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Assembly of a Heterobinuclear 2-D Network: A Rare Example of Endo- and Exocyclic Coordination of Pd^{II}/Ag^{I} in a Single Macrocycle

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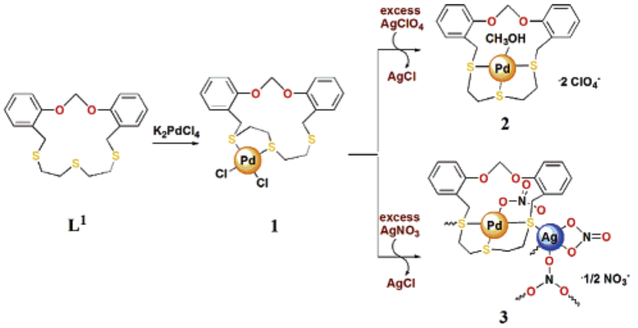
The S_3O_2 macrocycle $\mathbf{L^1}$ was synthesized by a dithiol–dihalide coupling reaction under high-dilution conditions. The reaction of $\mathbf{L^1}$ with K_2PdCl_4 afforded an exocoordinated complex **1**, [*cis*-$Cl_2Pd(\mathbf{L^1})$], which can then be manipulated to provide a heterobinuclear complex **3**, $\{[Pd(\mathbf{L^1})Ag(NO_3)_{2.5}](NO_3)_{0.5}\}_n$, utilizing endocyclic Pd^{II} and exocyclic Ag^{I} in a single macrocycle through a successive reaction with $AgNO_3$. The network of **3** contains a unique honeycomb-like 2-D sheet made up of the repeating unit $[Ag_6(NO_3)_6]$.

Research on macrocyclic binuclear complexes has grown in recent decades and has been a subject of numerous reports.[1] The reasons for such interest include their relevance to bimetallic bioinorganic systems and their potential applications in catalysis. A number of macrocyclic binuclear complexes involve two main categories: linked macrocycles[2] and large macrocycles.[3] In particular, the versatility of S-containing macrocycles makes them useful for a range of products because the S donor is expected to favor binding toward "softer" metals such as Pd^{II}, Pt^{II}, and Ag^{I} in either exo- or endocyclic mode; the complexes in such a mode have been investigated by us[4] and others.[5] As part of ongoing efforts, we therefore focused our attention on the macrocyclic complexes that would potentially contain two different metals positioned inside and outside the cavity, respectively.

Scheme 1. Compounds Prepared



One possible strategy for the preparation of heterobimetallic complexes is the use of metal complexes as ligands, that is to say, metal complexes containing potential donor atoms or those with available coordination sites.[6] In this work, we were able to prepare the exocoordinated *cis*-dichloropalladium(II) complex of a S_3O_2 macrocycle, leaving one S donor uncoordinated (see compound **1** in Scheme 1). This result was enough to motivate works on the preparation of new types of heterobinuclear macrocyclic complexes. The expectation has been realized through the stepwise approach, as depicted in Scheme 1. Herein, we present the stepwise synthesis and structural characterization of the heterobinuclear 2-D network utilizing endocyclic Pd^{II} and exocyclic Ag^{I} in a single macrocycle.

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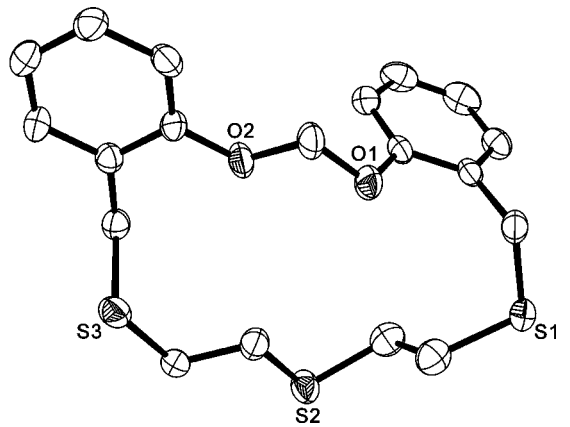


Figure 1. Molecular structure of $\mathbf{L^1}$.

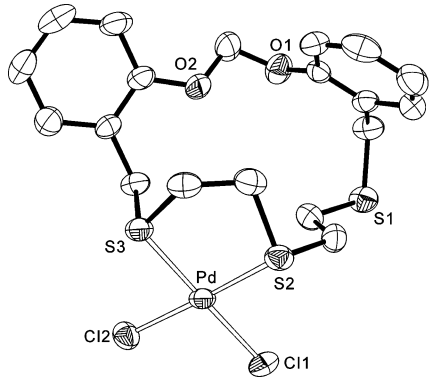
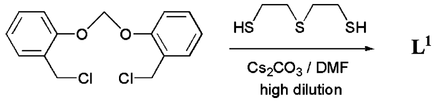


Figure 2. Molecular structure of exocoordinated **1**, [*cis*-$Cl_2Pd(\mathbf{L^1})$].

Scheme 2. Synthesis of $\mathbf{L^1}$



$\mathbf{L^1}$ was synthesized by a coupling reaction from corresponding dichloride and dithiol (Scheme 2). The single crystals of $\mathbf{L^1}$ were obtained by slow evaporation of a methanol solution, and the crystal structure was characterized (Figure 1). In $\mathbf{L^1}$, two O atoms are oriented in an endodentate fashion, while three S atoms are positioned exodendate.[7]

The reaction of $\mathbf{L^1}$ with K_2PdCl_4 afforded an orange crystalline product, **1**. The mass spectrum of **1** showed a peak at *m/z* 519 corresponding to $[Pd(\mathbf{L^1})Cl]^+$. The crystal structure reveals that **1** is an exodentate complex of formula $[Pd(\mathbf{L^1})Cl_2]$ (Figure 2). The Pd atom is outside the cavity in a cis-type square-planar arrangement coordinated by two S donors from $\mathbf{L^1}$ in a bent arrangement. Two Cl atoms are occupying the rest of the two binding sites. One S atom (S1), together with two O donors, is remaining uncoordinated. The bond distances of Pd−S2 [2.270(1) Å], Pd−S3 [2.274(1) Å], Pd−Cl1 [2.319(1) Å], and Pd−Cl2 [2.311(1) Å] compare well with those found in the other *cis*-Cl_2S_2-type Pd^{II} complexes.[8] The conformation of the macrocycle is different from that in free $\mathbf{L^1}$ because of the flexible nature of the thioether moiety. In view of the torsion angles between the neighboring donor atoms, the aliphatic segment of S−C−C−S−C−C−S shows an anti−anti arrangement in free $\mathbf{L^1}$, while in **1**, it changes to an anti−gauche arrangement because of its flexible nature.

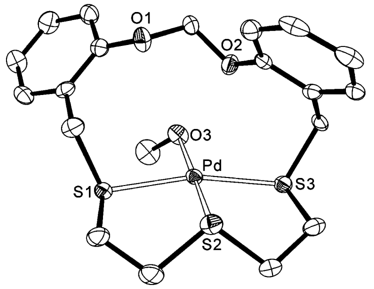


Figure 3. Molecular structure of endocoordinated **2**, $[Pd(\mathbf{L^1})(CH_3OH)]$-$(ClO_4)_2$. Noncoordinating anions are omitted.

The result for the crystal structure of **1** in which it has one unoccupied S donor and two easily removable Cl atoms leads to the idea that by successive reactions with thiaphilic metal salts generation of new types of complexes including heterobinuclear ones with novel structure may occur. If fact, the reactions of **1** with excess amounts of $AgClO_4$ and $AgNO_3$ afforded **2** and **3**, respectively. The AgCl precipitate formed was easily removed by filtration. By slow evaporation of each filtrate, the respective orange single crystals were obtained. Interestingly, the reactions of **1** with silver salts afforded two types of complexes (**2**, ClO_4^-; **3**, NO_3^-), in which their topologies and stoichiometries vary with the anion used.

First, **2** crystallizes in a 1:1 complex of formula $[Pd(\mathbf{L^1})$-$(CH_3OH)](ClO_4)_2$ (Figure 3). In marked contrast to **1**, the Pd atom in **2** is in the cavity, forming an endodentate environment. The Pd atom is in a distorted square plane with coordination sites occupied by three S donors from $\mathbf{L^1}$ and by one methanol molecule. The bond distances of Pd−S1 [2.320(1) Å] and Pd−S3 [2.321(1) Å] are longer than those of **1**, while that of Pd−S2 [2.215(2) Å] is shorter. The transformation of Pd^{II} coordination from exo (in **1**) to endo mode (in **2**) is noticeable. This rearrangement is activated by the cleavage of two Pd−Cl bonds as well as the existence of one unoccupied S donor in **1**.

On the other hand, **3** crystallizes as a 2-D network of formula $[Pd(\mathbf{L^1})Ag(NO_3)_{2.5}](NO_3)_{0.5}$ involving a heterobinuclear Pd^{II}/Ag^{I} complex unit (Figure 4). The structure shows an unusual arrangement, with the Ag atom coordinated exo fashion to the ring via one S donor and the Pd atom bound with three S donors in endo fashion to the ring. $\mathbf{L^1}$ also behaves as an exo-monodentate ligand through one S donor (S3) capable of bridging the endocyclic Pd atom and exocyclic Ag atom. The asymmetric unit contains one molecule of $\mathbf{L^1}$, one Pd atom, one Ag atom, and two and half nitrate ions as well as half of a free nitrate ion (not shown). The structural unit shown in Figure 4 is generated through a center of symmetry. The structure of the endocyclic

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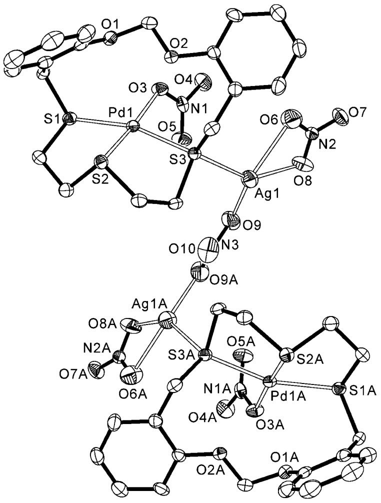

Figure 4. View of basic heterobinuclear unit $\{[Pd(\mathbf{L^1})Ag(NO_3)_{2.5}]$-$(NO_3)_{0.5}\}_2$ in **3**, $\{[Pd(\mathbf{L^1})Ag(NO_3)_{2.5}](NO_3)_{0.5}\}_n$. Noncoordinating anions are omitted.

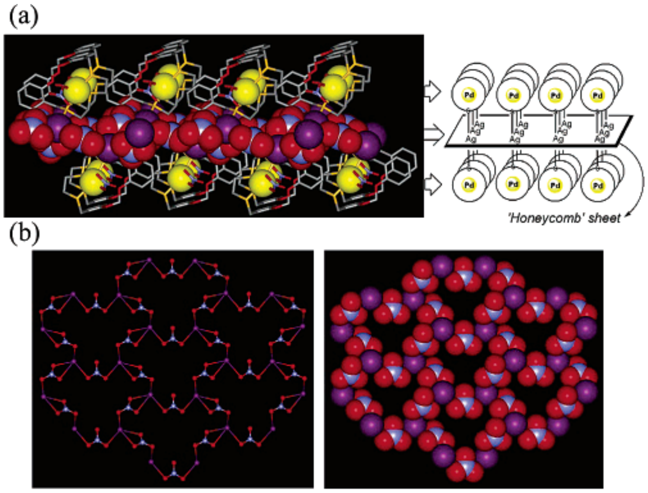

Figure 5. (a) 2-D network of **3** showing arrangement of endocyclic Pd^{II} complex units grafted up and down of the $[Ag_6(NO_3)_6]_n$ honeycomb sheet. (b) Ball-and-stick (left) and space-filling (right) representations of the honeycomb sheet. (Key: Pd, yellow; Ag, violet; N, light blue; O, red.)

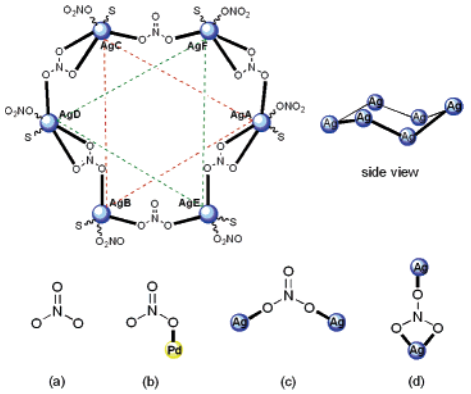

Figure 6. View of the $[Ag_6(NO_3)_6]$ hexagon unit from the honeycomb layer of **3** (top) and coordination modes of the nitrate ions (bottom).

Pd^{II} complex unit in **3** exhibits no significant differences from that of **2** except nitrate coordination instead of methanol. In fact, Ag^I is five-coordinated by one S donor from $\mathbf{L^1}$ and one bidentate and two monodentate nitrate ions (one is not shown; see Figure S4 in the Supporting Information) in an O_4S coordination sphere. The narrow bite angle [49.0(2)°] of the bidentate nitrate ion for Ag^I allows for a pseudotetrahedral coordination geometry. As we understand, this is the first example of a macrocyclic complex with μ_2-S-bridged Pd and Ag atoms. The exo- and endocyclic coordination in a single macrocycle is also very novel.

The continual symmetry operations about 2-fold axes passing through one nitrate ion lead to a 2-D sheet, which is made up of the repeating unit $[Ag_6(NO_3)_6]$ with a honeycomb-like conformation (Figure 5). Consequently, the endocyclic Pd^{II} complex units as pendants are arranged onto the layer from both sides by the S−Ag bond. The $[Ag_6(NO_3)_6]$ unit possesses a C_2 symmetry axis passing through its center and two bidentate nitrate ions. Furthermore, six Ag atoms in the $[Ag_6(NO_3)_6]$ hexagon unit are arranged in an alternating up-and-down fashion: three Ag atoms are placed on one plane and the other three Ag atoms share the other one with 2.026 Å of two triangular planes distance (Figure 6). As we understand, this is the first characterized structure derived from the aggregation of simple $AgNO_3$ molecules.

Interestingly, four kinds of nitrate anions with different coordination modes are presented in **3** (Figure 6): (a) noncoordinated, (b) monodentated bound to one Pd atom, (c) bidentated bridging two Ag atoms, and (d) tridentated bridging two Ag atoms in mono- and bidentate fashions, respectively. Consequently, the nitrate ions with diverse coordination modes provide a considerable variety of the network structure. We believe that the interest in the structural motifs of **3** is in not only the formation of an endo/exocyclic heterobinuclear complex but also the remarkable arrangement of network. The result of a comparative NMR experiment suggests that the solid structures of **2** and **3** are also retained in solution (Figure S6 in the Supporting Information).

In summary, the present paper demonstrates the stepwise assembly and structural characterization of the novel heterobinuclear 2-D network with endocyclic Pd^{II} and exocyclic Ag^I in a single macrocycle. The simple exocoordinated Pd^{II} complex with one unoccupied S donor provides an opportunity for the construction of a higher level of sophistication by combining reasonable soft metal salt systems.

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Supporting Information Available: Synthetic procedures and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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