Copper(II) Complexes with 4-Amino-*N*-[4,6-dimethyl-2-pyrimidinyl]benzenesulfonamide. Synthesis, Crystal Structure, Magnetic Properties, EPR, and Theoretical Studies of a Novel Mixed μ-Carboxylato, NCN-Bridged Dinuclear Copper Compound

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Received August 1, 2000

New Cu(II) complexes of sulfamethazine (4-amino-*N*-[4,6-dimethyl-2-pyrimidinyl]benzenesulfonamide, HL) $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**) and $\{[Cu(L)_2]\cdot 2H_2O\}_\infty$ (**2**) were prepared and structurally characterized. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 8.9486(9)$ Å, $b = 15.0956(12)$ Å, $c = 16.542(3)$ Å, $\beta = 105.584(15)°$, and $Z = 2$. Compound **2** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 13.8097(8)$ Å, $b = 14.5765(4)$ Å, $c = 13.7853(15)$ Å, $\beta = 96.033(9)°$, and $Z = 1$. In compound **1** two copper ions are linked by two syn−syn acetates and two nonlinear NCN bridging groups pertaining to the deprotonated sulfamethazine ligands. Each copper center presents a nearly square planar geometry. Magnetic susceptibility data for **1** show a strong antiferromagnetic coupling with $2J = -216.7$ cm^{-1}. The EPR spectra at the X- and Q-band frequencies present the signals corresponding to the dinuclear entity, being the zero-field splitting parameter, $D = 0.265$ cm^{-1}. The antiferromagnetic exchange coupling is discussed using DFT calculations on some model compounds with NCN bridging ligands and also on model structures with mixed μ-acetato and NCN bridges. The copper in the polymeric compound **2** is five coordinate. The CuN_5 chromophore has a highly distorted square pyramidal geometry with small axial N−Cu−N angles of 65.53(14) and 59.90(13)°. In the structure a sulfamethazinate anion binds to one copper through the sulfonamido and pyrimidine N atoms and to an adjacent copper via the amino N atom.

Introduction

Many dinuclear copper(II) complexes have been prepared, and the relationships between their magnetic properties and molecular structures have been extensively studied in order to understand the spin-exchange interaction. The magneto−structural correlations in di- or polynuclear metal complexes have not yet been completely identified because the type (antiferromagnetic or ferromagnetic) and magnitude of magnetic exchange interactions depend on several structural parameters.[1−5]

Numerous copper(II) carboxylate adducts have been isolated and their magneto−structural correlation studied.[6] In most cases, a general formula of the complexes is given by $[Cu_2(RCOO)_4L_2]$. These compounds are susceptible to core conversion on reactions with chelating bidentate ligands, usually bidentate amines, and the products are often dinuclear copper(II) complexes with a reduced number of carboxylate bridging ligands.[7]

We previously reported the crystal structure and the magnetic properties of an antiferromagnetic ($2J = -61.5$ cm^{-1}) dimer complex $[Cu_2(sulfathiazolato)_4]$ (sulfathiazole = 4-amino-*N*-(thiazol-2-yl)benzenesulfonamide).[8] The two coppers ions in this compound are quadruply bridged by the nonlinear NCN fragments of the ligands. This is an important feature of the ligand in view of the fact that the same types of bridges are also found in molecules such as adenine.[9−13] A matter of interest in these dinuclear copper(II) systems with nonlinear NCN bridges could be to study how the presence of μ-carboxylato bridging groups affects their magnetic properties.

In this paper, we report a dicopper(II) complex bridged by two carboxylates and two sulfamethazinates anions in a centrosymmetric fashion, $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**) (HL = sulfamethazine, 4-amino-*N*-[4,6-dimethyl-2-pyrimidinyl]benzenesulfonamide).

Additionally, the crystal structure and spectroscopic properties of a coordination polymer $\{[Cu(L)_2]\bullet 2H_2O\}_\infty$ (**2**) obtained as byproduct of **1** are described.

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10.1021/ic000869i CCC: \$20.00

Experimental Section

All reagents and chemicals were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N, S) were carried out at the microanalytical laboratory of the Universidad Politécnica of Valencia, Spain. The copper content was determined by atomic absorption spectroscopy.

Physical Measurements. The infrared spectra ($\nu = 400-4000$ cm^{-1}) were obtained on KBr pellets using a Mattson Satellite FTIR spectrophotometer. Solid electronic spectra were recorded on samples dispersed in Nujol using a Shimadzu 2101 PC spectrophotometer. EPR measurements for ground crystals were carried out on a Bruker ER200D at X-band frequencies and on a Bruker ESP300 at Q-band frequencies. The variable-temperature magnetic susceptibility measurement on a microcrystalline sample of complex **1** was carried out on a Quantum Design MPMS2 SQUID susceptometer equipped with a 55 kG magnet, 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 constants.

Synthesis of the Complexes. Solid sulfamethazine (0.27 g, 1 mmol) was dissolved by stirring in a solution of copper acetate monohydrate (0.1 g, 0.5 mmol) in 20 mL of dmf. Prismatic brown crystals of $[Cu_2(CH_3COO)_2(L)_2]$.2dmf (**1**) were obtained by slow evaporation of the resulting mixture at room temperature. They were isolated by filtration, washed with dmf, and air-dried. Yield: 57%. The filtrate was gradually evaporated at room temperature to give $\{[Cu(L)_2] \cdot 2H_2O\}_\infty$ (**2**) as prismatic brown crystals. Yield: 12%.

Anal. Calcd for $C_{34}H_{46}Cu_2N_{10}O_{10}S_2$ (**1**): C, 43.17; H, 4.90; N, 14.81. Found: C, 43.22; H, 4.84; N, 14.93. IR (KBr pellet; cm^{-1}): 3436, 3361, 3248 ($\nu(NH_2)$); 1649 ($\delta(NH_2)$); 1576 ($\nu_{as}(COO)$); 1436 ($\nu_s(COO)$); 1275, 1130 ($\nu(SO_2)$); 980 (ν(S−N)). Solid electronic spectra (Nujol) (λ_{max}, nm): 295 ($\pi-\pi^*$); 420 (LMCT); 560 (d−d). Anal. Calcd for $C_{24}H_{30}CuN_8O_6S_2$ (**2**): C, 44.06; H, 4.62; N, 17.13; S, 9.80; Cu, 9.71. Found: C, 44.95; H, 4.80; N, 17.10; S, 9.52; Cu, 9.58. IR (KBr pellet; cm^{-1}): 3545 (ν(O−H)); 3478, 3415, 3380, 3230 (ν (NH_2)); 1620 ($\delta(NH_2)$); 1273, 1140 ($\nu(SO_2)$); 982 (ν(S−N)). Solid electronic spectra (Nujol) (λ_{max}, nm): 330 ($\pi-\pi^*$); 440 (LMCT); 740 (d−d).

X-ray Crystal Structure Determination for Compounds 1 and 2. A brown prismatic crystal of $[Cu_2(CH_3COO)_2(L)_2] \cdot 2dmf$ (**1**) (0.35 × 0.35 × 0.35 mm) and a brown prismatic crystal of $\{[Cu(L)_2] \cdot 2H_2O\}_\infty$ (**2**) (0.25 × 0.10 × 0.10 mm) were mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection of **1** and **2** were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $11.8 < \theta < 21.0°$ for **1** and of $15.9 < \theta < 45.0°$ for **2** in a graphite-monochromated Enraf Nonius MACH3 automatic diffractometer (compound **1**) and in a graphite-monochromated Enraf Nonius CAD4 automatic diffractometer (compound **2**).[14] Data were collected at 293 K (Mo Kα radiation for **1**; Cu Kα radiation for **2**), using the ω-scan technique, and corrected for Lorentz and polarization effects.[15] A semiempirical absorption correction (ψ-scan)[16] was made for both complexes. The structures were solved by direct methods[17] and subsequent difference Fourier maps and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters.[18] For compound **1** all hydrogen atoms were located from difference Fourier maps except those of the methyl groups 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 from difference Fourier maps. The H atoms of the water molecules, O(1) and O(2), were not located. The located H atoms were refined isotropically. Atomic scattering factors were taken from ref 19. Molecular graphics were performed from ZORTEP[20] (complex **1**) and from PLATON99[21] (complex **2**). A summary of the crystal data, experimental details, and refinement results for **1** and **2** are listed in Table 1.

Table 1. Crystal Data and Structure Refinement for $[Cu_2(CH_3COO)_2(L)_2] \cdot 2dmf$ (**1**) and $\{[Cu(L)_2] \cdot 2H_2O\}_\infty$ (**2**) Compounds

	1	**2**
empirical formula	$C_{34}H_{46}Cu_2N_{10}O_{10}S_2$	$C_{24}H_{30}CuN_8O_6S_2$
fw	946.01	654.22
space group	$P2_1/n$	$P2_1/c$
a, Å	8.9486(9)	13.8097(8)
b, Å	15.0956(12)	14.5765(4)
c, Å	16.542(3)	13.7853(15)
β, deg	105.584(15)	96.033(9)
V, Å^3	2152.4(4)	2759.6(3)
Z	2	4
λ, Å	0.710 73	1.541 84
μ, cm^{-1}	11.49	30.14
ρ_{calcd}, g/cm^3	1.460	1.575
T, K	293(2)	293(2)
R1[a]	0.0409	0.0526
wR2[a]	0.1002	0.1318

[a] $R1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.6464P]$, where $P = (F_o^2 + 2F_c^2)/3$, for compound **1**. $w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 2.4757P]$, where $P = (F_o^2 + 2F_c^2)/3$, for compound **2**.

Computational Method. We recently showed the ability of hybrid density functional methods to provide accurate numerical estimates of the exchange coupling constant J in transition-metal molecular complexes.[22−24] The B3LYP method is the most popular form of the so-called hybrid functionals,[25] in which the exact exchange, calculated using Kohn−Sham orbitals,[26] is mixed with the pure generalized gradient approximation (GGA)[27,28] functional by fitting, in the B3LYP case, three mixing parameters to some sets of experimental data. For this purpose we use the B3LYP method as implemented in the GAUSSIAN package[29] combined with a modified broken-symmetry approach. We found that, when using DFT based wave functions, a reasonable estimate of the low spin state energy can be obtained directly from the energy of a broken-symmetry solution.[30]A triple-ζ basis set is used for the copper atom,[31] while double-ζ basis sets are employed for the rest of atoms.[32]

Calculations for model complexes were carried out using the following structural parameters for the description of the bridge, Cu−N = 2.01 Å, N−C = 1.338 Å, $Cu-O_{water}$ = 2.15 Å, $Cu-O_{acetato}$ = 2.01 Å, C−C = 1.384 Å, N−C−C=124°, and Cu−N−C = 126.4°, but for the adenine ligand $Cu-N_{pyrimidine}$ = 2.04 Å and Cu−N−C = 121.5 Å. In the model structures of sulfathiazole and sulfamethazine, to reduce the computer time, the aminophenyl group was replaced by a methyl group. For the other structural parameters, we employed angles and distances corresponding to the X-ray diffraction data.

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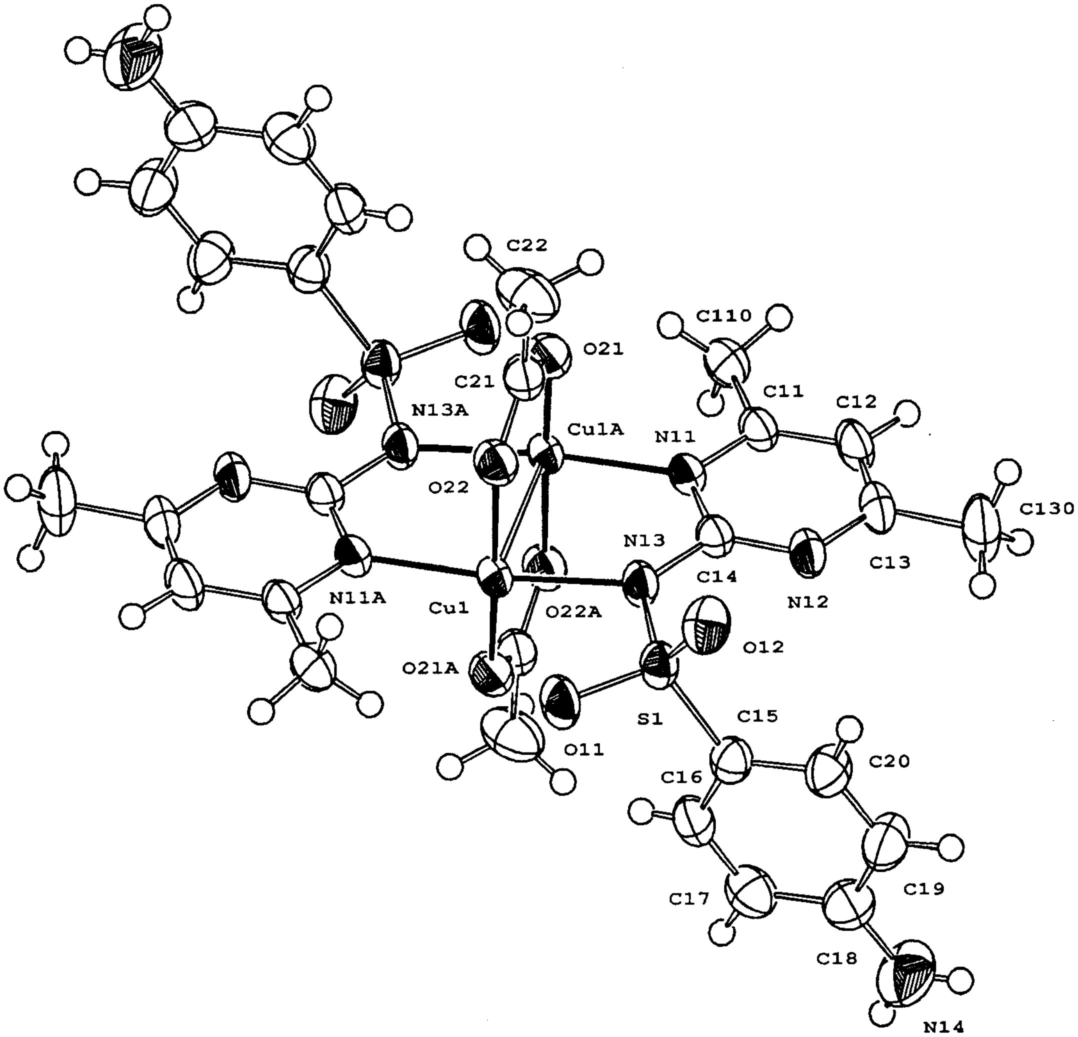
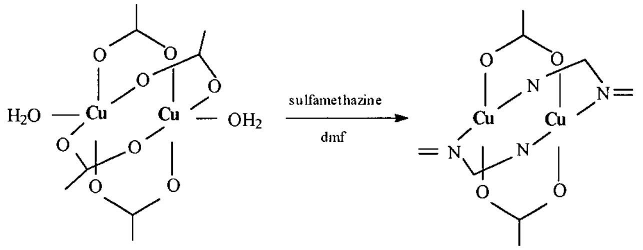


Figure 1. Molecular structure of $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**).

Scheme 1. Reaction of $Cu_2(CH_3COO)_4(H_2O)_2$ with Sulfamethazine in dmf



Results and Discussion

A reaction of $Cu_2(CH_3COO)_4(H_2O)_2$ with sulfamethazine in dimethylformamide leads to the formation of $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$, which has a novel type of quadruply bridged core. The reaction proceeds through the substitution of two axial waters and two bridging carboxylate in the precursor complex by two bridging sulfamethazinate ligands (Scheme 1). From the same reaction mixture a small amount of the polymer $\{[Cu(L)_2]\cdot 2H_2O\}_\infty$ (**2**) is also afforded.

Description of the Crystal Structure of Compound $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (1). A molecular drawing of complex **1** with the atomic numbering scheme is shown in Figure 1. Selected structural parameters are listed in Table 2. The crystal consists of dinuclear $[Cu_2(CH_3COO)_2(L)_2]$ units and two solvent dmf's. An inversion center ($-x$, $-y + 2$, $-z + 1$) is located at the center in the dinuclear entity. The copper centers are bridged by two syn−syn carboxylates and two triatomic NCN bridging groups of the deprotonated sulfamethazine ligands. Each copper ion is coordinated to two carboxylate oxygens, one pyrimidine N atom and one sulfonamide N atom. The two copper ions presents a nearly square planar geometry. The deviation of the Cu ion from the N_2O_2 plane is −0.1398 Å. The bridging pathway Cu−N−C−N−Cu is planar where the largest deviation is 0.025 Å.

The cis O−Cu−N angles are within the range of 88.10(8)−92.11(8)°. The trans O−Cu−O and N−Cu−N angles are 170.48(7) and 173.04(8)°, respectively. The Cu−O lengths [1.9767(18) and 1.9772(18) Å] and the Cu−N distances [1.9764(19) and 1.9995(19) Å] are almost identical.

The Cu···Cu distance is 2.5412(6) Å. It is shorter than that found in the dinuclear adenine complex, $[Cu(adenine)_4]\cdot 4H_2O$,[13] and it is comparable to that of the $[Cu_2(sulfathiazolate)_4]$.[8] Such a short distance appears to be determined by the width of the "bite" of the bridging sulfamethazine. Moreover, a comparison of the Cu···Cu distance in complex **1** with those in dinuclear copper(II) with two syn−syn carboxylates (Cu···Cu, ca. 3.1 Å)[33] and with four syn−syn carboxylates (Cu···Cu, ca. 2.6 Å)[34] indicates that the sulfamethazine NCN bridges allow an ap-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**) and $\{[Cu(L)_2]\cdot 2H_2O\}_\infty$ (**2**) Compounds[a]

1		**2**	
Cu(1)−N(11)#1	1.9764(19)	Cu(1)−N(23)	2.036(4)
Cu(1)−O(21)#1	1.9767(18)	Cu(1)−N(13)	2.040(4)
Cu(1)−O(22)	1.9772(18)	Cu(1)−N(11)	2.051(4)
Cu(1)−N(13)	1.9995(19)	Cu(1)−N(24)#2	2.068(5)
Cu(1)−Cu(1)#1	2.5412(6)	Cu(1)−N(21)	2.452(4)
N(24)−Cu(1)#3	2.068(5)		
N(11)#1−Cu(1)−O(21)#1	88.10(8)	N(23)−Cu(1)−N(13)	166.91(16)
N(11)#1−Cu(1)−O(22)	89.18(8)	N(23)−Cu(1)−N(11)	103.07(15)
O(21)#1−Cu(1)−O(22)	170.48(7)	N(13)−Cu(1)−N(11)	65.53(14)
N(11)#1−Cu(1)−N(13)	173.04(8)	N(23)−Cu(1)−N(24)#2	95.81(19)
O(21)#1−Cu(1)−N(13)	92.11(8)	N(13)−Cu(1)−N(24)#2	95.52(18)
O(22)−Cu(1)−N(13)	89.50(8)	N(11)−Cu(1)−N(24)#3	161.04(18)
N(11)#1−Cu(1)−Cu(1)#1	94.36(6)	N(23)−Cu(1)−N(21)	59.90(13)
O(21)#1−Cu(1)−Cu(1)#1	84.58(5)	N(13)−Cu(1)−N(21)	112.77(15)
O(22)−Cu(1)−Cu(1)#1	86.53(5)	N(11)−Cu(1)−N(21)	94.27(14)
N(13)−Cu(1)−Cu(1)#1	78.75(6)	N(24)#2−-Cu(1)−N(21)	93.71(16)
N(11)−Cu(1)−C(14)	32.44(13)	N(23)−Cu(1)−C(14)	135.39(15)
N(24)#2−Cu(1)−C(14)	128.60(18)	N(13)−Cu(1)−C(14)	33.14(14)
N(21)−Cu(1)−C(14)	107.10(14)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y + 2$, $-z + 1$; #2, $-x + 1$, $y + 1/2$, $-z + 3/2$; #3, $-x + 1$, $y - 1/2$, $-z + 3/2$.

Table 3. EPR Data for the $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**) Complex[a]

	X-band (calcd)	Q-band
$\Delta m_s = \pm 2$	*b*	5568
H_z1	722 (607)	8382
$H_{xy}1$	1680 (1526)	10477
H_z2	5262 (5126)	*c*
$H_{xy}2$	4555 (4416)	13130

[a] Resonance fields in gauss ($=10^{-4}$ T). [b] Not resolved from nearby $\Delta m_s = \pm 1$ band. [c] Hidden by stronger H_{xy^2} band.

proach similar to that of the carboxylate ones. This fact suggests that the removal of carboxylates and their substitution by the triatomic nonlinear NCN bridging groups do not have an influence on the Cu···Cu distance.

The crystal is electrostatically stabilized by hydrogen bonds formed between the amino N and carboxylate O atoms.

Description of the Crystal Structure of Compound $\{[Cu(L)_2]\cdot 2H_2O\}_\infty$ (2). An ORTEP drawing of complex **2** showing the atomic numbering scheme is presented in Figure 2. Selected bond lengths and angles are given in Table 2.

The crystal structure consists of an infinite tridimensional arrangement of water and $[Cu(L)_2]$ molecules. The copper ion is five-coordinate and is bound to five nitrogen atoms from three sulfonamide ligands, one of which belongs to an adjacent asymmetric unit. The metal ion adopts a distorted square pyramidal stereochemistry ($\tau = 0.097$) with the equatorial plane defined by two sulfonamidate N atoms [N(13) and N(23)] in the trans position, a pyrimidine N [N(11)], and one amino N atom [N(24B)]. The axial site is occupied by the pyrimidine N [N(21)]. The axial Cu−N(21) bond length is markedly longer than the equatorial Cu−N ones (T = 0.83). It is worth noting that the equatorial N(13)−Cu−N(11) and the axial N(11)−Cu−N(21) angles have small values of 65.53(14) and 59.90(13)°, respectively. Such small axial angle also has been observed in complexes with the related ligand sulfathiazole.[35]

The coordination behavior of the deprotonated sufamethazine differs from that exhibited by the sulfamethazine anion in compound **1**. In complex **2** the sulfonamidate ligands bind to a metal ion through the sulfonamidato and pyrimidine N atoms, giving rise to a four-membered chelate ring and connect to an adjacent copper(II) through the amino N one.

Owing to the presence of a sulfonamide ligand bridging two adjacent metal cations (Cu···Cu average distance, 9.72 Å), the crystal structure is stabilized by a three-dimensional network. Some relatively weak hydrogen bonds (O···N = 2.921(1)−3.296(7) Å) also take part in the stabilization of the crystal.

Magnetic Properties. Magnetic susceptibility measurements of **1** were performed on crystals in the temperature range 2−350 K. The temperature dependence of the magnetic susceptibility per Cu is shown in Figure 3. The dominant features of the data are a maximum around 200 K and a rapid decrease to zero at lower temperatures. The solid curve in Figure 3 is the best fit of the data to the Bleaney−Bowers equation for the exchange-coupled copper(II) dimers

$$\chi_{\mathrm{M}} = (Ng^2\beta^2/KT[3 + \exp(-2J/KT]\}^{-1} \qquad (1)$$

which results from a consideration of the eigenvalues of $H = -2JS_1S_2$ and where the symbols have the usual meanings. An excellent fit of the data was obtained when $-2J = 216.7$ cm^{-1}, $g = 2.16$, and $R = 6 \times 10^{-4}$.

The antiferromagnetic interaction of compound **1** is found to be intermediate between that which is exhibited by copper(II) dimer complexes with Cu···Cu distances of ca. 2.6 Å and that present four carboxylate bridges or four nonlinear NCN bridges (see Tables 4 and 5). An analysis of this *J* value will be made below using DFT calculations on model compounds.

EPR Spectra. The X- and Q-band EPR spectra of complex **1** at room temperature are shown in Figures 4 and 5, respectively.

The spin Hamiltonian for the triplet state of dimeric compounds is given by the equation[36]

$$H = g\beta BS + DS_{z^2} + E(S_{x^2} - S_{y^2}) - 2D/3 \qquad (2)$$

where *D* and *E* are zero-field splitting parameters and β is the Bohr magneton. As shown by Wasson et al.,[37] two allowed

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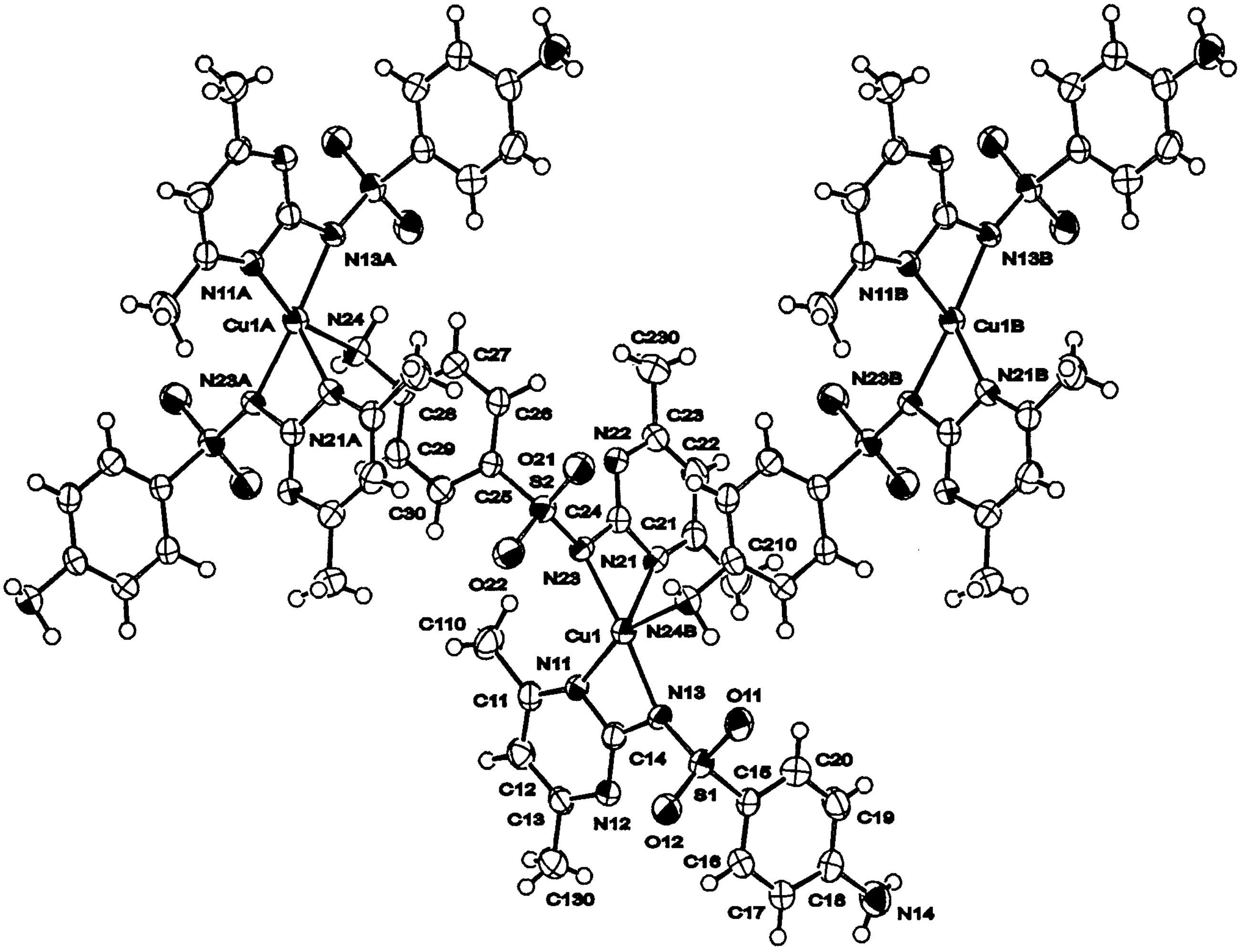

Figure 2. Molecular structure of $\{[Cu(L)_2]\cdot 2H_2O\}_\infty$ (**2**).

transitions by the selection rule ($\Delta m_s = \pm 1$) will result in each principal direction and six resonance fields can be determined. The six resonance fields are H_{x^1}, H_{y^1} , H_{z^1}, H_{x^2}, H_{y^2}, and H_{z^2}, whose equations are proposed by Wasserman et al.[38] When D is lower than $h\nu$, as is usually the case in compounds containing dimers, the solution of spin Hamiltonian yields four allowed transitions ($\Delta m_s = \pm 1$) at resonance fields H_{z^1}, H_{z^2} , H_{xy^1}, and H_{xy^2} given by the equations

$$H_{z^1} = (g_e/g_z)(H_0 - D') \tag{3}$$

$$H_{xy^1} = (g_e/g_{xy})^2 H_0(H_0 - D') \tag{4}$$

$$H_{z^2} = (g_e/g_z)(H_0 + D') \tag{5}$$

$$H_{xy^2} = (g_e/g_{xy})^2 H_0(H_0 + D') \tag{6}$$

In addition, the formally forbidden transition ($\Delta m_s = \pm 2$) is given by the equation[39]

$$H_{\min} = (1/2)g\beta[(h\nu)^2 - 4(D^2/3 + E^2)]^{1/2} \tag{7}$$

The observed transitions are summarized in Table 3. There is a good agreement between the experimental and calculated fields. Values of $g_{\|} = 2.35$, $g_{\perp} = 2.04$, and $D = 0.265$ cm^{-1} are calculated from the observed transitions. The D value is intermediate between those found for dimers with only carboxylate bridges and those reported for copper dimers with nitrogen donors in the bridges.[40] The values of H_{z^2} and H_{xy^2} must be virtually coincident at the Q-band frequency, and consequently, the low-intensity H_{z^2} is hidden by the much stronger H_{xy^2} band. Changing the microwave frequency to X-band enables a clear separation of these transitions to be made (Figure 4). Conversely, the H_{z^1}, H_{xy^1}, and $\Delta m_s = \pm 2$ transitions

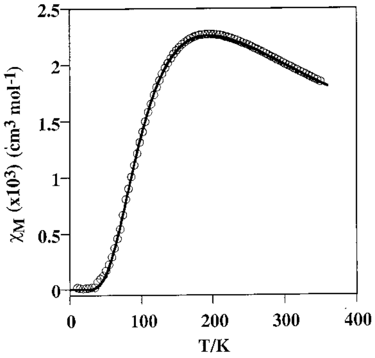

Figure 3. Temperature dependence of $\chi_M T$ for $[Cu_2(CH_3COO)_2(L)_2]\cdot 2dmf$ (**1**). The solid line represents the fitted function according to eq 1.

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Table 4. Experimental Structural Data and Exchange Coupling Constants for Cu(II) Binuclear Complexes Containing NCN Bridges with the Corresponding Refcodes Employed in the Cambridge Structural Database Indicated for Such Structures

compd[a]	J_{exp}/cm^{-1}	refcode	ref
$[Cu_2(adenine)_4(H_2O)_2](ClO_4)_4$	−312	adaqcu	13
$[Cu_2(adenine)_4Cl_2]Cl_2$	−285	cadcuc	13
$[Cu_2(adenine)_4(H_2O)_2](SO_4)_2$	−305	qqqaar	13
$[Cu_2(naphthyridine)_2Cl_2]Cl_2$	−278	baxrib	44
$[Cu_2(adenine)_4(H_2O)_2]$	−179		45
$[Cu_2(adenine)_4(Pip)_2]$	−246		13
$[Cu_2(sulfathiazolato)_4(H_2O)_2]$	−62	runvax	8
$[Cu_2(CH_3COO)_2(L)_2]$ (**1**)	−216	This work	

[a] Solvation molecules not included in the formulas. L = sulfamethazinato.

Table 5. Calculated Exchange Coupling Constants for Cu(II) Binuclear Models Containing NCN and OCO Bridges and the Available Experimental Data[a]

model	J_{calcd}/cm^{-1}	J_{exp}/cm^{-1}
$[Cu_2(sulfathiazolato)_4]$	−57	−62
$[Cu_2(sulfathiazolato)_4(H_2O)_2]$	−43	
$[Cu_2(L)_4(H_2O)_2]$	−55	
$[Cu_2(adenine)_4(H_2O)_2]$	−100	−179
$[Cu_2(Hadenine)_4(H_2O)_2]^{4+}$	−181	−305, −312
$[Cu_2(CH_3COO)_2(L)_2]$ (**1**)	−202	−217
$[Cu_2(CH_3COO)_2(L)_2(H_2O)_2]$	−134	
$[Cu_2(sulfathiazolato)_2(CH_3COO)_2(H_2O)_2]$	−141	
$[Cu_2(adenine)_2(CH_3COO)_2(H_2O)_2]$	−175	
$[Cu_2(CH_3COO)_4(H_2O)_2]$	−261	−298

[a] See references in Table 4. L = sulfamethazinato.

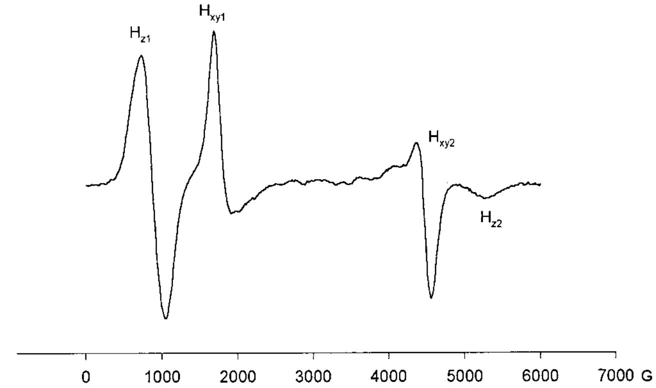

Figure 4. X-band powder EPR spectra of $[Cu_2(CH_3COO)_2(L)_2]{\cdot}2dmf$ (**1**) at room temperature.

could not have been unambiguously assigned from the X-band results alone because of the appreciable overlapping of bands at this frequency. However, these transitions are clearly resolved and readily assigned at the Q-band frequency (Figure 5). The value of $g_o = 2.14$ correlates well with the value obtained from the magnetic data.

The observed *D* value is expressed as $D_{obs} = D_{dd} + D_{exch}$, where D_{dd} and D_{exch} arise from dipole−dipole and exchange interactions, respectively. D_{dd}, which is expected to be negative, is approximately calculated[41] from the equation based on a point dipole model, $R^3 = 0.65g_z^2/D_{dd}$, where *R* is the copper−copper distance. Use of the equation gives $D_{dd} = 0.247$ cm^{-1} and therefore $D_{exch} = 0.512$ cm^{-1}. Rough correlations between D_{exch} and 2*J* have been made by means of the equation $D_{exch} = -2J[(g_z - 2)^2/4 - (g_{xy} - 2)^2]/8$.[30] From this equation a value of $-2J = 136$ cm^{-1} is obtained whereas the experimental value is 216.7 cm^{-1}. The difference between the calculated and the experimental values may be due to the approximations assumed in deriving the equations and also to the fact that the singlet−triplet splitting is not simply related to the strength of the exchange interaction as pointed out elsewhere.

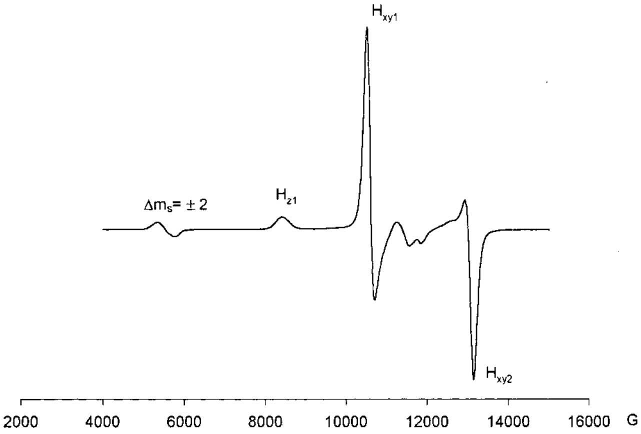

Figure 5. Q-band powder EPR spectra of $[Cu_2(CH_3COO)_2(L)_2]{\cdot}2dmf$ (**1**) at room temperature.

The room-temperature X-band EPR spectrum obtained for a powder sample of **2** is rhombic with $g_1 = 2.20$, $g_2 = 2.15$, and $g_3 = 2.05$. The lines corresponding to g_1 and g_2 are considerably broader than the g_3 line, as expected. However, they are not well resolved due to the hyperfine structures based on copper (^{63}Cu, ^{65}Cu) and nitrogen (^{14}N).[42] A value of $R = (g_2 - g_1)/(g_3 - g_2) = 0.5$ suggests that the distortion from the regular geometry is strong.[43]

Theoretical Results. There are different families of dinuclear Cu(II) complexes supported by NCN bridges between the two copper atoms. For all the complexes indicated in Table 4,[8,13,44,45] all SOMO's are oriented toward the four nitrogen atoms of the bridging ligands ($x^2 - y^2$ type orbital) except for the naphthyridine complex, with a trigonal bipyramid coordination environment where the z^2 type SOMO's are directed toward the two unique naphthyridine ligands. The *J* values indicate in all cases the existence of antiferromagnetic coupling. However, important changes in the magnitude of the coupling constant have been observed depending on whether the NCN bridges belong to a ligand with two condensed rings (adenine and naphthyridine; see Chart 1) or with one single ring (sulfathiazole; see Chart 2). To understand these changes in the coupling constant, we calculated *J* for some model structures with four NCN bridging ligands The calculated values (Table 5) show a very good agreement with the available experimental data, especially considering that we are used model structures.

On the other hand, the calculated values reproduce the experimental trends correctly: the adenine ligand shows a larger antiferromagnetic coupling than the one single ring ligands, and the protonation of the adenine ligands also enhances the exchange coupling considerably. This last effect can easily be rationalized using the Hay−Thibeault−Hoffman model.[46] In principle, due to the similarity of the two structures, the bielectronic contributions can be considered similar in both cases. Thus, the analysis of the SOMO's energies indicates an

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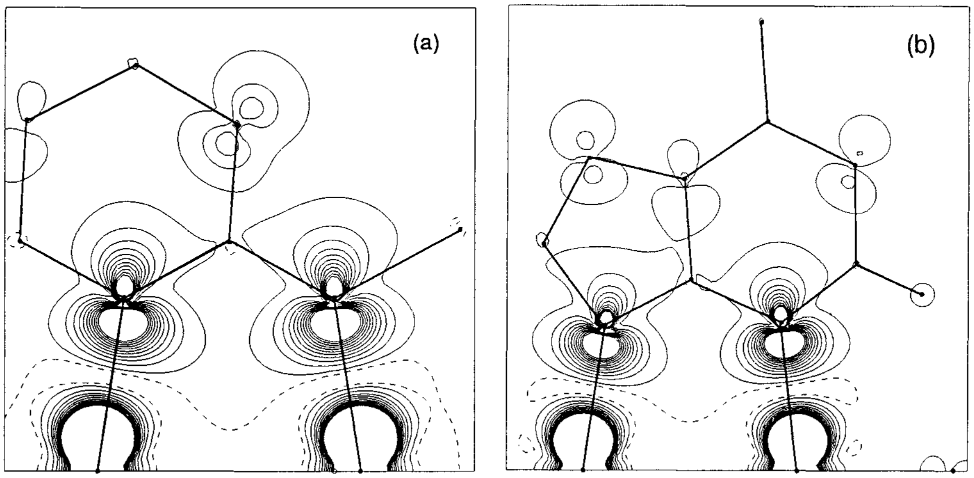
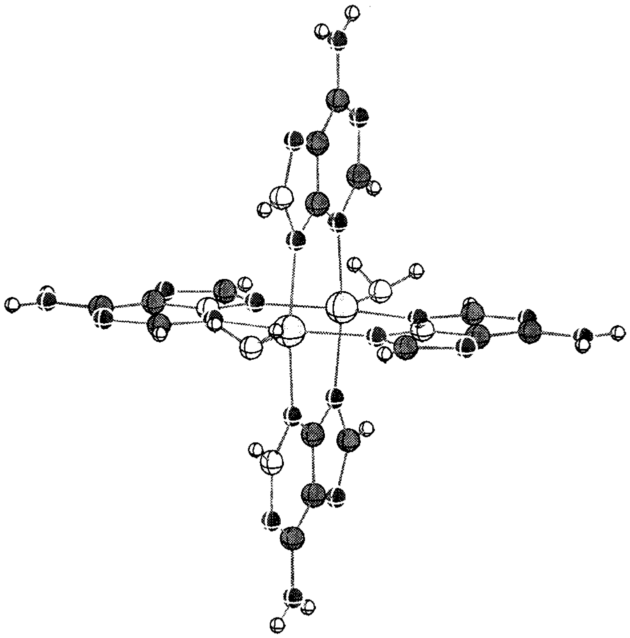


Figure 6. Calculated spin population map for the sulfamethazine bridging ligand in the $[Cu_2(CH_3COO)_2(L)_2]$ complex (a) and for the adenine ligand in the $[Cu_2(CH_3COO)_2(adenine)_2(H_2O)_2]$ complex (b). Solid lines indicate positive levels and dashed negative ones. The contour values are between -0.0005 and $+0.0005$ e$^-$/Å^3 with steps of 0.0020 e$^-$/Å^3.

Chart 1. Dinuclear Cu(II) Model with Four NCN Bridges Belong to a Ligand with Two Condensed Rings

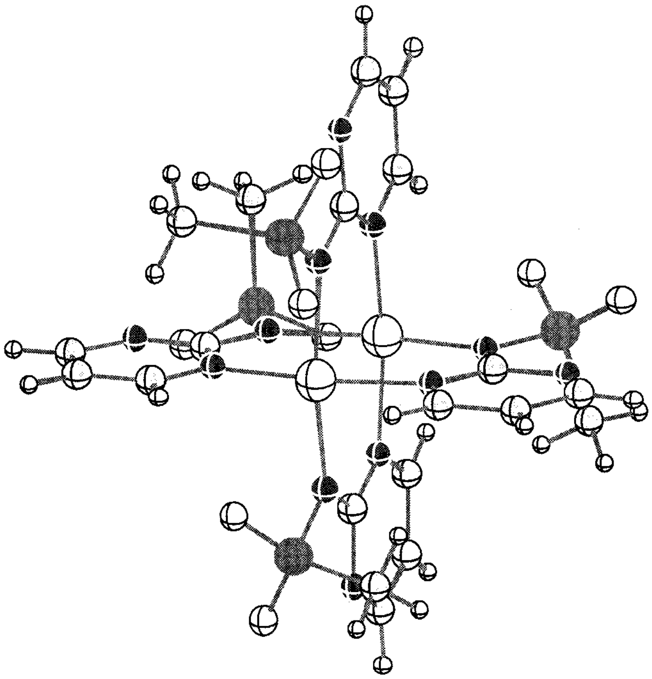


increase in the energy gap due to the protonation, this being the source for a larger antiferromagnetic coupling for the protonated ligand.

Furthermore, we have calculated the coupling constant for model complexes with two acetates and two NCN bridges. The calculated *J* value for these complexes was very close to the average of the *J* values of the corresponding complex with four identical bridging ligands and of the copper acetate. In previous work, we found a similar behavior when mixing different carboxylato bridging ligands: the *J* values were always very close to those corresponding to the average between the two complexes with four identical ligands.[47] One should have expected a larger antiferromagnetic coupling for the NCN bridges than for the OCO ones, but in this case, the asymmetry of the NCN bridging ligands also enhanced the ferromagnetic contribution.[48]

We also performed the calculation of the *J* value for the $[Cu_2(CH_3COO)_2(L)_2]$ (**1**) complex using the whole X-ray structure for the molecule obtaining a value of -158 cm^{-1}. Surprisingly, the value obtained with the model structure (see Table 5) was slightly closer to the experimental one of -216.7 cm^{-1}.

Chart 2. Dinuclear Cu(II) Model with Four NCN Bridges Belong to a Ligand with One Single Ring



To analyze the coupling mechanism of the adenine ligands in comparison with the sulfamethazine ligand, we plotted the spin population maps for these two complexes (see Figure 6). The spin population map for the triplet state was calculated in order to avoid the well-known problem in the definition of the spin density of the broken-symmetry solutions.[26] The maps for the adenine and sulfamethazine ligand were quite similar in both cases: the predominant mechanism in the neighboring nitrogen atom was the spin delocalization.[49] However, in the bridging carbon atom a very small negative value indicated a polarization

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mechanism on the bridge. For the other atoms of the rings the delocalization mechanism was predominant and only a carbon atom in the sulfamethazine ligand showed a negative spin density population.

We also studied the effect on the exchange coupling of the presence of water molecules occupying the axial coordination position. For this purpose we carried out the calculations both with and without water molecules for the two complexes that do not have water molecules in the X-ray structure, $[Cu_2(CH_3COO)_2(L)_2]$ (**1**) and $[Cu_2(\text{sulfathiazolato})_4]$. In both cases, the inclusion of water molecules decreased the strength of the antiferromagnetic interaction (see Table 5). The considerable change predicted for the exchange coupling constant due to the presence of the axial water molecules for the $[Cu_2(CH_3COO)_2(L)_2]$ (**1**) complex was remarkable. The effect found in the J value when including axial ligands was unusual, because normally the axial ligand induces a larger hybridization of the d_{z^2} orbital in the xy plane.[50] Thus, it would favor the interaction of the orbitals bearing the unpaired electrons with the orbitals of the bridging group and, following Kahn's model, an increase in the antiferromagnetic coupling would be expected.[51] However, in this case the SOMO's gap remained almost unchanged. Thus, the mechanism related to the hybridization of $d_{x^2-y^2}$ orbitals did not seem to be responsible for the reduction of the antiferromagnetic coupling. Nevertheless, we found an enhancing of the localization of the spin population of the copper atom when the axial ligands were included which resulted in a decrease of the spin population in the bridging ligand. This decrease of the spin population could be responsible for the observed reduction of the antiferromagnetic coupling.[49]

Acknowledgment. G.A. and J.B. thank the CYCIT (Project PM97-0105-C02-01) and A.C. thanks the Xunta de Galicia (Project XUGA20309B97) for financial support. E.R. and A.R-F. acknowledge financial support provided by the DGES through Project No. PB98-1166-C02-01. A.R.-F. thanks the CIRIT, Generalitat de Catalunya, for a doctoral fellowship. The computing resources were generously made available by the Centre de Computació de Catalunya (CESCA) with a grant provided by Fundació Catalana per a la Recerca (FCR) and the Universitat de Barcelona. The authors thank Prof. Teofilo Rojo (Universidad del Pais Vasco, Spain) for the Q-band EPR measurements and Prof. J. A. Real (Universidad de Valencia, Burjassot, Spain) for the magnetic measurements.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares planes and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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