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Polar 2D Sheet versus Nonpolar 1D Helix Metallosupramolecular Architectures Based on $M_6M'_8$ (M = Pd^{II}, Ni^{II}; M′ = Cu^{I}, Ag^{I}) Cage Clusters with D-Penicillaminate

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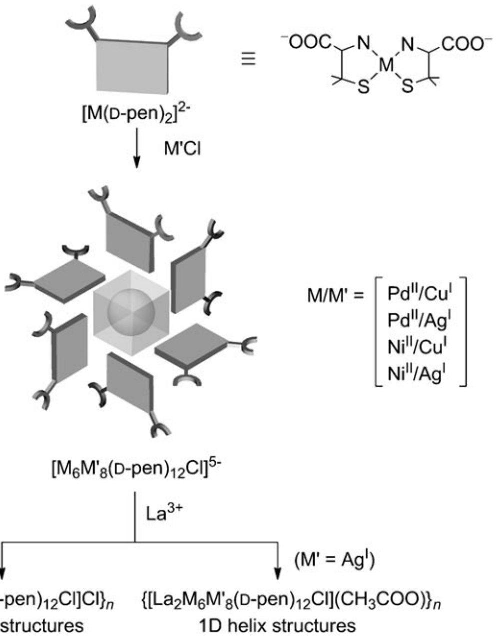
The rational design and synthesis of metallosupramolecular architectures that show unique structures and properties have been an active research subject over the past decade.[1–4] In many case, this class of architectures have been constructed by using multifunctional organic ligands as building units that are linked by appropriate transition-metal ions through coordination bonds.[2] On the other hand, examples of the use of preformed metal clusters with donor sites, instead of organic ligands, are relatively rare, although this approach is attractive with respect to the expansion of sizes, geometries, and functions in created metallosupramolecular structures, as well as the appearance of synergistic properties due to multiple metal centers.[3,4] This is mainly because of the lack of suitable metal clusters with plural donor sites, the structures of which are retained in the course of the reactions with metal ions. To date, such candidates are almost limited to oxido-, chalcogenido-, or halogenido-bridged inorganic clusters, represented by polyoxometalates[3] and $[M_6E_8(CN)_6]^{n-}$ (M = transition metal, E = chalcogenide),[4] which contain oxo or cyanide groups as donor sites. Thus, it is highly desirable to develop new metal clusters with functional groups available for coordination to metal centers and to investigate their aggregations into metallosupramolecular structures assisted by metal ions. Herein, we report on the rational synthesis of a series of S-bridged $M_6M'_8$ cage-type clusters with a cubane $[M'_8Cl]^{7+}$ core, $[M_6M'_8(\text{D-pen})_{12}Cl]^{5-}$ (M = Ni^{II}, Pd^{II}; M′ = Cu^{I}, Ag^{I}; D-pen = D-penicillaminate), by using square-planar $[M(\text{D-pen})_2]^{2-}$ as the starting complex (Scheme 1). A notable feature of these chiral $M_6M'_8$ clusters is the presence of twelve free carboxylate groups, which are expected to be used as coordination sites to metal centers. Indeed, these clusters were found to bind to La^{3+} ions through carboxylate groups, leading to the formation of dimensional heterotrimetallic supramolecular structures. Remarkably, the supramolecular structures created were markedly dependent on whether the clusters contain Cu^{I} or Ag^{I} in a cubane $[M'_8Cl]^{7+}$ core.



Scheme 1. Stepwise construction of cluster-based architectures.

The reaction of $Na_2[Pd(\text{D-pen})_2]$[5] with a slight excess of CuCl in water under reflux gave a dark yellow solution, from which a dark brown powder (**1**) was isolated by adding ethanol. X-ray fluorescence spectrometry indicated that **1** contains Pd and Cu atoms in a 3:4 ratio, and the presence of fully deprotonated D-pen ligands in **1** was confirmed by the IR spectrum, which has a $\nu(C{=}O)$ band at 1603 cm^{-1}.[6,7] The absorption spectrum of **1** is characterized by an intense absorption band at 362 nm, the molar extinction coefficiency

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of which ($\varepsilon = 4.5 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$) is significantly greater than that ($\varepsilon = 1.6 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$) of a sulfur-to-palladium charge-transfer band observed for $[\text{Pd}(\text{D-pen})_2]^{2-}$ at 330 nm.[8] The ^{1}H NMR spectrum of **1** in D_2O shows two methyl ($\delta = 1.70$, 2.50 ppm) and a methine ($\delta = 3.42$ ppm) proton signals due to D-pen ligands, which locate at much lower magnetic fields relative to the corresponding signals for $\text{Na}_2[\text{Pd}(\text{D-pen})_2]$ (Figure 1). The appearance of a single set of D-pen signals implies that **1** has a highly symmetrical structure.

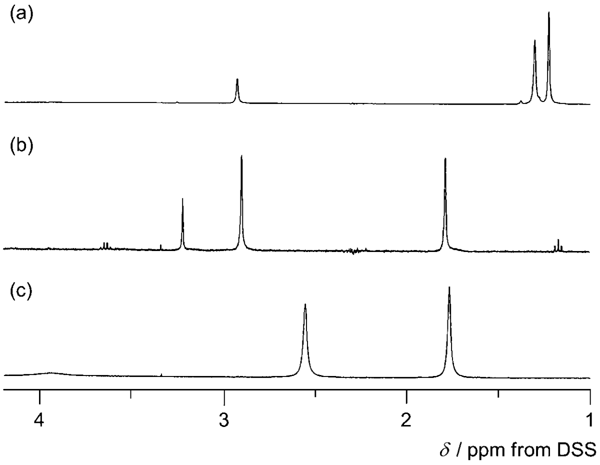

Figure 1. ^{1}H NMR spectra of $\text{Na}_2[\text{Pd}(\text{D-pen})_2]$ (a), **1** (b), and **2** (c) in D_2O.

The structure of **1** was determined by X-ray analysis, using a single crystal (**1**·NaCl) that was obtained by the slow evaporation of a solution containing **1** and NaCl in water/DMF (Figure 2).[9] The complex anion of **1** consists of six square-planar *cis*-$[\text{Pd}(\text{D-pen})_2]^{2-}$ units that bind to a $[\text{Cu}_8\text{Cl}]^{7+}$ core through S atoms, forming a cage-type $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ 14-nuclear cluster, $[\text{Pd}_6\text{Cu}_8(\text{D-pen})_{12}\text{Cl}]^{5-}$. In the $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster, there are twelve noncoordinating carboxylate groups that point in different directions with the largest intramolecular O···O separation of about 16.9 Å. Each thiolato S atom in the *cis*-$[\text{Pd}(\text{D-pen})_2]^{2-}$ units coordinates to two Cu^{I} atoms, while each Cu^{I} atom is coordinated by three S atoms from three different *cis*-$[\text{Pd}(\text{D-pen})_2]^{2-}$ units in a trigonal-planar geometry. The overall structure of this $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster in **1** is very similar to that of an analogous $\text{Cu}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster with a T symmetry, $[\text{Cu}_{14}(\text{D-pen})_{12}\text{Cl}]^{5-}$,[10] which has been prepared by the one-pot reaction of CuCl_2 and D-H_2pen. However, in **1**·NaCl, a chloride ion binds to one of eight Cu^{I} ions ($\text{Cu-Cl}_{\text{terminal}} = 2.473(4)$ Å) to have a C_3 symmetrical structure, and thus the $[\text{Cu}_8\text{Cl}]^{7+}$ core is highly distorted from a regular cubane with one of eight $\text{Cu}\cdots\text{Cl}_{\text{center}}$ distances (3.651(3) Å) being much longer than the others (2.7514(13)–2.9357(13) Å). Since the ^{1}H NMR spectrum of **1**·NaCl is identical to that of **1**, it is considered that the terminal chloride ion is liberated from a Cu^{I} coordination sphere to adopt an averaged T-symmetrical structure in solution.

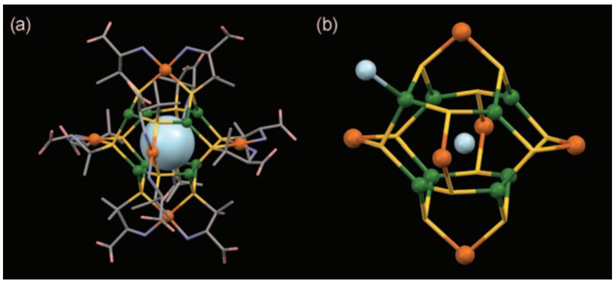

Figure 2. Perspective views of the $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster (a) and its core structure (b) in **1**·NaCl. Pd: orange, Cu: green, Cl: pale blue, C: gray, N: blue, O: red, S: yellow.

A similar reaction of $\text{Na}_2[\text{Pd}(\text{D-pen})_2]$ with AgCl in water at room temperature gave a yellow solution, from which a yellow powder (**2**) was obtained by adding ethanol.[6] While **2** does not exhibit a characteristic absorption band in the region >300 nm, the ^{1}H NMR spectrum is very similar to that of **1**, giving only two methyl ($\delta = 1.62$, 2.24 ppm) and a methine ($\delta = 3.41$ ppm) proton signals at magnetic fields much lower than those of $\text{Na}_2[\text{Pd}(\text{D-pen})_2]$ (Figure 1). In addition, the presence of fully deprotonated D-pen ligands in **2** was confirmed by the IR spectrum, which gives a ν(C=O) band at 1596 cm^{-1}.[6] From these observations, together with X-ray fluorescence and elemental analytical results, compound **2** is confidently assigned as an S-bridged $\text{Pd}^{\text{II}}_6\text{Ag}^{\text{I}}_8$ 14-nuclear cluster, $\text{Na}_5[\text{Pd}_6\text{Ag}_8(\text{D-pen})_{12}\text{Cl}]$, analogous to **1**.[11]

To examine the coordination ability of carboxylate groups in $[\text{Pd}_6\text{M}'_8(\text{D-pen})_{12}\text{Cl}]^{5-}$ ($\text{M}' = \text{Cu}^{\text{I}}$, Ag^{I}), compounds **1** and **2** were each treated with LaCl_3 in a sodium acetate buffer solution (pH 5), which afforded dark-brown crystals (**3**) and yellow crystals (**4**), respectively.[6] X-ray fluorescence spectrometry indicated that **3** and **4** each contain La atoms, besides Pd and Cu/Ag atoms, and their elemental analysis data were consistent with the formula for a 1:2 adduct of $[\text{Pd}_6\text{M}'_8(\text{D-pen})_{12}\text{Cl}]^{5-}$ and La^{3+}. Although the structural information for **3** and **4** was not gained from solution NMR spectroscopy owing to insolubility in any common solvents, the presence of $[\text{Pd}_6\text{M}'_8(\text{D-pen})_{12}\text{Cl}]^{5-}$ in **3** and **4** as building units was suggested by the IR spectral features, which are nearly the same as those of **1** and **2** over the whole region.[6]

The crystal structures of **3** and **4** were established by single-crystal X-ray analyses (Figure 3).[9] Crystal **3** is composed of S-bridged $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster units ($[\text{Pd}_6\text{Cu}_8(\text{D-pen})_{12}\text{Cl}]^{5-}$) and La^{3+} ions in a 1:2 ratio. The structure of each cluster unit in **3** is very similar to that of the $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster in **1**·NaCl, although the $[\text{Cu}_8\text{Cl}]^{7+}$ core in **3** is not so deviated from a regular cubane structure with similar Cu···Cl distances (2.739(3)–3.1265(14) Å) because of the absence of an outer chloride ion bound to a Cu^{I} atom. The overall molecular symmetry of each $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster unit in **3** is best described as T symmetry with four threefold axes passing through Cu-Cl-Cu lines of the $[\text{Cu}_8\text{Cl}]^{7+}$ core. Each $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster unit symmetrically binds to six La^{3+} ions through six carboxylate groups in a chelating mode (av. $\text{La-O} = 2.610(19)$ Å), while each La^{3+} ion is chelated by three carboxylate groups from three different $\text{Pd}^{\text{II}}_6\text{Cu}^{\text{I}}_8$ cluster

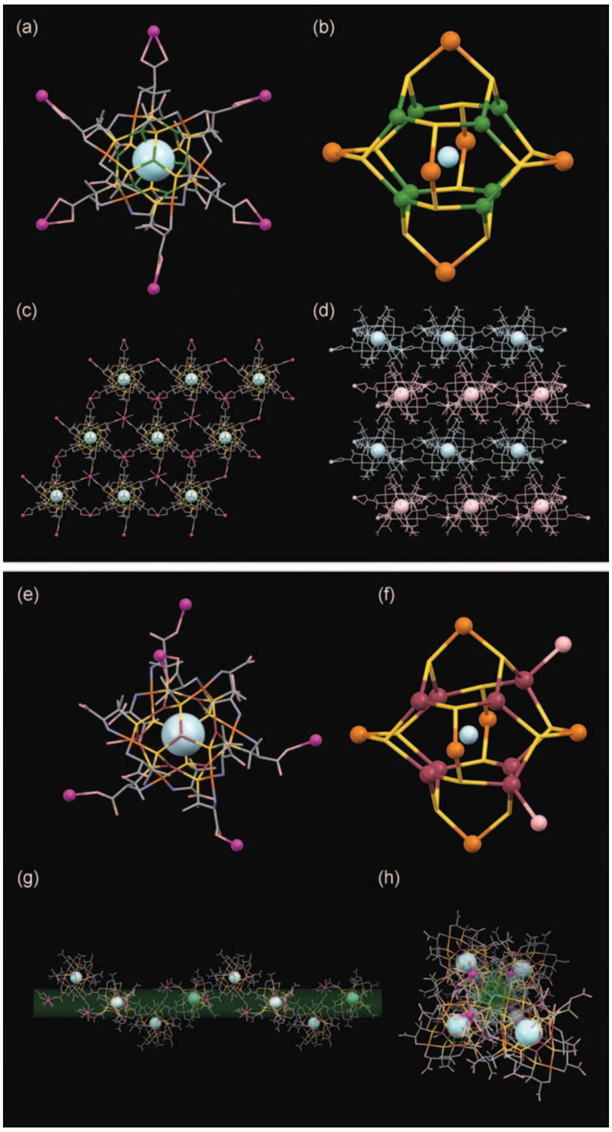

Figure 3. Perspective views of the $\mathrm{Pd^{II}_6Cu^{I}_8}$ cluster bound by $\mathrm{La^{3+}}$ ions (a), the core structure of the complex anion (b), the 2D sheet structure (c), and the packing drawing looking down the *b* axis (d) in **3**. Perspective views of the $\mathrm{Pd^{II}_6Ag^{I}_8}$ cluster bound by $\mathrm{La^{3+}}$ ions (e), the core structure of the complex anion (f), the 1D helix structure looking down the *b* axis (g), and the 1D helix structure from the *c* axis (h) in **4**. La: purple, Pd: orange, Cu: green, Ag: red purple, Cl: pale blue, C: gray, N: blue, O: red, S: yellow.

units, besides water molecules. As a result, a 2D sheetlike $\mathrm{(La^{III}_2Pd^{II}_6Cu^{I}_8)}_n$ supramolecular structure, in which three $\mathrm{Pd^{II}_6Cu^{I}_8}$ cluster units are connected alternately by three $\mathrm{La^{3+}}$ ions to form a huge hexagon with a side of about 10.8 Å, is constructed in an *ab* plane. Furthermore, the 2D supramolecular sheets are piled up in an AB stacking mode through $\mathrm{NH_2\cdots OOC}$ hydrogen bonds, completing a lattice structure very close to hexagonal close packing. In **3**, chloride anions are located between the supramolecular sheets to balance the total charge, together with water molecules of crystallization.

Crystal **4** is composed of S-bridged 14-nuclear cluster units ($\mathrm{[Pd_6Ag_8(D\text{-}pen)_{12}Cl]^{5-}}$) and $\mathrm{La^{3+}}$ ions in a 1:2 ratio, as in the case of **3**. The structure of each cluster unit in **4** corresponds well with that in **3**, except that a cubane core is made up of $\mathrm{Ag^{I}}$ atoms in place of $\mathrm{Cu^{I}}$ atoms. However, in each cluster unit of **4**, two of eight $\mathrm{Ag^{I}}$ atoms are each bound by a water molecule (Ag–O = 2.523(9), 2.596(12) Å) to form a highly distorted $\mathrm{[Ag_8Cl]^{7+}}$ cubane core, in which two of eight Ag···Cl separations (3.662(3), 3.862(3) Å) are much longer than the others (2.811(3)–3.282(3) Å).[12] Owing to this distortion, the molecular symmetry of each $\mathrm{Pd^{II}_6Cu^{I}_8}$ cluster unit is lowered from T to C_2 with a twofold axis passing through a Pd-Cl-Pd line. The most striking structural feature in **4**, which is markedly different from that in **3**, is the formation of a 1D helix supramolecular structure with a 4_1 screw axis, in which the $\mathrm{Pd^{II}_6Ag^{I}_8}$ cluster units are alternately linked by $\mathrm{La^{3+}}$ ions through monodentate carboxylate groups (av. La–O = 2.485(9) Å). The supramolecular helixes uniformly adopt a right-handedness and are linked in parallel by other $\mathrm{La^{3+}}$ ions through carboxylate groups. It appears that the low symmetry of each $\mathrm{Pd^{II}_6Ag^{I}_8}$ cluster unit in **4**, induced by the binding of water molecules to the $\mathrm{[Ag_8Cl]^{7+}}$ core, results in the unsymmetrical binding of carboxylate groups to $\mathrm{La^{3+}}$ ions, thus forming a unique helix $\mathrm{(La^{III}_2Pd^{II}_6Ag^{I}_8)}_n$ supramolecular structure. In **4**, an acetate ion, which balances the total charge, coordinates to a $\mathrm{La^{3+}}$ ion, together with carboxylate groups from the $\mathrm{Pd^{II}_6Ag^{I}_8}$ cluster units and water molecules.

With the aim of checking whether the construction of 2D sheet versus 1D helical supramolecular structures is dependent on metal ions ($\mathrm{Ag^{I}}$, $\mathrm{Cu^{I}}$) incorporated in the cubane core, analogous S-bridged $\mathrm{Ni^{II}_6Cu^{I}_8}$ and $\mathrm{Ni^{II}_6Ag^{I}_8}$ clusters, $\mathrm{K_5[Ni_6Cu_8(D\text{-}pen)_{12}Cl]}$ (**5**) and $\mathrm{K_5[Ni_6Ag_8(D\text{-}pen)_{12}Cl]}$ (**6**), were prepared by using $\mathrm{K_2[Ni(D\text{-}pen)_2]}$ as the starting complex,[13] instead of $\mathrm{Na_2[Pd(D\text{-}pen)_2]}$, which was treated with CuCl and AgCl, respectively.[6] The assignment of these clusters was made by the absorption, CD, IR, and ^{1}H NMR spectroscopy results, together with X-ray fluorescence and elemental analyses.[6] The successive reactions of **5** and **6** with $\mathrm{LaCl_3}$ gave dark-brown crystals of **7** and red crystals of **8**, respectively, which were determined to contain $\mathrm{[Ni_6(Cu\ or\ Ag)_8(D\text{-}pen)_{12}Cl]^{5-}}$ and $\mathrm{La^{3+}}$ in a 2:1 ratio by means of single-crystal X-ray analyses. Crystals **7** and **8** have 2D sheet $\mathrm{(La^{III}_2Ni^{II}_6Cu^{I}_8)}_n$ and 1D helix $\mathrm{(La^{III}_2Ni^{II}_6Ag^{I}_8)}_n$ supramolecular structures composed of $\mathrm{[Ni_6Cu_8(D\text{-}pen)_{12}Cl]^{5-}}$ and $\mathrm{[Ni_6Ag_8(D\text{-}pen)_{12}Cl]^{5-}}$ cluster units, respectively.[9] The supramolecular structures in **7** and **8** are the same as those in **3** and **4**, which consist of the $\mathrm{[Pd_6Cu_8(D\text{-}pen)_{12}Cl]^{5-}}$ and $\mathrm{[Pd_6Ag_8(D\text{-}pen)_{12}Cl]^{5-}}$ cluster units, respectively. Like in the $\mathrm{Pd^{II}_6Ag^{I}_8}$ cluster unit of **4**, two water molecules bind to the $\mathrm{[Ag^{I}_8Cl]^{7+}}$ core in the $\mathrm{Ni^{II}_6Ag^{I}_8}$ cluster unit of **8** to cause distortion from a regular cubane structure. On the other hand, the $\mathrm{[Cu^{I}_8Cl]^{7+}}$ core in the $\mathrm{Ni^{II}_6Cu^{I}_8}$ cluster unit of **7** has a much less distorted cubane structure without the coordination of water molecules, like in the $\mathrm{Pd^{II}_6Cu^{I}_8}$ cluster unit of **3**. Thus, it is reasonable to conclude that the metallosupramolecular structures constructed from $\mathrm{[M_6M'_8(D\text{-}pen)_{12}Cl]^{5-}}$

and La^{3+} are not affected by metal ions involved in the outer *cis*-$[M(\text{D-pen})_2]^{2-}$ square-planar units, but are largely dependent on metal ions that constitute an inner $[M'_8Cl]^{7+}$ ($M' = Cu^I$, Ag^I) cubane core.

Importantly, the two types of metallosupramolecular structures are discriminated not only by dimensionalities but also by polarities. That is, compounds **3** and **7** with a 2D sheet structure crystallize in the $P6_3$ space group belonging to the polar C_6 point group, whereas **4** and **8**, with a 1D helical structure, crystallize in the $P4_12_12$ space group belonging to the nonpolar D_4 point group.[14] It is known that polar materials often exhibit attractive dielectric properties, such as ferroelectricity, pyroelectricity, and piezoelectricity.[15] To observe the dielectric behavior of cluster-based frameworks, the relative permittivity measurements were performed for **3**, **4**, **7**, and **8** at variable temperatures (308–383 K) and frequencies (1–10^5 Hz) after the removal of solvated water molecules by heating at 383 K in vacuo.[16] Unfortunately, compounds **3** and **4** did not show any detectable dielectric response over the whole ranges of temperature and frequency.[6] However, compound **7** showed a small, but non-negligible dielectric response in a high temperature range (>330 K) and a low frequency range (1–10 Hz), which is indicative of the pyroelectricity. On the other hand, no detectable dielectric response was observed for compound **8** over the whole ranges. The appearance of a dielectric response for **7**, but not for **8**, is compatible with the polarity difference between **7** and **8**, and its observation at the low frequency range is most likely due to a slow fluctuation of the big $Ni^{II}{}_6Cu^I{}_8$ cluster units in the solid state. The lack of a dielectric response for **3** may be explained by stronger Pd–S than Ni–S bonds, which restricts a fluctuation of the $Pd^{II}{}_6Cu^I{}_8$ cluster units under the measurement conditions.[17]

In conclusion, we have developed the rational synthesis of a series of S-bridged 14-nuclear clusters with twelve free carboxylate groups, $[M_6M'_8(\text{D-pen})_{12}Cl]^{5-}$, by employing $[M(\text{D-pen})_2]^{2-}$ ($M = Pd^{II}$, Ni^{II}) as the starting complex, in combination with thiophilic metal ions ($M' = Cu^I$, Ag^I). These clusters were found to be available as chiral building units for the construction of metallosupramolecular architectures thanks to the presence of free carboxylate groups, as evidenced by the reactions with La^{3+} ions. Remarkably, the $La^{III}{}_2M_6Cu^I{}_8$ (**3** and **7**) and the $La^{III}{}_2M^6Ag^I{}_8$ (**4** and **8**) compounds formed polar 2D sheets and nonpolar 1D helical structures, respectively. This difference originates from the difference in the degree of distortion of the $[M'_8Cl]^{7+}$ core due to the binding/nonbinding of water molecules. Thus, it was shown that a slight structural distortion of molecular building units leads to dramatic changes in dimensional topologies and polarities when they are aggregated into highly organized supramolecular structures.

Experimental Section

Experimental details, together with spectroscopic data, are given in the Supporting Information.

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Keywords: amino acids · cluster compounds · dielectric properties · supramolecular chemistry

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[1] a) L. F. Lindoy, *Coord. Chem. Rev.* **2001**, *222*, 1–2; b) J. A. Thomas, *Chem. Soc. Rev.* **2007**, *36*, 856–868; c) S. Kitagawa, R. Matsuda, *Coord. Chem. Rev.* **2007**, *251*, 2490–2509; d) D. Tanaka, S. Kitagawa, *Chem. Mater.* **2008**, *20*, 922–931; e) E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret, M. Julve, *Dalton Trans.* **2008**, 2780–2805; f) M. W. Cooke, D. Chartrand, G. S. Hanan, *Coord. Chem. Rev.* **2008**, *252*, 903–921; g) M. P. Suh, Y. E. Cheon, E. Y. Lee, *Coord. Chem. Rev.* **2008**, *252*, 1007–1026.

[2] a) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; b) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; c) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841; d) E. C. Constable, *Coord. Chem. Rev.* **2008**, *252*, 842–855; e) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257–1283; f) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417.

[3] For example, see:a) M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem.* **2000**, *112*, 3036–3038; *Angew. Chem. Int. Ed.* **2000**, *39*, 2914–2916; b) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, Y.-G. Li, and L. Xu, *Angew. Chem.* **2006**, *118*, 7571–7574; *Angew. Chem. Int. Ed.* **2006**, *45*, 7411–7414.

[4] For example, see:a) V. E. Fedorov, N. G. Naumov, Y. V. Mironov, A. V. Virovets, S. B. Artemkina, K. A. Brylev, S. S. Yarovoi, O. A. Efremova, U. H. Peak, *J. Struct. Chem.* **2002**, *43*, 669–684; b) Y. V. Mironov, N. G. Naumov, K. A. Brylev, O. A. Efremova, V. E. Fedorov, K. Hegetschweiler, *Angew. Chem.* **2004**, *116*, 1317–1321; *Angew. Chem. Int. Ed.* **2004**, *43*, 1297–1300; c) K. A. Brylev, N. G. Naumov, A. V. Virovets, S.-J. Kim, V. E. Fedorov, *J. Clust. Sci.* **2009**, *20*, 165–176.

[5] N. Yoshinari, Y. Hirai, T. Kawamoto, A. Igashira-Kamiyama, K. Tsuge, T. Konno, *Chem. Lett.* **2009**, *38*, 1056–1057.

[6] See the Supporting Information.

[7] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 5th ed., Wiley Interscience, New York, **1997**.

[8] The intense absorption band at 362 nm for **1** was assigned as arising from intracluster transitions from Cu(3d)-S(p) to Pd(4d)-S(p) orbitals on the basis of single-point and time-dependent DFT calculations for the model complex, $[Pd_6Cu_8(SH)_{12}Cl(NH_3)_{12}]^{7+}$ (**9**).[6]

[9] Crystal data for **1**·NaCl·10.5 H_2O: $C_{60}H_{129}Cl_2Cu_8N_{12}Na_6O_{34.5}Pd_6S_{12}$; $M_r = 3311.03$; crystal size $0.40 \times 0.40 \times 0.40$ mm^3; cubic; space group $I2_13$; $a = 38.483(7)$ Å; $V = 56990(19)$ Å^3; $Z = 8$; $\rho_{calcd} = 0.772$ g cm^{-3}; $\mu = 1.097$ mm^{-1}; $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å); $T = 200(2)$ K; $2\theta_{max} = 47.6°$; 106126 reflections measured, of which 14452 unique ($R_{int} = 0.137$), 414 parameters, $R_1 = 0.065$ ($I > 2\sigma(I)$), $wR_2 = 0.188$ (all data), flack parameter = 0.07(2), residual electron density 0.347/−0.274 e Å^{-3}. **3**·51.5 H_2O: $C_{60}H_{211}Cl_2Cu_8La_2N_{12}O_{75.5}Pd_6S_{12}$; $M_r = 4189.57$; crystal size $0.40 \times 0.25 \times 0.22$ mm^3; hexagonal; space group $P6_3$; $a = 18.1980(12)$, $c = 25.236(2)$ Å; $V = 7237.5(9)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.922$ g cm^{-3}; $\mu = 2.754$ mm^{-1}; $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å); $T = 200(2)$ K; $2\theta_{max} = 55.0°$; 70946 reflections measured, of which 11091 unique ($R_{int} = 0.0525$), 530 parameters, $R_1 = 0.045$ ($I > 2\sigma(I)$), $wR_2 = 0.117$ (all data), flack parameter = 0.022(15), residual electron density 2.665/−1.668 e Å^{-3}. **4**·36 H_2O: $C_{62}H_{183}Ag_8ClLa_2N_{12}O_{62}Pd_6S_{12}$; $M_r = 4288.55$; crystal size $0.35 \times 0.10 \times 0.05$ mm^3; tetragonal; space group $P4_12_12$; $a = 24.927(4)$, $c = 46.045(10)$ Å; $V = 28610(7)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.991$ g cm^{-3}; $\mu = 2.661$ mm^{-1}; $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å);

$T = 200(2)$ K; $2\theta_{max} = 55.1°$; 192404 reflections measured, of which 32969 unique ($R_{int} = 0.0855$), 1381 parameters, $R_1 = 0.060$ ($I > 2\sigma(I)$), $wR_2 = 0.149$ (all data), flack parameter = 0.00(2), residual electron density 2.877/−4.710 e Å^{-3}. **7**·52.5 H_2O: $C_{60}H_{213}N_{12}Cl_2Cu_8La_2Ni_6O_{76.5}S_{12}$; $M_r = 3921.44$; crystal size 0.40 × 0.10 × 0.10 mm^3; hexagonal; space group $P6_3$; $a = 18.0422(2)$, $c = 25.1499(5)$ Å; $V = 7089.99(18)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.837$ g cm^{-3}; $\mu = 2.848$ mm^{-1}; $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å); $T = 200(2)$ K; $2\theta_{max} = 54.9°$; 69840 reflections measured, of which 10583 unique ($R_{int} = 0.0626$), 521 parameters, $R_1 = 0.063$ ($I > 2\sigma(I)$), $wR_2 = 0.178$ (all data), flack parameter = 0.05(2), residual electron density 1.572/−3.943 e Å^{-3}. **8**·36.5 H_2O: $C_{62}H_{184}N_{12}Ag_8ClLa_2Ni_6O_{62.5}S_{12}$; $M_r = 4011.42$; crystal size 0.40 × 0.15 × 0.15 mm^3; tetragonal; space group $P4_12_12$; $a = 24.4191(5)$, $c = 47.6380(9)$ Å; $V = 28406.2(10)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.876$ g cm^{-3}; $\mu = 2.716$ mm^{-1}; $Mo_{K\alpha}$ radiation ($\lambda = 0.71075$ Å); $T = 200(2)$ K; $2\theta_{max} = 55.0°$; 279226 reflections measured, of which 32508 unique ($R_{int} = 0.1174$), 1379 parameters, $R_1 = 0.1151$ ($I > 2\sigma(I)$), $wR_2 = 0.2628$ (all data), flack parameter = 0.09(3), residual electron density 2.123/−3.526 e Å^{-3}. CCDC-779324 (**1**·NaCl), 779325 (**3**), 779326 (**4**), 779327 (**7**), 779328 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] a) P. J. M. W. L. Birker, H. C. Freeman, *J. Chem. Soc. Chem. Commun.* **1976**, 312–313; b) P. J. M. W. L. Birker, H. C. Freeman, *J. Am. Chem. Soc.* **1977**, *99*, 6890–6899.

[11] The $Pd^{II}{}_6Ag^{I}{}_8$ and $Ni^{II}{}_6Ag^{I}{}_8$ cluster compounds, $[Co(NH_3)_6]_5[Pd_6Ag_8(\text{D-pen})_{12}Cl]_3$ and $[Co(NH_3)_6]_5[Ni^{II}{}_6Ag^{I}{}_8(\text{D-pen})_{12}Cl]_3$, have been prepared by one-pot reactions of D-H_2pen, MCl_2 (M = Pd or Ni), $AgNO_3$, and $[Co(NH_3)_6]Cl_3$. P. J. M. W. L. Birker, J. Reedijk, G. C. Verschoor, *Inorg. Chem.* **1981**, *20*, 2877–2882.

[12] The $[Ag^{I}{}_8Cl]^{7+}$ core in **4** (*cis*-Ag···Ag = 3.3689(15)–3.9851(15) Å) is greater than the $[Cu^{I}{}_8Cl]^{7+}$ core in **3** (*cis*-Cu···Cu = 3.3465(11)–3.4255(13) Å) owing to the longer Ag–S bonds (av. 2.517(4) Å) than the Cu–S bonds (av. 2.2795(18) Å). This is most likely responsible for the coordination of water molecules to the $[Ag_8Cl]^{7+}$ core, together with the high oxophilic character of Ag^{I}. S. F. Lincoln, D. T. Richens, A. G. Sykes in *Comprehensive Coordination Chemistry II: From biology to Nanotechnology, Vol. 1*, (Eds.: J. A. McCleverty, T. B. Meyer), Elsevier, Oxford, **2004**, pp. 515–555.

[13] N. Baidya, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1991**, *30*, 3967–3969.

[14] *International Tables for Crystallography, Volume A: Space-Group Symmetry* 2nd ed.(Ed.: T. Harn), Reidel, Dordrecht, Holland, **1987**.

[15] W. Zhang, H.-Y. Ye, R.-G. Xiong, *Coord. Chem. Rev.* **2009**, *253*, 2980–2997.

[16] The removal of water at this temperature was confirmed by the TG/DTA analysis.

[17] J. R. Gispert, *Coordination Chemistry*, Wiley, New York, **2008**.

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