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Absence of a magnetic interaction in a dinuclear copper complex? The case of a crossed axial–equatorial oxalate coordination mode

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ABSTRACT

A simple and easy preparation of the hydrogen oxalate ligand $(HOOCCOO)^-$, with only one deprotonated carboxylic function, is described. ^{13}C NMR spectroscopy furnishes a straightforward characterization of this interesting ligand. This ligand coordinates in its monodeprotonated form to a Cu^{II} complex with a free coordination position, yielding a complex that presents a very weak antiferromagnetic interaction. In a subsequent step, the second deprotonation allows the isolation of an oxalato-bridged dinuclear Cu^{II} complex, which is characterized by structural determination, the copper ions being pentacoordinate in an equivalent centrosymmetry-related environment. DFT calculations show that the magnetic interaction through the oxalato bridge is strictly equal to 0 cm^{-1}, demonstrating that the singlet and triplet states of this oxalato-bridged dinuclear Cu^{II} complex have the same energy. This dinuclear complex presents a rhombic EPR spectrum, with three well-defined *g* values, at room temperature as well as at 100 K.

1. Introduction

Oxalic acid has been used so extensively for the preparation of di or polynuclear complexes of 3d ions that it seems impossible to give an exhaustive list of references dealing with that subject [1–5]. Indeed the resulting deprotonated oxalate ligand is a good chelating agent of 3d ions and also a good transmitter of magnetic interactions. The different topologies obtained for the coordination geometries of oxalate with transition metal ions and lanthanides have been reported [6]. At variance, the hydrogen oxalate ligand, in which only one carboxylic function is deprotonated, has only been reported in two papers dealing with the structural determination of Cr^{III} and Cu^{II} compounds [7,8]. In both cases, the ligand was prepared by serendipity, protonation of the starting oxalato ligand or complexation after degradation of squaric acid. However, this ligand can be isolated in large amounts and then used in the synthesis of a copper complex without further deprotonation. Afterwards, deprotonation of this entity yields a dinuclear oxalato-bridged copper compound. In this contribution, we focus on the formation of this interesting ligand, its characterization in solution by ^{13}C NMR spectroscopy and its use as a ligand towards Cu^{II} ions.

2. Experimental

2.1. Materials

Oxalic acid, piperidine and $LiOH{\cdot}H_2O$ (Aldrich) were used as purchased. High-grade solvents (acetone, diethyl ether and methanol) were used for the syntheses of the ligands and the complexes. The copper complex [9], bis(μ-acetato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))dicopper(II), $[(LCu(CH_3COO)]_2$, and the dideprotonated oxalate $(pipH)_2^+(Ox)^{2-}$ [10] were prepared as described previously.

2.2. Ligand

$(pipH)^+(HOOCCOO)^-$. To oxalic acid (3 g, 33.3 mmol) dissolved in acetone (100 mL) was added an acetone solution (20 mL) containing piperidine (2.83 g, 33.3 mmol). The white precipitate which appeared immediately, was stirred at room temperature for 30 min and filtered off, washed with acetone and diethyl ether, and then dried. Yield: 5 g (86%). *Anal.* Calc. for $C_7H_{13}NO_4$ (175.0): C, 48.0; H, 7.5; N, 8.0. Found: C, 47.8; H, 7.8; N, 8.2%. ^{13}C NMR (DMSO) δ (ppm): 168.1 (HOOCCOO), 46.9 ($N{-}C_{ortho}$), 24.6 (C_{meta}), 23.8 (C_{para}).

2.3. Complexes

$LCu(HOOCCOO)(H_2O)$ **1**. To $[(LCu(CH_3COO)]_2$ (0.5 g, 1.9 mmol), dissolved in distilled water (15 mL) was added $(pipH)^+(OxH)^-$

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(0.33 g, 1.9 mmol) as a solid. A few minutes later a blue precipitate appeared in the blue solution, which was stirred for 30 min at room temperature. The precipitate was filtered off by suction, washed with acetone and diethyl ether, and then dried. Yield: 0.2 g (34%). *Anal.* Calc. for $C_9H_{16}CuN_2O_6$ (311.8): C, 34.7; H, 5.2; N, 9.0. Found: C, 34.3; H, 5.0; N, 8.9%. IR (ATR, cm^{-1}): 3379w, 3315m, 3238m, 3153m, 2951w, 1661m, 1616m, 1586s, 1509s, 1461m, 1443w, 1403s, 1355w, 1337m, 1310m, 1275m, 1218w, 1136m, 1092m, 1073w, 1015m, 947w, 790m, 753m, 700w, 647w.

[LCu(Ox)CuL]·2H$_2$O **2**. As the yield of the previous reaction is rather low, the filtrate was kept and $LiOH·H_2O$ (0.04 g, 1 mmol) was added to the filtrate. The resulting solution was kept undisturbed for three days, yielding blue crystals. Yield: 0.15 g (30%). *Anal.* Calc. for $C_{16}H_{30}Cu_2N_4O_8$ (533.5): C, 36.0; H, 5.7; N, 10.5. Found: C, 35.8; H, 5.4; N, 10.2%. IR (ATR, cm^{-1}): 3451m, 3393m, 3324m, 3266m, 2929w, 1663s, 1596m, 1586m, 1504s, 1462m, 1437m, 1414s, 1396m, 1339m, 1314w, 1281w, 1261w, 1216w, 1137w, 1123w, 1087m, 1010m, 941m, 915w, 796m, 741m, 668w.

This compound was also prepared in a more classical way by the addition of $(pipH)_2{}^{+}(Ox)^{2-}$ (0.26 g, 1 mmol) to a water solution of $[(LCu(CH_3COO)]_2$ (0.26 g, 1 mmol). The precipitate that appeared quickly in 80% yield gave the same infrared and analytical data.

2.4. Crystal structure

Crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of the corresponding water solution. The selected crystal of 2 (yellow parallelepiped, 0.50 × 0.20 × 0.10 mm3) was mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected at 293 K up to 27° in the $\omega-2\theta$ scan mode and reduced with the MOLEN package [11]. Absorption corrections [12] from ψ scans were applied (Tmin − max = 0.7831 − 0.9972).

The structure was solved using SHELXS-97 [13] and refined on F^2 by full-matrix least-squares using SHELXL-97 [14] with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in the calculations using the riding model. Isotropic U_H factors were 1.1 times higher than those of the atom to which they were bonded. The atomic scattering factors and anomalous dispersion terms were taken from a standard compilation [15]. The maximum and minimum peaks on the final difference Fourier map were 0.633 and −0.310 e Å^{-3} for **2**. A drawing of the molecule was performed with the program ZORTEP [16]. Crystal data collection and refinement parameters are given below, and selected bond distances and angles are gathered in the figure caption.

2.4.1. Crystal data for 2

$C_{16}H_{30}Cu_2N_4O_8$, M = 533.52, monoclinic, $P2_1/c$ (N°14), Z = 2, a = 14.499(2), b = 6.0623(16), c = 12.8240(18) Å, β = 91.899(12)°, V = 1126.6(4) Å^3, 2554 collected reflections, 2455 unique reflections (R_{int} = 0.0214), R = 0.0336, R_w = 0.0623 for 1788 contributing reflections [$I > 2\sigma(I)$].

2.5. Physical measurements

C, H and N elemental analyses were carried out at the Laboratoire de Chimie de Coordination Microanalytical Laboratory in Toulouse, France. IR spectra were recorded with a Perkin-Elmer Spectrum 100FTIR using the ATR mode. 1D ^{13}C spectra using ^1H broadband decoupling $\{^1H\}^{13}C$ were performed with a Bruker WM250 apparatus working at 62.89 MHz using $(CD_3)_2SO$ as solvent. Chemical shifts are given in ppm versus TMS. Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 2–300 K temperature range under a 0.1 T applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants [17]. Isothermal magnetization measurements were performed up to 5 T at 2 K. The magnetic susceptibilities have been computed by exact calculations of the energy levels associated with the spin Hamiltonian through diagonalization of the full matrix with a general program for axial symmetry [18], and with the MAGPACK program package [19] in the case of magnetization. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT [20].

2.6. Computational details

All theoretical calculations were carried out at the density functional theory (DFT) level using the hybrid B3LYP exchange-correlation functional [21], as implemented in the GAUSSIAN 09 program [22]. A quadratic convergence method was employed in the self-consistent-field process [23]. The triple-ζ quality basis set proposed by Ahlrichs and co-workers has been used for all atoms [24]. Calculations were performed on complexes built from experimental geometries as well as on model complexes. The electronic configurations used as starting points were created using Jaguar 7.9 software [25].

3. Results

Addition of piperidine to a DMF solution of oxalic acid yields a white precipitate that corresponds to the dideprotonated oxalate salt along with two piperidinium cations. When carried out in acetone, the same reaction yields only the monodeprotonated oxalic acid with a piperidinium countercation. This monodeprotonation is clearly shown by ^{13}C NMR spectroscopy. Oxalic acid gives a single signal at 160.9 ppm for the COOH carbon atom, while the deprotonated COO^- of the $(pipH)_2{}^{+}(Ox)^{2-}$ species appears at 175.7 ppm. In our $(pipH)^{+}(HOOCCOO)^{-}$ compound, we could expect two signals corresponding to the COOH and COO^- carbon atoms, but we observed a unique signal at 168.1 ppm. This is due to the presence of a fast proton exchange between the carboxylate and carboxylic functions, with an intermediately located signal, in between those corresponding to the non-deprotonated and dideprotonated forms. However, the signals of the piperidinium cations are quite similar in the two different species, $(pipH)^{+}(HOOCCOO)^{-}$ and $(pipH)_2{}^{+}(Ox)^{2-}$. Three signals are observed at 46.9, 24.6 and 23.8 ppm in the two samples, for the carbon atoms in ortho, meta and para positions of the nitrogen atom, respectively. $(pipH)^{+}$(-HOOCCOO)$^-$ reacts with $[(LCu(CH_3COO)]_2$ in a 1:1 ratio to give the neutral $LCu(HOOCCOO)(H_2O)$ blue complex for which we have not been able to isolate crystals suitable for X-ray structure determination. Addition of a base, lithium hydroxide, to the blue filtrate of the reaction yielded nice blue crystals corresponding to a dinuclear copper complex in which the two copper ions are linked by the dideprotonated oxalate ligand. Infrared spectra of complexes **1** and **2** differ in the 3500–3000 and 1670–1560 cm^{-1} regions. In the first region, there is an additional stretching OH vibration, not easy to assign among the bands originating from the stretching NH_2 and water vibrations. In the other area, a band at 1663 cm^{-1} and two bands of equal intensity appear at 1596 and 1586 cm^{-1} for complex **2**, while two intense bands at 1661 and 1586 cm^{-1}, along with a band of lower intensity at 1616 cm^{-1} are present for complex **1**. The bands around 1600 cm^{-1} are attributable to the C=O and C=N stretching vibrations originating from the ligand, by comparison with other LCuX complexes (X = N_3, SCN) [26] and the band at 1663–1661 cm^{-1} corresponds to the ν_{asym} COO vibration of the deprotonated oxalato function. We have then concluded that the band at 1586 cm^{-1} originates from the carboxylic acid of the hydrogen oxalato $HOOCCOO^-$ ligand.

Solution visible spectra (DMSO) of complexes **1** and **2** are characterized by very similar d–d transitions at 640 nm for **1** and 636 nm for **2**. These spectra are consistent with at least a pentacoordination of the Cu ions.

3.1. Structural determination

A view of the dinuclear complex **2** is shown in Fig. 1 while selected bond lengths and angles are listed in the figure caption. Two LCu cationic units are linked by the deprotonated oxalate, thus yielding a neutral dinuclear complex. There is an inversion center located in the middle of the C–C oxalate bond. The copper ion is pentacoordinate, in a distorted (4 + 1) geometry. The four equatorial bond lengths span the range 1.923(2)–2.001(2) Å; they involve the three Cu–O and the Cu–N bonds to the ligand and one of the Cu–O oxalato bonds. We note the large difference between the two Cu–O oxalate bond lengths, 2.001(2) for Cu–O2 and 2.287(2) Å for Cu–O3. The plane defined by the three ligand donor atoms and the copper ion makes an angle of 86.9(1)° with the oxalate plane, and the two planes containing the three ligand donor atoms and the copper ion are strictly parallel, the distance between the two planes being equal to the Cu···Cu distance of 5.541(3) Å. The non-coordinated water molecules are involved in hydrogen bonds between two symmetry-related oxalato oxygen atoms and the keto oxygen atoms of the tridentate ligand, which results in the formation of 1D chains that are linked together through other hydrogen bonds involving the other two symmetry-related oxalato oxygen atoms and the coordinated primary amine functions, thus yielding a 2D lattice.

3.2. Magnetic properties

The magnetic susceptibility of complexes **1** and **2** has been measured in the 2–300 K temperature range under an applied magnetic field of 0.1 T. The thermal variation of the $\chi_M T$ product for **2** is displayed in Fig. 2, χ_M being the molar magnetic susceptibility of the dinuclear species corrected for the diamagnetism of the ligands. From 300 to 15 K, $\chi_M T$ is equal to 0.81 cm^3 mol^{-1} K, which corresponds to the value expected for two uncoupled copper ions with $g = 2$ (0.75 cm^3 mol^{-1} K). Lowering the temperature results in a slow decrease of $\chi_M T$ down to 2 K (0.38 cm^3 mol^{-1} K). This behavior indicates that a weak antiferromagnetic interaction operates at low temperature. A qualitative analysis has been performed with a simple isotropic Hamiltonian, $H = -2J(S_{Cu1}.S_{Cu2})$, while intermolecular interactions through the hydrogen bonding network were taken into account by the mean-field Hamiltonian [27]. The resulting interaction parameter is very weak, $J_{CuCu} = -1.15$ cm^{-1}, $zj = -0.22$ cm^{-1}, with $g = 2.13$ and a nice agreement factor $R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2$ equal to 6×10^{-5}. As the structure of complex **1** is unknown, it was first analyzed as a mononuclear complex, but the $\chi_M T$ decrease at low temperature confirms presence of a higher nuclearity. By analogy with the starting dinuclear acetate complex, a dinuclear model was been investigated. The corresponding $\chi_M T$ product is constant (0.75 cm^3 mol^{-1} K) from 300 to 50 K, and then decreases to 0.03 cm^3 mol^{-1} K at 2 K (Fig. 3). This larger decrease means that a slightly larger magnetic interaction occurs in this expected dinuclear complex. Applying the above Hamiltonian yields $J_{CuCu} = -3.9$ cm^{-1}, $zj = -0.68$ cm^{-1}, with $g = 2.11$ and $R = 2 \times 10^{-5}$. It should be noted that a fitting of these data with a chain model does not give satisfactory results.

EPR spectra are interesting because they allow a straightforward characterization of complexes **1** and **2**. In the solid state, a spectrum of axial symmetry, with $g_{par} = 2.225$ and $g_{per} = 2.084$, is associated with complex **1** (Fig. 4). A very weak half-field transition can be shown with a 1600 amplification gain, in agreement with the presence of weak Cu–Cu magnetic interactions (Fig. S3). A

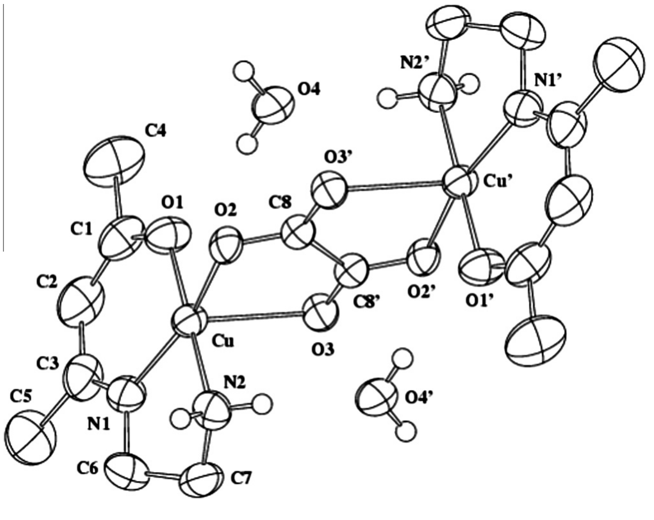

Fig. 1. Molecular structure of the oxalate-bridged dinuclear [LCu(Ox)CuL].2H_2O complex **2** with the partial atom numbering scheme. H atoms, except those of water molecules and primary amine functions, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu–O1 1.923(2), Cu–O2 2.0005(18), Cu–O3 2.2869(18), Cu–N1 1.940(2), Cu–N2 1.983(3), O1–Cu–N1 93.86(9), N1–Cu–N2 85.10(10), O2–Cu–O3 77.78(6), O1–Cu–O3 91.30(8).

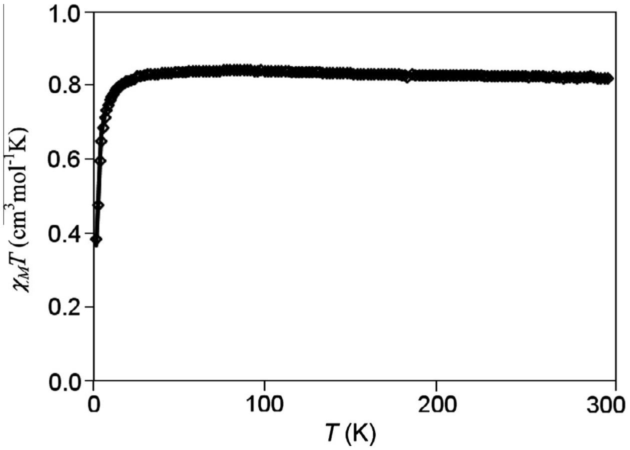

Fig. 2. Temperature dependence of the $\chi_M T$ product for complex **2**. The solid line corresponds to the best data fit, see text.

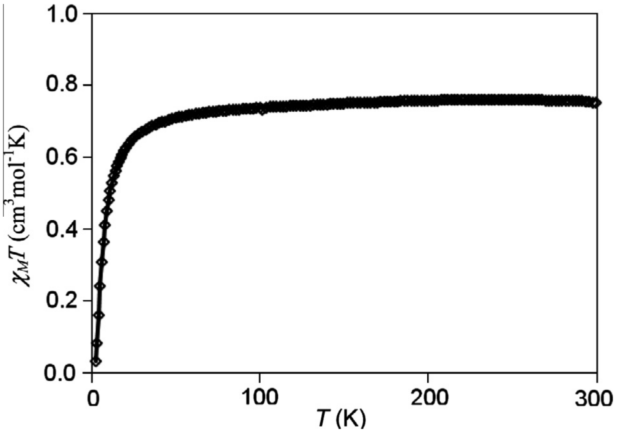

Fig. 3. Temperature dependence of the $\chi_M T$ product for complex **1**. The solid line corresponds to the best data fit, see text.

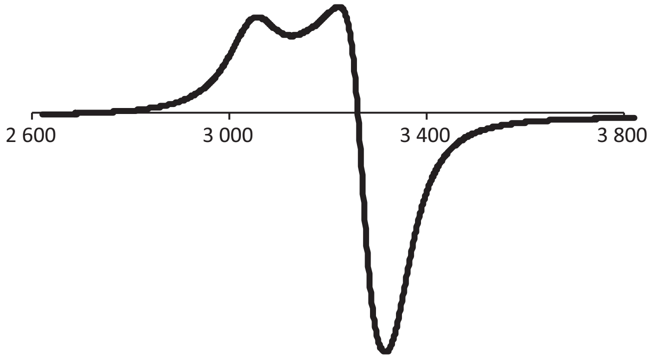

Fig. 4. X-band EPR spectrum of complex **1**.

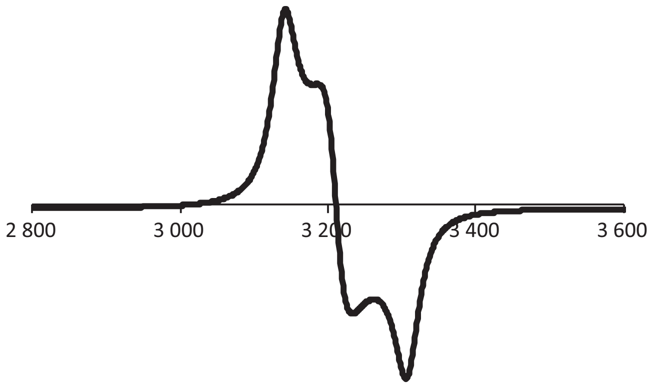

Fig. 5. X-band EPR spectrum of complex **2**.

rhombic spectrum with three g values, $g_1 = 2.166$, $g_2 = 2.120$, $g_3 = 2.057$, is seen for complex **2** (Fig. 5). This observation along with the absence of half-field transition should be in relation to the weak magnetic interaction found for this complex.

In order to confirm the very weak magnetic coupling observed in complex **2**, we have performed DFT calculations following the Broken-Symmetry (BS) approach from the model crystal structure described above. The exactly zero value found for the exchange coupling constant (*J*) means an equal energy value of the two possible magnetic states, namely the parallel-spin (triplet) and the opposite-spin (singlet) states. This behavior should be ascribed to the relative orientation of the bridge between neighboring Cu^{II} ions, suggesting the existence of a unique operative magnetic path connecting the equatorial and axial positions, thus leading to non-coupled magnetic centers. This exchange pathway always produces, if any, negligible magnetic interactions regardless of the structural parameters of the bridge [28]. This is because the magnetic orbital on the Cu^{II} is located in the equatorial plane (the d_{x2-y2} magnetic orbital is directed toward the nitrogen and oxygen atoms of the L ligand on each copper moiety) and, therefore, the spin density on its axial position is expected to be almost zero, as it appears in the spin density map depicted in Fig. 6. We have also collected some representative spin density values in Table 1.

Although the crystal structure of complex **1** is still unknown, DFT calculations have been carried out, starting with the model crystal structure of the $[LCu(CH_3COO)]_2$ complex previously published [9], in which the mono-*O*-acetato bridging ligand is replaced by a monodeprotonated oxalato ligand acting in the same bridging mode. We have indeed calculated two different structures called **1a** and **1b**, in which all the atoms (including the oxygen bridging atom) have the same positions as found in the crystal structure, except for the C_2O_3H fragment which should be properly accommodated. The structure **1a** has the same $CuO_{bridged}C$ angle as the acetato ligand in the parent compound, whereas **1b** has been modified by an in plane displacement of the oxalato moieties by 10° away from the corresponding neighboring ligands in order to avoid some steric hindrance occurring between the oxalato group and the close ligand, see Fig. 7. For these structures, we have found coupling constant (*J*) values of -0.02 and $+0.09\ cm^{-1}$, respectively, confirming the small exchange coupling exhibited by these systems.

4. Discussion

Potassium and sodium oxalate ligands have been used for a long time to yield oxalato bridged transition metal complexes. There are so many complexes that we cannot furnish an exhaustive list. Organic bases such as piperidine have been used as countercations to provide more soluble oxalate salts [29]. Following this route, it is possible to isolate the monodeprotonated form of oxalic acid $HOOCCOO^-$ in large amounts, by using acetone as the solvent. The resulting hydrogen oxalate ligand is nicely characterized by its ^{13}C NMR spectrum. This ligand can also be linked to a copper complex in this form, without deprotonation of the second carboxylic function, using distilled water as the solvent. In methanol, a mixture of complexes **1** and **2** was obtained, complex **2** being the most abundant. Unfortunately, the structure of compound **1** remains unknown. This ancillary $COOHCOO^-$ ligand can coordinate to the copper ion as a chelate or only through the deprotonated oxygen atom, as does the acetato ligand in a complex involving the same LCu unit in the $[LCu(CH_3COO)]_2$ dinuclear complex [9]. These two possibilities result at least in a pentacoordination of

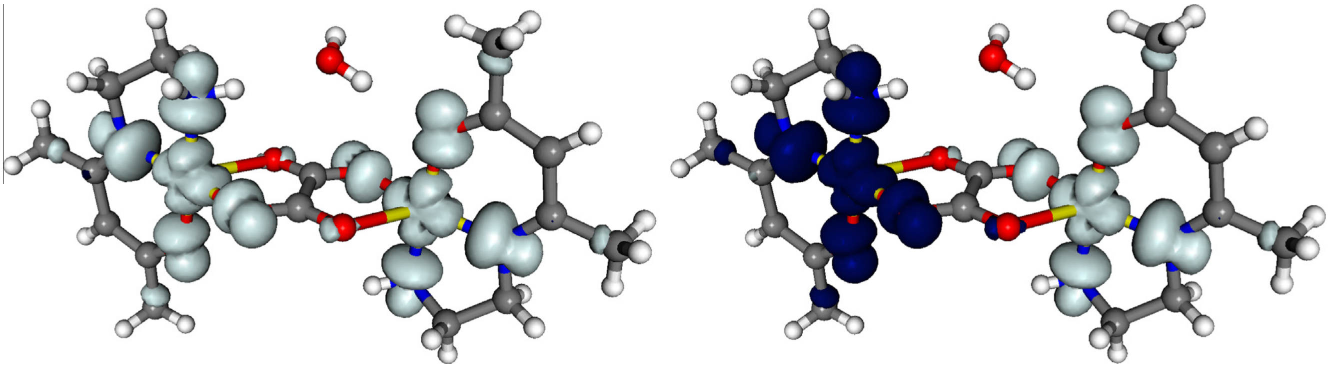

Fig. 6. Calculated spin densities for complex **2** in the triplet (left) and singlet (right) states. The represented isodensity surfaces correspond to a cut-off value of 0.0015 e $Bohr^{-3}$. Grey and blue colors correspond to positive and negative values, respectively. (Colour online).

Table 1
Spin density values (in e^-) on selected atoms for complex **2**.

Atoms[a]	Parallel-spin (triplet) state	Opposite-spin (singlet) state
Cu1/Cu2	+0.6219/+0.6261	−0.6216/+0.6258
$N1_{amine}/N2_{amine}$	+0.0945/+0.0908	−0.0943/+0.0907
$N1_{imine}/N2_{imine}$	+0.1076/+0.1065	−0.1075/+0.1065
$O1_{enolate}/O2_{enolate}$	+0.1013/+0.0929	−0.1012/+0.0929
$O1_{oxalate\text{-}eq}/O2_{oxalate\text{-}eq}$	+0.0724/+0.0792	−0.0707/+0.0783
$O1_{oxalate\text{-}ax}/O2_{oxalate\text{-}ax}$	+0.0069/+0.0056	+0.0016/−0.0001

[a] Indexes 1 and 2 refers to the Cu1 and Cu2 moieties, respectively.

the Cu^{II} ion, in agreement with the d-d transition at 640 nm. In a recent work [8], the structural determination of a copper complex of this hydrogen oxalate ligand, originating from the decomposition of squaric acid, indicates that $COOHCOO^-$ is chelated through two oxygen atoms to the Cu^{II} ion and that the outer oxygen atom is able to enter the coordination sphere of the neighbouring Cu^{II} ion in the apical position to yield a 1D chain compound. Such a coordination in our case would yield again a 1D chain, with a hexacoordinated Cu^{II} ion, which it is not in accordance with the observation of a visible spectrum similar to that of complex **2**, along with the impossibility to obtain an acceptable fit of the magnetic data to a 1D chain model.

Adding a base to a solution of complex **1** allows complex **2** to be generated, in which the oxalato dianion bridges two cationic LCu units, thus yielding a neutral compound. The structural determination shows that the copper ions are in a pentacoordinated (4 + 1) coordination mode, with four short bond lengths and a fifth longer bond. The SHAPE program [30] allows the confirmation that the Cu^{II} ion can be equally considered in a vacant octahedron ($S_{Oh} = 2.76$) or a square pyramidal environment ($S_{SP} = 2.66$). Importantly, the mean coordination planes involving the donor atoms of the tridentate ligand and the copper ions are strictly parallel, separated by a distance of 2.019(2) Å. Indeed, when two Cu^{II} ions are chelated to an oxalato ligand, the two copper magnetic orbitals can be coplanar, perpendicular, parallel or in a trigonal-bipyramidal topology [31]. These four orientations have been experimentally found. In the parallel case, the magnetic interaction is weak, varying from −37 to +1.2 cm^{-1}. In a more recent example, a ferromagnetic interaction of +5.4 cm^{-1} has been reported [32]. These examples involve mainly complexes made with polyamine ligands. In comparison with these polyamine ligands, a partial electronic delocalization occurs in the tridentate ligand coordinated to copper in complex **2**, thus defining a planar equatorial plane around the copper ion. The presence of a crystallographic inversion center in the middle of the C–C oxalato bond constrains the two copper magnetic orbitals to be in a parallel orientation, which results in the perfect absence of a magnetic interaction, as estimated in a previous work [2]. The observation of a nice rhombic EPR spectrum without any half-field transition does confirm that there is no magnetic interaction between the two equivalent Cu^{II} ions. It has also been shown by DFT calculations that the triplet and singlet states have the same energy, in agreement with the presence of non-coupled magnetic Cu^{II} centers.

5. Conclusion

We have described a synthetic pathway able to yield large amounts of the hydrogen oxalate $HOOCCOO^-$ ligand. This ligand can be coordinated to a copper complex possessing a free equatorial position without further deprotonation. In spite of the lack of structural determination, the magnetic study is in agreement with a dinuclear compound including a five coordinate Cu^{II} ion. Such a result can be reached in two ways, the hydrogen oxalato $HOOCCOO^-$ ligand bridging two copper ions through a single oxygen atom, as observed in the $[LCu(CH_3COO)]_2$ complex [9] or through a more classical two oxygen atoms bridge, as in the copper acetate complex. In view of a recent X-ray study of a Cu^{II} compound including the sole hydrogen oxalate ligand [8], the second possibility should be considered. Complete deprotonation by addition of base to a water solution of the above complex yields a dinuclear complex in which the two symmetry-related Cu^{II} ions are pentacoordinate and linked by the oxalato ligand. The absence of a magnetic interaction through the oxalato bridge is confirmed by the constant $\chi_M T$ product from 300 to 15 K, the absence of half-field transition in the rhombic EPR spectrum and by DFT calculations evidencing that the singlet and triplet states have the same energy. The low $\chi_M T$ product in the 2–10 K temperature range could result from the hydrogen bonding network through the water molecules. We note that deprotonation of the $LCu(HOOCCOO)(H_2O)$ complex should yield polynuclear Cu-3d or Cu-4f complexes. Unfortunately, the expected complexes have not been characterized to date.

Appendix A. Supplementary data

CCDC 945567 contains the supplementary crystallographic data for complex **2**. 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. The ^{13}C NMR spectrum of the monodeprotonated oxalic acid and

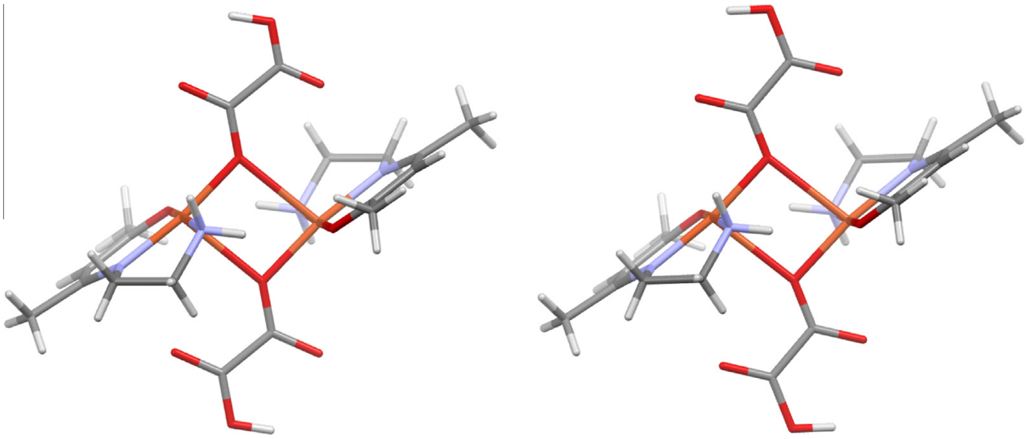

Fig. 7. DFT calculated structures **1a** (left) and **1b** (right). In **1b**, the oxalate moieties were symmetrically rotated by 10° away the neighboring ligands.

EPR spectra of the complexes are given in the Supplementary Material. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.06.054.

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