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Oxalate-templated synthesis of di-zinc macrocycles

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ABSTRACT

Herein we report that oxalate serves as a template in the formation of di-zinc macrocycles featuring bis(imino)pyridine chelating units linked by *p*-xylylene or *m*-xylylenes linkers. The resulting complexes were characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography. NMR spectroscopy indicates highly symmetrical (C_{2v} or D_{2h}) structures of the macrocyclic complexes in solution. Solid-state structures, determined by X-ray crystallography (obtained only for the *m*-xylylene bridged macrocycles), revealed hexa-coordinate zinc centers with μ^2-κ^2,κ^2-bound oxalate, meridional NNN chelates, and an additional ligand (DMF or H_2O) bound to zinc centers. Cyclic voltammetry demonstrates series of reductions associated with the redox-active bis(imino)pyridine chelates; no oxidation was observed up to 1 V. We have attempted to extract oxalate from the macrocycle using calcium bromide, ethylenediaminetetraacetic acid (EDTA), trimethyl silyl chloride (TMSCl), acetic acid, or hydrochloric acid (HCl). Of the above, EDTA, TMSCl, acetic acid, and HCl in ether failed to remove oxalate or to form a new isolable product, while calcium bromide transformed μ^2-κ^2,κ^2-bound oxalate into the μ^2-κ^1,κ^2-bound form. The addition of aqueous HCl enables observation of the oxalate-free complex by mass spectrometry as one of the major products.

1. Introduction

There is a significant interest in the synthesis of dinuclear metal complexes due, in part, to the possible metal–metal cooperativity in the activation of small molecules and catalysis [1,2]. Macrocyclic ligands constitute particular useful frameworks for the stabilization of bimetallic and polymetallic complexes as they generally allow well-defined metal–metal distances which are paramount to a catalyst design [2a–c,3]. Schiff-base containing macrocycles are relatively common [4]. Their assembly, however, often relies on the use of templating agents, most commonly metal ions [4]. In addition, some bridging ligands (for example, imidazole, acetate, or azide) capable of binding two metals have been used as templating agents in the formation of dinuclear macrocycles [5,6]. Of all bridging ligands, oxalate is among the most common – a CSD search revealed ca. 4800 compounds containing bridging oxalate. Although oxalate is frequently encountered as a bridging ligand in bimetallic complexes, we are unaware of its use as a template to form macrocycles.

We are investigating dinuclear complexes featuring redox active chelating groups. One particular aspect of our research efforts focuses on the cooperative effects that such complexes may have in the activation of heteroallenes [7]. Specifically, we are targeting dinuclear reductive coupling or reductive splitting of carbon dioxide and related heteroallenes, to yield oxalate or carbon monoxide, respectively. We have recently reported dinuclear di-Ni complexes supported by open-chain dinucleating ligands in which two iminopyridine chelates were linked by *p*-xylylene diamine [7a–c]. Some of these complexes were found to ligate two molecules of carbon disulfide per one molecule of dinuclear complex; η^2-bound carbon disulfide was reduced to the $[CS_2]^{2-}$ state [7b,c]. However, no cooperativity was observed between the reduced CS_2 molecules. We postulated that the lack of reactivity resulted, among other reasons, from the highly flexible nature of these open-chain complexes. We have also demonstrated that these open-chain systems are capable of efficient and reversible binding of oxalate, with oxalate positioned in the intramolecular cavity, thus serving as chemosensors for oxalate [7d]. We decided next to pursue more rigid macrocyclic systems with two tridentate bis(imino)pyridine chelates linked by *p*-xylylene- or *m*-xylylenediamine linkers. We note that our previous (open-chain) systems incorporated *p*-xylylene linkers; thus, present work would be a direct extension of an open-chain system featuring one *p*-xylylene linker to a macrocyclic system containing two such linkers. As for the choice of *m*-xylylene linkers, similar macrocyclic systems bridged by a *m*-xylylene linker have been previously synthesized using

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imidazole [6]. We decided to investigate oxalate as a template. The oxalate is the product of the reductive coupling of carbon dioxide. We hypothesized that a bimetallic system templated by oxalate would have the appropriate intramolecular cavity size for its binding and thus may facilitate its formation via reductive coupling. Herein we report successful oxalate-templated syntheses of di-zinc macrocycles and their structural, spectroscopic, and electrochemical characterization. The focus of this work on zinc chemistry is due to the fact that zinc(II) enables the use of NMR spectroscopy as an easily accessible characterization method for the products of the exploratory synthesis; following a success of zinc chemistry, it could be further extended to other transition metals. We also describe our endeavors to extract the oxalate from the di-zinc macrocycles, including the structure of the di-zinc complex containing asymmetrically bound partially removed oxalate.

2. Results and discussion

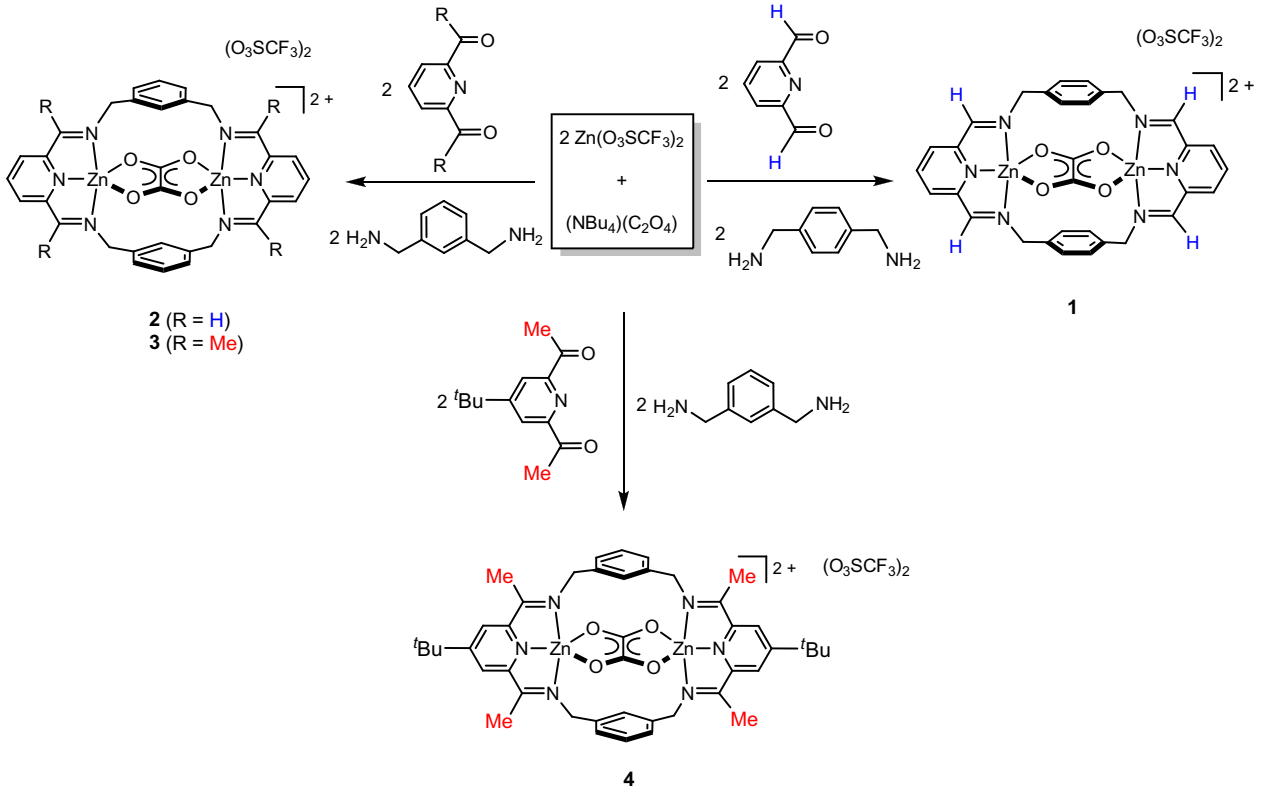
2.1. Synthesis of macrocycles **1**–**4**

Open-chain bis(iminopyridine) ligands can be synthesized by the addition of two equivalents of an aldehyde/ketone to the diamine in the absence of any templating agent [6]. A similar approach to the syntheses of the desired macrocycle employing various combinations of 2,6-pyridinedicarboxyadehyde/2,6-diacetylpyridine with *para*-xylylene (*p*-xylylene) and *meta*-xylylene (*m*-xylylene) diamines failed to produce soluble products, which suggests that the desired macrocycles were not obtained (see Section 4 for details). We were not able to characterize these products due to their lack of solubility in common organic solvents. We hypothesize that polymeric material was formed instead of the macrocycles.

Thus, we turned next to the template synthesis. Treatment of a solution of zinc triflate and tetrabutylammonium oxalate [7b] (Scheme 1) in methanol with solutions of 2,6-diformylpyrine (2,6-pyridinedicarboxalydehyde) and *p*-xylylene diamine consecutively resulted in the formation of a cloudy solution. The solution was stirred at room temperature overnight, after which the volatiles were removed and the resulting white solid was washed with THF. Drying the product afforded the macrocyclic complex $[(Zn_2(L^1)(C_2O_4)](O_3SCF_3)_2$ (**1**), containing bis(aldimino) chelates, in 79% yield. In contrast to the facile formation of the bis(aldimino)macrocycle linked by the *p*-xylylene bridge, the reaction of 2,6-diacetylpyridine with *p*-xylylene diamine failed to produce the corresponding bis(ketimino) macrocycle.

We have also investigated the formation of *m*-xylylene bridged macrocycles. Treatment of the mixture of zinc triflate with tetrabutylammonium oxalate in methanol with the solutions of 2,6-dicarboxypyridine and *m*-xylylene diamine forms the aldimino-based macrocyclic complex $[(Zn_2(L^2)(C_2O_4)](O_3SCF_3)_2$ (**2**) isolated as a white solid in 86% yield. A similar reaction sequence using 2,6-diacetylpyridine instead of 2,6-dicarboxypyridine forms the macrocyclic complex $[(Zn_2(L^3)(C_2O_4)](O_3SCF_3)_2$ (**3**) incorporating ketimino groups. Complex **3** was isolated as an orange solid in 73% yield. Thus, while the *p*-xylylene diamine linker enables only the formation of an aldimino-containing macrocycle, *m*-xylylene is capable of supporting both aldimino and ketimino macrocycles. The origin of this difference in reactivity is not entirely clear. One could speculate that in *p*-xylylene the amino nitrogens are further away from each other than in *m*-xylylene diamine and thus are less predisposed to support formation of small entropically unfavorable 2×2 macrocycles. While the more reactive formyl groups undergo facile condensation and cyclization with both *p*-xylylene diamine and *m*-xylylene diamine, the reaction is more sluggish with less electrophilic acetyl groups, and therefore only *m*-xylylene forms the desired 2×2 macrocycle.

We note that this "template effect" in the formation of the di-zinc complexes of the bis(imino)pyridine macrocycles described above is selective for oxalate. We have carried out similar self-assembly reactions using zinc triflate, 2,6-diacetylpyridine, and



Scheme 1. Oxalate-templated synthesis of di-zinc macrocycles **1**–**4**.