

Observation of Dominant Ferromagnetic Interaction in Fumarate-Bridged 1-D Polymer of Cu(II)

Partha Sarathi Mukherjee,[†] Tapas Kumar Maji,[†] Golam Mostafa,[‡] Joan Ribas,^{*,§,||}
Mohamed Salah El Fallah,[§] and Nirmalendu Ray Chaudhuri^{*,†,⊥}

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta-700032, India, Department of Physics, Krishnath College, Berhampur 742109, India, and Departament de Quimica Inorganica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain

Received August 17, 2000

The reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{C}_4\text{H}_2\text{O}_4$ (disodium fumarate) in dilute ammonia solution produces 1-D polymeric chain $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$. The crystal structure of the compound has been solved. The compound crystallizes in the monoclinic system, space group $C2/m$ (No. 12), with chemical formula $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_5\text{-Cu}$, $a = 13.955(5)$ Å, $b = 7.330(3)$ Å, $c = 8.927(2)$ Å, $\beta = 102.39(3)^\circ$, $Z = 4$. The interesting feature of the complex is that one of the carboxylic acid groups acts as a monodentate coordinating ligand whereas the remaining carboxylate moiety acts as a monoatomic bridging bidentate ligand. This unusual coordination behavior of fumarate anion produces a chain with alternate repetition of 4- and 14-member rings. The magnetic properties of the compound have been studied from room temperature to 4 K, which reveal the existence of a dominant ferromagnetic interaction with exchange coupling parameter values of $J_F = +12 \text{ cm}^{-1}$ and $J_{AF} = -3.8 \text{ cm}^{-1}$, using an alternating ferro- and antiferromagnetic chain model for $S = 1/2$ local spin. The ferromagnetic interaction arises from the alkoxo-bridged dimeric part of the chain. The fitting of the $\chi_M T$ vs T data continued until the maximum in the experimental data using a single dinuclear model resulted in $J = +7.8 \text{ cm}^{-1}$.

Introduction

In the past few years chemists have dedicated their efforts to the study of molecular-based magnets with the need to understand the fundamental science associated with magnetic interactions between the paramagnetic metal ions and the bridging ligand to develop the magnetostructural correlation, enabling the design synthesis of interesting magnetic materials.^{1–4} These magnetic materials can be constructed to yield dimers, tetramers, and mono-, bi-, and three-dimensional extended structures,^{5–7} with the paramagnetic metal ions using bridging ligands that act as a superexchange pathway between the metal centers. This superexchange pathway determines the exchange coupling parameter J .

Recently the use of organic spacers, particularly the dicarboxylic acid,^{8,9} as superexchange pathways between the metal

ions is of growing interest in the field of molecular magnetism. Major studies have been done on oxalato-bridged^{10–13} metal complexes with a few examples using terephthalic acid and malonic acid as superexchange pathways.⁸ Previous reports reveal that dicarboxylic acid can coordinate to a metal ion in either a chelating bisbidentate or bismonodentate or a bridging bismonodentate.^{14–16} Though the use of various dicarboxylic acids to form bridges between paramagnetic metal centers has been extensively studied, the use of fumaric acid as a bridging block between metal centers is scanty in the literature. To our knowledge, only one metal complex¹⁷ has been structurally characterized to date using fumarate anion as a bridging block between paramagnetic Mn(II) centers that are not magnetically characterized. Herein, we report the synthesis, crystal structure, and magnetostructural correlation of a Cu(II) complex using fumarate as a bridging block. The coordination behavior of the fumarate ligand in our complex is totally different from the fumarate complex of manganese(II) reported earlier.

The most interesting fact in our complex is that one of the carboxylate acid groups acts as a monodentate coordinating

* To whom correspondence should be addressed.

[†] Indian Association for the Cultivation of Science.

[‡] Krishnath College.

[§] Universitat de Barcelona.

^{||} E-mail: jribas@kripto.qui.ub.es. Fax: 34-93-4907725.

[⊥] E-mail: icnrc@mahendra.iacs.res.in. Fax: 91-33-473 2805.

- (1) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.
- (2) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392.
- (3) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635.
- (4) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40.
- (5) Escuer, A.; Vicente, R.; Ribas, J.; Solans, X. *Inorg. Chem.* **1995**, *34*, 1793.
- (6) Ribas, J.; Monfort, M.; Diaz, C.; Bastos, C.; Solans, X. *Inorg. Chem.* **1994**, *33*, 484.
- (7) Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.* **1996**, *35*, 6386.
- (8) Deakin, L.; Arif, M. A.; Miller, J. S. *Inorg. Chem.* **1999**, *38*, 5072.
- (9) Bakalbassis, E.; Bergerat, P.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Dromzee, Y.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 625.

- (10) Girerd, J. J.; Kahn, O.; Verdager, M. *Inorg. Chem.* **1980**, *19*, 274.
- (11) Julve, M.; Verdager, M.; Gleizes, A.; Philoche-Lavisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.
- (12) Julve, M.; Faus, J.; Verdager, M.; Gleizes, A. *J. Am. Chem. Soc.* **1984**, *106*, 3808.
- (13) Tapper, A. E.; Billo, E. J.; Golen, J. A. *Inorg. Chim. Acta.* **1993**, *210*, 71.
- (14) Cano, J.; DeMunno, G.; Sanj, J. L.; Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Caneschi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1915.
- (15) Burger, K. S.; Chaudhuri, P.; Weighardt, K.; Nuber, B. *Chem.—Eur. J.* **1995**, *1*, 583.
- (16) Bakalbassis, E.; Bergerat, P.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Dromzee, Y.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 625.
- (17) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Khan, M. A.; Roberts, P. J. *Inorg. Chem.* **1979**, *18*, 2433.

ligand where the remaining group functions as a monoatomic bridging ligand to form a 1-D chain with alternate repetition of 4- and 14-member rings. The monoatomic bridging behavior of the carboxylic acid group is very rare because to our knowledge only three examples are reported^{17,18} to date where the carboxylic acid group shows such bridging behavior. Low-temperature susceptibility data show that the present complex is primarily ferromagnetic, and this ferromagnetic interaction arises from the monoatomic-bridged copper(II) dimeric part of the complex through the large Cu—O—Cu angle (104.1°).

Experimental Section

Synthesis. Disodium fumarate (1 mmol) dissolved in water (10 mL) was added to an aqueous solution (10 mL) of copper(II) chloride dihydrate (1 mmol) with continuous stirring. A sky-blue solid was filtered out and washed with water. It was treated with water (10 mL) and stirred well to form a slurry. A dilute aqueous solution of ammonia was slowly added to it drop by drop to dissolve it completely. The resulting deep-blue solution yields suitable single crystals for X-ray diffraction when the solution is kept in a refrigerator for a week. Anal. Calcd: C, 20.9; H, 4.35; N, 12.2. Found: C, 20.75; H, 4.43; N, 11.9. IR: $\nu(\text{COO}^-)$, 1370, 1592 cm^{-1} ; $\nu(\text{N—H})$, 2900 cm^{-1} ; $\nu(\text{O—H})$, 3400–3300 cm^{-1} . TGA: 8% (110–120 °C) and 15.2% (160–180 °C).

Physical Measurements. IR spectra were recorded on a Nicolet 520 FTIR spectrometer as KBr pellets. Thermal analysis (TGA) was carried out using a Shimadzu DT-30 thermal analyzer under a flow of nitrogen (30 mL min^{-1}). The sample (particle size 50–200 mesh) was heated at a rate of 10 °C min^{-1} with inert alumina as a reference. The magnetic measurement was carried out on a polycrystalline sample with a pendulum type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat, working in the temperature range 300–4 K, and a Bruker BE15 electromagnet. The magnetic field was approximately 15 000 G. The instrument was calibrated by magnetization measurements of a standard ferrite. Diamagnetic corrections were estimated from Pascal constants.¹⁹

Crystal Data Collection and Refinement. A crystal suitable for X-ray analysis was mounted on a Nicolette R3/m single-crystal diffractometer equipped with graphite monochromator and Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The unit cell parameter and orientation matrix were determined by least-squares refinements of the setting angles of 25 reflections ($2.3^\circ < \theta < 25^\circ$). Crystal and instrument stabilities were monitored with a set of three standard reflections measured over 100 reflections; in all cases variations were insignificant. The collected intensity data were corrected for the Lorentz polarization effect. A total of 899 reflections were measured and 731 were assumed observed, applying the condition $I > 2\sigma(I)$. Extinction of reflections of this crystal indicated the space group to be $C2$ (acentric), Cm (acentric), or $C2/m$ (centric). An analysis of centric E statistics preliminarily resolved the ambiguity. The correct space group, as confirmed by structure refinement, was $C2/m$. Also, the chemical evidence that the density indicated $Z = 4$ and that the copper atom possesses the inversion center leads us to choose unambiguously the space group as $C2/m$. The structure was solved by Patterson synthesis²⁰ and refined through full-matrix least squares on F^2 using SHELXL93²¹ with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon and nitrogen atoms (C—H, 0.97 Å; N—H, 0.90 Å). The R_{int} value is 0.039, and no correction was made for extinction because we did not get any evidence of primary or secondary extinction. During refinement, the water molecule was found to be disordered over two positions with a site occupancy ratio 0.8/0.2. The refinement converged to residual indices $R1 = 0.053$ and $wR2 = 0.149$ with $I > 2\sigma(I)$. The final difference Fourier map showed maximum and minimum peak heights of 0.94 and -1.23 e/\AA^3 , respectively. All

Table 1. Crystal Data and Details of the Structure Determination for $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$

chemical formula	$\text{C}_4\text{H}_{10}\text{N}_2\text{O}_5\text{Cu}$	fw	229.5
a [Å]	13.955(5)	space group	$C2/m$ (No. 12)
b [Å]	7.330(3)	temp (K)	293
c [Å]	8.927(2)	λ (Mo K α) [Å]	0.710 73
α, β, γ [deg]	90, 102.39(3), 90	μ [cm^{-1}]	24.37
V [Å ³]	891.9(5)	ρ_{calc} [g/cm^3]	1.711
Z	4	$R(F_o)^a$	0.053
		$R_w(F_o)^b$	0.149

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

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n^a$

Cu—O(1)	1.973(5)	Cu—N	1.975(5)
Cu—O(3a)	1.994(5)	Cu—O(3c)	2.458(6)
C(1)—O(1)	1.266(10)	C(1)—O(2)	1.247(10)
C(4)—O(3)	1.261(9)	C(4)—O(4)	1.262(10)
C(1)—C(2)	1.489(10)	C(2)—C(3)	1.303(11)
C(3)—C(4)	1.489(10)		
O(1)—Cu—N	90.23(13)	O(1)—Cu—O(3a)	171.0(2)
O(1)—Cu—O(3c)	95.1(2)	O(1)—Cu—N(f)	90.23(13)
O(3a)—Cu—N	90.66(13)	O(3c)—Cu—N	95.59(13)
N—Cu—N(f)	168.73(19)	O(3c)—Cu—O(3a)	75.90(19)
O(3a)—Cu—N(f)	90.66(13)	O(3c)—Cu—N(f)	95.59(13)
Cu—O(1)—C(1)	114.3(5)	O(3)—C(4)—O(4)	124.0(7)
O(1)—C(1)—O(2)	123.2(7)		

$$^a \text{(a) } x, y, -1 + z. \text{ (c) } 1 - x, y, 2 - z. \text{ (f) } x, -y, z.$$

calculations were carried out using SHELXL97,²² SHELXL93,²¹ ZORTEP,²³ and PLATON99²⁴ programs. The crystallographic data are given in Table 1, and selected bond distances and bond angles are given in Table 2.

Results and Discussion

The IR spectrum of the title compound shows a strong band in the region 3400–3300 cm^{-1} (O—H stretching vibrations) and is consistent with the presence of water. The bands at 1592 and 1370 cm^{-1} are assigned to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ stretching vibrations, respectively, and the strong bands at 2900 cm^{-1} is assigned to the N—H stretching mode.

Thermogravimetric analysis of the complex shows that the weight loss of 8% takes place in the temperature range 110–120 °C and a weight loss of 15.2% in the temperature range 160–180 °C, corresponding to the loss of one water and two ammonia molecules, respectively.

Structure Description. In the crystal structure of the title compound, the copper centers are interlocked by fumarate ligands, giving a novel $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$ infinite chain as shown in Figure 1. Each copper is in a distorted square pyramidal environment. Two nitrogens of the coordinated ammonia and two oxygens of two different fumarate units define the equatorial plane of the pyramid. The axial position is occupied by an oxygen of the third fumarate anion. Thus, each Cu(II) center is linked to three different fumarate anions. The bond lengths in the equatorial plane are the following: Cu—N, 1.975(5) Å; Cu—O(1), 1.973(5) Å; Cu—O3, 1.994(5) Å. The axial bond length is 2.458(6) Å. Two carboxylate groups of the fumarate ligand have two different coordination modes. In the first mode, the carboxylate group acts as a monoatomic bridge linked to two Cu(II) ions. This bridging mode is very rare; only a few examples are reported to date.^{17,18} The

(18) Shi, Z.; Zhan, L.; Gao, S.; Jang, G.; Hua, J.; Gao, L.; Feng, S. *Inorg. Chem.* **2000**, *39*, 1990.

(19) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: London, 1968.

(20) Sheldrick, G. M. SHELXL-86, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 476.

(21) Sheldrick, G. M. SHELXL-93, Program for Solution of Crystal Structure; University of Gottingen: Gottingen, Germany, 1993.

(22) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; University of Gottingen: Gottingen, Germany, 1997.

(23) Zsolnai, L. ZORTEP, Program for Presentation of Thermal Ellipsoids; University of Heidelberg: Heidelberg, Germany, 1994.

(24) Spek, A. L. PLATON, Molecular Geometry Program; University of Utrecht: Utrecht, The Netherlands, 1999.

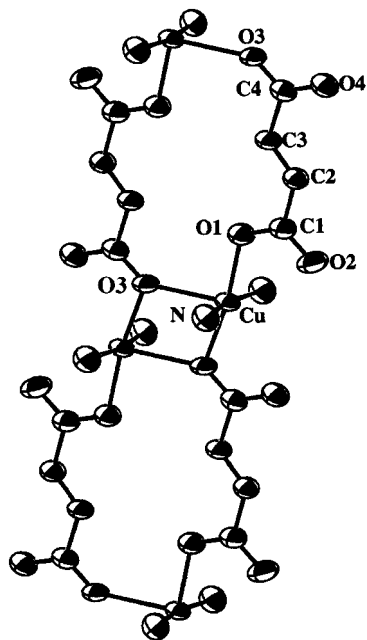


Figure 1. ORTEP diagram of $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$ with labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

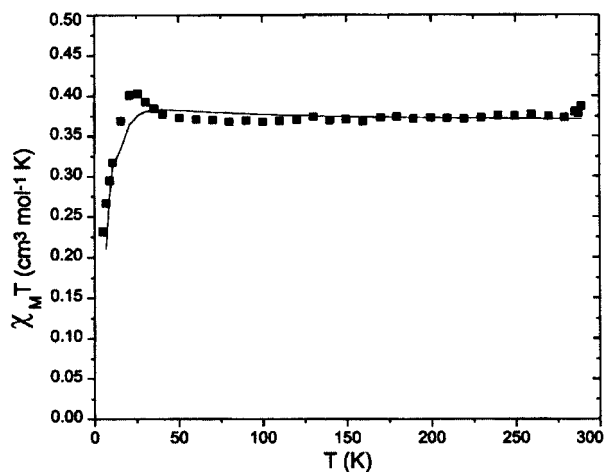


Figure 2. $\chi_M T$ vs T plot in the 4–300 K range of temperatures of a polycrystalline sample for $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$. The solid line shows the best fit obtained by using the Borrás equation (see text).

interesting feature of the structure is that in the dimeric $\text{Cu}-\text{O}_2-\text{Cu}$ part of the chain one of the bridging oxygens is in the axial position of the first $\text{Cu}(\text{II})$ center whereas the same oxygen is in the equatorial position of the second $\text{Cu}(\text{II})$. The other bridging oxygen of this dimeric part is linked to two $\text{Cu}(\text{II})$ in a reverse manner. Another oxygen atom of this carboxylate group O(4) forms a hydrogen bond, $\text{N}-\text{H}(2\text{ N})\cdots\text{O}(4)$, with the coordinated ammonia of the neighboring chain with a distance 3.073(7) Å. In the second mode it serves as a monodentate ligand. Two first-mode carboxylate groups bond to Cu ions, forming a four-membered ring ($\text{Cu}-\text{O}_2-\text{Cu}$). The second mode of the fumarate anion produces a 14-membered ring. The overall bridging mode of the fumarate anion produces a Cu fumarate infinite chain with alternate repetition of 4- and 14-membered rings.

Magnetic Properties. The $\chi_M T$ vs T plot for the titled complex is shown in Figure 2. The $\chi_M T$ values are almost constant up to 50 K. When the temperature is further decreased, the $\chi_M T$ values gradually increase and reach a maximum (0.82

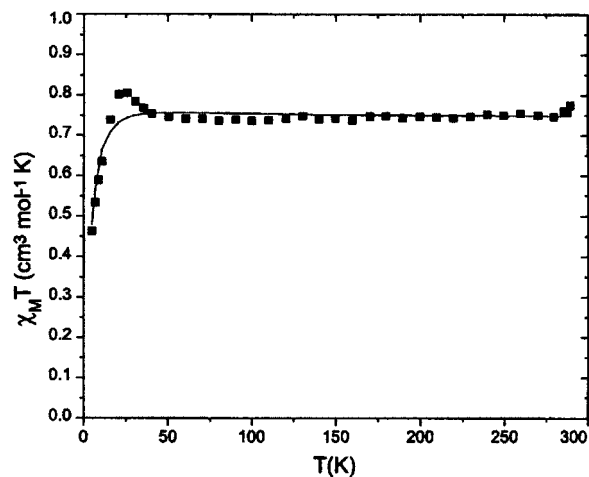


Figure 3. Fitting of the $\chi_M T$ vs T data for the complex $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$, using the formula for a $\text{Cu}(\text{II})$ dimeric system with intermolecular interactions. The solid line represents the best fit.

$\text{cm}^3 \text{mol}^{-1} \text{K}$) at 25 K. This nature of the $\chi_M T$ vs T curve is a signature of the global ferromagnetic behavior of the compound. According to the X-ray crystal structure determination, there are two different pathways in the polymeric chain: the first through the ring created by the fumarate anion, the coupling through which will be very small and antiferromagnetic because of the long-length exchange pathways, and the second through the ring $\text{Cu}-\text{O}_2-\text{Cu}$, which can produce ferro- or antiferromagnetic interaction.²⁵

Thus, according to the structure, we have fitted the data in three different ways.

(a) Assuming the system as an alternating ferro- and anti-ferromagnetic chain, the susceptibility data are fitted (Figure 2) on the basis of the strategy given by Borrás et al.²⁶ for alternating $S = 1/2$ chains using the exchange Hamiltonian

$$H = - \sum_{i=1}^{N-1} [J_1 S_{2i} S_{2i+1} + J_2 S_{2i} S_{2i-1}]$$

with the coefficients for the polynomials valid in the range $2 \leq \alpha \leq 8$, $\alpha = J_2/|J_1|$, where J_2 and J_1 are the ferro- and antiferromagnetic coupling constants, respectively. The best-fitting parameters are $J_2 = +12 \text{ cm}^{-1}$, $\alpha = 3.15$, $g = 2.08$, and R (reliability factor) = 4.1×10^{-4} , which are consistent with a dominant ferromagnetic coupling.

(b) The second method of fitting the susceptibility data involves considering the system as dinuclear and assuming J_1 through the long-length fumarate pathway is zero, but fitting the decreasing part of the curve (Figure 3) with the parameter θ in the dinuclear law for a $\text{Cu}(\text{II})-\text{Cu}(\text{II})$ dimeric system. θ includes the zero-field splitting of the ground-state $S = 1$ ($1/2 + 1/2$) and the antiferromagnetic interactions between the dimers. An alternative explanation for this downturn would be some type of long-range ordering event. In this case, results of the best fit are $J = +15 \text{ cm}^{-1}$, $\theta = -3.17$, $g = 2.1$, and $R = 9.0 \times 10^{-4}$. The interpretation is poor compared to that of the former fitting because the R value is high.

(c) The susceptibility data are also fitted until the maximum is reached in the experimental curve, assuming the system as a single dinuclear one (Figure 4). In this case only two parameters are necessary: $J = +7.8 \text{ cm}^{-1}$; $g = 2.06$ and $R = 3.1 \times 10^{-4}$.

(25) Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.

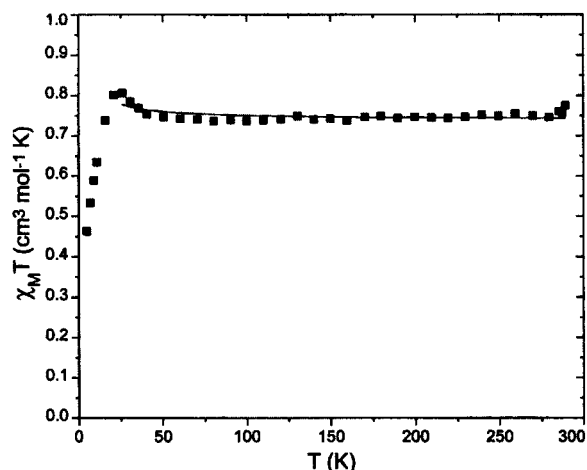


Figure 4. $\chi_M T$ vs T data fitting for the complex $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n \cdot (\text{H}_2\text{O})_n$ using the Bleaney–Bowers formula up to 25 K. The solid line shows the best fit.

Here the R factor is best (minimum) and the J (ferro) value seems to be completely reasonable for the shape of the curve. The formula for fitting a dinuclear of Cu(II) (Bleaney–Bowers formula)²⁷ is exact, and any approximation is not necessary.

In conclusion, none of these models provide an adequate description of the observed behavior. This is itself not surprising because magnetic interactions are often complex and hard to model. As a conclusion, we can only state that the magnetic coupling is dominated by the short pathway Cu–O₂–Cu that shows an angle 104.1° and creates an intramolecular ferromagnetic coupling.

Magnetostructural Correlation. The superexchange pathway in the titled complex that leads to the ferromagnetic interaction is attributed to the monoatomic (alkoxo type) bridged dimeric unit of the molecule. The details of the magnetostructural correlation in the case of hydroxo, oxo, and chloro-bridged parallel-planar Cu(II) dinuclear systems have been well explored, and it is found that the nature of the magnetic interaction is dictated by the bridge angle.^{28–30} Generally, the complex with a Cu–O–Cu angle larger than 97° shows antiferromagnetic interaction³¹ between the metal ions, and when this angle increases, the coupling parameter ($-J$) increases. However, in our complex, although the Cu–O–Cu angle is 104.1°, it still shows ferromagnetic interaction. This can be easily accounted for if we look at the exact environment around the copper(II) in the alkoxo-bridged dimeric unit. The crystal structure shows that each Cu(II) is in distorted square pyramidal environment where one of the bridging oxygens (O_x) is in an axial position (Figure 5) to Cu (1), whereas the same atom (O_x) is in an equatorial position of the Cu(2) environment. The other bridging oxygen (O_y) is in an axial position around Cu(2), whereas it occupies the equatorial position of the Cu(1). The equatorial bond lengths are shorter than the axial bond lengths (2.45 Å), indicating that the spin-unpaired electron is located in the $d_{x^2-y^2}$ orbital and that the d_z^2 orbital contains spin-paired electrons. Thus, here the magnetic orbitals ($d_{x^2-y^2}$) of the two copper(II)

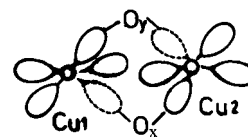


Figure 5. Orbital orientation ($d_{x^2-y^2}$ and d_z^2) of the Cu(II) ions in the Cu–O₂–Cu dimeric part of the molecule.

atoms do not interact via the bridging oxygen in the parallel plane to give antiferromagnetic interaction; rather, only one Cu(II) atom interacts with the bridging oxygen via the magnetic orbital ($d_{x^2-y^2}$), whereas the other interacts via d_z^2 . Because the d_z^2 orbital does not contain spin-unpaired electrons, this orientation of the overlapping orbitals around each Cu(II) is responsible for showing ferromagnetic interaction through this large Cu–O–Cu angle.⁸ Again, the origin of the smaller coupling parameters for both fumarate and Cu–O–Cu paths can be easily accounted for by considering the geometry around the copper atoms. The magnetic orbital describing the single electron on each copper is lying in the basal plane of the copper atoms and has a very small contribution to the axis perpendicular to this plane. The consequence is a good delocalization of the Cu(2) electron density toward the bridging O_x atom while the delocalization is poor from Cu(1) because O_x occupies an apical position with longer distance. The overlap between the Cu(1) and Cu(2) magnetic orbitals is thus expected to be very weak, leading to a small exchange coupling parameter as observed. The situation for the fumarate pathway is due to a long superexchange pathway and smaller coupling parameter for this path; compared to the former the fumarate bridging entity has six atoms instead of one in the former case.

Concluding Remarks

We have presented here the synthesis, single-crystal structure, and magnetostructural correlation of a novel 1-D fumarate-bridged copper(II) chain. The structural characterization shows a rare monoatomic bridging mode of an acid group and that the remaining carboxylate group acts as a monodentate coordinating ligand. Such a coordination mode of the bridging fumarate anion produces a chain with alternate repetition of 4- and 14-membered rings. From the magnetic point of view the complex shows an overall intrachain ferromagnetic interaction. Fitting of the data using the model of ferro- and antiferromagnetic alternating chain for Cu(II) system gave the coupling parameters $J_1 = -3.8$ and $J_2 = +12 \text{ cm}^{-1}$ for fumarate and monoatomic bridged Cu–O₂–Cu pathways, respectively. In our opinion, a wide variety of molecular architectures with varied Cu–O–Cu angles with different intensities of magnetic interaction can be constructed using different nonchelating monodentate ligands instead of ammonia.

Acknowledgment. The authors are grateful to the National Single Crystal Diffractometer Facility at I.A.C.S for providing single-crystal data. We also thank Dr. Bimal Dirghangi and Mr. Swarup Chattopadhyay for their help during single-crystal data collection. Funding for this work is provided by the Council of Scientific and Industrial Research (New Delhi) Grants Scheme and is gratefully acknowledged. J.R. and M.S.El F. acknowledge the financial support from Spanish DGICYT (Grant PB96/0163).

Supporting Information Available: An X-ray crystallographic data file, in CIF format, giving data and details of the structure determination, bond lengths, bond angles, atomic and hydrogen coordinates, equivalent displacement parameters, and anisotropic parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC000949M

- (26) Borrás-Almenar, J. J.; Coronado, E.; Curely, J.; Georges, R.; Gianduzzo, J. C. *Inorg. Chem.* **1994**, *33*, 5171.
 (27) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.
 (28) McKee, V.; Zvagulis, M.; Dagdigan, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.
 (29) Haddad, M. S.; Wilson, W. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384.
 (30) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228.
 (31) Kahn, O. *Molecular Magnetism*; VCH: Heidelberg, 1993.