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Dinuclear Paddle-Wheel Copper(II) Carboxylates in the Catalytic Oxidation of Carboxylic Acids. Unusual Polymeric Chains Found in the Single-Crystal X-ray Structures of [Tetrakis(μ-1-phenylcyclopropane-1-carboxylato-*O,O′*)bis(ethanol-*O*)dicopper(II)] and *catena*-Poly[[bis(μ-diphenylacetato-*O*:*O′*)dicopper](μ_3-diphenylacetato-1-*O*:2-*O′*:1′-*O′*)-(μ_3-diphenylacetato-1-*O*:2-*O′*:2′-*O′*)]

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The X-ray structures and spectroscopic and magnetic properties of [tetrakis(μ-1-phenylcyclopropane-1-carboxylato-*O,O′*)bis(ethanol-*O*)dicopper(II)], **1**, and *catena*-poly[[bis(μ-diphenylacetato-*O*:*O′*)dicopper](μ_3-diphenylacetato-1-*O*:2-*O′*:1′-*O′*)(μ_3-diphenylacetato-1-*O*:2-*O′*:2′-*O′*)], **2**, two extended-chain copper(II) carboxylates with dinuclear *paddle-wheel* subunits, are reported. **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 6.8873(3)$ Å, $b = 11.7367(6)$ Å, $c = 13.7899(7)$ Å, $\alpha = 107.076(4)°$, $\beta = 93.545(4)°$, $\gamma = 103.967(4)°$, $Z = 1$. The Cu···Cu distance is 2.6009(4) Å, and the Cu···carboxylate O distances are in the range 1.937(2)−1.962(2) Å. The ethanol at the apex forms an unsymmetrical bifurcated H bond to two carboxylate oxygens of another dinuclear unit with O···O distances 2.980(3) and 3.108(3) Å, thereby extending the structure along the *a*-axis. The magnetic structure consists of isolated antiferromagnetically coupled dinuclear copper units, with a $-2J$ value of 242 cm^{-1}, in concurrence with the EPR parameters, *viz.*, $g_x = 2.03(1)$, $g_y = 2.07(1)$, $g_z = 2.35(1)$, $A_{\|} = 0.064(2)$ cm^{-1}, $D = 0.316(15)$ cm^{-1}, $E = 0.005(1)$ cm^{-1}. The $-2J$ value is the smallest value measured for dinuclear copper carboxylates with oxygen-donor ligands at the axial position and no electron-withdrawing carboxylate R groups. **2** crystallizes in the monoclinic space group $P2_1/c$, with $a = 15.953(2)$ Å, $b = 5.385(6)$ Å, $c = 28.322(10)$ Å, $\beta = 120.22(3)°$, $Z = 2$. The compound contains tetrakis(diphenylacetato)dicopper(II) units, forming a polymeric structure along the b-axis by axial coordination of a carboxylate oxygen to copper of a subsequent dinuclear unit, at 2.323(11) Å. The intradimer Cu···Cu distance is 2.594(4) Å; the interdimer Cu···Cu distance is 3.425(5) Å. The $-2J$ value of 321 cm^{-1} was interpreted as originated from isolated antiferromagnetically coupled dinuclear copper units. The EPR parameters are $g_x = 2.07(1)$, $g_y = 2.02(1)$, $g_z = 2.33(1)$, $D = 0.347(10)$ cm^{-1}, $E = 0.0034(5)$ cm^{-1}. The dinuclear subunits are likely candidates for the catalytically active Cu species in copper(II)-catalyzed oxidation of carboxylic acids.

Introduction

During our investigations of the copper(II)-catalyzed oxidation of carboxylic acids,[1] it was found that dinuclear copper(II) carboxylates are present under catalytic reaction conditions.[2] Therefore it was decided to investigate the structure of these, possibly catalytically active, complexes in more detail. In general copper(II) carboxylates exhibit the dinuclear *paddle-wheel* cage structure. Some 250 X-ray crystal structures containing the $Cu_2(OOCR)_4$ core can be found in the Cambridge Structural Database, of which 126 are of the type $Cu_2(OOCR)_4L_2$, where L is an apical ligand with an oxygen or a nitrogen donor atom.[3]

Carboxylate anions are versatile ligands, because each carboxylate oxygen atom carries two lone pairs. Various coordination modes are thus possible. In most structures only one of the lone pairs of each oxygen atom is involved in coordination, like in the dinuclear paddle-wheel structure. However, if the second lone pair is donated to a metal ion of another paddle-wheel unit, the stepped polymeric structure **I** (Figure 1) results. Although only a few crystal structures of this type have been reported,[4−10] it is generally accepted that all anhydrous copper(II) carboxylates adopt this type of structure. This bonding

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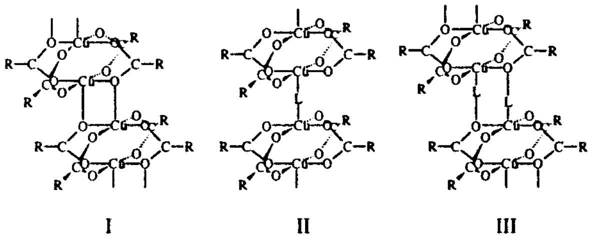

Figure 1. General structures of polynuclear copper(II) carboxylates: **I**, stepped without additional ligands; **II**, ligands bridging between two Cu; **III**, ligands bridging between Cu and O.

mode is common in all silver(I) carboxylates.[11] From the reinvestigated kinetics and regiochemistry of the thermal decomposition of copper(II) benzoate in benzoic acid,[12] the critical step in the DOW phenol process,[13] a tetranuclear structure of this type was proposed as a key intermediate. A mechanism involving this species is more feasible than the radical-cage mechanism accepted thus far, which completely neglects the preferred coordination of carboxylate ligands to copper(II) ions.[14]

Polymeric structures can also be obtained by means of ligands which are able to bridge between dinuclear units, as in **II** (Figure 1). The two Cu ions may coordinate to the same or to different donor atoms of the bridging ligand. Structures have been reported with bridging pyrazine,[15] *N,N*′-hexamethylene-tetramine,[16] 2-aminopyrimidine,[17] dioxane,[18] and 2-aminopyrimidine,[19] which are all bifunctional ligands coordinating axially to two copper ions of different dinuclear paddle-wheel units. In most cases a linear polynuclear structure results; in some cases the structure is zigzag, as with *N,N*′-hexamethylenetetramine[16] and 2-aminopyrimidine.[19] If the bridging ligand coordinates axially to a Cu ion and at the same time interacts with a carboxylate oxygen atom of another paddle-wheel unit, a third type of polymer, type **III** (Figure 1), results, which can be regarded as intermediate between types **I** and **II**. Examples of type **III** structures are [tetrakis(μ-acetato-*O,O*′)bis(methanol-*O*)dicopper(II)][20] and [bis(aqua)bis(μ-acetato-*O,O*′)bis(2,6-μ-dimethoxybenzoato-*O,O*′)dicopper],[21] where the coordinated methanol and water, respectively, at the apex forms an *intermolecular* hydrogen bridge to a carboxylate oxygen of a next dinuclear unit.

In the present paper the structures and spectroscopic and magnetic properties of [tetrakis(μ-1-phenylcyclopropane-1-carboxylato-*O,O*′)bis(ethanol-*O*)dicopper(II)], **1**, and *catena*-poly[[bis(μ-diphenylacetato-*O*:*O*′)dicopper](μ_3-diphenylacetato-1-*O*:2-*O*′:1′-*O*′)(μ_3-diphenylacetato-1-*O*:2-*O*′:2′-*O*′)], **2**, are reported. Compound **1** has a structure derived from type **III**, with an ethanol molecule bridging two dinuclear units in a unique fashion: the ethanol oxygen coordinates axially to a Cu ion of one dinuclear unit, whereas the hydroxylic H forms an unsymmetric bifurcated H bond to two carboxylate oxygen atoms of another dinuclear unit.

Experimental Section

Syntheses of the complexes were carried out using commercially available chemicals and solvents of reagent grade, which were used as received. Copper(II) diphenylacetate and copper(II) 1-phenylcyclopropanecarboxylate were prepared by the precipitation method.[22] An aqueous 1 M $CuSO_4$ solution was slowly added to a 1 M aqueous solution of the appropriate Na carboxylate, with vigorous stirring. After the complete addition, the temperature was raised to 55−60 °C and the solution was kept at this temperature for 1 h, while the stirring was continued. After cooling to room temperature, the precipitated product was filtered off, and subsequently washed extensively with water to remove Na_2SO_4. The product was dried at 100 °C and 200 mbar during several hours to yield the monohydrated copper(II) carboxylate. **1** was obtained by recrystallization from ethanol, and **2** by recrystallization from methanol. Single crystals of X-ray quality were obtained by slow evaporation of the solvent. Dry crystals of **2** are sensitive to moist air and should thus be handled preferably in a dry atmosphere or in their mother liquor.

Metal analyses were carried out complexometrically with Na_2H_2-edta as complexing agent.

C,H,O,N analyses were performed at the Microanalytical Laboratory in Dublin. Elemental analyses of **1** (calculated values in parentheses) gave Cu 14.5 (14.71), C 61.21 (61.17), H 5.58 (5.60), O 18.61 (18.52). Values obtained for **2**: Cu 12.8 (13.07), C 69.02 (69.20), H 4.52 (4.56), O 13.31 (13.17).

Temperature dependent magnetic susceptibilities of solid samples were measured on a fully automated Manics DSM-8 susceptometer (Faraday balance) equipped with a TBT continuous-flow cryostat (4−300 K) and a Drusch EAF 16 NC electromagnet operating at ca. 1.4 Tesla. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.[23] Magnetic data were fitted to the modified Bleaney−Bowers equation by means of a Simplex routine[24] using a locally developed BASIC computer program. The parameters *J* and *p* were varied independently during the fitting procedure, minimizing the function $R = [\sum|X_{obs} - X_{calc}|^2/\sum X_{obs}^2]^{1/2}$; the *g* value was set at the average *g* value calculated from EPR spectra.

Infrared spectra in the 4000−180 cm^{-1} range of the samples as KBr pellets or as Nujol mulls were recorded either on a Perkin-Elmer 580B spectrophotometer, equipped with a Perkin-Elmer data station, or on a Bruker IFS 113V FTIR spectrophotometer.

Electronic spectra (28000−5000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station, as solids in standard diffuse-reflectance mode with MgO as reference.

Electron paramagnetic resonance measurements were carried out using solid samples on a JEOL RE2x ESR spectrometer operating at X-band frequency (9.0 GHz at 77K), or on a Bruker ESP380E ESR spectrometer equipped with a Varian E-110 Q-band microwave bridge operating at 35 GHz, at approximately 100 K, using a Varian model E-266 cylindric resonator TE-011. The resonance field values in X-band spectra were corrected using 1,1-diphenyl-2-picrylhydrazil (dpph) as external reference. The parameters of the triplet spectra were calculated by minimizing the function $R = \sum|H_{obs} - H_{calc}|$, using the equations of organic triplet systems,[25] calculated by means of a locally developed PASCAL program.

X-ray Data Collection and Structure Refinement. X-ray data for complex **1** were collected at 150 K on an Enraf Nonius CAD4T/rotating anode diffractometer, using graphite-monochromated Mo Kα radiation,

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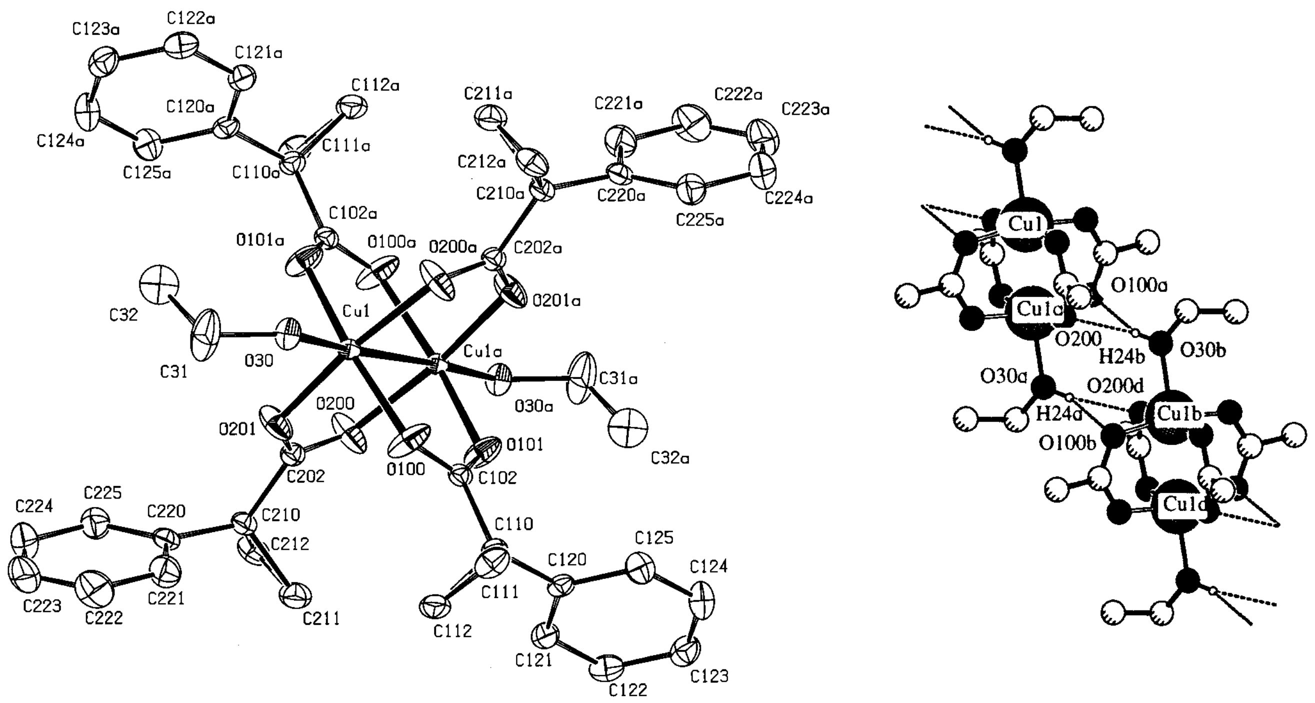

Figure 2. PLATON[29] projection of the molecular structure (left), with thermal ellipsoids drawn at the 50% probability level, and a PLUTON[31] projection of the chain extension by H bonding (right) of **1**.[32] H atoms, except for the ethanolic H, have been omitted for clarity; on the right side all C atoms except for the carboxylate and α-C atoms have been omitted for clarity.

for a greenish transparent cut-to-shape crystal of 0.15 × 0.20 × 0.50 mm. Accurate unit cell parameters were derived from the SET4 setting angles of 25 reflections in the range $10 < \theta < 14°$. A total of 7138 reflections were scanned ($\omega/2\theta$ scan; $\Delta\omega = 0.63 + 0.35 \tan \theta°$; $\theta(\max) = 27.5°$). Data were corrected for Lp and absorption (DIFABS,[26] correction range 0.91−1.07) and averaged ($R(\text{int}) = 0.037$) into a unique set of 4095 observed reflections with $I > 2.5\ \sigma(I)$. The structure was solved with DIRDIF/PATT[27] and refined on F with SHELX76.[28] The terminal methyl moiety of the coordinating ethanol was found to be disordered over two positions (0.79:0.21). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were refined isotropically. The positions of the ethanol hydrogen atoms were refined riding on their carrier atom or with a bond restraint (O−H). Refinement converged at $R = 0.034$ for 4095 observed reflections and 329 parameters. A final difference map showed no residual density outside -0.46 e Å^{-3} $< \Delta\rho <$ 0.46 e Å^{-3}. Geometrical calculations were done with PLATON.[29]

X-ray data for complex **2** were collected at 150 K on an Enraf Nonius CAD4T/rotating anode diffractometer, using graphite-monochromated Mo Kα radiation, on a small blue-green needle-shaped crystal (0.025 × 0.025 × 0.38 mm). Crystals were found to reflect poorly, resulting in a relatively high residual R value. Cell dimensions were derived from the SET4 setting angles of 25 reflections in the range $5 < \theta < 14°$; the space group was derived from observed systematic extinctions. A total of 4517 reflections were scanned ($\omega/2\theta$ scan; $\Delta\omega = 0.80 + 0.35 \tan \theta°$; $\theta(\max) = 22.5°$), corrected for Lp and absorption (DIFABS,[26] correction range 0.84−1.56) and averaged ($R(\text{int}) = 0.21$) into a unique set of 2740 reflections. The structure was solved with DIRDIF/PATT[27] and refined on F^2 with SHELXL93[30] to a final $R = 0.11$ for 980 reflections with $I > 2.5\ \sigma(I)$ ($wR_2 = 0.21$ for 2740 reflections and 193 parameters). The limited quality of the dataset did not allow the anisotropic refinement of all non-hydrogen atoms. Hydrogen atoms were taken into account at calculated positions, riding on their carrier atom. No residual density outside the range -1.01 e Å^{-3} $< \Delta\rho <$ 0.80 e Å^{-3} was observed in a difference density map. Geometrical calculations were done with PLATON.[29]

Results and Discussion

General Procedure. The hydrated copper(II) carboxylates were synthesized by the precipitation method.[22] Subsequent recrystallization of **1** from ethanol or **2** from methanol afforded green crystals of X-ray quality in both cases. In the case of **1** the crystals were regularly-formed rectangular needles; in the case of **2** the needles were slightly twisted. PLATON[29] projections with thermal ellipsoids, and PLUTON[31] projections of the molecular and crystal structures, are shown in Figures 2 and 3 for **1** and **2**, respectively. Atomic coordinates are listed in Tables 2 and 4, and selected bond distances and angles are listed in Tables 3 and 5, respectively.

Description of the Structure of [Tetrakis(*μ*-1-phenylcyclopropane-1-carboxylato-*O*,*O′*)bis(ethanol-*O*)dicopper(II)], 1. The structure consists of centrosymmetric dinuclear units, with space group $P\bar{1}$. Each Cu(II) ion has four oxygens of different carboxylate groups in equatorial positions, with Cu···O distances in the range 1.937−1.962 Å, and an ethanolic oxygen at 2.1533(15) Å at the apex, completing the square pyramidal coordination geometry. The four carboxylates bridge between both copper ions, forming a paddle-wheel type cage with a Cu(1)···Cu(1)a distance of 2.6009(4) Å. The Cu···basal plane (formed by the four O atoms in equatorial positions) distance is 0.193(2) Å. An infinite chain along the *a*-axis is formed by means of an unsymmetrical (bifurcated) hydrogen bond from the ethanolic oxygen at the apex to two of the carboxylic oxygens of a subsequent dinuclear unit. Distances O(30)b···O(200)[$1-x,-y,-z$] and O(30)b···O(100)[$1+x,y,z$] are

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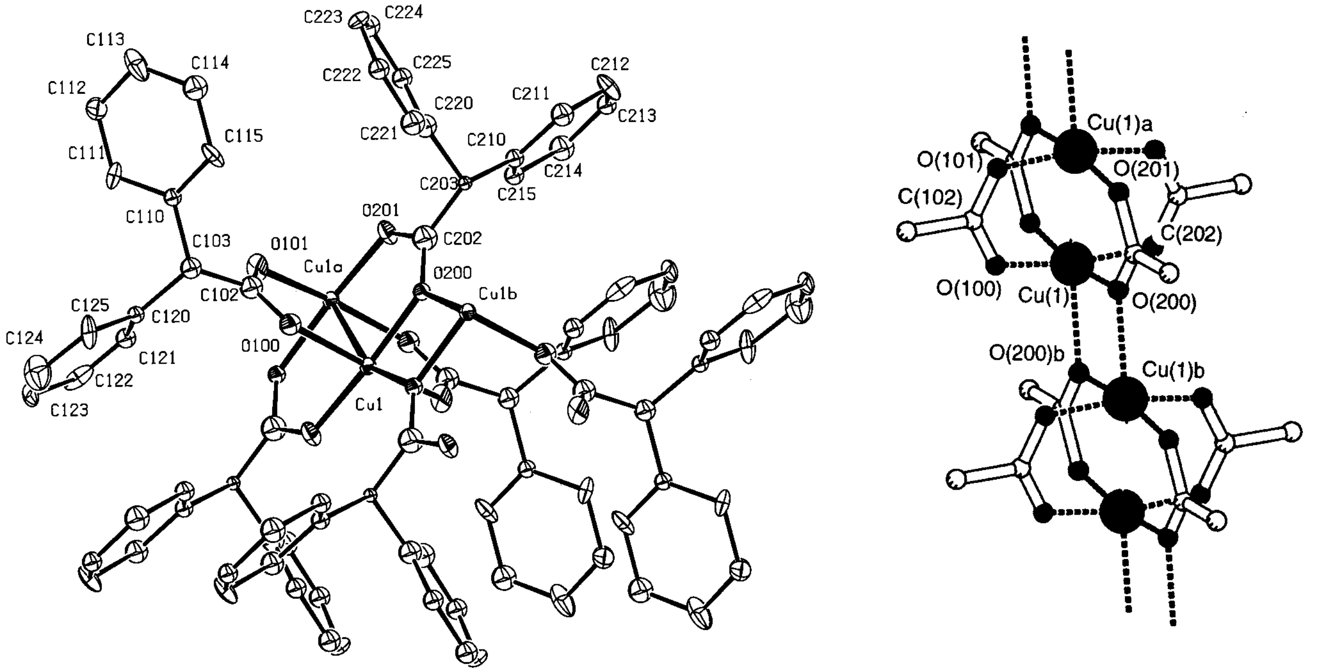

Figure 3. PLATON[29] projection of the molecular structure (left), with thermal ellipsoids drawn at the 50% probability level, and a PLUTON[31] projection of the chain extension by H bonding (right) of **2**. H atoms have been omitted for clarity; on the right side all C atoms except for the carboxylate and α-C atoms have been omitted for clarity.

Table 1. Crystallographic Data for [Tetrakis(*μ*-1-phenylcyclopropane-1-carboxylato-*O*,*O*′)bis(ethanol-*O*)dicopper(II)], **1**, and *catena*-Poly[[bis(*μ*-diphenylacetato-*O*:*O*′)dicopper](*μ*$_3$-diphenylacetato-1-*O*:2-*O*′:1′-*O*′)(*μ*$_3$-diphenylacetato-1-*O*:2-*O*′:2′-*O*′)], **2**

	1	**2**
empirical formula	$C_{44}H_{48}Cu_2O_{10}$	$C_{56}H_{44}Cu_2O_8$
formula weight	863.95	972.06
space group	$P\bar{1}$	$P2_1/c$
a (Å)	6.8873(3)	15.953(2)
b (Å)	11.7367(6)	5.385(6)
c (Å)	13.7899(7)	28.322(10)
α (deg)	107.076(4)	90
β (deg)	93.545(4)	120.22(3)
γ (deg)	103.967(4)	90
V (Å^3)	1023.42(9)	2102(3)
Z	1	2
D(calc) (g/cm^3)	1.402	1.536
μ (Mo Kα) (cm^{-1})	11.0	10.7
λ (Mo Kα) (Å)	0.710 73	0.710 73
temp (K)	150	150
R^a	0.034	0.11
$R_w{}^b$	0.050	
w$R_2{}^c$		0.21

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] w$R_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$.

2.980(3) and 3.108(3) Å, respectively, which are typical values for O···H···O hydrogen bonded systems.[33] The hydrogen bonding to two carboxylate oxygens renders the four carboxylate oxygens coordinated to copper pairwise inequivalent: the distances of Cu(1)c to O(200) and O(100)c, the oxygens involved in H bonding, are equal, 1.962(2) Å, whereas the other two equatorial Cu···O distances are slightly shorter, 1.937(2) and 1.947(2) Å. The ethanolic methyl group is disordered; the occupancy factors of the two positions are 0.79 and 0.21, respectively. H bridging is uncommon for this kind of copper compound,[9] and the formation of a chain structure of type **1**, by means of bifurcated interdimer H bonding, has to our knowledge not yet been reported for copper(II) carboxylates.[3]

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters with Esd's of the Non-Hydrogen Atoms for [Tetrakis(*μ*-1-phenylcyclopropane-1-carboxylato-*O*,*O*′)bis-(ethanol-*O*)dicopper(II)], **1**

atom	x	y	z	U(eq) (Å^2)^a
Cu(1)	0.16871(4)	0.02362(2)	0.05939(2)	0.0139(1)
O(30)	0.4639(2)	0.06358(16)	0.14388(12)	0.0222(5)
O(100)	−0.1806(3)	0.13969(16)	0.02715(15)	0.0374(6)
O(101)	0.1082(3)	0.17823(16)	0.12674(14)	0.0321(6)
O(200)	0.2798(3)	0.0954(2)	−0.04388(15)	0.0362(6)
O(201)	−0.0084(3)	0.05934(18)	−0.14291(14)	0.0329(6)
C(31)	0.5250(6)	0.0904(4)	0.2505(2)	0.0524(11)
C(32)	0.4454(7)	0.1866(4)	0.3145(3)	0.0454(10)
C(102)	−0.0423(3)	0.20848(19)	0.09851(16)	0.0170(6)
C(110)	−0.0538(3)	0.3369(2)	0.15079(17)	0.0185(6)
C(111)	−0.2610(4)	0.3597(2)	0.1461(2)	0.0279(8)
C(112)	−0.1186(4)	0.4025(2)	0.0798(2)	0.0285(8)
C(120)	0.1027(3)	0.41199(19)	0.24201(17)	0.0187(6)
C(121)	0.2903(4)	0.4779(2)	0.22972(18)	0.0232(7)
C(122)	0.4360(4)	0.5469(2)	0.3133(2)	0.0276(7)
C(123)	0.3961(4)	0.5505(2)	0.41129(19)	0.0280(7)
C(124)	0.2112(4)	0.4837(3)	0.4242(2)	0.0319(8)
C(125)	0.0652(4)	0.4149(2)	0.34024(19)	0.0262(7)
C(202)	0.1765(3)	0.10973(19)	−0.11530(16)	0.0170(6)
C(210)	0.2817(3)	0.1962(2)	−0.16841(17)	0.0181(6)
C(211)	0.3974(4)	0.3227(2)	−0.0929(2)	0.0276(8)
C(212)	0.5096(4)	0.2362(2)	−0.1497(2)	0.0260(7)
C(220)	0.1748(3)	0.1940(2)	−0.26763(17)	0.0204(6)
C(221)	0.0153(4)	0.2471(3)	−0.2675(2)	0.0309(8)
C(222)	−0.0771(5)	0.2506(3)	−0.3580(3)	0.0434(10
C(223)	−0.0116(6)	0.2009(3)	−0.4496(2)	0.0441(10)
C(224)	0.1442(5)	0.1466(3)	−0.4510(2)	0.0414(10)
C(225)	0.2368(4)	0.1428(2)	−0.35991(19)	0.0283(8)

[a] U(eq) = one-third of the trace of the orthogonalized **U** tensor.

The shortest interdimer Cu···Cu distance is 5.0425(5) Å, and the *stacking period* amounts to 6.8873(3) Å. The angle which the paddle-wheel "discs" form with the chain axis, calculated as the angle of the C(102) C(102)a C(202) C(202)a plane with the *a*-axis, is 54.84(5)°.

In the IR spectrum recorded as a Nujol mull $\nu_{asym}(COO^-)$ is observed at 1612 cm^{-1}, and three $\nu_{sym}(COO^-)$ are seen at 1468 (s), 1420 (m), and 1386 (m) cm^{-1}. When the IR spectrum is

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(33) Bellamy, L. J.; Owen, A. J. *Spectrochim. Acta* **1969**, *A25*, 329.

Table 3. Selected Bond Distances (Å) and Angles (deg) of [Tetrakis(μ-1-phenylcyclopropane-1-carboxylato-*O*,*O*′)bis(ethanol-*O*)dicopper(II)], **1**, with Esd's[a]

Cu(1)−O(30)	2.1533(15)
Cu(1)−O(100)	1.962(2)
Cu(1)−O(201)	1.947(2)
Cu(1)−Cu(1)a	2.6009(4)
Cu(1)−O(101)a	1.937(2)
Cu(1)−O(200)a	1.962(2)
O(30)−C(31)	1.423(3)
O(100)−C(102)	1.254(3)
O(101)−C(102)	1.249(3)
O(200)−C(202)	1.254(3)
O(201)−C(202)	1.249(3)
O(30)−Cu(1)−O(100)	93.09(8)
O(30)−Cu(1)−O(201)	98.88(8)
Cu(1)a−Cu(1)−O(30)	173.95(4)
O(30)−Cu(1)−O(101)a	98.17(8)
O(30)−Cu(1)−O(200)a	92.40(8)
O(100)−Cu(1)−O(201)	88.06(8)
Cu(1)a−Cu(1)−O(100)	84.56(6)
O(100)−Cu(1)−O(101)a	168.65(9)
O(100)−Cu(1)−O(200)a	89.37(9)
Cu(1)a−Cu(1)−O(201)	86.62(6)
O(101)a−Cu(1)−O(201)	91.62(8)
O(200)a−Cu(1)−O(201)	168.55(9)
Cu(1)a−Cu(1)−O(101)a	84.09(6)
Cu(1)a−Cu(1)−O(200)a	82.02(6)
O(101)a−Cu(1)−O(200)a	88.71(9)
Cu(1)−O(30)−C(31)	130.46(19)
Cu(1)−O(100)−C(102)	122.35(17)
Cu(1)a−O(101)−C(102)	124.32(16)
Cu(1)a−O(200)−C(202)	124.99(18)
Cu(1)−O(201)−C(202)	120.72(16)
O(30)−C(31)−C(32)	112.9(3)
O(100)−C(102)−C(110)	117.9(2)
C(102)−C(110)−C(111)	117.10(19)
C(111)−C(110)−C(120)	119.5(2)
C(31)−C(32)	1.459(6)
C(102)−C(110)	1.491(3)
C(110)−C(111)	1.515(4)
C(110)−C(112)	1.518(3)
C(110)−C(120)	1.497(3)
C(111)−C(112)	1.481(4)
C(202)−C(210)	1.496(3)
C(210)−C(211)	1.530(3)
C(210)−C(212)	1.508(4)
C(210)−C(220)	1.503(3)
C(211)−C(212)	1.493(4)
C(112)−C(110)−C(120)	118.1(2)
C(110)−C(111)−C(112)	60.88(17)
C(110)−C(112)−C(111)	60.67(16)
C(110)−C(120)−C(121)	120.5(2)
C(110)−C(120)−C(125)	121.0(2)
O(200)−C(202)−O(201)	124.4(2)
O(200)−C(202)−C(210)	117.4(2)
O(201)−C(202)−C(210)	118.2(2)
C(202)−C(210)−C(211)	112.20(19)
C(202)−C(210)−C(212)	117.47(19)
C(202)−C(210)−C(220)	118.04(19)
C(211)−C(210)−C(212)	58.88(17)
C(211)−C(210)−C(220)	117.5(2)
C(212)−C(210)−C(220)	118.8(2)
C(210)−C(211)−C(212)	59.81(16)
C(210)−C(212)−C(211)	61.31(17)
C(210)−C(220)−C(221)	120.3(2)
C(210)−C(220)−C(225)	120.9(2)
C(102)−C(110)−C(112)	114.88(19)
C(111)−C(110)−C(112)	58.45(16)
O(100)−C(102)−O(101)	124.5(2)
O(101)−C(102)−C(110)	117.6(2)
C(102)−C(110)−C(120)	116.31(19)

[a] Symmetry code: a = $-x$, $-y$, $-z$.

measured as a KBr pellet, only one ν_{asym} at 1610 and one ν_{sym} at 1420 cm^{-1} are observed. The three ν_{sym} absorptions confirm that the carboxylate bridges are inequivalent. The values of $\Delta(\nu_{\mathrm{asym}}-\nu_{\mathrm{sym}})$, a measure for the bridging mode of carboxylate anions,[34] amount to 144, 192, and 226 cm^{-1}, respectively. The relatively weak 1420 cm^{-1} absorption is attributed to isolated dinuclear impurities, most likely formed in sample preparation during the mulling in nujol due to exposure to moisture; this appears to be the same species present in the KBr pellet, indicating that the pressure exerted in mulling the sample changes the structure to *syn*,*syn* didentate bridged dinuclear carboxylates. The 1386 and 1468 cm^{-1} resonances are attributed to the carboxylate bridges involved in the bifurcated H bridge, since this involves a *syn*,*syn*,*anti* carboxylate bonding mode with one monatomic bridge,[22b] which results in a reduced value for $\Delta(\nu_{\mathrm{asym}}-\nu_{\mathrm{sym}})$.[34] The IR spectrum also shows a very broad ν(OH) at approximately 3420 cm^{-1}, which is shifted to lower frequencies by 280 cm^{-1} compared to the free OH absorption,[33] $\Delta\nu$(OH), due to an increase of the effective mass. The broadness is the result of delocalization over many possible states, the more since this H bond is bifurcated. O−H···O distances can be calculated by an empirical relationship between $\Delta\nu$(OH) and the O−H···O distances, proposed by Bellamy and Owen.[33] Applied to single hydrogen bonding, as in [tetrakis(μ-1-phenylcyclopentane-1-carboxylato-*O*,*O*′)bis(ethanol-*O*)dicopper(II)] bis(ethanol),[35] the calculated and measured distances correspond very well. In this case, however, the calculated O−H···O distance is 2.802 Å, whereas the measured distances amount to 2.980 and 3.108 Å. Due to the bifurcated nature of the hydrogen bond, the effective mass is even larger; thus the $\Delta\nu$(OH) is larger than predicted.

The ligand field spectrum shows a Cu d-d transition of 14.4 × 10^3 cm^{-1}, the *xy*-polarized band I, being a $d_{x^2-y^2} \rightarrow d_{xz},d_{yz}$ transfer,[22c] and a LMCT at 25 × 10^3 cm^{-1}, the *z*-polarized band II,[22c] present as a shoulder on a very intense charge transfer band.

Description of the Structure of *catena*-Poly[[bis(μ-diphenylacetato-*O*:*O*′)dicopper](μ_3-diphenylacetato-1-*O*:2-*O*′:1′-*O*′)(μ_3-diphenylacetato-1-*O*:2-*O*′:2′-*O*′)], 2. This structure also contains centrosymmetric dinuclear Cu units with the paddle-wheel cage structure. The four carboxylate oxygens in equatorial positions are at a distance in the range 1.936−1.955 Å, and the Cu(1)···Cu(1)a distance is 2.594(4) Å. The distance between Cu and the basal plane, formed by O(100), O(200), O(101)a, and O(201)a, amounts to 0.185(2) Å. In this case one of the carboxylate oxygens of a neighboring $Cu_2(OOCR)_4$ unit coordinates at the apical position on 2.323(11) Å, thus extending the structure to an infinite chain along the *b*-axis. This apical distance is exceptionally large compared to other dinuclear copper carboxylates with axial O-donor ligands. This is due to the relatively large carboxylate side groups, which initially were expected to prevent this type of stacking of paddle-wheel units. The equatorial Cu···O distance of the O involved in the chain extension is slightly shorter than the other three Cu···O$_{\mathrm{eq}}$ distances: 1.936(11) versus 1.955(13), 1.948(13), and 1.952(13) Å. The shortest interdimer Cu···Cu distance is 3.425(5) Å, and the *stacking period* amounts to 5.385(8) Å. The mean plane of the dinuclear "disks" is at an angle of

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(34) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(35) Agterberg, F. P. W.; Provó Kluit, H. A. J.; Driessen, W. L.; Oevering, H.; Buijs, W.; Lakin, M.; Veldman, N.; Spek, A. L.; Reedijk, J. *Inorg. Chim. Acta.*, in press.

Table 4. Fractional Coordinates and Equivalent Isotropic Thermal Parameters with Esd's of the Non-Hydrogen Atoms for *catena*-Poly[[bis(μ-diphenylacetato-*O*:*O*′)dicopper](μ_3-diphenylacetato-1-*O*:2-*O*′:1′-*O*′)(μ_3-diphenylacetato-1-*O*:2-*O*′:2′-*O*′)], **2**

atom	*x*	*y*	*z*	*U*(eq) (Å^2)^a
Cu(1)	0.00962(14)	0.2069(4)	−0.02025(10)	0.0122(6)
O(100)	0.1427(7)	0.166(3)	0.0397(5)	0.020(3)
O(101)	0.1279(6)	−0.190(3)	0.0747(5)	0.024(4)
O(200)	−0.0270(6)	0.369(2)	0.0277(4)	0.013(3)
O(201)	−0.0394(7)	0.011(2)	0.0651(5)	0.021(4)
C(102)	0.1756(11)	−0.014(4)	0.0726(7)	0.022(4)
C(103)	0.2849(6)	−0.012(2)	0.1111(4)	0.019(4)
C(110)	0.3195(6)	−0.069(2)	0.1702(4)	0.013(4)
C(111)	0.3771(6)	−0.274(2)	0.1970(4)	0.033(7)
C(112)	0.4144(10)	−0.309(4)	0.2536(6)	0.024(6)
C(113)	0.3975(11)	−0.129(4)	0.2830(8)	0.034(8)
C(114)	0.3384(11)	0.069(4)	0.2550(7)	0.026(5)
C(115)	0.3002(11)	0.101(4)	0.1979(7)	0.025(7)
C(120)	0.3329(9)	−0.164(3)	0.0863(6)	0.012(4)
C(121)	0.2902(11)	−0.393(3)	0.0576(7)	0.017(4)
C(122)	0.3312(11)	−0.526(4)	0.0367(7)	0.025(6)
C(123)	0.4247(11)	−0.467(4)	0.0451(8)	0.031(8)
C(124)	0.4677(11)	−0.255(4)	0.0731(8)	0.041(8)
C(125)	0.4230(10)	−0.110(4)	0.0942(8)	0.025(7)
C(202)	−0.0455(11)	0.260(4)	0.0619(8)	0.027(5)
C(203)	−0.0732(9)	0.382(3)	0.0970(6)	0.008(4)
C(210)	−0.1701(9)	0.309(4)	0.0928(6)	0.014(4)
C(211)	−0.2042(11)	0.468(4)	0.1182(7)	0.022(4)
C(212)	−0.2906(10)	0.415(4)	0.1182(7)	0.022(6)
C(213)	−0.3401(9)	0.208(4)	0.0928(6)	0.016(4)
C(214)	−0.3088(11)	0.056(4)	0.0669(7)	0.026(5)
C(215)	−0.2222(10)	0.102(3)	0.0671(7)	0.016(4)
C(220)	0.0066(10)	0.374(3)	0.1563(7)	0.022(4)
C(221)	0.0747(10)	0.567(4)	0.1755(7)	0.025(4)
C(222)	0.1475(10)	0.576(4)	0.2308(7)	0.018(4)
C(223)	0.1513(11)	0.399(4)	0.2657(7)	0.034(7)
C(224)	0.0837(9)	0.195(4)	0.2446(6)	0.020(4)
C(225)	0.0145(9)	0.193(4)	0.1912(6)	0.017(4)

^{a} *U*(eq) = one-third of the trace of the orthogonalized **U** tensor.

57.6(5)° with the stacking direction, calculated as the angle of the C(102) C(102)a C(202) C(202)a plane with the *b*-axis.

Cu···Cu distances in polynuclear compounds of type **2** are among the shortest known in coordination compounds.[36] In paddle-wheel structures the Cu···Cu distance generally increases as the acid strength increases and at the same time the Cu atom moves out of the basal plane of its square pyramidal coordination polyhedron. For CuO$_4$O chromophores Cu···Cu and Cu···basal plane distances vary from 2.575 to 2.702 and from 0.165 to 0.225 Å, respectively.[3,14] Differences between Cu···O distances in the equatorial plane, between the O atom involved in the chain extension and the other carboxylate oxygens, are much larger in other, earlier reported, structures of type **2**. This is also encountered for Cu···O$_{ax}$ distances, which are affected by the changed geometry of the Cu ion. Differences can be well compared when considering the general numbering scheme depicted in Figure 4.

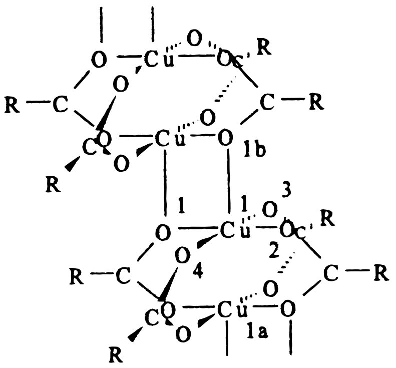

Figure 4. Schematic atom labeling of stepped polymeric structures.

Whereas the Cu1−O1 distance is shortened for Cu propanoate[4] (1.853 Å), and elongated (2.002−2.121 Å) for all other literature compounds,[5−10] only in compound **2** does this distance (1.936 Å) have a value common for copper(II) carboxylates.[14] Copper octanoate[6] and decanoate[7] exhibit a large distortion from the common square pyramidal geometry. In Cu octanoate Cu−O1b (1.913 Å) is very short compared to the corresponding distance in all other compounds, with also a short Cu−O4 distance (1.841 Å); in copper decanoate Cu−O1b (2.241 Å) is in the "normal" range, but Cu−O4 (2.083 Å) is very long. The deviation from square pyramidal geometry, as expressed by Addison's τ,[37] is thus largest for copper octanoate[6] ($\tau = 0.082$) and copper decanoate ($\tau = 0.128$)[7] and quite small for **2** ($\tau = 0.012$). This difference might well be due to van der Waals interactions, which, in the latter two cases, have a pronounced effect due to the difference in length of the (aliphatic) tails of the carboxylate fragments.

In the IR spectrum of **2**, ν_{asym} is at 1585 cm^{-1} and split and ν_{sym} is observed at 1399 cm^{-1}. The value of $\Delta(\nu_{asym}-\nu_{sym})$[34] is 186 cm^{-1}, which is smaller than usually observed for dinuclear copper(II) carboxylates,[34] *viz.*, the acetone and acetonitrile adducts of copper(II) diphenylacetate. The latter have Δ values of 234 and 205 cm^{-1}, respectively.[35] This is also in agreement with reduction of Δ upon obtaining the *syn,syn,anti* coordination mode in the chain extension. The split ν_{asym} is the result of the inequivalence of the carboxylate bridges. Unlike **1**, the spectrum recorded as Nujol mull is identical to the KBr pellet spectrum.

The ligand field spectrum shows one Cu d−d transition at 15.5 × 10^3 cm^{-1} (band I);[22c] band II was not observed, which probably was too broad to form the usual shoulder on the large LMCT starting at approximately 400 nm.

Magnetic Properties. The temperature dependent bulk magnetic susceptibilities of compounds **1** and **2** were measured and have been interpreted as isolated antiferromagnetically coupled dinuclear copper units. The $S = 1$ system arises from spin interactions between the two d^9 Cu(II) ions via the conjugated π-system of the carboxylate bridges, the so-called *superexchange mechanism*.[38] For paddle-wheel-type copper(II) carboxylates this interaction is strongly antiferromagnetic, because unpaired electron density from both Cu ions is transferred to the same orbital of the bridging carboxylate ligand. The coupling is given by the isotropic exchange Hamiltonian (eq 1). Best fits were obtained by using the modified Bleaney−Bowers equation (2) for exchange-coupled pairs of $S = {}^1/_2$ ions, which also accounts for paramagnetic (mononuclear) impurities, present in fraction *p*, which unavoidably are present in dinuclear Cu^{II} compounds and are relatively important at low temperatures; χ_p was calculated assuming a Curie law (eq 3). All symbols have their usual meanings.[33]

$$\hat{H} = -2J(\hat{S}_A \cdot \hat{S}_B) \tag{1}$$

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[36] O'Reilly, E. J.; Smith, G.; Kennard, C. H. L. *Inorg. Chim. Acta* **1984**, 63.

[37] Addison, A. W.; Rao, T. N.; Reedijk, J; Van Rijn, J.; Verschoor; G. C. *J. Chem. Soc., Chem., Dalton Trans.* **1984**, 1349.

[38] (a) Mabbs, F. E.; Collison, D. *Electron Paramagnetic Resonance of d Transition Metal Compounds*; Elsevier: Amsterdam, 1992; p 974, (b) p 90.

Table 5. Selected Bond Distances (Å) and Angles (deg) of *catena*-Poly[[bis(μ-diphenylacetato-*O*:*O*′)dicopper](μ_3-diphenylacetato-1-*O*:2-*O*′:1′-*O*′)(μ_3-diphenylacetato-1-*O*:2-*O*′:2′-*O*′)], **2**[a]

Cu(1)−O(100)	1.952(13)	C(202)−C(203)	1.43(3)
Cu(1)−O(200)	1.936(11)	C(203)−C(210)	1.54(2)
Cu(1)−Cu(1)a	2.594(4)	C(203)−C(220)	1.51(2)
Cu(1)−O(101)a	1.948(13)	O(201)−C(202)	1.34(2)
Cu(1)−O(201)a	1.955(13)	C(103)−C(110)	1.507(14)
Cu(1)−O(200)b	2.323(11)	C(110)−C(111)	1.392(15)
O(100)−C(102)	1.26(2)	C(102)−C(103)	1.52(2)
O(101)−C(102)	1.24(3)	C(103)−C(120)	1.51(2)
O(200)−C(202)	1.29(2)		

Cu(1)−O(200)−C(202)	125.9(12)	O(100)−C(102)−C(103)	115.1(16)
O(100)−Cu(1)−O(200)	91.2(5)	C(102)−C(103)−C(110)	116.2(11)
Cu(1)a−Cu(1)−O(100)	80.6(5)	C(110)−C(103)−C(120)	114.7(10)
O(100)−Cu(1)−O(101)a	169.1(6)	C(103)−C(110)−C(115)	116.6(12)
O(100)−Cu(1)−O(201)a	89.1(6)	Cu(1)−O(200)−Cu(1)b	106.7(5)
O(100)−Cu(1)−O(200)b	93.6(5)	Cu(1)b−O(200)−C(202)	126.8(12)
Cu(1)a−Cu(1)−O(200)	86.1(3)	Cu(1)a−O(201)−C(202)	126.0(12)
O(101)a−Cu(1)−O(200)	87.7(5)	C(103)−C(120)−C(121)	121.1(14)
O(200)−Cu(1)−O(201)a	169.8(5)	C(103)−C(120)−C(125)	122.9(15)
O(200)−Cu(1)−O(200)b	73.3(4)	O(200)−C(202)−O(201)	118.0(17)
Cu(1)a−Cu(1)−O(101)a	88.5(5)	O(200)−C(202)−C(203)	125.4(18)
Cu(1)a−Cu(1)−O(201)a	83.9(4)	O(201)−C(202)−C(203)	116.6(17)
Cu(1)a−Cu(1)−O(200)b	158.6(3)	C(202)−C(203)−C(210)	118.5(15)
O(101)a−Cu(1)−O(201)a	90.2(6)	C(202)−C(203)−C(220)	112.1(15)
O(101)a−Cu(1)−O(200)b	96.5(5)	C(210)−C(203)−C(220)	109.2(13)
O(200)b−Cu(1)−O(201)a	116.9(4)	C(203)−C(210)−C(211)	116.2(17)
Cu(1)−O(100)−C(102)	126.5(13)	C(203)−C(210)−C(215)	124.7(16)
Cu(1)a−O(101)−C(102)	118.2(13)	C(203)−C(220)−C(221)	117.7(15)
O(100)−C(102)−O(101)	126.0(18)	O(101)−C(102)−C(103)	118.8(16)
C(102)−C(103)−C(120)	109.2(11)	C(103)−C(110)−C(111)	122.7(9)
C(203)−C(220)−C(225)	123.4(15)		

[a] Symmetry code: a = −*x*, −*y*, −*z*; b = −*x*, 1/−*y*, −*z*.

$$\chi_\mathrm{m} = (1 - p)\frac{N\beta^2 g^2}{3\mathrm{k}T}\,\frac{1}{3 + \exp(-2J/\mathrm{k}T)} + \chi_p p \qquad (2)$$

$$\chi_\mathrm{p} = \frac{N\beta^2 g^2}{3\mathrm{k}T}S(\mathrm{S} + 1) \qquad (3)$$

Although in cases of so-called short H bonds,[39] with O⋯O distances of approximately 2.4 Å, magnetic exchange has been reported, this is not expected to be the case with the longer bifurcated H bonds of **1**. Furthermore, little unpaired electron density is expected in the d_{z^2} orbital, since the $d_{x^2-y^2}$ and d_{z^2} orbitals are orthogonal as is generally the case for dinuclear square planar based Cu(II) carboxylates. The magnetic parameters calculated are listed in Table 6.

For structure **1** the $-2J$ value was calculated at 242 cm^{-1} (g = 2.15, obtained from EPR measurements); this is quite small compared to values of 280−330 cm^{-1} generally observed for dinuclear copper(II) carboxylates;[14b,40] in fact, it is the smallest value measured for dinuclear copper carboxylates with oxygen-donor ligands at the axial position and no electron-withdrawing carboxylate R groups (i.e., haloalkyl). Although copper(II) carboxylates exhibit the shortest Cu⋯Cu distances known, the $-2J$ value is known to be relatively insensitive to this factor.[41] The main aspect which determines the magnitude of the antiferromagnetic interaction is the electronic structure of the bridging O−C−O-moiety. Very important herein is the bending of the Cu−O−C−O−Cu bridge (ϕ_bend), the dihedral angle between the Cu−O−O−Cu and the carboxyl moiety, which would lead to a decrease in $-2J$ due to reduced overlap of the Cu $d_{x^2-y^2}$ orbital and the $2p_x$ carboxylate oxygen orbital in the symmetric HOMO.[42] This factor may contribute significantly in the case of **1**, since this angle amounts to 4.0(3)°, and this angle is in the range 7−11° in structures where the $-2J$ value is decreased considerably for this reason.[42] In general the $-2J$ value increases as the apical ligands become stronger electron donors.[14] Contrary to this, hydrogen bonding involving the ethanolic oxygen is expected to increase the electron donor capacity of the ethanol, and since also the apical Cu⋯O distance is not unusual, the significantly smaller $-2J$ value must thus be due to the smaller donor capacity of carboxylate oxygens at the equatorial positions as a result of H bonding. This is a quite reasonable explanation, since all carboxylate bridges are involved in hydrogen bonding. This is in accordance with correlations found between the pK_a and $-2J$ values by some authors;[14,43] indeed smallest $-2J$ values were observed with copper carboxylates with electron-withdrawing R groups.[20]

For **2** the $-2J$ value is 321 cm^{-1} (g = 2.14), which is in the normal range for dinuclear copper(II) carboxylates.[14b,40] It is comparable to the values for the acetone and acetonitrile adducts of copper diphenylacetate, being 303 and 330 cm^{-1}, respectively.[35] This indicates that, although the compound crystallographically is a polymer, magnetically it can be considered as a dinuclear species without magnetic interdimer interactions. The $-2J$ value of **2** differs considerably from the literature values of 360 and 363 cm^{-1} determined for anhydrous copper(II) diphenylacetate.[40,44] Regarding our data for three analogous compounds, the latter numbers seem to be too large.

The powder EPR spectra at 77 K exhibit well-resolved resonance bands typical for randomly oriented triplet states with

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(39) See, for example: (a) Jones, D. J.; Roziere, J.; Lehmann, M. S. *J. Chem. Soc., Dalton Trans.* **1986**, 651. (b) Ortega, R. B.; Tapscott, R. E.; Campana, C. F. *Inorg. Chem.* **1982**, *21*, 2517. (c) Ribas, J.; Monfort, M.; Costa, R.; Solans, X. *Inorg. Chem.* **1993**, *32*, 695.

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Table 6. Magnetic Parameters, with Esd's

compd	$-2J$ (cm^{-1})	g_x	g_y	g_z	$A_{\|\|}$ (cm^{-1})	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})
1	242(10)	2.03(1)	2.07(1)	2.35(1)	0.064(2)	0.316(15)	0.0050(10)
2	321(16)	2.07(1)	2.02(1)	2.33(1)	*a*	0.347(10)	0.0034(5)

[a] Not determined due to poor resolution.

axial symmetry and have been interpreted in terms of the effective spin Hamiltonian:

$$\hat{H} = g\beta H\hat{S} + D\hat{S}_{z^2} + E(\hat{S}_{x^2} - \hat{S}_{y^2}) - (2/3)D \qquad (4)$$

where D and E are the zero-field splitting parameters (axial and rhombic, respectively) and the other symbols have their usual meanings.[14] The values for $|D|$ calculated are 0.316(15) and 0.347(10) cm^{-1}, respectively for **1** and **2**, and exceed the microwave quantum applied in X-band EPR spectroscopy (9 GHz). Thus only four of the six allowed $\Delta m_s = 1$ transitions can be observed; for this reason also Q-band EPR spectra (35 GHz) were measured, in which case all allowed $\Delta m_s = 1$, and forbidden $\Delta m_s = 2$ transitions are observed. Remarkable is the observed axial anisotropy in the half-field signal ($H_{\min}$) in the Q-band spectra. The high resolution of the X-band spectra allows the determination of the small rhombic ZFS parameter $|E|$ and the axial hyperfine coupling parameter $A_{||}$ from the unusually well-resolved seven-line patterns on H_{Z^1} and H_{Z^2} of **1**. The value of $A_{||}$ of structure **1** is indeed approximately half the usual value for Cu(II) ions in a square pyramidal CuO_5 environment.[38b] The resolution of the EPR spectra shows a large temperature dependence; at higher temperatures considerable broadening of the lines due to exchange interaction between excited triplet states is observed. It is quite likely that this is due to the polymeric chain structure, as suggested by Mrozinski *et al.*[43]

The rhombicity of the spectra indicates an inequivalence of the carboxylate anions in the magnetic *xy*-plane of Cu in both compounds. Assuming that the magnetic axes do not differ much from the geometric axes, this confirms the geometric inequivalences in the *x*- and *y*-directions observed in the X-ray and IR data of both compounds.

Concluding Remarks

The retainment of paddle-wheel dinuclear units of copper(II) carboxylates in solutions is known from literature[45] and has been confirmed with EPR.[2] This type of structure may thus be the catalytically active species in the copper(II)-catalyzed oxidation of carboxylic acids. In fact, the rate-determining step in oxidative decarboxylation of copper(II) carboxylates in carboxylic acids is known to be the inner-sphere electron transfer from a coordinated carboxylate ligand to a copper(II) ion.[1] This electron transfer then occurs in the paddle-wheel structure, the second copper ion facilitating the electron transfer. In carboxylic acid solution the ligand at the apex will generally be a carboxylic acid coordinated as in $[Cu_2(OAc)_4(AcOH)_2]$,[20] but possibly a second-order reaction between two dinuclear paddle-wheel units yields intermediate tetramers stacked as in **2**; these tetramers probably account for the large variation in reaction orders in [Cu] in the DOW phenol reaction, observed by different authors.[12] Further work will deal with a search for the mechanism of the copper-catalyzed oxidative decarboxylation.

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Supporting Information Available: Tables listing crystal data and details of the structure determination, atomic coordinates and equivalent isotropic thermal parameters of all atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and unit cell and packing diagrams (22 pages). Ordering information is given on any current masthead page.

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