Experimental Section

Synthesis of IRPM-1: In a typical synthesis, $[Co(bpdc)(H_2O)_2]\cdot H_2O$ (0.3 mmol, white-gray), prepared as previously reported[8], and bpy (0.1 mmol) were stirred in DMF (10 mL) and well mixed. The solution was then transferred into an acid digestion bomb, which was closed and heated at 150 °C for 3 days, giving rise to deep-purple columnar crystals of IRPM-1 in high yield (129.1 mg, ≈94.5 %). IRPM-1 can also be synthesized solvothermally by direct reaction of $Co(NO_3)_2\cdot 6H_2O$ with bpy and bpdc in a DMF solution at 150 °C for three days. A 13.5 mg of the ground product was immersed in distilled water for 30 min, yielding $[Co(bpdc)(H_2O)_2]\cdot H_2O$ in quantitative yield (10.4 mg, calcd 10.5 mg). Powder X-ray diffraction (PXRD) analysis of the product was in excellent agreement with the calculated PXRD pattern produced by single crystal data.

Sorption Experiments: The sorption studies were conducted on a computer-controlled DuPont Model 990 TGA. The hydrocarbon partial pressure was varied by changing the blending ratios of hydrocarbon-saturated nitrogen and pure nitrogen gas streams. The zeolite and IRPM-1 samples were initially activated at 500 and 200 °C in nitrogen, respectively. At 80 °C, the measured sorption capacities for propylene ($p = 600$ Torr, $p/p_o = 0.023$), *n*-hexane ($p = 90$ Torr, $p/p_o = 0.084$), and cyclohexane $p = 55$ Torr, $p/p_o = 0.074$) of IRPM-1 are 12, 15, and 19 wt %, respectively, where p is the sorption pressure of the sorbate and p_o is the calculated vapor pressure at the sorption temperature. Measurements of cyclohexane sorption rate on IRPM-1, H-Y, and H-ZSM-5 samples were performed at 80 °C.

Photolysis of *o*-MeDBK: IRPM-1 (about 50 mg) was prepared as a slurry in pentane, and transferred to a branched quartz cell. Argon was used to evaporate the solvent, and the sample was then heated to 150 °C for an hour at 1 Torr. A sample of *o*-MeDBK (2 mg) in pentane/ether (0.3 mL; 1:1) was added to IRPM-1 at room temperature under Ar. The mixture was allowed to soak for 2 h, then flushed with Ar, and pumped to 2×10^{-5} Torr and left overnight. It was then irradiated with a 500 W medium-pressure mercury lamp for one hour. Procedure 1: The irradiated sample was then extracted with ether. Procedure 2: After procedure 1 sample was soaked in water until the color turned to white–gray and then extracted with an excess amount of ether. Procedures 1 and 2 gave ≈30 % and ≈30 % **AB**, respectively, and >40 % of the alcohol (**CP**).

Received: August 5, 2002 [Z19888]

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[9] $[Co_3(bpdc)_3(bpy)]\cdot 4DMF\cdot H_2O$ (IRPM-1) crystallizes in the orthorhombic crystal system, space group *Pbcn*, with $a = 14.195(3)$, $b = 25.645(5)$, $c = 18.210(4)$ Å, $V = 6629(2)$ Å^3, $Z = 4$, and $d_{calc} = 1.367$ g cm^{-3}. Analysis was done at wavelength λ ($Mo_{K\alpha}$) = 0.71073 Å. The structure was solved by direct methods and successive Fourier difference syntheses. The refinement by full-matrix least squares gave a final value $R = 0.056$ from 3662 reflections with intensity $I \geq 2\sigma(I)$ for 384 variables. The analytical data for IRPM-1 are as follows: calcd C 57.11, H 4.53, N 6.02 %; found C 56.4, H 4.58, N 6.16 %. The evacuated IRPM-1, $[Co_3(bpdc)_3(bpy)]$, crystallizes in the orthorhombic crystal system, space group *Pbcn*, with $a = 13.950(3)$, $b = 25.999(5)$, $c = 18.089(4)$ Å, $V = 6561(2)$ Å^3, $Z = 4$ and $d_{calc} = 1.067$ g cm^{-3}. The analytical data for $[Co_3(bpdc)_3(bpy)]$ are as follows: calcd C 59.3, H 3.06, N 2.66 %; found C 59.24, H 3.27, N 2.75 %. CCDC-188406 (IRPM-1) contains 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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Chiral Metallahelicates

The Preparation of a Double Metallahelicate Containing 28 Copper Atoms

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Molecules of great complexity that are prepared by the self-organization of simple components have garnered considerable recent attention. Among these compounds are metallamacrocycles such as the helicates,[1a–d] molecular squares,[2a,b] and the metallacrowns.[3a–e] The latter molecular class is reminiscent of organic crown ethers; however, the $\{O\text{-}C\text{-}C\}_n$ repeat unit is substituted by heteroatoms, such as $\{O\text{-}M\text{-}N\}_n$. Metallacrowns have been prepared with ring sizes ranging from 9-metallacrown-3 (9-MC-3) to 30-MC-10.[4a–c] The 15-

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  0044-8249/03/11505-0564 $ 20.00+.50/0

MC-5 complexes, in particular, have been of interest as these can be prepared using α-amino acid-derived ligands. As such they are inherently chiral and can form cavities capable of selective anion recognition[5a] or resolved, fourfold symmetric, amphiphilic metallahelices.[5b] Herein, we demonstrate that a new class of self-assembled complex, a metallahelicate, can also be isolated by our synthetic strategy.

The standard preparation of a 15-MC-5 complex entails the addition of a stoichiometric ratio (5:5:2) of copper acetate, an α-aminohydroxamic acid, and ammonium chloride, respectively, followed by the addition of one equivalent of a lanthanide(III) salt. Before the addition of the lanthanide, a slightly soluble green material can be observed in the aqueous solvent. Recent work by Dallavalle and Tegoni,[6] in which L-phenylalanine hydroxamic acid (L-H_2pheha) was employed, proposed a 12-MC-4 model for this green material. Such a structure, however, should be relatively unstable, as the ring of a 12-MC-4 complex is highly strained when composed of ligands with fused 5,5-membered chelate rings.

In an attempt to improve our understanding of the nature of this green intermediate, we adjusted the copper/L-norvaline hydroxamic acid (L-H_2norvalha)/chloride ratios to 5:4:2, and changed our solvent system to pure methanol. Crystalline material was observed after three weeks of slow methanol evaporation.

The compound ion $[\mathbf{1}]^{2+}$[7,8] ($M_W = 5328.7$) contains copper atoms in seven different donor environments (Figure 1), with an overall stoichiometry of $[Cu_{28}L_{20}(OAc)_{10}Cl_4(MeOH)_5(H_2O)_3]$. Additional unbound solvent molecules and anions ($2\,Cl^-$) are present in the crystal structure, to give an overall molecular weight of 5952.1. This remarkable molecule is over three nanometers long and is constructed from two $\{Cu_{14}L_{10}(OAc)_4\}$ strands that are related by a noncrystallographic twofold symmetry axis. Each strand contains three structural domains; a central "body" (composed of four Cu^{II} atoms and four [L-norvalha]$^{2-}$ ligands), two sets of "wings" (each composed of four Cu^{II} atoms and three [L-norvalha]$^{2-}$ ligands) and two $[Cu(OAc)]^+$ bridges that link together the body and wing domains. The relationship between the body, the "hinge" copper atom, and the wing is illustrated in Figure 2. The coordination of the copper ions is, with the exception of the hinges, essentially square planar with a weaker interaction perpendicular to the plane. The body of the metallahelicate contains two collapsed 12-MC-4 units[9] oriented cofacially, with *n*-propyl groups pointing away from the central plane of the body, thus forming two pockets (one on each side) that each surround a chloride counterion (Figure 3). The wings that form the upper and lower domains of the structure are capped by dicopper sites, which display simultaneous μ-alkoxy (using the oxygen atom of the carbonyl hydroxamate) and μ-acetato bridged copper centers

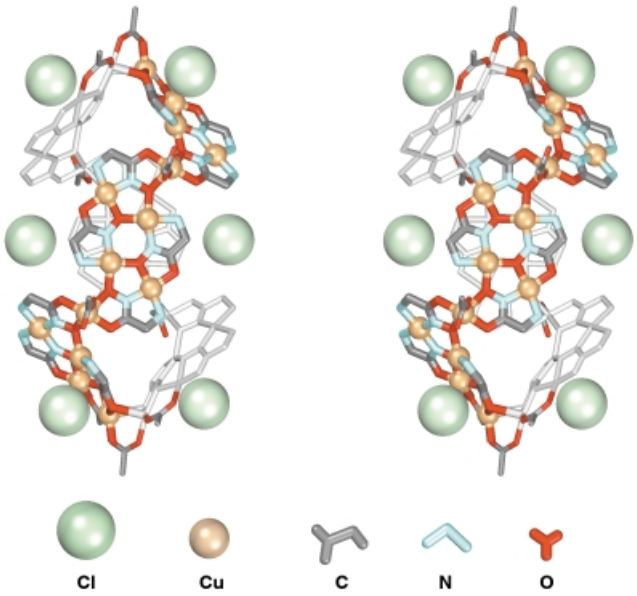

Figure 1. A stereoview of **1**·2Cl with lattice solvent, coordination solvent, and alkyl groups removed for clarity.

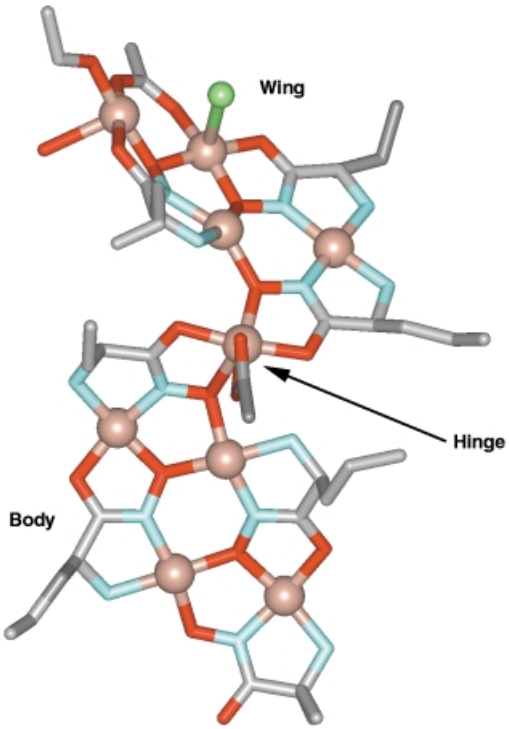

Figure 2. A side view of the collapsed metallacrown core of the "body" portion of **1**·2Cl.

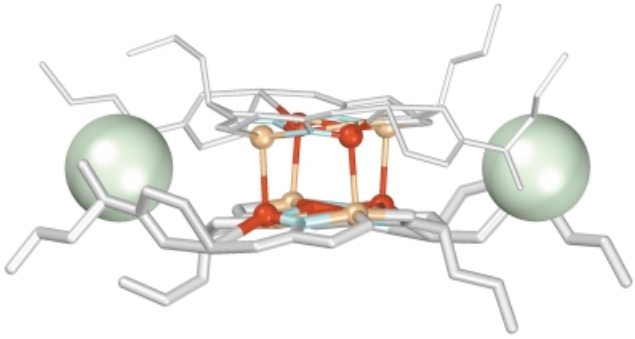

Figure 3. A minimal representation of the connectivity in the metallahelicate showing one body unit, one wing unit, and one hinge Cu^{II} center of the complex.

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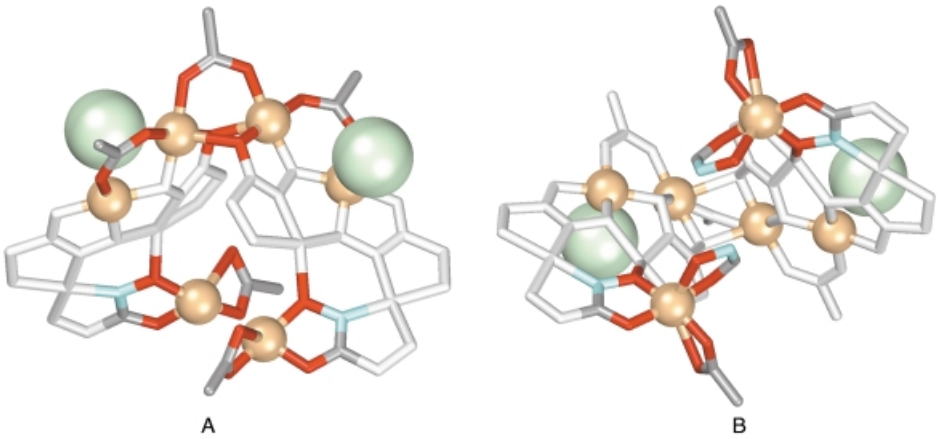

Figure 4. A) A side view of the top "wing" of the $[\mathbf{1}]^{2+}$ unit displaying the binuclear copper centers with bridging acetate groups and coordinated chloride ions; B) a view along the pseudo-twofold axis of the $[\mathbf{1}]^{2+}$ unit showing two of the unique "hinge" copper atoms and their pseudo-Δ propeller geometry.

(Figure 4 A). There is a nearly planar tetranuclear fragment on either side of the wing, related by a twofold axis, with each wing containing one of these binuclear copper atoms. To satisfy the coordination geometry about the capping copper dimer, the planes of the two tetranuclear fragments must twist with respect to one another. One of the three remaining Cu^{II} ions has a coordinated chloride ion. The conformational complexity of the $[\mathbf{1}]^{2+}$ ion is further defined by the absolute stereochemical configurations of the four chiral copper atoms (hinge atoms) that form the links between the body and wings of the structure. In the $[\mathbf{1}]^{2+}$ unit, all four Cu^{II} ions have a Δ configuration (Figure 4 B) while in the $[\mathbf{2}]^{2+}$ ion, prepared from D-H_2norvalha,[10] they have a Λ configuration.

Finally, upon combining all structural domains and stereochemical restrictions, a metallahelicate topology is generated if one begins at one of the top binuclear copper atoms and traces the connectivity of adjacent copper atoms throughout the molecule. This suggests that helicate-like molecules should be accessible using a binuclear cap with an appropriate helix-inducing organic ligand.

This new supermolecule[11] offers a unique set of potential attachment points for a variety of ligand sets, as well as providing a potential synthon for metallacrown formation. Currently, we are exploring the incorporation of mesogenic groups onto the periphery of these noncentrosymmetric metal clusters to observe possible nonlinear optical phenomena that may be apparent as a result of liquid-crystalline ordering.[12a–c]

Experimental Section

The syntheses of L-H_2norvalha and D-H_2norvalha were accomplished by a literature method.[13] m.p. = 168–171 °C (L-H_2norvalha); m.p. = 163–168 °C (D-H_2norvalha).

Compound **1**·2 Cl was synthesized by the addition of L-norvalha (0.67 mmol) to a stirred slurry of $Cu^{II}(OAc)_2{\cdot}H_2O$ (0.93 mmol) in predried methanol (10 mL). After stirring the capped reaction solution for 30 min, NH_4Cl (0.20 mmol) was added. The mixture was then stirred for 2 h to give a dark-green solution, which was subsequently filtered by gravity into a vial (27 × 165 mm) and allowed to stand uncapped for 48–72 h. Suitable green blocks were obtained for X-ray diffraction study. Yield 28.6 %; m.p. = 198–200 °C (decomp); elemental analysis (%) calcd for $C_{131}H_{320}Cl_6Cu_{28}N_{40}O_{94}$: C 26.43, H 5.42, N 9.41; found: C 26.62, H 4.94, N 9.66.

Compound **2**·2 Cl was prepared in the same manner as **1**·2 Cl, but with D-H_2norvalha as the ligand. Yield 8.1 %; m.p. = 196–199 °C (decomp); elemental analysis (%) calcd for $C_{135}H_{330}Cl_6Cu_{28}N_{40}O_{95}$: C 26.91, H 5.52, N 9.30; found: C 25.05, H 4.71, N 9.37.

Received: September 16, 2002 [Z50160]

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[8] Crystal data for **1**·2Cl ($[Cu_{28}L_{20}(OAc)_{10}Cl_6(MeOH)_{11}(H_2O)_{23}]$): $M_W = 5952.09$, monoclinic, space group $P2_1$, $a = 14.2512$, $b = 26.9615(19)$, $c = 34.476(3)$ Å, $\alpha = 90.00$, $\beta = 90.049(2)$, $\gamma = 90.00°$, $V = 13246.8(16)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.492$ g cm^{-3}; $2.73 < \theta < 28.34°$; crystal dimensions $0.24 \times 0.38 \times 0.42$ mm^3; $\mu = 23.35$ cm^{-1}; $T = 123(2)$ K; 172045 reflections collected; 63307 unique reflections and 2727 parameters were used for the full-matrix least-squares refinement on F^2; $R1 = 0.0394$, $wR2 = 0.1012$.

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[10] Crystal data for **2**·2Cl ($[Cu_{28}L_{20}(OAc)_{10}Cl_6(MeOH)_{15}(H_2O)_{20}]$): $M_W = 6026.21$, monoclinic, space group $P2_1$, $a = 14.1740(12)$, $b = 26.753(2)$, $c = 34.535(3)$ Å, $\alpha = 90.00$, $\beta = 90.314(3)$, $\gamma = 90.00°$, $V = 13095.7(19)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.528$ g cm^{-3}; $2.70 < \theta < 22.78°$; crystal dimensions $0.10 \times 0.14 \times 0.22$ mm^3; $\mu = 23.63$ cm^{-1}; $T = 150(2)$ K; 84037 reflections collected; 34295 unique reflections and 2767 parameters were used for the full-matrix least-squares refinement on F^2; $R1 = 0.0651$, $wR2 = 0.1270$. Note that **2**·2Cl differs from **1**·2Cl in that the bound solvent composition is 6 MeOH and 2 H_2O for the former and 5 MeOH and 3 H_2O for the latter.

[11] Here we define a "supermolecule" (see ref. [1c]) as composed of receptors (that is, α-aminohydroxamic anions and acetates) and substrates (copper and chloride ions) held together weakly by intermolecular forces, thus giving a larger discreet superstructure.

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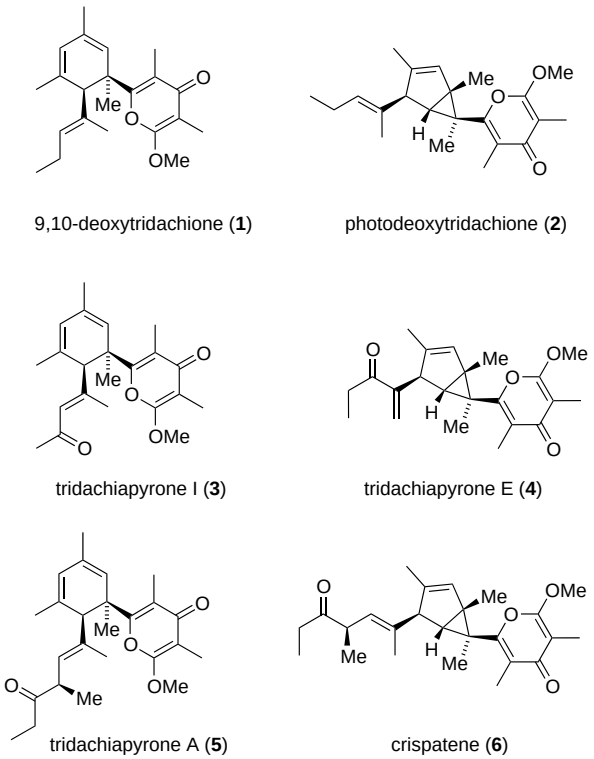

Scheme 1. Molluscan polypropionates. The absolute stereochemistry shown is arbitrary.

Lewis Acids in Total Synthesis

Total Synthesis of (±)-Photodeoxytridachione through a Lewis Acid Catalyzed Cyclization**

*Aubry K. Miller and Dirk Trauner**

Certain sacoglossan molluscs sequester active chloroplasts from algae and use these organelles to carry out photosynthesis in their own tissues.[1] These fascinating animals lack a protective shell and thus rely on chemical defense against predators. Not surprisingly, they have yielded a range of interesting biologically active natural products.[2] Many of these are highly unsaturated polypropionates that feature an α-methoxy-γ-pyrone moiety (Scheme 1).

Architecturally, these natural products, which have been largely ignored by the synthetic community,[3] fall into two categories. Whereas 9,10-deoxytridachione (**1**), tridachiapyrone I (**3**), and tridachiapyrone A (**5**) are cyclohexadiene derivatives, photodeoxytridachione (**2**), tridachiapyrone E (**4**), and crispatene (**6**) feature a bicyclo[3.1.0]hexene core. The isomeric nature of these ring systems raises questions about their mutual biogenetic relationship.[4] In 1979, Ireland and Scheuer demonstrated that 9,10-deoxytridachione (**1**) can be photochemically converted in vivo and in vitro into photodeoxytridachione (**2**).[1] This transformation could proceed through conrotatory photochemical retro-electrocyclization followed by a "photochemical Diels–Alder reaction"—that is a $[_\pi 4_a +_\pi 2_s]$ cycloaddition.[5] However, since no racemization occurs, the reaction was proposed to proceed as a photochemical $[_o 2_a +_\pi 2_a]$ rearrangement.[4]

Although these results suggest that **2** is biosynthesized via **1**, it is also, at least in principle, conceivable that both compounds are *directly* derived from a common acyclic precursor **7** (Scheme 2). The cyclohexadiene **1** may originate from this hypothetical intermediate through thermal disrotatory 6π electrocyclization. In contrast, the bicyclo[3.1.0]hexene **2** could arise in one step from a thermal $[_\pi 4_a +_\pi 2_a]$ cycloaddition of the same precursor. Provided that such a reaction could be realized in the laboratory, a unified synthetic approach toward both classes would be possible, since 6π electrocyclizations of hexatrienes are well-prece-

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[**] The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as a sponsoring member and Novartis as a supporting member.