Strong Ferromagnetic Coupling in Linear Mixed μ-Acetato, μ-Hydroxo Trinuclear Copper(II) Complexes with *N*-sulfonamide derivatives − Synthesis, Structure, EPR and Magnetic Properties

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Two new trinuclear copper(II) complexes have been synthesised and structurally characterised: $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) [HL1 = *N*-(pyrid-2-ylmethyl)benzenesulfonylamide] and $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**) [HL2 = *N*-(pyrid-2-ylmethyl)naphthalenesulfonylamide]. In both complexes the central copper ion has a regular square planar geometry. The coordination spheres of the terminal copper atoms are square pyramidal, the apical positions being occupied by a DMF oxygen atom in **1** and by a sulfonamido oxygen of the contiguous trimer in **2**, as a consequence the latter can be considered a chain of trinuclear species. For the two compounds the three copper atoms are in a strict linear arrangement and adjacent coppers are connected by a hydroxo bridge and a bidentate *syn-syn* carboxylato group. The mixed bridging by a hydroxide oxygen atom and a bidentate carboxylato group leads to a noncoplanarity of the adjacent basal coordination planes with a dihedral angle of 54.4(1)° for compound **1** and 58.34(3)° for compound **2**. Susceptibility measurements (2–300 K) reveal a strong ferromagnetic coupling, J = 94.0 and 59.1 cm^{-1}, respectively, in the mixed-bridged moiety leading to a quadruplet ground state that is confirmed by the EPR spectra. The ferromagnetic coupling arising from the countercomplementarity of the hydroxo and acetato bridges has been discussed on the basis of DFT calculations on model compounds.

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Introduction

There is a great deal of interest in multimetallic complexes due to the special chemical and physical properties resulting from the mutual interaction of two or more metal centres.[1] Investigations of trinuclear transition metal complexes have been of increasing interest in recent years. One reason for this was the lack of metallobiomolecules for which the trinuclear core can act as a synthetic analogue. The MCD spectroscopic proof of a trinuclear active site in laccase,[2] the recent discovery of a ferromagnetically coupled Cu^{II} triad in a subunit of methane mono-oxygenase[3] and an X-ray structure analysis of ascorbate oxidase from zucchini,[4] which revealed an angled trimeric Cu^{II} unit as well as a mononuclear type 1 copper(II) centre, have all stimulated an increasing interest in the study of trinuclear copper systems.

Very recently we have reported a ferromagnetically coupled copper(II) triad that has been synthesised and structurally as well as magnetically characterised.[5] This compound presents a linear arrangement of the three copper(II) atoms linked by μ-hydroxo and μ-carboxylato bridges. Until now this complex and that previously reported by Haase et al.[6] are the only ferromagnetic linear trinuclear copper(II) complexes fully characterised.

The importance of these systems does not arise only from the occurrence of this bridging unit in several metalloproteins.[7] These studies are also related to the properties of quadruplet ground states, to magnetostructural correlations in mixed bridged systems, to ferromagnetic exchange coupling, and to long-range coupling effects between terminal copper centres.

Within this framework and following our current study on multiatom-bridged exchange-coupled systems we report here the synthesis, X-ray structure and magnetic properties of two trinuclear copper(II) complexes, $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and $[Cu_3(L2)_2(CH_3COO)_2$-

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$(OH)_2]_\infty$ (**2**) {HL1 = [*N*-(pyrid-2-ylmethyl)benzenesulfonylamide)] and HL2 = [*N*-pyrid-2-ylmethylnaphthalenesulfonylamide]}. In both compounds the copper atoms are bridged by hydroxo and acetate groups. In compound **2** the trinuclear units are linked by a sulfonamide oxygen atom from the HL2 ligand leading to a three dimensional network. The complexes display a linear arrangement of the copper centres and a strong ferromagnetically coupled pair of copper atoms.

Results and Discussion

Crystal Structure of $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (1)

The trinuclear entity of compound **1** with the atomic labelling scheme used is shown in Figure 1. Selected bond lengths and angles are collected in Table 1. The complex molecule consists of a neutral symmetrical trinuclear unit and two disordered dimethylformamide molecules along with the Cu(2) at the symmetry centre. The terminal copper atoms Cu(1) and Cu(1a) have a distorted square pyramidal geometry (τ parameter 0.30) coordinated by two nitrogen atoms N(1) and N(2) of the pyridyl ring and of the sulfonamidato group of the deprotonated ligand ($L1^-$), the O(1) of the hydroxo bridge, the O(21) of the acetate bridge and the O(30) from a dimethylformamide solvent. The central Cu(2) presents a regular square plane geometry formed from the O(1), O(1a), O(22) and O(22a) atoms of the hydroxo and acetate bridging groups, respectively [deviation of the O(1), O(22), O(1a), O(22a), and Cu(2) atoms from the plane, 0.000].

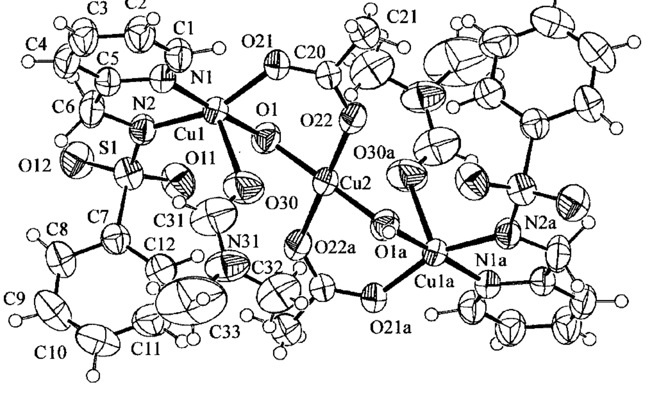

Figure 1. Molecular structure of $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**)

Adjacent copper centres are bridged by the oxygen atom of the hydroxo ligand [Cu(1)−O(1)−Cu(2) = 113.33(15)°] and two oxygen atoms of a bidentate *syn-syn* carboxylato group leading to a mixed-bridged coplanar coordination geometry with Cu(1)···Cu(2) = 3.1656(6) Å. The Cu(2)−O(1) and Cu(2)−O(22) bond lengths are 1.899(3) Å and 1.959(3) Å, respectively. The Cu(1)−N(1) and Cu(1)−N(2) lengths are 2.004(3) Å and 2005(3) Å, respectively, and the Cu(1)−O(1) and Cu(1)−O(21) bond lengths are 1.890(3) Å and 1.981(3) Å. The apical bond length Cu(1)−O(30) is 2.398(4) Å. The two O(30) and O(30a) atoms from the DMF molecules linked to the Cu(1) and Cu(1a) centres are at 2.776(5) Å from the Cu(2). The Cu(1)−O(11) and Cu(1)−O(12) distances are 3.420(2) and 4.422(3) Å indicating that the Cu^{II} ions do not interact with the oxygen atoms of the sulfonamido group. Bond lengths are similar to those of the previously reported $[Cu_3(L)_2(CH_3COO)_2(OH)_2(DMF)_2]$ [HL = *N*-(pyrid-2-ylmethyl)toluensulfonylamide] compound[5] except for the Cu−O(30) bond length, which is significantly shorter (ca. 0.12 Å) in the present compound.

The Cu(1) atom is 0.1706 Å from the square plane formed by the N(1), N(2), O(1) and O(21) atoms. The skeleton Cu(1a)−O(1)−Cu(2)−O(1a)−Cu(1) is in a zigzag with the three copper ions forming a straight line with an angle of 180°. The mixed bridging leads to a noncoplanarity of the basal N(1)N(2)O(1)O(2) and O(1)O(22)O(22A)O(21A) planes characterised by a folding angle of 54.4(1)°.

Crystal Structure of $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (2)

The trinuclear entity with the atomic labelling scheme used is shown in Figure 2. Selected bond lengths and angles are listed in Table 1. The polymer compound consists of trinuclear copper fragments $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]$. The sites of the central and terminal copper ions are nonequivalent. The geometry around the terminal copper atoms Cu(1) and Cu(1A) is distorted square pyramidal (τ parameter 0.22) with a $CuN_2O_2\cdots O$ chromophore. The basal plane is described by the two nitrogen atoms N(1) and N(2) of the pyridyl ring and of the sulfonamidato group of the deprotonated ligand ($L2^-$), the O(1) of the hydroxo bridge and O(21) of the acetate bridge. The apical position is occupied by a sulfonamide O atom [O(11B)] of another $L2^-$ ligand pertaining to a contiguous asymmetric unit. For the central Cu(2) a regular square plane geometry is realised with the O(1), O(1A), O(22) and O(22A) atoms from the hydroxo and acetate bridging groups, respectively.

The Cu−O and Cu−N distances are similar to those found in complex **1**. The Cu(2)−O(1) and Cu(2)−O(22) bond lengths are 1.883(8) Å and 2.005(7) respectively. The Cu(1)−N(1) and Cu(1)−N(2) lengths are 2.022(10) Å and 1.991(9) Å, respectively, and the Cu(1)−O(1) and Cu(1)−O(21) bond lengths are 1.914(7) Å and 1.981(8) Å. The apical bond length Cu(1)−O(11A) is 2.460(8) Å. The Cu(1) atom lies 0.0985 Å above the square plane formed by the N(1), N(2), O(1) and O(21) atoms.

In the same way as in complex **1**, adjacent copper centres are bridged by the oxygen atom O(1) of the hydroxo ligand [Cu(1)−O(1)−Cu(2) = 112.6(4)°] and two oxygen atoms O(21) and O(22) of a bidentate *syn-syn* carboxylato group leading to a mixed-bridged non coplanar coordination geometry [dihedral angle between the mean equatorial planes N(1)N(2)O(1)O(2) and O(1)O(22)O(22A)O(21A), 58.3(3)°]. In the trinuclear entity, the three copper ions are arranged in a strict linear fashion [Cu(1)−Cu(2)−Cu(1A) = 180°]

Table 1. Selected bond lengths [Å] and angles [°] for $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**); symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z + 1$ (compound **1**); #1 x, $-y + 1$, $z - 1/2$ #2 $-x + 1/2$, $-y + 3/2$, $-z$ (compound **2**)

1		**2**	
Cu(1)−O(1)	1.890(3)	Cu(1)−O(1)	1.914(7)
Cu(1)−O(21)	1.981(3)	Cu(1)−O(21)	1.981(8)
Cu(1)−N(1)	2.004(3)	Cu(1)−N(2)	1.991(9)
Cu(1)−N(2)	2.005(3)	Cu(1)−N(1)	2.022(10)
Cu(1)−O(30)	2.398(4)	Cu(1)−O(11)#1	2.460(8)
Cu(1)−Cu(2)	3.1656(6)	Cu(1)−Cu(2)	3.1589(15)
Cu(2)−O(1)#1	1.899(3)	Cu(2)−O(1)#2	1.883(8)
Cu(2)−O(1)	1.899(3)	Cu(2)−O(1)	1.883(8)
Cu(2)−O(22)#1	1.959(3)	Cu(2)−O(22)#2	2.005(7)
Cu(2)−O(22)	1.959(3)	Cu(2)−O(22)	2.005(7)
Cu(2)−O(30)#1	2.776(5)		
Cu(2)−O(30)	2.776(5)		
O(1)−Cu(1)−O(21)	90.59(13)	O(1)−Cu(1)−O(21)	89.4(3)
O(1)−Cu(1)−N(1)	177.85(13)	O(1)−Cu(1)−N(2)	102.3(4)
O(21)−Cu(1)−N(1)	88.46(12)	O(21)−Cu(1)−N(2)	162.9(4)
O(1)−Cu(1)−N(2)	98.61(13)	O(1)−Cu(1)−N(1)	176.6(4)
O(21)−Cu(1)−N(2)	159.83(13)	O(21)−Cu(1)−N(1)	87.5(4)
N(1)−Cu(1)−N(2)	81.71(13)	N(2)−Cu(1)−N(1)	81.1(4)
O(1)−Cu(1)−O(30)	87.82(15)	O(1)−Cu(1)−O(11)#1	87.8(3)
O(21)−Cu(1)−O(30)	88.58(14)	O(21)−Cu(1)−O(11)#1	94.6(4)
N(1)−Cu(1)−O(30)	94.07(15)	N(2)−Cu(1)−O(11)#	98.3(3)
N(2)−Cu(1)−O(30)	109.57(14)	N(1)−Cu(1)−O(11)#1	90.9(4)
O(1)#1−Cu(2)−O(1)	180.00(17)	O(1)#2−Cu(2)−O(1)	180.0(4)
O(1)#1−Cu(2)−O(22)#1	91.96(13)	O(1)#2−Cu(2)−O(22)#2	91.8(3)
O(1)−Cu(2)−O(22)#1	88.04(13)	O(1)−Cu(2)−O(22)#2	88.2(3)
O(1)#1−Cu(2)−O(22)	88.04(13)	O(1)#2−Cu(2)−O(22)	88.2(3)
O(1)−Cu(2)−O(22)	91.96(13)	O(1)−Cu(2)−O(22)	91.8(3)
O(22)#1−Cu(2)−O(22)	180.00(7)	O(22)#2−Cu(2)−O(22)	180.00(7)
O(1)#1−Cu(2)−O(30)#1	77.21(12)	Cu(1)#2−Cu(2)−Cu(1)	180.0
O(1)−Cu(2)−O(30)#1	102.79(12)		
O(22)#1−Cu(2)−O(30)#1	83.17(14)		
O(22)−Cu(2)−O(30)#1	96.83(14)		
O(1)#1− Cu(2)−O(30)	102.79(12)		
O(1)−Cu(2)−O(30)	77.21(12)		
O(22)#1−Cu(2)−O(30)	96.83(14)		
O(22)−Cu(2)−O(30)	83.17(14)		
O(30)#1−Cu(2)−O(30)	180.0		

with Cu(2) on the inversion centre and a Cu(1)···Cu(2) distance of 3.1589(15).

As for the coordination mode of the ligand, it is noteworthy that HL2 coordinates to one copper ion in a bidentate fashion through the pyridyl and sulfonamidato N atoms and to another copper(II) of another asymmetric unit through the sulfonamide O atom giving an infinite tridimensional network of trinuclear units. As a consequence of the coordination of the $O_{sulfonamidate}$ atom to the copper ion, there is a small difference between the S−O bond lengths [S−O(11): 1.452 Å, S−O(12): 1.434 Å] the former being larger due to the O(11) that is linked to the copper ion. However, the S−O bond lengths in compound **1** and in the compound previously reported[5] are the same, 1.443 Å, because in these complexes there is no interaction between the copper ion and the $O_{sulfanomidate}$ atom of the SO_2 group.

IR and Electronic Spectra

The IR spectra of both complexes present a similar pattern to that of the previously reported trinuclear compounds with the related *N*-(pyrid-2-ylmethyl)toluensulfonylamide ligand.[5] The IR spectrum of complex **2** shows a band at 3530 cm^{-1} characteristic of the O−H bridging group.[7] The characteristic vibrations of the acetato group in the spectra of both complexes confirm that it acts as a bridging bidentate ligand [$\Delta\nu = \nu_{asymm.}(COO) - \nu_{symm.}(COO) = 144$ and 142 cm^{-1} for compounds **1** and **2**, respectively].[8] The spectrum of complex **1** exhibits a new band at 1653 cm^{-1}, which is assigned to the $\nu(C{=}O)$ vibration of the dimethylformamide. As a consequence of the deprotonation and coordination of the sulfonamido N atom the characteristic bands of the SO_2 group are shifted to lower frequencies. The $\nu(SO_2)_{asymm.}$ vibrations present the

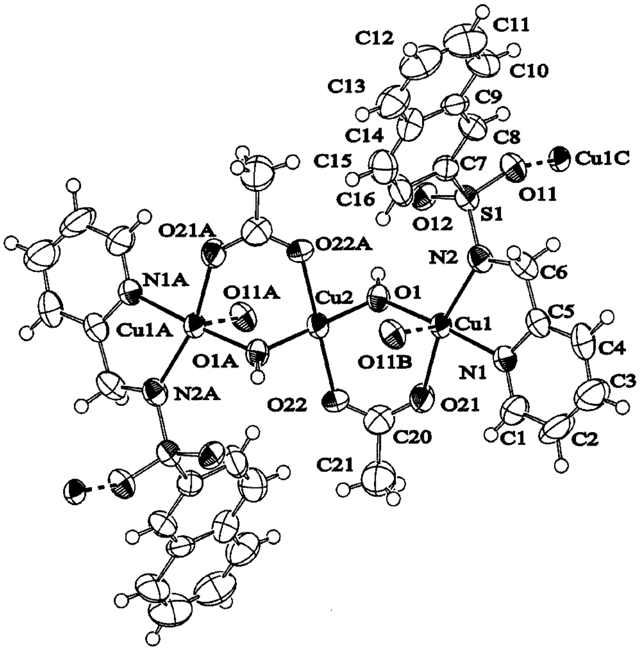

Figure 2. Molecular structure of $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**)

same band at 1256 cm^{-1} for both complexes, however the $\nu(SO_2)_{symm.}$ vibrations are different, 1130 cm^{-1} in compound **1** and 1120 cm^{-1} in compound **2**, probably due to the interaction of one of the oxygen atoms of the sulfonamido group with the metal ion in complex **2**.

The solid-state spectra of both trinuclear complexes exhibit a broad band at about 15314 cm^{-1} (**1**) and 15873 cm^{-1} (**2**) that corresponds to the two chromophores, CuN_2O_2 and CuO_4, present in the compounds.[9] In dichloromethane solution, the d-d band of the complexes is slightly shifted. The small shift of ca. 500 cm^{-1} to lower frequencies in complex **1** and ca. 700 cm^{-1} to higher frequencies in complex **2** can be attributed to solvent effects.

Magnetic Properties

The temperature dependence of the $\chi_M T$ product for $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**) (χ_M being the magnetic susceptibility per trimer unit and T the absolute temperature) in the temperature range 2−300 K is shown in Figure 3. As expected, the magnetic behaviour of both complexes is similar and resembles that of the related trinuclear compound $[Cu_3(L)_2(CH_3COO)_2(OH)_2(DMF)_2]$ [HL = *N*-(pyrid-2-ylmethyl)toluensulfonylamide].[5] At room temperature $\chi_M \cdot T$ is 1.51 and 1.32 $cm^3 \cdot mol^{-1} \cdot K$, respectively, a value which is somewhat larger than that expected for a magnetically uncoupled trinuclear Cu^{II} compound (1.23 $cm^3 \cdot mol^{-1} \cdot K$, $g = 2.1$). Upon cooling of the sample, $\chi_M \cdot T$ increases and reaches a value of 2.18 $cm^3 \cdot mol^{-1} \cdot K$ (compound **1**) and of 2.00 $cm^3 \cdot mol^{-1} \cdot K$ (compound **2**) in the 6−15 K temperature range. This behaviour is indicative of strong ferromagnetic coupling between the adjacent Cu^{II} atoms in the trinuclear species. Below 5 K, $\chi_M T$ decreases rapidly down to 1.9 $cm^3 \cdot mol^{-1} \cdot K$ (compound **1**) and to 1.8 $cm^3 \cdot mol^{-1} \cdot K$ (compound **2**), which is most likely due to zero-field splitting (ZFS) within the quadruplet ground state. The occurrence of intermolecular antiferromagnetic interactions may also be operative at very low temperatures.

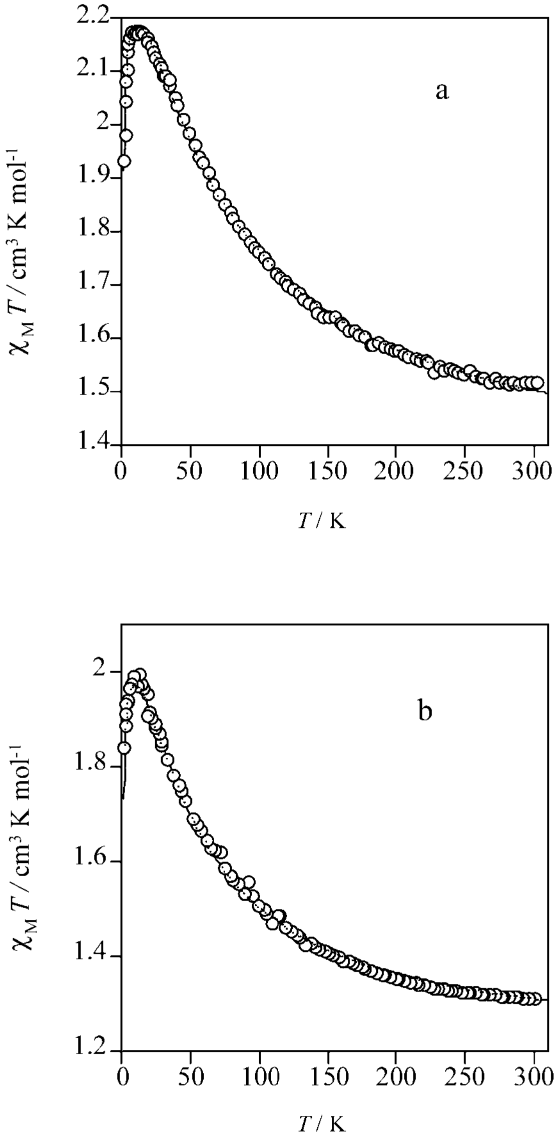

Figure 3. a) Temperature dependence of $\chi_M T$ for $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**); b) temperature dependence of $\chi_M T$ for $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**)

The spin Hamiltonian that is appropriate for describing the exchange interaction in a linear symmetric trimer has the form:

$$H = -J(S_1S_2 + S_2S_3) - J'\, S_1S_3 + D\,[S_z^2 - S(S+1)/3] + g\beta HS \quad (1)$$

where the occurrence of axial ZFS between the ±3/2 and ±1/2 Kramer's doublets arising from the $S = 3/2$ ground state have been included. The exchange parameters J and

J' refer to the interaction between two adjacent centres and the interaction between the terminal centres, respectively. The resulting spin multiplets are two doublets ($S = 1/2$) and one quadruplet ($S = 3/2$).[10] D denotes the half energy gap between the above mentioned Kramer's doublets.

In a first step we have set $D = 0$ in expression (1). In this case, the fitting of the experimental data for $T > 10$ K to this Hamiltonian confirms that the values of J and J' are strongly correlated in determining the temperature dependence of the magnetic susceptibility, as has already been observed for other similar systems.[5,11] The fitting to the experimental data, including the low temperature region where D is operative, shows a similar correlation between J and J'. The solid and broken lines in Figure 3 represent typical fits with $J = 94$ cm^{-1}, $J' = -3.6$ cm^{-1}, $|D| = 1.76$ cm^{-1}, $g = 2.17$ and $R = 3.10{-}5$ (Figure 3a) and $J = 59.1$ cm^{-1}, $J' = -4.6$ cm^{-1}, $|D| = 1.76$ cm^{-1}, $g = 2.06$ and $R = 3.10{-}4$ (Figure 3b), respectively [R values obtained from the expression $R = \{\Sigma_i[(\chi_M T)_{\mathrm{obs},i} - (\chi_M T)_{\mathrm{calcd},i}]^2/\Sigma_i[(\chi_M T)_{\mathrm{obs},i}]^2\}$. These J and J' values are indicative of a strong ferromagnetic and a weak antiferromagnetic coupling, respectively.

It is well-known that in dinuclear copper(II) complexes with *syn-syn* carboxylato bridges and hydroxo bridges, with an angle at the hydroxo bridge larger than 97.5°, antiferromagnetic coupling occurs;[12] the magnetic coupling in **1** and **2** should therefore be antiferromagnetic. However, when the bridging ligands are different, the two bridges may either increase or cancel out these effects. This phenomenon is known as orbital complementarity and countercomplementarity,[13−20] respectively, and was observed by us for the previously reported $[Cu_3(L)_2(CH_3COO)_2(OH)_2(DMF)_2]$[5] [HL = *N*-(pyrid-2-ylmethyl)toluensulfonylamide]. In this case, the antiferromagnetic contributions of each bridge almost cancelled each other out (these bridges show an orbital countercomplementarity) and the ferromagnetic term dominates ($J_T = J_{AF} + J_F$ with $|J_{AF}|$ being smaller than $|J_F|$). Here, both complexes **1** and **2** are good examples of the countercomplementarity effect imposed by the carboxylato bridge, which attenuates the effect of the antiferromagnetic hydroxo bridge to the point where strong ferromagnetic behaviour is observed.

EPR Spectra

The X-band EPR spectra of complexes **1** and **2** at room temperature are dominated by a transition at 2000 and 2100 G, respectively, which identifies an $S = 3/2$ ground state. The Q-band EPR spectrum at room temperature of compound **1** is shown in Figure 4, where the strong transition at 8000 G confirms the ferromagnetic behaviour of the compound.

For the complex $[Cu_3(L)_2(CH_3COO)_2(OH)_2(DMF)_2]$[5] [HL = *N*-(pyrid-2-ylmethyl)toluensulfonylamide] we have reported variable temperature studies in detail that revealed a strong shift of this resonance towards higher fields upon raising the temperature. This effect was explained from the temperature-dependent contribution of the resonance fields of the three spin states to a composite EPR signal. In the present work, due to the similarity between the structures, magnetic properties and EPR spectra of the compounds $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**) and the complex $[Cu_3(L)_2(CH_3COO)_2(OH)_2(DMF)_2]$, we assumed a similar g-temperature dependence for **1** and **2**.

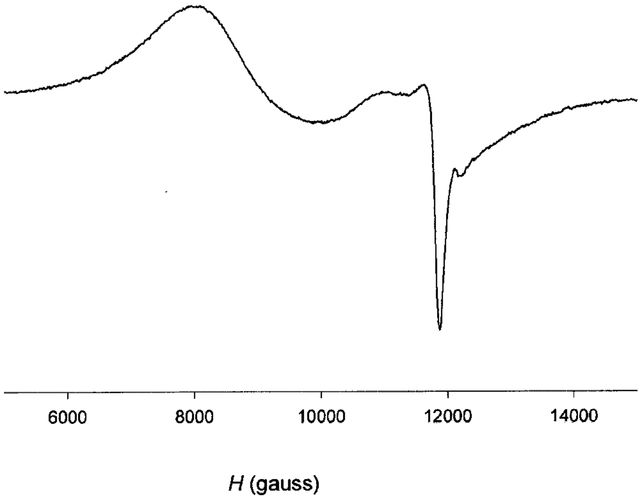

Figure 4. Q-band EPR spectrum at room temperature for $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**)

DFT Calculations

In previous work[5] we stated that the nature of the magnetic interaction in this kind of compound is governed by orbital countercomplementarity phenomena, in particular the SOMOs (Singly Occupied Molecular Orbital). In other words, two different bridging ligands can interact with the magnetic orbitals in the metal ions in a different way, destabilising the in-phase combination in one case (Φ_{AS}), and the out-of-phase (Φ_S) in the other. So, in the systems with two bridging ligands, there is a counterbalance and a compensation of their effects in the formation of the SOMOs. This leads to an increase in the energy gap, $\Delta = E_{AS} - E_S$, between the SOMOs, and therefore a reduction in the antiferromagnetic contribution to the magnetic coupling.[5] The antiferromagnetic contributions of each bridge almost cancel each other out and the ferromagnetic term dominates.

When we compare the J values of compounds **1** (94 cm^{-1}), **2** (59.1 cm^{-1}) and that of the related trinuclear complex of ref.[5] (96 cm^{-1}) and try to correlate them with the CuOCu angle φ (113.3°, 112.6° and 114.9° respectively) (Figure 5), we find that the J value of **2** is significantly smaller than the values of the other two compounds, when into account the φ angle is taken.

Several structural parameters can modify the exchange coupling constant value, J, in the family of the compounds studied. The CuOCu angle, φ, can have a dominant influence. As is well-known, there is a strong dependence be-

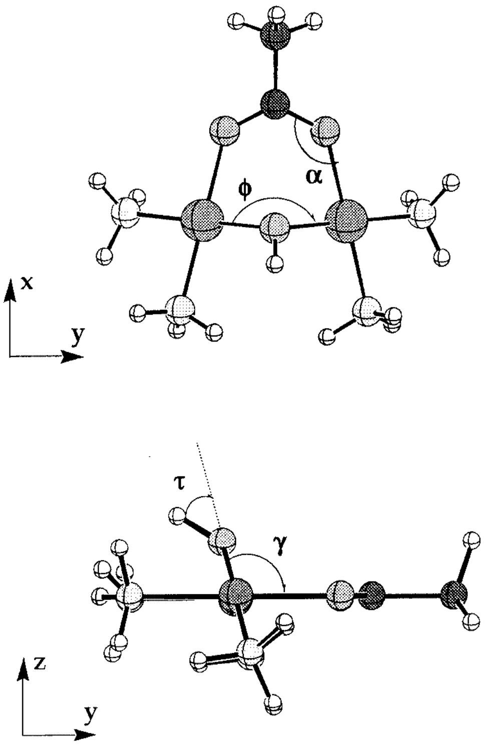

Figure 5. The structural parameters studied in the model **III**

tween the *J* constant and the φ angle in the binuclear bis(μ-hydroxo)Cu^{II} complexes[12,21] $[Cu_2(\mu\text{-}OH)_2]^{2+}$. So, in the last complexes small changes in the φ values produce important variations in the magnitude and the nature of the magnetic interaction. Wieghardt and co-workers[18] have proposed a magneto-structural correlation between the coupling constant *J* and the CuOCu angle φ for μ-hydroxo-μ-carboxylatodicopper(II) complexes. Using this correlation the values of *J* obtained for the trinuclear complexes **1** and **2** are approximately −20 cm^{-1}, which are not in agreement with the experimental results. Later, Chakravarty et al.[22] proposed a linear magneto-structural correlation $[-2J = 11.48\varphi(\text{deg}) - 1373]$ for μ-alkoxo/hydroxo-μ-carboxylato dicopper(II) systems. Using this empirical relationship the value of *J* for the three compounds (**1**, **2** and that of ref.[5]) are 36.1, 40.1 and 26.9 cm^{-1}, respectively, which, as in the previous correlation, are not in agreement with the experimental measurements.

In order to understand the different *J* values found in these trinuclear compounds we have performed DFT calculations on three model compounds derived from the structure of the complexes: model **I** [two copper(II) atoms bridged by an acetato group], model **II** [two copper(II) atoms bridged by a hydroxo group] and model **III** [two copper(II) atoms bridged by an acetato and a hydroxo group]. To avoid the extra influences in the *J* constant, we have frozen most of the structural parameters in the variation of φ. Only the α angle (see Figure 5) has been varied in the φ change process. This angle (α), which governs the carboxylate-copper ion conformation (*syn-syn* or *anti-anti*), varies between 123.8 (φ = 90°) and 135.0° (φ = 130°) in the calculated models. The calculations with model **I** have shown that this small change in α causes a slight shift to weaker magnetic interactions for the smaller α values (−12.3 to −50.7 cm^{-1}) because of a loss of overlap between the magnetic orbitals in the metal ions and the HOMO's of the carboxylate ligand.

For a certain value of φ, a zero value for Δ is expected for model **II**, as in the $[Cu_2(\mu\text{-}OH)_2]^{2+}$ complexes. When this angle increases, a splitting of the SOMOs is observed. This energy gap has the opposite sign to the one found for model **I** (see Figure 6). This phenomenon is more pronounced as the φ value increases, and a stronger ferromagnetic character is expected for the magnetic interaction. So, a total counterbalance is found and a maximum ferromagnetic interaction must be observed. From here, the energy gap in the SOMOs of the hydroxo ligand will be bigger than that caused by the carboxylate ligand, and, consequently, a decrease in the ferromagnetic interaction is expected. Similar results have been found for the calculation on model **III**. All these comments are summarised in Figure 6. For model **III** a maximum of *J* is obtained for a φ value of 102.8° (see Figure 7). The more stable structure appears for a φ value of 118.7°, which is slightly bigger than that in the $[Cu_2(\mu\text{-carboxylate})(\mu\text{-}OH)]^{2+}$ complexes.

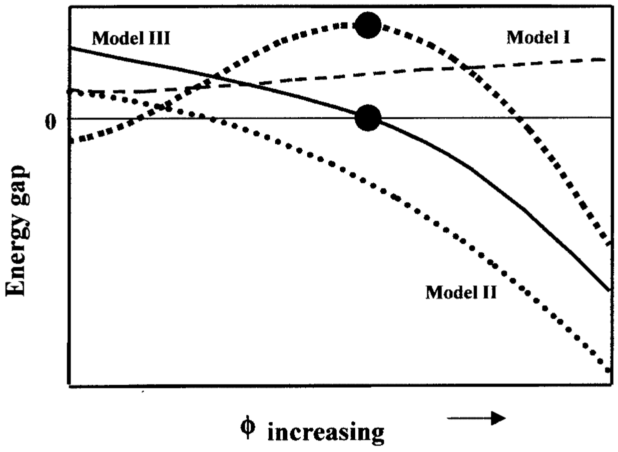

Figure 6. Theoretical dependence of Δ (energy gap) with the φ angle for the models **I** (- - -), **II** (···) and **III** (——); the variation of *J* as a function of φ is shown as a (···) line; the maximum *J* value for the model **III** coincides with the zero value in the energy gap (Δ) (black circles)

Figure 7 shows the theoretical *J* values for model **III**, the experimental ones of dinuclear copper(II) complexes reported in the literature (shown as circles), those found for the trinuclear compounds described here and that described in ref.[5] (shown as crosses). In the range from 103 to 135° the magnetic coupling becomes more antiferromagnetic when φ increases. It should be emphasised that the compounds with an aliphatic peripheral ligand [18−19,23] show φ angles bigger than those with an aromatic peripheral one.[7,24−25] However, our compounds show an intermediate φ value. This is probably due to the trinuclear topology adopted in our series of compounds. We have therefore found

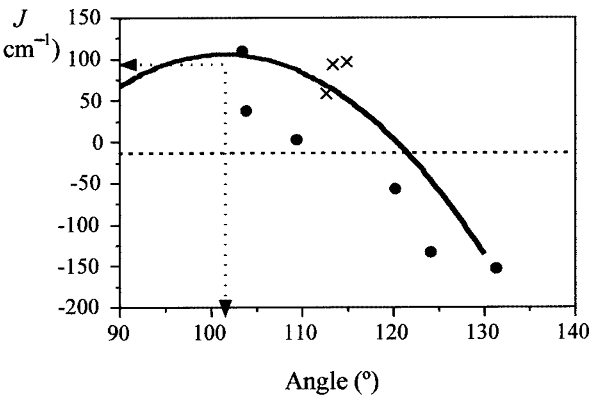

Figure 7. Calculated dependence of *J* with the φ angle for the model **III**; the arrows point to the maximum *J* value; experimental *J* values of dinuclear copper(II) complexes reported in the literature (·) and those of compounds **1**, **2** and that described in ref.[5] (x)

a way to tune the magnitude and the nature of the magnetic interaction through the peripheral ligand and the molecular nuclearity. On the other hand, Figure 7 shows that the experimental *J* values of trinuclear compounds (**1**, **2** and the compound from ref.[5]) are higher than that found experimentally in dinuclear complexes for similar φ angles. The formation of trinuclear entities implies a change in the coordination sphere. Thus, the compounds in the literature (dinuclear complexes) present a N_2O_2 environment, while the trinuclear complexes show both N_2O_2 and O_4 ones. The higher *J* value shown by the title compounds could be explained by taking into account the effect of the nature of the donor atoms of the peripheral ligands on the magnetic interaction magnitude.[26] Nevertheless, it is not uncommon that a relatively large range of values for the *J* constant is observed for a family of complexes with similar φ angles.

To explain this phenomenon, we have studied several structural distortions found in the real systems: changes in the $Cu-N_{\text{peripheral ligand}}$, $Cu-O_{\text{bridging ligands}}$ distances, the dihedral angle γ (Figure 5) between the $CuO_{\text{hydroxo}}Cu$ and $CuOO_{\text{carboxylate}}Cu$ planes, distortions in the carboxylate group, etc. No important effects on the *J* constant values have been found. Only the relative position of the hydrogen atom in the hydroxo group, defined by the τ angle (see Figure 5), as in the $[Cu_2(\mu\text{-}OH)_2]^{2+}$ complexes, is able to cause meaningful changes in the *J* constant. Although, as in the $[Cu_2(\mu\text{-}OH)_2]^{2+}$ complexes, a structural correlation can exist between the φ and τ angles[12,21] (the same electronic reasons), there are other factors, such as hydrogen bonds, that can govern the hydrogen-atom position or the τ value. Unfortunately, in many cases, the exact positions of these hydrogen atoms have not been determined by X-ray diffraction; however, it is possible to estimate this position when a solvent molecule or anion forms a hydrogen bond with the hydroxo groups. The hydrogen atom can then be placed in the direction of this bond. In this way the τ angle for these compounds lies between 0 and 51°, with a maximum value for the compound with the anomalous stronger ferromagnetic interaction. In any case, for model **III**, based on compound **2** ($\tau = 58.5°$) and **1** ($\tau = 0°$) we have found *J* values (36.4 and 85.4 cm^{-1}, respectively) that are in good agreement with the tendency found experimentally.

Although two parameters mostly govern the nature and magnitude of the magnetic interaction in this family of compounds, a lot of other structural parameters exist that have negligible influences.

Experimental Section

General Remarks: The infrared spectra ($\tilde{\nu} = 400-4000$ cm^{-1}) were obtained on a Mattson Satellite FTIR spectrophotometer. Elemental Analyses were performed on a Carlo Erba AAS instrument. The variable temperature magnetic susceptibility measurements were carried out on a microcrystalline sample using a Quantum Design MPMS2 SQUID susceptometer equipped with a 55 kG magnet and operating at 10 kG in the range of 1.8−400 K. The susceptometer was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 12H_2O$. The corrections for the diamagnetism were estimated from Pascal's constants. Diffuse Reflectance and UV/Vis spectra were recorded on a Shimadzu 2101 PC spectrophotometer. The EPR spectra of ground crystals were carried out at the X-band with a Bruker ELEXSYS and at the Q-band frequencies with a Bruker ESP300 spectrometer.

***N*-(pyrid-2-ylmethyl)benzenesulfonylamide (HL1) and *N*-(pyrid-2-ylmethyl)naphthalenesulfonylamide (HL2):** The ligands were obtained by condensation of 2-picolylamine and the corresponding sulfonyl chloride (benzenesulfonyl chloride or 2-naphthalenesulfonyl chloride) following the synthesis procedure previously described.[5] **HL1** (yield 1.38 g, 56%). $C_{12}H_{12}N_2O_2S$ (248): calcd. C 58.1, H 4.8, N 11.3, S 12.9; found C 57.3, H 4.7, N 11.1, S 12.7. IR (KBr): $\tilde{\nu}$ = 1330, 1160 ν(SO_2), 850 cm^{-1} ν(S−N). **HL2** (yield 2.11 g, 71%). $C_{16}H_{14}N_2O_2S$ (298): calcd. C 64.4, H 4.7, N 9.4, S 10.7; found C 61.5, H 4.8, N 8.9, S 10.4. IR (KBr): $\tilde{\nu}$ = 1329, 1162 ν(SO_2), 954 cm^{-1} ν(S−N).

Bis(μ-acetato)-bis(μ-hydroxo)-bis[*N*-(pyrid-2-ylmethyl)benzenesulfonylamidate(DMF)$_2$]tricopper(II) (1) and Bis(μ-acetato)-bis(μ-hydroxo)-bis[*N*-(pyrid-2-ylmethyl)naphthalenesulfonylamidate]-tricopper(II) (2): Both copper complexes were prepared by the reaction of the metal acetate (1 mmol in 25 mL DMF) with the ligand (1 mmol in 25 mL DMF). Slow evaporation of the resulting solution at room temperature provided well-developed blue crystals of both compounds suitable for X-ray diffraction. Microanalysis of the dried crystals was satisfactory. **1** (yield 354 mg, 24%). $C_{17}H_{22}Cu_{1.5}N_3O_6S$ (**1**) (491.75): calcd. C 41.48, H 4.47, N 8.54, S 6.50; found C 40.94, H 4.40, N 8.30, S 6.53. IR (KBr): $\tilde{\nu}$ = 3530 ν(O−H), 1567 ν_{as}(COO), 1423 ν_s(COO), 1256, 1130 ν(SO_2), 970 cm^{-1} ν(S−N). Diffuse Reflectance: (λ_{max}) = 15314 cm^{-1} (653 nm). UV/Vis (dichloromethane/THF/acetic acid): λ_{max} = 14837 cm^{-1} (674 nm), 26882 cm^{-1} (sh) (372 nm). **2** (yield 281 mg, 20%). $C_{36}H_{34}Cu_3N_4O_{10}S_2$ (**2**) (937): C 46.10, H 3.62, N 5.97, S 6.63; found C 45.91, H 3.69, N 6.02, S 6.47. IR (KBr): $\tilde{\nu}$ = 3530 ν(O−H), 1569 ν_{as}(COO), 1427 ν_s(COO), 1256, 1120 ν(SO_2), 975 cm^{-1} ν(S−N). Diffuse Reflectance: λ_{max} = 15150 cm^{-1} (660 nm). UV/Vis (dichloromethane): λ_{max} = 15873 cm^{-1} (630 nm), 27030 cm^{-1} (sh) (370 nm).

X-ray Crystallographic Study: A blue prismatic crystal of $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and a blue plate crystal of $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**) were mounted on a glass fibre. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $15.884 < \theta < 45.488°$ (compound **1**)

Table 2. Crystal data and structure refinement for $[Cu_3(L1)_2(CH_3COO)_2(OH)_2(DMF)_2]$ (**1**) and $[Cu_3(L2)_2(CH_3COO)_2(OH)_2]_\infty$ (**2**)

	1	**2**
Empirical formula	$C_{17}H_{22}Cu_{1.50}N_3O_6S$	$C_{36}H_{34}Cu_3N_4O_{10}S_2$
Formula weight	491.75	937.41
Temperature	293(2) K	293(2) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
Unit cell dimensions	a = 11.390(2) Å b = 13.6125(14) Å c = 13.2216(13) Å β = 93.271(7)°	a = 29.3948(11) Å b = 14.4396(7) Å c = 10.7455(6) Å β = 108.826(4)°
Volume	2046.7(5) $Å^3$	4316.9(4) $Å^3$
Z, Calculated density	2, 1.596 Mg/m^3	4, 1.442 Mg/m^3
Absorption coefficient	3.334 mm^{-1}	3.089 mm^{-1}
F(000)	1010	1908
Crystal size	0.35 × 0.25 × 0.25 mm	0.25 × 0.15 × 0.10 mm
θ range	4.67 to 75.89°	3.18 to 77.78°
Limiting indices	$-14 \le h \le 14$, $-17 \le k \le 0$, $-16 \le l \le 0$	$-33 \le h \le 37$, $-17 \le k \le 0$, $-13 \le l \le 9$
Reflections collected/unique	4454/4269 [R(int) = 0.0271]	5099/4056 [R(int) = 0.1316]
Completeness to θ	75.90, 100.0%	77.78, 87.9%
Absorption correction	ψ-scan	ψ-scan
Max. and min. transmission	0.979 and 0.922	0.979 and 0.802
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4269/0/310	4056/0/251
Goodness-of-fit on F^2	1.065	0.970
Final R[a] indices [$I > 2\sigma(I)$]	$R1 = 0.0583$, $wR2 = 0.1610$	$R1 = 0.0515$, $wR2 = 0.1715$
R indices (all data)	$R1 = 0.0680$, $wR2 = 0.1698$	$R1 = 0.1242$, $wR2 = 0.2162$
Largest diff. Peak and hole	0.917 and -0.525 $e{\cdot}A^{-3}$	1.143 and -1.036 $e{\cdot}A^{-3}$

[a] $R = \mid |F_o| - |F_c| \mid / |F_o|$; $R_w = \{[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}$

and 16.039° < θ < 45.208° (compound **2**) on an Enraf Nonius CAD4 automatic diffractometer.[27] Data were collected at 293 K using Cu-K_α radiation (λ = 1.54184 Å) and the ω-scan technique, and corrected for Lorentz and polarisation effects.[28] A semi-empirical absorption correction (Ψ-scans) (DIFABS) was made.[29] The structure was solved by direct methods[30] and subsequent difference Fourier maps, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[31] For compound **1** all hydrogen atoms were located from difference Fourier maps except those of two of the phenyl group and of DMF which were located in their calculated positions (C−H 0.93−0.97 Å). The located H atoms were refined isotropically, whereas the calculated H atoms were refined using a riding model. For compound **2** all hydrogen atoms were located in their calculated positions (C−H: 0.93−0.97 Å) and were refined using a riding model. Atomic scattering factors were obtained from the International Tables for X-ray Crystallography.[32] Molecular graphics were obtained from PLATON-98[33] (compound **2**) and from PLATON-99[34] (compound **1**). A summary of the crystal data, experimental details and refinement results are listed in Table 2.

CCDC-168013 (**1**) and -168014 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: A detailed description of the computational strategy adopted in this work has been described elsewhere[12] and is only briefly reviewed here. For the evaluation of the coupling constants of dinuclear models, two separate calculations were carried out by means of density functional theory,[35] one for the triplet state and another for the singlet state. The hybrid B3LYP method,[36] as implemented in Gaussian98,[37] was used in all calculations, mixing the exact Hartree−Fock exchange[38] with Becke's expression for the exchange and with the Lee−Yang−Parr correlation functional.[39] Double-ζ quality and triple-ζ quality basis sets proposed by Ahlrichs[40] were employed for nonmetallic and metallic atoms, respectively. Also, for the metallic atoms, we added two extra polarisation p functions. The presence of a low-energy singlet made it difficult to evaluate, accurately, the energy of the lowest singlet by a single-determinant method. To solve this problem, broken-symmetry wave functions, as proposed by Noodleman et al., were used.[41−44] Previously, it has been found among the most common functionals, that the B3LYP method combined with the broken-symmetry treatment is the strategy that provides the best results for calculating coupling constants.[5,12,45−49] It is clear that for broken-symmetry, Hartree−Fock calculations are necessary to make a correction due to the multideterminant character of the wave function of the low-multiplicity state.[48] On the other hand, for DFT calculations we adopted single-determinant wave functions for which DFT is well defined.[50−52] Then, we used the broken-symmetry energy calculated by DFT methods as the real energy of the state.

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