The First Two Novel Metallomacrocycles Constructed from Cubane-Like Cu_4I_4 Cluster Units and Ditopic Diamines

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Two novel metallomacrocycles made up of difunctional 4,4′-diaminodiphenylmethane (DADPM) or 4,4′-diaminodiphenyl ether (DADPE) and cubane-like Cu_4I_4 cluster units have been prepared by the reaction of CuI and DADPM or DADPE in MeCN/H_2O. The X-ray crystal structural analyses show that the topology of the cubane-like Cu_4I_4 cluster units is maintained in the assembly process.

Introduction

Much effort has been devoted to the design and construction of metal-containing supramolecular and coordination polymers from building blocks possessing useful properties such as nonlinear optical properties, bulk magnetism, light emission and porosity.[1−8] Metallomacrocycles based on specific building blocks have recently received a great deal of attention in chemistry and material science owing to their potential applications in various materials.[9−24] A number of discrete macrocycles have been constructed by ditopic or oligotopic ligands, in particular di- or polypyridyl ligands and suitable metal ions.[15−23] For instance, discrete square or rectangular metallomacrocycles with nanometer-sized cavities have been obtained by the assembly of pyridine-based ligands, such as 4,4-bipyridine or its derivatives, and metal ions with square-planar coordination geometry, such as Pd^{II} or Pt^{II}.[15−21] However, discrete macrocycles consisting of metal clusters and organic ligands are less well-known.[23,24]

It is known that the reaction of copper(I) iodide with aniline derivatives, such as *p*-toluidine, *p*-chloroaniline, *p*-anisidine, *o*-ethylaniline, 2,6-dimethylaniline or 6-ethyl-*o*-toluidine, produces complexes containing a single cubane-like Cu_4I_4 cluster in which the aniline derivatives act as the terminal ligands coordinating to copper(I) centers.[25−28] Thus, it is reasonable to expect the formation of macrocyclic complexes constructed from Cu_4I_4 cluster units by replacing the aniline derivatives with difunctional diamine ligands containing suitable spacers. Considering the flexibility and electronic structures of diamine ligands, such as 4,4′-diaminodiphenylmethane (DADPM) and 4,4′-diaminodiphenyl ether (DADPE), we recently began work on the reaction of diamine ligands and Cu^I, with the hope of isolating some interesting complexes constructed by cubane-like Cu^I cluster units. Herein, we report two novel macrocyclic complexes $[(Cu_4I_4)(MeCN)_2(DADPM)]_2\cdot 2MeCN$ (**1**) and $[(Cu_4I_4)(MeCN)_2(DADPE)]_2\cdot 2MeCN$ (**2**) assembled from DADPM, DADPE and CuI, respectively. To the best of our knowledge they are the first two discrete macrocyclic complexes constructed from cubane-like Cu_4I_4 clusters.

Results and Discussion

Complex **1** was synthesized in a high yield from the reaction of DADPM and CuI with a metal-to-ligand ratio of 1:1 in MeCN/H_2O at 60 °C. Single crystal X-ray diffraction analysis revealed that **1** is a discrete metallomacrocycle possessing a crystallographic center of symmetry, in which two cubane-like Cu_4I_4 cluster units are linked by two DADPM ligands (Figure 1).

Each DADPM ligand acts as a μ_2-bridge linking two cubane-like Cu_4I_4 units through its two nitrogen atoms. The dihedral angle of the two phenyl rings and the C(4)−C(5)−C(6) bond angle in the DADPM ligand are 89.2° and 112.7(10)°, respectively, resulting in a twisted-rhombus macrocycle. Two opposite phenyl rings in the macrocycle are parallel to each other at a distance of 10.53 Å, while the distance between the C(7)−C(8)−I(4A) and C(7A)−C(8A)−I(4) planes is 4.04 Å. Thus the dimension of the distorted macrocycle is 10.53×4.04 Å which compares well with the value of 8.36×4.10 Å for the macrocycle formed from DADPM and Cu^{II} ions.[22] Two uncoordinated MeCN molecules lie in two sides of the macrocycle as space fillers. Each Cu_4I_4 unit displays a cubane-like arrangement with Cu^I and iodide atoms occupying alternate corners of the cube; no crystallographic symmetry element is present for this unit. All Cu^I centers are in a distorted NI_3 tetrahedral geometry in which the coordination geometry of

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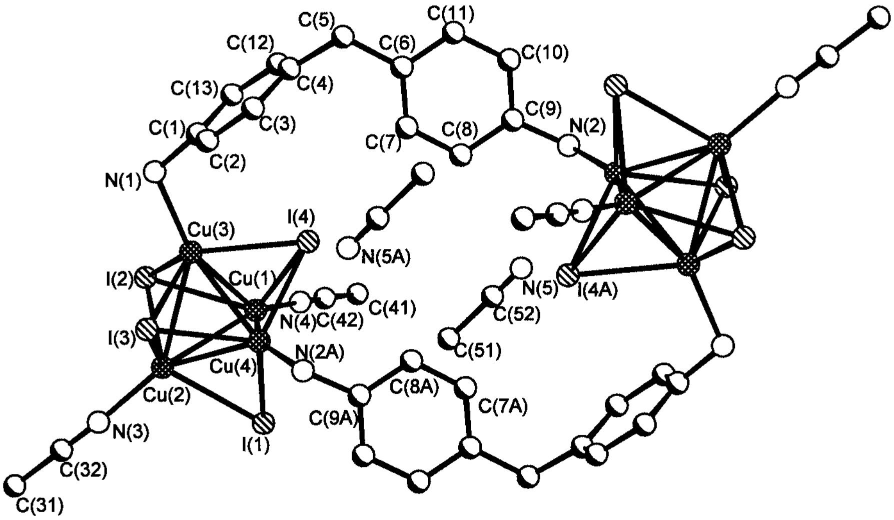

Figure 1. A view of the macrocyclic structure of **1**

two of the Cu^I ions is completed by the nitrogen atoms of two MeCN ligands and that of the other two Cu^I ions is completed by the nitrogen atoms of different DADPM ligands. All the bond lengths and bond angles of the Cu_4I_4 units in **1** are normal.[25−28] The Cu−Cu bond lengths, ranging from 2.670(3) to 2.777(3) Å (average value 2.724 Å), are within the range suggested by Mehrotra and Hoffman.[29]

Complex **2** was obtained in an analogous procedure except that DADPE was used instead of DADPM. The X-ray crystallographic analysis reveals that its structure is very similar to that of complex **1**, consisting of a centrosymmetrical metallomacrocycle formed from two cubane-like Cu_4I_4 cluster units and two bridging DADPE ligands. As shown in Figure 2, each DADPE ligand acts as a μ_2-bridge linking two Cu_4I_4 cluster units, the dihedral angle of two phenyl rings and the C(4)−O(1)−C(5) bond angle in DADPE are 90.4° and 117.1(7)°, respectively, resulting in a twisted-rhombus metallomacrocycle with dimensions of 9.99 × 3.88 Å. This is slightly smaller than in **1**, but larger than in other complexes obtained from the reaction of transitional metal ions and 1,2-bis(4-pyridyl)ethane.[19−21]

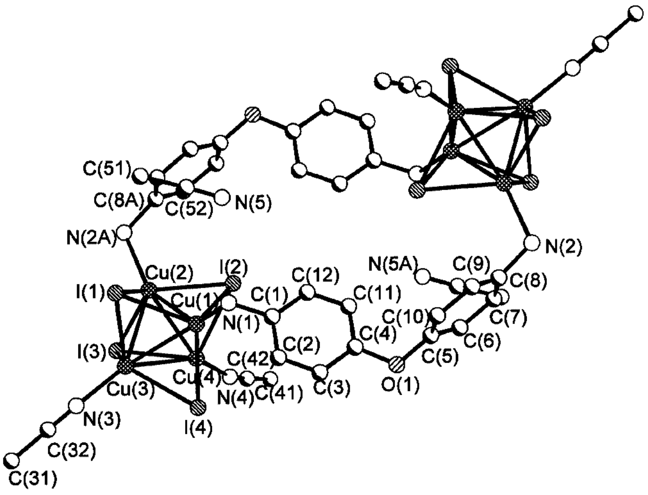

Figure 2. A view of the macrocyclic structure of **2**

There are no apparent differences in the bond lengths and bond angles in the Cu_4I_4 cluster units in complexes **1** and **2** and in the reported $[Cu_4I_4L_2(MeCN)_2]$ (L = aniline derivatives) complexes.[25−28] This result suggests that the topology of the cubane-like Cu_4I_4 cluster units is maintained during the assembly process and is not influenced by the linker ligands used.

In the solid state, the emission spectra for **1** and **2** were recorded after irradiating with light at a wavelength of 310 nm. Compounds **1** and **2** show a similar emission band in the 320−630 nm range despite the fact that free DADPM and DADPE have different emission spectra at the same excitation wavelength. Compared with single cubane-like $[Cu_4I_4L_2(MeCN)_2]$ (L = aniline derivatives) complexes[25,26] and luminescent Cu^I complexes,[30−33] the high energy emission at 350−460 nm might be ascribed to an intraligand interaction, and the weak emission which appears as a shoulder at around 500 nm might be ascribed to a metal-centered transition.

Conclusion

We have successfully assembled cubane-like Cu_4I_4 cluster units and difunctional diamines containing a spacer to form two discrete metallomacrocycles in which the topology of the Cu_4I_4 clusters is maintained. Previous reports have predicted that the tetranuclear chalcogenide Cu_4 or Ag_4 d^{10} clusters are good building blocks for the formation of materials with desirable physical and chemical properties.[33] Our report may open a new way to assembly Cu_4 clusters into desirable materials.

Experimental Section

General: All chemicals were purchased from Acros and used as received. The IR spectra were recorded as KBr discs on a Magna 750 FT-IR spectrophotometer. Elemental analyses were determined on an Elementar Vario ELIII elemental analyzer by the elemental analysis laboratory of this institute. NMR spectra were recorded on a Varian Unity 500 spectrophotometer. The fluorescent data were collected on an Edinburgh FL-FS920 TCSPC system by the Spectroscopy Laboratory of Fuzhou University.

Synthesis of [$(Cu_4I_4)(MeCN)_2$(DADPM)]$_2$·2MeCN (1): A solution of DADPM (0.10 g, 0.5 mmol) in H_2O (10 mL) was added slowly to a solution of CuI (0.10 g, 0.5 mmol) in MeCN (20 mL). The reaction mixture was stirred at 60 °C for 30 min and gave a colorless solution, which was then filtered. The gray crystals of complex **1** were obtained by allowing the resulting solution to stand in the air for three days. Yield: 0.107 g, (0.049 mmol, 79% based on CuI). Addition of CuI and DADPM in a 2:1 ratio under otherwise identical experimental conditions gave the same complex. $C_{38}H_{46}Cu_8I_8N_{10}$ (2166.37): calcd. C 21.07, H 2.14, N 6.47; found C 21.23, H 2.17, N 6.54. IR (KBr): $\tilde{\nu}$ = 3396m, 3321s, 3265s, 3228m, 3140w, 3030w, 2922w, 2904w, 1612m, 1587m, 1510vs, 1433w, 1242m, 1178w, 1095w, 1018s, 985s, 941m, 850w, 825w, 812m, 777w, 766w, 704w, 577m, 515m cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.08 (m, 9 H, MeCN), 3.68 (s, 2 H, -CH_2-), 4.33 (s, 4 H, NH_2), 6.83 and 6.37 (m, 8 H, -C_6H_4-) ppm.

Synthesis of [$(Cu_4I_4)(MeCN)_2$(DADPE)]$_2$·2MeCN (2): The experimental procedure was similar to the synthesis of complex **1** except that DADPE (0.10 g, 0.5 mmol) was used instead of DADPM. Yield: 0.086 g (0.040 mmol, 63% based on CuI). Changing the metal-to-ligand ratio has no influence on the product of the reaction. $C_{36}H_{42}Cu_8I_8N_{10}O_2$ (2170.32): calcd. C 19.92, H 1.95, N 6.46; found C 20.07, H 2.03, N 6.57. IR (KBr): $\tilde{\nu}$ = 3315s, 3253s, 3128w, 3061w, 3018w, 1572m, 1498vs, 1441w, 1284m, 1265s, 1221s, 1165w, 1090w, 1014m, 978s, 926w, 877w, 843w, 825m, 785m, 552w, 517w, 503w cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.09 (m, 9 H, MeCN), 4.29 (s, 4 H, NH_2), 6.66 and 6.43 (m, 8 H, -C_6H_4-) ppm.

Table 1. Crystallographic data for compounds **1** and **2**

	1	2
Empirical formula	$C_{38}H_{46}Cu_8I_8N_{10}$	$C_{36}H_{42}Cu_8I_8N_{10}O_2$
Mol. wt.	2166.37	2170.32
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	10.473(3)	13.3142(2)
b, Å	21.458(8)	10.3433(3)
c, Å	13.660(7)	21.4439(6)
β, deg	94.10(3)	100.194(1)
V, Å^3	3062(2)	2906.48(13)
Z	2	2
D_c, g cm^{-3}	2.350	2.480
μ, cm^{-1}	6.789	7.155
Diffractometer	CAD4 four-circle	Siemens Smart CCD
T [K]	293(2)	293(2)
λ(Mo-K_α) [Å]	0.71073	0.71073
Reflections collected	6343	8489
Unique reflections	6008	5100
R_{int}	0.1158	0.0343
Parameters	289	289
S on F^2	1.045	1.009
$R1$ [$I > 2\sigma(I)$][a]	0.0621	0.0475,
$wR2$ (all data)[b]	0.1810	0.1318

[a] $R = \|F0\| - \|Fc\|)/\|F0\|$. [b] $wR = [w(F0^2 - Fc^2)^2/w(F0^2)^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for compound **1**[a]

Cu(1)−N(4)	1.993(15)	Cu(2)−N(3)	1.975(12)
Cu(3)−N(1)	2.078(10)	Cu(4)−N(2A)	2.108(11)
Cu(1)−I(1)	2.709(3)	Cu(1)−I(2)	2.723(2)
Cu(1)−I(4)	2.693(2)	Cu(2)−I(1)	2.666(2)
Cu(2)−I(2)	2.742(2)	Cu(2)−I(3)	2.683(2)
Cu(3)−I(2)	2.675(2)	Cu(3)−I(3)	2.738(2)
Cu(3)−I(4)	2.675(2)	Cu(4)−I(1)	2.643(2)
Cu(4)−I(3)	2.731(2)	Cu(4)−I(4)	2.640(2)
Cu(1)−Cu(2)	2.729(3)	Cu(1)−Cu(3)	2.670(3)
Cu(1)−Cu(4)	2.733(3)	Cu(2)−Cu(3)	2.777(3)
Cu(2)−Cu(4)	2.727(3)	Cu(3)−Cu(4)	2.709(3)
N(4)−Cu(1)−I(1)	107.5(5)	N(4)−Cu(1)−I(2)	105.3(5)
N(4)−Cu(1)−I(4)	107.5(4)	N(3)−Cu(2)−I(1)	107.5(4)
N(3)−Cu(2)−I(2)	102.1(4)	N(3)−Cu(2)−I(3)	110.0(4)
N(1)−Cu(3)−I(2)	107.0(3)	N(1)−Cu(3)−I(4)	107.9(3)
N(1)−Cu(3)−I(3)	102.6(3)	N(2A)−Cu(4)−I(1)	109.8(3)
N(2A)−Cu(4)−I(3)	99.0(3)	N(2A)−Cu(4)−I(4)	108.8(3)
I(1)−Cu(1)−I(2)	113.66(8)	I(4)−Cu(1)−I(1)	108.86(8)
I(4)−Cu(1)−I(2)	113.60(8)	I(1)−Cu(2)−I(3)	112.65(8)
I(1)−Cu(2)−I(2)	114.45(8)	I(3)−Cu(2)−I(2)	109.56(7)
I(2)−Cu(3)−I(3)	109.92(7)	I(2)−Cu(3)−I(4)	115.78(8)
I(4)−Cu(3)−I(3)	112.60(7)	I(1)−Cu(4)−I(3)	111.85(7)
I(4)−Cu(4)−I(1)	112.57(7)	I(4)−Cu(4)−I(3)	113.97(7)
Cu(1)−I(2)−Cu(2)	59.91(7)	Cu(2)−I(1)−Cu(1)	61.02(7)
Cu(2)−I(3)−Cu(3)	61.63(6)	Cu(2)−I(3)−Cu(4)	60.49(6)
Cu(3)−I(2)−Cu(1)	59.28(6)	Cu(3)−I(2)−Cu(2)	61.67(6)
Cu(3)−I(4)−Cu(1)	59.65(6)	Cu(4)−I(1)−Cu(1)	61.40(6)
Cu(4)−I(1)−Cu(2)	61.83(6)	Cu(4)−I(4)−Cu(1)	61.64(6)
Cu(4)−I(3)−Cu(3)	59.37(6)	Cu(4)−I(4)−Cu(3)	61.26(6)
Cu(1)−Cu(2)−Cu(3)	58.00(7)	Cu(1)−Cu(3)−Cu(2)	60.09(8)
Cu(1)−Cu(3)−Cu(4)	61.07(7)	Cu(2)−Cu(1)−Cu(4)	59.91(7)
Cu(2)−Cu(4)−Cu(1)	59.98(7)	Cu(3)−Cu(1)−Cu(2)	61.90(7)
Cu(3)−Cu(1)−Cu(4)	60.16(7)	Cu(3)−Cu(4)−Cu(1)	58.77(7)
Cu(3)−Cu(4)−Cu(2)	61.46(7)	Cu(4)−Cu(2)−Cu(1)	60.12(7)
Cu(4)−Cu(2)−Cu(3)	58.94(7)	Cu(4)−Cu(3)−Cu(2)	59.60(7)
C(4)−C(5)−C(6)	112.7(10)		

[a] Symmetry transformations used to generate equivalent atoms: A: $-x$, $-y$, $-z$.

X-ray crystallography: The crystal data and a structure determination summary for **1** and **2** are listed in Table 1. Selected bond lengths and bond angles for **1** and **2** are listed in Table 2 and 3, respectively. Intensity data for **1** and **2** were measured on a CAD4 four-circle and Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K, respectively. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and all calculations were performed using the SHELXL PC program. The positions of the H atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The structure was refined by full-matrix least-squares minimization of $\Sigma(F_o - F_c)^2$ with anisotropic thermal parameters for all atoms except the H atoms. CCDC-175784 (**1**) and CCDC-175785 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected bond lengths [Å] and angles [°] for compound **2**[a]

Cu(1)−N(1)	2.073(8)	Cu(2)−N(2A)	2.119(8)
Cu(3)−N(3)	1.985(11)	Cu(4)−N(4)	2.005(11)
I(1)−Cu(1)	2.7357(16)	I(1)−Cu(2)	2.7299(16)
I(1)−Cu(3)	2.6892(16)	I(2)−Cu(1)	2.6192(16)
I(2)−Cu(2)	2.6777(16)	I(2)−Cu(4)	2.7087(17)
I(3)−Cu(2)	2.6597(15)	I(3)−Cu(3)	2.7289(17)
I(3)−Cu(4)	2.7602(17)	I(4)−Cu(1)	2.6367(15)
I(4)−Cu(3)	2.6844(16)	I(4)−Cu(4)	2.6743(17)
Cu(1)−Cu(2)	2.7764(19)	Cu(1)−Cu(3)	2.731(2)
Cu(1)−Cu(4)	2.772(2)	Cu(2)−Cu(3)	2.747(2)
Cu(2)−Cu(4)	2.6951(18)	Cu(3)−Cu(4)	2.765(2)
N(1)−Cu(1)−I(1)	100.6(2)	N(1)−Cu(1)−I(2)	104.6(3)
N(1)−Cu(1)−I(4)	114.0(2)	N(2A)−Cu(2)−I(1)	101.0(3)
N(2A)−Cu(2)−I(3)	107.7(2)	N(2A)−Cu(2)−I(2)	108.6(2)
N(3)−Cu(3)−I(1)	110.4(3)	N(3)−Cu(3)−I(3)	101.0(3)
N(3)−Cu(3)−I(4)	108.1(3)	N(4)−Cu(4)−I(2)	101.7(3)
N(4)−Cu(4)−I(3)	103.5(3)	N(4)−Cu(4)−I(4)	117.5(3)
I(2)−Cu(1)−I(1)	111.16(5)	I(2)−Cu(1)−I(4)	112.18(6)
I(4)−Cu(1)−I(1)	113.43(6)	I(2)−Cu(2)−I(1)	109.56(5)
I(3)−Cu(2)−I(1)	111.07(5)	I(3)−Cu(2)−I(2)	117.57(5)
I(1)−Cu(3)−I(3)	110.20(5)	I(4)−Cu(3)−I(1)	113.40(6)
I(4)−Cu(3)−I(3)	113.03(6)	I(2)−Cu(4)−I(3)	113.16(5)
I(4)−Cu(4)−I(2)	108.25(6)	I(4)−Cu(4)−I(3)	112.35(6)
Cu(1)−I(2)−Cu(2)	63.21(4)	Cu(1)−I(2)−Cu(4)	62.68(5)
Cu(1)−I(4)−Cu(3)	61.75(5)	Cu(1)−I(4)−Cu(4)	62.93(5)
Cu(2)−I(1)−Cu(1)	61.06(4)	Cu(2)−I(3)−Cu(3)	61.27(5)
Cu(2)−I(2)−Cu(4)	60.04(4)	Cu(2)−I(3)−Cu(4)	59.60(4)
Cu(3)−I(1)−Cu(1)	60.44(5)	Cu(3)−I(1)−Cu(2)	60.90(4)
Cu(3)−I(3)−Cu(4)	60.48(5)	Cu(4)−I(4)−Cu(3)	62.12(5)
Cu(1)−Cu(3)−Cu(2)	60.91(5)	Cu(1)−Cu(3)−Cu(4)	60.59(5)
Cu(2)−Cu(4)−Cu(1)	61.02(5)	Cu(2)−Cu(3)−Cu(4)	58.55(5)
Cu(2)−Cu(4)−Cu(3)	60.39(5)	Cu(3)−Cu(1)−Cu(2)	59.83(5)
Cu(3)−Cu(1)−Cu(4)	60.31(5)	Cu(3)−Cu(2)−Cu(1)	59.26(5)
Cu(3)−Cu(4)−Cu(1)	59.10(5)	Cu(4)−Cu(1)−Cu(2)	58.12(5)
Cu(4)−Cu(2)−Cu(1)	60.86(5)	Cu(4)−Cu(2)−Cu(3)	61.06(5)
C(5)−O(1)−C(4)	117.1(7)		

[a] Symmetry transformations used to generate equivalent atoms: A: $-x$, $-y$, $+ 1$, $-z$.

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