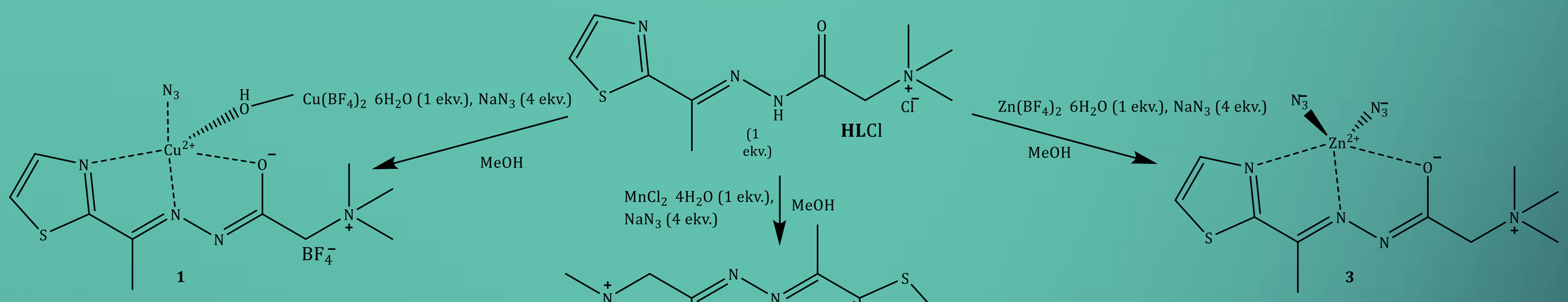
# Cu(II), Mn(II) and Zn(II) complexes of hydrazones with quaternary ammonium moiety: Synthesis, characterization and DFT calculation

Nevena Stevanović[a], Matija Zlatar[b], Mima Jevtović[c], Maja Gruden[a], Maja Šumar[a], Katarina Anđelković[a], Božidar Čobeljić[a]

[a]*University of Belgrade-Faculty of Chemistry, , Studentski trg 12–16, 11000 Belgrade, Serbia*
[b]*University of Belgrade-ICTM, Department of Chemistry, Njegoševa 12, 11000 Belgrade, Serbia*
[c]*Innovative Centre of Faculty of Chemistry, Studentski Trg 12-16, 11000 Belgrade, Serbia;*
e-mail: nstevanovic@chem.bg.ac.rs

The **HL**Cl ligand with metal salts $Cu(BF_4)_2 \cdot 6H_2O$ / $MnCl_2 \cdot 4H_2O$ / $Zn(BF_4)_2 \cdot 6H_2O$ and $NaN_3$, in methanol form mononuclear penta coordinated complexes $[Cu\mathbf{L}(N_3)(CH_3OH)]BF_4$ (**1**) and $[Zn\mathbf{L}(N_3)_2]$ (**2**) and binuclear $[Mn_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 2CH_3OH$ (**3**) complex.



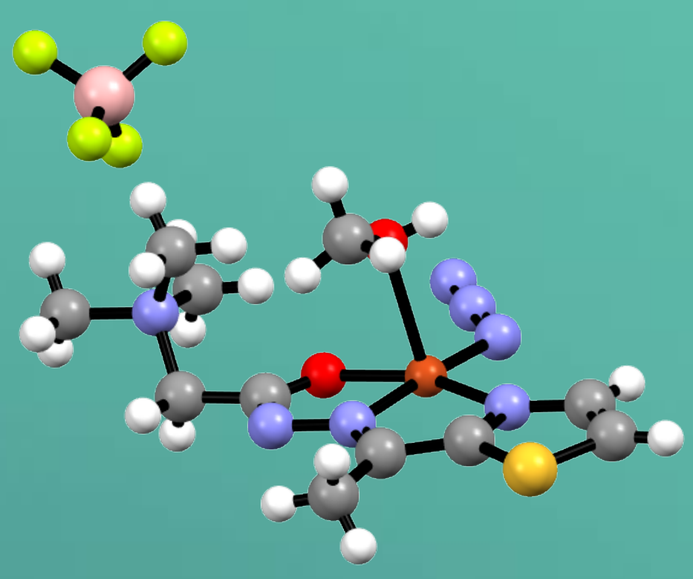



**Fig. 1** $[Cu\mathbf{L}(N_3)(CH_3OH)]BF_4$ complex

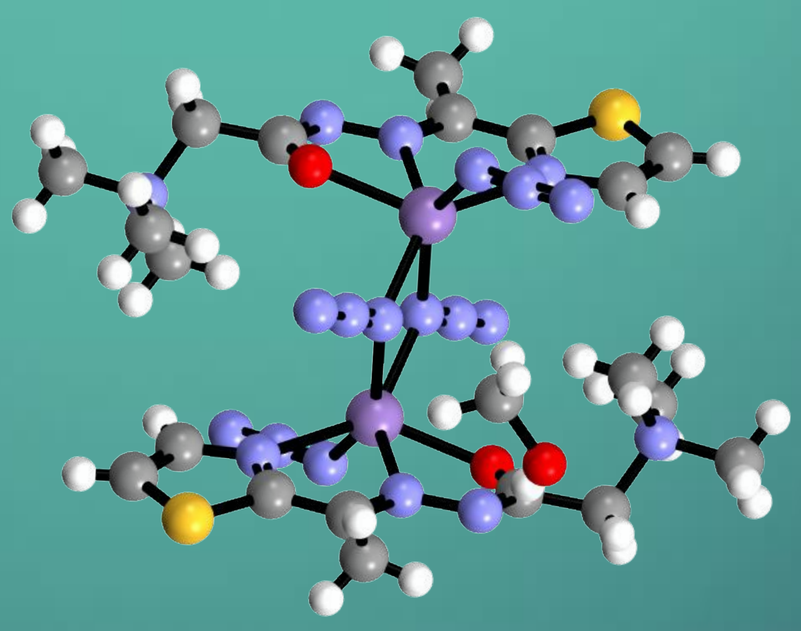


**Fig. 2** $[Mn_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 2CH_3OH$

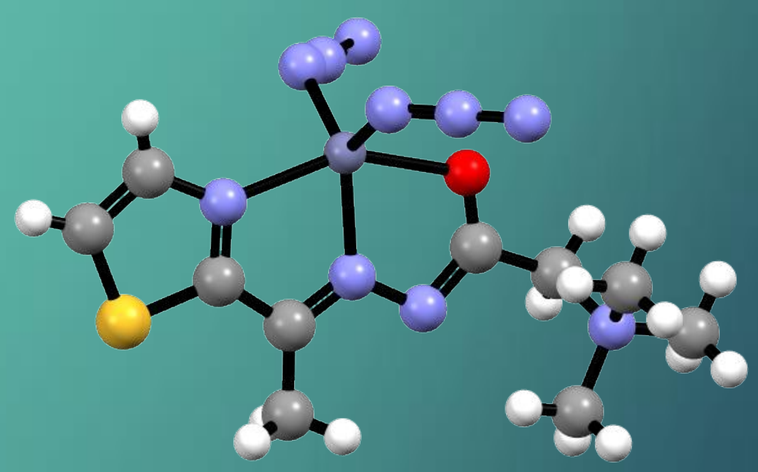


**Fig. 3** $[Zn\mathbf{L}(N_3)_2]$ complex

Complexes **1**, **2** and **3** were characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, and DFT calculations. In all three complexes ligand ($\mathbf{L}^1$) is coordinated in deprotonated formally neutral form *via* NNO donor set atoms. Complexes **1** and **3** crystallize in the monoclinic crystal system with space group No. 14 ($P2_1/n$ and $P2_1/c$ cell settings, respectively) and complex **2** in the triclinic crystal system with space group $P-1$ (No. 2).

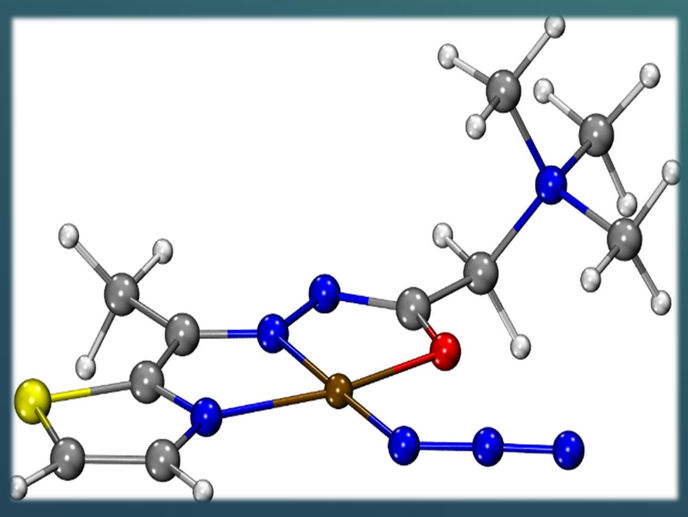


**Fig. 4** Structure of $[Cu\mathbf{L}^1(N_3)]^+$ complex ion optimized at ZORA-BP86-D3/TZP-COSMO(DMSO) level of theory

According to the DFT studies, Cu(II) complex is the most stable in square-planar geometry, while in the same DMSO solution, Mn(II) complex is the mixture of $[Mn\mathbf{L}(N_3)_2]$ and $[Mn_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$ complexes.

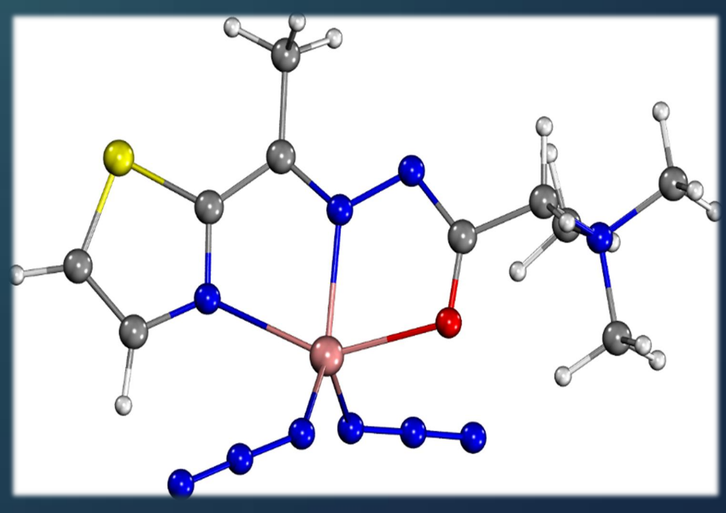


**Fig. 5** Structure of $[Mn\mathbf{L}^1(N_3)_2]$ complex optimized at ZORA-BP86-D3/TZP-COSMO(DMSO) level of theory

*Acknowledgment:* This research was supported by the Science Fund of the Republic of Serbia, #7750288, Tailoring Molecular Magnets and Catalysts Based on Transition Metal Complexes – TMMagCat.