

A Lower Rim *Tert*-butyl Calix[4]arene Derivative that Binds Ag(I)

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The X-ray structures of a *tert*-butyl calix[4]arene derivative with $-O-H$ and $-O-(CH_2)_2-NH-(P=S)(OCH_2CH_3)_2$ pendant arms (**EPS**) as molecular complexes with methanol, **EPS**(MeOH), **1**, with dichloromethane, **EPS**(Cl₂CH₂), **2**, and its complex with silver(I) and acetonitrile, Ag**EPS**(MeCN)K.(ClO₄)₂.H₂O, **3**, were determined. The structures were solved from 17027 (**1**), 8810 (**2**) and 7729 (**3**) reflections with $I > 2\sigma(I)$ collected at T=100 K, and refined to R1-factors of 0.054 (**1**), 0.049 (**2**) and 0.090 (**3**). In all compounds, a pair of strong O-H...O(pend) bonds in the lower rim produces relatively open chalices. This, in turn, promotes the hydrophobic interaction with the solvent molecules found included in these cavities. The upper half of the **EPS** pendant arms is anchored by N-H...O(ox) intramolecular bonds where now the phenol oxydryl oxygen atoms act as H-bond acceptors. Despite the relative rigidity of the upper half of the hydrophilic cavity, the lower half is pre-organized towards soft metal ion complexation at the thiophosphorous sulphur binding site by unhindered torsion movements, mainly around the N-P σ -bond. The silver(I) complex with **EPS**, exhibits an approximate C₂ symmetry around the calix axis. The Ag(I) ion is sited on this axis, linearly coordinated to the sulphur atoms of the pendant arms [Ag-S distances of 2.414(2) and 2.422(2) Å, $\angle(S-Ag-S)=171.99(8)^\circ$]. We thank FAPESP (Brazil) and EU (Contract ICA CT 2000-30006) for support.

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