Synthesis, crystal structure and magnetic properties of a Cu(II) paddle-wheel complex with mixed bridges

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ABSTRACT:

The synthesis and characterization of a mixed carboxylate paddle-wheel copper complex, with formula [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 (Pip = piperonylate or 1,3-benzodioxole-5-carboxylate and MeCO2 = acetate), is here reported. The described compound is a binuclear complex, each pair of similar carboxylate ligands occupyingmutually trans bridging positions,while the methanol occupies the apical positions. The dimers are arranged into 2D layers in the bc plane through a network of O-H···O hydrogen bonds established between themethanol and the acetate ligand. Magnetic studies showed a strong antiferromagnetic Cu···Cu interaction (J = −308 cm−1), in agreement with the presence of four μ-κO-κO′ carboxylates bridging the metallic centers in the binuclear complex.

1. INTRODUCTION

Copper(II) complexes involving carboxylate ligands are particularly interesting due to the versatility of this ligand that can adopt different coordinationmodes, thus allowing the building of awide range of structures [1–5]. The paddle-wheel structure is a very frequent architecture found for binuclear complexes. Until now, and only considering copper compounds, more than 1300 crystal structures that contain [Cu2L4] (L = carboxylate) core have been reported [6,7]. In these compounds, carboxylate ligands occupy the equatorial copper coordination positions, in a syn-syn coordinationmode, establishing four bridges between themetal centers. Otherwise, the axial positions could be occupied by a variety of donor molecules. This structure is frequently found in different materials, from discrete complexes to 1D coordination polymers and in metal organic frameworks. In the vast majority of those compounds, all carboxylate ligands have the same nature, however, only eight mixed carboxylate [Cu(L)(L′)(X)]2 have been described [6,8–15], six of them having two acetate anion ligands [9–12, 14, 15]. In a pair of these few examples, the presence of bulky carboxylate ligands could favors the formation of mixed carboxylates dimers [12,14].

We are interested in the synthesis of [Cu(Pip)2(X)]2 (Pip = piperonylate, X = solvent) compounds, with the objective of replacing X for bulky amine derivatives, thus, aiming to build up novel supramolecular systems with potential applications in catalysis and gas storage/separation. During this investigation, crystals of [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 were unexpectedly obtained while using MeOH as solvent and 1Cu:1Pip molar ratio, a new mixed carboxylate paddlewheel copper complex. Full characterization of this new compound is here presented, intending to understand the factors that favor the formation of mixed carboxylate paddle-wheel complexes. In the present case, there is not steric hindrance for the formation of homoleptic piperonylate, and in fact we have isolated a [Cu(μ-Pip)2(BzPy)]2 paddle wheel complex [16]. However, reported works discuss the effect of solvent's polarity in the formation of either the homoleptic or heteroleptic compounds [9]. A heteroleptic compound containing vanillinate and acetate ligands [Cu2(μ-C8H7O4)(μ-MeCO2)(MeOH)]2 is obtained when working in MeOH, whereas homoleptic compound [Cu2(C8H7O4)4(H2O)2] is obtained when working in H2O (C8H8O4 = vanillic acid). In the present work, the designed synthetic method produces bulk quantities of [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 complex, [17] whose structure is shown in Fig. 1. The obtained product is a green crystalline powder. The elemental analysis of this sample gives satisfactory C and H values. Moreover, powder X-ray diffraction shows that the structure of the bulk powder matches the one of the single-crystal, with only a small displacement of the peaks due to the different characterization temperature applied in the powder (room temperature) and monocrystal (100 K) measurements (Fig. 2).

ATR-FTIR spectrum of this compound shows significant shifts in the ν(C_O) and ν(C\\O) stretching with respect to the spectra of free ligands, hence confirming the coordination of the Cu(II) to the carboxylate groups of the Pip and MeCO2 ligands. Additionally, the coordination mode of the carboxylate groups can be inferred from the difference between the asymmetry and symmetric

vibrations of the COO– groups (Δ = νCOOasym − νCOOsym) [18,19]. The values of the compound show a bidentate bridging mode for the carboxylate ligands [20–23]. Another characteristic band, appearing at 3279 cm−1 and assignable to ν(O\\H) vibration, is in agreement with the presence of MeOH in the complex. The shape and position of this band suggest that the hydroxyl group participates in a hydrogen bond interaction [22,23].

The structure was determined by single crystal X-ray diffraction [24]. X-ray studies confirmed that the compound [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 has a paddle-wheel binuclear Cu(II) structure, with four bridging carboxylate ligands in a syn-syn coordination mode (Fig. 1). Each Cu metal atom was coordinated to five oxygen atoms, four from different carboxylate groups (two of Pip ligands and two of acetate groups) at the equatorial positions and another oxygen atom fromMeOHmolecule at the apical position completing the square pyramidal coordination geometry (τ = 0) [25]. The Cu-Ocarbox bond distances range from 1.9546(17) to 1.9774(18), and the angles O-Cu-O(eq) between 88.45 and 90.72°, while the Cu-OMeOH bond length is larger than previous with a value of 2.1388(17) Å. The metal atoms are displaced in the axial direction towards the methanol molecules from the oxygen plane, as indicated by the Ocarbox-Cu-OMeOH angles, with values in the range from 90.07(7) to 100.29(7)°. The intramolecular Cu···Cu distance is 2.5930(6) Å, which is very similar to values previously reported in the literature (2.58–2.76 Å) [26–28]. Selected distances and angles are provided in Table 1.

The most important intermolecular interaction present in the compound is the hydrogen bond between methanol's hydroxyl and one of the oxygens from the acetate ligand (O7-H7O···O5, 1.900 Å; O7···O5, 2.725 Å; O7-H70-O5, 166.95°). The propagation of these hydrogen bonds defines a two-dimensional supramolecular network, parallel to the bc plane (Fig. 3, up). The strength of this interaction involves the approximation of adjacent atoms, and, hence, the formation of O-H7···C9 and O-H7···C10 interactions. Furthermore, in these layers weaker CH··· O (O1···H10B 2.515 Å; O6···H10A, 2.555 Å) interactions can also be found. The dioxole groups protrude perpendicularly to the layer plane, and alternatively in opposite directions (Fig. 3, down). The layers are stacked in such a manner that dioxole groups are interleaved, being able to establish C-H···O interactions that connect the 2D layers yielding a 3D supramolecular network. Hydrogen atoms of the CH2 coming from the dioxole group (H6A) interact with acetate's oxygen (O6···H6A, 2.506 Å). The same hydrogen atom establishes a weak interaction with carboxylate oxygen from piperonylate group (O2···H6A, 2.655 Å).

Supramolecular networks, with tunable self-organized units, have attracted much attention during the past years [29–31]. This interest comes from the possibility of fabricate materials with desirable properties, just by controlling the intermolecular interactions between molecular building units. Therefore, researchers are focusing on designing new functional complexes with well-defined structures to accomplish a desired function. In particular, hydrogen bonds play an important role in the formation of crystal structures [32–34]. The extended 2D supramolecular network of [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 shows a great number of H-bond interactions. This strong network explains its insolubility in methanol and in other tested solvents such as H2O, EtOH and DMF. Consequently,

during the substitution of acetate ligands for piperonylate ligands, the formation of that strong networks of H-bond causes the precipitation of the compound. This fact may prevent the formation of the homoleptic compound, resulting in an easy isolation of this new mixed carboxylate structure. The mixed carboxylate [Cu(μ-PhCO2)(μ-MeCO2)(CH3OH)]2 shows a similar 2D supramolecular hydrogen bond network [10].Methanol also plays a key role in the hydrogen bonding supramolecular 2D network of [Cu(μ-C8H7O4)(μ-MeCO2)(CH3OH)]2 (C8H7O4 = vanillic acid), in this case interacting with the phenol groups [9].

In Fig. 4, the thermal variation of the χpT is presented for the [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 compound. The bridging carboxylate groups are very efficient in transmitting super-exchange interactions between paramagnetic centers [31,35,36]. The magnetic susceptibility of this compound shows a rounded maximum near room temperature which decreases by lowering the temperature, reaching a minimum at ca. 50 K and a divergence at lower temperatures. This behavior suggests the presence of a strong antiferromagnetic Cu···Cu interaction, as expected fromthe structure of this compound. The divergence at lowtemperature indicates the presence of a paramagnetic contribution from a small percentage of impurities (ρ). The magnetic behavior of the compound can be modeled by the classical Bleaney and Bowers S = ½ dimer model [37]. In order to reproduce the divergence at low temperature, we have included a paramagnetic contribution (ρ) with the same g value as the Cu(II) ions in the dimer. The model reproduces very satisfactorily the magnetic properties, in the whole temperature range, including the divergence at low temperatures with the parameters (g=2.12; J(cm−1)=−308; ρ(%)=1.13;H=−JSiSi+1). These values also agree with the reported values for many other similar Cu(II) paddle-wheel dimers, including the original acetate complex (J = −284 cm−1) [38].

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2. CONCLUSIONS

In summary, a binuclear complex based in the piperonylate and acetate ligands, with formula [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2, was prepared and characterized. The compound reported here constitute one of the very rare examples ofmixed carboxylate paddle-wheel copper dimers (8/1300). The dimeric complex shows a strong intradimer antiferromagnetic Cu···Cu interaction, in agreement with previous observation in similar dimeric complexes.

ACKNOWLEDGEMENTS

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[17] HPip (506 mg, 3.05 mmol) was added to a green solution of Cu(MeCO2)2·H2O (601 mg, 3.01 mmol) in MeOH (60 ml) and stirred for one hour. A green solid appeared that was filtered, washed with cold methanol and dried at room temperature. Yield: 0.704 (73.5%). This compound has also been obtained working with other metal to ligand ratios. From mother liquors, green crystals suitable for single crystal diffraction were obtained. Analysis for C22H24O14Cu2 calc/found (%): C, 41.32/41.29; H, 3.78/3.83. ATR-FTIR (cm−1): 3279(m),

1591(s), 1492(w), 1441(m), 1389(s), 1264(m), 1118(m), 1021(s), 922(m), 884(w), 803(w), 775(s), 683(s). Bulk powder XRD pattern is similar to single crystal XRD pattern (Fig. 2).

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[24] Experimental X-ray structure determination of the [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 complex: A green prism-like crystal (0.103 × 0.104 × 0.126 mm) was measured on a D8 Venture system equipped with a Multilayer monochromate and a Mo microfocus (λ = 0.71073 Å). C22H24Cu2O14, M = 639.49, Monoclinic space group P(21/c) with Z = 2, and a = 11.9625(6), b = 13.0173(7), c = 7.9398(4) Å, β = 95.112(2)°, and V=1231.46(11) Å3. The integration of the data using a monoclinic unit cell yielded a total of 14640 reflections to a maximumθ angle of 26.39° (0.80 Å resolution), ofwhich 2502were independent (average redundancy 5851, completeness= 99.6%, Rint=4.72%, Rsig=3.14%) and 2114 reflections (84.49%) were greater than 2σ(F2). The refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6892 and 0.7454. The structure was solved using the Bruker SHELXTL, and refined using SHELXL program. The final anisotropic full-matrix least squares refinement on F2 with 174 variables converged at R1 = 3.05%, for the observed data and wR2 = 7.34% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.649 eÅ−3 and the largest hole was −0.358 eÅ−3 with a RMS deviation of 0.091 eÅ−3. On the basis of the final model, the calculated density was 1.725 g cm−3 and F(000) was 652.

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247 **Legends to figures**

248

249 **Figure 1.** ORTEP drawing of [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2, showing all non-hydrogen atoms and
250 the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

251

252 **Figure 2.** Comparison of the powder XRD pattern of bulk [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2 (down,
253 black line) and the pattern simulated from de crystal structure refinement (up, red line). Small
254 displacement of the peaks was due to the different temperature characterization of the powder (room
255 temperature) and the monocrystal (100 K).

256

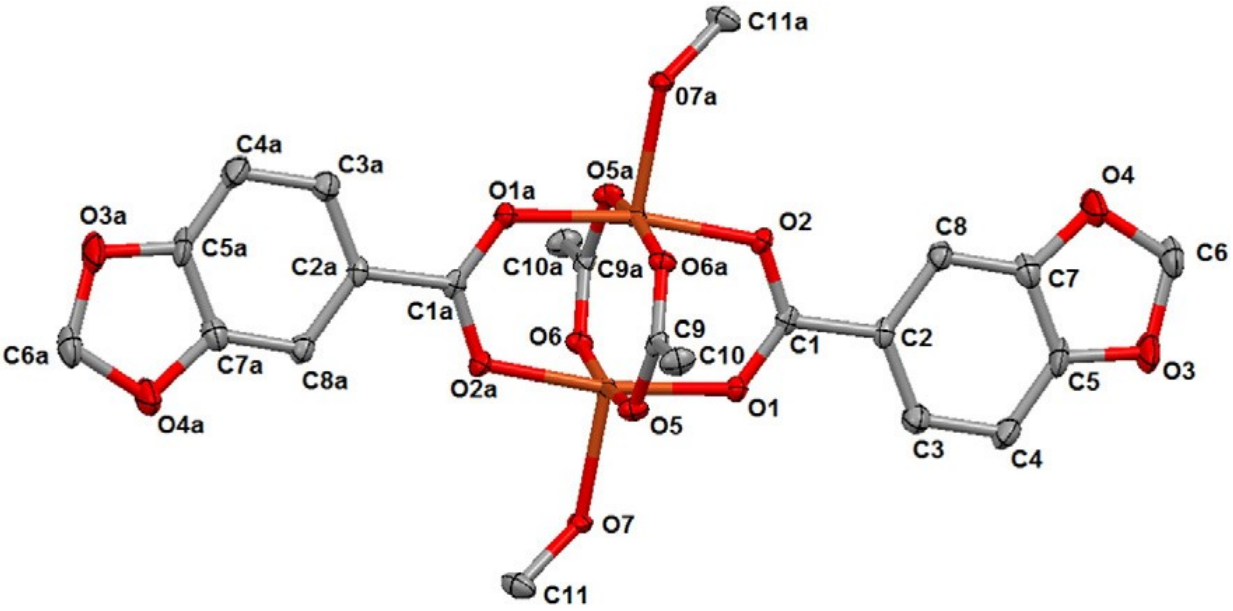
257 **Figure 3**. Supramolecular 2D network generated by the propagation of the hydrogen bond (green line)
258 between the hydrogen fromthemethanol (O···H7) and an oxygen atomof the acetate ligand (O5). Only
259 the hydrogen atoms involved in this intermolecular interaction are displayed for clarity. Up, projection
260 down the a axis; down, projections down the b axis, left and the c axis, right.

261

262 **Figure 4.** Thermal variation ofχmT for complex [Cu(μ-Pip)(μ-MeCO2)(MeOH)]2. Solid red line
263 is the best fit to the S = 1/2 dimer model (see text).

264

FIGURE 1.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C9a
O6a
C7
C1a
O6
C9
C1
C2
C6a
C7a
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O7
C11

FIGURE 2.

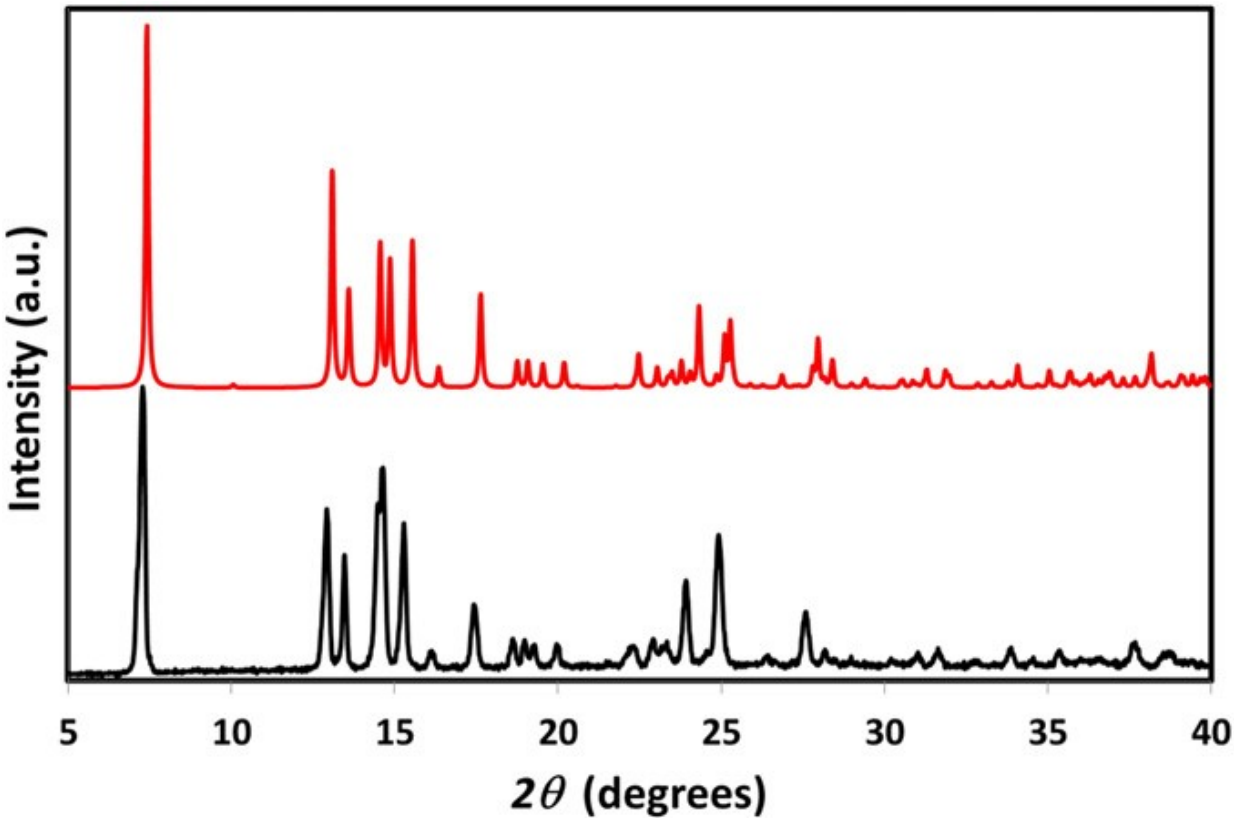

FIGURE 3.

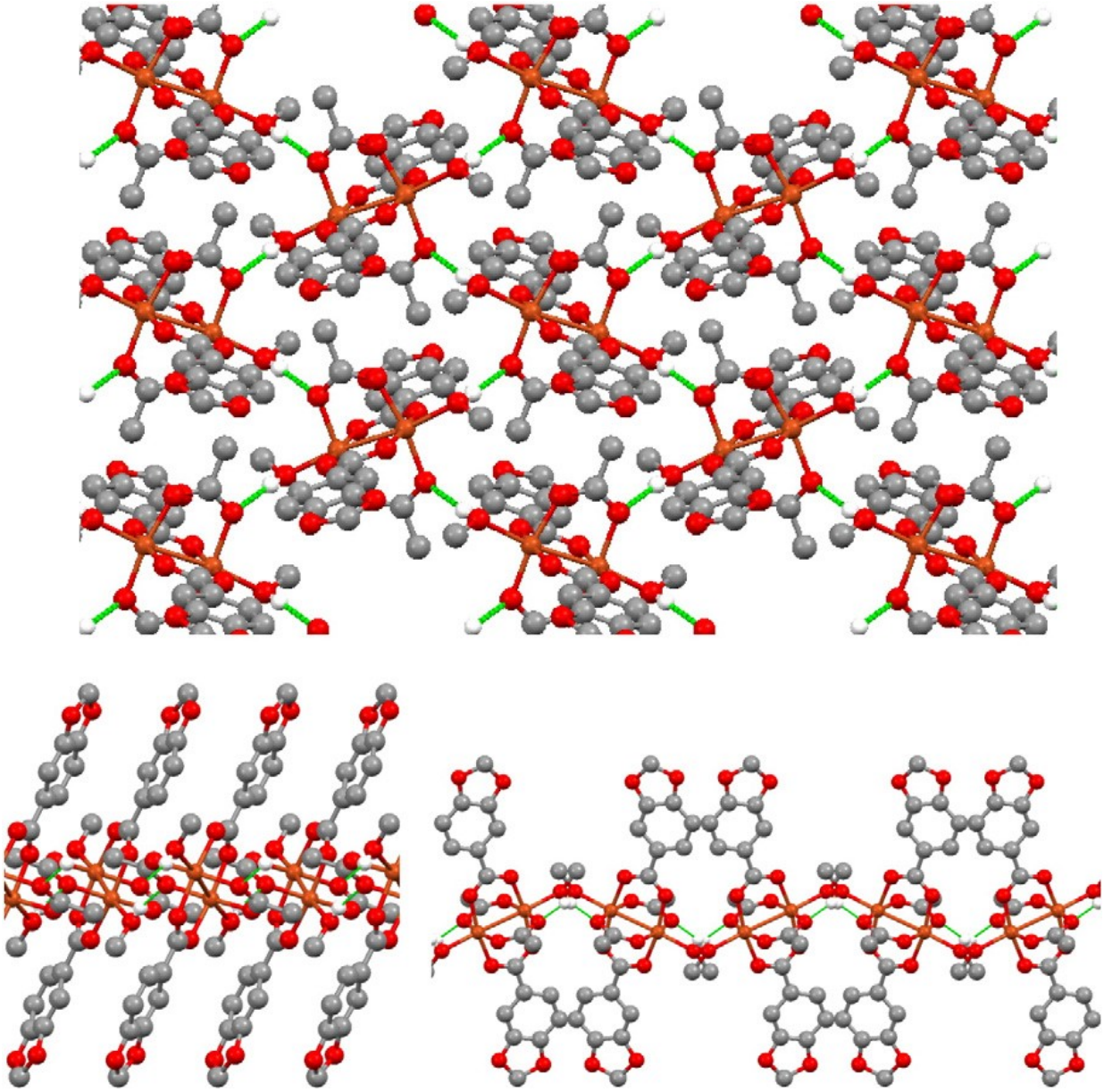

FIGURE 4.

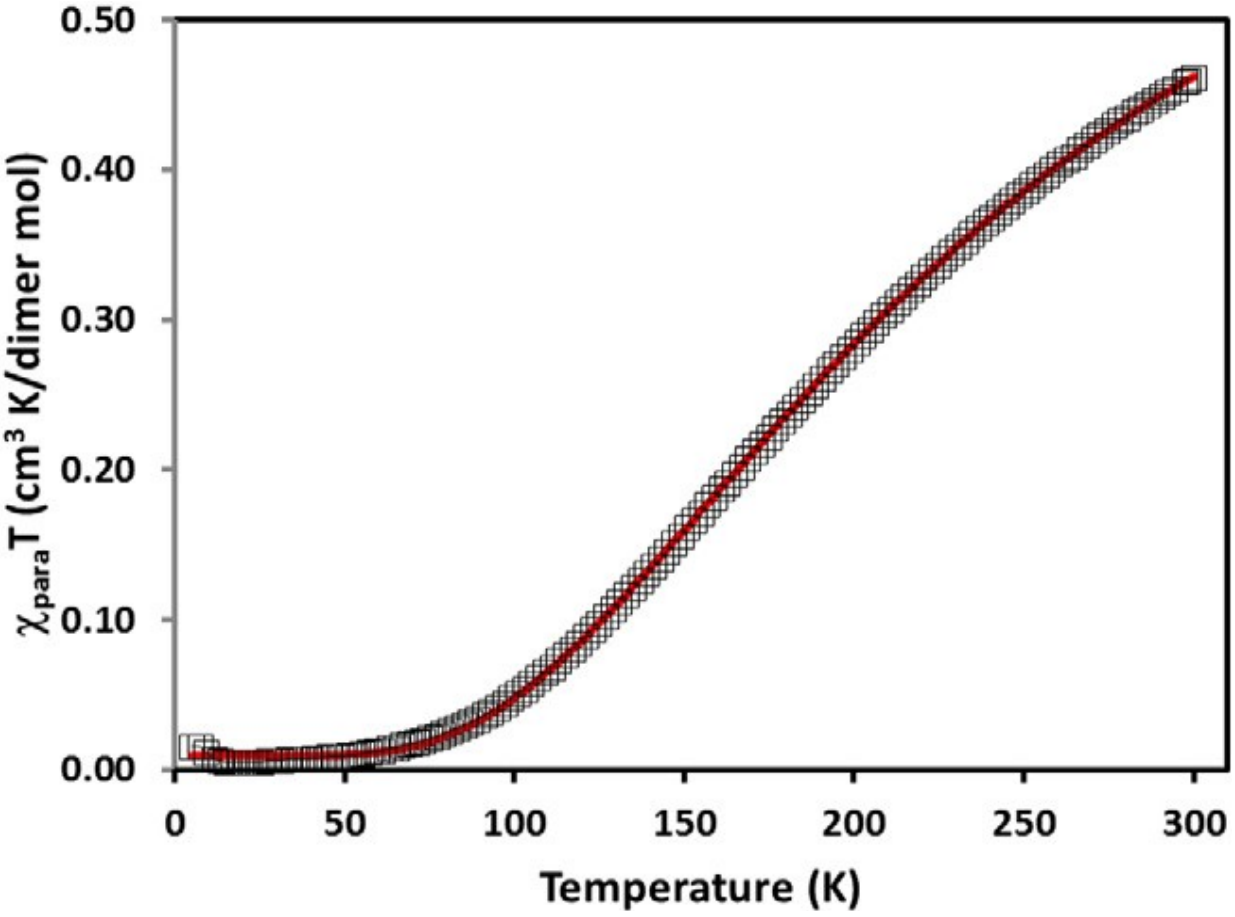
0.50
0.40
0.30
0.20
0.10
0.00
χpara T (cm3 K/dimer mol)
0
50
100
150
200
250
300
Temperature (K)

Table 1 Selected bond lengths (Å) and bond angles (°) values for the [Cu(μ-Pip)(μ-MeCO2) (MeOH)]2 complex. The estimated standard deviations (e.s.d.s.) are shown in parentheses.

Bond lengths (Å)			
Cu(1)-O(2)	1.9546(17)	Cu(1)-O(5)	1.9774(18)
Cu(1)-O(1)#1	1.9603(18)	Cu(1)-O(7)	2.1388(17)
Cu(1)-O(6)#1	1.9720(18)	Cu(1)-Cu(1)#1	2.5930(6)
Bond angles (°)			
O(2)-Cu(1)-O(1)#1	168.55(7)	O(6)#1-Cu(1)-O(5)	168.55(7)
O(2)-Cu(1)-O(6)#1	89.45(8)	O(2)-Cu(1)-O(7)	94.48(7)
O(1)#1-Cu(1)-O(6)#1	90.72(7)	O(1)#1-Cu(1)-O(7)	95.96(7)
O(2)-Cu(1)-O(5)	88.45(8)	O(6)#1-Cu(1)-O(7)	90.07(7)
O(1)#1-Cu(1)-O(5)	89.50(8)	O(5)-Cu(1)-O(7)	100.29(7)