



# Barium(II) thiocyanate templating Schiff-base lateral macrobicycles derived from 1,10-diaza-15-crown-5

David Esteban, Carlos Platas-Iglesias, Fernando Avecilla, Andrés de Blas<sup>\*</sup>,  
Teresa Rodríguez-Blas<sup>\*</sup>

*Departamento de Química Fundamental, Facultad de Ciencias, Universidade da Coruña, Campus da Zapateira s/n 15071 A Coruña, Spain*

Received 7 August 2004; accepted 16 November 2004

Available online 9 December 2004

## Abstract

Previously we have proved that barium perchlorate is a highly effective template agent in the formation of the Schiff-base lateral macrobicycles  $L^1$  and  $L^2$  (receptors derived from the condensation of *N,N'*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 with 2,6-diformylpyridine and 2,6-diformyl-4-methylphenol, respectively). Aiming to understand the effect that the nature of the counteranion present in the reaction medium has on the barium template potential, we have carried out the corresponding template synthesis in the presence of barium thiocyanate. We have found that considerably longer reaction times are required to obtain both receptors when barium thiocyanate is employed. The barium template remains trapped into the formed macrobicyclic cavity and compounds of formula  $Ba(L^1)(SCN)_2 \cdot H_2O$  (**1**) and  $Ba(L^2)(SCN)_2 \cdot 2H_2O$  (**2**) were isolated. The X-ray crystal structure of **1** shows the metal ion coordinated to the eight donor atoms of the receptor and to the nitrogen atom of a isothiocyanate group, the coordination polyhedron being best described as a monocapped distorted dodecahedron. In **1**, the metal ion is nearly centred inside the macrobicyclic cavity of  $L^1$ , whereas NMR studies in solution indicate that in **2** the barium ion is asymmetrically situated in the macrobicyclic cavity of  $L^2$ . This asymmetric coordination is attributed to the proton transfer from the phenol group to the nitrogen atom of one of the imine groups.

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*Keywords:* Lateral macrobicyclic; X-ray crystal structures; Template synthesis; Barium; Thiocyanate

## 1. Introduction

The coordination chemistry of macrocyclic ligands [1,2] is a fascinating area of intense study for inorganic chemists. One aspect of the interest that macrocyclic ligands have promoted stems from the fact that depending on features such as the nature, number and arrangement of the ligand donors, as well as ligand conjugation, substitution and flexibility, it is possible to tailor-make different types of macrocyclic molecules for specific uses. In particular, the cyclic framework of crown ethers and cryptands affords an interesting plat-

form for the complexation of metal ions [3]. Likewise, according to the number of connecting bridges used for their construction as well as to the nature of the subunits used as building blocks, a variety of macropolycyclic structures may be envisaged. Lateral macrobicycles (described as dissymmetrical molecules structurally based on the combination of two different binding units, a chelating one and a macrocyclic one) are one of them [4]. Taking into account the peculiar structural features that the lateral macrobicycles show, it is easy to understand that this type of macropolycyclic architectures exhibit a range of interesting and potentially useful molecular recognition properties [5]. However, to date the coordinative properties of lateral macrobicycles remain considerably unexplored.

<sup>\*</sup> Corresponding authors. Tel.: +34981167000; fax: +34981167065.  
E-mail address: [mayter@udc.es](mailto:mayter@udc.es) (A. de Blas).

In the recent past a great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate given metal ions [6]. In particular, macrocyclic Schiff bases and Schiff-base derived cryptands and cryptates have successfully been proposed as excellent systems in the complexation of metal ions. However, no example of a Schiff-base lateral macrobicyclic was reported until 1999 when we described, at the first time, examples of Schiff-base lateral macrobicycles [7]. These macrobicycles, shown in Scheme 1, structurally derive from bibracchial lariat ethers incorporating pendant aniline moieties. Subsequent studies demonstrated that these systems possess promising coordinating properties [8–10]. We have found that these Schiff-base lateral macrobicycles cannot be prepared by direct reaction between the organic precursors; but barium perchlorate can act as a template, thereby facilitating the formation of the desired macrobicycles in high yields. In fact, it is known that the direct synthesis of a free macrocycle from its organic precursors often results in a low yield of the desired cyclic product, with side reactions such as polymerisation predominating. Consequently, some synthetic strategies such as the use of high dilution conditions, the incorporation of a rigid group in the open chain precursors, and the use of template agents have been developed. Particularly, template Schiff base condensations between dicarbonyl compounds and diamines are among the simplest and most popular methods for macrocycle synthesis [11].

Previously, we have demonstrated that the effectiveness of barium(II) perchlorate to template the macrobicycles **L**<sup>1</sup> to **L**<sup>4</sup> comes from its ability to arrange the pendant arms of the diamine precursor [*N,N'*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (for **L**<sup>1</sup> and **L**<sup>2</sup>) or *N,N'*-bis(2-aminobenzyl)-4,13-diaza-18-crown-6 (for **L**<sup>3</sup> and **L**<sup>4</sup>)] in a *syn* conformation (Fig. 1) [12]. Aiming to

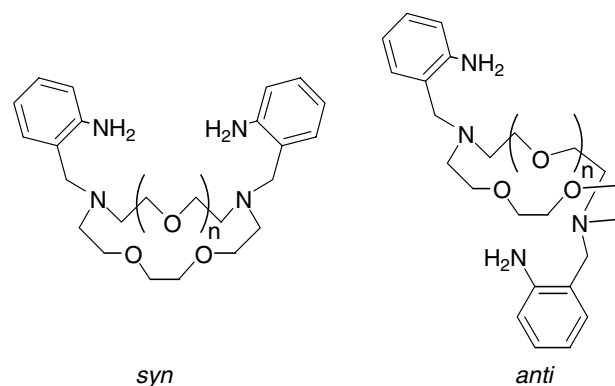


Fig. 1. The *syn* and *anti* conformations of the diamine precursors used for the preparation of macrobicycles **L**<sup>1</sup> and **L**<sup>2</sup> ( $n = 1$ ) or **L**<sup>3</sup> and **L**<sup>4</sup> ( $n = 2$ ).

understand the effect that the nature of the counteranion present in the medium reaction had on the barium template potential, we also carried out the corresponding template synthesis in the presence of barium thiocyanate under the same experimental conditions used with barium perchlorate, finding that whereas barium thiocyanate can also template the formation of the largest macrobicycles **L**<sup>3</sup> and **L**<sup>4</sup>, it was not able to do it with the smallest **L**<sup>1</sup> and **L**<sup>2</sup> [7]. We have now slightly modified the synthetic conditions, and in this paper we discuss the formation of macrobicycles **L**<sup>1</sup> and **L**<sup>2</sup> in the presence of barium thiocyanate. We also describe the structures of the corresponding barium complexes both in solution and in the solid state, and we compare them to those previously described for their perchlorate analogues [7,13].

## 2. Experimental

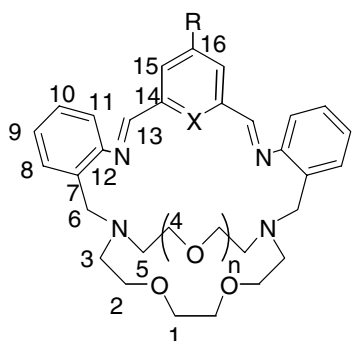
### 2.1. Reagents

2,6-Diformylpyridine and 2,6-diformyl-4-methylphenol were synthesised according to literature methods [14–16]. The diamine *N,N'*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 was prepared as previously described by us [8]. All other chemicals were purchased from commercial sources and used without further purification. Solvents were of reagent grade purified by the usual methods.

### 2.2. Template synthesis

#### 2.2.1. $Ba(L^1)(SCN)_2 \cdot H_2O$ (**1**)

A solution of  $Ba(SCN)_2 \cdot H_2O$  (0.072 g; 0.266 mmol) in absolute ethanol (50 mL) was added with stirring to a solution of the diamine *N,N'*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 (0.114 g; 0.266 mmol) also in absolute ethanol (120 mL). The mixture was vigorously stirred



- L**<sup>1</sup>:  $n = 1$ ,  $R = H$ ,  $X = N$   
**L**<sup>2</sup>:  $n = 1$ ,  $R = CH_3$ ,  $X = C-OH$   
**L**<sup>3</sup>:  $n = 2$ ,  $R = H$ ,  $X = N$   
**L**<sup>4</sup>:  $n = 2$ ,  $R = CH_3$ ,  $X = C-OH$

Scheme 1.

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