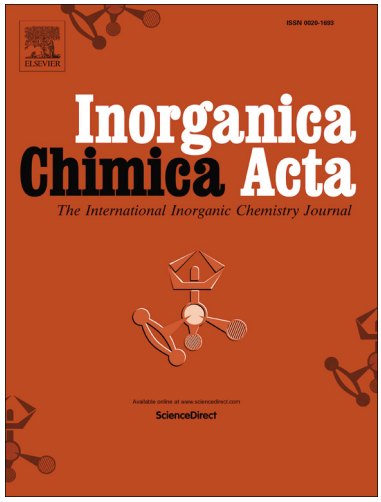

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Róbert Csonka,[a] Dóra Lakk-Bogáth,[a] Ágnes Gömöry,[b] László Drahos,[b] Michel Giorgi,[c] Gábor Speier,[a] Róbert K. Szilágyi,[d,*] József Kaizer[a,*]

[a] *Department of Chemistry, University of Pannonia, 8201 Veszprém, Hungary.*

[b] *Hungarian Academy of Sciences, Research Centre for Natural Sciences, H-1117 Budapest, Hungary*

[c] *Aix Marseille Université, CNRS, Centrale Marseille, Spectropole FR1739, 13397 Marseille, France*

[d] *Department of Chemistry & Biochemistry, Montana State University, Bozeman, MT 59717, USA*

Abstract

A mononuclear copper complex $[Cu^{II}(asN4Py)(MeCN)](O_3SCF_3)_2$ (**1**) and its mixed mono- and trinuclear $[Cu(pic)_2(ClO_4)_2][Cu_3(asN4Py)_2(pic)_2(ClO_4)_2](ClO_4)$ derivatives (**2**) were synthesized containing *N*,*N*-bis(2-pyridylmethyl)-1,2-di(2-pyridyl)-ethylamine (asN4Py) chiral ligands and 2-picolinate (pic) bridges. The structures were elucidated using single crystal X-ray diffraction and spectroscopic methods. Due to the non-trivial assignments of the formal Cu oxidation states, the d-electron count and the location of electron holes were assigned by broken-symmetry electronic structure calculations using a spectroscopically validated, hybrid density functional theory with saturated basis set. The ground state description of the mononuclear complexes is trivial; thus, they were used to validate the computational level of theory and the modelling approach. The experimental structure of the trinuclear complex can only be described by considering two asymmetric resonance structures in the crystal structure containing Cu^{II}-Cu^{II}-Cu^{I}/Cu^{I}-Cu^{II}-Cu^{II} metal centres.

Keywords: Copper(II); Pentadentate; Chiral; X-ray crystal structure; Computation.

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*To whom correspondence should be addressed. Address: Department of Chemistry, University of Pannonia, H-8201 Veszprém, Wartha V. u. 1., Hungary. E-mail: kaizer@almos.vein.hu. Tel.: (+36)88624720.