

MS05-2-4 TREN and TMPA capped calix[6]arene metal complexes as ds-DNA/RNA binders
#MS05-2-4A. Višnjevac ¹, N. Nyssen ², I. Nikšić-Franjić ¹, I. Piantanida ¹, B. Colasson ², O. Reinaud ²¹Institut Ruđer Bošković - Zagreb (Croatia), ²Universite de Paris - Paris (France)**Abstract**

TMPA and TREN capped calix[6]arene derivatives are specially designed for an easy coordination of variety of transition metal dications and specific intra-cavity inclusion of small organic species attracted (and coordinated) by this cations. Within the frame of a project aimed to investigate capability of these remarkable edifices to recognize various ds-DNA or ds-RNA structures and to study structural particularities of so formed non-covalent assemblies, we are reporting single crystal X-ray structures of a TMPA capped calixarene copper (II) complex, [Cu(II)X6(NMe3+)3tmpaOMe(MeCN)][NO3-]5 (1) and two isostructural TREN capped calix[6]arene cobalt (II) complexes, [Co(II)X6trenOMe(MeCN)][ClO4-]2 (2) and [Co(II)X6trenOMe(OH)]ClO4- (3). In all complexes, four metal coordination valences are occupied by four nitrogen donor atoms from TMPA (in 1) and TREN (in 2 and 3). While the fifth coordination site in 1 and 2 is occupied by an intra-cavity coordinated acetonitrile molecule, in 3, this site is taken by a hydroxide anion. In all three structures, metal lies in a centre of a slightly distorted trigonal bipyramid, with an apical compression in the case of Cu(II) complex 1, and elongation in the case of Co(II) complexes 2 and 3. The apical compression of the pyramid as observed in 1 indirectly confirms the oxidation state of the copper, which was impossible to establish crystallographically, due to an overwhelming disorder of the two nitrate counter anions. Charge of the Co(II) is expectedly balanced by two extra cavity perchlorate counter anions in 2 and by one in 3 (as the other negative charge here emanates from the intra-cavity bound OH). While there are no classic hydrogen bonds in the structure of 1, in cobalt complexes 2 and 3, a network of hydrogen bonds involving the perchlorate anion guides crystallographic packing by a formation of hydrogen-bonded perchlorate bridged head-to-tail molecular chains.

Both, experimentally (fluorimetric experiments by Ethidium bromide and DAPI displacement) and computationally (molecular dynamics simulations), it was confirmed that the metal complex 1, with water or hydroxide instead of acetonitrile bound in the cavity, efficiently binds to the DNA minor groove, as well as corresponding calixarene with no metal cation attached. In contrast, the calixarene analogue in which the positively charged trimethylammonium feet are replaced with neutral amino groups does not bind to the ds-DNA, whereas its Cu (II) complex does. These findings confirm the crucial role of the positive charge in these molecules for the efficient DNA binding.

