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Discrepancy between the structural and magnetic dimensionality in the (μ-terephthalato)bis[(diethylenetriamine)Cu(II)]perchlorate complex

Evangelos Bakalbassis, Constantinos Tsipis*
Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, P.O.B. 135, 54006 Salonica (Greece)

Anastasios Bozopoulos
Applied Physics Laboratory, Department of Physics, Aristotle University of Thessaloniki, 54006 Salonica (Greece)

Wolfgang Dreissig
Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, 1000 Berlin 33 (F.R.G.)

Hans Hartl
Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstrasse 34–36, 1000 Berlin 33 (F.R.G.)

and **Jerzy Mrozinski**
Institute of Chemistry, University of Wroclaw, 14 F. Joliot-Curie Street, 50383 Wroclaw (Poland)

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Abstract

The crystal structure of [(dien)Cu(μ-tp)Cu(dien)]$(ClO_4)_2$, where tp is the dianion of terephthalic acid and dien is diethylenetriamine, has been determined by direct X-ray methods. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a=8.911(6)$, $b=8.002(5)$, $c=19.61(2)$ Å, $\beta=90.2(1)°$, $Z=2$ and $V=1398.3$ Å^3. Solution of the structure of a twin crystal of the compound led to final values of $R=0.069$ and $R_W=0.079$ with 174 least-squares parameters for 2263 unique reflections with $I>2\sigma(I)$. The compound is a perchlorate salt of a dicationic centrosymmetric binuclear copper(II) complex, $[(dien)Cu(\mu\text{-tp})Cu(dien)]^{2+}$ — the crystallographic inversion center being located at the center of the benzene ring of the tp bridging ligand. Within the binuclear unit the copper(II) ions are bridged by tp ligand in a bis-unidentate fashion, the coordination geometry about each Cu(II) ion is distorted octahedral; the Cu–Cu distance in each binuclear entity is 11.006(5) Å. Moreover, two Cu(II) centers of two different dimeric units are bridged by an oxygen atom of a carboxylate group. Thus, chains along the *b* direction and layers parallel to (100) are formed. The variable-temperature (4.2–290 K) magnetic susceptibility data of the complex, interpreted with a dimer law with a molecular field approximation, yielded to *J*, *g* and *zJ'* values of -3.66 cm^{-1} 2.07 and -0.03 cm^{-1}, respectively. An orbital interpretation of the coupling is proposed.

Introduction

It is now well documented that 11.25 Å is not the limit for the intramolecular magnetic interaction between two Cu(II) ions, provided that the Cu(II) atoms and the bridging ligand have the proper symmetry. Moreover, quite recently, Chaudhuri *et al.* [1] provided strong evidence that our first observation concerning the moderate strong antiferromagnetism, seen in the $[Cu_2(bipy)_2(OH_2)_2(\mu\text{-terephthalato})](ClO_4)_2$ complex [2] is correct. Hence, the mechanistic aspects of the magnetic exchange interactions of these systems — being the subject of our recent research interest [2–4] — retain their fundamental importance. Within this framework, the clear evidence for a both intrachain ferromagnetic and an interchain antiferromagnetic exchange interaction in the μ-terephthalato complexes has been recently given by us [3b], through the study of the crystal structure and magnetic behavior of the first copper(II) μ-terephthalato zigzag chain.

As a result of our continuing interest in this field, we report herein on the crystal structure and the interpretation of the magnetic behavior — in correlation with the structural data and EHMO calculations — of the two-dimensional, polymeric

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*Author to whom correspondence should be addressed.

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{[(μ-terephthalato)bis[diethylenetriamineCu(II))]}-(perchlorate) complex. The interpretation of the magnetic behavior of the complex had been previously fitted by a dimer law by Kahn and co-workers [5], and reinvestigated by us in a previous paper [3a].

Experimental

Synthesis

The dark blue single crystals, suitable for the structure and the magnetic determination, were obtained by slow evaporation from the corresponding reaction mixture which has been described in a previous paper [3a].

Anal. Calc for $Cu_2C_{16}H_{30}N_6O_{12}Cl_2$: Cu, 18.25; C, 27.59; H, 4.34; N, 12.07; O, 27.57; Cl, 10.18. Found: Cu, 18.05; C, 27.34; H, 4.45; N, 11.91; O, 27.96; Cl, 10.29%.

X-ray data collection and refinement

A first interpretation of rotation, Weissenberg and precession photographs of divers crystals led to the orthorhombic space group. However, the systematic absences ($h0l$ with $I = 2n + 1$ and $0k0$ with $k = 2n + 1$) were not relevant to this crystal system.

Precession and Weissenberg photographs showed that the $h00$ reflections only exhibited an unusual broadening. This was further substantiated on the basis of profile analyses on a STOE diffractometer. The increasing broadening and even splitting of *hkl* reflections (although this was not also the case with the 0*kl* reflections), for increasing *h* values, indicated the existence of twinned crystals, the twin plane being the (011) one. All these led to the corrected space group, $P2_1/c$.

An irregularly shaped leaflet crystal of 0.04 × 0.2 × 0.3 mm was used for intensity data collection. The sums of the $I_{hkl} + I_{h\bar{k}l}$ intensities of the two twin individuals were measured at 293 K with a STOE-diffractometer using graphite monochromated Mo Kα radiation and the $\theta/2\theta$ scan mode. Data were collected for $4 \leqslant 2\theta \leqslant 50°$ in the hemisphere with $10 \geqslant h \geqslant -10$, $-9 \leqslant k \leqslant 0$ and $0 \leqslant l \leqslant 23$. Periodical measurements of the intensities of two reflections showed that the crystal was not subject to decay. The intensities of 2475 unique reflections were measured, 212 of which having $I < 2\sigma(I)$ were considered to be unobserved. Data were corrected for Lorentz and polarization effects but not for absorption (μ(Mo Kα) = 17.85 cm^{-1}). The unit cell parameters were determined by least-squares refinement from diffractometer setting angles for 0*kl* reflections and *hkl* ones splitted into two maxima.

TABLE 1. Crystallographic data for the complex

Formula	$C_{16}H_{30}Cl_2Cu_2N_6O_{16}$
Formula weight	760.51
Space group	$P2_1/c$
a (Å)	8.911(6)
b (Å)	8.022(5)
c (Å)	19.61(2)
β (°)	90.2(1)
V (Å^3)	1398.3
Z	2
λ (Mo Kα) (Å)	0.71069
D_m (g cm^{-3})	1.647
D_c (g cm^{-3})	1.651
μ (cm^{-1})	17.85
Total no. reflections collected	2475
No. reflections with $I > 2\sigma(I)$	2263
R (%)	6.9
R_w (%)	7.9

The structure was solved by direct methods — by using the MULTAN80 [6] program — and successive difference Fourier syntheses. The use of the summed intensities ($I_{hkl} + I_{h\bar{k}l}$) for the least-squares refinement [7] of the positional and anisotropic thermal parameters, yielded $R = 13.5\%$. At this point the least-squares program SFLS [8] suitable for twinned crystals was used. Full matrix least-squares refinement of positional and anisotropic thermal parameters, with isotropic extinction coefficient and a scale factor along with a factor considering the volume ratio of the two twin individuals (1:0.8), led to a much better result. A final R value of 0.069 for 172 parameters and 2263 reflections ($R = 0.078$ with the inclusion of the 212 unobserved reflections) was derived; minimizing function was $\Sigma_i w_i(|F_o| - |F_c|)^2$ with unit weights. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [9]. A final difference Fourier map showed a maximum electron density of 1.1 e Å^{-3} in the region of the Cu atom. Hydrogen atoms were not included in the calculations. General crystallographic information is given in Table 1.

Magnetic and EPR measurements

The procedure for the variable-temperature magnetic susceptibility determination and the EPR measurements have been previously described [3a].

Results and discussion

Description of the structure

Each unit cell contains two formula units (Fig. 1). The crystal structure of the complex is built up by isolated perchlorate anions and polymeric [(dien)Cu(μ-tp)Cu(dien)]$^{2+}$ dications. Each dication consists of two Cu(II) centers bridged by tp dianions, coordinated in a bis-unidentate fashion through the

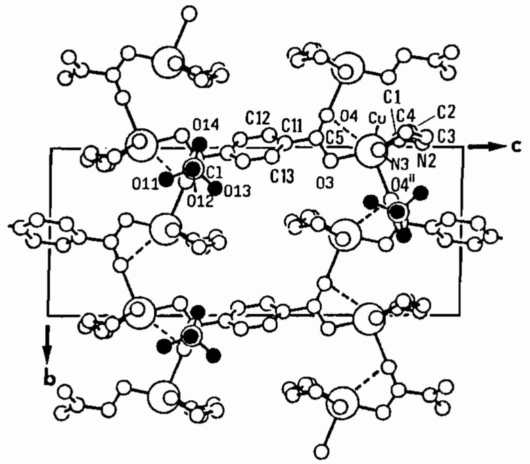


Fig. 1. Normal projection of the complex on (100).

O(3) and O(3^i) atoms (Cu–O(3) = 1.982(5) Å) of their carboxylate groups. Moreover, the second oxygen atom, O(4), of each carboxylate group bridges two Cu(II) centers (Cu–O(4^{ii}) = 2.485(5) Å) of two different dimeric units. Thus, layers parallel to (100) are formed. Moreover, the Cu–O bond of 2.485(5) Å, is the key one in joining the dimeric dications either along the *b* or approximately along the [011] direction. However, the latter chain exhibits higher symmetry as compared to the former. A crystallographic inversion center is located at the center of the benzene ring of the tp bridging ligand. The non-coordinated perchlorate ions are situated between the layers.

The Cu(II) ions are in 4+2 surroundings (Fig. 2). Each basal plane includes the three nitrogen atoms of the dien ligand and the O(3) atom of a carboxylate group of the tp dianion. The two axial positions are occupied by two O(4) atoms belonging to two different tp bridging units. Due to both the markedly different Cu–O distances (Cu–O(4) = 2.760(5) Å, Cu–O(4^{ii}) = 2.484(5) Å) and angles (O(4)–Cu–O(4^{ii}) = 151.0(2)°, O(4)–Cu–N(2) = 113.9(2)° and O(4^{ii})–Cu–N(2) = 94.4(2)°) the coordination polyhedron around Cu(II) could be described as a distorted octahedron, CuO_3N_3, with a *mer*-configuration concerning the O and N atoms. The largest deviation of the three nitrogen atoms of the dien ligand and the O(3) atom from their mean basal plane is 0.24 Å; Cu deviates by only 0.09 Å.

All Cu–N bond distances, ranging from 1.988(7) to 2.044(7) Å are comparable with the ones found in other analogous Cu(II) amine complexes [3b, 10, 11]. The Cu–O 'short' distance of 1.982(5) Å is also in line with the corresponding ones found in other analogous μ-terephthalato complexes [3b, 5]. The 'long' Cu–O distances of 2.760(5) and 2.485(5) Å are also comparable with the corresponding ones found in the above Cu(II) complexes.

Two Cu(II) ions, connected by the same tp dianion in the *c* direction, are separated by 11.006(5) Å; this Cu–Cu separation is close to the corresponding ones reported previously [3b, 5]. The shortest Cu–Cu separation in the *b* direction (2_1 axis, along the same chain) is 4.179(3) Å.

The six carbon atoms of the benzene ring of the tp ligand do not deviate less than the standard deviations of their atomic positions from their respective mean plane. The dihedral angles between the carboxylate planes and the benzene ring are 51.9(3)°. The non-coordinated perchlorate anions as usual show large thermal ellipsoids due to orientational disorder. The atomic coordinates of the non-hydrogen atoms and the main bond lengths and angles are given in Tables 2 and 3, respectively. See also 'Supplementary material'.

The spectroscopic characterization of the complex has been given in a previous paper [3a].

Magnetic data and their interpretation

Variable-temperature (4.2–295 K) magnetic susceptibility data were collected for a solid sample of the complex. See also 'Supplementary material'.

The magnetic behavior of the complex, in the form of a $\chi_M T$ versus T plot, χ_M being the corrected molar magnetic susceptibility per dimer and T the temperature, has been presented previously [3b]. At 290 K, $\chi_M T$ is equal to 0.818 cm^3 K mol^{-1}. When

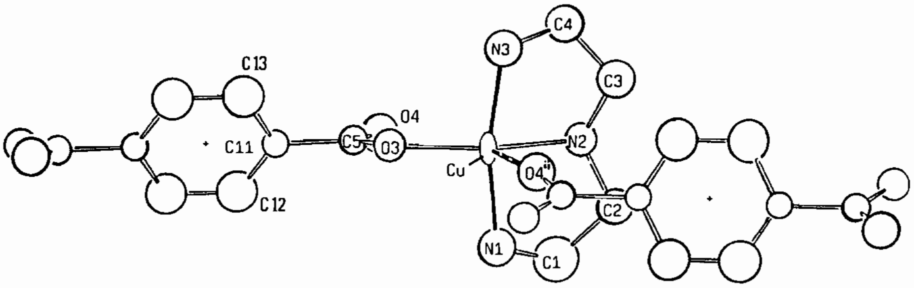


Fig. 2. The Cu(II) ions surroundings.

TABLE 2. Atomic parameters for the non-hydrogen atoms (e.s.d.s in parentheses) and their equivalent isotropic temperature factors (×100)

Atom	x/a	y/b	z/c	U_{eq} (Å^2)[a]
Cu	0.0075(1)	0.0196(1)	0.78057(4)	2.9
N(1)	−0.2206(7)	0.043(1)	0.7856(3)	5.0
N(2)	−0.0167(7)	−0.0907(7)	0.8717(3)	3.4
N(3)	0.2271(7)	0.0128(9)	0.7984(3)	4.2
C(1)	−0.2748(9)	−0.047(1)	0.8461(4)	5.5
C(2)	−0.155(1)	−0.027(1)	0.9024(4)	5.0
C(3)	0.127(1)	−0.062(1)	0.9108(4)	4.8
C(4)	0.255(1)	−0.089(1)	0.8623(4)	5.6
C(5)	−0.0010(8)	−0.0569(9)	0.6468(3)	3.0
O(3)	0.0269(6)	0.0750(6)	0.6825(2)	3.4
O(4)	−0.0312(7)	−0.1942(6)	0.6715(3)	4.3
C(11)	−0.0041(8)	−0.0279(8)	0.5703(3)	2.7
C(12)	−0.1234(8)	−0.0755(9)	0.5318(3)	3.3
C(13)	0.1238(8)	0.0499(9)	0.5393(3)	3.4
Cl	0.4996(3)	0.1181(4)	0.3475(2)	8.2
O(11)	0.470(2)	0.179(2)	0.2811(7)	22.6
O(12)	0.6524(8)	0.120(1)	0.3456(4)	9.0
O(13)	0.448(2)	0.234(2)	0.401(1)	27.8
O(14)	0.427(2)	−0.022(2)	0.3610(9)	22.4

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 3. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses[a]

(a) Bond lengths			
Cu...Cu^{ii}	4.179(3)	Cu...Cu^{i}	11.006(5)
Cu–N(1)	2.044(7)	N(1)–C(1)	1.47(1)
Cu–N(2)	2.005(6)	C(1)–C(2)	1.54(2)
Cu–N(3)	1.988(7)	C(2)–N(2)	1.47(1)
Cu–O(3)	1.982(5)	N(2)–C(3)	1.50(1)
Cu–O(4)^{ii}	2.485(5)	C(3)–C(4)	1.50(2)
Cu–O(4)	2.760(5)	C(4)–N(3)	1.51(1)
C(5)–O(3)	1.289(8)	Cl–O(11)	1.41(2)
C(5)–O(4)	1.231(9)	Cl–O(12)	1.36(1)
C(5)–C(11)	1.518(9)	Cl–O(13)	1.47(2)
C(11)–C(12)	1.36(1)	Cl–O(14)	1.32(2)
C(11)–C(13)	1.43(1)		
C(12)–C(13)	1.41(1)		
(b) Bond angles			
N(1)–Cu–N(2)	83.6(3)	O(3)–C(5)–O(4)	124.1(6)
N(1)–Cu–N(3)	166.6(3)	O(3)–C(5)–C(11)	114.4(6)
N(1)–Cu–O(3)	96.7(3)	O(4)–C(5)–C(11)	121.4(6)
N(1)–Cu–O(4)^{ii}	88.8(3)	Cu–O(4)^{ii}–Cu^{ii}	105.5(2)
N(1)–Cu–O(4)	88.5(2)	Cu–N(1)–C(1)	108.8(5)
N(2)–Cu–N(3)	86.6(3)	N(1)–C(1)–C(2)	107.3(7)
N(2)–Cu–O(3)	166.7(3)	C(1)–C(2)–N(2)	104.5(6)
N(2)–Cu–O(4)^{ii}	94.4(2)	Cu–N(2)–C(2)	107.8(5)
N(2)–Cu–O(4)	113.9(2)	Cu–N(2)–C(3)	107.1(5)
N(3)–Cu–O(3)	94.9(3)	N(2)–C(3)–C(4)	107.5(6)
N(3)–Cu–O(4)^{ii}	82.9(3)	C(3)–C(4)–N(3)	109.1(7)
N(3)–Cu–O(4)	103.8(3)	Cu–N(3)–C(4)	108.4(5)
O(3)–Cu–O(4)^{ii}	98.8(2)	O(4)–Cu–O(4)	151.0(2)
O(3)–Cu–O(4)	53.0(2)		
O–Cl–O	98.8(8)–112.7(10)	(ClO_4)	
C–C–C	118.3(6)–121.2(6)	(C_6-Ring)	

[a] Symmetry codes: (i) $-x$, $-y$, $1-z$; (ii) $-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$.

the system cools down from room temperature, $\chi_M T$ decreases slightly and reaches a value of 0.756 cm^3 K mol^{-1} at *c*. 20 K, where upon it decreases again down to a value of 0.522 cm^3 K mol^{-1} at 4.2 K. Qualitatively, the interpretation of these magnetic properties is as follows. Deviations from Curie behavior, not inconsistent with weak intramolecular AF interactions are observed for the high-temperature range; still a very weak intermolecular AF interaction occurs below 20 K. Moreover, the absence of a clear sharp maximum of $\chi_M T$ (and χ_M) in the low-temperature range accounts well for the absence of a three dimensional AF ordering [12].

In an attempt to probe deeper into the magnetic superexchange interactions, the magnetic behavior of the complex is closely combined with its molecular and crystal structure. As was shown in the previous section, the complex has an unusual, very interesting crystal structure, built from magnetic planes parallel to (100) separated by the non-coordinated perchlorate anions. A careful examination of the magnetic planes of the complex clearly demonstrates that, despite the identical coordination sphere [CuN_3O_3] of the Cu(II) magnetic centers these latter are mutually coupled in two ways: the first coupling is the one through the bridging terephthalato dianions along the *c* direction (with a Cu–Cu separation of *c*. 11 Å), whereas the second is the one along the *b* direction via the O(4) carboxylic atoms (a Cu–Cu separation of *c*. 4.179 Å). However, due to both the long Cu–O(4) separation (2.48 Å) and the nature of the magnetic orbital centered on each Cu(II), pointing mainly toward its four nearest-neighbor N(1), N(2), N(3) and O(3) atoms, the spin density on O(4) should be very low and/or zero. Consequently, although the crystal structure suggests a one- and/or a two-dimensional structure, the compound should behave magnetically as a chain of weakly interacting binuclear units. In other words, the magnetic dimensionality is not the structural dimensionality. Therefore, the experimental data from room temperature down to 4.2 K were least-squares fitted with a dimer law with a molecular field approximation [13] in order to account for the weak interdimer interactions of the complex. In the frame of this approximation (with the interaction Hamiltonian: $\mathscr{H} = -J\hat{S}_1\hat{S}_2$), values of -3.41 cm^{-1}, 2.07 and -0.03 cm^{-1} were obtained for *J*, *g* and *zJ'*, respectively, with a very good *R* value of $R = 1.21 \times 10^{-4}$ (*R* is the agreement factor defined as $R = \Sigma_i[(\chi_{obs})_i - (\chi_{theor})_i]^2/\Sigma_i(\chi_{obs})_i^2$). In a three-parameter fitting with *J*, *g* and *zJ'* variables, a *J* value of -3.41 cm^{-1} was obtained along with

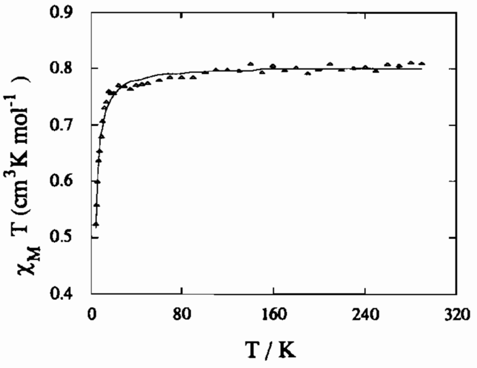


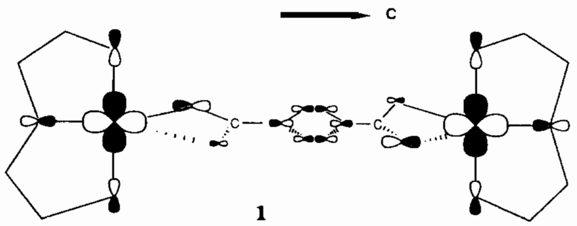
Fig. 3. Experimental (Δ) and theoretical (——) temperature dependence (290–4.2 K) of $\chi_{Cu}T$.

a theoretical *g* value almost identical to the experimental one. Moreover, the very good fitting derived (see Fig. 3), accounts also well for the lack of magnetic exchange interactions between the magnetic planes of the compound.

The question asked now is as follows: is it possible to rationalize the inter- and intradimer interactions on an orbital basis? In an attempt to answer this question the experimental results discussed above are combined with the quantum-chemical results of the EHMO type in the next section.

Quantum-chemical interpretations and mechanism of superexchange interactions

It was shown in the previous sections that the copper(II) ions are in octahedral surroundings. Therefore, the unpaired electron around each Cu(II) magnetic center is described by a x^2–y^2-type magnetic orbital pointing from the metal toward the four-nearest neighbor atoms, N1, N2, N3 and O3 in the equatorial plane. This magnetic orbital overlaps the corresponding x^2–y^2-type magnetic orbital centered on Cu(II), through the terephthalato bridge. The weak σ-type orbital 'channels', seen in the SOMO1 (**1**) of the aforementioned hypothetical binuclear entity ('binuclear entity along the *c* direction') could account well for the intramolecular magnetic exchange interactions of the complex.



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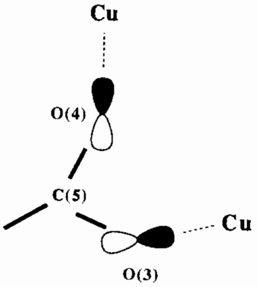
The interaction between the two Cu(II) ions through the O(3)–C(5)–O(4) bridge, is examined next. The ability of the carboxylate group to propagate the exchange interaction between two Cu(II) ions separated by more than 5 Å has well been demonstrated in the case of (μ-oxalato)copper(II) compounds [14, 15]. As a matter of fact, a 2*J*/*k* value of −558 K was found [14] in [(tmen(H_2O)Cu-(C_2O_4)Cu(H_2O)tmen](ClO_4)$_2$, thanks to the *syn–syn* configuration [16] of its carboxylato bridge. However, due to the *syn–anti* configuration of its carboxylato bridge, the [Cu(NH_3)$_2$(CH_3COO)Br] polymeric complex exhibited [17] a *J*/*k* value of −4.3 K. The problem at hand is then this: how strong would the exchange through the O(3)–C(5)–O(4) carboxylate bridge be?

Based upon the results of EHMO calculations, carried out with the crystal data available for our complex, the unpaired electron around each Cu(II) magnetic center is mainly described by a magnetic orbital of x^2–y^2-type pointing toward the four nearest neighbors (O(3), N(1), N(2) and N(3) atoms) in the equatorial plane. That, along with the large Cu–O(4) separation and the fact that the admixture of a z^2-type orbital points toward the O(4)^{ii} atom in the apical position, rules out a strong interaction through the O(4) atom. Moreover, along the chain structure, the magnitude of the antiferromagnetic interaction is governed by the overlap of two magnetic orbitals of this kind centered on the nearest-neighbor Cu(II) ions [18]. Owing to the symmetry of the Cu–O(3)–C(5)–O(4)–Cu bridging network, exhibiting a *syn–anti* carboxylato-bridge configuration (see **2**), the contributions of the 2p orbitals of the O(3) and O(4), belonging to the magnetic orbitals centered on the two successive Cu atoms along the *b* direction, are unfavorably oriented to give a strong overlap, accounting also for the very weak intermolecular antiferromagnetism of the compound.



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Supplementary material

Tables of anisotropic temperature coefficients U_{ij} for the non-hydrogen atoms, structure factor listing and the least-squares planes with displacements of selected atoms from the plane, as well as Tables of experimental and calculated magnetic susceptibility data, are available from the authors on request.

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