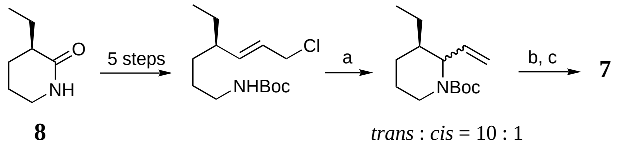
S. V. Ley, *Tetrahedron* **1991**, *47*, 1311; T. Shono, Y. Matsumura, T. Fujita, *Tetrahedron Lett.* **1991**, *32*, 6723.

[9] The structure of each isomer was confirmed by comparison of the spectral data with those of **7** synthesized from **8** by an alternative route (Scheme 4). K. Takao, Y. Nigawara, E. Nishino, I. Takagi, K. Maeda, K. Tadano, S. Ogawa, *Tetrahedron* **1994**, *50*, 5681.



Scheme 4. Alternative synthetic route to intermediate **7**. a) nBu$_4$NI, NaH, [Pd(Ph$_3$P)$_4$], THF; b) CF$_3$CO$_2$H, CH$_2$Cl$_2$; c) (CH$_3$CH$_2$CO)$_2$O, Et$_3$N, CH$_2$Cl$_2$.

[10] For related examples, see M. J. Fisher, L. E. Overman, *J. Org. Chem.* **1990**, *55*, 1447; T. Hosaka, Y. Torisawa, M. Nakagawa, *Tetrahedron Lett.* **1997**, *38*, 3535.

[11] M. Narisada, I. Horibe, F. Watanabe, K. Takeda, *J. Org. Chem.* **1989**, *54*, 5308.

[12] D. A. Evans, T. C. Britton, J. A. Ellman, *Tetrahedron Lett.* **1987**, *28*, 6141.

[13] L. Kisfaludy, M. Löw, O. Nyeki, T. Szirtes, I. Schön, *Justus Liebigs Ann. Chem.* **1973**, 1421. This process was superior to other lactamizations in terms of both yield and convenience.

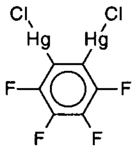
[14] The structure of the synthetic fluvirucinine A$_1$ was also confirmed by comparison of the spectral data of the methoxy(trifluoromethyl)phenylacetic acid (MTPA) esters of synthetic and natural fluvirucinine A$_1$.[1c] We thank Professor Takenori Kusumi of Tokushima University and Professor Hiroshi Kakisawa of the University of Tsukuba for kindly providing spectral data of the fluvirucins.

Micropore Decoration with Bidentate Lewis Acids: Spontaneous Assembly of 1,2-Bis(chloromercurio)tetrafluorobenzene[**]

Martin Tschinkl, Annette Schier, Jürgen Riede, and François P. Gabbaï[*]

Dedicated to Professor Hubert Schmidbaur
on the occasion of his 65th birthday

Polydentate Lewis acids constitute a rapidly growing class of molecular compounds made up of simple bidentate derivatives[1–8] as well as more elaborate polydentate macrocycles.[9–11] The importance of these derivatives is coming to light in several aspects of chemistry including activation of organic reactions,[1] organometallic catalysis,[2] and molecular[3, 5–10] and anion recognition.[6–11] It occurred to us that the incorporation of polydentate Lewis acid functionalities in supramolecular nanoporous structures[12] could also be of interest for the design of new materials with unusual guest affinity[13] or catalytic activity.[14] We now report that 1,2-bis(chloromercurio)tetrafluorobenzene (**1**), a rigid bifunctional Lewis acid,[15] assembles into a microporous solid with internal Lewis acidic sites while retaining the integrity of its bidentate character. In addition, we report that guest exchange is readily observed within the host lattice. This work is part of our current interest in the chemistry of bifunctional Lewis acids as supramolecular synthons.[16]



1

Slow evaporation of a solution of **1** in DMSO affords crystals of composition **1**·(DMSO)$_3$ (**2**), as determined by elemental analysis.[17] The IR spectrum of this novel compound revealed an unresolved broad absorption in the S=O stretching frequency region, suggesting the presence of chemically nonequivalent DMSO molecules.[17] Solid-state MAS NMR spectroscopy confirmed this view, as two sets of methyl resonances could be detected in the ^{13}C NMR spectrum.[17]

As determined by single-crystal X-ray diffraction analysis,[18] the asymmetric unit of **2** consists of one molecule of **1**·(μ_2-DMSO)$_2$ and one noncoordinating solvate DMSO molecule (Figure 1). Each of the coordinated DMSO molecules is chelated by the bidentate Lewis acidic pincer. The resulting Hg–O bonds (av 2.70 Å) are shorter than the sum of

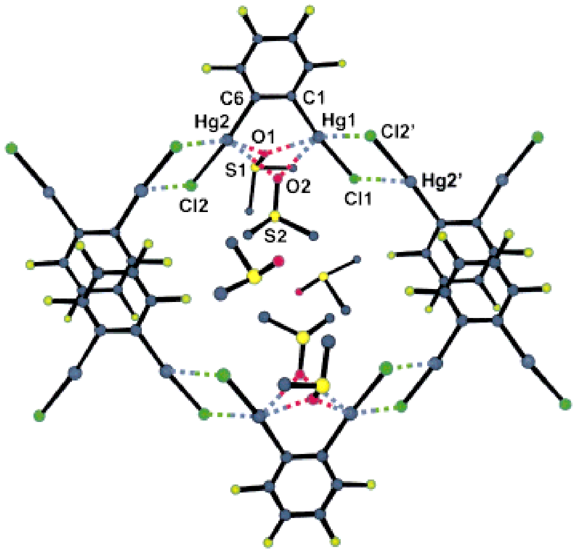


Figure 1. Ball-and-stick diagram showing the structure of **2**. The Hg···Cl and π–π contacts are evident from this view. Selected bond lengths [Å] and angles [°]: Hg1–C1 2.063(7), Hg1–Cl1 2.315(2), Hg1–O1 2.689(6), Hg1–O2 2.785(5), Hg2–C6 2.050(6), Hg2–Cl2 2.319(2), Hg2–O1 2.623(5), Hg2–O2 2.686(5), S1–O1 1.497(6), S2–O2 1.521(2); C1-Hg1-Cl1 173.6(2), C1-Hg1-O1 89.9(2), Cl1-Hg1-O1 94.67(13), C1-Hg1-O2 87.2(2), Cl1-Hg1-O2 98.28(11), O1-Hg1-O2 73.6(2), C6-Hg2-Cl2 174.9(2), C6-Hg2-O1 91.6(2), Cl2-Hg2-O1 91.10(13), C6-Hg2-O2 89.3(2), Cl2-Hg2-O2 95.53(11).

---

[*] Prof. F. P. Gabbaï, Dipl. Chem. M. Tschinkl
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255 (USA)
Fax: (+1) 409-845-4719
E-mail: gabbai@mail.chem.tamu.edu

Dr. A. Schier, J. Riede
Anorganisch-chemisches Institut der Technischen
Universität München
Lichtenbergstrasse 4, D-85747 Garching (Germany)

[**] We thank the Department of Chemistry at Texas A&M University and the Lehrstuhl of Prof. H. Schmidbaur at the TU München for making this work possible. Financial support from the State of Bavaria/Technische Universität München and the DAAD (Promotionsstipendium, grant to M.T.) is gratefully acknowledged.

1433-7851/99/3823-3547 $ 17.50+.50/0

the van der Waals radii of oxygen (1.54 Å)[19] and mercury (1.73–2.00 Å),[20] and can be compared to the Hg–O distances of 2.793 and 2.804 Å in the DMSO chelate complex 1,8-bis(chloromercurio)-naphthalene · μ_2-DMSO.[4]

Examination of the cell-packing diagram reveals the existence of infinite two-dimensional sheets. The cohesion within each sheet results from the interplay of two types of interactions. The formation of chains along the *y* axis can be recognized. In these chains, molecules of **1** are linked by formation of Hg_2Cl_2 bridges (Hg1–Cl2′ 3.261, Hg2′–Cl1 3.555 Å; van der Waals radius of Cl: 1.58–1.78 Å,[19] Hg: 1.73–2.00 Å),[20] as often encountered for organomercurio halides in the solid state.[21] These chains are parallel and interact with one another through π–π contacts of 3.54 Å involving pairs of juxtaposed phenylene rings.[22] In this pairs, the polar molecules of **1** adopt a slightly offset[23] and antiparallel arrangement similar to that observed for other 1,2-substituted tetrafluorobenzene derivatives.[24, 25] In the crystal, the successive sheets are parallel to one another and form a layered structure. The shortest interlayer distance is 3.116 Å and occurs between the fluorine atoms at the 3- and 4-positions of proximate monomers belonging to different sheets. This overall arrangement leads to the formation of channels along the *x* axis (Figure 2). The cross-section of the channels adopts the shape of a parallelogram whose effective diagonals are 10 and 7 Å.

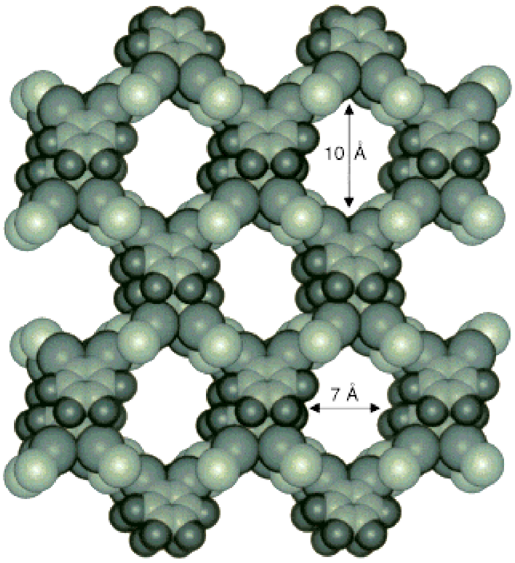
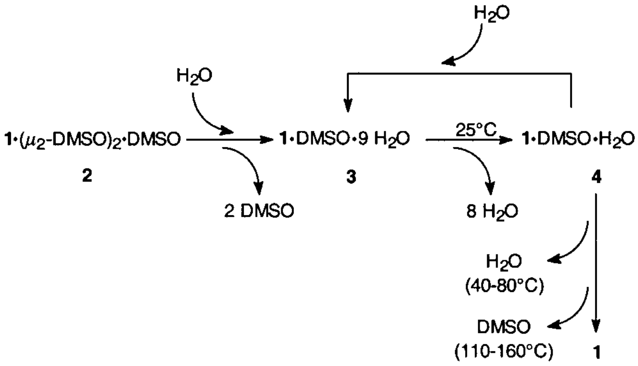


Figure 2. Space-filling model of the lattice of **2**. The DMSO molecules are omitted for clarity.

Compound **1** is insoluble in water. In water, single crystals of **2** become rapidly opaque. The opaque crystals (**3**) can be recovered and physically dried. Gravimetric analysis reveals that **3** undergoes a weight loss of 17.0(±0.5) % at room temperature to yield **4**, which was identified as **1** · DMSO · H_2O by elemental analysis as well as IR and ^1H NMR spectroscopy.[26] When this experiment is run in D_2O, analysis of the supernatant by ^1H NMR spectroscopy indicates the presence of two equivalents of dissolved DMSO (internal standard: 3-trimethylsilyl 1-propanesulfonic acid, sodium salt (TSP)), while ^{19}F NMR confirms the absence of dissolved **1**. Finally, an overall weight loss of 16.5(±0.5) % is observed in going from **2** to **4**, which supports the loss of two equivalents of DMSO and addition of one equivalent of water.

These data indicate that when **2** is placed in water, displacement of two DMSO molecules by nine water molecules occurs to provide **3** (Scheme 1). When **3** is taken out of the aqueous solution, part of the water components spontaneously desorbs to yield **4**. This hydration–dehydration process is reversible, as **3** can be regenerated when **4** is immersed in water. Assuming that the pores in **3** are saturated with liquid water, the effective pore volume of **4** is 0.20 $cm^3 g^{-1}$. The X-ray powder pattern of **4**, which indicates high crystallinity, suggests that significant structural changes occur on going from **2** to **4**.[27] Finally, as shown by thermogravimetric analysis (TGA), **4** undergoes successive dehydration (40–80 °C) and DMSO loss (110–160 °C) accompanied by melting at 143–144 °C. We are currently investigating the structure of **4** by X-ray powder methods.



Scheme 1. **2** is converted into **3** by immersion in water. In air, at 25 °C, **3** loses water to yield **4**. **4** can be converted back into **3** by addition of water or back into **1** by heating.

Received: June 7, 1999 [Z13522IE]
German version: *Angew. Chem.* **1999**, *111*, 3769–3771

Keywords: host–guest chemistry · Lewis acids · mercury · microporosity · supramolecular chemistry

---

[1] a) T. Ooi, T. Miura, K. Maruoka, *Angew. Chem.* **1998**, *110*, 2524–2526; *Angew. Chem. Int. Ed.* **1998**, *37*, 2347–2349; b) T. Ooi, N. Asao, K. Maruoka, *J. Synth. Org. Chem. Jpn.* **1998**, *56*, 377–385.
[2] L. Jia, X. Yang, C. Stern, T. J. Marks, *Organometallics* **1994**, *13*, 3755–3757.
[3] J. D. Wuest, *Acc. Chem. Res.* **1998**, *32*, 81–89.
[4] H. Schmidbaur, H.-J. Öller, D. L. Wilkinson, B. Huber, *Chem. Ber.* **1989**, *122*, 31–36.
[5] a) F. P. Gabbaï, A. Schier, J. Riede, M. J. Hynes, *Chem. Commun.* **1998**, 897–898; b) K. Nozaki, M. Yoshida, H. Takaya, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2043–2052; c) H. E. Katz, *J. Org. Chem.* **1989**, *54*, 2179–2183.
[6] J. D. Wuest, B. Zacharie, *Organometallics* **1985**, *4*, 410–411.
[7] V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3244–3245; b) W. Uhl, F. Hannemann, W. Saak, R. Wartchow, *Eur. J. Inorg. Chem.* **1998**, 921–926; c) M. Tschinkl, A. Schier, J. Riede, F. P. Gabbaï, *Inorg. Chem.*

1997, *36*, 5706–5711; d) H. E. Katz, *J. Org. Chem.* **1985**, *50*, 5027–5032.

[8] R. Altmann, K. Jurkschat, M. Schurmann, D. Dakternieks, A. Duthie, *Organometallics*, **1998**, *17*, 5858–5866.

[9] M. Newcomb, J. H. Horner, M. T. Blanda, P. J. Squattrito, *J. Am. Chem.* Soc. **1989**, *111*, 6294–6301.

[10] M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.* **1997**, *30*, 267–276.

[11] I. A. Tikhonova, F. M. Dolgushin, A. I. Yanovsky, Yu. T. Struchkov, A. N. Gavrilova, L. N. Saitkulova, E. S. Shubina, L. M. Epstein, G. G. Furin, V. B. Shur, *J. Organomet. Chem.* **1996**, *508*, 271–273.

[12] For a nanoporous networks with accessible Lewis sites, see a) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1999**, *121*, 1651–1657; b) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186–2187.

[13] a) H. J. Choi, T. S. Lee, M. P. Suh, *Angew. Chem.* **1999**, *111*, 1490–1493; *Angew. Chem. Int. Ed.* **1999**, *38*, 1405–1408; b) H. Gudbjartson, K. Biradha, K. M. Poirier, M. J. Zaworotko, *J. Am. Chem. Soc.* **1999**, *121*, 2599–2600; c) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem.* **1999**, *111*, 190–193; *Angew. Chem. Int. Ed.* **1999**, *38*, 140–143; d) C. J. Kepert, D. Hesek, P. D. Beer, M. J. Rosseinsky, *Angew. Chem.* **1998**, *110*, 3335–3337; *Angew. Chem. Int. Ed.* **1998**, *37*, 3158–3160; e) K. Biradha, D. Dennis, V. A. MacKinnon, C. V. K. Sharma, M. J. Zaworotko, *J. Am. Chem. Soc.* **1998**, *120*, 11894–11903; f) L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676–2677; g) P. Brunet, M. Simard, J. D. Wuest, *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738; h) O. M. Yaghi, G. Li, H. Li, *Nature* **1995**, *378*, 703–705; i) D. Venkataraman, G. B. Gardner, S. Lee, J. S. Moore, *J. Am. Chem. Soc.* **1995**, *117*, 11600–11601.

[14] a) T. Sawaki, T. Dewa, Y. Aoyama, *J. Am. Chem. Soc.* **1998**, *120*, 8539–8540; b) K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 4117–4122; c) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.

[15] The solution host–guest properties of **1** have been recently reported: M. Tschinkl, A. Schier, J. Riede, F. P. Gabbaï, *Organometallics* **1999**, *18*, 1747–1753.

[16] F. P. Gabbaï, A. Schier, J. Riede, *Angew. Chem.* **1998**, *110*, 646–648; *Angew. Chem. Int. Ed.* **1998**, *37*, 622–624.

[17] Analytical data for **2**: M.p. 133–134 °C; elemental analysis calcd for $C_{12}H_{18}Cl_2F_4Hg_2O_3S_3$: C 16.85, H 2.11; found: C 16.69, H 2.10; IR (KBr): $\tilde{\nu} = 3401$, 2998, 2917, 1617, 1590, 1473, 1414, 1310, 1283, 1076, 1020, 999, 951, 897, 810, 762, 706 cm^{-1}; CP-MAS ^{13}C NMR: $\delta = 41.8$, 41.1.

[18] Crystal structure data for **2**: $C_{12}H_{18}Cl_2F_4Hg_2O_3S_3$, $M_r = 854.52$, monoclinic, space group $P2_1/c$, $a = 8.149(1)$, $b = 14.245(1)$, $c = 19.214(1)$ Å, $\beta = 96.90(1)^\circ$, $V = 2214.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.563$ g cm^{-3}, $F(000) = 1568$, Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $T = -82$ °C. Data were corrected for Lorentz, polarization, and absorption effects (DIFABS). The structure was solved by direct methods and refined by full-matrix least-square methods against F^2 (SHELXTL-PLUS, SHELXL-93). Of 4794 measured reflections, 4512 were used for refinement. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized geometry and allowed to ride on their corresponding carbon atom with $U_{iso} = 1.5\,U_{eq}$ of the attached carbon atom. The structure converged for 235 refined parameters to $R1 = 0.0347$ and $wR2 = 0.0887$; max./min. residual electron density $+1.427/-2.291$ e Å^{-3}. 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-124679. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[19] S. C. Nyburg, C. H. Faerman, *Acta Crystallogr. Sect. B.* **1985**, *41*, 274–279.

[20] A. J. Canty, G. B. Deacon, *Inorg. Chim. Acta* **1980**, *45*, L225–L227.

[21] R. G. Gerr, M. Y. Antipin, N. G. Furmanova, Yu. T. Struchkov, *Sov. Phys. Crystallogr. Engl. Transl.* **1979**, *24*, 543–546.

[22] This distance corresponds to the normal spacing between the planes formed by each phenylene ring.

[23] W. L. Jorgensen, D. L. Severance, *J. Am. Chem. Soc.* **1990**, *112*, 4768–4774.

[24] D. S. Brown, T. K. Mistry, A. G. Massey, *J. Organomet. Chem.* **1986**, *308*, 207–210.

[25] R. E. Cobbledick, R. A. Copes, F. W. B. Einstein, *Acta Crystallogr. Sect. B* **1977**, *33*, 2914–2916.

[26] Analytical data for **4**: M.p. 143–144 °C; elemental analysis calcd for $C_8H_8Cl_2F_4Hg_2O_2S$: C 13.70, H 1.14, S 4.57; found: C 13.90, H 0.90, S 4.56; IR (KBr): $\tilde{\nu} = 3570$, 3443, 1617, 1590, 1477, 1415, 1310, 1288, 1084, 1079, 1047, 1026, 1002, 952, 898, 817, 763 cm^{-1}.

[27] X-ray powder diffration (XRPD) data for **4**: d spacing [Å] (I/I_o): 10.85 (100), 6.26 (86.8), 4.57 (64.72), 4.20 (52.46), 3.91 (41.85), 3.36 (28.00), 3.27 (83.92), 3.22 (21.76), 3.16 (25.95), 2.97 (27.25), 2.93 (23.68), 2.63 (22.47), 2.57 (26.51), 2.39 (26.03). Simulated XRPD for **2** (intense peaks are given for comparison purposes): d spacing [Å] (I/I_o): 11.41 (57.48), 9.54 (92.87), 8.09 (100), 6.84 (71.73), 6.57 (15.97), 5.83 (53.45), 5.81 (44.38), 4.98 (33.54), 4.05 (22.68), 3.90 (16.25), 3.80 (17.24), 3.73 (20.69), 3.69 (33.31), 3.54 (31.58), 3.50 (19.89), 3.29 (28.99), 3.04 (20.70).

X-Ray Structure of a Heterochiral, Sulfoximine-Stabilized Dilithiomethane Derivative

Jürgen F. K. Müller,* Markus Neuburger, and Bernhard Spingler

Dilithiomethane and some of its heteroatom-stabilized analogues have been the subject of intensive research during recent years. On the one hand the elucidation of the nature and the structures of the compounds were pursued, whilst on the other hand several investigations addressed the synthetic utility of these reagents.[1] The structure of dilithiomethane, the simplest polylithiated compound, has been determined in the solid state by X-ray analysis and NMR spectroscopy, whereas in solution no experimental data are available.[2] Some experimental evidence for the existence of a dimeric species in the gas phase has been reported.[3] Computational studies suggest that dilithiomethane and its higher aggregates have tetrahedral and planar structures, respectively.[4] The structures of heteroatom-stabilized geminal dianions, including dilithiated phosphonates,[5] phosphinimines,[6] sulfones, and nitriles[7] have been determined in the solid state, in solution, and theoretically. The α,o-dilithiated intermediates known for structurally related sulfones and sulfoximines mimic the reactivity of an α,α-dianion in trapping reactions with electrophiles.[8] This is also the case for the so called

---

[*] Dr. J. F. K. Müller, M. Neuburger
Institut für Anorganische Chemie der Universität
Spitalstrasse 51, CH-4056 Basel (Switzerland)
Fax: (+41) 61-267-10-18
E-mail: muellerju@ubaclu.unibas.ch

Dr. B. Spingler
Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139 (USA)