Copper Fixation to Guaiacyl Lignin Units by Nitrogen Donor Ligands

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Several new copper(II) complexes with guaiacyl lignin models vanillin (HL1) \([\text{Cu(L1)}_2(\text{nia})_2]\) \((1)\) (nia = nicotinamide) or vanillic acid (HL2) \([\text{Cu(L2)}_2(\text{nia})_2]\) \((2)\) \([\text{Cu}_2(\mu-\text{L2})_4(\text{nia})_2]\) \((3)\), and \([\text{Cu(L2)}_2(\text{Hetam})_2]\) \((4)\) (Hetam = ethanolamine) were isolated and characterized. The molecular structure of complex \(1\) reveals bidentate vanillin (HL1) coordination via the methoxy and the deprotonated hydroxy groups. On the other hand, the vanillic acid (HL2) complexes \(2–4\) show a deprotonated carboxylate group with chelating coordination mode in \(2\), bridging in \(3\) and monodentate coordination in \(4\). The mononuclear complexes \(1, 2\) and \(4\) show a distorted trans octahedral coordination sphere with pairs of monodentate and chelating ligands. A replacement of the monodentate nicotinamide ligand in \(2\) with the bidentate ethanolamine ligand in \(4\) changes the coordination mode of the vanillic acid anion from bidentate (complex \(2\)) to monodentate (complex \(4\)). This shift inside the coordination sphere reveals different O–Cu–O Jahn-Teller axes by the vanillic acid anion in \(2\) and ethanolamine in \(4\). Empty channels are present in the crystal structure of the dinuclear complex \(3\), stabilized by hydrogen bonds and \(\pi-\pi\) stacking.

Key words: Copper, Guaiacyl, Lignin, Vanillin, Vanillic Acid, N-Donor Ligands