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Article

Metal–Organic Architectures of Silver(I), Cadmium(II), and Copper(II) with a Flexible Tricarboxylate Ligand

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Three novel metal–organic architectures, $[Ag_3(bta)]\cdot 1.5H_2O$ (**1**), $[Cd_3(bta)_2(H_2O)_7]\cdot 5H_2O$ (**2**), and $[Cu_{11}(bta)_6(Hbta)_2(H_2O)_{10}]\cdot 29H_2O$ (**3**), were obtained by reactions of the corresponding metal salts with a flexible tripodal ligand, benzene-1,3,5-triacetic acid (H_3bta), and their structures were determined by single-crystal X-ray diffraction studies. The results revealed that, in complexes **1** and **2**, the carboxylate groups of the bta^{3-} ligand adopted varied coordination modes to link metal atoms and further to form three-dimensional structures with open channels occupied by water molecules, while in complex **3**, for the first time, the flexible H_3bta acted as a secondary building unit to generate a novel nanometer-sized metallocage, which is composed of a Cu^{II} paddle wheel (square secondary building units) and $bta^{3-}/Hbta^{2-}$ organic links (triangular secondary building units). The photoluminescence properties of complexes **1** and **2** were investigated, and the results showed that **2** exhibited photoluminescence in the solid state at room temperature.

Introduction

Metal−organic architectures with large cavities have evoked wide attention because of their structural diversity and potential applications in many fields.[1] Recently, Kitagawa and co-workers reported methane gas adsorption and hydrogen storage properties of porous frameworks.[2] On the other hand, Yaghi and some other groups have succeeded in obtaining multidimensional porous frameworks by using a 1,3,5-benzenetricarboxylate (btc; Chart 1) ligand and various metal salts.[3,4] Because of the diversity of the binding modes of the carboxylate group with metal atoms, novel and fantastic frameworks can be achieved by reactions of carboxylate-containing ligands with various metal salts. Up to now, extensive works have been carried out by using carboxylate-containing ligands in addition to btc, for example, 1,3-benzenedicarboxylic acid (m-H_2bdc), 1,4-ben-

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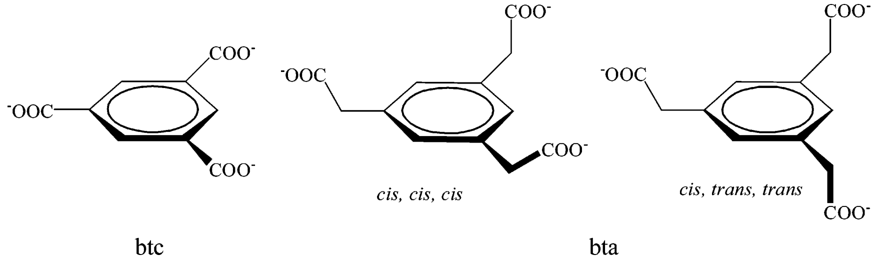
Chart 1



zenedicarboxylic acid (p-H_2bdc), 4,4′,4″-benzene-1,3,5-triyltribenzoic acid (H_3btb), and 1,2,4,5-benzenetetracarboxylic acid (H_4btec).[5−8] In these reports, most of the bridging ligands used in the construction of the frameworks are rigid because the carboxylate groups in these ligands are attached to the central aromatic ring directly. Metal−organic architectures assembled by metal salts with flexible carboxylate-containing ligands are not well done up to now, possibly because of the difficulties in predicting the structures of the resulting complexes.[9] We report herein the synthesis, structural characterization, and luminescence properties of two novel three-dimensional (3D) complexes, $[Ag_3(bta)]\cdot 1.5H_2O$ (**1**) and $[Cd_3(bta)_2(H_2O)_7]\cdot 5H_2O$ (**2**), and one nanometer-sized metallocage $[Cu_{11}(bta)_6(Hbta)_2(H_2O)_{10}]\cdot 29H_2O$ (**3**), where bta^{3-} is a flexible tripodal ligand, benzene-1,3,5-triacetate, which can adopt at least two different conformations (Chart 1) upon coordination with metal atoms, while in the cases of rigid ligands, such as btc^{3-}, btb^{3-}, etc., there are no such great conformational changes.

Table 1. Crystallographic Data for Complexes **1**−**3**

complex	**1**	**2**	**3**
chemical formula	$C_{12}H_{12}Ag_3O_{7.50}$	$C_{24}H_{42}Cd_3O_{24}$	$C_{96}H_{152}Cu_{11}O_{87}$
fw	599.83	1051.78	3397.12
cryst syst	triclinic	monoclinic	tetragonal
space group	$P\bar{1}$	$P2_1/c$	$I4/m$
a, Å	4.7143(3)	11.344(3)	17.5189(4)
b, Å	11.7344(8)	39.266(6)	17.5189(4)
c, Å	13.6823(10)	8.1324(18)	20.3167(6)
α, deg	67.666(2)	90.00	90.00
β, deg	89.269(3)	102.908(18)	90.00
γ, deg	82.096(2)	90.00	90.00
V, Å^3	692.82(8)	3530.8(13)	6235.4(3)
Z	2	4	2
T, K	200	296	200
μ(Mo Kα), mm^{-1}	4.234	1.883	1.957
D_{calcd}, g cm^{-3}	2.870	1.979	1.809
λ, Å	0.7107	0.7107	0.7107
R_{int}	0.0217	0.0285	0.0262
R $[I > 2\sigma(I)]^a$	0.0283	0.0305	0.0450
wR $[I > 2\sigma(I)]^b$	0.0742	0.0748	0.1089

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR = |\sum w(|F_o|^2 - |F_c|^2)|/\sum|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Experimental Section

Materials and Measurements. All commercially available chemicals are of reagent grade and were used as received without further purification. Solvents were purified according to the standard methods. The compound H_3bta was prepared according to the method reported in the literature.[10] Elemental analyses of C and H were carried out on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. Thermogravimetric analysis (TGA) of the powder sample was performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 at a heating rate of 10 °C min^{-1} from room temperature to 600 °C. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a Xe arc lamp as the light source. In the measurements of emission and excitation spectra, the pass width is 5.0 nm. A SLM 48000 DSCF fluorescence spectrometer was used to perform the lifetime measurements.

Preparation of the Complexes. $[Ag_3(bta)]\cdot 1.5H_2O$ (1). A solution of H_3bta (12.6 mg, 0.05 mmol) in ethanol (5 mL) was added slowly to a layer of a freshly prepared solution of $[Ag(NH_3)_2]NO_3$ (0.05 mmol) in water (4 mL) in a tube. Single crystals of **1** suitable for X-ray crystal diffraction analysis were obtained with a yield of 43% after 10 days of standing. Anal. Calcd for $C_{12}H_{12}Ag_3O_{7.5}$: C, 24.03; H, 2.02%. Found: C, 23.89; H, 2.00%.

$[Cd_3(bta)_2(H_2O)_7]\cdot 5H_2O$ (2). H_3bta (50.4 mg, 0.2 mmol) and NaOH (24.1 mg, 0.6 mmol) were dissolved in 20 mL of water. To this solution was added an aqueous solution (10 mL) of $CdCl_2$ (55.0 mg, 0.3 mmol) at room temperature. The mixture was stirred for 30 min and then filtered. The clear filtrate was allowed to stand for 2 weeks, and the colorless crystals of **2** suitable for X-ray diffraction were obtained (yield 53%). Anal. Calcd for $C_{24}H_{42}Cd_3O_{24}$: C, 27.41; H, 4.03%. Found: C, 27.35; H, 4.03%.

$[Cu_{11}(bta)_6(Hbta)_2(H_2O)_{10}]\cdot 29H_2O$ (3). Compound **3** was prepared by a layering method at room temperature. H_3bta (25.2 mg, 0.1 mmol) and $KHCO_3$ (30.0 mg, 0.3 mmol) were dissolved in water (4 mL), and then the mixture was added slowly to a layer of

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**−**3**

1[a]							
Ag1−O3	2.200(3)	Ag3−O6	2.253(3)	Ag1−O1	2.261(3)	Ag2−O5	2.442(3)
Ag1−O1#1	2.433(3)	Ag3−O2	2.479(3)	Ag1−Ag2	2.8453(5)	Ag3−C6	2.460(4)
Ag1−Ag1#2	3.1429(6)	Ag3−O6#4	2.543(3)	Ag2−O4	2.225(3)	Ag3−O5#3	2.515(3)
Ag2−O2	2.234(3)						
O3−Ag1−O1	160.50(11)	O2−Ag2−Ag1	83.97(7)	O3−Ag1−Ag2	82.46(8)	O5−Ag2−Ag1	169.81(7)
O1−Ag1−O1#1	77.88(10)	O6−Ag3−C6	161.27(12)	O1#1−Ag1−Ag2	158.00(6)	O6−Ag3−O2	108.92(10)
O1−Ag1−Ag2	80.16(7)	C6−Ag3−O2	88.48(11)	O1−Ag1−Ag1#2	74.23(8)	O6−Ag3−O5#3	94.36(11)
O3−Ag1−Ag1#2	109.34(8)	C6−Ag3−O5#3	92.30(11)	Ag2−Ag1−Ag1#2	74.226(14)	O2−Ag3−O5#3	90.56(9)
O1#2−Ag1−Ag1#2	100.81(7)	O6−Ag3−O6	74.16(12)	O4−Ag2−O5	99.64(11)	C6−Ag3−O6#4	87.72(12)
O4−Ag2−O2	159.70(11)	O2−Ag3−O6#4	172.19(10)	O4−Ag2−Ag1	79.41(8)	O5#3−Ag3−O6#4	96.40(10)
O2−Ag2−O5	98.76(10)	O3−Ag1−O1#1	118.97(10)				
2							
Cd1−O5	2.232(3)	Cd2−C112	2.750(4)	Cd1−O14	2.363(3)	Cd2−O16	2.295(3)
Cd1−O15	2.286(3)	Cd3−O3	2.243(3)	Cd1−O1	2.467(3)	Cd2−O18	2.299(3)
Cd1−O13	2.310(3)	Cd3−O19	2.276(3)	Cd1−C12	2.744(4)	Cd3−O10	2.381(3)
Cd1−O2	2.312(3)	Cd3−O11	2.328(3)	Cd2−O9	2.242(3)	Cd3−O12	2.433(3)
Cd2−O17	2.361(3)	Cd3−O6	2.376(3)	Cd2−O7	2.279(3)	Cd3−C152	2.742(4)
Cd2−O8	2.525(3)						
O5−Cd1−O15	116.47(11)	O7−Cd2−C112	27.06(12)	O15−Cd1−O1	133.28(10)	O9−Cd2−O17	89.10(11)
O5−Cd1−O13	87.82(12)	O16−Cd2−C112	115.99(13)	O13−Cd1−O1	88.02(11)	O7−Cd2−O17	83.66(12)
O15−Cd1−O13	100.10(12)	O18−Cd2−C112	85.27(12)	O2−Cd1−O1	54.32(10)	O16−Cd2−O17	90.04(12)
O5−Cd1−O2	163.89(10)	O17−Cd2−C112	90.18(12)	O14−Cd1−O1	78.83(10)	O18−Cd2−O17	171.78(11)
O15−Cd1−O2	79.65(11)	O8−Cd2−C112	26.88(11)	O5−Cd1−C12	136.90(11)	O9−Cd2−O8	99.48(10)
O13−Cd1−O2	89.29(13)	O3−Cd3−O19	139.97(11)	O15−Cd1−C12	106.24(12)	O19−Cd3−O12	85.02(10)
O5−Cd1−O14	95.76(11)	O3−Cd3−O11	83.02(11)	O13−Cd1−C12	90.34(12)	O11−Cd3−O12	54.47(10)
O15−Cd1−O14	89.67(11)	O19−Cd3−O11	136.98(11)	O2−Cd1−C12	27.24(11)	O6−Cd3−O12	93.24(11)
O13−Cd1−O14	166.82(11)	O3−Cd3−O6	108.71(11)	O14−Cd1−C12	78.37(11)	O10−Cd3−O12	91.20(11)
O2−Cd1−O14	83.76(11)	O19−Cd3−O6	74.53(10)	O1−Cd1−C12	27.20(10)	O3−Cd3−C152	108.14(12)
O5−Cd1−O1	109.71(10)	O11−Cd3−O6	92.24(12)	O9−Cd2−O7	151.32(11)	O19−Cd3−C152	111.47(11)
O7−Cd2−O8	53.92(10)	O3−Cd3−O10	89.52(12)	O9−Cd2−O16	118.13(11)	O11−Cd3−C152	27.22(11)
O16−Cd2−O8	142.11(11)	O19−Cd3−O10	75.98(10)	O7−Cd2−O16	89.68(11)	O6−Cd3−C152	93.81(11)
O18−Cd2−O8	83.77(11)	O11−Cd3−O10	114.45(11)	O9−Cd2−O18	99.11(11)	O10−Cd3−C152	103.51(11)
O17−Cd2−O8	95.24(11)	O6−Cd3−O10	149.65(11)	O7−Cd2−O18	89.21(12)	O12−Cd3−C152	27.26(11)
O9−Cd2−C112	125.88(12)	O3−Cd3−O12	133.13(11)	O16−Cd2−O18	85.83(12)		
3[b]							
Cu1−O2	1.975(3)	Cu3−O4B	2.353(14)	Cu1−O5	1.989(3)	Cu3−Cu4	2.628(2)
Cu1−O7	2.126(5)	Cu4−Cu5	1.593(4)	Cu1−Cu2	2.6361(9)	Cu4−O4	1.961(6)
Cu2−O1	1.947(3)	Cu4−O10	2.128(8)	Cu−O6	1.967(3)	Cu5−O4B	1.914(12)
Cu2−O8	2.092(5)	Cu4−O4B#1	2.229(11)	Cu3−O3	1.982(8)	Cu5−O4	2.414(6)
Cu3−O3	1.982(8)	Cu5−O3#1	2.136(7)	Cu3−O9	2.193(14)		
O2−Cu1−O2#2	89.36(18)	Cu5−Cu4−O10	180.000(3)	O2−Cu1−O5	90.79(13)	O4−Cu4−O10	95.10(17)
O2−Cu1−O5#2	168.96(12)	O4−Cu4−O4B#4	81.4(4)	O5−Cu1−O5#2	86.96(18)	Cu5−Cu4−O4B#1	57.3(4)
O2−Cu1−O7	97.10(14)	O4#1−Cu4−O4B#1	28.4(4)	O5−Cu1−O7	93.83(15)	O4−Cu4−O4B#1	141.6(5)
O2−Cu1−Cu2	83.70(8)	O10−Cu4−O4B#1	122.7(4)	O5−Cu1−Cu2	85.35(9)	O4−Cu4−O4B#3	93.0(4)
O7−Cu1−Cu2	178.87(16)	O4B#3−Cu4−O4B#4	114.5(8)	O1−Cu2−O1#2	88.99(19)	O4B#1−Cu4−O4B#3	73.0(4)
O1−Cu2−O6	90.35(13)	O4−Cu4−Cu3	84.90(17)	O1#2−Cu2−O6	167.27(13)	O10−Cu4−Cu3	180.000(1)
O6−Cu2−O6#2	87.50(18)	O4B#1−Cu4−Cu3	57.3(4)	O1−Cu2−O8	96.28(14)	Cu4−Cu5−O4B	78.3(5)
O6−Cu2−O8	96.44(14)	O4B−Cu5−O4B#1	156.6(9)	O1−Cu2−Cu1	84.53(9)	O4B−Cu5−O4B#3	87.65(18)
O6−Cu2−Cu1	82.74(9)	O4B−Cu5−O3#4	106.2(4)	O8−Cu2−Cu1	178.86(15)	Cu4−Cu5−O3#1	112.7(2)
O3−Cu3−O3#1	167.8(4)	O4B#1−Cu5−O3#1	36.6(4)	O3−Cu3−O3#3	89.35(5)	O4B−Cu5−O3#1	163.6(5)
O3−Cu3−O9	96.1(2)	O4B−Cu5−O3#3	83.0(4)	O3−Cu3−O4B#4	76.1(4)	O3#3−Cu5−O3#4	134.6(5)
O3#4−Cu3−O4B	96.4(4)	O3#1−Cu5−O3#3	81.44(17)	O3#1−Cu3−O4B	135.1(4)	O3#1−Cu5−O4#1	58.9(2)
O3−Cu3−O4B	33.2(3)	Cu4−Cu5−O4	54.01(15)	O9−Cu3−O4B	127.2(3)	O4B#1−Cu5−O4	131.9(5)
O4B−Cu3−O4B#1	105.6(6)	O4B−Cu5−O4	25.1(4)	O4B−Cu3−O4B#3	68.6(3)	O4B#3−Cu5−O4	88.6(5)
O3−Cu3−Cu4	83.9(2)	O3#4−Cu5−O4	107.7(3)	O9−Cu3−Cu4	180.000(2)	O3#1−Cu5−O4	165.8(3)
O4B−Cu3−Cu4	52.8(3)	O3#3−Cu5−O4	98.6(2)	Cu5−Cu4−O4	84.90(17)	O4−Cu5−O4#1	108.0(3)
O4−Cu4−O4#4	89.55(3)	O4B−Cu5−O4#3	77.6(4)	O4−Cu4−O4#1	169.8(3)	O4−Cu5−O4#3	69.80(15)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z$; #2, $-x + 1$, $-y$, $-z$; #3, $x - 1$, y, z; #4, $-x + 1$, $-y - 1$, $-z + 1$.
[b] Symmetry transformations used to generate equivalent atoms: #1, $1 - x$, $1 - y$, z; #2, x, y, $-z + 1$; #3, $-y + 1$, x, z; #4, y, $-x + 1$, z.

an aqueous solution (4 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (20.6 mg, 0.06 mmol) in a tube. Single crystals suitable for X-ray crystal diffraction analysis were obtained with yield of 50% after several days of standing at room temperature. Complex **3** is insoluble in water and common organic solvents. Anal. Calcd for $C_{96}H_{152}Cu_{11}O_{87}$: C, 33.94; H, 4.51%. Found: C, 34.01; H, 4.34%.

Crystallographic Analyses. The X-ray diffraction measurements for complexes **1** and **3** were carried out on a Rigaku RAXIS−RAPID imaging-plate diffractometer at 200 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data collection for complex **2** was made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at 296 K. The structures were solved by direct methods using SIR92 and expanded using Fourier techniques.[11,12] The O23 atom in **2** has two positions with site occupation factors of 0.75(2) and 0.25(2),

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(11) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

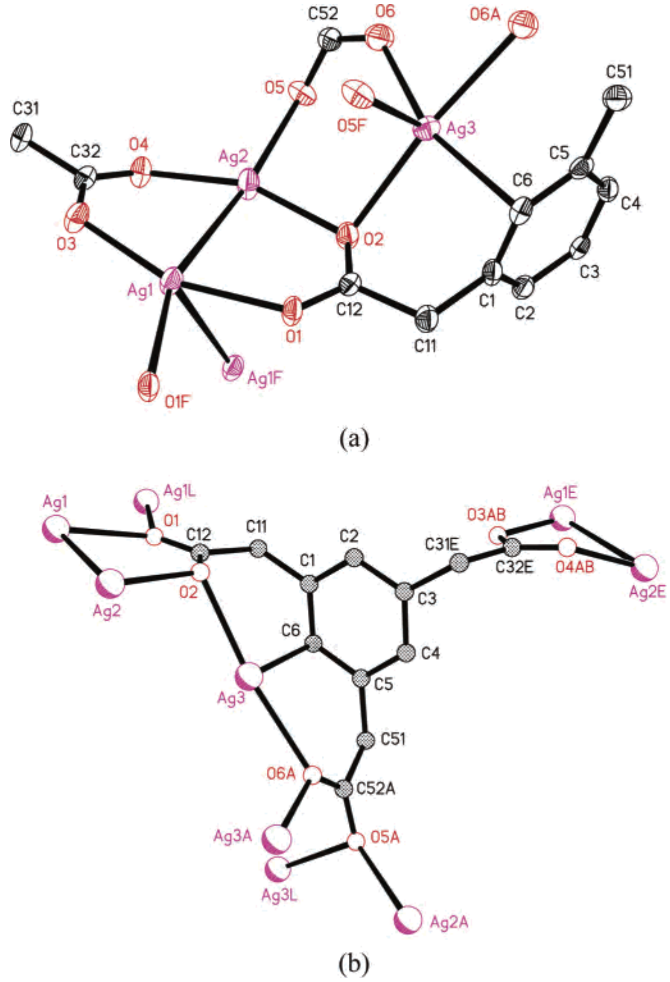

Figure 1. (a) Coordination environment of Ag^{I} with the ellipsoids drawn at the 50% probability level. The H atoms and uncoordinated water molecules are omitted for clarity. (b) Coordination mode of the bta^{3-} ligand in **1**.

respectively. The O24 atom in **2** has two positions with site occupation factors of 0.56(7) and 0.44(7), respectively. All data were refined anisotropically by the full-matrix least-squares method on F^2 for non-H atoms. The H atoms except for those of water molecules were generated geometrically. The crystal parameters, data collection, and refinement results for compounds **1**−**3** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2. Further details are provided in the Supporting Information.

Results and Discussion

Description of the Crystal Structures. 1. In complex **1**, there are three crystallographically independent Ag atom centers in the structure, and each Ag atom has a different coordination environment (Figure 1a). Both Ag1 and Ag3 atoms are unusual five-coordinate with distorted square-pyramid geometry.[13] The Ag1 atom is coordinated by three O atoms from three different bta ligands and two Ag atoms, while in the case of the Ag3 atom, it is bound by four O atoms from three different bta ligands and one C atom. The distance of 2.460(4) Å between Ag3 and C6 implies the existence of a Ag−C bond. Similar Ag−C bond distances ranging from 2.420(5) to 2.766(4) Å have been observed in Ag^{I} polymers with pyrene and perylene.[14] The Ag2 atom is coordinated with three O atoms from three different ligands and one Ag atom with distorted square-planar coordination geometry. In turn, each bta^{3-} ligand coordinates to nine Ag^{I} atoms, with three carboxylate groups adopting μ_4-η^2:η^2- and μ_2-η^1:η^1-bridging coordination modes (Figure 1b).

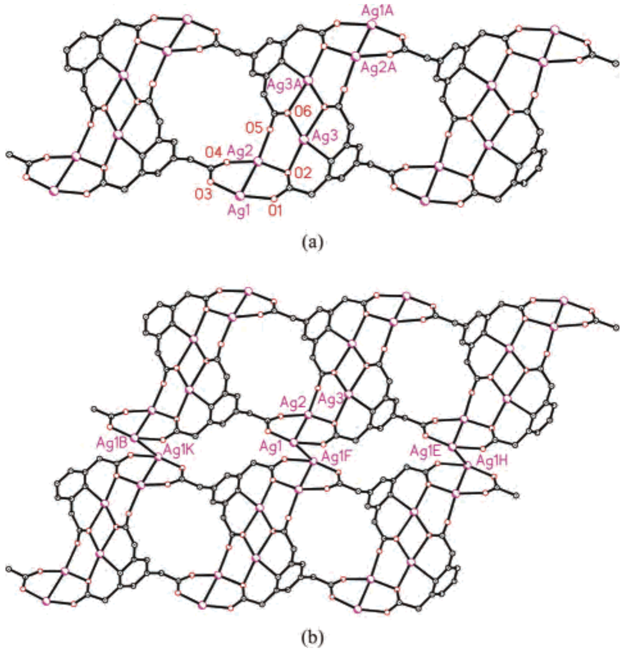

Figure 2. (a) 1D chain structure of **1**. (b) 2D network structure of **1** connected by Ag^{I}−Ag^{I} bonds.

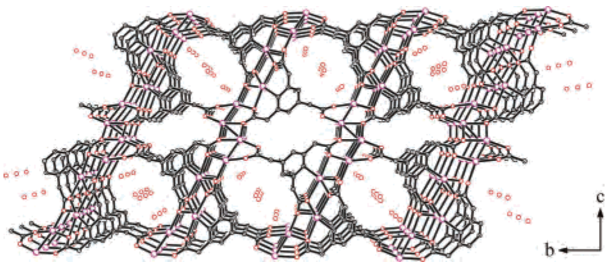

Figure 3. Packing diagram of **1** on the *bc* plane with open channels.

As shown in Figure 2a, ligand bta^{3-} coordinates to seven Ag^{I} atoms to form a one-dimensional (1D) chain, which includes 20-membered macrocyclic rings with dimensions of 6.6 × 8.4 Å. Also, there exists a bimetallic (Ag1 and Ag2) dicarboxylate unit, with a short Ag−Ag internuclear separation of 2.8453(5) Å. It is known that bimetallic tetracarboxylate units are a common arrangement for many transition-metal carboxylates such as Cu, Rh, Mo, etc.[3,5,15] A tetranuclear Ag^{I} cluster bridged by carboxylate groups has

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(12) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF94 Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

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(14) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903.

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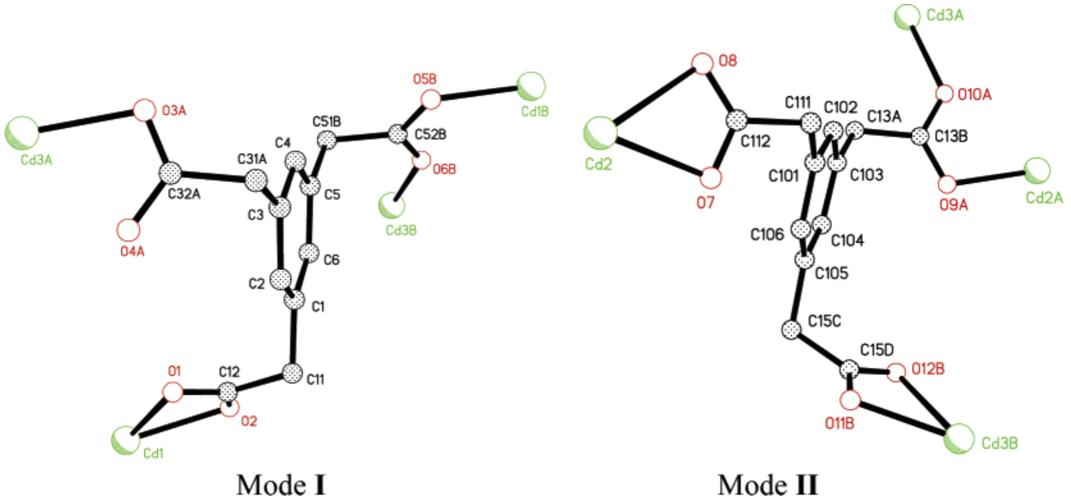

Figure 4. Coordination modes of the bta^{3-} ligand in **2**.

been reported to have a Ag−Ag distance of 2.938(1) Å, which is longer than that observed in complex **1**.[15b] The distance of two Ag atoms of two adjacent chains is 3.1429(6) Å, which is shorter than the Ag−Ag van der Waals contact distance of 3.40 Å and indicates the presence of Ag−Ag interactions.[16] Thus, the 1D chains were further linked by Ag−Ag interactions to give a two-dimensional (2D) network structure (Figure 2b), and the 20-membered macrocyclic rings with 4.0 × 11.7 Å dimensions were formed between two adjacent 1D chains. Furthermore, the 2D sheets were connected by Ag−O bonds to give a 3D framework with open channels (Figure 3), which were occupied by water molecules via C−H···O hydrogen bonds (Table 3). Therefore, complex **1** is a novel metal−organic architecture constructed through Ag−O coordination and Ag−Ag and Ag−C interactions.

2. As shown in Figure 4, the bta^{3-} ligands display two kinds of coordination modes in each repeat unit of **2**. In mode **I**, the bta^{3-} ligand connects four Cd^{II} atoms with the carboxylate group, adopting μ_1-η^1:η^0-monodentate, μ_1-η^1:η^1-chelating, and μ_2-η^1:η^1-bridging coordination modes. In the case of mode **II**, the bta^{3-} ligand connects four Cd^{II} atoms with two kinds of coordination modes: μ_1-η^1:η^1 chelating and μ_2-η^1:η^1 bridging. The asymmetric unit of **2** contains three Cd^{II} atoms with distorted octahedral coordination geometry (Figure 5a). Each Cd1 or Cd2 is coordinated by three O atoms of three water molecules and three O atoms of two carboxylate groups. In turn, each ligand bta^{3-} coordinates to two Cd1 or two Cd2 atoms to form chains **A** and **B** (Figure 5b), while Cd3 is bound by one O atom of the water molecule, two O atoms of two carboxylate groups from two **A** chains, and three O atoms of two carboxylate groups from two **B** chains. That is to say, the Cd3 atom links **A** and **B** chains into a 3D structure with open channels in dimensions of 8.0 × 11.2 Å, which is occupied by water molecules by forming O−H···O hydrogen bonds (Table 3, Figure 6, and Figure S1 in the Supporting Information).

Table 3. H Bonds Data for Complexes **1** and **2**

D−H···A	distance of D···A (Å)	angle of D−H−A (deg)
	$[Ag_3(bta)]\cdot1.5H_2O$ (**1**)[a]	
C4−H2···O8#1	3.424(15)	164
C11−H4···O2#2	3.461(5)	147
	$[Cd_3(bta)_2(H_2O)_7]\cdot5H_2O$ (**2**)[b]	
O13−H19···O5#1	2.832(5)	160
O13−H20···O20#2	2.721(5)	173
O14−H21···O1#3	2.731(4)	167
O14−H22···O4#4	2.787(4)	166
O15−H23···O24#5	2.69(2)	159
O15−H24···O19	2.743(4)	167
O16−H25···O15#6	2.812(5)	150
O16−H26···O4	2.878(5)	170
O17−H27···O8#7	2.742(5)	165
O17−H28···O21#2	2.756(6)	162
O18−H29···O12#6	2.751(5)	167
O18−H30···O9#8	2.886(4)	169
O19−H31···O20#2	2.719(5)	162
O19−H32···O17	2.754(4)	155
O20−H33···O21	2.791(7)	145
O20−H34···O14#9	2.891(5)	165
O21−H35···O23	2.666(10)	172
O21−H36···O22	2.795(8)	129
O22−H37···O11#10	2.728(6)	152
O22−H38···O2#9	2.692(6)	164
O23−H39···O3#11	2.834(10)	172
O23−H40···O24#4	2.75(2)	125
O24−H42···O22	2.48(2)	165
O24−H43···O23#6	2.75(2)	125
C106−H12···O22#2	3.413(6)	153

[a] Symmetry transformations used to generate equivalent atoms: #1, $1 - x, -2 - y, 1 - z$; #2, $-1 + x, y, z$. [b] Symmetry transformations used to generate equivalent atoms: #1, $3 - x, -y, 2 - z$; #2, $1 + x, y, z$; #3, $3 - x, -y, 3 - z$; #4, $x, y, 1 + z$; #5, $1 + x, y, 1 + z$; #6, $x, y, -1 + z$; #7, $x, \frac{1}{2} - y, \frac{1}{2} + z$; #8, $x, \frac{1}{2} - y, -\frac{1}{2} + z$; #9, $-1 + x, y, -1 + z$; #10, $-2 + x, y, -1 + z$; #11, $-2 + x, y, z$.

It is noteworthy that the bta^{3-} ligands in complexes **1** and **2** adopt a cis,trans,trans conformation and all of the three carboxylate groups of each bta participate in the coordination with metal atoms to generate the 3D frameworks. Four different coordination modes of the carboxylate groups are found in these two complexes, namely, μ_4-η^2:η^2 bridging, μ_2-η^1:η^1 bridging, μ_1-η^1:η^1 chelating, and μ_1-η^1:η^0 monodentate (Chart 2), in which μ_4-η^2:η^2 bridging is an unusual coordination mode for the carboxylate group.[17]

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[16] (a) Fei, B. L.; Sun, W. Y.; Okamura, T.-a.; Tang, W. X.; Ueyama, N. *New J. Chem.* **2001**, *25*, 210. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173. (c) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942.

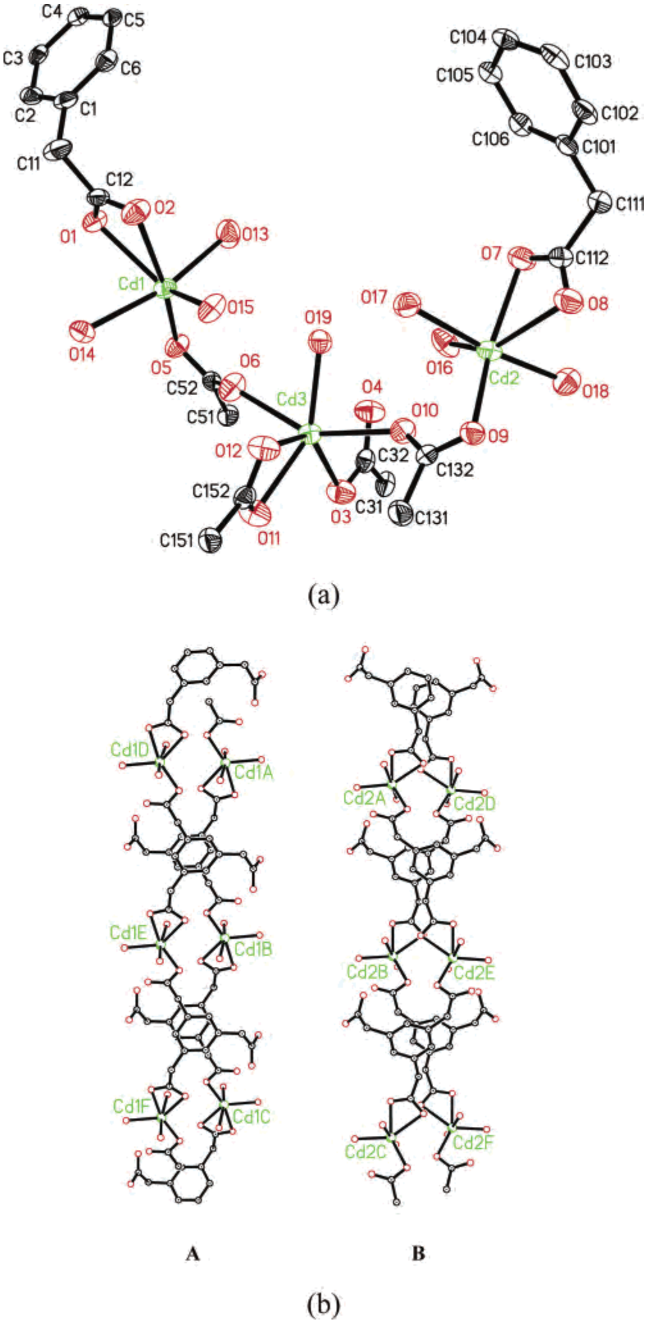


Figure 5. (a) Asymmetric unit of **2** with the ellipsoids drawn at the 50% probability level. The H atoms and uncoordinated water molecules are omitted for clarity. (b) 1D chain structures composed of Cd1 (**A**) or Cd2 (**B**) of **2**.

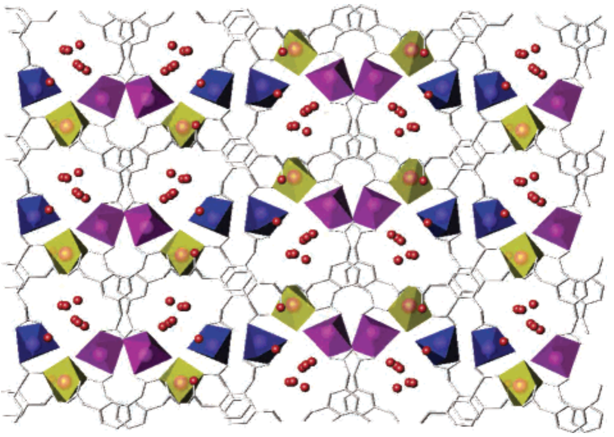
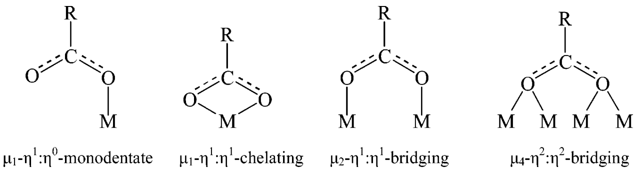


Figure 6. Packing diagram of **2** on the *ab* plane with open channels. The polyhedral presentation indicates the coordination environments for Cd1 (navy), Cd2 (magenta), and Cd3 (yellow).

Chart 2



3. Single crystals of **3** were obtained by a diffusion method between an aqueous solution of H_3bta and $KHCO_3$ and an aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ at room temperature. In contrast to the mild conditions for the preparation of **3**, the reported frameworks with a carboxylate ligand were usually obtained by thermal or solvothermal methods under high temperature and high pressure to increase the dimensionality of the resulting complexes.[3,7] The result of crystal structural analysis of **3** indicates that there are 11 Cu^{II} atoms and 8 bta ligands in each cage of **3**, as illustrated in Figure 7a. It is interesting that the Cu^{II} atoms in **3** have two different coordination environments: octahedral and square planar. In the repeat unit, Cu5 was found between Cu3 and Cu4 in the Fourier map and disordered carboxyl groups were found near these Cu atoms. Cu3 and Cu4 form a paddle-wheel cluster with an occupancy of 0.5, while Cu5 also with an occupancy of 0.5 is only four-coordinate, in which two of the four carboxylates must be protonated because no other cation was found in the crystal analysis of **3** even at 200 K. In the other reported metallocages, all of the metal atoms in each compound have the same coordination geometry.[18] Thus, in each cage of **3**, there are five, not six, paddle-wheel dimeric cupric tetracarboxylate units, with short Cu−Cu internuclear separations of 2.6361(9) (Cu1−Cu2) and 2.628(2) (Cu3−Cu4) Å. Such bimetallic tetracarboxylate units have been observed in many transition-metal (e.g., Cu, Rh, Mo) carboxylate frameworks.[3,5,15a] The previously reported metallocage $[Cu_{24}(m\text{-bdc})_{24}(DMF)_{14}(H_2O)_{10}](H_2O)_{50}(DMF)_6(C_2H_5OH)_6$ (where DMF = dimethylformamide), obtained by the reaction of a 1,3-benzenedicarboxylate ligand, rather than a tricarboxylate one, with copper(II) nitrate, has 12 $Cu_2(COO)_4$ paddle-wheel secondary building units.[5] Therefore, the structure of **3** can be described as a near cuboctahedron composed of square (paddle wheels and planar) and triangular secondary building units (organic bta links), as illustrated in Figure 7b.

It is noteworthy that only the cis,cis,cis conformation of the bta^{3-} ligand was observed in **3**, though there are two possible conformations (Chart 1) when the flexible bta^{3-}

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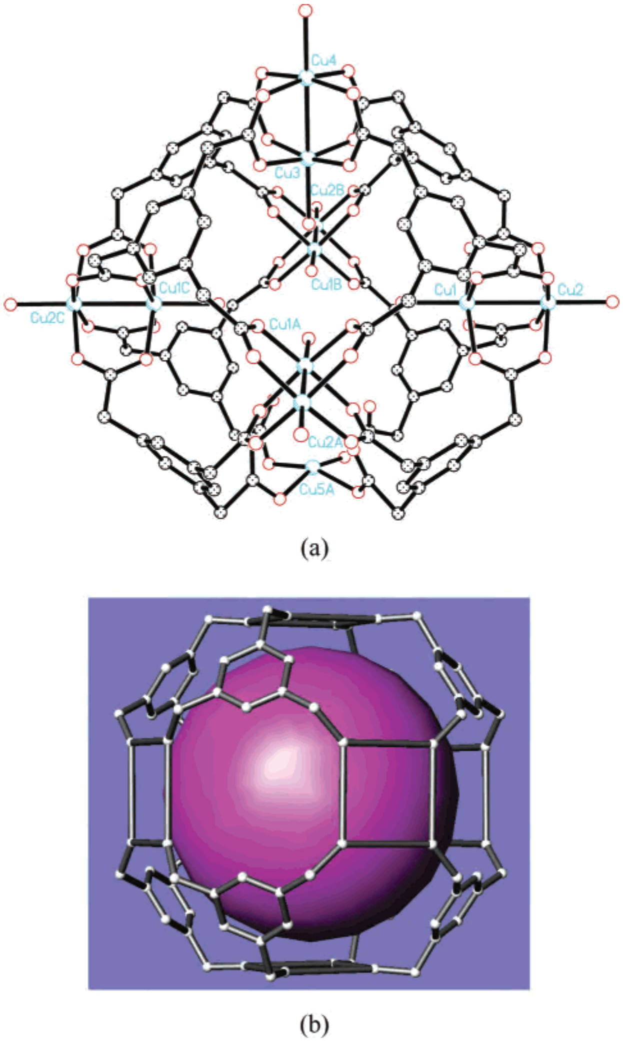

Figure 7. (a) Crystal structure of **3** with Cu^{II} atom numbering. The H atoms and solvent water molecules are omitted for clarity. (b) Simplified metallocage **3** with a large void (magenta sphere). The square secondary building units were obtained by linking together only the carboxylate C atoms in the bta ligands.

reacts with metal salts, as was demonstrated in the previous studies for imidazole-containing tripodal ligands such as 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene.[19]

Complex **3** is a nanometer-sized metallocage because the distances between Cu1 and Cu1C and between Cu3 and Cu5A (Figure 7a) are 10.25 and 10.92 Å, respectively. Each $Cu_2(COO)_4$ paddle-wheel unit has two terminal water molecules coordinated to the inside and outside Cu^{II} atoms of the cage. The overall size of the cage is 19.7 Å (with terminal ligands) or 15.5 Å (without terminal ligands) in diameter. In the reported cagelike complex $[Cu_{24}(m\text{-bdc})_{24}(DMF)_{14}(H_2O)_{10}](H_2O)_{50}(DMF)_6(C_2H_5OH)_6$, water or DMF molecules coordinated to the Cu^{II} atoms as terminal ligands and gave an overall size of 34 Å (with terminal ligands) or 25 Å (without terminal ligands) in diameter.[5] The distance from the cavity center to the bta centroid is 6.9 Å (a diameter of 13.8 Å and a volume of 1375 Å^3), which is longer than that of the reported complex $[Cu^{II}_{12}(tapp)_8]$ (H_3tapp = 2,4,6-triazophenyl-1,3,5-trihydroxybenzene) but shorter than the corresponding distance of $[Cu_{24}(m\text{-bdc})_{24}(DMF)_{14}(H_2O)_{10}](H_2O)_{50}(DMF)_6(C_2H_5OH)_6$.[5,20] The crystallographic study provides direct evidence of **3** with a large inner cavity capable of accommodating many solvent molecules. A total of 29 well-defined water molecules were found in each cage **3** (Figure S2 in the Supporting Information). Four disordered water molecules (each has two positions with site occupancy factors of 0.5) are located outside, while the other 25 are inside of **3**. The presence of the water molecules was confirmed by TGA. Unfortunately, the structure collapsed after removal of the water molecules and could not be recovered. In the crystal packing, each cage of **3** is surrounded by eight cages (Figure S3 in the Supporting Information).

The compound H_3bta was used for the first time as a secondary building unit to construct metal−organic architectures. Namely, the present study provides the first example of a supramolecular complex with a flexible tricarboxylate bta^{3-} ligand and a nice example of a nanometer-sized metallocage. Compound **3** is a new metallocage composed of Cu paddle-wheel square secondary building units and bta organic links (triangular secondary building units).

In our previous studies, the bta^{3-} ligand was used to react with main-group metal salts of Ca^{II} and Ba^{II}, transition-metal salts of Co^{II} and Ni^{II}, and various lanthanide salts, and metal complexes with 1D, 2D, and 3D structure were obtained.[21] The results of previous and present studies indicate that the flexible bta^{3-} ligand is versatile in the formation of metal−organic architectures because different conformations of the ligand and different coordination modes of the carboxylate group. On the other hand, the metal atoms with different coordination numbers and coordination geometries also enrich the structure of the resulting complexes. It is worth noting that the metal atoms in each complex of **1**−**3** have two or three different coordination environments, while in the case of Co^{II} and Ni^{II} complexes, all of the metal atoms have the same coordination environment.[21b] Furthermore, the Ag−O coordination, together with the Ag−Ag and Ag−C interactions, makes complex **1** a unique structure.

Properties of Complexes 1 and 2. Both **1** and **2** are air stable. TGA for complexes **1** and **2** was carried out to exam their thermal stabilities by heating of the samples up to 600 °C. The TGA data of **1** show that a weight loss of 4.8% (calculated 4.5%) corresponding to the liberation of the water molecules was observed below 80 °C, and then no further weight loss was observed until 220 °C. The TGA data of **2** show that a weight loss of 20.0% (calculated 20.6%) corresponds to a loss of lattice and coordinated water molecules below 205 °C, and then the residue starts to decompose from 350 °C.

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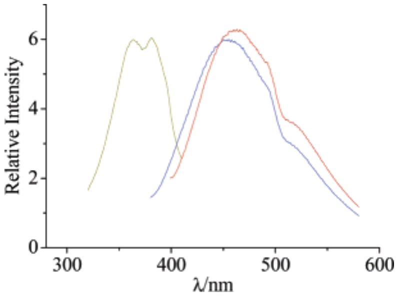

Figure 8. Excited (left) and emission (right) spectra of **2** (red line, excited at 381 nm; blue line, excited at 364 nm) in the solid state at room temperature.

Photoluminescent properties of frameworks **1** and **2** as well as the H_3bta ligand were investigated in the powdered solid state at room temperature. No clear luminescence was detected for the H_3bta ligand and its Ag^I complex **1** under the experimental conditions. It has been reported that Ag^I complexes may emit weak photoluminescence at low temperature and that the luminescence at room temperature is weak or unobservable.[22] In contrast to complex **1** and the H_3bta ligand, the Cd^{II} complex **2** shows intense violet-blue photoluminescence under the same conditions. Complex **2** exhibits photoluminescence with an emission maximum at ca. 463 nm (lifetime $\tau = 2.84$ ns) upon excitation at 381 nm, as illustrated in Figure 8. When complex **2** was excited at 364 nm, the emission maximum was slightly blue shifted to 455 nm. Because no emission was observed for the H_3bta ligand, photoluminescence of complex **2** was attributed to the coordination of the bta^{3-} ligand to the Cd^{II} atoms, as was observed in the previously reported cadmium(II) carboxylate complexes.[23] An intense emission was observed for the Cd^{II} complex of a trimellitic salt, while no emission was detected for the trimellitic acid.[23a] In the case of Cd^{II}btc complexes, the observed photoluminescence has been assigned to ligand-to-metal charge transfer.[23b]

Conclusion

Three metal complexes with a flexible bta^{3-} ligand, **1**−**3**, were synthesized, and the single-crystal X-ray diffraction analysis revealed that different conformations of the bta ligand and different coordination modes of the carboxylate group as well as different coordination numbers and coordination geometries of the metal atoms make the complexes interesting 3D framework structures (**1** and **2**) and a discrete cagelike structure (**3**). The results of the luminescence investigation showed that the Cd^{II} complex exhibited violet-blue photoluminescence, while no emissions were observed for the Ag^I complex.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant 20231020) and the National Science Fund for Distinguished Young Scholars (Grant 20425101).

Supporting Information Available: X-ray crystallographic file in CIF format and crystal packing diagrams for **2** and **3** (Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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