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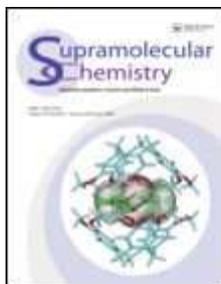
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A proton complex of *p*-tert-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide): NMR evidence and probable structure

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Using ¹H and ¹³C NMR together with density functional theoretical (DFT) calculations, we show that *p*-tert-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) (1) forms a stable equimolecular complex with proton in the form of hydroxonium ion in nitrobenzene-*d*₅. Protons were offered by hydrogen bis(1,2-dicarbolyl) cobaltate (HDCC) and converted to hydroxonium ions by traces of water. The complex 1·H₃O⁺ adopts a slightly asymmetric but rapidly motionally averaged conformation, which is distinctly more cone-like than ligand 1. The hydroxonium ion H₃O⁺ is bound partly to thiocarbonyl sulphur atoms and partly to phenoxy oxygen atoms of 1 by strong hydrogen bonds and other electrostatic interactions.

Keywords: Calixarene complex; protonation; NMR; DFT

INTRODUCTION

Calixarene-based molecules produced in rich diversity [1] have received intense attention in the last years. The **some** calixarenes **having** **four and five member rings** bear some resemblance to the natural cyclodextrins [2] in as much they possess a cone-like cavity, which is able to act as a host for a number of guest molecules. As such, they find applications as

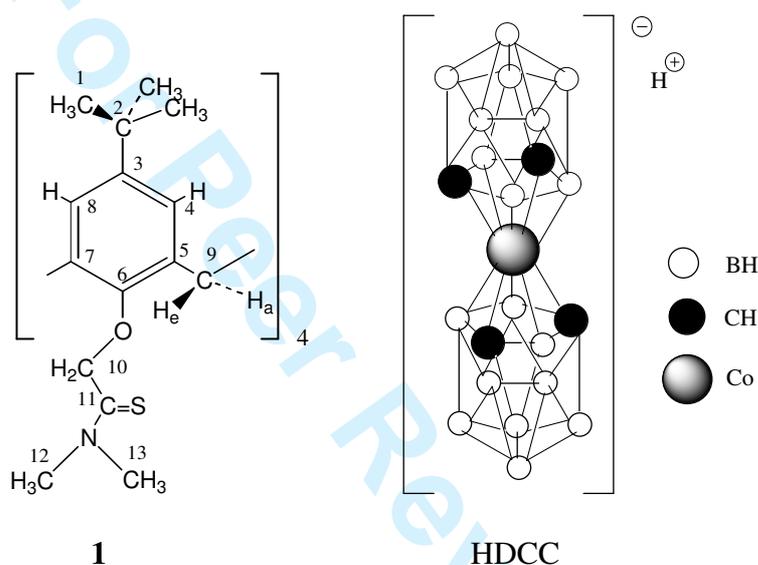
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3 selective binders and carriers, analytical sensors, catalysts and model structures for
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5 biomimetic studies [1].
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8 In addition, they can be modified by attaching carbonyl, ester, amide or thioamide groups
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10 to their lower rim. Due to their number (usually four or more) and restricted conformation,
11
12 these groups often serve as efficient coordination site for various cations. Many studies have
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14 focused on their binding ability toward metal ions, predominantly alkali and alkaline-earth but
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16 also transition and heavy metal cations. [3-11] As experimentally proved, coordination of a
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18 metal ion to the groups (say carbonyls) at the lower rim exerts a conformation change on the
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20 whole calixarene unit, which usually adopts a more cone-like form changing thus subtly its
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22 host properties for a guest molecule. The actual conformation change appears to be strongly
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24 dependent on the nature of the ion as well as the calixarene itself. The study of ion
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26 coordination to modified calixarenes, including non-metallic ions, first of all proton or
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28 hydroxonium ion, thus can be of primary interest to supramolecular chemistry.
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34 Up to now, no complex of proton with any calixarene has been reported. We have studied
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36 interactions of H_3O^+ with calix[4]arenes bearing ester, amide and thioamide groups. All of
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38 these substances clearly form an equimolecular complex with H_3O^+ . However, the
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40 dimethylamide-derivative apparently is not available in a sufficiently pure form, the
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42 commercial product being partly complexed with Na^+ ions and thus not suitable for
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44 demonstrative purposes. The interaction of the analogue bearing ester groups is somewhat
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46 complicated and will be described in a separate study. [18] In this work, we present NMR
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48 evidence for a complex of H_3O^+ with the thioacetamide derivative known as lead ionophore,
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50 namely *p-tert*-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (**1**, cf. Scheme 1). On
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52 the grounds of ^1H and ^{13}C NMR spectra and DFT calculations, we suggest its most probable
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54 structure.
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RESULTS AND DISCUSSION

Similarly as in our previous papers [13,14], hydrogen bis(1,2-dicarbollyl)cobaltate (HDCC) (Ref.12, for structure see Scheme 1) as a proton source, was used in nitrobenzene-*d*₅. A 2.5 mol excess of water to HDCC converts the protons to the hydroxonium ions H₃O⁺. HDCC is well soluble in nitrobenzene, but calixarene **1** did not allow concentrations above 5×10⁻³ mol/L.



Scheme 1

In the following NMR spectra, the signal assignment (which was checked by means of 2D COSY-LR and NOESY NMR spectra for ¹H and HSQC and HMBC spectra for ¹³C) corresponds to Scheme 1 where the protons have the same number as the carbons they are attached to. Figure 1 shows ¹H NMR spectra of **1** and its 2:1 and 1:1 mol/mol mixtures with HDCC in nitrobenzene-*d*₅. There are relative shifts of almost all signals in a similar direction and magnitude as in the case of complexation of metallic ions by calixarene ligands [3-5], evidencing the formation of a complex of **1** with H₃O⁺ (in Fig. 1B, the signal of proton 13 is broadened and placed under the number 6). Under higher excess of HDCC, no further shift is observed proving thus that the complex is equimolecular and its stability constant is high

(well above 10^3). At HDCC/**1** ratios between 0 and 1 mol/mol, the signals gradually shift and broaden. At the ratio 1:1, the signals are further shifted but narrow again. Evidently, an exchange between free and bound ligand **1** takes place. Its rate is only moderate considering the signal broadening. The corresponding correlation times of exchange τ_{ex} (in ms) calculated from the broadening of the signals and the relative shifts between the free and bound states are given in Fig. 1 B, while the relative shifts are shown in Figure 1 C. These values are rather formal, however, considering the complexity of motions discussed below.

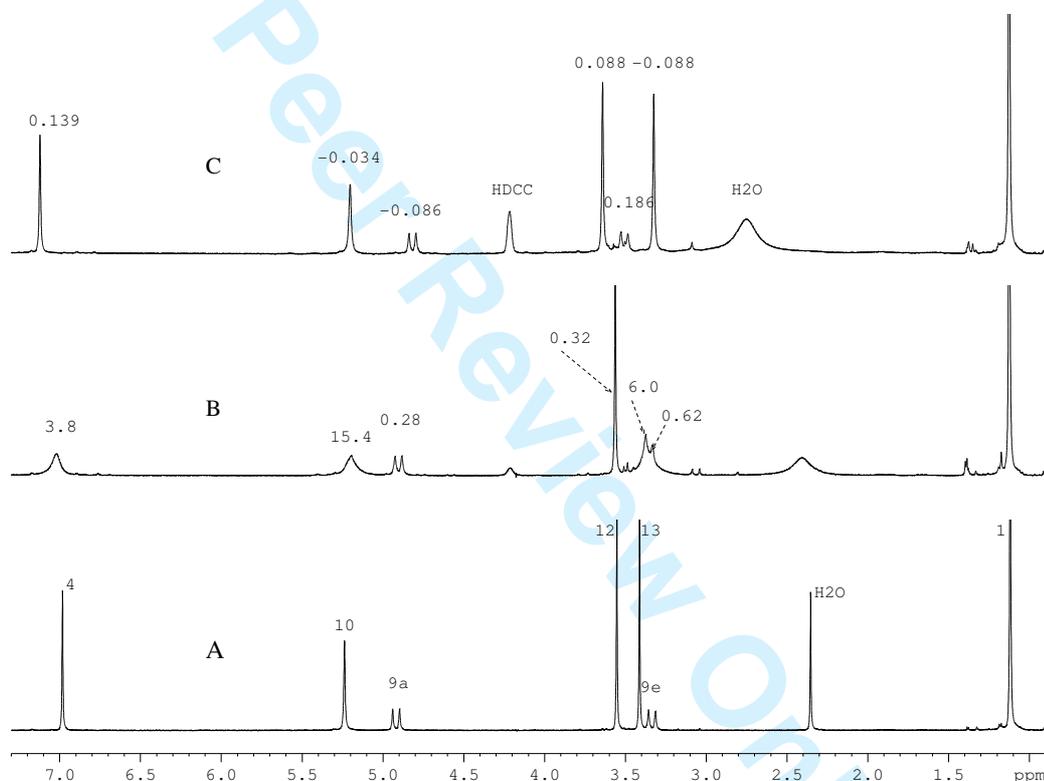


Fig. 1 ^1H NMR spectra of 0.005 mol/L solution of **1** (A) and its 2:1 (B) and 1:1 (C) (mol/mol) mixtures with HDCC. Signal assignment (cf. Scheme 1) in A, approximate exchange correlation times τ_{ex} (in ms) in B, relative chemical shifts (in ppm) in C.

Two dynamic processes are clearly operative here: i) a fast exchange between free and bound ligand **1** and ii) the *pinched cone* – *pinched cone* interconversion. It is well documented that calix[4]arene derivatives adopt a *pinched cone* conformation with C_{2v} symmetry of the macrocycle (neglecting conformations of the lower rim substituents that may further decrease

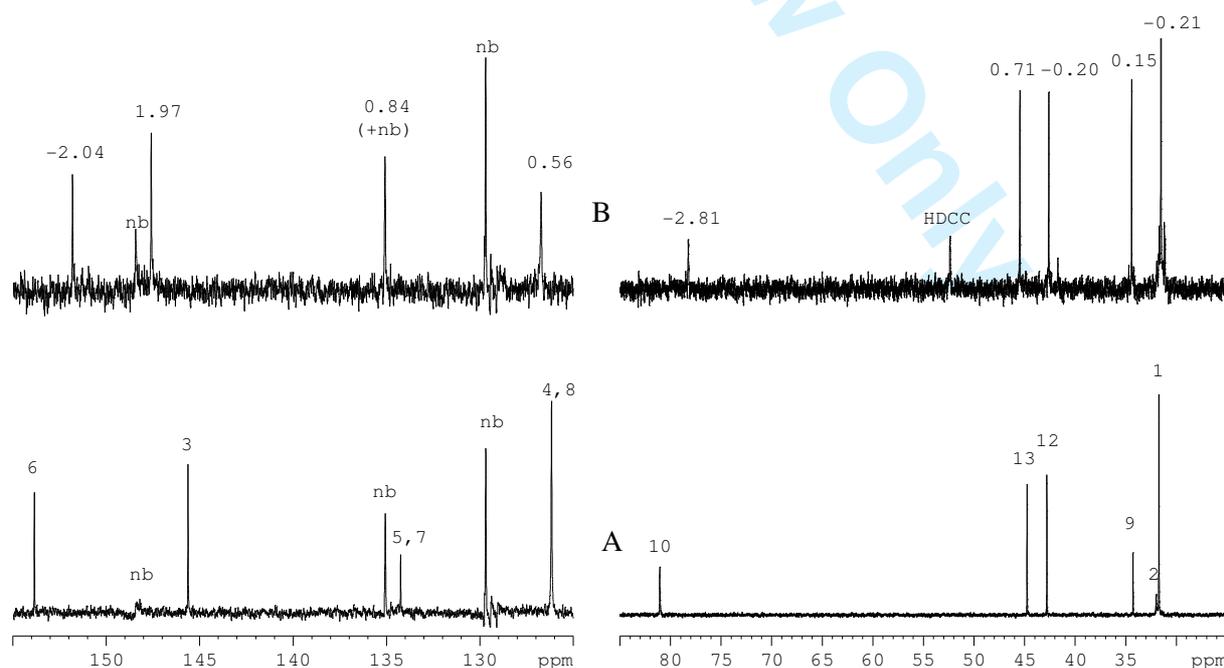
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3 the actual symmetry) rather than the effective C_4 symmetry that can be deduced from 1H
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5 NMR spectra [15,19]. The average spectral shape is caused by a rapid interconversion
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7 between two identical structures (*pinched cone*). The free energy barrier is usually as low as 9
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9 kcal/mol [19], which makes this motion fairly difficult to be detected by NMR. A significant
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11 line broadening due to this process occurs at very low temperatures (around 188 K) when
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13 most of solvents become frozen. An evidence of the *pinched cone* conformation of **1** is also a
14
15 chemical shift difference of the axial and equatorial bridging methylene protons 9 [15], which
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17 is as large as 1.534 ppm.
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22 It is obvious that attachment of hydroxonium or metal cation hinders the *pinched cone*
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24 – *pinched cone* interconversion. In the presence of the fast chemical exchange of
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26 hydroxonium cations (on 1H chemical shift time scale), the calix[4]arene molecule is allowed
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28 to interconvert only in between the periods when the complex is formed. This results in
29
30 overall decrease of *pinched cone* – *pinched cone* interconversion rate and thus broadening of
31
32 some of the signals.
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36 When all of **1** is bound to H_3O^+ , the calix[4]arene part of the molecule is fixed in a C_4
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38 symmetry so that no interconversion takes place and the NMR signals are narrow again. The
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40 decrease of the difference of chemical shifts of diastereotopic methylene protons 9 to 1.311
41
42 ppm shows that the cavity adopts a flatter, more cone-like form, presumably due to nearer
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44 proximity of the lower-rim polar groups interacting with H_3O^+ . Despite of the high stability
45
46 constant of the complex, the hydroxonium cation remains mobile and it samples different
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48 orientations within a single ligand averaging thus the whole structure so that there is only one
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50 set of signals in Figure 1C.
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52
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54 Somewhat more information about the structure of the complex $\mathbf{1}\cdot H_3O^+$ can be
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56 obtained from ^{13}C NMR spectra depicted in Figure 2. In order to overcome the low sensitivity
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58 at 5 mmol/L concentration and overshadowing by huge signals of nitrobenzene- d_5 , four types
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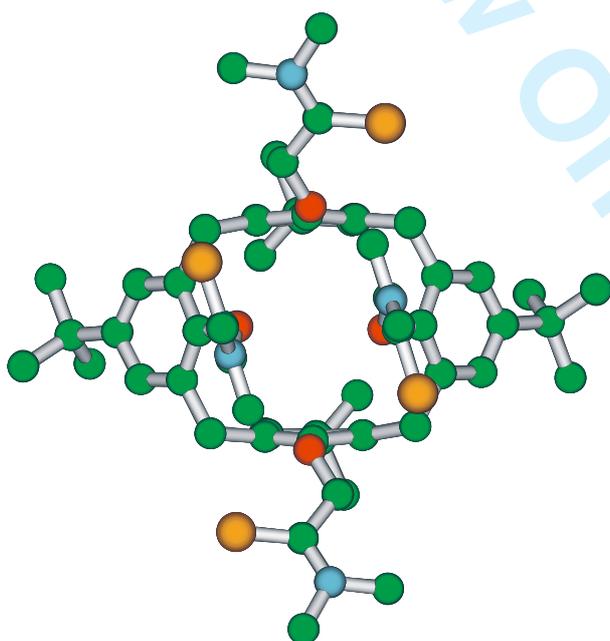
of DEPT45 and DEPT-LR spectra are combined here. The signals of C=S carbon 11 did not show up in DEPT spectra but can be found in ordinary ^{13}C NMR spectra, their shifts being 197.97 and 195.99 ppm in **1** and the complex, respectively. The down-field shifts of carbon signals 4(8) and 5(7) probably indicate formation of the conical structure that is close to C_4 symmetry. Quite similar ^{13}C complexation induced shifts were reported by Arduini et al. [4] for complex of tetraamide derivative of calix[4]arene with KSCN. The up-field shift of 6 may be attributed to a decreased electron density on the phenoxy oxygen atom due to a hydrogen bond with H_3O^+ . At the same time, 1.98 ppm up-field shift of carbon 11 shows a strong hydrogen bond of the ion H_3O^+ with a C=S group. As these shifts indicate really strong hydrogen bonds, the most probable structure appears to be that of H_3O^+ directly bonded to both phenoxy oxygen and thiocarbonyl sulphur atoms. We have only one signal for each type of carbon including 11, which indicates a C_4 symmetry of the whole molecule; the simplicity of the corresponding proton spectrum points to the same conclusion. As it is hardly possible to have the H_3O^+ ion equally bound by hydrogen bonds to all four C=S groups and all four phenoxy oxygen atoms as well we have to assume a rapid motion of H_3O^+ within the coordination site averaging the structure in the time window of NMR (see below).



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4 **Fig. 2** Combined ^{13}C NMR DEPT45 and DEPT-LR spectra of 0.005 mol/L solution of **1** (A)
5 and its 1:1 (mol/mol) mixture with HDCC (B). Signal assignment (cf. Scheme 1) in A,
6 relative chemical shifts (in ppm) in B; in both parts, nb means residual signals of
7 nitrobenzene.
8
9

10 In order to confront our experimental findings with theoretical predictions, the
11 equilibrium geometries of ligand **1** and its complex with H_3O^+ were calculated at the
12 B3LYP/6-31G(d) level. DFT calculations have been found to offer good results for H-bonded
13 structures [20] although their full reliability in this field was recently criticized [21,22].
14
15 However, recommended more rigorous methods like Moeller-Plesset perturbation approach
16 MP2 [21] or modified functionals with wider basis sets [22] are not practicable for such large
17 systems as **1** or its complex. Considering the rather mild deviations apparently produced by
18 the conventional DFT method, we believe that our calculations give a reasonable
19 approximation to our structures.
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31 In Fig. 3, the optimized structure of **1** is given. As it can be seen, the cone is predicted
32 to be distorted in the way suggested by NMR, i.e. two opposite aromatic rings are much more
33 parallel than it would be expected in ligand **1**. As explained above, it is in a good agreement
34 with NMR spectra.
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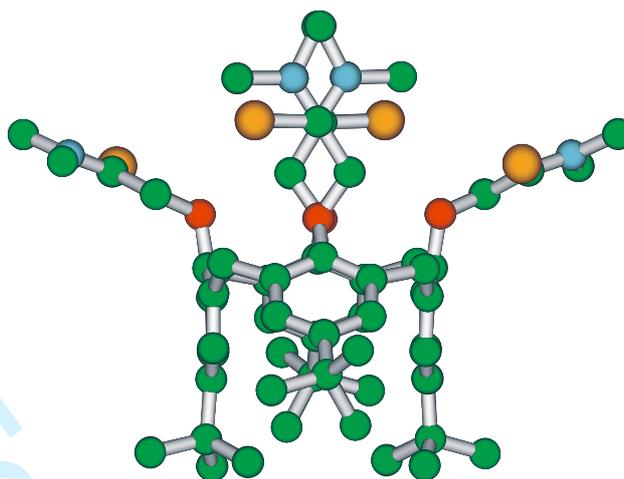


Fig. 3 Two projections of the DFT-optimized structure of free **1** (B3LYP/6-31G(d), hydrogen atoms omitted).

In Fig. 4, the lowest-energy-level structure obtained by optimization of the $\mathbf{1}\cdot\text{H}_3\text{O}^+$ complex is illustrated. In good agreement with NMR, the calixarene part of the considered complex is more cone-like and distinctly more symmetric than free ligand **1**. The hydroxonium ion, also in agreement with NMR, is bound by two strong H-bonds to phenoxy oxygen atoms as well as by a two-center H-bond to thiocarbonyl sulphur and phenoxy oxygen atoms. Considering their orientation, the remaining two thiocarbonyl sulphur atoms are probably bound by electrostatic interaction with H_3O^+ , too.

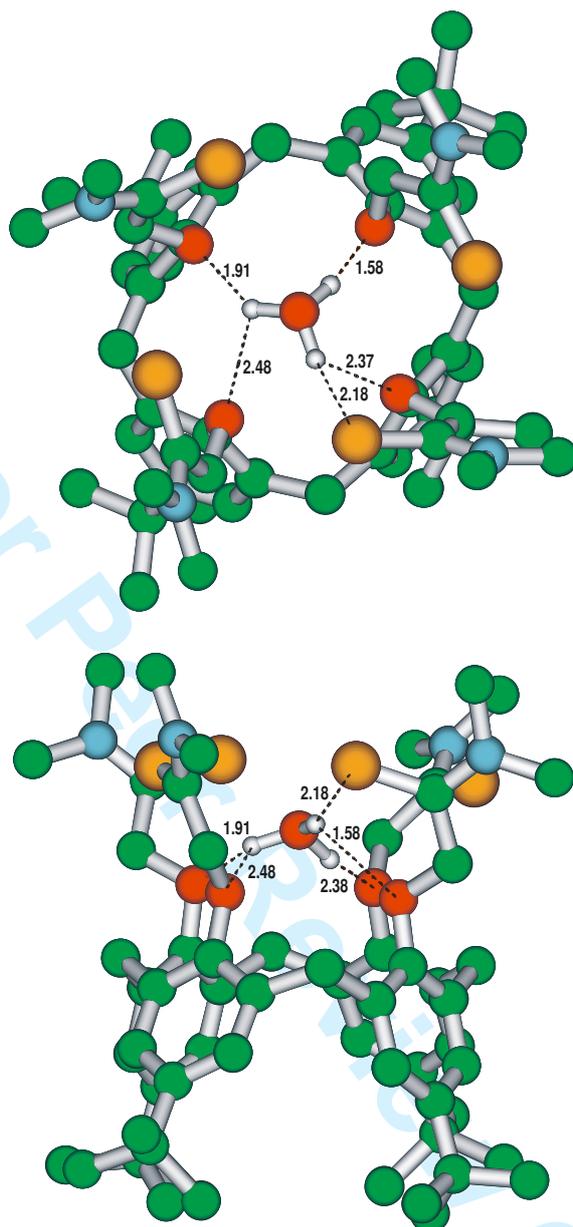


Fig. 4 Two projections of the DFT-optimized structure of the $1 \cdot \text{H}_3\text{O}^+$ complex (B3LYP/6-31G(d), hydrogen atoms omitted except those of H_3O^+).

Although the symmetry of the calixarene part is predicted to be fairly near to C_4 (cf. Fig. 4), the strong hydrogen bonds are not symmetrically distributed as it would seem to be so by NMR spectra. The above explanation that the structure is averaged by a fast motion of the H_3O^+ ion in the coordination cavity seems to be hampered by a too high energy barrier connected with the necessary breaking of three to four hydrogen bonds. There is a high probability, however, that such barrier either does not exist or is much lower due to the

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3 relative nearness of two other sulfur atoms, which form weak hydrogen bonds with the ion.
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5 As the ion rotates, some hydrogen bonds are strengthened simultaneously as other are
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8 weakened and the energy surface traversed by this motion has shallow ripples rather than high
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10 peaks and deep valleys. It is also probable that the rotation can tunnel through these low
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12 barriers.
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15 Finally, the calculated stabilization energy of the $\mathbf{1}\cdot\text{H}_3\text{O}^+$ complex is 100.4 kcal/mol,
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17 which is a rather high value expressing high stability of the complex under study. This again
18
19 is in agreement with the findings of NMR. The determination of the actual stability constant
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21 of the complex $\mathbf{1}\cdot\text{H}_3\text{O}^+$ in the organic phase of the two-phase water-nitrobenzene extraction
22
23 system is underway in our laboratories.
24
25

26
27 In conclusion, we found that H_3O^+ not only binds to $\mathbf{1}$ but, in doing so, influences its
28
29 overall conformation forcing its calixarene cavity to adopt a more symmetric and open shape.
30
31 This surely influences its properties as a host for some guest molecules. One can thus
32
33 speculate that inclusion interactions of $\mathbf{1}$ and similar modified calixarenes could be changed
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35 by adding protons to the system, which opens interesting possibilities.
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41 EXPERIMENTAL

42
43 **Materials and samples.** Nitrobenzene- d_5 and *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-
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45 dimethylthioacetamide) ($\mathbf{1}$) were purchased from Fluka, Buchs, Switzerland and were used as
46
47 obtained. Preparation of hydrogen bis(1,2-dicarbollyl) cobaltate (HDCC) was described in
48
49 Ref. [14]. Briefly, the cesium (CsDCC) analogue was prepared in the Institute of Inorganic
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51 Chemistry, Řež, Czech Republic, using the method published by Hawthorne et al. [17]. In
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53 order to obtain its hydrogen analogue, HDCC, 0.2 mol/L solution of CsDCC in nitrobenzene
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55 was twice shaken with equal volumes of 15% v/v *n*-propanol in 1 mol/L H_2SO_4 in distilled
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57 water, followed by tenfold equilibrium shaking with equal amounts of 1 mol/L H_2SO_4 and
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59
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two equilibrations with distilled water. After separation of the phases, nitrobenzene was removed by distillation. The product was dried under high vacuum to a constant weight for two weeks. For NMR samples, 5×10^{-6} mol of **1** was dissolved in a mixture of appropriate amounts of nitrobenzene- d_5 and 0.001 mol/L solution of HDCC in the same solvent.

NMR measurements. ^1H and ^{13}C NMR spectra were measured at 300.13 and 75.45 MHz frequency, respectively, with an upgraded Bruker Avance DPX300 spectrometer collecting 64 scans for ^1H NMR and 2×10^4 scans for each type of ^{13}C NMR spectra. In the latter case, DEPT45 sequence was used and spectra with coherence evolution delays adapted for the spin interaction constants J_{CH} 145, 20, 12, and 6 Hz, respectively, were superimposed in the presented ^{13}C NMR spectra. COSY-LR and NOESY 2D ^1H NMR spectra as well as HSQC and HMBC ^1H - ^{13}C 2D correlation spectra were measured using an inverse-detection z-gradient probe taking 1 kpoints and 256 increments in 640 scans. Phase shifted sine-bell weighting function was applied before Fourier transform.

Computational procedures. All calculations were performed using the GAUSSIAN 03 suite of programs [16]. The molecular equilibrium geometries were fully optimized without geometry constrains by using the Becke's three parameter functional of density functional theory with the correlation of Lee-Yang-Parr (B3LYP) and the 6-31G(d) basis set. Several local configurations near the achieved energy minimum were examined. As the renewed optimizations converged to the same molecular geometry, we believe the achieved energy minimum to be the global one.

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