

Copper(II) Complexes With Lignin Model Compound Vanillin

Bojan Kozlevčar,* Branka Mušič, Nina Lah, Ivan Leban, and Primož Šegedin

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, P.O. Box 537, SI 1001 Ljubljana, Slovenia

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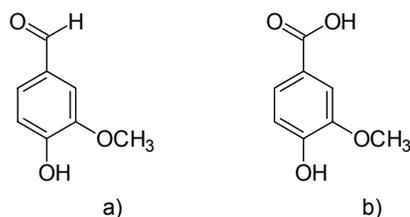
Abstract

Three copper(II) coordination compounds with vanillinate ion *trans*-[Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O **1**, [Cu(C₈H₇O₃)₂(H₂O)₂] **2** and [Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O **3** were synthesized and characterized. The structure analysis of air-unstable complex **1** reveals *trans* arrangement of two vanillinate ligands around copper(II) ion, coordinated via methoxy (Cu–O3 2.3266(14) Å) and deprotonated hydroxy group (Cu–O4 1.9383(13) Å). In the octahedral coordination sphere, two water molecules are also present (Cu–Ow1 2.0113(15) Å). Copper(II) ions in air-stable vanillinate complexes **2**, **3** and **1a** ([Cu(C₈H₇O₃)₂(H₂O)₂]; partially decomposed **1**), that show very similar vibrational and electronic spectra, represent isolated paramagnetic centers ($\mu_{\text{eff}} > 1.73$ BM). The most significant differences in IR spectra are above 3000 cm⁻¹ for **1a** (partial decomposition of **1** and different H-bonding), and in electronic spectra for non-typical orange coloured **2** with respect to yellow-green **1a** and **3**.

Key words: copper, vanillin, lignin, model, structure

Introduction

Application of copper compounds in wood protection, due to their fungicidal activity, is known for a long time.¹ Although such protection is very commonly used, the mode of copper action and its way of binding to wood are still not known accurately.² Possible binding site for copper is lignin, due to several different oxygen atoms present in its structure and its high abundance in wood. Lignin is composed of several different subunits of phenylpropane derivatives, mutually connected in many ways. Exact structure is not known, since all attempts of isolation revealed some changes in the basic structure. In this aspect, the lignin model compounds and their copper complexes seem to be a suitable basis for research of copper to wood interactions.³ So far, a few vanillinate (= 4-formyl-2-methoxyphenolate) copper complexes with additional nitrogen ligands²⁻⁶ and one vanillic acid anion (= 4-hydroxy-3-methoxybenzoate)⁷ copper complex were described (Scheme 1). In this paper, several new copper(II) complexes with lignin model compound vanillin are presented and described by structural, magnetic and spectroscopic parameters.



Scheme 1. Lignin model compounds vanillin (a) and vanillic acid (b).

Results and discussion

Description of the crystal structure of *trans*-diaquabis(vanillinato(*O,O'*))copper(II) dihydrate **1**. The copper(II) ion in [Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O (**1**) is surrounded by two didentate vanillinate ions and two water molecules in *trans* orientation (Figure 1). The basal plane in an elongated octahedral chromophore CuO₆ is composed of two deprotonated hydroxy groups (Cu–O4 1.9383(13) Å) and two water molecules (Cu–Ow1 2.0113(15) Å). Elongated Jahn-Teller axis in the octahedron is described by two methoxy oxygen atoms (Cu–O3 2.3266(14) Å). Significant rhombic distortion of an octahedron is probably due to rigidity of the vanillinate ion (O4–Cu–O3 76.43(5)°) and several hydrogen bonds present in the structure (Table 1). Two additional water molecules are more distant from copper ion. Each of them is hydrogen bonded to one coordinated water molecule (Ow2–H21···Ow1 2.971(3) Å) and by a pair of H-bonds (Ow2–H22···Ow2ⁱⁱⁱ 2.812(3) Å) to the neighbouring non-coordinated water molecule (Figure 1). The coordinated water molecule is connected with much stronger intermolecular hydrogen bonds also to the aldehyde group (Ow1–H12···O11ⁱ 2.686(2) Å) and to the hydroxy group of the adjacent mononuclear unit (Ow1–H11···O4ⁱⁱ 2.650(2) Å). A projection of the mononuclear units in **1** reveals parallel layers (Figure 2). The C–O distances are similar as found in the structure of free vanillin.⁸ X-ray diffraction data of **1** were collected at 150 K, due to instability of the compound outside the solution at room temperature. As confirmed by elemental analysis, the diversity between

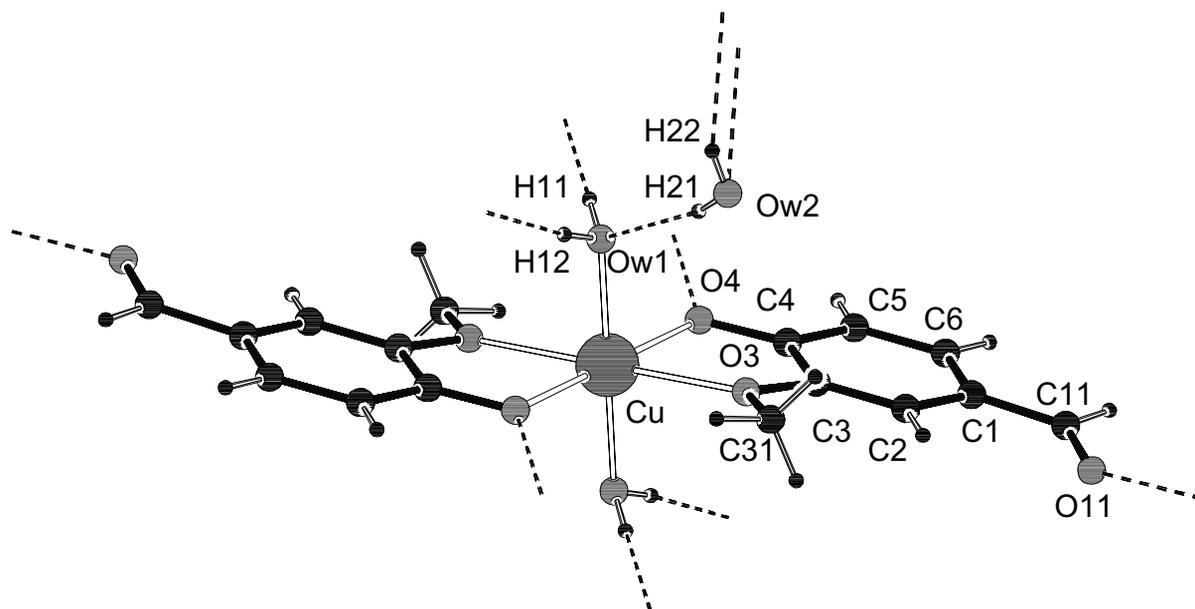


Figure 1. The hydrogen-bonding pattern in the structure of **1**.

Table 1. Selected bond distances (Å) and angles (°) in the structure of **1**.

Cu–O4	1.9383(13)	O4–Cu–Ow1	90.04(6)	
Cu–Ow1	2.0113(15)	O4–Cu–O3	76.43(5)	
Cu–O3	2.3266(14)	Ow1–Cu–O3	89.47(6)	
Hydrogen-bonding geometry (Å,°)				
D–H···A	D–H	H···A	D···A	D–H···A
Ow2–H21···Ow1	0.785(32)	2.197(33)	2.971(2)	169(3)
Ow1–H12···O11 ⁱ	0.787(29)	1.902(29)	2.686(2)	174(3)
Ow1–H11···O4 ⁱⁱ	0.809(31)	1.841(31)	2.650(2)	179(3)
Ow2–H22···Ow2 ⁱⁱⁱ	0.686(56)	2.209(53)	2.813(3)	148(6)
Symmetry code: (i) $-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $1-x, 1-y, 2-z$;				

the XRD powder data, obtained at room temperature, and calculated via the structural data,^{9,10} can be ascribed to some structural rearrangements, occurring after release of two uncoordinated water molecules. This partial decomposition of **1** in air yields **1a**.

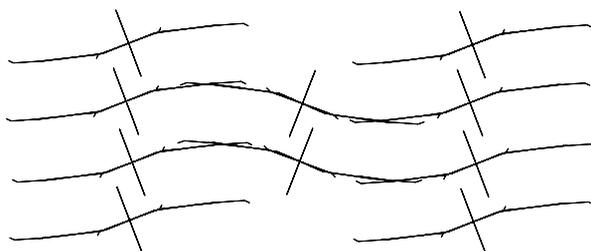


Figure 2. A parallel wave-like orientation of the mononuclear units in the structure of **1**. Hydrogen atoms are omitted for clarity.

Another two vanillinate complexes, orange $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2]$ **2** and green $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ **3** (XRD powder pattern is different than for **1a** or calculated for **1**)^{9,10} are stable in air. Due to isolated paramagnetic Cu(II) centers for three vanillin compounds **1a**, **2**, **3** ($\mu_{\text{eff}} \sim 1.9$ BM), mononuclear coordination sphere is proposed for them. The electronic spectra of almost identically coloured solutions, obtained by dissolution of differently coloured solids **1a**, **2**, **3** in methanol or acetonitrile, indicate that the coordinated species in all three compounds are rearranged into the same one (Figure 3). In the mull spectrum of **2**, very weak $d-d$ signal at 810 nm and much stronger shoulder at 500 nm (next to LMCT and $\pi-\pi$ transitions in the UV region)¹¹ were observed, visible also as copper(II) non-typical orange colour. Both signals of similar intensity ratio were also found in the spectra of yellow-green **1a** and **3**, but at lower energies (470(sh), 675 nm **1a**; 485(sh), 695 nm **3**).

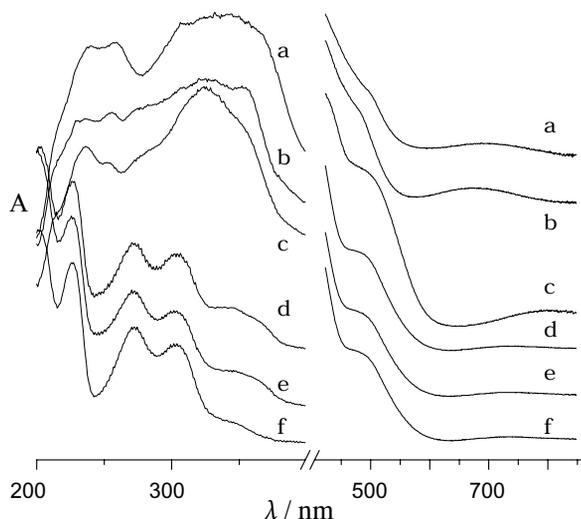


Figure 3. The electronic spectra of **1a** (b,e), **2** (c,f) and **3** (a,d) as nujol suspensions (a,b,c) and acetonitrile solutions (d,e,f). Due to very low intensity of the *d*–*d* transition signals, higher concentration of the solutions (200–400 nm, 3.0×10^{-6} M; 400–860 nm, 3.0×10^{-4} M) and higher density of the suspensions were used for the visible light region spectra.

Air-stable complexes **2** and **3** show similar broad IR signal in the $3400\text{--}3100\text{ cm}^{-1}$ region, while for **1a** a sharp band at 3445 cm^{-1} was observed. The origin of these bands are probably in water molecules,¹² since the hydroxy group was found deprotonated in **1**, **2**, and **3**. Strong similarities in the spectra of **1a**, **2**, **3** and free vanillin were found in $1700\text{--}1400\text{ cm}^{-1}$ region, where also the $\nu(\text{C}=\text{O})$ aldehyde band at 1650 cm^{-1} was found, indicating non-coordination via the aldehyde group.

To correlate three very similar formulations **1**–**3** more unambiguously, in the continuation of this work we will try to obtain single crystals of the compounds **2** and **3** for structural characterization of the complexes, together with the EPR characterization of all three species.

Conclusions

Three copper(II) complexes with lignin model compound vanillin were synthesized. The structure of $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ **1** reveals didentate coordination of vanillinate via methoxy oxygen atom and deprotonated hydroxy oxygen atom in mononuclear species, as observed in other copper vanillinate complexes,^{2–6} confirming the bonding role of copper to lignin.¹³

In all Cu-vanillinate complexes found in the literature, additional nitrogen donor ligands are also present. This is the most significant difference with regard to compounds **1**–**3** described here, where only oxygen donor ligands are found. Since these complexes

were synthesized from nitrogen ligand free aqueous solutions, the nitrogen ligands are not necessary for copper coordination at lignin models.

Experimental

Materials: All starting compounds and solvents were used as purchased, without any further purification.

X-ray crystallography: The crystal data were collected on Kappa CCD Nonius diffractometer with graphite monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods,¹⁴ and the figures were drawn using PLATON.^{9,10} Refinements were based on F^2 values and done by full-matrix least-squares¹⁵ with all non-H atoms anisotropic. Hydrogen atoms were located from a ΔF synthesis and included in the refinement at calculated positions and with the isotropic displacement parameters of 1.2 times the U_{eq} value of their respective attached heavy atom, 1.5 times for the methyl hydrogens. Crystal data: $\text{C}_{16}\text{H}_{22}\text{CuO}_{10}$ **1**, $F_r = 437.89$, monoclinic, $a = 4.90380(10)$, $b = 19.6635(5)$, $c = 9.4786(2)$ Å, $\beta = 92.0300(10)^\circ$, $V = 913.41(4)$ Å³, $T = 293(2)$ K, space group $P2_1/c$ (No. 14). $Z = 4$, $\mu(\text{Mo } K\alpha) = 1.249\text{ mm}^{-1}$, 3814 reflections measured, 1818 unique ($R_{\text{int}} = 0.0326$) which were used in all calculations. The final $wR(F^2)$ was 0.0395 (all data).

Physical measurements: Metal analysis was carried out electrogravimetrically with Pt electrodes. C,H analysis was performed with a Perkin Elmer, Elemental Analyzer 2400 CHN. Interplanar spacings were obtained by the Guinier camera (Huber), Cu $K\alpha$ radiation. The magnetic susceptibility of the substances was determined at room temperature by powdered samples with a Sherwood Scientific MSB-1 balance. Diamagnetic corrections were estimated from Pascal's constants.¹⁶ Infrared spectra were measured on mineral oil mulls, using a Perkin-Elmer FT-IR 1720X spectrometer. Electronic spectra were recorded as nujol mulls with a Perkin-Elmer UV/VIS/NIR spectrometer Lambda 19.

Synthesis: *trans*- $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**); $[\text{Cu}(\text{C}_8\text{H}_7\text{O}_3)_2(\text{H}_2\text{O})_2]$ (**1a**): 0.320 g of $[\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ was dissolved in 10.0 mL of water while stirring and slow heating. The solution was added to 0.244 g of vanillin. Yellow-green needle-like crystals of **1** were filtered off after three days and dried in air for a day, when the crystals dimed (**1** change to **1a**). The crystal structure was obtained from undecayed single crystal of **1**, frozen immediately after removing from the mother liquid, while for the other characterization methods, the dried sample of **1a** was used. Yield 30%. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{CuO}_8$ (**1a**): C 47.8, H 4.51, Cu 15.8. Found: C 47.2, H 4.34, Cu 15.7. UV-Vis (CH_3CN)

λ_{\max} , 225, 270, 300, 350(sh), 490(sh), 720 nm. UV-Vis (mull) λ_{\max} , 235, 255, 325, 400(sh), 470(sh), 675 nm. IR (mull) $\bar{\nu}$ 3445, 1658, 1582, 1557, 1494, 1468, 1432, 1307 cm^{-1} . μ_{eff} (RT) 1.87 BM.

[Cu(C₈H₇O₃)₂(H₂O)₂] (2): [Cu₂(O₂CCH₃)₄(H₂O)₂] (0.160 g) was dissolved at room temperature in 10.0 mL of acidified water (one drop of glacial acetic acid). The solution and solid vanillin (0.244 g) were slowly heated in two separated flasks. When vanillin had melted, the acetate solution was put over melted vanillin that turned red and dissolved in ~5 seconds. Orange crystals of **2** were filtered off next day and dried in air for a day. If the temperature is not high enough, the dissolution might take longer, while too high temperature (over 100 °C) partly change vanillin (black particles), both leading in partial precipitation of compounds **1** and **2** (after two days mostly **1** was present). Yield 20%. Anal. Calcd for C₁₆H₁₈CuO₈: C 47.8, H 4.51, Cu 15.8. Found: C 47.5, H 4.33, Cu 15.7. UV-Vis (CH₃CN) λ_{\max} , 225, 270, 300, 350(sh), 490(sh), 720 nm. UV-Vis (mull) λ_{\max} , 235, 325, 410(sh), 500(sh), 810 nm. IR (mull) $\bar{\nu}$ 3400–3100, 1648, 1579, 1550, 1503, 1463, 1337 cm^{-1} . μ_{eff} (RT) 1.91 BM.

[Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O (3): Similar procedure as for **1** was applied. The starting compounds [Cu₂(O₂CCH₃)₄(H₂O)₂] (0.320 g) and vanillin (0.244 g) were added to water without further heating and stirring. Soon, yellow-green compound **1** was observed and after three days also green cube-like crystals of **3**. After two weeks only compound **3** was present, filtered off and dried for a day in air. Yield 35%. Anal. Calcd for C₁₆H₂₂CuO₁₀: C 43.9, H 5.06, Cu 14.5 %. Found: C 43.6, H 4.87, Cu 14.9. UV-Vis (CH₃CN) λ_{\max} , 225, 270, 300, 350(sh), 490(sh), 720 nm. UV-Vis (mull) λ_{\max} , 235, 255, 345, 410(sh), 485(sh), 695 nm. IR (mull) $\bar{\nu}$ 3600–3100, 1658, 1583, 1551, 1503, 1454, 1306 cm^{-1} . μ_{eff} (RT) 1.89 BM.

CCDC-240144 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax:

(internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Povzetek

Tri bakrove(II) koordinacijske spojine z vanilinatnim ionom *trans*-[Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O **1**, [Cu(C₈H₇O₃)₂(H₂O)₂] **2** in [Cu(C₈H₇O₃)₂(H₂O)₂]·2H₂O **3** so bile sintetizirane in karakterizirane. Strukturna analiza na zraku neobstoje spojine **1** pokaže *trans* usmeritev dveh vanilinatnih ligandov okoli bakrovega(II) iona, koordinirana preko metoksi (Cu–O3 2.3266(14) Å) in deprotonirane hidroksilne skupine (Cu–O4 1.9383(13) Å). V oktaedrični koordinacijski sferi sta prisotni tudi dve molekuli vode (Cu–Ow1 2.0113(15) Å). V spojinah **2**, **3** in **1a** ([Cu(C₈H₇O₃)₂(H₂O)₂]; **1** po delnem razpadu), ki so na zraku obstojne in imajo podobne vibracijske in elektronske spektre, predstavljajo bakrovi(II) ioni izolirana paramagnetna jedra ($\mu_{\text{eff}} > 1.73$ BM), obdana s podobnimi koordinacijskimi sferami. V IR spektrih so opazne razlike v območju nad 3000 cm^{-1} pri **1a** (delno razpadla **1** ter spremenjene vodikove vezi), in v elektronskem spektru spojine **2**, ki je, v primerjavi z rumeno zeleno obarvanima spojinama **1a** in **3**, obarvana netipično oranžno.