Crystal Growth of Extended Solids by Nonaqueous Gel Diffusion

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Progress in many areas of chemistry continues to hinge upon accessing reaction products as single crystals in order to allow the precise identification of their molecular structure by X-ray diffraction techniques. Crystal growth in aqueous gels has been known since the end of the last century to be an effective method for preparing large single crystals of metals[1a] and simple ionic solids.[1b−f] Although such gels have been extensively exploited in many other areas of materials science such as sol−gel processing, nanocomposites, and biomineralization,[2,3] their development as crystallization and diffusion media for *nonaqueous* assembly systems with organometallic, metalorganic, and inorganic constituents remains primitive at best.[4] Given the tremendous emerging interest in designing and constructing extended solids from molecular building blocks,[5] and the undesired tendency of their assembly reactions to yield amorphous and poorly crystalline materials,[6] we believe that developing crystal growth techniques for such systems is an imperative step toward furthering this area and uncovering new structures and properties.

In this report, the utility of nonaqueous poly(ethylene oxide) (PEO) gel[7] in the synthesis of large crystals of coordination solids is demonstrated by the assembly of $Zn(HBTC)(NC_5H_5)_2{\cdot}C_2H_5OH$ (HBTC $= 1,3,5\text{-}C_6H_3(CO_2)_2\text{-}(CO_2H)$) from zinc(II) nitrate, 1,3,5-benzenetricarboxylic acid (H_3BTC), and pyridine in ethanol. The preparation of this compound was attempted as part of our continuing efforts to elaborate on the parameters governing the formation of 1-D, 2-D, and 3-D M-BTC porous frameworks. Apparently, the resulting framework dimensionality is markedly affected and perhaps determined by the base strength, the lability of the base as a ligand, as well as its solubility in the solvent employed.[8] By manipulating these conditions, it was possible to generate porous coordination solids exhibiting unprecedented inclusion properties.[9] However, unlike most of these solids, the present compound did not yield to analogous conditions that were designed to produce single crystals of sufficient quality for X-ray structure determination.

The addition of pyridine (0.20 mL, 2.5 mmol) to an absolute ethanol mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (200 mg, 0.672 mmol) and H_3BTC (210 mg, 1.00 mmol) causes the immediate precipitation of a white microcrystalline solid. This product was washed with absolute ethanol (3 × 10 mL) and diethyl ether (3 × 10 mL) to give 190 mg (60% yield based on zinc) of pure $Zn(HBTC)(NC_5H_5)_2{\cdot}C_2H_5OH$.[10] Inspection of the microcrystalline product using an optical microscope revealed that the overall quality of the speciments was inappropriate for single-crystal diffraction study as shown in Figure 1a. It was not possible to recrystallize this solid by the usual dissolution/reprecipitation process,[11] because it reacts with water and it is insoluble in common organic solvents such as *N*,*N*-dimethylformamide, ethanol, acetonitrile, and acetone. Further attempts to obtain single crystals by slowly diffusing pyridine into the reaction mixture and/or changing the concentration of reactants and ambient conditions proved unsuccessful. However, large block-shaped crystals were obtained by employing a PEO gel as a reaction medium.[12] The crystals thus obtained are shown in Figure 1b, which

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[1] (a) For example: copper metal crystals were obtained by chemical reduction of copper sulfate that has been incorporated in gel: Holmes, H. N. *Colloide Chemistry*; Alexander, J., Ed.; Chemical Catalog Co.: New York, 1926. Dendritic crystals of lead were found in a gel containing lead acetate and metallic zinc: Simon, A. L. *Kolloid Z.* **1913**, *12*, 171. (b) Henisch, H. K. *Crystals in Gels and Liesegang Rings*; Cambridge University Press: Cambridge, 1988. (c) McCauley, J. W.; Roy, R. *Am. Mineral.* **1974**, *59*, 947. (d) Holmes, H. N. *J. Franklin Inst.* **1917**, *184*, 743. (e) Cody, A. M.; Horner, H. T.; Cody, R. D. In *Scanning Electron Microscopy*; SEM Inc.: AMF O'Hare, Chicago, IL, 1982. (f) Suib, S. L. *J. Chem. Educ.* **1985** *62*, 81.

[2] (a) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: San Diego, CA, 1990. (b) *Nanophase Materials: Synthesis-Properties-Applications*; Hadjipanayis, G. C., Siegal, R. W., Eds.; NATO ASI Series E.: Applied Sciences; Kluwer Publishers: Dordrecht, The Netherlands, 1994; Vol. 260.

[3] *Biomineralization: Chemical and Biological Perspectives*; Mann, S., Webb, J., Williams, R. J. P., Eds.; VCH Publishers: New York, 1989.

[4] Large crystals of molecular organic compounds have been successfully obtained from nonaqueous gels. For example: (a) 2-phenyl-1,4-hydroquinone-2-phenyl-1,4-benzoquinone complex; grown using Sephadex LH-20 (alkylated cross-linked dextran) gel in aromatic hydrocarbons: Desiraju, G. R.; Curtin, D. Y.; Paul I. C. *J. Am. Chem. Soc.* **1977**, *99*, 6148. Also see: (b) phenol−benzoquinone complex: Sakurai, T. *Acta Crystallogr.* **1968**, *B24*, 403. Harding, T. T.; Wallwork, S. C. *Acta Crystallogr.* **1952**, *6*, 791. (c) Naphthalene−picric acid: Baddar, F. G.; Mikhail, H. *J. Chem. Soc.* **1949**, 2927.

[5] (a) Atwood, J. L., MacNicol, D. D., Davies, J. E. D., Vogtle, F., Lehn, J.-M., Eds. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 1−10. (b) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558. (c) Fagan, P. J.; Ward, M. D. *Sci. Am.* **1992**, *267*, 48. (d) Bein, T., Ed. *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*; American Chemical Society: Washington, DC, 1992. (e) Dagai, R. *Chem. Eng. News* **1991**, *69*, 24−30.

[6] (a) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262. (b) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554.

[7] Although PEO polymeric matrixes have been used to study the complexation of metals ions and to prepare nanocrystals of extended inorganic solids (Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci.* **1968**, *6*, 1509. Bianconi, P. A.; Lin, J.; Strzelecki, A. R. *Nature* **1991**, *349*, 315), we are not aware of reports of their use for the preparation of *large single* crystals of extended covalent solids.

[8] (a) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096. (b) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703−706. (c) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.

[9] Yaghi, O. M. In *Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, M. F., Eds. Plenum: New York, 1995; p 111.

[10] Anal. Calcd for $C_{21}H_{20}N_2O_7Zn$: C, 52.79; H, 4.22; N, 5.86; Zn, 13.68. Found: C, 52.21; H, 4.19; N, 6.05; Zn, 13.09.

[11] Holden, A.; Morrison, P. *Crystals and Crystal Growing*; MIT Press: Cambridge, 1982.

[12] PEO solid (500 mg, MW = 100 000) was placed in a 20 mL vial containing 1,2-dichloroethane (2.0 mL) and stirred for 1 min to give a gel. An absolute ethanol solution (3.33 mL) containing $Zn(NO_3)_2{\cdot}6H_2O$ (100 mg, 0.336 mmol) was immediately added to it, and the resulting mixture was stirred for 2 min to give a slightly turbid gel. This gel material was transferred into a 15 mL test tube (12 mm i.d. and 130 mm long) and an absolute ethanol solution (5 mL) containing H_3BTC (70.0 mg, 0.333 mmol) and pyridine (0.033 mL, 0.410 mmol) was layered above the gel and the tube covered with paraffin film then allowed to stand at room temperature for 4 days. Large block-shaped colorless crystals appeared just below the gel/solution interface. At this point, the solution and most of the gel surrounding the crystals were decanted using a pipet; then the crystals adhering to the inside surface of the tube were washed with absolute ethanol (2 × 6 mL) and collected on a medium frit.

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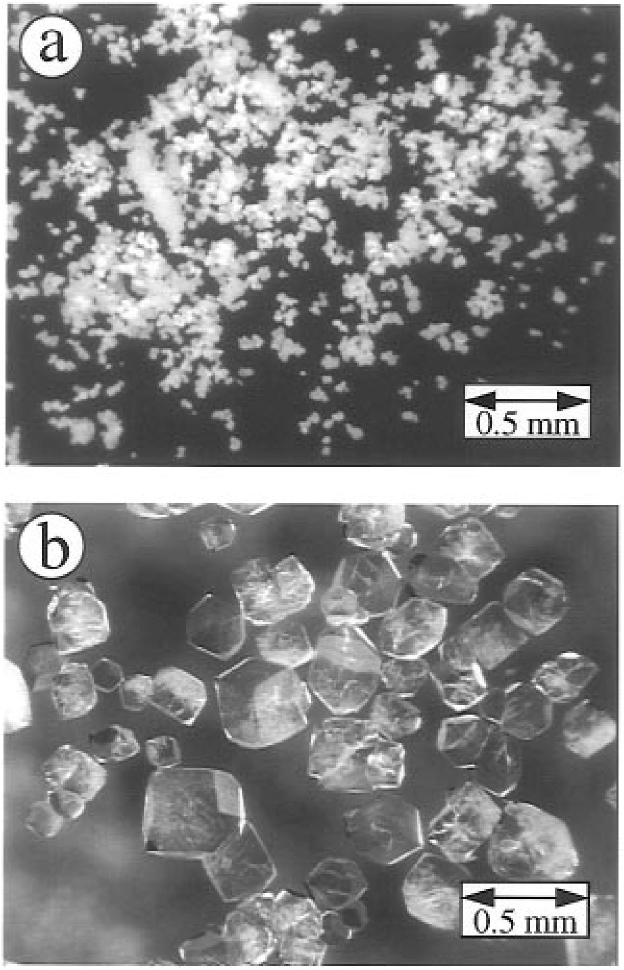

Figure 1. Optical photographs showing the difference in crystal quality and size of $Zn(HBTC)(NC_5H_5)_2{\cdot}C_2H_5OH$ material grown in the absence (a) and in the presence of PEO gel (b).

clearly attests to the striking contrast in size and morphology of this material relative to that prepared in the absence of gel. The elemental microanalysis[10] and X-ray powder diffraction (XRPD) pattern[13] of these crystals are coincident to those of the microcrystalline solid; indicating the same bulk composition, homogeneity, and purity.[14] We found that these crystals are easily obtained under the aforementioned conditions, however, crystal size and crystal habit are affected by numerous parameters relating to reaction temperature, viscosity of the gel, diffusing concentration gradients, and the solvent employed in the preparation of the gel.[15]

X-ray structure analysis[16] of the single crystals confirmed the composition and revealed an extended solid composed of the building units shown in Figure 2. Here, zinc(II) is linked to two pyridine ligands (N11 and N12) and two HBTC units, which are bound to zinc in a monodentate fashion (O1 and O5A). These units are copolymerized with zinc using such monodentate interactions through O1A and O5 to form zigzag chains, where one oxygen (O3) of the third carboxylate unit of HBTC is hydrogen-bonded to an interstitial ethanol molecule (O1S) to form a strong interaction (O3···O1S = 2.588(3) Å).[17] The acidic proton in HBTC is likely to be on O3 since C−O3 = 1.313(12) Å is slightly elongated

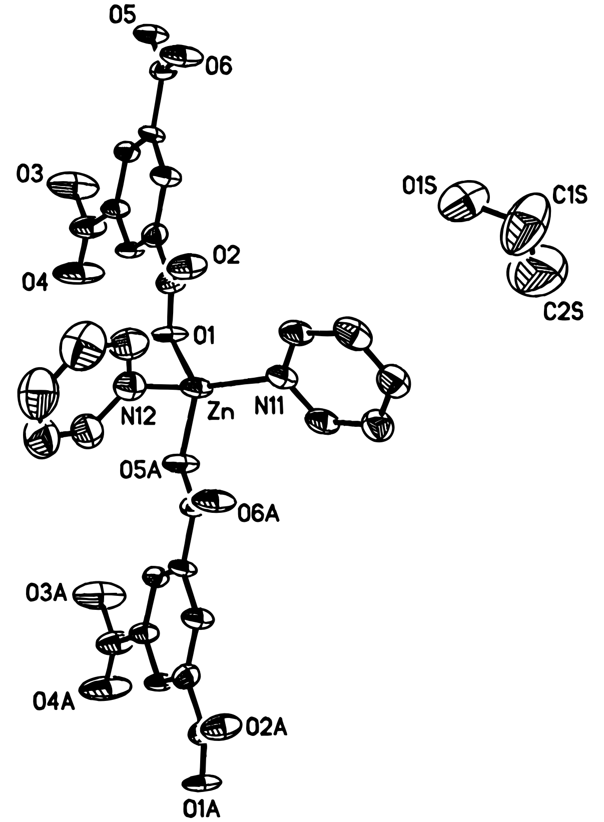

Figure 2. Building unit present in the extended solid-state structure of $Zn(HBTC)(NC_5H_5)_2{\cdot}C_2H_5OH$ shown with the non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with an additional letter *A* are related by symmetry to those without such designation.

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[13] XRPD data for the most prominent lines with *d* spacings in Å and the relative intensities placed in parentheses. Observed: 10.316 (100), 9.291 (76), 7.468 (50), 7.318 (48), 6.309 (28), 5.552 (44), 5.142 (39), 5.000 (58), 4.862 (37), 4.753 (39), 4.581 (42), 4.136 (96), 4.040 (60), 3.828 (36), 3.526 (31), 3.426 (56), 3.046 (23), 2.825 (29). Calculated: 10.274 (100), 9.248 (26), 7.448 (21), 6.308 (8), 5.713 (14), 5.200 (7), 5.021 (10), 4.863 (10), 4.624 (12), 4.183 (29), 4.049 (19), 3.820 (8), 3.536 (3), 3.451 (17), 3.192 (6), 2.826 (10).

[14] The homogeneity of the bulk product was confirmed by comparison of the observed and calculated XRPD patterns. The calculated pattern was produced using the SHELXTL-XPOW program with the single-crystal data.[15]

[15] Even though, the process of growing such large crystals appears to be more of an art than a science, we learned that the task of determining the optimum conditions for crystal growth of metalorganic solids in PEO media is greatly simplified by consideration of these general guidelines: (a) The preparation of PEO gel or polymeric medium is best done in nonaqueous solvents such as methanol, ethanol, propanol, *N*,*N*-dimethylformamide, acetonitrile, and dimethyl sulfoxide, where 0.5 g of PEO (MW = 100 000) is mixed with approximately 2 mL of the desired solvent in the presence of 1,2-dichloroethane. (b) In some cases, it appears to be crucial that the layering solvent be the same as that used to prepare the solution containing the reagent to be impreganted into the gel. (c) The ligand or the metal ion may be used to impregnate the gel. (d) Using test tubes of the size mentioned above along with those volume proportions at room temperature appears to give high-quality crystals.

[16] Single crystals of $Zn(HBTC)(NC_5H_5)_2{\cdot}C_2H_5OH$ were analyzed at 20 ± 1 °C: monoclinic, space group $P2_1/c$ (No. 14) with $a = 10.162(2)$ Å, $b = 20.548(4)$ Å, $c = 10.552(2)$ Å, $\beta = 101.07(2)°$, $V = 2162(1)$ Å^3, $Z = 4$, $d_{calcd} = 1.468$ g cm^{-3} ; μ_a(Mo Kα) = 1.18 mm^{-1}. A total of 2975 independent absorption-corrected relections having 2θ(Mo Kα) < 45.8° (the equivalent of 0.6 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using "direct methods" techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence {R_1 (unweighted, based on F) = 0.045 for 1545 independent absorption-corrected reflections having 2θ(Mo Kα) < 45.8° and $I > 3\sigma(I)$} using counter-weighted, full-matrix, least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen and isotropic thermal parameters for all included hydrogen atoms.

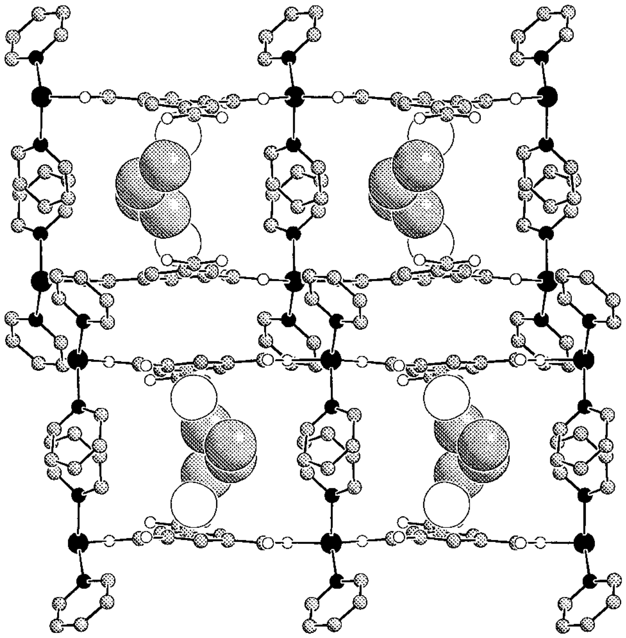

Figure 3. View of the solid-state structure of Zn(HBTC)-$(NC_5H_5)_2 \cdot C_2H_5OH$ along the c-axis. The zinc carboxylate layers with the pyridine ligands are shown as sphere-and-stick representation: Zn, large dark; N, small dark; C, small shaded; O, small open. The ethanol guest molecules are shown in the space-filling van der Waals radii with C and O atoms drawn as large shaded and open spheres, respectively. The hydrogen atoms have been omitted for clarity.

compared to C−O4 = 1.186(10) Å. Ethanol is also hydrogen-bonded to another carboxylate oxygen (O2) on an adjacent chain (O1S···O2 = 2.675(4) Å) to give an overall closely hydrogen-bonded sheet structure. These sheets are stacked in pairs with each pair being held together by $\pi-\pi$ interacting HBTC units of different sheets (distance between centers of such HBTC units is 3.586(5) Å). Closer examination of the structure reveals that the double sheets are stacked further along the *b* axis through $\pi-\pi$ interacting pyridine ligands with a typical distance of 2.771(6) Å. This structural arrangement results in a 3-D network with square channels of nearly 6 Å pores extended along the *c* axis, where ethanol molecules reside as shown in Figure 3. Ongoing experimentation is aimed at exploring the inclusion chemistry of this network and the possibility of removing or exchanging the ethanol guests without destruction of the framework as observed in an earlier study.[8a]

These findings demonstrate the utility and suitability of nonaqueous gels for crystal growth of extended solid products resulting from the assembly of metalorganic molecular building blocks. The results of this work are currently being applied to other systems involving the construction of extended networks from organometallic and inorganic clusters.

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Supporting Information Available: Crystallographic data for $Zn(HBTC)(NC_5H_5)_2 \cdot C_2H_5OH$ including crystal structure analysis report, positional parameters and thermal parameters, and interatomic distances and angles (18 pages). Ordering information is given on any current masthead page.

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