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Complexes with lignin model compound vanillic acid. Two different carboxylate ligands in the same dinuclear tetracarboxylate complex [Cu₂(C₈H₇O₄)₂(O₂CCH₃)₂(CH₃OH)₂]

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Abstract

Two copper(II) coordination compounds with vanillic acid $C_8H_8O_4$ (1), namely $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ (2) and $[Cu_2(C_8H_7O_4)_4(H_2O)_2]$ (3), were synthesized and characterized. Single crystals of 1–3 were obtained and their crystal structures determined. The structure of **2** shows dinuclear cage structure of copper acetate hydrate type, however with two different carboxylates, acetates and vanillic acid anions, respectively. Both bridging anions are in pairs in *trans* orientation. Methanol molecules are apically coordinated (Cu–O7 2.160(2) Å), fulfilling square-pyramidal coordination sphere around both copper ions. The compound **2** decomposes outside mother-liquid (yielding $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(H_2O)_2]$ (**2a**)) with the removal of methanol, but without significant change of the dicopper tetracarboxylate cage structure, as noticed by μ_{eff} 1.48 BM for **2a**. Similar was found also in the X-band EPR spectra with three signals H_{z1} , $H_{\perp 2}$ and H_{z2} in the region from 0 to 600 mT. The structure of free vanillic acid **1** is composed of dimeric units of two molecules, connected by two parallel hydrogen bonds between carboxylate group of each other (O1–H…O2 2.642(3) Å), while the structure of **3** is of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ type. Interestingly, an additional signal in the EPR spectra of **3** is found at 80 mT ($H_{\perp 1}$) at 298 and at 116 K, next to three signals H_{z1} , $H_{\perp 2}$ and H_{z2} .

Keywords: Copper; Vanillic acid; Dinuclear; Heterocarboxylate; $H_{\perp 1}$; EPR

1. Introduction

Copper fungicides play a very important role in the wood protection [1]. To investigate copper to wood interactions, copper complexes with lignin model compounds (Scheme 1) were prepared. So far, several vanillin complexes [2–7] and one vanillic acid coordination compound [8] have been presented. It appeared that Cu–vanillin compounds might be obtained either with or without the presence of a nitrogen donor ligand. The main analogy in Cu–vanillin complexes is in the didentate (deprotonated hydroxy and methoxy group) coordination of vanillin, yielding *trans* or *cis* mononuclear species. The didentate coordination was observed also in the copper complex with very similar lignin model compound vanillic acid $[Cu_2(C_8H_7O_4)_4(H_2O)_2]$ [8], however the structure is dinuclear and the carboxylate group serves as a bridge as observed in $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ type of complexes. Vast majority of the described dinuclear *paddle-wheel* complexes is with four identical carboxylates for all four bridges in a dinuclear unit, and only rare examples of different carboxylate anions in one dinuclear unit are known [9–12]. A more detailed description of copper– vanillic acid system of compounds might help in better evaluation of the coordination role of the oxygen groups

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Scheme 1. Two lignin model compounds vanillin $(C_8H_8O_3)$ and vanillic acid $(C_8H_8O_4)$ (1).

on benzene ring, present in simple lignin model compounds (Scheme 1).

A dinuclear heterocarboxylate copper *paddle-wheel* compound with vanillic and acetic acid anions $[Cu_2-(C_8-H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ was synthesized and characterized. It was compared to a related homocarboxylate complex $[Cu_2(C_8H_7O_4)_4(H_2O)_2]$.

2. Experimental

2.1. Synthesis

All starting compounds and solvents were used as purchased, without any further purification. The single crystals of vanillic acid ($C_8H_8O_4$) (1), suitable for X-ray analysis, were obtained by a recrystallization from ethylacetate.

 $[Cu_{2}(C_{8}H_{7}O_{4})_{2}(O_{2}CCH_{3})_{2}(CH_{3}OH)_{2}](2), [Cu_{2}(C_{8}H_{7}O_{4})_{2}](2), [Cu_{2$ $(O_2CCH_3)_2(H_2O)_2$ (2a): Vanillic acid (0.061 g; 0.36 mmol) was added to a hot methanol solution (10.0 mL) of [Cu₂- $(O_2CCH_3)_4(H_2O)_2$ (0.040 g; 0.10 mmol). Next day, a dark green precipitate of 2 was filtered off, washed three times with methanol and then left for a day on air, yielding 2a. Yield 80%. Anal. Calc. for C₂₀H₂₄Cu₂O₁₄ (2a): C, 39.0; H, 3.93; Cu, 20.7. Found: C, 38.9; H, 4.17; Cu, 20.7%. UV–Vis–NIR (DMSO) λ_{max} , 260, 290, 450(sh), 720 nm; (mull) λ_{max} , 230, 265, 290, 360(sh), 695 nm. IR, 3420 v(O-H), 1623 v_{as}(CO₂), 1602, 1591 v_{as}(CO₂), 1518, 1417 $v_{\rm s}({\rm CO}_2)$, 1398 $v_{\rm s}({\rm CO}_2)$, 780 cm⁻¹. EPR (298 K), $g_{\perp} = 2.09$, $g_{\parallel} = 2.36, D = 0.329 \text{ cm}^{-1}, 2J = 278 \text{ cm}^{-1}; (116 \text{ K}), g_{\perp} =$ 2.07, $g_{\parallel} = 2.36$, $A_{z1} = 5.6 \text{ mT}$, $D = 0.326 \text{ cm}^{-1}$, 2J = 237cm⁻¹. μ_{eff} (298 K), 1.48 BM. The single crystals of **2**, suitable for X-ray analysis, were obtained by a similar procedure, but at lower concentration of the starting compounds. The crystals were frozen immediately after removal from mother-liquid, to prevent their decomposition due to evaporation of methanol and its probable replacement with water molecules (elemental analysis, IR).

 $[Cu_2(C_8H_7O_4)_4(H_2O)_2]$ (3): The starting compounds and a procedure was different as already described [8]. 0.160 g (0.40 mmol) of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ was dissolved in 10 mL of hot water. The solution was added to 0.244 g (1.45 mmol) of vanillic acid. Green crystallites were filtered off next day and then dried one day in a desiccator. Yield 80%. *Anal.* Calc. for C₃₂H₃₂Cu₂O₁₈ (**3**): C, 46.2; H, 3.88; Cu, 15.3. Found: C, 46.0; H, 4.18; Cu, 15.2. UV–Vis–NIR (DMSO) λ_{max} , 260, 290, 450(sh), 720 nm; (mull) λ_{max} , 230, 265, 300, 380(sh), 690 nm. IR, 3456 v(O–H), 1615, 1596, 1570 v_{as} (CO₂), 1518, 1455, 1426 v_{s} (CO₂), 1394 v_{s} (CO₂), 774 cm⁻¹. EPR (298 K), $g_{x} = 2.05$, $g_{y} = 2.06$, $g_{z} = 2.34$, D = 0.306 cm⁻¹, E = 0.0025 cm⁻¹, 2J = 241 cm⁻¹; (116 K), $g_{x} = 2.05$, $g_{y} = 2.06$, $g_{z} = 2.35$, $A_{z1} = 7.0$ mT, D = 0.303 cm⁻¹, E = 0.0030 cm⁻¹, 2J = 231 cm⁻¹. μ_{eff} (298 K), 1.56 BM. The single crystals of **3**, suitable for X-ray analysis, were obtained by a similar procedure, but at lower concentration of the starting compounds.

2.2. X-ray structure analysis

Details of the crystal data, data collection and refinement parameters for 1, 2 and 3 are listed in Table 1. The selected distances and angles are presented in Table 2. A colorless plate of compound 1 was glued, while green prisms of compounds 2 and 3 were greased on a glass thread. The diffraction data for 1-3 were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Ka radiation. A Cryostream Cooler (Oxford Cryosystems) was used for cooling the samples of 2 and 3. The data were processed using DENZO [13]. Structures of 1 and 2 were solved by direct methods using SIR97 [14] and refined using XTAL 3.6 [15] by a full-matrix least-squares procedure based on F. Structure of 3 was solved by direct methods implemented in SHELXS-97 [16] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [17]. All of the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms in 1 and 2 were obtained from the difference Fourier maps. Positional parameters of H atoms for 1, while positional and isotropic displacement parameters of H atoms for 2, were refined. The water hydrogen atoms in 3 were visible in the last stages of the refinement and were refined freely, while the other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

2.3. Physical measurements

Metal analysis was carried out electrogravimetrically with Pt electrodes. C,H analysis was performed with a Perkin–Elmer, Elemental Analyzer 2400 CHN. 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 [18]. Infrared spectra were measured on mineral mulls, using a Perkin–Elmer FT-IR 1720X spectrometer. Electronic spectra were recorded as nujol mulls and DMSO solutions with a Perkin–Elmer

Table 1 Relevant crystal data and data collection summary

| | 1 | 2 | 3 |
|--|--------------------------------|---|---|
| Formula | $C_8H_8O_4$ | C ₂₂ H ₂₈ Cu ₂ O ₁₄ | C ₃₂ H ₃₂ Cu ₂ O ₁₈ |
| Formula weight | 168.15 | 643.54 | 831.66 |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space group | $P2_{1}/c$ | $P\overline{1}$ | $P2_1/n$ |
| a (Å) | 3.9101(1) | 8.3217(2) | 8.2747(4) |
| <i>b</i> (Å) | 17.3900(6) | 8.9495(2) | 19.5282(11) |
| <i>c</i> (Å) | 11.3267(5) | 9.7552(3) | 10.0006(5) |
| α (°) | 90 | 69.633(1) | 90 |
| β (°) | 95.313(1) | 76.824(1) | 102.725(3) |
| γ (°) | 90 | 64.165(1) | 90 |
| $V(Å^3)$ | 766.87(5) | 610.52(3) | 1576.31(14) |
| Z | 4 | 1 | 2 |
| D_{calc} (g/cm ³) | 1.456 | 1.750 | 1.752 |
| $\mu (\mathrm{mm}^{-1})$ | 0.118 | 1.812 | 1.438 |
| $T(\mathbf{K})$ | 293 | 150 | 150 |
| Crystal color | colorless | green | green |
| Crystal shape | plate | prism | prism |
| Crystal size (mm) | $0.25 \times 0.25 \times 0.10$ | $0.15 \times 0.10 \times 0.09$ | $0.23 \times 0.10 \times 0.10$ |
| θ_{\max} (°) | 27.5 | 25.0 | 27.5 |
| R _{int} | 0.049 | 0.024 | 0.035 |
| Refined parameters | 133 | 172 | 248 |
| Total data | 10029 | 7267 | 5813 |
| Independent data | 1715 | 2130 | 3420 |
| Observed data $[F^2 > 2\sigma(F^2)]$ | 981 | 1985 | 2869 |
| $R^{\rm a}$ (observed) | 0.052 | 0.031 | 0.067 |
| $R_{\rm w}^{\rm b}$, $w R_2^{\rm c}$ (observed) | 0.056^{b} | 0.026 ^b | 0.135 ^c |
| $\Delta \rho_{\min,\max} (e \text{ Å}^{-3})$ | -0.408, 0.281 | -0.807, 0.555 | -0.520, 1.294 |

 $\begin{array}{l} ^{\rm a} \ R = \sum (||F_{\rm o}| - |F_{\rm c}||) / \sum |F_{\rm o}|. \\ ^{\rm b} \ R = \sum (w(|F_{\rm o}| - |F_{\rm c}|)) / \sum (w|F_{\rm o}|). \\ ^{\rm c} \ wR_2 = (\sum [w(F_{\rm o}^2 - F_{\rm c}^2)^2] / \sum (wF_{\rm o}^2)^2)^{1/2}. \end{array}$

Table 2

Selected bond distances (Å) and angles (°) in the structures 2 and 3

| 2 | | | | 3 | | | |
|---------------------|---------------|----------------------|-----------------------|-------------|------------------|---------------------|------------|
| Cu⊷Cu | 2.608(1) | O1–Cu–O2 | 169.31(5) | Cu···Cu | 2.611(1) | O3–Cu–O2 | 169.51(16) |
| Cu–O1 | 1.960(1) | O1-Cu-O5 | 89.99(6) | Cu–O3 | 1.956(3) | O3–Cu–O5 | 87.06(15) |
| Cu–O2 | 1.951(1) | O1–Cu–O6 | 90.22(6) | Cu–O2 | 1.958(3) | O2–Cu–O5 | 90.37(15) |
| Cu–O5 | 1.965(2) | O1–Cu–O7 | 97.85(5) | Cu–O5 | 1.977(3) | O3–Cu–O4 | 86.93(15) |
| Cu–O6 | 1.984(2) | O2–Cu–O5 | 89.02(6) | Cu–O4 | 1.981(3) | O2–Cu–O4 | 93.61(15) |
| Cu–O7 | 2.160(2) | O2–Cu–O6 | 88.76(7) | Cu–O6 | 2.170(4) | O5–Cu–O4 | 167.67(15) |
| | | O2–Cu–O7 | 92.83(5) | | | O3–Cu–O6 | 97.29(16) |
| | | O5–Cu–O6 | 169.13(5) | | | O2–Cu–O6 | 93.11(16) |
| | | O5–Cu–O7 | 96.87(6) | | | O5–Cu–O6 | 96.76(17) |
| | | O6–Cu–O7 | 93.87(6) | | | O4–Cu–O6 | 94.68(17) |
| Hydrogen-bon | ding geometry | | | | | | |
| O7–H7···O4 2.735(2) | | $169(5)^{i}$ | O6−H1···O10 |) 2.877(6) | | $167(8)^{a}$ | |
| | | | O6–H2···O9 2.959(6) | | | 159(7) ^b | |
| O4–H4···O6 2.751(2) | | 157(3) ⁱⁱ | O10-H10···O5 2.873(5) | | 155 ^c | | |
| O4-H4···O3 2.707(2) | | 102(2) | O9–H9···O7 2.679(6) | | | 114 | |
| | ~ / | | . / | O10−H10···O | 08 2.731(6) | | 111 |

Symmetry codes: (i) 2 - x, 1 - y, 1 - z; (ii) x, 1 + y, -1 + z.

(a) 1/2 + x, 1/2 - y, -1/2 + z; (b) -x, -y, 1 - z; (c) 1/2 - x, 1/2 + y, 5/2 - z.

UV/Vis/NIR spectrometer Lambda 19. EPR spectra of the powdered samples were recorded by a Bruker ESP-300 spectrometer, operating at X-band (9.59 GHz) at room temperature and at 116 K. The values of parameters g, A, D, E and 2J were calculated directly from the signal positions in the spectra [19–21].

3. Results and discussion

3.1. The structure of free vanillic acid $C_8H_8O_4$ (1)

Two molecules of free vanillic acid are strongly Hbonded by two mutual H-bonds between their carboxylate groups (O1–H···O2' 2.642(3) Å), thus forming a centrosymmetrical dimeric unit (Fig. 1), as often found at carboxylic acids. Another H-bond is intramolecular, formed by the hydroxy group and the methoxy group (O4–H···O3 2.631(3) Å). A comparison to the structure of related lignin model compound vanillin (Scheme 1) [22] reveals significantly different intermolecular H-bonding, due to the aldehyde group instead of the carboxylic group. The vanillin molecules are packed in chains, where strong H-bonds connect aldehyde and phenolato groups on positions 1 and 4 of the benzene ring (O–H···O 2.712(2)–2.743(3) Å).

3.2. The structure of bis(μ-(4-hydroxy-3-methoxybenzoato-O:O'))bis(μ-(acetato-O:O'))bis(methanol) dicopper(II) (2)

The centrosymmetric *paddle-wheel* central core $[Cu_2 (C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ (2) is of copper(II) acetate hydrate type, however with two different carboxylates (two acetates and two vanillic acid anions) in *trans* orientation, while methanol molecules occupy the apical positions (Fig. 2). The phenolate group is involved in all three hydrogen bonds, either intra-molecularly to methoxy oxygen atom (O4–H···O3 2.707(2) Å), or inter-molecularly to methanol molecule (O7–H···O4 2.735(2) Å) and acetate group (O4–H···O6 2.751(2) Å).

3.3. The structure of tetrakis(μ -(4-hydroxy-3-methoxybenzoato-O:O'))bis(aqua) dicopper(II) (3)

The structure of complex $[Cu_2(C_8H_7O_4)_4(H_2O)_2]$ (3) was already reported [8], but was redetermined due to unavailability of the atom positions from the CSD [25]. Complex 3



Fig. 1. The dimeric structure of free vanillic acid with two hydrogenbonds between the carboxylic groups of the vanillic acid molecules [23,24].



Fig. 2. Two types of carboxylate anions in a dinuclear copper(II) tetracarboxylate complex $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ (2) [23,24]. The intermolecular H-bonds are connecting the phenolate group (O4) with the acetate anion (O6) and methanol molecules (O7).

is of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ type with four identical carboxylate ligands. Similar pattern, as in **2**, is found in the vanillic acid anion, with the phenolate group involved in all H-bonds and an intra-molecular H-bond between hydroxy and methoxy groups. Each hydroxy group is Hbonded also inter-molecularly to axially coordinated water molecules (O6–H1···O10 2.876(6) Å, O6–H2···O9 2.958(6) Å), giving two H-bonds with each water molecule.

Two H-bonds (3) to the axial ligand instead of one (2) and better volatility of methanol (2) than water (3) may be the main reasons for better stability of 3 than 2 outside mother-liquid. Interestingly, only two vanillic acid anions in 3 are forming another H-bond to carboxylate oxygen atom (O10–H10···O5 2.873(5) Å), while for another two, no such connections were found, probable due to steric reasons. This is very probable reason that only two vanillic acid anions are replaced with acetates in 2. Small acetates enable stronger (shorter) inter-molecular H-bonds, possibly due to less steric hindrance (see Table 2). Additionally, stronger stabilization in 3 than in 2 is found also in π -stacking interaction (mean inter-planar separation 3.30 Å (3.37 Å) for 3 (2), centroid \cdots centroid distance 3.94 Å (4.22 Å) for 3 (2)). It seems that the decisive factors for the competition between the homocarboxylate (3) and heterocarboxylate (2) are inter-molecular interactions. Either weaker H-bonds, stronger π -stacking and two Hbonds to the axial ligand (3), or stronger H-bonds, weaker π -stacking and one H-bond to the axial ligand (2).

3.4. Spectroscopic and magnetic analysis

Although the compound 2 is not stable outside motherliquid, yielding 2a, the μ_{eff} 1.48 BM (2a) suggests only partial decomposition of 2 and a retainment of the dinuclear tetracarboxylate central core in the compound 2a (1.55 BM for 3). This is in agreement with almost identical solution or mull UV-Vis-NIR spectra for 2a and 3, respectively, and with EPR spectra, where typical signals $(H_{z1},$ $H_{\perp 2}$, H_{z2} [19], Fig. 3) for the triplet state S = 1 of $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ type of compounds may be observed at room temperature and at 116 K (see Section 2). In the low temperature EPR spectra, the splitting of a H_{z1} signal to septet, $H_{\perp 2}$ to H_{x2} and $H_{\nu 2}$ and an appearance of the signal of mononuclear species H_{mono} at 330 mT were noticed. Such phenomena are often found in the low temperature spectra of the dinuclear copper(II) tetracarboxylates. Differences in the H_{z1} splitting, the hyperfine constant A_{z1} (5.6 mT; 7.0 mT), and the $H_{\perp 2}$ separation for the spectra of 2a and 3 may be related to a different role of the bridging anions present in both complexes, and/or replacement of the apical ligand $(2 \rightarrow 2a)$ that might not enable full equivalency of both Cu ions in the dinuclear unit after rearrangement. Close to the H_{z1} signal in the spectra of 3, an additional distinctive signal may be observed at 80 mT (Fig. 3). This signal is assigned as $H_{\perp 1}$ (H_{x1}, H_{y1}) that is observable, since $D \le hv$, and may be described by the equations [19–21]:



Fig. 3. Three signals H_{z1} , $H_{\perp 2}$ (H_{x2} , H_{y2}) and H_{z2} , characteristic for $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ type of compounds for **2a** and **3**, and an additional signal $H_{\perp 1}$ (H_{x1} , H_{y1}) at 80 mT, in the spectra of **3** at room temperature (RT) and at 116 K.

$$H_{x1}^{2} = \left(\frac{g_{e}}{g_{x}}\right)^{2} (H_{0} - D' + E')(H_{0} + 2E'),$$
(1)

$$H_{y1}^{2} = \left(\frac{g_{e}}{g_{y}}\right)^{2} (H_{0} - D' - E')(H_{0} - 2E'),$$
⁽²⁾

$$H_0 = hv/g_e\beta$$
, $D' = D/g_e\beta$, $E' = E/g_e\beta$.
Such signal and its assignment was, up to o

our knowledge, so far not reported for dicopper(II) tetracarboxylates, but only for $[Cu_2(O_2CCH_3)_2L_2(dmf)_2]$, with two O-C-O and two N-C-N bridges in Cu tetracarboxylate analogue [26]. Similar signal was noticed also in the spectra of copper(II) dinuclear complex with four O–C–N bridges in $[Cu_2(chp)_4]$ [27]. The partial coordination sphere in these two complexes is distorted square-planar CuO₂N₂ (only coordination atoms from bridges and without the axial ligand). The presence of the $H_{\perp 1}$ signal for these two tetracarboxylate analogues is in agreement with low D values (0.265; $0.275 \text{ cm}^{-1} \Rightarrow D < hv$). Structurally, the complex 3 is related to these two complexes by a relatively large torsion angle 6.0° for two trans O-Cu-··Cu-O moieties (both O atoms are from the same carboxylate group; Fig. 4). For $[Cu_2(chp)_4]$, the O-Cu···Cu-N torsion angle is 5.1-8.6°, while for $[Cu_2(O_2CCH_3)_2L_2(dmf)_2]$, O-Cu···Cu-O 3.4° and N-Cu-··Cu-N 0.9°, respectively. Comparable angles for 2 and for $[Cu_2(O_2CCH_3)_4(H_2O)_2]$ are significantly smaller ($<1.2^\circ$, $<2^\circ$) [28]. The Cu···Cu distances for both complexes 2 and 3 (2.608(1), 2.611(1) A) are similar and typical for dicopper tetracarboxylates [29], therefore this distance can not be directly correlated to the appearance of the $H_{\perp 1}$ signal in the EPR spectra of 3.

Since herein, the complex 3 is structurally characterized with 2, and with 2a by EPR, this correlation may not be absolutely exact. Maybe some additional information from the EPR spectra of the undecayed 2 (powder inside traces



Fig. 4. Torsion in the O–Cu $\cdot\cdot$ Cu–O angles in 3 [23–25]. The second central copper ion is positioned behind the first one. All hydrogen atoms and aromatic rings are omitted for clarity.

of mother solution) or from the frozen solution spectra could be obtained.

A broad band at $3600-3300 \text{ cm}^{-1}$ in the IR spectrum of **2a** agrees with the presence of water instead of methanol (a narrow band for O–H bond would be expected for **2**). One strong band in the region $1650-1550 \text{ cm}^{-1}$ found for **3** (1570 cm^{-1}) and two strong bands in the spectrum of **2a** (1623, 1591 cm^{-1}) are probably due to the asymmetric stretching vibration [30] of one (vanillic acid anion) and two (acetate, vanillic acid anion) types of carboxylate anions in the compounds **2a** and **3**, respectively. Since in $[Cu_2(O_2CCH_3)_4(H_2O)_2]$, an acetate analogue of **3**, $v_{as}(CO_2)$ was observed at 1605 cm^{-1} [31], the higher energy band at 1623 cm^{-1} in the spectrum of **2a** is assigned to the acetate, while the 1591 cm^{-1} band to the vanillic acid anion.

4. Concluding remarks

The compounds $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ (2) and $[Cu_2(C_8H_7O_4)_4(H_2O_2)]$ (3) precipitate from the solution of the same starting compounds $[Cu_2(O_2CCH_3)_4]$ (H₂O)₂] and vanillic acid, however in different polar solvent methanol or water for 2 or 3, respectively. Heterocarboxylate compound $[Cu_2(C_8H_7O_4)_2(O_2CCH_3)_2(CH_3OH)_2]$ (2) is unstable outside mother-liquid. Its decomposition is partial, since the central carboxylate cage remains, however water molecules replace the apical methanol molecules. On the other hand, the homocarboxylate compound [Cu₂- $(C_8H_7O_4)_4(H_2O_2]$ (3) is stable also in air, probably due to two H-bonds to the axial ligand instead of one (2) and less volatile water (3) than methanol (2). Significant differences were found in the EPR spectra, resulting in an unexpected signal at 80 mT in the spectra of 3, next to H_{z1} , $H_{\perp 2}$ and H_{z2} , typical for S = 1 spin state. This signal is assigned as $H_{\perp 1}$, due to low D axial zero field splitting parameter value $(D \le hv)$. The appearance of this signal is probably related to a relatively large torsion angle O-Cu-··Cu-O, found in compound 3, and not with the $Cu \cdot \cdot Cu$ distance inside a dinuclear molecule. Coordination of the acetates, together with vanillic acid anions, in **2** and **2a**, yields stronger H-bonds and much less torsion in dicopper tetracarboxylate central core than in **3**, and seems to be an appropriate alternative to more extensive H-bonding with the axial ligand and more effective π -stacking in homocarboxylate complex **3**.

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Appendix A. Supplementary data

The final atomic and geometrical parameters, crystal data and details concerning data collection and refinement for all three compounds have also been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers 277423 (1), 277424 (2) and 277425 (3), respectively. These data can be obtained, free of charge via http://www.ccdc.cam. ac.uk/const/retrieving.html. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2005.08.031.

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