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An unexpected carboxylato-bridged-only hexanuclear copper compound

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ABSTRACT

The reaction of copper acetate with 3,4,5-tri(ethoxy)benzoic acid leads to the formation of dodecakis((μ-(3,4,5-tri(ethoxy)benzoato-κ²O:O′)-hexa(copper(II)), [Cu₆(O₂CC₆H₂(OCH₂CH₃)₃)₁₂]. The new compound crystallizes in the triclinic system, space group *P*1̄ with *Z* = 2, solvated by disordered cyclohexane molecules. The Cu(II) ions are placed in O₅ pentacoordinated environments provided by four carboxylate oxygen atoms in a pseudo square planar arrangement and a fifth oxygen atom that belongs to a more distant carboxylate group in the axial position. The Cu(II) centers occupy the corners of a trigonal antiprism. A carboxylato network links each copper center with other four, providing potential paths for exchange coupling between the Cu(II) centers. Variable temperature magnetic susceptibility measurements show a maximum at 8 K. An analysis based on the spin-Hamiltonian formalism and DFT-based broken symmetry computations provides insight into the magnetic exchange interactions between the metal centers.

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1. Introduction

Many well-known copper carboxylates are dinuclear systems of general formula [Cu₂(O₂CR)₄L_x] (RCO₂⁻: equatorial carboxylates; L: axial ligands, *x* = 0–2) [1,2] and Lantern-type structure. This kind of compounds have been employed in basic research in the field of molecular magnetism, as biologically active substances [3] and as potential building blocks for advanced materials based on oligomeric and polymeric arrangements [4]. In addition, the use of Lantern-type copper carboxylates to develop metal-containing liquid crystalline materials (metallomesogens) has attracted many groups, including ours [5]. The ubiquitous role of these species in the molecular magnetism field is mostly due to three different reasons: (i) Cu(II) compounds are usually friendly from the synthetic point of view, (ii) Each Cu(II) carries only one unpaired electron, a fact that tremendously simplifies the analysis, (iii) Carboxylato bridges usually promote significant antiferromagnetic (AF) coupling between the *S* = ½ Cu(II) centers, leading to exchange coupling constants *J* with absolute values that can be even higher than 175 cm⁻¹ (*H* = -2*J*₁·*S*₂) [2,6,7].

In a systematic approach to understand the influence of the substitution pattern of the aryl groups on the mesomorphism of

Lantern-type copper benzoates, we employed 3,4,5-tri(ethoxy)benzoate. Unexpectedly, we isolated a species with an unusual temperature dependent magnetic susceptibility behavior consistent with, at most, weak exchange interactions. The X-ray analysis of a crystalline sample revealed the presence of a hexanuclear copper species [Cu₆(O₂CC₆H₂(OCH₂CH₃)₃)₁₂]. This molecule comprises six pentacoordinated Cu(II) centers in a close to idealized *D*_{3d} trigonal antiprism arrangement. In recent years a significant amount of discrete copper species with nuclearity higher than two has been reported [8], but only a few hexanuclear compounds that hold oxygen-only coordination spheres have been properly characterized [9]. To our knowledge, this is the first example of a hexanuclear Cu(II) species where all oxygen atoms in the coordination sphere of the metals belong exclusively to carboxylate functional groups. The bridging framework involve *syn-syn* bridges, *syn-anti* bridges, and O atoms bridging different Cu(II) centers in either *syn* or *anti* conformations. In this report, we focus on the molecular structure and the magnetic properties of this new species, as it stands as an ideal case to explore, both experimentally and theoretically, the different roles that carboxylates could play in setting the magnetic interactions between metal centers. There are not many examples displaying combined *syn-syn* and *syn-anti* bridging modes in the same compound, and in those cases the resulting interaction scheme may not be easily unraveled. We analyze the temperature dependent susceptibility by means of a proper spin-Hamiltonian, DFT calculations and Broken-symmetry analysis in order to

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provide an interpretation of the magnetic interactions between the spin carrying metal centers.

2. Experimental

2.1. Preparation of $[Cu_6(O_2CC_6H_2(OCH_2CH_3)_3)_{12}]$

Two hundred and ninety-seven milligrams of $Cu_2(O_2CCH_3)_4 \cdot 2H_2O$ (0.744 mmoles) dissolved in 85 mL of methanol were added dropwise to a well stirred solution of 964 mg of 3,4,5-tri(ethoxy)benzoic acid (3.79 mmoles) dissolved in 15 mL of ethanol. A light green-blue precipitate developed immediately. The solid was collected by filtration, recrystallized twice from cyclohexane and dried in vacuo. Yield: 701 mg (83%). Elemental analysis: Calculated for Cu_6L_{12} ($Cu_6C_{156}H_{204}O_{60}$, Mr 3420.57), C: 54.8%; H: 6.0%. Found: C: 54.8%; H: 5.9%. FT-IR (KBr disc ν/cm^{-1}) 2980m (νCH_3 , as), 2933w (νCH_2 , as), 2890w (νCH_2 , s), 1611s (ν aromatic ring), 1576s (νCO_2 , as), 1422s (δCH_2 , as), 1414s (νCO_2 , s), 1383s, 1358m (δCH_3), 1320w (δCH_2), 1227m ($\nu PhOC$), 1125s, 1115m (ωCH_3), 1030m, 900w, 782w and 769w (aromatic ring). UV-Vis ($CHCl_3$) $\nu_{max} = 14.6 \times 10^3 cm^{-1}$ ($\epsilon = 505 M^{-1} cm^{-1}$) with a shoulder at $11.1 \times 10^3 cm^{-1}$.

Green crystals suitable for X-ray analysis were obtained in a reproducible way by slowly cooling (5 °C/day) a concentrated solution of Cu_6L_{12} in cyclohexane. The crystals were kept in contact with the mother liquor in order to prevent rapid loss of the solvent.

2.2. Physical measurements

FT-IR spectra (KBr pellets) were collected on a FT-IR Avatar 320 spectrometer. Elemental analysis was performed on a Carlo Erba EA 1108 analyzer. UV-Vis spectra were recorded on a Shimadzu UV3100 spectrophotometer. Electrospray ionization mass spectra were recorded using a Finnigan MAT 95 spectrometer, Finnigan GmbH, Bremen, Germany. Magnetic susceptibility measurements were performed in fine powdered samples with a Quantum Design Squid magnetometer model MPMS XL5, using calibrated gelatin capsules as sample holders having small diamagnetic contribution. The magnetic susceptibility was measured in the temperature interval 2–300 K, with an applied field of 0.05 T. The contribution of the gelatin capsule was subtracted from the measured values. The diamagnetic correction was estimated from Pascal's constants as $\chi_{dia} = -1793 \times 10^{-6} cm^3 mol^{-1}$. The use of this value leads to a TIP of $2610 \times 10^{-6} cm^3 mol^{-1}$. This last number is larger than the expected for a Cu(II) hexamer ($400 \times 10^{-6} cm^3 mol^{-1}$) [10]. The disagreement might originate in the estimation of χ_{dia} for such a large molecule. Significant differences between the measured and calculated values of χ_{dia} for related high molar mass compounds have previously been reported [11].

2.3. X-ray data collection and analysis

A green single crystal of $Cu_6L_{12} \cdot 2.25 C_6H_{12}$, was coated with perfluoropolyether, picked up with a nylon loop and mounted in the nitrogen cold stream of the diffractometer to prevent solvent loss. Intensity data were collected at 100 K using a Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source. Graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was used. Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensities of redundant reflections were used to correct for absorption using the program SADABS [12]. The structure was readily solved by Patterson methods and subsequent difference Fourier techniques. The Siemens SHELXTL software package [13] was used for solution and artwork of the structures, SHELXL97 [14] was used for the refinement. All

non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

The two crystallographically independent complex molecules, residing on an inversion center, were found to be severely disordered. Split atom models were refined for some tris(ethoxy)benzoate ligands using EADP, SAME and SADI instruction of SHELXL. Two molecules of cyclohexane were found to crystallize on general positions of which one was refined with a split atom model. An additional cyclohexane molecule with a low occupation factor resides on an inversion center. The occupation factor of the three symmetry independent carbon atoms refined to about 0.5 giving a total of 2.25 cyclohexane molecules per hexanuclear complex unit.

2.4. Theoretical calculations

Theoretical calculations were performed with density functional theory (DFT) as implemented in the GAUSSIAN 03 package [15]. We used Becke's three parameter hybrid functional with the correlation functional of Lee, Yang and Parr formalized as the B3LYP hybrid functional [16] and three different basis sets which proved to be suitable for computing the electronic properties of coordination compounds containing first row transition metal centers: TZV [17], 6-31G⁺⁺ [18] and LanL2DZ [19]. Unrestricted open-shell calculations were performed in every case. The SCF calculations were of the spin-polarized type and were tightly converged.

Single point DFT calculations have been employed to estimate the exchange coupling between pairs of copper centres linked by different bridge configurations. The case of a large number of coupled spins is difficult to address theoretically [20]. For this reason we adopted a strategy where only pairs of interacting spin-carrying Cu centers were considered and the remaining metallic centers were replaced by Zn(II) ions, which have a similar q/r ratio but are diamagnetic (Doped Cluster Approach) [20]. In all our computations the replacement of Cu(II) ions by Zn(II) did not perturb significantly the electronic distribution of the rest of the molecule as revealed by the Mulliken charge and spin density atomic values, which remained essentially unaltered.

We calculated the high spin ($HS; M_S = S_A + S_B$) and broken symmetry ($BS; M_S = |S_A - S_B|$) wave functions and energies, and combined them to estimate the exchange coupling parameter J involved in the Heisenberg-Dirac-van Vleck Hamiltonian:

$$\hat{H}_{HDVV} = -2J\hat{S}_A\hat{S}_B \quad (1)$$

We employed the broken symmetry formalism, originally developed by Noodleman for SCF methods [21], which involves a variational treatment within the restrictions of a single spin-unrestricted Slater determinant built upon using different orbitals for different spin. This approach has been later applied within the frame of DFT. We preferred the use of the approximation described by Yamaguchi and co-workers [22] to link the exchange coupling parameter with the energies and expectation values of the spin-squared operator for the HS and BS states [22,23].

$$J = -\frac{E_{HS} - E_{BS}}{\langle \hat{S}_{HS}^2 \rangle - \langle \hat{S}_{BS}^2 \rangle} \quad (2)$$

We also employed the BS-type spin unrestricted solution after a corresponding orbital transformation as a means to visualize the interacting non-orthogonal magnetic orbitals [24]. Note that these orbitals do not have a well-defined orbital energy. In the figures showing such orbitals, we therefore do not give orbital energies explicitly. Our main interest is the occupation and spin-coupling patterns.

3. Results and discussion

3.1. Synthesis and basic characterization

The reaction between copper acetate ($\text{Cu}_2(\text{O}_2\text{CCH}_3)_4 \cdot 2\text{H}_2\text{O}$) and 3,4,5-tri(ethoxy)benzoic acid ($(3,4,5\text{-}(\text{CH}_3\text{CH}_2\text{O})_3\text{C}_6\text{H}_2\text{CO}_2\text{H}, \text{LH})$) in a methanol/ethanol mixture lead to immediate precipitation of a light green-bluish precipitate. This material was only marginally soluble in both polar and non-polar solvents. However, the solubility in hydrocarbons increases significantly at high temperatures, allowing recrystallization from cyclohexane. The presence of L^- in the coordination sphere of Cu(II) was confirmed by its characteristic IR spectral features, see experimental section. The elemental analysis of the material obtained was compatible with two units of L^- per copper center, as expected for a Lantern-type compound Cu_2L_4 , though the green color of the material is uncommon. A UV–Vis spectrum recorded in chloroform solution (Fig. S1) shows a band centered at about $14.6 \times 10^3 \text{ cm}^{-1}$ with a noticeable shoulder at $11.1 \times 10^3 \text{ cm}^{-1}$.

The MS–ESI (+) spectrum obtained from a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution (Fig. S2) consists of a complex pattern arising from species containing different Cu/L ratios, which could eventually be compatible with the fragmentation of a multinuclear cluster larger than expected.

3.2. Crystal structure

X-ray analysis revealed the presence of discrete $[\text{Cu}_6\text{L}_{12}]$ hexanuclear clusters. The unit cell contains two crystallographically independent $[\text{Cu}_6\text{L}_{12}]$ molecules which reside on inversion centers and disordered cyclohexane molecules (Table 1). The clusters are roughly globular, with the copper ions occupying the core region (Fig. 1). Six L^- molecules are arranged around the equatorial section while the six remaining L^- occupy the axial positions of the

cluster. The carboxylate end of L^- point towards (and actually bridge) the Cu(II) ions while the aromatic rings substituted with O-ethyl chains constitute the outer shells of the molecules. The two $[\text{Cu}_6\text{L}_{12}]$ molecules show a different degree of disorder, particularly in the outer O-ethyl chains. An atom-by-atom comparison between both molecules (Fig. S3) reveals significant differences (RMSD considering all non-hydrogen atoms of 1.93 Å) mostly due to different conformations of the phenyl groups and the flexibility of the outer chains. On the contrary, the core regions are virtually superimposable, with RMSD of 0.24 Å if all the atoms placed within 4 Å of the Cu(II) centers are taken into account in the computation. In the following, we concentrate on the description of the copper sites, and for that purpose we employ information derived from the less disordered of the two $[\text{Cu}_6\text{L}_{12}]$ clusters.

The six copper atoms are settled in two parallel equilateral triangles rotated 60° one with respect to the other and separated by about 1.72 Å yielding a trigonal antiprism. The Cu(II) centers on the corners are 5.1 Å apart and are bridged by a single μ -carboxylate moiety in *syn-anti* conformation (Fig. 2a). The shortest distance between metal ions in different triangles is 3.4 Å. These two centers are linked by two μ -carboxylate bridges, one in *syn-syn* conformation and the other in *syn-anti* conformation, and an extra κ -O-carboxylate bridge (Fig. 2b). Each copper atom is pentacoordinated by five carboxylic O-atoms in a pseudo square pyramidal environment: four O-atoms in the roughly planar base (Fig. 2c) and a more distant one in the apical position. The ligand environments around the six Cu(II) ions are not strictly identical (Table 2). The presence of an inversion center groups the metals in pairs, leaving three non-equivalent copper sites. In spite of slight differences in distances and angles between the metal centers and the O-atoms of the first coordination sphere (RMSD in the range of 0.05–0.09 Å), the Cu(II) sites are roughly equivalent and the whole symmetry of the molecular core is very close to idealized D_{3d} . The mean value of the Cu–O bond lengths for O-atoms located in the square plane is 1.95 Å, which is typical for dimeric copper carboxylates (usually in the range between 1.95 and 1.98 Å). The average Cu–O distance for the axial positions is considerably longer at 2.24 Å. The O-alkyl substituents have different conformations in each position of each crystallographically independent benzoate group. They are quite flexible and therefore severely disordered. Nevertheless, some intramolecular interactions between ethyl groups of one or different ligands as well as C–H... π interactions between ligands seem to operate, as revealed by a number of short contacts (Table S1). The two crystallographically independent hexanuclear compounds interact with each other only by weak Van der Waals forces.

To the best of our knowledge, there are only two previous examples of cyclic oligomeric copper species containing only carboxylates as bridges: hexakis(2,4,6-triisopropylbenzoato)-tricopper(II), $\text{Cu}_3(\text{O}_2\text{CC}_{15}\text{H}_{23})_6$, a trinuclear compound characterized by Clérac et al., [25] and dodekakis(phenoxyacetato)hexacopper(II), $\text{Cu}_6(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_{12}$, a hexanuclear cluster characterized by Carruthers et al. [9]. The latter exhibits a bridging scheme slightly different from the one operating in the case of $[\text{Cu}_6\text{L}_{12}]$, because the coordination sphere of the ions involves oxygen atoms that belong to ether groups. Both compounds exhibit intramolecular interactions along the external groups of the ligands, a fact that could help to stabilize the oligomeric arrangement with respect to the more usual dinuclear presentation.

3.3. Magnetic behavior

The temperature dependency of the magnetic susceptibility of a microcrystalline sample of $[\text{Cu}_6\text{L}_{12}] \cdot 2.25\text{C}_6\text{H}_{12}$ in the range 2–300 K is displayed in Fig. 3. The $\chi_m T$ values at high temperature are consistent with six independent $S = 1/2$ spin centers. The maximum in

Table 1

Crystal data and structure refinement for $[\text{Cu}_6\text{L}_{12}] \cdot 2.25\text{C}_6\text{H}_{12}$.

Empirical formula	$\text{C}_{169.5} \text{H}_{231} \text{Cu}_6 \text{O}_{60}$
Formula weight	3609.78
Temperature (K)	100(2)
Wavelength (Mo K α) (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$, No.2
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	17.6341(5)
<i>b</i> (Å)	21.1791(6)
<i>c</i> (Å)	24.6752(7)
α (°)	81.987(4)
β (°)	84.308(3)
γ (°)	83.583(3)
Volume (Å ³)	9035.6(4)
<i>Z</i>	2
Density (Calc.) (Mg m ⁻³)	1.327
Absorption coefficient (mm ⁻¹)	0.777
<i>F</i> (0 0 0)	3804
Crystal size (mm)	0.14 × 0.10 × 0.08
θ Range for data collection (°)	2.93–26.00
Index range	–21 ≤ <i>h</i> ≤ 21, –25 ≤ <i>k</i> ≤ 26, –30 ≤ <i>l</i> ≤ 30
Reflections collected	131372
Independent reflections	35432 [$R_{\text{int}} = 0.0521$]
Completeness to $\theta = 26.00$	99.7%
Absorption correction	semi-empirical from equivalents
Maximum and minimum transmission	0.9404 and 0.8990
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	35432/634/2281
Goodness-of-fit on F^2	1.017
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0609$, $wR_2 = 0.1516$
<i>R</i> indices (all data)	$R_1 = 0.0965$, $wR_2 = 0.1747$

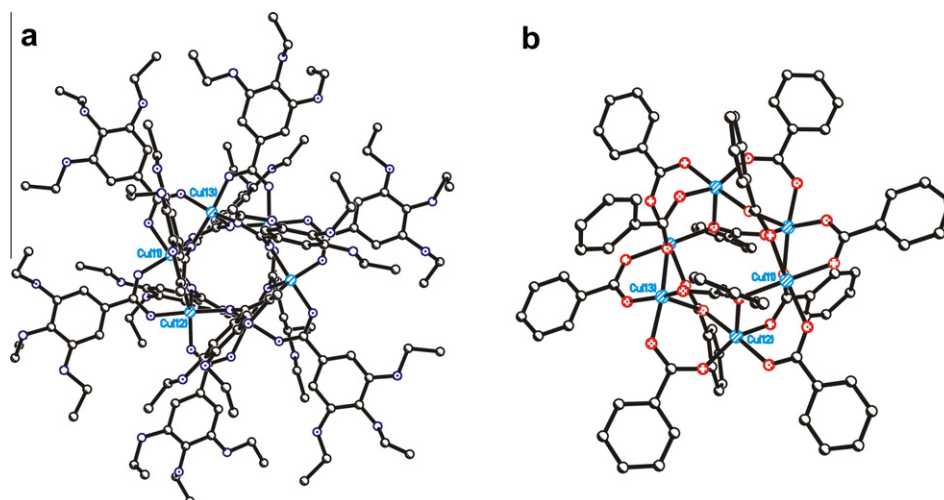


Fig. 1. Crystalline structure for compound $[\text{Cu}_6\text{L}_{12}] \cdot 2.25 \text{C}_6\text{H}_{12}$. (a) Top view where the hydrogen atoms were removed for better viewing. (b) Lateral view where also the side chains were removed.

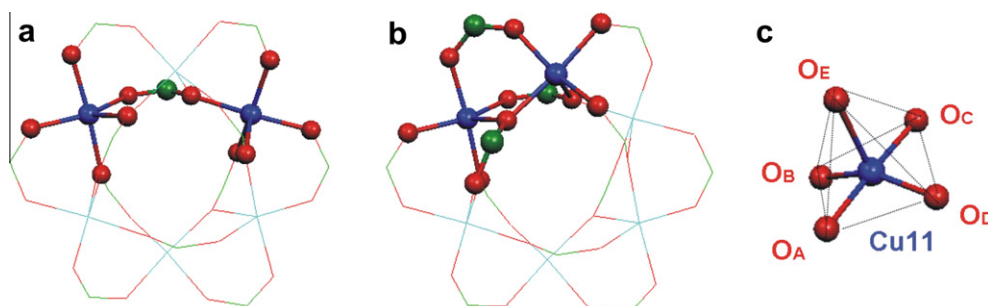


Fig. 2. Simplified molecular structure showing Cu centers and carboxylate bridges. (a) Bridges connecting a pair of Cu at 5.1 Å. (b) Bridges connecting a pair of Cu at 3.4 Å. (c) Labeling scheme around a copper center.

Table 2
Selected geometric parameters; distances (Cu–O_x) are shown in Å and angles (O_x–Cu–O_y) in degrees. Cu₁–Cu₃ and Cu₁₁–Cu₁₃ identify the independent Cu-sites in the crystallographically non-equivalent subunits (see text). Oxygen atoms are labeled according to the numbering scheme in Fig. 1.

	Cu ₁	Cu ₂	Cu ₃	Cu ₁₁	Cu ₁₂	Cu ₁₃
Cu–O _A	1.951(3)	1.966(3)	1.965(3)	1.967(3)	1.961(3)	1.960(3)
Cu–O _B	1.962(14) ^a	1.939(3)	1.946(3)	1.963(3)	1.959(3)	1.954(3)
Cu–O _C	1.934(3)	1.947(13) ^a	1.935(3)	1.936(3)	1.930(3)	1.928(3)
Cu–O _D	1.935(3)	1.941(3)	1.948(3)	1.958(3)	1.952(3)	1.952(3)
Cu–O _E	2.270(3)	2.236(3)	2.254(3)	2.226(2)	2.251(2)	2.238(3)
O _A –Cu–O _B	93.2(9)	93.14(13)	92.62(12)	93.28(11)	94.11(11)	92.98(11)
O _A –Cu–O _C	174.90(12)	172.9(9) ^a	174.20(13)	176.81(11)	177.21(11)	172.91(12)
O _A –Cu–O _D	90.35(11)	91.44(12)	91.06(13)	89.90(11)	91.57(11)	90.78(11)
O _A –Cu–O _E	93.35(11)	93.65(11)	93.01(11)	91.19(10)	93.28(10)	92.96(10)
O _B –Cu–O _C	86.1(8) ^a	84.4(9) ^a	85.14(13)	85.77(11)	84.07(12)	84.44(11)
O _B –Cu–O _D	155(1) ^a	156.38(14)	155.18(12)	154.95(11)	151.58(11)	157.97(12)
O _B –Cu–O _E	98(2) ^a	94.58(13)	99.19(12)	100.25(10)	100.31(10)	94.81(10)
O _C –Cu–O _D	88.22(13)	89(1) ^a	88.78(14)	89.69(11)	89.06(12)	89.20(11)
O _C –Cu–O _E	91.75(11)	91.3(5) ^a	92.63(12)	91.98(10)	89.12(10)	93.85(11)
O _D –Cu–O _E	106.15(12)	108.24(11)	105.12(11)	104.52(10)	107.14(10)	106.68(10)

^a The values correspond to the average over two disordered positions and have therefore higher uncertainties.

χ_m versus T at 8 K is an indication of (moderate) magnetic interactions between the Cu(II) ions.

The existence of six spin-carrying metal centers yields in principle a total of 15 different exchange interactions between pairs of centers: six of them involving Cu(II) ions 3.4 Å apart, other six involving Cu(II) ions separated 5.1 Å and further three between metal centers distant 6 Å from each other (the latter involve metal centers that are not directly connected by carboxylate units). In

order to prevent over-parameterization of the problem, it is necessary to introduce a certain number of constraints (approximations) when building the spin-Hamiltonian of the system. Some derive immediately from geometry considerations: if an idealized D_{3d} point group symmetry is assumed for the cluster, only three different exchange interactions have to be considered. Others come from the previous research in the field of molecular magnetism: since the historical paper by Bleanny and Bowers [6], a keystone for

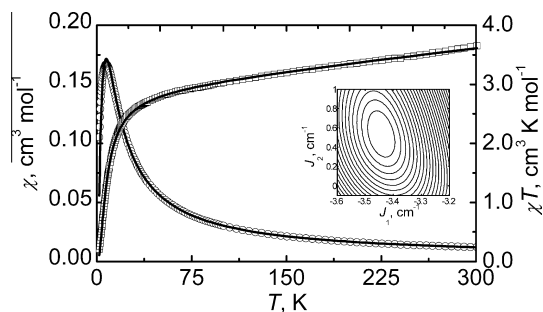


Fig. 3. Plot of χ vs. T (circles) and χT vs. T (squares) for a powder sample of $[\text{Cu}_6\text{L}_{12}] 2.25 \text{ C}_6\text{H}_{12}$. The solid lines represent the best fit to the spin Hamiltonian for the system (see text). Inset: Contour plot of $|\chi_{\text{calc}} - \chi_{\text{exp}}|/T$ vs. (J_1, J_2) in steps of $0.02 \text{ cm}^3 \text{ K mol}^{-1}$.

the understanding of exchange coupling in dinuclear and multinuclear coordination compounds, detailed magneto-structural correlations have been explored for carboxylato bridged transition metal containing systems. It is well established that the bridging carboxylates play a crucial role in the magnitude of exchange interaction between the metal centers [6,25,26]. This suggests that the interactions between the non-bridged centers are negligible for the analysis.

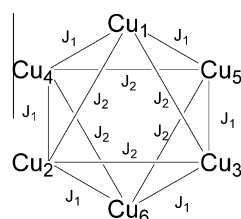
The magnetic interactions were therefore modeled taking into account the following considerations: (a) There is only one type of $[\text{Cu}_6\text{L}_{12}]$ molecule. (b) The system is magnetically dilute. (c) The six Cu(II) centers are identical. (d) The g -values of the $S = 1/2$ Cu(II) centers are considered to be isotropic. (e) The magnetic interactions between the metal centers propagate through the carboxylato net. There are only two independent exchange coupling constants associated to the interactions between Cu(II) centers with connectivity patterns described in Scheme 1. Our DFT calculations on this system (vide infra) are consistent with this assumption.

The spin Hamiltonian that results from these approximations has the form:

$$H = \mu \sum_{i=1, \dots, 6} S_i g_{\text{iso}} H - 2J_1(S_1S_4 + S_1S_5 + S_2S_4 + S_2S_6 + S_3S_5 + S_3S_6) - 2J_2(S_1S_2 + S_1S_3 + S_2S_3 + S_4S_5 + S_4S_6 + S_5S_6) \quad (3)$$

The experimental data for the magnetic susceptibility are satisfactorily reproduced for $J_1 = -3.5 \text{ cm}^{-1}$; $J_2 = 0.5 \text{ cm}^{-1}$ and $g_{\text{iso}} = 2.28$ (Fig. 3). The experimental g -value is consistent with the one derived from the UV–Vis spectrum in non-coordinating solvents ($g_{\perp} = 2.11$; $g_{\parallel} = 2.60$; $g_{\text{iso}} = 2.29$) [27] if the lowest energy transitions are assigned as d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ in origin, respectively [28]. The agreement is also an indication that the overall coordination environment of the metal centers are similar in solution and in the solid state, suggesting that the $[\text{Cu}_6\text{L}_{12}]$ clusters might not dissociate in this medium.

The rationalization of the experimental J values in terms of the connectivities between the metal centers requires a careful analysis. In the Lantern-like dinuclear compounds, the strong AF interaction has been ascribed to an exchange pathway that



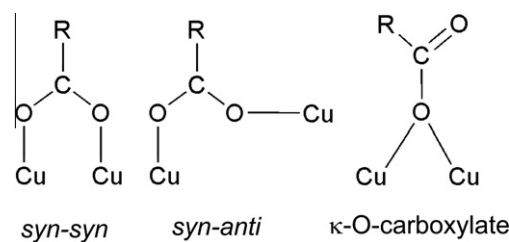
Scheme 1.

involves a *syn-syn* conformation of the carboxylato bridges [29], Scheme 2. On the contrary, when carboxylato bridges exhibit *syn-anti* conformation, much smaller AF exchange coupling constants have been found [29,30], and even ferromagnetic (F) exchange has been reported [31]. This difference could be qualitatively interpreted on the basis of current models for the interpretation of magnetic interactions [32]. The overlap between magnetic orbitals (usually $d_{x^2-y^2}$ in square pyramidal or related geometries) through an O–C–O framework approaches its maximum for a *syn-syn* conformation, but tends to zero for an idealized *syn-anti* conformation. This same kind of qualitative interpretation suggests that systems containing approximately *syn-anti* conformations could exhibit either weak AF or weak F interactions. A third possible linking pattern involves one O atom of a carboxylato group bridging simultaneously two different Cu(II) centers, one with *syn* conformation, the other with *anti* conformation. In such situations the magnetic interaction is still AF, but the reported J values are consistently smaller [33].

On this basis, we can reasonably justify the F nature of the exchange coupling between the Cu ions linked by a single carboxylato fragment in *syn-anti* conformation. However, the interpretation of AF exchange between the triply bridged metal centers is not straightforward due to the different nature of the three carboxylato bridges.

In order to gain a better understanding of the exchange coupling pathways and validate the assumptions made to interpret the magnetic results, we explored the system by means of the broken symmetry (BS) approach. Due to the high number of interacting spins, we performed these calculations under the doped cluster approximation (see Section 2) [20]. The large size of the molecule (426 atoms) prompted us to choose the LanL2DZ basis set sacrificing accuracy in the sake of a lower computational cost. Nevertheless, in order to assess the impact of this choice we performed similar calculations with two additional basis sets: TZV, 6-31G⁺⁺ but on a slightly smaller model compound, $\text{Cu}_6(\text{O}_2\text{CC}_6\text{H}_5)_{12}$, in which the substituents on the aromatic rings were replaced by H atoms. Both TZV and 6-31G⁺⁺ are typically employed on systems containing metals of the first transition series [20,34]. In spite of slight differences in the calculated exchange coupling parameters, the results from the three basis sets, collected in Table 3, were very similar. Complementary, the computational methodology was validated with the trinuclear species $\text{Cu}_3(\text{O}_2\text{CC}_{15}\text{H}_{23})_6$, a simpler system whose magnetic properties are well studied in the literature [25,35]. The results, also reported on Table 3, show excellent agreement between theory and experiment ($J_{\text{exp}} = -75.1 \text{ cm}^{-1}$).

The computational results obtained on the hexanuclear system (Table 3) fully support the analysis performed so far. On one hand, the evaluation of all possible exchange pathways reveal only three sets of exchange coupling constants, which is consistent with the idealized D_{3d} symmetry. On the other hand, the computed interactions between Cu atoms 3.4 Å apart, linked by two μ -carboxylate bridges and one κ -O-carboxylate were in all cases AF, while those between Cu atoms 5.1 Å apart and linked by one μ -carboxylate bridge were F . Finally, the Cu atoms further apart (6 Å) were not coupled at all ($J < 0.01 \text{ cm}^{-1}$).



Scheme 2.

Table 3
Coupling constants J (in cm^{-1}) for the studied compounds, as calculated from DFT-BS approach. J_1 refers to pairs of Cu atoms at 3.4 Å; J_2 refers to pairs of Cu atoms at 5.1 Å

Coupling constant	TZV	6-31G ⁺⁺	LanL2DZ
J in $\text{Cu}_3(\text{O}_2\text{C}_{16}\text{H}_{23})_6$	−91.9	−74.5	−91.2
J_1 in $[\text{Cu}_6\text{L}_{12}]$	–	–	−18.0
J_1 in $[\text{Cu}_6(\text{O}_2\text{CC}_6\text{H}_5)_{12}]$	−16.8	−10.3	−19.0
J_2 in $[\text{Cu}_6\text{L}_{12}]$	–	–	7.3
J_2 in $[\text{Cu}_6(\text{O}_2\text{CC}_6\text{H}_5)_{12}]$	7.9	5.0	8.4

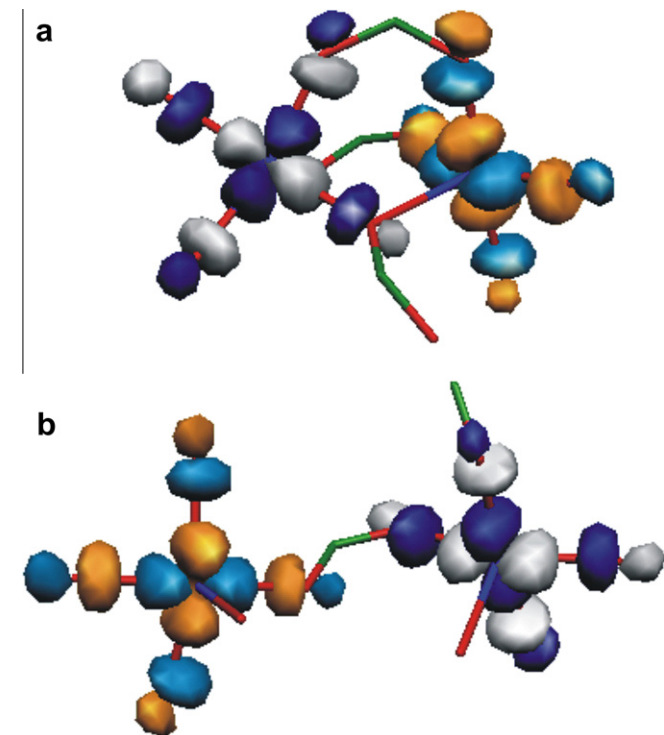


Fig. 4. Magnetic orbital for compound $[\text{Cu}_6\text{L}_{12}] \cdot 2.25 \text{C}_6\text{H}_{12}$ at the B3LYP level of theory, as obtained from the corresponding orbital transformation. (a) Cu atoms linked by two μ -carboxylate bridges and one κ -O-carboxylate. (b) Cu atoms linked by one μ -carboxylate bridge.

The spin density is mainly located on the Cu(II) centers, with only partial polarization on the neighboring O-atoms. The magnetic orbital of each copper center is displayed in Fig. 4. The representation is the result of a corresponding orbital transformation (COT) performed on the spin unrestricted computation output [24]. The SOMO is essentially the $d_{x^2-y^2}$ orbital, destabilized with respect to the d_{z^2} orbital due to the absence of a sixth atom in the axial direction. The distance between the metal centers and the orientation of the magnetic orbitals rule out the possibility of direct through-space interactions. The overlap integrals between the magnetic orbitals are small, due to the orientation of the magnetic orbitals. The AF exchange pathway between Cu(II) centers at 3.4 Å involves the *syn*–*syn* and κ -carboxylate bridge orbitals with virtually no contribution of the *syn*–*anti* bridge. This combination yields an overlap integral $S = 0.029$. The interaction between Cu atoms 5.1 Å apart mediated by a bridge in *syn*–*anti* configuration is even smaller ($S = 0.013$) because of the relative orientation of the orbitals involved, resulting in *F* exchange.

4. Conclusion

A hexameric copper compound of unusual structure and globular appearance was isolated and crystallized reproducibly. The

cluster arrangement seems to gain stabilization from the presence of bulky substituents on the carboxylate groups, a condition also met by other carboxylate-bridged-only copper oligomeric systems. In spite of the severe disorder induced by the flexibility of the outer O-ethyl chains we succeeded to solve the crystal structure, which provided valuable details about the coordination environment and the bridging modes between the metal centers.

In contrast with other carboxylate-bridged systems, this system revealed only moderate magnetic exchange interactions. The overall temperature dependent magnetic susceptibility behavior could be modeled on the basis of a simplified Hamiltonian. Two different types of intramolecular exchange coupling pathways could be identified, one AF in nature and one F. Both are weak and reflect the molecular geometry of the complex. DFT broken symmetry computations based on the doped cluster approach allowed us to rationalize this behavior and provide a representation of the magnetic orbitals and exchange pathways.

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Appendix A. Supplementary material

UV-Vis spectrum in CHCl_3 , MS-ESI (+) spectrum ($\text{CH}_2\text{Cl}_2/\text{MeOH}$), atom-by-atom comparison between non-equivalent units and Van der Waals and C–H $\cdots \pi$ interactions in $[\text{Cu}_6\text{L}_{12}] \cdot 2.25\text{C}_6\text{H}_{12}$. The crystallographic data of the structure described in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 812288. [Supplementary data](#) associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.025.

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