Table 6: Relative energies (in kcal mol^{-1}) of [Cy(CH$_2$)(B-H)(YH$_2$)] (Y = Si, Ge, Sn) with pyramidal (C_1) and planar (C_s) boron atoms, calculated at the B3LYP/LANL2DZ level of theory. θ is the pyramidalization angle at boron, given in degrees.

		Si	Ge	Sn
E_{rel} + ZPVE	C_1	0	0.0	0.0
	C_s	−0.1	6.5	11.2
θ	C_1	14.1	7.7	6.5

If one Si atom causes pyramidalization, two of them should enhance the effect. We have calculated the Si_2BH_5 structure at various levels and found it to have a C_s structure (**7**) with a pyramidal boron atom. The corresponding C_{2v} structure (**8**) with a planar boron center is found to be higher in energy. The calculated value of θ is larger than that of **1**. The energy differences are also found to be considerably higher (Table 5).

The heavier group 14 elements, Ge and Sn, must also influence the pyramidalization of boron. Calculations at the B3LYP/LANL2DZ level show that θ decreases as Si (14.1°) is replaced by Ge (7.7°) or Sn (6.5°; Table 6). However, the inversion barrier increases in going from Si (0.7) to Ge (7.5) to Sn (12.7 kcal mol^{-1}). The unexpected nonplanar arrangement of the tricoordinate boron center in **1** provides another demonstration of the many novel structural patterns that the heavier elements of the main group can contribute to the first-row elements, and invites experimental verification.

Received: July 4, 2002
Revised: October 22, 2002 [Z19666]

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Ship-in-Bottle Photochemistry

ℝPM-1: A Recyclable Nanoporous Material Suitable for Ship-In-Bottle Synthesis and Large Hydrocarbon Sorption[**]

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Zeolites and related molecular sieves, which contain rigid frameworks and accessible internal channels and/or cages, have been dominating the porous material world for a long time, because of their widespread applications in catalytic and separation science.[1,2] Although there is an increasing demand for materials with tunable structures, the structural design of zeolites is limited by their requirement for

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[**] The Rutgers University team is grateful to the National Science Foundation for its generous support (MDR-0094732). This work was supported in part by the MRSEC Program of the National Science Foundation under Award Number DMR-9809687, and by the National Science Foundation and the Department of Energy under Grant No. NSF CHE9810367 to the Environmental Molecular Sciences Institute at Columbia University.

0044-8249/03/11505-0560 $ 20.00+.50/0

tetrahedral oxide skeletons. Another impediment in the applications of zeolites is the difficulty in framework dissolution or removal, which is required for ship-in-bottle synthesis.[3] In such a reaction, synthesis is conducted within the internal framework of the zeolite to produce a product (ship) that is difficult to remove from the pores of the zeolite internal surface (bottle) for some technical reason. In most of these cases, concentrated acids or bases must be used to "break the bottle", that is, to remove or dissolve the host framework. Such a harsh processes may not only rupture the framework but also cause severe damage to the products.[4,5]

Recently, organometallic materials have demonstrated great potential as zeolite mimics, with some properties of the mimic being superior to those of zeolites. For example, highly porous organometallic structures can be rationally synthesized and tuned by a suitable choice of organic ligands and metal ions to control their framework architecture and functionality.[6,7] However, it remains a challenge to synthesize reversibly recyclable systems in which the frameworks can be effectively removed and rebuilt. We have met this challenge through the synthesis of a thermally stable, 3D nanoporous organometallic material, RPM-1 (Rutgers Recyclable Porous Materials) via a nonporous 1D precursor. This compound has demonstrated a strong capability in sorption of large hydrocarbons and outstanding shape selectivity in the photolysis of *ortho*-methyldibenzylketone (*o*-MeDBK), to give a cage effect of 100 % of the α-cleavage products, and a high yield of the cyclization product. By breaking the framework of RPM-1, a mass balance of 100 % is achieved. Thus, not only does RPM-1 demonstrate a similar (or better) performance in sorption and catalysis than some of the most commonly used zeolites (ZSM-5, X, and Y), but it is also the first recyclable organometallic nanoporous compound whose framework (the bottle) can be completely broken down under mild conditions to allow a full recovery of photochemical products (the ship; see Figure 1).

The targeted 3D network was prepared from a previously reported 1D structure, $[Co(bpdc)(H_2O)_2]\cdot H_2O$ (bpdc = biphenyldicarboxylate).[8] A key earlier observation was that all materials, 1D or 2D, which belong to a Co–bpdc–py (py = pyridine) family readily convert to this 1D compound when immersed in water, regardless of their initial dimensionality.[8] This remarkable feature is highly desirable for designing a recyclable process in which 1) an open 3D framework is made from the nonporous 1D $[Co(bpdc)(H_2O)_2]\cdot H_2O$ phase (hereafter referred to as the precursor) by substitution of an ancillary water molecule in the precursor with a bpy ligand (bpy = 4,4′-bipyridine) and 2) the open 3D framework is readily broken down and converted back into the precursor when immersed in water.

$[Co_3(bpdc)_3(bpy)]\cdot 4\,DMF\cdot H_2O$ (hereafter referred to as RPM-1) was synthesized by a solvothermal reaction. The product, RPM-1, remained stable in common organic solvents. When immersed in water, RPM-1 quickly and quantitatively converted into the precursor. Upon heating the precursor in DMF and bpy, RPM-1 was recovered in high yield [Eq. (1)].

$$\underset{\text{(precursor)}}{[Co(bpdc)(H_2O)_2]\cdot H_2O + bpy} \xrightleftharpoons[\text{H}_2\text{O, RT}]{\text{DMF, 150°C}} \underset{\text{(RPM-1)}}{[Co_3(bpdc)_3bpy]\cdot 4DMF\cdot H_2O} \qquad (1)$$

An X-ray structural analysis performed on a single crystal of RPM-1 revealed a structure possessing a two-fold interpenetrating 3D network constructed with a unique building block, $[Co_3(bpdc)_6]$, as shown in Figure 2.[9] The structure

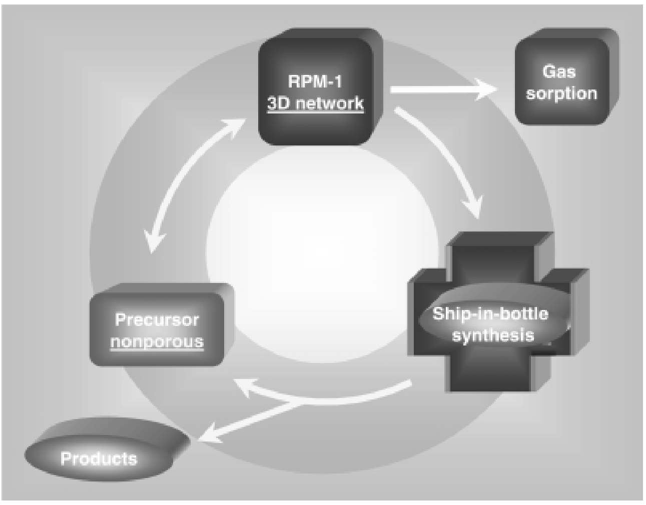


Figure 1. Schematic representation of the recycling process involving RPM-1.

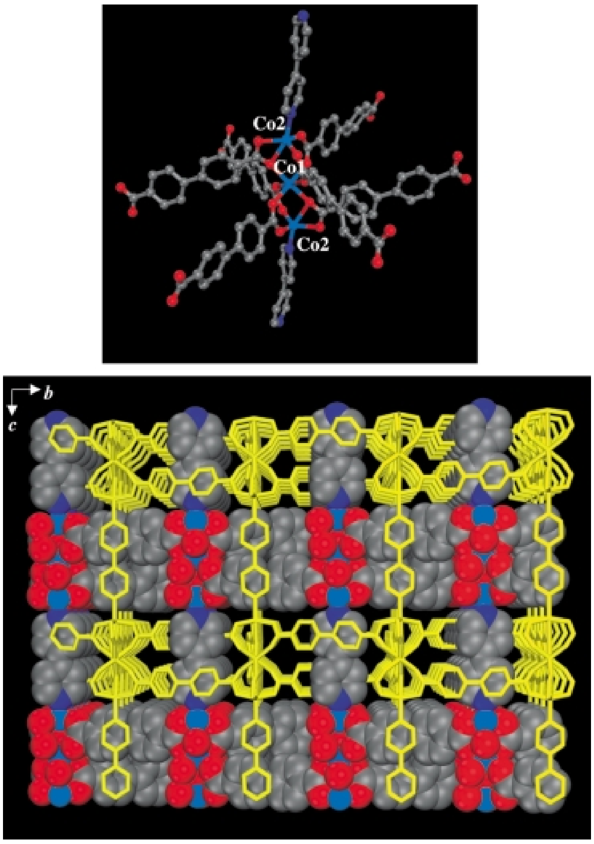


Figure 2. Single crystal structure of RPM-1. Top: the $[Co_3(bpdc)_6(bpy)_2]$ building unit. Bottom: View down the *a* axis showing two interpenetrating 3D networks. Co (light blue), O (red), N (blue), C (gray).

contains two crystallographically independent cobalt centers. The octahedrally coordinated Co1 is located on the two-fold rotation axis and is connected to two adjacent Co2 centers with distorted trigonal bipyramidal geometry, through six bpdc ligands (Figure 2, top). Each of the two Co1···Co2 pairs is connected through three carboxylate groups by two μ_2 and one μ_3 bonding modes. The Co_3 unit, which acts as a node, is connected to six adjacent nodes through six bpdc ligands to form a 2D layer parallel to the *ab* (*xy*) plane. The remaining coordination sites of the two Co2 centers in each building block are occupied by nitrogen atoms of bpy ligands that act as pillars, and which bind the adjacent 2D layers to generate a pillared 3D framework. Such a pillared 3D structure composed of "double" metal–carboxylate layers (Figure 2, bottom) is rare. Two of these pillared 3D motifs, identical in structure, interpenetrate to yield a new type of catenated network consisting of large, open, 1D channels (Figure 3). All aromatic rings self-assemble to line up approximately with their planes parallel to the *z* axis, and act as sidewalls of the channels. The free space accommodates four DMF molecules and one H_2O molecule per formula unit. As illustrated in Figure 3a, these channels contain large diameter supercages (approximately 11 × 11 × 5 Å, based on the van der Waals radius of carbon atoms) and smaller windows (triangular, with an effective maximum dimension of about 8 Å), and thus are shaped dramatically differently from most other organometallic open frameworks, which usually have straight channels.[10]

IRPM-1 has demonstrated an unusually high thermal stability with respect to organometallic materials.[6] Thermogravimetric (TG) analyses were performed both in air and nitrogen atmosphere. A weight loss of $\approx$22.7% was observed at around 180 °C in both cases, which corresponds to the weight of all guest solvents (calcd 22.7%). Upon further heating in air, the desolvated samples showed no signs of decomposition up to 400 °C (see Supporting Information). The crystal structure of the evacuated sample of IRPM-1 was determined from a single crystal after the removal of all the guest molecules at 300 °C. The structure remained essentially unchanged.[9]

The adsorption and catalytic properties of IRPM-1 were examined under experimental conditions that are identical or similar to those employed with conventional zeolites. IRPM-1 displays a high sorption capacity for hydrocarbons, in accordance with the large channels observed. A pore volume of 0.25 $cm^3 g^{-1}$ is estimated for IRPM-1, based on the *n*-hexane ($p = 90$ Torr, $p/p_o = 0.48$) sorption capacity (17 wt %) at 30 °C. This volume is between those for the large-pore zeolite H-Y (0.32 $cm^3 g^{-1}$)[11a] and medium-pore zeolite H-ZSM-5 (0.19 $cm^3 g^{-1}$).[11b] At 80 °C, the sorption capacity for cyclohexane ($p = 55$ Torr, $p/p_o = 0.074$) of IRPM-1 is 19 wt% (corresponding to 2.4 molecules per cage, see Supporting Information), which exceeds that of H-Y (17 wt %), one of the most widely used large-pore zeolites; this demonstrates the high porosity of this material. The higher uptake of cyclohexane in IRPM-1, despite its lower pore volume, may be caused by more efficient packing of the molecules and/or their stronger interaction with the walls than in the case of H-Y. IRPM-1 is capable of adsorbing even larger hydrocarbon molecules: The sorption capacities at 80 °C for mesitylene (7 Å, $p = 1.4$ Torr, $p/p_o = 0.27$) and triisopropylbenzene (8.5 Å) are 17 and 12 wt%, respectively. From these pore-gauging data, a pore window with a maximum dimension of $\approx$8 Å is deduced. A series of sorption isotherms for *n*-hexane at various temperatures are shown in Figure 4a. IRPM-1 demonstrates remarkable stability on repetitive gas sorption and desorption trials, even at high temperatures up to at least 250 °C. To our knowledge, this study represents the first

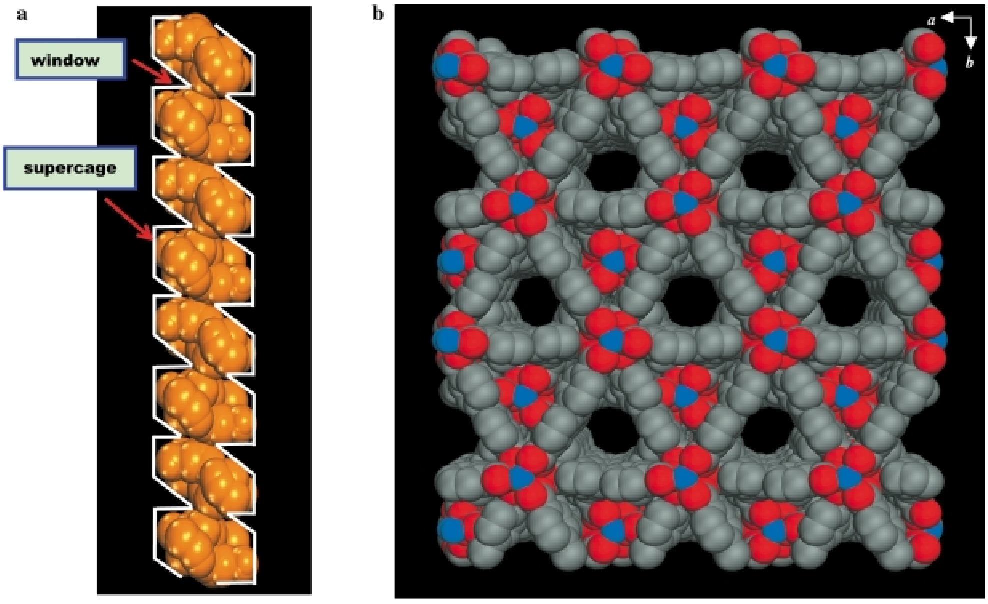


Figure 3. a) Side view (100) of one-dimensional channel in IRPM-1 with solvent molecules (gold). The narrower window has an effective maximum dimension of about 8 Å (calculated based on the van der Waals radius of carbon atoms), and the size of the supercage is 11 × 11 × 5 Å; b) top view (001) of the channels showing the window openings. The same labeling scheme as in Figure 2 is used here.

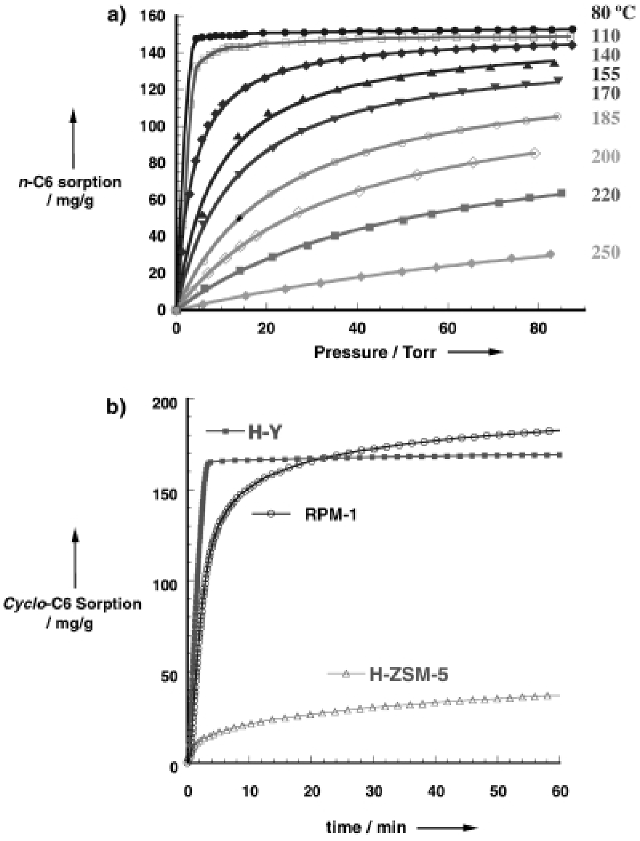
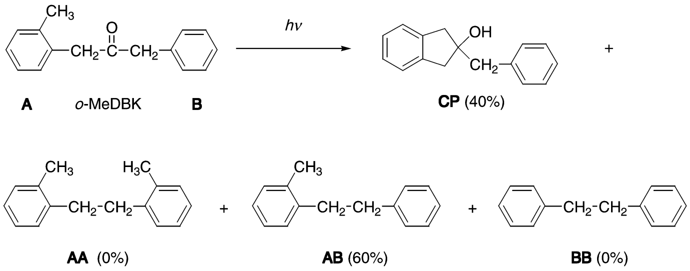


Figure 4. a) The *n*-hexane sorption isotherms of IRPM-1 measured at various temperatures; b) the cyclohexane uptake on H-Y, IRPM-1, and H-ZSM-5 as a function of sorption time, measured at 80 °C

investigation of zeolite-like sorption properties of a organometallic compound at temperatures above 100 °C. The heat of *n*-hexane sorption on IRPM-1 (66 kJ mol^{-1}) is considerably larger than that of H-Y (45.5 kJ mol^{-1}), and is close to that of H-ZSM-5 (68.8 kJ mol^{-1}).[12] The high isosteric heat, unexpected for the large pore size of IRPM-1, suggests the strong sorption of these hydrocarbons in the channels. Comparison of Henry constants[13] of *n*-hexane sorption isotherms measured at 250 °C: 0.0070, 0.0060, and 0.0038 Torr^{-1} for H-ZSM-5, IRPM-1, and H-Y, respectively, confirms the strong hydrocarbon molecule–pore-wall interaction in IRPM-1. The sorption rate can be used to estimate the size of the effective pore windows in porous materials.[2] As clearly seen in Figure 4 b, the sorption rate of cyclohexane in IRPM-1 is slower than that in H-Y, which contains 12-membered ring windows with openings of 7.4 × 7.4 Å, and faster than that in H-ZSM-5, which has 10-membered ring windows with apertures of 5.3 × 5.6 Å. The retardation in rate for IRPM-1 for the nearly spherical cyclohexane molecule (kinetic diameter 6.0 Å) suggests a minimum window dimension of ≤ 6 Å. Another interesting feature of IRPM-1 is that it is hydrophobic (1 wt % water sorption at 15 Torr at 30 °C). We attribute this hydrophobicity to the hydrophobic surface of the pores in IRPM-1, which are composed mainly of aromatic carbon and hydrogen atoms. It is also worth noting that IRPM-1 retains its porous framework against water vapor (15 Torr) in the temperature range of 30 to 80 °C.

IRPM-1 was examined for its ability to serve as a host for photochemical reactions.[14] The photochemistry of dibenzylketone (DBK) and its derivatives adsorbed on classical FAU and MFI zeolites has been thoroughly investigated.[3] *o*-MeDBK was selected as a test substrate in consideration of the specific shape of the 1D channels of IRPM-1. This molecule, when adsorbed on FAU or MFI zeolites, undergoes two photoreactions as shown in Scheme 1: 1) α cleavage, followed by loss of carbon monoxide to form a geminate pair of hydrocarbon radicals, which undergo geminate (product AB) or random combination (products **AA**, **AB**, and **BB**), and 2) an intramolecular hydrogen abstraction followed by cyclization to form a cyclopentanol, **CP**. Photolysis of *o*-MeDBK@IRPM-1 produced only **AB** with 60 % yield in reaction 1, which corresponds to a "cage effect" of 100 % (compared to a cage effect of 70 % for photolysis of *o*-MeDBK in NaX). The yield of **CP** is 40 % in reaction 2. This yield of **CP** is much higher than the values found in other zeolites (e.g. NaX) where the maximum yield is approximately 10 %. More significantly, only ≈50 % of the overall products could be extracted before breaking the IRPM-1 framework.[14] The remaining 50 % of the products were recovered only after IRPM-1 was immersed in water and completely converted into a nonporous 1D precursor, to give a 100 % mass balance (compared to ca. 60–70 % mass balance of NaX). The results from the photolysis demonstrate the unique potential of IRPM-1 to serve as "smart" porous host for "ship-in-bottle" photochemistry and other reactions.[14]



Scheme 1. The ship-in-bottle photochemical reaction.

In conclusion, IRPM-1 is a thermally stable, nanoporous, organometallic structure containing unique open channels formed by narrower windows and larger supercavities. It exhibits a high sorption capacity for large hydrocarbons over a wide temperature range. IRPM-1 also possesses superior size/shape selectivity for the in situ photolysis of *o*-MeDBK. Most notably, the 3D framework of IRPM-1 can be readily broken down into a nonporous structure under mild conditions. This would allow a full recovery of product molecules in a ship-in-bottle synthesis application. Such a structural conversion is completely reversible. The structural reversibility of IRPM-1 may provide significant economic and technical advantages for recyclable use of this material.

Experimental Section

Synthesis of ℝPM-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 ℝPM-1 in high yield (129.1 mg, ≈94.5 %). ℝPM-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 ℝPM-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 ℝPM-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 ℝPM-1, H-Y, and H-ZSM-5 samples were performed at 80 °C.

Photolysis of *o*-MeDBK: ℝPM-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 ℝPM-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] $[Co_3(bpdc)_3(bpy)]\cdot 4DMF\cdot H_2O$ (ℝPM-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 ℝPM-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 ℝPM-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 (ℝPM-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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