJ\ mol^{-1}$ K^+	16.2 ± 0.2	17 ± 1	[d]	[d]	31.7 ± 0.8
$-\Delta H/kJ\ mol^{-1}$ Rb^+	27.2 ± 0.4	25.2 ± 0.1	12.6 ± 0.2	12.5 ± 0.8	52 ± 1
$-\Delta H/kJ\ mol^{-1}$ Cs^+	35.7 ± 0.3	29.7 ± 0.1	11.4 ± 0.7	11 ± 1	56.2 ± 2
$-\Delta H/kJ\ mol^{-1}$ NH_4^+	25.4 ± 0.2	–	–	–	–
$T\Delta S/kJ\ mol^{-1}$ Na^+	[d]	[d]	[d]	[d]	–
$T\Delta S/kJ\ mol^{-1}$ K^+	11.1 ± 0.5	6.8 ± 0.9	[d]	[d]	−8.3 ± 1.5
$T\Delta S/kJ\ mol^{-1}$ Rb^+	4 ± 1	0.0 ± 0.3	13 ± 0	13 ± 1	−27 ± 1
$T\Delta S/kJ\ mol^{-1}$ Cs^+	−0.3 ± 0.4	−2 ± 1	17 ± 2	17 ± 2	−29 ± 4
$T\Delta S/kJ\ mol^{-1}$ NH_4^+	5.7 ± 0.2	–	–	–	–

[a] Data obtained from this work. Average and σ for 3–5 runs.

[b] Data obtained from Ref. [6], solvent: acetonitrile, log K values obtained by UV absorption spectrophotometry, other values obtained from titration calorimetry.

[c] Same as [b], but solvent is methanol.

[d] Too little heat to measure.

It is interesting to compare the thermodynamic values for 12C4C6-cation complexation reactions to thermodynamic data from other related complexation systems. Arnaud-Neu *et al.* carried out calorimetric measurements for the related bis-calixcrowns C4C6C6, BC4C6C6 and NC4C6C6 (Fig. 1) [8]. These results are presented in Table I. Comparison of the thermodynamic data in Table I gathered by Arnaud-Neu *et al.* for C4C6C6, BC4C6C6, and NC4C6C6 can be carried out on two fronts. First, a comparison of the complexing properties of bis-crown derivatives in acetonitrile and methanol shows differences in solvent effects upon complex formation. Second, a comparison between the bis-crown derivatives and 12C4C6 illustrates differences in how these ligands form complexes with cations.

Table I illustrates the primary thermodynamic difference between bis-calix-crown complex formation in acetonitrile, as compared to complex formation in methanol. Comparison of data for C4C6C6 complexes in both solvents shows that complex formation in acetonitrile is more entropically favored and less enthalpically stabilized. Arnaud-Neu *et al.* proposed that this is because alkali metal cations K^+, Rb^+ and Cs^+ are slightly more solvated in acetonitrile than in methanol, and possibly the ligand is likewise more solvated in acetonitrile than in methanol [8]. Using X-ray crystallography, Vicens *et al.* demonstrated that one acetonitrile molecule is associated inside each crown ether loop of the uncomplexed bis-calix-crown [12, 13]. This result confirms that bis-calixcrowns are highly solvated in acetonitrile and supports Arnaud-Neu *et al.*'s second hypothesis that differences in entropic contributions to complex formation are due, in the case of acetonitrile and methanol, partly to ligand solvation differences.

When comparing complex formation data for C4C6C6, BC4C6C6 and NC4C6C6 in acetonitrile, one notices that selectivity of Cs^+/Rb^+ for BC4C6C6 and NC4C6C6 complexes is entropically driven. This can be explained simply by the increased conformational rigidity of the substituted crown-ether loops in these complexes, which leads to a less negative entropic effect upon forming complexes [8]. It should also be noted that of the bis-calix-crown derivatives

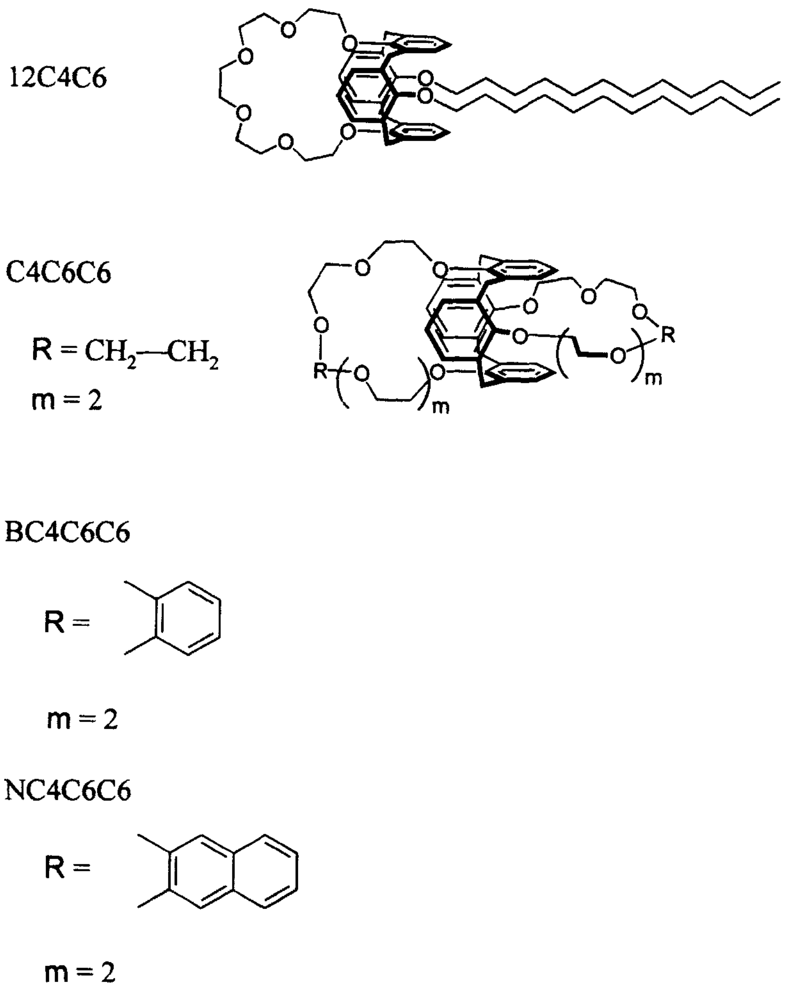

FIGURE 1 Structures of calixcrown ligands.

presented here, Cs^+/Na^+ selectivity ($\alpha = K(M_1^+)/K(M_2^+)$) is greatest for NC4C6C6.

The results for bis-calix-crown complex formation presented in Table I assume that only one of the two binding sites present in bis-calixcrowns is used at a time, *i.e.*, only 1:1 cation/ligand complexes are formed. Although Arnaud-Neu *et al.* [8], Asfari *et al.* [14] and Hill *et al.* [3] agreed that only 1 : 1 complexes are formed, a later paper authored by D'Aprano *et al.* shows conductivity measurement evidence that 2 : 1 cation/ligand complexes do form with K^+, Rb^+ and Cs^+ cations [15]. This conclusion is further supported by Shinkai *et al.*, who used ^1H NMR spectroscopy to show 2 : 1 complex formation with a bis-calixarene-crown-5 derivative [9].

The presence of 2 : 1 complex formation could possibly affect the results of Arnaud-Neu *et al.* [8] presented in Table I. However, D'Aprano *et al.* began noticing significant deviations in expected conductivity only when [ligand]/[cation] ≤ 0.5. [15]. In making calorimetric measurements of complexation reactions with relatively high ($> 10^4$) K values, the useful data were collected with [ligand]/[cation] < 0.5. Review of Arnaud-Neu *et al.*'s experimental conditions [8, 16] reveals that in all probability their data are not skewed by any significant 2 : 1

cation/calixarene complex formation occurring during their calorimetric determinations.

The comparison between thermodynamic values of complex formation for 12C4C6 and C4C6C6 presents some striking similarities and differences, as illustrated in Figure 2. The Cs^+/K^+ selectivity is about 25 for 12C4C6 and about 6 for C4C6C6. Cs^+/K^+ selectivity is also important in nuclear waste separation applications, though not as important as Cs^+/Na^+ selectivity, for which we do not have data to compare [17]. All complexation reactions investigated were clearly more enthalpically and entropically favorable with 12C4C6 than with C4C6C6. This is interesting, because the ligands are quite similar and the experimental conditions of our determinations and those of Arnaud-Neu *et al.* are almost identical. The only difference in our experimental conditions involves our use of alkali metal thiocyanate salts to make our solutions, where they used sodium perchlorate and potassium, rubidium, and cesium iodide [8,16]. Although molecular dynamics simulations of bis-calix-crown complexation with alkali metal cations predict that a picrate anion will interact with a cation/ligand complex to "pull" the cation further outward in the calix-crown cavity (particularly small cations) [11], the small difference in anion electronegativity between CNS^- and I^- seems unlikely to cause significant effects.

Anion aside, one particular difference between complexation by 12C4C6 and C4C6C6 with alkali metal cations lies in the fact that C4C6C6 possesses two possible binding cavities. Shinkai *et al.* have performed ^1H NMR spectroscopy experiments with alkali metal cation/calix[4]arene-bis-crown-5 complexes which demonstrate that a complexed cation can traverse the π-basic tube formed by the calix-crown's phenyl groups [9]. In fact, their measurements indicate that the activation energy for potassium and sodium cations' tunneling through the calix tube is significantly less than the activation energy required for those cations' entrance to, or exit from, the calix-crown cavity. This suggests that at a moderate temperature these cations probably traverses the calix tube much more frequently than it enters and exits the calix-crown. The time it spends in the elevated energy state as it passes through the tube thus causes the overall energy state of the complex to be higher than otherwise, making complex formation less energetically favorable. This effect does not necessarily clarify the results for cesium as cesium ions are large enough to make tunneling improbable.

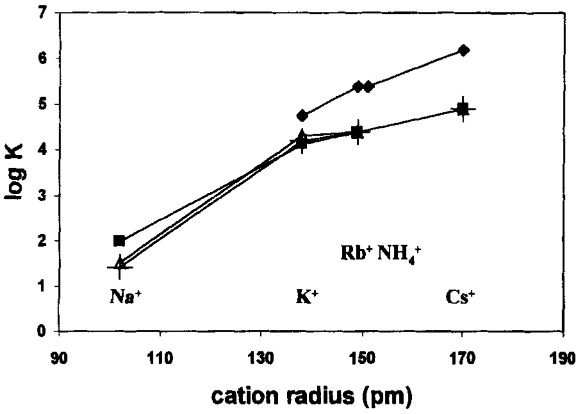

FIGURE 2 Log K *versus* cation radius for complexation with ◆ 12C4C6, △ BC4C6C6, □ C4C6C6, + NC4C6C6 in acetonitrile.

MATERIALS AND METHODS

Thermodynamic data for the complexation of 12C4C6 with the alkali metal cations were determined by titration calorimetry using a Tronac 450 isoperibol calorimeter, isoperibol meaning that the process takes place at nearly constant temperature and at ambient pressure. Metal thiocyanate in acetonitrile was titrated into ligand solution and the heat evolved was measured as a function of titrant volume added [18].

The reaction vessel was a 25-mL Dewar flask which was filled with 25-mL of 0.5 mM 12C4C6 in acetonitrile. The titrant was added by means of a precision buret driven by a synchronous motor. The titrant solutions were all prepared with concentrations between 20 and 25 mM of the metal thiocyanate salts. The reaction vessel was stirred constantly with a glass stirrer attached to another synchronous motor to make sure the reaction system was well mixed. The whole system was submerged in a water bath held at 25.0000 ± .002°C, and both reactant solutions were brought to the water bath temperature before beginning the titration. Specifically, the solution in the buret was allowed to equilibrate to the bath temperature on its own, while the solution in the dewar was heated *via* a heating wire in the reaction vessel.

To obtain data for a ligand-metal complexation, three types of runs must be performed: heat capacity runs, dilution runs and complexation runs.

In a heat capacity run, the reaction vessel was filled with 25 mL of acetonitrile. Then a known amount of heat (calculated by monitoring the voltage and current through the heater) was added through a resistance heating wire. The temperature change of the system with time, was monitored and the heat capacity of the reaction system was calculated. In a dilution run, only one reactant was used, the other solution being pure solvent. Thus, the heats of dilution of the reactants were measured and used to correct the reaction data. In our analysis we made correction for the titrant heat of dilution only because the heat of dilution for the titrate was found to be insignificant. In complexation runs, one reactant was titrated into the other and the heat of reaction measured at regular time intervals.

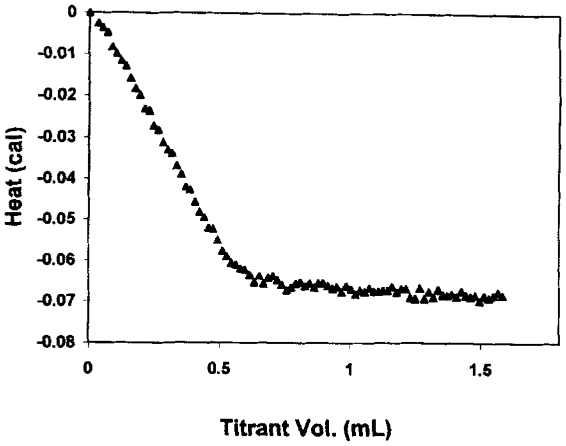

FIGURE 3 Example plot of heat *versus* volume added (Q–V) in the titration of ammonium thiocyanate into 12C4C6 in acetonitrile at 25°C.

The data collected for the runs was reduced to the desired thermodynamic values using the computer programs ENPLT, AVDIL, EQDH and REACTIONS. The ENPLT program was used to calculate the reaction system heat capacity and convert the raw temperature data to a matrix of heat and volumes of titrant added. A sample "QV" (heat/volume) plot for the titration of ammonium ion is shown in Figure 3. AVDIL was used to subtract the heat of dilution from the original QV data and the resultant corrected QV data were processed by a least squares method in the EQDH program to obtain K and ΔH values simultaneously. In cases where log K > 5.5, the endpoint of the titration is too sharp to allow calculation of log K in this way. Therefore, to determine the log K value for Cs^+ complexation, a competition titration was performed with equimolar 12C4C6/KSCN serving as titrate and CsSCN as titrant. Using the log K for K^+ determined earlier, the log K for Cs^+ complexation could then be calculated using the REACTIONS least square fit program.

The solvent used for the titrations was Fischer HPLC grade acetonitrile. Reagent grade thiocyanate salts of all five cations (Na^+, K^+, Rb^+, Cs^+, NH_4^+) were used. This anion was chosen mainly for its solubility in acetonitrile. Ligand 12C4C6 (1,3-alternate conformer) was synthesized and purified as published elsewhere [5].

Acknowledgements

Appreciation for support of this research is expressed to the US Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division (Grant No. DE-FGO3-95ER14506).

References

[1] U. S. Department of Energy. Hanford: Making Progress...Getting Results! Richland Operations Office Fiscal Year 1998 Report. http://www.hanford.gov/doe/98annualrp/98annualrp.pdf (accessed Apr., 2000).

[2] U. S. Department of Energy. New Data Confirms DOE Report on Cesium in Hanford Soils. http://www.hanford.gov/press/1996/96-116.htm (accessed Apr., 2000).

[3] Hill, C., Dozol, J.-F., Lamare, V., Rouquette, H., Eymard, S., Tournois, B., Vicens, J., Asfari, Z., Bressot, C., Ungaro, R. and Casnati, A. (1994). *J. Inclusion Phenom. Mol. Recognit. Chem.*, **195**, 399–408.

[4] Bunker, B., Virden, J., Kuhn, B. and Quinn, R. (1995). *Encyclopedia of Energy Technology and the Environment*, John Wiley: New York, pp. 2023–2032.

[5] Levitskaia, T., Macdonald, D., Lamb, J. and Moyer, B. (2000). *Physical Chemistry and Chemical Physics*, **007**, 1481–1491.

[6] Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M.-J., Egberink, R. J. M., de Jong, F. and Reinhoudt, D. N. (1995). *J. Am. Chem. Soc.*, **117**, 2767–2777.

[7] Shannon, R. D. and Prewitt, C. T. (1969). *Acta Cryst.*, **B25**, 925–946.

[8] Arnaud-Neu, F., Asfari, Z., Souley, B. and Vicens, J. (1996). *New J. Chem.*, **20**, 453–463.

[9] Koh, K. N., Araki, K., Shinkai, S., Asfari, Z. and Vicens, J. (1995). *Tetrahedron Lett.*, **36**, 6095–6098.

[10] Wipff, G. and Lauterbach, M. (1995). *Supramol. Chem.*, **6**, 187–207.

[11] Varnek, A. and Wipff, G. (1996). *J. Comput. Chem.*, **17**, 1520–1531.

[12] Thuéry, P., Nierlich, M., Asfari, Z. and Vicens, J. (1997). *J. Inclusion Phenom. Mol. Recognit. Chem.*, **27**, 169–178.

[13] Thuéry, P., Nierlich, M., Bryan, J. C., Lamare, V., Dozol, J.-F., Asfari, Z. and Vicens, J. (1997). *J. Chem. Soc. Dalton Trans.*, pp. 4191–4202.

[14] Asfari, Z., Bressot, C., Vicens, J., Hill, C., Dozol, J.-F., Rouquette, H., Eymard, S., Lamare, V. and Tournois, B. (1995). *Anal. Chem.*, **67**, 3133–3139.

[15] D'Aprano, A., Vicens, J., Asfari, Z., Salomon, M. and Iammarino, M. (1996). *J. Solution Chem.*, **25**, 955–970.

[16] Arnaud-Neu, F., Barrett, G., Fanni, S., Marrs, D., McGregor, W., McKervey, M. A., Schwing-Weill, M.-J., Vetrogon, V. and Wechsler, S. (1995). *J. Chem. Soc. Perkin Trans.*, **2**, 453–461.

[17] Haverlock, T. J., Bonnesen, P. V., Sachleben, R. A. and Moyer, B. A. (1997). *Radiochim. Acta*, **76**, 103–108.

[18] Ott, J. B. (1997). *Thermochim. Acta*, **300**, 255–281.