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Article

A Quasi-Tetrahedral Cu_4 Cluster and a Helical-Chain Copper(II) Complex with Single Syn–Anti Carboxylate Bridges: Crystal Structure and Magnetic Properties

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A tridentate Schiff base carboxylate ligand, derived from the condensation of pyridine 2-carboxaldehyde with anthranilic acid, reacts with copper trifluoroacetate salt to give rise to the helical chain complex $[Cu(C_{13}H_9N_2O_2)(F_3CCO_2)]_n$ (**1**) and with copper nitrate to give rise to the tetranuclear complex $[\{Cu_4(C_{13}H_9N_2O_2)_4(H_2O)_4\}\cdot 3.5NO_3\cdot 0.5N_3]$ (**2**) with the addition of azide salt. The structures of these complexes have been solved by X-ray crystallography. The Cu(II) ions are in a distorted square-pyramidal environment in complex **1**. They are sequentially bridged by carboxylate groups in the syn–anti conformation, resulting in the formation of an infinite helix like chain along the crystallographic *c*-axis. The crystal structure of complex **2** consists of tetranuclear $[Cu_4(L)_4(H_2O)_4]^{4+}$ ($L = C_{13}H_9N_2O_2^-$) cations and isolated NO_3^- and N_3^- anions in the ratio 1:3.5:0.5, respectively, involving bridging carboxylate groups in the syn–anti conformation. For **1** the carboxylato–Cu(II) coordination is apical–basal, while for **2** it is basal–basal. From the magnetic susceptibility measurements the complex **1** is found to exhibit very weak antiferromagnetic interaction whereas a weak ferromagnetic coupling has been established for complex **2**. The magnetic behavior can be satisfactorily explained on the basis of the structural data for these and related complexes.

Introduction

A recent feature in the development and progress of chemical research has been the concern with molecular assemblies, ensembles, and all manner of structured aggregates.[1] 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.[2−7] Recent attention has focused particularly on the construction of various supramolecular structures such as molecular squares,[8,9] cylindrical molecular boxes,[10] molecular cages,[11] and helical structures[12] as well as the supramolecules exhibiting switching ability,[13] whose structure

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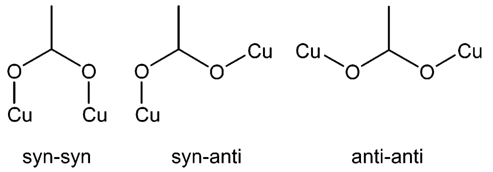
Chart 1



and/or physicochemical properties change by input of external information. Polynuclear copper(II) clusters are of present interest in bioinorganic modeling, multielectron transfer, catalysis, and magnetostructural research. Among the multiatom bridging ligands, carboxylate has been extensively studied.

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.[14−16] In these complexes, a carboxylate group can assume many types of bridging conformations, the most important being triatomic syn−syn, anti−anti, and syn−anti and monatomic.[17] The magnetic properties are closely related to the bridging (Chart 1) conformation adopted by the carboxylate group in these polynuclear systems. Thus, for copper(II) complexes, the former conformation mediates large antiferromagnetic interactions,[14,18] the second mediates medium or weak antiferromagnetic or ferromagnetic interactions,[17e,19] and the latter exhibits weak antiferromagnetic exchange interactions.[20] As expected on the basis of their respective geometries, the syn−syn configuration favors the formation of dinuclear complexes[21] while the anti−anti and syn−anti configurations generally correspond to chain or layer compounds.[22−25] Working with the tridentate Schiff base H_2L and two different counteranions (see Experimental Section), we succeeded in obtaining two new polynuclear complexes with bridging COO^- groups in the syn−anti configuration but with complete different dimensionality: one of them, **1**, is a one-dimensional helical chain with the carboxylato giving basal−apical coordination, and the second, **2**, is a new tetranuclear complex, in which the carboxylato shows basal−basal coordination. The tetrameric complex contains a $(-Cu-O-C-O)_4$ ring folded in such a manner that the four copper ions fall at the corners of a pseudotetrahedron. It should be noted that complex **2** represents one of the very few examples of singly carboxylate-bridged tetranuclear complexes reported so far.[26,27] This paper is devoted to the structural and magnetochemical studies of these two complexes.

Experimental Section

Physical Measurements. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 883-IR spectrophotometer using KBr pellets. Magnetic susceptibility measurements in the range 2−300 K have been carried out using an MPMS SQUID magnetometer.

Materials. Pyridine-2-carboxyldehyde, anthranillic acid (Aldrich), copper carbonate, copper nitrate, trifluoroacetic acid, and sodium azide (Merck) were used as received. Copper trifluoroacetate was prepared by standard method.[28]

Preparation of the Complexes. The ligand LH_2 was prepared by coupling anthranillic acid with pyridine 2-carboxaldehyde in methanol by the procedure reported elsewhere.[29]

The complex $[Cu(C_{13}H_9N_2O_2)(F_3CCO_2)]_n$ (**1**) was prepared by slowly adding 10 mL of methanolic solution of LH_2 (1 mmol) to a 15 mL methanolic solution of copper trifluoroacetate (0.225 g, 1 mmol) at room temperature with constant stirring, and it was kept at room temperature. Deep green rectangular shaped crystals appeared after 36 h, from which suitable crystals for X-ray analysis were separated. Yield: 95%. Anal. Calcd for $C_{15}H_9CuF_3N_2O_4$: C, 44.78; H, 2.24; N, 6.97; Cu, 15.81. Found: C, 44.81; H, 2.26; N, 6.95; Cu, 15.80. IR (KBr; cm^{-1}): ν(N−H), 3170−3345; ν_s(COO), 1667; ν_{as}(COO), 1395.

$[\{Cu_4(C_{13}H_9N_2O_2)_4(H_2O)_4\}\cdot 3.5NO_3\cdot 0.5N_3]$ (2). This complex was prepared by addition of the Schiff base (1 mmol) to a methanolic solution of copper nitrate (0.18 g, 1 mmol). The resulting mixture was stirred for 15 min, and sodium azide (0.5 mmol) in 2 mL of water was added to it with the solution kept at room temperature. Shiny green rectangular crystals appeared after 24 h, from which suitable crystals for X-ray analysis were separated. Yield: 90%. Anal. Calcd for $C_{52}H_{44}Cu_4N_{13}O_{22.50}$: C, 42.58; H, 3.00; N, 12.49; Cu, 17.33. Found: C, 42.59; H, 3.02; N, 12.50; Cu, 17.31. IR (KBr; cm^{-1}): ν(N−H) and ν(O−H), 3140−3405; ν_s(COO), 1688; ν_{as}(COO), 1401.

X-ray Data Collection and Structure Refinement. X-ray intensity data for the compounds **1** and **2** were collected on a Bruker-Nonius CAD 4 diffractometer and a CCD area detector, respectively, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The lattice constants were determined by least-squares refinements of the setting angles for 25 reflections ($17 \geq \theta \geq 16°$) for **1** and for all the observed reflections in the entire data set for **2**. The data for **1** were corrected for absorption effects

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Table 1. Crystal Data and Structure Refinement for $[Cu(C_{13}H_9N_2O_2)(F_3CCO_2)]_n$ (**1**) and $[\{Cu_4(Cl_3H_9N_2O_2)_4(H_2O)_4\}\cdot 3.5NO_3\cdot 0.5N_3]$ (**2**)

	1	**2**
empirical formula	$C_{15}H_9CuF_3N_2O_4$	$C_{52}H_{44}Cu_4N_{13}O_{22.50}$
fw	401.78	1465.16
temp, K	150(2)	150(2)
radiation, graphite monochromated	Mo Kα	Mo Kα
wavelength, Å	0.710 73	0.710 73
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a, Å	10.419(2)	21.2320(2)
b, Å	16.289(5)	21.1793(2)
c, Å	8.937(4)	27.1400(4)
α, deg	90	90
β, deg	107.83(3)	107.8660(4)
γ, deg	90	90
Z	4	8
cryst size, mm^3	0.35 × 0.30 × 0.30	0.10 × 0.10 × 0.08
V, $Å^3$	1443.9(9)	11 615.8(2)
ρ(calcd), Mg/m^3	1.848	1.676
θ range for data collcn, deg	2.92−25.38	2.92−27.50
reflcns collcd	2839	22 946
indpdt reflcns	2628 [R(int) = 0.0307]	13 102 [R(int) = 0.0233]
goodness-of-fit on F^2	1.029	1.023
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0431, wR2 = 0.1073	R1 = 0.0583, wR2 = 0.1643
R indices (all data)	R1 = 0.0608, wR2 = 0.1135	R1 = 0.0719, wR2 = 0.1748
largest diff peak and hole	0.615 and −0.617 e $Å^{-3}$	2.918 and −1.352 e $Å^{-3}$

using the ψ-scan method incorporated in WINGX,[30] and those for **2**, by using multiple and symmetry-related data measurements via SORTAV.[31] The structures were solved by direct methods (SHELXS-97)[32] and refined on F^2 by full-matrix least-squares using all unique data (SHELXL-97).[33] For **1**, all non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions (riding model). For **2**, both the hydrogen atoms on the coordinated water molecules O(10) and O(12) were experimentally located but not refined. The hydrogen atoms of the other two coordinated water molecules in this structure could not be located from the difference map and were ignored, while those on the rings were included in calculated positions. The nitrate and azide anions in this structure were somewhat disordered, and refinement was carried out with the constraints N−O distances = 1.250(5) Å and ISOR = 0.005 $Å^2$ for all the atoms in these groups. The structures were finally refined to the conventional *R*-values of 0.0431 and 0.0583 for **1** and **2**, respectively. The crystal data, conditions for the intensity data collection, and important features of the structural refinements for both compounds are listed in Table 1. Selected bond lengths and angles for the two complexes are presented in Tables 2 and 3, respectively, and the dimensions of some hydrogen bonds are in the Supporting Information.

Results and Discussion

The reactions of the tridentate carboxylate containing ligands with copper trifluoro acetate and copper nitrate molecules 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 reactions for the synthesis of **1** and **2** are carried out by using Cu(II) trifluoroacetate and copper nitrate molecules, the differences between the $\nu_{as}(COO)$ and $\nu_{sym}(COO)$ stretching frequencies are near 287 and 272 cm^{-1}, respectively, reflecting the coordination modes of the carboxylate ligands.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu(C_{13}H_9N_2O_2)(F_3CCO_2)]_n$ (**1**)[a]

Cu(1)−O(1)	1.911(3)	Cu(1)−O(3)	1.940(3)
Cu(1)−N(2)	2.002(3)	Cu(1)−N(1)	2.010(3)
Cu(1)−O(2)	2.144(3)	O(1)−C(13)	1.271(4)
O(2)−C(13)	1.248(4)	O(2)−Cu(1)	2.144(3)
O(3)−C(14)	1.268(5)	O(4)−C(14)	1.210(4)
O(1)−Cu(1)−N(2)	91.47(11)	O(3)−Cu(1)−N(2)	164.38(12)
O(1)−Cu(1)−N(1)	160.26(12)	O(3)−Cu(1)−N(1)	89.21(12)
N(2)−Cu(1)−N(1)	81.45(12)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) *x*, −*y* + 1/2, *z* − 1/2; (#2) *x*, −*y* + 1/2, *z* + 1/2.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[\{Cu_4(Cl_3H_9N_2O_2)_4(H_2O)_4\}\cdot 3.5NO_3\cdot 0.5N_3]$ (**2**)[a]

Cu(1)−O(4)	1.936(3)	Cu(1)−O(1)	1.957(3)
Cu(1)−N(2)	1.976(4)	Cu(1)−N(1)	2.017(4)
Cu(1)−O(9)	2.174(4)	Cu(2)−O(8)	1.935(3)
Cu(2)−O(3)	1.953(3)	Cu(2)−N(4)	1.973(4)
Cu(2)−N(3)	2.007(4)	Cu(2)−O(10)	2.170(4)
Cu(3)−O(2)	1.931(3)	Cu(3)−O(5)	1.960(3)
Cu(3)−N(6)	1.974(3)	Cu(3)−N(5)	2.022(4)
Cu(3)−O(11)	2.169(3)	Cu(4)−O(6)	1.930(3)
Cu(4)−O(7)	1.956(3)	Cu(4)−N(8)	1.976(3)
Cu(4)−N(7)	2.011(4)	Cu(4)−O(12)	2.158(4)
O(1)−C(13)	1.257(5)	O(2)−C(13)	1.269(5)
O(3)−C(26)	1.254(5)	O(4)−C(26)	1.266(5)
O(5)−C(39)	1.252(5)	O(6)−C(39)	1.263(5)
O(7)−C(52)	1.254(5)	O(8)−C(52)	1.273(5)
N(2)−Cu(1)−O(4)	176.33(14)	N(4)−Cu(2)−O(8)	175.42(15)
N(6)−Cu(3)−O(2)	176.46(14)	N(8)−Cu(4)−O(6)	175.83914)
N(1)−Cu(1)−O(1)	142.81(15)	N(3)−Cu(2)−O(3)	144.00(15)
N(5)−Cu(3)−O(5)	143.34(15)	N(7)−Cu(4)−O(7)	144.85(15)
N(1)−Cu(1)−N(2)	81.64(16)	N(3)−Cu(2)−N(4)	81.89(15)
N(5)−Cu(3)−N(6)	81.82(16)	N(7)−Cu(4)−N(8)	82.02(15)
O(1)−Cu(1)−N(2)	89.12(14)	O(3)−Cu(2)−N(4)	88.94(14)
O(5)−Cu(3)−N(6)	89.22(14)	O(7)−Cu(4)−N(8)	89.19(14)

[a] Symmetry transformations used to generate equivalent atoms: (#1) −*x* + 1, *y*, −*z* + 1/2; (#2) −*x* + 1, −*y*, −*z*; (#3) −*x* + 1, −*y* + 1, −*z* + 1.

Crystal Structures of Complexes 1 and 2. Both the structures of **1** and **2** are based on the tridentate Schiff base ligand $C_{13}H_9N_2O_2^-$, but they represent two structural varieties as discussed below.

The crystal structure of $[Cu(L)(F_3CCO_2)]_n$ ($L = C_{13}H_9N_2O_2^-$) (**1**) is polymeric, and it results from the fact that the copper(II) ions are bridged sequentially by syn−anti carboxylate groups. A view of the molecular fragment showing the immediate environments of the copper atom together with the atom numbering scheme and formation of a bridge between two copper centers is illustrated in Figure 1. The carboxylate group belonging to the Schiff base ligand is bidentate/bridging involving both the oxygen atoms, while that in the trifluroacetate group is monodentate with only one of the oxygen atoms being bonded to one copper center. The polymeric chain is helical and propagates along the *c*-axis, as shown in Figure 2.

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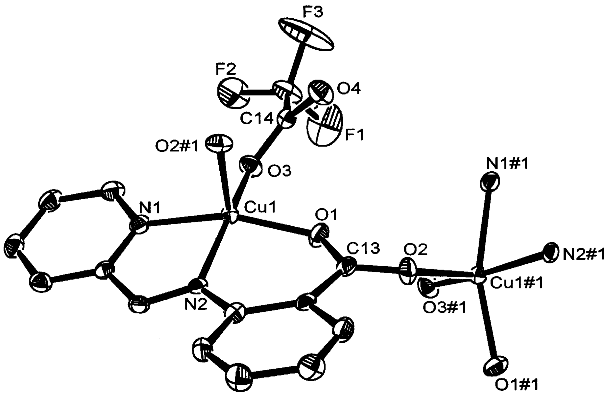

Figure 1. General view of the molecular fragment of the structure **1** showing the immediate environments of the copper atom together with the atom-labeling scheme.

The coordination geometry around the copper atom may be described as a distorted square pyramidal, the basal plane being defined by O(3), O(1), N(2), and N(1) and the apical position being occupied by O(2)#1 from another carboxylate oxygen atom of a Schiff base. The N(1), N(2), O(1), and O(3) atoms show deviations of 0.046(2), −0.045(2), 0.042(2), and −0.043(2) Å, respectively, from the mean plane of these atoms, indicating a tetrahedral distortion from planarity. As expected, the Cu(1) atom is displaced from this plane by 0.282(2) Å toward the apical O(2)#1 atom. The Schiff base ligand is tridentate with respect to one copper center, but it is in fact tetradentate when the bridging bond is considered. It forms one five- and one six-membered chelate ring with the metal, producing considerable distortions in the chelate rings. Thus, the N(1)−Cu(1)−N(2) and O(1)−Cu(1)−N(2) chelate angles are 81.45(12) and 91.47(11)°, respectively. The five-membered chelate ring is slightly nonplanar [maximum atomic displacement ±0.016(2) Å], while the six-membered chelate ring is significantly nonplanar [atomic displacement ±0.165(2) Å]. The two fused ring systems are also folded along the common Cu(1)−N(2) axis by 14.6(2)°.

Within the coordination sphere, four short bonds are formed in the basal plane with two nitrogen atoms [Cu(1)−N(2) = 2.002(3), Cu(1)−N(1) = 2.010(3) Å] and one oxygen atom [Cu(1)−O(1) = 1.911(3) Å] from the Schiff base ligand and one oxygen atom [Cu−O(3) = 1.940(3) Å] from the F_3CCO_2 ion, while the other oxygen atom forming the bridge between two copper atoms is placed at the axial position and coordinated at a longer distance [Cu(1)−O(2)#1 = 2.144(3) Å].

The two C−O distances in each carboxylate group are different [C(13)−O(1) = 1.271(4), C(13)−O(2) = 1.248(4) Å; C(14)−O(3) = 1.268(5), C(14)−O(4) = 1.210(4) Å], and these differences may be correlated with their involvement in bonding with copper. The shortest C(14)−O(4) bond does not interact with the metal. Other bond lengths and angles associated with the Schiff base and trifluoroacetate ligands are as expected.

As noted earlier, each carboxylate group in the Schiff base ligand is in the syn−anti conformation and bridges two copper atoms via its two oxygen atoms. The bridging Cu−O−C−O−Cu pathway observed here gives rise to a very interesting helical chain polymer running along the crystallographic *c*-axis as shown in Figure 2. The Cu···Cu separation in the polymer is 5.283(1) Å. A similar helical chain has been recently reported by Colacio et al. with another tridentate Schiff base carboxylate-containing ligand.[26]

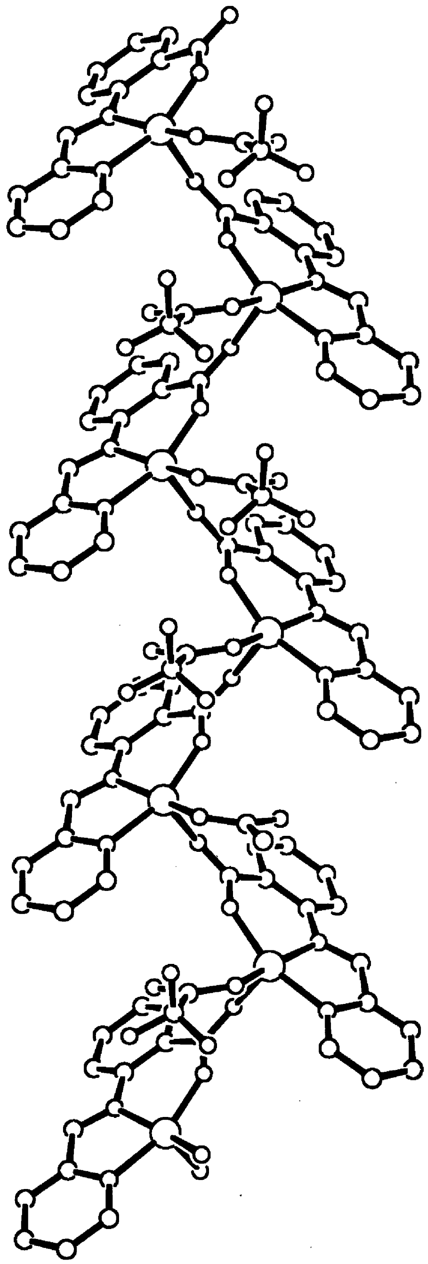

Figure 2. Perspective view of the structure of **1** showing the formation of the helical polymeric chain propagated along the crystallographic *c*-axis.

The crystal structure of complex **2** consists of tetranuclear $[Cu_4(L)_4(H_2O)_4]^{4+}$ ($L = C_{13}H_9N_2O_2^-$) cations and isolated NO_3^- and N_3^- anions in the ratio 1:3.5:0.5, respectively. The cationic complex is formed from four $\{Cu(L)(H_2O)\}^+$ units bridged by the carboxylate groups of the four Schiff base ligands. A general view of the complex together with the formation of the carboxylate bridges and the immediate environments of the copper atoms is illustrated in Figure 3 with atom-labeling scheme. 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

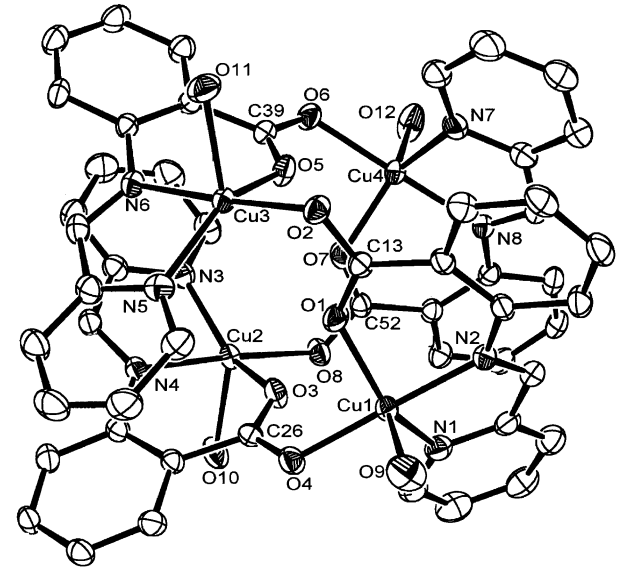

Figure 3. Perspective view of the formation of the carboxylate bridges and the immediate environment of the copper atoms of complex **2** with atom-labeling scheme.

flattened tetrahedron. The Cu···Cu separations are ∼5.17 Å along the two flattened [Cu(1)···Cu(4), Cu(2)···Cu(3)] edges and ∼4.73 Å along the other four edges. Each copper is five coordinate and bonded to two nitrogen and one carboxylate oxygen atoms of a Schiff base ligand, one water molecule, and an oxygen atom of the carboxylate group from another Schiff base ligand. All the donor atoms of the Schiff base ligands are thus utilized in the chelating and bridging modes of bonding with the copper atoms. The structure is very similar to the unique one recently reported by Colacio et al.[26]

The coordination geometry around each copper may be conveniently described as highly distorted square pyramidal. For Cu(1), the base of the pyramid is defined by the three atoms N(1), N(2), and O(1) from the same Schiff base and O(4) from another Schiff base ligands, and the apical position is occupied by the water molecule O(9). Similarly, for each of the other copper atoms, the corresponding four atoms from two Schiff base ligands occupy the basal and one water molecule occupies the apical positions. All the copper atoms in this structure have equivalent coordination environments with similar geometric distortions. In the basal plane, the N(2)−Cu(1)−O(4), N(4)−Cu(2)−O(8), N(6)−Cu(3)−O(2), and N(8)−Cu(4)−O(6) angles [176.33(14), 175.42(15), 176.46(14), and 175.83(14)°, respectively] are close to 180°, whereas the N(1)−Cu(1)−O(1), N(3)−Cu(2)−O(3), N(5)−Cu(3)−O(5), and N(7)−Cu(4)−O(7) angles [142.81(15), 144.00(15), 143.34(15), and 144.85(15)°, respectively] show significant deviations from linearity. These deviations are mainly due to the geometric restrictions associated with the formation of five- and six-membered chelate rings by each Schiff base with a metal atom, as well as its involvement in the bridge formation with another metal. The bite angles in the five-membered chelate rings are N(1)−Cu(1)−N(2) = 81.64(16), N(3)−Cu(2)−N(4) = 81.89(15), N(5)−Cu(3)−N(6) = 81.82(16), N(7)−Cu(4)−N(8) = 82.02(15)°, and those in the six-membered chelate rings are O(1)−Cu(1)−N(2) = 89.12(14), O(3)−Cu(2)−N(4) = 88.94(14), O(5)−Cu(3)−N(6) = 89.22(14), and O(7)−Cu(4)−N(8) = 89.19(14)°. These values are close to the corresponding values in **1**. All the chelate rings are significantly nonplanar, and the Schiff base ligands undergo considerable strain due to the formation of the tetranuclear species.

The Cu−N/O bond lengths around each copper in **2** follow a pattern similar to that observed in **1**. Thus, the axial bond for each copper [Cu(1)−O(9) = 2.174(4), Cu(2)−O(10) = 2.170(4), Cu(3)−O(11) = 2.169(3), Cu(4)−O(12) = 2.158(4) Å] is always longer than the corresponding four basal bonds [Cu(1)−N(1)/N(2)/O(1)/O(4) = 2.017(4)/1.976(4)/1.957(3)/1.936(3), Cu(2)−N(3)/N(4)/O(3)/O(8) = 2.007(4)/1.973(4)/1.953(3)/1.935(3), Cu(3)−N(5)/N(6)/O(5)/O(2) = 2.022(4)/1.974(3)/1.960(3)/1.931(3), Cu(4)−N(7)/N(8)/O(7)/O(6) = 2.011(4)/1.976(3)/1.956(3)/1.930(3) Å]. It is observed that the two Cu−N bonds for each Schiff base ligand are slightly different and the longer bond is always associated with the terminal amino nitrogen atom. Similarly, the two Cu−O(carboxylate) bonds in the basal plane follow a definite trend. Thus, the Cu−O bond associated with the six-membered chelated for each Schiff base ligand is slightly but systematically longer than the Cu−O(COCu) bridge bond. This difference in the Cu−O bond lengths for each carboxylate group is also reflected in the two C−O distances [C(13)−O(1)/O(2) = 1.257(5)/1.269(5), C(26)−O(3)/O(4) = 1.254(5)/1.266(5), C(39)−O(5)/O(6) = 1.252(5)/1.263(5), C(52)−O(7)/O(8) = 1.254(5)/1.273(5) Å]. These variations in the C−O distances are small and statistically insignificant, but the effects are probably real. Certainly they follow a trend and appear to be correlated with the corresponding Cu−O bond distances. As mentioned earlier, similar effects are also observed for **1**.

It should be pointed out that, in **2**, each copper atom, in addition to the five bonding interactions discussed above, has a long Cu−O interaction at Cu(1)···O(3) = 2.826(4), Cu(2)···O(7) = 2.862(4), Cu(3)···O(1) = 2.845(4), and Cu(4)···O(5) = 2.876(4) Å. These distances are nonbonding, but the oxygen atoms are sterically placed to block the “sixth” coordination site in an “octahedral” arrangement of ligands around the metal atoms.

The presence of water molecules in the structure of **2** enables it to form several hydrogen bonds with the nitrate and azide groups. Location of the hydrogen atoms on the water molecules O(10) and O(12) has established the following hydrogen bonds: O(12)−H(12B)···N(16); O(12)−H(12A)···O(13); O(10)−H(10A)···O(18); O(10)−H(10B)···O(20).

Magnetic Properties and Correlations of Complexes 1 and 2. The global feature of the $\chi_M T$ vs T curve in **1** is characteristic of a very weak antiferromagnetic interaction. The value of $\chi_M T$ at 300 K is 0.421 $cm^3\ mol^{-1}$ K, which is as expected for one uncoupled copper(II) ion (0.40 $cm^3\ mol^{-1}$ K/one Cu^{II} with $g = 2.08$). The $\chi_M T$ values are constant in all the range of temperature, decreasing to the value of 0.408 $cm^3\ mol^{-1}$ at very low temperature. The χ_M curve starts at 1.4×10^{-3} $cm^3\ mol^{-1}$ at room temperature and increases in an uniform way to 0.204 $cm^3\ mol^{-1}$ at 2 K. The shape of

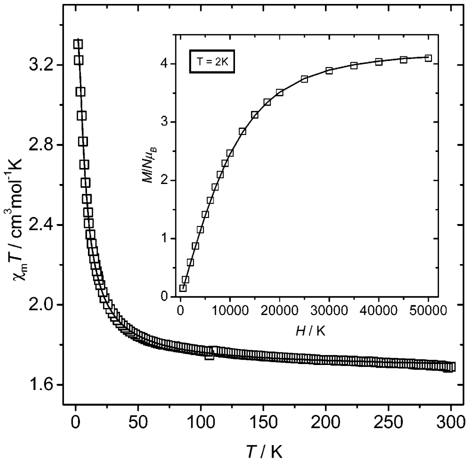

Figure 4. Magnetic behavior of the complex **2** in the form of $\chi_M T$ vs T plot and the field dependence of the reduced magnetization ($M/N\mu_B$) (per Cu_4 entity) vs H plot at 2 K (inset). The solid lines correspond to the best fit (see text).

this curve is a typical one for the Curie law. The field dependence of the reduced magnetization ($M/N\beta$) (0−5 T) vs H measured at 2 K tends to 1.0 electrons which is close to the expected $S = {}^1/_2$ for one Cu^{II} ion. As shown in the crystallographic part, the complex **1** structure consists of copper entities linked between them by the carboxylate group of the ligand giving a 1D system. Thus, only one coupling parameter (J) must be considered to interpret a possible magnetic interaction in the complex.

Taking into account this consideration, the experimental magnetic data have been fitted using the equation which is derive from the Bonner−Fisher calculation[34] on the basis of the isotropic Heisenberg Hamiltonian:

$$H = -J\sum(S_i S_{i+1})$$

The best fit parameters from 300 down to 2 K are found as $J = -0.11$ cm^{-1} and $g = 2.08$ with an error $R = 2.5 \times 10^{-5}$, where $R = \sum[(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{exp}]^2$. The low value of the superexchange parameter can be related to the nature of the bridging among the neighbor copper(II) atoms. In this case the coordination between the copper atoms is through the carboxylato group of the ligand in syn−anti conformation, with basal−apical coordination. As pointed out for other similar situations, the magnetic pathway in apical−basal coordination gives typically very weak ferro- or antiferromagnetic behavior.[35] As it has been recently pointed out by Colacio et al.,[26] when carboxylato groups link copper(II) in equatorial−axial positions, the coupling through the bridging ligand should be negligible regardless of the structural parameter of the bridge.

The magnetic behavior of the complex **2** in the form of a $\chi_M T$ vs T plot is shown in Figure 4. The global feature is characteristic of weak ferromagnetic interaction. The value of $\chi_M T$ at 300 K is 1.69 cm^3 mol^{-1} K, which is as expected for four magnetically quasi-isolated spin doublets (1.65 cm^3 mol^{-1} K/4 Cu^{II} with $g = 2.1$). The $\chi_M T$ values smoothly increase from room temperature to ca. 50 K (1.83 cm^3 mol^{-1} K) and then quickly increases at lower temperature reaching a maximum value of 3.30 cm^3 mol^{-1} K (5.14 μ_B) at 2 K. This is consistent with that expected for a spin-aligned ground state in which all spins are parallel arising from the intramolecular interactions between the four Cu(II). The field dependence of magnetization (0−5 T) measured at 2 K is shown in Figure 4 (inset) in the form of $M/N\mu_B$ (per Cu_4 entity) vs H. The magnetization tends to 4.09 e, which is close to the expected $S = 2$ for the four Cu^{II} ions system. This feature agrees to the global weak ferromagnetic coupling within the four copper(II) ions.

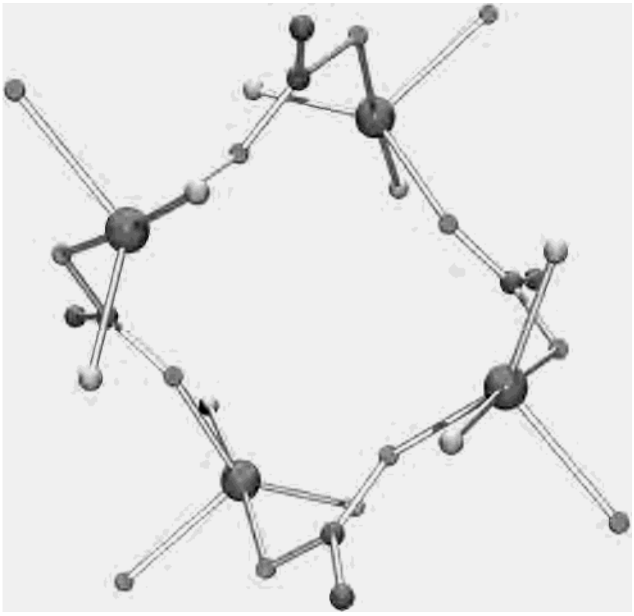

Figure 5. Interpretation of the magnetic interaction of a cyclic system in complex **2** considering only one kind of coupling parameter.

As shown in the crystallographic part, complex **2** is made by Cu_4 entities linked between them by the carboxylato part of the ligand 2-(2-pyridylmethylidene)aminobenzoic acid, giving a cyclic system (Figure 5). Thus, four of one kind of coupling parameter J must be considered to interpret the magnetic properties of complex **2**. Another possible transmission of the coupling among two neighbor copper ions through the same ligand is discarded, because it can be considered nil (such as Cu3−O2−C13−C12−C7−N2−Cu1).

On the basis of this consideration, the experimental magnetic data have been fitted using the isotropic Heisenberg Hamiltonian:[36]

$$H = -J(S_1 S_2 + S_2 S_3 + S_3 S_4 + S_4 S_1)$$

Here the numbering of the spins follows the numbering of the copper atoms in Figure 5. In this Hamiltonian all J values between Cu(II) atoms are considered to be equal. The best fit parameters from 300 down to 2 K are found as $J = +6.88$

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cm^{-1} and $g = 2.12$ with $R = 3.3 \times 10^{-5}$, where $R = \sum[(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2/\sum[(\chi_M T)_{exp}]^2$. The TIP was assumed to be 240×10^{-6} cm^3 mol^{-1}.

The value of the superexchange parameter $J = +6.88$ cm^{-1} for complex **2** can be considered as normal, taking into account the structural and magnetic data found in the literature. As indicated above, weak ferro- or antiferromagnetic interactions are observed in these carboxylato-bridged copper(II) complexes when the carboxylato adopts the syn−anti conformation, assuming axial−axial coordination.[37−45] The small overlap between the magnetic orbitals of the copper atom through the anti−syn carboxylato bridge for a Cu−O−C−O−Cu skeleton that is planar accounts for the weak antiferromagnetic coupling observed. This overlap is significantly reduced for cases where the Cu−O−C−O−Cu skeleton deviates from planarity (out-of-phase exchange pathway), thus reducing the antiferromagnetic contribution, and the ferromagnetic term becomes dominant.[39,44] The magnetic orbital at each copper atom is defined by the short equatorial bonds, and it is of the $d_{x^2-y^2}$ type with possible some mixture of the d_{z^2} character in the axial position. In the case of complex **2**, the conformation is not planar, but it is varying between 37 and 40° (0° stands for planarity and 90° for orthogonality), enhancing the ferromagnetic coupling. Theoretical DFT calculations also corroborate this weak ferromagnetic coupling for the syn−anti conformation.[45]

Conclusion

The reaction of a tridentate Schiff base carboxylato ligand with copper(II) in the presence of trifluoroacetate or nitrate/azide anions allows the synthesis of two new polynuclear systems, one one-dimensional helical chain and another tetranuclear with a flattened tetrahedron shape, with the carboxylates linking the copper(II) ions in syn−anti conformation. In the one-dimensional system, **1**, this coordination is basal−apical, while in the tetranuclear complex, **2**, it is basal−basal. The magnetic properties agree with these features: **1** shows very small antiferromagnetic coupling, whereas **2** shows small ferromagnetic coupling, typical of these basal−basal syn−anti nonplanar structures. The synthesis from this tridentate Schiff base carboxylato ligand corroborates the recently reported perspectives made by Colacio et al.[26] about the possibility of obtaining new interesting complexes by blocking three of the coordination sites of the copper(II) ion.

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Supporting Information Available: X-ray crystallographic files, in CIF format, and tables of hydrogen bonds for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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