

Supporting Information for:

Drastic Effects of the Second Coordination Sphere on Neutral vs. Anionic Guest Binding to a Biomimetic Cu(II) center embedded in a calix[6]azacryptand

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Experimental section

General. All solvents and reagents were obtained commercially. All solvents used have been distilled and kept under N₂. IR spectra were recorded with a Perkin-Elmer Spectrum One spectrometer.

EPR spectra were recorded using a Bruker Elexys spectrometer (X-band). Fitting of the EPR spectra was performed using Xepr & Xsophe suite (Bruker). The vis-NIR spectra were recorded with a Jasco V-570 spectrophotometer. Elemental analysis was performed at the Institut des Substances Naturelles, Gif sur Yvette, France.

[Cu(calix[6]tmpa)(H₂O)](ClO₄)₂: To a solution of the ligand calix[6]tmpa (30 mg ; 22.3 μmol) in DCM (2 mL) was added a stoichiometric amount of Cu(ClO₄)₂(H₂O)₆ (8.3 mg, 22.3 μmol) in THF (100 μL). The cloudy suspension became clear after a few minutes. The green solution was stirred for one hour, concentrated and filtered over celite. Pentane was added and the resulting green precipitate was collected by centrifugation (25 mg, 68 %).

Mp 185 °C (decomp)

IR (KBr, cm⁻¹): 2961 ; 2906 ; 2869 ; 1608 ; 1580 ; 1480 ; 1384 ; 1362 ; 1295 ; 1245 ; 1202 ; 1144 ; 1120 ; 1088 ; 1007 ; 939 ; 877 ; 800 ; 624.

Anal. Calcd for C₉₀H₁₁₀Cl₂CuN₄O₁₅, CH₂Cl₂, 2 H₂O: calculated C 62.70, H 6.71, N 3.21, found C 62.43, H 6.75, N 3.72.

[Cu(calix[6]tmpa)(OH)](ClO₄): To a solution of the ligand calix[6]tmpa (50 mg ; 37 μmol) in DCM (3 mL) was added a stoichiometric amount of Cu(ClO₄)₂(H₂O)₆ (13.8 mg, 37 μmol) in THF (100 μL). The cloudy suspension became clear after a few minutes. The green reaction mixture was stirred for one hour, NEt₃ was added as a 3.7 10⁻² M solution in DCM (100 μL, 37 μmol) and the resulting mixture was stirred for one hour. The blue solution was then concentrated, pentane (4 mL) was added and the precipitate was collected by centrifugation. This solid was then redissolved in DCM (0.3 mL), PrOH (3 mL) was added and the precipitate was collected by centrifugation (40 mg, 66 %).

Mp 190 °C (decomp)

Anal. Calcd for C₉₀H₁₀₉ClCuN₄O₁₁, 3 H₂O: calculated C 68.59, H 7.36, N 3.56, found C 68.14, H 6.97, N 3.38.

(Due to their potentially explosive character, the Cu perchlorate complexes were not completely dried.)

Comparative behaviour between the calix[6]tren and tmpa-based Cu(II) complexes for anion binding.

i) EPR experiments

To a CH₂Cl₂ solution of complex [calix[6]trenCu(II)(H₂O)](ClO₄)₂ (0.04 M) was progressively added either lutidine, Et₃N or *i*Pr₂EtN.

After a total addition of 90 equiv. of lutidine, no significant change of the EPR spectrum could be observed.

After a total addition of 40 equiv. of Et₃N, no significant change of the EPR spectrum could be observed. With 90 equiv., free Cu(II) was partially released.

After a total addition of 40 equiv. of *i*Pr₂EtN, no significant change of the EPR spectrum could be observed. With 90 equiv., free Cu(II) was partially released.

ii) UV-vis experiments

When to a CH₂Cl₂ solution of complex [calix[6]trenCu(II)(DMF)](ClO₄)₂ (0.004 M) was progressively added first Et₃N (up to 2500 equiv.), then *n*Bu₄Cl (up to 140 equiv.), no spectroscopic change was observed: the UV-vis spectrum (beside some increase of the ϵ value) or the EPR spectrum remained essentially the same. When *n*Bu₄Cl was added to the aqua complex in CH₂Cl₂ (under similar experimental conditions), decoordination occurred.

In strong contrast, complexes [calix[6]tmpaCu(II)(L)](ClO₄)₂ in CH₂Cl₂ solution (0.003 M, L = H₂O or DMF) were quantitatively converted with less than 5 equiv. of lutidine into the hydroxo species [calix[6]tmpaCu(II)(OH)]⁺ (this was checked by UV-vis and EPR spectroscopies). Similarly, the addition of 2 equiv. of Cl⁻ was sufficient to produce [calix[6]tmpaCu(II)(Cl)]⁺.

The pK_a values of [Cu(tmpa)(H₂O)]²⁺ and [Cu(tmpa)(H₂O)]²⁺ in water are 9.4 and 7.4, respectively (see A. Neubrand, F. Thaler, M. Körner, A. Zahl, C. D. Hubbard, R. V Rudick, *J. Chem. Soc. Dalton trans* **2002**, 957-961 and ref. cited therein).

The pK_a value of lutidine is 6.75 in H₂O and 4.46 in DMSO, while the one of Et₃N is 10.75 in H₂O and 9.00 in DMSO (for *i*Pr₂EtN, it is 18.1 in MeCN. See Evan's pK_a table and: A. M. Kelly-Rowley, V. M. Lynch, E. V. Anslyn, *J. Am. Chem. Soc.* **1995**, *117*, 3438-3447.).

This implies that the basicity of a tertiary amine is more than 4 orders of magnitude higher than that of lutidine, whereas there are only 2 orders of magnitude between the pK_a of the tren and tmpa complexes. Knowing that less than 10 equiv. of the weakest base (lutidine) are required to fully deprotonate the more acidic complex (calix[6]tmpa-based), and 1000 equiv. of the strongest base (Et₃N) are inefficient at deprotonating the calix[6]trenCu(II) aqua complex (in dilute solution), we can stipulate that there is a factor of $100 \times 10^4 = 10^6 \Leftrightarrow 6$ pK_a units separating the acidity constants of these calix-based Cu(II) complexes. This value is much higher than that measured for the simple tren and tmpa Cu(II) aqua systems (2 pK_a units of difference), thus emphasizing the drastic effect of the calixarene core on the relative stabilization of the acid-base species. The latter can be estimated as $6 - 2 = 4$ pK_a units, which corresponds to *ca.* 20 kJ.M⁻¹.

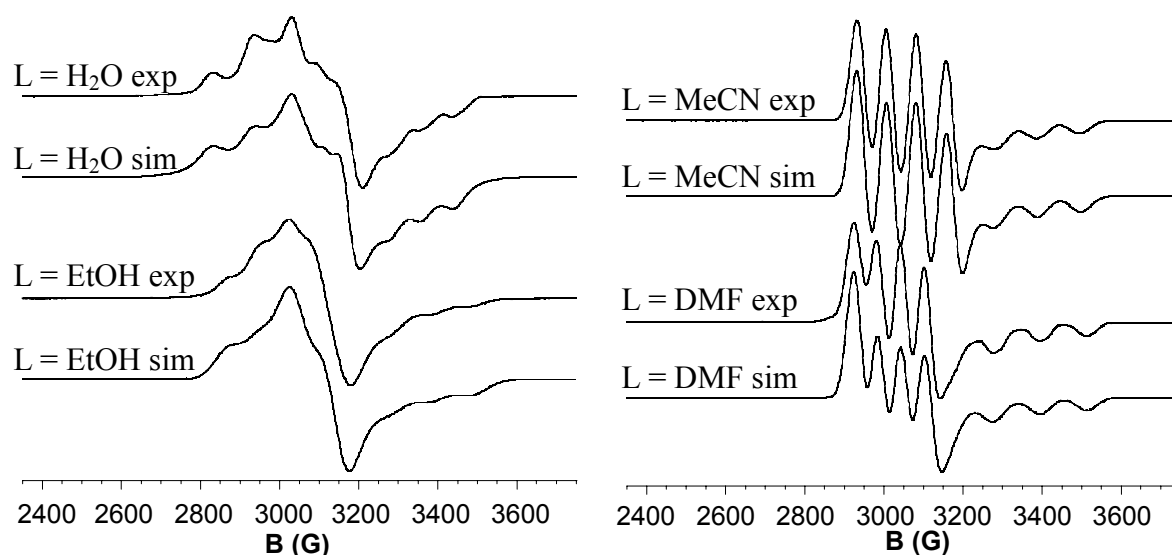


Fig. S1. Experimental and simulated EPR spectra (X band) of $[\text{Cu}(\text{calix}[6]\text{tmpa})(\text{L})](\text{ClO}_4)_2$ in frozen CH_2Cl_2 (100 K) with 10% (v/v) of guests (for $\text{L} \neq \text{H}_2\text{O}$).

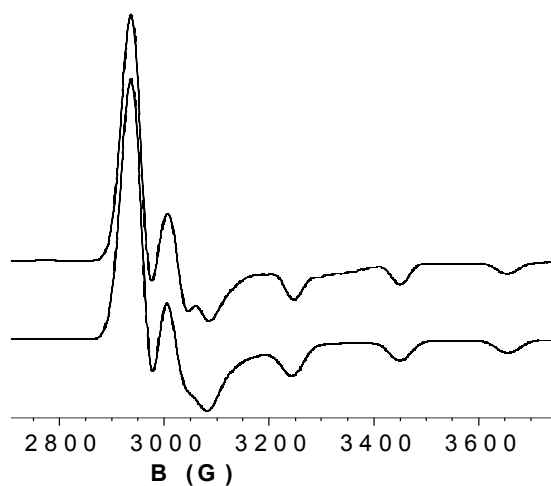


Fig. S2. Experimental and simulated EPR spectrum (X band) of complex $[\text{Cu}(\text{calix}[6]\text{tmpa})(\text{OH})](\text{ClO}_4)$ in frozen CH_2Cl_2 (100 K).

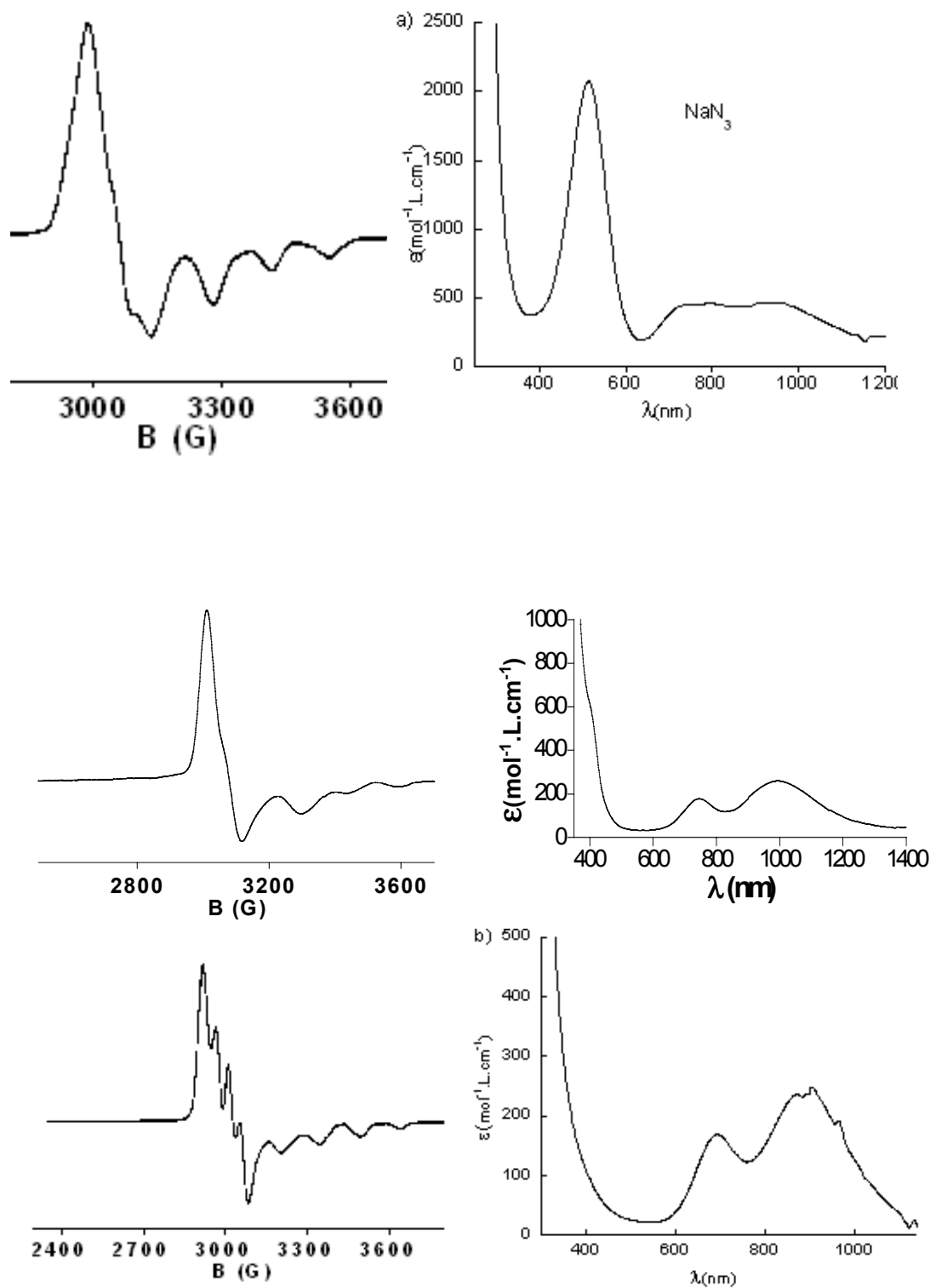


Fig S3. EPR (100 K, left) and UV-vis-NIR (right, 293 K) spectra of $[\text{Cu}(\text{calix}[6]\text{tmpa})\text{X}]^+$ resulting from the addition of 1 equiv. of NaN_3 diluted in DMF (top, $\text{X} = \text{N}_3$, $g_{\perp} = 2.18 > g_{\parallel} = 1.99$, $A_{\parallel} = 136 \times 10^{-4} \text{ cm}^{-1}$), NEt_4Cl diluted in DMF (middle, $\text{X}^- = \text{Cl}^-$, $g_{\perp} = 2.19 > g_{\parallel} = 2.00$, $A_{\parallel} = 150 \times 10^{-4} \text{ cm}^{-1}$), NBu_4F diluted in CH_2Cl_2 (bottom, $\text{X}^- = \text{F}^-$, $g_{\perp} = 2.23$, $A_{\perp} = 45.5 \times 10^{-4} > g_{\parallel} = 1.95$, $A_{\parallel} = 145 \times 10^{-4} \text{ cm}^{-1}$). Conditions: $[\text{Cu}] = 1\text{-}3 \text{ mM}$.

XRD determination of complex [Cu(calix[6]tmpa)(MeCN)](ClO₄)₂.

A green crystal (0.30 x 0.10 x 0.06 mm³) was mounted with Paratone-N oil (Hampton Research) coating and immediately placed under a nitrogen cold stream. X-ray intensity data were collected at 100 K on a Bruker-Nonius X8-APEX2 CCD area-detector diffractometer using Mo-*K*_α radiation ($\lambda = 0.71073 \text{ \AA}$). Seven sets of narrow data frames (30 s per frame) were collected at different θ values for 6 and 1 initial values of ϕ and ω , respectively, using 0.5° increments of ϕ or ω . Data reduction was accomplished using SAINT V7.03¹. The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10)¹ to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELXTL V6.14.² Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms. Several disordered molecules were initially modelled as discrete ClO₄⁻ counter-ions but they were ultimately removed from the structure. The data set was corrected with the program PLATON/SQUEEZE³.

1 APEX2 version 1.0-8; Bruker AXS: Madison, WI, 2003

2 SHELXTL version 6.14; Bruker AXS: Madison, WI, 2001

3 P Van der Sluis, A. L. Spek, Acta Cryst., A46, 194-201, 1990