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Synthesis and characterization of two new tetrapyrazolic macrocycles for the selective extraction of cesium cation

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ABSTRACT

The synthesis of two macrocycles containing two bipyrazolic subunits, with different side arms is reported. These structures were characterised by ^{1}H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis. The macrocycle bearing a hydroxyl group in the side arms, crystallizes in triclinic (S.G.: P-1) systems, with the unit cell parameters: [11.3086(4), 13.6865(5), 14.6311(5), 108.774(3), 105.408(3), 107.131(3), V=1879.28(15) Å^3]. It possesses 3D crystal structure with molecules interacting through weak H-bonds. The complexing properties of new macrocycles towards alkaline metal ions (Li^+, Na^+, K^+ and Cs^+) were studied by a liquid–liquid extraction process. The percentage values of extraction were determined by atomic absorption measurements and UV spectroscopy. Their macrocyclic cavities are better adapted to extract the Cs^+ cation. The macrocycle with side chains bearing donor groups shows the best extraction due to its participation in complexation.

1. Introduction

The design of new macrocyclic receptors has attracted considerable interest in recent years because of their encapsulating properties towards numerous guests making them important molecules in the fields of molecular recognition, transport, biological models or selective catalysis.[1–3] The first macrocycles were the crown ethers synthesized in 1967 by Pedersen, which have a circular pre-organized cavity and present selective complexation properties vis-à-vis the alkali and alkaline earth cations,[4] and the cryptands and spherands of Lehn and Cram, respectively.[5,6]

One of our research interests is the study of properties of macrocycles incorporating pyrazole subunits, which have the ability to extract and complex hard and soft cations such as alkali and transition metals.[7–9] Many modifications of polypyrazolic macrocycles, such as changing the ring size, the kind of substituents, and the type of donor atoms, can change their complexation properties.[10–13] In addition, it is reported in the literature that the presence of a donor atom in a side chain of lariat ethers increases the binding ability of the macrocycle towards cations.[14–16] Furthermore, ligands with side arms attached to nitrogen (N-pivot lariat ethers) instead of a carbon (C-pivot lariat ethers) present the best binding properties. This bonding improvement could be attributed to the higher flexibility of the side chain with nitrogen, which facilitates the optimal bonding geometry.[17] Therefore, it is interesting to study the effect of the nature of the side arm of pyrazolic macrocycles on their abilities to extract the alkali metal ions.

Moreover, several macrocyclic receptors were developed for the selective removal of Cs^+ from aqueous mediums.[18–22] Indeed, its radioactive isotope $^{137}Cs^+$ presents a real danger to both environmental and human health.[23,24] Thus, the extraction of cesium cation is an urgent necessity.

Previously, we reported the synthesis of tetrapyrazolic macrocycles for the extraction and transport of alkali cations through synthetic polymer membranes.[25] These macrocycles showed a pronounced selectivity of extraction and transport for K^+ ions. Therefore, it was interesting to increase the size of the cage of these macrocycles, to develop a new series of macrocycles for the selective extraction of cesium.

In this context, we describe in this work, the synthesis of two new tetrapyrazolic macrocycles having the same cavity size, but differing by the nature of the two side arms to verify the effect on the binding ability of these ligands. Their selectivities were examined using a liquid–liquid extraction process.

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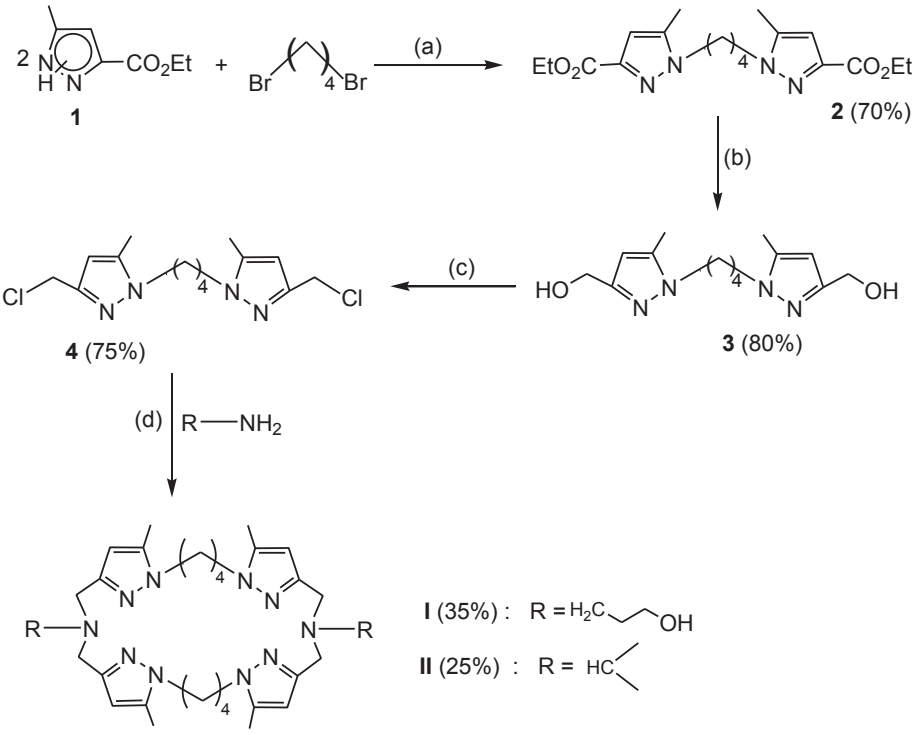
2. Results and discussion

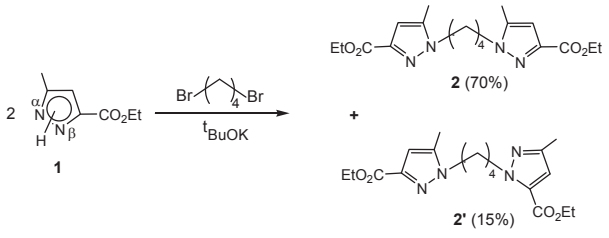
2.1. Synthesis

The route used to prepare the desired macrocycles is shown in Scheme 1.



Scheme 1. Synthesis of the macrocycles **I** and **II**. Reagent and conditions (a) ^{t}BuOK, THF, Reflux, 15 h (b) $LiAlH_4$, THF, Reflux, 4 h (c) $SOCl_2$, CH_2Cl_2, RT, 12 h (d) Na_2CO_3; CH_3CN, 24 h.

2.1.1. Synthesis of the bipyrazolic precursor ***4****.* The synthesis of macrocyclic precurseur compound **4** starts by alkylation of the pyrazolic ester **1** using the 1,4-dibromobutane. This reaction led to the formation of the diester **2**[26] due to αα alkylation. This product was isolated by recrystallization from diethyl ether in good yield (70%). However, TLC showed the existence of another product in the filtrate which was isolated by column chromatography with a low yield (15%). According to NMR spectroscopy, this compound was the minor isomer **2′**, due to αβ alkylation (Scheme 2).



Scheme 2. Isomers resulting from the alkylation of ester pyrazole **1**.

The first isomer **2** has a center of symmetry; and presents a single signal for each kind of protons, which is the case of the ^{1}H NMR spectrum corresponding to the major product (Fig. 1A). By contrast, the ^{1}H NMR spectrum of the minor product (Fig. 1B) presents duplicate signals due to the presence of dissymmetry in this product.

To ensure that the major product corresponds to the structure of the isomer **2**, and not to the isomer coming from the ββ alkylation, which also has a center of symmetry, we performed X-ray crystallographic analysis on single crystals obtained by recrystallization of the major product from diethyl ether. The results displayed in Fig. 2 confirms that the molecular structure of the major product is the isomer **2**.

Major isomer **2** was then converted in the presence of lithium aluminium hydride using a modified procedure documented in the literature[27] to give 80% yield of the hydroxy product **3**. This reaction was followed by the addition of thionyl chloride to compound **3** to give the precursor **4** with a yield of 75%, which should be used immediately to avoid its hydrolysis.

2.1.2. Synthesis of the macrocycles. In order to achieve the desired macrocycles **I** and **II**, we condensed the dichlorinated derivative **4** with the corresponding primary amines: 3-aminopropan-1-ol and isopropylamine respectively, under high dilution conditions to promote [2+2] cyclisation over the linear condensation. The two products were isolated and characterized by ^{1}H NMR, ^{13}C NMR and mass spectrometry.

However, it should be noted that the [1+1] cyclization of chlorinated derivative **4** with these primary amines can also occur, and gives monofunctional bipyrazolic macrocycles (Fig. 3) due to the flexibility of compound **4**.

The ^{1}H NMR and ^{13}C NMR spectra of both macrocycles should be identical, which does not allow to differentiate them as reported in our previous work.[25] In the order to check the obtained macrocyclic structures, we used the mass spectrometry. Mass spectra of the two