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New copper(II) clusters and coordination polymers from the amalgamation of azide/benzoate/di-2-pyridyl ketone ligands

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ABSTRACT

The employment of the di-2-pyridyl ketone $[(py)_2CO]/PhCO_2^-/N_3^-$ ligand combination in copper(II) chemistry has provided access to the hexanuclear cluster $[Cu_6(O_2CPh)_4(N_3)_2\{(py)_2CO_2\}_2\{(py)_2C(OH)O\}_2]$ (**1**), and the coordination polymers $[Cu_4(O_2CPh)_2(N_3)_4\{(py)_2C(OMe)O\}_2]_n$ (**2**) and $[Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}]_n$ (**3**). The structural type (cluster versus polymer) depends on the reaction solvent. Complex **1** has a $[Cu^{II}_6(\mu_3\text{-}OR'')_2(\mu\text{-}OR'')_4]^{6+}$ core based on a central defective cubane unit and two additional Cu^{II} atoms across the missing edges. Complex **2** consists of zig-zag chains and complex **3** consists of extended 2D networks that adopt the herringbone architecture which is not based on T-shaped nodes. Cluster **1** is antiferromagnetically coupled with an $S = 0$ ground state.

1. Introduction

Two classes of compounds which currently attract the intense interest of inorganic chemists are molecular clusters [1] and coordination polymers [2]. There are many reasons for this, not least of which is the aesthetic beauty of their structures. Moreover, such compounds exhibit interesting and often fascinating physical properties and have a variety of potential applications. For example, few 3d-metal clusters function as nanoscale magnetic particles (the so named single-molecule magnets, SMMs [3]), while the current great interest in the synthesis of new coordination polymers stems from their potential applications [4] in fields and areas, such as catalysis, electrical conductivity, luminescence, non-linear optics, magnetism, medicine, gas storage, anion separation and ion exchange.

An important synthetic parameter for the preparation of molecular clusters and coordination polymers with interesting structures and properties is the appropriate selection of the ligand(s). A modern synthetic trend is the use of two or even three ligands in the reaction systems (combination of ligands or 'ligand blends'). The loss of a degree of the synthetic control [5] is more than compensated for by the vast diversity of structural types using the combination of ligands. The present report represents efforts along this line in copper(II) chemistry.

We have been exploring the ternary $(py)_2CO/R'CO_2^-/N_3^-$ ligand combination in 3d-metal chemistry as a source to high-nuclearity clusters [$(py)_2CO$ is di-2-pyridyl ketone, see Scheme 1]. Studies with Mn [6], Fe [7], Co [8] and Ni [9] were fruitful and led to a plethora of high-spin molecules, some of which are SMMs [6,7]. We have thus decided to extend the investigation of this general ligand combination in copper(II) chemistry. We herein report that the $Cu^{II}/(py)_2CO/PhCO_2^-/N_3^-$ reaction system leads to remarkable clusters and coordination polymers.

The highly activated carbonyl group of $(py)_2CO$ makes this ligand special [10]. Water and alcohols (ROH), amongst other [11] nucleophiles, have been shown to add to the carbonyl group *upon coordination* of the carbonyl oxygen and/or the 2-pyridyl rings forming the ligands $(py)_2C(OH)_2$ [the *gem*-diol form of $(py)_2CO$] and $(py)_2C(OR)(OH)$ [the hemiacetal form of $(py)_2CO$], respectively (Scheme 1). Upon deprotonation, the latter becomes monoanionic, whereas the former can function either as mono- or dianionic depending on the reaction conditions. The great coordinative flexibility and versatility of the $(py)_2CO$-based anionic ligands [10] and the well known μ_2–μ_4 potential of the RCO_2^- and N_3^- [12] anions, prompted us to combine the three ligand systems to aim for polynuclear copper(II) complexes. Our belief was that the simultaneous employment of the three types of ligands in Cu^{II} chemistry would

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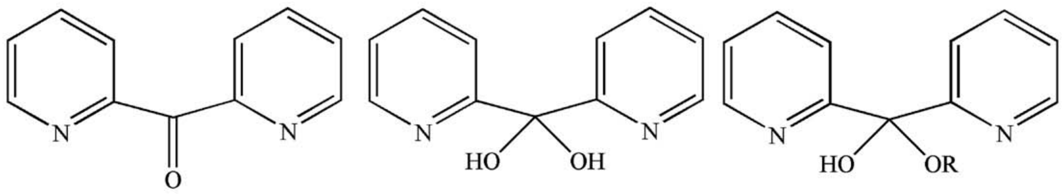


$(py)_2CO$ $(py)_2C(OH)_2$ $(py)_2C(OR)(OH)$

Scheme 1. The $(py)_2CO$-based ligands discussed in the text; note that $(py)_2C(OH)_2$ and $(py)_2C(OR)(OH)$ and their anions exist *only* in their respective metal complexes (R = Me, Et, etc.).

give an extraordinary structural flexibility in the $(py)_2CO/R'CO_2^-/N_3^-$ mixed ligand system. This has, indeed, turned out to be the case. Preliminary results of this work have been communicated [13].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. $Cu(O_2CPh)_2 \cdot 2H_2O$ was prepared as described elsewhere [14]. *Caution*! Although no such behavior was observed during the present work, azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyzer. IR spectra (4000–450 cm^{-1}) were recorded on Perkin–Elmer 16 PC and Nicolet 520 FTIR spectrometers with samples prepared as KBr pellets. Magnetic susceptibilities were measured on polycrystalline powders with a Cryogenic S600 SQUID magnetometer. Powders were pressed in a pellet to prevent preferential crystallite orientation with the magnetic field.

2.2. Compound preparation

2.2.1. $[Cu_6(O_2CPh)_4(N_3)_2\{(py)_2CO_2\}_2\{(py)_2C(OH)O\}_2] \cdot 2H_2O \cdot 4.5MeCN$ ($\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$)

Method A: To a stirred solution of $(py)_2CO$ (0.06 g, 0.30 mmol) and $LiOH \cdot H_2O$ (0.01 g, 0.30 mmol) in MeCN (20 ml) was added solid NaN_3 (0.02 g, 0.30 mmol). The mixture was stirred for 15 min and then solid $Cu(O_2CPh)_2 \cdot 2H_2O$ (0.21 g, 0.60 mmol) was added under vigorous stirring, which caused a rapid color change from blue to dark green. The resulting solution was stirred for a further 1 h, filtered, and the filtrate was layered with Et_2O (40 ml). After 10 days, X-ray quality dark-green prismatic crystals of $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$ were collected by filtration, washed with MeCN (2×5 ml) and Et_2O (2×5 ml), and dried in air. Yield 55%. The dried sample analyzed as $\mathbf{1} \cdot 2H_2O$. *Anal.* Calc. for $C_{72}H_{58}Cu_6N_{14}O_{18}$: C, 48.35; H, 3.27; N, 10.96. Found: C, 48.51; H, 3.14; N, 10.91%. Selected IR data (KBr pellet, cm^{-1}): 3428m, 2058vs, 1602s, 1562s, 1474m, 1442m, 1382vs, 1298w, 1224w, 1158w, 1126w, 1078s, 980w, 776w, 722m, 684w, 652w, 462w, 424w.

Method B: To a stirred solution of $(py)_2CO$ (0.06 g, 0.30 mmol) in MeCN (20 ml) was added solid NaN_3 (0.02 g, 0.30 mmol). The mixture was stirred for 35 min and then solid $Cu(O_2CPh)_2 \cdot 2H_2O$ (0.21 g, 0.60 mmol) was added under vigorous stirring, which caused a rapid color change from blue to dark green. The resulting solution was stirred for a further 1 h, filtered, and the filtrate was layered with Et_2O (40 ml). After 13 days, X-ray quality dark-green prismatic crystals of $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$ were collected by filtration, washed with MeCN (2×5 ml) and Et_2O (2×5 ml), and dried in air. Yield 13%. The identity of the product was confirmed by elemental analysis (C, H, N) and IR spectroscopic comparison with authentic material from Method A.

2.2.2. $[Cu_4(O_2CPh)_2(N_3)_4\{(py)_2C(OMe)O\}_2]_n$ (**2**) and $[Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}]_n$ (**3**) in a mixture

To a stirred solution of $(py)_2CO$ (0.06 g, 0.30 mmol) in MeOH (20 ml) was added solid NaN_3 (0.02 g, 0.30 mmol). The mixture was stirred for 15 min and then solid $Cu(O_2CPh)_2 \cdot 2H_2O$ (0.21 g, 0.60 mmol) was added under vigorous stirring, which caused a rapid color change from blue to dark green. The solution was stirred for a further 30 min, filtered, and the filtrate was layered with Et_2O (40 ml). After 20 days, X-ray quality dark-green plate-like crystals of **2** *and* dark-green needles of **3** were collected by filtration, washed with cold MeOH (2×5 ml) and Et_2O (2×5 ml), and dried in air. The two products were separated manually and individually identified as complexes **2** and **3** (both by single-crystal X-ray crystallography), respectively. Typical yields were ~20% (**2**) and ~10% (**3**).

2.3. Single-crystal X-ray crystallography

The crystallographic data and structure refinement details for the three complexes are summarized in Table 1. Selected crystals of $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$ ($0.30 \times 0.40 \times 0.65$ mm) and **3** ($0.05 \times 0.10 \times 0.55$ mm) were mounted in capillary, whereas a selected

Table 1
Crystallographic data for complexes $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$, **2** and **3**.

Parameter	$\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$	**2**	**3**
Formula	$C_{81}H_{71.50}Cu_6N_{18.50}O_{18}$	$C_{38}H_{32}Cu_4N_{16}O_8$	$C_{19}H_{16}Cu_2N_8O_4$
Formula weight	1973.31	1094.96	547.48
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
α (Å)	16.289(8)	21.690(10)	12.994(6)
b (Å)	17.295(8)	12.867(9)	8.630(4)
c (Å)	18.125(8)	16.810(10)	19.302(9)
α (°)	69.870(10)	90	90
β (°)	69.18(2)	114.46(2)	102.13(3)
γ (°)	73.48(2)	90	90
V (Å^3)	4404(4)	4270(4)	2116.2(17)
Z	2	4	4
ρ_{calc} (g cm^{-3})	1.488	1.703	1.718
Radiation	Mo Kα	Cu Kα	Cu Kα
λ (Å)	0.71073	1.54180	1.54180
Temperature (K)	298	298	298
μ (mm^{-1})	1.499	2.859	2.884
Data collected/ unique (R_{int})	16118/15406 (0.0205)	6410/6174 (0.0373)	3152/3044 (0.0270)
Data with $I > 2\sigma(I)$	11619	5448	2310
R_1 ($I > 2\sigma(I)$)[a]	0.0478	0.0389	0.0485
wR_2 ($I > 2\sigma(I)$)[b]	0.1253	0.1025	0.1189

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

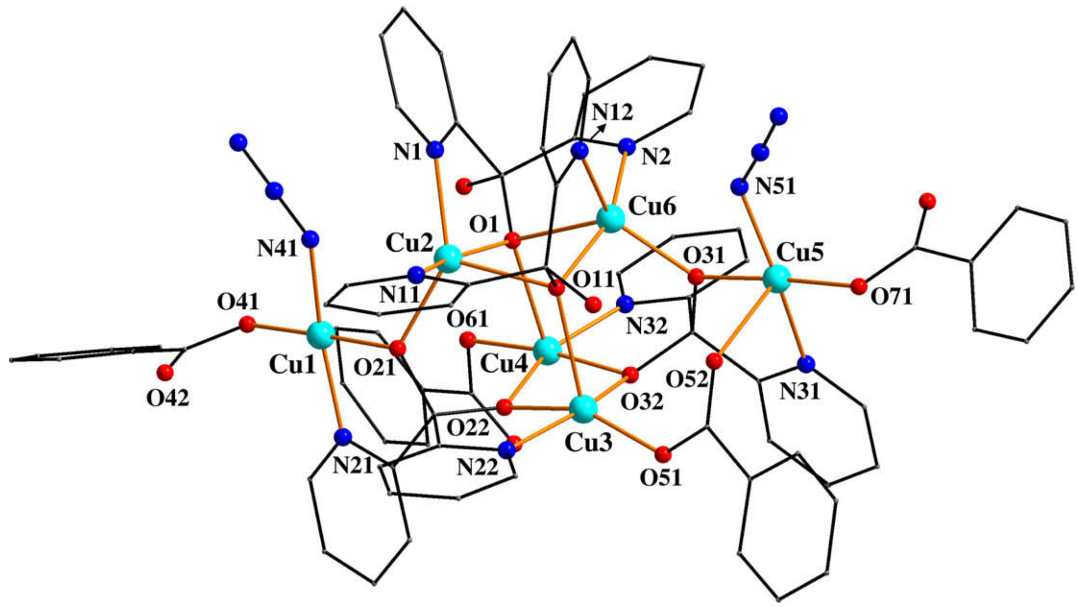


Fig. 1. Molecular structure of **1**. Color scheme: Cu^{II}, sky blue; O, red; N, dark blue; C, gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

crystal of **2** (0.05 × 0.15 × 0.25 mm) was mounted in air. Diffraction measurements for $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$ were made on a Crystal Logic Dual Goniometer diffractometer using graphite-monochromated Mo radiation. Crystallographic data for complexes **2** and **3** were collected on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic using graphite-monochromated Cu radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$ (for $\mathbf{1} \cdot 2H_2O \cdot .5MeCN$) and $22° < 2\theta < 54°$ (for **2** and **3**). Intensity data were recorded using a θ–2θ scan to a maximum 2θ value of 50° (for $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$) and 118° (for **2** and **3**). Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using CRYSTAL LOGIC software. All three structures were solved by direct methods using SHELXS-97 [15a] and refined on F^2 by full-matrix least squares techniques with SHELXL-97 [15b]. All H atoms were located by Fourier difference maps and refined isotropically, except those on the solvent molecules ($\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$) which were introduced at calculated positions as riding on bonded atoms. All non-H atoms were refined anisotropically.

3. Results and discussion

3.1. Syntheses and IR spectroscopy

The reaction of $Cu(O_2CPh)_2 \cdot 2H_2O$, $(py)_2CO$, LiOH and NaN_3 in a 2:1:1:1 molar ratio in MeCN gave a dark green solution which upon conventional workup gave cluster **1** (as the $\mathbf{1} \cdot 2H_2O \cdot 4.5MeCN$ solvate) in good yield, see the balanced equation (1). The Cu^{II}-mediated nucleophilic attack of H_2O (from the solvent and/or the starting material) is responsible for the formation of the *gem*-diolate(-1) ligand $(py)_2C(OH)O^-$ (Scheme 1) [10]. Complex **1** was also obtained in the absence of

$$6Cu(O_2CPh)_2 \cdot 2H_2O + 4(py)_2CO + 2NaN_3 + 2LiOH \xrightarrow{MeCN} \underset{\mathbf{1}}{[Cu_6(O_2CPh)_4(N_3)_2\{(py)_2CO_2\}_2\{(py)_2C(OH)O\}_2]} + 2NaO_2CPh + 2LiO_2CPh + 4PhCO_2H + 10H_2O \quad (1)$$

external OH^-s, but the yields were appreciably lower. In this case, the deprotonation of '$(py)_2C(OH)_2$' is achieved solely by the $PhCO_2^-$ groups and the formation of the cluster can be summarized by the balanced equation (2):

$$6Cu(O_2CPh)_2 \cdot 2H_2O + 4(py)_2Co + 2NaN_3 \xrightarrow{MeCN} [Cu_6(O_2CPh)_4(N_3)_2\{(py)_2CO_2\}_2\{(py)_2C(OH)O\}_2] + 2NaO_2CPh + 6PhCO_2H + 8H_2O \quad (2)$$

with the identity of **1** established, we also tried several other $Cu(O_2CPh)_2/(py)_2CO/OH^-/N_3^-$ ratios, and particularly with a large excess of N_3^- ions, to see if azido-bridged products could be obtained, but in all cases **1** was the isolated product, in varying yields.

The chemical and structural identity of the products from the $Cu(O_2CPh)_2/(py)_2CO/N_3^-$ reactions systems depends on the solvent used. Exactly the same preparative and crystallization

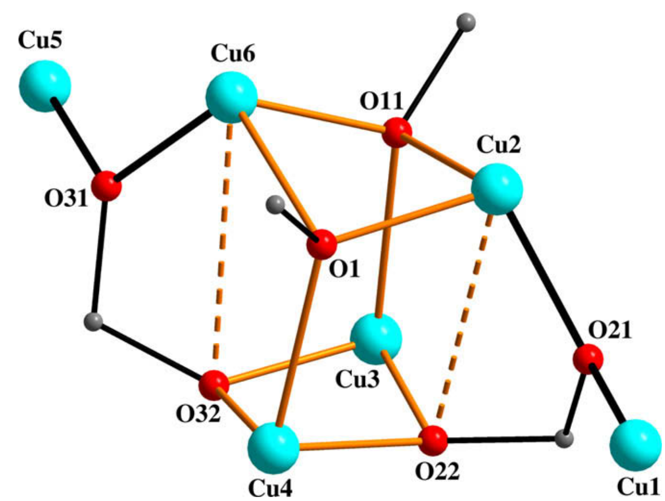


Fig. 2. The $[Cu^{II}_6(\mu_3\text{-}OR'')_2(\mu\text{-}OR'')_4]^{6+}$ core of **1**, emphasizing the central defective cubane subcore (orange thick lines). The orange dashed lines represent the two missing edges of the cubane unit. Color scheme: Cu^{II}, sky blue; O, red; C, gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

procedures as those of **1** but employing MeOH instead of MeCN, gave a mixture of dark-green plate- and needle- like crystals, crystallographically characterized as the 1D and 2D coordination polymers $[Cu_4(O_2CPh)_2(N_3)_4\{(py)_2C(OMe)O\}_2]_n$ (**2**) and $[Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}]_n$ (**3**), respectively. Although polymeric in nature, the non-optimized yields were rather low (~20% and ~10% for **2** and **3**, respectively). The formation of the complexes can be summarized by the balanced equations (3) and (4):

$$4n\mathrm{Cu(O_2CPh)_2}\cdot 2\mathrm{H_2O} + 2n(\mathrm{py})_2\mathrm{CO} + 4n\mathrm{NaN_3} + 2n\mathrm{MeOH} + 2n\mathrm{LiOH} \xrightarrow{\mathrm{MeOH}} \underset{\mathbf{2}}{[\mathrm{Cu_4(O_2CPh)_2(N_3)_4\{(py)_2C(OMe)O\}_2}]_n} + 4n\mathrm{NaO_2CPh} + 2n\mathrm{LiO_2CPh} + 10n\mathrm{H_2O} \quad (3)$$

$$2n\mathrm{Cu(O_2CPh)_2}\cdot 2\mathrm{H_2O} + n(\mathrm{py})_2\mathrm{CO} + 2n\mathrm{NaN_3} + n\mathrm{MeOH} + n\mathrm{LiOH} \xrightarrow{\mathrm{MeOH}} \underset{\mathbf{3}}{[\mathrm{Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}}]_n} + 2n\mathrm{NaO_2CPh} + n\mathrm{LiO_2CPh} + 5n\mathrm{H_2O} \quad (4)$$

Mainly due to the identical $Cu^{II} : PhCO_2^- : N_3^- : (py)_2C(OMe)O^-$ (2:1:2:1) ratio present in the two complexes, the two polymeric compounds could not be isolated separately. Changes in the crystallization procedures also failed to lead to the separate isolation of the two materials.

The IR spectra of **1**–**3** do not exhibit a band in the region of the carbonyl stretching vibration [$\nu(CO)$] as expected, with the nearest bands at ~1600 cm^{-1} assigned as a 2-pyridyl stretching vibration [this band also has a $\nu_{as}(CO_2)$ character] raised from 1582 cm^{-1} on coordination as observed earlier [16] upon complex formation involving hydration of $(py)_2CO$. In the spectrum of **1**, the strong band at 1562 cm^{-1} is also assigned [17] to $\nu_{as}(CO_2)$; the $\nu_s(CO_2)$ modes appear at 1442 and 1382 cm^{-1}. The appearance of two distinct bands for each mode reflects the presence of two different types of $PhCO_2^-$ ligands in the complex. The 1602 and 1382 cm^{-1} pair [$\Delta = \nu_{as}(CO_2) - \nu_s(CO_2) = 220$ cm^{-1}] are assigned [17] to the monodentate $PhCO_2^-$ groups, while the 1562 and 1442 cm^{-1} pair ($\Delta = 120$ cm^{-1}) to the bidentate bridging $PhCO_2^-$ group. The differ-

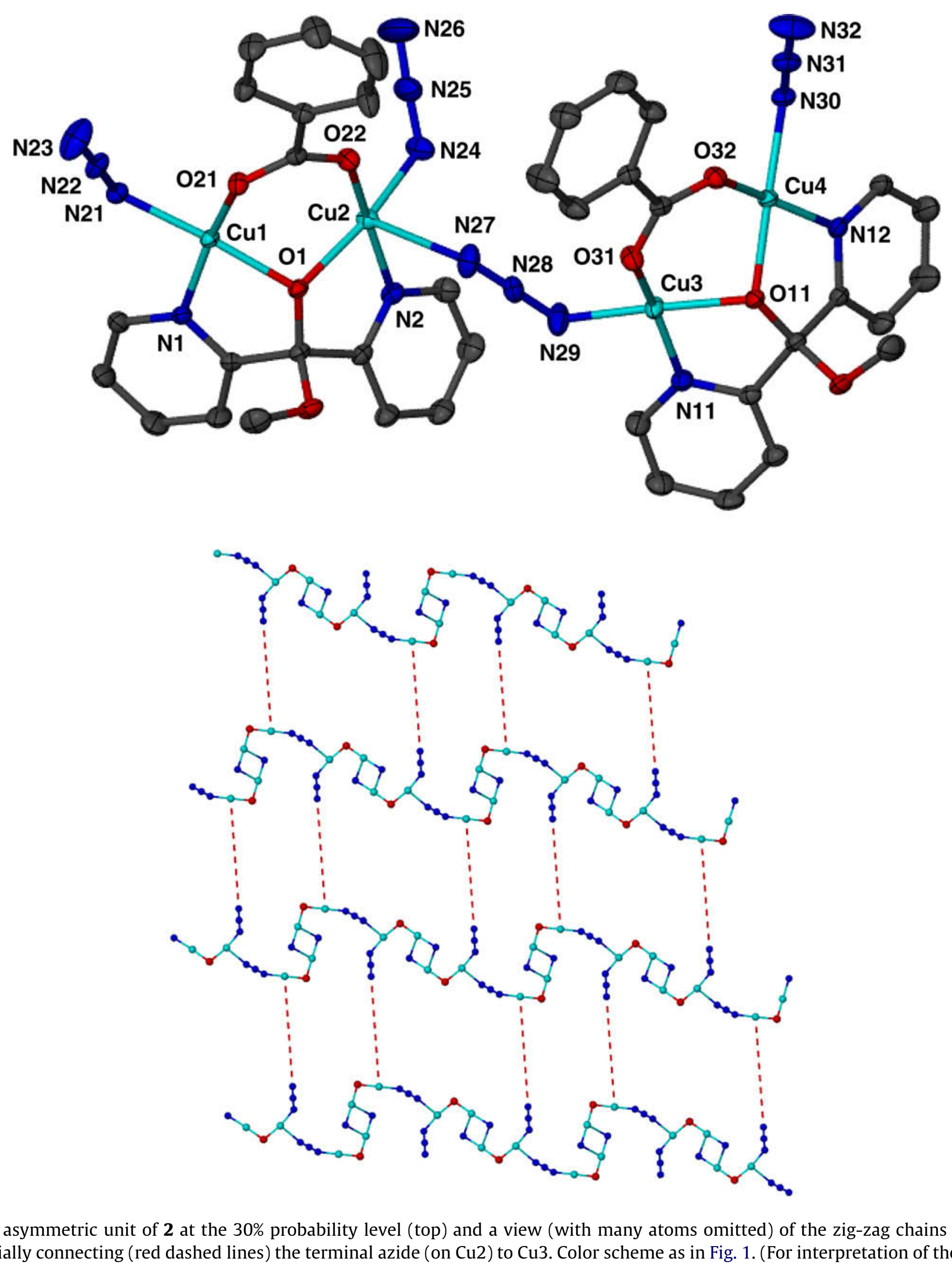


Fig. 3. ORTEP view of the asymmetric unit of **2** at the 30% probability level (top) and a view (with many atoms omitted) of the zig-zag chains and the herringbone layer (bottom) formed by artificially connecting (red dashed lines) the terminal azide (on Cu2) to Cu3. Color scheme as in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ences are more (220 cm^{-1}) and less (120 cm^{-1}) than the Δ value for NaO_2CPh (184 cm^{-1}), as expected for the monodentate and bidentate modes, respectively, of carboxylate ligation. The Δ values for **2** and **3** are ~140 cm^{-1} in accordance with the crystallographically established bidentate bridging ligation mode of the $PhCO_2^-$ groups [17]. The strong band at 2045–2065 cm^{-1} in the spectra of **1**–**3** is assigned to the asymmetric stretching mode of the azido ligands [18].

3.2. Description of structures

The molecular structure of complex **1** is depicted in Fig. 1, whereas ORTEP representations of the asymmetric units of **2** and **3** are shown in Figs. 3 and 4, respectively. Selected interatomic distances and angles for compounds **1**–**3** are listed in Tables 2 and 3.

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The hexanuclear molecule (Fig. 1) is held together by two 4.2211 (Harris notation [19]) $(py)_2CO_2^{2-}$ ligands, two 3.3011 $(py)_2C(OH)O^-$ groups and a single *syn,anti*-2.11 $PhCO_2^-$ group. Peripheral ligation is provided by three monodentate (1.10) $PhCO_2^-$ groups and two terminal (1.100) N_3^- ligands. The new core (Fig. 2) consists of four, 5-coordinate Cu^{II} atoms [Cu(2,3,4,6)] located at four alternate vertices of a central defective cubane unit (a cubane missing two opposite edges), two μ_3 O atoms (O1, O11) from the 3.3011 $(py)_2C(OH)O^-$ groups and two μ O atoms (O22, O32) from two different 4.2211 $(py)_2CO_2^{2-}$ ligands (these four O atoms occupy the remaining vertices of the cube), two additional satellite Cu^{II} atoms (Cu1 is square planar; Cu5 is 5-coordinate) across the missing edges, and two μ O atoms (O21, O31) that belong to the two different $(py)_2CO_2^{2-}$ groups and each links the cubane unit with a satellite metal ion.

Analysis of the shape-determining angles using the approach of Reedijk, Addison and co-workers [20] yields trigonality index, τ, values of 0.35, 0.08, 0.22, 0.18 and 0.28 for Cu2, Cu3, Cu4, Cu5 and Cu6, respectively ($\tau = 0$ and 1 for perfect *spy* and *tbp* geometries, respectively). This suggests that the coordination geometry of Cu(3,4,5,6) is slightly to moderately distorted square pyramidal; the coordination polyhedron of Cu2 is very distorted and can be considered either as a square pyramid or as a trigonal bipyramid.

Complex **1** joins a very small family of hexanuclear Cu^{II}_6/N_3^- clusters; however, in the three previous examples the azido ligands were bridging [21]. This nuclearity is the second highest in copper(II) azide chemistry [12] after the impressive $(Cu^{II}_7)_2/N_3^-$ cluster synthesized by Thompson's group [22].

The asymmetric unit of **2** (Fig. 3, top) consists of two similar $Cu^{II,II}_2$ subunits A (Cu1, Cu2) and B (Cu3, Cu4) bridged by a single end-to-end (EE or $\mu_{1,3}$) N_3^- ligand through the square pyramidal Cu2 ($\tau = 0.07$) and the square planar Cu3 ions. The two Cu^{II} centers within each dinuclear unit are bridged by one 2.2011 $(py)_2C(OMe)O^-$ ligand and one *syn,syn*-2.11 $PhCO_2^-$ group. Two end-on (EO or $\mu_{1,1}$) N_3^- ligands bridge two Cu1 atoms from two dinuclear units A. Similarly two dinuclear units B are bridged through two EO N_3^- ligands via two Cu4 centers. Both Cu1 ($\tau = 0.21$) and Cu4 ($\tau = 0.19$) are in distorted square pyramidal environments with azido nitrogens at the apical positions. Thus, tetranuclear units A = A and B = B form, while one EE azido ligand bridges the tetranuclear units A=A and B=B, giving rise to a an octanuclear repeating unit of –A=A–B=B–, where "=" and "–" denote double EO and single EE azide bridges, respectively. The AABB repeating unit forms an infinite zigzag chain running along the *ac* diagonal (Fig. 3, bottom). Therefore, chemically **2** is best formulated as $[Cu_8(O_2CPh)_4(N_3)_8\{(py)_2C(OMe)O\}_4]_n$.

The asymmetric unit of **3** (Fig. 4, top) consists of dinuclear $[Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}]$ moieties, where the two square pyramidal Cu^{II} centers (Cu1, $\tau = 0.13$; Cu2, $\tau = 0.25$) are bridged (as in **2**) by one 2.2011 $(py)_2C(OMe)O^-$ ligand and one *syn,syn*-2.11 $PhCO_2^-$ group. The dinuclear units assemble with two EO azido ligands that bridge the Cu2 atoms to form a tetranuclear unit (Fig. 4, middle). The latter are linked through the Cu1 centers via four EE azido ligands to form a 2D layer along the (1 0 −1) plane (Fig. 4,

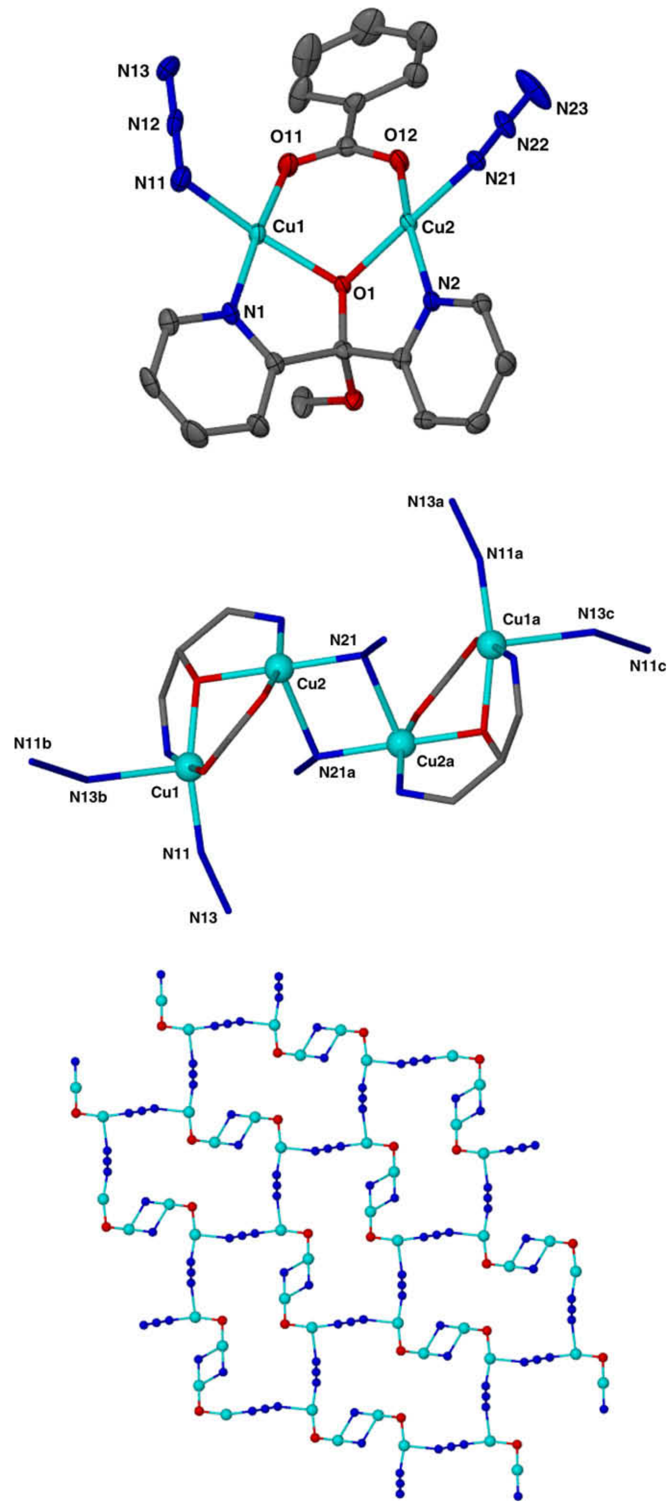


Fig. 4. ORTEP view of the asymmetric unit of **3** at the 30% probability level (top), the assembly of two dinuclear units (middle) of **3** and the 2D layer running along the (1 0 −1) plane (bottom). Symmetry code: a: 2 − *x*, −*y*, −*z*; b: 1.5 − *x*, 0.5 + *y*, 1.5 − *z*; c: 0.5 + *x*, −0.5 − *y*, 0.5 + *z*. Color scheme as in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Selected bond lengths (Å) and angles (°) for complex **1** · $2H_2O$ · 4.5MeCN.

Parameter		Parameter	
Cu(1)···Cu(2)	3.317(3)	Cu(2)···Cu(6)	3.085(7)
Cu(1)···Cu(3)	5.431(7)	Cu(3)···Cu(4)	3.003(2)
Cu(1)···Cu(4)	4.238(3)	Cu(3)···Cu(5)	4.327(2)
Cu(1)···Cu(5)	8.833(7)	Cu(3)···Cu(6)	3.557(1)
Cu(1)···Cu(6)	6.031(4)	Cu(4)···Cu(5)	5.452(5)
Cu(2)···Cu(3)	3.729(5)	Cu(4)···Cu(6)	3.659(1)
Cu(2)···Cu(4)	3.561(5)	Cu(5)···Cu(6)	3.335(4)
Cu(2)···Cu(5)	6.103(5)	Cu(4)–O(1)	2.379(3)
Cu(1)–O(21)	1.929(3)	Cu(4)–O(22)	1.950(3)
Cu(1)–O(41)	1.928(3)	Cu(4)–O(32)	1.945(3)
Cu(1)–N(21)	1.979(4)	Cu(4)–O(61)	1.956(3)
Cu(1)–N(41)	1.938(5)	Cu(4)–N(32)	1.993(4)
Cu(2)–O(1)	1.941(3)	Cu(5)–O(31)	1.947(3)
Cu(2)–O(11)	2.299(3)	Cu(5)–O(71)	1.930(3)
Cu(2)–O(21)	1.989(3)	Cu(5)–N(31)	2.003(4)
Cu(2)–N(1)	2.030(4)	Cu(5)–N(51)	1.949(4)
Cu(2)–N(11)	1.974(3)	Cu(6)–O(1)	2.338(3)
Cu(3)–O(11)	2.437(3)	Cu(6)–O(11)	1.950(3)
Cu(3)–O(22)	1.937(3)	Cu(6)–O(31)	1.979(3)
Cu(3)–O(32)	1.931(3)	Cu(6)–N(2)	1.993(3)
Cu(3)–O(51)	1.933(3)	Cu(6)–N(12)	2.024(4)
Cu(3)–N(22)	1.970(4)		
Cu(1)–O(21)–Cu(2)	115.7(2)	Cu(3)–O(11)–Cu(6)	107.9(1)
Cu(2)–O(1)–Cu(4)	110.7(1)	Cu(3)–O(22)–Cu(4)	101.1(1)
Cu(2)–O(1)–Cu(6)	91.8(1)	Cu(3)–O(32)–Cu(4)	101.6(1)
Cu(2)–O(11)–Cu(3)	103.8(1)	Cu(3)–O(32)–Cu(6)	83.8(1)
Cu(2)–O(11)–Cu(6)	92.8(1)	Cu(4)–O(1)–Cu(6)	101.7(1)
Cu(2)–O(22)–Cu(3)	91.8(1)	Cu(4)–O(32)–Cu(6)	86.9(1)
Cu(2)–O(22)–Cu(4)	85.8(1)	Cu(5)–O(31)–Cu(6)	116.3(2)
O(21)–Cu(1)–O(41)	176.9(2)	O(32)–Cu(4)–O(61)	171.3(1)
N(21)–Cu(1)–N(41)	168.1(2)	O(22)–Cu(4)–N(32)	158.0(1)
O(1)–Cu(2)–N(11)	159.5(1)	O(31)–Cu(5)–O(71)	176.5(1)
O(21)–Cu(2)–N(1)	138.8(1)	N(31)–Cu(5)–N(51)	165.6(2)
O(51)–Cu(3)–O(22)	153.7(1)	O(11)–Cu(6)–N(2)	156.7(1)
O(32)–Cu(3)–N(22)	158.5(1)	O(31)–Cu(6)–N(12)	139.7(1)

Table 3
Selected bond lengths (Å) and angles (°) for complexes **2** and **3**.

Parameter[a]		Parameter	
Complex ***2***			
Cu(1)···Cu(1a)	3.302(2)	Cu(2)···Cu(3)	5.829(4)
Cu(1)···Cu(2)	3.112(4)	Cu(2)···Cu(4)	6.703(5)
Cu(1)···Cu(3)	8.676(1)	Cu(3)···Cu(4)	3.026(7)
Cu(1)···Cu(4)	9.741(1)	Cu(4)···Cu(4b)	3.255(1)
Cu(1)–O(1)	1.956(2)	Cu(3)–O(11)	1.952(2)
Cu(1)–O(21)	1.932(2)	Cu(3)–O(31)	1.919(3)
Cu(1)–N(1)	1.966(3)	Cu(3)–N(11)	1.966(3)
Cu(1)–N(21)	1.986(3)	Cu(3)–N(29)	1.920(4)
Cu(2)–O(1)	1.958(2)	Cu(4)–O(11)	1.949(2)
Cu(2)–O(22)	1.950(3)	Cu(4)–O(32)	1.941(3)
Cu(2)–N(2)	2.006(3)	Cu(4)–N(12)	1.962(3)
Cu(2)–N(24)	1.934(3)	Cu(4)–N(30)	1.989(3)
Cu(2)–N(27)	2.496(3)		
Cu(1)–O(1)–Cu(2)	105.3(1)	O(22)–Cu(2)–N(2)	169.2(1)
Cu(3)–O(11)–Cu(4)	101.7(1)	O(11)–Cu(3)–N(29)	173.6(1)
O(1)–Cu(1)–N(21)	176.5(1)	O(31)–Cu(3)–N(11)	163.0(1)
O(21)–Cu(1)–N(1)	164.0(1)	O(11)–Cu(4)–N(30)	177.5(1)
O(1)–Cu(2)–N(24)	164.9(1)	O(32)–Cu(4)–N(12)	165.9(1)
Complex ***3***			
Cu(1)···Cu(1a)	6.058(1)	Cu(1)–N(13b)	2.425(5)
Cu(1)···Cu(2)	3.070(1)	Cu(2)–O(1)	1.954(3)
Cu(2)···Cu(2a)	3.328(1)	Cu(2)–O(12)	1.930(4)
Cu(1)–O(1)	1.971(3)	Cu(2)–N(2)	1.976(4)
Cu(1)–O(11)	1.925(4)	Cu(2)–N(21)	1.991(4)
Cu(1)–N(1)	1.981(4)	Cu(2)–N(21a)	2.495(4)
Cu(1)–N(11)	1.964(5)		
Cu(1)–O(1)–Cu(2)	102.9(2)	O(11)–Cu(1)–N(1)	172.3(2)
Cu(2)–N(21)–Cu(2a)	95.1(2)	O(1)–Cu(2)–N(21)	178.1(1)
O(1)–Cu(1)–N(11)	164.7(2)	O(12)–Cu(2)–N(2)	163.3 (2)

[a] Atoms designated by a and b are related by symmetry operators.

bottom). The 2D layer of **3** adopts the "herringbone" or "parquet floor" architecture. The familiar herringbone network is based on T-shaped 3-connected nodes bridged by linear spacers (Fig. 5, left), while in **3** each tetranuclear unit serves as two fused 3-connected nodes that self-assemble to create the herringbone architecture (Fig. 5, right). Alternatively, **3** can be described as the assembly of tetranuclear clusters bridged by four EE azido ligands that serve as linear spacers. To the best of our knowledge, **3** joins only a handful of extended 2D networks that adopt the herringbone architecture which is *not* based on T-shaped nodes [23].

A detailed examination of the crystal structures of **2** and **3** reveals that the 2D structure of the latter "contains" the 1D chains of the former. Complex **3** could have derived from **2** if the terminal azide ligand on Cu2 in **2** (Fig. 3) had bridged the Cu3 atom in an EE fashion (Fig. 6). Complexes **2** and **3** are the first copper(II) coordination polymers with any $(py)_2CO$-based ligand/N_3^- combination; this combination has been found in the recently reported tetranuclear structure $[Cu^{II}_4(N_3)_2\{(py)_2C(OMe)O\}_4][Cu^{I}Cl_2]$ [24].

3.3. Magnetochemistry

Solid-state direct current magnetic susceptibility (χ_M) data on dried **1** · $2H_2O$ were collected in an 0.1 T field in the 2.0–300 K range and are plotted as $\chi_M T$ versus T, and χ_M versus T in Fig. 7. χ_M increases from 48×10^{-4} emu mol^{-1} at room temperature to a maximum value of 56×10^{-4} emu mol^{-1} at 170 K and then decreases drastically to a minimum of 3×10^{-4} emu mol^{-1} at 20 K, before increasing again to the value of 21×10^{-4} emu mol^{-1} at 6 K. Based on the room-temperature $\chi_M T$ value of 1.43 emu mol^{-1} K, which is lower than the value expected for six $S = 1/2$ uncoupled spins (2.25 emu mol^{-1} K with $g = 2.0$) and the maximum in the χ_M versus T plot at 170 K, we conclude that strong antiferromagnetic exchange interactions between the Cu^{II} atoms are operative within the cluster. The Curie tail in the low temperature susceptibility data reveals the existence of a paramagnetic, possibly monomeric, impurity. According to the core (Fig. 2) a simplified spin Hamiltonian that describes the exchange interactions in **1** is

$$H = -2J_1(S_1 \cdot S_2 + S_5 \cdot S_6) - 2J_2 S_2 \cdot S_6 - 2J_3 S_3 \cdot S_4 \quad (5)$$

Magnetic susceptibility data were fitted using the MAGPACK [25] program (based on the Irreducible Tensor Operator method for diagonalization of the energy matrix) employed with the non-linear, least-squares curve-fitting program, DSTEPIT [26]. Best-fit (solid lines in Fig. 7) parameters are $J_1 = -94(5)$ cm^{-1}, $J_2 = -110(5)$ cm^{-1}, $J_3 = -116(5)$ cm^{-1}, $g = 2.05$, and $\rho = 0.15\%$, leading to an overall $S = 0$ ground state. Antiferromagnetic exchange interactions are often found in copper(II) complexes with $(py)_2CO$-based bridging ligands [27]. A fourth exchange parameter (J_4) incorporating the

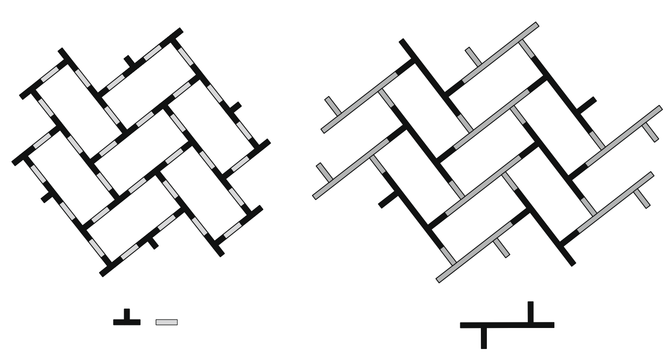
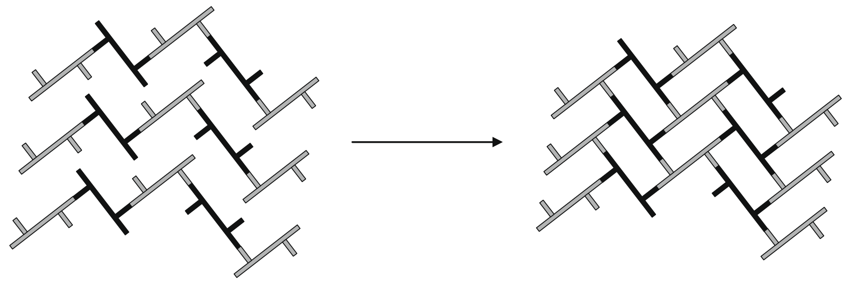


Fig. 5. The familiar herringbone motif based on T-shaped 3-connected nodes and spacers (left), and the herringbone architecture of **3** based on the tetranuclear units which serve as two fused 3-connected nodes (right).



2 3

Fig. 6. The transformation of the one-dimensional polymer **2** to the two-dimensional polymer **3**.

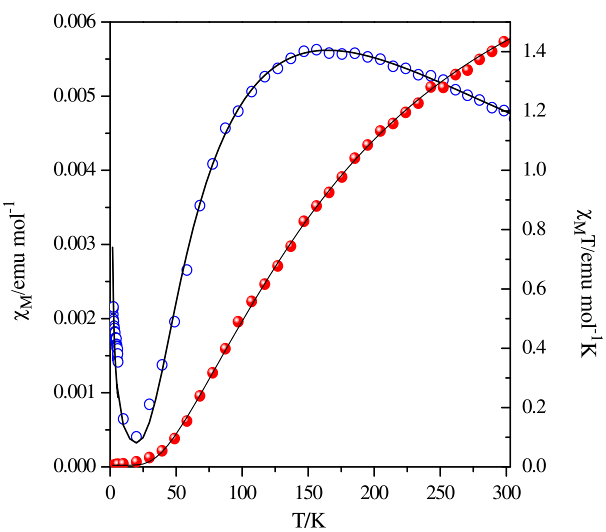


Fig. 7. χ_M vs. T (open blue cycles) and $\chi_M T$ vs. T (solid red cycles) plots for **1** · $2H_2O$ in a 1 kG field. The solid lines are the fit of the data; see the text for the fit parameters.

S_2S_3, S_2S_4, S_3S_6 and S_4S_6 magnetic interactions was not considered because the relevant Cu···Cu distances are rather long (3.56–3.73 Å, see Table 1); incorporation of J_4 leads to significant correlations between the fitted parameters. Efforts to employ a 2-J model, assuming $J_2 = J_3$, did not give a satisfactory fit.

4. Conclusions

An important chemical message from this work is that the $(py)_2CO/PhCO_2^-/N_3^-$ ligand combination looks like a promising candidate system for the generation of interesting copper(II) clusters and coordination polymers. The hexanuclear cluster **1** has a novel core, while the coordination polymers **2** and **3** exhibit interesting structural features. The products provide an example of the dependence of the structural type (cluster versus polymers) on the reaction solvent. The three complexes augur well that they are merely the first member of a new family of $Cu^{II}/(py)_2CO$-based ligands/$R'CO_2^-/N_3^-$ compounds. Preliminary results reveal that the nature of the carboxylate ligand, i.e. the nature of R′, affects the identity of the products.

5. Supplementary data

CCDC 702630, 702631 and 702629 contain the supplementary crystallographic data for **1** · $2H_2O$ · 4.5MeCN, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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