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Keywords: spin-coupled biradical anions, magnetic properties, tetrachlorosemiquinone anion radical

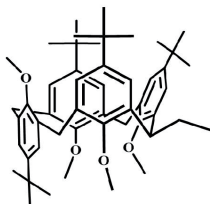
MS24.P48

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Crystal engineering of Calix[4]arenes. Chemical straightening of guest channels

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Three solvate crystal structures of the laterally ethyl substituted tetra-*tert*-butyltetraamethoxycalix[4]arene (**1**) with THF, CHCl₃ and CH₂Cl₂ are compared to the corresponding solvent free structure using single crystal X-ray structure determination, isostructurality and molecular isometricity calculations [1]. To study the effect of the lateral substitution, the laterally non-substituted host with the guest THF is also included to the comparison.



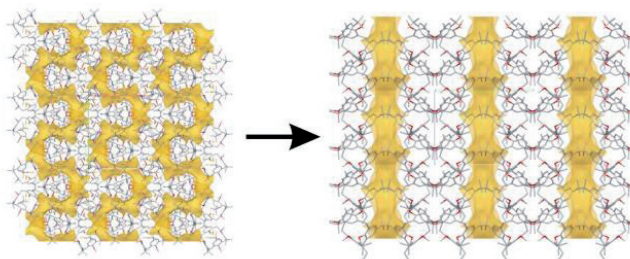
The calixarene molecules due to the absence of any intramolecular hydrogen bonding at the lower rim all adopt a *partial cone* conformation, which has already been calculated to be the lowest energy conformer [2]. The guest molecules are always being positioned interstitially.

The presence of solvent molecules induces the formation of the higher symmetrical orthorhombic crystal structures of the laterally substituted calixarene, being isostructural irrespective of the included guest molecule. The packing arrangement of all structures is controlled by weak intermolecular C-H... π -interactions and van der Waals forces, whereas π ... π interactions are absent.

The introduction of the lateral ethyl substituent expands the total room available for guest molecule inclusion by nearly 30%, being a promising fact for crystal inclusion chemistry.

The serpentine like channels disposable of the solvent guest molecules in the crystal structures straighten as the effect of lateral substitution of the host calix[4]arene. This fact seems to be an

interesting crystal engineering aspect, as the channel geometry of a calixarene lattice can be straightened by the effect of a simple lateral monosubstitution to the host molecule.



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Two reversible thermochromic phase transitions of copper(II) diiminate

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Two thermal reversible first-order phase transitions for solid copper(II) diiminate Cu[-N(H)-C(CF₃)=C(F)-C(CF₃)=N(H)-]₂ (**1**) at 68.6 °C ($\alpha \rightarrow \beta$) and 87.5 °C ($\beta \rightarrow \gamma$) have been found by differential scanning calorimetry. They are accompanied by *green* (α) – *yellow* (β) – *red* (γ) thermochromism.

The α (monoclinic, $P2_1/n$, $Z = 2$), β (tetragonal, $P4_2/n$, $Z = 4$) and γ (monoclinic, $P2_1/n$, $Z = 4$) phases of **1** have been studied by X-ray single-crystal structural analysis and powder diffraction. It has been revealed that the solid phase transitions are related to the transformations of six-membered metallocycle geometry from bent to planar ($\alpha \rightarrow \beta$) and Cu(II) coordination from square-planar to tetrahedral ($\beta \rightarrow \gamma$). Presumably, these transformations are explained by (i) Jahn-Teller effect of Cu(II) (d^9 -system), (ii) the intramolecular repulsion between NH-groups, and (iii) the short intermolecular Cu...F and F...F contacts. The high-temperature β and γ phases exist at room temperature in a metastable state and slowly transform into the stable α phase for some days. However, these processes proceed very fast on further cooling. The crystal densities of the studied phases decrease in the range of α (2.278 g/cm³) > β (2.162 g/cm³) > γ (2.065 g/cm³).

Solid state thermochromic behaviour is of special interest in the design of devices for visual and prompt monitoring of temperature changing. The reversible interconversion in copper(II) diiminate **1** can provide a new class of thermochromic materials.

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Keywords: Cu(II) diiminate, reversible thermochromic phase transitions, X-ray single-crystal and powder diffraction