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INFLUENCE OF HYDROGEN BRIDGES ON THE MAGNETIC PROPERTIES OF COPPER(II) BIS(TRIFLUOROACETATE) COMPLEXES

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In memoriam of Doctor Guido S. Canessa C.

RESUMEN

Unidades monometálicas de trifluoroacetato de cobre(II) con tres moléculas de agua coordinadas cristalizan en forma de cadenas lineales vía puentes de hidrogeno, rodeadas por moléculas de dioxano de solvatación. El complejo $[Cu(H_2O)_3(OOCCF_3)_2]\cdot 2(C_4H_8O_2)$ **(1)** cristaliza en el sistema triclínico grupo espacial P1, con a = 6.067(1)Å, b = 12.153(3)Å, c = 15.057(3)Å, α= 100.09(2), β= 99.15(2), γ= 101.00(2) y Z = 2. El EPR de **(1)** muestra dos señales ($g\perp = 2.19$ y $g|| = 2.39$) y un multiplete débil a g = 4.55. El espectro EPR de (1) se interpreta en términos de un acoplamiento débil entre los iones cúpricos en la estructura de cadena observada por difracción de rayos-X. Se propone que el camino de intercambio pasa por una molécula de agua axial y por los grupos carboxilato de una unidad coordinada vecina. La susceptibilidad magnética de **(1)** conduce a un valor constante para el momento magnético de alrededor de 1.93 B.M..

El complejo bis(1,3-diaminopropan-2-ol)bis(trifluoroacetato)cobre(II) **(2)** $[Cu(DAP)_2(OOC\text{-}CF_3)_2]$ (DAP=1,3-diamino propan-2-ol) cristaliza en el sistema monoclínico, grupo espacial $P2_1/c$ con a = 9.951(3)Å, b = 8.521(2) Å, c = 11.224(3)Å, β= 109.83(2) y Z = 2. Existe una red de puentes de hidrogeno entre los grupos DAP y trifuoroacetatos de unidades monometálicas vecinas. El complejo **(2)** presenta un intercambio magnético débil entre los iones cúpricos, la susceptibilidad magnética se ajusta a la ecuación de Curie-Weiss con θ= -3.86 K y g = 2.1. El momento magnético efectivo de **(2)** decae continuamente desde 2.01 B.M. a temperatura ambiente hasta 1.5 B.M. a 6 K.

PALABRAS CLAVES: Enlace de hidrogeno, intercambio magnetico, cobre (II), trifluoroacetato.

SUMMARY

Copper(II) trifluoroacetate with three coordinated water molecules and two dioxane molecules **(1)** crystallized as a linear chain surrounded by a net of hydrogen bonds to the dioxane and trifluoroacetate. This complex $[Cu(H_2O)_3(OOC\text{-}CF_3)_2]\cdot 2(C_4H_8O_2)$ crystallizes in the triclinic space group P1 with a = 6.067(1)Å, b = 12.153(3)Å, c = 15.057(3)Å, α= 100.09(2), β= 99.15(2), γ= 101.00(2) and Z = 2. The single crystal EPR spectrum of **(1)** shows to signals ($g\perp = 2.19$ and $g|| = 2.39$), and a weak multiplet at g = 4.55. The EPR spectrum of complex **(1)** is interpreted as a weak exchange occurring in the chain structure found by X-ray diffraction. A hydrogen bond occurring between the axial water on one copper and the carboxylate group of a neighbor copper is proposed to transmit the magnetic exchange found by EPR. The magnetic susceptibility of **(1)** gave a constant value for the magnetic moment of 1.93 B.M.

Bis(1,3-diaminopropan-2-ol)bis(trifluoroacetate)copper(II) complex **(2)** $[Cu(DAP)_2(OOC\text{-}CF_3)_2]$ (DAP=1,3-diamino propan-2-ol) forms a net of hydrogen bonds in the plane of the DAP ligand with adjacent trifluoroacetates. This complex crystallizes in the monoclinic space group $P2_1/c$ with a = 9.951(3)Å, b = 8.521(2) Å, c = 11.224(3)Å, β= 109.83(2) and Z = 2. Complex **(2)** present a weak magnetic coupling; the magnetic data fits to the Curie-Weiss equation, with θ= -3.86 K and g = 2.1. The effective magnetic moment of **(2)** decays steadily from 2.01 B.M. at room temperature down to 1.5 B.M. at 6 K.

KEYWORDS: *Hydrogen bonding, magnetic exchange, copper(II), trifluoroacetate.*

INTRODUCTION

Complexes with bifunctional ligands, for example amino-acid or amino-alcohol molecules,[1] are important because these complexes are convenient compounds to model properties of metal ions in biological systems.[2] The crystal and molecular structure, electronic and magnetic properties and theoretical studies of copper compounds have been focused on linear chain or layered spin systems, where the exchange interaction occurs primarily in one or two dimensions.[3-6] Besides, a long list of copper(II) carboxylate dimers is known with carboxylate forming bridges between two copper centers, in which antiferromagnetic coupling dominates.[7] In these dimers usually an antiferromagnetic path between copper ions is favored.[7,8] The carboxylate ion may link two copper centers in many ways, and the magnetic behavior of these compounds has been related to its bridging mode.[9] A complete understanding of the electronic and geometrical fundamental basis of the coupling has been reached making theoretical calculations at different levels of approximation on this kind of bridged systems.[10-13] One interesting result has been obtained by Bürger et al., who showed that for long distance coupling in copper(II) aromatic dicarboxylate bridged complexes intramolecular H-bonding plays a mayor role, and that ferromagnetic coupling may occur over distances greater than 15 Å when favorably aligned. [14]

If structurally compared di or polynuclear copper carboxylate bridged compounds with mononuclear copper complexes, the latter are relatively scarce and less studied from a magneto-structural point of view. The principal reason for this situation is simple: mononuclear copper compounds lead in general to simple paramagnetic systems which are of low interest to researchers. In this kind of systems copper ions may weakly interact through hydrogen bonds, leading to a non simple magnetic behavior. By nature, hydrogen bonds can only lead to weak interactions between copper ions. The experimental evaluation of this interaction is difficult because of its magnitude. Very low temperature magnetic susceptibility or oriented single crystal EPR measurements are required to detect a weak interaction. EPR and specific heat studies in mononuclear copper aminoacid complexes lead to coupling constant values ranging between 0.05 and 1.5 K, depending of the nature of the exchange path.[15-17]

In contrast to the extensively investigated copper acetate bridged systems, compounds with trifluoroacetate ligand have been less studied, although of its wide use in synthesis. Usually trifluoroacetate does not bridge two copper(II) centers. Trifluoroacetate is more frequently found as terminal carboxylate[18] and eventually forming a linear polymer of copper(I).[19] The aim of this work is to present the synthesis and structure of two mononuclear copper(II) compounds with trifluoroacetate, and discuss the experimentally observed magnetic behavior in terms of coupling interactions through hydrogen bonds.

EXPERIMENTAL

Preparation of the complexes. All chemicals were purchased from Aldrich Chemicals and were used without further purification. Solvents were distilled over metallic sodium and dried by standard methods under nitrogen. FT-IR spectra of complexes **(1)** and **(2)** were recorded on a Brucker IFS spectrometer. IR spectrum for **(1)** was measured in NaCl pellets to prevent decomposition of the copper trifluoroacetate complex in KBr dispersions, while complex **(2)** was measured in KBr pellets.

Synthesis of $[Cu(CF_3COO)_2(H_2O)_3].2C_4H_8O_2$ (1). Copper(II) trifluoroacetate was prepared by dissolving metallic copper in 60% aqueous trifluoroacetic acid and the resulting crystals twice recrystallized from a saturated dioxane solution layered with toluene under inert atmosphere. Large blue prismatic hexagons crystallized from toluene at -10ºC over a period of 4 weeks. The crystals loose dioxane standing in an open container.
$[Cu(CF_3COO)_2(H_2O)_3]\cdot 2\ C_4H_8O_2$ (Found: C, 23.8, H, 3.1. $[Cu(CF_3COO)_2(H_2O)_3]\cdot 1.2\ C_4H_8O_2$ requires C, 23.5, H, 3.5. The formula considers the loss of solvent.).
IR(NaCl pellet): $\underline{\nu}_{max}/cm^{-1}$: 1791w, 1684b, 1444w, 1202s, 1149s, 1684b, 1202m.

Synthesis of $[Cu(DAP)_2(CF_3COO)_2]$ (2). 50 mL of tetrahydrofuran solution of 1,3-diaminopropan-2-ol (397mg, 4.4 mmol) was mixed with stirring at room temperature with $Cu(CF_3COO)_2$

(1154mg, 2.2 mmol) for 8 hr. The insoluble solid was then filtered off (80% yield aprox.). A fine microcrystalline compound was obtained immediately. Blue crystals of complex **(2)** suitable for x-ray diffraction were obtained after two weeks standing at room temperature.
$[Cu(C_3H_{10}N_2O)_2(CF_3COO)_2]$(Found C, 25.5, H, 4.1, N, 11.9. $C_{10}H_{20}CuF_6N_4O_6$, requires C, 25.3, H, 4.2, N, 11.9). IR(KBr pellet): $\overline{\nu}_{max}$/cm^{-1} : 2923w, 2878w, 1671s, 1582s, 1423w, 1197s, 1134s, 1042s, 835w, 802w.

Single Crystal X-Ray measurements . Crystal data, data collection and processing, structure analysis and refinement for complexes **(1)** and **(2)** are summarized in Table 1. A blue prism of **(1)** was mounted on a capillary glass tube containing a drop of mother liquor and sealed. A purplish blue plate of **(2)** was mounted on a glass fibber. For both complexes preliminary examination and data collection were performed on a Siemens R3m Diffractometer (oriented graphite monochromator; MoKα radiation). Cell parameters were calculated from the least-squares fitting for 25 high-angle reflections (15º ≥ 2θ ≥ 30º). Two standards reflections, collected every 98 measured reflections, showed no decay. Lorentz and polarization corrections were applied. The structures were solved by direct methods using XS in SHELXTL package.[20] The structure were refined using XL in SHELXTL.[20] In the case of **(1)**, the water hydrogen atoms were located from difference Fourier map; hydrogen-oxygen distance was restricted to be 0.85 Å. Dioxane hydrogen atoms were placed using geometrical considerations. No hydrogen atom in **(1)** was subsequently refined in least squares fitting. For **(2)** all the hydrogen atoms were placed based on geometrical considerations and were not refined, except the alcohol hydrogen atom, located from Fourier difference map, and refined in least squares cycles. In the case of complex **(2)**, certain disorder on the fluorine atoms of the CF_3 group is evident from the difference Fourier map. Five position for fluorine atoms around the carbon atom of CF_3 group were considered. The occupation of every position was then refined, with the constrain that the sum over the five positions is 3 and that the carbon fluorine distance is restrained to be 1.26 Å (free to refine) Final occupation factors are F1: 0.40, F2: 0.75, F3: 0.60, F4: 0.46, F5: 0.75.

Table I. Crystallographic and refinement details for $[Cu(H_20)_3(TFA)_2]$ • 2 Dx (1) and $[Cu(DAP)_2(TFA)_2]$ (2).

	(1)		(2)	
Empirical Formula	$C_{12}H_{22}O_{11}F_6Cu$		$C_{10}H_{20}O_6N_4F_6Cu$	
Formula Weight	519.84		469.8	
Crystal Size (mm)	0.8 x 0.7 x 0.6		0.4 x 0.2 x 0.02	
Crystal System	Triclinic		Monoclinic	
Space Group	P-1		$P2_1/c$	
Cell Dimensions (Å, º)	a:6.067(1)	α:100.09(2)	a:9.951(3)	α:90
	b:12.153(3)	β:99.15(2)	b: 8.512(2)	β:109.83(2)
	c:15.057(3)	γ:101.00(2)	c:11.224(3)	γ:90
Cell Volume (Å³)	1051.4(4)		894.3(4)	
Z	2		2	
D_{calc} (g/cm³)	1.642		1.745	
μ (mm^{-1})	1.141		1.317	
F(000)	530		478	
2θ range	3.50 to 55.12		4.36 to 50.08	
Index ranges	$0 \leq h \leq 7$		$0 \leq h \leq 11$	
	$-15 \leq k \leq 15$		$0 \leq k \leq 10$	
	$-19 \leq l \leq 19$		$-13 \leq l \leq 12$	
Reflections Collected(n)	4789		1583	
Observed Reflections ($F_o^2 > 2\sigma(F_o^2)$)	3955		1111	
Absorption Correction	ψ scan		ψ scan	
Max. and Min. Transmission Factors	0.505 and 0.424		0.974 and 0.532	
Number of l.s. param.(p)	272		153	
R*, wR2** ($F_o^2 > 2\sigma(F_o^2)$)	0.0446,0.0750		0.0592, 0.1375	
R*, wR2** (all data)	0.0542,0.1383		0.0959, 0.1599	
Goodness of fit***	1.057		1.088	
Largest e$^-$ Density Peak and Hole (e/Å³)	1.023, -0.500		0.810, -0.680	

$*R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$;$**wR2=[\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)2]]^{1/2}$,$***S=[\Sigma[w(Fo^2-Fc^2)2]/(n-p)]^{1/2}$

Magnetic measurements. Samples were used as powders for magnetic susceptibility measurements. Magnetic susceptibility data were obtained between 5 and 300K using a SHE 906 SQUID magnetometer, at a field of 1 kOe (10^{-3} Am^{-1}). Pascal's constants were used to estimate the diamagnetic correction of the sample. TIP for copper was taken from the literature.[21]

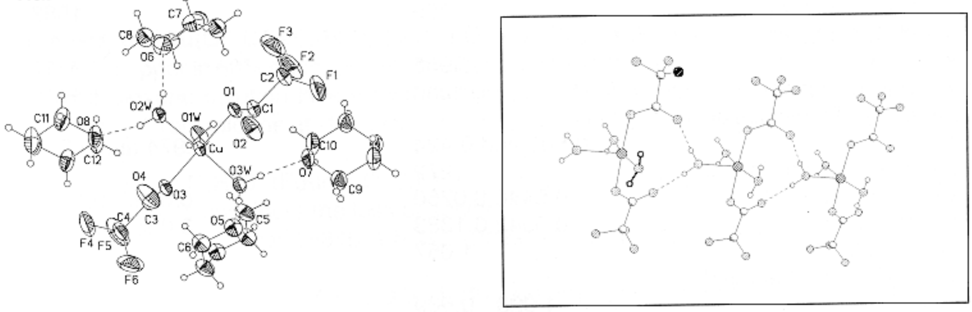
EPR measurements. EPR spectrum was obtained on a Bruker 106 spectrometer working in the X-band (9.78 GHz) at room temperature. The crystalline sample of **(1)** (2 x 2 x 3 mm) was held in a Rexolite stand and rotated to obtain the best signal to noise ratio. The microwave power was set at 1 mW to avoid saturation, and modulation amplitude was set at 4.8 Gauss. The low field signal was obtained after 4 scans with a 10 fold increase in the receiver gain. Since large crystals were not obtained for complex **(2)**, a powder spectrum was obtained in a 2 mm quartz capillary at liquid nitrogen temperature. The work frequency was 9.48 GHz and the power was 0.97 mW.

EHMO and PM3 Calculations. The EHMO parameters were those from program ICON EHMO,[22] with K = 1.75 as usual and results were plotted by CACAO.[23] Parametrization of PM3 was that from the SpartanPlus[24] package.

RESULTS AND DISCUSSIONS

The perspective view of $[Cu(H_2O)_3(OOC\text{-}CF_3)_2]\cdot 2(C_4H_8O_2)$ **(1)** and $[Cu(DAP)_2(OOC\text{-}CF_3)_2]$ **(2)** are given in Fig.1a and Fig.1b respectively, together with the atom numbering scheme. Table 2 contains a summary of bond lengths, angles and hydrogen bond distances. Complex **(1)** is a monometallic copper carboxylate, and the coordination geometry at the copper atom corresponds to a distorted square pyramid. The basal plane is defined by two trans water oxygen atoms and two trans trifluoroacetate oxygen atoms. A water molecule O(1W) occupies the apical position. The copper to water distance (Cu-O(1W), 2.195(2)Å) in the apical position is longer than the oxygen to copper distance in the basal plane (Cu-O(2W), 1.967(2)Å; Cu-O(3W), 1.974(2)Å). The trifluoroacetate group acts as a monodentate ligand, with its two non coordinating oxygen atoms (O2, O4) located trans to the apical water molecule (O1W). Least squares plane defined by carbon and oxygen atoms of trifluoroacetate group defines a dihedral angle of 76.0(1)° (O1, O2, C1, C2) and 75.1(1)((O3, O4, C3, C4) with the coordinated basal plane (Cu, O2W, O3W, O1, O3). In the crystal packing of **(1)** there are two non coordinating dioxane molecules per copper complex. The inversion center of the centrosymmetric P1 space group coincides with the inversion center of the chair conformation of the dioxane molecules. The crystal packing of **(1)** shows two types of hydrogen bond connecting the mononuclear copper units. The first kind of H-bond corresponds to the hydrogen atoms of the water molecules in the basal plane, which are directed toward the oxygen atoms of dioxane solvate, defining the following distances: H2WA-O8: 1.896Å, H2WB-O6: 1.869Å, H3WA-O7: 1.881Å, H3WB-O5: 1.864Å. The second kind of hydrogen bond in the lattice of **(1)** is defined by the apical water hydrogen atoms and the two non-coordinating trifluoroacetate oxygen atoms, as shown in the insert of Fig.1a. The distance between copper atoms connected through the first kind of hydrogen bond is in average 10.2Å. The separation found between adjacent copper atoms related by the second path is 6.067Å.

1.a.



1.b.

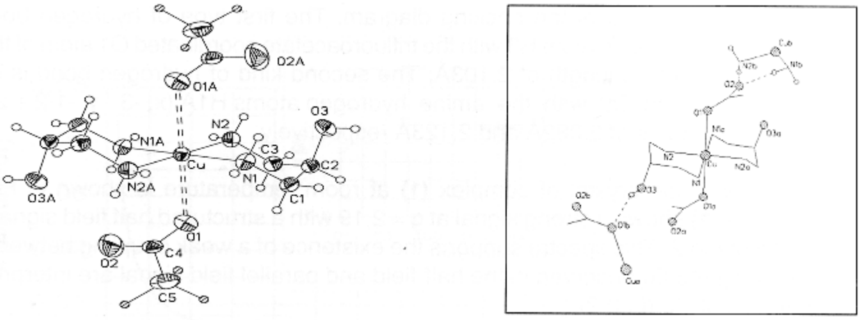


Fig1. a. Molecular structure diagram of $[Cu(H_2O)_3(CF_3COO)_2].2C_4H_8O_2$ (1) showing 33% displacement ellipsoids and atom numbering scheme. Insert: Packing of complex (1), dioxane molecules omitted for clarity. **b.** Molecular structure diagram of $Cu(DAP)_2(CF_3COO)_2$ (2) showing 33% displacement ellipsoids and atom numbering scheme. Insert: Packing of complex (2).

Table II. Selected bond lengths (Å), angles (º), and hydrogen bond lenghts (Å) for $[Cu(H_20)_3(TFA)_2]$ • 2 Dx **(1)** and $[Cu(DAP)_2(TFA)_2]$ **(2)**.

$[Cu(H_20)_3(TFA)_2]$ • 2 Dx **(1)**			
Cu-O(1)	1.942(2)	Cu-O(3)	1.946(2)
Cu-O(1W)	2.195(2)	Cu-O(2W)	1.967(2)
Cu-O(3W)	1.974(2)		1.255(4)
O(1)-Cu-O(3)	176.4(1)	O(1)-Cu-O(2W)	89.2(1)
O(3)-Cu-O(2W)	90.45(8)	O(1)-Cu-O(3W)	91.1(1)
O(3)-Cu-O(3W)	88.5(1)	O(2W)-Cu-O(3W)	168.2(1)
O(1)-Cu-O(1W)	91.6(1)	O(3)-Cu-O(1W)	92.0(1)
O(2W)-Cu-O(1W)	95.3(1)	O(3W)-Cu-O(1W)	96.5(1)
C(1)-O(1)-Cu	120.7(2)	O(2)-C(1)-O(1)	129.4(3)
H3WB···O5	1.864	H3WA···O7	1.869
H2WB···O6	1.881	H2WA···O8	1.896
O2···H1WA#1	1.935	O4···H1WB#1	1.912
#1: 1+x, y, z			
$[Cu(DAP)_2(TFA)_2]$ **(2)**			
Cu-N(1)	2.017(4)	Cu-N(2)	2.029(5)
Cu-O(1)	2.617(6)		
N(1)-Cu-N(1)#3	180.0	N(1)-Cu-N(2)#3	92.7(2)
C(3)-N(2)-Cu	117.4(4)	C(1)-N(1)-Cu	118.3(3)
H3···O1#2	2.103	O2···H1A#3	2.082
O2···H2B#4	2.123		
#2:x,-3/2-y,-1/2-z	#3:x,-3-y,-1/2+z		
#4:-x,y-1/2,-1/2-z			

Complex **(2)** is also a monometallic copper carboxylate. In this case, the coordination geometry around copper atom corresponds to a tetragonaly distorted octahedron. In attention to the copper-ligand atom distances (see Table 2) the equatorial plane can be considered defined by four nitrogen atoms of two chelating 1,3-diaminopropan-2-ol molecules (DAP) and the axial positions defined by two trifluoroacetate oxygen atoms, which as in **(1)** act as monodentate ligands. The copper atom in (2) lies on a special position in the space group $P2_1/c$ (type a, corresponding to the inversion center). In this way the asymmetrical unit corresponds to one half of the complete monometallic unit $Cu(DAP)_2(OOC\text{-}CF_3)_2$, and the non-coordinating oxygen atoms of the DAP ligands are located on the opposite sides of the coordinated basal plane. The value of the copper-trifluoroacetate oxygen distance is 2.617(6)Å, noticeably longer than the corresponding values in **(1)** (Cu-O(1), 1.942(2)Å; Cu-O(3) 1.946(2)Å). This fact is not surprising if one considers that in **(1)** the trifluoroacetate oxygen atoms are bonded to the copper atom at the basal plane, and that in **(2)** these are bonded to axial positions, subject to Jahn-Teller distortion. The dihedral angle between the trlifluoroacetate (O1, O2, C4, C5) least squares plane and the basal coordinated plane (Cu, N1, N1a, N2, N2a) is 37.7(1)º. The copper centers in **(2)** are connected by two kinds of hydrogen bonds. The insert of Fig.1b shows the packing diagram. The first type of hydrogen bond implies the interaction of the alcohol-hydrogen atom H3 with the trifluoroacetate coordinated O1 atom of the symmetrical unit x, -3/2 - y, -1/2 + z; with a length of 2.103Å. The second kind of hydrogen bond is defined by the trifluoroacetate oxygen atom O2 with the amine hydrogen atoms H1A (x, -3 - y, -1/2 + z) and H1B (-x, -1/2 + y, -1/2 - z), with lengths of 2.082Å and 2.123Å respectively.

The EPR of a single crystal of complex **(1)** at room temperature is shown in Fig.2. The EPR spectrum for complex **(1)** shows a strong signal at g = 2.19 with a structured half field signal at g = 4.55 as shown in the insert of Fig.2. This spectra supports the existence of a weak coupling between copper ions. The hyperfine splitting (45 G) observed in the half-field and parallel field signal are interpreted as arising from the nuclear spin of Cu (I= 3/2).

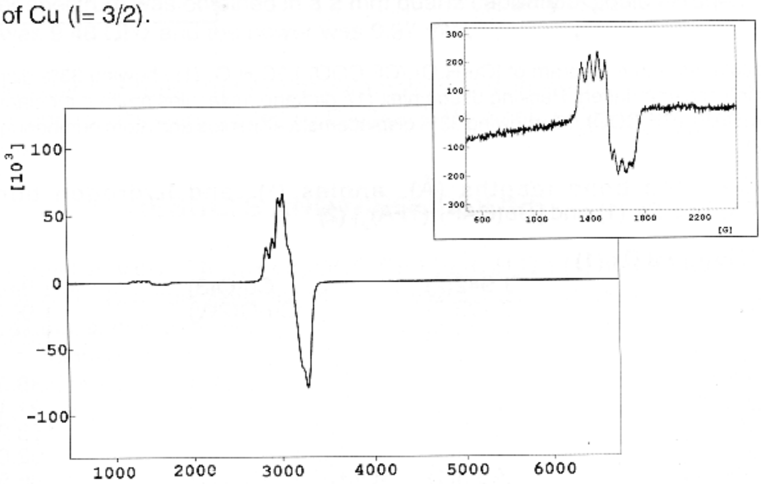
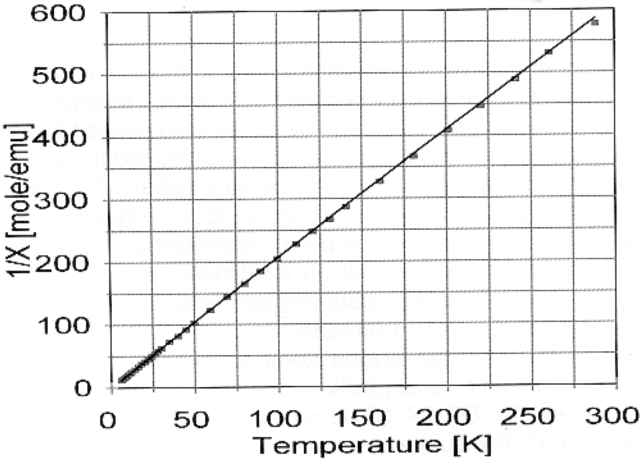


Fig.2. EPR spectra of complex **(1)**. Insert : low field spectra of complex **(1)**.

Molar magnetic susceptibility data for complex **(1)** fit better to a Curie-Weiss model with θ of 0.09 K and a g factor of 1.95 (the agreement factor r is $2\cdot10^{-5}$ for 36 points and two independent variables, θ and g). The reciprocal of molar susceptibility as a function of temperature for complex **(1)** is shown in Fig.3a. The magnetic moment (1.93 B.M.) remains constant over the entire range of temperature. Since complex **(2)** did not give large crystal which could be used to record a single crystal EPR spectrum, a powder EPR spectrum was recorded at liquid nitrogen temperature. The spectrum shows a broad structureless band centered at g = 2.10. The molar magnetic susceptibility of complex **(2)** can be interpreted in terms of a Curie-Weiss behavior with a θ = -3.86 K and g = 2.1 (see Fig 3b), where the agreement factor r is 6.1×10^{-3} for 32 points. A magnetic moment of 2.01 B.M is calculated at room temperature.

3 a.



3 b.

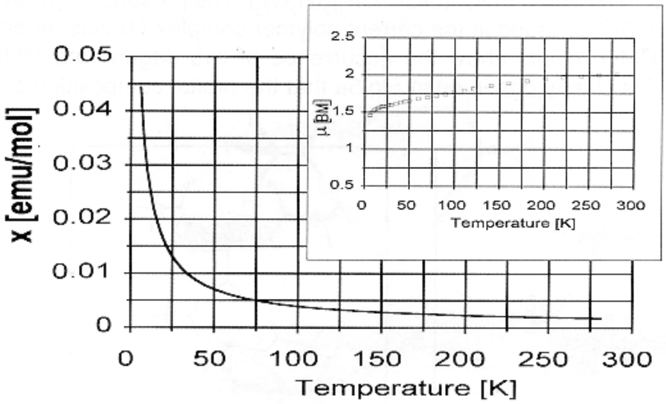
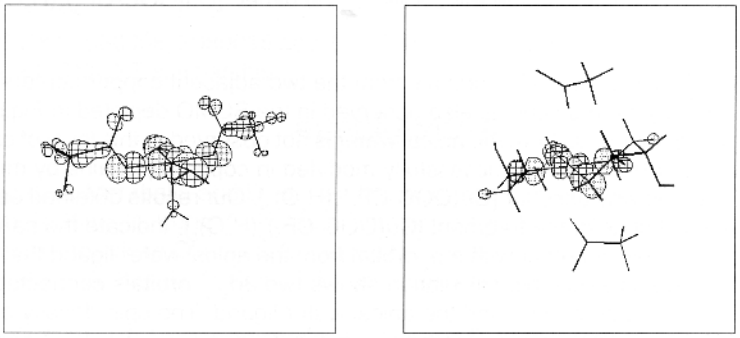


Fig.3. a. Reciprocal of the molar magnetic susceptibility as function of temperature for complex **(1)**. Full line correspond to Curie-Weiss fit (g = 1.95, q = 0.09K). **b.**Molar magnetic susceptibility as function of temperature for complex **(2)**. Full line correspond to Curie-Weiss fit (g = 2.1, q = -3.86K). Insert : Magnetic moment as function of temperature.

A steady decrease of the magnetic moment to 1.45 B.M. at 5.95 K as shown at insert in figure 3b indicates some degree of interaction between the copper centers.

In order to explain the weak spin exchange observed by EPR in complex **(1)**, we modeled the fragment $[Cu(OOC\text{-}CF_3)_2(H_2O)_3]$ as well as two adjacent monomers $[Cu(OOC\text{-}CF_3)_2(H_2O)_3]$ by EHMO theory and PM3 method. The distortion from square pyramidal geometry found in complex **(1)** was taken into account for these calculations. In order to study the influence of the water bridge with the neighbor complex, a second apical water molecule forming a pseudo octahedral fragment $[Cu(OOC\text{-}CF_3)_2(H_2O)_3.H_2O]$ was studied as shown below.

As seen in Fig.4a the atomic orbital composition of the SOMO in the $[Cu(OOC\text{-}CF_3)_2(H_2O)_3]$ complex is dominated by atomic orbitals from the oxygen atoms of the equatorial water and trifluoroacetate as well as the copper $d_{x^2-y^2}$ orbital. A small contribution from the pz orbital belonging to the apical water molecule to the SOMO is observed. The participation of the entire trifluoroacetate is clearly portrayed in this calculation. The nearest occupied orbital below the SOMO contains the expected σ contribution of all the ligands and the d_{z^2} orbital. Energy gap between these orbitals is 1.36 eV. This doubly occupied MO contains a larger contribution of the apical water molecule. The presence of a fourth water molecule along the z axis, from the neighbor complex $[Cu(OOC\text{-}CF_3)_2(H_2O)_3.H_2O]$ does not alter the composition of the



a

b

Fig.4. a. SOMO molecular orbital in the $[Cu(OOC\text{-}CF_3)_2(H_2O)_3]$ calculated at the EHMO level. **b.** SOMO molecular orbital calculated at the EHMO level for $[Cu(OOC\text{-}CF_3)_2(DAP)_2]$, complex (2).

monomer itself nor mixes with the SOMO of [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]. The presence of a second molecule of complex [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$] as found in the current polymer complex (1) was modeled by EHMO method, see Fig.4a. The EHMO results show the occurrence of two degenerate MOs with similar composition and symmetry. It is clearly observed in Fig.5a that the orbital composition of the SOMO of [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]$_2$ involves the $d_{x^2-y^2}$ orbitals from the two adjacent copper centers. In addition, the involvement of the carboxylate σ system is also observed in the SOMO depicted in Fig.5a. However the participation of the hydrogen bonds from the apical water is not observed at this level of calculation. Since the magnetic exchange path has been successfully modeled in copper(II) chains by means of the PM3 method,[3] this same method was used for [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]. Our results obtained using the Spartan-PM3 method on the triplet state of the fragment [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]$_2$ indicate the participation of both copper(II) $d_{x^2-y^2}$ and d_{z^2}orbitals together with a p_x orbital from the apical water ligand that is not present in the EHMO calculation. Remarkably this calculation shows two $3d_{x^2-y^2}$ orbitals connected through the 2p orbitals from the trifluoroacetate groups and the apical water ligand. The spin density of the triplet state was calculated and plotted by PM3 method for the moeity [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]$_2$, as seen in Fig.5b. This figure clearly shows some spin density over the bridging water O(1W) together with the carboxylate manifold. From the current structural data and theoretical calculation results for **(1)** we propose an exchange path connecting the copper(II) ions through the axial water molecule to the carboxylate groups of the neighbor copper(II) complex, as shown in the scheme below.

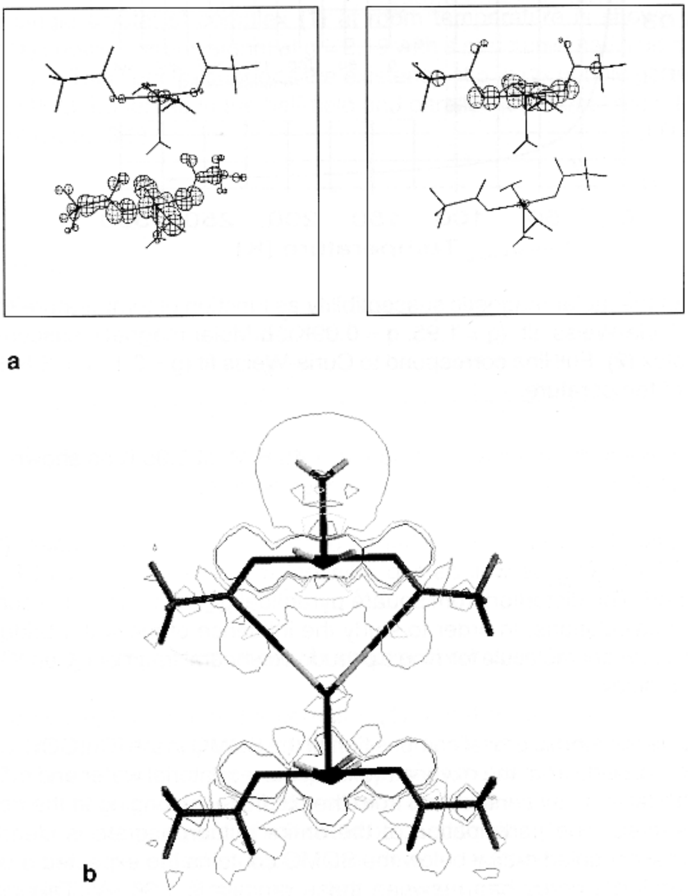
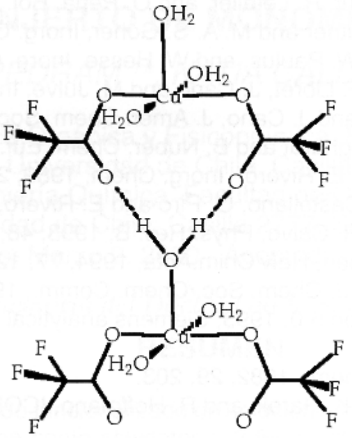


Fig.5. **a.** SOMO molecular orbitals calculated for the dimer [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]$_2$ at the EHMO level. **b.** Spin density contours calculated at the PM3 level for the dimer [Cu(OOC-CF$_3$)$_2$(H$_2$O)$_3$]



The exchange path described through the hydrogen bonds of complex **(1)** explains how the adjacent copper(II) complexes are magnetically connected, although the magnitude of the exchange is not evident from susceptibility data. It is frequent to observe a weak magnetic exchange by EPR spectroscopy in copper(II) complexes connected through hydrogen bonds.[25] The estimated exchange coupling constant in these systems is in the order of a few tenth of a wavenumber, which explains that our magnetic susceptibility measurements are almost insensitive to this kind of phenomenon. Since some degree of magnetic interaction between copper centers in complex **(2)** is evident from magnetic susceptibility measurements (θ =-3.86) EHMO calculations were performed in order to obtain an explanation for this observation. The results show that the SOMO is composed exclusively of p_x and p_y orbitals from DAP molecule mixed with the copper $d_{x^2-y^2}$ orbital, as seen in Fig.4b. The participation of the carboxylate group in the SOMO is ruled out in view of these results and the long distance (2.616Å) between the copper(II) center and the trifluoroacetate ion. On the other hand, we also modeled complex **(2)** complex at the PM3 level. The SOMO obtained for complex **(2)** by this method is identical to that obtained at the EHMO level. That is the unpaired electron resides in a $3d_{x^2-y^2}$ orbital mixed with the 2p orbitals of the axial nitrogen atoms.

Since EHMO and PM3 calculations show no participation of the trifluoroacetate group in the magnetic orbitals and the structurally observed hydrogen bonds in complex **(2)** implies in all cases the weakly coordinated trifluoroacetate oxygen atoms, we can not propose any exchange path that could account for the magnetic behavior.

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REFERENCES

1 J. A. Bertrand, C. Marabella and D. G. Van Der Veer, Inorg. Chim. Acta,1977, 25, L69.
2 M. Johnson, R. King, D. Kurtz, C. Kutal, M. Norton and R. Scott in Electron Transfer in Biology and the Solid State. American Chemical Society, Washinton, DC 1990, USA.
3 C. A. White, G. P. A. Yap, N. P. Raju, J. E. Greedan and R. J. Crutchley, Inorg. Chem., 1999, 38, 2548.
4 O. Guillou, O. Kahn, R. Oushoorn, K. Boubekeur and P. Batail, Inorg. Chim. Acta, 1992, 119, 198.
5 J. Miller and A. Epstein, Angew. Chem. Int. Ed. Engl., 1994, 33, 385.
6 S. Barlow and D. O'Hare, Chem. Rev., 1997, 97, 637.
7 R. W. Jotham, S. F. A. Kettle and J. A. Marks, J. Chem. Soc. Dalton Trans.,1972, 428.
8 O. Kahn, Inorg. Chim. Acta, 1982, 62, 3.

9 A. M. Atria, E. Spodine, J. Manzur, R. Letelier, and O. Peña, Bol. Soc. Chil. Quim.,1992, 37, 323.
10 A. Escuer, R. Vicente, F. A. Mautner and M. A. S. Goher, Inorg. Chem., 1997, 36,1233.
11 S. P. Gehring, H. Fleischhauer, W. Paulus, and W. Hesse, Inorg. Chem., 1993, 32, 54.
12 L. K. Thompson, S. S. Tandon, F. Lloret, J. Cano and M. Julve, Inorg. Chem., 1997, 36, 3301.
13 E. Ruiz, P. Alemany, S. Alvarez and J. Cano, J. Amer. Chem. Soc., 1997, 119, 1297.
14 K. Burger, P. Chaudhuri, K. Wieghardt and B. Nuber, Chem. Eur. J., 1995, 1, 583.
15 C. Steren, R. Calvo, O. Piro and E. Rivero, Inorg. Chem, 1989, 28, 1933.
16 P. R. Levstein, R. Calvo., E. E. Castellano, O. Piro and E. Rivero, Inorg. Chem, 1990, 29, 3918.
17 M. L. Siqueira, R. E. Rapp and R. Calvo, Phys. Rev. B, 1993, 48, 3257.
18 T. Becht, K. Gerfin and H. Dahmen, Helv.Chim.Acta, 1994, 77, 1288.
19 P. F. Rodesiler and E. L. Amma, J. Chem. Soc. Chem. Comm., 1974, 599.
20 Sheldrick, G.M. SHELXTL version 5.0, 1993, Siemens analytical X-ray Instruments Inc. Madison, Wisconsin, USA.
21 C. J. O'Connor, Prog. Inorg. Chem., 1982, 29, 203.
22 J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffmann, ICON program, 1977, QCPE, 5, No. 344.
23 C. Mealli and D. M. Proserpio, CACAO program. J. Chem. Ed., (1990), 67, 399.
24 B. J. Deppmeier, A. J. Driessen, W. J. Herhe, T. Herhe, P. E. Klunzinger, L. Lou and J. Yu, SPARTAN PLUS program, 1999.
25 C. D. Brondino, N. M. C. Casado, M. C. G. Passeggi and R. Calvo, Inorg. Chem.,1993, 32, 2078.