

PYRAZOLE-BASED POLYDENTATE COMPLEXES OF THE FIRST-ROW TRANSITION METALS AS LOW-WEIGHT BIOMIMETICS

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The series of first-row transition metal complexes with polypyrazole, N-scorpionate: tris(3,5-dimethylpyrazol-1-ylmethyl)amine (L) or N-pincer: bis(1-(3,5-dimethylpyrazolyl)methyl)amine (L') type ligands is presented. The complexes are compounds of Cu^{II}, Co^{II}, Zn^{II}, Fe^{II} and Fe^{III} with structural diversity - monomeric: [Cu(NCS)₂(L')], [Fe(NCS)₂(L)]·CH₃CN, dimeric: [Fe₂(μ-Cl)₂L₂][BPh₄]₂·2CH₃CN, [FeLCl(μ-O)FeCl₃]·CH₃CN as well as cationic-anionic structures: [Zn(NCS)L]₂[Zn(NCS)₄], [CuCIL]₂[CuCl₄] and [CoCIL][CoCl₃L'].

Since scorpionate-type ligands, analogous to polypyrazole ligands introduced by Trofimenko[1], are a good choice as ligands for the synthesis of complexes with potential enzymatic activity, we have tested our complexes as functional enzyme models. The presented transition metal complexes have been tested as biomimetics in three different reactions, namely:

- 1) [Cu(NCS)₂(L')] and [Zn(NCS)L]₂[Zn(NCS)₄] complexes as inhibitors of xanthine oxidase (XO).[2] Both compounds acted as mixed-type inhibitors of XO, and the difference in their activity was confirmed by molecular docking.
- 2) [CuCIL]₂[CuCl₄] and [CoCIL][CoCl₃L'] as catechol oxidase (CO) mimetics.[3] Interestingly, from the tested complexes, only Cu^{II} one possesses CO catalytic activity. Moreover, catalytic results for the Cu^{II} complex showed that its activity is mainly due to the cationic form and is solvent-dependent, consistent with theoretical studies.
- 3) [Fe(NCS)₂(L)]·CH₃CN, [Fe₂(μ-Cl)₂L₂][BPh₄]₂·2CH₃CN and [FeLCl(μ-O)FeCl₃]·CH₃CN as mimetics of RPE65 protein. The complexes were tested in the reaction with retinyl acetate as potential catalysts for the synthesis of cis-retinoids. The changes in the electronic structure of the central metal ions were tracked during the reaction using XAS/XES measurements with the synchrotron radiation and supported with quantum chemical calculations.

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[1] S. Trofimenko, *J. Am. Chem. Soc.*, 1967, 89, 6288.

[2] J. Masternak, M. Zienkiewicz-Machnik, K. Kazimierczuk, B. Barszcz, *Polyhedron*, 2018, 142, 93.

[3] M. Zienkiewicz-Machnik, A. Kubas, et. al, *Dalton Trans.*, 2025, 54, 5268.