

Supramolecular and Coordination Polymer Complexes Supported by a Tripodal Tripyridine Ligand Containing a 1,3,5-Triethylbenzene Spacer

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By combining a tripodal tripyridine ligand containing a 1,3,5-triethylbenzene spacer (**L**) with several divalent transition-metal chlorides, we have selectively prepared a capsule-type supramolecular complex, $[\text{Pd}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O}$, and one-dimensional (1D) coordination polymer complexes, $[\text{Cu}^{\text{II}}(\text{L})\text{Cl}_2] \cdot \text{C}_2\text{H}_5\text{OH}$, $[\text{Co}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{CH}_2\text{Cl}_2$, and $[\text{Zn}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O}$, with a zigzag polymer chain, a linear polymer chain, and a ladder polymer chain structure, respectively. All the structures were established in detail by single-crystal X-ray diffraction analysis, and the factors inducing the structural differences among the complexes are discussed by taking account of the differences in coordination geometry (square planar vs tetrahedral) as well as metal–ligand binding strength in the complexes.

Development of supramolecular and coordination polymer complexes has recently attracted considerable attention due to the fundamental interest in self-assembly processes of transition-metal complexes, supramolecular chemistry, and crystal engineering.¹ Rational design of the molecular architectures is essential for the creation of new functional materials with solvent-inclusion or gas-adsorption characteristics or with electronic or nonlinear optical properties.^{2,3} So far, a wide variety of supramolecular complexes and coordination polymer complexes exhibiting different types of network topologies have been prepared to demonstrate that the supramolecular structure and the polymer framework

primarily depend on the structural functionality of ligands as well as the coordination geometry of the metal center.¹ Thus, a great deal of effort in this area has recently been devoted to develop novel multidentate ligands that can accommodate a unique supramolecular structure and a new network topology of coordination polymer.¹

On the other hand, the 1,3,5-triethylbenzene derivatives have attracted much recent attention as efficient building blocks for the development of functional molecules such as molecular receptors and metal ligands in the fields of molecular recognition chemistry and supramolecular chemistry.⁴ The 1,3,5-triethylbenzene spacer plays an important role in controlling the steric configuration of the functional groups introduced into its 2,4,6-positions. Namely, the functional groups, the metal binding moieties in the present ligand system, attached at the 2,4,6-positions are forced to position at the same side of the benzene ring of the spacer, since the *ababab* configuration (*a* denotes “above”, and *b* denotes “below”) is the most thermodynamically stable configuration due to the steric repulsion between the neighboring substituents as illustrated in Figure 1B.⁵ So far, the 1,3,5-triethylbenzene derivatives have been applied mainly for the synthesis of active site models for metalloenzymes,⁶ organometallic compounds,⁷ shape-selective anion and cation receptors,⁸ and supramolecules.⁹ However, little

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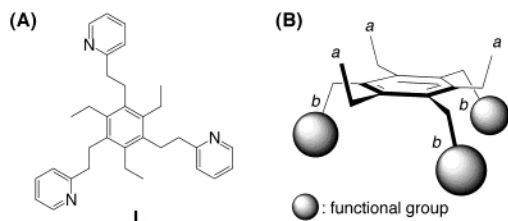


Figure 1. (A) Ligand **L**. (B) Schematic representation of the steric configuration of the substituents of the 1,3,5-triethylbenzene derivative.

attention has been focused on the application of 1,3,5-triethylbenzene as a building block of coordination polymers.¹⁰

In this study, we have developed a new tripodal tripyridine ligand (**L**) containing a 1,3,5-triethylbenzene spacer shown in Figure 1A to provide a capsule-type supramolecular complex and one-dimensional (1D) coordination polymer complexes with a variety of network topologies.

The tripodal tripyridine ligand (**L**) was prepared by the reaction of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene¹¹ and 2-picoyllithium, generated in situ by the reaction of 2-picoline and *n*-BuLi in THF at $-80\text{ }^{\circ}\text{C}$.¹² Slow liquid-phase diffusion between a MeOH solution of ligand **L** and a DMSO solution of $[\text{Pd}^{\text{II}}(\text{CH}_3\text{CN})_2\text{Cl}_2]$ in a glass tube ($\varnothing = 0.6\text{ cm}$) gave a Pd^{II} complex as a pale yellow single crystal. The crystal structure of the complex determined by the X-ray crystallographic analysis is shown in Figure 2.¹³ It is a trinuclear Pd^{II} complex supported by two ligands, providing a capsule-type supramolecule with $M_w = 1521.32$. The distances between the two triethylbenzene spacers is about 5 Å. Each Pd center has a four-coordinate square planar structure with the N_2Cl_2 donor set, where the two pyridine nitrogen atoms possess the *trans*-configuration, and so do the chloride anions. The complex looks like it has C_3

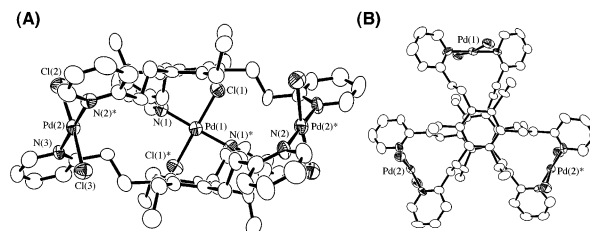


Figure 2. ORTEP drawings of $[\text{Pd}^{\text{III}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O}$ showing 50% probability thermal ellipsoids: (A) side view and (B) top view. Hydrogen atoms and water molecules are omitted for clarity.

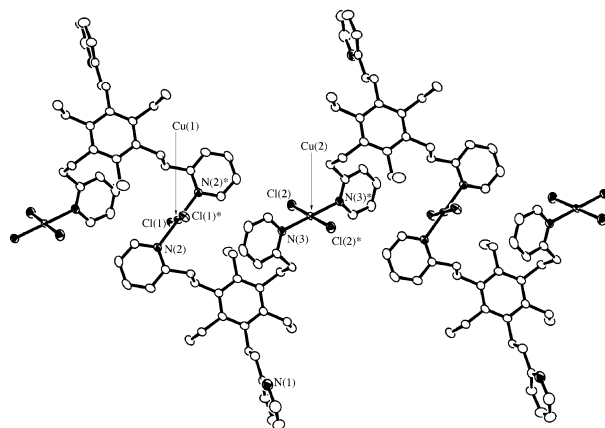


Figure 3. ORTEP drawing of $([\text{Cu}^{\text{II}}(\text{L})\text{Cl}_2] \cdot \text{CH}_3\text{CH}_2\text{OH})_n$ showing 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

symmetry (Figure 2B), but detailed inspection of the crystal structure indicated that there is a C_2 axis that is perpendicular to the $\text{Pd}(1)$ -coordination plane. Thus, the Pd ions are arranged as an isosceles triangle shape with a shorter Pd–Pd distance of 9.508(1) Å and a longer Pd–Pd distance of 10.054(1) Å.

The copper(II) complex obtained by liquid-phase diffusion between a CH_3CN solution of CuCl_2 and an ethyl acetate solution of **L** exhibits a violet color and a totally different structure from that of the Pd complex shown in Figure 2, even though the coordination geometry of the metal centers of both complexes is nearly the same (square planar, see below). In Figure 3 is shown the X-ray structure of the copper complex. The compound is a polymer complex consisting of CuCl_2 and the ligand in a 1:1 ratio. Each ligand is connected by CuCl_2 through the coordination of two of the three pyridine nitrogens, N(2) and N(3), constructing a 1D zigzag polymer chain structure, in which copper ions are linearly aligned with 7.6(4) Å separation. Thus, the remaining pyridine nitrogen N(1) does not participate in the metal coordination (Figure 3). The copper ion has a four-coordinate square planar structure with the N_2Cl_2 donor set having the *trans*-configuration with respect to the pyridine nitrogen atoms and the chloride ions, respectively.

Mechanistic details about the complex formation processes of the trinuclear Pd^{II} complex and the 1D-polymer Cu^{II} complex are not clear at present. One of the most important factors controlling the complex structures (capsule vs polymer) may be strength of the metal– N_{Py} (pyridine nitrogen) coordination bond. Namely, the stronger $\text{Pd}^{\text{II}}-\text{N}_{\text{Py}}$ bond may be practically irreversible, thus providing a

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- (12) Experimental details for the syntheses and characterizations are presented in the Supporting Information.
- (13) Details of the structural determination and the crystallographic data are deposited in the Supporting Information as a CIF.

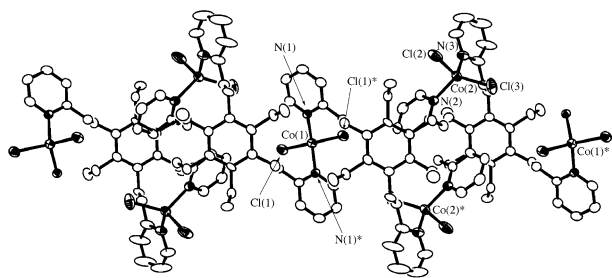


Figure 4. ORTEP drawing of $([\text{Co}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{CH}_2\text{Cl}_2)_n$ showing 50% probability thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

kinetically controlled product, that is, the capsule-type trinuclear complex, while the weaker $\text{Cu}^{\text{II}}-\text{N}_{\text{Py}}$ bonding may be reversible, thus affording a thermodynamically more stable polymer complex. In fact, there is no axially located ligand that might affect the complex structures in both the $\text{Pd}(\text{II})$ and $\text{Cu}(\text{II})$ complexes.

Replacement of CuCl_2 with CoCl_2 resulted in a drastic change in the polymer structure as shown in Figure 4. In this case as well, the compound has a 1D linear polymer structure, but the metal:ligand ratio of 3:2 is different from that of the copper complex ($\text{Cu}:\text{L} = 1:1$). As a result, all three pyridine ligands, N(1), N(2), and N(3), participate in the metal coordination to make the triangular arrangement of the three cobalt ions, and this triangular unit is repeated throughout the 1D linear polymer. One of the big reasons for the difference in structure between the copper complex and the cobalt complex may be the difference in coordination geometry between Cu^{II} and Co^{II} . Namely, the four-coordinate tetrahedral structure of the cobalt center brings the neighboring ligands closer each other, making it possible to construct the triangular unit of cobalt (see above), while the square planar structure of the metal center in the copper complex cannot adapt to such a ligand arrangement.

Adoption of ZnCl_2 induced further structural change of the polymer complex as shown in Figure 5. The colorless Zn^{II} complex exhibits a ladder polymer structure, in which the three pyridine rings of each ligand bind to a different Zn^{II} ion exhibiting a tetrahedral geometry (see also Scheme 1). Since the bond lengths and the coordination geometry of metal centers are relatively similar between the Co^{II} and Zn^{II} complexes, the reversibility of the metal– N_{Py} bonding and/or the solvent molecules incorporated into the crystal lattice (CH_2Cl_2 in the Co^{II} complex and H_2O in the Zn^{II} complex) may induce the structural difference between the Co^{II} and Zn^{II} polymer complexes.

In summary, a variety of complexes, $[\text{Pd}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O}$, $([\text{Cu}^{\text{II}}(\text{L})\text{Cl}_2] \cdot \text{CH}_3\text{CH}_2\text{OH})_n$, $([\text{Co}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{CH}_2\text{Cl}_2)_n$, and $([\text{Zn}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O})_n$, exhibiting totally different structures have been obtained by the treatment of the simple tridentate ligand **L** and divalent transition-metal chlorides as illustrated in Scheme 1. Although the mechanistic details of the complex

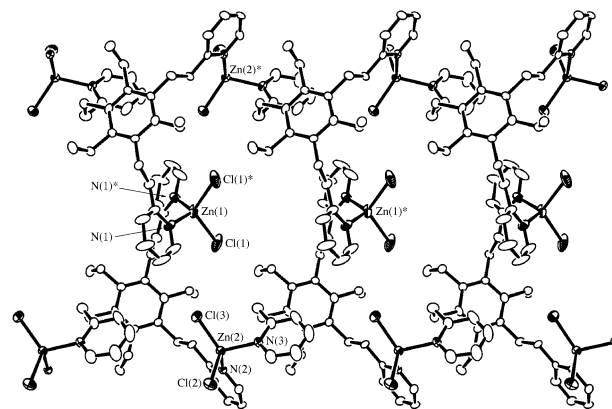
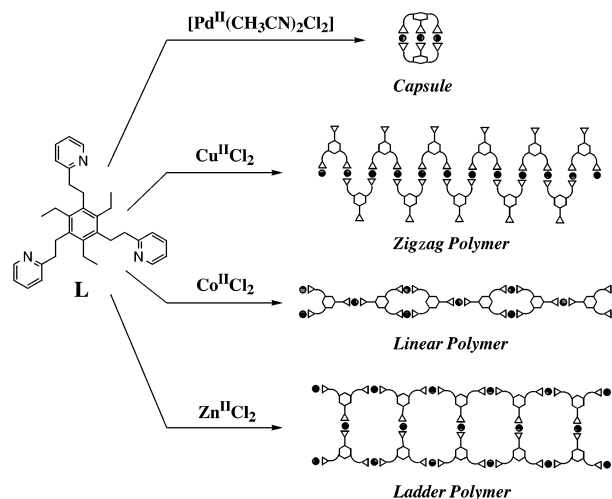


Figure 5. ORTEP drawing of $([\text{Zn}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O})_n$ showing 50% probability thermal ellipsoids. Hydrogen atoms and water molecules are omitted for clarity.

Scheme 1



formation processes have yet to be clarified, reversibility of the metal– N_{Py} bonding as well as the coordination geometry (square planar vs tetrahedral) of the metal center may be the important factors that control the supramolecular and polymer complex structures. The functional aspects of the present complexes are now under investigation.

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Supporting Information Available: Experimental details for the syntheses of the ligand and complexes. X-ray structural determination and details of the crystallographic data in a CIF-format file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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