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Complexes of copper(II) formate with 2-(phenylamino)pyridine and 2-(methylamino)pyridine: New copper formato *paddle-wheel* compounds

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Abstract

The derivatives of $Cu(HCOO)_2 \cdot 4H_2O$ with 2-(phenylamino)pyridine and 2-(methylamino)pyridine, $[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**), $[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**) and $Cu(HCOO)_2(MeNHpy)_2$ (**3**), have been synthesized and characterized. Compounds **1** and **2** show the *paddle-wheel* structure of $[Cu_2(\mu\text{-}HCOO)_4L_2]$, with four *syn–syn* bridging formato groups and two molecules of PhNHpy or MeNHpy coordinated to the axial positions, respectively. Intramolecular hydrogen bonds are formed in both cases: two in each dimer of **1** and four in the dimer of compound **2**. The dimer units are oriented in two different directions. Dimers with the same orientation form rows along the "*c*" and the "*a*" axis in compounds **1** and **2**, respectively, with a π–π stacking of the pyridine rings. In compound **1**, an intercalation of the phenyl rings of contiguous rows of dimers gives rise to a succession of phenyl rings at a distance of 4.38 Å and an angle of 30.44° between alternate rings. They are antiferromagnetic. Signals of the triplet state are observed in their EPR spectra and the zero-field splitting parameter has been determined. Compound **3** obeys the Curie–Weiss law and the magnetic results indicate the absence of magnetic interaction between Cu(II) atoms.

Keywords: Copper; Hydrogen bonds; Dimers; Formate; Antiferromagnetism; EPR

1. Introduction

The dinuclear copper acetate dihydrate $[Cu_2(\mu\text{-}OAc)_4(H_2O)_2]$ and the adducts $[Cu_2(\mu\text{-}OAc)_4L_2]$ with different ligands in the axial positions are among the most studied dinuclear compounds of Cu(II) in their structural and magnetic aspects [1–6]. On the contrary, few compounds containing the *paddle-wheel* dinuclear group $[Cu_2(\mu\text{-}HCOO)_4]$, with four *syn–syn* formate groups are known. This structure is present in some complexes: molecular dimers as $[Cu_2(\mu\text{-}HCOO)_4(urea)_2]$ [7], $[Cu_2(\mu\text{-}HCOO)_4(dmso)_2]$ [8] and $[Cu_2(\mu\text{-}HCOO)_4(dmf)_2]$ [9], chains of dimers as …dioxane–$[Cu_2(\mu\text{-}HCOO)_4]$–dioxane–$[Cu_2(\mu\text{-}HCOO)_4]$–… [10] and dimers or chains of dimers with pyrazine and different isomers of dimethylpyrazine [11].

The copper(II) formate tetrahydrate, $Cu(HCOO)_2 \cdot 4H_2O$, does not have the dinuclear unit $[Cu_2(\mu\text{-}HCOO)_4]$, similar to that of the copper(II) acetate. It consists of chains …–$Cu(H_2O)_2$–$(\mu\text{-}HCOO)_2$–$Cu(H_2O)_2$–$(\mu\text{-}HCOO)_2$–…, with *anti–anti* bridging $HCOO^-$, linked by hydrogen bonds through additional water molecules [12].

In previous papers, we reported the study of the complexes with 2-(phenylamino)pyridine and 2-(methylamino)pyridine, $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ [13] and $[Cu_2(\mu\text{-}OAc)_4(MeNHpy)_2]$ [14], respectively. In both cases, the

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structural and magnetic results were similar to those of the copper acetate hydrate. The ligands are coordinated in the axial positions of the dimer through the pyridinic nitrogen atom. Two intramolecular hydrogen bonds are formed between each ligand and an oxygen atom of one acetate group.

In this paper, we describe the interaction between Cu-$(HCOO)_2 \cdot 4H_2O$ and the ligands 2-(phenylamino)pyridine (PhNHpy), and 2-(methylamino)pyridine (MeNHpy), with the purpose of observing the difference between OAc^- and $HCOO^-$ and the influence of the substitution of Ph for Me in the molecule of the additional ligand. Magnetic and EPR results are also described.

2. Experimental

2.1. Synthesis of $[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**)

A solution of $Cu(HCOO)_2 \cdot 4H_2O$ (225.6 mg, 1 mmol) in MeOH (20 ml) was added to a solution of PhNHpy (851 mg, 5 mmol) in MeOH (10 ml). The green solution was stirred during 24 h. The formed precipitate was filtered off, washed with MeOH/Et_2O (1:1) and Et_2O and dried by air suction and in vacuo over $CaCl_2$. Yield: 184 mg (56%). *Anal.* Calc. for $C_{26}Cu_2H_{24}N_4O_8$ (647.59): C, 48.22; H, 3.74; N, 8.65. Found: C, 47.91; H, 3.65; N, 8.70%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the complex in CH_2Cl_2.

2.2. Synthesis of $[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**)

To a solution of 2-(methylylamino)pyridine (0.216 ml, 2 mmol) in MeCN (20 ml), solid $Cu(HCOO)_2 \cdot 4H_2O$ (450 mg, 2 mmol) was added. The mixture was stirred during 15 h and the remaining solid filtered off. The solution was carried next to dryness in the rotavapour. The residue was collected with CCl_4. The solid was filtered off, washed with Et_2O and dried by air suction and in vacuo over $CaCl_2$. Yield: 260 mg (49%). *Anal.* Calc. for $C_{16}Cu_2H_{20}N_4O_8$ (523.44): C, 36.71; H, 3.85; N, 10.70. Found: C, 36.87; H, 3.83; N, 10.75%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the complex in CH_2Cl_2.

2.3. Synthesis of $Cu(HCOO)_2(MeNHpy)_2$ (**3**)

To a solution of 2-(methylylamino)pyridine (1 ml, 10 mmol) in MeCN (25 ml), solid $Cu(HCOO)_2 \cdot 4H_2O$ (450 mg, 2 mmol) was added. The mixture was stirred during 4 h and the solution was carried next to dryness in the rotavapour. The residue was collected with CCl_4. The solid was filtered off, washed with a minimum volume of MeCN and with Et_2O, and dried by air suction and in vacuo over $CaCl_2$. Yield: 441 mg (60%). *Anal.* Calc. for $C_{14}CuH_{18}N_4O_4$ (369.87): C, 45.46; H, 4.91; N, 15.15. Found: C, 45.33; H, 4.89; N, 15.20%.

2.4. Measurements

C, H and N were analysed in a Leco 932-CHNS Elemental Analyser. IR spectra were recorded on a Nicolet FT-IR 510 spectrometer in the range 4000–400 cm^{-1} using KBr pellets. Electronic spectra were recorded on a Shimadzu UV-265 FW spectrophotometer. Magnetic measurements were carried out with a magnetometer SQUID MPMSXL of Quantum Design. Diamagnetic corrections were applied [2]. The EPR spectra were recorded on a Bruker ESP 300 spectrometer with a Bruker ER 035 M gaussmeter and HP 5325 frequency counter.

2.5. X-ray crystallographic study

Data collection was carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), operating at 50 kV and 30 mA, in the φ and ω scanning mode. The data were collected over a hemisphere of the reciprocal space by a combination of three exposure sets. Each exposure covered 0.3 in ω. The cell parameters were determined and refined by a least-squares fit of all reflections. The first 50 frames were recollected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A summary of the fundamental crystal and refinement data are given in Table 1.

Table 1
Crystallographic and structure refinement data for compounds **1** and **2**

Compound	$[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**)	$[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**)
Empirical formula	$C_{13}H_{12}N_2O_4Cu$	$C_8H_{10}N_2O_4Cu$
Formula weight	323.79	261.72
T (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	15.154(2)	7.772(1)
b (Å)	11.156(2)	13.408(2)
c (Å)	7.888(1)	10.279(2)
β (°)	92.970(3)	107.806(3)
V (Å^3)	1331.8(3)	1019.8(3)
Z	4	4
D_{calc} (g cm^{-3})	1.615	1.705
Absorption coefficient μ (mm^{-1})	1.654	2.137
$F(000)$	660	532
θ Range for data collection (°)	1.35–25.00	2.58–25.00
Index ranges	(−17, −13, −9) to (17, 11, 9)	(−9, −10, −12) to (9, 15, 11)
Reflections collected	6773	5248
Independent reflections (R_{int})	2332 (0.0721)	1796 (0.0672)
Completeness to $\theta = 25.00°$ (%)	99.7	99.8
Data/restraints/parameters	2332/0/181	1796/0/137
Goodness-of-fit on F^2	0.928	0.900
Final R indices $[I > 2\sigma(I)]$ (observed reflections)	R_1[a] $= 0.0453$ (1414)	$R_1 = 0.0426$ (1043)
R indices (all data)	wR_2[b] $= 0.1158$	$wR_2 = 0.1088$

[a] $\sum[|F_o| - |F_c|]/\sum|F_o|$.

[b] $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Both structures were solved by direct methods and refined by full-matrix least-square procedures on F^2 [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms, except H2, bonded to the nitrogen atom, which has been located in a Fourier synthesis included and their coordinates fixed. The largest peaks and holes in the final difference map were 0.626 and -0.457 e Å^{-3} and 0.480 and -0.394 e Å^{-3} for **1** and **2**, respectively.

3. Results and discussion

By the reaction of $Cu(HCOO)_2 \cdot 4H_2O$ with 2-(phenylamino)pyridine in 1:5 proportion, the dimer $[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**) was obtained and with 2-(methylylamino)pyridine the dimer $[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**) and the complex of composition $Cu(HCOO)_2(PhNHpy)_2$ (**3**) were obtained using 1:1 and 1:5 proportions, respectively.

3.1. Characterization

The molar conductivity values for **1**, **2** and **3** in methanol correspond to non-ionic compounds. The most significant bands in the IR spectra are those assigned to the stretching ν(N–H) at 3409, 3317 and 3300 cm^{-1} for **1**, **2**, and **3**, respectively.

The diffuse reflectance spectra show a broad d → d band centred at 730, 740 and 640 nm for **1**, **2**, and **3**, respectively. The wavelength of the absorption increases with the presence of the dimeric unit.

3.2. Crystal structure of $[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (1)

Compound **1** consists of centrosymmetric dinuclear *paddle-wheel* units in which four formato groups are bridging the two copper atoms, in a *syn–syn* disposition, and a PhNHpy ligand occupies the axial position of each copper atom, coordinated to them through the pyridine nitrogen atom. Fig. 1 shows the ORTEP view of dimer **1**, showing the atomic numbering scheme (35% probability ellipsoids). Some carbon atoms and hydrogen atoms have been ommitted for clarity; only H(2), involved in an hydrogen bond, is included. The selected interatomic distances and angles are listed in Table 2.

Table 2
Selected interatomic distances (Å) and angles (°) for compounds **1** and **2**

Compound	$[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**)	$[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**)
Interatomic distances (Å)		
Cu(1)–O(1)	1.984(3)	1.980(4)
Cu(1)–O(2)	1.963(4)	1.979(4)
Cu(1)–O(3)	1.969(3)	1.981(4)
Cu(1)–O(4)	1.971(4)	1.971(4)
Cu(1)–N(1)	2.226(4)	2.177(4)
Cu(1)···Cu(1)*	2.710(1)	2.710(1)
N(2)–H(2)	0.987	0.977
Bond angles (°)		
O(4)–Cu(1)–O(2)	166.2(2)	166.4(2)
O(4)–Cu(1)–O(1)	90.2(2)	89.1(2)
O(2)–Cu(1)–O(1)	88.7(2)	89.7(2)
O(4)–Cu(1)–O(3)	88.5(2)	89.5(2)
O(2)–Cu(1)–O(3)	89.2(2)	88.5(2)
O(1)–Cu(1)–O(3)	166.3(2)	166.4(1)
O(4)–Cu(1)–N(1)	99.2(2)	96.9(2)
O(2)–Cu(1)–N(1)	94.6(2)	96.7(2)
O(1)–Cu(1)–N(1)	98.3(1)	99.5(2)
O(3)–Cu(1)–N(1)	95.4(1)	94.2(2)
N(1)–Cu(1)–Cu(1)*	177.7(1)	177.3(1)
Torsion angles (°)		
O(1)–Cu(1)–N(1)–C(7)	−7.5(4)	−41.1(4)
O(2)–Cu(1)–N(1)–C(7)	−97.0(4)	−131.9(4)
O(3)–Cu(1)–N(1)–C(7)	173.3(4)	139.1(4)
O(4-)Cu(1)–N(1)–C(7)	84.0(4)	49.2(4)

Symmetry transformations used to generate equivalent atoms: *, $-x+1$, $-y+1$, $-z+1$.

Each copper atom lies in a square-planar pyramidal coordination, with four oxygen atoms in a plane, at an average distance of 1.971 Å; the fifth coordination position is occupied by the pyridine nitrogen, N(1), of a molecule of ligand, at 2.226(4) Å. The Cu···Cu distance is 2.710(1) Å. The trigonality index, $\tau < 0.002$, corresponds clearly to a square pyramidal coordination [16]. The angle between phenyl and pyridine rings of each ligand is of 53.7°.

The hydrogen atom, H(2), bonded to the anilinic nitrogen, N(2), is involved in an hydrogen bond to the oxygen, O(1), of a formato group (Table 3). Only two of the four formato groups are involved in the intramolecular hydrogen bonds.

The dimers are oriented in the crystal in two different directions, which form between them an angle of 17°, as is observed in Fig. 2. In each row of dimers along the *c*-axis the pyridine rings are stacked with a distance of 7.888 Å

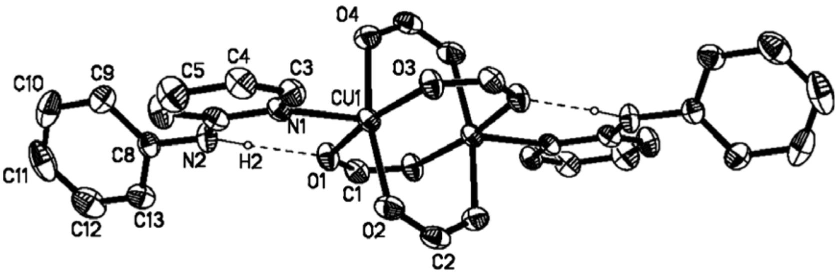

Fig. 1. ORTEP view of the dimer $[Cu_2(\mu\text{-}HCOO)_4(PhNHpy)_2]$ (**1**).

Table 3
Hydrogen bonds data for compounds **1** and **2**

Compound	N–H···O	d(N–H) (Å)	d(H···O) (Å)	d(N···O) (Å)	∠NHO (°)
$[Cu_2(\mu\text{–}HCOO)_4(PhNHpy)_2]$ (**1**)	N(2)–H(2)···O(1)	0.99	1.87	2.856(5)	172.6
$[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**)	N(2)–H(2)···O(1)	0.98	2.18	3.078(6)	152.8
	N(2)–H(2)···O(4)	0.98	2.56	3.263(6)	128.9

(c). There is an intercalation of phenyl rings of ligands of contiguous dimers rows, so that the phenyl ring centroids define a zig-zag line along the "*c*"-direction. The distance between phenyl rings centroids is 4.38 Å and the angle between alternate phenyl rings is 30.44°. The intercalation of phenyl rings makes possible a bidimensional interaction which gives rise to the formation of a sort of sheets parallel to the "*bc*"-plane (Fig. 2). These intercalations were not observed in the structure of $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ [13]. In this case, the dimers adopt a unique orientation in the crystal and are arranged in rows along the "*b*"-axis.

3.3. Crystal structure of $[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (2)

Similar to compound **1**, compound **2** consists of centrosymmetric dinuclear *paddle*-*wheel* units in which four formato groups are bridging the two copper atoms, in a *syn–syn* disposition. A molecule of MeNHpy occupies the axial position of each copper atom, coordinated to them through the pyridine nitrogen atom. Fig. 3 shows the ORTEP view of the dimer showing the atomic numbering scheme (35% probability ellipsoids). The hydrogen atoms, except H2, have been ommitted for clarity. Selected interatomic distances and angles are listed in Tables 2 and 3. The trigonality index is practically zero, $\tau < 0.0002$, and corresponds clearly to a square pyramidal coordination [16].

The hydrogen atom, H(2), bonded to the anilinic nitrogen, N(2), is involved in this case in two hydrogen bonds to the oxygen atoms O(1) and O(4) of two formato groups (Table 3). The formato groups in the dimer are involved in four intramolecular hydrogen bonds and not only in two, as in complex **1**. According to this fact, the values of the torsion angles around the N–Cu bond (Table 2) make clear that the pyridine plane bisects the O(1)Cu(1)O(4) and O(2)Cu(1)O(3) angles in complex **2**, whilst it is coplanar with the plane defined by O(1)Cu(1)O(3) in complex **1**.

The dimers are oriented in the crystal in two different modes as is observed in Fig. 4. They form rows of dimers along the *a*-axis with the pyridine rings stacked at a distance of 7.772 Å (a). The disposition of these rows gives rise to the formation of a sort of sheets parallel to "*bc*"-plane. All the dimers in a sheet have the same orientation. In the acetate complex, $[Cu_2(\mu\text{-}OAc)_4(MeNHpy)_2]$, similar rows of dimers along the "*a*"-axis are observed, but all the dimers in the crystal present the same orientation [14].

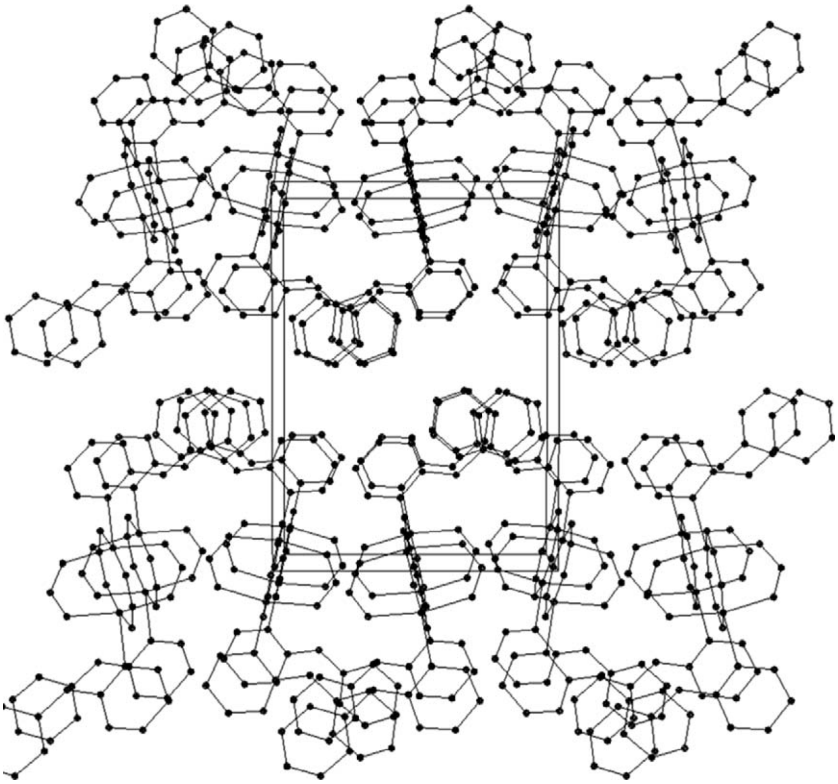

Fig. 2. View of compound **1** along the "*c*"-axis.

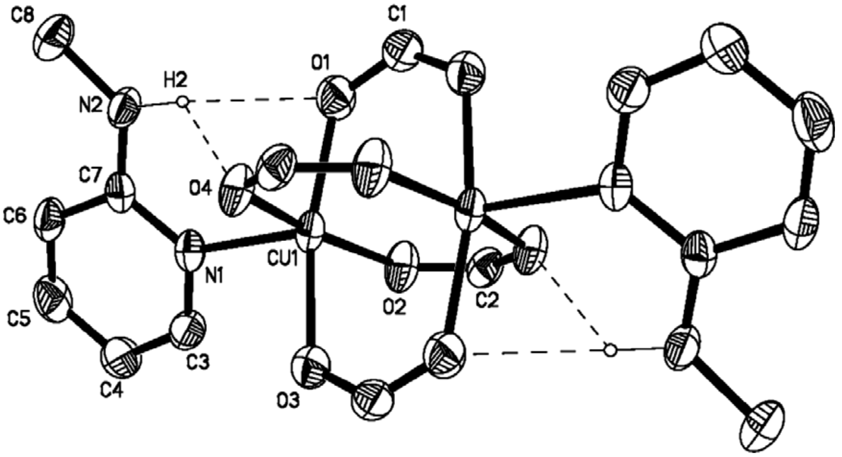

Fig. 3. ORTEP view of the dimer $[Cu_2(\mu\text{-}HCOO)_4(MeNHpy)_2]$ (**2**).

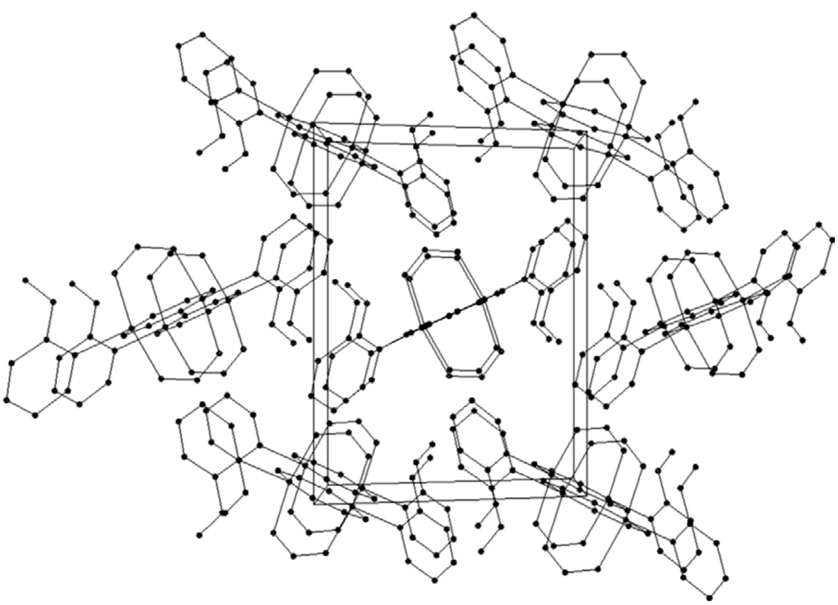

Fig. 4. Crystal structure of **2** viewed along the *a*-axis.

3.4. Magnetic and EPR results

Compounds **1** and **2** show a strong antiferromagnetism. The magnetic moments decrease from 1.12 μ_B and 1.25 μ_B at 300 K, to 0.16 μ_B and 0.17 μ_B at 5 K, for complexes **1** and **2**, respectively. The plot of $\chi_M T$, per mole of dimer, versus temperature (T) for compound **1** is shown in Fig. 5. The plot is similar for compound **2**.

The data, from 50 to 300 K, were fitted to the Bleaney–Bowers equation for a dimer with $S_1 = S_2 = 1/2$, modified by the inclusion of the fraction of monomeric impurity [17]:

$$\chi_M(2Cu) = 2\{[C e^x(1-\rho)/(1+3e^x)] + C\rho/4 + N\alpha\}$$

where $C = Ng^2\beta^2/kT$, $x = 2J/kT$, $2J$ = separation between singlet and triplet states, ρ is the fraction of monomeric impurity and $N\alpha$ is the temperature independent paramagnetism (TIP).

The results for the best fit for $g = 2.14$ (EPR result) and $N\alpha = 60 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$ are collected in Table 4.

The antiferromagnetic parameter, $2J$, is similar to those found for other complexes with the group $[Cu_2(\mu\text{-}HCOO)_4]$ and higher than those found for the analogous compounds of acetate. These results agree with the conclusions of Rodríguez-Fortea et al. in a density functional study of the exchange coupling in carboxylato-bridged dinuclear copper(II) compounds [18]: in $[Cu_2(\mu\text{-}RCOO)_4]$ groups, the antiferromagnetic interaction strength decreases with the presence of electron-with-drawing R groups. This explains the difference between $2J$ values for acetato and formato derivatives.

The powder EPR spectra of **1** and **2**, at Q band and room temperature, are similar and show the signals of the triplet state ($S = 1$) for $D \neq 0$ and $E \approx 0$. Fig. 6 corresponds to the spectrum of compound **2**. The spectra were

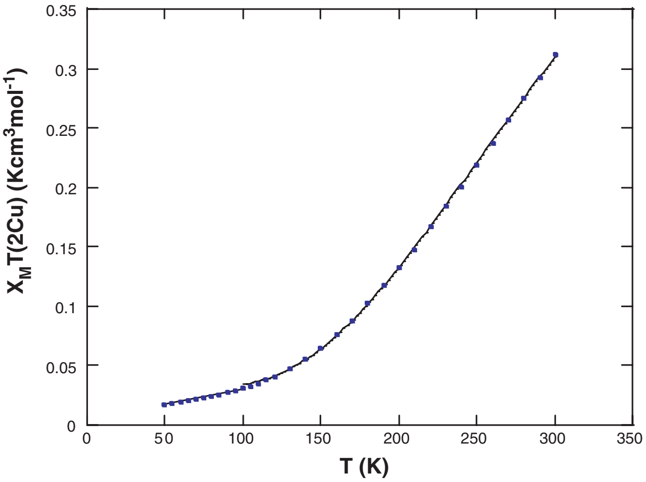

Fig. 5. Plot of $X_M T$ vs. T, per mole of dimer, for **1**.

Table 4
Magnetic results for compounds **1** and **2**

Compound	$2J$ (cm^{-1})	ρ	R	Reference
1	−455	0.024	5.31×10^{-4}	
2	−403	0.048	4.83×10^{-4}	
$[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$	−288	0.054	1.16×10^{-3}	[13]
$[Cu_2(\mu\text{-}OAc)_4(MeNHpy)_2]$	−285	0.06		[14]
$[Cu_2(\mu\text{-}HCOO)_4(urea)_2]$	−408			[7]
$[Cu_2(\mu\text{-}HCOO)_4(dmso)_2]$	−434			[8]
$[Cu_2(\mu\text{-}HCOO)_4(dmf)_2]$	−470			[9]

$R = \sum(\chi_M T_{i\mathrm{exp}} - \chi_M T_{i\mathrm{cal}})^2 / \sum(\chi_M T_{i\mathrm{exp}})^2$.

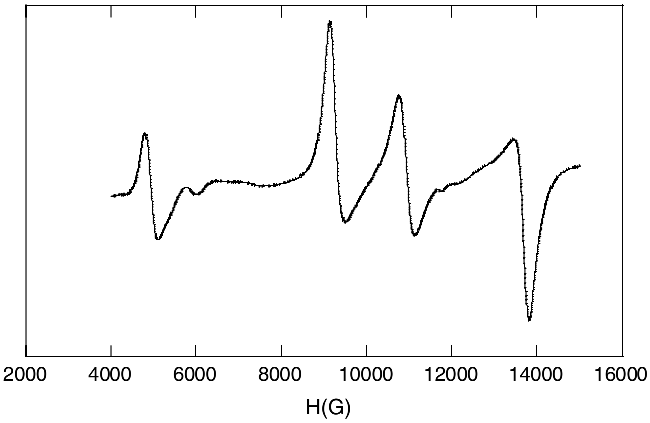

Fig. 6. EPR Q band (ν = 33.9645 GHz) spectrum of powdered compound **2**, at room temperature.

interpreted according to the Wasserman, Snyder and Yager equations [19,20], based on the Hamiltonian $H = gHS\beta + D[S_z^2 - 2/3] + E[S_x^2 - S_y^2]$, with $D \neq 0$ and $E = 0$.

For $\Delta M = \pm 1$:

$$H_{\parallel} = (g_e/g_{\parallel})(H_o - D')$$
$$H_{\perp 1} = (g_e/g_{\perp})[H_o(H_o - D')]^{1/2}$$
$$H_{\perp 2} = (g_e/g_{\perp})[H_o(H_o + D')]^{1/2}$$

For $\Delta M = \pm 2$:

$$H_{\min} = (g_e/g_{\min})[(H_o^2/4) - (D'^2/3)]^{1/2}$$
$$H_{dq} = (g_e/g_{av})[H_o^2 - D'^2/3]^{1/2}$$
$$H_o = h\nu/g_e\beta; \quad D' = D/g_e\beta$$

The experimental values of H and the calculated parameters: $g_{\parallel}$, $g_{\perp}$, g_{av} and D are collected in Table 5. The zero-field splitting parameter is, in both cases, higher than that found for the acetate complexes, $[Cu_2(\mu\text{-}OAc)_4(PhNHpy)_2]$ (0.33 cm^{-1}) [13] and $[Cu_2(\mu\text{-}OAc)_4(MeNHpy)_2]$ (0.36 cm^{-1}) [14], and similar to that of formate derivatives with pyrazine and dimethylpyrazines (0.42–0.43 cm^{-1}) [11].

For compound **3** the magnetic moment value is practically constant, from 1.84 μ_B at room temperature to 1.83 μ_B at 5 K. The fit of the experimental data to the Curie–Weiss law leads to $\theta = 0.054$ K, indicating the absence of magnetic interaction between the copper atoms. Even though the structure of **3** is unknown, the magnetic results allow to conclude that it does not include the antiferromagnetic $[Cu_2(\mu\text{-}HCOO)_4]$ group.

The powder Q band spectrum for **3** (Fig. 7), at room temperature, shows four signals. H = 10 758, 11 225, 11 502 and 11 800. They could be compatible with the existence in the structure of two different copper atoms, responsible for a triple signal (g = 2.26; 2.16; 2.06) and an isotropic signal (g = 2.11), respectively.

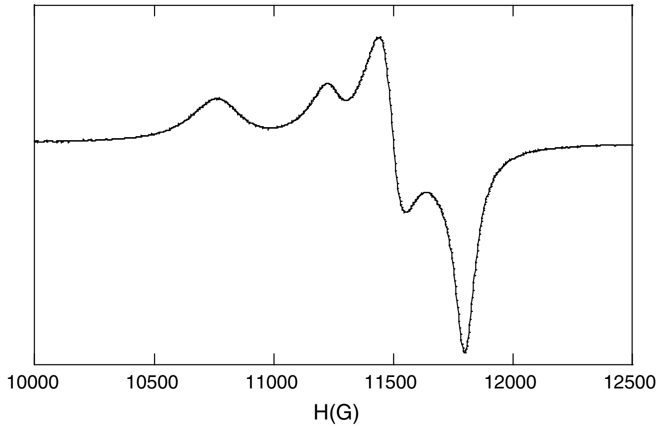

Fig. 7. EPR Q band spectrum (ν = 33.9708 GHz) of powdered **3**, at room temperature.

Table 5
EPR results for **1** and **2**

Compound	$H_{\min}$ (G)	$H_{\parallel}$ (G)	$H_{\perp 1}$ (G)	$H_{\perp 2}$ (G)	H_{dq} (G)	$g_{\parallel}$	$g_{\perp}$	g_{av}	D (cm^{-1})
1	5000	6850	9200	13 870	10 980	2.27	2.06	2.14	0.44
2	4970	6550	9160	13 850	10 990	2.26	2.07	2.14	0.44

4. Supplementary material

CCDC No. 289007 and CCDC No. 289008 contain the supplementary crystallographic data for **1** and **2**, respectively. 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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