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Substituent-Controlled Constructions of M$_2$L$_4$ Cage and 1D Network Structures for Cu(II) Complexes with Bis-benzimidazole Ligands

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1 Multicopper(II) complexes were synthesized using bis-
2 benzimidazole ligands expressed as B–CH$_2$–C$_6$R$_4$–CH$_2$–
3 B (B = benzimidazole, R = Me (bbitrb), OMe
4 (bbitrmob)). For the reactions with Cu(ClO$_4$)$_2$·6H$_2$O and
5 CuSO$_4$·5H$_2$O, bbitrb gave M$_2$L$_4$ cage complexes, while
6 bbitrmob gave a M$_2$L$_4$ cage complex and a new 1D
7 coordination polymer. The substituent-controlled
8 syntheses of the Cu(II) complexes are described.
9
10 Keywords: bis-benzimidazole, M$_2$L$_4$ cage, Coordination
11 polymer.

12 Constructions of multinuclear metal complexes with
13 cage and network structures have attracted much attention
14 because of the unique functions of such complexes, such as
15 separation, and storage of guest molecules or guest ions in
16 the space created in the frameworks.[1-4] Among the various
17 bridging ligands that have been used for their syntheses, bis-
18 benzimidazole ligands expressed as B–CH$_2$–C$_6$R$_4$–CH$_2$–B
19 (B = benzimidazole, R = H, Me, or OMe) have afforded
20 unique M$_2$L$_2$,[5] M$_2$L$_4$,[5-11] and M$_2$L$_3$ cages,[5,6] as well as
21 network structures.[7,11,12]
22 It has been shown that 1,4-bis((1H-imidazol-1-
23 yl)methyl)benzene (*p*-bix), which is the ligand with R = H,
24 affords [Cu(*p*-bix)](ClO$_4$)$_2$,[13] which has a 1D network
25 structure, by the reaction with Cu(ClO$_4$)$_2$·6H$_2$O. We have
26 reported previously that the tetramethyl derivative, 1,4-
27 bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (*p*-biteb),
28 affords a M$_2$L$_4$ cage complex [ClO$_4$ ⊂ Cu$_2$(*p*-
29 biteb)$_4$(ClO$_4$)$_2$]ClO$_4$ by the reaction with Cu(ClO$_4$)$_2$·6H$_2$O.[8]
30 These results indicate that the R groups of B–CH$_2$–C$_6$R$_4$–
31 CH$_2$–B affect the framework motifs of the obtained metal
32 complexes. Although control of the framework motifs by
33 the R groups is an attractive subject, it has not been well
34 explored.
35 In the series of B–CH$_2$–C$_6$R$_4$–CH$_2$–B ligands, 1,3-
36 bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene
37 (bbitrb) has been widely used for the synthesis of
38 multinuclear metal complexes.[5,6,14] To study the effects of R
39 on the structures of the obtained complexes, and which
40 create the new multinuclear metal complexes, we
41 synthesized a new bridging ligand 1,3-bis(benzimidazol-1-
42 ylmethyl)-2,4,6-trimethoxybenzene (bbitrmob), the
43 trimethoxy derivative of bbitrb, and then characterized the
44 Cu(II) complexes obtained with this ligand. The structures
45 of bbitrb and bbitrmob are illustrated in Scheme 1.
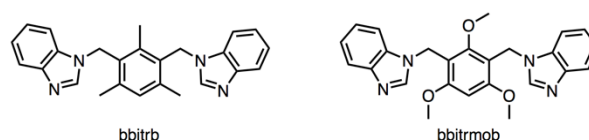
46
47 **Scheme 1.** Structures of bbitrb and bbitrmob.
48
49 The M$_2$L$_4$ complex [ClO$_4$ ⊂ Cu$_2$(bbitrb)$_4$(ClO$_4$)](ClO$_4$)$_2$
50 (**1a**) was characterized by Su et al.[5] as a reaction product of
51 Cu(ClO$_4$)$_2$·6H$_2$O with bbitrb. Because of the relatively poor
52 quality of the reported crystal structure of **1a**, we proceeded
53 to isolate the M$_2$L$_4$ complex from the reaction of bbitrb with
54 Cu(ClO$_4$)$_2$·6H$_2$O, in a mixed solution of THF/Me$_2$CO, and
55 then (in this work) we redetermined the structure of the
56 complex for structural comparison with other complexes.
57 We have previously shown that the M$_2$L$_4$ cage
58 complex [SO$_4$ ⊂ Cu$_2$(bbitrb)$_4$](SO$_4$) is obtained by the
59 reaction of CuSO$_4$·5H$_2$O with bbitrb.[10] In this work, we
60 found that bbitrmob also gave a M$_2$L$_4$ cage complex [ClO$_4$
61 ⊂ Cu$_2$(bbitrmob)$_4$](ClO$_4$)$_3$(MeCN)$_2$(H$_2$O)$_2$ (**2**) by the
62 reaction with Cu(ClO$_4$)$_2$·6H$_2$O. Furthermore, the ligand did
63 not afford the M$_2$L$_4$ cage complex by the reaction with
64 CuSO$_4$·5H$_2$O, but yielded a 1D coordination polymer
65 [Cu$_2$(SO$_4$)$_2$(bbitrmob)$_2$](MeCN)(H$_2$O) (**3**). This paper
66 describes the syntheses and structures of the Cu(II)
67 complexes with bis-benzimidazole ligands, and the effects
68 of the methoxy groups (as R) of the ligands on the obtained
69 structures.
70 The ligand bbitrmob was prepared from 1,3,5-
71 trimethoxybenzene, following a general procedure.
72 Treatment of the starting material with 1,3,5-trioxane and
73 30% HBr in glacial acetic acid afforded 2,4-
74 bis(bromomethyl)-1,3,5-trimethoxybenzene. Reaction of the
75 precursor with benzimidazole and KOH then afforded the
76 target ligand, bbitrmob. The details are shown in the
77 Supporting Information.
78 Diffusion of an Me$_2$CO solution of bbitrb (prepared
79 according to a method reported in the literature) into a
80 MeOH solution of Cu(ClO$_4$)$_2$·6H$_2$O afforded [ClO$_4$ ⊂
81 Cu$_2$(bbitrb)$_4$(ClO$_4$)](ClO$_4$)$_2$(Me$_2$CO)$_4$ (**1b**) as purple crystals.
82 Complex **2** was also isolated as purple crystals after
83 diffusion of an MeCN solution of bbitrmob into an Me$_2$CO
84 solution of Cu(ClO$_4$)$_2$·6H$_2$O. Figure 1 shows the M$_2$L$_4$ cage
85 structures of **1b** and **2**.[15] For **1b**, there is a crystallographic
86 $C4$ axis, which runs through the two Cu^{II} centers. For **2**,
87 there is a crystallographic inversion center in the M$_2$L$_4$ cage.
88 The Cu–N distances around the Cu^{II} centers are 1.9975
89 (19) and 1.984 (2) Å (avg. 1.991 Å) for **1b**; for **2** they are in

the range 1.983–1.996 Å (avg. 1.987 Å). The values are referred to in the caption of Figure 1. Both complexes include a ClO_4^- in the cage and three ClO_4^- outside the cage. The ClO_4^- in **1b**, which is disordered at the four positions due to the crystallographic *C*4 axis, associates weakly with the two Cu^{II} centers (Cu(1)---O(1) = 2.664 Å and Cu(2)---O(2) = 2.458 Å, avg. 2.561 Å). These distances are shorter than the sum of the van der Waals radii of Cu (1.4 Å) and O (1.52 Å). The ClO_4^- in the cage of **2**, which is disordered at the four positions, also weakly associates with the Cu^{II} centers (Figure S3). The Cu---O distances, which are in the range 2.51–2.61 Å (avg. 2.55 Å), are close to those of **1b**.
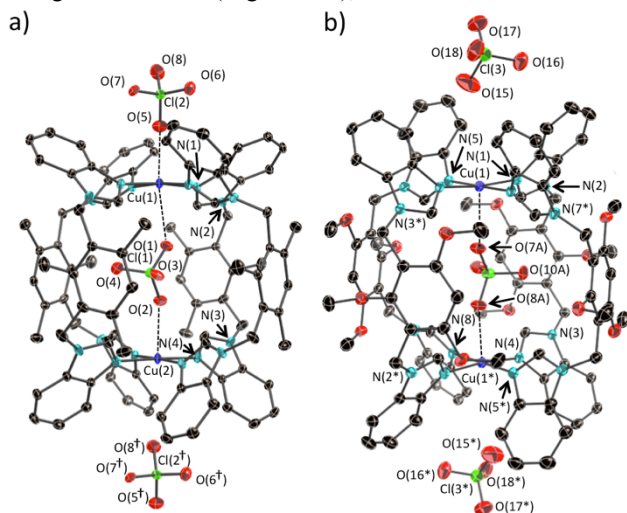
Figure 1. Thermal ellipsoids of the molecular structures of **1b** (a) and **2** (b) at 30% probabilities. Disordered ClO_4^-, guest organic molecules, other ClO_4^- located side the cage, and hydrogen atoms are omitted for clarity. Color code: blue, copper; red, oxygen; green, chlorine; cyan, nitrogen; black, carbon. Symmetry operation † *X, Y, −1+Z*, * *−X, −Y, −Z*. Selected bond distances for **1b** are Cu(1)–N(1) = 1.9975 (19); Cu(2)–N(4) = 1.984 (2) Å, and for **2** are Cu(1)–N(1) = 1.983 (2); Cu(1)–N(5) = 1.996 (2); Cu(1)–N(4*) = 1.9799 (19); Cu(1)–N(8*) = 1.987 (2) Å.

Of the three ClO_4^- outside the cage of **1b**, one ClO_4^- associates with the Cu^{II} center (Cu(1)---O(5) = 2.401 Å). Although this anion locates between the two Cu^{II} centers of the two different M_2L_4 cages, it does not associate with the other Cu^{II} center (Cu(2)---O(8†) = 3.847 Å). That is, there are no coordinating molecules or anions above the Cu(2) center. As a result, Cu(1) is based on the elongated octahedral, while Cu(2) is based on the distorted square pyramidal. In the case of **2**, although ClO_4^- outside the cage is observed above each Cu^{II} center, the anion does not associate with the Cu^{II} center (Cu(1)---O(15) = 4.22 Å). Furthermore, the two Cu^{II} centers of **2** are based on the distorted square pyramidal. For both complexes, the other ClO_4^- are located in the hydrophobic space created among the M_2L_4 cages.
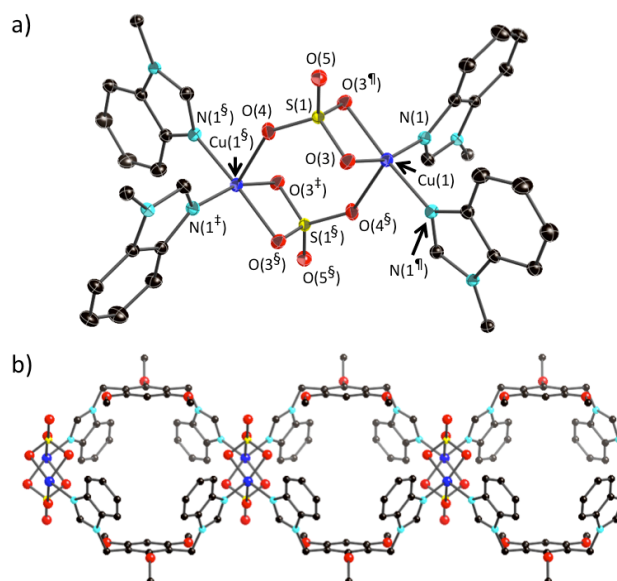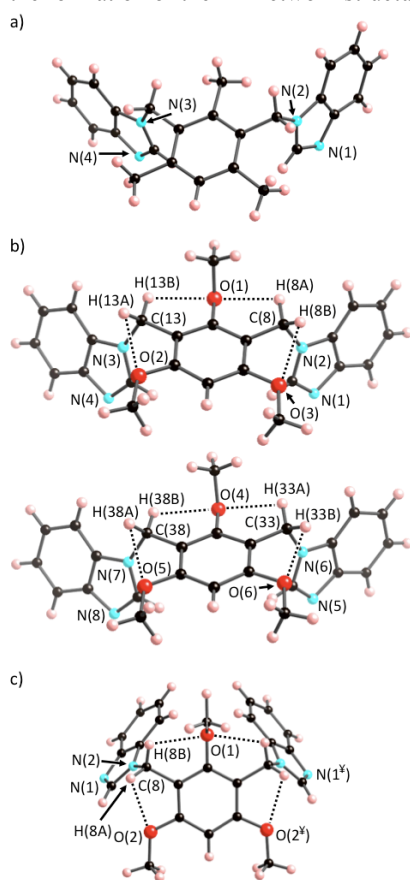

Figure 2. Thermal ellipsoids of the coordination environments of **2** at 30% probabilities (a) and the 1D structure, which is constructed by bridging the $Cu_2(SO_4)_2$ units with bbitrmob (b). Symmetry operation ¶ *X, −Y, Z*, § 1−*X, Y, 1−Z*, ‡ 1−*X, −Y, 1−Z*.

Complex **3** was isolated as blue crystals by diffusion of an MeCN solution of bbitrmob into a MeOH solution of $CuSO_4·5H_2O$. The 1D framework is constructed by bridging the $Cu_2(SO_4)_2$ units with 2 equiv bbitrmob. Figure 2 shows the coordination circumstances around the Cu^{II} centers and structure of the 1D chain. The two Cu^{II} ions are connected by two SO_4^{2-}. Each SO_4^{2-} binds to two Cu^{II} centers in the monodentate and bidentate chelating fashions, respectively. Two bbitrmob connect these units, producing a 1D network along the *b* axis (Figure 2b). There are crystallographic mirrors perpendicular to the chains, and the *C*2 axis runs through the 1D chain. The space created by the two $Cu_2(SO_4)_2$ units and two bbitrmob in the chain has a size of about 8.5 × 7.5 Å^2 at the middle part. For the bbitrmob, the plane-plane angle defined by the benzimidazole ring and phenyl ring with methoxy groups is 68.7(1)°. The size of the void space, which has volume of about 225 Å^3, in the 1D chain decreases to about 6.0 × 5.0 Å^2 at the top and bottom of the space due to capping by the phenyl rings of the benzimidazole and methoxy groups of the bbitrmob. A H_2O molecule is trapped in the space, with remarkable disorders, which were solved at O(6A), O(7B), O(8C), and O(9A) with occupancies of 0.10, 0.10, 0.15, and 0.20, respectively.

As mentioned above, the reaction of $Cu(ClO_4)_2·6H_2O$ with bbitrmob gave a M_2L_4 cage complex, while the reaction of $CuSO_4·5H_2O$ with the ligand gave the 1D coordination polymer. The ligands B–CH$_2$–C$_6$R$_4$–CH$_2$–B often give the M_2L_4 cage complexes that trap a ClO_4^-.[5-9] We have shown that this tendency is because the ClO_4^- functions as the template guest for the M_2L_4 cage constructions due to the hydrophobic surface.[11] In contrast to ClO_4^-, SO_4^{2-} would not function as the template guest for

the M_2L_4 cage constructions due to the hydrophilic surface. The formation of the M_2L_4 cage that traps a SO_4^{2-} would result from strong Cu---O bond formations between the Cu^{II} center and SO_4^{2-}, as reflected by the shorter Cu---O distances. For example, the distances (about 2.1 Å) observed in $[SO_4 \subset Cu_2(bbitrb)_4](SO_4)$[10] are remarkably shorter than those of **1b** (avg. 2.561 Å) and **2** (avg. 2.55 Å).

The Cu—N distances (avg. 1.986 Å) of **2** are slightly shorter than those (avg. 1.991 Å) of **1b**. It is well known that a methoxy group has stronger electron-donating properties than a methyl group. The stronger electron-donating property of bbitrmob would form stronger Cu—N bonds, and then decreases the acidity at the Cu^{II} center. This effect would weaken the Cu---O bonds between the Cu^{II} center and SO_4^{2-} in the M_2L_4 cage with bbitrmob. As a result, the $[SO_4 \subset Cu_2(bbitrmob)_4]^{2+}$ structure becomes unstable, leading to the formation of the 1D network structure.

One of the unique features of the bbitrmob ligand is the formation of the intraligand C–H···O interactions. The C–H···O interaction is a type of hydrogen bond. When the interactions are formed, in most cases, the C---O distance is shorter than 3.0 Å, and the C–H···O angle is in the range 90–180°. Figure 3b and 3c illustrates the plausible C–H···O interactions with dotted lines. Table 1 summarizes the C–H···O angles and C---O and O···H distances estimated from the crystal structures. It was found that all methoxy groups of bbitrmob form C–H···O interactions with hydrogen atoms of methylene groups in **2** and **3**, although the C(38)–H(38A)···O(5) interaction in **2** is significantly weak, as estimated by the significantly small C–H···O angle (85.90°) and long O···H distance (2.64 Å). Their bond formations would stabilize the structures of the obtained complexes. These interactions would be useful for the construction of new multinuclear structures for metal complexes. Studies are in progress.

Table 1. The C-H···O angles α (°) and the estimated C···O (d_1) and O···H distances d_2 (Å) in bbitrmob of **2** and **3**.

C-H···O interactions	α	d_1	d_2
Complex **2**			
C(8)—H(8A)···O(1)	104.65	2.84	2.42
C(8)—H(8B)···O(3)	91.86	2.73	2.51
C(13)—H(13A)···O(2)	89.39	2.70	2.52
C(13)—H(13B)···O(1)	106.06	2.87	2.44
C(33)—H(33A)···O(4)	100.74	2.84	2.46
C(33)—H(33B)···O(6)	97.59	2.76	2.44
C(38)—H(38A)···O(5)	85.90	2.75	2.64
C(38)—H(38B)···O(4)	108.10	2.84	2.38
Complex **3**			
C(8)—H(8A)···O(2)	92.21	2.71	2.49
C(8)—H(8B)···O(1)	105.75	2.86	2.43

Figure 3. Structures of bbitrmob in **1b** (a), **2** (b), and **3** (c). Symmetry operation ¥ X, $1-Y$, Z.

Figure 3 shows X-ray structures of the ligands in **1b**, **2**, and **3**. Complex **2** has two crystallographically independent bbitrmob ligands with similar structures. It is evident that conformations of the ligands in the M_2L_4 cages, i.e., bbitrb in **1b** and bbitrmob in **2**, are similar, and quite different from that of bbitrmob in **3**. The conformation of B–CH_2–C_6R_4–CH_2–B would be fixed sterically in the M_2L_4 cage structures.

In summary, we have designed a new bis-benzimidazole ligand, bbitrmob. Reactions of the ligand with $Cu(ClO_4)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$ gave a M_2L_4 cage complex and 1D coordination polymer. The formation of Cu^{II} complexes with different structures is in contrast to products obtained with the ligand bbitrb, which gave M_2L_4 cage complexes after similar treatment. The structure formation obtained when using bbitrmob would be the result of a decrease in the acidity at the Cu^{II} center due to the strong electron-donating effects of the three methoxy groups. These results imply that the structures of the complexes obtained are conveniently controlled by the R groups in the ligands.

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15. Data collections were carried out on a Rigaku VariMax diffractometer using multi-layer mirror monochromated Mo-Kα radiation (1.2-kW rotating anode) and a PILATUS 200K detector. Crystallographic data for **1b**: $C_{112}H_{120}Cl_4Cu_2N_{16}O_{20}$ (MW: 2279.11), tetragonal, space group *I*4 (No. 79), a = 18.5297(2), c = 15.9530(3) Å, V = 5477.46 (16) Å^3, Z = 2, ρ(cacld) = 1.382 g cm^{-3}, μ(Mo Kα) = 0.562 mm^{-1}, T = 173 K, λ = 0.71073 Å, ω scan, reflections collected/unique reflections/ parameters refined: 7257/6545/416, Rint = 0.0518, final R1 = 0.0378 (I > 2σ(I)), wR2 = 0.1001 (all data), GOF = 1.040. CCDC 1988632. Crystallographic data for **2**: $C_{104}H_{106}Cl_4Cu_2N_{18}O_{30}$ (MW: 2356.99), triclinic, space group *P*-1 (No. 2), a = 14.1410 (11), b = 14.3853 (18), c = 15.646 (2) Å, α = 117.163(4), β = 92.640(3), γ = 91.279(2)°, V = 2825.4 (6) Å^3, Z = 1, ρ(cacld) = 1.385 g cm^{-3}, μ(Mo Kα) = 0.554 mm^{-1}, T = 173 K, λ = 0.71075 Å, ω scan, reflections collected/unique reflections/ parameters refined: 38608/12754/854, Rint = 0.0563, final R1 = 0.0592 (I > 2σ(I)), wR2 = 0.1690 (all data), GOF = 0.856. CCDC 1988630. Crystallographic data for **3**: $C_{27}H_{29}CuN_5O_8S$ (MW: 647.16), monoclinic, space group *C*2/*m* (No. 12), a = 18.2894 (10), b = 11.8659 (5), c = 16.1202 (8) Å, β = 117.9210 (14)°, V = 3091.2 (3) Å^3, Z = 4, ρ(cacld) = 1.390 g cm^{-3}, μ(Mo Kα) = 0.828 mm^{-1}, T = 173 K, λ = 0.71075 Å, ω scan, reflections collected/unique reflections/ parameters refined: 24329/3693/244, Rint = 0.0197, final R1 = 0.0472 (I > 2σ(*I*)), wR2 = 0.1414 (all data), GOF = 1.100. CCDC 1988631.