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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

**Source:** Inorganic Chemistry, 49 (17): 7941-7952 SEP 6 2010

**Language:** English

**Document Type:** Article

**KeyWords Plus:** Spin-state crossover; Tris(Pyrazolyl) Methane ligands; Peroxidative oxidation; Molecular materials; Infrared spectra; Angular-Overlap; Iron(II); Palladium(II); Units; Zinc

**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  $\text{VCl}_3$  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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**Publisher:** AMER CHEMICAL SOC

**Publisher Address:** 1155 16TH ST, NW, WASHINGTON, DC 20036 USA

**ISSN:** 0020-1669

**DOI:** 10.1021/ic100966u

**29-char Source Abbrev.:** INORG CHEM

**ISI Document Delivery No.:** 642QT