

COMPLEXES OF MAGNESIUM AND BARIUM CATIONS WITH CROWN ETHERS  
ATTACHED TO AN ANTHRAQUINONE UNIT IN THE REDUCED FORM

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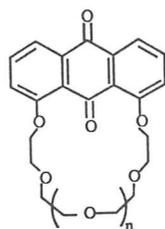
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**Summary:** The electrochemical behaviour and complexation properties of synthetic macrocyclic crown ethers with six and seven oxygen donor atoms in the macroring and attached to an anthraquinone unit towards the alkaline-earth cations,  $Mg^{2+}$  and  $Ba^{2+}$ , are examined by cyclic voltammetry. The results indicate different cation binding enhancements with these electrochemically switched systems. The larger cation size and larger number of macroring donor atoms favour a stronger interaction between the cations and the reduced ligands.

Crown ethers form an important group of synthetic macrocyclic polyethers which have been subject of a wide study as complexing agents towards several ionic species. These ionophoric compounds can form complexes with high stability and show selective recognition for specific metal cations.<sup>1,2</sup> These properties can be altered by the presence of electroactive groups attached to the crown ether systems if they are appropriately situated to interact with the cations. The binding strength and cationic selectivity given by these ionophores can be modified and controlled by electrochemical processes relatively to the properties shown by the hosts in their neutral form.<sup>3,4</sup>

In this work we report some results of a study on the electrochemical characteristics and complexation behaviour of receptor molecules (L) with six and seven oxygen donor atoms in the macroring together with an anthraquinone moiety (scheme I) towards the alkaline-earth metal cations  $Mg^{2+}$  and  $Ba^{2+}$ . The study was carried out in 0.1 M tetrabutylammonium perchlorate + acetonitrile, using conventional cyclic voltammetry. Experimental details are as previously described.<sup>4</sup>

The results obtained from the cyclic voltammograms (CVs) in the absence and presence of metal cations for various ligand-to-cation ratio



scheme 1

Compound	n
A	1
B	2

are summarized in Table 1. The electrochemical reduction of the host molecules A and B provided CVs exhibiting two successive one electron reductions as a result of the formation of anion radicals  $L \rightarrow L^{\cdot -}$  ( $E_1^0$ ) and dianions  $L^{\cdot -} \rightarrow L^{2-}$  ( $E_2^0$ ).<sup>4</sup> The addition of  $Mg(ClO_4)_2$  and  $Ba(ClO_4)_2$  to the solutions of crown ethers A and B shifted the electrochemical response to a more positive potential range than that corresponding to the uncomplexed ligands. The new redox waves were attributed to the reduced complexed ligands,  $M^{2+}L \rightarrow M^{2+}L^{\cdot -}$  ( $E_1^{\prime 0}$ ) and  $M^{2+}L^{\cdot -} \rightarrow M^{2+}L^{2-}$  ( $E_2^{\prime 0}$ ). The formal potential shifts for more positive values reflect a stronger binding strength of the cations to the electrochemically reduced ligands than to their unreduced forms. These shifts,  $\Delta E_1^0$  and  $\Delta E_2^0$ , should be taken as a quantitative estimate of the effective increase of the cation binding on the species formed.<sup>5</sup>

The cations interact with the neutral ligands through the macrocyclic oxygen atoms by electrostatic forces of the ion-dipole type. The electrochemical reduction of the ligands producing anion radicals, should induce an additional intramolecular charge-charge interaction between the monoreduced electronic acceptor group belonging to the macrocyclic ring and the macrocyclic bound cation. The electronic charge density of the anion radicals being appropriately situated within the macrocyclic ring will contribute to a more effective interaction with the macrocyclic bound cations. The electrochemical formation of the dianions does not induce such strong binding enhancements as is shown by the

Table 1. Electrochemical data for the free and complexed ligands A and B with  $Mg^{2+}$  and  $Ba^{2+}$  cations, a, b, c

Compound	$M^{2+}$	$-E_1^0/V$ d	$-E_2^0/V$ d	$-E_1^{\prime 0}/V$ d	$-E_2^{\prime 0}/V$ d	$\Delta E_1^0/V$ e	$\Delta E_2^0/V$ e
A	-	1.24	1.76				
	$Mg^{2+}$	1.23	- <sup>f</sup>	1.06 <sup>g</sup>	1.68	0.17 <sup>h</sup>	0.08
	$Ba^{2+}$	1.22	-	0.92	1.64	0.32	0.12
B	-	1.36	1.82				
	$Mg^{2+}$	1.35	1.80	1.08	-	0.28	-
	$Ba^{2+}$	1.40	1.88	0.95	1.74 <sup>g</sup>	0.41	0.14 <sup>h</sup>

<sup>a</sup> potentials are reported vs.  $Ag/0.01 M Ag^+$  in acetonitrile; <sup>b</sup> values recorded were obtained from  $L/M^{2+} = 1/1$ ; <sup>c</sup> scan rate =  $100 mV s^{-1}$ ; <sup>d</sup>  $E_1^0$  and  $E_2^0$  are the formal potentials of the uncomplexed ligands,  $E_1^{\prime 0}$  and  $E_2^{\prime 0}$  are the formal potentials of the complexed ligands; they were estimated from the cathodic and anodic peak potentials  $E_{red}$  and  $E_{ox}$  as  $(E_{red} + E_{ox})/2$ ; <sup>e</sup>  $\Delta E_1^0 = E_1^{\prime 0} - E_1^0$  and  $\Delta E_2^0 = E_2^{\prime 0} - E_2^0$ ; <sup>f</sup> (-) no redox couple was observed; <sup>g</sup> a reduction peak and not a redox couple was observed; <sup>h</sup>  $\Delta E^0$  values were deduced from the reduction potentials of the complexed and free ligands.

smaller values of the parameter  $\Delta E_2^0$  compared to  $\Delta E_1^0$  corresponding to the monoanion formation. The carbonyl group which does not belong to the macrocyclic ring, is in a position physically incapable of interacting directly and strongly with the macrocyclic bound cation. At the same time, its negative electric charge should influence the association with the cation and therefore the binding enhancement is smaller than with the anion radical.

Besides this generic behaviour, the data indicate that  $Mg^{2+}$  and  $Ba^{2+}$  have different levels of complexation and affinity with the reduced ligands. The relative size of the macrocyclic cavity to cation and the structural flexibility of the crown ether subunit of the ligand will play a relevant role in the interaction strength and in the complexing characteristics.<sup>6</sup> The macrocyclic ring of the hosts is sufficiently flexible to adopt a more favourable structural organization in its coordination to the cation, that favours the contact between the two species and consequently contributes for an enhancement of the coordination strength. The dimensions of the  $Mg^{2+}$  and  $Ba^{2+}$  cations allows both of them to enter and to be held bound inside the cavity of the neutral macrocyclic ring.<sup>7</sup> In spite of its stronger electric field,  $Mg^{2+}$  fits less well

into the cavity of the neutral macrocyclic polyethers owing to its smaller size and therefore the contact among the donor oxygen atoms of the macroring and  $Mg^{2+}$  is not so favoured as in the case of  $Ba^{2+}$  cation.  $Mg^{2+}$  has more difficulty to organize the available macroring donor atoms around itself after electrochemical reduction and thus inducing smaller binding increases,  $\Delta E^0_1$ . The binding of  $Ba^{2+}$  is larger when the ligands are reduced because its larger size fits better to the macroring cavity and induces a larger cation enhancements as is shown by the larger  $\Delta E^0_1$ .

The compound B with seven oxygen atoms in the macroring and a larger cavity shows similar voltammetric behaviour to compound A, meanwhile the binding affinities of the reduced compound B are different from the affinities of the reduced compound A. The order of binding increase of the cations is retained and the larger enhancements for the reduced compound B may reflect the influence of the larger number of binding sites in the crown ether macroring.

The results obtained suggest that the ligands A and B in the reduced form are more effective complexing agents towards the alkaline-earth metal ions  $Mg^{2+}$  and  $Ba^{2+}$  than their neutral forms. Moreover, the larger cation size favours the larger increase in its interaction with the reduced ligands.

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## THE ELECTROOXIDATION OF SMALL ORGANIC MOLECULES AND COMPARATION BETWEEN NOBLE AND NON-NOBLE ELECTRODE SURFACES

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### Summary

The electrooxidation of methanol and iso-propanol has been examined on Au(100) and compared with the electrooxidation on non-modified and modified glassy carbon electrodes. The studies with Au(100) have pointed out the role of the  $OH^-$  layer formation for the beginning of the electrooxidation of alcohols in alkaline solution (1,2) on noble metals. The small differences in the structure of alcohol ( $CH_3OH$  and iso-propanol) cause the big differences in an electrochemical behaviour on noble electrochemical surfaces. The usually prepared GC electrode (3) is not active for the electrooxidation of alcohols at all and modified, Ag/GC electrode shows the different way of the adsorption-desorption processes of both alcohols connected with the electrochemical activity only deeply in the oxide region (5). The comparison with the electrooxidation of  $CH_2O$  on noble (4) and non-noble electrodes (5) indicates that the most simple molecule with the aldehyde group exhibits the unexpected electrocatalytic behaviour at Ag-GC surfaces in the region of the potential before the oxide formation. That means the general conclusion is not possible to make; each molecule requires a special explanation of the electrocatalytic phenomena.

The experimental part has been described in (2), (3) and (4).

In Fig. 1 is presented the electrooxidation of 0.01 M  $CH_3OH$  and 0.01 M iso-propanol on Au(100) at different values of the sweep rate.

It is obvious that sweep rate = 50 mV/sec is too fast for the exhibition of any electrocatalytical process in a case of both alcohols. With sweep rate = 5 mV/sec and 0.5 mV/sec the expected shape of the voltammograms are obtained in a case of iso-propanol, very similar to those, obtained with glycerol at Au(100)(2). The incipient potential of the reaction corresponds to the potential of AuOH formation on Au(100).

$CH_3OH$  remains unactive at sweep = 5 mV/sec and even at sweep rate = 0.5 mV/sec there is no signs of any significant oxidation processes. It can be said that only adsorption-desorption processes of  $CH_3OH$  occur at Au(100) under the experimental