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Title: Synthesis and Coordination Chemistry of a New N-4-Polydentate Class of Pyridyl-Functionalized Scorpionate Ligands: Complexes of Fe-II, Zn-II, V-IV, Pd-II and Use for Heterobimetallic Systems

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Abstract: The new potentially N-4-multidentate pyridyl-functionalized scorpionates 4-((tris-2,2,2-(pyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy, (1)) and 4-((tris-2,2,2-(3-phenylpyrazol-1-yl)ethoxy)methyl)pyridine (TpmPy(Ph), (2)) have been synthesized and their coordination behavior toward Fe-II, Ni-II, Zn-II, Cu-II, Pd-II, and V-III centers has been studied. Reaction of (1) with $\text{Fe}(\text{BF}_4)(2) \cdot 6\text{H}_2\text{O}$ yields $[\text{Fe}(\text{TpmPy})(2)](\text{BF}_4)(2)$ (3), that, in the solid state, shows the sandwich structure with trihapto ligand coordination via the pyrazolyl arms, and is completely low spin (LS) until 400 K. Reactions of 2 equiv of (1) or (2) with Zn-II or Ni-II chlorides give the corresponding metal complexes with general formula $[\text{MCl}_2(\text{TpmPy}^*)(2)]$ ($\text{M} = \text{Zn, Ni}$; $\text{TpmPy}^* = \text{TpmPy, TpmPy(Ph)}$) (4-7) where the ligand is able to coordinate through either the pyrazolyl rings (in case of $[\text{Ni}(\text{TpmPy})(2)\text{Cl}_2]$ (5)) or the pyridyl-side (for $[\text{ZnCl}_2(\text{TpmPy})(2)]$ (4), $[\text{ZnCl}_2(\text{TpmPy(Ph)})(2)]$ (6) and $[\text{NiCl}_2(\text{TpmPy(Ph)})(2)]$ (7)). The reaction of (1) with VCl_3 gives $[\text{VOCl}_2(\text{TpmPy})]$ (8) that shows the N-3-pyrazolyl coordination-mode. Moreover, (1) and react with $\text{cis-}[\text{PdCl}_2(\text{CH}_3\text{CN})(2)]$ to give the disubstituted complexes $[\text{PdCl}_2(\text{TpmPy})(2)]$ (9) and $[\text{PdCl}_2(\text{TpmPy(Ph)})(2)]$ (10), respectively, bearing the scorpionate coordinated via the pyridyl group. Compounds (9) and (10) react with $\text{Fe}(\text{BF}_4)(2)$ to give the heterobimetallic Pd/Fe systems $[\text{PdCl}_2(\mu\text{-TpmPy})(2)\text{-Fe}](\text{BF}_4)(2)$ (11) and $[\text{PdCl}_2(\mu\text{-TpmPy(Ph)})(2)\text{-Fe-}2(\text{H}_2\text{O})(6)](\text{BF}_4)(4)$ (13), respectively. Compound (11) can also be formed from reaction of (3) with $\text{cis-}[\text{PdCl}_2(\text{CH}_3\text{CN})(2)]$, while reaction of (3) with $\text{Cu}(\text{NO}_3)(2) \cdot 2.5\text{H}_2\text{O}$ generates $[\text{Fe}(\mu\text{-TpmPy})(2)\text{-Cu}(\text{NO}_3)(2)](\text{BF}_4)(2)$ (12), confirming the multidentate ability of the new chelating ligands. The X-ray diffraction analyses of compounds (1), (3), (4), (5), and (9) are also reported.

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