Inorg. Chem. **2009**, *48*, 420−422

Inorganic Chemistry
Communication

A Novel Supramolecular Tetrahedron Assembled from Tetranuclear Copper(I) Cluster Molecules via Aryl Embrace Interactions

Wei Wei,[†,‡] Mingyan Wu,[†] Qiang Gao,[†,‡] Qingfu Zhang,[†,‡] Yougui Huang,[†] Feilong Jiang,[†] and Maochun Hong[*,†]

The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China, and Graduate School of the Chinese Academy of Sciences, Bejing 100039, People's Republic of China

Received October 19, 2008

An intriguing supramolecular tetrahedral aggregate $[Cu_4I(ptt)_3(Hptt)_3]_4$ (**1**; Hptt = 1-phenyl-1*H*-tetrazole-5-thiol) based on novel copper(I) iodide thiolate clusters in the solid state has been synthesized and characterized. Four tetra-copper(I) cluster molecules join together with the cooperation of multiple offset face-to-face $\pi-\pi$ stacking (**OFF**) and edge-to-face $C-H\cdots\pi$ (**EF**) interactions in the form of aryl embrace of a $(\mathbf{EF})_3(\mathbf{OFF})_3$ motif, which leads to the formation of this tetrahedral aggregate. Furthermore, this complex exhibits a temperature-dependent green photoluminescence.

Supramolecular chemistry describes the spontaneous assembly of noncovalently linked molecular polyhedra of unique shape and composition. In the past decade, the coordination-driven[1] and conventional hydrogen-bonding-directed[2] self-assembly of a high-symmetry conglomerate has been developed rapidly based on the edge- or face-directed strategies.[1a,e] However, it is still a great challenging subject to construct supramolecular polyhedra merely via weaker affinities such as aromatic−aromatic interaction because of the weak attraction of an individual interaction.[3] To overcome this difficulty, multiple concerted aromatic−aromatic interactions will be required, thus resulting in a collective contribution to the formation of a reliable supramolecular synthon, which would be used to interlink ambient individual molecules into a regular aggregation like a supramolecular polyhedron, as is found to be prevalent in many biological molecules. One of the supramolecular synthons has been described as a multiple aryl embrace by Dance and co-workers,[4,5] which is a concerted set of interactions between aryl groups through a combination of offset face-to-face $\pi-\pi$ stacking (**OFF**) and edge-to-face $C-H\cdots\pi$ (**EF**) interactions.[3a] Actually, these multiarmed, concerted, and attractive motifs are frequently observed in crystals of molecules with multiple aryl groups on the surfaces.[5,6] In this respect, we chose 1-phenyl-1*H*-tetrazole-5-thiol (Hptt) as the ligand, which obviously could be divided into two parts: thiotetrazole and phenyl groups. The former is expected to be bridging groups in the construction of copper(I) clusters like other N-heterocyclic thiolate ligands,[7] while the latter can offer additional noncovalent aromatic interactions to modulate and influence the assembly and packing of copper(I) cluster molecules. Also, we fortunately obtained a delicate supramolecular tetrahedron $[Cu_4I(ptt)_3(Hptt)_3]_4$ (**1**) in the solid state, which is assembled from four novel copper(I) iodide thiolate cluster molecules via many cooperative aromatic−aromtic interactions. In this Communication, we will report its synthesis and crystal structure, together with temperature-dependent green photoluminescence and its considerable thermal stability.

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[*] To whom correspondence should be addressed. E-mail: hmc@fjirsm.ac.cn.

[†] The Chinese Academy of Sciences.

[‡] Graduate School of the Chinese Academy of Sciences.

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10.1021/ic801972e CCC: $40.75

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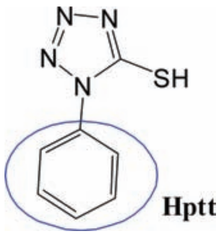
Published on Web 12/15/2008



Reaction and evaporation at ambient temperature of the Hptt ligand and CuI at a ratio of 1:1 in CH_3CN afford colorless prismatic crystals.[8] Single-crystal X-ray diffraction reveals that **1** crystallizes in the noncentrosymmetric cubic group $P\bar{4}3n$.[9] The structure of **1** features a discrete tetracopper(I) cluster linked by ptt anion and neutral Hptt ligands.[10] As shown in Figure 1, there are only two crystallographically independent Cu atoms in the asymmetric unit. Cu1 is located on the crystallographic C_3 axis and is ligated by three S2 atoms from three ptt ligands in a triangle geometry with a bond length of 2.287 Å (Cu1−S2). In contrast to Cu1, Cu2 shows a distorted tetrahedron geometry: two S atoms and one N atom from the ptt and Hptt ligands create its tapered bottom, and I^- occupies its apex to complete the configuration. Here, similar to Cu1, I^- also locates on the C_3 axis and has an occupancy of one-third. The distance of Cu2−I1 is measured to be 2.8034(7) Å, which is slightly longer than those found in other copper(I) complexes containing Cu−I bonds.[11] The separation between Cu1 and Cu2 is 2.8234(9) Å, which is close to the sum of the van der Waals radii (2.80 Å) of Cu^I centers, implying the existence of weak Cu−Cu interactions. Thus, the connectivity of four Cu ions and one I anion gives rise to a novel tetrametal core of $[Cu_4I]$ with C_{3v} symmetry. Additionally, there are relatively few examples known of the simultaneous incorporation of competitive iodide and thiolate anions bridging adjacent coinage metal ions.[12]

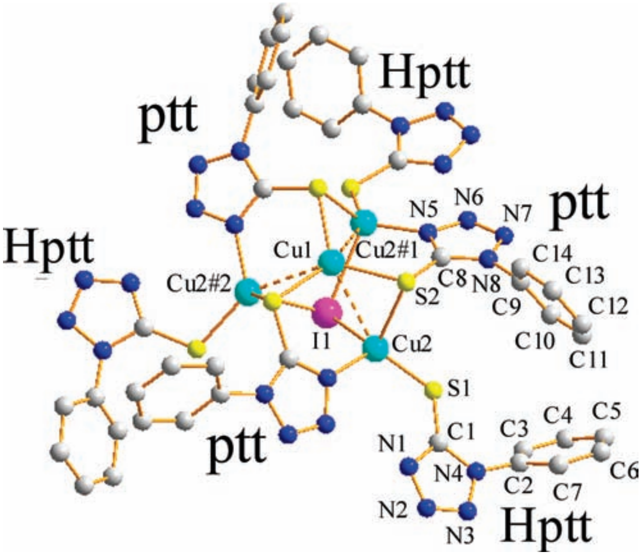


Figure 1. View of the metal−cluster molecule with C_3 symmetry in **1**. All H atoms have been omitted for clarity. Two types of ligands are marked with Hptt and ptt. Symmetry code: #1, $1 - y, z, 1 - x$; #2, $1 - z, 1 - x, y$.

Because the copper(I) cluster molecule is electrically neutral and hydrophobic, it lacks charge-compensating interactions like ion−dipole interaction and conventional hydrogen bonding. Consequently, the self-assembly force for the construction of supramolecular conglomerates mainly comes from the concerted aromatic−aromatic interactions, which are originated from the tetrazole ring and protruding phenyl group of the ligands. As shown in Figure 2a, a trimer generated from C_3 symmetry operation can be extracted from packing topology to expound the complicated aromatic−aromatic interactions. It is obvious that three types of aromatic−aromatic interactions exist among the trimer: (I) edge-to-face CH···π interactions (red dashed lines) between two neighboring phenyl rings, ab. **EF**; (II) offset face-to-face phenyl−tetrazole stacking (dark dashed lines), ab. **OFF**; (III) tetrazole−tetrazole stacking interctions (yellow dashed lines). All of these interaction separations and angles are listed in Table 1. Primarily, three phenyl rings from different copper(I) cluster molecules interact with each other through three **EF** ($d_{CH\cdots centroid} = 2.82$ Å) in a concerted manner, which gives rise to a concerted $(\mathbf{EF})_3$ motif. At the same time, tetrazole moieties from adjacent molecules also affect the phenyl ring by the formation of **OFF** interaction ($d_{centroid\cdots centroid} = 3.78$ Å). In this manner, each phenyl ring, acting as both a proton acceptor and a donor, is sandwiched with interactions of two **EF** and one **OFF** motifs from three other aromatic rings. Thus, for the whole trimer, it includes an extended array of aryl embrace of $(\mathbf{EF})_3(\mathbf{OFF})_3$. In addition, tetrazole moieties from ptt ligands of neighboring molecules are involved in another type of energetically favorable π deficient−π deficient stacking,[13] and the close contact (3.14 Å) between N atoms of two tetrazole rings indicates considerable tetrazole−tetrazole interaction. As a result, by means of the aryl embrace of the $(\mathbf{EF})_3(\mathbf{OFF})_3$ motif and the tetrazole−

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(8) Synthesis of the compound: The ligand Hptt (89 mg, 0.50 mmol) and CuI (90 mg, 0.50 mmol) were mixed with 10 mL of CH_3CN and stirred for 2 h. After 48 h, slow evaporation of the solution in air afforded a large number of fine colorless crystals. Yield: 68% (with respect to Hptt supplied). Anal. Calcd for $[C_{42}H_{33}N_{24}S_6ICu_4]$: C, 34.85; H, 2.30; N, 23.23. Found: C, 35.27; H, 2.32, N, 23.15. IR (KBr, cm^{-1}): 3073(m), 2920(m), 2771(m), 1594(m) 1497(s), 1376(s), 1313(s), 761(s), 687(m), 566(m).

(9) Crystal data for **1**: $C_{42}H_{33}N_{24}S_6ICu_4$, $M_W = 1447.3$, cubic, $P\bar{4}3n$ (No. 218), $a = 22.4646$ (3) Å, $V = 11336.9$ (3) Å^3, $Z = 8$, $D_c = 1.692$ g/cm^3, $F_{000} = 5744$, $\mu = 2.30$ mm^{-1}, $S = 1.068$, R1 = 0.0374, wR2 = 0.1053. Considering the long distance of Cu1 and I1, ca. 3.12 Å, we infer that there is no interaction between them.

(10) It is distinct that there are two different coordination modes of the ligand in **1**. As judged by the distance of C1···S1 atoms [1.668 (4) Å, distinctly shorter in comparison to the C8−S2 single bond length 1.717(4) Å] and the conservation of electroneutrality of the component molecule, the C1−S1 bond is a double covalent bond and proton transfer from S1 to N1 has occurred. Thus, the monodentate ligand possessing a S1 atom is electrically neutral, which is marked with Hptt, and the ptt anion ligand containing μ-S (S2) is represented as ptt.

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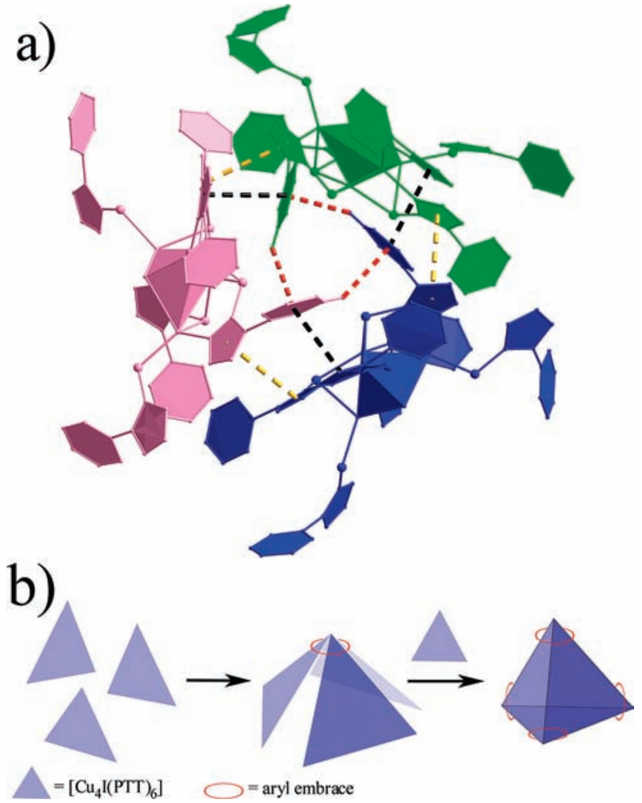

Figure 2. (a) View of the formation of a trimer along the C_3 axis via the CH$\cdots\pi$ (red dashed lines), phenyl−tetrazole stacking (dark dashed lines), and additional tetrazole−tetrazole stacking interactions (yellow dashed lines). (b) Cartoon representation of the hypothetical formation of the trimer depicted as an open cone with C_3 symmetry and finally a supramolecular tetrahedron.

Table 1. Aromatic−Aromatic Interactions Existing in the Crystal Structure of **1**

interaction group	interaction type	central separation/ Å	shortest contact/ Å	angle/ deg
phenyl−phenyl	C−H$\cdots\pi$	2.82[a]		$\theta = 141$
phenyl−tetrazole	$\pi-\pi$ stacking	3.78	3.52	$\beta = 17.31$
tetrazole−tetrazole	$\pi-\pi$ stacking	3.92	3.14	$\beta = 22.23$

[a] Separation of an H atom and π ring centroid; θ = angle of C−H$\cdots$ring centroid in C−H$\cdots\pi$ interactions; β = angle between the ring normal and centroid−centroid vector in $\pi-\pi$ stacking.

tetrazole interactions, the assembly of the trimer can be depicted as the formation of an open cone with C_3 symmetry (Figure 2b). On the other hand, the copper(I) cluster molecule itself also has a C_3 symmetry. Accordingly, simultaneous satisfaction of the two 3-fold symmetry axes can only be achieved by the formation of a supramolecular tetrahedron via 30 aromatic−aromatic interactions (Figure 3). Interestingly, we cannot find any appreciable interactions among these tetrahedra, implying an independence of the supramolecular conglomerates in crystal packing. Thermogravimetric analysis indicates that the highly symmetric structure with a void of ca. 160 Å^3 can survive until 180 °C. This tetramer structure is reminiscent of the hemoglobin molecule, which is also a tetramer of four globular protein subunits composed of heme groups containing metal ions and protein chains. Additionally, it is also assembled via weak hydrogen bonds, $\pi-\pi$ stacking, and van der Waals contacts.

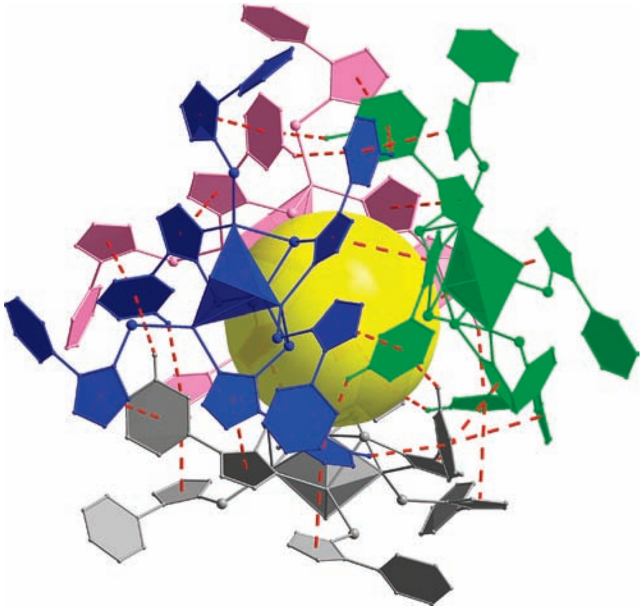

Figure 3. Formation of a supramolecular tetrahedron via 30 aromatic−aromatic interactions. The interactions are represented as red dashed lines.

The other attractive characteristic of this complex is its temperature-dependent green photoluminescent property. At ambient temperature, **1** does not display any obvious emission. However, at the low temperature of 10 K, excitation of solid samples at $\lambda = 380$ nm produces a broad green emission with a peak maximum at 528 nm (Figure S3 in the Supporting Information). More detailed theoretical and spectroscopic studies are being pursued.

In summary, an interesting supramolecular tetrahedron complex based on novel tetracopper(I) clusters has been synthesized and characterized. These tetrametal cluster molecules join together with the cooperation of C−H$\cdots\pi$ and $\pi-\pi$ stacking interactions in the form of an aryl embrace of the (**EF**)$_3$(**OFF**)$_3$ motif, which leads to the formation of a supramolecular tetrahedron in the solid state. This crystal structure serves as a useful example of these weak aromatic−aromatic interactions for organization into highly symmetric architectures with considerable stabilization, which affords a significant approach to the biological simulation. Furthermore, this complex exhibits a temperature-dependent green photoluminescence deserving further investigations of the emissive mechanism.

Acknowledgment. We thank the 973 Program (2006CB932900), the National Natural Foundation of China and the Natural Science Foundation of Fujian Province for funding this research.

Supporting Information Available: Crystallographic data in CIF format, table of selected bond lengths and angles, XRPD patterns, TG-MS analyses, solid-state emission spectrum, space-filling representation, and packing diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

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