Supplementary data for article:

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Supplementary materials for:

Dinuclear copper(II) octaazamacrocyclic complex in a PVC coated GCE and graphite as a voltammetric sensor for determination of gallic acid and antioxidant capacity of wine samples

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1. Details of molecular modeling and DFT calculations

Results of CDS search [1-S] have shown that during the forming of dinuclear complexes with transition metal ions *tpmc* ligand can adopt three different conformations: "boat", "symmetric chair" and "unsymmetric chair" conformation. Geometry optimization study on $[Cu_2tpmcGA]^{3+}$ complex ion with DFT method have shown that, independently of the starting geometry, optimized geometry is always in the "unsymmetric chair" conformation (Fig. 1) with gallic acid acting as the bidentate bridging ligand between two copper(II) ions.

In the optimized structure of $[Cu_2tpmcGA]^{3+}$ complex there are two different geometries around two copper(II) ions. Geometry around first Cu(II) ion (labeled Cu1 in Fig. 1) is close to trigonal-bipyramidal geometry (τ parameters 0.81) with two nitrogen atoms from *tpmc* and

oxygen atom from gallic acid in equatorial position and the other two nitrogen atoms from *tpmc* axial position. Ligating atoms around the second copper ion (Cu2, Fig. 1) are arranged in square-pyramidal geometry (τ parameters 0.115) with three nitrogen atoms from *tpmc* and oxygen atom from gallic acid in in-plane position. The fourth *tpmc* nitrogen atom is in apical position.

The crystal structures of all dinuclearcopper(II) complexes with *tpmc* and another bidentante ligand (CO_3^{2-} [2-S], NO_3^- [3-S], $HCOO^-$[4-S], CH_3COO^-[4-S], succinato [5-S] and $C_6H_5COO^-$ [5-S]) are also in "unsymmetric chair" conformation.

In order to obtain better insight in the stability of $[Cu_2tpmcGA]^{3+}$ complex ion, the energy of isodesmic reaction (1) in water solution was calculated using UB3LYP method. Solvation of molecules and ions participating in the reaction was simulated with SMD implicit solvation method [6-S].

$$[Cu_2tpmc(H_2O)_2\ ]^{4+} + GA^- \rightarrow [Cu_2tpmcGA]^{3+} + 2\ H_2O \qquad (1)$$

References

[1-S] B.B. Petković, M. Milčić, D. Stanković, I. Stambolić, D. Manojlović, V.M. Jovanović, S.P. Sovilj, Complexation Ability of Octaazamacrocyclic Ligand Towards Co^{2+}, Ni^{2+}, $Cu^{2+}$and Zn^{2+} Metal Cations; Experimental and Theoretical Study, Electrochim. Acta 89 (2013) 680–687.

[2-S] A.M. Appel, R. Newell, D.L. Du Bois, M.R. Du Bois, Concentration of Carbon Dioxide by Electrochemically Modulated Complexation with a Binuclear Copper Complex, Inorg. Chem. 44 (2005) 3046–3056.

[3-S] E. Asato, H. Toftlund, S. Kida, M. Mikuriya, K. Murray, Preparation and characterization of copper(II) complexes with 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, Inorg. Chim. Acta 165 (1989) 207–214.

[4-S] G.A. Bogdanović, Z.M. Miodragović, G. Vučković, R. Marković, A. Spasojević-de Bire, Synthesis and X-raycrystal analysis of $[Cu_2(HCOO)tpmc]$-$[Cu_2(CH_3COO)tpmc](ClO_4)_6 \cdot 6H_2O$(tpmc = N,N′,N″,N‴-tetrakis-(2-pyrydimethil)-1,4,8,11-tetraazacyclotetradecane). Preparation and characterization of $[Cu_2(HCOO)tpmc](ClO_4)_3 \cdot H_2O$, Synth. React. Inorg. Met-Org. Chem. 31 (2001) 1189–1203.

[5-S] G. Vučković, M. Antonijević-Nikolić, T. Lis, J. Mrozinski, M. Korabik, D.D. Radanović, X-ray analyses, spectroscopic and magnetic properties of $[Cu_4(succinato)(tpmc)_2](ClO4)_6 \cdot 2C_2H_5OH \cdot 4H_2O$ and $[Cu_2(C_6H_5COO)tpmc](ClO_4)_3 \cdot 0.5CH_3OH \cdot 0.5H_2O$ complexes, J. Mol. Struct. 872 (2008) 135–144.

[6-S] A.V. Marenich, C.J. Cramer, and D.G. Truhlar, Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, J. Phys. Chem. B113 (2009) 6378–6396.