



## Rigid ferrocenophane and its metal complexes with transition and alkaline-earth metal ions

Xiuling Cui<sup>a</sup>, Rita Delgado<sup>a,b,\*</sup>, Judite Costa<sup>c</sup>, Michael G.B. Drew<sup>d</sup>, Paulo J. Costa<sup>e</sup>, Vítor Félix<sup>e</sup>

<sup>a</sup> Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República - EAN, 2780-157 Oeiras, Portugal

<sup>b</sup> Instituto Superior Técnico, Departamento de Química e Bioquímica, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

<sup>c</sup> CBT-iMed.UL, Fac. de Farmácia de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal

<sup>d</sup> School of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

<sup>e</sup> Departamento Química, CICECO and Secção Autónoma de Ciências da Saúde, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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### ABSTRACT

The rigid [6]ferrocenophane,  $L^1$ , was synthesised by condensation of 1,1'-ferrocene dicarbaldehyde with *trans*-1,2-diaminocyclohexane in high dilution at r.t. followed by reduction. When other experimental conditions were employed, the [6,6]ferrocenophane ( $L^2$ ) was also obtained. Both compounds were characterised by single crystal X-ray crystallography. The protonation of  $L^1$  and its metal complexation were evaluated by the effect on the electron-transfer process of the ferrocene (fc) unit of  $L^1$  using cyclic voltammetry (CV) and square wave voltammetry (SWV) in anhydrous  $CH_3CN$  solution and in 0.1 M  $^nBu_4NPF_6$  as the supporting electrolyte. The electrochemical process of  $L^1$  between  $-300$  and  $900$  mV is complicated by amine oxidation. On the other hand, an anodic shift from the fc/ $fc^+$  wave of  $L^1$  of 249, 225, 81 and 61 mV was observed by formation of  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Pd^{2+}$  and  $Cu^{2+}$  complexes, respectively. Whereas  $Mg^{2+}$  and  $Ca^{2+}$  only have with  $L^1$  weak interactions and they promote the acid-base equilibrium of  $L^1$ . This reveals that  $L^1$  is an interesting molecular redox sensor for detection of  $Zn^{2+}$  and  $Ni^{2+}$ , although the kinetics of the  $Zn^{2+}$  complex formation is much faster than that of the  $Ni^{2+}$  one. The X-ray crystal structure of  $[Pd(L^1Cl_2)]$  was determined and showed a square-planar environment with Pd(II) and Fe(II) centres separated by 3.781(1) Å. The experimental anodic shifts were elucidated by DFT calculations on the  $[ML^1Cl_2]$  series and they are related to the nature of the HOMO of these complexes and a four-electron, two-orbital interaction.

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### 1. Introduction

Ion sensors represent a very active research area because ions play a fundamental role in biology, chemical processes, and environmental pollution. These systems are usually composed of a signalling unit (antenna) incorporated into the receptor, so that ion recognition is reported by a measurable physical change. Receptors were designed to sense a specific ion through a variety of physical responses, such as electrochemical, optical (UV–Vis absorption or fluorescence), etc. [1–4].

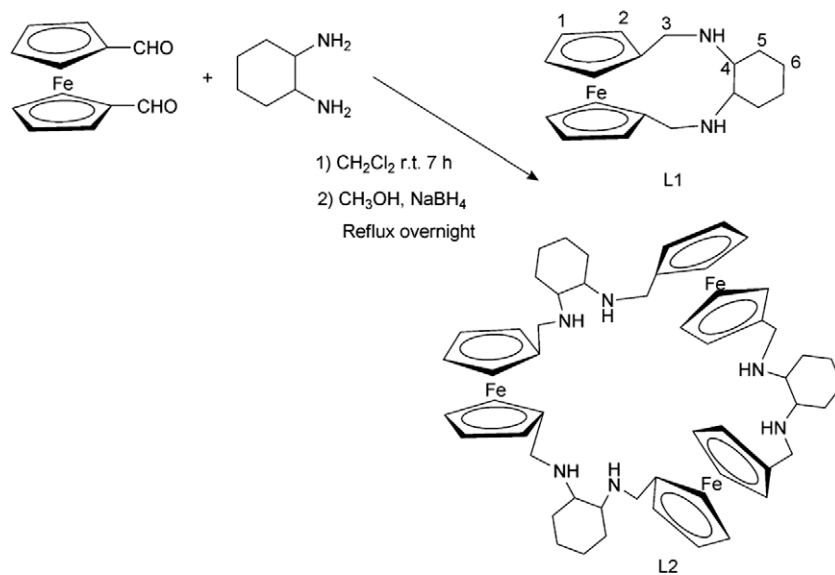
We are especially interested in the design of molecular redox sensors for metal ions [5,6] or anions [7]. In this context, ferrocene is a versatile unit that can be covalently bound and included as an antenna in multiple types of receptors to sense ions [2,5–11]. The metal ion (or anion) binding at an adjacent site of a ferrocene-based receptor induces a positive (or negative) shift in the redox

potential of the ferrocene/ferrocenium couple, either by through-bond and/or through space electrostatic interactions, interference or conformational change, and the ion recognition ability of the receptor can be reversibly switched on or off by varying the applied electrochemical potential. The efficiency of these receptors crucially depends on the electronic communication between the fc unit and the substrate involved. This communication is favourable when the donor atoms of the receptor are very close or directly attached to the fc unit [9–12]. Additionally, from a synthetic point of view, ferrocene is a very convenient building block because it can easily be functionalized and incorporated into many structures, and its electrochemical and UV–Vis spectroscopic properties can be perturbed by the proximity of the substrate [2,8,10,11].

In the present work two ferrocenophanes ( $L^1$  and  $L^2$ ) were synthesised and characterised by single crystal X-ray diffraction. The redox behaviour of  $L^1$  to protonation and to metal complexation with  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Pd^{2+}$  metal ions was studied in  $CH_3CN$  solution and in 0.1 M  $^nBu_4NPF_6$  in order to evaluate this ligand as a potential molecular sensor. To our knowledge the number of nitrogen-containing rigid macrocycles with bridged

\* Corresponding author. Address: Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República - EAN, 2780-157 Oeiras, Portugal. Tel.: +351 214469737; fax: +351 214411277.

E-mail address: [delgado@itqb.unl.pt](mailto:delgado@itqb.unl.pt) (R. Delgado).



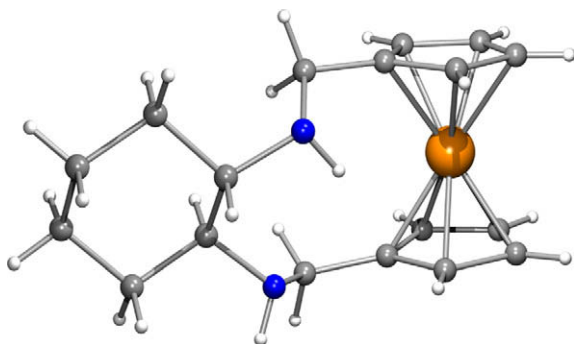
**Scheme 1.** Synthetic procedure of  $L^1$  and  $L^2$ .

ferrocenyl units is very limited [9,11–13], and its peculiar behaviour justifies more research in this area.

## 2. Results and discussion

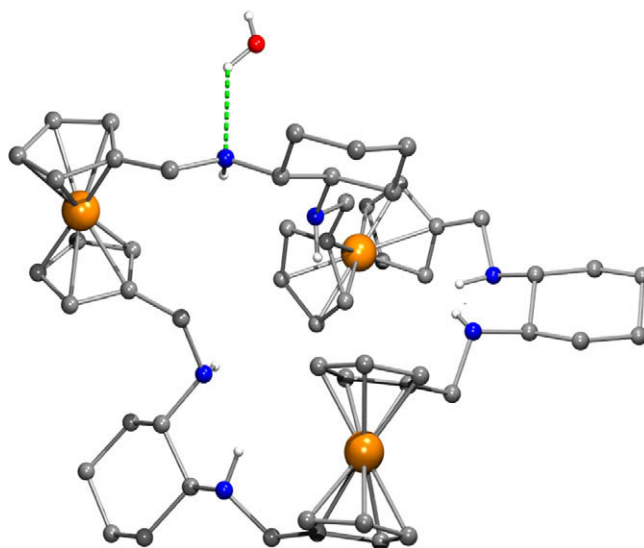
### 2.1. Syntheses and X-ray structures of $L^1$ and $L^2$

$L^1$  and  $L^2$  were obtained by condensation of 1,1'-ferrocenedi-carbaldehyde with *trans*-1,2-diaminocyclohexane at r.t. followed by reduction with  $\text{NaBH}_4$  in dry MeOH, see Scheme 1. By this simple synthetic pathway, the formation of [6,6,6]ferrocenophane ( $L^2$ ) and diverse oligomers were impossible to avoid. However the hexaimine precursor ( $L^{2*}$ ) of this compound has been obtained before by another strategy [14]. By a high dilution technique the yield of the [6]ferrocenophane,  $L^1$ , was improved, and the pure compound was then obtained by recrystallization from a chloroform/hexane mixture of solvents. Recently V. Dimitrov and coworkers proposed a different way for the synthesis of  $L^1$  but the final yield was only slightly better [15]. Compound  $L^2$  was isolated from the mixture of compounds at low temperature ( $-15\text{ }^\circ\text{C}$ ) in an amount only sufficient for analytical and single crystal X-ray characterisation. Ligand  $L^1$  was also characterised by single crystal X-ray diffraction analysis.



**Fig. 1.** PLATON view of  $L^1$  showing its molecular structure. Carbon atoms are shown in grey, hydrogen in white, nitrogen in blue and iron(II) in brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The unit cell of [6]ferrocenophane is composed of eight discrete molecules of  $L^1$  exhibiting the molecular structure showed in Fig. 1. The crystal structure of [6,6,6]ferrocenophane is built up from an asymmetric unit composed of one molecule of  $L^2$  and one water molecule assembled by one weak  $\text{N}\cdots\text{O}$  hydrogen bond with a  $\text{N}\cdots\text{O}$  distance of  $3.040(6)\text{ \AA}$  and an  $\text{N}\cdots\text{O}$  angle of  $120^\circ$ . The water molecule is outside the macrocyclic cavity. The molecular structure of  $L^2$  is presented in Fig. 2. In both structures the Cp rings of the ferrocene units adopt an almost eclipsed arrangement and the cyclohexane rings exhibit chair conformations. In the metallomacrocyclic  $L^2$  the three iron centres are held at long distances of  $7.810(1)$ ,  $8.538(1)$  and  $7.724(1)\text{ \AA}$ , which prevent any electronic communication between them. These distances are longer than the ones found in the two crystal structures of the assembled molecules of the  $L^2$  imine precursor [ $(R)-L^{2*}$ ] with (*R*)-1,1'-bi-2-naphthol, which were



**Fig. 2.** PLATON view of asymmetric unit of  $L^2$  showing the hydrogen bonding interaction between the water molecule and the [6,6,6]ferrocenophane. The C–H hydrogen atoms have been omitted for clarity. The oxygen atom is in red and the colour scheme of the remaining atoms is given in Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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