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# Isomeric Molecular Rectangles Resulting from Self-Assembly of Dicopper Complexes of Macrocyclic Ligands

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Dinuclear copper complexes containing hexaazacyclophane macrocyclic ligands react with the disodium salt of terephthalic acid resulting in the self-assembly of rectangular molecules with the general formula $[(Cu_2L)_2(p\text{-}(O_2CC_6H_4CO_2)_2)]X_4$, where X = $CF_3SO_3$ and $ClO_4$ (**$3X_4$**, L = Me2p and **$4X_4$**, L = Me2m). Tetranuclear complexes **$3(CF_3SO_3)_4$** (as polymorphs **3a** and **3b**) and **$4(ClO_4)_4$** have been characterized by single-crystal X-ray diffraction analysis providing definitive proof of their structure as well as their metrical parameters. **3a** contains, in its unit cell, two isomeric cationic units (**3a*syn*** and **3a*anti***) that differ in the relative position of the two O carboxylate atoms which bind to the Cu atoms of the different macrocyclic complexes, leading to boxes with different metrical parameters. ESI-MS analyses of solutions of the tetranuclear complexes **$3(CF_3SO_3)_4$** and **$4(CF_3SO_3)_4$** exhibit cluster ions which match the solid state formulation, thus demonstrating that the cages are retained in solution.

## Introduction

Self-assembly processes and their regulation by self-recognition mechanisms are important topics because of their implication in biology, chemistry, and materials science.[1−10] Hydrogen-bonding and metal−ligand interactions are among the most powerful directing forces for the self-assembly processes which allow the construction of large suprastructures. In particular, such interactions have allowed the development of discrete cyclic nanostructures containing metal centers, which hold potential use in molecular recognition, photophysics, and catalysis.[1,2,11−14] To date, $Cu^I$, $Pd^{II}$, and $Pt^{II}$ constitute the most common metal ions of choice for this purpose, though a handful of other transition metals have been occasionally described.[4,7,9,10,12,14] Reports on supramolecular structures resulting from the self-assembly of $Cu^{II}$ complexes appear to be rarer. This is presumably because of the odd $d^9$ ion configuration, which tends to favor asymmetric coordination geometries. These irregular shapes are more difficult to integrate into regular frameworks.[15−20] Yet, macrocyclic complexes based on crown ethers or

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**Table 1.** Crystallographic Data for **1(CF$_3$SO$_3$)$_4$**, **2(CF$_3$SO$_3$)$_4$**, **3a(CF$_3$SO$_3$)$_4$**, **3b(CF$_3$SO$_3$)$_4$**, and **4(ClO$_4$)$_4$**

| | **1(CF$_3$SO$_3$)$_4$** | **2(CF$_3$SO$_3$)$_4$**·2CH$_3$CN | **3a(CF$_3$SO$_3$)$_4$**·$x$CH$_3$CN |
|---|---|---|---|
| empirical formula | $C_{32.5}H_{46}Cu_2F_8N_6O_{10}S_4$ | $C_{46}H_{68}Cu_2F_{12}N_{12}O_{12}S_4$ | $C_{85.67}H_{117.5}Cu_4F_{12}N_{14.84}O_{20}S_4$ |
| fw | 1088.07 | 1464.44 | 2285.51 |
| cryst syst | orthorhombic | triclinic | triclinic |
| space group | *Cmcm* | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 14.2529(8) | 10.6473(10) | 11.059(3) |
| $b$, Å | 26.1686(18) | 12.4122(12) | 22.177(5) |
| $c$, Å | 27.4119(16) | 14.1083(14) | 26(152(6) |
| α, deg | 90 | 64.789(3) | 114.566(6) |
| $\beta$, deg | 90 | 75.012(4) | 90.690(6) |
| $\gamma$, deg | 90 | 65.012(4) | 99.175(6) |
| $V$, Å$^3$ | 10 224.0(11) | 1521.9(3) | 5737(2) |
| formula units/cell | 4 | 1 | 2 |
| temp, K | 153(2) | 153(2) | 100(2) |
| $\lambda$(Mo Kα), Å | 0.710 73 | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.414 | 1.598 | 1.323 |
| $\Theta_{max}$, deg | 31.57 | 31.55 | 33.48 |
| reflns measured | 66 074 | 20 829 | 61 339 |
| unique reflns | 8473 [$R_{int}$ = 0.1669] | 8622 [R$_{int}$ = 0.1075] | 37 393 [R$_{int}$ = 0.0627] |
| param | 510 | 403 | 1540 |
| $\mu$, mm$^{-1}$ | 1.076 | 0.940 | 0.888 |
| $R_1$,[a] $wR_2$[b] [$I > 2\sigma(I)$] | 0.1044, 0.2751 | 0.0624, 0.1256 | 0.1203, 0.3301 |
| $R_1$,[a] $wR_2$[b] (all data) | 0.2296, 0.3264 | 0.1720, 0.1565 | 0.1908, 0.3788 |
| GOF (F$^2$) | 0.920 | 0.830 | 1.020 |

| | **3b(CF$_3$SO$_3$)$_4$**·$x$CH$_3$CN | **4(ClO$_4$)$_4$**·$x$CH$_3$CN·$x$H$_2$O |
|---|---|---|
| empirical formula | $C_{90.67}H_{123}Cu_4F_{12}N_{17.33}O_{22}S_4$ | $C_{81}H_{115.5}Cu_4N_{14.5}Cl_4O_{25}$ |
| fw | 2418.13 | 2088.34 |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | *C*2/c |
| $a$, Å | 13.1376(15) | 41.432(5) |
| $b$, Å | 16.701(2) | 12.453(2) |
| $c$, Å | 26.734(3) | 26.216(3) |
| α, deg | 105.424(3) | 90 |
| $\beta$, deg | 100.280(3) | 127.805(5) |
| $\gamma$, deg | 93.037(3) | 90 |
| $V$, Å$^3$ | 5532.6(11) | 10687(3) |
| formula units/cell | 2 | 4 |
| temp, K | 100(2) | 100(2) |
| $\lambda$(Mo Kα), Å | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.452 | 1.298 |
| $\Theta_{max}$, deg | 32.63 | 33.22 |
| reflns measured | 79 963 | 78 964 |
| unique reflns | 37 559 [$R_{int}$ = 0.0369] | 19 778 [$R_{int}$ = 0.0608] |
| param | 1480 | 616 |
| $\mu$, mm$^{-1}$ | 0.927 | 0.956 |
| $R_1$,[a] $wR_2$[b] [$I > 2\sigma(I)$] | 0.0905, 0.2653 | 0.0687, 0.1795 |
| $R_1$,[a] $wR_2$[b] (all data) | 0.1363, 0.3046 | 0.0864, 0.1916 |
| GOF ($F^2$) | 1.037 | 1040 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2\ ]]\}^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP]i$. $P = (F_o^2 + 2F_c^2)/3$.

polyamines were among the first ligand backbones reported to create controlled cavities in which the selective recognition of cationic, anionic, or neutral molecules could take place.[21−23] Despite this fact, their use as building blocks in the assembly of larger supramolecular structures has, so far, only been explored in rather limited examples.[24−26] In this work, we report the self-assembly of molecular rectangles resulting from the dimerization of dicopper hexaazamacrocyclic building blocks.

## Experimental Section

**Materials.** Solvents were purchased from SDS and were of reagent grade. Acetonitrile was distilled over CaH$_2$ and stored over molecular sieves prior to use. Diethyl ether was distilled over

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**Table 2.** Selected Bond Lengths (Å) and Angles (degrees) for **1**$(CF_3SO_3)_4$, **2**$(CF_3SO_3)_4$, **3a***syn*$(CF_3SO_3)_4$, **3a***anti*$(CF_3SO_3)_4$, **3b**$(CF_3SO_3)_4$, and **4**$(ClO_4)_4$

| **1**$(CF_3SO_3)_4$ | **2**$(CF_3SO_3)_4$ | **3a***syn*$(CF_3SO_3)_4$ |
|---|---|---|
| Cu1−O1 1.912(5) | Cu1−N4 2.010(4) | Cu1B−O3B 1.928(4) |
| Cu1−N1 1.980(6) | Cu1−N2 2.029(4) | Cu1B−N2B 2.009(5) |
| Cu1−N2 2.067(6) | Cu1−N1 2.084(4) | Cu1B−N1B 2.098(6) |
| Cu2−O2 1.931(7) | Cu1−N3 2.096(3) | Cu1B−N3B 2.115(8) |
| Cu2−N4 1.975(7) | Cu1−N5 2.198(4) | Cu2B−O1B 1.923(4) |
| Cu2−N3 2.037(6) | N4−Cu1−N2 176.52(15) | Cu2B−N5B 2.000(5) |
| O1−Cu1−N1 178.1(3) | N4−Cu1−N1 91.72(14) | Cu2B−N6B 2.075(6) |
| O1−Cu1−N2 93.95(13) | N2−Cu1−N1 85.95(15) | Cu2B−N4B 2.076(6) |
| N1−Cu1−N2 85.82(13) | N4−Cu1−N3 95.04(15) | O3B−Cu1B−N2B 167.4(2) |
| N2−Cu1−N2 164.0(3) | N2−Cu1−N3 85.98(15) | O3B−Cu1B−N1B 94.1(2) |
| O2−Cu2−N4 180.0(4) | N1−Cu1−N3 153.96(13) | N2B−Cu1B−N1B 85.4(3) |
| O2−Cu2−N3 93.65(16) | N4−Cu1−N5 87.46(15) | O3B−Cu1B−N3B 98.6(2) |
| N4−Cu2−N3 86.36(16) | N2−Cu1−N5 95.61(14) | N2B−Cu1B−N3B 84.8(3) |
| N3−Cu2−N3 163.9(3) | N1−Cu1−N5 104.16(14) | N1B−Cu1B−N3B 162.3(2) |
| | N3−Cu1−N5 101.24(14) | O1B−Cu2B−N5B 166.2(2) |
| | | O1B−Cu2B−N6B 95.23(19) |
| | | N5B−Cu2B−N6B 86.1(2) |
| | | O1B−Cu2B−N4B 97.0(2) |
| | | N5B−Cu2B−N4B 85.1(2) |
| | | N6B−Cu2B−N4B 162.1(2) |

| **3a***anti*$(CF_3SO_3)_4$ | **3b**$(CF_3SO_3)_4$ | **4**$(ClO_4)_4$ |
|---|---|---|
| Cu1−O3 1.904(4) | Cu1−O8 1.916(3) | Cu1−O1 1.9643(19) |
| Cu1−N5 2.017(5) | Cu1−N2 1.995(3) | Cu1−N2 1.984(2) |
| Cu1−N4 2.060(5) | Cu1−N1 2.059(4) | Cu1−N1 2.074(3) |
| Cu1−N6 2.061(5) | Cu1−N3 2.072(4) | Cu1−N3 2.092(3) |
| Cu2−O1 1.911(4) | Cu2−O1 1.924(2) | Cu1−O2 2.351(2) |
| Cu2−N2 2.003(5) | Cu2−N5 1.986(3) | Cu2−O3 1.961(2) |
| Cu2−N1 2.092(5) | Cu2−N4 2.079(3) | Cu2−N5 1.973(3) |
| Cu2−N3 2.102(5) | Cu2−N6 2.088(3) | Cu2−N4 2.062(3) |
| O3−Cu1−N5 166.6(2) | Cu3−O4 1.923(2) | Cu2−N6 2.098(3) |
| O3−Cu1−N4 96.11(19) | Cu3−N8 2.001(3) | Cu2−O4 2.397(2) |
| N5−Cu1−N4 85.3(2) | Cu3−N7 2.058(3) | O1−Cu1−N2 170.86(9) |
| O3−Cu1−N6 96.07(19) | Cu3−N9 2.073(3) | O1−Cu1−N1 96.35(9) |
| N5−Cu1−N6 86.3(2) | Cu4−O5 1.924(3) | N2−Cu1−N1 86.85(10) |
| N4−Cu1−N6 160.7(2) | Cu4−N11 1.993(4) | O1−Cu1−N3 93.17(9) |
| O1−Cu2−N2 170.0(2) | Cu4−N12 2.085(6) | N2−Cu1−N3 86.44(10) |
| O1−Cu2−N1 96.1(2) | Cu4−N10 2.093(6) | N1−Cu1−N3 160.22(10) |
| N2−Cu2−N1 85.3(2) | O8−Cu1−N2 165.62(11) | O1−Cu1−O2 61.03(8) |
| O1−Cu2−N3 90.6(2) | O8−Cu1−N1 96.94(14) | N2−Cu1−O2 109.87(9) |
| N2−Cu2−N3 85.6(2) | N2−Cu1−N1 85.26(13) | N1−Cu1−O2 105.83(9) |
| N1−Cu2−N3 163.9(2) | O8−Cu1−N3 97.05(14) | N3−Cu1−O2 93.95(9) |
| | N2−Cu1−N3 84.46(13) | O3−Cu2−N5 177.70(10) |
| | N1−Cu1−N3 160.76(13) | O3−Cu2−N4 91.98(11) |
| | O1−Cu2−N5 165.97(11) | N5−Cu2−N4 87.29(12) |
| | O1−Cu2−N4 98.94(13) | O3−Cu2−N6 94.73(10) |
| | N5−Cu2−N4 84.67(12) | N5−Cu2−N6 85.54(11) |
| | O1−Cu2−N6 95.20(13) | N4−Cu2−N6 166.32(10) |
| | N5−Cu2−N6 84.56(13) | O3−Cu2−O4 60.01(8) |
| | N4−Cu2−N6 161.25(11) | N5−Cu2−O4 122.28(9) |
| | O4−Cu3−N8 165.07(11) | N4−Cu2−O4 101.14(10) |
| | O4−Cu3−N7 98.30(12) | N6−Cu2−O4 92.53(9) |
| | N8−Cu3−N7 85.72(14) | |
| | O4−Cu3−N9 95.30(12) | |
| | N8−Cu3−N9 84.75(14) | |
| | N7−Cu3−N9 160.33(13) | |
| | O5−Cu4−N11 165.59(14) | |
| | O5−Cu4−N12 99.11(18) | |
| | N11−Cu4−N12 84.6(2) | |
| | O5−Cu4−N10 94.79(17) | |
| | N11−Cu4−N10 84.9(2) | |

sodium/benzophenone under nitrogen prior to use. Unless noted otherwise, all reagents were purchased from commercial sources and used as received.

3,6,9,16,19,22-hexamethyl-3,6,9,16,19,22-hexaazatricyclo-[22.2.2.211,14]triaconta-(26),11(12),13,24,27,29-hexaene, Me2p, and 3,6,9,17,20,23-hexamethyl-3,6,9,17,20,23-hexaazatricyclo[23.3.1.111,15]triaconta-1(29),11(30),12,14,25,27-hexaene, Me2m,[27−30] were prepared according to or through slight modifications of the published procedures.

**Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. While we have not encountered any problems, it is advisable to use only small amounts and to handle the compounds with care.

**Physical Measurements.** FT-IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer containing a MKII Golden Gate Single Reflection ATR System. Elemental analyses were conducted in a Carlo Erba Instrument, model CHNS 1108. UV−vis spectroscopy was performed on a Cary 50 Scan (Varian)

UV−vis spectrophotometer with 1 cm quartz cells. Low-resolution electrospray mass spectra were recorded on a Bruker Biotof II spectrometer.

**Syntheses. Terephthalic Acid Disodium Salt.** Terephthalic acid (4.56 g, 27 mmol) was added to an aqueous solution of NaOH (1.98 g in 10 mL of water, 49 mmol). The solution was filtered (to remove the excess diacid), and the disodium salt was precipitated by adding diethyl ether (50 mL) and methanol (75 mL). The product was filtered and washed with diethyl ether (4.2 g, 82%). FT-IR $\nu$: 1561, 1383 cm$^{-1}$ (COO$^{-}$). Elem Anal. Calcd (%) for $C_8H_4O_4Na_2$ (210.09): C, 45.73; H, 1.92. Found: C, 45.36; H, 1.78.

**[$Cu_2$(Me2p)($OH_2$)$_2$]($CF_3SO_3$)$_4$·$CH_3CN$·$H_2O$·$^1/_2Et_2O$, 1($CF_3SO_3$)$_4$·$CH_3CN$·$H_2O$·$^1/_2Et_2O$.** Me2p (49.9 mg, 0.10 mmol) and Cu($CF_3SO_3$)$_2$ (71.9 mg, 0.19 mmol) were charged in a 10 mL flask and dissolved in 20:1 $CH_3CN/H_2O$ (2.5 mL) to form a reddish-blue solution. The mixture was stirred for 30 min and then filtered through Celite. Ether diffusion after 2 days affords red rectangular plates. The solvent was decanted and the crystalline solids dried under vacuum (90.4 mg, 0.07 mmol, 70%). FT-IR $\nu$: 3445 (OH), 1472 (C═C arom.), 1244, 1161, 1027, 635 cm$^{-1}$ ($CF_3SO_3$). Elem Anal. Calcd (%) for $C_{34}H_{54}N_6Cu_2O_{14}F_{12}S_4$·$CH_3CN$·$H_2O$·$^1/_2Et_2O$ (1350.29): C, 33.80; N, 7.26; H, 4.78; S, 9.50. Found: C, 33.76; N, 7.12; H, 4.82; S, 9.44. UV−vis ($CH_3CN$) $\lambda_{max}$ ($\epsilon$): 521 (466 M$^{-1}$cm$^{-1}$).

**[$Cu_2$(Me2m)($CH_3CN$)$_4$]($CF_3SO_3$)$_4$·2$CH_3CN$·2$H_2O$, 2($CF_3SO_3$)$_4$·2$CH_3CN$·2$H_2O$.** Me2m (33.2 mg, 0.067 mmol) and Cu($CF_3SO_3$)$_2$ (48.6 mg, 0.13 mmol) were charged in a 10 mL flask and dissolved in 20:1 $CH_3CN/H_2O$ (1.5 mL) to form a bright blue solution. The mixture was stirred for 30 min and then filtered through Celite. Ether diffusion into this solution affords blue needles. The solvent was decanted and the crystalline solids dried under vacuum (77.5 mg, 0.058 mmol, 89%). FT-IR $\nu$: 1473 (C═C arom.), 1278, 1242, 1153, 1027, 633 cm$^{-1}$ ($CF_3SO_3$). Elem Anal. Calcd (%) for $C_{34}H_{50}N_6Cu_2O_{12}F_{12}S_4$·2$CH_3CN$·2$H_2O$ (1336.27): C, 34.16; N, 8.39; H, 4.53; S, 9.60. Found: C, 33.88; N, 8.37; H, 4.17; S, 9.33. UV−vis ($CH_3CN$) $\lambda_{max}$ ($\epsilon$): 623 (588 M$^{-1}$cm$^{-1}$).

**[$Cu_4$($O_2CC_6H_5CO_2$)$_2$(Me2p)$_2$]($CF_3SO_3$)$_4$·4$H_2O$, 3($CF_3SO_3$)$_4$·4$H_2O$.** Me2p (51.1 mg, 0.10 mmol) and Cu($CF_3SO_3$)$_2$ (76.2 mg, 0.21 mmol) were charged in a 10 mL flask and dissolved in 20:1 $CH_3CN/H_2O$ (2.5 mL) to form a reddish-blue solution. The mixture was stirred for 30 min to allow the total formation of **1($CF_3SO_3$)$_4$**. Then, 21.7 mg of terephthalic acid disodium salt (0.10 mmol) was added directly as a solid to the stirred solution. The resulting dark blue solution was stirred for 20 h and then filtered through Celite. Ether diffusion after 3 days affords large blue rectangles. The solvent was decanted and the crystalline solids dried under vacuum (88.9 mg, 0.040 mmol, 80%). FT-IR $\nu$: 3511 (OH), 1615, 1340 (C═O), 1251, 1225, 1156, 1028, 635 cm$^{-1}$ ($CF_3SO_3$). Elem Anal. Calcd (%) for $C_{80}H_{108}N_{12}Cu_4O_{20}F_{12}S_4$·4$H_2O$ (2240.27): C, 42.89; N, 7.50; H, 5.22; S, 5.73. Found: C, 42.67; N, 7.66; H, 4.99; S, 5.53. UV−vis ($CH_3CN$) $\lambda_{max}$ ($\epsilon$): 236 (31 750), 281 (28 490), 506 (448), 630 (664 M$^{-1}$cm$^{-1}$). MS (ESI) *m*/*z*: 934 (100) [**3($CF_3SO_3$)$_4$**−2$CF_3SO_3$]$^{+2}$, 573 (75) [**3($CF_3SO_3$)$_4$**−3$CF_3SO_3$]$^{+3}$.

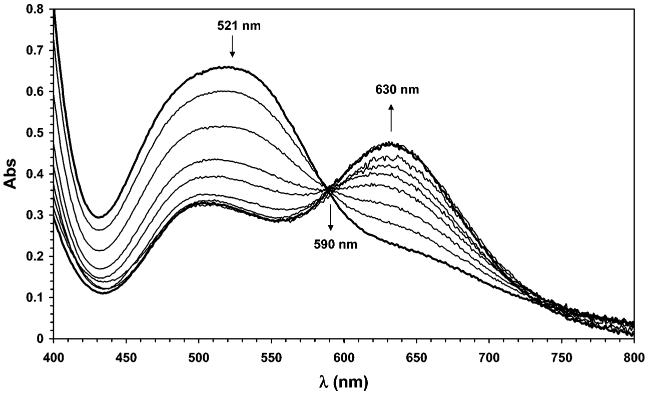
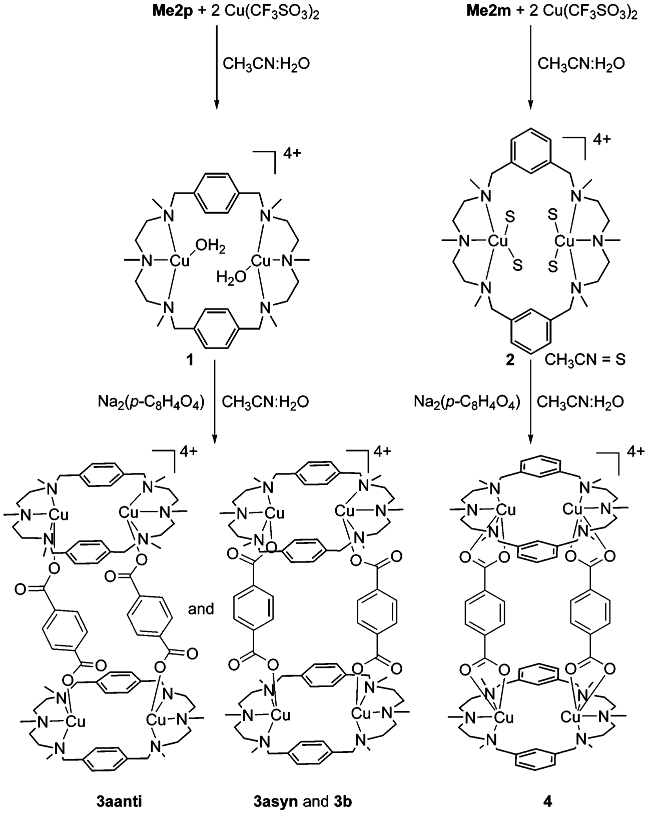


**Figure 1.** UV−vis titration of **1($CF_3SO_3$)$_4$** with terephthalic acid disodium salt (0−1 equiv) in $CH_3CN$ to form **3($CF_3SO_3$)$_4$**.

**Scheme 1.** Schematic Diagram of the Complexes Prepared in This Work



**[$Cu_4$($O_2CC_6H_4CO_2$)$_2$(Me2m)$_2$]($CF_3SO_3$)$_4$·4$H_2O$, 4($CF_3SO_3$)$_4$·4$H_2O$.** Me2m (54.9 mg, 0.11 mmol) and Cu($CF_3SO_3$)$_2$ (81.9 mg, 0.22 mmol) were charged in a 10 mL flask and dissolved in 20:1 $CH_3CN/H_2O$ (2.5 mL) to form a bright blue solution. The mixture was stirred for 30 min to allow the total formation of **2($CF_3SO_3$)$_4$**. Then, 23.3 mg of terephthalic acid disodium salt (0.11 mmol) was added directly as a solid to the stirred solution. The resulting blue solution was stirred for 20 h and then filtered through Celite. Ether diffusion after 2 days affords blue needles. The solvent was decanted and the crystalline solids dried under vacuum (101.6 mg, 0.045 mmol, 82%). FT-IR $\nu$: 3610 (OH), 1574, 1368 (C═O), 1340 (C═C arom.), 1247, 1225, 1158, 1028, 636 cm$^{-1}$ ($CF_3SO_3$). Elem Anal. Calcd (%) for $C_{80}H_{108}N_{12}Cu_4O_{20}F_{12}S_4$·4$H_2O$ (2240.27): C, 42.89; N, 7.50; H, 5.22; S, 5.73. Found: C, 43.14; N, 7.76; H, 5.23; S, 5.35. UV−vis ($CH_3CN$) $\lambda_{max}$ ($\epsilon$): 240 (33 480), 292 (24 890), 636 (829 M$^{-1}$cm$^{-1}$). MS (ESI) *m*/*z*: 934 (100) [**4($CF_3SO_3$)$_4$**−2$CF_3SO_3$]$^{+2}$, 573 (65) [**4($CF_3SO_3$)$_4$**−3$CF_3SO_3$]$^{+3}$. Single crystals of **4($ClO_4$)$_4$** suitable for X-ray diffraction analysis were obtained by slow diethyl ether diffusion into acetonitrile solutions of **4($CF_3SO_3$)$_4$** containing $NaClO_4$.

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**Crystal Data Collection, Structure Solution, and Refinement Details for Compounds 1(CF$_3$SO$_3$)$_4$, 2(CF$_3$SO$_3$)$_4$, 3a(CF$_3$SO$_3$)$_4$, 3b(CF$_3$SO$_3$)$_4$, and 4(ClO$_4$)$_4$.** Crystal structure determinations for **1(CF$_3$SO$_3$)$_4$** and **2(CF$_3$SO$_3$)$_4$** were carried out using a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co rotating anode with Mo K$\alpha$ radiation, a graphite monochromator, and a Siemens low-temperature device LT2 ($T = -120$ °C). Full sphere data collection $\omega$ and $\varphi$ scans were performed. The programs used were, for data collection, Smart version 5.060 (BrukerAXS, 1999), for data reduction, Saint+ version 6.02 (Bruker AXS, 1999), and for absorption correction, SADABS (Bruker AXS, 1999). Crystal structure solution was achieved using direct methods as implemented in SHELXTL version 5.10 (Sheldrick, Universität Göttingen, Germany, 1998) and was visualized using the XP program. Crystal structure determinations for **3a(CF$_3$SO$_3$)$_4$**, **3b(CF$_3$SO$_3$)$_4$**, and **4(ClO$_4$)$_4$** were carried out using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with Mo K$\alpha$ radiation, Montel mirrors as a monochromator, and a Kryoflex low-temperature device ($T = -173$ °C). Full sphere data collection $\omega$ and $\varphi$ scans were performed. The programs used were, for data collection, Apex2 version 1.0-22 (Bruker-Nonius, 2004), for data reduction, Saint+ version 6.22 (Bruker-Nonius, 2001), and for absorption correction, SADABS version 2.10 (Bruker AXS, 2003). Crystal structure solution was achieved using direct methods as implemented in SHELXTL version 6.10 (Sheldrick, Universität Göttingen, Germany, 2000) and was visualized using the XP program. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. A least-squares refinement on F2 using all measured intensities was carried out using the program SHELXTL version 6.10 (Sheldrick, Universität Göttingen, Germany, 2000). All non-hydrogen atoms were refined including anisotropic displacement parameters.

The crystals used for structure determination contain, in most of the cases, solvent molecules, which make its manipulation extremely difficult, and also have disordered anions. Because of these difficulties, some of the data sets are complicated to collect and not of the best quality for refinement.

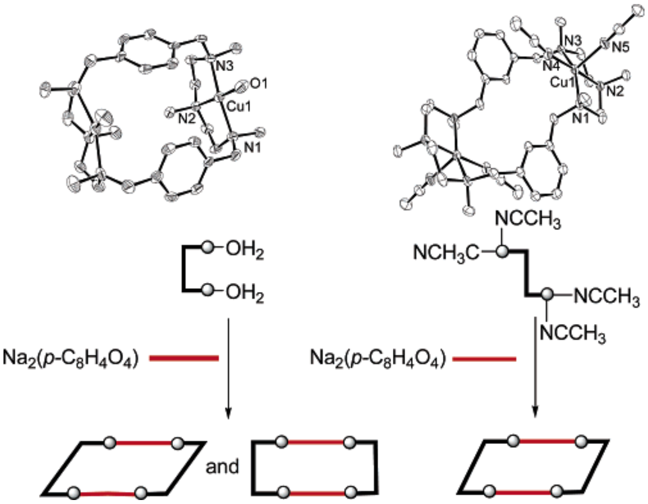
Table 1 summarizes the crystallographic refinement parameters for complexes **1(CF$_3$SO$_3$)$_4$**, **2(CF$_3$SO$_3$)$_4$**, **3a(CF$_3$SO$_3$)$_4$**, **3b(CF$_3$SO$_3$)$_4$**, and **4(ClO$_4$)$_4$**. A list of selected bond lengths (Å) and angles (degrees) for complexes reported in this work is collected in Table 2.

## Results and Discussion

**Preparation of the Complexes.** Reactions of the corresponding para and meta phenyl-substituted hexaazacyclophanes (Me2p and Me2m, Scheme 1) with 2 equiv of Cu(CF$_3$SO$_3$)$_2$ in 20:1 CH$_3$CN/H$_2$O yield the solvato dinuclear Cu$^{II}$ complexes [Cu$_2$(Me2p)(OH$_2$)$_2$]$^{4+}$, **1**, and [Cu$_2$(Me2m)(CH$_3$CN)$_4$]$^{4+}$, **2**. Triflate salts of the complexes could be isolated as crystalline materials by slow diethyl ether diffusion into acetonitrile solutions in 70% and 89% yields, respectively.

**1(CF$_3$SO$_3$)$_4$** and **2(CF$_3$SO$_3$)$_4$**, prepared in situ, were reacted with a para-substituted diacid aromatic linker. Fast reaction was evidenced by UV−vis spectroscopy, which revealed a quantitative disappearance of the starting dinuclear complexes after the addition of 1 equiv of the terephthalic acid disodium salt. Tetrametallic [Cu$_4$(O$_2$CC$_6$H$_5$CO$_2$)$_2$(Me2p)$_2$](CF$_3$SO$_3$)$_4$, **3(CF$_3$SO$_3$)$_4$**, and [Cu$_4$(O$_2$CC$_6$H$_5$CO$_2$)$_2$(Me2m)$_2$](CF$_3$SO$_3$)$_4$, **4(CF$_3$SO$_3$)$_4$**, were isolated in crystalline form from these reactions in 80% and 82% yields, respectively. Interestingly, UV−vis titration of **1(CF$_3$SO$_3$)$_4$** with terephthalic acid disodium salt reveals that the transformation from **1** to **3** occurs with an isosbestic point at $\lambda = 590$ nm, without the accumulation of any reaction intermediate (Figure 1). This observation strongly suggests that, after binding of the first dicarboxylate bridge, the formation of rectangle **3** by coordination of the second terephthalate unit is a cooperatively accelerated process. The analogous titration of **2** to form rectangle **4** suggests a similar behavior (Figure S1, Supporting Information).

**Scheme 2.** ORTEP Diagram of the Cationic Portions of **1(CF$_3$SO$_3$)$_4$** (Left) and **2(CF$_3$SO$_3$)$_4$** (Right) along with the Schematic Representation of the Self-Assembled Rectangles **3** and **4**



**Crystallographic Characterization of the Complexes. 1(CF$_3$SO$_3$)$_4$ and 2(CF$_3$SO$_3$)$_4$.** The molecular structures of the dinuclear complexes were established by single-crystal X-ray analysis (Scheme 2). Unfortunately, **1(CF$_3$SO$_3$)$_4$** suffers from serious solvent disorder, which prevents a discussion of the metrical parameters of the complex. Nevertheless, reliable information about the overall topology, chemical composition, and coordination geometry of metal ions could be extracted from this analysis. Crystallographic characterization of **1(CF$_3$SO$_3$)$_4$** and **2(CF$_3$SO$_3$)$_4$** reveals that, in both complexes, each of the copper ions are bound to three nitrogen atoms of the macrocyclic ligand, but the coordination geometry, the nature and number of external ligands, and the intramolecular Cu···Cu distance are different. Thus, the copper ions in **1(CF$_3$SO$_3$)$_4$** are square planar with a water molecule completing their coordination environment, and the copper centers are separated by 6.9 Å. Instead, **2(CF$_3$SO$_3$)$_4$** is a rare example of a square pyramidal Cu$^{II}$ complex ($\tau = 0.38$)[31] containing two acetonitrile ligands in cis orientations per metallic ion.[32] Remarkably, the acetonitrile occupying the axial position lies along a tetragonally elongated axis and the corresponding Cu−N distance is significantly longer than the one associated with the equatorially bound nitrile ($\Delta r_{\text{Cu−N}} \sim 0.2$ Å). The Cu···Cu distance

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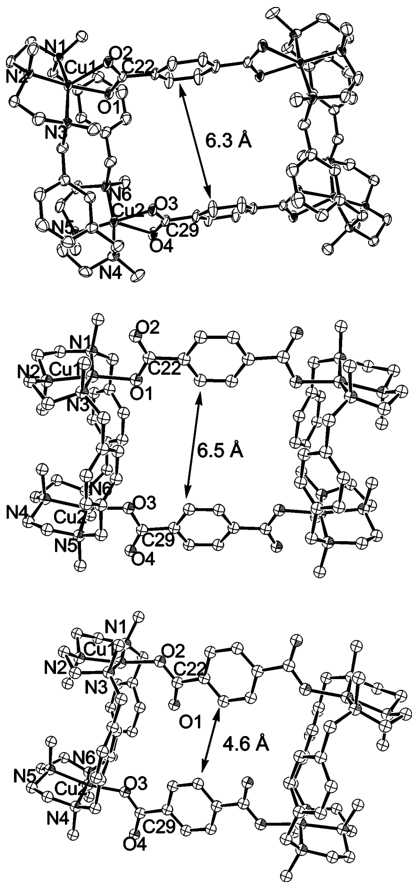


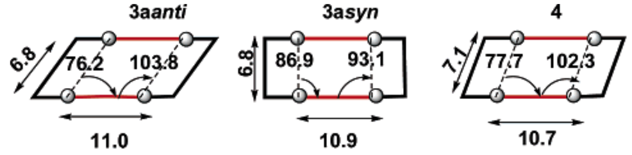
**Figure 2.** ORTEP diagram (50%) of the cationic portions of **3a*anti*** (bottom), **3*asyn*** (middle), and **4** (top).

is substantially elongated to 7.5 Å relative to **1**. Most remarkable is the distinct shape of the respective macrocyclic cavity; a box-like shape could be easily identified in **1**, which we envisioned as a potential building block for supramolecular assemblies via coordination through the Cu ions, provided self-recognition phenomena apply. However, the elongated cavity exhibited by **2** and the opposing orientations of the respective Cu coordination polyhedra render self-assembly predictions difficult.

**$3(CF_3SO_3)_4$ and $4(ClO_4)_4$.** Single crystals of **$3(CF_3SO_3)_4$** and **$4(ClO_4)_4$** were obtained by slow diethyl ether diffusion into acetonitrile solutions of the complexes (the latter containing $NaClO_4$), and their structures were established by X-ray crystallography (Figure 2). For compound **3**, two different polymorphs were measured, **3a** and **3b**.

Both cationic **3** and **4** adopt rectangular topologies resulting from a 2 + 2 self-assembly process. Interestingly, compound **3a** crystallizes as an equimolar mixture of two isomers (**3a*syn*** and **3a*anti***). The isomers differ in the relative position of the carboxylate oxygen atoms bound to the metal ion (Figure 2), but the square planar coordination environment of the copper ions is almost superimposable in **1** and in the two isomeric forms of **3a**. The relative orientation of the bridging aromatic rings differs in **3a** and **4**. In **3a*syn*** and **3a*anti***, the rings are side to side, but they appear face to face in **4** (Figure 2). In addition, the carboxylate binds in a monodentate O $\eta^1$ mode in both **3a*syn*** and **3a*anti***, whereas in **4**, it is bound in a O,O′:$\eta^1$,$\eta^1$ terminal mode. Despite the similarities in the copper coordination spheres of the isomeric forms observed for **3**, **3a*syn*** and **3a*anti*** contain cavities with remarkably different geometric parameters. The structure of **3b** is identical to the conformer **3a*syn***.

**Scheme 3.** Schematic Representation of the Self-Assembled Rectangles **3a*anti*** (Left), **3a*syn*** (Middle), and **4** (Right) with the Corresponding Metrical Parameters (Distances in Å, Angles in Degrees)[a]



[a] Bond distances and angles are obtained by considering Cu ions as the vertex of the quadrilaterals.

Interestingly, the binding mode and relative orientation of the terephthalate group in **3a*syn***, and its topology, are reminiscent of a Pt-based rectangle recently reported by Stang et al.[33] although, in that case, there is no evidence for additional isomeric rectangles analogous to **3a*anti***. The overall dimensions and shape of the macrocyclic entities could be extracted by considering the four coplanar metal ions as the hypothetical corners of a quadrilateral (Scheme 3). Thus, the dimensions of the rectangle in the syn isomer **3a*syn*** are 6.8 × 10.9 Å$^2$ and the respective angles deviate slightly from 90° (86.9° and 93.1°). **3a*anti*** exhibits a nearly identical Cu···Cu axis (6.8 × 11.0 Å) but exhibits distorted angles of 76.2° and 103.8°. The metal-defined quadrilateral in **4** is even less regular in shape, and the respective metrical parameters are characterized by slightly longer intramolecular (7.1 Å) and shorter intermolecular (10.7 Å) Cu···Cu distances, as well as similarly distorted angles (77.7° and 102.3°). In this case, the Cu ions are five-coordinate and exhibit square pyramidal geometries ($\tau \sim 0.18$).

A closer examination of the structures reveals that the unoccupied internal cavity is accessible to external molecules and could be better defined by the shortest Cu···Cu distance and by the shortest interaromatic $C_{ar}-C_{ar}$ distance (Figure 2). The latter is 6.3 Å in **4** and 6.5 Å in **3a*syn*** and decreases down to 4.6 Å in **3a*anti***. This clearly indicates that the empty space in the cavities of **3a*syn*** and **3a*anti*** is substantially different, such that they could be thought of as the *opened* and *closed* isomeric forms. Interestingly, inspection of the crystalline lattice in **3a** (Figure 3) reveals that **3a*syn*** packs forming channels along the *a* crystallographic axis, in contrast with **3a*anti***, which does not form such macroscopic structures. The cationic unit in **4** also forms channels along the *b* axis; although in this case, they are occupied by acetonitrile molecules.

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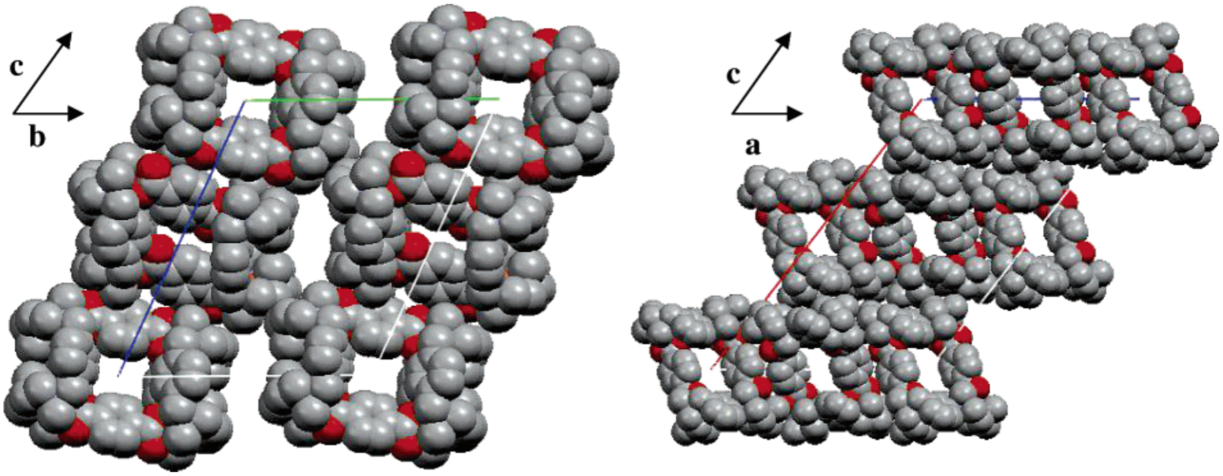

**Figure 3.** Space-filling diagram of **3a(CF$_3$SO$_3$)$_4$** (left) along the *a* axis and **4(ClO$_4$)$_4$** (right) along the *b* axis showing the channels. H atoms and acetonitrile molecules have been omitted for clarity.

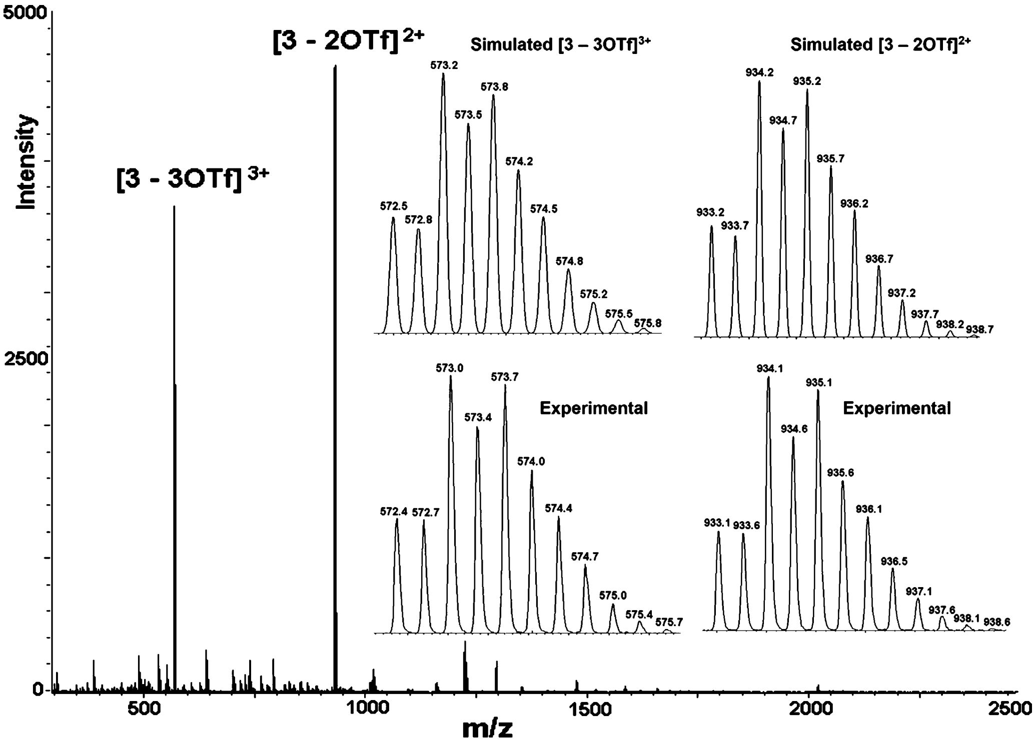

**Figure 4.** ESI-MS spectrum of **3(CF$_3$SO$_3$)$_4$** in a 1:1 CH$_3$CN/H$_2$O solution. Simulated (top) and experimental (bottom) isotopic distributions for the cationic species [**3(CF$_3$SO$_3$)$_4$**−3CF$_3$SO$_3$]$^{3+}$ and [**3(CF$_3$SO$_3$)$_4$**−2CF$_3$SO$_3$]$^{2+}$ are shown (OTf stands for CF$_3$SO$_3$).

**Spectroscopic Characterization of the Complexes.** Molecular rectangles **3(CF$_3$SO$_3$)$_4$** and **4(CF$_3$SO$_3$)$_4$** were spectroscopically characterized by FT-IR and UV−vis spectroscopy. The most distinctive features of their respective IR spectra are two strong bands at 1615 and 1340 cm$^{-1}$ for **3** and at 1574 and 1368 cm$^{-1}$ for **4**. The high-energy band is assigned to the $\nu_{asym}$ COO stretching mode, while the lower-energy component corresponds to the corresponding $\nu_{sym}$ mode. The larger $\Delta(\nu_{asym} - \nu_{sym})$ difference exhibited by **3** in comparison with **4** clearly reflects the different binding mode of the carboxylate ligand,[34] as unambiguously ascertained by X-ray crystallography. On the other hand, the UV−vis spectra of the four copper complexes reported in this work (Figure S2, Supporting Information) are characterized by relatively weak features between 500 and 700 nm characteristic of ligand field transitions of d$^9$ ions.[35] The energy of these features is relatively high compared with the spectroscopic behavior observed in mononuclear trigonal bipyramidal copper complexes containing tripodal amine ligands, which strongly suggests that the solid-state coordination geometries of the complexes described in this work are retained in solution.[36,37]

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**Integrity of the Rectangles in Solution.** ESI-MS measurements of **$3(CF_3SO_3)_4$** and **$4(CF_3SO_3)_4$** in $CH_3CN/H_2O$ solutions give similar results (Figure 4 and Figure 4S, Supporting Information). In both cases, the more intense peaks appear at *m*/*z* = 934.1 and 573.0 with isotopic patterns that match the cationic species $\{[Cu_4(O_2CC_6H_5CO_2)_2L_2](CF_3SO_3)_2\}^{2+}$ ([**X**-$2CF_3SO_3]^{2+}$) and $\{[Cu_4(O_2CC_6H_5CO_2)_2L_2](CF_3SO_3)\}^{3+}$ ([**X**-$3CF_3SO_3]^{3+}$) [X = **$3(CF_3SO_3)_4$**, L = Me2p or X = **$4(CF_3SO_3)_4$**, L = Me2m] respective formulations. The single bimetallic macrocyclic complex is not observed in the ESI-MS measurements, thus strongly suggesting that the macrocyclic tetrametallic boxes are retained in solution. In addition, cluster ions that could be identified as larger nuclearity assemblies were not observed.

## Conclusions

The self-assembly of macrocyclic dinuclear complexes via the coordination of terephthalate bridges has led to the preparation of a new family of molecular rectangles with unprecedented isomeric diversity. These structures bear a resemblance to the cavitands prepared by the self-assembly of calixarene building blocks.[38−40] The wealth of information arising from studies over the past decades on the physicochemical properties and potential applications of crown ethers and related aza analogues such as the ones employed in this work warrant a myriad of potential uses for the type of complexes herein described.[21−23,26]

**Acknowledgment.** This research has been financed by MCYT of Spain through Project BQU2000-0458. A.L. is grateful to CIRIT Generalitat de Catalunya (Spain) for the Distinction Award and the aid SGR2001-UG-291. A.C. thanks MEC for a Ph.D. grant. R.M. thanks MEC of Spain for postdoctoral support.

**Supporting Information Available:** UV−vis spectra of the complexes reported in this work, UV−vis titration of **2** with terephthalic acid disodium salt to give **4**, and ESI-MS of **4**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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