Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Structure 796 (2006) 160–164
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Single-metal-ion-based molecular building blocks (MBBs) approach to the design and synthesis of metal–organic assemblies

Jacilynn A. Brant, Yunling Liu, Dorina F. Sava, Derek Beauchamp, Mohamed Eddaoudi *

Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620, USA

Received 25 January 2006; accepted 23 February 2006

Abstract

The single-metal-ion-based molecular building blocks (MBBs) approach for the construction of metal–organic assemblies, in which hetero-coordinated single metal ions are rendered rigid and directional via nitrogen–oxygen chelation with judiciously selected ligands, has been implemented. Single-metal-ion-based MBBs of the general formula $MN_x(CO_2)_y$ constitute the building units of metal–organic frameworks (MOFs) and metal–organic polyhedra (MOPs) presented herein. The octahedral MBB, $MN_2(CO_2)_4$, can occur as two structural isomers depending on the positioning of nitrogen atoms. The $MN_2(CO_2)_4$ MBBs contain two rings of heterochelation, and depending on the position of the oxygen atoms involved in heterochelation it is possible to generate three different building units (BUs) from the *cis*-$MN_2(CO_2)_4$ MBB and two BUs from the *trans*-$MN_2(CO_2)_4$ MBB. Assembly of the different BUs derived from the *cis*-$MN_2(CO_2)_4$ MBB, through a bifunctional ligand such as 2,5-pyridinedicarboxylic acid, permits the construction of diverse assemblies, such as a metal–organic 2D Kagomé lattice, a discrete octahedron, and a 3D diamondoid-like network. The *fac*-$MN_3(CO_2)_3$ MBB mediates a BU with the appropriate geometry to facilitate the formation of a metal–organic cube, and the BU resulting from the *mer*-$MN_3(CO_2)_3$ MBB is T-shaped. Tetrahedral building units (TBUs) can be derived either from $MN_4(CO_2)_2$ or $MN_4(CO_2)_4$ MBBs, from which zeolite-like MOFs have been constructed. Foremost, rationalization and systemization of such findings offer great potential toward the pursuit of the logical synthesis of functional metal–organic assemblies.

Keywords: Coordination polymers; Metal–organic frameworks (MOFs); Zeolite-like metal–organic frameworks; Porous materials; Single-metal-ion based MBBs

As the goals of design become attainable, the possibility of constructing solid-state materials with tailor-made functional properties, which can be adjusted and acclimated, becomes probable [1]. The ability to design and synthesize utilitarian porous materials is an ongoing challenge in solid-state chemistry. Zeolites [2] and synthetic microporous analogues [3], such as aluminophosphates (AlPOs) [4] and silicoaluminophosphates (SAPOs) [5] are inorganic porous materials of major commercial significance, however, alterations of their composition and structural features for applications beyond those of small guest molecules is generally difficult. The emerging field of coordination polymers offers a means to a novel class of potentially designable materials [6] and substantial progress has been made towards design as the use of molecular building blocks is becoming ubiquitous among solid-state synthetic chemistries [7–10]. The pathways for rational discovery of functional, unprecedented metal–organic assemblies, the solid-state materials of focus, are successfully developing as countless efforts to rationalize and systemize serendipitous discoveries progress into methods that are based on building blocks. One approach to the design and synthesis of metal–organic materials is to utilize premeditated single-metal-ion-based molecular building blocks (MBBs), which can be produced in situ from single metal ions heterochelated by multifunctional ligands. Depending on the coordination number of the single metal ion and the configuration of coordination, MBBs of various geometries can be synthesized. The challenge remains to control synthetic conditions in order to form targeted MBBs and thus synthesize intended metal–organic materials. Multitopic ligands that contain strategically placed coordinating groups, such as nitrogen atoms and carboxylate groups, capable of locking metal ions into position via bidentate chelation are used as bridging linkers. In conjunction, suitable single-metal-ions must be able to accommodate such ligands and permit the formation of high

---

* Corresponding author. Tel.: +1 8139749622; fax: +1 8139743203.
E-mail address: eddaoudi@cas.usf.edu (M. Eddaoudi).

0022-2860/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.02.064

coordination complexes. The ability to control several attributes, synthetic and geometric, is vital to the rational assembly of metal–organic materials; and much consideration and deliberation has been given to the selection of organic ligands to be used as linkers.

At the beginning of the 1990's, a plethora of experimentation and contemplation was put forth towards the selection, design and synthesis of nitrogen-based organic ligands for utilization in the construction of coordination polymers [11–14]. A metal–organic framework (MOF) based on a nitrogen-donating ligand, adiponitrile, has been reported in the literature as early as 1959 [15]. One particular class of ligands, 4,4′-bipyridine and its corresponding analogues, has received abundant attention and the involvement of these ligands in the enrichment of the metal–organic assemblies repertoire still continues [16,17]. Monodentate coordination results in a lack of building block rigidity and directionality, thus the reported 4-connected, three-dimensional nitrogen-based frameworks are commonly related to the cubic diamond net [12,18,19]. Frequent interpenetration renders their inherent pores inadequate for guest inclusion applications and when void space is present due to lack of interpenetration, the frameworks tend to collapse upon partial or complete removal of the guest molecules [20,21].

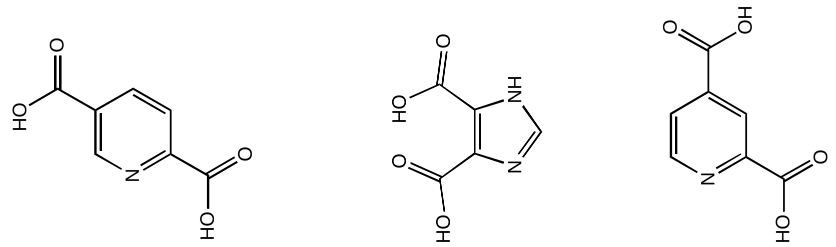
In the mid 1990's, a new class of compounds, which employ carboxylates as the coordinating entity, so as to introduce rigidity through multidentate coordination, has emerged. Carboxylate-based ligands can form secondary building units (SBUs) based on metal clusters [22] or MBBs consisting of single-metal-ions. Frameworks based on carboxylate clusters, where metal ions are locked in position, have proven to be porous due to the introduced rigidity in the inorganic building blocks [21,23–25].

Here, we present our strategy toward the logical synthesis of metal–organic assemblies, which consists of forming rigid and directional single-metal-ion-based MBBs, namely $MN_x(CO_2)_y$ (containing x N–, O– chelating moieties, and y bridging carboxylates). Our approach focuses on rendering each N–, O– single metal, formed in situ, rigid and directional using ligands, which permit the completion of the metal coordination sphere via a heterochelating functionality. Such ligands, which possess both the chelating and bridging functionality, are shown in Fig. 1. Hetero-coordinated single-metal-ions, MN_xO_y, have been employed in the construction of robust metal–organic assemblies by means of single-metal-ion-based MBBs, $MN_x(CO_2)_y$, specifically, $MN_2(CO_2)_4$, $MN_3(CO_2)_3$, $MN_4(CO_2)_2$, and $MN_4(CO_2)_4$.

Two types of structural isomers, *cis*- and *trans*-, are accessible in the octahedral hetero-coordinated single metal ion MN_2O_4, resulting in various types of $MN_2(CO_2)_4$ MBBs induced by ligand coordination through two sets of N–, O– heterochelation where the two remaining metal coordination sites are occupied by the monodentate carboxylate oxygen atoms. The different MBBs allow the generation of geometrically distinctive BUs, MN_2O_2, depending on the position of coordination of the chelated and monodentate carboxylate oxygen atoms. The *trans*-$MN_2(CO_2)_4$ MBB can yield a square-planar-like BU [26] and a see-saw-like BU, and the *cis*-$MN_2(CO_2)_4$ MBB affords two types of see-saw-like BUs as well as a square planar-like BU (Fig. 2).

We have previously reported [27] the use of a single-metal-ion-based MBB, with the general formula $InN_2(CO_2)_4$, in the assembly of two supramolecular isomers, a Kagomé lattice and a M_6L_{12} octahedron (Fig. 3). The metal–organic Kagomé lattice consists of a 6-coordinate $InN_2(CO_2)_4$ MBB, which functions as a 4-connected square-planar BU. The discrete M_6L_{12} octahedron is constructed from an $InN_2(CO_2)_4$ MBB, which constitutes a *trans* pyramidal BU, that results from distortion of the conceptual see-saw-like BU in which monodentate oxygen atoms are *trans*. Yet another MOF, involving the multifunctional 2,5-pyridinedicarboxylate ligand, has been constructed from the $MN_x(CO_2)_y$ MBB, namely $FeN_2(CO_2)_4$, which is derived from the *cis*-isomer of the 6-coordinate single-metal-ion MN_2O_4. The $FeN_2(CO_2)_4$ MBB represents the third type of *cis*-$MN_2(CO_2)_4$ MBB in which monodentate oxygen atoms are *cis* resulting in a see-saw-like BU. In this type of see-saw, two different types of atoms are present in the lever and the fulcrum, as opposed to the see-saw-like BU found in the octahedron structure that has one type of atom in the lever (oxygen) and the other type (nitrogen) in the fulcrum. The see-saw-like MBBs assemble through the multifunctional linkers to yield a MOF related to the cubic diamond net (Fig. 3).

The MN_3O_3 octahedral single-metal-ion can exist as two possible structural isomers, the *fac*-isomer and the *mer*-isomer (Fig. 4). Examples of the *mer*-$MN_3(CO_2)_3$ MBB exist [28–30], but to our knowledge, these types of MBBs involving five-member rings of chelation have not yet been reported as part of extended coordination polymers. We recently have reported the occurrence of *fac*-$NiN_3(CO_2)_3$, in



2,5-pyridinedicarboxylic acid 1*H*-imidazole-4,5-dicarboxylic acid 2,4-pyridinedicarboxylic acid

Fig. 1. Examples of ligands containing the chelating and bridging functionalities.