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Structural Reliability of Building Blocks in Coordination Framework Design

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ABSTRACT: *The use of the building-block methodology in designing coordination framework materials are discussed, with particular reference to the structural reliability of a given building block. The term structural reliability is defined for a given metal containing moiety as the degree to which that building block reproducibly adopts a given, predicted, coordination arrangement when reacted with a series of chemically related bridging ligands. This terminology is discussed with respect to a range of coordination frameworks constructed using Cd(NO$_3$)$_2$ as a building -block, which is demonstrated to be structurally unreliable.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:574–577, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10092

INTRODUCTION

The development of inorganic supramolecular networks and coordination polymers is an area of chemistry that is extremely topical [1]. This is due to the fundamental interest in not only self-assembly processes and supramolecular chemistry but perhaps, most significantly, crystal engineering [2]. The rational design of 3D molecular architectures is also of great importance when synthesizing new materials as the arrangement of the components within a material inherently affects its properties. Some success has recently been achieved in the synthesis of materials with solvent-inclusion [3] or gas adsorption characteristics [4], and with nonlinear optical properties [5].

Inorganic coordination networks are typically constructed using a building-block methodology, which allows a high degree of design through variation of metal, ligand or anion [6]. Our research in this area has to date focused on the *control* of network structure and topology through ligand modification, [7] and by developing new understanding of the more subtle effects of the anion [8], and crystallization conditions [9].

One of the most intriguing features of the building-block approach is that by judicial choice of components an almost limitless range of framework topologies can be prepared. These include both structures that mimic naturally occurring minerals and entirely new *unnatural* structural types. The most common types of coordination network include 3D diamondoid frameworks (Scheme 1a) [10], constructed using tetrahedral metal cations and linear bridging ligands, 2D square-grid (4,4) networks (Scheme 1b) [11], constructed using square-planar metal cation connecting nodes, and the family of compounds prepared by using “T-shaped” building blocks (Scheme 2) [12–21].

The latter family of compounds forms the basis of this article and in particular the Cd(NO$_3$)$_2$ building-block. T-shaped building-blocks have been typically introduced into coordination networks via the M(NO$_3$)$_2$ {M = Co [12,13], Ni [14], Zn [9], and Cd [9,15–19]} units. The potential to use such units as T-shaped connectors in combination with three pyridyl donors was first recognized by Fujita et al. who developed the original, earlier, structural characterization of M(NO$_3$)$_2$(py)$_3$ (M = Co, Zn, Cd; py = pyridine) (Fig. 1) [20].

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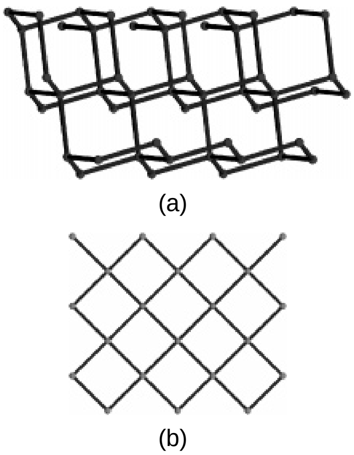
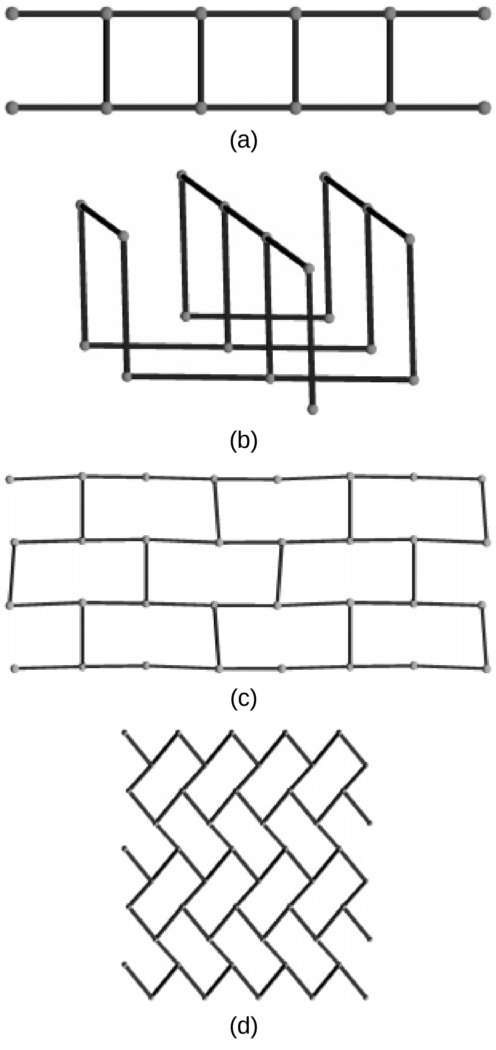


SCHEME 1 Diamondoid (a) and square-grid (4,4) grid structures (b) constructed using tetrahedral and square-planar building-blocks, respectively.



SCHEME 2 Representative motifs observed for coordination frameworks constructed using T-shaped building-blocks: (a) ladder, (b) bilayer, (c) brick-wall, and (d) herringbone.

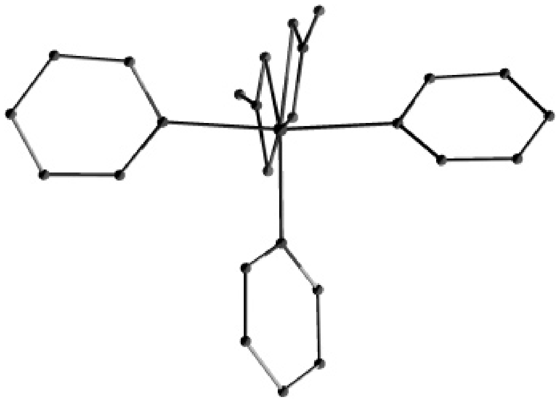


FIGURE 1 The "T-shaped" structure adopted by M$(NO_3)_2$-$(py)_3$ (M = Co, Zn, Cd) [20].

It is clear from the single crystal X-ray structures of these mononuclear complexes that the pyridine donors are arranged in a near perfect T-shape. Therefore, replacement of these pyridine donors with multi-pyridyl bridging ligands should afford extended structures based upon the T-shaped building-block. To utilize the T-shaped geometry induced by the M$(NO_3)_2$ moiety, a 2:3 M/L stoichiometry has to be targeted when using bidentate bridging ligands such as 4,4-bipyridine and its derivatives. Such a combination of T-shaped connector and rod-like bridges can give rise to a variety of 1D, 2D, and 3D structures (Scheme 2). These structures can be considered to be supramolecular isomers, of which, the simplest is the 1D molecular ladder (which has 1D polymeric propagation) [9,12]. Two-dimentional polymers are observed for herringbone [15–17], brick-wall [18], and bilayer structures [14]. Three-dimentional structures are less common but have been observed by using Co$(NO_3)_2$ with 4,4′-bipyridine as the connecting unit [13]. The balance between these structures, which is observed is extremely subtle and can often be influenced by the incorporation of even slightly different guest molecules.

Many of these structures have been observed when Cd$(NO_3)_2$ has been used as the T-shaped connector and these are summarized in Table 1. However, careful inspection of the literature will demonstrate to the reader that Cd$(NO_3)_2$ is far from a reliable building-block in that it does not uniformly adopt a T-shaped arrangement with pyridyl donors. Thus, early studies by Fujita illustrated that Cd$(NO_3)_2$ reacts with 4,4′-bipyridine to afford a (4,4) square grid structure in which each Cd(II) cation is coordinated by four pyridyl donors and each NO_3^- anion coordinates in a mono rather than the required bidentate fashion [11].

TABLE 1 Summary of Previously Reported Examples of $Cd(NO_3)_2$ Structures Which Contain the T-Shaped Connecting Node

Compound	*Framework Topology*	*Reference*
$[Cd_2(NO_3)_4(bpmebz)_3]_\infty$	Ladder	[18]
$[Cd_2(NO_3)_4(bpmefbz)_3]_\infty$	Brickwall	[18]
$[Cd_2(NO_3)_4(bpethyne)_3]_\infty$	Ladder	[17]
$[Cd_2(NO_3)_4(bpethyne)_3]_\infty$	Herringbone	[16]
$[Cd_2(NO_3)_4(apy)_3]_\infty$	Herringbone	[15]
$[Cd_2(NO_3)_4(3,3'\text{-pytz})_3]_\infty$	Ladder	[9]
$[Cd_2(NO_3)_4(4,4'\text{-pytz})_3]_\infty$	Ladder	[19]
$[Cd_2(4,4'\text{-pytz})_3(\mu\text{-}NO_3)\text{-}(NO_3)_2(MeOH)](OH)\}_\infty$	Polyknot	[19]

bpmebz = 1,4-bis-(pyrid-4-yl)methyl benzene; bpmefbz = 1,4-bis-(pyrid-4-yl)methyl 2,3,5,6-tetrafluorobenzene; bpethane = 1,2-bis-(pyrid-4-yl)ethane; bpethyne = 1,2-bis-(pyrid-4-yl)ethyne; apy = trans-4,4′-azobis(pyridine)]; 3,3′-pytz = 1,4-bis-(pyrid-3-yl)-2,3,5,6-tetrazine; 4,4′-pytz = 1,4-bis-(pyrid-4-yl)-2,3,5,6-tetrazine.

The coordinative flexibility of the $Cd(NO_3)_2$ moiety was further demonstrated for a series of compounds by using either 1,4-bis(pyrid-3-yl)-2,3,5,6-tetrazine (3-pytz) [9] or 1,4-bis(pyrid-4-yl)-2,3,5,6-tetrazine (4-pytz) [19]. Both ligands have been used to afford molecular ladders but the formation of these species is extremely sensitive to the solvent of crystallization. Indeed, 3-pytz reacts with $Cd(NO_3)_2$ in MeOH to afford a 1D chain, irrespective of M/L reaction stoichiometry, in which one molecule of the solvent occupies a coordination site thus preventing the formation of a T-shaped $Cd(NO_3)_2$ node. Using longer chain alcohols (EtOH, ^{i}PrOH) results in the formation of molecular ladders. In the case of 4-pytz, reaction in EtOH also affords a molecular ladder but in MeOH an extremely unusual structure (Fig. 2) is observed [19]. Not only is MeOH coordinated to the Cd(II) cation, but one of the NO_3^- anions bridges Cd(II) nodes such that what would otherwise be interpenetrating molecular ladders are linked into a single *polyknotted* 3D structure.

Indeed, bridging by NO_3^- anions is quite regularly observed when using $Cd(NO_3)_2$ building-blocks, often resulting in unusual structural types. The reaction between $Cd(NO_3)_2$ and 2,4-bis(4-pyridyl)-1,3,5-triazine (dpt) in MeCN affords a structure in which each Cd(II) node is coordinated by only two dpt ligands, which bridge the adjacent metal nodes to form tetranuclear metallacycles [21]. These metallacycles are linked via NO_3^- anions to yield a 2D sheet structure, $[Cd_2(NO_3)_4(dpt)_2(MeCN)]_\infty$, of 4.8^2 topology. These sheets are doubly interpenetrated in a parallel fashion to give a 2D supermolecule (Fig. 3). Indeed, when EtOH is used as a crystallization solvent, a 1D chain structure is observed when dpt reacts with $Cd(NO_3)_2$ even though the same solvent can be used to generate molecular ladders with 3-pytz and 4-pytz.

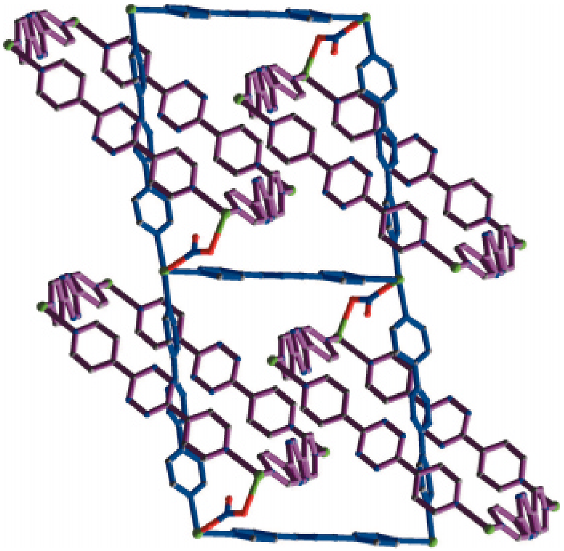


FIGURE 2 Polyknotted structure propagated via NO_3^- anion bridging of Cd(II) cations [19].

It can be seen from these reports that although the reaction of bridging dipyridyl ligands with the $Cd(NO_3)_2$ building-block can generate coordination polymer structures with T-shaped connections, this

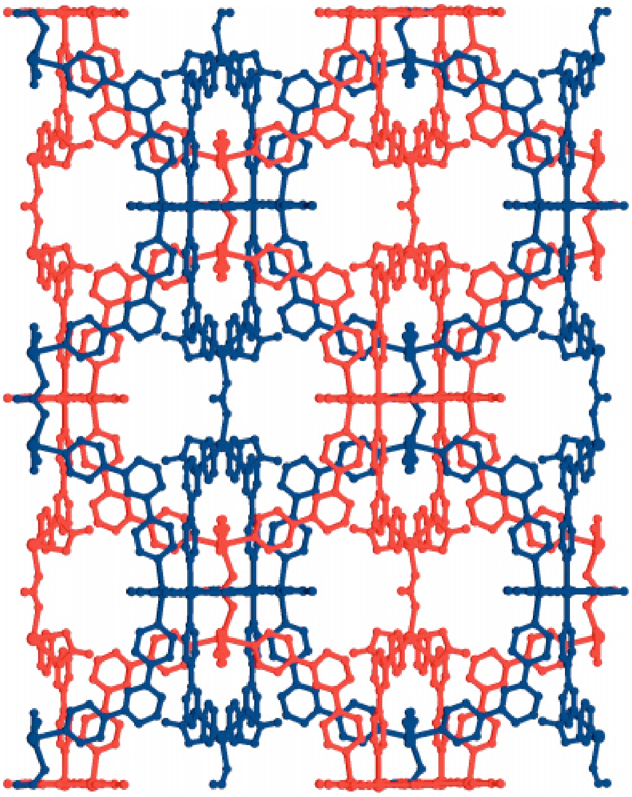


FIGURE 3 Interpenetrating 4.8^2 sheets of $[Cd_2(NO_3)_4\text{-}(dpt)_2(MeCN)]_\infty$ [21].

is a far from reliable methodology. Indeed, the $Cd(NO_3)_2$ building-block is sensitive to crystallization solvent and NO_3^- anion bridging between Cd(II) cations is regularly observed leading to unusual structures such as a polyknotted arrangement and the first observation of interpenetrated 4.8^2 sheets.

Structural reliability is clearly an important property for a building-block when designing and preparing coordination frameworks. Thus, if a framework with T-shaped connections is desired then it is preferable to use a structurally reliable building-block. Although other $M(NO_3)_2$ building-blocks may be more reliable, in particular $Co(NO_3)_2$, $Cd(NO_3)_2$ is certainly the most unreliable. However, this unreliability with respect to the formation of T-shaped connections should not necessarily be viewed as a disadvantage. Indeed, the structural flexibility of the $Cd(NO_3)_2$ moiety leads to the discovery of unusual structural phenomena and thus opens new avenues of research using coordination frameworks.

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