

COMBINED EXPERIMENTAL AND THEORETICAL STUDIES OF Cu(II) AND Co(II) CATIONIC-ANIONIC COMPLEXES WITH N-SCORPIONATE LIGAND – SIMILAR STRUCTURES BUT DIFFERENT REACTIVITY

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Herein, we report the structural and spectroscopic characterization supported by quantum chemical studies of two novel Cu(II): $[\text{CuLCl}]_2[\text{CuCl}_4]$ (**1**) and Co(II): $[\text{CoLCl}][\text{CoL}^+\text{Cl}_3]$ (**2**) cationic-anionic complexes with N-scorpionate type ligand: N, N, N-tris(3,5-dimethylpyrazol-1-ylmethyl)amine (L) (Fig. 1).

The obtained complexes are the first reported examples of cationic-anionic coordination compounds tested on catecholase activity. Interestingly, from the tested Cu(II) and Co(II) complexes, only Cu(II) one (**1**) possesses catalytic activity in the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC). Moreover, catalytic results obtained for **1** revealed that the solvent's nature significantly affects the catecholase activity of the Cu(II) complex.

Experimental UV-Vis spectroscopy of **1** shows that essential features of the solid-state spectrum are maintained in DMSO and MeOH solvents, i.e. those that support the highest activity. On the contrary, the build-up of a new feature around 475 nm for **1** in ACN was noted, along with negligible activity. Using high-level quantum chemical methods at single- and multireference levels, we found that this feature could be attributed to intermolecular charge transfer excitation from $[\text{CuCl}_4]^{2-}$ to $[\text{CuLCl}]^{1+}$ species. It shifts to lower energies as compared to solid-state as the two charged fragments get closer due to Coulomb interactions. In DMSO, the solvent molecule serves as a labile ligand in a $[\text{CuLCl}]^{1+}$ fragment, while in MeOH the solvent effectively stabilizes $[\text{CuCl}_4]^{2-}$ via H-bond network. In both cases, the free coordination site is accessible, thus allowing a substrate molecule to bind.

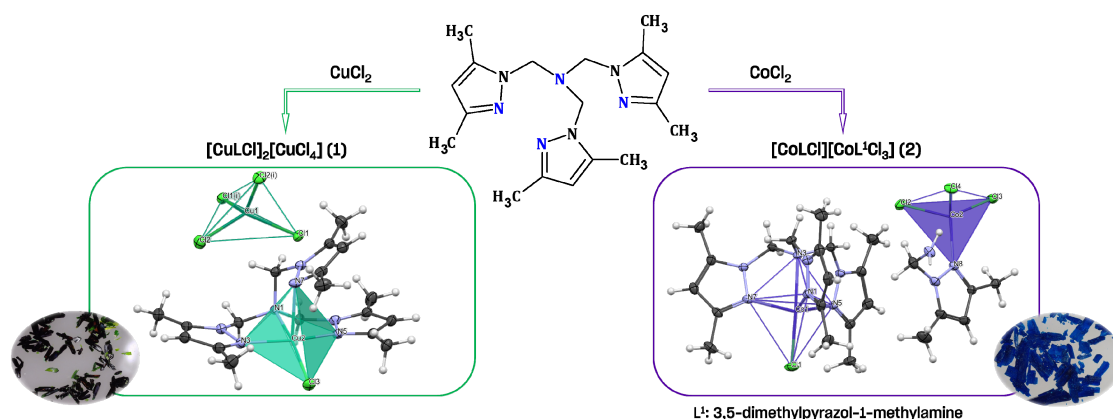


Fig. 1. Molecular structures of the Cu(II) and Co(II) complexes with N, N, N-tris(3,5-dimethylpyrazol-1-ylmethyl)amine (L)