Available online at www.sciencedirect.com

ScienceDirect

Polyhedron 26 (2007) 1483–1492

POLYHEDRON

www.elsevier.com/locate/poly

Construction of macrocycle-based molecular stairs having pendant 4-aminopyridine, 4-dimethylaminopyridine and isonicotinonitrile groups

Wei Huang [a,b,*], Zhaolian Chu [a], Shaohua Gou [a,*], Takuji Ogawa [b,*]

[a] *State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

[b] *Research Center for Molecular Nanoscience, Institute for Molecular Science, Okazaki National Research Institutes, 5-1 Higashiyama, Myodaiji-cho, Okazaki, Aichi 444-8787, Japan*

Received 24 October 2006; accepted 15 November 2006
Available online 21 December 2006

Abstract

Self-assembly directed by dinuclear zinc(II) macrocyclic species with 4-aminopyridine, 4-dimethylaminopyridine and isonicotinonitrile produces four novel *trans* macrocycle-based complexes, namely three molecular stair elements and one one-dimensional (1D) polymeric stair. Controlled synthesis of the *cis* or *trans* isomers of 4-aminopyridine macrocyclic complexes (**2a** or **2b**), where the same rigid macrocyclic platform and counterion are used, can be achieved merely by the substitution of a protonic solvent for a non-protonic solvent, and that is further verified by theoretical calculations. However, when the two hydrogen atoms of the amino group are replaced by methyl groups (i.e. 4-dimethylaminopyridine) in order to block the formation of effective hydrogen bonds, only the *trans* isomers (**3a** and **3b**) can be obtained, either in protonic or non-protonic solvents. Moreover, when an isonicotinonitrile molecule, which has a stronger coordination ability and may act as a bidentate bridging ligand, is used, an infinite 1D macrocycle-based stair (**4b**) is generated *via* compensatory coordinative bonds as well as hydrogen bonding and face-to-face π–π stacking interactions.

Keywords: Macrocyclic complexes; *cis* or *trans* isomers; Molecular stairs; Controlled synthesis; Supramolecular interactions

1. Introduction

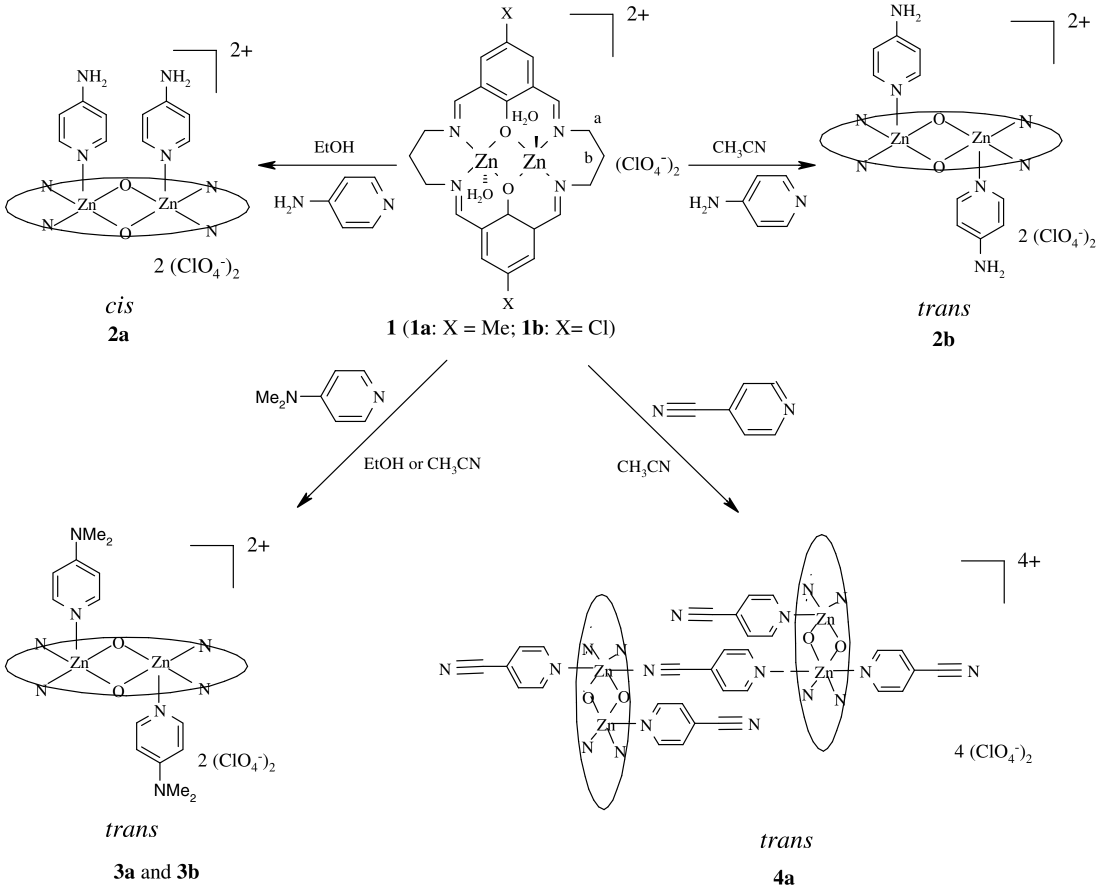
Coordinative bond driven self-assembly has received much attention in recent years, because such a method offers a new and effective approach for the construction of well-defined structures with a variety of topologies [1]. The resulting coordination polymers and networks have exhibited very interesting properties in many aspects of catalytic, magnetic, fluorescent, host-guest chemistry and racemic resolution [2]. Nowadays rational design and possible applications of these products are the main focus of crystal engineering [3]. Robson-type binucleating macrocyclic dianionic ligands have been found to be useful candidates for the modelling of metallobiosites and in the search for appropriate systems for activating simple molecules, owing to their special coordination ability with transition metals [4]. Some of these macrocycles have rigid planar structures where two metal ions are positioned in proximity, therefore they can serve as building blocks or metal sources (in terms of supramolecular chemistry) for self-assembly studies with organic functional groups.

---

[*] Corresponding authors. Address: State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. Fax: +86 2583314502.

E-mail addresses: whuang@nju.edu.cn (W. Huang), sgou@nju.edu.cn (S. Gou), ogawat@ims.ac.jp (T. Ogawa).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.11.055



Scheme 1. Schematic illustration for the preparation of the macrocyclic complexes.

For the dinuclear Zn(II) centers $[Zn_2L(H_2O)_2](ClO_4)_2$ (**1**) (Scheme 1), prepared from the [2+2] sodium template condensation of 1,3-diaminopropane and 2,6-diformyl-4-substitutedphenol, both penta-coordinate and hexa-coordinate modes are common, depending on the ligands used [5]. Weakly coordinated water molecules at each side of the macrocyclic framework [6] can be replaced by an additive ligand bearing strong coordination atoms. If small or linear ligands such as CH_3COO^- [7a] and N_3^- [7b] anions are applied to react with **1**, the *trans* positional isomers will be the dominant products in order to minimize the spatial hindrance, since the two zinc(II) ions are positioned in a distance less than 3.3 Å. Nevertheless, if ligands containing aromatic rings are involved, *cis* and *trans* conformations, with respect to the rigid macrocylic skeletons, are accessible upon interaction at the supramolecular level. Compared to conventional means, X-ray single-crystal diffraction is the most powerful tool to characterize these two possible isomers. In our previous reports, we have described two *cis* molecular ladder elements by using 4-aminopyridine and 4-pyridinecarboxylate [8] as well as two infinite coordinative bond driven 1D ladders in which macrocyclic platforms are connected by 4,4-bipyridine [9]. All of these complexes are further stabilized by complementary hydrogen binding and face-to-face π–π interactions.

Recently, there have been a few reports on 1D chains of this type of macrocycle with mono μ_2-bridging ligands, such as formate bridged dinuclear Zn(II) [10], 1,3-diaminopropane bridged dinuclear Ni(II) [11], acetylenedicarboxylate [12] and 7,7,8,8-tetracyanoquinodimethane bridged dinuclear Cu(II) complexes [13]. Moreover, several sandwich-like dimacrocyclic complexes with double μ_2-oxygen bridges like tetranuclear Zn(II) [14] and tetranuclear Fe(III) [15] complexes have also been documented. Additionally, we have reported two coordinative bond free donor-acceptor hydrogen-bond-supported layer complexes bearing 2-methylquinoline [14a] and 8-methylquinoline [16]. However, the motif of a molecular stair, where two aromatic rings adopt a *trans* conformation with respect to the macrocyclic plane, is a relatively new topology that is rarely reported to date [17]. Moreover, the study of regulating the *cis* and *trans* macrocyclic subunits has not been mentioned. In this paper, we report the self-assembly study of macrocyclic complexes having pendant 4-aminopyridine (4-ampy), 4-dimethylaminopyridine (4-dmampy) and isonicotinonitrile (4-cnpy) groups, in which these pyridine rings are *trans* relative to the rigid macrocyclic plane. Controlled synthesis of the *cis* and *trans* isomers can be achieved for the 4-ampy subunits and the experimental result is supported by DFT calculations.