The Inclusion Mode of *tert*-Butylbenzene in the 1-D Channel of Microporous *β*-Bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxy-acetylacetonato) copper(II)

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Abstract

Inclusion of *tert*-butylbenzene into the l-D channel of the title host matrix results in a β-[CuL$_2$]·1/3(*tert*-butylbenzene) inclusion compound (trigonal, space group $R\bar{3}$; a = 24.495(3), c = 10.510(2) Å, V = 5461(1) Å^3, Z = 9; R = 0.049). The observed guest–host mole ratio of 1/3 was confirmed by X-ray diffraction and arises from the stoichiometric filling of the larger wide segments of the channel. This contrasts with the benzene inclusion compound studied previously, where both the larger and smaller wide segments were occupied to give a 2/3 guest–host stoichiometry. A comparison of these two structures explains the experimental fact that the guest–host mole ratios for inclusions of the title host lie between values of 1/3 and 2/3 for 20 different benzene derivatives.

Introduction

β-[CuL$_2$] (L = {CF$_3$COCHCOC(OMe)Me$_2$}$^-$) is a new microporous solid exhibiting zeolite-like behavior (unlike the α-form of the complex, which is a dense polymorph unable of acting as a sorbent) [2]. The 3-D assembly of the porous β-structure arises from metal-coordination bonding that connects the basic building blocks so as to form a 1-D channel of variable diameter. The channels have constrictions (Figure 1, top), the intervening broad portions having the character of large and small cavities. The unit cell contains 9 host units, and 3 of each type of cavity. In the benzene inclusion compound studied by X-ray crystallography [2], each cavity, large and small, is filled with one guest molecule (Figure 1, bottom), leading to a guest–host ratio of 2/3. Among 20 inclusion compounds of benzene derivatives only those of fluorobenzene, chlorobenzene, toluene, *o*-dichlorobenzene (and possibly *o*-xylene) have guest–host ratios that approach complete filling of the available cavities. Other inclusion compounds have smaller guest contents, implying non-stoichiometric character. This explains the failure of attempts to locate guest species from X-ray diffraction analysis for some of the compounds in question. In addition, two or three compounds have guest–host ratios close to 1/3, which may indicate the stoichiometrical filling of only one type of cavity, or the filling of two adjacent cavities by a single guest. The present study is devoted to an X-ray diffraction study of the β-inclusion compound of *tert*-butylbenzene.

Experimental

A full description of the synthesis of the title complex host as well as its inclusion compounds was given in our previous work [2]. There it was shown that exposure of host material to *tert*-butylbenzene guest vapor (isopiestic method) resulted in a powder product, stable in air, with the equilibrium guest–host ratio of 0.34(1) very near to a value of 1/3. For this study, inclusion compound crystals were prepared in the course of slow evaporation of the host solution in neat guest. A blue prism of 0.5 mm size was used. Data were collected on a Siemens SMART CCD diffractometer (monochromic Mo-K$_\alpha$-radiation, λ = 0.7107 Å; ω scan mode; 1.7–29° θ range; −33/33, −32/33, −14/14 h, k, l-range; room temperature). An empirical absorption correction utilised the SADABS routine associated with the Siemens diffracto-meter.

The structure was solved by direct methods using the SHELXS [3] system of programs. Refinement (anisotropic for the host non-hydrogen atoms) was performed on F^2 with SHELXL [4] using all data with positive intensities. The methoxy-*tert*-butyl fragment was found to be disordered over two orientations. Qualitatively, the second orientation (17%) may be produced from the main one through a 60° rotation around the C(14)—C(15) bond followed by a 180° turn around the O(15)—C(18) bond (for numbering scheme see Figure 2). Real rotations should be excluded for steric reasons, however. Atoms in this second orientation were refined isotropically with a general thermal factor fixed as a free variable and with bond lengths and valence angles fixed to be equal to those for the main orientation. Some constraints were applied also for the disordered trifluoromethyl group. The disorder assumes its rotation around the C(11)—

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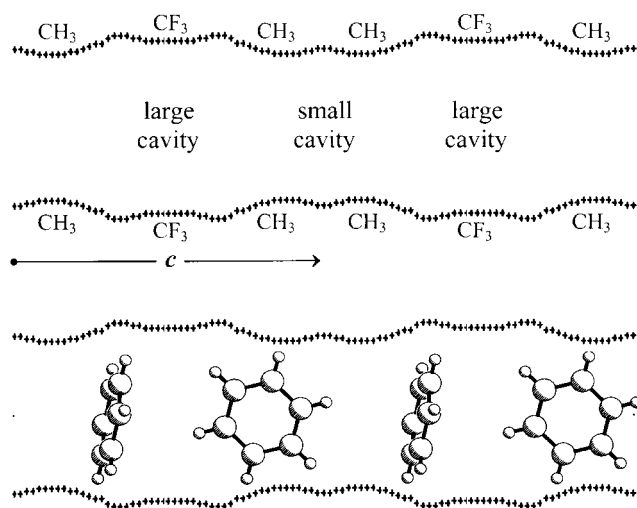
Figure 1. *Top*: Profile of the channel in β-[CuL$_2$]·2/3(benzene) as the diameter of the inscribed sphere along the channel axis. The groups making up the different parts of the channel and the disposition of the cavities are indicated. *Bottom*: Location of guest benzene species along the channel (one of possible variants). Each cavity, of both types, accommodates one guest molecule to give the 2/3 guest–host stoichiometry.
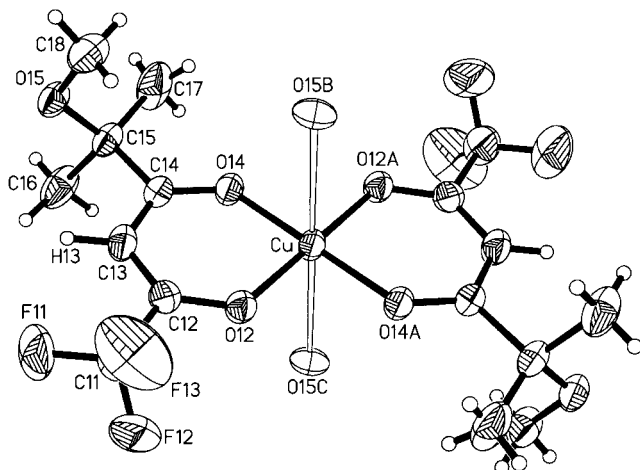
Figure 3. Channels in the 3-D host molecular assembly with the unit cell content along the *c*-axis; the guest is not shown.

e/Å^3) remaining in the residual density map was found at the $\bar{3}$ site (Wyckoff position b), whereas the next largest maximum was only 0.30 e/Å^3.

The structure was analyzed with standard programs. The profile of the channel was outlined using the CLAT program package [5]; the following system of van der Waals radii was applied: C, 1.71; H, 1.16; Cu, 1.40; F, 1.35: O, 1.29 Å.

Salient experimental details and the essential structural parameters are listed in Table 1. Selected geometric parameters for the structure are given in Table 2. Final fractional atomic coordinates as well as the remaining structural information has been deposited with the Cambridge Crystallographic Data Centre as CCDC 136730.

Figure 2. Host molecule and oxygen atom of neighboring hosts in β-[CuL$_2$]·1/3(*tert*-butylbenzene). A-labeled atoms are generated through centrosymmetry, O(15B) and O(15C) from O(15) with $(1/3 - y, 1/3 + x - y, -1/3 + z)$ and $(2/3 + y, 1/3 - x + y, 4/3 - z)$ operators, respectively.

C(12) bond as the group sticks out into the channel space (cf. Figures 1 and 3). Host hydrogen atoms were unconstrained, but isotropic thermal factors 1.2 or 1.5 greater than those for adjacent carbon atoms were applied.

Two symmetrically independent orientations of the guest *tert*-butylbenzene molecule were found. Because of the 6-fold symmetry arising from the $\bar{3}$-axis along the channel, the guest molecules were badly distorted; in the course of further refinement they were constrained to the ideal geometry with only the *tert*-butyl group rotating. The guest atoms were refined isotropically with fixed thermal factors. Site occupancy factors for both orientations were refined independently to give a value of 0.262(7) + 0.077(8) = 0.34(1) for the guest–host mole ratio. In the final cycles of refinement the total occupancy was fixed at an exact value of 1/3, the resulting R-value being 0.049. The only maximum (0.56
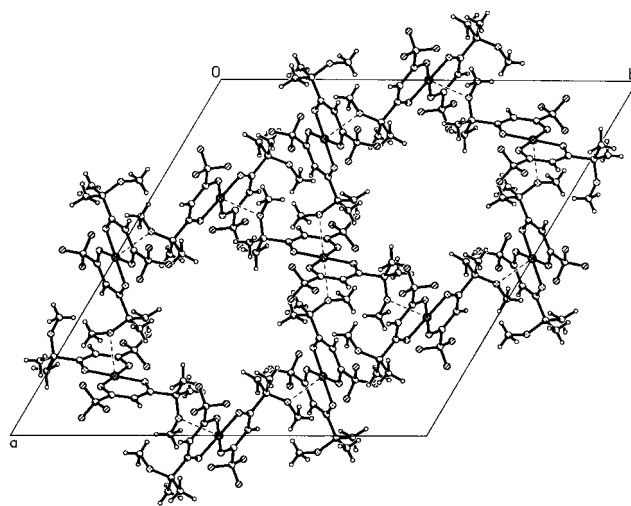
Results and discussion

The present study confirms the inclusion character and the expected stoichiometry of the compound studied, allowing its formulation as β-[CuL$_3$]-1/3(*tert*-butylbenzene). The structure consists of 3-D assembled electrically neutral [CuL$_2$] units and guest *tert*-butylbenzene species included in the available 1-D channel space. Topologically, the compound should be classified as a tubulate.

An ORTEP-drawing of the host unit is shown in Figure 2. It is centrosymmetric and thus is *trans*-configured. The copper(II) center is in the square-planar environment of four oxygen donors from two deprotonated acetylacetone units acting as bidentate ligands with Cu—O distances of 1.91–1.93 Å. The copper coordination is complete because of the apical methoxy oxygen donated by neighoring molecules at a distance of 2.79 Å. The methoxy oxygens also may be involved in intramolecular hydrogen bonding, with an O(15)···C(13) distance of 2.89 Å. The oxygen atom in the low-occupancy orientation of the —C(OMe)Me$_2$ fragment O(15′) forms a stronger bond to C(13) and a weaker bond to copper (Table 2). The main orientation of the —C(OMe)Me$_2$ fragment gives rise to a stronger intermolecular assembly through coordination bonding whereas

Table 1. Details of the structural determination and the main parameters for the structure.

Formula	β-[CuL$_2$]·1/3 (*tert*-butylbenzene)
Empirical formula	C$_{19,33}$H$_{24,67}$CuF$_6$O$_6$
Formula weight	530.6
Crystal system	Trigonal
Space group	$R\bar{3}$ (No. 148)
Unit cell parameters:	
a, Å	24.495(3)
c, Å	10.510(2)
V, Å	5461(1)
Z	9
Calculated density, g cm^{-3}	1.452
Absorption coefficient (MoK$_\alpha$), cm^{-1}	9.76
Number of unique reflections:	
Used ($I > 0$)	3148
Intense ($I > 2\sigma(I)$)	2507
Number of refined parameters	355
R-values:	
R_{int} (all data)	0.039
$RI = \Sigma \parallel F_o\| - \|F_c \parallel /\Sigma\|F_o\|$ (intense data)	0.049
$wR2$ (intense data)	0.123
Goodness-of-fit on F^2	1.091

Table 2. Selected host geometric parameters for β-[CuL$_2$]·1/3(*tert*-butylbenzene) (distances, Å; angles, deg.; for the numbering scheme see Figure 2)

Bond	Distance	bond type
Coordination bonds:		
Cu—O(12)	1.907(2)	Intramolecular
Cu—O(14)	1.929(2)	Intramolecular
Cu—O(15)B	2.786(2)	Intermolecular
Cu—O(15′)B	2.835(6)	Intermolecular
Covalent bonds:		
C(11)—F(11)	1.285(3)	
C(11)—F(12)	1.286(3)	
C(11)—F(13)	1.285(3)	
C(11)—C(12)	1.533(4)	
C(12)—O(12)	1.269(3)	
C(12)—C(13)	1.363(4)	
C(1IJ)—C(14)	1.390(4)	
C(14)—O(14)	1.259(3)	
C(14)—C(15)	1.557(4)	
C(15)—O(15)	1.433(4)	
C(15)—C(17)	1.502(6)	
C(15)—C(16)	1.537(5)	
O(15)—C(18)	1.422(4)	

Angles:			
O(12)—Cu—O(14)	92.47(7)	C(11)—C(12)—C(13)	118.9(2)
O(12)—Cu—O(14)A	87.53(7)	C(11)—C(12)—O(12)	112.2(2)
O(12)—Cu—O(15)B	93.59(7)	O(12)—C(12)—C(13)	128.9(2)
O(12)—Cu—O(15)C	86.41(7)	C(12)—O(12)—Cu	124.1(2)
O(14)—Cu—O(15)B	82.76(8)	C(12)—C(13)—C(14)	122.7(2)
O(14)—Cu—O(15)C	97.24(8)	C(13)—C(14)—C(15)	118.8(2)
O(12)—Cu—O(15′)B	76.5(2)	C(13)—C(14)—O(14)	124.4(2)
O(12)—Cu—O(15′)C	103.5(2)	O(14)—C(14)—C(15)	116.7(2)
O(14)—Cu—O(15′)B	90.8(3)	C(14)—O(14)—Cu	127.1(2)
O(14)—Cu—O(15′)C	89.2(3)	O(15)—C(15)—C(16)	105.6(3)
F(11)—C(11)—F(12)	106.7(2)	O(15)—C(15)—C(17)	108.3(4)
F(12)—C(11)—F(13)	106.8(2)	C(16)—C(15)—C(17)	114.6(6)
F(13)—C(11)—F(11)	107.1(2)	C(14)—C(15)—O(15)	107.5(2)
F(11)—C(11)—F(12)	112.3(2)	C(14)—C(15)—C(16)	109.7(3)
F(12)—C(11)—F(12)	111.9(2)	C(14)—C(15)—C(17)	110.8(3)
F(13)—C(11)—F(12)	111.7(2)	C(15)—O(15)—C(18)	115.0(3)

Intramolecular hydrogen bonds ($D \ldots H$—A):				
Atom D	Atom A	$D \ldots A$	Atom H	$D \ldots H$
O(15)	C13	2.886(4)	H13	2.60(4)
O(15′)	C13	2.839(7)	H13	2.48(4)

the second orientation contributes more to intramolecular interactions.

The 3-D host assembly (Figure 3) shows the channels lying along the c crystallographic axis. The inner surface of the channel is comprised of methyl and trifluoromethyl host moieties. The profile of the channel along the c-axis is shown in Figure 3. The channel diameter changes significantly, the minimum and maximum values being 4.85 to 6.36 Å, respectively. This variability of the channel diameter and chemical environment explain the preferences of the guest species for occupancy of definite sites that depend on guest polarity and geometry. Therefore, two types of sorption sites alternating along the channel have been identified (cf. Figure 1). The first, associated with the Wyckoff special position a ($\bar{3}$), is referred to as the "small cavity", while the second, at Wyckoff position b (also $\bar{3}$), is the "large cavity". In β-[CuL$_2$]·2/3 benzene [2] both are filled with benzene guest molecules (Figure 1). In the title compound, the guest species completely fill the large cavities (Figure 4) to give half the guest–host mole ratio of 1/3. The main orientation of the guest tert-butylbenzene (77%) lies almost along the channel axis inside the large cavity and has a slightly higher thermal parameter. The second orientation is inclined, and the phenyl moiety partially extends into the space of the small cavity.

The guest site identified for *tert*-butylbenzene is likely to be characteristic of medium-sized molecules like the substituted benzenes. Most likely, the value of 1/3 is the lower limit for the stoichiometry of compact guest molecules capable of being included into β-[CuL$_2$]. Remarkably, the guest–host values for 20 inclusion compounds with benzene derivatives lie between values of 1/3 and 2/3. Thus, the preferences in stoichiometry are well explained in relation to the microstructure of the host matrix.

Knowledge of the microstructure of the void space, including the dimensionality, geometry, the physical and chemical environment, makes it possible to explain and predict sorption behavior and selectivity of the host material. The 1-D urea channel nearly has a constant diameter and a homogeneous environment that results in the dense filling of available space with hydrocarbon and alcohol guest molecules without any special compositions or special preferences for guest length (though there is a remarkable selectivity for guest "thickness" separating unbranched species) [6]. Other matrices that possess less homogeneous cavity space reveal complicated preferences. Besides, the preferences may change with the quantity of absorbed guest
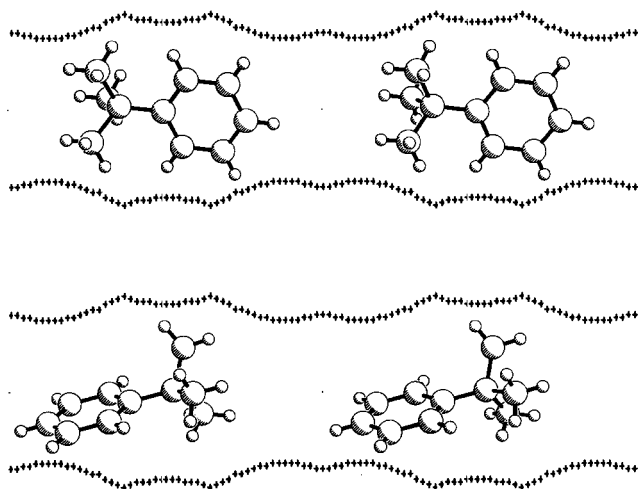
Figure 4. Location of guest species in the first orientation (*top*) and the second orientation (*bottom*) in the 1-D channel of β-[CuL$_2$]·1/3(*tert*-butylbenzene). All symmetrically equivalent positions are eliminated for clarity.

or they could induce the inclusion of two or more guest types at once to fill different types of sorption sites. In the structure studied, the sorption sites referred to as "small" cavities remain unoccupied whereas the presence of a second, help component, could lead to inclusion compounds of host·1/3(guest1)·1/3(guest2) stoichiometry. A similar situation was observed previously for the trigonal 1-D channel clathrates [M(4-MePy)$_4$(NCS)$_2$]·2/3(4-MePy)·l/3(H$_2$O), with water filling the small isthmuses between main cavities [7]. The presence of different sorption sites in the 3-D space of the β-[Ni(4-MePy)$_4$(NCS)$_2$] host [8] was used to explain sorption modes and the resulting compositions for a variety of guests [9].

The observations discussed may be useful, as the title material was found to reveal zeolite-like behavior, keeping its open structure even after complete guest removal [2]. Empty β-[CuL$_2$] is able to reabsorb an endless variety of organic species starting with the simplest hydrocarbon, methane. Thus, general principles may be applied to the title host, taking into account the unique channel microstructure of the host matrix.

Acknowledgement

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