the large vesicles by the self-assembly of the entrapped polymer under conditions similar to those which led to the formation of the outermost vesicle. The variation in the number of layers depends on the polymer concentration and the size of the outermost vesicles. This formation process may resemble that occurring in small-molecule amphiphile systems.[9] The entrapped vesicles found previously[13] are probably formed by the same solution process.

The onions with spaces and solid onions described above are the latest additions to the family of block-copolymer vesicles (Table 1). The various vesicular structures can be controlled by thermodynamic parameters through such external factors as the diblock composition, the polymer concentration, the type of common solvents, the water content, and the presence of additives. The wall thickness, which affects the strength and the ability of small molecules to penetrate the vesicle walls, is tunable by varying the core-forming block length and the type of common solvent. The shorter the core-forming block, the thinner the wall. The size of the vesicles is mainly controlled by the swelling of the core and by the polymer concentration (Table 1).

Different vesicles are of interest for applications in drug delivery, encapsulation, or in cosmetics. Small vesicles with a narrow size distribution can be targeted at applications that involve size limitations, while the larger vesicles can increase the capacity of encapsulation. Entrapped vesicles may slow down the delivery of some of encapsulated species, but may not be able to function as time-release devices because they lack multiple layers. The presence of chambers between layers allows the onions with spaces to be considered as potential time-release devices which would function by the progressive breaking or erosion of the layers, or by gradual diffusion through the walls. The newly found onions with spaces are unique for block copolymers and extend the range and the control of vesicular structures.

Experimental Section

Block copolymers, PS_{132}-*b*-P(*t*BuA)$_{20}$ (*t*BuA: *tert*-butyl acrylate) and PS_{260}-*b*-P4VP$_{70}$, were synthesized by anionic polymerization.[5] After the hydrolysis of the P(*t*BuA) blocks, the PAA systems were fractionated to remove any homopolystyrene;[5] P4VP blocks were quaternized by using decyl iodide.[14] Onions with spaces were prepared by dissolving 10 wt % PS_{132}-*b*-PAA_{20} in dioxane, then adding water over a three-month period until the water content was 40 wt %, and finally freeze-drying a drop of the colloidal solution on copper grids for TEM observation.[5] Solid onions were prepared by dissolving 1 wt % PS_{260}-*b*-P4VPDecI$_{70}$ in THF, then adding water dropwise at a rate of 1 wt % per minute until the water content was 50 wt %, and finally dialyzing the resulting solution against water. A similar preparation method was also used for preparing other types of vesicles (Table 1) and has been described.[13, 14]

Received: March 27, 2000
Revised: May 16, 2000 [Z14898]

[1] a) L. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728; b) L. Zhang, K. Yu, A. Eisenberg, *Science* **1996**, *272*, 1777; c) L. Zhang, C. Bartels, Y. Yu, H. Shen, A. Eisenberg, *Phys. Rev. Lett.* **1997**, *79*, 5034; d) K. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 3509; e) K. Yu, C. Bartels, A. Eisenberg, *Macromolecules* **1998**, *31*, 9399; f) N. S. Cameron, M. K. Corbierre, A. Eisenberg, *Can. J. Chem.* **1999**, *77*, 1311.

[2] a) J. P. Spatz, S. Mößmer, M. Möller, *Angew. Chem.* **1996**, *108*, 1673; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1510; b) J. Ding, G. Liu, *Macromolecules* **1997**, *30*, 655; c) G. Liu, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200; d) J. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **1998**, *120*, 9533; e) A. V. Kabanov, T. K. Bronich, V. A. Kabanov, K. Yu, A. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 9941; f) S. A. Jenekhe, X. L. Chen, *Science* **1998**, *279*, 1903; g) J. J. L. M. Cornelissen, M. Fischer, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **1998**, *280*, 1427; h) E. Kramer, S. Forster, C. Goltner, M. Antonietti, *Langmuir* **1998**, *14*, 2027; i) R. R. Netz, J. F. Joanny, *Macromolecules* **1998**, *31*, 5123; j) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*, 1111; k) R. R. Netz, *Europhys. Lett.* **1999**, *47*, 391; l) A. Harada, K. Kataoka, *Science* **1999**, *283*, 65; m) Z. Li, Y. Liang, F. Li, *Chem. Commun.* **1999**, *16*, 1557; n) K. Fischer, M. Gerle, M. Schmidt, *Polym. Mater. Sci. Eng.* **1999**, *80*, 133.

[3] a) B. M. Discher, Y. Y. Won, D. S. Ege, J. C. M. Lee, F. S. Bates, D. E. Discher, D. A. Hammer, *Science* **1999**, *284*, 1143; b) B. M. Discher, Y. Y. Won, J. C. M. Lee, H. Bermudez, F. S. Bates, D. A. Hammer, D. E. Discher, *Biophys. J.* **2000**, *78(1)*, 1950.

[4] *Vesicles* (Ed.: M. Rosoff), Dekker, New York, **1996**, Chap. 9 – 10.

[5] a) H. Shen, A. Eisenberg, *J. Phys. Chem. B* **1999**, *103*, 9473; b) H. Shen, A. Eisenberg, *Macromolecules* **2000**, *33*, 2561.

[6] J. Ding, G. Liu, *J. Phys. Chem. B* **1998**, *1023*, 6107.

[7] a) D. J. Kinning, K. I. Winey, E. L. Thomas, *Macromolecules* **1988**, *21*, 3502; b) E. L. Thomas, J. R. Reffner, J. Bellare, *Colloq. Phys.* **1990**, *C7* (363), 15.

[8] a) K. Prochazka, T. J. Martin, S. E. Webber, P. Munk, *Macromolecules* **1996**, *29*, 6526; b) M. R. Talingting, P. Munk, S. E. Webber, Z. Tuzar, *Macromolecules* **1999**, *32*, 1593.

[9] a) A. Sein, J. B. F. N. Engberts, *Langmuir* **1993**, *9*, 1714; b) D. Danino, Y. Talmon, R. Zana, *J Colloid Interface Sci.* **1997**, *185*, 84; c) M. Bergmeier, M. Gradzielski, H. Hoffmann, K. Mortensen, *J. Phys. Chem. B* **1999**, *103*, 1605.

[10] a) F. Gauffre, D. Roux, *Langmuir* **1999**, *15*, 3738; b) O. Regev, F. Guillemet, *Langmuir* **1999**, *15*, 4357.

[11] J. Zipfel, P. Lindner, M. Tsianou, P. Alexandridis, W. Richtering, *Langmuir* **1999**, *15*, 2599.

[12] J. Ding, G. Liu, *Macromolecules* **1999**, *32*, 8413.

[13] Y. Yu, A. Eisenberg, *J. Am. Chem. Soc.* **1997**, *119*, 8383.

[14] H. Shen, L. Zhang, A. Eisenberg, *J. Am. Chem. Soc*. **1999**, *121*, 2728.

Hydrogen-Bonded Hexamolybdenum Clusters: Formation of Inorganic – Organic Networks**

Nicholas Prokopuk, Charles S. Weinert, David P. Siska, Charlotte L. Stern, and Duward F. Shriver*

The increasing importance of solid materials in catalysis, nonlinear optics, chemical sensors, separation technology, and electronics has created a demand to control the chemical and physical properties of solids.[1] Solution chemists typically approach this problem by synthesizing discrete molecules that spontaneously self-assemble into extended arrays.[2] The significance and impact of self-assembly are demonstrated by the porous zeolites that combine the acidic properties of the aluminosilicate with the channels and pores of the

[*] Prof. D. F. Shriver, N. Prokopuk, C. S. Weinert, D. P. Siska, C. L. Stern
Department of Chemistry
Northwestern University
2145 Sheridan Rd., Evanston, IL 60208 (USA)
Fax: (+1) 847-491-7713
E-mail: shriver@chem.nwu.edu

[**] This work was supported by the National Science Foundation (grant CHE-9417250).

  1433-7851/00/3918-3312 $ 17.50+.50/0

supramolecular structure to generate catalytically important materials.[3] Recently molecular self-assembly has been achieved by hydrogen bonds between organic components.[4] An advantage of this approach is that hydrogen bonds are relatively easy to direct.[5] In addition, the growth of crystals with minimal defects is aided by the ease with which hydrogen bonds are broken and reformed. Together, these properties facilitate the synthesis of crystalline materials with molecular components in controlled geometric orientations. By increasing the number of intermolecular hydrogen bonds, organic solids with large void volumes and structural integrity have been prepared.[6] Despite the promise of diverse electronic, magnetic, and catalytic properties, few transition metal cluster compounds have been linked directly into extended arrays through proton donor–acceptor bonds.[7]

Herein we describe the synthesis and self-assembly of hydrogen-bonded organic–inorganic networks containing the octahedral cluster $\{Mo_6Cl_8\}^{4+}$. Reaction of the sodium or sodium cryptand salt of $[Mo_6Cl_8(OCH_3)_6]^{2-}$ with six equivalents of p-$HOC_6H_4CONH_2$ in CH_3OH results in the formation of the new cluster **1**. A shift in ν(C–O) from 1213 cm^{-1} for the free ligand p-$HOC_6H_4CONH_2$ to 1240 cm^{-1} for **1** indicates that the p-$OC_6H_4CONH_2^-$ ligand coordinates to the $\{Mo_6Cl_8\}^{4+}$ core through the oxygen atom of the phenoxide group. This bonding mode disposes the amide moieties away from the cluster core and the self-assembly of **1** is accomplished by intermolecular hydrogen bonding between these amide moieties.

$[Mo_6Cl_8(p\text{-}OC_6H_4CONH_2)_6]^{2-}$ **1**

The sodium cryptand salt of **1**, crystallizes from a mixture of $DMF/H_2O/CH_3OH/Et_2O$[8] or DMF/Et_2O[9] yielding different structures, **1A** and **1B**, respectively. In both structures the $\{Mo_6Cl_8\}^{4+}$ core is virtually identical to previously synthesized compounds containing the molybdenum chloride cluster.[10] An interesting feature of these structures is the influence of hydrogen bonding on the packing of the cluster anions and the anion–cation interactions. In **1A**, the cluster anions are arranged in layers with four p-$OC_6H_4CONH_2^-$ ligands of each cluster hydrogen-bonded to four adjacent clusters (Figure 1a). Each amide group acts as both a proton donor and proton acceptor within the cluster layer. The N···O distances range from 2.857 to 2.967 Å, in accord with the donor–acceptor distances of hydrogen-bonded amide groups.[11] The lamella of **1A** are connected through hydrogen bonds between the two remaining p-$OC_6H_4CONH_2^-$ ligands which are not involved in intraplanar hydrogen bonding but instead form donor–acceptor bonds with the p-$OC_6H_4CONH_2^-$ ligands in adjacent layers, resulting in a three-dimensional hydrogen-bonded network (Figure 2a). The sodium cryptand ions occupy the space between the cluster layers, leaving small channels running parallel (5×7 Å) and perpendicular (6×8 Å) to the lamella which are filled with solvent molecules.

The crystallization of $(cryptNa)_2$**1** from DMF/Et_2O mixtures with higher concentrations of $(crypNa)_2$**1** or Et_2O/DMF ratios provides structure **1B** with **1** arranged in layers. At lower concentrations of $(cryptNa)_2$**1** or lower Et_2O/DMF ratios yellow plate crystals formed which have a different unit cell than **1B**, but the crystals were not of a suitable quality for a full structure determination: space group: $P2_1/n$ (no. 14), $a = 22.736(2)$, $b = 25.551(2)$, $c = 35.028(3)$ Å, $\beta = 91.551(2)^\circ$. The resulting intraplanar hydrogen-bonded scheme is similar to that of **1A** (Figure 1b). A significant difference in the packing of the clusters is the spacing of the $\{Mo_6Cl_8\}^{4+}$ units within the planes which are separated by 17 Å in **1A** compared to 10 Å for **1B**. The packing of **1** in **1B** causes the $(cryptNa)^+$ counterions to crowd together and forces the molybdenum cluster layer spacing to 22 Å compared to 11 Å for **1A** (Figure 2b). A result of the tighter packing of the cluster anions within a layer and the increased layer spacing for **1B** is that the p-$OC_6H_4CONH_2^-$ ligands form interplanar hydrogen bonds that are too far apart to interconnect the cluster layers. Thus, the hydrogen bonding extends in only two directions in **1B**, leaving void space between the layers, which is occupied by solvent molecules.

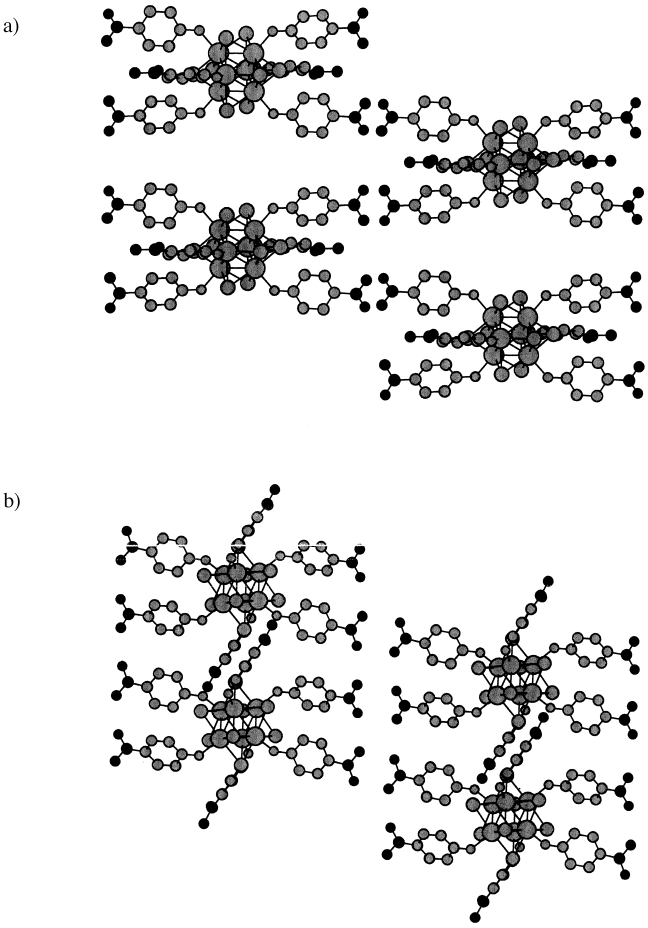


Figure 1. Planes of $[Mo_6Cl_8(OC_6H_4CONH_2)_6]^{2-}$ ions in **1A** (a) and **1B** (b). The amide groups are in black and the rest of the cluster is in gray.

The photophysical and redox properties of the $\{Mo_6Cl_8\}^{4+}$ core make these extended structures potential candidates for solar energy storage.[12] In this connection, the octahedral Group 6 metal halide clusters have unusually long-lived excited states and a red-shifted luminescence spectrum.[13] Composite materials containing $\{Mo_6Cl_8\}^{4+}$ clusters imbedded in a polymer matrix or oxide support have been prepared[14] and the excited state $\{Mo_6Cl_8\}^{4+}$ has been used to facilitate the oxidation of alkenes and alcohols.[14b, 15] The emission spec-

  1433-7851/00/3918-3313 $ 17.50+.50/0

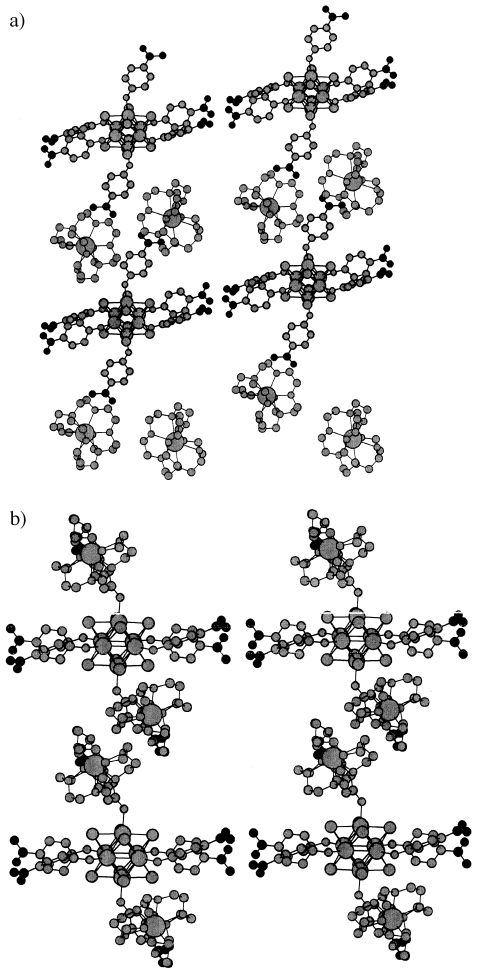


Figure 2. View of **1A** (a) and **1B** (b) parallel to the cluster planes. The solvent molecules are omiited for clarity. Amide groups are in black, and the cluster and cryptNa are in gray.

trum of crystalline **1A** exhibits a red-shifted luminescence (Figure 3), which is similar to the emission spectrum of $(cryptNa)_2$**1** in DMF and that of the all chloro cluster $[Mo_6Cl_8Cl_6]^{2-}$.[13a] Similar spectra are observed for crystals of **1B**. These data demonstrate that the photophysical properties of the molecular components are retained in these supramolecular solids, thus the self-assembly of $\{Mo_6Cl_8\}^{4+}$ clusters into extended arrays incorporates a known photocatalyst into a solid with specific pore sizes and channels, and may lead to a new generation of heterogeneous catalysis.

Experimental Section

Na_2**1**: A solution of *p*-$HOC_6H_4CONH_2$ (52 mg, 0.381 mmol in 9 mL dry methanol) was added to a solution of $Na_2[Mo_6Cl_8(OCH_3)_6]$ (50 mg, 0.046 mmol in 5 mL dry methanol) under a flow of nitrogen, allowed to stir for 12 h, and then concentrated to about 1 mL under vacuum. Dry diethyl ether was added dropwise to the stirred solution until precipitation of the yellow solid was complete. The solid was isolated by filtration, washed with dry diethyl ether (5 mL), and dried under vacuum. Total yield 35 mg (44%). Elemental analysis calcd for $C_{42}H_{36}N_6O_{12}Cl_8Mo_6Na_2$ (%): C 29.29, H 2.11, N 4.88; found: C 31.14, H 2.59, N 4.25. The sodium cryptand salt was prepared by adding two equivalents of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane to the reaction mixture.

Received: April 25, 2000 [Z15038]

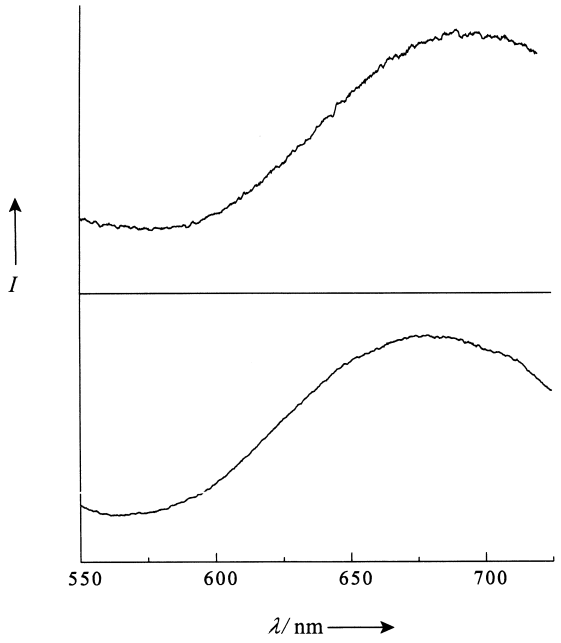


Figure 3. Emission spectra of $(cryptNa)_2[Mo_6Cl_8(OC_6H_4CONH_2)_6]$ in DMF (upper) and crystalline state (lower). Excitation wavelength is 385 nm.

[1] a) H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe, *J. Am. Chem. Soc.* **1996**, *118*, 368; b) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981; c) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *271*, 49; d) J. Real, E. Andres, M. Munoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* **1995**, *268*, 265; e) H. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn, *Science* **1993**, *261*, 447.

[2] a) G. Whitesides, J. Mathias, C. Seto, *Science* **1991**, *254*, 1312; b) A. Stein, S. Keller, T. Mallouk, *Science* **1993**, *259*, 1558.

[3] a) Q. Huo, D. Margolese, U. Ciesla, P. Feng, T. Gier, P. Sieger, R. Leon, P. Petroff, F. Schuth, G. Stucky, *Nature* **1994**, *368*, 317; b) C. Dresge, M. Leonowicz, W. Roth, J. Vartuli, J. Beck, *Nature* **1992**, *359*, 710; c) M. Davis, C. Saldarriaga, C. Montes, J. Garces, C. Crowder, *Nature* **1988**, *331*, 698; d) M. Estermann, L. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, *Nature* **1991**, *352*, 320.

[4] a) M. Hollingsworth, M. Brown, B. Santarsiero, J. Huyffman, C. Goss, *Chem. Mater.* **1994**, *6*, 1227; b) G. Whitesides, E. Simanek, J. Mathias, C. Seto, D. Chin, M. Mammen, D. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37; c) G. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441; d) A. Burrows, C. Chan, M. Chowdhry, J. McGrady, D. Mingos, *Chem. Soc. Rev.* **1995**, 329.

[5] a) W. Hamilton, J. Ibers, *Hydrogen Bonding in Solids*, W. A. Benjamin, New York, **1968**; b) M. Joesten, L. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, **1974**.

[6] X. Wang, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1994**, *116*, 12119.

[7] a) S. B. Copp, S. Subramanian, M. J. Zaworotko, *Angew. Chem.* **1993**, *105*, 755; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 706; b) S. Copp, K. Holman, J. Sangster, S. Subramanian, M. Zaworotko, *J. Chem. Soc. Dalton Trans.* **1995**, 2233.

[8] Crystal structure analysis of $(cryptNa)_2$**1**$\cdot 2DMF \cdot 6H_2O \cdot 4CH_3OH$ (**1A**): space group *C*2/*c* (no. 15), $a = 40.2779(2)$, $b = 12.3127(2)$, $c = 24.9961(4)$ Å, $\beta = 106.814(1)^\circ$, $V = 11956.7(3)$ Å^3, $\rho = 1.522$ g cm^{-3}, 14840 unique reflections, 5467 observed ($I > 3\sigma I$), $R = 0.072$, $R_w = 0.088$.[9b].

[9] a) Crystal structure analysis of $(cryptNa)_2$**1**$\cdot 6DMF$ (**1B**): space group $P\bar{1}$ (no. 2, $a = 9.9582(7)$, $b = 15.1884(10)$, $c = 20.819(1)$ Å, $\alpha = 96.3054(12)$, $\beta = 100.6521(12)$, $\gamma = 99.6380(12)^\circ$, $V = 3018.5(3)$ Å^3, $\rho = 1.505$ g cm^{-3}, 13465 unique reflections, 10208 observed ($I > 3\sigma I$), $R = 0.050$, $R_w = 0.130$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary

  1433-7851/00/3918-3314 $ 17.50+.50/0

publication no. CCDC-142907 (**1A**) and CCDC-142908 (**1B**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] N. Perchenek, A. Simon, *Z. Anorg. Allg. Chem.* **1993**, *619*, 98.

[11] a) S. Weinstein, L. Leiserowitz, *Acta Crystallogr. Sect. B* **1980**, *36*, 1406; b) L. Leiserowitz, M. Tuval, *Acta Crystallogr. Sect. B* **1978**, *34*, 1230.

[12] H. B. Gray, A. W. Maverick, *Science* **1981**, *214*, 1201.

[13] a) D. G. Nocera, H. B. Gray, *J. Am. Chem. Soc.* **1984**, *106*, 824; b) A. W. Maverick, H. B. Gray, *J. Am. Chem. Soc.* **1981**, *103*, 1298.

[14] a) L. M. Robinson, D. F. Shriver, *Coord. Chem. Rev.* **1996**, *37*, 119; b) J. A. Jackson, M. D. Newsham, C. Worsham, D. G. Nocera, *Chem. Mater.* **1996**, *8*, 558; c) J. H. Golden, H. Deng, F. J. DiSalvo, J. M. Frechet, P. M. Thompson, *Science* **1995**, *268*, 1463.

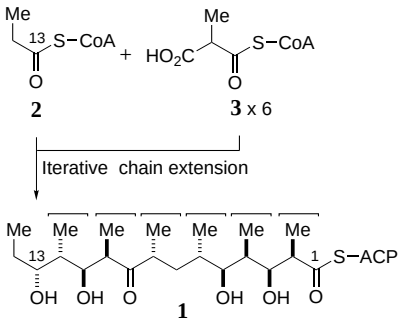
[15] J. A. Jackson, R. D. Mussell, D. G. Nocera, *Inorg. Chem.* **1993**, *32*, 4643.

A Combinatorial Approach to Polyketide-Type Libraries by Iterative Asymmetric Aldol Reactions Performed on Solid Support**

Ian Paterson,* Monica Donghi, and Kai Gerlach

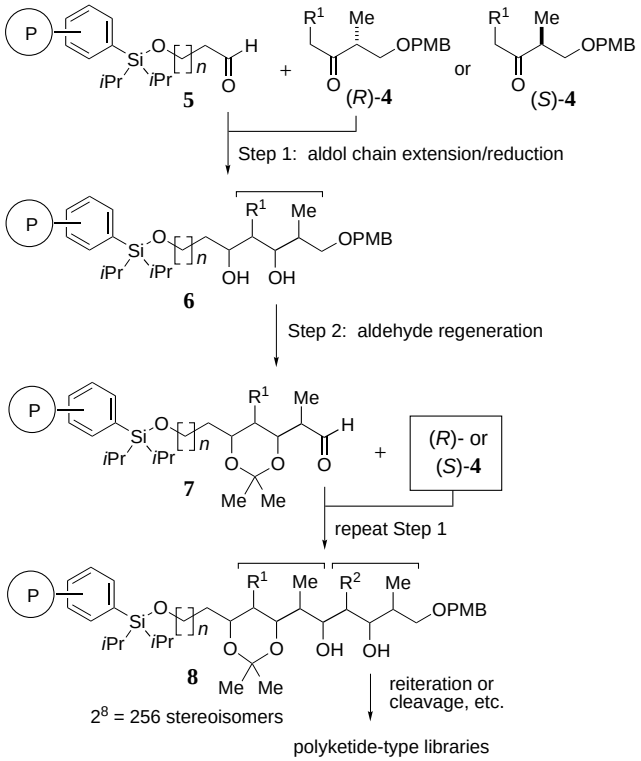
The polyketides represent a rich reservoir of structurally complex, bioactive, natural products, with many having therapeutic importance (as antibiotics, anticancer agents, antifungals, antiparasitics, immunosuppressants, and cardiovascular agents).[1] As a source of pharmaceutically relevant, molecular diversity, they are attractive targets for developing a combinatorial approach to library generation, particularly if this can be accomplished on solid phase, where purification procedures are simplified and automation becomes feasible. Solid-phase synthesis, routinely applied to the preparation of peptides and oligonucleotides, has been adapted in recent years to oligosaccharides and small molecules.[2] However, the synthesis of elaborate polyketide sequences (e.g. **1**, the acyclic precursor of the erythromycin antibiotics, Scheme 1) involving the controlled formation of multiple stereocenters remains a challenge,[3, 4] requiring the transfer of more sophisticated chemistry for achieving asymmetric carbon–carbon formation to solid phase.

In the archetypal case of erythromycin, the heptaketide precursor **1** is assembled biosynthetically by the polyketide synthase from a starter unit **2** and six extender units **3**, with the growing chain bound to the acyl carrier protein (ACP).[5, 6] By mimicking this processive mechanism in the laboratory using a greater variety of chain extending units, a combinatorial synthetic approach might be developed, leading to much greater molecular diversity. As part of studies towards this goal,[3] herein we demonstrate the utility of the chiral ketones **4** (see Scheme 2) for performing efficient polyketide synthesis on solid support, providing wide-ranging opportunities for structural and stereochemical diversification.



Scheme 1. Biosynthesis of the heptaketide precursor **1** of erythromycin. ACP = acyl carrier protein. CoA = coenzyme A.

In this new approach to expanding polyketide diversity (Scheme 2), a suitable aldehyde starter unit, such as **5**, is attached to a polystyrene support (which functions as a surrogate for the ACP) through a silyl ether linker. By using stereoregulated aldol chemistry, employing the reagents (*R*)- or (*S*)-**4** for chain extension and a subsequent ketone reduction to produce the 1,3-diol **6** (Step 1), followed by regeneration of the aldehyde functionality in **7** (Step 2), repetition provides the more elaborate 1,3-diol **8**. This leads progressively to the synthesis of polyketide-type sequences of



Scheme 2. Solid-phase synthesis of polyketide-type libraries using iterative chain extension of resin-supported aldehydes **5** and **7** with ketones (*R*)- or (*S*)-**4**. P = polystyrene resin (styrene–1% divinylbenzene, 200–400 mesh), PMB = *p*-methoxybenzyl.

[*] Dr. I. Paterson, Dr. M. Donghi, Dr. K. Gerlach
University Chemical Laboratory
Lensfield Road, Cambridge, CB2 1EW (UK)
Fax: (+44) 1223-336362
E-mail: ip100@cus.cam.ac.uk

[**] We thank the European Commission (TMR Network ERB-FMR XCT 96-0011 and IHP Network HPRN-CT-2000-00014), EPSRC, Pfizer, and Merck for support.

  1433-7851/00/3918-3315 $ 17.50+.50/0