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Design, Self-Assembly, and Molecular Structures of 3D Copper(II) Capsules Templated by BF_4^- Guest Anions

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The synthesis of two 3D M_2L_4 copper(II) capsules, $\{[BF_4\subset(CH_3CN)_2Cu_2(L^1)_4][BF_4]_3\}$ (**1**) and $\{[BF_4\subset(BF_4)_2Cu_2(L^1)_4][BF_4]\}$ (**2**), by using 1,3-(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene (L^1) as a semirigid exobidentate ligand and $[Cu(CH_3CN)_4][BF_4]_2$ as a metallobrick is reported. Single-crystal X-ray diffraction studies show the encapsulation of a BF_4^- anion in **1** and **2**. Moreover, **2** displayed three coordinated BF_4^- anions, which is rare in supramolecular coordination host–guest chemistry. Remarkably, in both metallocages the weakly coordinated BF_4^- anion acts as a template and interacts with the metal center through a weak Cu···F contact.
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Introduction

The rational construction of well-defined discrete structures possessing a central cavity capable to receive guest molecules has attracted great interest[1] not only because of their appealing structures but also due to their importance in molecular recognition,[2] ion exchange,[3] chemical sensors,[4] or even more recently as nanoreactors for chemical transformations.[5] In the latter, it has been shown that size, shape, and the chemical environment of the cavities provide new approaches to nanovessel catalysts. For example, Raymond, Bergman, and Fujita showed that an encapsulated organometallic catalyst within space-restricted media may be used for stereoselective transformations.[5,6]

The self-assembly of metal ions and bridging ligands rationally chosen allowed the efficient and elegant preparation of a variety of original well-characterized entities.[7] Whereas large metallomacrocycles of the type M_4L_6 (M = metal, L = ligand), $M_{12}L_8$, and M_6L_8 cages[8] have been intensively described in the literature, surprisingly simple 3D di- or trinuclear architectures such as M_3L_2, M_2L_3, or M_2L_4 have received less attention.[9] In particular, examples of copper(II) cages are rare. To the best of our knowledge, just three types of Cu_2L_4 molecular boxes[10] have been reported with the use of exobidentate ligands.

Pursuing our research in this area we recently reported the self-assembly of unusual inorganic cobalt cages that encapsulate a tetrafluoroborate anion.[11] Remarkably, a discrete 3D cage in which three BF_4^- ions are coordinated was described; this is a rare finding in supramolecular chemistry. However, the originality of this work stems from the fact that the encapsulated BF_4^- anion shows a direct M···F interaction with the metal center. In this work we extend our methodology to tetragonal Cu^{II} capsules templated by weakly anion guests. In fact, Cu^{II} coordination chemistry is very different from that of Co^{II} and because only few examples of Cu^{II} cages are known,[10] we felt that the rational design and synthesis of such metallocages represent an attractive challenge to overcome. In contrast, we note that examples of supramolecular metallomacrocycles with different metal centers that act as anion receptors have been reported by other groups.[12]

In this paper we report the preparation and structural characterization of two new tetragonal copper(II) cages, $\{[BF_4\subset(CH_3CN)_2Cu_2(L^1)_4][BF_4]_3\}$ (**1**) and $\{[BF_4\subset(BF_4)_2Cu_2(L^1)_4][BF_4]\}$ (**2**), with the use of 1,3-(benzimidazol-1-ylmethyl)-2,5-dimethoxy-4,6-dimethylbenzene (L^1) as a bidentate assembling ligand.

Results and Discussion

Treatment of L^1 (2 equiv.) with $[Cu(CH_3CN)_4][BF_4]_2$ in a solution of acetonitrile/chloroform for several hours followed by reaction workup provided a violet microcrystalline precipitate in 73% yield (Scheme 1). Recrystallization from CH_3CN/Et_2O afforded suitable crystals of $\{[BF_4\subset(CH_3CN)_2Cu_2(L^1)_4][BF_4]_3\}$ (**1**), as identified by single-crystal X-ray diffraction study (vide infra).

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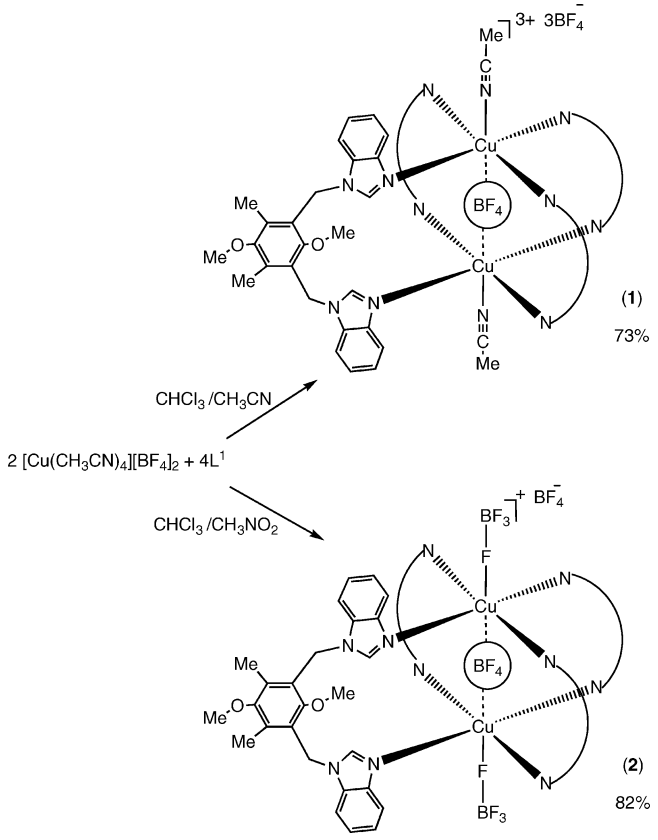

Scheme 1. Synthesis of metallocages **1** and **2**.

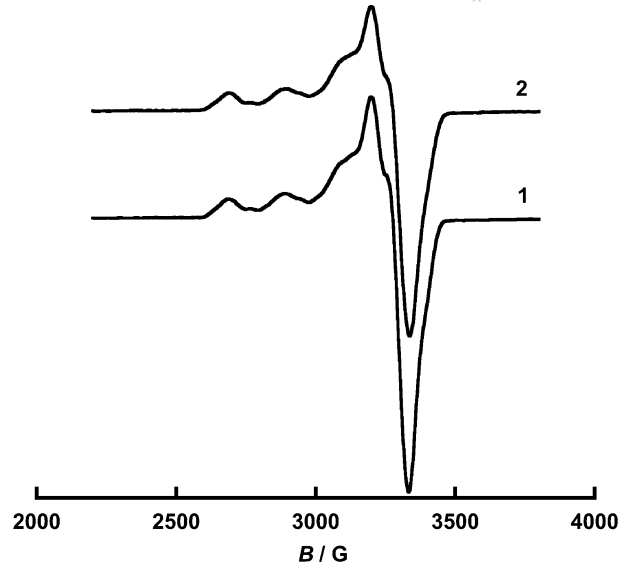

Figure 1. EPR spectra of **1** and **2**. Recording conditions: 1 mM (solvent in the text), 100 K, microwave frequency: 9.384 GHz, microwave power: 3.2 mW, modulation amplitude: 2.5 G, modulation frequency 100 kHz, sweep time: 167.77 s, time constant: 40.96 ms.

Repeating the above reaction but in nitromethane/chloroform solvent mixture instead afforded a deep-purple microcrystalline precipitate in 82% yield, which was ascertained by X-ray analysis to be $\{[BF_4\subset(BF_4)_2Cu_2(L^1)_4]\text{-}[BF_4]\}$ (**2**). In both cases, complexes were isolated pure and analyzed elementally. The infrared spectra showed the presence of tetrafluoroborate anions for both metallomacrocycles **1** and **2**. The paramagnetic copper cages **1** and **2** gave, as might be expected, nonrecordable ^{1}H NMR spectra. In the same way, the encapsulated BF_4^- anions could not be observed by ^{11}B and ^{19}F NMR techniques, as only signals attributed to the free anions were identified. This is not surprising and is attributed to the paramagnetic nature of copper and has been reported previously.[13] The paramagnetic nature of metallomacrocycles **1** and **2** was confirmed by EPR. The spectra were recorded in solution for **1** (CH_3CN/toluene, 1:1) and **2** (CH_3NO_2/toluene, 1:1; see Figure 1). They display similar spectra showing a typical anisotropic copper(II) signal with four lines in parallel region arising from the hyperfine coupling of the $S = 1/2$ electron spin of Cu^{II} with its nuclear spin $I = 3/2$. Approximate g and A values were obtained from the spectra: for **1**, $g_\parallel = 2.25$ and $g_\perp = 2.04$, $A_\parallel/g_\parallel\beta = 200$ G; for **2**: $g_\parallel = 2.25$ and $g_\perp = 2.04$, $A_\parallel/g_\parallel\beta = 219$ G. The morphology of both spectra ($g_\parallel > g_\perp$) is consistent with a Cu^{II} ion in an axial elongated square-pyramidal geometry, which is that obtained in the solid state as described below.

Furthermore, crystals of $\{[BF_4\subset(CH_3CN)_2Cu_2(L^1)_4]\text{-}[BF_4]_3\}$ (**1**) were grown by vapor diffusion of diethyl ether into a solution of the complex in CH_3CN. The compound crystallized in the monoclinic space group $P2_1/n$. The structure shows the formation of a novel type of a $[Cu_2(L^1)_4]$ tetragonal cage (Figure 2), where each copper atom adopts a square pyramidal geometry. Four benzimidazole arms of the bridging ligands L^1 fill the equatorial positions, whereas two coordinating solvents were found to occupy the apical positions of the dicopper box. Further, a BF_4^- anion is encapsulated inside the cage cavity through a weak metal–anion interaction with Cu···F 2.558 Å; this distance is longer than that reported for $\{[BF_4\subset(CH_3CN)_2Co_2(L^1)_4]\text{-}[BF_4]_3\}$ (**3**) with Co···F 2.405 Å.[11b] Three BF_4^- anions are located outside the cavity. It is worth mentioning that the encapsulated BF_4^- anion was found to be disordered, in particular the two nonbridging fluorine atoms and the boron center (···F*BF2*F···). Each atom occupies two sites and each was refined with half-occupancy. The Cu–N bond lengths lie in the range 2.016–2.042(3) Å. The Cu···Cu distance is 7.412 Å, and the average distance between two facing phenyl rings is nearly 11 Å. Thus, the cavity size is slightly bigger than that of homologous tetragonal cobalt cage **3**.

Crystals of **2** were grown by vapor diffusion of diethyl ether into a solution of the complex in a noncoordinating solvent, CH_3NO_2. The compound crystallized in the triclinic space group $P\bar{1}$. The structure shows, as before, the formation of a novel type of a $[Cu_2(L^1)_4]$ tetragonal cage (Figure 3), where each copper atom adopts a square pyramidal geometry. Unlike previous cage **1**, there are two coordinated BF_4^- anions that bind externally (apical positions) to the two copper centers instead of a coordinating solvent with Cu···F 2.475(3) Å. Four benzimidazole arms of the

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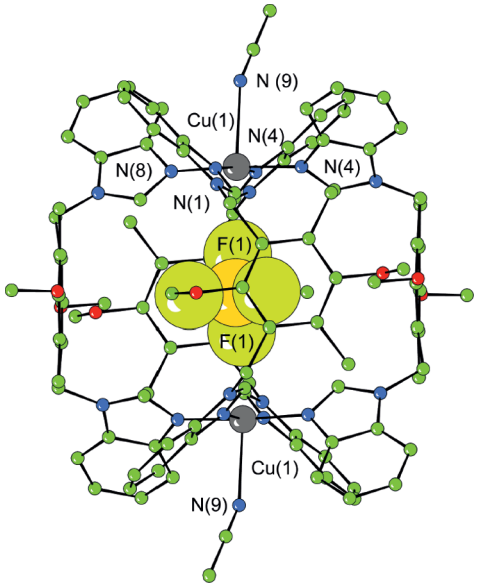

Figure 2. X-ray crystal structure of $[BF_4{\subset}(CH_3CN)_2Cu_2(L^1)_4]^{3+}$ showing the encapsulated BF_4^- anion in space-filling representation (C green, O red, N blue, B yellow, F pale green, Cu gray; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 2.016(3), Cu1–N4 2.022(3), Cu1–N5 2.042(3), Cu1–N8 2.032(3), Cu1–N9 2.553, Cu1–F1 2.558, N1–Cu1–N5 91.27(13), N5–Cu1–N4 88.96(13), N4–Cu1–N8 88.98(13), N8–Cu1–N1 90.42(13).

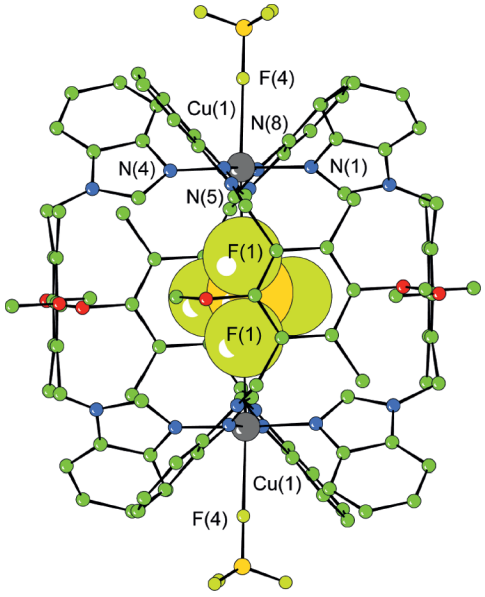

Figure 3. X-ray crystal structure of $\{[BF_4{\subset}(BF_4)_2Cu_2(L^1)_4]^+\}$ showing the encapsulated BF_4^- anion in space-filling representation as well as the two other coordinated BF_4^- anions (C green, O red, N blue, B yellow, F pale green, Cu gray; H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N1 2.030(3), Cu1–N4 2.022(3), Cu1–N5 2.030(3), Cu1–N8 2.015(3), Cu1–F1 2.461(3), Cu1–F4 2.475(3), N1–Cu1–N5 90.74(13), N5–Cu1–N4 90.02(13), N4–Cu1–N8 89.43(13), N8–Cu1–N1 89.74(13).

bridging ligands L^1 fill the equatorial positions. Further, a third BF_4^- anion is encapsulated inside the cage cavity through a metal–anion weak interaction Cu···F 2.461(3) Å; this encapsulated BF_4^- anion was also found to be disordered in a similar way to that found in cage **1**. This bond length is shorter than that described for **1** (vide supra) but longer than that reported for $\{[BF_4{\subset}(BF_4)_2Co_2(L^1)_4][BF_4]\}$ (**4**) in which Co···F 2.312(3) Å.[11a] The fourth BF_4^- anion is located outside the cavity. The Cu–N bond lengths lie in the range 2.015(3)–2.032(3) Å, which is very close to that observed in previous cage **1**. The Cu···Cu distance is 7.244 Å, and the average distance between two facing phenyl rings is 11 Å. Thus, the cavity size is slightly smaller than that of **1**. At this stage, a short comment on the nature of the M···BF_4^- direct contact is required, as such an interaction is unusual and unlike H···BF_4^- anion hydrogen bonding. Only a few metallomacrocycles showing such an interaction are reported in the literature.[10a,14] In contrast, however, we note that several simple mononuclear Cu^{II} complexes displaying a Cu···F weak interaction with two BF_4^- anions are reported. It is clear that these examples are intrinsically different from our work.[15] Thus, the 3D capsule $\{[BF_4{\subset}(CH_3CN)_2Co_2(L^1)_4][BF_4]_3\}$ (**3**) with three coordinated BF_4^- anions is a rare finding in supramolecular coordination chemistry.

Overall we note that in 3D Cu^{II} cages **1** and **2**, the cavities are bigger than their homologous Co^{II} metallomacrocycles.[11] These two examples beautifully illustrate the crucial role of BF_4^- anions. In fact, such an anion is ideally suited for these kinds of cages and can be considered as a "strong template" around which four ligand L^1 and two copper inorganic bricks self-assemble.[16] This requires a perfect adequacy between the coordination geometry of metal ions, the topology of the ligand, and the shape of the guest. The number of papers describing the recognition and complexation by cationic and neutral guests is well developed in the literature, but in contrast, the encapsulation of anionic guests is still in its infancy, despite the fact that anions play important roles in chemistry and biology.[12] The unusual Cu···F interaction in both cases may play a determining part in the inclusion of the BF_4^- anion inside the tetragonal cage and may dictate the final supramolecular structure.

Conclusions

In summary, the use of BF_4^- as a template combined with L^1 exobidentate ligands and Cu^{II} bricks allowed an elegant and rational preparation of two new 3D discrete paramagnetic copper cages, $\{[BF_4{\subset}(CH_3CN)_2Cu_2(L^1)_4][BF_4]_3\}$ (**1**) and $\{[BF_4{\subset}(BF_4)_2Cu_2(L^1)_4][BF_4]\}$ (**2**), in high yield. The characterization of these supramolecular assemblies in solution was not possible by ^1H, ^{11}B, and ^{19}F NMR spectroscopy. On the basis of the EPR spectrum, the oxidation state +2 for the copper metal centers in **1** and **2** was confirmed. The identities of **1** and **2** were ascertained structurally, and in both cases one anion is encapsulated inside the cavity. Further, the X-ray structure of **2** shows the coordination of three BF_4^- anions to the copper center, which is a rare finding in host–guest coordination macro-

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cycles. Compared to their homologous 3D discrete cobalt(II) capsules, **1** and **2** are slightly bigger. Cages **1** and **2** are quite interesting examples of self-assembly using tetrafluoroborate anion as a template in which the recognition takes place through a weak direct interaction with the metal. Efforts to construct new architectures involving other weak coordinating anions such as PF_6^- are currently under investigation.

Experimental Section

General Methods: All solvents used were reagent grade or better. Commercially available reagents were used as received. Ligand L^1 was synthesized as previously reported.[11b] $[Cu(CH_3CN)_4][BF_4]_2$ was prepared following a published procedure.[17] IR spectra were recorded with a Bruker Tensor 27 instrument equipped with a Harrick ATR. Elemental analysis was performed by the Microanalytical Laboratory of the Université Pierre et Marie Curie Paris-6. EPR measurements were recorded with a Bruker Elexis 500 spectrometer at the ICMMO, University Paris-Sud 11, at 100 K, in a frozen CH_3CN/toluene (1:1) mixture for **1** and in a frozen CH_3NO_2/toluene (1:1) mixture for **2**. The difference in solvent was imposed by the different solubilities of the two compounds and toluene was added to obtain a good glass when frozen. The instrument parameters used are described in the legend of Figure 1.

{$[BF_4 \subset (CH_3CN)_2Cu_2(L^1)_4][BF_4]_3$} (1): Ligand L^1 (852 mg, 2 mmol) in CH_2Cl_2 (15 mL) was added to a blue solution of $[Cu(CH_3CN)_4][BF_4]_2$ (401 mg, 1 mmol) in CH_3CN (15 mL). The solution was stirred at room temperature for 4 h, during which a blue-deep blue color appeared. The solvents were then removed. The obtained blue precipitate was washed with CH_2Cl_2 and dried under vacuum. Yield: 73%. Recrystallization (CH_3CN/Et_2O) afforded quantitatively violet crystals. $C_{108}H_{110}B_4Cu_2F_{16}N_{18}O_8 \cdot 2Et_2O$ (2262.46): calcd. C 57.79, H 5.44, N 10.46; found C 57.92, H 5.79, N 10.34. IR: $\tilde{\nu}$ = 1074 [ν(B–F)] cm^{-1}.

{$[BF_4 \subset (BF_4)_2Cu_2(L^1)_4][BF_4]$} (2): Compound **2** was obtained following a similar procedure described for **1** but with the use of CH_3NO_2 instead of CH_3CN. Yield: 82%. Recrystallization (CH_3NO_2/Et_2O) afforded quantitatively deep-purple crystals. $C_{104}H_{104}B_4Cu_2F_{16}N_{16}O_8$ (2301.49): calcd. C 57.29, H 4.81, N 10.28; found C 58.00, H 5.26, N 10.37. IR: $\tilde{\nu}$ = 1059 [ν(B–F)] cm^{-1}.

Data Collection and Structure Refinement: A single crystal of compound **1** or **2** was selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo-K_α radiation. Unit-cell parameter determination and data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs.[18] Multiscan absorption correction was applied.[19] The structure was solved by direct methods using the SIR92 program[20] and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package.[21] The encapsulated BF_4^- anion in cage **1** is disordered on two positions. The atom sites outside the Cu1···F1···F1···Cu1 axis, that is, B1, F2, and F3, are on 50% site occupation. The encapsulated BF_4^- anion in cage **2** is disordered on two positions. The atom sites outside the Cu1···F1···F1···Cu1 axis, that is, B1, F2, and F3, are on 50% site occupation. In contrast, the outer BF_4^- anions coordinated to the copper atoms are disordered around the B2–F4···Cu1····Cu1···F4–B2 axis, leading to two orientations, and the populations of the orientations A and B are 0.5 (F5, F6, and F7). The free BF_4^- anions in the lattice is located on a center of symmetry (B3 atom), and the four F atoms are disordered accordingly with a 0.5 site occupation factor.

Crystal data for $[BF_4 \subset (CH_3CN)_2Cu_2(L^1)_4][BF_4]_3 \cdot CH_3CN$ ($1 \cdot CH_3CN$): Violet crystals, $C_{112}H_{116}B_4Cu_2F_{16}N_{20}O_8$, monoclinic, $P2_1/n$, a = 14.347(3) Å, b = 22.752(4) Å, c = 18.866(3) Å, α = 90°, β = 104.999(11)°, γ = 90°, V = 5948.4(17) Å^3, Z = 2, T = 200(2) K, μ = 0.445 mm^{-1}, 78012 reflections measured, 13535 independent (R_{int} = 0.0768), 7485 observed [$I \geq 2\sigma(I)$], 734 parameters, final R indices R_1 [$I \geq 2\sigma(I)$] = 0.0687 and wR_2 (all data) = 0.2376, GOF(on F^2) = 1.057, max/min residual electron density r = 1.267/–0.607 e Å^{-3}.

Crystal data for $[BF_4 \subset (BF_4)_2Cu_2(L^1)_4][BF_4] \cdot 5CH_3NO_2$ ($2 \cdot 5CH_3NO_2$): Deep-purple crystals: $C_{111}H_{125}B_4Cu_2F_{16}N_{23}O_{22}$, triclinic, $P\bar{1}$, a = 14.3540(13) Å, b = 14.521(3) Å, c = 17.055(2) Å, α = 90.136(12)°, β = 109.874(12)°, γ = 91.006(11)°, V = 3342.5(8) Å^3, Z = 1, T = 250(2) K, μ = 0.411 mm^{-1}, 68164 reflections measured, 19259 independent (R_{int} = 0.0685), 9673 observed [$I \geq 2\sigma(I)$], 840 parameters, final R indices R_1 [$I \geq 2\sigma(I)$] = 0.0859 and wR_2 (all data) = 0.3043, GOF(on F^2) = 1.033, max/min residual electron density r = 1.796/–0.492 e Å^{-3}.

CCDC-734169 (for **1**) and -734170 (for **2**) 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.

Acknowledgments

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