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# Designed Self-Assembly of Molecular Necklaces

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***Abstract:*** This paper reports an efficient strategy to synthesize molecular necklaces, in which a number of small rings are threaded onto a large ring, utilizing the principles of self-assembly and coordination chemistry. Our strategy involves (1) threading a molecular "bead" with a short "string" to make a pseudorotaxane and then (2) linking the pseudorotaxanes with a metal complex with two cis labile ligands acting as an "angle connector" to form a cyclic product (molecular necklace). A 4- or 3-pyridylmethyl group is attached to each end of 1,4-diaminobutane or 1,5-diaminopentane to produce the short "strings" (**C4N4**$^{2+}$, **C4N3**$^{2+}$, **C5N4**$^{2+}$, and **C5N3**$^{2+}$), which then react with a cucurbituril (CB) "bead" to form stable pseudorotaxanes (**PR44**$^{2+}$, **PR43**$^{2+}$, **PR54**$^{2+}$, and **PR53**$^{2+}$, respectively). The reaction of the pseudorotaxanes with Pt(en)$(NO_3)_2$ (en = ethylenediamine) produces a molecular necklace [4]MN, in which three molecular "beads" are threaded on a triangular framework, and/or a molecular necklace [5]MN, in which four molecular "beads" are threaded on a square framework. Under refluxing conditions, the reaction with **PR44**$^{2+}$ or **PR54**$^{2+}$ yields exclusively [4]MN (**MN44T** or **MN54T**, respectively), whereas that with **PR43**$^{2+}$ or **PR53**$^{2+}$ produces exclusively [5]MN (**MN43S** or **MN53S**, respectively). The products have been characterized by various methods including X-ray crystallography. At lower temperatures, on the other hand, the reaction with **PR44**$^{2+}$ or **PR54**$^{2+}$ affords both [4]MN and [5]MN. The supermolecules reported here are the first series of molecular necklaces obtained as thermodynamic products. The overall structures of the molecular necklaces are strongly influenced by the structures of pseudorotaxane building blocks, which is discussed in detail on the basis of the X-ray crystal structures. The temperature dependence of the product distribution observed in this self-assembly process is also discussed.

## Introduction

One of the most significant developments in supramolecular chemistry during the past two decades is efficient synthesis of mechanically interlocked structures[1] such as catenanes, rotaxanes, and knots, which have attracted considerable attention due to not only their aesthetic appeal but also their potential applications as, for instance, molecular machines or switches.[2,3] The introduction of various template strategies has made the preparation of such topologically intriguing supermolecules much more feasible than before.[4−6] For example, Sauvage et al. exploited a metal ion as a template in their elegant synthesis of [2]catenanes.[4] Stoddart et al. prepared a series of catenanes and rotaxanes through covalent synthesis assisted by weak intermolecular interactions including π-donor−acceptor interactions.[5] However, these syntheses are generally carried out

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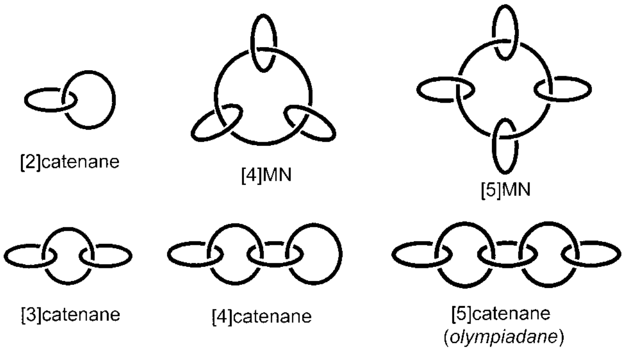
under kinetic control, which normally leads to a mixture of products. Therefore, efficient synthesis of complicated interlocked supermolecules remains challenging.

Another significant development in supramolecular chemistry during the past decade is the construction of discrete cyclic nanostructures by modular approaches based on coordination interactions of transition metal ions.[7−18] For example, Fujita et al.[8] and Stang et al.[9] independently reported the self-assembly of nanometer-sized supermolecules such as molecular squares and cages invoking simple graph theory and utilizing the square-planar coordination preference of Pd(II) and Pt(II). Furthermore, Fujita demonstrated that this approach can be successfully employed in the synthesis of elaborate catenanes.[7b]

For the past several years, we have been interested in transition-metal-directed self-assembly of interlocked supramolecular species. For example, we reported a simple approach to construct one- (1D),[19] two- (2D),[20] and three-dimensional (3D)[21] polyrotaxanes containing cucurbituril (CB)[22,23] as a "bead". CB has several desirable properties, making it an excellent molecular "bead" to synthesize interlocked structures: (i) a highly symmetrical structure with exceptional chemical stability, (ii) an internal cavity of $\sim$5.5 Å diameter which is accessible from the exterior by two carbonyl laced portals of $\sim$4 Å diameter, (iii) the ability to form stable inclusion complexes with protonated diaminoalkanes,[24] and (iv) its ability to move along the alkyl chain on external stimulation.[3d,25]

Having successfully synthesized 1D and 2D polyrotxanes, we turned our attention to the discrete interlocked structures, molecular necklaces in which a number of small rings are threaded onto a large ring. From the topology point of view, they constitute a subset of catenanes. For a given number of rings, a molecular necklace is uniquely defined. A molecular necklace consisting of $(n - 1)$ rings threaded on a large ring (total $n$ rings) is denoted as [$n$]MN, which is a topological stereoisomer of classical [$n$]catenane, where $n$ rings are mechanically interlocked in a linear fashion (Chart 1). For example, the molecular necklace [5]MN and "olympiadane"[5d] ([5]-catenane) synthesized by Stoddart et al. are topological stereoisomers. The minimum molecular necklace is [4]MN; the smaller molecular necklaces [2]MN and [3]MN are equivalent to [2]catenane and [3]catenane, respectively.

***Chart 1***



The first molecular necklaces were discovered by accident. In a synthesis of [3]catenanes, Sauvage and co-workers observed

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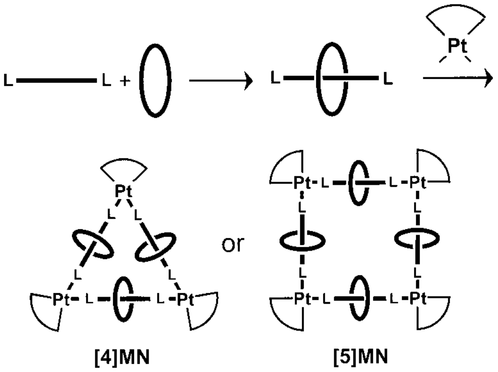
unexpected formation of a mixture of [*n*]MN ($n = 4-7$), some of which could be isolated and characterized by electrospray mass spectrometry.[26] Stoddart and co-workers also isolated and characterized a [4]MN in the synthesis of oligocatenanes.[27] These molecular necklaces, however, are kinetic products, and the desired products are usually accompanied by a host of byproducts, underlining the synthetic difficulties in the conventional template route.

To obtain the desired molecular necklaces exclusively under thermodynamic control, we have combined the strategy used to construct the polyrotaxanes with that for molecular squares developed by Fujita, Stang, and others. Herein we report the self-assembly of [4]MN and [5]MN from molecular "beads", "strings", and "angle connectors". Preliminary results in this area have been communicated.[28]

## Results

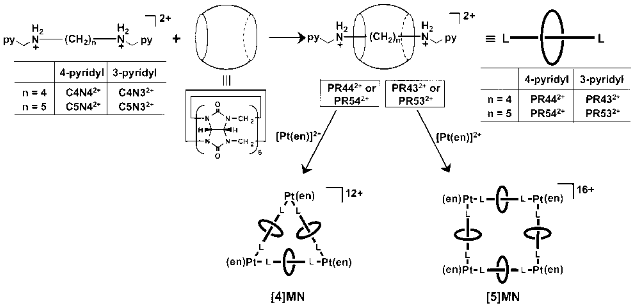
**Synthetic Strategy for Molecular Necklaces.** Our strategy for the construction of molecular necklaces is (1) to thread a molecular "bead" with a short "string" to make a pseudorotaxane and then (2) to link the pseudorotaxanes into a metal complex with two cis labile ligands acting as "angle connectors" to form a cyclic product (molecular necklace), as shown in Scheme 1.

***Scheme 1***



To achieve this, we designed short "strings" incorporating terminal donors in such a way that they not only form stable inclusion complexes with a CB "bead" but also are able to bind transition metal ions. A pyridylmethyl group with different pyridyl nitrogen positions was attached to each end of 1,4-diaminobutane or 1,5-diaminopentane to produce the short "strings" (**C4N4**$^{2+}$, **C4N3**$^{2+}$, **C5N4**$^{2+}$, and **C5N3**$^{2+}$, Scheme 2). These short "strings" react with a CB "bead" to form stable pseudorotaxanes (**PR44**$^{2+}$, **PR43**$^{2+}$, **PR54**$^{2+}$, and **PR53**$^{2+}$, respectively, Scheme 2). The overall 2+ charge of the pseudorotaxanes makes them soluble in water, although CB itself is sparingly soluble. The metal complex Pt(en)$(NO_3)_2$ (en = ethylenediamine) with two labile nitrate ligands at the cis positions is used as a "90° angle connector" to form molecular necklaces [4]MN and/or [5]MN upon reaction with the pseudorotaxanes.

***Scheme 2***



**Molecular Necklaces MN44T and MN44S.** The molecular necklace **MN44T** was obtained in near quantitative yield (by $^1$H NMR) by reacting **PR44**$(NO_3)_2$ with Pt(en)$(NO_3)_2$ in refluxing water for 24 h. The same product can be obtained when the three components, i.e., CB, **C4N4**$(NO_3)_2$, and Pt(en)$(NO_3)_2$, are allowed to react in equimolar amounts under similar reaction conditions. Figure 1 shows evolution of the $^1$H NMR spectra of the reaction mixture during the formation of **MN44T**. As the reaction proceeds, the initial singlet peak (marked with ◆) for ethylenediamine attached to Pt decreases while two new singlet peaks (marked with ● and $*$**)** grow downfield (Figure 1c). The downfield singlet peak ($*$) gradually replaces the two earlier peaks (Figure 1d). A similar evolution of the peaks corresponding to the pyridyl protons is also observed. Upon completion of the reaction, the spectrum of the reaction mixture becomes simple; only one set of signals was detected for the **PR44**$^{2+}$ and Pt complex (Figure 1e). This result suggests the quantitative self-assembly of a single supermolecule with a highly symmetric structure.

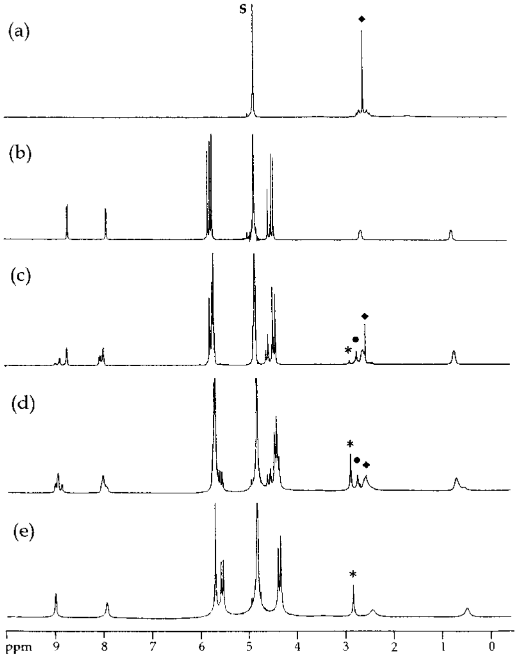


***Figure 1.*** Evolution of $^1$H NMR (300 MHz, $D_2O$) spectra during the formation of **MN44T**: (a) Pt(en)$(NO_3)_2$, (b) pseudorotaxane **PR44**$(NO_3)_2$, (c) a few minutes after beginning of the reaction between Pt(en)$(NO_3)$ and **PR44**$(NO_3)_2$ in refluxing $H_2O$, (d) after 6 h, and (e) after 24 h.

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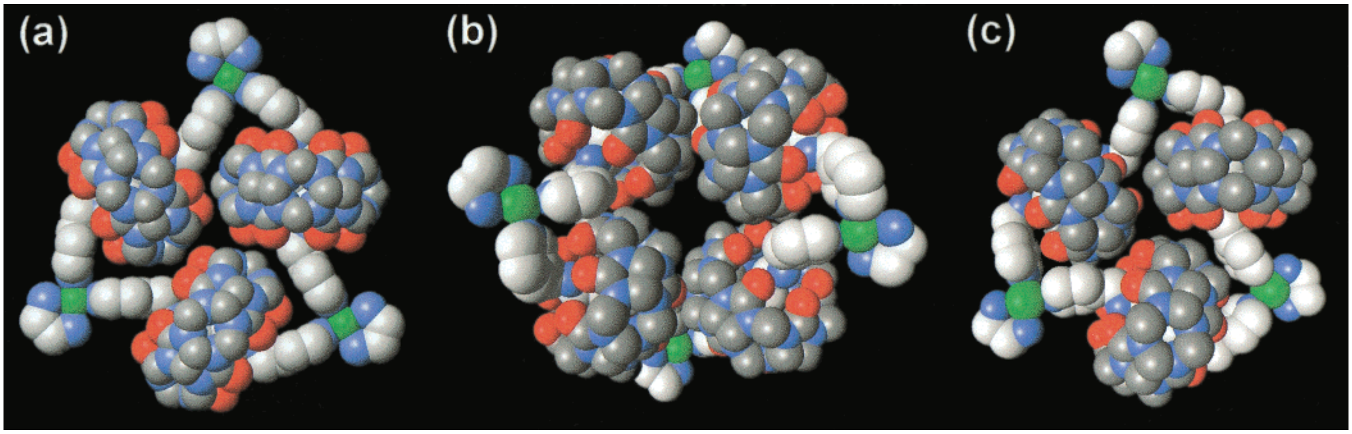


***Figure 2.*** Space-filling representions for the X-ray crystal structures of (a) **MN44T**, (b) **MN43S**, and (c) **MN54T**. Hydrogen atoms are omitted for clarity. Color codes: carbon, gray; nitrogen, purple; oxygen, red; Pt ion, green.

Since the pseudorotaxane **PR44**$^{2+}$ usually acts as a linear bridging ligand,[19a,20] our initial guess for the structure of **MN44T** was a square-shaped [5]MN with four platinum atoms at the corner. However, to our surprise, the electrospray ionization (ESI) mass data of **MN44T** are consistent with a [4]MN structure. This conclusion was confirmed by single-crystal X-ray structure analysis. The structure of **MN44T** reveals a [4]MN structure in which three CB molecular "beads" are threaded on a molecular triangle[17] (Figures 2a and 3a). In the crystal, the molecular necklace **MN44T** is sitting on a mirror plane, and a 3-fold symmetry axis perpendicular to the mirror plane passes through the center of the supermolecule. Each corner of the triangle is occupied by a Pt(en) moiety and each side by a sigmoidal-shaped pseudorotaxane unit **PR44**$^{2+}$, which links the two Pt moieties by coordination with its terminal pyridyl groups (Pt$\cdots$Pt = 19.476(1) Å). No unusual bond parameters are observed including the Pt$-$N$_{py}$ distances and the N$_{py}-$Pt$-$N$_{py}$ angle: Pt$-$N$_{py}$ = 2.029(12) and 2.025(10) Å, and N$_{py}-$Pt$-$N$_{py}$ = 89.3(4)°.

A CB molecular "bead" is held tightly on each side of the molecular triangle by strong hydrogen bonds between the protonated amines of the "string" and the oxygen atoms at the CB portals. It is interesting to note that the three CB molecular "beads" in **MN44T** are arranged in such a way that almost no vacant space exists inside the molecular triangle. A close contact between a CB oxygen and an equator carbon of the neighboring CB is observed: O(8)$\cdots$C(13′) = 2.975(10) Å (see Supporting Information), and the separation between the centroids of two CB "beads" is 12.073 Å.

When the reaction is carried out at room temperature for 70 h rather than under refluxing condition, a 1:1.1 mixture of [4]-MN(**MN44T**) and [5]MN(**MN44S**) is obtained, as confirmed by $^1$H NMR spectroscopy (Figure 4). From the product mixture, **MN44S** was isolated and characterized by NMR spectroscopy and ESI mass spectrometry, but its X-ray crystal structure remains to be determined.

**Molecular Necklace MN43S.** The reaction of **PR43**$^{2+}$ with Pt(en)(NO$_3$)$_2$ under refluxing conditions for 7 d produces molecular necklace **MN43S**. The $^1$H NMR spectrum of **MN43S** is very simple, similar to that of **MN44T**. The ESI mass spectrum of **MN43S**, however, is consistent with a [5]MN structure. In the X-ray crystal structure of **MN43S**, four CB

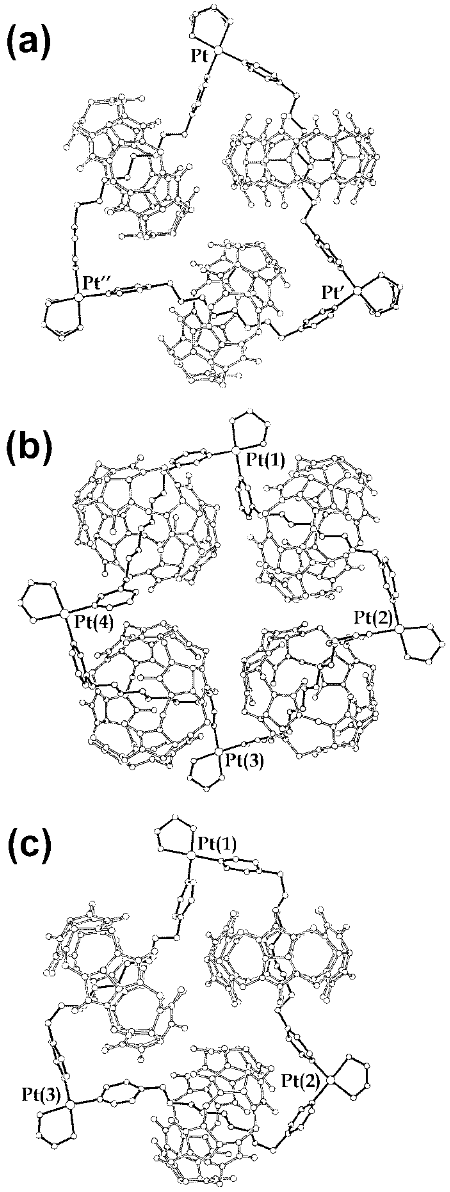


***Figure 3.*** Ball and stick representions for the X-ray crystal structures of (a) **MN44T**, (b) **MN43S**, and (c) **MN54T**. Hydrogen atoms are omitted for clarity.

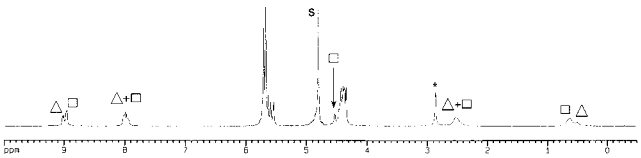


*Figure 4.* $^1$H NMR (300 MHz, $D_2O$) spectrum taken after the reaction of Pt(en)($NO_3$) and **PR44**($NO_3$)$_2$ in $H_2O$ at room temperature for 70 h, indicating the formation of a ~1:1.1 mixture of **MN44T** (△) ([4]MN) and **MN44S** (□) ([5]MN). The peaks for ethylenediamine attached to Pt are marked with *.

molecular beads are threaded on a square framework whose corners are occupied by the four Pt(en) units (Figures 2b and 3b). The average neighboring Pt···Pt distance is ~17.7 Å. It has a butterfly structure with a bend angle of 77.7°, and the distance between the two wingtips is ~22 Å (Figure 5a). The molecular necklace **MN43S** crystallizes in a chiral space group $P2_1$, which suggests that **MN43S** exists as two enantiomeric forms (Figure 5b). The bulk material of **MN43S** is a racemic mixture of the two enantiomers, but attempts to separate them by chrial columns have been unsuccessful.

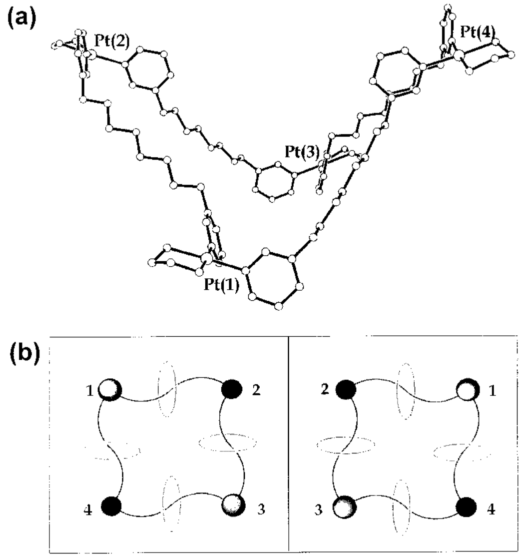


*Figure 5.* (a) Crystal structure of **MN43S** showing a butterfly structure of the framework; CB beads are omitted for clarity. (b) Schematic diagram for **MN43S** illustrating existence of two enantiomers.

**Molecular Necklaces MN54T and MN54S.** The reaction of **PR54**($NO_3$)$_2$ with Pt(en)($NO_3$)$_2$ in refluxing water affords molecular necklace **MN54T**. The X-ray crystal structure of **MN54T** reveals a [4]MN in which three CB molecular beads are threaded on a molecular triangle (Figures 2c and 3c). As in **MN44T**, each corner of the triangle is occupied by a Pt(en) moiety and each side by a rotaxane unit **PR54**$^{2+}$ linking the two Pt corners by coordination with its terminal pyridyl groups. Interestingly, the average Pt···Pt distance and the separation between the centroids of adjacent CB "beads" (18.38 and 11.96 Å, respectively) are shorter than those of **MN44T** (19.45 and 12.07 Å, respectively), which means that the triangular **MN54T** is smaller and sterically more congested than **MN44T**, even though one might expect that the rotaxane unit **PR54**$^{2+}$ would be longer than **PR44**$^{2+}$.

As seen in the reaction with **PR44**, when the reaction of **PR54**($NO_3$)$_2$ with Pt(en)($NO_3$)$_2$ is carried out at a lower temperature (80 °C), a mixture of [4]MN(**MN54T**) and [5]MN-(**MN54S**) is obtained in a ratio of 1:1.9, as confirmed by $^1$H NMR spectroscopy (Figure 6) and ESI mass spectrometry.

**Molecular Necklace MN53S.** The molecular necklace **MN53S** was obtained by the reaction of **PR53**($NO_3$)$_2$ with Pt(en)($NO_3$)$_2$ in refluxing water for 7 d. The product was characterized by $^1$H NMR spectroscopy, electrospray mass spectrometry, and elemental analysis. The $^1$H NMR spectrum of **MN53S** also shows a very simple pattern indicative a highly symmetric structure. The ESI mass spectrum of the product **MN53S** is consistent with a [5]MN structure, in which four molecular beads are threaded on a square framework. The crystal structure of **MN53S**, however, remains to be determined.

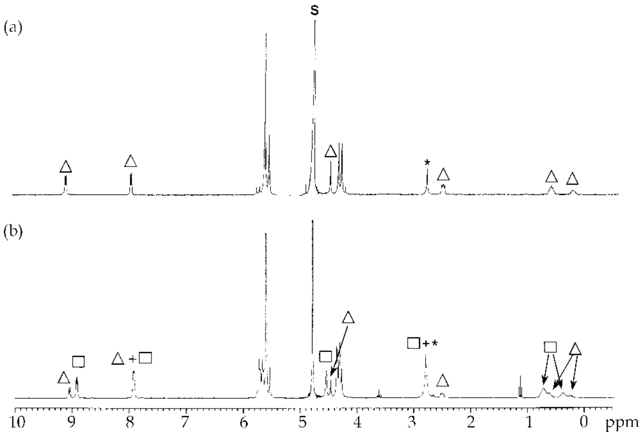


*Figure 6.* $^1$H NMR (300 MHz, $D_2O$) spectra taken after the reaction of **PR54**($NO_3$)$_2$ and Pt(en)($NO_3$)$_2$ (a) in fluxing $H_2O$ for 3 d and (b) in at 80 °C for 7 d. Peaks corresponding to **MN54T** ([4]MN) and **MN54S** ([5]MN) are marked with △ and □, respectively. The peaks for ethylenediamine attached to Pt are marked with *.

## Discussion

As illustrated by elegant work of Fujita, square-planar metal complexes with two cis labile ligands such as Pd(en)($NO_3$)$_2$ and Pt(en)($NO_3$)$_2$ have been successfully employed in self-assembly of molecular squares, cage, and catenanes.[8] However, attempts to construct molecular necklaces by reaction of the pseudorotaxanes with Pd(en)($NO_3$)$_2$ failed because the reaction always produces a mixture of oligomers, as indicated by complicated NMR patterns. On the other hand, the reaction of the pseudorotaxanes with Pt(en)($NO_3$)$_2$ yields the desired molecular necklaces in excellent yields, even though the process requires higher temperatures and longer reaction times than that with the corresponding Pd complex due to the stronger and more inert nature of a Pt−py (py = pyridine) bond compared to a Pd−py bond.

The structural features of the molecular necklaces **MN44T**, **MN43S**, and **MN54T** are compared in Table 1. The overall structures of the molecular necklaces depend on the structures of pseudorotaxanes and the reaction conditions, particularly reaction temperature.

The structures of pseudorotaxanes have a strong influence on the overall structure of the molecular necklace. In these pseudorotaxanes, the CB moiety is held tightly onto the linear string through hydrogen bonding between the protonated amines and the CB portal oxygens. As described in our previous studies[29] on transition-metal-directed self-assembly of polyrotaxanes, the preferred geometries of the pseudorotaxanes are dependent upon (i) the length of the linear "string" vis-à-vis

***Table 1.*** Comparison of Some Structural Parameters for **MN44T**, **MN43S**, and **MN54T**[a]

| | topology | $\theta_1$, $\theta_2$ (°) | $\phi$ (°) | P1···P2 (Å) | Pt···Pt′ (Å) |
|---|---|---|---|---|---|
| **MN44**[b] | [4]MN | 43.6, 17.0 | 180 | 13.47 | 19.48 |
| **MN43** | [5]MN | 59.9, 65.7 | 169.8 | 13.53 | 17.68 |
| | | 46.1, 75.6 | 154.3 | 13.56 | 17.67 |
| | | 57.6, 70.6 | 163.0 | 13.61 | 17.64 |
| | | 46.8, 70.7 | 160.2 | 13.44 | 17.72 |
| **MN54** | [4]MN | 59.7, 23.2 | 175.8 | 13.05 | 18.38 |
| | | 58.7, 21.2 | 169.7 | 12.90 | 18.28 |
| | | 54.9, 35.0 | 110.6 | 13.35 | 18.46 |

[a] The "bending" angles $\theta_1$ and $\theta_2$ are the angles between vectors **Pt−P1** and **P1−P2** and between vectors **Pt−P2** and **P1−P2**, respectively, and $\phi$ is the dihedral angle **Pt−P1−P2−Pt′**, where **P1** and **P2** are the centroids of the terminal pyridyl groups of a pseudorotaxane. [b] All of the rotaxanes are crystallographically equivalent.

the distance between the two carbonyl portals of CB and (ii) the position of the nitrogen atom on the terminal pyridine groups. To compare the structural features of the pseudorotaxanes, we define "coordinate vectors" and "ligand vector" as illustrated in Figure 7. The former represents the vector connecting the centroid of the terminal pyridyl group and the metal to which the pyridyl group is coordinated, while the latter represents the vector passing through two centroids of the terminal pyridyl groups. The "bending angles" ($\theta_1$ and $\theta_2$) are defined as the angles between the coordinate vectors and the ligand vector, and the dihedral angle between the two coordinate vectors is given as $\phi$. These values for the molecular necklaces **MN44T**, **MN43S**, and **MN54T** are collected in Table 1.

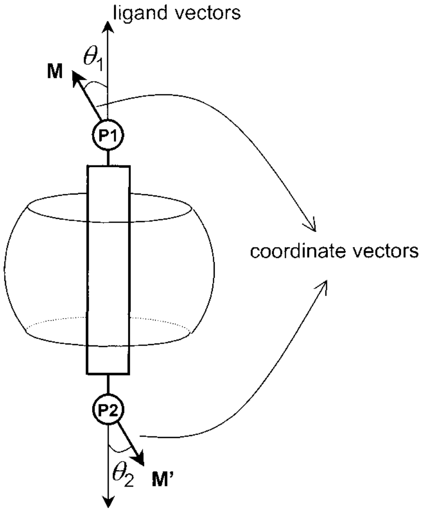


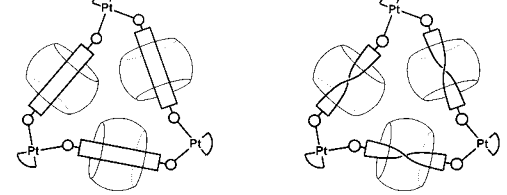
***Figure 7.*** "Ligand" vector, "coordinate" vector, and bending angles ($\theta_1$ and $\theta_2$). **P1** and **P2** are the centroids of the terminal pyridyl groups of a rotaxane, and **M** and **M′** are the two metal ions to which the rotaxane unit is coordinated.

Our previous studies[29] on transition-metal-directed self-assembly of one-dimensional polyrotaxanes showed marked differences in the overall structure of the polyrotaxanes from the pseudorotaxanes, **PR44**$^{2+}$ and **PR43**$^{2+}$. In both cases, the distance between the two ammonium nitrogen atoms of the "string" (**C4N4**$^{2+}$ or **C4N3**$^{2+}$) well matches the separation between two portals of CB when the "string" is fully stretched with all methylene units in anti conformation. Since the interactions between the "bead" and the "string" are maximized in this conformation, the flexible "string" turns into a rigid, bulky ligand upon formation of the pseudorotaxane **PR44**$^{2+}$ or **PR43**$^{2+}$. In both cases, however, the coordinate vectors are inclined at a certain angle from the ligand vector and at the same time point in opposite directions with respect to each other ($\phi$ = ~180°). Therefore, the pseudorotaxane behaves like a rigid, ditopic ligand with a sigmodal shape. While the distance between the centroids of two terminal pyridyl groups is almost the same in the two pseudorotaxanes, the "bending" angles in **PR43**$^{2+}$ ($\theta_1$, $\theta_2$: ~45−75°) are considerably larger than those in **PR44**$^{2+}$ ($\theta_1$, $\theta_2$: ~10−40°) since the former has meta-substituted pyridine groups whereas the latter has para-substituted ones. This leads to a shorter distance ("linking" distance) between the two metal centers bridged by **PR43**$^{2+}$ (~17.5 Å) compared to that bridged by **PR44**$^{2+}$ (~20 Å), as also observed in the transition-metal-linked 1D polyrotaxanes.

These structural differences between **PR44**$^{2+}$ and **PR43**$^{2+}$ may explain the fact that the former forms a [4]MN with a triangular framework (**MN44T)** and the latter forms a [5]MN with a square framework (**MN43S**) upon reaction with Pt(en)($NO_3$)$_2$ under refluxing condition. The larger "bending" angle and smaller "linking" distance of **PR43**$^{2+}$ compared to those in **PR44**$^{2+}$ make it difficult to form a stable [4]MN structure with **PR43**$^{2+}$, as such a structure would lead to strong steric repulsion among the three bulky CB beads threaded onto a small triangular framework.

Compared to **PR44**$^{2+}$ and **PR43**$^{2+}$, on the other hand, **PR54**$^{2+}$ and **PR53**$^{2+}$, having five methylene units between the two ammonium nitrogen atoms of the "string", exhibit more flexibility in conformation because the separation between the two nitrogen atoms does not match that between the two portals of CB. All three **PR54**$^{2+}$ units in the crystal structure of **MN54T** have a sigmodal shape similar to that of **PR44**$^{2+}$ in **MN44T** (Figure 3c): two of the three **PR54**$^{2+}$ units in **MN54T** take an "anti" conformation ($\phi$ = ~170°) for the two coordinate vectors, whereas the remaining unit has a "gauche" conformation ($\phi$ = ~110°).[30] A close inspection of the structure further reveals that the "string" (**C5N4**) of the pseudorotaxane (**PR54**$^{2+}$) is considerably "twisted" to achieve the overall sigmodal structure (Figure 3c and Chart 2). The severe "bending" ($\theta_1$, $\theta_2$: ~25−60°) and "twisting" of the "string" in **PR54**$^{2+}$ compared to **PR44**$^{2+}$ makes the "linking" distance of the former (Pt···Pt ~18.4 Å) considerably shorter than that of the latter (~19.5 Å), which results in a more sterically congested triangular structure for **MN54T**.

***Chart 2***



The effect of the shape and length of organic "strings" on the structures of molecular necklaces is further illustrated by

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[29] Park, K.-M.; Whang, D.; Lee, E.; Heo, J.; Kim, K. *Chem. Eur. J.* **2002**, *8*, 498.

[30] If the "string" (**C5N4**) of **PR54**$^{2+}$ were in a fully stretched conformation, the coordinate vectors of **PR54**$^{2+}$ would be inclined from the ligand vector in the same directions ($\phi$ = ~0°), and the angle between the coordinate vectors would be ~107.5°.

another pseudorotaxane, **PR53**$^{2+}$. Although X-ray crystal structures of molecular necklaces made of **PR53**$^{2+}$ have not been determined yet, those of 1D and 2D polyrotaxanes built with **PR53**$^{2+}$ are available.[19b,29] According to these structures, the meta-substituted pyridine terminal groups of **PR53**$^{2+}$ in general make the "linking distance" shorter compared to that of **PR54**$^{2+}$ with para-substituted pyridine terminal groups. From these structural features one might expect that **PR53**$^{2+}$ would form a [5]MN as a thermodynamic product rather than a sterically congested [4]MN, which has been indeed confirmed by ESI mass spectrometry.

As described above, when **PR44**$(NO_3)_2$ and **PR54**$(NO_3)_2$ are reacted with $Pt(en)(NO_3)_2$, a [4]MN is exclusively obtained under refluxing condition, but both [4]MN and [5]MN are produced at a lower temperature. The origin of the temperature dependence of the product distribution in this self-assembly process has not been fully understood. A simple explanation may be that [4]MN is a thermodynamic product while [5]MN is a kinetic product formed during the self-assembly process at a lower temperature. However, another possibility is that it is a consequence of competition between enthalpy and entropy effects. More specifically, when an enthalpically favored supermolecule is in equilibrium with an entropically favored one in a self-assembly process, lowering reaction temperature can make the enthalpy effects more prominent than the entropy effects. Therefore, under refluxing conditions, entropic effects may overcome the enthalpic cost associated with the sterically congested and strained [4]MN structure.[31] However, the strain-free [5]MN and entropically favored [4]MN may coexist at a lower temperature, where the enthalpic and entropic factors compete with each other. If it is the case, thermal or entropic effects strongly affect the equilibrium in this thermodynamically controlled self-assembly reaction. However, a more careful study is needed to establish the origin of the temperature dependence of the product distribution. Whatever the origin may be, it is interesting to observe such a temperature dependence of the product distribution in the metal-ion-directed self-assembly process, although several examples of concentration-dependent equilibria between the molecular square and triangle in the self-assembly process have been reported.[18]

Finally, because the necklace formation reaction is carried out in the highly polar medium, the hydrophobic interactions between the bulky CB beads with the alkyl chains may contribute to the formation of trigonal-shaped **MN44T** and **MN54T** and stabilize the structures. It is well known that such hydrophobic interaction in polar media can be a key factor in the metal-ion-mediated self-assembly of interlocked supermolecules.[8d]

## Conclusion

In this paper, we have presented an efficient strategy to synthesize molecular necklaces, particularly [4]MN and [5]MN utilizing the principles of self-assembly and coordination chemistry. The supermolecules reported here are the first series of molecular necklaces obtained as thermodynamic products. The overall structures of the molecular necklaces are influenced by the structures of pseudorotaxane building blocks and the reaction conditions, particularly reaction temperature.

By varying the structures of bridging pseudorotaxanes and angle connectors and carefully choosing the reaction conditions, one should be able to construct a variety of molecular necklaces with different sizes, shapes, and numbers of molecular beads. For example, we have recently succeeded in the synthesis of molecular necklaces [5]MN using preorganized L-shaped pseudorotaxanes and metal ions or metal complexes as angle connectors.[32] Furthermore, the present approach to molecular necklaces can be followed to construct other extended or discrete interlocked structures. For example, we have recently demonstrated a new synthetic strategy to modular porous solids, which utilizes molecular necklaces as secondary building blocks.[33] Finally, such a highly efficient synthesis of topologically intriguing supramolecular species may provide insights into construction of other nanoscale assemblies with well-defined structures and functions.

## Experimental Section

**General Methods.** All reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied without further purification. $^1H$ NMR spectra were recorded on a Bruker DRX500 or AM300 spectrometer. The electrospray mass spectrometry data[34] were obtained with a JEOL JMS-700T mass spectrometer. The counterions of samples for mass analysis were exchanged with $PF_6^-$ ions.

**MN44T. Method A.** A mixture of **PR44**$(NO_3)_2$ (110.0 mg; 79.0 $\mu$mol) and $Pt(en)(NO_3)_2$ (30.0 mg; 79.0 $\mu$mol) in water (40 mL) was heated at reflux for 24 h. After the volume of the solution was reduced to ~3 mL under a reduced pressure, ethanol was added to the solution to precipitate the product **MN44T**, which was filtered, washed with ethanol, and dried (135.2 mg, 91%).

**Method B.** Cucurbituril decahydrate (53 mg; 53 $\mu$mol), **C4N4**$(NO_3)_2$ (21 mg; 53 $\mu$mol), and $Pt(en)(NO_3)_2$ (20 mg; 53 $\mu$mol) were added to water (20 mL). The mixture was heated at reflux for 24 h. After the volume of the solution was reduced to ~3 mL under a reduced pressure, ethanol was added to the solution to precipitate the product **MN44T**, which was filtered, washed with ethanol, and dried (89.6 mg, 90%). Slow recrystallization of the crude product from water/ethanol gave the crystalline product (65.5 mg, 66%). Mp > 220 °C dec. $^1H$ NMR (300 MHz, $D_2O$): $\delta$ 0.47 (br, 12H), 2.43 (br, 12H), 2.82 (s, 12H), 4.31 (s, 12H), 4.34 (d, $J = 15.5$ Hz, 36H), 5.54 (d, $J = 15.5$ Hz, 36H), 5.68 (s, 36H), 7.93 (s, br, 12H), 8.99 (d, $J = 5.3$ Hz, 12H). ESI-MS: $m/z$ 1433.0 (**MN44T** $- 4PF_6^-)^{4+}$, 1117.5 (**MN44T** $- 5PF_6^-)^{5+}$, 907.0 (**MN44T** $- 6PF_6^-)^{6+}$, 756.9 (**MN44T** $- 7PF_6^-)^{7+}$. Anal. Calcd for $Pt_3C_{162}H_{204}N_{102}O_{72}\cdot 18H_2O$: C, 34.49; H, 4.29; N, 25.32. Found: C, 34.31; H, 4.03; N, 25.03.

**Low-Temperature Synthesis of MN44T and MN44S.** A mixture of **PR44**$(NO_3)_2$ (43.0 mg; 30.3 $\mu$mol) and $Pt(en)(NO_3)_2$ (11.5 mg; 30.3 $\mu$mol) in water (20 mL) was stirred at room temperature for 70 h. After the volume of the solution was reduced to ~3 mL under a reduced pressure, ethanol was added to the solution to precipitate a ~1:1.1 mixture of **MN44T** and **MN44S**, which was filtered, washed with ethanol, and dried (51.0 mg). Slow recrystallization of the product mixture from water/ethanol gave pure crystalline **MN44T**. After recrystallization of triangular **MN44T**, ethanol was added to the mother liquor to precipitate the product square **MN44S** (24.0 mg, 45%). Mp > 220 °C dec. $^1H$ NMR (300 MHz, $D_2O$): $\delta$ 0.60 (br, 16H), 2.49 (br, 16H), 2.82 (s, 16H), 4.37 (d, $J = 15.6$ Hz, 48H), 4.49 (s, 16H), 5.65

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[31] Preliminary molecular mechanical calculation suggests that the structure of MN44T is more sterically congested and strained than that of MN44S.

[32] (a) Roh, S.-G.; Park, K.-M.; Park, G.-J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 638. (b) Kim, S.-Y.; Roh, S.-G.; Park, K.-M.; Park, G.-J.; Sakamoto, S.; Yamaguchi, K.; Kim, K., manuscript in preparation.

[33] Lee, E.; Kim, J.; Heo, J.; Whang, D.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 399.

[34] Sakamoto, S.; Fujita, M.; Kim, K.; Yamaguchi, K. *Tetrahedron* **2000**, *56*, 955.

(s, 48H), 5.72 (d, *J* = 15.6 Hz, 48H), 7.99 (d, *J* = 6.4 Hz, 16H), 8.93 (d, *J* = 6.4 Hz, 16H). ESI-MS: *m*/*z* 1538.1 ($\mathbf{MN44S} - 5PF_6^-)^{5+}$, 1257.7 ($\mathbf{MN44S} - 6PF_6^-)^{6+}$, 1057.5 ($\mathbf{MN44S} - 7PF_6^-)^{7+}$, 907.2 ($\mathbf{MN44S} - 8PF_6^-)^{8+}$.

**MN43S.** A mixture of **PR43**$(NO_3)_2$ (191.9 mg; 129.4 $\mu$mol) and Pt(en)$(NO_3)_2$ (50.0 mg; 129.4 $\mu$mol) in water (50 mL) was heated at reflux for 7 d. The solvent was evaporated in vacuo (217.6 mg, 84%). The resulting colorless solid was dissolved in water (3 mL), and EtOH was allowed to vapor diffuse into the solution to produce the crystalline product (87.7 mg, 34%). Mp > 225 °C dec. $^1$H NMR (300 MHz, $D_2O$): $\delta$ 0.54 (br, 16H), 2.47 (br, 16H), 2.86 (s, 16H), 4.34 (s, 16H), 4.42 (d, *J* = 15.5 Hz, 48H), 5.59 (d, *J* = 15.5 Hz, 48H), 5.72 (s, 48H), 7.82 (t, *J* = 6.1 Hz, 8H), 8.53 (d, *J* = 8.0 Hz, 8H), 9.04 (d, *J* = 5.5 Hz, 8H), 9.19 (s, 8H). ESI-MS: *m*/*z* 4280.18 ($\mathbf{MN43S} - H^+ + (PF_6^-))^{2-}$, 4352.94 ($\mathbf{MN43S} + 2(PF_6^-))^{2-}$. Anal. Calcd $Pt_4C_{216}H_{272}N_{136}O_{96}\cdot 49H_2O$: C, 32.54; H, 4.68; N, 23.89. Found: C, 32.67; H, 4.34; N, 23.57.

**MN54T. PR54**$(NO_3)_2$ (96.9 mg; 64.4 $\mu$mol) and Pt(en)$(NO_3)_2$ (25.0 mg; 64.4 $\mu$mol) were dissolved in distilled water (40 mL) and refluxed for 3 d. The solvent was evaporated and dried in vacuo. The resulting colorless solid was dissolved in 3 mL of distilled water, and EtOH was allowed to vapor diffuse into the solution to produce the crystalline product (103.62 mg, 85%). Mp > 225 °C dec. $^1$H NMR (300 MHz, $D_2O$): $\delta$ 0.30 (br, 6H), 0.60 (br, 12H), 2.50 (br, 12H), 2.82 (s, 12H), 4.35 (d, *J* = 15.5 Hz, 36H), 4.51 (s, 12H), 5.63 (s, 36H), 5.73 (d, *J* = 15.5 Hz, 36H), 7.94 (d, *J* = 6.4 Hz, 12H), 9.06 (d, *J* = 6.1 Hz, 12H). ESI-MS: *m*/*z* 3249.1 ($\mathbf{MN54T} - H^+ + (PF_6^-))^{2-}$, 3321.7 ($\mathbf{MN54T} + 2(PF_6^-))^{2-}$.

**Low-Temperature Reaction of PR54$(NO_3)_2$ with Pt(en)$(NO_3)_2$. PR54**$(NO_3)_2$ (111.3 mg; 73.9 $\mu$mol) and Pt(en)$(NO_3)_2$ (28.7 mg; 73.9 $\mu$mol) were dissolved in distilled water (40 mL) and heated at 80 °C for 7 d. After the volume of the solution was reduced by evaporation, EtOH was added slowly to yield a mixture of **MN54T** and **MN54S**, which was filtered and dried in vacuo (111.9 mg, 80%). $^1$H NMR (300 MHz, $D_2O$): $\delta$ 0.30 (br, 6H, **MN54T**) 0.40 (br, 8H, **MN54S**), 0.60 (br, 12H, **MN54T**), 0.75 (br, 16H, **MN54S**), 2.50 (br, 12H, **MN54T**), 2.82 (s, 44H, **MN54T** + **MN54S**), 4.31 (d, *J* = 15.5 Hz, 36H, **MN54T**), 4.36 (d, *J* = 15.6 Hz, 48H, **MN54S**), 4.48 (s, 12H, **MN54T**), 4.56 (s, 24H, **MN54S**), 5.55 (s, 36H, **MN54T**), 5.60 (s, 48H, **MN54S**), 5.68 (d, *J* = 15.5 Hz, 36H, **MN54T**), 5.71 (d, *J* = 15.6 Hz, 48H, **MN54S**), 7.92 (d, *J* = 6.4 Hz, 28H, **MN54T** + **MN54S**), 8.91 (d, *J* = 5.9 Hz, 16H, **MN54S**), 9.04 (d, *J* = 6.1 Hz, 12H, **MN54T**). ESI-MS: *m*/*z* 3322.1 ($\mathbf{MN54T} + 2(PF_6^-))^{2-}$, 4381.0 ($\mathbf{MN54S} + 2(PF_6^-))^{2-}$.

**MN53S.** This compound was prepared by the same procedure as that for **MN43S** described above except that **PR53**$(NO_3)_2$ instead of **PR43**$(NO_3)_2$ was used (209.8 mg, 86%). Mp > 230 °C dec. $^1$H NMR (300 MHz, $D_2O$): $\delta$ 0.47 (br, 8H), 0.74 (br, 16H), 2.08 (br, 32H), 4.39 (d, *J* = 15.5 Hz, 48H), 4.50 (s, 16H), 5.64 (d, *J* = 15.5 Hz, 48H), 5.67 (s, 48H), 7.72 (t, *J* = 6.4 Hz, 8H), 8.50 (d, *J* = 7.6 Hz, 8H), 8.92 (d, *J* = 5.8 Hz, 8H), 9.18 (s, 8H). ESI-MS: *m*/*z* 4309.00 ($\mathbf{MN53S} - H^+ + (PF_6^-))^{2-}$, 4381.13 ($\mathbf{MN53S} + 2(PF_6^-))^{2-}$. Anal. Calcd $Pt_4C_{220}H_{280}N_{136}O_{96}\cdot 22H_2O$: C, 35.11; H, 4.31; N, 25.32. Found: C, 35.31; H, 4.45; N, 24.97.

**Crystal Structure Analysis.** Crystals of **MN44T**, **MN43S**, and **MN54T** suitable for X-ray work were grown by slow diffusion of EtOH vapor into aqueous solutions of the molecular necklaces in 2 d, 20 d, and 2 months, respectively. Their crystallographic data are listed in Table S1 (Supporting Information). The data collection was performed at 188 K on a Siemens SMART diffractometer (MoK$\alpha$, $\lambda = 0.71073$ Å) equipped with a CCD area detector. Due to an unexpected power failure, only a part of (54.5%) the complete data set (to $\theta = 24.11°$) was collected for **MN54T**. An empirical absorption correction was applied (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXTL). In the crystal structure of **MN54T**, a free CB molecule was found in the lattice. The origin of the free CB molecule is not clear, but it may come from decomposition of **MN54T** during the crystallization. For **MN44T** and **MN43S**, all the non-hydrogen atoms except for the disordered ones were refined anisotropically. For **MN54T**, however, only Pt atoms were refined anisotropically due to the limited number of reflections collected. Some counteranions were found to be disordered; they were refined with suitable disorder models. Final *R* factors are listed in Table S1.

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**Supporting Information Available:** Detailed X-ray crystallographic information including structural diagrams (PDF); an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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