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From Discrete Linear Zn^{t}Bu$_2$ Molecules to 1D Coordination Polymers and 2D Fabrics

Janusz Lewiński,*,† Maciej Dranka,† Wojciech Bury,† Witold Śliwiński,† Iwona Justyniak,*,‡ and Janusz Lipkowski‡

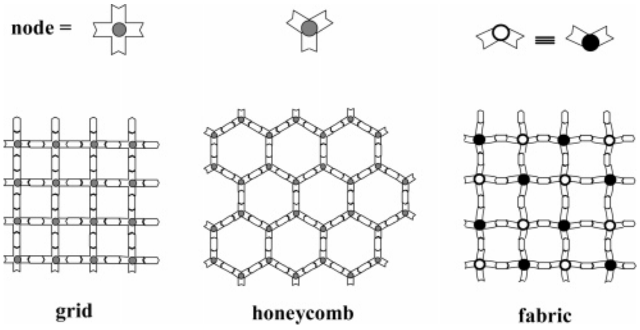
Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland, and Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Received October 9, 2006; E-mail: lewin@ch.pw.edu.pl

Structural studies of the homoleptic main group metal alkyls are of fundamental interest to rationalize their physical behavior and reactivity, and they provide novel supramolecular structures with remarkable topologies and often unusual metal−ligand interactions. For instance, the structure of heavier group 13 trimethyls is topologically equivalent to the well-known zeolite type structures,[1] and the structure characterization of Mg^{t}Bu$_2$ (i.e., the simplest dialkylmagnesium compound to be structurally authenticated) revealed that intra- and intermolecular $CH_3\cdots Mg$ agostic interactions play a substantial role in the molecular assembly.[2] As noted by Seyferth in the seminal paper on the history of zinc alkyls chemistry, in recent years, there has been a renaissance in dialkylzinc chemistry due to the utility of this family of compounds in important synthetic processes.[3] Up to now, however, the structurally authenticated homoleptic dialkylzincs consist of sterically strongly encumbered methylsilyl ligands,[4] though some of lower zinc alkyls were investigated by a host of techniques[5] including molecular weight determination, NMR and IR spectroscopy, gas electron diffraction, and photoelectron spectroscopy.[6] Other structurally known examples are restricted to a very recently reported divinylzinc compound[7] and some diarylzinc compounds, including the unique structure of diphenylzinc, in which the monomeric $ZnPh_2$ units are associated into unsymmetrical dimers that are linked by further weaker interactions into tetrameric units.[8] Moreover, systematic investigations on the structure and relative stability of the $ZnR_2(L)_n$ adduct as a function of the character of both the R substituent and L ligand are also relatively sparse. For instance, to our knowledge, of the Lewis acid−base adducts involving Zn^{t}Bu$_2$, only the three-coordinate $ZnR_2(L)$ complexes with the iminato ligand have been structurally authenticated.[9,10]

On the other hand, during the past decade, the controlled self-assembly of metal−ligand complexes has attracted great attention owing to their wide potential applications as functional materials, and many supramolecular compounds with intriguing structures have been synthesized and characterized, such as the 1D chains, 2D layers, and 3D open frameworks.[11] In regard to 2D metal−organic frameworks, where honeycomb, brick wall, grid, square, or rectangular networks are known, nanofabrics still await their realization (Chart 1).[12] We report here a system involving Zn^{t}Bu$_2$ and bipyridine ligands that brings together the major features mentioned above: the molecular structure of homoleptic metal alkyl and self-assembly of a metal−ligand complex leading to unprecedented topology of the 2D framework based on coordination polymers sustained by organometallic nodes.

Chart 1



The limited experimental structural data for *tert*-butylzinc derivatives stimulated our interest in Zn^{t}Bu$_2$ (**1**) and its adducts with pyridine ligands. The homoleptic starting compound **1** was prepared in high yield according to the literature procedure.[13]

Colorless crystals of **1** suitable for X-ray single-crystal determination were obtained by sublimation at 30 °C under vacuum (5×10^{-2} Torr), which proves the anticipated monomeric linear structure (Figure 1a). Compound **1** crystallizes in the orthorhombic *Pnma* space group, and the crystal structure consists of discrete monomeric molecules with two-coordinate zinc atoms. The Zn1

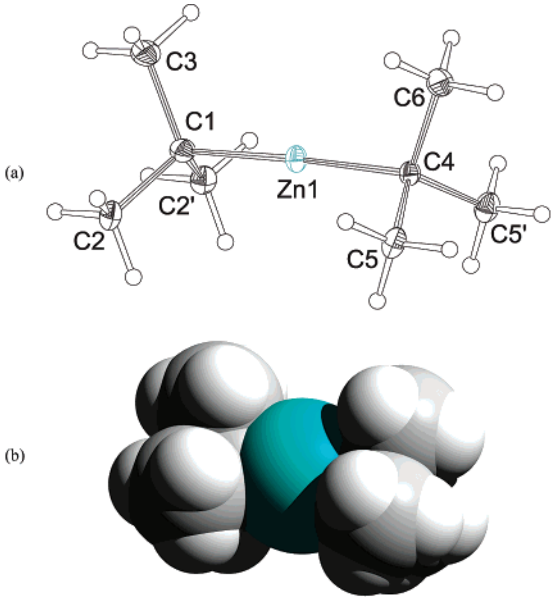


Figure 1. (a) Molecular structure of **1** with thermal ellipsoids drawn at the 30% probability level. (b) Space-filling representation of **1**.

[†] Warsaw University of Technology.
[‡] Polish Academy of Sciences.

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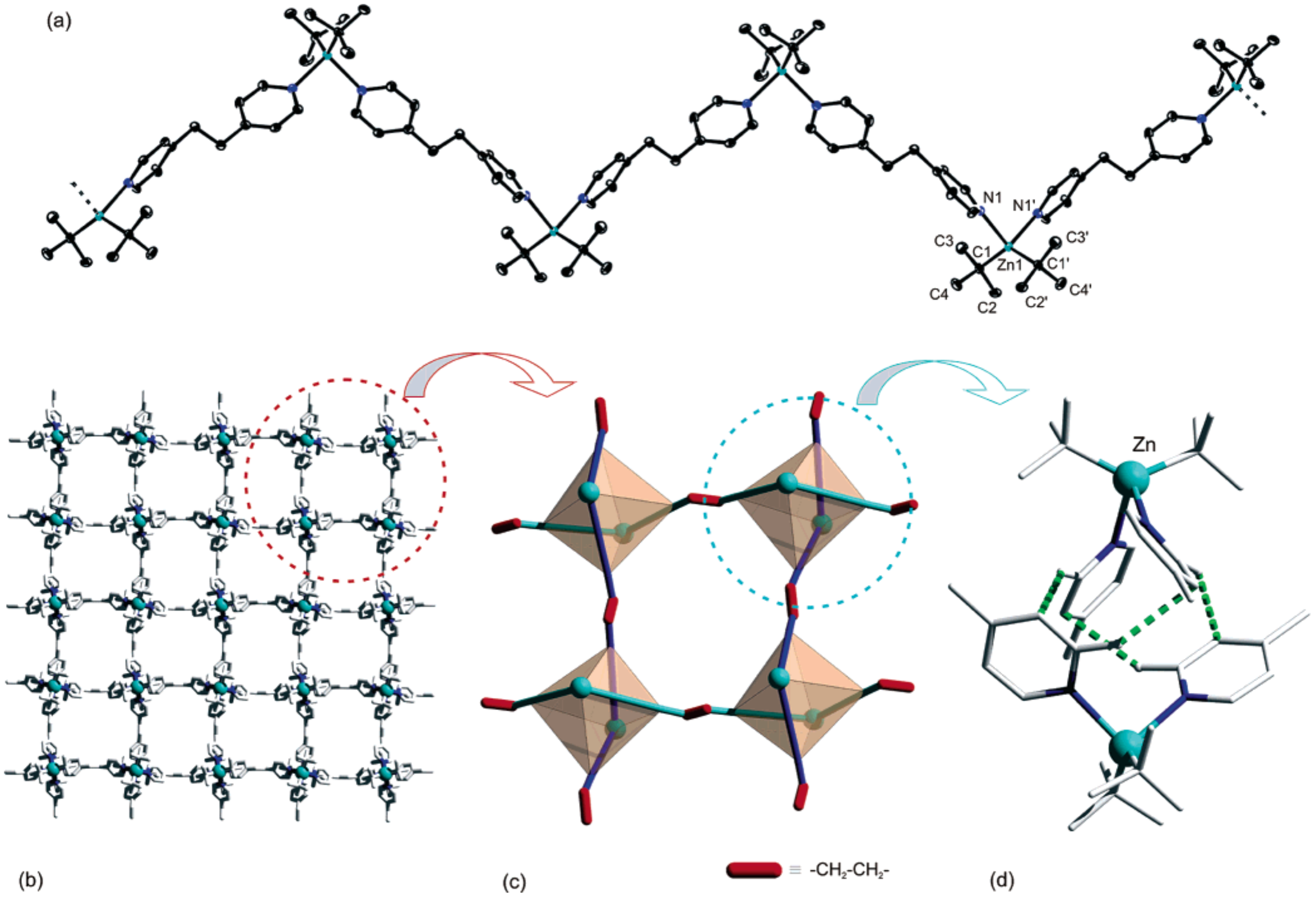

Figure 2. (a) ORTEP diagram of the zigzag-like 1D coordination polymer formed by **2**. (b) View toward the *ab* plane of the 2D framework in **2**. (c) View showing the network topology of polymer threads in a fabric. (d) Noncovalently bonded cage as a node responsible for coordination polymers weaving.

atom is coordinated by two terminal *tert*-butyl groups in a linear mode (C1−Zn1−C4 177.41(13)°), with the bond length of Zn1−C1 being 1.977(4) Å. The slight deviation of the C−Zn−C angle from the linear geometry may likely result from crystal packing forces or a very weak nonbonding interaction between the central zinc atom and two methyl groups from the neighboring Zn^{t}Bu$_2$ molecule (Figure S1). Strikingly, the ^{t}Bu groups adopt an eclipsed conformation with an idealized D_{3h} molecular symmetry, in contrast to the staggered conformation observed in Zn[C(SiMe$_3$)$_3$]$_2$;[4a] the reported DFT structure optimizations at the B3LYP/SDD level also predicted the staggered conformation of Zn^{t}Bu$_2$ with the D_{3d} molecular symmetry as the global minimum.[6] The observed conformation likely results from crystal packing forces; nevertheless, the space-filling representation of **1** shows that steric repulsion between alkyl groups is absent for the eclipsed conformation (Figure 1b).

The most common approach to build supramolecular architectures is the rational combination of organic spacers containing appropriate donor sites and metal ion nodes bearing a specific coordination geometry. In this regard, both zinc(II) ions and *N*,*N*-bidentate ligands are frequently employed as nodes and spacers, respectively, in metal−organic framework synthesis.[14] So, we anticipated that bipyridine ligands are ideal candidates for studying the coordination abilities of Zn^{t}Bu$_2$ and the self-assembly process involving dialkylzinc species. The treatment of **1** with 1 equiv of 1,2-bis(4-pyridyl)ethane (bpe)[15] in THF afforded the Lewis acid−base adduct [Zn^{t}Bu$_2$(bpe)] (**2**), which is soluble in THF and sparingly soluble in aromatic solvents. Square-like yellow crystals of **2** were obtained from a THF/toluene solution at 0 °C over a few hours. X-ray crystallographic analysis of **2** revealed the formation of an unprecedented 2D fabric structure.[12]

Compound **2** belongs to the tetragonal system with *I*41/*acd* space group. In the structure, each tetrahedral zinc center is coordinated by two bridging bipyridine molecules and two terminal *tert*-butyl groups with the bond lengths of Zn−N and Zn−C being 2.220(3) and 2.035(3) Å, respectively. The Zn−N distances are normal and comparable with those in the literature. The two pyridine ligands around a zinc center are nearly perpendicular to each other, with the N−Zn−N bond angle being 93.90(13)°. The zinc(II) ions, separated at ca. 13.645 Å, are bridged by 1,2-bis(4-pyridyl)ethane ligands. The bipyridine spacer adopts an *anti* conformation with the corresponding dihedral angle of 173.8°, and the two aromatic rings are not coplanar with each other (the twist angle between the rings is 69.29°). Strikingly, the zigzag-like inorganic−organic hybrid polymeric chains are weaved perpendicularly in the *ab* plane to form crystallographically independent lamellar fabric structures that are built of square meshes of 11.467 Å in size (Figure 2b). The hybrid chains are assembled into a 2D framework by C−H$\cdots\pi$ interactions involving pyridine rings (the shortest C−H$\cdots\pi$ contacts range from 2.848(3) to 3.005(4) Å). Formally, these interactions led to noncovalently bonded cages in the crossing points as is shown in Figure 2d. Thus, the weaving is controlled by the cooperative C−H$\cdots\pi$ interactions in the crossing points, and topologically, the resulting framework may be described as

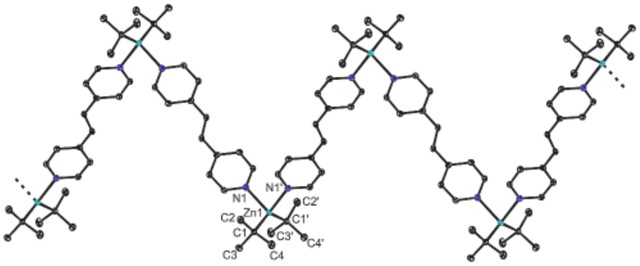

Figure 3. Zigzag-like 1D coordination polymer formed by [Zn^{t}Bu$_2$(bpene)] (**3**).

square layers with the noncovalently bonded cages as planar nodes and ethane backbones as linkers. The adjacent 2D grids in **2** stack along the *c*-axis with an offset of 1/2 along the *a*-axis and are shifted by 1/4 along the *c*-axis.

One of the major aims of crystal engineering is targeted at the predictable assembly of molecular species into extended architectures. To obtain more indepth understanding of the noncovalent assembly of molecules into the fabric structures and various factors that may have an influence over such processes, in the next step, we reacted **1** with 1,2-bis(4-pyridyl)ethylene (bpene). We anticipated that the latter bipyridine ligand of the inherent *anti* conformation is an ideal candidate for further probing the role of noncovalent forces in the supramolecular organization involving the bipyridine ligand. Needlelike dark red crystals of the Lewis acid−base adduct [Zn^{t}Bu$_2$(bpene)] (**3**) were obtained from a THF solution at 0 °C. X-ray crystallographic analysis of **3** revealed the formation of the 1D zigzag-like inorganic−organic hybrid polymeric chains (Figure 3). The geometric parameters of **3** are similar to those of **2**, with pyridine ligands completing a pseudotetrahedral Zn(II) coordination sphere. Both aromatic rings in the bipyridine spacer are essentially coplanar and are not involved in C−H···π interactions.

While the exchange of the central backbone from the C−C to C═C bond did not change the immediate environment around Zn(II) centers, it did have a major influence on the supramolecular structure of **3**. In the latter structure, the building blocks are still arranged in 1D coordination polymers, but the bipyridine spacer is not further involved in the self-assembly process. This can be interpreted by a more rigid configuration of 1,2-bis(4-pyridyl)-ethylene and a decrease in the freedom of rotation of pyridyl rings due to the π-conjugation of the unsaturated bond system. Upon coordination as a bridge, the ligand is locked into a planar conformation, and its participation in self-assembly is strongly limited. In the case of **2**, two aromatic rings are joined by the C−C single bond and the pyridyl rings can be more effectively involved in molecular recognition through C−H···π interactions. Thus, one may conclude that 1,2-bis(4-pyridyl)ethane is more structurally adaptive for the formation of noncovalent networks, and the mode of assembly of molecules in crystals is strongly influenced by the nature of the intermolecular interactions.

In conclusion, we have authenticated the molecular and crystal structure of Zn^{t}Bu$_2$ and constructed the unprecedented 2D fabric structure using the *tert*-butylzinc molecules and 1,2-bis(4-pyridyl)-ethane as simple building blocks. The X-ray crystal structure analysis revealed that the inorganic−organic polymeric chains weave to form fabric structures by the concerted C−H···π interactions involving the pyridine rings. We have also demonstrated that minor modifications in the organic linker caused by the introduction of the ethylene group lead to the decrease in the dimensionality of the supramolecular architecture; that is, Zn^{t}Bu$_2$ and 1,2-bis(4-pyridyl)ethylene are assembled into 1D zigzag-like chains. Thus, this work furnished a strategy for the generation of a new class of organometallic coordination polymers. Ongoing research is being focused on the use of various metal alkyls and *N*,*N*-linkers in order to elucidate subtle factors governing self-assembly processes. A simple access to this new class of coordination polymers opens also opportunities to probe their potentially intriguing chemistry.

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Supporting Information Available: Additional experimental, spectroscopic, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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