Helical-Chain Copper(II) Complexes and a Cyclic Tetranuclear Copper(II) Complex with Single Syn−Anti Carboxylate Bridges and Ferromagnetic Exchange Interactions

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Tridentate Schiff-base carboxylate-containing ligands, derived from the condensation of 2-imidazolecarboxaldehyde with the amino acids β-alanine (H_2L^1) and 2-aminobenzoic acid (H_2L^5) and the condensation of 2-pyridinecarboxaldehyde with β-alanine (HL^2), D,L-3-aminobutyric acid (HL^3), and 4-aminobutyric acid (HL^4), react with copper(II) perchlorate to give rise to the helical-chain complexes $\{[Cu(\mu-HL^1)(H_2O)](ClO_4)\}_n$ (**1**), $\{[Cu(\mu-L^2)-(H_2O)](ClO_4)\cdot 2H_2O\}_n$ (**2**), and $\{[Cu(\mu-L^3)(H_2O)](ClO_4)\cdot 2H_2O\}_n$ (**3**), the tetranuclear complex $\{[Cu(\mu-L^4)(H_2O)]-(ClO_4)\}_4$ (**4**), and the mononuclear complex $[Cu(HL^5)(H_2O)](ClO_4)\cdot^1/_2H_2O$ (**5**). The reaction of copper(II) chloride with H_2L^1 leads not to a syn−anti carboxylate-bridged compound but to the chloride-bridged dinuclear complex $[Cu(HL^1)(\mu-Cl)]_2$ (**6**). The structures of these complexes have been solved by X-ray crystallography. In complexes **1**−**4**, roughly square-pyramidal copper(II) ions are sequentially bridged by syn−anti carboxylate groups. Copper-(II) ions exhibit CuN_2O_3 coordination environments with the three donor atoms of the ligand and one oxygen atom belonging to the carboxylate group of an adjacent molecule occupying the basal positions and an oxygen atom (from a water molecule in the case of compounds **1**−**3** and from a perchlorate anion in **4**) coordinated in the apical position. Therefore, carboxylate groups are mutually cis oriented and each syn−anti carboxylate group bridges two copper(II) ions in basal−basal positions with Cu···Cu distances ranging from 4.541 Å for **4** to 5.186 Å for **2**. In complex **5**, the water molecule occupies an equatorial position in the distorted octahedral environment of the copper(II) ion and the Cu−O carboxylate distances in axial positions are very large (>2.78 Å). Therefore, this complex can be considered as mononuclear. Complex **6** exhibits a dinuclear parallel planar structure with C_i symmetry. Copper(II) ions display a square-pyramidal coordination geometry ($\tau = 0.06$) for the N_2OCl_2 donor set, where the basal coordination sites are occupied by one of the bridging chlorine atoms and the three donor atoms of the tridentate ligand and the apical site is occupied by the remaining bridging chlorine atom. Magnetic susceptibility measurements indicate that complexes **1**−**4** exhibit weak ferromagnetic interactions whereas a weak antiferromagnetic coupling has been established for **6**. The magnetic behavior can be satisfactorily explained on the basis of the structural data for these and related complexes.

Introduction

Research for extended systems on the relationship between structure and magnetic properties has been particularly active in the last two decades with the aim of understanding the fundamental factors governing magnetic properties.[1−6] This information can be applicable to the design and preparation of new molecular materials exhibiting expected magnetic proper-

ties, such as molecular-based magnets, or to the investigation of the structure of the active sites in metalloproteins with interacting paramagnetic centers. In this regard, studies on metal carboxylate complexes as models for metalloproteins have long been of interest.[7−9] Moreover, because, in metalloproteins, carboxylate ligands are provided by side amino acid chains, polydentate chelating ligands containing a carboxylate group are of biological relevance.[10]

It is well-known that a carboxylate group can bridge two metal ions to give rise to a wide variety of polynuclear complexes ranging from discrete entities to three-dimensional systems.[11−13] In these complexes, a carboxylate group can assume many types of bridging conformations, the most

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important being triatomic syn−syn, anti−anti, and syn-anti and monatomic.[14] As expected, the magnetic properties are closely related to the bridging conformation adopted by the carboxylate group in these polynuclear systems. Thus, for copper(II) complexes, the former two conformations mediate large and weak to medium antiferromagnetic interactions,[11,14] respectively, whereas the latter two exhibit weak magnetic exchange interactions.[15,16] It should be noted that, as far as we know, only a few fully structurally and magnetically characterized singly syn-anti carboxylate-bridged copper(II) complexes have been reported so far,[16−19] which usually exhibit ferromagnetic exchange coupling and in a few instances exhibit antiferromagnetic coupling. To analyze in a thorough manner the structural factors leading to these differences in magnetic behavior, more examples of these kinds of complexes are needed. We have previously shown that tridentate ligands with carboxylate groups can undergo self-assembly processes promoted by metal ions leading to either anti-anti or syn-anti carboxylate-bridge copper-(II) complexes. Thus, from [M(hfac)$_2$] (M = Mn(II), Ni(II), Cu-(II); hfac = hexafluoroacetylacetonate) and the tridentate ligand derived from 2-imidazolecarboxaldehyde and β-alanine (H$_2$L^1), anti-anti zigzag-chain [M(HL^1)(hfac)]$_n$ complexes were obtained[14] whereas, from [(carboxyphenyl)azo]pyrimidine tridentate ligands and copper(II) perchlorate, a series of oligomeric copper(II) complexes, ranging from dinuclear to chain complexes, could be prepared.[16] Within this framework and with the aim of preparing new syn-anti carboxylate-bridged copper-(II) complexes, we have used tridentate Schiff-base ligands derived from the condensation of 2-imidazolecarboxaldehyde and 2-pyridinecarboxaldehyde with the amino acids β-alanine, D,L-3-aminobutyric acid, 4-aminobutyric acid, and 2-aminobenzoic acid (see Chart 1). On reacting with copper(II) perchlorate, the Schiff-base ligands derived from β-alanine and D,L-3-aminobutyric acid produce the syn-anti carboxylate-bridged helical-chain copper(II) complexes {[Cu(μ-HL^1)(H$_2$O)](ClO$_4$)}$_n$ (**1**), {[Cu(μ-L^2)(H$_2$O)](ClO$_4$)·2H$_2$O}$_n$ (**2**), {[Cu(μ-L^3)(H$_2$O)]-(ClO$_4$)·2H$_2$O}$_n$ (**3**), whereas the reaction of copper(II) perchlorate with the Schiff-base ligand derived from 4-aminobutyric acid produces the distorted square-planar cyclic tetranuclear copper(II) complex {[Cu(μ-L^4)(H$_2$O)](ClO$_4$)}$_4$ (**4**). With H$_2$L^5, the mononuclear complex [Cu(HL^5)(H$_2$O)](ClO$_4$)·^{1}/$_2$H$_2$O (**5**) is obtained, and the reaction of H$_2$L^1 with copper(II) chloride leads to the chloride-bridged dinuclear complex [Cu(HL^1)(μ-Cl)]$_2$ (**6**). This paper is devoted to the structural and magnetochemical studies of these complexes.

Experimental Section

Physical Measurements. Elemental analyses and diffuse-reflectance spectra were obtained at the Centro de Instrumentación Científica of the University of Granada on a Fisons-Carlo Erba model EA 1108 analyzer and a Varian Cary-5E spectrometer, respectively. IR spectra were recorded on a Perkin-Elmer 983 G spectrometer using KBr pellets. Variable-temperature magnetic susceptibility data were collected for

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Chart 1
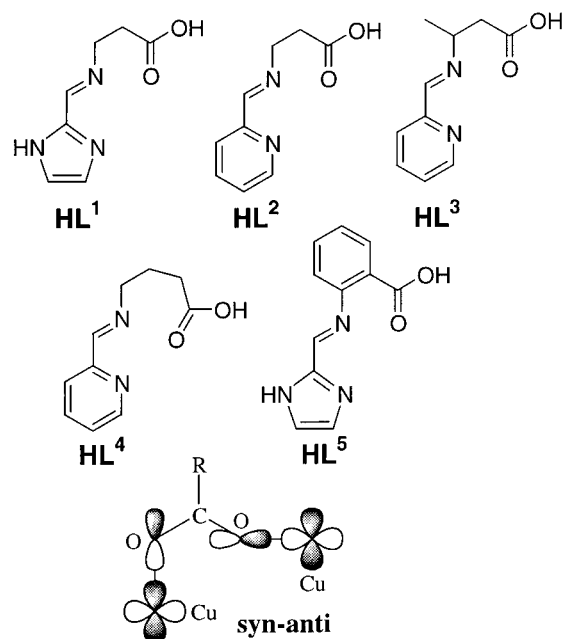
powdered samples of the compounds on a Quantum Design MPMS instrument with the use of a SQUID-based sample magnetometer. Data were corrected for the diamagnetism of the ligands using Pascal's constants. Variable-temperature EPR spectra were measured with a Bruker ESP 300E spectrometer.

Caution! Perchlorate salts are potentially explosive and should only be handled in small quantities.

All reagents were of analytical grade and were used without further purification.

Preparations of the Compounds. All complexes were prepared using the same method, which is described in detail for {[Cu(μ-HL^1)-(H$_2$O)](ClO$_4$)}$_n$ (**1**) as an example. This complex was prepared by refluxing 2-imidazolecarboxaldehyde (0.2 g, 2.08 mmol) and β-alanine (0.185 g, 2.08 mmol) for 1 h in 30 mL of an MeOH/H$_2$O mixture (3/1, v/v). To the cold, filtered yellow solution was added dropwise, with stirring, Cu(ClO$_4$)$_2$·6H$_2$O (0.77 g, 2.08 mmol) in 30 mL of MeOH. The resulting deep blue solution, kept at room temperature for 2 days, provided blue prism-like crystals, which were isolated by filtration and air-dried. Yield: 90%. Anal. Calcd for C$_7$H$_{10}$N$_3$O$_7$ClCu: C, 24.19; H, 2.88; N, 12.09. Found: C, 23.75; H, 3.00; N, 12.04. IR (KBr; cm^{-1}): ν(N$_{im}$−H) 3122; ν(CO) 1610, 1437; ν(Cl−O) 1086, 1179. d−d band (λ, nm): 692.

{[Cu(μ-L^2)(H$_2$O)](ClO$_4$)·2H$_2$O}$_n$ (2) was obtained as greenish-blue crystals. Yield: 65%. Anal. Calcd for C$_9$H$_{15}$N$_2$O$_9$ClCu: C, 27.41; H, 3.81, N, 7.11. Found: C, 27.46; H, 3.79; N, 7.56. IR (KBr; cm^{-1}): ν(CO) 1600, 1442; pyridine skeleton 1589, 1471, 1433; ν(Cl−O) 1093, 1120. d−d band (λ, nm): 698.

{[Cu(μ-L^3)(H$_2$O)](ClO$_4$)·2H$_2$O}$_n$ (3) was obtained as blue crystals. Yield: 92%. Anal. Calcd for C$_{10}$H$_{17}$N$_2$O$_9$ClCu: C, 29.41; H, 4.17; N, 6.86. Found: C, 29.70; H, 3.79; N, 6.53. IR (KBr; cm^{-1}): ν(CO) 1600, 1430; pyridine skeleton 1586, 1472, 1445; ν(Cl−O) 1094, 1121. d−d band (λ, nm): 692.

[Cu(μ-L^4)(ClO$_4$)]$_4$ (4) was obtained as dark blue crystals. Yield: 83%. Anal. Calcd for C$_{10}$H$_{13}$N$_2$O$_7$ClCu: C, 33.79; H, 3.66; N, 7.88. Found: C, 33.75; H, 3.24; N, 7.67. IR (KBr; cm^{-1}): ν(CO) 1606, 1433; pyridine skeleton 1585, 1467, 1445; ν(Cl−O) 1090. d−d band (λ, nm): 635.

[Cu(HL^5)(H$_2$O)](ClO$_4$)·^{1}/$_2$H$_2$O (5) was obtained as olive-green crystals. Yield: 60%. Anal. Calcd for C$_{11}$H$_{11}$N$_3$O$_{7.5}$ClCu: C, 32.65; H, 2.72; N, 10.39. Found: C, 32.12; H, 2.97; N, 10.08. IR (KBr; cm^{-1}): ν(N$_{im}$−H) 3145; ν(CO) 1621, 1428; ν(Cl−O) 1087, 1120. d−d band (λ, nm): 651.

[Cu(HL^1)(μ-Cl)]$_2$ (6) was obtained as light blue crystals. In this case, CuCl$_2$ was used instead of Cu(ClO$_4$)$_2$·6H$_2$O. Yield: 90%. Anal. Calcd

Table 1. Crystal Data and Structure Refinement Details for **1**−**6**

	1	2	3	4	5	6
empirical formula	$C_7H_{10}ClCuN_3O_7$	$C_9H_{15}ClCuN_2O_9$	$C_{10}H_{17}ClCuN_2O_9$	$C_{40}H_{44}Cl_4Cu_4N_8O_{24}$	$C_{11}H_{11}ClCuN_3O_{7.5}$	$C_{14}H_{16}Cl_2Cu_2N_6O_4$
fw	347.17	394.22	408.25	1416.80	404.22	530.30
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	rhombohedral	triclinic
space group (No.)	$C2/c$ (15)	$P2_1/c$ (14)	$P2_1/c$ (14)	$C2/c$ (15)	$R\bar{3}$ (148)	$P\bar{1}$ (2)
a (Å)	14.606(3)	12.954(3)	13.1234(10)	26.658(5)	19.948(3)	8.199(5)
b (Å)	7.704(2)	7.487(2)	7.7098(4)	7.966(2)	19.948(3)	8.942(6)
c (Å)	21.836(4)	16.085(3)	16.126(2)	26.508(5)	19.405(4)	6.866(4)
α (deg)	90	90	90	90	90	103.85(5)
β (deg)	95.77(3)	101.53(3)	100.432(8)	92.25(3)	90	108.51(4)
γ (deg)	90	90	90	90	120	69.32(5)
V (Å^3)	2444.6(9)	1528.6(5)	1604.6(2)	5625(2)	6687(2)	442.0(5)
Z	8	4	4	4	18	1
d_{calcd} (Mg m^{-3})	1.887	1.713	1.690	1.673	1.807	1.992
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	193(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
abs coeff (mm^{-1})	2.039	1.649	1.574	1.768	1.694	2.746
final R indices [$I > 2\sigma(I)$]: R1,[a] wR2[b]	0.0472, 0.1217	0.0641, 0.1211	0.0437, 0.1133	0.0989, 0.1879	0.0675, 0.1456	0.0306, 0.0828

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [b] wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

for C$_7$H$_8$N$_3$O$_2$ClCu: C, 31.69; H, 3.01; N, 15.84. Found: C, 32.46; H, 2.91; N, 15.71. IR (KBr; cm^{-1}): $\nu(N_{im}-H)$ 3150; $\nu(CO)$ 1626, 1373. d−d band (λ, nm): 686.

X-ray Data Collections and Structure Determinations. Intensity data for compounds **1**, **2**, **4**, and **5** were collected with a Siemens STADI4, data for **3** with a Siemens P4, and data for **6** with a Rigaku AFC-7S single-crystal diffractometer. In each case, Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator) was used and the scan type was $\omega/2\theta$. The data were corrected for Lorentz and polarization effects and for absorption (empirical ψ scan). The structures of the compounds were solved by direct methods[20] combined with subsequent Fourier analyses.[21] Further details of the crystal data collections and structure determinations are given in Table 1.

Results and Discussion

Syntheses. The reactions of the new tridentate carboxylate-containing ligands with copper(II) perchlorate generally lead to syn-anti carboxylate-bridged complexes. Because the tridentate ligands do not saturate the coordination positions on the copper(II) ions, self-assembly reactions may occur through the deprotonated carboxylate groups, leading to carboxylate-bridged polynuclear complexes. When the reaction for the synthesis of **1** is carried out by using copper chloride as the starting material, the chloride ligands remain bonded to the Cu(II) ion, a self-assembly reaction takes place not through carboxylate groups but through the chloride ligands, and a chloride-bridged dinuclear complex is obtained. For complexes **1**−**4** the difference between $\nu_{as}(COO)$ and $\nu_{sym}(COO)$ stretching frequencies is near 170 cm^{-1}, thus suggesting a bridging coordination mode for the carboxylate group. Complexes **5** and **6** exhibit larger values for that difference of 193 and 253 cm^{-1}, respectively, pointing toward a terminal monodentate coordination mode of the carboxylate group.

Structures. The structures of the complexes **1**−**3** are very similar and consist of roughly square-pyramidal copper(II) ions which are sequentially bridged by syn-anti carboxylate groups to form infinite helical chains. Perspective views of the mononuclear fragments for complexes **1**−**3**, together with the corresponding atom-labeling schemes, are given in Figure 1, and a view of the helical chain for **2** is given in Figure 2 as an example. Selected bond lengths and angles are listed in Table 2.

Each monodeprotonated ligand acts as a tridentate ligand toward a copper(II) ion and as a monodentate ligand toward a neighboring copper(II) center. Copper(II) ions exhibit CuN$_2$O$_3$ coordination environments, in which four short bonds close to 2 Å are formed with three donor atoms of the ligand and one oxygen atom belonging to the carboxylate group of an adjacent molecule, while a water molecule is coordinated at a longer distance, >2.35 Å. According to the procedure described by Addison,[22] the shapes of the polyhedra can be considered as square-based pyramidal, since the τ values ($\tau = (\theta_1 - \theta_2)/60°$, where θ_1 and θ_2 are the largest angles in the coordination sphere) are 0.01, 0.16, and 0.06 for complexes **1**−**3**, respectively (τ has values of 1 and 0 for trigonal-bipyramidal (D_{3h}) and square-based-pyramidal (C_{4v}) geometries, respectively). In the C_{4v} description, the four short bonds occupy the basal positions, whereas the water molecule is bonded in the apical position. As usual, the copper ions deviate from the mean basal plane toward the axial oxygen donor.

Because the three donor atoms of the ligands occupy in-plane coordination positions, the carboxylate bridges are forced to be oriented in a mutually cis fashion and then placed in either basal−apical or basal−basal positions. For complexes **1**−**3**, the latter orientation is adopted and each syn−anti carboxylate group bridges two copper(II) ions in basal−basal positions with intrachain Cu···Cu distances of 4.844, 5.186, and 5.158 Å, respectively. Interestingly, both the cis orientations of the syn-anti carboxylate groups and the shifts of the copper(II) ions from the carboxylate planes lead to helicities in the chains. In the lattices, Λ and Δ helical chains alternate, resulting in optically inactive racemic crystals. Spontaneous resolution of left- and right-handed helices, though rare, has been observed, for instance, in helical chains containing chiral ligands.[23] For compound **3**, containing a chiral ligand, however, racemic crystals form. Figure 2 shows the space-filling diagram of the −CuCOOCu− backbone of Λ and Δ helical chains in compound **2**. It should be noted at this point that the helical structural motif is of current interest in supramolecular chemistry owing to its involvement in biological systems and enantioselective catalysis.[24]

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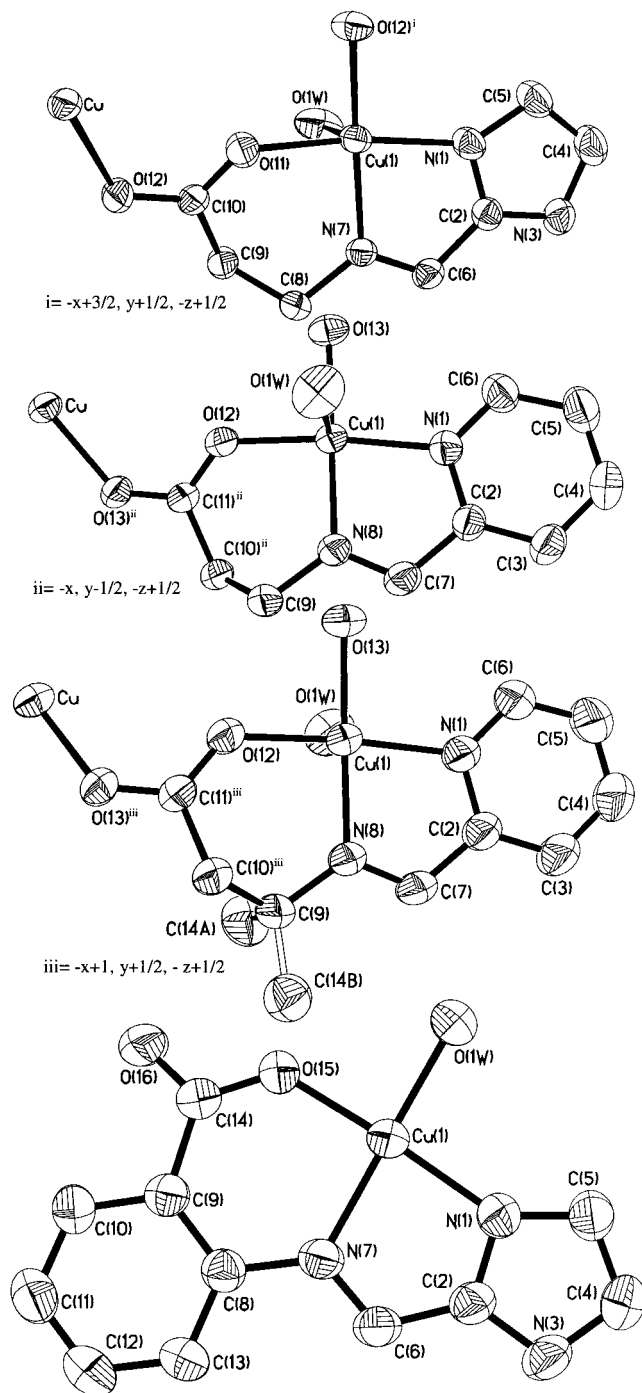
Figure 1. Perspective views of the mononuclear fragments for complexes **1** (top), **2, 3,** and **5** (bottom). Ellipsoids represent 40% of probability.

The polymeric chains are held together by an extensive network of hydrogen bonds involving the coordinated water molecule, the imidazole hydrogen atom, N(3)−H, and the perchlorate anion in **1** and the three water molecules and the perchlorate anion in **2** and **3**, with shortest interchain distances of 8.037, 7.889, and 8.091 Å, respectively. A few helical singly syn−anti carboxylate-bridged copper(II) chain structures similar to those observed for complexes **1**−**3** have been previously reported by us[25] and other authors.[17,18,26]
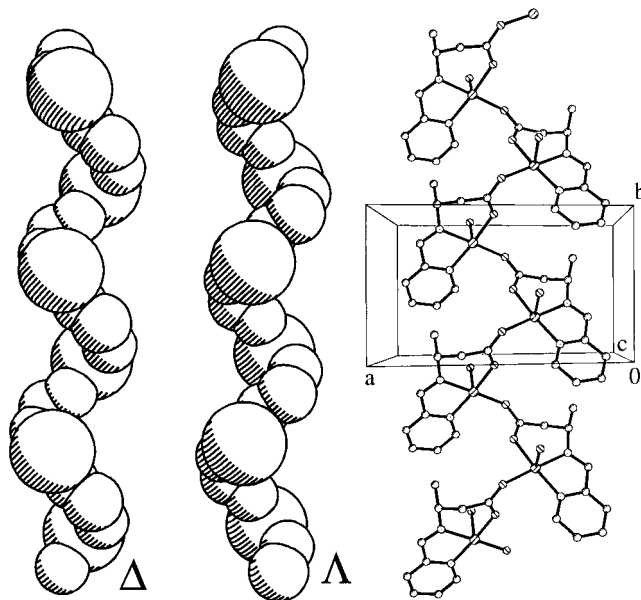

Figure 2. Space-filling diagram of two adjacent complementary helices in **2**. Only the Cu−O−C−O−Cu backbone is shown.

As indicated elsewhere, when the tridentate ligand HL^4 is allowed to react with $Cu(ClO_4)_2\cdot6H_2O$, the tetranuclear complex **4** is obtained instead of a chain compound. A perspective view of the structure of **4**, with the atom-numbering scheme, is given in Figure 3. Relevant interatomic distances and angles are given in Table 2. The structure of **4** consists of syn−anti carboxylate-bridged cyclic tetranuclear molecules $[Cu(\mu-L^4)(ClO_4)]_4$ with C_2 symmetry. The two crystallographically independent copper-(II) ions, as in the helical-chain copper(II) complexes **1**−**3**, exhibit square-pyramidal CuN_2O_3 chromophores (τ values for Cu(1) and Cu(2) are 0.04 and 0.05, respectively) with the oxygen atoms of the carboxylate bridging ligands occupying cis basal positions. In this case, however, the apical position is occupied by one oxygen atom of the perchlorate anion instead of the oxygen atom of a water molecule. The carboxylate bridging groups and copper(II) ions form a 16-membered ring ($-Cu-O-C-O)_4$ with the four copper ions located at the corners of a quite flattened tetrahedron. In fact, according to the Muetterties procedure,[27] the actual geometry lies on the $T_d \leftrightarrow D_{4h}$ deformation pathway with 62.4% D_{4h} character and the shape of the polyhedron can be better described as an approximate molecular parallelogram of sides 4.541 Å (between Cu(1) and Cu(2)) and 4.616 Å (between Cu(1) and Cu(2A)). Finally, there are no close intermolecular contacts in the structure and the tetranuclear molecules are well isolated, with a shortest intermolecular Cu···Cu distance of 7.375 Å.

The formation of the tetranuclear instead of the chain structure in **4** may be related to the fact that the amino acid chain in HL^4 is longer than those in the other ligands. This provides sufficient flexibility for HL^4 to be folded in such a way in its coordination to Cu(II) that the tetranuclear structure can be formed. It should be noted that **4** represents one of the very few examples of singly carboxylate-bridged tetranuclear copper(II) complexes reported so far.[28]

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**–**6**[a]

Complex **1**			
Cu(1)−O(11)	1.940(2)	Cu(1)−O(12)[i]	1.961(2)
Cu(1)−N(1)	1.988(3)	Cu(1)−N(7)	2.002(2)
O(1W)−Cu(1)	2.533(4)		
O(11)−Cu(1)−O(12)[i]	87.98(10)	O(11)−Cu(1)−N(1)	171.61(10)
O(12)[i]−Cu(1)−N(1)	98.07(11)	O(11)−Cu(1)−N(7)	91.19(9)
O(12)[i]−Cu(1)−N(7)	171.88(9)	N(1)−Cu(1)−N(7)	82.00(10)
O(1W)−Cu(1)−N(1)	93.83(13)	O(1W)−Cu(1)−N(7)	84.77(10)
O(1W)−Cu(1)−O(11)	90.41(12)	O(1W)−Cu(1)−O(12)[i]	103.31(10)
Complex **2**			
Cu(1)−N(8)	1.970(3)	Cu(1)−O(12)	1.972(3)
Cu(1)−O(13)	1.979(2)	Cu(1)−N(1)	2.009(3)
Cu(1)−O(1W)	2.310(3)		
N(8)−Cu(1)−O(12)	92.36(12)	N(8)−Cu(1)−O(13)	179.13(12)
O(12)−Cu(1)−O(13)	87.84(11)	N(8)−Cu(1)−N(1)	81.45(13)
O(12)−Cu(1)−N(1)	173.23(11)	O(13)−Cu(1)−N(1)	98.30(12)
N(8)−Cu(1)−O(1W)	96.30(13)	O(12)−Cu(1)−O(1W)	95.33(13)
O(13)−Cu(1)−O(1W)	84.53(12)	N(1)−Cu(1)−O(1W)	88.13(13)
Complex **3**			
Cu(1)−O(13)	1.970(2)	Cu(1)−O(12)	1.969(2)
Cu(1)−N(8)	1.980(2)	Cu(1)−N(1)	2.005(3)
Cu(1)−O(1W)	2.351(3)		
O(13)−Cu(1)−O(12)	88.18(9)	O(13)−Cu(1)−N(8)	178.58(10)
O(12)−Cu(1)−N(8)	93.05(10)	O(13)−Cu(1)−N(1)	97.03(10)
O(12)−Cu(1)−N(1)	174.79(9)	N(8)−Cu(1)−N(1)	81.74(11)
O(13)−Cu(1)−O(1W)	85.04(10)	O(12)−Cu(1)−O(1W)	92.52(11)
N(8)−Cu(1)−O(1W)	95.60(12)	N(1)−Cu(1)−O(1W)	87.93(12)
Complex **4**			
Cu(1)−O(141)	1.957(9)	Cu(1)−O(13)	1.949(9)
Cu(1)−N(1)	2.002(13)	Cu(1)−N(8)	1.999(12)
Cu(1)−O(44)[iv]	2.423(12)	Cu(2)−O(131)	1.946(9)
Cu(2)−O(14)	1.959(9)	Cu(2)−N(81)	1.969(12)
Cu(2)−N(11)	1.990(12)	Cu(2)−O(32B)	2.46(7)
O(141)−Cu(1)−O(13)	92.0(4)	O(141)−Cu(1)−N(1)	92.0(5)
O(13)−Cu(1)−N(1)	174.0(5)	O(141)−Cu(1)−N(8)	171.5(5)
O(13)−Cu(1)−N(8)	93.6(5)	N(1)−Cu(1)−N(8)	82.0(5)
O(141)−Cu(1)−O(44)[iv]	99.1(5)	O(13)−Cu(1)−O(44)[iv]	92.0(4)
N(1)−Cu(1)−O(44)[iv]	91.9(5)	N(8)−Cu(1)−O(44)[iv]	87.1(5)
O(131)−Cu(2)−O(14)	91.9(4)	O(131)−Cu(2)−N(81)	94.7(5)
O(14)−Cu(2)−N(81)	172.5(5)	O(131)−Cu(2)−N(11)	175.7(5)
O(14)−Cu(2)−N(11)	92.4(4)	N(81)−Cu(2)−N(11)	81.0(5)
O(131)−Cu(2)−O(32B)	81.4(14)	O(14)−Cu(2)−O(32B)	94(2)
N(81)−Cu(2)−O(32B)	91(2)	N(11)−Cu(2)−O(32B)	98.1(14)
Complex **5**			
Cu(1)−O(15)	1.883(3)	Cu(1)−O(1W)	1.944(4)
Cu(1)−N(1)	1.969(4)	Cu(1)−N(7)	2.010(4)
O(15)−Cu(1)−O(1W)	87.8(2)	O(15)−Cu(1)−N(1)	174.8(2)
O(1W)−Cu(1)−N(1)	95.5(2)	O(15)−Cu(1)−N(7)	92.8(2)
O(1W)−Cu(1)−N(7)	178.9(2)	N(1)−Cu(1)−N(7)	84.0(2)
Complex **6**			
Cu−O(11)	1.935(2)	Cu−N(1)	1.978(3)
Cu−N(7)	2.019(3)	Cu−Cl	2.288(2)
Cu−Cl[v]	2.724(2)	Cu−Cl−Cu[v]	87.03(6)
O(11)−Cu−N(1)	168.09(10)	O(11)−Cu−N(7)	92.48(11)
N(1)−Cu−N(7)	80.93(11)	O(11)−Cu−Cl	93.07(8)
N(1)−Cu−Cl	92.52(9)	N(7)−Cu−Cl	171.72(8)
O(11)−Cu−Cl[v]	97.16(8)	N(1)−Cu−Cl[v]	93.05(9)
N(7)−Cu−Cl[v]	92.42(9)	Cl−Cu−Cl[v]	92.97(6)

[a] Symmetry transformations: (i) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (iv) $x + \frac{1}{2}$, $y - \frac{1}{2}$, z; (v) $-x$, $-y + 1$, $-z$.

When the ligand HL[5] is used, the reaction with Cu(ClO$_4$)$_2$ produces not a genuine carboxylate-bridged copper(II) complex but the mononuclear complex [Cu(HL[5])(H$_2$O)](ClO$_4$)·$^1/_2$H$_2$O (**5**). A perspective view of the structure, together with the atom-labeling scheme, is given in Figure 1. Selected bond distances and angles are listed in Table 2. The copper(II) ion exhibits a 4 + 2 distorted octahedral geometry. The equatorial positions are occupied by the three donor atoms of the ligand and the
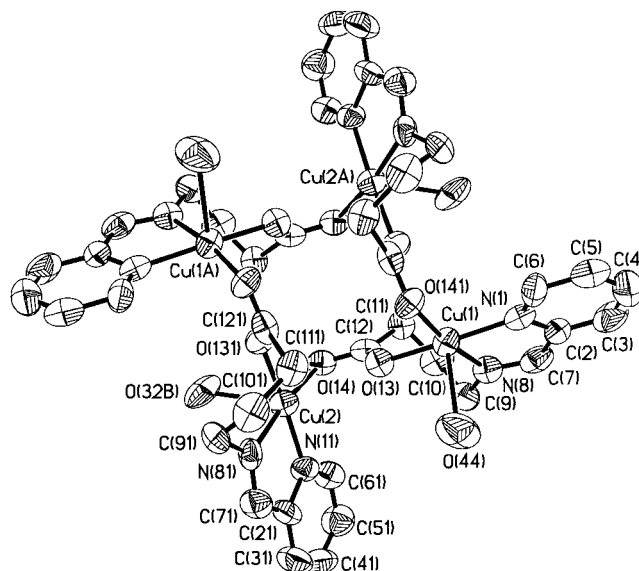

Figure 3. Molecular structure of the tetranuclear complex **4**. Perchlorates and hydrogen atoms are omitted for clarity. Ellipsoids represent 40% probability.

oxygen atom of a water molecule at distances close to 2 Å, whereas the oxygen atoms from a semicoordinated and disordered perchlorate anion and from the carboxylate group of an adjacent molecule occupy the axial positions at distances longer than 2.78 Å. As indicated above, in this case, in contrast to that observed for complexes **1**–**4**, the water molecule coordinates at an equatorial position and the Cu(II) ion has two empty axial coordination sites for the binding of the carboxylate group from a neighboring molecule. The Jahn−Teller distortion of the Cu(II) ion, however, leads to relatively large Cu−O$_{axial}$ bond distances, thus avoiding the formation of a genuine carboxylate-bridged complex. The formation of a strong hydrogen bond involving the O(16) carboxylate oxygen atom and the water molecule of a symmetry-related molecule may also help to weaken the Cu−O(16) bond.

The reaction of HL[1] with CuCl$_2$ leads not to the syn−anti carboxylate-bridged chain analogue of **1** but to the chloride-bridged dinuclear complex [Cu(HL[1])(μ-Cl)]$_2$ (**6**). In this case, the chloride ligands remain coordinated to the copper(II) ion, thus preventing a self-assembly reaction through the carboxylate group. The structure consists of dinuclear molecules with C_i symmetry, the center of symmetry being located at the center of the Cu(μ-Cl$_2$)Cu bridging unit. A perspective view of the dinuclear molecule, with the atom-labeling scheme, is given in Figure 4. Selected bond distances and angles are given in Table 2. The copper(II) ion exhibits a square-pyramidal coordination geometry ($\tau = 0.06$) for the N$_2$OCl$_2$ donor set, where the basal coordination sites are occupied by one of the bridging chlorine atoms and the three donor atoms of the tridentate ligand, whereas the apical site is occupied by the remaining bridging chlorine atom. Each chloride ligand bridges two copper(II) ions in the equatorial-axial mode, with Cu−Cl$_{ax}$ and Cu−Cl$_{eq}$ distances of 2.724(2) Å and 2.288(2) Å, respectively, leading to a parallel planar dinuclear structure. Within the planar Cu(μ-Cl)$_2$Cu bridging unit, the Cu−Cl−Cu and Cl−Cu−Cu bond angles of 87.03 and 92.97°, respectively, are close to 90°, as expected for an almost perfect square-pyramidal coordination geometry for the Cu(II) ion, and the Cu···Cu distance is 3.466 Å. Finally, the amine proton at N(3) is involved in an intermolecular N−H···O hydrogen bond to the coordinated carboxylate oxygen atom O(11).
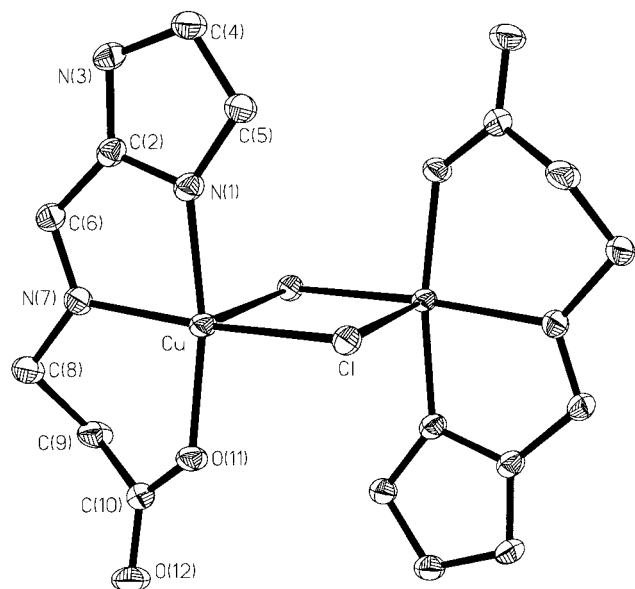
Figure 4. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Ellipsoids represent 40% probability.

EPR and Magnetic Properties. The X-band EPR spectra of polycrystalline samples of **1** and **2** at 100 K and that of **3** at 77 K appear axial with two main features attributable to $g_\parallel$ and $g_\perp$ (2.23 and 2.06 for **1**, 2.24 and 2.05 for **2**, and 2.17 and 2.06 for **3**), indicating, as expected for square-based-pyramidal coordination polyhedra, $(d_{x^2-y^2})^1$ electronic configurations for the copper(II) ions. In addition, signals of low intensity are observed between the two main features. The spectra are devoid of any hyperfine structure or half-field signal. Analogous spectra have been observed for other ferromagnetic chain complexes with syn−anti[25] and anti−anti[14] carboxylate bridges. The frozen methanol solution spectra are typical of electronically isolated Cu(II) species ($g_\parallel$, $g_\perp$, and $A_\parallel$ are 2.30, 2.07, and 170 cm^{-1} for **1**, 2.27, 2.05, and 174 cm^{-1} for **2**, and 2.29, 2.05, and 165 cm^{-1} for **3**, respectively), thus suggesting that these complexes deaggregate in solution and the copper(II) ions adopt elongated octahedral or square-planar coordination geometries.

The powder magnetic susceptibilities were measured under a 1 T applied magnetic field in the 2−300 K temperature range. The magnetic behaviors of complexes **1**−**3** are illustrated in Figure 5 in the form χT vs T. At room temperature the χT product values correspond well with that expected for isolated copper(II) ions. On lowering of the temperature to 2 K, χT gradually increases, thus indicating the existence of weak ferromagnetic exchange interactions between copper(II) ions. The results of the magnetization experiments on these complexes as a function of the applied field at 5 K are also shown in Figure 5, together with the Brillouin function for isolated Cu(II) ions. The experimental magnetization values are greater than those predicted by the Brillouin function for a system with a spin value of $^1/_2$, thus confirming the ferromagnetic nature of the interaction. The magnetic susceptibility data were quantitatively analyzed by means of the expression of Baker et al.[29] for one-dimensional infinite chains with $J > 0$, where the spin Hamiltonian is defined as $H = -J\sum S_i S_{i+1}$. A molecular field term was added to describe interchain interactions that were expected in the chains. The expression for the magnetic susceptibility becomes

(29) Baker, G. A.; Rushbrooke, G. S.; Gilbert, H. E. *Phys. Rev.* **1964**, *135*, A1272.
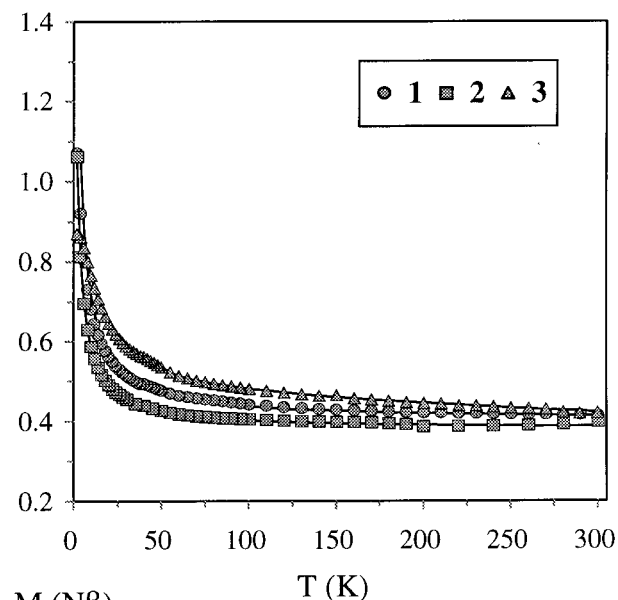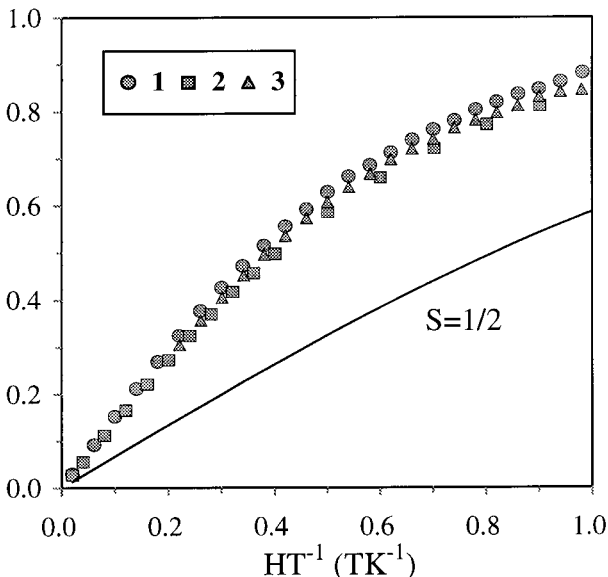

Figure 5. Plots of the experimental and calculated (solid lines) temperature dependences of $\chi_M T$ (top) and field dependences of the magnetization (the solid line corresponds to the Brillouin function for a system with $S = ^1/_2$) at 5 K (bottom) for complexes **1**−**3**.

$$\chi_M^{mf} = \frac{\chi_M}{1 - 2zJ'\chi_M/Ng^2\beta^2}$$

where χ_M is the molar susceptibility given by Baker's expression. The best fit parameters are given in Table 3, together with some structural and magnetic data for other syn−anti carboxylate-bridged copper(II) complexes, in which each bridge links two basal positions on square-pyramidal copper(II) ions. The best fits are shown in Figure 5 as solid lines.

The thermal dependence of the χT product per tetranuclear unit for **4** is given in Figure 6. At room temperature, χT corresponds well with that expected for four isolated copper-(II) ions. As can be seen, the χT product steadily increases as the temperature is lowered to reach a maximum value of 3.43 cm^3 mol^{-1}K at 2 K, which would correspond to a state characterized by $S = 2$ and $g = 2.14$ and thus to ferromagnetic

Table 3. Magnetostructural Data for the Cu−O−C−O−Cu Fragment

compd	Cu−O[a]	OCO[b]	CuOC[b] syn/anti	Cu dev[c]	$\sum$|Cu dev|[d]	Cu···Cu[a] cis/trans	J[e]	g[e] zJ'
1	1.943	121.0	120.3	↑↑	0.234	5.186	5.8	2.08
	1.962		128.0			cis		−0.3
2	1.950	123.5	124.3	↑↓	0.315	4.844	4.3	2.01
	1.965		127.5			cis		−0.1
3	1.968	122.6	127.7	↑↑	0.356	5.158	6.3	2.07
	1.970		129.8			cis		−1.1
4	1.946	119.8	<113.2	↑↓	0.205	<4.616	4.2	2.14
	1.959	119.5	>125.4	↑↑	0.072	cis	7.8	
Cu₃[f]	1.880	121.4	123.0	↑↑	0.655	4.797	2.7	
	1.941		126.5			trans		
Cu_n[g]	1.902	120.9	127.0	↑↓	0.366	4.962	3.4	
	1.995		131.8			cis		
Cu_n[h]	1.995	125.0	115.0	↑↓	0.284	4.950	2.8	
	1.983		118.3			cis		
Cu_n[i]	1.995	120.0	117.9		0	4.879	−3.0	
	2.001		123.3			cis		

[a] Angstroms. [b] Degrees. [c] Deviations of the copper ions with respect to the OCO plane: ↑↑, both metal ions are above the OCO plane; ↑↓, one copper ion is above and the other is below the OCO plane. [d] Sum of deviations in absolute value. [e] Best fit parameters; J and zJ' in cm^{-1}. [f] {Cu(H₂O)₄[Cu(HL)(H₂O)(ClO₄)]₂(ClO₄)₂}·2H₂O (L = 6-(methylamino)-1,3-dimethyl-5-[(2-carboxyphenyl)azo]uracil); from ref 16. [g] [Cu(L)(H₂O)]_n (L = 1,3-dimethyl-5-[(2-carboxyphenyl)azo]barbituric acid); from ref 25. [h] [Cu(CTH)(OAc)]_n (CTH = D,L-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane); from ref 18. [i] [Cu(NH₃)₂(OAc)(Br)]_n; from ref 31.

interactions among copper(II) ions. In keeping with the structure of **4**, the magnetic data were analyzed with the spin Hamiltonian for a rectangular system of four $S = \frac{1}{2}$ spins (see inset of Figure 6), $H = g\beta S - 2[J_1(S_1 S_2 + S_{1A} S_{2A}) + J_2(S_1 S_{2A} + S_{1A} S_2)]$. The energies of the low-lying states deduced from the above Hamiltonian by Jotham and Kettle,[30] using an energy matrix diagonalization method, and labeled according to the point group D_2 are

$$E(^5A) = -(J_1 + J_2)$$

$$E(^3B_3) = J_1 - J_2$$

$$E(^3B_2) = J_2 - J_1$$

$$E(^3B_1) = J_1 + J_2$$

$$E(^1A_a) = J_1 + J_2 - 2(J_1^2 + J_2^2)^{1/2}$$

$$E(^1A_b) = J_1 + J_2 + 2(J_1^2 + J_2^2)^{1/2}$$

Therefore there are two spin singlets, three triplets, and one quintet. In the case of ferromagnetic coupling, the quintet ^5A is the ground state. The theoretical expression for the magnetic susceptibility per mole of tetranuclear complex obtained from the above energy levels and the Van Vleck equation, taking into consideration that g values for multiplets and the local g values for the copper(II) ions are all equal, is

$$\chi_M = \frac{2Ng^2\beta^2}{kT}[5\exp(Q/kT) + R]/[5\exp(Q/kT) + 3R +$$
$$\exp((S - Q)/kT) + \exp(-(S + Q)/kT)]$$

$$Q = J_1 + J_2$$

$$R = \exp((J_1 - J_2)/kT) + \exp((J_2 - J_1)/kT) +$$
$$\exp(-(J_1 - J_2)/kT)$$

$$S = 2(J_1^2 + J_2^2 - J_1 J_2)^{1/2}$$

The best fit parameters are given in Table 3. In this case, the

(30) Jotham, R. W.; Kettle, S. F. A. *Inorg. Chim. Acta* **1970**, *4*, 145.

experimental magnetization data at 2 K (Figure 6) can be well fitted to the theoretical expression for an $S = 2$ system with $g = 2.10$. This result nicely supports the quintuplet nature of the ground-state deduced from magnetic susceptibility measurements.

The room-temperature spectrum of a powdered sample of the tetranuclear complex **4** shows an intense, almost isotropic, featureless resonance at $g = 2.12$. When the temperature is lowered from room temperature to 5 K, the overall aspect of the spectrum and the position of the resonance are not altered but the line width (measured at half-height) decreases from 138 to 83 G, respectively. This fact might be due to depopulation of the $^3B_2$ and $^3B_1$ triplets at 4.2 K. It should be noted that similar EPR spectra have been observed for other tetranuclear copper(II) complexes. The frozen methanol solution spectrum of **4** at 100 K exhibits an isotropic signal centered at $g = 2.12$, indicating that, in contrast to the structures of the chain complexes **1−3**, the tetranuclear structure of **4** seems to be retained in methanol.

For comparison purposes, the structural and magnetic data for complexes **1−4** and those for other *syn-anti* carboxylate-bridged copper(II) complexes with $d_{x^2-y^2}$ magnetic orbitals and carboxylate bridges linking two basal positions are given in Table 3. Data for analogous complexes with carboxylate groups linking equatorial−axial positions have not been considered, since the equatorial−axial coupling of coppers(II) through the bridging ligand should be negligible regardless of the structural parameters of the bridge. As can be observed in Table 3, all of the complexes, with the exception of [Cu(NH₃)₂Br(μ-CH₃-CO₂)]_n, show small exchange interactions that are ferromagnetic. This behavior can be explained in terms of the topology of the bridge between copper(II) ions. It is well-known that the magnetic coupling constant, J, can be expressed as a sum of both ferromagnetic (J_F) and an antiferromagnetic contributions (J_{AF}). Whereas ferromagnetic contributions are usually small, the magnitudes of the antiferromagnetic ones are each proportional to the square of the overlap integral between magnetic orbitals. Thus, the resulting sign of a magnetic interaction depends, to a great extent, on the amplitude of that overlap. As pointed out by us and other authors,[28,31] for syn−anti Cu−O−C−O′-Cu′ complexes, the contributions from the 2p orbitals of the O and O′ atoms belonging to the magnetic orbitals centered
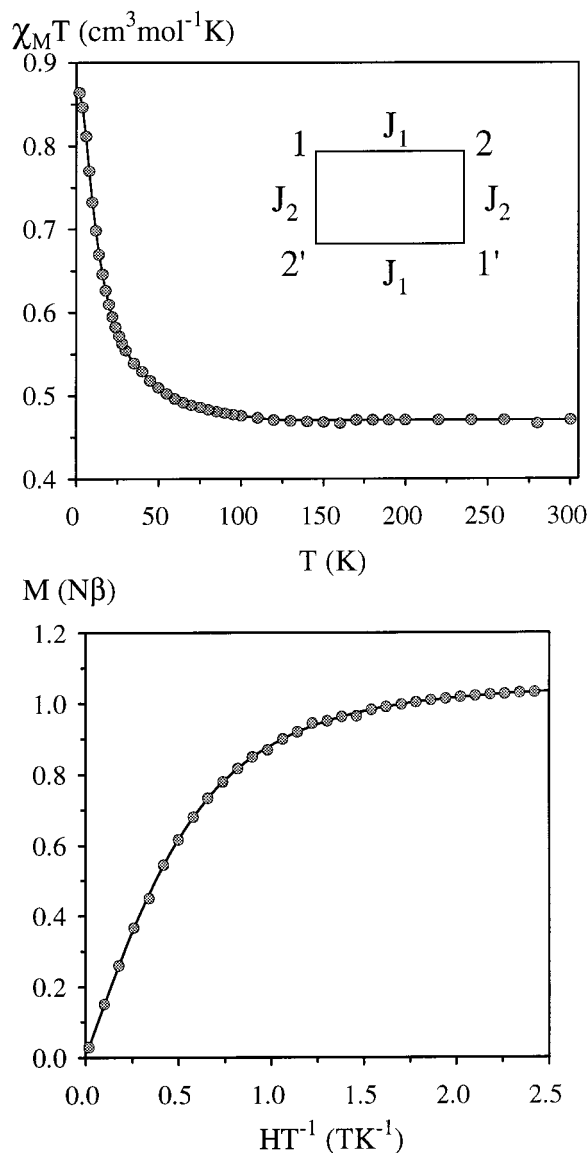
Figure 6. Temperature dependence of $\chi_M T$ (top) and field dependence of the magnetization at 2 K (bottom) for complex **4**. Solid lines represents the theoretical fits.

on Cu and Cu′ are unfavorably oriented to give a significant overlap (Chart 1); therefore, $J_{AF} \approx 0$ and a weak ferromagnetic interaction is observed. The nonplanarity of the Cu−O−C−O−Cu bridging network is also expected to decrease the overlap of the magnetic orbitals in the bridging region, thus favoring ferromagnetic exchange couplings. In fact, complexes with copper(II) ions that deviate from the carboxylate plane are all ferromagnetic. The sign reversal for [Cu(NH₃)₂Br(μ-CH₃-CO₂)]ₙ[31] might be the result of both the planarity of the Cu−O−C−O−Cu skeleton and the existence of relatively strong interchain hydrogen-bond contacts. Thus, the former would reduce the intrachain ferromagnetic interaction to such an extent that the intermolecular antiferromagnetic interaction mediated by the latter would be predominant. The low J value for the trinuclear compound {Cu(H₂O)₄[Cu(HL⁶)(H₂O)(ClO₄)]₂(Cl-O₄)₂}·2H₂O, with a very nonplanar bridging skeleton, may be due to the existence of strong hydrogen bonds that can efficiently transmit the antiferromagnetic interaction between copper(II)

ions, thus reducing the ferromagnetic interaction. On the other hand, structural factors such as Cu−O bond lengths and Cu···Cu distances seem not to be essential in determining the sign of the exchange coupling.

Finally, the temperature dependence of the magnetic susceptibility for **6** was measured in the range 300−4.2 K. From 300 to 50 K, $\chi_M T$ per dinuclear unit remains practically constant and equal to 0.84 cm³ mol⁻¹ K, which is the value expected for two isolated copper(II) ions. From 50 K, $\chi_M T$ continuously decreases with cooling and reaches a value of 0.32 cm³ mol⁻¹ K at 4.2 K, indicating the existence of a weak antiferromagnetic interaction between copper(II) ions through the chloride bridging groups. According to the dinuclear structure of **6**, magnetic susceptibility data were fitted to the Bleaney−Bowers equation for exchange-coupled dinuclear copper(II) complexes. A good agreement was obtained, with $J = -1.7$ cm⁻¹ ($H = -2JS_1S_2$; $S_1 = S_2 = \frac{1}{2}$) and $g = 2.01$. For bis(μ-chloro)-bridged copper(II) dimers with parallel planar structures, as is the case for **6**, Hatfield[32] has shown that a correlation between the structural parameter relation ϕ/R (ϕ is the Cu−Cl−Cu angle and R is the Cu−Cl axial distance) and the coupling constant J exists. The trend of J with ϕ/R predicts antiferromagnetic interactions for ϕ/R values higher than 33.5° Å⁻¹, which increase as does ϕ/R. In view of this, for **6**, with a ϕ/R value of 34.1° Å⁻¹, a weak antiferromagnetic interaction would be expected, in good accordance with the experimental results.

The polycrystalline EPR spectrum of **6** at 100 K is axial with $g_\parallel = 2.24$ and $g_\perp = 2.06$, as expected for copper(II) ions with square-pyramidal geometries and $(d_{x^2-y^2})^1$ electronic configurations. Neither a half-field signal nor a hyperfine structure is observed in this spectrum. The frozen methanol solution spectrum at 100 K shows, besides signals attributable to electronically isolated Cu(II) species ($g_\parallel = 2.25$, $A_\parallel = 166$ cm⁻¹), more than 14 resonances in the 3150−3650 G range, which may correspond to $\Delta M = 1$ transitions of the triplet spectrum. Indeed, the low g value of 1.86 for one of the resonances suggests significant zero-field-splitting effects. In view of these facts, it seems reasonable to assume that the dinuclear structure of **6** is at least partially retained in methanol solution.

Concluding Remarks

The use of tridentate Schiff-base carboxylate-containing ligands from the condensation of amino acids and 2-imidazole-or 2-pyridinecarboxaldehyde has been shown to be a good tool to build singly syn−anti carboxylate-bridged copper(II) complexes, in which carboxylate groups link two basal positions. The length of the amino acid chain seems to have a direct influence on the structure. Thus, when the amino acid chain contains two carbon atoms (between the amino and acid groups), helical-chain complexes are obtained, while with three carbon atoms, the chain has sufficient flexibility to form a cyclic tetranuclear structure. All of these complexes exhibit weak ferromagnetic exchange interactions. From the experimental data for these and other similar compounds, one can conclude that the basal−basal (or equatorial−equatorial) syn−anti carboxylate bridging mode in copper(II) complexes always must lead to intramolecular ferromagnetic interactions. Moreover, when the syn−anti bridging network is nonplanar, the overall magnetic interaction is ferromagnetic regardless of whether intermolecular hydrogen bonds are present or not. When the Cu−O−C−O−

(31) Carlin, R. L.; Kopinga, K.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1986**, *25*, 1786.

(32) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series, Vol. 140; D. Reidel: Dordrecht, The Netherlands, 1985; p 555.

Cu skeleton is planar, however, the ferromagnetic interaction should decrease and, depending on the magnitude of the intermolecular magnetic interactions, an overall antiferromagnetic coupling might be observed. Further work, experimental and theoretical, is needed to support our conclusion. When copper(II) chloride is used instead of copper(II) perchlorate, the reaction with the tridentate ligand leads not to the syn−anti carboxylate-bridged complex but to a parallel planar chloride-bridged dinuclear complex.

Supporting Information Available: X-ray crystallographic files, in CIF format, for **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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