Unique Formation of a Crystal Phase Containing Cyclic Oligomers and Helical Polymers of the Same Monomeric Fragment

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Over the last years we have been actively working in the field of metal diazolates, with the aim of finding efficient and selective catalysts for oxidation.[1] In our studies, we tackled the problem of structurally characterizing binary species, precursors of the catalytic species, which are only obtained as fine, insoluble, powdered samples. An appropriate ab initio structure determination technique from X-ray powder diffraction (XRPD) data has been successfully developed,[2] which has led to the complete characterization of, among others, α-[{Cu(pz)}$_n$], β-[{Cu(pz)}$_n$], [{Ag(pz)}$_n$], [{Ag(pz)}$_3$], [{Ag(dmpz)}$_3$], [{Cu(dmnpz)}$_3$], [{Ag(imz)}$_n$], and [{Ag(pymo)}$_6$] (Hpz = pyrazole, Hdmpz = 3,5-dimethylpyrazole, Hdmnpz = 3,5-dimethyl-4-nitropyrazole, Himz = imidazole, Hpymo = 2-hydroxypyrimidine).[3, 4]

The many interesting features displayed by some of these compounds include the existence of different cyclic oligomers and polymeric species for the same monomeric unit and ready accessibility by selective synthetic routes. To our surprise, upon hydration/dehydration the [{Ag(pymo)}$_6$] hexamer[4] reversibly transforms into the [{Ag(pymo)}$_n$]$\cdot$2H_2O polymer.[5] Here we report on the synthesis and XRPD structural characterization of the copper analogue.[6]

Treatment of a hot solution in ethanol of an equimolecular amount of [Cu(CH_3CN)$_4$][BF_4] and Hpymo with NEt_3 causes the sudden precipitation of a yellow microcrystalline powder, which was analyzed to be [Cu(pymo)] (**1**). This very insoluble species could only be characterized by IR spectroscopy[7] and, thanks to its satisfactory degree of crystallinity, by the newly emerging technique of ab initio XRPD.[8] At variance with the spectrum observed for [{Ag(pymo)}$_6$] ($\tilde{\nu}_{CO} = 1618\ \text{cm}^{-1}$),[4] the IR spectrum of **1** evidences at least two different CO environments ($\tilde{\nu}_{CO} = 1614$ and $1590\ \text{cm}^{-1}$), which suggests a more complex structure. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of **1** under an N_2 atmosphere revealed no phase transitions nor solvent desorption up to about 350 °C, where decomposition to metallic copper occurred. We have tried to synthesize different crystal phases by changing the synthetic method or by applying heat or pressure (up to 1 GPa for 24 h), but we always observed the XRPD pattern of **1**. Solubilization of **1** was only possible by reaction with PPh_3 in CH_2Cl_2 to afford the monomeric complex [Cu(PPh_3)$_2$(pymo)].[9]

The XRPD pattern, collected in the range $4 < 2\theta < 94°$ on an annealed sample of **1** (3 h at 200 °C under N_2), was fully indexed with TREOR[10] [monoclinic P, $a = 8.63$, $b = 13.81$, $c = 9.81$ Å, $\beta = 112.5°$, $V = 1080$ Å^3, $M(20)$[11] = 19, $F(20)$[12] = 36 (0.012, 43)]. Unfortunately, the 367 extracted intensities (with $2\theta < 64°$) did not afford any reasonable Patterson map, nor were direct methods successful in offering a suitable structural model in the "compatible" space groups. Only the search for higher symmetry metrics and supercells[13] evidenced a possible relationship between the available cell and a trigonal/hexagonal cell with a much larger (6×) cell volume (ca. 6500 Å^3). Suddenly, we recognized that our problem fell into one of the special cases studied by Mighell and Santoro.[14] They foresaw that different lattices with different reduced cell volumes may afford identical peak positions (in the monodimensional 2θ space), leading to ambiguous cell choices (clearly, such ambiguity does not exist in three-dimensional single-crystal diffractometry). Therefore, a new R-centered cell ($a = 27.58$, $c = 9.81$ Å) was used (with $Z = 54$!). However, owing to the 1-D projection of the reciprocal space inherent in powder experiments, the Laue group was still uncertain and a number of possible space groups, and therefore a multitude of structure-solution processes, had to be considered ($R\bar{3}m$ or one of its subgroups).

No matter which space group was chosen, the approximate locations of the metal atoms could be derived by Patterson and/or direct methods. This showed that the copper atoms were roughly arranged in columns running parallel to c, with interatomic distances of about $c/3$. After optimization of lattice parameters, background, and peak shape by the Le Bail technique,[15] refinement of the locations of the copper atoms in the space groups $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$ versus the high-angle data ($2\theta > 30°$) clearly revealed $R\bar{3}$ as the best candidate (with three crystallographically independent copper atoms), while a refinement in $R3$ was found to be unstable. A significant asymmetrization of the initial Cu$\cdots$Cu contacts was achieved; two interactions are markedly shorter than the third (ca. 3 versus ca. 4 Å).

These distances are much shorter than those expected for metals bridged by N,N'-pymo ligands (ca. 5.5–6.0 Å) and similar to those found for many unsupported Cu$\cdots$Cu intermolecular interactions; therefore, the ligands must be roughly oriented in the ab plane. Analysis of the possible connectivity patterns (consistent with linearly bicoordinated metals) derived by joining metals which are about 5.7 Å apart in the space group $R\bar{3}$ revealed the existence of heterochiral helices (winding up about the 3_1 and 3_2 axes), leaving holes suitable for a cyclic hexamer of $\bar{3}$ crystallographic symmetry. Consistently, a difference Fourier map confirmed the presence of peaks near the positions expected for the nitrogen atoms from the above topological analysis. The remaining atoms were then determined by a combination of several difference Fourier maps and geometrically restrained Rietveld refinements. However, owing to the non-holoedric nature of the Laue group of **1**, the initial location of the C, N, and O atoms was of poor quality and the refinements were slow and rather unstable. Therefore, an

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additional intermediate geometry optimization was performed (to minimize the overall (steric + packing) energy of the crystal) with the aid of a locally developed molecular mechanics program capable of dealing with, inter alia, polymers.[16] Our experience[17] has shown that the imperfect parametrization of the metal force field only marginally affects the geometry of the crystal packing once the positions of the metal atoms are fixed in their experimental locations. Indeed, feeding the optimized coordinates into the program GSAS[18] afforded an R_{wp} value as low as 0.09, which was a very good starting point for the final refinement against powder data only (with some intramolecular restraints for the pymo rings).

The crystal structure determination[19] surprisingly led to the formulation of **1** as a crystal phase containing separate hexamers (Figure 1a) and helical polymers (Figure 1b) in a 1:2 ratio. The digonal copper atoms are bound to bidentate *N,N'*-pymo ligands (N7-Cu1-N8 177(1), N24-Cu13-N26 174(1), N25-Cu12-N27 175(1)°).[20] Therefore, **1** is better described as a $1/6[\{Cu(pymo)\}_6]\cdot 1/n[\{Cu_2(pymo)_2\}_n]$ adduct (stoichiometrically consistent with the original [Cu(pymo)] formulation). The helices contain six Cu(pymo) monomers per turn (with a pitch of 9.79 Å)—that is, they possess rare (noncrystallographic) 6_1 (or 6_5) character[21]—and are heavily compenetrated; each helix is trigonally surrounded by three helices of opposite chirality (Figure 2). This trigonal packing (hexagonality value $H = 1.73$), which is typical for heterochiral helices, is indeed favored by large compenetration.[22] It is noteworthy that adjacent helices are displaced by about one-third (and not one-half) of their pitch. In the space left by the packing of six adjacent helices, a closed cavity is formed (Figure 3) which perfectly matches the size and shape of $[\{Cu(pymo)\}_6]$.[23] Thus, once the hexamers fill this space, there are no other (solvent-accessible) holes in the packing of the helices in **1**. The helical nature of the polymeric portion of **1** closely ressembles that of poly(*m*-phenylene)[24] and the polyheterocyclic strand recently reported by Lehn et al.[25] Our observations thus confirm that *meta*-coordinated aromatic moieties (directly linked or connected by linear spacer(s) such as Cu^I atoms in **1**) favor helicity in their open oligomers and polymers.[26]

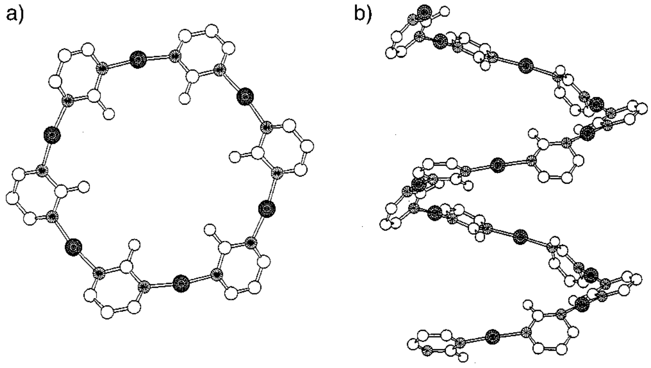

Figure 1. Molecular drawing of a) the $[\{Cu(pymo)\}_6]$ hexamer and b) a portion of the infinite helix of $[\{Cu_2(pymo)_2\}_n]$.

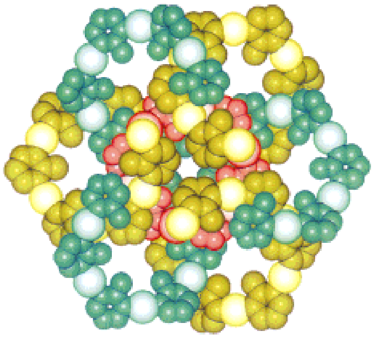

Figure 2. A packing diagram of compound **1**, viewed along [001]. Helices of different polarity are depicted by different colors (yellow and green). Within this trigonal packing of helices, the closed cavity about the origin hosts the $[Cu(pymo)]_6$ hexamer (red).

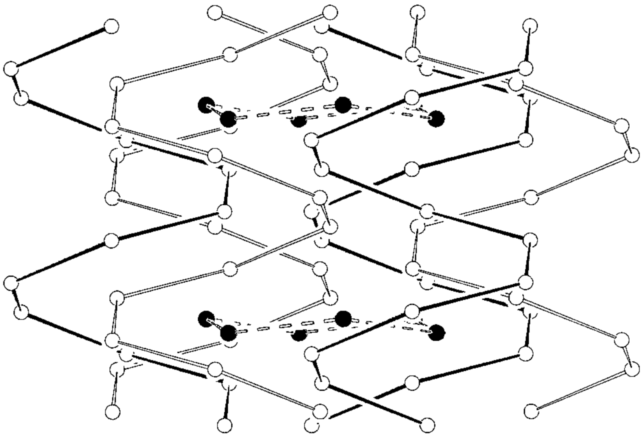

Figure 3. Schematic drawing of the *pseudo*-channel, defined by six adjacent helices, containing the $[Cu(pymo)]_6$ hexamers, viewed along [010] (the vertical axis is [001], black and white helices have opposite polarity). This channel periodically widens about the hexamers and shrinks above and below them.

Interestingly, all ligand-unsupported Cu ··· Cu contacts between adjacent helices (Cu12 ··· Cu13 2.69(1) Å) are much shorter than those between helices and oligomers (Cu1 ··· Cu13 2.96(1), Cu1 ··· Cu12 4.36(1) Å), and fall well below the range observed in a number of related compounds.[3a] To our knowledge these contacts are the shortest ever observed in the absence of bridging ligands. This indicates either that the coupling of helices about these hinges might be the driving force for formation of the cavities or that the intrinsic size of the oligomers forces the helices to couple. This coupling offers evidences for a correlation between intermetallic distances and the color of the species: All analogues of general formulae $[\{CuL\}_n]$ (L = a monoanionic diazolate) are white and show longer (>2.96 Å) distances.[3a] In contrast, **1** is yellow—like $[\{Cu(pz^*)\}_3]$ (Hpz* = 2-[3(5)-pyrazolyl]pyridine; 2.90 Å) and $[\{Cu(bmip)\}_2][ClO_4]_2$ (bmip = 2,6-bis(1-methylimidazol-2-yl)pyridine; 2.82 Å)[27]—while the $[\{Cu(dpad)\}_3]$ (dpad = 1,5-ditolyl-1,4-pentaazadien-3-ide) trimer is red even in solution due to the presence of very short intramolecular contacts (2.35 Å).[28]

With respect to metal diazolates, our structural study is novel in that 1) nondegenerate (i.e., non-2_1) helices were observed for the first time, and 2) the $[Cu(pymo)]_6$ unit has a unique, high-symmetry (S_6) conformation.[4, 29] Above all, the fact that a polymer and one of its cyclic oligomers coexist in an ordered fashion in the same crystal lattice has never been reported before in any field.[30] Since such coordination polymers possessing labile metal–nitrogen bonds rarely dissolve without depolymerization, it is very unlikely that hexameric and polymeric molecules of **1** exist in solution. Thus, the rapid and unique formation of solid **1** can only be explained by a very selective self-recognition process at the crystal/solution interface promoting the actual crystal phase, but not the individual separate end members. This means that the nucleation process simultaneously controls the kinetics of the crystallization and the nature of the products. Hence, mixed phases similar to **1** may not be rare in the realm of "catenated" coordination compounds if a suitable nucleus is formed.[31]

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[1] G. LaMonica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151–238, and references therein.

[2] N. Masciocchi, A. Sironi, *J. Chem. Soc. Dalton Trans.* **1997**, 4643–4650.

[3] N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia, G. LaMonica, *J. Am. Chem. Soc.* **1994**, *116*, 7668–7676; N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia, G. LaMonica, *J. Chem. Soc. Dalton Trans.* **1995**, 1671–1675; N. Masciocchi, P. Cairati, A. Sironi, *Powder Diffr.* **1998**, *13*, 35–40; G. A. Ardizzoia, S. Cenini, G. LaMonica, N. Masciocchi, A. Maspero, M. Moret, *Inorg. Chem.* **1998**, 4284–4292.

[4] N. Masciocchi, E. Corradi, M. Moret, G. A. Ardizzoia, A. Maspero, G. LaMonica, A. Sironi, *Inorg. Chem.* **1997**, *36*, 5648–5650.

[5] M. Quiros, *Acta Crystallogr. Sect. C* **1994**, *50*, 1236–1238.

[6] We have also prepared the "[Au(pymo)]" analogue, but, despite its evident polycrystalline nature, we were not able to determine its structure from the rather complex XRPD pattern. However, we can easily rule out its being isomorphous with [{Ag(pymo)}$_6$] or **1**.

[7] IR spectral data for **1** (nujol): $\tilde{\nu} = 1614$ (s), 1590 (s), 1368 (s), 1356 (s), 1280 (s), 1268 (s), 1130 (m), 1089 (m), 1043 (m), 1002 (w), 973 (w), 798 (s), 771 (m), 764 cm^{-1} (m).

[8] A. K. Cheetham in *The Rietveld Method* (Ed.: R. A.Young), Oxford University Press, New York, **1993**; K. D. M. Harris, M. Tremayne, *Chem. Mater.* **1996**, *8*, 2554–2560; J. I. Langford, D. Louër, *Rep. Prog. Phys.* **1996**, *59*, 131–234; D. M. Poojary, A. Clearfield, *Acc. Chem. Res.* **1997**, *30*, 414–422.

[9] G. A. Ardizzoia, G. LaMonica, M. Moret, N. Masciocchi, unpublished results.

[10] P. E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* **1985**, *18*, 367–370.

[11] P. M. De Wolff, *J. Appl. Crystallogr.* **1968**, *1*, 108–113.

[12] G. S. Smith, R. L. Snyder, *J. Appl. Crystallogr.* **1979**, *12*, 60–65.

[13] Y. Le Page, *J. Appl. Crystallogr.* **1982**, *15*, 255–259; A. K. Spek, *J. Appl. Crystallogr.* **1988**, *21*, 578–579.

[14] A. D. Mighell, A. Santoro, *J. Appl. Crystallogr.* **1975**, *8*, 372–377.

[15] A. Le Bail, H. Duroy, J. L. Fourquet, *Mater. Res. Bull.* **1988**, *23*, 447–452.

[16] P. L. Mercandelli, M. Moret, A. Sironi, *Inorg. Chem.* **1998**, *37*, 2563–2569.

[17] E. Corradi, N. Masciocchi, G. Palyi, R. Ugo, A. Vizi-Orosz, C. Zucchi, A. Sironi, *J. Chem. Soc. Dalton Trans.* **1997**, 4651–4655; N. Masciocchi, F. Ragaini, S. Cenini, A. Sironi, *Organometallics* **1998**, *17*, 1052–1057.

[18] A. C. Larson, R. B. Von Dreele, LANSCE, MS-H805, Los Alamos National Laboratory, New Mexico, **1990**.

[19] a) Crystal data for **1**, $C_4H_3CuN_2O$: $M_r = 158.62$, trigonal, space group $R\bar{3}$, $a = b = 27.581(1)$, $c = 9.7870(6)$ Å, $V = 6447.8(5)$ Å^3, $Z = 54$, $\rho_{calcd} = 2.206$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 53.61$ cm^{-1}, $F(000) = 4210$; $R_{wp} = 0.052$, $R_p = 0.032$, and $\chi2 = 3.80$ for 107 parameters, 84 restraints, and 4051 data points collected in the range $8 < 2\theta < 89°$ (1173 reflections, $R_F = 0.067$) on a Rigaku D-III/MAX powder diffractometer equipped with Soller slits and a secondary beam graphite monochromator; optics used: DS/AS/RS 1.0/1.0/0.3°, θ:2θ step scan, $\Delta 2\theta = 0.02°$, $t = 12$ s step^{-1}. The structure was solved by Patterson methods, difference Fourier transformation, and geometrical modeling, and refined by GSAS.[18] The C–C (1.35 Å), C–N (1.35 Å), C–O (1.20 Å), and C–H bond distances (0.95 Å) and pymo ring angles (120°) were restrained at the values given. The refined isotropic thermal parameters (U_{iso}) for copper and the lighter atoms were 0.057(1) and 0.077(1) Å^2, respectively. The final Rietveld refinement plot is shown in Figure 4. b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101957. 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).

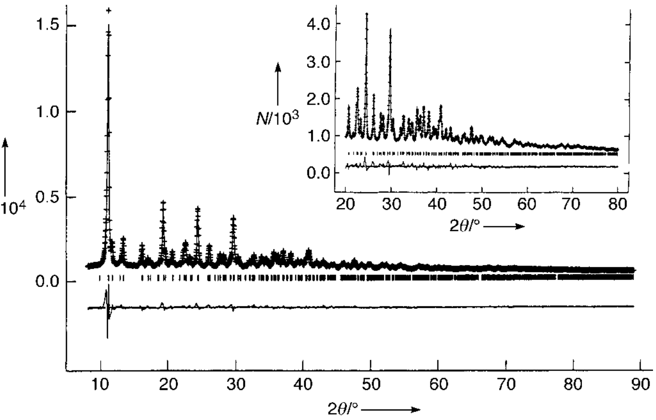

Figure 4. Rietveld refinement plot in the range $8 < 2\theta < 89°$ ($\lambda = 1.5405$ Å). The peak markers and the difference plot are given at the bottom. The insert shows an enlargement of the high-angle region. N = number of counts.

[20] The atom numbers refer to the atom sequence in the table of fractional atomic coordinates deposited with the Cambridge Crystallographic Data Centre.[19b]

[21] Recent examples: S. R. Batten, B. F. Hoskins, R. Robson, *Angew. Chem.* **1997**, *109*, 652–653; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 636–637; M. A.Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. Schroeder, *Angew. Chem.* **1997**, *109*, 2421–2423; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2327–2329.

[22] S. V. Meille, G. Allegra, *Macromolecules* **1995**, *28*, 7764–7769.

[23] Heterochiral helices alone could pack in the same space group with no cavities but with a shorter pitch (ca. 6.50 Å) to ensure constancy of the crystal density.

[24] D. J. Williams, H. M. Colquhoun, C. A. O'Mahoney, *J. Chem. Soc. Chem. Commun.* **1994**, 1643–1644.

[25] G. S. Hanan, J. M. Lehn, N. Kyritsakas, J. Fischer, *J. Chem. Soc. Chem. Commun.* **1995**, 765–766.

[26] A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65–71; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 63–68.

[27] K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 2942–2943; R. F. Carina, G. Berardinelli, A. F. Williams, *Angew. Chem.* **1993**, *105*, 1483–1485; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1463–1465.

[28] J. Beck, J. Strähle, *Angew. Chem.* **1985**, *97*, 419–420; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 409–410.

[29] R. G. Raptis, H. H. Murray III, J. P. Fackler, Jr., *J. Chem. Soc. Chem. Commun.* **1987**, 737–739; H. H. Murray III, R. G. Raptis, J. P. Fackler, Jr., *Inorg. Chem.* **1988**, *27*, 26–31.

[30] From a formal point of view, also $NaCD_3$ (E. Weiss, S. Corbelin, J. K. Cockroft, A. N. Fitch, *Angew. Chem.* **1990**, *102*, 728–729; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 650–652; E. Weiss, S. Corbelin, J. K. Cockroft, A. N. Fitch, *Chem. Ber.* **1990**, *123*, 1629–1634) contains oligomers (in this case, tetramers) and polymeric chains. However, owing to a number of short intermolecular Na–C contacts between the two structural units, this distinction is not so evident.

[31] Indeed, a recent single-crystal structure determination performed in our laboratory on $[Ag(pyridazine)]NO_3$ has shown the copresence of dimers and 2_1-helical polymers: L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Inorg. Chem.* **1998**, in press.

Combinatorial Material Libraries on the Microgram Scale with an Example of Hydrothermal Synthesis**

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Dedicated to Sir John Meurig Thomas
on the occasion of his 65th birthday

As a consequence of the large number of possible polynary mixtures of oxidic materials, together with the potential use of many template molecules, it is attractive to apply combinatorial methods to hydrothermal synthesis.[1] While combinatorial methods are already established as important tools for the development of new lead structures in the areas of organic, biochemical, and pharmaceutical chemistry,[2] there are only a few examples known in the area of inorganic materials research or technical catalyst development. In particular the groups of P. G. Schultz and W. H. Weinberg have been actively involved since the mid 1990s in the development of combinatorial synthesis of new materials. These activities concentrated on the search of new compositions with superconducting,[3] magnetoresistant,[4] or luminescent[5] properties.

These applications are based on the deposition of the compounds as thin films through electron beam evaporation or RF sputtering. The library structure was obtained by the use of physical masks with lattice sizes between 100 × 100 and 200 × 200 μm^2. Libraries with up to 25 000 different materials have been prepared and investigated by routine methods and new lead structures have already been "discovered".[3–5]

The most challenging problem is the analysis and characterization of the properties of interest. The amount of each sample is extremely small because of the miniaturized dimensions necessary for the generation of large libraries of materials. Akporiaye, Karlsson, and Wendelbo[6] published recently the application of combinatorial methods for hydrothermal synthesis. They developed an autoclave that allows 100 hydrothermal syntheses to be run in parallel at temperatures up to 200 °C. The phase diagram obtained in such a single experiment has been used to demonstrate the potential strengths of combinatorial approaches in the area of the synthesis of solid-state materials. In these experiments the reaction volumes were still in the range of 0.5 mL. The identification of the phases prepared still required manual removal of the solids from the reactors, followed by individual measurements with conventional X-ray diffraction techniques. The authors give no information on concentration and amounts of product actually achieved, but the amounts required were in the range of 1–10 mg. The sample handling after synthesis is still quite cumbersome. Every sample has to be prepared individually. Since we have been engaged for some time in the area of combinatorial methods for material synthesis, the above publication prompted us to present the results of our work.

The advantage of our reactor is the direct preparation of a library of materials, whose components can be identified automatically on the library substrate by X-ray microdiffraction. Another advantage is the reaction volume, which is smaller by a factor of 250 relative to that used in reference [6]. Figure 1 shows the construction with dimensions of the pressure reactor. For simplification the model shown has only 37 reaction chambers (each of diameter 1.4 mm and height 4 mm). There is no technical problem in reducing the size and

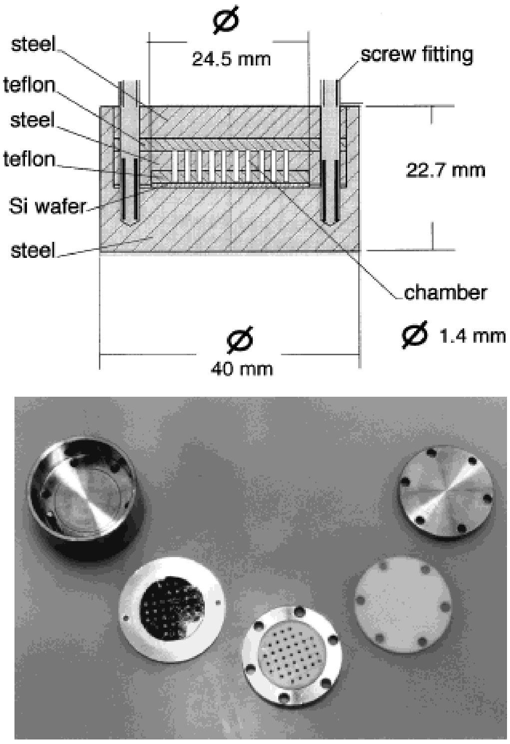

Figure 1. A cross-section of the multireactor autoclave (top) and a photograph of the individual reactor parts (bottom) with the orignial library on the Si wafer (second disk from the left).

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