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A Coordination Polymer Containing Inorganic Buckybowl Analogues

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Two photoluminescent coordination polymers, $\{[Cu_{10}(\mu_3\text{-}Mtta)_3(\mu_4\text{-}Mtta)_7]\cdot 2H_2O\}_n$ (**1**), containing 2-D wavy motifs with inorganic buckybowl analogues, and $[Cu_5(\mu_3\text{-}Mtta)_2(\mu_4\text{-}Mtta)_3(NH_3)_2]_n$ (**2**, Mtta = 5-methyl tetrazolate), were obtained by the control of solvents and auxiliary complexing agent. The ligand Mtta is a likely candidate for the construction of metal-organic, fullerene-like molecules. The luminescent properties of **1** and **2** are discussed.

Introduction

As a bridge between the fullerene family and flat aromatic compounds, buckybowls, curved-surface fragments of fullerenes, were found a few years ago, and only a few examples are available to date.[1] Great attention has been paid to the coordination chemistry of transition-metal buckybowl complexes because of their intriguing curvatures and reactivity.[2] On the other hand, substantial effort has recently been directed towards studies of metal-containing, inorganic, fullerene-like molecules that comprise five- and six-membered rings mapping onto the surface of the C_{60} analogue.[3] The design and construction of inorganic, fullerene-like molecules, even of their fragments, are still a great challenge for inorganic chemists because of the difficulty to control the formation of the curvature. The five-membered ring tetrazole is possibly a potential candidate for constructing fullerene-like fragments. In our continuing research of designing novel coordination networks,[4] herein we report the synthesis and the structural characterization of a supramolecular network containing inorganic buckybowl analogs, and of another 2D polymeric network for comparison, by using Sharpless' cycloaddition reactions of nitriles and azides.[5]

Results and Discussion

Reactions of $Cu(NO_3)_2$, NaN_3, and CH_3CN with 2, 2′-bipyridine/H_2O or toluene/$NH_3\cdot H_2O$ (v/v, 2:1) gave two complexes $\{[Cu_{10}(\mu_3\text{-}Mtta)_3(\mu_4\text{-}Mtta)_7]\cdot 2H_2O\}_n$ (**1**) or $[Cu_5(\mu_3\text{-}Mtta)_2(\mu_4\text{-}Mtta)_3(NH_3)_2]_n$ (**2**), respectively, (Mtta = 5-methyltetrazolate). Interestingly, 2, 2′-bipiridine does not appear in **1**. The influence of bipyridine on the self-assembly of the complex is obvious because **1** cannot be synthesized in the absence of bipyridine.

X-ray single-crystal analyses of **1** and **2** confirm the formation of 5-methyl tetrazolate. Complex **1** is composed of guest water molecules and a 3D neutral microporous framework based on copper(I) and the ligand Mtta, with a space group of *C2/m* (Figure 1a, and Figures S1 and S2 in the Supporting Information). The elliptic cavities along the *c* axis in the 3D framework of **1** are constructed by stacking two different kinds of 2D layers (Part A and Part B, Figure 1b and Figure 1c, respectively) in the alternative mode ABAB. Approximately 18.3% of the crystal volume can be occupied by free water molecules, with a volume of ca. 958.6 Å^3 in each cell unit.[6]

In Part A (Figure 1b), each Cu^I center adopts a distorted tetrahedral geometry. The copper atoms bound to the tetradentate Mtta ligands show significant out-of-plane displacements with respect to the "best plane" of the heterocycle (in the range +0.1328 to +1.6078 Å). Markedly, the out-of-plane displacements result in the formation of a buckybowl analogue that possesses 26 inorganic core atoms of $Cu_6(Mtta)_4$ with four five-membered rings and five six-membered rings (Figure 2a). In the buckybowl analogue, each N_4C ring of Mtta is surrounded by six-membered N_4Cu_2 rings. Adjacent buckybowl analogues facing the opposite direction in an alternating convex and concave fashion are linked by Cu–N coordination bonds to form a wavy ribbon along the *b* direction (Figure 2b). Adjacent ribbons are fused by the Cu–N bonds into a 2D wavy layer (Figure 1b, Figure S3). The ligand Mtta possesses a μ_4-η^1:η^1:η^1:η^1 coordination mode which is rare in tetrazolate derivatives.[7] Because of the tetrahedral coordination sphere of the Cu^I ions, the nonplanar, six-membered rings formed are folded along the Cu···Cu axis by about 131–170°. The existence of carbon atoms that cannot be coordi-

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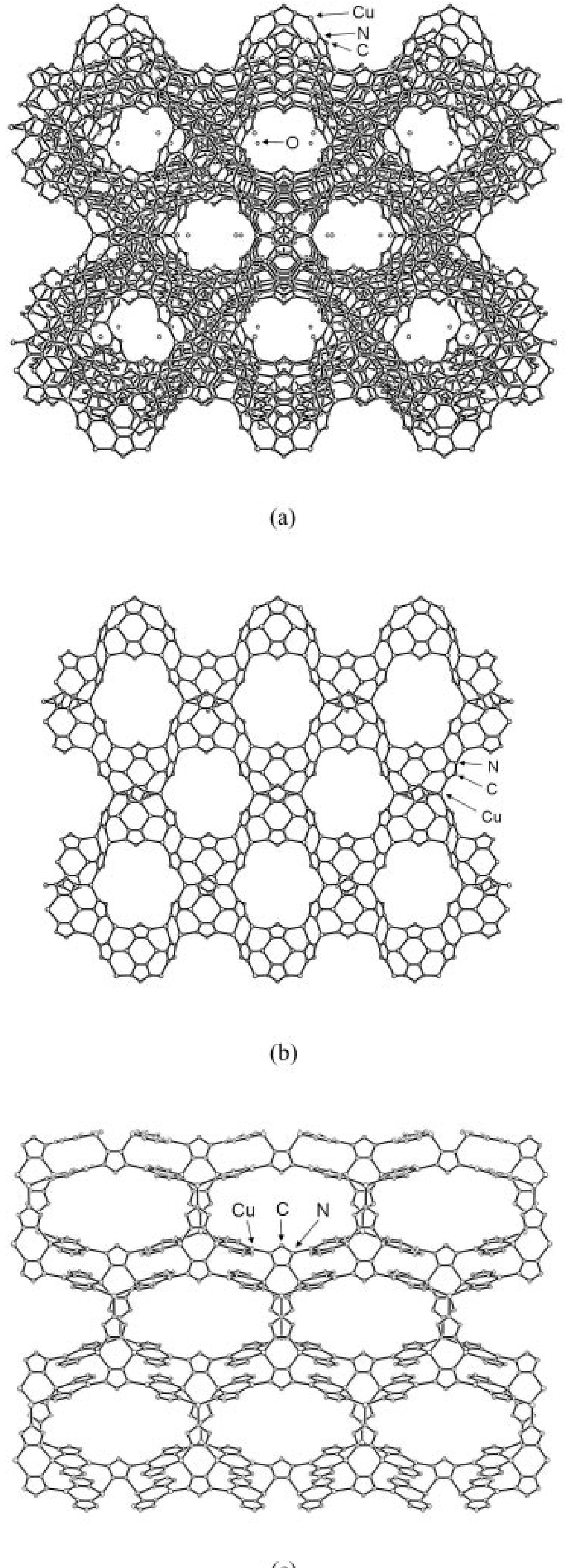

Figure 1. Structure of **1**: (a) Three dimensional packing diagram along the *ab* plane; (b) 2D layer of Part A; (c) 2D layer of Part B.

nated and the steric hindrance of methyl groups most likely prevents the assembly from developing a larger fullerene-like fragment.

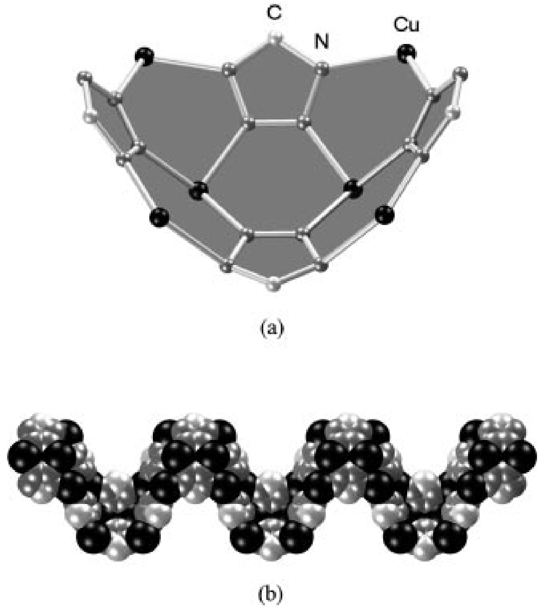

Figure 2. View of the buckybowl composed of Cu$_6$(Mtta)$_4$ with four five-membered rings and five six-membered rings. (b) 1D wavy ribbon constructed by alternating convex and concave buckybowls.

In Part B, the copper(I) centers adopt two types of coordination geometries: the trigonal planar copper(I) center that binds three nitrogen atoms from three different ligands, and the distorted tetrahedral copper(I) center that binds four nitrogen atoms from four different ligands. The Mtta ligand bridges the copper atom through μ_3 and μ_4 bridging modes (in the ratio 1:1) to form a 2D double-layer plane with an approximately rectangular cavity (Figure 1c). All Mtta ligands located above and below the double-layer plane occupy the fourth coordination site of the copper atoms of Part A and form Cu–N bonds to construct the final 3D framework (Figure S2).

In **2**, there are four crystallographically unique copper atoms, which adopt trigonal and tetrahedral geometries (Figures S4 and S5). The Mtta ligand bridges the copper atom through μ_3 and μ_4 bridging modes (in the ratio 2:3) to form a 2D double-layer plane with rectangular cavities as shown in Figure 3. The coordination geometry around the rectangular cavities is identical to that of our previously reported 3D network [Cu(μ_4-Mtta)]$_n$[4c] shown in Figure S6 (top). The NH$_3$ molecules most likely act as a “molecular scissor” to cut the 3D network of [Cu(μ_4-Mtta)]$_n$ along the *b* axis to form the 2D layer and to occupy the vacancy of the Cu^I center.

The tetrazolate group in Part B of **1** and **2**, which bears a μ_3 bridging mode, does not allow for the formation of a buckybowl. It seems that the μ_4-η^1:η^1:η^1:η^1 coordination mode is crucial for the construction of an arched surface.

Both **1** and **2** in the solid state show strong photoluminescence at room temperature with emission maxima at 469 nm and 497 nm, respectively (Figure 4). In comparison

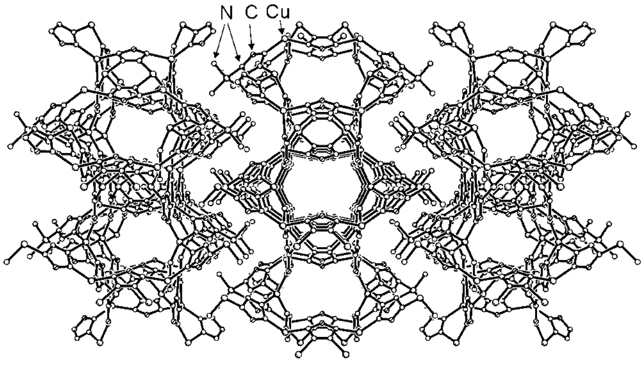

Figure 3. 2D double-layer plane with rectangular cavitivies in complex **2**.

with the photoluminescence of Cu^I azolate,[8] the possibility of an MLCT [Cu→Mtta] excited state in the two complexes may be suggested. The similar emission spectra of these two complexes imply that the properties of the excited state are related only to the local coordination geometry. This explains the red shift of the bands in the spectrum of complex **2** relative to that of complex **1**, since the d* energy level in trigonal planar Cu^I is higher than that in tetrahedral Cu^I.

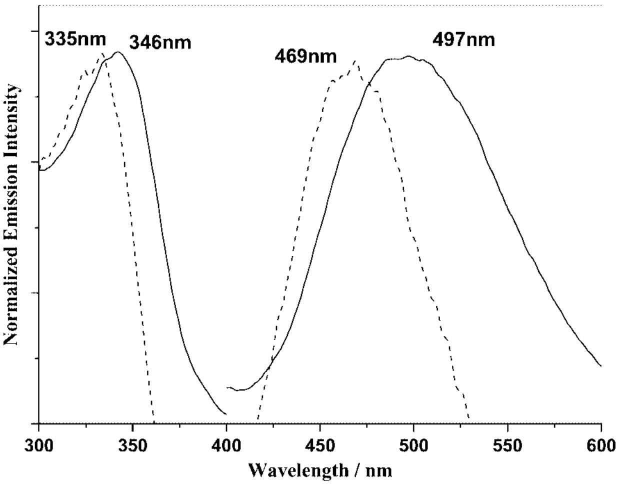

Figure 4. Solid-state excitation (left) and emission (right) spectra of complex **1** (dashed line) and **2** (solid line) at room temperature.

The TG curve of **1** shows a weight loss of 2.28% (calcd. 2.39%) from 45–230 °C that corresponds to the release of lattice water (Figure S7). After a stable platform, complex **1** begins to decompose at 298 °C and finally sublime at 415 °C. The observed weight loss that corresponds to NH_3 (5.15%) in complex **2** is in good agreement with the calculated value from 202–229 °C. A very stable platform from 229–276 °C is observed, which increases the possibility of the solid transformation from **2** to $[Cu(\mu_4\text{-Mtta})]_n$, and this is followed by an abrupt decline (approximately 100%). Unfortunately, the XPRD pattern of the solid prepared by heating complex **2** at 250 °C under argon for 0.5 h is different from the simulated pattern of $[Cu(\mu_4\text{-Mtta})]_n$ (Figure S8), which implies that the solid transformation from **2** to $[Cu(\mu_4\text{-Mtta})]_n$ was unsuccessful.

Conclusions

In summary, we obtained a 3D coordination network containing inorganic buckybowl analogues. The ligand Mtta with a μ_4-η^1:η^1:η^1:η^1 coordination mode is most likely a good candidate for the construction of inorganic, fullerene-like molecules. Furthermore, the N_5 ring may be an optimal component, demonstrating the great potential for the synthesis of other half shells, nano-sized molecules, and full-shell structural motifs. This work provides a new avenue for designing and constructing an inorganic, fullerene-like molecule.

Experimental Section

Preparation of Complex 1: A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.241 g, 1.0 mmol), NaN_3 (0.065 g, 1.0 mmol), 2, 2′-bipyridine (0.156 g, 1.0 mmol), and acetonitrile (5.0 mL) was stirred for 10 min in air, and then transferred and sealed in a 15-mL Teflon-lined reactor. The reactor was heated in an oven to 140 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. The pale-yellow block crystal was attained in a reasonable yield (35.5%, 0.053 g) based on $Cu(NO_3)_2\cdot 3H_2O$. $C_{20}H_{34}Cu_{10}N_{40}O_2$ (1502.27): calcd. H 2.28, C 15.99, N 37.29; found H 2.31, C15.90, N 37.34. IR data (KBr): 2921 (m), 1634 (m), 1499 (s), 1384 (s), 1135 (m), 1045 (m), 698 (w) cm^{-1}.

Preparation of Complex 2: A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (0.241 g, 1.0 mmol), NaN_3 (0.065 g, 1.0 mmol), acetonitrile (5.0 mL), and aqueous ammonia (25%, 5.0 mL) was stirred for 10 min in air, and then transferred and sealed in a 15-mL Teflon-lined reactor. The reactor was heated in an oven to 140 °C for 50 h and then cooled to room temperature at a rate of 5 °C h^{-1}. The colorless, bar crystal was attained in a reasonable yield (46.3%, 0.036 g) based on $Cu(NO_3)_2\cdot 3H_2O$. $C_{10}H_{21}Cu_5N_{22}$ (767.19): calcd. H 2.76, C 15.66, N 40.17; found H 2.72, C15.71, N 40.60. IR data (KBr): 3419 (s), 2921 (m), 1646 (m), 1482 (s), 1372 (s), 1123 (s), 1083 (m), 702 (w) cm^{-1}.

X-ray Crystallographic Study: Data collections of **1** and **2** were performed on a Bruker Smart Apex CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å), using frames of 0.3° oscillation ($2\theta \le 56°$). The structures were solved with direct methods and refined with the full-matrix least-squares technique with the SHELXTL programs. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C–H = 0.960 Å). The crystallographic calculations were conducted with the SHELXL-97 programs.[9] Crystal data for **1**: $C_{20}H_{34}Cu_{10}N_{40}O_2$, monoclinic, space group *C2/m* (no. 12), Mr = 1502.27, a = 21.5327(12) Å, b = 16.4443(9) Å, c = 14.8195(8) Å, β = 92.5190(10)°, V = 5242.4(5) Å^3, Z = 4, D_c = 1.903 g cm^{-3}, μ = 4.036 mm^{-1}, $F(000)$ = 2960, T = 298(2) K, 16576 reflections measured, 6175 unique (R_{int} = 0.0268), final R_1 = 0.0553, wR_2 = 0.1483, S = 1.083 for all data. Crystal data for **2**: $C_{10}H_{21}Cu_5N_{22}$, monoclinic, space group *C2/m* (no. 12), Mr = 767.19, a = 11.5328(6) Å, b = 30.1639(17) Å, c = 8.8471(5) Å, β = 130.2320(10)°, V = 2349.6(2) Å^3, Z = 4, D_c = 2.169 g cm^{-3}, μ = 4.504 mm^{-1}, $F(000)$ = 1520, T = 298(2) K, 7343 reflections measured, 2762 unique (R_{int} = 0.0185), final R_1 = 0.0294, wR_2 = 0.0791, S = 1.108 for all data. CCDC-279776 and CCDC-279777 contain 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.

Supporting Information (see footnote on the first page of this article): Additional figures for structural illustration (Figures S1–S6), TG analysis of complexes **1** and **2** (Figure S7), and XPRD pattern of the solid prepared by heating complex **2** (Figure S8) are available.

Acknowledgments

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