

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231530111>

α - and β -Bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxyacetylacetonato)copper(II): Transforming the Dense Polymorph into a Versatile New Microporous Framework†

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · APRIL 1999

Impact Factor: 12.11 · DOI: 10.1021/ja981443u

CITATIONS

142

READS

13

7 AUTHORS, INCLUDING:



Dmitriy Soldatov

University of Guelph

103 PUBLICATIONS 1,835 CITATIONS

SEE PROFILE



John A. Ripmeester

National Research Council Canada

716 PUBLICATIONS 15,782 CITATIONS

SEE PROFILE

α - and β -Bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxyacetylacetonato)copper(II): Transforming the Dense Polymorph into a Versatile New Microporous Framework[†]

D. V. Soldatov,^{‡,§} J. A. Ripmeester,^{*,‡} S. I. Shergina,[‡] I. E. Sokolov,[‡] A. S. Zanina,[‡] S. A. Gromilov,[§] and Yu. A. Dyadin[§]

Contribution from the Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa K1A 0R6, Canada, Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia, and Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia

Received April 27, 1998

Abstract: Bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxy-acetylacetonato)copper(II) was prepared in two polymorphic modifications. The orthorhombic α -form is stable and densely packed, with four trans and four cis square bischelate building blocks per unit cell. These are connected through additional coordination bonds to form a dense polymer network. For the trigonal β -form, the square bischelate complex units are present exclusively as the trans isomers. The distinctive assembly of these units results in a lattice with an open pore volume of about 17% that is accessible to a wide range of guests. The compound has a remarkably strong affinity for the porous β -form as evident from the efficient α -to- β conversion on contact not only with liquid guests but also with organic vapors at pressures well below the saturation pressure. Although the open β -form is metastable, it has a remarkable kinetic stability, most likely because of the trans-to-cis isomerization that must accompany the β -to- α transformation. Many sorbents play a dual role as stabilizing guest and as catalyst promoting the α -to- β or β -to- α conversion. Because of its versatile sorption properties and relative robustness, the β -form of the complex can be classified as a novel organic zeolite mimic.

Introduction

There is considerable interest in the design of novel organic and metal–organic materials that exhibit zeolite-like behavior. Materials that have a predisposition toward forming open structures often show a rapidity and reversibility of guest inclusion that facilitate their function as zeolite mimics. Potential applications include processes such as separation and purification, catalysis, stereoselective syntheses, sensor applications, or the preservation of unstable or highly reactive species.¹ Despite extensive efforts, only a few host types forming stable porous matrixes have been discovered so far,² as most either collapse when the templating guest is removed or lose their crystallinity. Here we report a novel host matrix capable of supporting a remarkably robust channel structure. Stable kinetically, it is sufficiently labile that controlled transformation of the dense to the open forms and vice versa can be contemplated as a design feature. The host shows considerable versatility in sorption behavior and an unusually strong affinity for the formation of inclusions with aliphatic hydrocarbon gases and offers insight into possible new design concepts for the development of

microporous architectures with the ability to switch between dense and open forms.

The crystal structure of the title complex in its open form was recently reported.³ The presence of solvent species, however, was not clearly established. Our work has revealed that the quantities of included solvent must have been significant, from both the unit cell volume of 5486 Å³ and the melting point of 94 °C (cf. 5450 Å³ and 157 °C for the pure complex, respectively, according to the present work). Here we report the synthesis and structure of both dense and open forms, as well as data on the versatility as inclusion host of the title compound.

Results and Discussion

α -Form of [CuL₂]. The reaction of CF₃COCH₂COC(OMe)-Me₂ (=HL) with Cu(II) salts in basic water/ethanol solution

* To whom correspondence should be addressed. E-mail: jar@ned1.sims.nrc.ca. Fax: (613) 998-7833.

[†] Issued as NRCC No. 40910.

[‡] National Research Council of Canada.

[§] Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences.

[‡] Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences.

(1) *Comprehensive Supramolecular Chemistry*, Vol. 10, Supramolecular Technology; Reinhoudt, D. N., Ed.; Pergamon: Oxford, 1996.

(2) (a) Allison, S. A.; Barrer, R. M. *J. Chem. Soc. A* **1969**, 1717–1723. (b) Ibragimov, B. T.; Talipov, S. A.; Aripov, T. F. *J. Inclusion Phenom.* **1994**, *17*, 317–324. (c) Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745–8756. (d) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600–11601. (e) Mak, T. S. W.; Bracke, B. R. F. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, p 39. (f) Gdaniec, M.; Ibragimov, B. T.; Talipov, S. A. *Ibid.* 139–140. (g) Reference 18c, pp 697–698. (h) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738. (i) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (j) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (k) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

(3) Gromilov, S. A.; Baydina, I. A.; Zharkova, G. I. *Zh. Strukt. Khim.* **1997**, *38*, 946–953 (in Russian).

Table 1. Parameters for the X-ray Experiments, Crystal Data and Structure Analysis for the Two Polymorphs of the Complex and Its Benzene Clathrate

	α -[CuL ₂]	β -[CuL ₂]	β -[CuL ₂] $\cdot\frac{2}{3}$ C ₆ H ₆
	Single-Crystal Experiment		
formula	C ₁₆ H ₂₀ CuF ₆ O ₆		C ₂₀ H ₂₄ CuF ₆ O ₆
formula weight	485.9		537.9
crystal color, habit	blue, massive		blue, prism
system, space group	orthorhombic, <i>Cmc</i> 2 ₁ (no. 36)		trigonal, <i>R</i> 3 (no. 148)
unit cell dimensions	<i>a</i> = 14.463(1) Å <i>b</i> = 15.827(1) Å <i>c</i> = 18.742(2) Å		<i>a</i> = 24.492(1) Å <i>c</i> = 10.624(1) Å
unit cell volume	4290(1) Å ³		5519(1) Å ³
<i>Z</i>	8		9
calculated density	1.504 g cm ⁻³		1.457 g cm ⁻³
absorption coefficient	11.0 cm ⁻¹		9.7 cm ⁻¹
total reflections	22 996 (<i>R</i> _{int} = 0.029)		13 098 (<i>R</i> _{int} = 0.033)
number of unique reflections (<i>I</i> > 0)	5410		2879
number of unique reflections (<i>I</i> > 2σ(<i>I</i>))	4708		2408
number of parameters	438		288
unweighted agreement factor, <i>R</i> (data with <i>I</i> > 2σ(<i>I</i>))	0.042		0.040
weighted agreement factor	0.097		0.098
<i>R</i> _w ² (data with (<i>I</i> > 2σ(<i>I</i>)) ^a	<i>k</i> = 0.0469, <i>m</i> = 3.06		<i>k</i> = 0.0555, <i>m</i> = 3.71
goodness of fit	1.038		1.050
absolute structure parameter	0.04(2)		
residual extrema	+0.44, -0.33 e Å ⁻¹		+0.58, -0.17 e Å ⁻¹
	Powder Experiment		
number of used reflections	20	17	17
system	orthorhombic	trigonal	trigonal
unit cell dimensions	<i>a</i> = 14.468(4) Å <i>b</i> = 15.842(5) Å <i>c</i> = 18.734(9) Å	<i>a</i> = 24.417(2) Å <i>c</i> = 10.555(2) Å	<i>a</i> = 24.500(3) Å <i>c</i> = 10.623(3) Å
unit cell volume	4294(3) Å ³	5450(1) Å ³	5522(2) Å ³
	Packing Analysis		
packing coefficient	0.565(1)	0.498(1)	0.577(1)

$$^a R_w^2 = \sum [w(F_o^2 - F_c^2)^2] / \{ \sum [w(F_o^2)^2] \}^{1/2}; w = 1/[\sigma^2(F_o^2) + (kP)^2 + mP], \text{ where } P = (\max(F_o^2) + 2F_c^2)/3.$$

Table 2. Lengths (Å) and Angles (deg) of Additional Bonds in the Compounds Studied^a

compound	bond type	atom D	atom A	D...A	atom H	D...H	D...H-A
α -[CuL ₂]	coordination, intermolecular	O15B*2	Cu1A	2.804(3)			
	coordination, intermolecular	O15B*3	Cu1A	2.804(3)			
	coordination, intermolecular	O25B*2	Cu1A	2.702(8)			
	coordination, intermolecular	O25B*3	Cu1A	2.702(8)			
	hydrogen, intermolecular	O15A	C13A	2.615(6)	H13A	2.220(4)	104.6(3)
	hydrogen, intermolecular	O25A	C23A	2.846(7)	H23A	2.573(6)	97.3(3)
	coordination, intermolecular	O25A	Cu1B	2.695(5)			
	coordination, intermolecular	F23A*4	Cu1B	3.253(5)			
	hydrogen, intermolecular	O15B	C13B	2.834(5)	H13B	2.505(4)	101.1(3)
	hydrogen, intermolecular	O25B	C13B	2.913(9)	H13B	2.66(1)	96.6(3)
β -[CuL ₂] $\cdot\frac{2}{3}$ C ₆ H ₆	coordination, intermolecular	O15#2	Cu	2.800(2)			
	coordination, intermolecular	O15#3	Cu	2.800(2)			
	coordination, intermolecular	O25#2	Cu	2.879(6)			
	coordination, intermolecular	O25#3	Cu	2.879(6)			
	hydrogen, intermolecular	O15	C13	2.892(3)	H13	2.648(2)	93.6(2)
	hydrogen, intermolecular	O25	C13	2.773(7)	H13	2.429(8)	102.8(2)

^a Symmetry operators: (*2) = (-1/2 - *x*, 3/2 - *y*, 1/2 + *z*); (*3) = (1/2 + *x*, 3/2 - *y*, 1/2 + *z*); (*4) = (-*x*, 1 - *y*, -1/2 + *z*); (#2) = (1/3 - *y*, *x* - *y* - 1/3, *z* - 1/3); (#3) = (2/3 + *y*, 1/3 - *x* + *y*, 4/3 - *z*).

gives blue [CuL₂] bischelate. Ethanol and water are able to coordinate to the molecules, thus giving green products, but these solvents are easily removed by drying in air or by warming. Vacuum sublimation of the blue complex results in the pure crystalline α -form of [CuL₂] (see Figure 5 for a powder diffractogram). This is the stable polymorphic modification of the complex without pore space for guest inclusion. It sublimes at temperatures above 150 °C and melts congruently in a sealed tube at 157 °C to give green liquor.

From X-ray structure determination (Tables 1 and 2) α -[CuL₂] is orthorhombic, with two crystallographically independent complex units (labeled A and B). Both have square-planar coordination of the Cu(II) cation by four donor oxygens from

two chelate ligands (Figure 1). The Cu-O bond lengths are quite short at 1.90–1.92 Å. The difference between A and B molecules is in the arrangement of the ligands; molecule A has a trans configuration, while that of unit B is cis. The crystal is therefore an equimolar mixture of two isomers of the compound situated in an ordered crystal lattice.⁴

The trans molecule A is located on a mirror plane perpendicular to the crystallographic *a* direction. The copper atom and chelate rings lie in the plane, while the trifluoromethyl and

(4) This phenomenon is interesting itself, and is analogous to contact conformational isomerism (coexistence of different conformations in the same structure)⁵ and contact stabilization of molecules.⁶ It may be referred to as "contact coordinational isomerism".

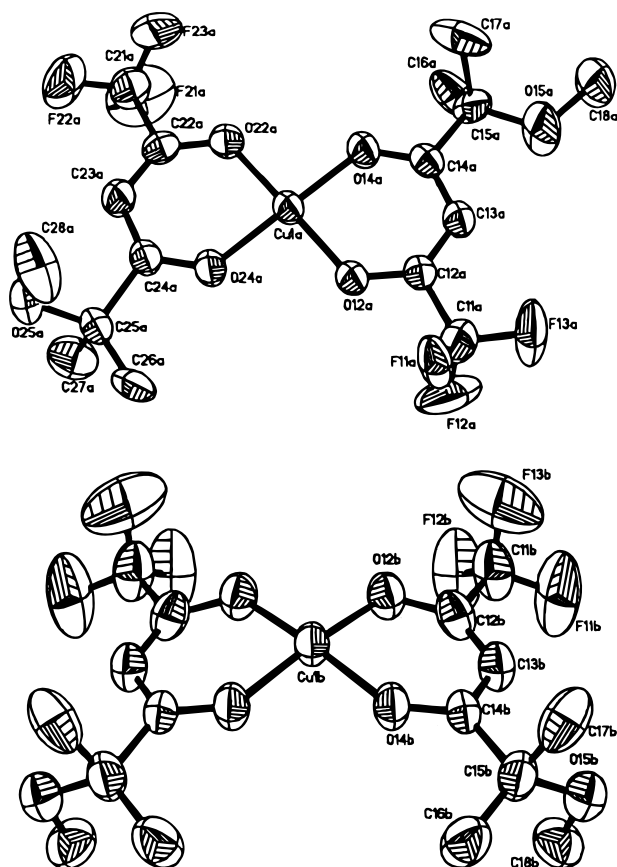


Figure 1. Two complex units found in α -[CuL₂]: top, trans isomer; bottom, cis isomer. Each unit cell contains four trans and four cis units.

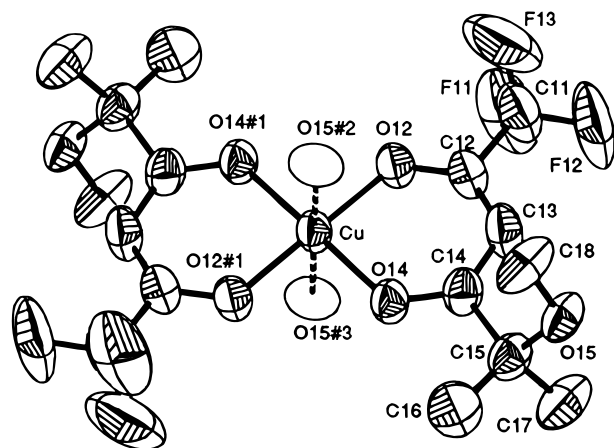


Figure 2. Host molecule and oxygen atoms of neighboring hosts in β -[CuL₂] \cdot $\frac{2}{3}$ C₆H₆.

methoxy-*tert*-butyl substituents are disordered on either side of the plane. The molecule is asymmetric but roughly approximates centrosymmetry (cf. the molecule in the benzene inclusion, Figure 2). Molecule B is cleaved by a mirror plane through the copper atom, the molecule thus consisting of two symmetrically placed halves in a cis configuration. Also, the bischolate fragment is bent, with the dihedral angle between chelate rings as large as 20°.

Each isolated molecule has two extra coordination sites on the copper cation and two donor oxygen atoms associated with the methoxy groups. There also are two hydrogen atoms whose acidity is promoted by the participation of adjacent carbons in the π -system of the chelate ring and the shifting of electron density toward the copper cation. Therefore, two additional types

of specific interactions occur in the structure (Table 2). All possible intramolecular C—H \cdots O hydrogen bonds are observed. As for the additional apical coordination to copper, this interaction is impossible within the same molecule and thus of necessity becomes intermolecular. Except for atom O15A, all methoxy oxygens participate in both types of interaction. It is interesting that the methoxy-*tert*-butyl fragment of molecule B is disordered over a main (89%) and a secondary (11%) orientation. The oxygen atom associated with the main orientation, O15B, coordinates to Cu1A at 2.80 Å and is linked to C13B at 2.83 Å by hydrogen bonding. The atom associated with the second orientation, O25B, is coordinated more strongly to Cu1A at 2.70 Å and forms a weaker connection to C13B at 2.91 Å. Ligation of atom O15A to copper is not observed, and instead one of the apical positions on Cu1B is occupied by fluorine F23A. Although the Cu—F bond is much weaker than Cu—O, its presence is evident from the interatomic distance of 3.25 Å, the mutual arrangement of the atoms, and the fact that the trifluoromethyl group containing F23A is the only one which is not disordered. Thus, the apical coordination sites on copper in molecule A are occupied by two oxygen donors, while in molecule B there are one oxygen and one fluorine atom.

α -[CuL₂] turns out to have a somewhat cumbersome, complicated crystal structure for such a simple molecule: it has a large unit cell with eight formula units, two crystallographically distinct molecules, isomerism within the same structure, a distorted geometry of the bischolate fragment in molecule B, and, finally, coordination of a trifluoromethyl fluorine atom to copper in the presence of available oxygen. All of these observations suggest that molecular packing is inefficient, and assembly to give a dense structure is difficult.^{75–7} Such problems of inefficient packing are overcome in the second, β -architecture of the compound. Although the packing arguments do not tell the entire story, they do give qualitative insight into the factors contributing to the relative thermodynamic stabilities of the two forms.

β -Inclusion with Benzene, β -[CuL₂] \cdot $\frac{2}{3}$ C₆H₆. When α -[CuL₂] is contacted by an appropriate (see below) liquid or gaseous organic guest, there is a significant increase in mass and a phase transformation to the trigonal β -modification (see, e.g., Figure 5a,b). Among the adducts with aromatics (Table 3), the benzene compound itself has remarkable stability: crystals of the compound show no mass decrease in a vacuum (0.03 Torr) for 24 h. In a closed volume the compound is stable up to 141 °C, at which point it melts incongruently into the solid α -form and green liquor.

The single-crystal X-ray diffraction study (Table 1) illustrates the inclusion character of the compound. The host complex molecule is centrosymmetric (Figure 2), closely resembling the trans configuration of molecule A in the α -form. There is square-planar ligation by two pairs of chelating oxygens from within the molecule. Donor oxygens associated with the methoxy groups take part in the formation of intramolecular hydrogen bonds with C—H groups of the chelate fragments, and at the same time ligate to the apical coordination sites on copper atoms of the adjacent molecules (Table 2). As for the α -form, disorder of the methoxy-*tert*-butyl tail is present. The oxygen atom in the main orientation (81%), O15, is coordinated to Cu at 2.80

(5) Zorkii, P. M.; Razumaeva, A. E. *Zh. Strukt. Khim.* **1979**, 20 (3), 463–466 (in Russian); *Chem. Abstr.* **1979**, 91, 174710a.

(6) (a) Dyadin, Yu. A.; Kislykh, N. V. *Mendeleev Commun.* **1991**, 134–136. (b) Dyadin, Yu. A.; Soldatov, D. V.; Logvinenko, V. A.; Lipkowski, J. J. *Coord. Chem.* **1996**, 37, 63–75.

(7) Kitaigorodsky, A. I. *Mixed Crystals*; Nauka: Moscow, 1983 (in Russian).

Table 3. β -[CuL₂] and Its Inclusions^a

N	guest	unit cell parameters			composition G:H	
		<i>a</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³	method A	method B
1	(empty phase)	24.417(2)	10.555(2)	5450(1)		
2	benzene, C ₆ H ₆	24.500(3)	10.623(3)	5522(2)	0.661(4)	0.68
		<i>24.492(1)</i>	<i>10.624(1)</i>	<i>5518(1)</i>		
3	fluorobenzene, C ₆ H ₅ -F	24.544(3)	10.655(2)	5559(2)	0.659(4)	0.68
4	chlorobenzene, C ₆ H ₅ -Cl	24.572(5)	10.720(8)	5605(4)	0.650(8)	0.66
5	bromobenzene, C ₆ H ₅ -Br	24.512(3)	10.618(2)	5525(2)		0.58
6	iodobenzene, C ₆ H ₅ -I	24.458(6)	10.581(3)	5481(3)		0.48
7	trifluoromethylbenzene, C ₆ H ₅ -CF ₃	24.517(5)	10.539(4)	5486(3)	0.474(5)	0.50
8	trichloromethylbenzene, C ₆ H ₅ -CCl ₃	24.456(5)	10.519(4)	5448(3)		0.39
9	nitrobenzene, C ₆ H ₅ -NO ₂	24.500(4)	10.555(3)	5487(2)		0.53
10	benzaldehyde, C ₆ H ₅ -CHO	24.488(6)	10.604(3)	5507(3)		ca. 0.3
11	toluene, C ₆ H ₅ -CH ₃	24.650(5)	10.720(4)	5641(3)	0.657(9)	0.66
12	ethylbenzene, C ₆ H ₅ -C ₂ H ₅	24.505(4)	10.525(3)	5473(2)	0.386(8)	0.46
		<i>24.519(4)</i>	<i>10.522(3)</i>	<i>5479(2)</i>		
13	cyclopropylbenzene, C ₆ H ₅ -CH(CH ₂) ₂	24.462(5)	10.525(4)	5454(3)	0.36(1)	0.40
		<i>24.491(5)</i>	<i>10.546(2)</i>	<i>5478(2)</i>		
14	propylbenzene, C ₆ H ₅ -C ₃ H ₇	24.455(4)	10.502(4)	5432(3)	0.34(1)	0.37
		<i>24.467(4)</i>	<i>10.503(2)</i>	<i>5445(2)</i>		
15	<i>tert</i> -butylbenzene, C ₆ H ₅ -C(CH ₃) ₃	24.513(6)	10.520(5)	5475(3)	0.34(1)	0.39
		<i>24.514(5)</i>	<i>10.531(2)</i>	<i>5481(2)</i>		
16	4-fluorotoluene, 4-F-C ₆ H ₄ -CH ₃	24.483(5)	10.526(4)	5464(3)	0.413(8)	0.48
17	4-fluoroanisole, 4-F-C ₆ H ₄ -OCH ₃	24.460(6)	10.521(5)	5451(3)	0.38(1)	0.41
18	<i>o</i> -xylene, <i>o</i> -CH ₃ -C ₆ H ₄ -CH ₃	24.652(6)	10.661(5)	5611(3)	0.62(1)	0.63
19	<i>m</i> -xylene, <i>m</i> -CH ₃ -C ₆ H ₄ -CH ₃	24.555(5)	10.564(5)	5516(3)	0.34(1)	0.41
		<i>24.542(6)</i>	<i>10.579(2)</i>	<i>5518(2)</i>		
20	<i>p</i> -xylene, <i>p</i> -CH ₃ -C ₆ H ₄ -CH ₃	24.487(4)	10.566(3)	5487(2)	0.36(1)	0.41
		<i>24.500(5)</i>	<i>10.554(2)</i>	<i>5486(2)</i>		
21	<i>o</i> -dichlorobenzene, <i>o</i> -Cl-C ₆ H ₄ -Cl	24.784(6)	10.741(4)	5714(3)		0.66
22	hexafluorobenzene, C ₆ F ₆	24.541(6)	10.609(5)	5533(3)	ca. 0.4	
23	mesitylene, 1,3,5-(CH ₃) ₃ -C ₆ H ₃			does not react		

^a Unit cell parameters from powder patterns are given in normal type with those from the single-crystal measurement (if available) in italics. For an explanation of methods A and B see the text. The experimental error in method B is ~3%.

Å and connected to C13 at 2.89 Å by hydrogen bonding, whereas the atom of the secondary orientation (19%), O25, is coordinated more weakly to Cu at 2.88 Å but connected more strongly to C13 at 2.77 Å.

The remarkable advantage of the β - over the α -framework is that all of the additional interactions possible involving the methoxy oxygen indeed occur in the former material. The polymer-like assembly results in a trigonal porous structure with straight channels along the *c* direction (Figure 3). The inner surface of each channel is formed by methyl and trifluoromethyl groups (Figure 3 (bottom)). The channel consists of alternating large and small cavities (Figures 4 and 6): the large cavity at $z/c = 0.3$ – 0.7 has two openings of more than 6.4 Å each, and the small cavities have one wide part at $z/c = 0.8$ – 1.2 and two constrictions at 5.3 Å. When each cavity is filled with one guest molecule, the guest-to-host molar ratio equals 2/3, a value that is actually observed for the benzene inclusion (see Table 3). Two orientations for the guest benzene molecule have been found (Figure 3). The first orientation is almost perpendicular to the channel direction in the large cavity, and there are two such sites symmetrically located on either side of the cavity center. Its low thermal parameters (see the Supporting Information) suggest that this benzene is particularly tightly bound and may be responsible for the high stability of the compound by tightly blocking the channel. The second orientation corresponds to a longitudinal displacement of the tilted guest into the small cavities, and again there are two such sites symmetrically displaced from the cavity center; the thermal parameters are twice those of the first orientation. Since the sites overlap, the cavity can be occupied by only one molecule. This and the approximately 50% distribution between the perpendicular and tilted orientations imply alternation of these two orientations

along the channel direction so that each cavity is occupied by one benzene molecule (Figure 4).

Inclusions with Benzene Derivatives. Data for inclusions of the complex with benzene derivatives are summarized in Table 3. These were prepared and analyzed by two independent methods. In method A (isopiestic method),^{2a,8} the reactions take place by gas-phase guest transport and result in a complete phase transformation into the β -form (cf. Figure 5a,b). It should be noted that reproducible results were obtained only with the thoroughly purified complex, and two or three sorption–desorption cycles often were necessary to avoid oversaturation and wetting of the samples. This requirement probably arises because of a side process by which α -[CuL₂] dissolves in excess liquid guest. Taking the process through a number of cycles also is likely to produce crystals that are not too dissimilar in size and therefore capable of a uniform response to the solvation or desolvation process. The isopiestic method also served for the determination of equilibrium compositions. Method B involved crystallization of α -[CuL₂] from neat guests. Unit cell parameters were obtained from powder patterns in an atmosphere of the corresponding guest. For inclusions that were stable enough, unit cell parameters were also determined on a single-crystal diffractometer. Inclusions of benzene and *m*- and *p*-xylenes are examples of the most stable compounds in the series. The majority of inclusions lost guest material in air, revealing the type of decomposition that is typical of solid solutions;⁹ the crystals cracked, retaining their habit and transparency. Often it was even possible to observe a decrease

(8) (a) Angla, B. *Ann. Chim.* **1949**, 4, 639–698; *Chem. Abstr.* **1950**, 44, 3442c. (b) Schlenk, W. *Justus Liebigs Ann. Chem.* **1949**, 565, 204–240; *Chem. Abstr.* **1950**, 44, 3900a.

(9) (a) Kemula, W.; Lipkowski, J.; Sybilska, D. *Rocz. Chem.* **1974**, 48, 3–12. (b) Reference 18a, p 94.

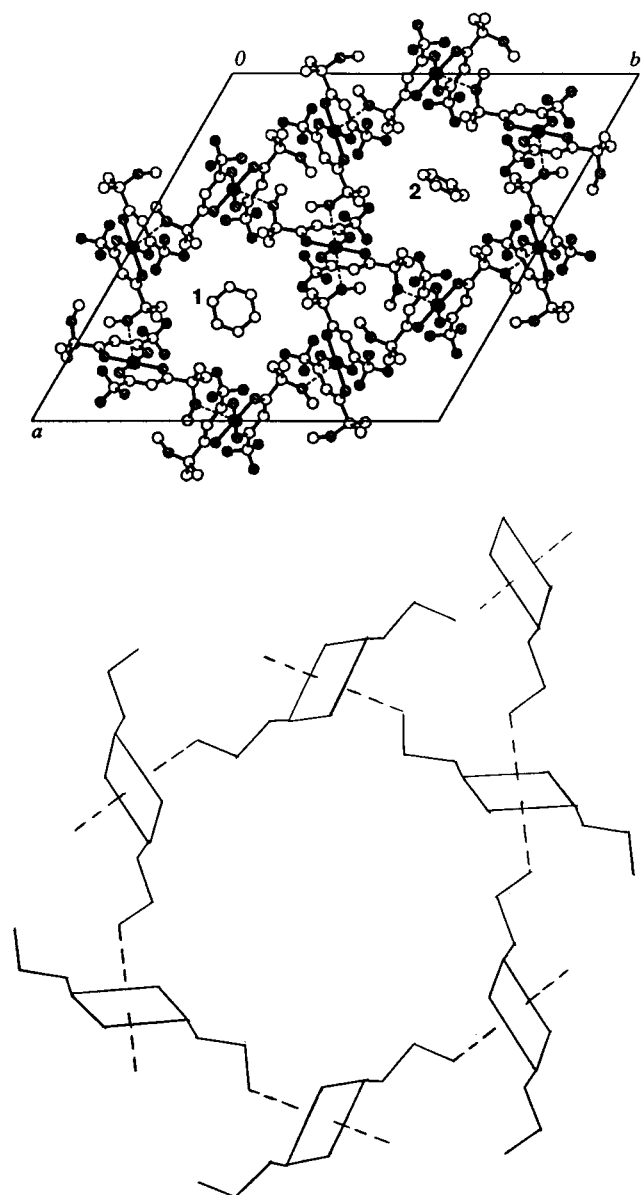


Figure 3. Molecular packing and mode of assembly in $\beta\text{-}[\text{CuL}_2]\cdot\frac{2}{3}\text{C}_6\text{H}_6$. Top: the host framework along the channel direction, showing the included benzene molecules. For clarity, two independent orientations of the guest molecules are shown in the two channels; hydrogen atoms are not shown. Bottom: schematic showing how the copper chelate building blocks are linked to form the channel. The rectangles represent the roughly square-planar ligation around the copper atoms located at the center of the rectangles. Each copper chelate uses one donor (O—Cu) and one acceptor (Cu—O) link (shown as dashed lines) to connect to other building blocks forming the channel, and the other donor and acceptor links connect to building blocks forming neighboring channels.

in unit cell parameters on repeating single-crystal X-ray experiments every 2 h. The least stable in the series were inclusions of hexafluorobenzene and *o*-xylene. Guest-to-host ratios were determined with ^1H NMR analysis.

As one can see from Table 3, all inclusions are isostructural and have a trigonal *R* cell. There is some difference in composition for the same inclusions obtained by methods A and B. Taking into account different synthetic conditions for the methods, we suggest that method A defines the lower limit of the equilibrium guest content, whereas method B gives the maximum (but not necessarily the equilibrium) guest content in the crystalline inclusions. This assumption is supported by

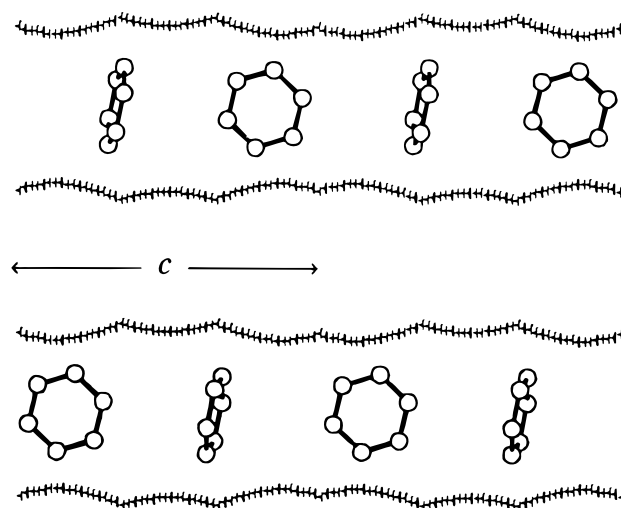


Figure 4. Possible variants of local ordering of benzene molecules in the channels of $\beta\text{-}[\text{CuL}_2]\cdot\frac{2}{3}\text{C}_6\text{H}_6$.

the fact that for compact, sterically simple guests the compositions coincide within experimental error.

From Table 3, the organic guests may be divided into three groups with regard to their ability to be included. First is the group of small, relatively compact molecules that are included with molar ratios close to the ideal value of 2/3. These are benzene, its F, Cl, and Me derivatives, and the *ortho* isomers of xylene and dichlorobenzene. The second group consists of molecules that are small enough to be included, but that are too long to fill all available cavities stoichiometrically. The resulting inclusions are typical solid solutions with nonstoichiometric compositions that depend on the guest size and the *P*–*T* conditions during synthesis. The final group consists of compounds that are too large to be included: mesitylene is an example of this and thus is a convenient choice as a nonincluded solvent for the title complex.

Sorption of Gases, Phase Conversion Catalysis, and Empty $\beta\text{-}[\text{CuL}_2]$. In the course of our experimental work we encountered an interesting phenomenon: the complex in its α -form reacts with hydrocarbons that are gases under ambient conditions. Reactions occur at room temperature and atmospheric pressure and result in a complete transformation to the β -form.¹⁰ With ~ 0.5 g samples the reactions with neopentane (bp +9.5 °C), *n*-butane (bp –0.5 °C), isobutylene (bp –7 °C), and isobutane (bp –11.7 °C) were complete after several hours, the rates correlating with boiling points and decreasing in the given sequence. During the reaction, the samples revealed mass increases of about 7 wt % due to the absorbed gas, the first portions of which disappeared again quickly when the material was removed from the gas stream. In air, the samples showed a gradual return to the original α -form.

These observations are exciting as they have bearing on the potential of the host material for applications involving gases where conventional host materials are not effective. In addition, the transformation itself demonstrates an amazingly strong affinity of the host for the channel form. Finally, the results provide convincing evidence of the relative robustness of the empty framework. Indeed, we have developed an elegant method of preparing pure, empty $\beta\text{-}[\text{CuL}_2]$ by finding a suitable

(10) This should be clearly distinguished from other types of processes with participation of gaseous guests: (a) trapping of gas molecules into the closed cages of clathrate hydrates, β -hydroquinone, Dianin's compound,¹¹ and calixarenes.¹² (b) Sorption into ready-made empty matrixes.^{2a,13} (c) Reactions with guest vapor at full saturation.¹⁴

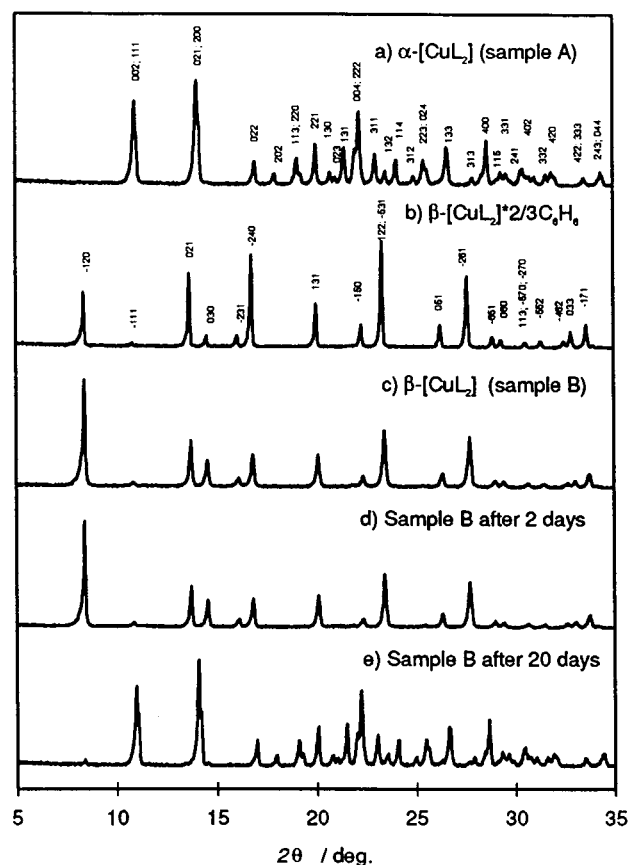
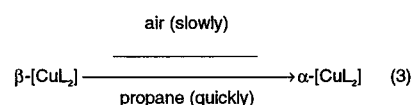
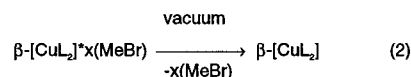
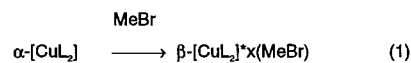


Figure 5. Selected powder diffractograms ($\lambda = 1.7902 \text{ \AA}$): (a) α -[CuL₂] after vacuum sublimation (sample A); (b) sample A after saturation with benzene for 24 h (the mass increase corresponds to 0.67 mol of benzene); (c) sample A after treatment with methyl bromide (2 h), followed by evacuation (3 h); the final mass equals that of the original sample (sample B); (d, e) sample B after 2 and 20 days, respectively.

“transforming” gas. Methyl bromide (bp +3.6 °C), with a compact molecule of maximum van der Waals diameter of 5.6 Å, is easy to remove from the framework. After α -[CuL₂] (Figure 5, “sample A”) is treated with methyl bromide for 2 h (eq 1) followed by 3 h of evacuation (eq 2), the product (“sample B”) is the empty β -framework. The weight gain on transforming to the methyl bromide- β -[CuL₂] compound varied from 16.8% to 19%, which amounts to about 0.9 mol of guest for each host molecule. The compound quickly loses methyl bromide on exposure to air, and exposure to vacuum leads to a quantitative removal of the guest species as judged by the weight loss. X-ray powder diffraction confirmed that the product was the β -form; also the stability of the empty β -[CuL₂] framework (Figure 5) and He pycnometry confirmed the presence of void space accessible to helium (see below). Some structural parameters of β -[CuL₂] are given in Table 1. The very low packing coefficient of 49.8% is possible only because of sufficiently strong intermolecular bonds that sustain the porous structure.

Kept in air in a closed container, the empty β -[CuL₂] is stable for some days, eventually returning again to the α -form (eq 3). The rate of transformation depends on sample purity. For instance, treatment with propane accelerates the reversion to the α -form (eq 3).

The reversion is direct evidence that the empty β -form is thermodynamically unstable with respect to the α -form. The relative kinetic stability, however, is remarkable, and can be explained as follows. According to the above structural data, the α -form has half of the Cu chelate molecules present as the



cis isomer, whereas in the β -form they are all trans isomers. The phase change therefore depends on the isomerization of half of the chelate building blocks and implies that at least two coordination bonds around the Cu center must break. This process is clearly affected by the presence of a sorbent, perhaps acting as a catalyst. Typically, sorbents play a double role in the inclusion compound formation process: stabilizing the empty β -form (thermodynamic action) and catalyzing the cis–trans isomerization necessary for phase transformation (kinetic aspect). However, even if the sorbent does not stabilize the β -lattice sufficiently as a guest molecule, apparently it can still trigger the β -to- α conversion (see, e.g., eq 3) or assist in the α -to- β transformation. This latter ability is demonstrated very well by the following example. The α -form does not react with paraffin oil upon wetting, and only small quantities of the β -phase form in the course of prolonged grinding of the mixture. At the same time, addition of a little mesitylene (which cannot be included as guest) completes the reaction within minutes. The results suggest that the processes involving the title material may be effectively controlled by applying certain “switching” substances, making the material a candidate for “smart” applications.¹⁵

Helium pycnometry provides further evidence of the kinetic stability of the guest-free framework. The effective density found for the empty β -[CuL₂] exposed to He gas is relatively high at 1.604(5) g cm⁻³ (cf. 1.333 g cm⁻³ from powder diffraction), which leads to a pore volume per unit cell (for He) of 925(15) Å³, or 17%.¹⁶ From Table 3, one finds that this “effective” volume may increase at least by up to 20% as a result of framework expansion during guest inclusion. Assuming that the pore space is a uniform channel, the average channel diameter is 6.10(5) Å,¹⁶ similar to that in medium-pore zeolites such as ZSM-12 and mordenite.¹⁷ Due to the properties outlined above, β -[CuL₂] can be classified as a novel metal–organic zeolite mimic. Longer-term stabilization of the empty framework may be possible by the introduction of a small quantity of a suitable “pillaring” guest. At the same time, chemical modification of the title complex may well lead to a series of similar structures with different pore sizes and shapes.

It is not entirely clear whether the mechanism of conversion of the α - to the β -form, which occurs both for the isopiestic

(11) *Inclusion Compounds*; Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D., Eds.; Academic Press: London, 1984. (a) Jeffrey, G. A.; Vol. 1, pp 135–190. (b) MacNicol, D. D.; Vol. 2, pp 1–46. (c) Davies, J. E. D.; Vol. 3, pp 37–68. (d) Davidson, D. W.; Ripmeester, J. A.; Vol. 3, pp 69–128.

(12) (a) Brouwer, E. B.; Enright, G. D.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 5404–5412. (b) Brouwer, E. B.; Enright, G. D.; Ripmeester, J. A. *Chem. Commun.* **1997**, 939–940.

(13) Manakov, A. Yu.; Lipkowski, J. *J. Inclusion Phenom.* **1997**, *29*, 41–55.

(14) Kaupp, G. In *Comprehensive Supramolecular Chemistry*; Davies, J. E. D., Ripmeester, J. A., Eds.; Pergamon: Oxford, 1996; Vol. 8, p 398.

(15) Newnham, R. E. *Mater. Res. Soc. Bull.* **1997** (May), *22* (5), 20–34.

(16) For details see the Experimental Section.

(17) *Atlas of Zeolite Structure Types*; Meier, W. M.; Olson, D. H., Eds.; Butterworth-Heinemann: London, 1992.

method and for the determination of composition and the synthesis of the empty form as described above, is identical in these two instances. It is likely that surface adsorption of guest material occurs, followed by capillary condensation, dissolution of the guest, and recrystallization, especially for guests that are rather high boiling. However, this seems less certain for low-boiling guests, especially light hydrocarbons in which the host is essentially insoluble. If the process is seen as the reaction of a gas with a disorganized surface (e.g., such as also takes place for ice to give clathrates), the concepts of phase rebuilding¹⁴ might be more appropriate. Kaupp¹⁴ discusses various possibilities for gas-surface reactions involving enclathration in light of information gained from application of scanning microscopy.

Comparison with Other Classes of Inclusion Compounds.

The host framework is built up of metal-chelate building blocks connected to each other by secondary coordination bonds. From this viewpoint, the hosts are intermediate between Werner hosts¹⁸ with their pure van der Waals interactions and typical coordination polymers such as the host complexes with 4,4'-dipyridyl¹⁹ or cyanide²⁰ ligands. It is peculiar in that despite the simplicity of the CuL₂ building blocks, the mode of their assembly is far from obvious (Figure 3 (bottom)). The "4 × 2" mode of assembly (coordination by four strong intermolecular and two weak intermolecular ligands, all with a single neutral building block) is worthy of investigation as a new strategy for the assembly of novel open frameworks. Note that coordination polymers based on chelated Cu(II) centers have been described elsewhere,²¹ and although no open channel frameworks were observed among them, these systems exemplify possible directions in such design.

Regarding symmetry, the β -[CuL₂] framework belongs to a very large group of trigonal (hexagonal) inclusion lattices, many of which have the same space group and similar unit cell dimensions and channel sizes. They may be found among the Werner clathrates,²² porphyrin-based frameworks,²³ Dianin's compound clathrates,²⁴ alicyclic diols,^{2c} "trigonal-symmetry" organic hosts,²⁵ etc.

The void space in the material is intermediate in character between that of true channel inclusions such as urea and

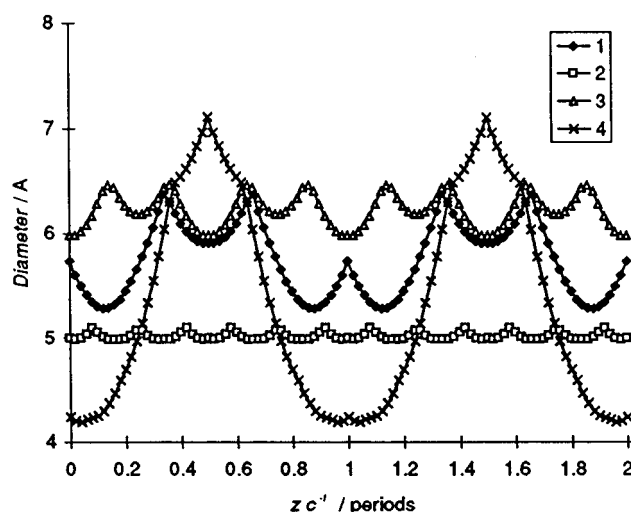


Figure 6. Characterization of the channel shape. The diameter of the inscribed sphere centered at (0, 0, z/c) versus z/c for the host frameworks: 1, β -[CuL₂] \cdot ²/₃C₆H₆; 2, urea; 3, thiourea; 4, Werner clathrate Mg(4-MePy)₄(NCS)₂. All are trigonal (hexagonal), with the channel along the z -axis; c parameters are between 10.6 and 12.6 Å.

thiourea²⁶ and that of the connected large cages typical of the trigonal Werner clathrates^{22c} (Figure 6).²⁶ This results in two qualitatively different types of inclusions: inherent nonstoichiometric ones such as classic inclusions of urea with hydrocarbons, and inclusions with compositions near the maximum structural stoichiometry. As one can see from Table 3, the β -[CuL₂] lattice is capable of some "adjusting" to a certain guest within a small range. Comparison of the data for β -[CuL₂] and the inclusions with X-C₆H₅ (X = H, F, Cl, Br, I) shows that elongation of the guest in one dimension results in a slight expansion of the framework at constant (maximum) stoichiometry. However, when the substituent is larger (bromo- or iodobenzene), the guest content drops sharply and the cell parameters of the framework tend to approach those of the empty lattice.

There is however a difference between nonstoichiometric inclusions of urea and β -[CuL₂]. In urea inclusions guest species are tightly packed, resulting in the appearance of an independent crystallographic period for the guest subsystem which does not coincide with the respective unit cell period of the urea host framework.^{27a} This was attributed to the thermodynamic and kinetic instability of the empty urea framework.²⁸ During experiments with the β -[CuL₂] inclusions we did not observe extra reflections in the powder diffraction patterns that could be assigned to independent "guest" periodicity. Most likely, the void space in our nonstoichiometric compounds is filled with disordered species, and if so, their inclusion into β -[CuL₂] resembles the sorption inside capillary tubes rather than the formation of densely packed supramolecular architectures.

(25) (a) Gardil, R. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, pp 243–252. (b) Allegra, G.; Farina, M.; Immirzi, A.; Colombo, A.; Rossi, U.; Broggi, R.; Natta, G. *J. Chem. Soc. B* **1967**, 1020–1028. (c) Freer, A. A.; MacNicol, D. D.; Mallinson, P. R.; Vallance, I. *Tetrahedron Lett.* **1992**, 33, 261–264.

(26) For channel geometry in urea and thiourea see also: (a) George, A. R.; Harris, K. D. M. *J. Mol. Graphics* **1995**, 13, 138–141. For Figure 3 X-ray data on clathrates of urea with n -hexadecane,^{27a} thiourea with adamantane,^{27b} and [Mg(4-MePy)₄(NCS)₂] with 4-MePy and water^{22c} were used.

(27) (a) Harris, K. D. M.; Thomas, J. M. *J. Chem. Soc., Faraday Trans. 1990*, 86, 2985–2996. (b) Gopal, R.; Robertson, B. E.; Rutherford, J. S. *Acta Crystallogr., Sect. C* **1989**, 45, 257–259.

(28) (a) Belosludov, V. R.; Lavrentiev, M. Yu.; Dyadin, Yu. A. *J. Inclusion Phenom.* **1991**, 10, 399–422. (b) Dyadin, Yu. A.; Bondaryuk, I. V.; Aladko, L. S. *J. Struct. Chem.* **1995**, 36, 995–1045.

(18) (a) Lipkowski, J. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 59–103. (b) Hanotier, J.; Radzitzki, P. *Ibid.* pp 105–134. (c) Lipkowski, J. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, pp 691–714.

(19) (a) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. In *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; pp 256–273. (b) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, 116, 1151–1152 and refs 2–4 therein. (c) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 23, 283–288. (d) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2127–2129.

(20) Iwamoto, T. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D.; Toda, F.; Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, pp 643–690.

(21) (a) Saalfrank, R. W.; Danion, D.; Hampel, F.; Hassa, J.; Struck, O.; Toupet, L. *Chem. Ber.* **1994**, 127, 1283–1286. (b) Saalfrank, R. W.; Struck, O. *Chem. Mater.* **1994**, 6, 1432–1436. (c) Saalfrank, R. W.; Harbig, R.; Struck, O.; Peters, E.-M.; Peters, K.; Schnering, H. G. *Z. Naturforsch. B* **1996**, 51, 399–408 (in German). (d) Saalfrank, R. W.; Harbig, R.; Struck, O.; Hampel, F.; Peters, E.-M.; Peters, K.; Schnering, H. G. *Z. Naturforsch. B* **1997**, 52, 125–134 (in German).

(22) Pervukhina, N. V.; Podberezskaya, N. V.; Davydova, I. V.; Kislykh, N. V.; Dyadin, Yu. A. *J. Inclusion Phenom.* **1992**, 13, 9–16. (b) Lipkowski, J.; Soldatov, D. V.; Kislykh, N. V.; Pervukhina, N. V.; Dyadin, Yu. A. *J. Inclusion Phenom.* **1994**, 17, 305–316. (c) Lipkowski, J.; Soldatov, D. V. *J. Inclusion Phenom.* **1994**, 18, 317–329.

(23) Krupitsky, H.; Stein, Z.; Goldberg, I. *J. Inclusion Phenom.* **1994**, 18, 177–192.

(24) (a) Ref 11b, 15. (b) Abriel, W.; Bois, A.; Zakrzewski, M.; White, M. A. *Can. J. Chem.* **1990**, 68, 1352–1356.

It is interesting to compare the title material with others that show similar zeolite-like behavior. Although a number of such systems are known,² currently only one has been studied in detail and continues to attract interest because of its high selectivity. This is the so-called β -phase of $[\text{Ni}(\text{4-MePy})_4(\text{NCS})_2]$ and some related complexes.^{18a,c} It is formed by van der Waals packing of coordinatively saturated units, and therefore it is rather flexible, expanding by as much as 9% during the inclusion process.²⁹ The sorption behavior of the material was studied and explained well in relation to its structure,^{13,18a} and attractive applications in chromatography have been suggested.³⁰ At the same time, a number of properties of the material, such as the thermal dissociation of the complex or the absence of changes in chemical bonding during the α - β -phase interconversions, place limits on its general application. In this sense, $[\text{CuL}_2]$ with the remarkable stability of the molecule and the possibility of catalytic switching between polymorphic forms gives real possibilities for its potential as a useful material.

Versatility, Chemical Stability, and Regeneration of the Host Material. The wide variety of guests (~ 100 guests have now been checked in addition to those given in Table 3) includes normal, branched, and cyclic hydrocarbons, their F, Cl, Br, I, and S derivatives, alcohols, ethers, esters, ethers of mineral acids, acid anhydrides, aldehydes, ketones, and compounds with nitro, amido, and nitrile functions.³¹ The material is thus versatile and is also stable in the presence of many classes of organic compounds. Inclusion of monomers such as isoprenes or lactones has potential for directed polymer syntheses inside the matrix. We also note the marked selectivity of inclusion. For example, the difference in stability and composition for inclusions of xylene isomers, as mentioned above, may well be useful for separation and purification processes.

Compounds with strong donor groups such as amines, or compounds with oxygen-containing functions capable of coordinating to copper centers, cause the loss of the capacity for inclusion of the host material. In many cases this type of reaction is easily reversed and may also be used for process control by a temporary "switching off" of the inclusion properties.

Although the synthesis of the host material requires considerable effort, the material itself is remarkably convenient, as it is completely recoverable. Unless highly reactive guest species such as aldehydes or weakly volatile guests such as iodobenzene are to be used, recovery can be quantitative. The regeneration of the pure host is based on two or more cycles of two processes. First is a recrystallization from hexane/benzene, where the former is the highly preferred guest and the latter is added to increase the solubility of the complex and to keep impurities in solution. The second process is a vacuum sublimation that makes it possible to separate the pure host from the volatile guest and nonvolatile impurities. In the course of this work, the loss of material after about 40 regenerations did not exceed 10%. Some of the coordination properties mentioned above might make even more effective recovery possible.

Conclusion

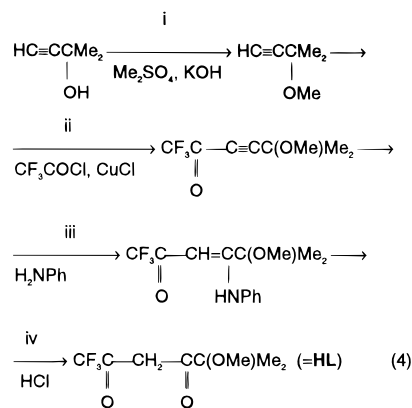
Molecular metal complexes are very attractive as building units for supramolecular architectures. This is because a wide possible variability of the units makes it possible to provide delicate control over selectivity, porosity, and sorption capability of these host materials. On the other hand, the simplicity of initiating self-assembly or the reversible destruction of such

systems by adding solvent or changing pH may be seen as an advantage in the design of future molecular-scale processes. This study demonstrates the extremely high potential for molecular complexes; the material presented here reveals novel properties such as the remarkable stability of the empty inclusion framework, catalytically induced switching between dense and open forms, and transformation from the dense to the porous form in an atmosphere of aliphatic hydrocarbon gases. At the same time, the mode of molecular assembly resulting in the open form of the title complex is neither obvious nor trivial. It is hoped that detailed analysis of such systems may well lead to the formulation of new approaches to supramolecular chemistry and crystal engineering for the creation of a new generation of novel materials.

Experimental Section

General Information. Reagent or analytical grade chemicals were used. For step (ii) of the HL synthesis all reagents and solvents were purified and dried by conventional methods. GLC analyses were performed on a Khrom-5 chromatograph with a flame ionization detector and a 360×0.4 cm column with 5% SE-30 on Inerton AW with nitrogen as the carrier gas. Elemental analyses were carried out at the Institute of Organic Chemistry, Novosibirsk. IR spectra were recorded on a BIO-RAD FTS-40A spectrometer. ^1H NMR spectra were obtained with a Bruker DRX-400 instrument and analyzed with the XWIN-NMR 2.0 program package.

$\text{CF}_3\text{COCH}_2\text{COC}(\text{OMe})\text{Me}_2$ (=HL). This diketone was synthesized according to the scheme



Step (i), adapted from Merz's method,³² involved methylation of commercially available ethynyltrimethylcarbinol; alternatively, reaction between acetylene and acetone followed by methylation of resulting dimethylcarbinol in situ was used.³³ Steps (ii),³⁴ (iii), and (iv)³⁵ were reported before without details. (i) $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ (49 mL, 0.5 mol; Aldrich), tetrabutylammonium iodide (1 g), and 50% aqueous NaOH (104 g, 1.3 mol) were equilibrated by stirring for 15 min. Then dimethyl sulfate (57 mL, 0.6 mol) was added dropwise for 1 h, and the temperature of the mixture was kept below 40 °C. Next, this was stirred vigorously (mechanically) for 3 h, and then for 30 min after adding concentrated aqueous NH_3 (10 mL). After the addition of excess water, the organic phase was separated, washed with water, and dried over MgSO_4 . A little xylene was used to avoid losses during the manipulations. Distillation at 80–82 °C gave 44 g (90%) of pure product, $\text{HC}\equiv\text{CC}(\text{OMe})\text{Me}_2$ (98.1) [registry no. 13994-57-5, supplied by author], n_D^{20} 1.4005. (ii) Into a flask equipped with a good mechanical stirrer was

(32) Merz, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 846–847.

(33) Sokolov, I. E.; Kotlyarevskii, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 202–203 (in Russian); *Chem. Abstr.* **1980**, *92*, 214840x.

(34) Shergina, S. I.; Sokolov, I. E.; Zanina, A. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, 158–160 (in Russian); *Chem. Abstr.* **1992**, *116*, 255138 g.

(35) Sokolov, I. E.; Shergina, S. I.; Zanina, A. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, 1390–1392 (in Russian); *Chem. Abstr.* **1993**, *118*, 124090d.

(29) Lipkowski, J.; Majchrzak, S. *Rocz. Chem.* **1977**, *49*, 1655–1660.

(30) Kemula, W.; Sybilka, D. *Nature* **1960**, *185*, 237–238.

(31) The details of that study will be the subject of our next paper.

suspended powdered CuCl (20 g, 0.2 mol) in dry benzene (150 mL) under flowing argon. Triethylamine (30.3 g, 0.3 mol) was added, and the mixture was stirred under argon for 10 min. HC≡CC(OMe)Me₂ (19.6 g, 0.2 mol) was then added, and CF₃COCl (28 g, 0.2 mol) was fed to the mixture instead of argon. (The latter was prepared from benzoyl chloride and trifluoroacetic acid.³⁶) The reaction mixture was stirred vigorously during the addition and for 2 h afterward, and its temperature was kept below 40 °C. Finally, the resulting solution was separated from the sticky solid, and the rest of the product was extracted from the solid with three portions of 50 mL of benzene. The combined volumes of benzene solution were washed three times with 5% HCl (75 mL each) and then with water to neutral pH and dried over MgSO₄. After benzene was removed on a rotary evaporator, vacuum distillation gave 24 g (60%) of the product, CF₃COC≡CC(OMe)Me₂: bp 62 °C (42 Torr); *n*_D²¹ 1.3880; IR (neat) 2218 (ν C≡C), 1742 (ν C=O) cm⁻¹. Anal. Calcd for C₈H₉F₃O₂ (194.2): C, 49.48; H, 4.67; F, 29.36. Found: C, 49.80; H, 4.75; F, 28.92. (iii, iv) The mixture of CF₃COC≡CC(OMe)Me₂ (19.5 g, 0.1 mol) and aniline (11 g, 0.12 mol) in 120 mL of dioxane was stirred at 60 °C for 3 h and, after addition of 25 mL of 15% aqueous HCl, for a further 3 h. After cooling, the organic phase was extracted with three portions of toluene (50 mL each), washed with water, and dried over CaCl₂. Vacuum distillation yielded 12 g (55%) of the product, CF₃COCH₂COC(OMe)Me₂ (=HL): bp 80 °C (35 Torr); *n*_D²⁰ 1.4080; ¹H NMR (CDCl₃) δ 6.39 (~1H, enol H—O), 3.23 (3H, OMe), 1.37 (6H, Me), 1.31 (~1H, enol HC=C) ppm. Anal. Calcd for C₈H₁₁F₃O₃ (212.2): C, 45.29; H, 5.23; F, 26.86. Found: C, 45.21; H, 5.16; F, 26.21.

α-[CuL₂]. To the solution of HL (2.2 g, 10 mmol) and Cu(NO₃)₂·2.5H₂O (1.2 g, 5.2 mmol) in ethanol (15 mL) was added the solution of NaOH (0.4 g, 10 mmol) in 10 mL of water/ethanol (1:1) for 5 min. After the solution was mixed for 30 min at 40 °C, water (100 mL) was added. The resulting green precipitate was washed with water and dried in air in a warm place until it turned blue. Sublimation (160–180 °C, 10⁻³ Torr) resulted in 2 g (80%) of powder, or a fine crystalline blue product. X-ray powder diffraction was used for product identification. The presence of the β-modification was revealed by its strong reflection (−1,2,0) (see Figure 5). Depending on the degree and the nature of contamination, the product could be improved by holding it in a warm place, by repeated sublimation, or by recrystallization from benzene/hexane (1:1) followed by a double sublimation.

Synthesis and Analysis of Clathrates by the Isopiestic Method (Method A). For this method [CuL₂] was thoroughly purified by two cycles of recrystallization and double sublimation as described above. The product was then recrystallized from mesitylene (Aldrich, 99%), dried, and ground into a fine powder. Samples of 100–200 mg were placed in closed vessels along with a saturated solution of the complex in the corresponding guest solvent. After the sample reached constant mass, it was allowed to decompose in air for some time, and the experiment was repeated until reproducible results were obtained. Two independent determinations were made. One cycle took from several hours to several weeks depending on the guest. Compositions *x* of the resulting β-[CuL₂]₂·*x*G inclusions were calculated from the formula *x* = (Δ*m*/*m*₀)(*M*_H/*M*_G), where Δ*m* and *m*₀ are the mass increase and starting sample mass and *M*_H and *M*_G are host and guest molecular masses, respectively.

Synthesis and Composition of Crystalline Clathrates (Method B). [CuL₂] is quite soluble in all aromatics. Cooling of warm green solutions gave blue crystals of the inclusions. They were of different habit depending on the guest used, usually isometric prisms or blocks but sometimes needles (with *o*-dichloro- and trichloromethylbenzenes). Compositions were obtained from ¹H NMR spectra of their 0.05 M solutions in CDCl₃. Host protons appeared in the spectra as broad bands at 1.75–1.97 (>CH), 3.35 (Me), and 5.34 (OMe) ppm, whereas guest resonances were sharp. The integration errors were ~3%.

(Empty) β-[CuL₂]. Ground α-[CuL₂] (500 mg) and analogous control samples were placed in an atmosphere of methyl bromide (0.1 L/min flow of gas) at 20 °C. After the control samples revealed the full transformation to the β-form (powder diffraction control, cf. Figure

5), the treatment continued for another hour (2 h total). Then the sample was allowed to decompose in air (0.5 h) and in a vacuum (3 h, up to 5 × 10⁻⁴ Torr) until it returned to its original mass.

Single-Crystal Diffraction Analysis. Data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (λ = 0.7107 Å) and a graphite monochromator. Unit cell parameters were measured using all collected data. Absorption corrections were made using SADABS-32. Solution and refinement were performed using direct methods (SHELXS-86) and full-matrix least squares on *F*² (SHELXL-93) using all positive data. All non-hydrogen atoms of complex molecules were refined anisotropically, whereas hydrogen atoms were fixed in the calculated positions with temperature factors 1.2 times exceeding those of adjacent carbon atoms. More experimental details are given in Table 1 and in the Supporting Information.

Single crystals of α-[CuL₂] were prepared by slow sublimation. For this, about 400 mg of pure complex was sealed under vacuum inside a 10 cm long Pyrex tube. One end of the tube was held at room temperature while the temperature of the end containing the complex was heated gradually from 150 to 200 °C over a 24 h period. The crystals that formed in the cold end were shapeless but quite suitable for crystallographic measurements.

Prismatic crystals of β-[CuL₂]₂·*x*C₆H₆ (*x* = 2/3) were prepared directly by crystallization. No precautions were needed to prevent decomposition during data collection. Because of strong disordering of the guest subsystem, benzene molecules were assigned their ideal geometry and were refined isotropically with the same thermal factor for all atoms of each orientation. In the course of the refinement the value of 0.70(1) was first obtained for the mole ratio *x*. In the last cycles however it was fixed at 2/3 exactly. For this situation, site occupancy factors of 52.4(7)% and 47.6(7)% were obtained for the perpendicular and tilted orientations, respectively.

A single-crystal diffraction measurement of the unit cell was also performed on the CCD diffractometer. The actual values were derived from 100–200 reflections randomly selected at different angles.

Powder Diffraction Measurements. The unit cell dimensions of both complex forms and all inclusions, obtained by method B, were determined from powder patterns recorded on a Rigaku Geigerflex diffractometer (Co Kα radiation, λ = 1.7902 Å). The powder patterns were cross-checked with those calculated from the single-crystal results. Inclusions were studied in an atmosphere of the corresponding guest. NaCl was added for the zero angle correction. Least-squares refinements were carried out using 15–20 reflections in a 5–40° 2θ range. The data are summarized in Table 3.

Analysis of Packing and Empty Space. Packing coefficients³⁷ and the geometry of the channel and sections for β-[CuL₂]₂·²/₃C₆H₆ were calculated on the basis of the crystallographic data using the CLAT software package and the Zefirov–Zorkii system of van der Waals radii (C, 1.71; H, 1.16; Cu, 1.40; F, 1.35; O, 1.29 Å).³⁸ Changes of molecular geometry due to the disordering of fragments were found not to exceed declared experimental errors. For calculating the packing coefficient for empty β-[CuL₂], the volume of the complex molecule as it was found in the benzene inclusion was used.

Helium Pycnometry. A sample of 400 mg of β-[CuL₂] was used for the experiment (AccuPyc 1330 pycnometer); three determinations were made. The pore volume was obtained from

$$V_{\text{emp}}^{(\text{He})} = V_{\text{u,cell}} - \frac{ZM \times 10^{24}}{d^{(\text{He})}N_A} = 925(15) \text{ Å}^3 \quad (5)$$

where *V*_{emp}^(He) is the volume of β-[CuL₂] accessible to He (Å³), *V*_{u,cell} = 5450(1) Å³ is the unit cell volume, *Z* = 9 is the number of molecules per unit cell, *M* = 485.9 g mol⁻¹ is the molar mass of the complex, *d*^(He) = 1.604(5) g cm⁻³ (at 30.3 °C) is the value from the pycnometry experiment, and *N*_A = 6.02 × 10²³ mol⁻¹ is Avogadro's number.

(37) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973; p 18.

(38) (a) Grachev, E. V.; Dyadin, Yu. A.; Lipkowski, J. J. *Struct. Chem.* **1995**, *36*, 876–879. (b) Zefirov, Yu. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1995**, *64*, 415–428.

(36) Henne, A. L.; Alm, R. M.; Smook, M. J. *Am. Chem. Soc.* **1948**, *70*, 1968.

The average channel diameter $d_{\text{av}}^{(\text{He})}$ was determined from the formula

$$V_{\text{emp}}^{(\text{He})} = 3c\pi(d_{\text{av}}^{(\text{He})}/2)^2 \quad (6)$$

where 3 is the number of channels going through the unit cell and $c = 10.555(2)$ Å is the period of the unit cell along the channel axis.

Acknowledgment. This work was supported by the NATO Science Program through a Research Visit Grant for D.V.S. (SRG 951535). We thank Professor I. K. Igumenov for suggesting the possibility of using the title compound as a host material, Professor M. S. Shvartsberg for continuing support of this work, Drs. K. A. Udachin and G. Enright for consulta-

tions on the crystallographic studies, Drs. C. I. Ratcliffe and G. Shimizu for helpful discussions, Dr. A. Yu. Manakov for useful suggestions on analytical procedures, E. V. Grachev for the CLAT software package, and Dr. T. V. Rodionova and N. V. Udachina for facilitating contact between the working groups.

Supporting Information Available: Full tables of crystal data and structural refinement, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom parameters for α -[CuL₂] and β -[CuL₂] $\cdot 2/3$ C₆H₆ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA981443U