

On the Complexation of Alkaline Earth Metal Cations in Propylene Carbonate by Macrocyclic Crown Ethers Featuring from Four to Ten Coordinating Sites

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The complexation of the alkaline earth ions by four crown ethers in anhydrous propylene carbonate has been investigated by a competitive potentiometric method using lead(II) as an auxiliary ion. The ligand-12-crown-4 forms bis-adducts with all the alkaline earths, the maximum stability being exhibited by the calcium complex. A fifteen-membered macrocycle, 4-*tert*-butylbenzo-15-crown-5 also forms 1:2 complexes but only with Sr^{2+} and Ba^{2+} . The larger ligands 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 and dibenzo-30-crown-10 bind strongly the alkaline earths, especially Sr^{2+} and Ba^{2+} . Moreover, the stability of the 1:1 adducts with dibenzo-30-crown-10 decreases regularly from Ba^{2+} to Mg^{2+} . The complexation trends are interpreted by taking into account the known structures of macrocyclic complexes in the solid. Finally, the stability of the adducts with the alkali metals, the alkaline earths and the di- and trivalent lanthanides are compared.

Introduction

Since their first recognition as selective complexing agents, the macrocycles excited considerable interest [1]. Nevertheless, information relating to the complexation of alkaline earth cations by crown ethers remains sparse compared to the extensive data which have been compiled for the complexation of the alkali ions [1].

In a series of previous publications [2–4], we have discussed in detail the factors influencing the formation of complexes of the alkali ions with 12-crown-4 and of complexes of the di- and trivalent lanthanide ions with various crown ethers. These studies were carried out in anhydrous propylene carbonate, a solvent particularly well suited for electrochemical measurements. The present paper reports a parallel investigation of the complexation of the alkaline earths by a series of crown ethers. This work was undertaken on the view that it would be useful to compare the complexation of uni-, di- and trivalent metal ions

by macrocyclic ethers in the same anhydrous aprotic solvent. We selected for this study four crown ethers featuring from four to ten oxygen atoms, namely the small 12-crown-4, the medium size 4-*tert*-butylbenzo-15-crown-5 and 4,4'(5')-di-*tert*-butylbenzo-18-crown-6 and finally the very large dibenzo-30-crown-10. The structural formulae of these ligands are shown in Fig. 1, along with the abbreviations used in the present paper.

Experimental

Solutions and Reagents

As described earlier [2–4], all solutions and reagents were stored and handled in a glove box filled with an inert recirculating atmosphere, the water content of which was monitored by means of a dew point meter and which was always below 20 ppm. Preparation, purification and dehydration of propylene carbonate, crown ethers, trifluoromethanesulfonate salts and tetraethylammonium perchlorate (TEAP) were performed as reported previously [2–4].

Alkaline earth perchlorates were prepared by reaction between the corresponding carbonate salt

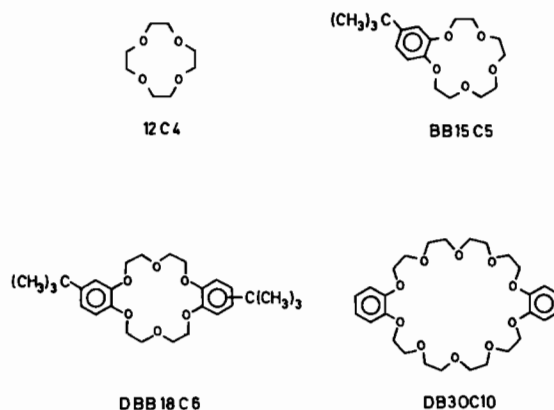


Fig. 1. Structural formulae of the macrocyclic crown ethers and abbreviated names used in the text.

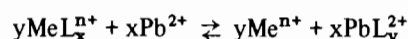
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(Merck) and the required amount of perchloric acid (Merck). They were dried overnight under vacuum at a temperature of 150 °C. Completeness of the dehydration was checked by Karl Fisher titration in anhydrous methanol and also by determining the metal content by potentiometric titration with EDTA, according to Reilley and Schmid [5].

All standard solutions were prepared by weighing the required amount of anhydrous salt and dissolving it in propylene carbonate. The water content of the solution (Karl Fisher titration) never exceeded 40 ppm at the end of each series of measurements.

Experimental Procedure and Calculations

The formation constants of the alkaline earth (Me) complexes with a macrocycle L were determined in anhydrous propylene carbonate at 25 °C (ionic strength adjusted to 0.1 with TEAP) by a competitive potentiometric method using Pb(II) as an auxiliary ion. The equilibrium position of the reaction



was shifted forward or backward by the addition of various aliquots of solutions of either an alkaline earth perchlorate or lead trifluoromethanesulfonate, or of a crown ether. Further details on the choice of the auxiliary ion, on the potentiometric technique or on the treatment of the experimental data by a non-linear best fit procedure may be found elsewhere [2–4]. The determination of the stoichiometries and stabilities of the lead crown adducts has also been discussed extensively in a previous publication [4].

Results and Discussion

The stability constants of the 1:1 and 1:2 complexes formed between the alkaline earth cations and four crown ethers are collected in Table I. Also included in this table, for comparison, are the stability constants of some complexes formed in anhydrous propylene carbonate by the alkali metal ions and by divalent samarium and ytterbium and trivalent lanthanum.

Alkaline Earth Complexes with 12-crown-4

The twelve-membered ligand 12-crown-4 (12C4) is a very small cycle which is unable to accommodate any of the alkaline earth ions in its internal cavity (radius: 0.57 Å [6]). Bis-complexes between this ligand and Na⁺, K⁺ or Rb⁺ have been prepared in the solid. The crystallographic structure of these complexes is a square antiprism, each squared face being occupied by a molecule of crown. The solid state structures of two alkaline earth–12C4 complexes which were synthesized in water have also been reported [7, 8]. In the 1:1 complex of magnesium, the cycle is not directly bonded to the metal ion which is surrounded by six molecules of water. Calcium also forms a 1:1 adduct with 12C4 but in this case the ligand is coordinated to the ion on one of the squared faces of a square antiprism while the other face consists of four water molecules.

Examining the results shown in Table I, it can be seen that all the alkaline earth cations form mono- and bis-complexes with 12C4. Our potentiometric measurements were carried out in anhydrous propyl-

TABLE I. Stability Constants ($\log \beta_n$) of the Alkaline Earth Cation Complexes with Macrocycles of Varying Size in Anhydrous Propylene Carbonate at 25 °C ($\mu = 0.1$). Comparison with the stability of macrocyclic complexes of alkali metal ions and of lanthanide ions.

	12C4		BB15C5		DBB18C6	DB30C10
	1:1	1:2	1:1	1:2	1:1	1:1
Mg ²⁺	2.61 ± 0.08	6.2 ± 0.1	6.72 ± 0.08	–	<1	2.89 ± 0.06
Ca ²⁺	5.53 ± 0.06	9.51 ± 0.05	6.05 ± 0.05	–	6.86 ± 0.02	5.23 ± 0.04
Sr ²⁺	5.29 ± 0.05	7.91 ± 0.07	5.55 ± 0.08	10.6 ± 0.1	7.82 ± 0.02	7.67 ± 0.03
Ba ²⁺	4.63 ± 0.04	7.9 ± 0.1	5.35 ± 0.04	10.4 ± 0.05	7.66 ± 0.01	9.33 ± 0.04
Li ⁺	2.93 ± 0.05 ^a	–	–	–	–	–
Na ⁺	3.5 ± 0.2 ^a	6.31 ± 0.04 ^a	–	–	5.20 ^d	–
K ⁺	2.15 ± 0.05 ^a	–	–	–	5.13 ^d	–
Rb ⁺	1.69 ± 0.04 ^a	–	–	–	3.91 ^d	–
Cs ⁺	1.43 ± 0.05 ^a	–	–	–	3.31 ^d	–
Sm ²⁺	–	8.4 ± 0.2 ^b	–	10.8 ± 0.1 ^b	7.60 ± 0.05 ^c	8.3 ± 0.1 ^b
Yb ²⁺	–	8.3 ± 0.2 ^b	–	8.4 ± 0.1 ^b	7.31 ± 0.10 ^c	7.5 ± 0.1 ^b
La ³⁺	5.00 ± 0.12 ^b	6.98 ± 0.15 ^b	3.26 ± 0.04 ^b	5.91 ± 0.08 ^b	5.14 ± 0.05 ^c	4.29 ± 0.04 ^b

^aTaken from ref. 2.

^bTaken from ref. 4.

^cTaken from ref. 3.

^dTaken from ref. 17, data obtained for dibenzo-18-crown-6.

elene carbonate and there is thus no water present to displace the ligand from the coordination sphere of the metal ions. The formation of a sandwich bis-adduct with calcium was thus expected since the tetrahydrated 1:1 complex of this ion with 12C4 already adopts a structure particularly favorable for the addition of a second molecule of ligand. The fairly high stability of the bis-adduct of magnesium is somewhat more surprising. When the ionic radius of the encapsulated ion decreases, the two 12C4 cycles are brought closer together and steric interactions are likely to increase. According to van Remoortere and Boer [6], 2.30 Å is the smallest cation–oxygen distance which can be reached by moving the two 12C4 rings near to each other without bringing two oxygen atoms at a smaller distance than two van der Waals radii (2×1.40 Å). This leaves enough space between the two cycles for a metal ion with a radius of 0.90 Å. Since, according to Shannon [9], the ionic radius of an eight-coordinated magnesium ion is 0.89 Å, one may assume that the formation of a bis-complex with this ion is not unreasonable even if steric interactions between the two cycles are more important than for larger ions.

As appears in Table I, the stability of the 1:2 sandwich complex of calcium with 12C4 is notably higher than in the case of the other alkaline earth cations. This observation can be correlated with other results obtained in anhydrous propylene carbonate. Sodium is the only alkali metal ion which forms [2] a stable bis-complex with 12C4. Moreover, the largest lanthanide ions, La^{3+} – Nd^{3+} , are involved in more stable 1:2 complexes than the smallest ions Sm^{3+} – Lu^{3+} [4]. It is interesting to note that the ions Na^+ , Ca^{2+} and La^{3+} – Nd^{3+} have very different charge densities but very similar ionic radii ($r = 1.12$ – 1.18 Å for a coordination number of eight). The particularly high stability of the bis-adducts of these ions with 12C4 is believed to be due, at least in part, to the structure of these complexes. Indeed, van Remoortere and co-workers [6–8] have shown that the ligand 12C4, when coordinated to Na^+ or Ca^{2+} , adopts a conformation in which all the methylene hydrogens are fully staggered and the oxygen lone pair orbitals are directed toward the center of the encapsulated metal ions. This particularly stable conformation cannot be maintained if the metals have an ionic radius either smaller or larger than 1.12–1.18 Å, thus leading to a reduced stability of the bis-adducts.

Alkaline Earth Complexes with 4-tert-butylbenzo-15-crown-5 and 4,4'(5')-di-tert-butylbenzo-18-crown-6

Ba^{2+} and Sr^{2+} are the only alkaline earth cations which form stable bis-adducts with 4-tert-butylbenzo-

15-crown-5 (BB15C5). These data were obtained by a best fit treatment of potentiometric measurements carried out with a lead amalgam electrode in the conditions $|\text{Me}|_{\text{tot}} < 3[|\text{L}|_{\text{tot}} + |\text{Pb}|_{\text{tot}}]$ or $|\text{L}|_{\text{tot}} < 3[|\text{Me}|_{\text{tot}} + |\text{Pb}|_{\text{tot}}]$ where Me is an alkaline earth ion. These concentration ranges are wide enough [4] to allow, if possible, the formation of 1:2 complexes. The error function calculated in the best fit treatment did not decrease in the case of magnesium and calcium if 1:2 adducts were taken into account in addition to 1:1 complexes; the existence of these species in our experimental conditions thus seems doubtful.

Our data are consistent with the maximum solid state stoichiometries reported by Parsons and Wingfield [10] for the alkaline earth complexes with benzo-15-crown-5. According to these authors, magnesium forms 1:1 complexes while 1:1 or 1:2 complexes of calcium can be obtained, depending on the complexing properties of the counter-ion. As mentioned above, we could not detect a bis-complex of calcium; the solvation by propylene carbonate is apparently sufficient to prevent the formation of this species. Moreover, Parsons and Wingfield [10] found that the reaction of strontium and barium with benzo-15-crown-5 yields only 1:2 adducts, in keeping with the high stability we measured for these complexes. The stability sequence of the 1:1 complexes with BB15C5 is also in agreement with the crystal structure of these complexes. Owen [11] reported that the Mg^{2+} ion lies exactly in the mean plane of the oxygen atoms of benzo-15-crown-5 while calcium sits 1.22 Å above this plane. Accordingly, the 1:1 complexes of magnesium are the most stable in the alkaline earth series. Also the large ions, Sr^{2+} and Ba^{2+} cannot fit into the internal cavity of BB15C5 and form 1:2 complexes. However, it is pertinent to note that solvation effects can alter the stability sequence given in Table I. Izatt and coworkers [12] investigated by calorimetry the complexation of the alkaline earth ions by 15-crown-5 in methanol. They found that magnesium is not complexed by this ligand and that strontium forms only a 1:1 adduct which is more stable than the corresponding adduct with calcium, in complete disagreement with our data obtained in an anhydrous aprotic medium.

The stability sequence of the 1:1 complexes of the alkaline earth cations with 4,4'(5')-di-tert-butylbenzo-18-crown-6 (DBB18C6) is also in agreement with the solid state structures reported for the adducts of these ions [10, 13]. The ions Sr^{2+} and Ba^{2+} were found [13] to lie above the macrocyclic ring of benzo-18-crown-6, but Sr^{2+} is closer to the center of this ring in keeping with the somewhat higher stability constant measured in propylene carbonate for the complex of Sr^{2+} with DBB18C6. Also, magnesium is only very weakly bonded by DBB18C6 because of the very poor fit between the cavity size of the ligand and the ionic radius of the metal ion.

Alkaline Earth Complexes with Dibenzo-30-crown-10

Strontium and barium adducts of 1:1 stoichiometry with the very large ligand dibenzo-30-crown-10 (DB30C10) have been isolated in the crystalline state, but no complex of calcium or magnesium could be synthesized [10]. The data listed in Table I show that 1:1 adducts with DB30C10 are formed in anhydrous propylene carbonate by all the alkaline earth cations. The stability of these complexes decreases regularly on proceeding from barium to magnesium. DB30C10 is a highly flexible ligand which can adopt a 'wrap around' conformation [14] of reduced cavity size in the presence of the potassium ion at the expense of a strongly negative entropy [1b]. A similar structure has been suggested for the cesium and barium complexes at DB30C10 in acetone and chloroform but was not found in the case of the smaller sodium ion [15]. It seems that the 'wrap around' conformation of DB30C10 becomes so rapidly strained when the ionic radius of the encapsulated ions decreases that the ligand is forced to adopt a less crowded, more open structure, in which the metal ions could be preferentially bonded to some of the oxygen atoms of the ligand [15, 1b]. The stability constants are then substantially lower [16]. This line of reasoning appears to be valid for both the alkali metal and the alkaline earth ions.

Concluding Remarks

Two other facts about the complexation of the alkaline earths by the crown ethers should be singled out for special note. On the one hand, the stability of the complexes depends on the number of coordinating sites of the ligand; on the other hand, an alkaline earth cation is bonded more strongly by the crown ethers than either the alkali metal ion or the trivalent lanthanide of the same ionic radius.

Because of its greater number of coordinating sites, DBB18C6 forms more stable 1:1 adducts than either 12C4 or B15C5 with all the alkaline earths except magnesium. It is likely that in the case of this ion, the greater number of oxygen atoms of DBB18C6 cannot offset the very poor fit between the size of the ion and the size of the ligand. The influence of the number of donor groups is also obvious if one compares the stability of the bis-adducts of Sr^{2+} or Ba^{2+} with BB15C5 and 12C4. On the contrary, the complexes with DB30C10 are not so stable as could have been anticipated by simply relying on the large number of coordinating sites of the ligand. Because of its ionic size, barium fills completely the internal cavity of DB30C10 in a 'wrap around' conformation and thus forms the most stable 1:1 complex investigated in the present work. However, examination of the data in Table I reveals that DB30C10 exhibits in

many cases a smaller affinity for Sr^{2+} , Ca^{2+} or Mg^{2+} than the other crown ethers either because the size of these ions no longer matches the size of the cavity of the 'wrapped' structure of DB30C10 or because an incomplete encapsulation takes place, as mentioned above. Similar trends have already been reported for the alkali metal ions [1].

A comparison of the complexation of uni-, di- and trivalent metal ions by crown ethers in anhydrous propylene carbonate is limited by the data available so far for the alkali metal ions. To our knowledge, the only stability constants determined for these ions in propylene carbonate are relative to the binding by 12C4 [2] and by dibenzo-18-crown-6 [17], a ligand which probably exhibits properties very similar to those of DBB18C6 (see Table I). Taking these limits into account, it is possible to compare the complexation of three ions of the same ionic radius [9] but of different charge, namely Na^+ , Ca^{2+} and La^{3+} . However, caution must be advised in accepting such a comparison because the dissociation of the perchlorate salts of the highly charged ions is incomplete in propylene carbonate despite the high dielectric constant (64.4) of this solvent. As appears in Table I, calcium is bonded more strongly by all the crown ethers than either sodium or lanthanum. Also, the complexes of the alkaline earths are systematically more stable than the adducts of the alkali metal ions of the same ionic radius. A greater charge density leads of course to increased interactions with both the ligand and the solvent. It is apparently for the divalent ions that the competition between the solvent and the ligand for the solvation of the metal ions is most in favour of the ligand. Different results have been obtained [12] in protic solvents (water and methanol) where 18-crown-6 prefers sodium over calcium in contrast with what we measured in propylene carbonate.

Finally, it is also of interest to compare the stability of the adducts of the alkaline earths and of two divalent lanthanide ions, Sm^{2+} and Yb^{2+} . Because they participate in similar electrostatic non-covalent bonds and because they have similar ionic radius [9], it was expected that Yb^{2+} and Ca^{2+} on the one hand, and Sm^{2+} and Sr^{2+} on the other hand, would form crown complexes of nearly identical stability. As can be seen in Table I, there is a fairly good agreement between the stability constants of the complexes of Sm^{2+} and Sr^{2+} but no such correlation exists in the case of Yb^{2+} and Ca^{2+} . However, it should be noted that the values of the complexation constants of the Yb^{2+} crown adducts are always enclosed between those of Ca^{2+} and Sr^{2+} . Because the coordination numbers of metal ions complexed by macrocycles are unknown, the exact value of the ionic radii is difficult to assess rigorously [9]. Taking these uncertainties into account we consider that there is indeed some parallelism between the complexation of the alkaline earth ions and the divalent lanthanides.

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