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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In order to elucidate the interactions of copper with wood, three mononuclear copper(II) coordination compounds with a vanillinate anion, *cis*-[Cu($C_8H_7O_3$)$_2$(H_2O)$_2$] (**1**), *trans*-[Cu($C_8H_7O_3$)$_2$(H_2O)$_2$]·2H_2O (**2**), and *trans*-[Cu($C_8H_7O_3$)$_2$(H_2O)$_2$] (**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 CuO$_6$ 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

Introduction

Despite the production of a variety of synthetic organic biocides, copper fungicides still predominate in the field of wood preservation [1]. Nevertheless, chromated copper arsenate (CCA), the most important wood preservative in the past century, will probably soon be replaced by the arsenic and chromium free copper based preservatives, due to its toxic side effects. An elucidation of interactions between copper and wood are therefore of importance in order to develop a new generation of effective copper based wood preservatives.

Preventing the leaching of the copper formulations from the protected wood is the main problem for this type of preservatives. Therefore, most investigations were focused on copper to wood fixation interactions.

For this purpose a fixation agent, such as chromium [2] or amine additive [3, 4] was used. These studies have indicated that copper-lignin and copper-hemicelluloses reactions in wood are the key processes. Unfortunately, the nature of copper-lignin interactions in the absence of amines, ammonia or chromium is still not completely understood.

Crystal structure determination is one of the most successful methods to describe the surrounding of selected atoms, but single crystals of the substrates are not always readily available. Biological systems (*e.g.* lignin) are especially delicate, and therefore certain compromises are often necessary. For these reasons, model systems are often used for the synthesis and complex investigation [5]. EPR spectroscopy is also well suited to study paramagnetic species (*e.g.* Cu(II)) as powders or in solution [6].

Table 1. Crystal data and data collection summary for **1** and **2**.

Compound	**1** 293 K	**2** 293 K	**2** 150 K
Emp. formula	$C_{16}H_{18}CuO_8$	$C_{16}H_{22}CuO_{10}$	$C_{16}H_{22}CuO_{10}$
Formula weight	401.84	437.88	437.88
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2/a$	$P2/a$
a [Å]	22.0422(3)	6.6963(5)	6.5434(1)
b [Å]	10.6891(2)	12.8247(8)	12.8853(3)
c [Å]	7.6668(1)	10.9532(13)	10.8852(3)
β [°]	104.8463(8)	100.446(3)	98.6110(10)
V (Å^3)	1746.08(5)	925.05(14)	907.43(4)
Z	4	2	2
D_x [g/cm^3]	1.529	1.572	1.603
μ [mm^{-1}]	1.291	1.233	1.257
Crystal colour	orange	yellow-green	yellow-green
Crystal shape	prism	prism	prism
Crystal size [mm]	0.20 × 0.15 × 0.12	0.35 × 0.32 × 0.25	0.20 × 0.16 × 0.15
θ max [°]	27.6	27.9	29.1
Refined params	126	143	157
Integr. reflexions	3797	6917	4312
Independent data	1985	2192	2422
Observed data [$I > 2\sigma(I)$]	1870	1984	2248
R (observed)	0.0256	0.0287	0.0239
wR (observed)	0.0723	0.0830	0.0654
R (all data)	0.0275	0.0317	0.0265
wR (all data)	0.0744	0.0861	0.0676
$\Delta\rho_{min,max}$ [eÅ^{-3}]	−0.282;0.328	−0.392;0.256	−0.423;0.405

The main goal of this work has been an EPR and structural investigation of different modifications of Cu(II) vanillinate (4-formyl-2-methoxyphenolate-*O:O'*; a lignin model compound) complexes with the CuO$_6$ chromophore [7]. These complexes were isolated from aqueous solutions, without an addition of any other stabilizing agent, and confirm that even in the absence of nitrogen or chromium; copper ions are able to form complexes with the lignin model compound. For these complexes, a strong correlation and complementarity of the results of the two methods (XRD, EPR) were noticed.

Results and Discussion

The structure of cis-di(4-formyl-2-methoxyphenolate-O:O')diaquacopper(II) (1)

XRD analysis of the orange compound *cis*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] (**1**) reveals two bidentate vanillinate anions and two water molecules in *cis* octahedral orientation around the central copper(II) cation, all symmetrically related by the 2-fold crystallographic axis (Fig. 1, Table 1). The anions are coordinated through the methoxy (Cu–O1 2.260(2) Å) and depro-
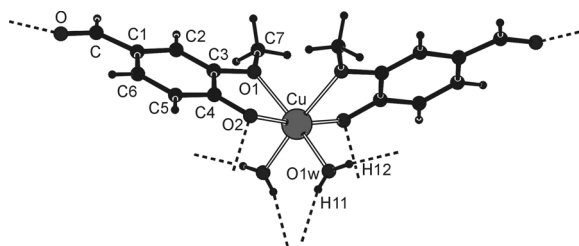
Fig. 1. The coordination sphere and the H-bonding in *cis*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] (**1**).
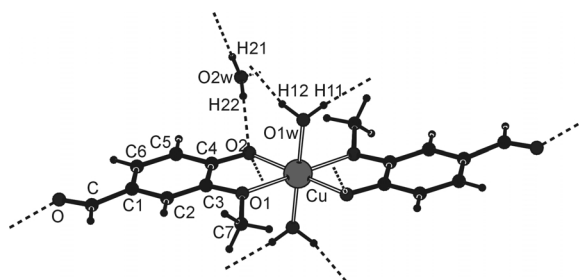
Fig. 2. The coordination sphere and the H-bonding in *trans*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O (**2**).

tonated hydroxy (Cu–O2 1.909(2) Å) oxygen atoms, as noticed for all complexes with this ligand [5, 7 – 11]. The water molecules (Cu–O1w 2.087(2) Å) and the methoxy oxygen atoms are in *trans* position, thus forming two non-symmetrical axes O1–Cu–O1w' of the same length, while the third axis with two hydroxy oxygen atoms O2–Cu–O2' is shorter. The distortion of the coordination octahedron is significant, notable also from their non-linear O1–Cu–O1w and O2–Cu–O2 (*x, y, z*) axes (Table 2). The water molecules allow for hydrogen bonding with the hydroxy and aldehyde groups (O1w–H11···O2 2.759(2) Å, O1w–H12···O 2.760(2) Å) to form an intermolecular network.

The structure of trans-di(4-formyl-2-methoxyphenolate-O:O')diaquacopper(II) dihydrate (2)

The coordinated groups in the structure of yellow-green [Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] · 2H$_2$O **2** are the same as in **1**, however they are *trans* oriented (Fig. 2). Two water molecules (Cu–O1w 1.994(2) Å) and two hydroxy oxygen atoms (Cu–O2 1.950(1) Å) are describing the basal plane of the octahedron, while the methoxy oxygen atoms are forming the elongated Jahn-Teller axis (Cu–O1 2.334(2) Å). The stabilization of the structure *via* H-bonding is similar as in **1**, with the key role of water molcules. On the other hand, the distortion of the CuO$_6$ octahedron is not so distinct, as seen in lin-

1	Cu–O2	1.9086(11)	O2–Cu–O1	77.31(4)	O1–Cu–O1	91.09(7)
	Cu–O1w	2.0869(13)	O1w–Cu–O1	88.74(6)	O1w–Cu–O1	169.97(5)
	Cu–O1	2.2603(12)	O1w–Cu–O1w	93.15(9)	O2–Cu–O1	95.00(5)
	O2–Cu–O2	169.14(7)	O2–Cu–O1w	94.75(6)	O2–Cu–O1w	92.71(6)
2	Cu–O2	1.9498(10)	O2–Cu–O2	180	O1w–Cu–O1w	180
	Cu–O1w	1.9940(13)	O2–Cu–O1w	88.97(5)	O2–Cu–O1	76.18(4)
	Cu–O1	2.3336(10)	O2–Cu–O1w	91.03(5)	O2–Cu–O1	103.82(4)
	O1–Cu–O1	180	O1w–Cu–O1	89.41(5)	O1w–Cu–O1	90.59(5)

Table 2. Selected bond distances (Å) and angles (°) in the structures of **1** and **2** (293 K).

Symmetry codes: [i] $-x, 1-y, 1-z$; [ii] $1/2+x, 1/2-y, 1/2+z$; [iii] $x, y, -1+z$; [iv] $1/2+x, 1/2-y, z$;

Hydrogen-bonding geometry					
D–H···A	D···A	D–H···A	D–H···A	D···A	D–H···A
1 O1w–H11···O2[i]	2.759(2)	166(3)	O1w–H12···O[ii]	2.760(2)	168(2)
2 O1w–H11···O[iii]	2.735(2)	171(3)	O1w–H12···O2w[iv]	2.684(2)	165(2)
O2w–H21···O2[iv]	3.069(2)	169(2)	O2w–H22···O2	2.820(2)	171(3)

Table 3. Selected EPR parameters of the vanillinate complexes **1**, **2** and **3** with the CuO_6 chromophore. The estimated errors are $H \pm 0.5$ mT, $g \pm 0.003$.

	— **1** —		— **2** —		— **3** —	
	298 K	115 K	298 K	115 K	298 K	115 K
H_1 (mT)		286.0	299.1	298.7	286.5	286.6
H_2 (mT)	297.4	309.2	316.6	315.2	327.0	327.8
H_3 (mT)	341.5	340.6	328.2	328.5	335.0	334.5
g_1		2.393	2.289	2.291	2.390	2.389
g_2	2.302	2.214	2.163	2.171	2.094	2.088
g_3	2.005	2.010	2.086	2.083	2.044	2.047

ear O–Cu–O axes, although these axes are not orthogonal (Table 2). This is obvious from the O(methoxy)–Cu–O(hydroxy) angle $\sim 76°$ (298 K and 115 K data), representing a rigid chelate vanillinate ligand.

The structure of **2**, solved from the 150 K data set, shows only small differences compared to the room temperature XRD analysis (Table 1). This unambiguously proves that the two *trans* complexes **2** and the previously reported **4** (= *trans*-[Cu($C_8H_7O_3$)$_2$(H_2O)$_2$]·$2H_2O$ [7]) are two different polymorphs, since significant structural differences were found. The compounds **1**, **2** and **3** (= [Cu($C_8H_7O_3$)$_2$(H_2O)$_2$], partly dehydrated **4**) are air stable, while **4** is not. The main reason for a decomposition **4** → **3** outside the mother liquor, the removal of the non-coordinated water molecules (O2w) in **4**, is probably due to weak H-bonding of O2w to the coordinated ligands. In the air-stable complex **2**, three such connections are present (to O1w, O2 and O2'; Table 2), but only one in the air unstable complex **4** (to O1w), since another two O2w H-bonds are mutually connecting both non-coordinated water molecules.

EPR

Spectra of the vanillinate complexes **1**–**3** were measured at different temperatures (298 K, 115 K; Fig. 3, 4). The room temperature spectrum of **1** shows an "inverse" axial pattern with $g_\perp (g_1 \sim g_2) > g_\parallel (g_3)$, usually representing a compressed octahedral geometry of the copper(II) coordination sphere suggesting a $\{d_{z^2}\}^1$ electronic ground state [12]. These observations are in agreement with the structural data, where inside a distorted octahedron CuO_6, two long and one shorter O–Cu–O axes were found. Interestingly, the low temperature spectrum changes to rhombic symmetry with $g_1 > g_2 > g_3$ (Fig. 3), for which the $\{d_{x^2-y^2}\}^1$ electronic ground state is more probable.

The room temperature spectrum of the *trans* isomer **2** shows three signals H_1 (299 mT), H_2 (317 mT), H_3 (328 mT) representing a rhombic distortion of the CuO_6 octahedron (Fig. 4). This deviates from the structural data, where only a small rhombic distortion (two O–Cu–O axes are similar and short, while the third is significantly longer; $\{d_{x^2-y^2}\}^1$ electronic ground state) is observed. Possible reason for the rhombic-axial discrepancy of the EPR-structural analysis of **2** are the distortions in the coordination octahedron noticed from non-orthogonal coordination axes and/or different coordinating oxygen atoms.

The slightly rhombically distorted spectrum $(g_\parallel (g_1) \gg g_\perp (g_2 > g_3))$ of [Cu($C_8H_7O_3$)$_2$(H_2O)$_2$] **3** (Fig. 4, Table 3) is in agreement with the structure of *trans*-[Cu($C_8H_7O_3$)$_2$(H_2O)$_2$]·$2H_2O$ **4** (undecayed **3**). Although a close correlation between **3** and **4** is not fully appropriate, at least a very similar geometry around the copper(II) ion might be expected (*trans*). On the other hand, a partial dehydration of **4**, due to a removal of two solvated water molecules leading to **3**, significantly changes the H-bonding network. This decomposition possibly allows for a more regular, elongated octahedral geometry of the CuO_6 chromophore, suggested by the EPR spectra of **3**. Lowering of the temperature to 115 K for **2** and **3** does not significantly change the shape of the signals as noticed for the *cis* isomer **1**.
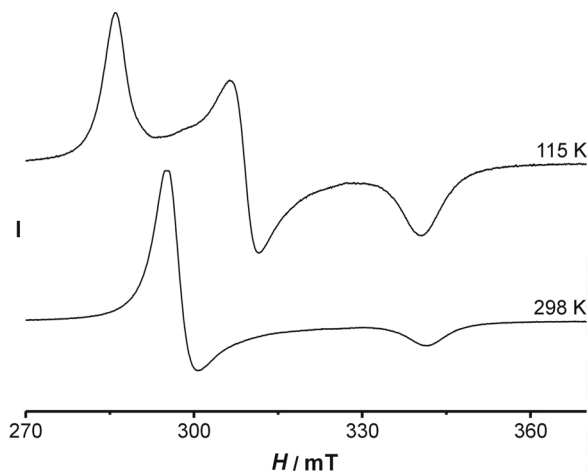
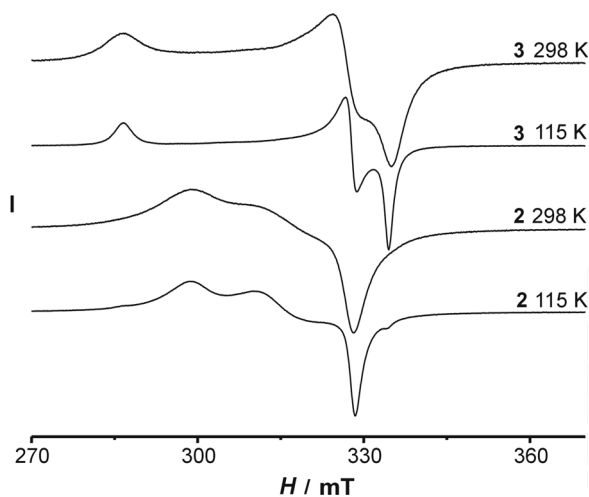Fig. 3. Temperature dependence of the EPR spectra of *cis*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] (**1**).

Fig. 4. The EPR spectra of the compounds **2** and **3** measured at two temperatures. The weak intensity signals at 285 and 335 mT in the 115 K spectrum of **2** may be explained by the presence of a small amount of **3** in the sample of **2**.

Conclusions

X-ray structure analysis of compounds **1** and **2** reveals *cis* and *trans* configurations of the mononuclear octahedron [Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$], where the chelate vanillinate anions and water molecules form the CuO$_6$ chromophores. Based on the different EPR spectra of **1** at different temperatures, a significant difference between the coordination spheres at 298 K and at 115 K is proposed, suggesting that the $\{d_{z^2}\}^1$ electronic ground state is uncertain, although the room temperature XRD and EPR data seem to confirm this. No similar change of coordination sphere with temperature was observed

for the *trans* complex **2**. At the first view different results of XRD and EPR for **2**, regarding the axial coordination bond distances and the rhombic EPR signals, may be explained by a non-orthogonality of the coordination axes, determined by different types of oxygen donor groups in three coordination axes, rigid vanillinate ions and water induced H-bonds. Due to the changes with temperature observed in the EPR spectra of the *cis* compound **1** and the coordination geometry / EPR discrepancy noticed for the *trans* compound **2**, it may be concluded that a description of the coordination sphere geometry from the EPR results and the determination of the electronic ground state by the XRD analysis may not always be unambigous. For more certain determination of these parameters, both methods may give a better insight, complemented by a comparison with the relevant data of related complexes.

Experimental Section

Synthesis

All starting compounds and solvents were used as purchased, without any further purification. *cis*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] **1**, *trans*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] · 2H$_2$O **2** and *trans*-[Cu(C$_8$H$_7$O$_3$)$_2$(H$_2$O)$_2$] **3** were synthesized as described previously [7].

X-ray crystallography

The crystal data for the vanillin complexes **1** (293 K) and **2** (293, 150 K) were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods [13], and the figures were drawn using PLATON [14]. Refinements were based on F^2 values and done by full-matrix least-squares [15]. All non-H atoms were treated anisotropically. Hydrogen atoms were located from a ΔF synthesis and included in the refinement at calculated positions and with isotropic displacement parameters of 1.2 times the U_{eq} value of their respective attached heavy atom, 1.5 times for the methyl hydrogens.

Details of the crystal data, data collection and refinement parameters for **1** and **2** are listed in Table 1. The selected bond lengths and angles and hydrogen bonds parameters for **1** and **2** (293 K) are listed in Table 2. All atoms parameters and other crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers 281654, 281655, 281656. These data can be obtained, free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html.

EPR

Spectra of the powdered samples were recorded by a Bruker ESP-300 spectrometer, operating at X-band (9.59 GHz) at 298 and 115 K. The g values were calculated directly from the signal positions $H(h\nu = g\beta_{\mathrm{e}}H)$.

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