reflections, 2495 unique reflections, 1700 used ($4° < 2\Theta < 49.36°$), $R_1 = 0.030$ (3344 reflections, $I > 10\sigma(I)$), $wR_2 = 7.4\%$ (all data), GOF = 0.97. Minimum and maximum peaks in the final difference map are −1.25 and 1.47 e Å^{-3}. CCDC-191383 (**1**), CCDC-191384 (**7**), CCDC-191385 (**22**), and CCDC-191386 (**24**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk)

[11] The nearest examples are [(η^6-$C_{10}H_8$)Ru(cod)], M. Crocker, M. Green, J. A. K. Howard, N. C. Norman, D. M. Thomas, *J. Chem. Soc. Dalton Trans.* **1990**, 2299; and [(η^4-$C_{10}H_8$)Rh(Cp)], G. Müller, P. E. Gaede, C. Hirsch, K. Qaio, *J. Organomet. Chem.* **1994**, *472*, 329–335.

[12] As determined by X-ray crystallography (**7**) and NMR, see Supporting Information.

[13] No other hapticity was noticed for the naphthalene ligand. For more structural and NMR information on related ruthenium–naphthalene complexes, see a) M. A. Bennett, H. Neumann, M. Thomas, X.-Q. Wang, P. Pertici, P. Salvadori, G. Vituilli, *Organometallics* **1991**, *10*, 3237–3245; b) M. A. Bennett, Z. Lu, X. Wang, M. Brown, D. C. R. Hockless, *J. Am. Chem. Soc.* **1998**, *120*, 10409–10415.

[14] For more information on the effect of arene methylation in {(η^6-arene)Rh^I} complexes, see: E. T. Singewald, C. S. Slone, C. L. Stern, C. A. Mirkin, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 3048–3056.

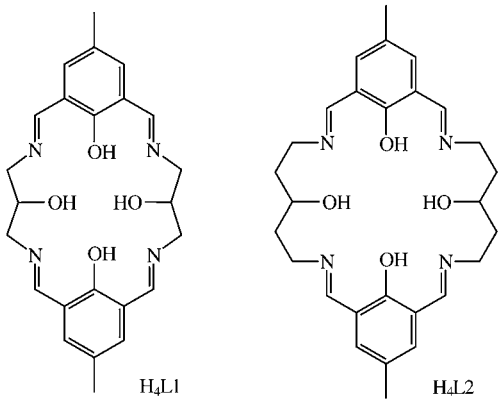
[15] See supporting information for details; yields given for the conversion of 2,3-dimethylbutadiene and propargyl methyl ether to the corresponding cyclohexadiene.

Di-, Tri-, and Tetracopper(II) Complexes of a Pseudocalixarene Macrocycle**

Julia Barreira Fontecha, Sandrine Goetz, and Vickie McKee*

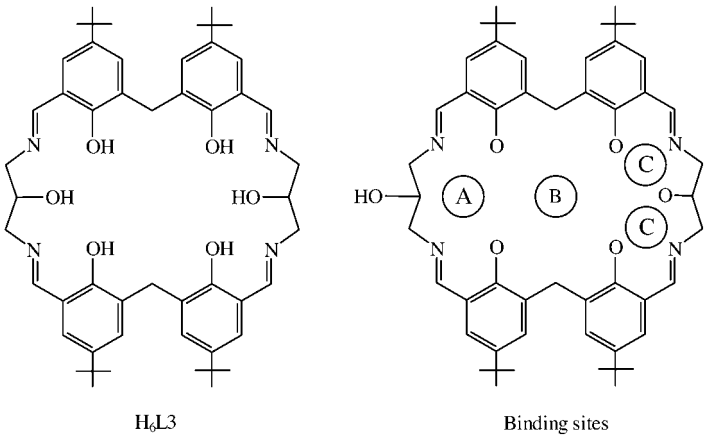
Schiff base Robson-type macrocycles containing two bridging phenol groups have been widely used to synthesize homo- and heterodinuclear complexes for many years. Detailed investigation of the chemistry of these systems has enabled insights in a number of areas, such as magnetochemistry, site selection, and bioinorganic model chemistry.[1] Expansion to larger macrocycles accommodating polynuclear assemblies has been achieved in the last ten years.[2,3] Interest in such complexes is centered on their ability to hold a number of metal ions in a fixed geometric relationship and has potential relevance in bioinorganic and catalytic chemistry as well as nanotechnological applications.

The macrocycle H_4L1 can form mono- and dinuclear complexes, but is unable to use the pendant alcohol groups to bind more than two metal ions within the macrocycle because of geometric constraints imposed by the overall



cavity size.[4] The longer saturated chain in H_4L2 permits formation of homo- and heterotetranuclear complexes, as well as complexes in which some sites are vacant.[3]

We have now synthesized the new dialdehyde dihydroxy-5,5′-di-*tert*-butyl-3,3′-methanediyldibenzaldehyde (dhtmb)[5] and used this group to expand the H_4L1 macrocycle. Schiff base condensation of dhtmb with 1,3-diaminopropan-2-ol in the presence of metal template ions yields complexes of the new macrocycle H_6L3 (Scheme 1). This ligand can be



Scheme 1. Pseudocalixarene ligand and binding sites.

considered as an expanded calix[4]arene containing two =$NCH_2CH(OH)CH_2N$= inserts. Unlike most aza- or oxocalixarenes (where inserts are placed between each pair of phenol rings),[6] H_6L3 preserves two methylene linkages while introducing imine and pendant alcohol donors.

Approximately planar conformations are sterically prohibited in genuine calix[*n*]arenes (where $n = 4$–6) and metal ions cannot take advantage of the bridging potential of the phenol groups, which generally leads to mononuclear complexes.[6,7] In contrast, H_6L3 can use some or all of the phenolic oxygen donors in the bridging mode and can be di- or polynucleating. The presence of relatively soft imine donors in addition to the phenolic oxygen atoms also widens the range of metal ions that might be expected to bind with high stability constants.

Three types of metal binding site are potentially available within H_6L3 (Scheme 1): site A is analogous to the conventional "Robson" site and is similar to that observed for complexes of H_4L1;[4] there are two of these in the macrocycle.

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The unique central calixarene-type site B involves the four phenol (or phenolate) donors. Finally, there are four equivalent sites of type C; occupation of similar sites has been reported for open-chain complexes based on 1,3-diaminopropan-2-ol[8] as well as in macrocyclic complexes of H_4L2.[3]

The macrocycle is formed by Schiff base condensation of dhtmb with 1,3-diaminopropan-2-ol in the presence of a metal template ion. When Cu^{II} is used as the template ion di-, tri-, and tetranuclear complexes can be isolated depending on the reaction conditions. Reaction of 1,3-diaminopropan-2-ol and dhtmb with equimolar amounts of $CuCl_2$ yields a green dicopper complex (**1**), while reaction with two equivalents of $Cu(NO_3)_2{\cdot}6H_2O$ yields a green tetracopper product (**3**) on short reflux. The tetranuclear complex converts into the brown tricopper species (**2**) on recrystallization from *N*,*N*-dimethylformamide (DMF). The structure of each complex has been investigated by X-ray crystallography.

The dicopper(II) cation of $[Cu_2Cl(H_4L3)]Cl{\cdot}1.6\,Et_2O{\cdot}EtOH$ (**1**$\cdot 1.6\,Et_2O{\cdot}EtOH$) is shown in Figure 1. The copper ions occupy the A sites, with each coordinated to two imine groups, two phenol oxygen atoms, and a bridging chloride ion. The geometry at each metal ion is square pyramidal, with the chloride ligand apical. The macrocycle adopts a saddle conformation with adjacent phenol rings inclined at 68.5(1) and 68.7(1)° to each other. This shape is maintained by three interactions: the Cu-Cl-Cu bridge (104.55(5)°) and two hydrogen bonds linking adjacent phenol oxygen atoms (O1···O2 2.414(4) and O4···O5 2.402(4) Å). The stoichiometry of the reaction suggests that the macrocycle is doubly deprotonated and the presence of the hydrogen bonds suggest that one proton is lost from each pair of phenols. The alcohol groups are not involved in bonding to the copper ions.

The tricopper(II) complex $[Cu_3(H_2L3)(NO_3)](NO_3)(dmf)_3$ (**2**) is dark brown, presumably because of charge transfer between the fully deprotonated phenolate groups and the Cu^{II} ions. The cations occupy the two A sites and the central C site (Figure 2), with each ion bound to four macrocyclic donors in its basal plane; the planes about Cu2 and Cu3 are inclined to that at Cu1 by 41.7(1) and 34.2(1)°, respectively. A coordinated nitrate counterion lies within the concave curve

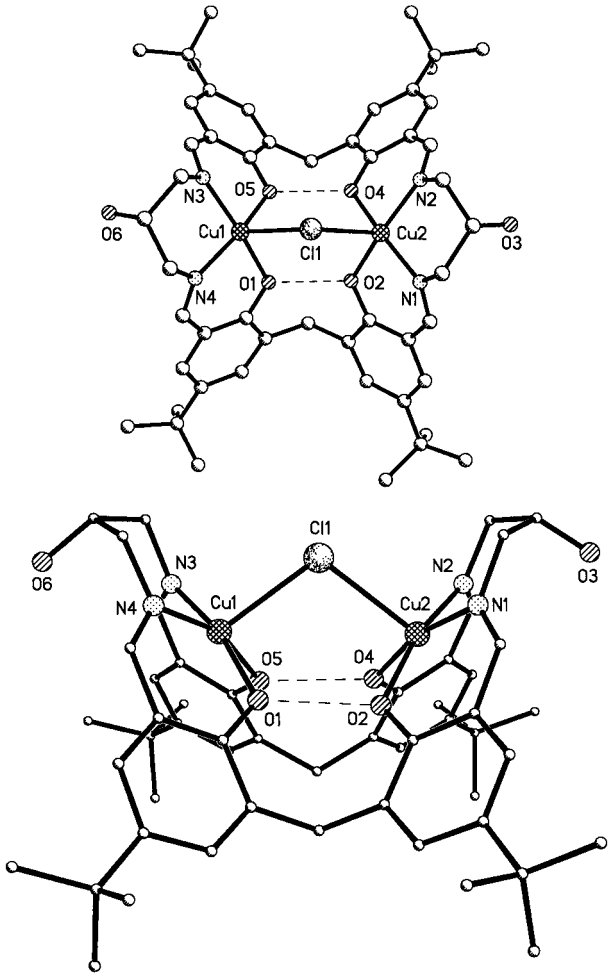

Figure 1. Two views of the $[Cu_2Cl(H_4L3)]^+$ ion of **1**, dotted lines represent hydrogen bonds. Selected bond lengths [Å] and angles [°]: Cu1-N3 1.952(4), Cu1-O1 1.958(3), Cu1-N4 1.978(4), Cu1-O5 1.989(3), Cu1-Cl1 2.5145(13), Cu2-O2 1.962(3), Cu2-N1 1.967(4), Cu2-O4 1.970(3), Cu2-N2 1.983(4), Cu2-Cl1 2.5423(14), O1-O2 2.414(4), O4-O5 2.402(4); Cu1-Cl1-Cu2 104.55(5).

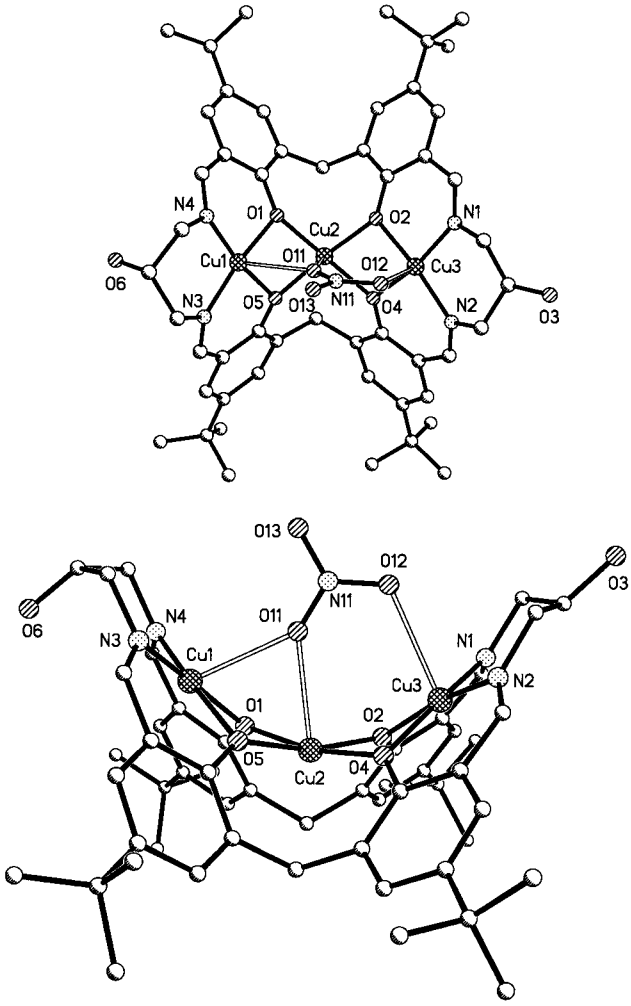

Figure 2. Two views of the $[Cu_3(H_2L3)(NO_3)]^+$ ion of **2**. Selected bond lengths [Å] and angles [°]: Cu1-O1 1.957(3), Cu1-O5 1.956(4), Cu1-N3 1.935(4), Cu1-N4 1.935(5), Cu1-O11 2.432(5), Cu1-Cu2 2.8428(8), Cu2-O1 1.918(3), Cu2-O5 1.925(3), Cu2-O2 1.928(3), Cu2-O4 1.929(3), Cu2-O11 2.490(5), Cu2-Cu3 2.8616(9), Cu3-O2 1.945(3), Cu3-O4 1.952(3), Cu3-N2 1.936(4), Cu3-N1 1.942(5), Cu3-O12 2.613(9); Cu2-O1-Cu1 94.38(14), Cu2-O2-Cu3 95.28(14), Cu2-O4-Cu3 95.02(14), Cu2-O5-Cu1 94.18(15).

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of the three copper sites. The nitrate is disordered (7:3) between two related positions; one site involves a single atom bridge between Cu1 and Cu2 and a three atom bridge between Cu2 and Cu3, while the minor site provides a single atom bridge between Cu3 and Cu2 with a three atom bridge linking Cu2 and Cu1. The conformation of the macrocycle is very similar to that in **1**.

The cation of $[Cu_4(H_2L3)(OH)_2(H_2O)(EtOH)](NO_3)_2$ (**3**) is shown in Figure 3; the Cu^{II} ions occupy the four equivalent B sites. As observed in complex **1**, each adjacent pair of phenols is monodeprotonated and linked by a hydrogen bond (O1···O2, 2.395(7); O4···O5, 2.417(6) Å). The overall conformation of the tetranuclear complex is, however, very different from that of **1** and **2**.

The saturated portions of the ring are fully extended to allow each alkoxo group to bridge two Cu^{II} ions and the macrocycle is sharply folded down its long axis, with each half approximately planar; the angles between adjacent phenol groups are 65.6(2) and 66.3(2)°. Each Cu^{II} ion has approximate square pyramidal geometry: the base comprises macrocyclic phenoxo, alkoxo, and imine donors as well as an exogenous μ_2-hydroxo group. The axial ligands are disordered and have been modeled as having 50% occupancy of water and ethanol at each site.

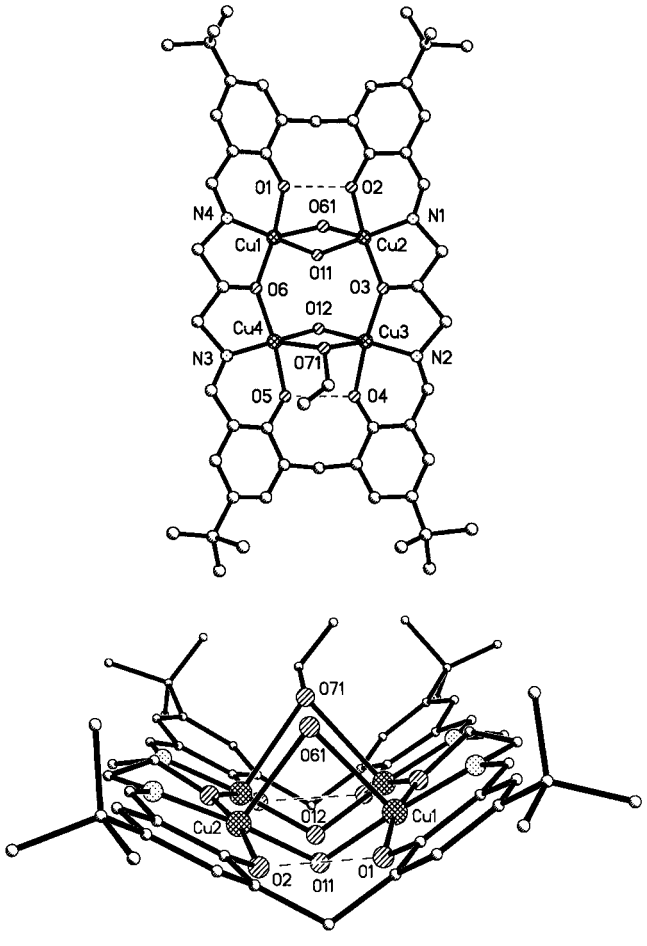

Figure 3. Two views of the $[Cu_4(H_2L3)(OH)_2(H_2O)(EtOH)]^{2+}$ ion of **3**, hydrogen bonds are shown as dotted lines. Selected bond lengths [Å] and angles [°]: Cu1-O11 1.927(5), Cu1-N4 1.932(8), Cu1-O6 1.961(5), Cu1-O1 1.995(5), Cu1-O61 2.420(6), Cu2-N1 1.904(6), Cu2-O11 1.928(5), Cu2-O3 1.963(5), Cu2-O2 1.977(5), Cu2-O61 2.402(6), Cu1-Cu2 3.143(1), Cu2-Cu3 3.681(1), Cu3-O12 1.889(5), Cu3-N2 1.935(7), Cu3-O3 1.963(5), Cu3-O4 2.007(5), Cu3-O71 2.520(7), Cu4-N3 1.898(7), Cu4-O12 1.909(5), Cu4-O6 1.979(5), Cu4-O5 1.997(5), Cu4-O71 2.527(7), Cu3-Cu4 3.160(1), Cu4-Cu1 3.677(1); Cu3-O3-Cu2 139.4(3), Cu1-O6-Cu4 137.9(3), Cu1-O11-Cu2 109.2(2), Cu3-O12-Cu4 112.6(2), Cu2-O61-Cu1 81.36(16), Cu3-O71-Cu4 77.54(18).

The most striking feature of this series of complexes is the variation in nuclearity within the same ligand system. This effect is linked to the variation in the extent of deprotonation of the ligand, the orientation of the phenol groups, and the overall shape of the macrocyclic host. Preliminary investigations suggest that the dicopper complex is only isolated in the presence of a good coordinating anion which is also large enough to fit the cavity defined by the hydrogen-bonding interactions of the ligand. When NO_3^-, ClO_4^-, or BF_4^- were used, the initial product of the template reaction was the tetracopper complex, irrespective of the stoichiometry of the template reaction.

Formally, the tricopper complex can be generated from the dinuclear analogue by displacement of the two central, hydrogen-bonding protons by a Cu^{II} ion. Comparison of Figures 1 and 2 shows that the two structures are closely related except that the saddle shape in **2** is maintained by the Cu^{II} ion in the central site and by two hydrogen bonds in **1**. Surprisingly, however, it seems that the tricopper complex is actually formed by rearrangement of the tetracopper complex. Extended reflux of the template mixture causes the green color to darken to brown and mixtures of **2** and **3** are formed, as indicated by FAB mass spectrometry. The same color change occurs within minutes if the tetracopper complex is dissolved in DMF and clean tricopper complex is obtained. Consequently, it seems that the tetranuclear complex (**3**) is the kinetic product of the template reaction and that **2** is the thermodynamic product. In view of the extensive structural rearrangement required, it is not unexpected that the rearrangement is slow in alcohol but faster in a solvent with better donor properties.

Experimental Section

2,2′-dihydroxy-5,5′-di-*tert*-butyl-3,3′-methanediyldibenzyl alcohol was synthesized from 4-*tert*-butylphenol following the literature procedure.[9] The alcohol groups were oxidized to aldehydes by MnO_2 after the phenol groups had been protected using allylbromide. The allyl groups were removed with 10% Pd on charcoal to yield 2,2′-dihydroxy-5,5′-di-*tert*-butyl-3,3′-methanediyl dibenzaldehyde (dhtmb) in 40% yield for the three-step process.[5] Elemental analysis calcd (%) for $C_{23}H_{28}O_4$: C 74.97, H 7.66; found: C 74.51, H 7.86. ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 9.86$ (s, 2H), 7.64 (d, 2H), 7.37 (d, 2H), 4.03 (s, 2H), 1.26 ppm (s, 18H).

$[Cu_2Cl(H_4L3)]Cl\cdot 2\,MeOH$ (**1**·2 MeOH). Anhydrous $CuCl_2$ (0.073 g 0.543 mmol) was dissolved in hot dry ethanol (40 ml) and added to a solution of dhtmb (0.20 g 0.543 mmol) in hot dry ethanol (35 mL). After 10 min reflux a solution of 1,3-diaminopropan-2-ol (0.52 g, 0.543 mmol) in dry methanol (20 mL) was added. The green solution was heated at reflux for 2 h, then cooled, filtered, and the volume reduced to give the product in 36% yield. Elemental analysis calcd (%) for **1**·2 MeOH: C 58.7, H 6.7, N 5.1; found: C 58.4, H 6.6, N 5.1. Emerald green crystals of the solvate **1**·1.6 Et_2O·EtOH were obtained by diffusion of diethyl ether into the filtrate. Crystal dimensions: $0.35 \times 0.14 \times 0.07$ mm^3, triclinic, space group $P\bar{1}$ $a = 13.707(3)$, $b = 14.568(3)$, $c = 16.827(4)$ Å, $\alpha = 103.472(3)$, $\beta = 95.935(3)$, $\gamma = 93.429(3)$°, $V = 3238(1)$ Å^3, $\rho_{calcd} = 1.237$ Mg m^{-3}. 22 822 reflections, 11 279 independent ($R_{int} = 0.0455$), $\mu = 0.792$ mm^{-1}, $T_{max} = 1.000$, $T_{min} = 0.880$, 830 least-squares parameters $R1 = 0.0579$ $wR2 = 0.1384$ (2σ data).

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$[Cu_3(H_2L3)(NO_3)](NO_3)(dmf)_4{\cdot}H_2O$ (**2**·4 dmf·H_2O). A mixture of $Cu(NO_3)_2{\cdot}6H_2O$ (0.321 g, 1.08 mmol) and dhtmb (0.20 g, 0.543 mmol) in dry ethanol (80 mL) were heated to reflux for 10 min and a solution of 1,3-diaminopropan-2-ol (0.052 g, 0.543 mmol) in dry methanol (20 mL) added dropwise. The emerald green solution darkened as reflux was continued for 2 h. the mixture was filtered, cooled, and concentrated under vacuum where upon a green solid precipitated (analyzed as $[Cu_4(H_4L)(NO_3)(OH)_2(H_2O)_4]$). This complex was dissolved in DMF and the color changed to brown; crystals of the trinuclear complex **2**·3 dmf were obtained in 40% yield by diffusion of diethyl ether into the solution. Elemental analysis calcd (%) for **2**·4 dmf·H_2O: C 51.8, H 6.4, N 9.4; found: C 52.1, H 6.5, N 9.4. Crystal dimensions: $0.45 \times 0.24 \times 0.04$ mm^3, monoclinic, space group $P2_1/c$, $a = 17.234(1)$, $b = 22.130(2)$, $c = 17.658(1)$ Å, $\beta = 103.488(1)°$, $V = 6549.0(8)$ Å^3, $\rho_{calcd} = 1.395$ Mg m^{-3}. 46 309 reflections, 11 521 independent ($R_{int} = 0.0424$), $\mu = 1.036$ mm^{-1}, $T_{max} = 1.000$, $T_{min} = 0.885$; 859 least-squares parameters $R1 = 0.0646$ $wR2 = 0.1638$ (2σ data).

$[Cu_4(H_2L3)(OH)_2(sol)_2](NO_3)_2$ (**3**·2 H_2O where sol = water or ethanol). A mixture of $Cu(NO_3)_2{\cdot}6H_2O$ (0.16 g, 0.543 mmol) and dhtmb (0.20 g, 0.543 mmol) in dry ethanol (70 mL) was heated to reflux for 10 min and a solution of 1,3-diaminopropan-2-ol (0.052 g, 0.543 mmol) in dry methanol (20 mL) added dropwise. The solution changed to emerald green and darkened as reflux was continued for 1 h. The solution was cooled, filtered, and evaporated to dryness. The residue was then dissolved in dichloromethane, filtered, and evaporated again before being dissolved in ethanol. Green $[Cu_4(H_2L3)(OH)_2(H_2O)_2](NO_3)_2{\cdot}2H_2O$ was obtained from this solution in 79% yield. Elemental analysis calcd (%) for **3**·2 H_2O: C 47.1, H 5.6, N 6.3; found: C 47.1, H 5.5, N 6.3. Crystals of $[Cu_4(H_2L3)(OH)_2(H_2O)(EtOH)](NO_3)_2{\cdot}2EtOH{\cdot}H_2O$ (**3**·2 EtOH·H_2O) were obtained by slow evaporation of a solution of **3**·2 H_2O in an ethanol/benzene/petroleum ether mixture. Crystal dimensions: $0.31 \times 0.13 \times 0.04$ mm^3, monoclinic, space group $P2_1/c$, $a = 11.867(2)$, $b = 14.125(3)$, $c = 41.220(7)$ Å, $\beta = 93.406(3)°$, $V = 6897(2)$ Å^3, $\rho_{calcd} = 0.352$ Mg m^{-3}. 47 670 reflections, 12 095 independent ($R_{int} = 0.0902$), $\mu = 1.285$ mm^{-1}, $T_{max} = 1.000$, $T_{min} = 0.766$; 696 least-squares parameters $R1 = 0.0763$ $wR2 = 0.21.19$ (2σ data). The uncoordinated solvate molecules and nitrate ions were highly disordered and were treated using the SQUEEZE program[10] (see the Supporting Information).

X-ray data were collected at 150(2) K on a Bruker SMART 1000 diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) to $2\theta_{max}$ of 25°. The structures were solved by direct methods and refined on F^2 using all the data.[11] Non-hydrogen atoms were refined with anisotropic ADPs and hydrogen atoms attached to full-occupancy carbon atoms were inserted at calculated positions. Details concerning treatment of disorders and of hydrogen atoms not bonded to carbon atoms are described in the Supporting Information. CCDC 190246.(**1**·1.6 Et_2O·EtOH) CCDC 190247 (**2**·3 dmf), and CCDC 190248 (**1**·2 H_2O) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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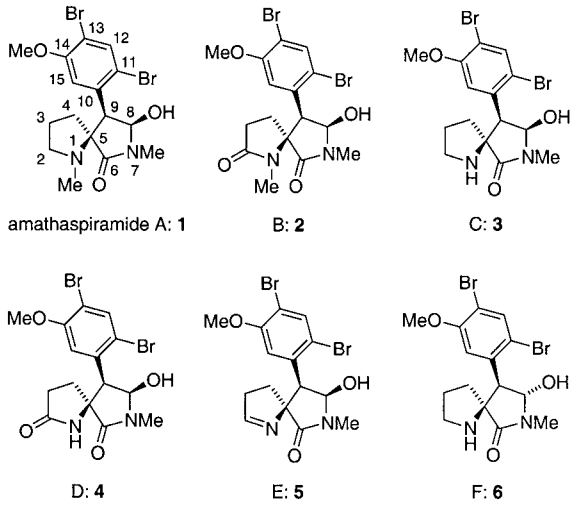
The Total Synthesis of (−)-Amathaspiramide F**

Chambers C. Hughes and Dirk Trauner*

The amathaspiramides A–F (**1**–**6**) are a family of marine alkaloids recently isolated from a New Zealand collection of the bryozoan *Amathia wilsoni*.[1,2] Marked by a dense array of polar functionality, the natural products feature a novel



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