Host–Guest Systems

DOI: 10.1002/ange.200502597

Simple and Quantitative Mechanochemical Preparation of a Porous Crystalline Material Based on a 1D Coordination Network for Uptake of Small Molecules**

Dario Braga, Marco Curzi, Anna Johansson, Marco Polito, Katia Rubini, and Fabrizia Grepioni**

Many research groups worldwide are engaged in the quest for nanoporous solids that are able to absorb and release small

[*] Prof. D. Braga, M. Curzi, Dr. A. Johansson, Dr. M. Polito, K. Rubini, Prof. F. Grepioni
Department of Chemistry, G. Ciamician
Via F. Selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-209-9456
E-mail: dario.braga@unibo.it
fabrizia.grepioni@unibo.it

[**] This work was supported by MIUR (PRIN2004, FIRB2001), the University of Bologna, and the Bertil Lundqvist Foundation.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

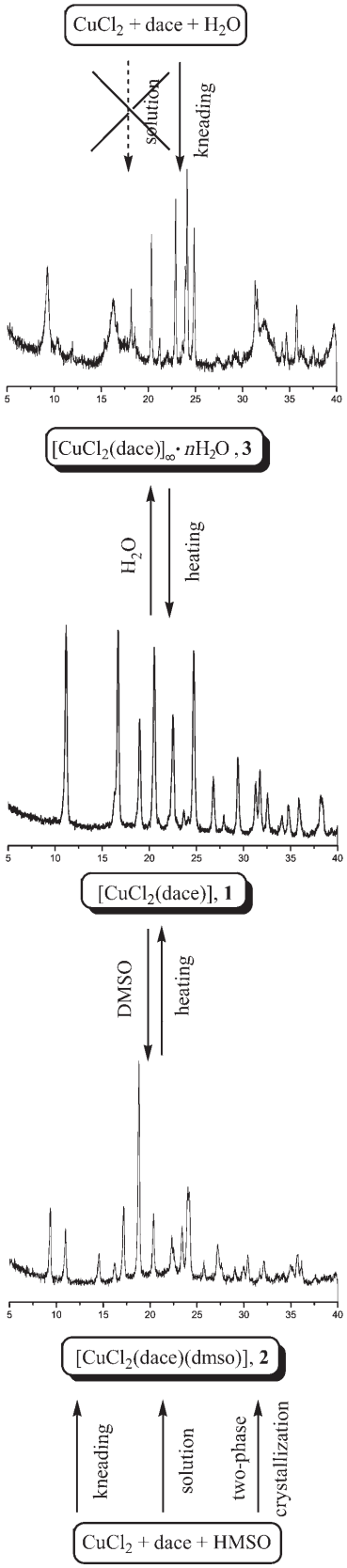
molecules in a controllable and selective fashion.[1] In many cases, coordination networks have been shown to allow formation of structures with channels and cavities (zeotypes), which can often be emptied and refilled without disruption of the crystalline edifice.[2] The preparation of zeotype compounds by hydrothermal methods or by reactions in solution, followed by crystallization, is often difficult because of the tendency of coordination networks to form highly insoluble materials. Recently we have begun to explore the use of solid-state, solvent-free methods for the preparation of molecular crystals[3] and more recently of coordination network compounds.[4,5]

It has long been known that co-grinding and co-milling of solid reactants are viable routes to molecular compounds or molecular crystals.[6] Early work dates back to the pioneering investigations of Etter and co-workers,[7] Rastogi and co-workers,[8] and Curtin, Paul, and co-workers.[9] Recently, mechanochemical methods have begun to be successfully applied also in the field of molecular crystal engineering[10] for solvent-free preparation of supramolecular aggregates,[11] cocrystals, and coordination networks.[12] Importantly, crystals formed by co-grinding of crystals in the absence of liquid can be different from those obtained from solutions or melts.[13]

Examples of the utilization of mechanochemical methods in coordination chemistry are not numerous, but these procedures are increasingly attractive because of environmental and sustainability issues. For example, *cis*-platinum complexes such as *cis*-$(Ph_3P)_2PtCl_2$ and *cis*-$(Ph_3P)_2PtCO_3$ have been prepared mechanochemically from solid reactants,[14] and the supramolecular self assembly of a number of two- or three-dimensional helicates has also been recently reported.[15]

Herein we describe the simple mechanochemical preparation of an inexpensive and versatile porous material based on the 1D coordination network $[CuCl_2(dace)]_\infty$ (**1**; dace = *trans*-1,4-diaminocyclohexane), which is able to absorb and release small molecules. Compound **1** can be obtained by mild thermal treatment of the hydrated compound $[CuCl_2(dace)]_\infty \cdot n H_2O$ (**3**) (see below), which is prepared as a polycrystalline material by manual kneading of solid $CuCl_2$ and dace in the presence of a small quantity of water (see Scheme 1). The system **1** reversibly absorbs small molecules either from solution or by simple kneading, whereas guest desorption invariably results in reversion to the unsolvated form **1**.

The structure of compound **1** is not known in crystallographic detail because the insolubility of the product does not permit the growth of X-ray crystallographic-quality single crystals. However, insight into the structure of **1** has been obtained from the knowledge of the structure of the dimethyl sulfoxide (DMSO) adduct $[CuCl_2(dace)(dmso)]_\infty$ (**2**), which has been fully characterized by single-crystal X-ray crystallographic diffraction (see the Experimental Section). As in the case of **3**, compound **2** can be easily and quantitatively prepared by kneading solid $CuCl_2$ and dace with a few drops of DMSO. Comparison of the X-ray powder diffractogram measured on the kneaded product with that calculated on the basis of the single crystal structure allowed unambiguous formulation of the former product as **2**.



Scheme 1. Preparation of compound **1** (middle) from its hydrated precursor **3** (top), and its behavior as a porous material to reversibly take up small guest molecules: in the example here (bottom) DMSO is absorbed to yield compound **2**.

Figure 1 shows how compound **2** is formed out of 1D coordination networks in which the $CuCl_2$ units are bridged by dace ligands located in chains. Parallel 1D $CuCl_2$–dace

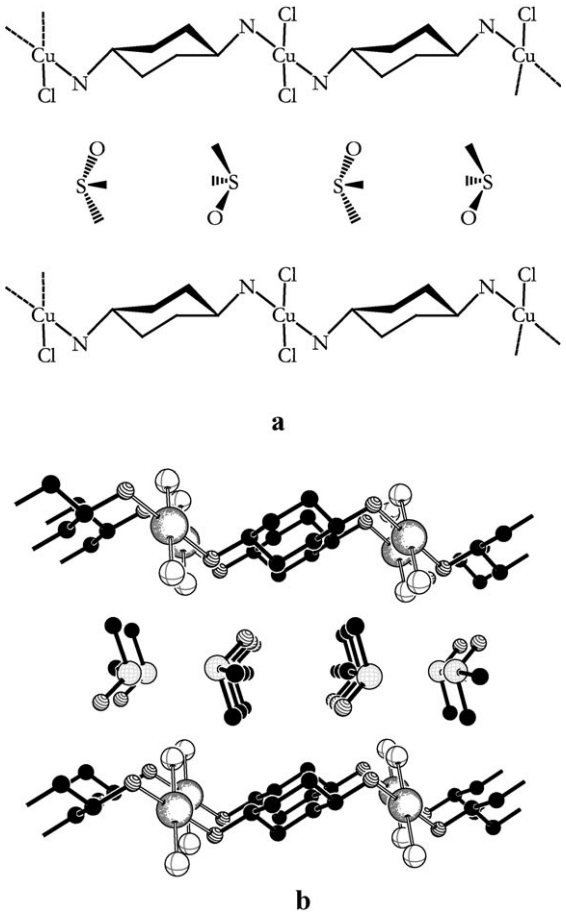
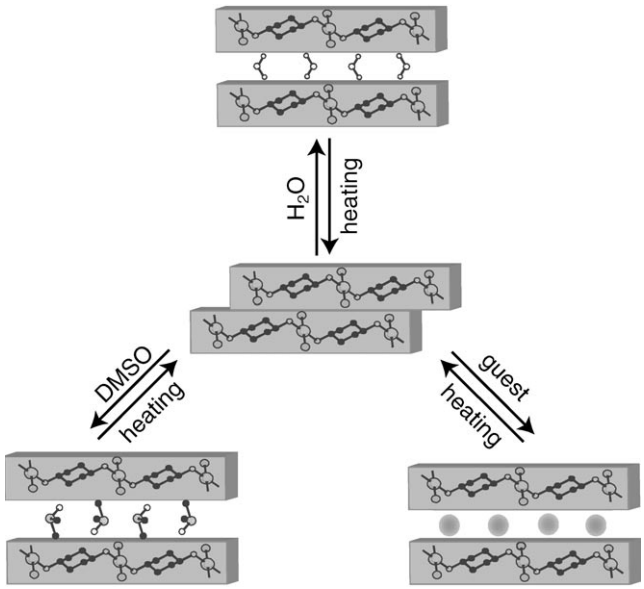


Figure 1. a) A schematic representation of the structure of **2**. b) A perspective view of the packing of **2**, showing the layers formed by parallel 1D networks of alternating $CuCl_2$ and dace units. H atoms omitted for clarity.

networks form layers, which host, in intercalation fashion, the cocrystallized DMSO molecules (see view of the packing in Figure 1b). The copper atoms in **2** adopt a square-planar coordination and the cyclohexane rings of dace are in the chair conformation. The earlier reported structure of *cis*-1,4-diaminocyclohexane, $PtCl_4$, and similar Pt compounds contain dace in the boat conformation.[16] Recently, we reported that solid-state and solution reactions between dace and silver acetate yield three isomeric forms of the coordination network $[Ag(H_2NC_6H_{10}NH_2)^+]_\infty$, all characterized by the presence of chevronlike Ag^+···dace···Ag^+···dace networks.[5]

The interest in compound **2** and its congeners stems not so much from their structures, but from their behavior upon thermal treatment. When polycrystalline **2**, which can be taken as a prototype of this family of compounds, is heated to 130 °C in TGA and DSC experiments, conversion into compound **1** is observed (Scheme 1). This was easily ascertained through comparison of X-ray powder diffractograms after and before DMSO absorption. The process is reversible, and the addition of a few drops of DMSO is sufficient to revert **1** into **2**. Compound **2** can also be obtained by mixing stoichiometric amounts of $CuCl_2$ and dace directly in DMSO with the resultant formation of an insoluble purple microcrystalline powder. In all cases, the products were identified unambiguously through comparison of X-ray powder diffraction patterns. From the structure of **2** and from the knowledge of its thermal behavior, it is possible to infer that the structure of **1** is based on a stacking sequence of layers as in **2**, but 'squeezed' at a shorter interlayer separation as a consequence of DMSO removal (Scheme 2). When the guest molecules enter between the layers, the spacing between the $CuCl_2$–dace chains is expanded and the layers are shifted back in position.



Scheme 2. Schematic representation of the stacking sequence of layers in compounds containing water (**3**), DMSO (**2**), and a generic guest molecule; in **1** a shorter interlayer separation is present, as a consequence of the guest removal.

Scheme 2 also shows that **1**, produced by guest removal, can in turn be used as a starting material in further uptake/release reactions. Table 1 lists the behavior of compound **1** towards a series of small molecules and how the formation of a host–guest compound depends on the preparation method, that is, kneading, suspension in the liquid guest, and kneading followed by suspension. This latter approach is the most productive; when suspended in the desired liquid guest, compound **1** only takes up relatively small molecules (DMSO, methanol, acetone, etc.). In contrast, kneading results in the uptake of other guest molecules as well, probably because the kneading procedure breaks crystallites and reduces surface clogging. Indeed, if polycrystalline **1** is first kneaded with a small amount of the desired liquid and then left to stir in the same liquid guest for 12 h, partial or complete filling of the compound is observed, independent of the guest molecule. Kneading is widely used in the pharmaceutical and food industry and also in the preparation of host–guest compounds

Table 1: Guest uptake by **1** as a function of the preparation route.

Guest	Kneading	Suspension[a]	Kneading followed by suspension[a]
1-hexanol	–	–	x
1-pentanol	–	–	x
acetone	x	–	x
acetonitrile	–	–	x
cyclohexane	–	–	x
dichloromethane	–	–	x
dioxane	–	–	x
dimethylsulphoxide	x	x	x
dimethoxyethane	–	–	x
dimethylformamide	–	–	x
ethylacetate	–	–	x
ethanol	x	x	x
glyme[b]	x	-	x
H_2O	x	x	x
hexane	–	–	x
2-propanol	x	–	x
methanol	x	x	x
tert-butyl alcohol	–	–	x
tetrahydrofuran	x	x	x
TMEDA[c]	x	x	x
toluene	–	–	x

[a] Suspension occurs in the liquid guest. [b] Glyme = ethylene glycol dimethyl ether. [c] TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

of cyclodextrins.[17] All uptake/release processes were monitored by powder diffraction (see Supporting Information).

In conclusion, we have found a simple way to prepare a relatively inexpensive material that absorbs and releases a variety of small molecules through an intercalation mechanism. Similar behavior is shown by intercalation compounds, such as metal calcogenides (TiS_2, ZrS_2, etc.) and metal oxides (MO_3, V_2O_5, $MOPO_4$, etc.). However, to the best of our knowledge, system **1** is the first example of a 1D coordination network with reversible intercalation capacity. Furthermore, guest uptake in **1** appears to be somewhat selective and depends on the method used.

Experimental Section

All starting materials were purchased from Aldrich. Reagent grade solvents and bidistilled water were used.

Kneading experiments; **1**: *trans*-1,4-Diaminocyclohexane (1.14 g, 1.0 mol) and $CuCl_2{\cdot}2H_2O$ (1.70 g, 1.0 mol) was ground together in an agate mortar to a fine powder, and water (0.5 mL) was then added. The mixture was kneaded for 5–10 min, and the water was then removed by thermal and vacuum treatment (100 °C under vacuum for 5 h).**2**: See synthesis of **1**, but DMSO was used instead of water.

3: In an agate mortar, **1** (0.2 g, 0.80 mmol) and water (0.5 mL) were kneaded for 5 min and left to stand for 1 h before measuring the powder diffractogram.

1·*n*(guest): see synthesis of **3**, with the exception that all the compounds listed in Table 1 were used instead of water.

Typical kneading experiment: See synthesis of **3**, but different solvents were used, and the product was left to stand for 1–6 h. Synthesis of **2** in DMSO: In a round-bottomed flask $CuCl_2{\cdot}2H_2O$ (1.70 g, 1 mol) was dissolved in DMSO (75 mL). A solution of *trans*-1,4-diaminocyclohexane (1.14 g, 1 mol) in DMSO (100 mL) was slowly added dropwise, and a blue-purple powder was formed in 92 % (2.86 g) yield.

A typical kneading experiment was followed by suspension in the same solvent that was used for the kneading process: After kneading, the powder mixture was left in suspension in the appropriate solvent for 12 h. In all cases, treatment of the product under vacuum and at 100 °C for 3 h quantitatively yields the solid reagent **1**.

Three-phase crystallization of **2**: In a sample tube, a saturated solution of *trans*-1,4-diaminocyclohexane in DSMO (0.5 mL), methanol/DMSO (1:1, 0.5 mL), and a saturated solution of $CuCl_2{\cdot}2H_2O$ in methanol (0.5 mL) was layered in three phases. A light-purple powder slowly formed between the DMSO layer and the methanol/DMSO layer after 3 days and in the powder a few single crystals of **1** of X-ray crystallographic quality were recovered.

Thermogravimetric measurements: Thermogravimetric investigations were carried out on dried samples by using a Perkin–Elmer TGA-7. Heating was performed under a nitrogen flow (20 $cm^3 min^{-1}$) by using a platinum crucible at a rate of 5 °C min^{-1} up to 450 °C. The weight of the samples was around 3 mg. Calorimetric measurements were performed by using a Perkin–Elmer DSC-7 equipped with a model PII intracooler. Temperature and enthalpy calibration were performed by using high purity standards (*n*-decane, benzene and indium). Heating was carried out at 5 °C min^{-1} in the temperature range 45–140 °C. Samples in the weight range from 5 to 10 mg were analyzed in open aluminum pans.

Crystal-structure determination: Data for **2** were collected at room temperature on an Enraf–Nonius CAD4 diffractometer, monochromator graphite. **2**: $C_6H_{14}Cl_2CuN_2\,2(C_2H_6OS)$, $M_r = 404.89$, light purple crystals, crystal dimensions: $0.2 \times 0.10 \times 0.10$ mm^3; triclinic $P\bar{1}$, $a = 5.911(2)$, $b = 8.515(2)$, $c = 9.621(4)$ Å, $\alpha = 86.81(3)$, $\beta = 78.09(4)$, $\gamma = 70.42(2)°$, $V = 446.4(3)$ $Å^3$, $Z = 1$, $\rho_{calcd} = 1.506$ g cm^{-3}, R_1 (wR_2) 0.0410 (0.0985) for 1547 observed independent reflections; $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 2θ range = 6.0–50.0. All non-hydrogen atoms were refined anisotropically. SHELXL97[18] was used for structure solution and refinement on F^2, and SCHAKAL[19] was used for the molecular graphics. CCDC-279106 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See Supporting Information for crystallographic data in CIF format, X-ray powder patterns for compounds **1**–**4**, and TGA and DSC measurements for **2**. Powder data were collected on a Philips X'Pert automated diffractometer with $Cu_{K\alpha}$ radiation, graphite monochromator. The program PowderCell 2.2 was used for calculation of X-ray crystallographic powder patterns.[20]

Received: July 25, 2005
Published online: November 21, 2005

Keywords: host–guest systems · mechanochemistry · porous materials · solid-state reactions

[1] a) M. Kruk, M. Jaroniec, *Chem. Mater.* **2001**, *13*, 3169–3183; b) P. J. Langley, J. Hulliger, *Chem. Soc. Rev.* **1999**, *28*, 279–291; c) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273–282; d) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109–119; e) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; f) S. Takamizawa, E.-i. Nakata, T. Saito, *CrystEngComm* **2004**, *6*, 39–41; g) S. Takamizawa, E.-i. Nakata, H. Yokoyama, K. Mochizuki, W. Mori, *Angew. Chem.* **2003**, *115*, 4367–4370; *Angew. Chem. Int. Ed.* **2003**, *42*, 4331–4334; h) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.* **2005**, *117*, 1850–1854; *Angew. Chem. Int. Ed.* **2005**, *44*, 1816–1820.

[2] a) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110–7118; b) H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. B. Go, M. Eddaoudi, A. J.

Matzger, M. O'Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523 – 527; c) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127 – 1130; d) L. C. Rowsell Jesse, R. Millward Andrew, S. Park Kyo, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, *126*, 5666 – 5667; e) O. Ohmori, M. Kawano, M. Fujita, *Angew. Chem.* **2005**, *117*, 1998 – 2000; *Angew. Chem. Int. Ed.* **2005**, *44*, 1962 – 1964; f) O. Ohmori, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 16292 – 16293; g) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Shakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem.* **2004**, *116*, 5739 – 5743; *Angew. Chem. Int. Ed.* **2004**, *43*, 5621 – 5625; h) D.-L. Long, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, D. M. Proserpio, C. Wilson, M. Schroeder, *Angew. Chem.* **2004**, *116*, 1887 – 1890; *Angew. Chem. Int. Ed.* **2004**, *43*, 1851 – 1854; i) A. N. Khlobystov, M. T. Brett, A. J. Blake, N. R. Champness, P. M. W. Gill, D. P. O'Neill, S. J. Teat, C. Wilson, M. Schroeder, *J. Am. Chem. Soc.* **2003**, *125*, 6753 – 6761.

[3] a) D. Braga, L. Maini, M. Polito, L. Mirolo, F. Grepioni, *Chem. Eur. J.* **2003**, *9*, 4362 – 4370; b) D. Braga, L. Maini, G. de Sanctis, K. Rubini, F. Grepioni, M. R. Chierotti, R. Gobetto, *Chem. Eur. J.* **2003**, *9*, 5538 – 5548; c) D. Braga, L. Maini, M. Polito, L. Mirolo, F. Grepioni, *Chem. Commun.* **2002**, 2960 – 2961.

[4] D. Braga, S. L. Giaffreda, F. Grepioni, M. Polito, *CrystEngComm* **2004**, *6*, 458 – 462.

[5] D. Braga, M. Curzi, F. Grepioni, M. Polito, *Chem. Commun.* **2005**, 2915 – 2917.

[6] a) G. W. V. Cave, C. L. Raston, J. L. Scott, *Chem. Commun.* **2001**, 2159 – 2169; b) K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025 – 1074; c) G. Rothenberg, A. P. Downie, C. L. Raston, J. L. Scott, *J. Am. Chem. Soc.* **2001**, *123*, 8701 – 8708; d) F. Toda, *CrystEngComm* **2002**, *4*, 215 – 222; e) G. Kaupp, *Compr. Supramol. Chem.* **1996**, *8*, 381 – 423; f) G. Kaupp, *CrystEngComm* **2003**, *5*, 117 – 133.

[7] a) M. C. Etter, *J. Phys. Chem.* **1991**, *95*, 4601 – 4610; b) M. C. Etter, S. M. Reutzel, C. G. Choo, *J. Am. Chem. Soc.* **1993**, *115*, 4411 – 4412; c) W. H. Ojala, M. C. Etter, *J. Am. Chem. Soc.* **1992**, *114*, 10288 – 10293.

[8] a) R. P. Rastogi, P. S. Bassi, S. L. Chadha, *J. Phys. Chem.* **1963**, *67*, 2569 – 2573; b) T. P. Rastogi, N. B. Singh, *J. Phys. Chem.* **1966**, *70*, 3315 – 3324; c) R. P. Rastogi, N. B. Singh, *J. Phys. Chem.* **1968**, *72*, 4446 – 4449.

[9] a) I. C. Paul, D. Y. Curtin, *Acc. Chem. Res.* **1973**, *6*, 217 – 225; b) C. C. Chiang, C. T. Lin, H. J. Wang, D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1977**, *99*, 6303 – 6308; c) A. O. Patil, D. Y. Curtin, I. C. Paul, *J. Am. Chem. Soc.* **1984**, *106*, 348 – 353.

[10] D. Braga, *Chem. Commun.* **2003**, 2751 – 2754.

[11] a) V. R. Pedireddi, W. Jones, A. P. Chorlton, R. Docherty, *Chem. Commun.* **1996**, 987 – 988; b) R. Kuroda, Y. Imai, N. Tajima, *Chem. Commun.* **2002**, 2848 – 2849; c) A. V. Trask, W. D. S. Motherwell, W. Jones, *Chem. Commun.* **2004**, 890 – 891.

[12] a) P. J. Nichols, C. L. Raston, J. W. Steed, *Chem. Commun.* **2001**, 1062 – 1063; b) W. J. Belcher, C. A. Longstaff, M. R. Neckenig, J. W. Steed, *Chem. Commun.* **2002**, 1602 – 1603.

[13] D. Braga, F. Grepioni, *Angew. Chem.* **2004**, *116*, 4092 – 4102; *Angew. Chem. Int. Ed.* **2004**, *43*, 4002 – 4011.

[14] a) V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *Chem. Commun.* **2002**, 724 – 725; b) V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *Chem. Commun.* **2002**, 1606 – 1607.

[15] A. Orita, L. Jiang, T. Nakano, N. Ma, J. Otera, *Chem. Commun.* **2002**, 1362 – 1363.

[16] a) A. R. Khokhar, S. Shamsuddin, Q. Xu, *Inorg. Chim. Acta* **1994**, *219*, 193 – 197; b) S. Shamsuddin, C. C. Santillan, J. L. Stark, K. H. Whitmire, Z. H. Siddik, A. R. Khokhar, *J. Inorg. Biochem.* **1998**, *71*, 29 – 35; c) S. Shamsuddin, J. W. van Hal, J. L. Stark, K. H. Whitmire, A. R. Khokhar, *Inorg. Chem.* **1997**, *36*, 5969 – 5971; d) J. D. Hoeschele, H. D. H. Showalter, A. J. Kraker, W. L. Elliott, B. J. Roberts, J. W. Kampf, *J. Med. Chem.* **1994**, *37*, 2630 – 2636; e) S. Shamsuddin, A. R. Khokhar, *J. Coord. Chem.* **1994**, *33*, 83 – 91.

[17] a) J. Shailaja, S. Karthikeyan, V. Ramamurthy, *Tetrahedron Lett.* **2002**, *43*, 9335 – 9339; b) F. Taneri, T. Gueneri, Z. Aigner, M. Kata, *J. Inclusion Phenom. Macrocyclic Chem.* **2002**, *44*, 257 – 260; c) R. Saikosin, T. Limpaseni, P. Pongsawasdi, *J. Inclusion Phenom. Macrocyclic Chem.* **2002**, *44*, 191 – 196; d) L. R. Nassimbeni, *Acc. Chem. Res.* **2003**, *36*, 631 – 637.

[18] G. M. Sheldrick, University of Göttingen, Germany, **1997**.

[19] E. Keller, SCHAKAL99, Graphical Representation of Molecular Models, University of Freiburg, Germany, **1999**.

[20] PowderCell, program by W. Kraus and G. Nolze (BAM Berlin) subgroups derived by Ulrich Müller (Gh Kassel).

