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A Nanometer-Sized Metallosupramolecular Cube with O_h Symmetry

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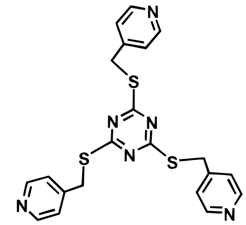
Construction of supramolecular architectures with inner cavities is a subject of current interest because of their ability for selective inclusion of ions and molecules, molecular recognition, and catalysis for specific chemical transformations.[1−6] The potential use of such species largely depends on their cavity size and type, which are mainly controlled by the ligands via appropriate metal ions.[2−6] A number of such species with inner cavities have been prepared and characterized.[7−13] Very recently, several metallosupramolecular capsules with enclosure-like systems and very large inner cavities were reported. Robson prepared and structurally characterized a $[Cu_{12}(tapp)_8]$ cubelike cage, which was derived from the self-assembly reaction of tri-bidentate ligand 2,4,6-triazophenyl-1,3,5-trihydroxybenzene (H_3tapp) and copper(II) ions.[14] Stang presented NMR and MS evidence for cuboctahedral and dodecahedral cations from tridentate and bidentate subunits.[15] Fujita obtained a trigonal-bipyramidal capsule with 36+ by reaction of $[Pd(NO_3)_2(en)]$ with 1,3,5-tris(3,5-pyrimidyl)benzene (tpb).[16] Herein reported is a stable neutral nanometer-sized metallosupramolecular cube cage $[Ni_6(tpst)_8Cl_{12}]$ (**1**) (tpst = 2,4,6-tri[(4-pyridyl)sulfanylmethyl]-1,3,5-triazine) with O_h symmetry, which was prepared from assembly reaction of $NiCl_2$ and the tpst ligand in DMF.

The tpst ligand, which was prepared from the reaction of 4-picolyl chloride hydrochloride and sodium trithiocyanuricate in MeCN, possesses exo-tridentate bonding sites. The three pyridyl rings and the central spacer in the ligand are connected by sulfanylmethyl groups. By using metal ions with square-planar or octahedral coordination geometry, such as Pd(II) or Ni(II), to link the three pyridyl groups of the tpst ligand, nanometer-sized supramolecular cages may be expected.



tpst

The reaction of $Ni(H_2O)_6Cl_2$ with tpst was carried out in a metal-to-ligand ratio of 3:4 in DMF/MeCN.[17] Slowly diffusing diethyl ether into the reaction solution produced light-green cubic crystals suitable for single-crystal X-ray diffraction. The crystallographic analysis of the complex[18] revealed that its structure is a supramolecular cube $[Ni_6(tpst)_8Cl_{12}]$ with a nanometer-sized inner cage. As can be seen in Figures 1 and 2, every tpst ligand bonds to three Ni(II) centers by the N atoms of the three pyridyl groups as expected. Each Ni center is in turn coordinated by four ligands and two chloride anions acquiring a distorted N_4Cl_2 octahedral coordination environment. Thus, fourteen building blocks, six Ni(II) centers, and eight tpst ligands dispose in an O_h space symmetrically around a central point and generate the cube cage. From the three 4-fold axis directions, the six cube faces are each effectively blocked off by one nickel atom and four pyridyl groups from four separate ligands (Figure 1). The six Ni atoms are located very close to the faces of the cube, 7.9 Å from the cavity center. The centroids of the eight C_3N_3 rings in the ligands are each located at the 3-fold inversion axes and very close to the corners of the cube (Figure 2). The distance from the cavity center to the C_3N_3 centroid is 13.2 Å. The volume of

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(17) Synthesis of the tpst ligand**:** A solution of 4-picolyl chloride hydrochloride (4.62 g, 30 mmol) and sodium trithiocyanuricate (1.77 g, 10 mmol) in NaOMe solution (1.62 g in 50 cm^3 MeOH) was heated to 50 °C for 5 h with vigorously stirring. After cooling, the pale yellow solution was filtered. Removal of the solvent afforded a light yellow powder, which was recrystallized from CH_2Cl_2/hexane (4.82 g, 75%). Anal. Calcd for $C_{21}H_{18}N_6S_3$: C, 56.0; H, 4.03; N, 18.7. Found: C, 55.2; H, 4.11; N, 18.5. ^1H NMR (500 MHz, dmso) 8.32 (pyridyl, 2H), 7.38 (pyridyl, 2H), 4.41 ($-SCH_2-$, 2H) ppm. Synthesis of $[Ni_6(tpst)_8Cl_{12}]$: A solution of the ligand tpst (0.45 g, 1 mmol) in acetonitrile (10 mL) was added to a solution of $Ni(H_2O)_6Cl_2$ (0.16 g, 0.7 mmol) in DMF (10 mL) and the reaction mixture was stirred for 2 h to give a light-green solution, which was filtered. Slow diffusion of diethyl ether into the resulting solution yielded a large amount of cubic crystals of the product (0.43 g, 59%). Anal. Calcd for $C_{240}H_{338}N_{72}O_{37}Ni_6Cl_{12}S_{24}$ (i.e., $[Ni_6(tpst)_8Cl_{12}]\cdot24DMF\cdot13H_2O$): C, 45.2; H, 5.35; N 15.8. Found: C, 45.0; H, 5.41; N, 15.5. ^1H NMR (500 MHz, dmso) 8.47 (pyridyl, 2H), 7.96 ($-CHO$, 1H), 7.35 (pyridyl, 2H), 4.37 ($-SCH_2-$, 2H), 2.89 ($-CH_3$, 3H), 2.72 ($-CH_3$, 3H) ppm. IR (KBr pellet): 3464 (s), 2983 (m), 2926.2 (w), 2875 (w), 2426 (w), 1655 (s), 1560 (s), 1481 (s), 1385 (s), 1248 (s), 850 (m), 789 (w), 680 (m) cm^{-1}.

(18) Crystallographic data: crystal dimensions 0.36 × 0.36 × 0.36 mm^3, formula $C_{240}H_{338}N_{72}O_{37}Ni_6Cl_{12}S_{24}$, FW 6370.9, cubic, space group $Pn\bar{3}n$, $a = 24.7269(14)$ Å, $V = 15118.5(15)$ Å^3, Z = 2, $R(wR) = 0.078(0.196)$ for 1206 reflections with $|F_o| \geq 2.0\ \sigma(|F_o|)$.

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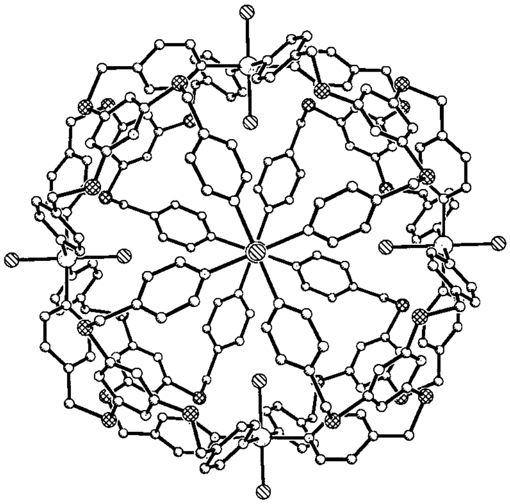

Figure 1. A view of the $[Ni_6(tpst)_8CL_{12}]$ cube cage from the 4-fold axis.

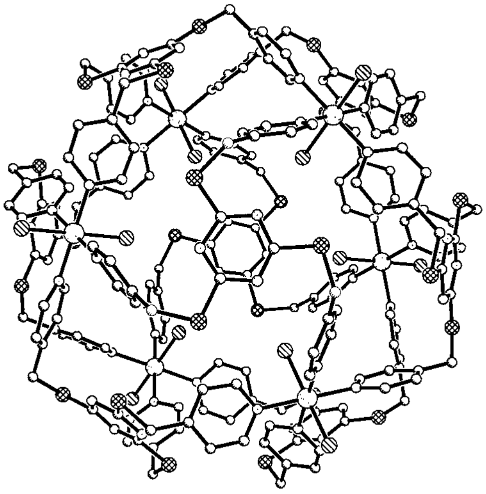

Figure 2. A view of the $[Ni_6(tpst)_8CL_{12}]$ cube cage from the 3-fold inversion axis.

the inner cavity is estimated to be ca. 1000 Å^3, implying that the complex can host many solvent molecules. Furthermore, the other interesting feature of this structure is its flexible windows. Because the sulfanylmethyl spacer groups result in the flexibility of the ligand, the cube opens twelve windows from the 2-fold axis directions of the cube edges. The water molecule inside the cage is well defined. A large number of peaks of electron densities are apparent inside and outside the cage. Occupancies of positions were therefore refined. Summation of the occupancies and symmetry operation of the positions gave rise to 8 DMF molecules in the cage and 16 DMF and 12 H_2O molecules between the cages. ^1H NMR spectra of the compound showed that the ratio of the $-SCH_2-$ signal intensity (or each of the two signals for the pyridyl groups) from the tpst ligand to that of $-CHO$ from DMF was about 2:1, indicating that each cage molecule contains 24 DMF. Both X-ray and NMR results are in agreement with that of the elemental analysis. The solvent exchange from the cage was studied. After the powder sample was soaked in water for 24 h, it was filtered and dried under vacuum. ^1H NMR spectra in the DMSO showed that the signals of DMF completely disappear, illustrating that the DMF molecules went out from the cage.

To our knowledge, such a large cage with O_h symmetry is seldom found in other metallosupramolecular species. This molecule represents the first example of a M_6L_8 metallosupramolecular cube cage and is also the first X-ray structure of the discrete nanometer-sized metallosupramolecular cage with O_h symmetry in this sort, although Stang[15] has presented NMR and MS evidence for cuboctahedral and dodecahedral cations and Winpenny[19] and Chen[20] have reported high nuclearity clusters of $[Cu_{12}La_8(\mu_3\text{-OH})_{24}(NO_3)]^{23+}$ and $[Cu_{12}Ln_6(\mu_3\text{-OH})_{24}(ClO_4)]^{17+}$ with noncrystallographic O_h symmetry, respectively. The other two examples known to us of larger coordinative capsules are Robson's $[Cu_{12}(tapp)_8]^{24+}$ and Fujita's trigonal-+bipyramidal capsule cation $[Pd_{18}(tpb)_{18}]^{36+}$ closure cages mentioned above,[14,16] of which the $[Cu_{12}(tapp)_8]^{24+}$ cavity is large enough to enclose approximately 6 DMF molecules.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (PDF). This material is available free of charge via the Internet at http:/pubs.acs.org.

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