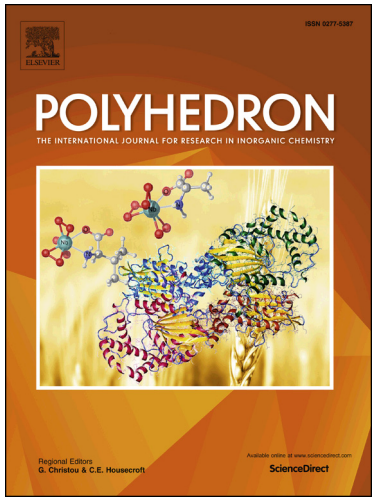

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Water-soluble NNN-pincer complexes of cobalt, nickel and palladium: Solid-state structures and catalytic activity

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Abstract. Neutral NNN-pincer ligand **1** based on a pyridyl core and cyclic amidine pendant arms was synthesized via a straightforward condensation reaction. Its square-planar palladium acetate complex **2** was prepared in methanol and featured a cyclic, hexameric solid-state structure assembled through moderately strong N···H···O hydrogen bonds involving the ligand backbone and the non-coordinated acetate group. The octahedral, diamagnetic Co(III) complex **3** was prepared via in-situ air oxidation of its Co(II) analog. Its solid-state structure confirmed the oxidation state of the metal and revealed the presence of weak bridging and terminal N-H···Cl hydrogen bonds. Paramagnetic nickel complex **4** was prepared in a similar fashion to **1** and was postulated to have a covalent attachment of the acetate moieties to the metal. Derivatives **2** and **3** had excellent water solubility and stability while **4** was sparingly soluble in water. Cyclic voltammetry revealed electrochemically reversible electron transfer steps corresponding to the Co(II)/Co(III) and Ni(II)/Ni(III) redox couples at -0.31 V and 1.04 V *vs.* SHE, respectively. Complex **4** displayed catalytic competency towards the thiolation of iodobenzene with dimethyldisulfide and zinc in DMF. In water, **4** was able to catalyze the Negishi cross-coupling of iodobenzene.

1. Introduction

Following the remarkable success of 2,2':6',6"-terpyridine ligands **I** (terpy or tpy) in coordination chemistry and catalysis (Chart 1),[1,2,3,4] other symmetric, neutral NNN-pincer ligands with pyridine central moieties and unsaturated nitrogen pendant donors have been pursued. An obvious further development was the replacement of the pyridine side arms with other aromatic six-membered nitrogen heterocycles such as pyrazine (**II**),[5,6] pyrimidine (**III**),[5,7] 1,3,5- and 1,2,4-triazine (**IV**[8] and **V**,[9,10,11] respectively) and 1,2,4,5-tetrazine (**VI**).[12,13,14,15] Ligand scaffolds having five-membered nitrogen heterocycles such as imidazole (**VII**),[16] pyrazole (**VIII**),[17,18,19,20,21] as well as 1,2,4- and 1,2,3-triazole (**IX**,[22] **X**,[23] and **XI**,[24,25] respectively) as pendant arms have been employed extensively, with **VIII** proving to be a particularly popular choice.[26,] Ligands **XII**,[27] **XIII**,[28] and **XV**[29] featuring oxazolyl, thiazolyl and thiazolinyl pendant