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# New Synthesis and Complexing Properties of *p-tert*-Butyldihomooxacalix[4]arene. Structure of Its 1 : 2 Complex with Tetrahydrofuran

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**Abstract.** A new method is described for the synthesis of isolated *p-tert*-butyldihomooxacalix[4]arene (CALO) with a 24% yield. The ability of CALO to form complexes in the solid state with small neutral molecules has been studied; the potential guests were common solvents bearing various chemical functions. The powder obtained after evaporation of the solvent has been characterized by the X-ray powder diffraction technique. Analysis of the patterns shows the non-complexation of linear alkanes and alcohols, but formation of complexes when the guest is cyclic or when it bears an amine or a ketone function. As illustration of the possible arrangement of molecules in complexes, the structure of the 1 : 2 complex with tetrahydrofuran (THF) is presented: the crystals are monoclinic, space group $P2_1/c$, $a = 9.459(2)$ Å, $b = 17.286(2)$ Å, $c = 30.469(6)$ Å, $\beta = 92.52(2)°$, $V = 4977(2)$ Å$^3$, $Z = 4$, $D_c = 1.099$ Mg m$^{-3}$, $\lambda = 1.54178$ Å, $\mu = 5.6$ cm$^{-1}$, $R = 0.086$ for 3590 reflections with $F > 4\sigma$ (F); one of the THF molecules is inside the cavity of the macrocycle, while the other, in the interhost space, exhibits disorder. In the CALO molecule, three out of the four *tert*-butyl groups are disordered which may induce the disorder of the THF molecule.

**Keywords:** Calixarene, complexation, crystal structure.

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## 1. Introduction

The ability of *p-tert*-butyldihomooxacalix[4]arene (CALO) to form complexes with small neutral molecules has been known since it was obtained as a component of the product mixture in calixarene synthesis [1]. Molecular compounds with *meta*-xylene[2] and triethylamine[3] have been obtained and their crystal structures have been determined. The substitution of one methylene bridge by a $CH_2$—O—$CH_2$ group gives more flexibility to the macrocycle and increases the size of the cavity. The aim of this work is to systematically test the ability of CALO to form molecular compounds with solvents, in the solid state, and then to

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show the arrangement of molecules in these compounds. The 1 : 2 complex with tetrahydrofuran is studied.

Due to the difficulty in isolating and purifying CALO from a mixture of other calixarenes, Gutsche has proposed an alternative method for its preparation using the bis-hydroxymethyl linear tetramer as an intermediate [4]. Our studies of the mechanisms of formation of calixarenes has proved that CALO molecules [5] are present during the reaction leading to the synthesis of calix[8]arene[6]. Reaction diagrams are used to find the best conditions for formation of CALO, and a fast and simple method giving isolated CALO with a 24% yield is elaborated.

Common solvents tend to be small neutral molecules with a wide range of chemical functions; because of their size, they can be potential guests for the macrocycle and their chemical functions may induce H bonds or $CH_3$—$\pi$ interactions leading to new compounds. Alcohols, ketones, alkanes, aromatics, amines, heterocycles and compounds containing chlorine, nitrogen and sulfur are used as solvents. Because the ability of the macrocycle to form molecular compounds is highly dependent on the experimental conditions, we have adopted a standardised procedure and the results concern only the solid state and special experimental conditions. After evaporation of the solvent in the CALO-solvent mixture, powders were mostly obtained which have been analysed by X-ray powder diffraction. With THF as solvent, crystals suitable for a X-ray analysis were obtained.

## 2. Experimental

### 2.1. SYNTHESIS

*p-tert*-Butylphenol (33.33 g, 0.22 mol), 11.67 g (0.389 mol) of *p*-formaldehyde and 200 mL of xylene were placed in a 500 mL, three necked, round-bottomed flask equipped with a nitrogen inlet, a mechanical stirrer, a Dean-Stark trap and a condenser. After 20 min, 0.667 mL (0.00667 mol) of 10N sodium hydroxyde were added. The reaction mixture was refluxed for 45 min, allowed to cool to room temperature and the precipitate separated by filtration. The filtrate was kept at 10 °C and after one day, a new precipitate was formed and collected as before. This precipitate, dissolved in 100 mL of chloroform, was washed with one part of 100 mL of 1N hydrochloric acid and three parts of 100 mL of water. The chloroform layer was dried over magnesium sulfate. The magnesium sulfate was removed by filtration and chloroform removed by rotary evaporation and the precipitate recrystallised in an acetone-methanol mixture. This filtered mixture gave 24% of CALO: HPLC and $^1$H-NMR analyses show the purity of the product: only one peak of CALO was detected by HPLC and the $^1$H-NMR data in $CDCl_3$ in ppm from TMS were 9.55 (s, 2, OH); 8.80 (s, 2, OH); 7.25–6.85 (m, 8, Ar—H); 4.63 (s, 4, Ar—$CH_2$—O—$CH_2$—Ar); 3.90 (s, 6, Ar—$CH_2$—Ar); 1.20 (s, 36, C $(CH_3)_3$).

### 2.2. METHODS OF PREPARATION AND IDENTIFICATION OF COMPLEXES

The calixarene was synthesized as described before and the solvents purchased from Aldrich were used without further purification.

A 3-mL portion of solvent was added to 100 mg of CALO; the mixture was then refluxed when possible or, if not, heated to 160 °C. When the calixarene dissolved, the solution was cooled slowly to room temperature and the solvent allowed to evaporate. The solid obtained was powdered for further analysis.

The characterization of the powder was made by the X-ray powder diffraction technique. The patterns were recorded on a Siemens D500 diffractometer at room temperature with Cu$K_\alpha$ radiation.

### 2.3. CRYSTAL STRUCTURE ANALYSIS OF THE THF COMPLEX

A needle-shaped crystal with approximate dimensions 0.08 × 0.14 × 0.4 mm was sealed in a capillary tube. X-ray diffraction data were measured at 20 °C on a Nonius CAD4 diffractometer (graphite monochromator, Cu$K_\alpha$ radiation). Lorentz and polarisation corrections were applied using XTAL3.2 programs [7]. Absorption effects were not corrected.

The crystal structure was solved by direct methods with the program MULTAN[8] and refined by SHELXL-93[9]. Successive Fourier $E$ maps progressively revealed all the non-hydrogen atoms. The disorder of the THF molecule situated in the interhost space was resolved using facilities included in SHELXL-93. The hydrogen atoms were calculated at theoretical positions. Anisotropic temperature factors were assigned to the non-hydrogen atoms, except C(234), C(235) and C(236) which correspond to positions with very low site occupation factors of disordered atoms. All hydrogens were refined isotropically as riding on the non-H atom to which they were connected. The final $R$ value was 0.086 for 3590 reflections considered as observed (with $F > 4\sigma(F)$). The cell constants and pertinent details about crystal data, data collection and refinement are given in Table I.

## 3. Results and Discussion

### 3.1. THE ABILITY OF CALO TO COMPLEX SMALL NEUTRAL MOLECULES IN THE SOLID STATE

We have analysed and compared the X-ray diffraction patterns obtained with uncomplexed CALO and with powders resulting from evaporation of solvent in CALO-solvent mixtures. Each diffraction diagram can be characterized by the positions ($d_{hkl}$) and the relative intensities ($I_{hkl}$) of the strongest reflections. Data for the pattern (P0) obtained with uncomplexed CALO, are given in Table II. Patterns similar to (P0) were obtained when the solvent was a linear alkane or an alcohol: it can be deduced that the powders consist mainly of microcrystals of the uncomplexed CALO and that no new molecular compound is formed. For other

TABLE I. Crystallographic data.

| | |
|---|---|
| *Crystal data* | |
| $C_{45}O_5H_{58}, 2C_4OH_8$ | Mol. wt = 823.2 |
| Monoclinic | $d_c = 1.099$ Mg m$^{-3}$ |
| $P2_1/c$ | Cell parameters from 25 reflections |
| $a = 9.459(2)$ Å | $\theta$ 9.0 → 33° |
| $b = 17.286(2)$ Å | $\lambda = 1.54178$ Å |
| $c = 30.469(6)$ Å | $\mu = 5.6$ cm$^{-1}$ |
| $\beta = 92.52(2)°$ | $T = 293$ °K |
| $V = 4977(2)$ Å$^3$ | |
| $Z = 4$ | |
| *Data collection* | |
| $\omega/2\theta$ scans | 3 standard reflections |
| $\theta$ : 1.0 → 73° | at frequency 60 mn. |
| $h$ : 0 → 11 | Intensity decrease 1.5% |
| $k$ : 0 → 21 | No of measured reflections: 9955 |
| $l$; −37 → 37 | No of observed reflections: 3937 |
| | $[I > 2\sigma(I)]$ |
| *Refinement* | |
| Refinement on $F^2$ | H atoms riding |
| $R[F > 4\sigma(F)] = 0.086$ | |
| $S = 1.061$ | $\Delta\rho_{\max} = 0.50$ e/Å$^3$ |
| 3590 reflections | $\Delta\rho_{\min} = -0.42$ e/Å$^3$ |
| 674 parameters | |
| Calculated weight $w = 1/[\sigma^2(F_0^2) + (0.1678P)^2 + 0.28P]$ where $P = (F_0^2 + 2F_c^2)/3$ | |

tested solvents (except ethyl acetate), the patterns differ from (P0): the powders consist mainly of microcrystals of new molecular compounds resulting from the complexation of CALO with the solvent accepted as guest molecule. Most of these patterns can be grouped into families: data for the patterns (P1), (P2) and (P3) obtained respectively when the solvent was toluene, acetone and THF, are given in Table II; many diffraction diagrams are very similar to (P1) or (P2) or (P3) and therefore can be grouped into corresponding families. A few unique patterns (P4)–(P9) were obtained. The final results concerning the ability of CALO to form, in the solid state, molecular compounds with small neutral molecules are given in Table III. This study leads to the following conclusions:

(1) For linear alkanes and alcohols the obtention of the X-ray diagram of the empty CALO shows that no new compound is obtained and that the powder is the uncomplexed CALO.

TABLE II. Characteristic X-ray powder diffraction patterns obtained with CALO and complexes with CALO.

| *Uncomplexed CALO* (P0) | | *Complex with toluene* (P1) | |
|---|---|---|---|
| $d_{(hkl)}$ | $I$ | $d_{(hkl)}$ | $I$ |
| 12.34 | 100 | 9.126 | 100 |
| 10.54 | 100 | 4.550 | 58 |
| 5.826 | 97 | 4.776 | 53 |
| 4.160 | 82 | 9.741 | 49 |
| 12.95 | 77 | 13.01 | 41 |

| *Complex with acetone* (P2) | | *Complex with THF* (P3) | |
|---|---|---|---|
| $d_{(hkl)}$ | $I$ | $d_{(hkl)}$ | $I$ |
| 16.87 | 100 | 15.22 | 100 |
| 12.40 | 26 | 11.44 | 35 |
| 8.424 | 23 | 3.888 | 27 |
| 14.38 | 16 | 4.470 | 24 |
| 7.217 | 15 | 4.406 | 22 |

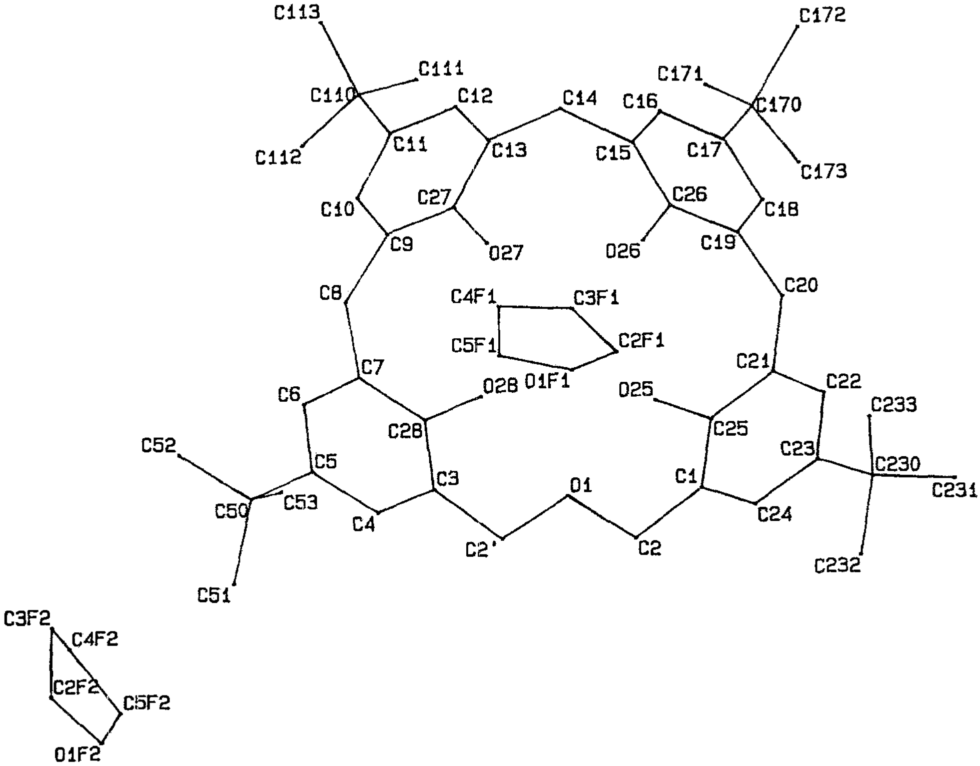

Fig. 1. Numbering scheme.

TABLE III. The ability of CALO in the solid state to form molecular compounds with small neutral molecules.

| Chemical function | Solvent as guest | Molecular compound | Pattern Type | Chemical function | Solvent as guest | Molecule Compound | Pattern Type |
|---|---|---|---|---|---|---|---|
| Alkane | *n*-hexane | NO | P0 | Amine | propylamine | YES | P8 |
| | *n*-heptane | NO | P0 | | triethylamine | YES | P9 |
| | cyclohexane | NO | P3 | | DMF | YES | P1 |
| Alcohol | methanol | NO | P0 | Aromatic | benzene | YES | P3 |
| | ethanol | NO | P0 | | toluene | YES | P1 |
| | 1-propanol | NO | P0 | | *m*-xylene | YES | P1 |
| | 2-propanol | NO | P0 | | *p*-xylene | YES | P1 |
| | 4-isopropyl benzylalcohol | NO | P0 | | *o*-xylene | YES | P1 |
| | | | | | chlorobenzene | YES | P1 |
| | ethylene glycol | NO | P0 | | anisole | YES | P1 |
| | 1,3-propanediol | NO | P0 | | 1,3-diisopropyl benzene | YES | P5 |
| | 1,4-butanediol | NO | P0 | | benzoyl chloride | YES | P6 |
| | 1,5-pentanediol | NO | P0 | | | | |
| | 2,4-pentanediol | NO | P0 | | | | |
| Ketone | acetaldehyde | YES | P2 | | | | |
| | acetone | YES | P2 | Heterocycle | morpholine | YES | P7 |
| | cyclopentanone | YES | P1 | | pyridine | YES | P2 |
| | cyclohexanone | YES | P1 | | 3-picoline | YES | P1 |
| | acetophenone | YES | P4 | | THF | YES | P3 |
| Ester | ethyl acetate | NO | P0 | Miscellaneous | acetonitrile | YES | P2 |
| Ether | *t*-butyl methyl ether | YES | P1 | | chloroform | YES | P2 |
| | | | | | carbon tetrachloride | YES | P3 |

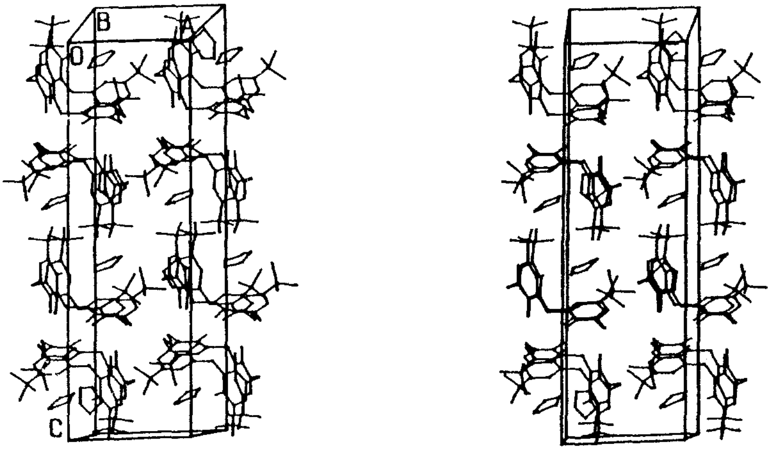

Fig. 2. Stereo view of the unit cell.

TABLE IV. Fractional atomic parameters and equivalent isotropic thermal parameters for non-H atoms.

| Atom | $x$ | $y$ | $z$ | $B$ (eq) |
|---|---|---|---|---|
| C(1) | 0.7735(5) | 0.0323(3) | 0.2751(2) | 5.5(1) |
| C(2) | 0.7070(6) | 0.1032(3) | 0.2561(2) | 6.5(2) |
| O(1) | 0.7621(4) | 0.1685(2) | 0.2802(1) | 6.14(9) |
| C(2′) | 0.7104(6) | 0.2391(3) | 0.2627(2) | 6.2(2) |
| C(3) | 0.7788(5) | 0.3041(3) | 0.2883(2) | 5.5(1) |
| C(4) | 0.6965(6) | 0.3587(3) | 0.3081(2) | 5.9(1) |
| C(5) | 0.7537(5) | 0.4228(3) | 0.3299(2) | 5.4(1) |
| C(50) | 0.6611(6) | 0.4827(4) | 0.3509(2) | 6.8(2) |
| C(51) | 0.538(2) | 0.507(1) | 0.3198(5) | 10.8(6) |
| C(52) | 0.737(1) | 0.5549(8) | 0.3675(8) | 10.4(6) |
| C(53) | 0.595(2) | 0.4454(9) | 0.3920(5) | 9.9(5) |
| C(54) | 0.685(2) | 0.561(1) | 0.326(1) | 9.5(7) |
| C(55) | 0.507(2) | 0.463(1) | 0.348(1) | 9.3(8) |
| C(56) | 0.703(3) | 0.485(2) | 0.3994(7) | 11.5(9) |
| C(6) | 0.9014(5) | 0.4298(3) | 0.3303(2) | 5.5(1) |
| C(7) | 0.9880(5) | 0.3756(3) | 0.3120(2) | 5.2(1) |
| C(8) | 1.1468(5) | 0.3873(3) | 0.3151(2) | 5.7(1) |
| C(9) | 1.2237(5) | 0.3384(3) | 0.3509(2) | 5.4(1) |
| C(10) | 1.2235(5) | 0.3627(3) | 0.3941(2) | 5.6(1) |
| C(11) | 1.2947(6) | 0.3217(4) | 0.4280(2) | 6.2(2) |
| C(110) | 1.2932(8) | 0.3469(5) | 0.4785(2) | 8.1(2) |
| C(111) | 1.263(3) | 0.283(1) | 0.5049(6) | 13.1(9) |
| C(112) | 1.177(5) | 0.406(2) | 0.4820(8) | 18(1) |
| C(113) | 1.435(3) | 0.383(3) | 0.4868(8) | 24(1) |
| C(114) | 1.18(1) | 0.302(8) | 0.497(2) | 36(6) |
| C(115) | 1.25(1) | 0.428(4) | 0.485(2) | 23(3) |
| C(116) | 1.429(4) | 0.338(5) | 0.501(1) | 19(3) |
| C(12) | 1.3673(5) | 0.2565(4) | 0.4159(2) | 6.2(2) |
| C(13) | 1.3704(5) | 0.2292(3) | 0.3737(2) | 5.5(1) |
| C(14) | 1.4502(5) | 0.1568(3) | 0.3628(2) | 6.0(1) |
| C(15) | 1.3607(4) | 0.0836(3) | 0.3661(2) | 5.3(1) |
| C(16) | 1.3477(5) | 0.0488(3) | 0.4058(2) | 5.7(1) |
| C(17) | 1.2662(5) | −0.0166(3) | 0.4122(2) | 5.6(1) |
| C(170) | 1.2499(6) | −0.0529(4) | 0.4575(2) | 6.6(2) |
| C(171) | 1.237(1) | 0.0103(5) | 0.4917(2) | 10.9(3) |
| C(172) | 1.3752(8) | −0.1041(6) | 0.4682(3) | 11.8(3) |
| C(173) | 1.1151(8) | −0.0998(5) | 0.4600(3) | 10.9(3) |
| C(18) | 1.2026(5) | −0.0483(3) | 0.3741(2) | 5.7(1) |
| C(19) | 1.2137(5) | −0.0167(3) | 0.3330(2) | 5.2(1) |
| C(20) | 1.1422(5) | −0.0563(4) | 0.2936(2) | 5.6(1) |
| C(21) | 0.9826(5) | −0.0445(3) | 0.2925(2) | 5.3(1) |
| C(22) | 0.8962(5) | −0.0996(3) | 0.3094(2) | 5.4(1) |

TABLE IV. Continued.

| Atom | $x$ | $y$ | $z$ | $B$ (eq) |
|---|---|---|---|---|
| C(23) | 0.7487(5) | −0.0914(3) | 0.3117(2) | 5.4(1) |
| C(230) | 0.6613(6) | −0.1514(4) | 0.3341(2) | 6.5(2) |
| C(231) | 0.682(1) | −0.2330(6) | 0.3143(5) | 9.9(4) |
| C(232) | 0.5014(9) | −0.1374(7) | 0.3288(6) | 9.8(4) |
| C(233) | 0.701(1) | −0.156(1) | 0.3821(4) | 12.0(5) |
| C(234) | 0.608(3) | −0.109(2) | 0.3752(9) | 9.1(8) |
| C(235) | 0.535(3) | −0.169(2) | 0.3019(9) | 8.2(6) |
| C(236) | 0.742(3) | −0.219(2) | 0.348(1) | 9.3(8) |
| C(24) | 0.6937(6) | −0.0244(3) | 0.2933(2) | 5.9(1) |
| C(25) | 0.9207(5) | 0.0221(3) | 0.2754(2) | 5.5(1) |
| O(25) | 1.0022(4) | 0.0806(2) | 0.2580(1) | 6.9(1) |
| C(26) | 1.2883(5) | 0.0520(3) | 0.3296(2) | 5.3(1) |
| O(26) | 1.2928(3) | 0.0869(2) | 0.2888(1) | 6.6(1) |
| C(27) | 1.2928(5) | 0.2713(3) | 0.3405(2) | 5.1(1) |
| O(27) | 1.2903(3) | 0.2449(2) | 0.2981(1) | 6.4(1) |
| C(28) | 0.9262(5) | 0.3124(3) | 0.2911(2) | 5.3(1) |
| O(28) | 1.0070(3) | 0.2572(2) | 0.2713(1) | 6.6(1) |
| O(1F1) | 0.7641(5) | 0.1418(4) | 0.4227(2) | 9.5(2) |
| C(2F1) | 0.850(1) | 0.0996(6) | 0.3955(3) | 12.5(3) |
| C(3F1) | 0.968(1) | 0.1453(9) | 0.3853(4) | 15.2(4) |
| C(4F1) | 0.946(1) | 0.2172(8) | 0.4047(5) | 17.2(5) |
| C(5F1) | 0.807(1) | 0.2158(6) | 0.4212(4) | 12.6(3) |
| O(1F2) | 0.118(3) | 0.642(3) | 0.3616(9) | 24.6(9) |
| C(2F2) | 0.227(5) | 0.693(3) | 0.360(1) | 22.4(8) |
| C(3F2) | 0.312(3) | 0.680(2) | 0.401(2) | 19(1) |
| C(4F2) | 0.212(5) | 0.659(3) | 0.4300(9) | 19(1) |
| C(5F2) | 0.109(4) | 0.613(3) | 0.402(1) | 21.3(8) |
| O(1F3) | 0.259(3) | 0.615(2) | 0.401(1) | 23(1) |
| C(2F3) | 0.262(4) | 0.673(3) | 0.370(2) | 22.5(9) |
| C(3F3) | 0.116(5) | 0.699(3) | 0.365(2) | 22(1) |
| C(4F3) | 0.062(4) | 0.688(2) | 0.405(2) | 22(1) |
| C(5F3) | 0.134(4) | 0.618(3) | 0.422(1) | 22.0(9) |

(2) For ketones, aromatics and for the other miscellaneous molecules the obtention of a new X-ray diagram shows that the powder is a new molecular compound corresponding to the complexation of the small molecule by CALO.

This work shows the very good ability of CALO to complex small molecules, in the solid state, with a wide range of chemical function and shapes of molecules.

TABLE V. Bond distances for non-H atoms.

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| C(1) | C(2) | 1.484(8) | C(11) | C(12) | 1.380(9) | C(22) | C(23) | 1.408(7) |
| C(1) | C(24) | 1,370(8) | C(110) | C(111) | 1.45(2) | C(23) | C(230) | 1.509(8) |
| C(1) | C(25) | 1.403(7) | C(110) | C(112) | 1.51(4) | C(23) | C(24) | 1.378(8) |
| C(2) | O(1) | 1.431(7) | C(110) | C(113) | 1.50(3) | C(230) | C(231) | 1.55(1) |
| O(1) | C(2′) | 1.412(7) | C(12) | C(13) | 1.372(8) | C(230) | C(232) | 1.53(1) |
| C(2′) | C(3) | 1.498(8) | C(13) | C(14) | 1.505(8) | C(230) | C(233) | 1.50(1) |
| C(3) | C(4) | 1.379(8) | C(13) | C(27) | 1.422(7) | C(25) | O(25) | 1.389(7) |
| C(3) | C(28) | 1.400(7) | C(14) | C(15) | 1.528(7) | C(26) | O(26) | 1.385(6) |
| C(4) | C(5) | 1.390(8) | C(15) | C(16) | 1.362(8) | C(27) | O(27) | 1.371(6) |
| C(5) | C(50) | 1.514(8) | C(15) | C(26) | 1.392(7) | C(28) | O(28) | 1.377(6) |
| C(5) | C(6) | 1.402(7) | C(16) | C(17) | 1.388(8) | O(1F1) | C(2F1) | 1.39(1) |
| C(50) | C(51) | 1.52(2) | C(17) | C(170) | 1.530(8) | O(1F1) | C(5F1) | 1.34(1) |
| C(50) | C(52) | 1.52(2) | C(17) | C(18) | 1.398(8) | C(2F1) | C(3F1) | 1.42(2) |
| C(50) | C(53) | 1.56(2) | C(170) | C(171) | 1.52(1) | C(3F1) | C(4F1) | 1.40(2) |
| C(6) | C(7) | 1.378(7) | C(170) | C(172) | 1.50(1) | C(4F1) | C(5F1) | 1.43(2) |
| C(7) | C(8) | 1.515(6) | C(170) | C(173) | 1.52(1) | O(1F2) | C(2F2) | 1.36(6) |
| C(7) | C(28) | 1.383(7) | C(18) | C(19) | 1.373(8) | O(1F2) | C(5F2) | 1.32(5) |
| C(8) | C(9) | 1.538(8) | C(19) | C(20) | 1.515(7) | C(2F2) | C(3F2) | 1.46(6) |
| C(9) | C(10) | 1.381(8) | C(19) | C(26) | 1.388(8) | C(3F2) | C(4F2) | 1.39(6) |
| C(9) | C(27) | 1.375(8) | C(20) | C(21) | 1.522(6) | C(4F2) | C(5F2) | 1.50(6) |
| C(10) | C(11) | 1.401(8) | C(21) | C(22) | 1.370(8) | | | |
| C(11) | C(110) | 1.520(9) | C(21) | C(25) | 1.383(8) | | | |
| | | | | | | O(1F3) | C(2F3) | 1.36(6) |
| | | | | | | O(1F3) | C(5F3) | 1.37(5) |
| C(50) | C(54) | 1.57(2) | C(110) | C(116) | 1.48(4) | C(2F3) | C(3F3) | 1.46(6) |
| C(50) | C(55) | 1.50(2) | C(230) | C(234) | 1.55(3) | C(3F3) | C(4F3) | 1.35(7) |
| C(50) | C(56) | 1.41(2) | C(230) | C(235) | 1.55(3) | C(4F3) | C(5F3) | 1.47(6) |
| C(110) | C(114) | 1.5(1) | C(230) | C(236) | 1.44(3) | | | |
| C(110) | C(115) | 1.48(7) | | | | | | |

## 3.2. CRYSTAL STRUCTURE OF THE 1 : 2 COMPLEX BETWEEN CALO AND THF

Final atomic coordinates are listed in Table IV. The numbering scheme is given in Figure 1. Bond lengths and bond angles are listed in Table V and Table VI.

The calixarene molecule exhibits a conical shape and a pseudosymmetrical conformation: the plane through O(1) and C(14) and perpendicular to C(8), C(14) and C(20) is a pseudo-mirror plane. The terminal —$CH_3$ of the *tert*-butyl groups connected to C(5), C(11) and C(23) are disordered with s.o.f. respectively of 60%, 68% and 70% for position C(51), C(52), C(53); C(111), C(112), C(113), and C(231), C(232) and C(233). The labels of the corresponding positions with lower s.o.f. are C(54), C(55), C(56); C(114), C(115), C(116), and C(234), C(235) and C(236). The *tert*-butyl group connected to C(11) has high thermal parameters

TABLE VI. Bond angles for non-H atoms.

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(2) | C(1) | C(24) | 121.1(5) | C(11) | C(110) | C(112) | 110(1) | C(22) | C(23) | C(230) | 121.7(4) |
| C(2) | C(1) | C(25) | 120.7(5) | C(11) | C(110) | C(113) | 107(1) | C(22) | C(23) | C(24) | 114.9(5) |
| C(24) | C(1) | C(25) | 118.1(5) | C(111) | C(110) | C(112) | 106(2) | C(230) | C(23) | C(24) | 123.9(5) |
| C(1) | C(2) | O(1) | 108.2(5) | C(111) | C(110) | C(113) | 112(2) | C(23) | C(230) | C(231) | 111.7(6) |
| C(2) | O(1) | C(2′) | 112.1(4) | C(112) | C(110) | C(113) | 110(2) | C(23) | C(230) | C(230) | 113.6(6) |
| O(1) | C(2′) | C(3) | 108.5(4) | C(11) | C(12) | C(13) | 124.3(5) | C(23) | C(230) | C(233) | 111.3(7) |
| C(2′) | C(3) | C(4) | 120.1(4) | C(12) | C(13) | C(14) | 121.6(5) | C(231) | C(230) | C(232) | 104.1(8) |
| C(2′) | C(3) | C(28) | 121.0(5) | C(12) | C(13) | C(27) | 117.2(5) | C(231) | C(230) | C(233) | 107(1) |
| C(4) | C(3) | C(28) | 118.9(5) | C(14) | C(13) | C(27) | 121.2(5) | C(232) | C(230) | C(233) | 108.4(9) |
| C(3) | C(4) | C(5) | 122.7(5) | C(13) | C(14) | C(15) | 112.9(4) | C(1) | C(24) | C(23) | 124.2(5) |
| C(4) | C(5) | C(50) | 121.7(5) | C(14) | C(15) | C(16) | 119.7(5) | C(1) | C(25) | C(21) | 120.7(5) |
| C(4) | C(5) | C(6) | 116.0(5) | C(14) | C(15) | C(26) | 121.8(5) | C(1) | C(25) | O(25) | 118.2(5) |
| C(50) | C(5) | C(6) | 122.2(5) | C(16) | C(15) | C(26) | 118.4(5) | C(21) | C(25) | O(25) | 121.1(4) |
| C(5) | C(50) | C(51) | 111.4(8) | C(15) | C(16) | C(17) | 123.7(5) | C(15) | C(26) | C(19) | 120.7(5) |
| C(5) | C(50) | C(52) | 115.3(7) | C(16) | C(17) | C(170) | 122.7(5) | C(15) | C(26) | O(26) | 120.9(5) |
| C(5) | C(50) | C(53) | 108.4(7) | C(16) | C(17) | C(18) | 115.1(5) | C(19) | C(26) | O(26) | 118.4(4) |
| C(51) | C(50) | C(52) | 109(1) | C(170) | C(17) | C(18) | 122.2(5) | C(9) | C(27) | C(13) | 120.3(5) |
| C(51) | C(50) | C(53) | 106.7(9) | C(17) | C(170) | C(171) | 109.8(5) | C(9) | C(27) | O(27) | 120.6(5) |
| C(52) | C(50) | C(53) | 106(1) | C(17) | C(170) | C(172) | 109.0(6) | C(13) | C(27) | O(27) | 119.1(5) |
| C(5) | C(6) | C(7) | 123.3(5) | C(17) | C(170) | C(173) | 112.4(5) | C(3) | C(28) | C(7) | 120.6(5) |
| C(6) | C(7) | C(8) | 119.3(5) | C(171) | C(170) | C(172) | 111.2(6) | C(3) | C(28) | O(28) | 118.2(5) |
| C(6) | C(7) | C(28) | 118.5(4) | C(171) | C(170) | C(173) | 105.1(6) | C(7) | C(28) | O(28) | 121.2(4) |
| C(8) | C(7) | C(28) | 122.2(5) | C(172) | C(170) | C(173) | 109.3(6) | C(2F1) | O(1F1) | C(5F1) | 107.2(7) |
| C(7) | C(8) | C(9) | 114.1(4) | C(17) | C(18) | C(19) | 123.7(5) | O(1F1) | C(2F1) | C(3F1) | 108.9(9) |
| C(8) | C(9) | C(10) | 119.2(5) | C(18) | C(19) | C(20) | 119.5(5) | C(2F1) | C(3F1) | C(4F1) | 106(1) |
| C(8) | C(9) | C(27) | 121.1(4) | C(18) | C(19) | C(26) | 118.0(5) | C(3F1) | C(4F1) | C(5F1) | 107(1) |
| C(10) | C(9) | C(27) | 119.8(4) | C(20) | C(19) | C(26) | 122.5(5) | O(1F1) | C(5F1) | C(4F1) | 108.2(9) |
| C(9) | C(10) | C(11) | 121.9(5) | C(19) | C(20) | C(21) | 111.5(4) | C(2F2) | O(1F2) | C(5F2) | 111(3) |
| C(10) | C(11) | C(110) | 122.6(5) | C(20) | C(21) | C(22) | 120.3(5) | O(1F2) | C(2F2) | C(3F2) | 106(3) |
| C(10) | C(11) | C(12) | 116.4(5) | C(20) | C(21) | C(25) | 121.6(5) | C(2F2) | C(3F2) | C(4F2) | 102(3) |
| C(110) | C(11) | C(12) | 121.0(5) | C(22) | C(21) | C(25) | 118.1(4) | C(3F2) | C(4F2) | C(5F2) | 102(3) |
| C(11) | C(110) | C(111) | 112(1) | C(21) | C(22) | C(23) | 123.9(5) | O(1F2) | C(5F2) | C(4F2) | 106(3) |
| C(5) | C(50) | C(54) | 107(1) | C(11) | C(110) | C(116) | 115(2) | C(234) | C(230) | C(236) | 110(2) |
| C(5) | C(50) | C(55) | 113(1) | C(114) | C(110) | C(115) | 103(6) | C(235) | C(230) | C(236) | 114(2) |
| C(5) | C(50) | C(56) | 107(1) | C(114) | C(110) | C(116) | 110(4) | C(2F3) | O(1F3) | C(5F3) | 110(3) |
| C(54) | C(50) | C(55) | 109(1) | C(115) | C(110) | C(116) | 103(4) | O(1F3) | C(2F3) | C(3F3) | 105(4) |
| C(54) | C(50) | C(56) | 114(2) | C(23) | C(230) | C(234) | 104(1) | C(2F3) | C(3F3) | C(4F3) | 105(4) |
| C(55) | C(50) | C(56) | 107(2) | C(23) | C(230) | C(235) | 106(1) | C(3F3) | C(4F3) | C(5F3) | 104(4) |
| C(11) | C(110) | C(114) | 108(4) | C(23) | C(230) | C(236) | 113(1) | C(1F3) | C(5F3) | C(4F3) | 105(4) |
| C(11) | C(110) | C(115) | 117(2) | C(234) | C(230) | C(235) | 110(2) |  |  |  |  |

TABLE VII. Characteristic torsional angles (deg).

| Atoms | | | | Angle |
|---|---|---|---|---|
| C(25) | C(1) | C(2) | O(1) | −60.4 (6) |
| C(2) | C(1) | C(25) | C(21) | −179.0 (5) |
| C(1) | C(2) | O(1) | C(2′) | 176.6 (4) |
| C(2) | O(1) | C(2′) | C(3) | −177.1 (4) |
| O(1) | C(2′) | C(3) | C(28) | 58.4 (6) |
| C(2′) | C(3) | C(28) | C(7) | 175.1 (5) |
| C(28) | C(7) | C(8) | C(9) | −78.8 (6) |
| C(8) | C(7) | C(28) | C(3) | −179.0 (5) |
| C(7) | C(8) | C(9) | C(27) | 100.5 (5) |
| C(8) | C(9) | C(27) | C(13) | 176.2 (4) |
| C(27) | C(13) | C(14) | C(15) | −89.9 (6) |
| C(14) | C(13) | C(27) | C(9) | −178.3 (4) |
| C913) | C(14) | C(15) | C(26) | 94.6 (6) |
| C(14) | C(15) | C(26) | C(19) | 176.3 (4) |
| C(26) | C(19) | C(20) | C(21) | −104.3 (5) |
| C(20) | C(19) | C(26) | C(15) | −175.5 (4) |
| C(19) | C(20) | C(21) | C(25) | 82.6 (6) |
| C(20) | C(21) | C(25) | C(1) | −179.2 (5) |

for the two disordered positions. The same observation can be made for the two possible positions (with s.o.f. 52% for F2 and 48% for F3) of THF molecules situated in the interhost space. Bond distances and angles have the expected values. In all the phenolic rings values between 121.9(5)° and 124.3(4)° for positions *meta* to the —OH and values between 114.9(5)° and 116.4(5)° for *para* positions correspond to the electron releasing character of the *tert*-butyl group. As with other dihomooxacalix[4]arenes, the plane C(8), C(14), C(20) is chosen as a reference plane (R). The phenolic rings containing C(28), C(27), C(26) and C(25) are called I, II, III and IV respectively; the angles between R and the four phenolic rings are 138.4(2), 127.1(2), 122.2(2) and 133.2(1)°. The four phenolic oxygens are less than 0.016(4) Å from their mean plane (P) which makes an angle of 14.4(3)° with (R). The oxygen belonging to the dimethyleneoxa bridge is inside the cavity, situated at 1.165(4) Å from (P). The lengths of O· · ·O contacts in the calixarene molecule are 2.838(5), 2.867(4), 2.747(5), 2.775(5) and 2.801(5) Å for O(1)· · ·O(25), O(25)· · ·O(26), O(26)· · ·O(27), O(27)· · ·O(28) and O(28)· · ·O(1). Torsional angles around atoms forming the macrocyclic ring are given in Table VII. Values of angles C(1)-C(2)-O(1)-C(2′) and C(2)-O(1)-C(2′)-C(3) show that atoms of the dimethyleneoxa bridge C(3), C(2′), O(1), C(2) and C(1) are nearly coplanar. The conformation of the CALO molecule, is very similar to the one found for the complex with *meta*-xylene.

One of the THF molecules is encapsulated by the macrocycle; (F1) is the mean plane of the five THF atoms; the angles between (F1) and (P) and (F1) and (I) are 45.7(3)° and 28.8(5)° respectively. The distance between (P) and atoms of the THF molecule are: 3.67(1) Å for C(3F1), 4.16(1) Å for C(4F1), 4.41(1) Å for C(2F1), 5.05(1) Å for C(5F1) and 5.363(5) for O(1F1): the molecule is oriented in such a way that its oxygen is situated as far as possible from the macrocycle ring. The other THF molecule is in the interhost space; it exhibits disorder and the angle between the two mean planes corresponding to the two disordered molecules is 63.(2)°. All the contacts between molecules correspond to van der Waals interactions.

Figure 2 is a stereo view of the structure. The axis of all the cones formed by the macrocycles are parallel to the $(\vec{a}\ \vec{c})$ plane. The structure consists of layers, parallel to the $(\vec{a}\ \vec{b})$ plane, formed by calixarene molecules, with the THF trapped inside the cavity, alternating with the non-trapped THF molecules. In one layer all the cones have their aperture in the same direction; the apertures of the cones in neighbouring layers are oriented in the opposite direction. As in the $(\vec{a}\ \vec{b})$ plane, molecules of calixarene and molecules of non-trapped THF molecules alternate in the $\vec{c}$ direction. Following the proposal for classification and nomenclature of host-guest type compounds given by Weber and Josel [10] this compound can be defined as a complex/intercalato-clathrate hybrid.

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