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# Supramolecular Aggregation of Pd(II) Monohelicates Directed by Discrete (H<sub>2</sub>O)<sub>8</sub> Clusters in a 1,4-Diaxially Substituted Hexameric Chairlike Conformation

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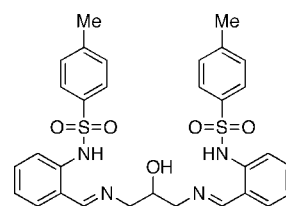
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**ABSTRACT:** We report the first structural evidence in the solid state of discrete water octamers with a 1,4-diaxially substituted hexameric chairlike conformation. These units were found to act as supramolecular glue in the aggregation of Pd(II) monohelicates to give a three-dimensional network through hydrogen-bonding.

In recent years, there has been increasing interest in the experimental and theoretical study of small water clusters<sup>1</sup> [(H<sub>2</sub>O)<sub>n</sub>, where  $n = 2$ –16] because these water assemblies are considered to be ideal research models to gain an insight into some of the unexplained properties of bulk water,<sup>1d,2</sup> into the processes that occur at the ice–liquid, ice–air, and liquid–air interfaces,<sup>3</sup> and into the nature of water–water and water–solute interactions.<sup>3a</sup> Among these clusters, the octamer is one of the lesser known systems, and just a few examples of this cluster have been observed in the solid state in organic or metallo-organic crystal hosts.<sup>4</sup> Theoretical predictions show that the octamer has two almost isoenergetic isomers, with  $S_4$  and  $D_{2d}$  symmetries,<sup>5</sup> and these models have been observed experimentally.<sup>6</sup> However, other conformations, including cubane,<sup>4a</sup> cyclic ring,<sup>4b</sup> opened cube,<sup>4c</sup> and book-shaped hexamer with two pendant water molecules,<sup>4d</sup> have also been characterized crystallographically. Very recently, a novel conformation for the (H<sub>2</sub>O)<sub>8</sub> cluster was observed in a dipicolinic acid/Ce(IV) host, and this consists of a hexameric chair with two handles in the 1,4-diaxial positions.<sup>4e</sup> Nevertheless, these octamers cannot be considered as discrete clusters since they are connected to one another and to other water molecules, giving rise to the formation of a complex infinite water network. Herein we report the first structural evidence in the solid state of a discrete water octamer with a 1,4-diaxially substituted hexameric chairlike conformation. The water clusters reported here are found to act as supramolecular glue<sup>7</sup> in the aggregation of discrete Pd(II) monohelicates to give a three-dimensional (3D) network through hydrogen bonding.

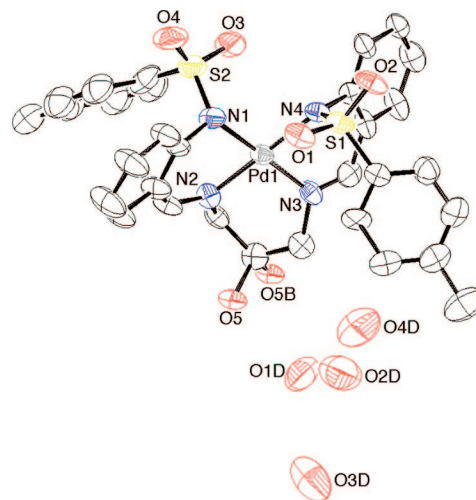
The metallo-supramolecular synthetic approach makes possible the assembly of a wide range of entities with defined size and shape.<sup>8</sup> However, the covalent synthesis of the ligands imposes a limit on the dimension of these arrays, and alternative synthetic methods are required to circumvent these severe limitations for obtaining nanometer-sized supramolecular systems. One possible approach for the generation of these nanoarchitectures is the assembly of discrete supramolecular units into larger arrays using structurally programmed interactions.<sup>9</sup> In this context, we have studied the use of helicates and other metal complexes as a means of producing larger arrays through their noncovalent aggregation.<sup>10</sup>

Scheme 1. Ligand H<sub>3</sub>L



Ligand H<sub>3</sub>L (Scheme 1) was synthesized in 88% yield by Schiff-base condensation of 2-tosylaminobenzaldehyde<sup>10</sup> and 1,3-diamino-2-propanol.<sup>11a</sup> Electrochemical oxidation<sup>11a–c</sup> of a palladium plate in a conducting acetonitrile solution of H<sub>3</sub>L yielded a yellow solution from which a yellow solid precipitated upon concentration. The FAB mass spectrum is consistent with the formation of a neutral monomeric species of formula [Pd(HL)], a process that involves the deprotonation of the two NH groups of the ligand in the electrochemical cell.<sup>12</sup>

Slow evaporation of a saturated 20:1 acetonitrile/water solution of the Pd(II) complex yielded dark yellow crystals that were suitable for X-ray diffraction studies.<sup>13</sup> The structure reveals the formation



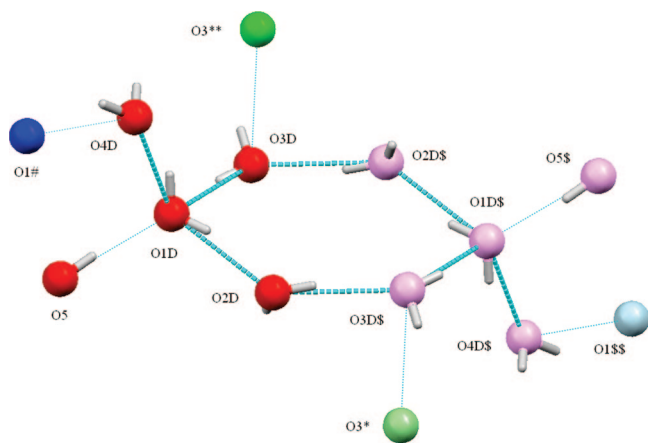
**Figure 1.** ORTEP representation of the molecular structure of [Pd(HL)]·4(0.85(H<sub>2</sub>O)) (1). Thermal ellipsoids are shown at 40% probability and hydrogen atoms have been omitted for clarity.

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**Figure 2.** Lattice water octamer (oxygen atoms labeled as D) found in the crystal cell of **1**, including hydrogen-bond contacts with the neighboring oxygen atoms (O1, O3, and O5) of the surrounding Pd(II) monohelicates. Symm code: # (1.5 − *x*, −0.5 + *y*, 0.5 − *z*); \* (1.5 − *x*, 0.5 + *y*, 0.5 − *z*); \*\* (−0.5 + *x*, 0.5 − *y*, 0.5 + *z*); \$ (1 − *x*, 1 − *y*, 1 − *z*); \$\$ (−0.5 + *x*, 1.5 − *y*, 0.5 + *z*).

of a single-stranded Pd(II) monohelicate solvated by four water molecules at 85% occupancy [Pd(HL)]·4[0.85(H<sub>2</sub>O)] (**1**) (Figure 1 and Supporting Information). A racemic mixture of both enantiomers is observed in the unit cell. The palladium(II) is tetra-coordinated by the four N donor atoms of the Schiff base ligand. The coordination environment of the metal ion can be considered as typical square planar, as the value N–Pd–N angles are in the usual range reported for this type of complex [88.1(5) to 92.4(5)°]. The intramolecular S1–S2 distance (ca. 4.60 Å) in **1** can be used to quantify the helical pitch of the monohelicate.<sup>14</sup>

The crystallographic analysis shows that the Pd(II) monohelicates have a disordered OH group in the spacer. A total of 15% of the complexes present in the unit cell of **1** are linked to one another by hydrogen bonding (see Supporting Information) to form an infinite one-dimensional (1D) supramolecular chain. Each monohelicate uses in this connection its OH group (O5B) and an oxygen atom (O1) from a tosyl group [O···O: 2.69(6) Å].

In the other 85% of the Pd(II) complexes of **1** the OH group (O5) is only connected to a lattice water molecule (O1D) by hydrogen bonding [O···O: 2.77(2) Å; see Figure 1]. Four lattice H<sub>2</sub>O molecules, with oxygen atoms O1D, O2D, O3D, O4D, are present in this 85% of the crystal cell of **1**. These water molecules, and their symmetry equivalents (1 − *x*, 1 − *y*, 1 − *z*), are arranged in close proximity to each other (Figure 2). The short separating distances and the angles between them (Table 1) suggest the occurrence of H-bonds,<sup>15</sup> which drive the formation of hydrophilic (H<sub>2</sub>O)<sub>8</sub> clusters. The water octamers have at their core a hexamer in the chair conformation, with two additional water molecules attached at two diagonally opposite ends of the chair at a distance of 10.80(10) Å. The average O···O distance in the hexamer is 2.85(3) Å. This distance is equal to those observed in liquid water (2.85 Å)<sup>16</sup> and is comparable to the corresponding value in hexagonal ice (*I*<sub>h</sub>, 2.76 Å).<sup>17</sup> Moreover, the average O···O angle in the hexamer is 116.77(8)°, which is a little higher than the

corresponding value in *I*<sub>h</sub> (109.3°). This 1,4-diaxially substituted hexameric chairlike conformation for a water octamer seems to be highly unstable with respect to other conformers of the cluster, as shown by theoretical calculations.<sup>4g</sup>

It must be remarked that the water octamers discussed here are discrete moieties that are not connected directly to one another through any noncovalent interaction. However, six Pd(II) monohelicates are connected to each water cluster by hydrogen bonding (Figure 3). Two of these monohelicates are linked through the OH group of the spacer (O5) to the O1D and O1D \$ atoms (symmetry code: 1 − *x*, 1 − *y*, 1 − *z*) of the hexameric core of the octamer, both in equatorial positions (O···O: 2.77 Å). The other four monohelicates are hydrogen bonded through an oxygen atom of a tosyl group (O1 or O3). Of these four complexes, two are connected to the nonhexameric water molecules of the octamer (O4D and O4D \$; O···O: 3.03 Å) and the other two are linked to the O3D and O3D \$ atoms of the hexameric core, both of which are also in equatorial positions (O···O: 2.87 Å). Overall, each Pd(II) monohelicate is hydrogen bonded to three octamers (Figure 4).

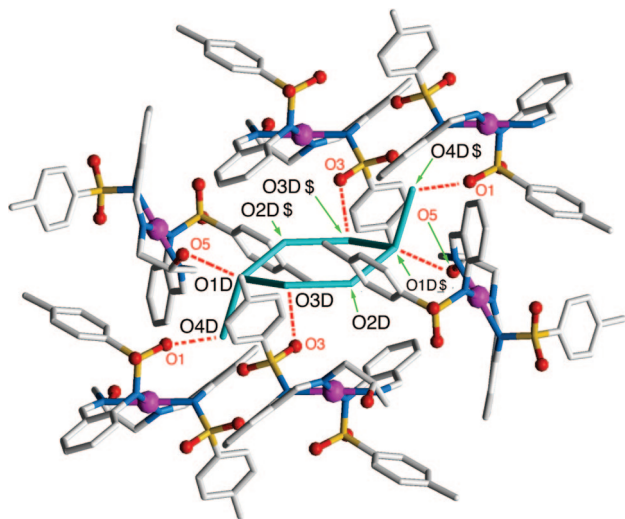
These multiple hydrogen-bonding interactions are extended into the solid to give an infinite array, which constitutes a 3D network of Pd(II) monohelicates. It could be viewed that the octameric water clusters behave as supramolecular glue between the metal complexes. To the best of our knowledge this is the first example of a 3D supramolecular network of Pd(II) monohelicates and also the first example of a 3D supramolecular network of monohelicates that is fully assembled by hydrogen bonding.

We decided to locate the hydrogen atoms in order to check that the proposed octamer motif really is viable within a single site in the crystal structure. For this analysis, the H atoms were positioned and refined using geometrical restraints (O–H distances and H–O···H angles). We found that it is possible to place the hydrogen atoms in the water octamer with reasonable interactions (Table 1). In this situation O1D acts as an H-bond acceptor for the OH group of the Pd(II) monohelicate [O5–H5···O1D] and as an H-bond donor both for O4D [O1D–H11D···O4D] and O2D [O1D–H12D···O2D]. Finally, O1 and O3 (tosyl oxygen atoms of the HL ligand) act as H-bond acceptors for O4D [O1···H41D–O4D] and O3D [O3···H31D–O3D], respectively (Figure 2). This arrangement of the hydrogen bonds is very similar to those observed in the octameric water cluster reported by Rajasekharan et al.<sup>4g</sup>

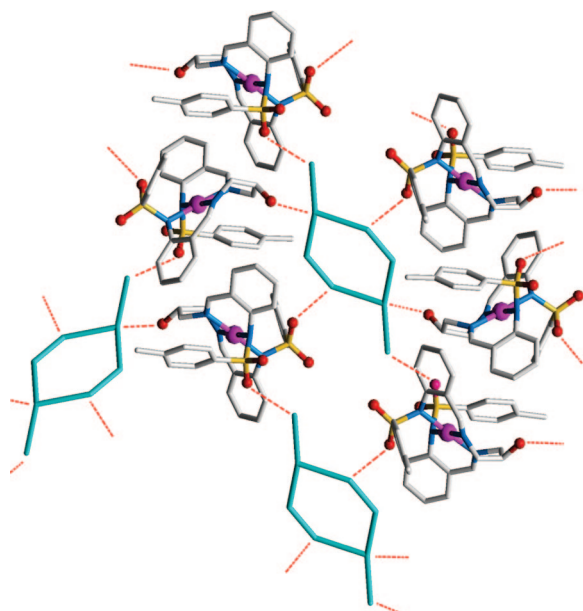
The thermal stability of the water clusters in **1** was studied by thermogravimetric analysis (TGA). The octameric water clusters remain stable in the crystal lattice of **1** at room temperature for an indefinite period. TGA studies showed total water loss occurs in one step: an 8.33% weight loss was observed between 70 and 150 °C, and this is almost equivalent to the loss of 3.56 water molecules (see Supporting Information). This behavior suggests that all water molecules are retained in the crystal lattice of **1** with the same strength. Finally, we studied the reversibility/irreversibility of the water loss from **1** by infrared spectroscopy. The stretching frequency of O–H bonds of the octameric water cluster present in **1** was observed as a large broadband at ca. 3445 cm<sup>−1</sup>. In the infrared spectrum of the same crystals, which were previously heated at 150 °C for a couple of hours, this band practically disappeared and did not appear again when the crystals were exposed to water vapor (see Supporting Information). These data suggest that the loss of water from **1** is irreversible.

**Table 1.** Geometrical Parameters of O···O Contacts and H···O Hydrogen Bonds for the Octamer and the Neighboring O Atoms Belonging to the Surrounding Pd(II) Monohelicates

| O <sub>donor</sub> –H···O <sub>acceptor</sub> | H···O (Å) | O···O (Å) | O–H···O (°) | O···O···O atoms         | O···O···O (°) |
|---|-----------|-----------|-------------|-------------------------|---------------|
| O(5)–H(5)···O(1D)                             | 1.93      | 2.76(2)   | 173         | O(4D)···O(1D)···O(2D)   | 117.1(7)      |
| O(1D)–H(11D)···O(4D)                          | 2.20(11)  | 2.91(3)   | 141(12)     | O(4D)···O(1D)···O(3D)   | 112.9(7)      |
| O(1D)–H(12D)···O(2D)                          | 2.00(16)  | 2.80(3)   | 162(14)     | O(3)**···O(3D)···O(1D)  | 117.9(7)      |
| O(2D)–H(22D)···O(3D)\$                        | 2.01(17)  | 2.84(3)   | 166(12)     | O(3)**···O(3D)···O(2D)  | 85.8(7)       |
| O(3D)–H(31D)···O(3)**                         | 2.16(19)  | 2.87(2)   | 142(12)     | O(1D)···O(2D)···O(3D)\$ | 138.9(8)      |
| O(3D)–H(32D)···O(1D)                          | 2.16(11)  | 2.91(2)   | 151(11)     | O(1D)···O(3D)···O(2D)\$ | 123.3(8)      |
| O(4D)–H(41D)···O(1#)                          | 2.20(6)   | 3.02(2)   | 145(5)      | O(3D)···O(1D)···O(2D)   | 88.1(7)       |



**Figure 3.** Ball and stick representation of the hydrogen-bonding associations between one octameric water cluster and six Pd(II) monohelicates in **1**.



**Figure 4.** Part of the unit cell of **1**, exhibiting the multiple hydrogen bonds established between the octamers and the metal complexes that give rise to the formation of a 3D supramolecular network of Pd(II) monohelicates.

In conclusion, we report the first structural evidence of a discrete water octamer cluster in a 1,4-diaxially substituted hexameric chairlike conformation. These octamers act as supramolecular glue in the aggregation of Pd(II) monohelicates to give a 3D network through hydrogen bonding. We believe that this novel discrete water assembly brings to light a novel mode of the cooperative association of water molecules in the solid state.

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**Supporting Information Available:** Crystallographic data for the structure **1** has been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications CCDC 687681 reference number. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: +(44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Thermogravimetric curve of compound **1**, IR spectra of the hydrated and dehydrated complex, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) A supramolecular glue could be defined as the noncovalent force (or set of noncovalent forces) that support the intermolecular 1D, 2D, or 3D aggregation of a certain discrete molecule, supramolecule or metal complex. For more details see Bermejo, M. R.; Fernández, M. I.; González-Noya, A. M.; Maneiro, M.; Pedrido, R.; Rodríguez, M. J.; Vázquez, M. *Eur. J. Inorg. Chem.* **2004**, 2769, and references therein.
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- (12) Selected data for [Pd(HL)]·4(0.85(H<sub>2</sub>O)) (**1**): Elemental analysis found: C, 47.6; H, 5.0; N, 7.2; S, 8.3. C<sub>31</sub>H<sub>30</sub>N<sub>4</sub>O<sub>5</sub>PdS<sub>2</sub>·4\*0.85(H<sub>2</sub>O) requires:



- C, 47.6; H, 4.9; N, 7.2; S, 8.2%. IR (KBr,  $\text{cm}^{-1}$ ) 3445 b; 1629 vs; 1283 s; 1258 s; 1138 s. Mass spectrometry (ESI):  $m/z = 709.0792$   $[\text{Pd}(\text{HL}) + \text{H}]^+$ .
- (13) X-ray crystallography: Data were collected with a CCD area detector diffractometer, using monochromatized  $\text{MoK}\alpha$  radiation. Data were processed using APPEX2 software (BRUKER AXS, 2005), and solved by SIR-97 (Giacovazzo et al., 1999). Finally, it was refined by full-matrix, least-squares based on  $F^2$  using SHELXL (Sheldrick, G. M. SHELXL-97. *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997). Crystal data for  $[\text{Pd}(\text{HL})] \cdot 4[(0.85(\text{H}_2\text{O}))]$  **1**:  $\text{C}_{31}\text{H}_{30}\text{N}_4\text{O}_5\text{PdS}_{2.4} \cdot 0.85(\text{H}_2\text{O})$   $M = 770.40$ , monoclinic, space group  $P121/n1$ ,  $a = 10.1084(6)$ ,  $b = 13.2472(7)$ ,  $c = 25.7538(16)$  Å,  $V = 3446.2(3)$  Å<sup>3</sup>,  $D_c = 1.485$  g  $\text{cm}^{-3}$ ,  $Z = 4$ ,  $\mu(\text{Mo K}\alpha) = 0.7107$  mm<sup>-1</sup>, 5896 unique reflections of which 3563 assumed as observed ( $I > 2\sigma(I)$ ). Final  $R$  indexes ( $I > 2\sigma(I)$ )  $R1 = 0.0923$ ,  $wR2 = 0.2667$ ;  $R$  index (all data)  $R1 = 0.1574$ .
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