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Self-Assembly of a Pd_6−Molecular Double-Square and a Cu_3-Trigonalbipyramidal Cage via a New Tripodal Flexible Ligand

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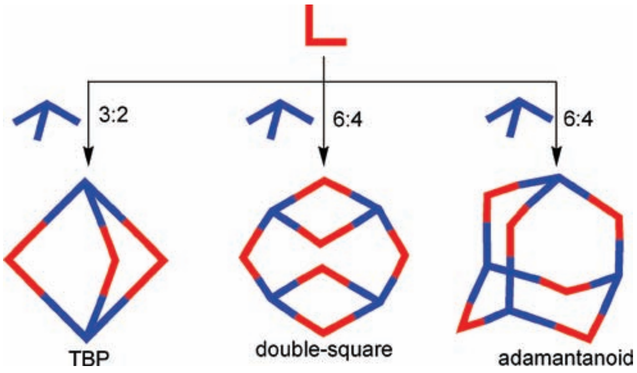
A new tripodal flexible ligand (**L**) containing pyrazolyl functionality has been prepared and successfully used to obtain a pd_6 (**1**) molecular double-square and a cu_3 trigonalbipyramidal cage (**2**), where complex **1** represents the first example of a double-square obtained using a flexible tripodal ligand.

Supramolecular self-assembly is the spontaneous association of more than one chemical entity to form larger aggregates through reversible noncovalent interactions.[1] Generally, such association is thermodynamically controlled[11] and the chemical entities organize themselves to the most thermodynamically stable aggregate. In synthetic self-assembly reaction, metal−ligand coordination bonding interaction has been considered to be very effective for designing large metallosupramolecules of finite shapes and sizes because of its stronger and high directional nature.[2] The organic backbone and the nature of the metal−ligand interaction usually control the structure, conformation, and topology of the final supramolecules.[1,2] A few recent examples are known where flexibility is also introduced into discrete assemblies by introducing organic ligands with arms containing flexible groups.[2f,3] The simplest combination for designing a 3D discrete architecture is the assembly of a 90° ditopic acceptor with a tritopic donor. Depending on the nature of the tritopic donor, three discrete 3D architectures are possible (Scheme 1).[4] Although a flexible tripodal donor prefers exclusively the formation of trigonalbipyramidal cage (TBP) or adamantanoid, a rigid tritopic planar donor prefers the formation of an octahedron.[5] Isolation of a 6:4 self-assembled double-square using a flexible tripodal ligand is yet to be reported. The present literature on Pd/Pt-based finite architectures is mainly dominated by the use of pyridyl donors with a few examples of other kinds of donors. Use of polypyrazole donors is very rare in this field, with a few recent examples where pyrazolate-bridged assemblies of dimetallic repeating unit are known.[6]

Scheme 1. Possible Discrete Architectures from [3 + 2] and [4 + 6] Self-Assembly of Tritopic Donor with a 90° Acceptor



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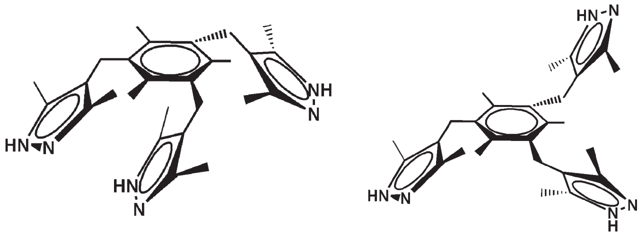
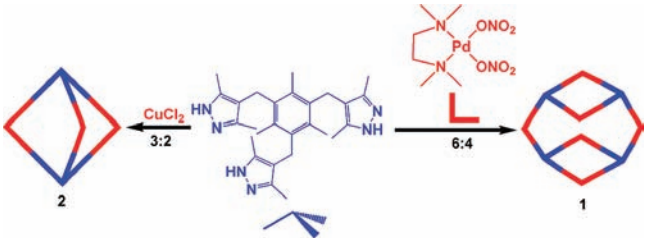


Figure 1. Possible cis, cis, cis (left) and cis, trans, trans (right) conformations of **L**.

Scheme 2. Self-Assembly of **1** and **2** from Their Precursor Units



Herein, we report the synthesis (see the Supporting Information) of a new flexible tripodal ligand 1,3,5-tris((3,5-dimethyl-1*H*pyrazol-4-yl)methyl)-2,4,6-trimethylbenzene (**L**) and its application to the design of an unexpected $[(\text{tmen})_6\text{Pd}^{\text{II}}_6\text{L}_4](\text{NO}_3)_{12}$ (**1**) (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) double-square and a $\text{Cu}^{\text{II}}_3\text{L}_2\text{Cl}_6$ (**2**) TBP cage by 4:6 and 2:3 self-assembly, respectively. Complex **1** represents the first example of a molecular double-square obtained from a flexible tripodal linker.

To introduce pyrazole functionality and flexibility, we have prepared a new flexible tripodal ligand (**L**) (see the Supporting Information). This ligand can adopt two different conformations: cis, cis, cis and cis, trans, trans conformations (Figure 1). Solution NMR of the free ligand indicated that it adopts the former symmetrical conformation.

Treatment of this flexible ligand with a cis-blocked 90° acceptor may yield a 2:3 self-assembled TBP cage or a 4:6 assembled double-square or adamantane-like structure. Adamantanoid geometry is thermodynamically more stable over TBP or double-square.[2b] For the L_2M_3-TBP cage or L_4M_6-adamantane-like structure, symmetrical cis, cis, cis conformation of the ligand is necessary, whereas a double-square geometry needs the ligand to adopt the other nonsymmetrical cis, trans, trans conformation. Reaction of **L** with *cis*-(tmen)Pd$(\text{NO}_3)_2$ [tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine] in 2:3 molar ratios in a MeOH−H_2O mixture yielded **1** (Scheme 2).

The ^{1}H NMR spectrum of this complex indicated a nonsymmetrical cis, trans, trans conformation of the ligand in **1**. Such conformation of the ligand in complex **1** ruled out the formation of an expected symmetrical TBP cage or adamantane-like geometry. The same reaction under different reaction conditions also yielded **1**. Five different kinds of protons were found in the aliphatic region of the spectrum. Each above kind of proton showed two peaks with 2:1 integration ratios.

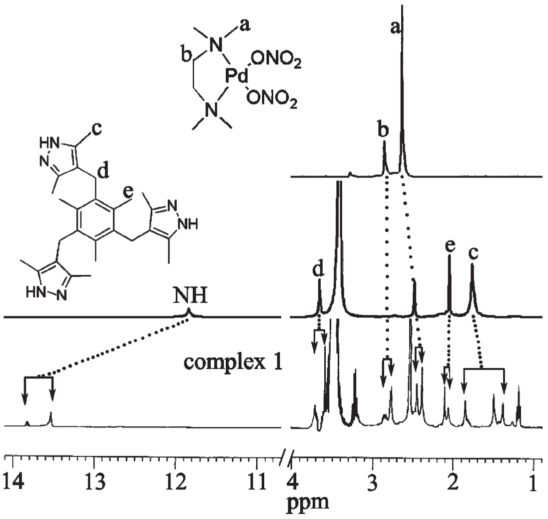


Figure 2. ^{1}H NMR spectra of **1**, **L** (D_6-dmso) and *cis*-(tmen)Pd$(\text{NO}_3)_2$ (CD_3OD).

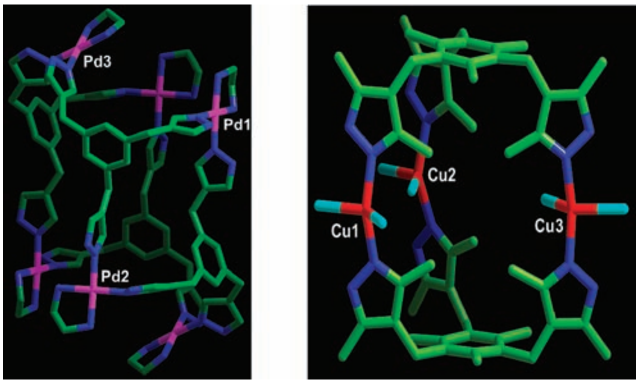


Figure 3. View of the molecular structures of **1** (left) and **2** (right). Color codes: green = C, blue = N, pink = Pd, red = Cu, cyan = Cl.

Significant downfield shift of the NH-proton from 11.9 in free ligand to 13.5 and 13.8 ppm in the complex **1** (Figure 2) was also an indication of the ligand to metal coordination and nonsymmetrical ligand conformation. Mass spectrometric analysis indicated a 4:6 composition of the ligand and *cis*-(tmen)Pd$(\text{NO}_3)_2$ in complex **1** by the appearance of peaks at 1293.8, 1222.42, and 709.9 due to $[\text{M} - 2\text{NO}_3^- - 6\text{tmen} - \text{L}]/2$, $[\text{M} - 3\text{NO}_3^-]/3$, and $[\text{M} - 5\,\text{NO}_3^-]/5$, respectively. Appearance of two peaks in NMR with 2:1 integration ratios for each kind of proton in complex **1** in combination with mass spectrometric analysis indicated the formation of the unusual molecular double-square. The final geometry of the complex is unique since flexible tripodal donors in all previous cases preferred the formation of TBP cage upon treatment with a 90° acceptor.

Finally, single-crystal X-ray diffraction study unambiguously (see the Supporting Information) confirmed the formation of double-square structure. Structural analysis revealed that each Pd(II) center is coordinated to two pyrazolyl moieties of two different ligands and attains almost square planar geometry. Interestingly, the centroids of two phenyl rings of two ligands and two similar Pd(II) centers (Pd1 and Pd2) form a square (Figure 3). Two such squares are clipped by two other Pd(II) centers (Pd3) via coordination through the pyrazolyl moieties of the ligands **L** to form a double-square structure (Figure 3). Thus, eight pyrazolyl

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units are involved in forming two squares and other four link these two squares via two Pd(3) centers. The distance between the palladium centers within squares is 11.94 Å while the Pd−Pd distance between the squares is 8.79 Å and thus the two squares are a bit bowed outward from each other. The distance between the two clipping palladium centers (Pd3−Pd3) is 17.23 Å (Figure 3). It looks as if the clipping palladium centers (Pd3) link the opposite square faces of a cube. The average Pd−N(Pyrazole) and Pd−N(tmen) bond distances are 2.022 Å and 2.057 Å, respectively. Because of the capping of the groups and bowed nature of the squares two opposite square faces of the cube make a nice porous channel which is clearly visible in the packing diagram (see the Supporting Information). The crystal packing diagram of **1** shows the formation of channels with counterions (NO_3^- and ClO_4^-) occupying the intermolecular regions (see the Supporting Information).

To explore the possibility of formation of discrete closed architecture using 3d metal ion, $CuCl_2$ was used instead of *cis*-(tmen)Pd$(NO_3)_2$. Interestingly, treatment of **L** with $CuCl_2 \cdot 2H_2O$ in methanol resulted a 2:3 self-assembled TBP cage [$Cu_3Cl_6L_2$] (**2**) as orange crystalline precipitate (Scheme 2) in 15 min. The elemental analysis and mass spectroscopic studies indicate the formation complex **2**. Formation of such a Cu(II) cage of finite shape is interesting because multidentate nitrogen donor flexible linkers generally prefer the formation of coordination polymers upon treatment with 3d series transition metals because of kinetically inert Cu−N bond formation. Compound **2** was unambiguously characterized by single-crystal X-ray structure analysis. X-ray diffraction quality crystals were grown by slow vapor diffusion of diethyl ether into the saturated DMF solution of **2**. Structure analysis revealed the formation of a TBP type nanoscopic cage. The conformation of the ligand **L** in **2** is symmetrical cis, cis, cis. Unlike in **1**, where the PdN_4 environment is almost square planar, the $CuCl_2N_2$ attains butterfly geometry (Figure 3) in complex **2**. The N−Cu−N bond angles range from 146 to 163° and Cl−Cu−Cl bond angles are between 133 and 135°; the average Cu−N bond length is 1.95 Å. Thus, two phenyl and six pyrazolyl moieties of the ligands in the [$Cu_3L_2Cl_6$] cage are bowed away from each other to keep the methyl substituents far away to reduce steric crowding and thereby leading to exclusively entropically favored molecular TBP architecture. The intramolecular Cu−Cu distances are 5.76, 8.17, and 8.99 Å, whereas the shortest intermolecular Cu−Cu distance between the neighboring cages is 3.75 Å. The neighboring molecules are linked by very weak Cu−Cl bridging and the Cu−Cl−Cu angle is 85°. Hydrogen bonding interactions were observed between the solvent (DMF) molecules present in the lattice with the pyrazolyl nitrogens of the complex **2** (see the Supporting Information). Variable-temperature magnetic study in the temperature range of 2−300 K revealed the presence of overall very weak ferromagnetic interaction. The intramolecular Cu−Cu separation is very large and thus magnetic interaction is expected to be weak. Susceptibility data were fitted using a Cu_3 model considering intertrimer interaction. Neighboring cages are bridged by weak Cu−Cl−Cu bridge and the angle is close to orthogonal. The magnetic data were fitted using a model of a triangle of Cu(II) [$S = 1/2$] considering intertrimer interaction. The best fit was obtained with the parameters J_1 (intratrimer) $= -4.03$ cm^{-1}, J_2 (intertrimer) $= 6.43$ cm^{-1} and $g = 2.17$ (see the Supporting Information). Thermogravimetric study on complexes **1** and **2** indicates that the ensembles are fairly stable up to 210 and 220 °C, respectively (see the Supporting Information).

In summary, a new tripodal flexible ligand containing three pyrazolyl groups has been synthesized, and has been successfully applied to construct a Pd_6 discrete molecular double-square and a Cu_3 TBP cage. Although the use of pyridyl donors has dominated the literature, a few polypyrazolate bridged discrete assemblies of Pt/Pd have been reported where both the nitrogen sites of pyrazole linked to metal. Interestingly, in both the present cages (**1** & **2**), pyrazole NH groups remain uncoordinated. Complex **1** represents the first example of a molecular double-square structure using a flexible tripodal linker because in all previous occasions flexible tripodal linkers preferred the formation of TBP cage in combination with 90° acceptor. A similar reaction using $CuCl_2 \cdot H_2O$ instead of *cis*-(tmen)Pd$(NO_3)_2$ yielded a Cu_3 TBP cage. Despite its tendency to form polymers due to the flexible nature, **L** assembles with metal acceptors into discrete finite cages. The use of flexible polypyrazole ligands with Pd(II)/Pt(II) metals and the formation of nanocages has potential to expand the coordination driven self-assembly for the construction of novel materials for practical application like gas adsorption, catalysis and host−guest chemistry.

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Supporting Information Available: Crystallographic information of **1** and **2** in CIF format; synthesis of **L**, **1**, and **2**; packing diagram of **1**; and variable-temperature magnetic susceptibility plot of **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.