

Fixation of Copper(II) Ions in Aqueous Solution to Lignin Model Compound Vanillin in an Absence of the Nitrogen Donor Ligands; Structural and EPR Correlation

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Z. Naturforsch. **60b**, 1273 – 1277 (2005); received September 5, 2005

In order to elucidate the interactions of copper with wood, three mononuclear copper(II) coordination compounds with a vanillinate anion, *cis*-[Cu(C₈H₇O₃)₂(H₂O)₂] (**1**), *trans*-[Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O (**2**), and *trans*-[Cu(C₈H₇O₃)₂(H₂O)₂] (**3**), have been characterized. X-ray structure analysis of the *cis* isomer **1** reveals two bidentate vanillinate ions coordinated *via* methoxy (Cu–O1 2.260(2) Å) and deprotonated hydroxy oxygen atoms (Cu–O2 1.909(2) Å), and two water molecules (Cu–O1w 2.087(2) Å) in the octahedral CuO₆ chromophore. Two axes O1–Cu–O1w' in the octahedron have the same length, while the third axis O2–Cu–O2' is shorter. This is in agreement with the room temperature EPR spectrum of **1**, showing two signals (*g*₁₂ 2.302, *g*₃ 2.005), but interestingly, three signals (*g*₁ 2.393, *g*₂ 2.214, *g*₃ 2.010) in the 115 K spectrum were found. The same coordination atoms were found also in the *trans* isomer **2** (Cu–O2 1.950(2), Cu–O1w 1.994(2), Cu–O1 2.334(2) Å), however here, two axes of almost equal length are short (O2–Cu–O2' O1w–Cu–O1w'), while the third axis is longer (O1–Cu–O1'). On the other hand, three (rhombic) signals (*g*₁ 2.289, *g*₂ 2.163, *g*₃ 2.086) in the room temperature EPR spectrum of **2** suggest three different axes in the coordination octahedron. In the EPR spectrum, of the second *trans* complex **3**, a slightly rhombically distorted elongated axial spectrum is found. The 115 K EPR spectra of the two *trans* complexes **2** and **3** do not differ significantly from the features observed at room temperature. These results indicate that there is not always a straightforward correlation between the results of XRD structure analysis and EPR spectroscopy. Nevertheless, both methods can act also complementarily and give a deeper insight into the nature of copper(II) chromophores.

Key words: Copper, EPR, Lignin Model Compound, Vanillin, XRD