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### *Biomimetic resorcinarene-based copper(II) complex*

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The synthesis, structural characterization, as well as the chemical activity studies of a Cu(II) "bowl complex", based on the resorcin[4]arene scaffold with three imidazole-containing coordinating arms grafted at the large rim, is presented. This complex is a biomimetic model of a metalloenzyme active site where a cofacial triade of amino-acid residues holds the metal ion in the active site [1]. The trisimidazole ligand reacts with a stoichiometric amount of copper(II) perchlorate to produce a Cu(II) diperchloratocomplex 1. Spectroscopic studies revealed a 5-coordinate SBP environment for the Cu(II) center provided by three imidazole arms, and two extra donors, one embedded in the resorcinarene cavity, the other exposed to the solvent, in exo position. These two labile sites are occupied by either coordinating solvent molecules or residual water, and are readily displaced by carboxylate donors, the position of which (endo or exo) is under tight control of the bowl-cavity. The reaction of 1 with CH<sub>3</sub>COONa led to a formation of the Cu(II) acetatocomplex 2. Molecular structure of 2 features a rigidified resorcinarene bowl, which was constructed by the addition of the four methylene bridges between the eight hydroxyl groups of the octol precursor [2]. The isolated resorcinarene basket reveals an approximate, non-crystallographic, 4mm point symmetry, and can easily host small guest molecules. Three methylimidazole-containing coordination arms at the large rim coordinate the Cu (II) ion. Its coordination sphere is completed by two O atoms from the intra-cavity bound acetate. The electron donors form a distorted square pyramide, where one of the nitrogens is at the apical position. The endo-coordination of the acetate is supported by an extensive network of intramolecular C-H...O and C-H... $\pi$  interactions. Complex 2 crystallizes in P21/c space group; a=32.3310 (4)Å, b=11.5490 (1)Å, c=21.6020 (2)Å, beta=102.281(3)°.

[1] Bertini, I; Gray, H. B.; Stiefel, E. I.; Valentine, J. S. *Biological Inorganic Chemistry, Structure and Reactivity*, University Science Books: Sausalito, CA, 2007., [2] Višnjevac, A; Gout, J; Ingert, N; Bistri, O; Reinaud, O, *Org. Lett.* 12 (2010) 2044 - 2047.

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