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Synthesis, Structure, and Properties of a Tetrametallic Ferrocenecarboxylato-Bridged Copper(II) Complex

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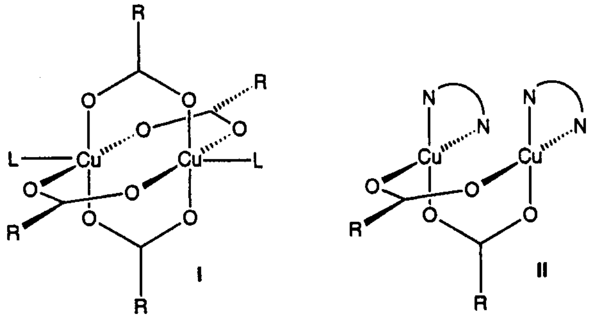
Introduction

Dinuclear copper(II) complexes have been early studied as useful models to establish magnetostructural correlations for spin exchange between metal ions.[1−3] Among them, copper(II) carboxylate adducts are one of the most extensively studied systems due to the limited variations observed in their tetra-bridged [Cu$_2$(μ-OOCR)$_4$L$_2$] cagelike core (Chart 1, **I**) when R and/or L are changed.[4−6] However, doubly *O,O′*-carboxylato-bridged dicopper(II) systems of magnetic and/or biological interest[7−25] are less common and most of them can be visualized as derived from the [Cu$_2$(μ-OOCR)$_4$] fragment either by replacement of two bridging carboxylato ligands by one monodentate O-donor group, giving [Cu$_2$(μ-OOCR)$_2$(μ-OR′)]$^{m+}$ species or by the incorporation of N-donor groups, producing [Cu$_2$(μ-OOCR)$_2$(NR″)$_y$]$^{m+}$ cores.[15−25] In the latter case, when the ligands are aromatic bidentate N-heterocycles, they tend to ocupy the basal positions of the square-pyramidal copper(II) environments (Chart 1, **II**):

Chart 1



On the other hand, despite a wide variery of transition metal complexes containing ferrocene derivatives that have been described in recent years,[26−30] examples of ferrocenecarboxylate anions acting as ligands are scarce.[31−36] Only three such compounds contain ferrocenecarboxylate as an *O,O′*-bridging ligand, leading to dimeric tetrabridged [M$_2$(μ-OOCFc)$_4$] cores [Fc = {(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$)} and M = Cu^{II}, Mo^{II}].[35,36] As far as we know, no examples of copper(II) compounds containing open-cage-like skeletons [Cu$_2$(μ-OOCFc)$_x$(L)$_y$]$^{m+}$ with $x < 4$ have been described so far.

On these bases, it seemed interesting to incorporate bulky ferrocenecarboxylato groups as bridging ligands into the [Cu$_2$(μ-OOCR)$_2$(L)$_y$]$^{m+}$ moieties and to study their influence upon the properties of this sort of dinuclear copper(II) complex. In this paper, we report the synthesis, the X-ray crystal structure, and the study of the magnetic and electrochemical behaviors of the first tetrametallic compound containing a [Cu$_2$(μ-OOCFc)$_2$(bpy)$_2$]$^{2+}$ core.

Experimental Section

Materials. Ferrocenecarboxylic acid, 2,2′-bipyridine (bpy), and Cu(ClO$_4$)$_2$·6H$_2$O were purchased from Aldrich and used as received. Na-

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(1) Willet, R. D.; Gatteschi, D.; Kahn, O. *Magneto-Structural Correlations in Exchange Coupled Systems*; Reidel: Dordrecht, The Netherlands, 1985; Vol. C140.
(2) Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. *Magnetic Molecular Materials*; Plenum: New York, 1991; Vol. E198.
(3) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
(4) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 1981.
(5) Hathaway, B. J. *Comprenhensive Coordination Chemistry*; Pergamon Press: Oxford, U.K., 1987.
(6) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *45*, 42.
(7) Porter, L. C.; Doedens, R. J. *Inorg. Chem.* **1985**, *24*, 1006.
(8) Tokii, T.; Nagamatsu, M.; Hamada, H.; Nakashima, M. *Chem. Lett.* **1992**, 1091.
(9) Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 3657.
(10) Christou, G.; Perlepes, S. P.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1990**, 746.
(11) Bertoncello, K.; Fallon, G. D.; Hodgkin, J. H.; Murray, K. S. *Inorg. Chem.* **1988**, *27*, 4750.
(12) Matsushima, H.; Koikawa, M.; Nakashima, M.; Tokii, T. *Chem. Lett.* **1995**, 869.
(13) Nishida, Y.; Tokii, T.; Mori, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 675.
(14) Perlepes, S. P.; Huffman, J. C.; Christou, G.; Paschalidou, S. *Polyhedron* **1995**, *14*, 1073.
(15) Colacio, E.; Dominguez-Vera, J.-M.; Kivekas, R.; Ruiz, J. *Inorg. Chim. Acta* **1994**, *218*, 109.
(16) Dung, N.-H.; Viossat, B.; Busnot, A.; Zafra, A. G. S.; Perez, J. M. G.; Gutierrez, J. N. *Inorg. Chim. Acta* **1990**, *169*, 9.
(17) Yawney, D. B. W.; Moreland, J. A.; Doedens, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 1164.
(18) Peng, S. M.; Lai, C. H. *J. Chin. Chem. Soc.* **1988**, *35*, 325.
(19) Dubler, E.; Häring, U. K.; Scheller, K. H.; Baltzer, P.; Sigel, H. *Inorg. Chem.* **1984**, *23*, 3785.
(20) Tokii, T.; Watanabe, N.; Nakashima, M.; Muto, Y.; Morooka, M.; Ohba, S.; Satto, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 364.
(21) Battaglia, P. L.; Bonamatini, A. C.; Lanelli, S.; Zoroddu, M. A.; Sanna, G. *J. Chem. Soc., Faraday Trans.* **1991**, 3863.
(22) Peng, S.-M.; Chen, H.-F. *Bull. Inst. Chem. Acad. Sin.* **1990**, *37*, 49.
(23) Meenakumari, S.; Chrakravarty, A. *Polyhedron* **1993**, *12*, 347.
(24) Mikuriya, M.; Kida, S.; Ueda, I.; Tokii, T.; Muto, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2464.
(25) Perlepes, S. P.; Huffman, J. C.; Christou, G. *Polyhedron* **1992**, *11*, 1471.
(26) Togni, A.; Hayashi, T. *Ferrocenes, Homogeneous Catalysis, Organic Synthesis. Material Science*; VCH: Weinheim, Germany, 1995.
(27) Benito, A.; Martínez-Mañez, R.; Payá, J.; Soto, J.; Tendero, M. J. L.; Sinn, E. *J. Organomet. Chem.* **1995**, *503*, 251.
(28) Benito, A.; Cano, J.; Martínez-Mañez, R.; Soto, J.; Payá, J.; Lloret, F.; Julve, M.; Faus, J.; Marcos, M. D. *Inorg. Chem.* **1993**, *32*, 1197.
(29) Bracci, M.; Ercolani, C.; Floris, B.; Basseti, M.; Chesi-Vila, A.; Guastini, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1357.
(30) Cano, J.; Benito, A.; Martínez-Mañez, R.; Soto, J.; Paya, J.; Lloret, F.; Julve, M.; Marcos, M. D. *Inorg. Chim. Acta* **1995**, *231*, 4556.
(31) Abuhijleh, A. L.; Woods, C. *J. Chem. Soc., Dalton Trans.* **1992**, 1249.
(32) Abuhijleh, A. L.; Pollitte, J.; Woods, C. *Inorg. Chim. Acta* **1994**, *215*, 131.
(33) Christie, S. D.; Subramanian, S.; Thompson, L. K.; Zaworotko, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2563.
(34) Lee, S.-M.; Cheung, K.-K.; Wong, W.-T. *J. Organomet. Chem.* **1996**, *506*, 77.
(35) Cotton, F. A.; Falvello, L. R.; Reid, A. H.; Tocher, J. H. *J. Organomet. Chem.* **1987**, *319*, 87.
(36) Churchill, M. R.; Li, Y.-J.; Nalewajer, D.; Schaber, P. M.; Dorfman, P. M. *Inorg. Chem.* **1985**, *24*, 2684.

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{87}H_{68}Cl_4Cu_4Fe_4N_8O_{29}$
fw	2308.85
space group	$P\bar{1}$ (No. 2)
a, Å	11.978(3)
b, Å	19.563(4)
c, Å	21.060(6)
α, deg	106.06(2)
β, deg	102.35(2)
γ, deg	90.55(2)
V, Å^3	4620(2)
Z	2
T, °C	20(2)
λ, Å	0.710 69
ρ_{calcd}, g cm^{-3}	1.660
μ(Mo Kα), cm^{-1}	1.711
R1(obs reflns)^a	0.079
wR2(all reflns)^b	0.229

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

[FcCOO] was prepared as described previously.[37] The organic solvents used in this work (CH_3OH and CH_3CN) were HPLC grade.

Safety Note: *Caution!* Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be handled, and this should be done with caution.

Preparation of $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2](ClO_4)_2\cdot{}^3/_2CH_3OH\cdot H_2O$ (1). A solution containing 156 mg (1 mmol) of bpy and 15 cm^3 of methanol was added slowly to a solution formed by $Cu(ClO_4)_2\cdot 6H_2O$ (370 mg, 1 mmol) and 5 cm^3 of methanol with continuous stirring at room temperature. The bluish precipitate formed during this period was dissolved by dropwise addition of water over the warmed reaction mixture. Afterward, 251 mg (1 mmol) of Na[FcCOO] dissolved in 10 cm^3 of methanol was added. The resulting deep green solution was stirred at room temperature for 10 min and filtered. Slow evaporation of the filtrate at ca. 20 °C produced green monocrystals of **1**. Anal. Calcd (found) for $C_{87}H_{84}Cl_4Cu_4Fe_4N_8O_{29}$: C, 44.94 (44.9); H, 3.64 (3.5); N, 4.82 (4.8); Cl, 6.10 (6.3).

Measurements. Elemental analyses (C, H, N, Cl) were carried out at the Institut de Química Bio-Orgànica, CSIC (Barcelona). The mass spectrum of an acetonitrile solution of **1** was recorded on a VG-QUATTRO spectrometer using the FAB(+) technique with NBA as a matrix. Susceptibility measurements were carried out in the 4−300 K temperature range on a polycrystalline sample of **1** with a pendulum type magnetometer (Manics-DSM8) equipped with a helium continuous-flow cryostat and a Drusch-EAF-16UE electromagnet. The measuring magnetic field was 1.58 T, and diamagnetic corrections were estimated from Pascal's constants. The EPR spectra of compound **1** were recorded at X-band frequencies (9.78 GHz) with a Bruker ES-200 spectrometer in the temperature range 4−298 K. Cyclic voltammograms were obtained on a VERSSTAT potentiostat under argon at 25 °C, using acetonitrile as solvent and $[Bu_4N][PF_6]$ (0.1 mol dm^{-3}) as supporting electrolyte. The potentials were referred to an Ag−$AgNO_3$ (0.1 mol dm^{-3}) electrode separated from the solution by a medium-porosity fritted disk. A platinum-wire auxiliary electrode was used in conjunction with a platinum-disk working electrode and a TACUSSEL-EDI rotatory electrode (3.14 mm^2). A cyclic voltammogram of a freshly prepared (10^{-2} mol dm^{-3}) solution of **1** in CH_3CN was recorded at 0.1 V s^{-1} in the 0.8 to −1.8 V range, and the values of the measured potentials were afterward referred to the ferrocene−ferrocenium couple, which was used as the internal reference ($E_{1/2} = 53$ mV versus Ag/$AgNO_3$ and $\Delta E = 90$ mV).

X-ray Structure Determination. A green prismatic crystal of **1** (dimensions 0.40 × 0.19 × 0.15 mm) was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Crystal data are reported in Table 1. Unit cell parameters were determined from the automatic centering of 25 reflections in the range $9° < \theta < 17°$ and refined by least-squares methods. The complex **1** was found to crystallize in the triclinic system. Intensities were collected with graphite-monochromated Mo Kα radiation using the $\omega - 2\theta$ scan technique with a θ range of 1.0−25.0°. Three reflections were measured every hour as intensity controls, and no significant intensity decay was observed. A ψ-scan absorption correction was attempted, but it led to a slightly worse R_{int} value; therefore, no correction was finally applied ($\mu R_{max} < 0.08$). A total of 17 239 reflections were collected (16 176 unique, $R_{int} = 0.0582$). The structure was solved by direct methods with the SHELXS-86[38] computer program and refined by full-matrix least-squares methods using the SHELXL-93[39] computer program. The function minimized was $\sum w(|F_o|^2 - |F_c|^2)$ where $w = [\sigma^2(|F_o|^2) + (0.1281P)^2 + 0.0000P]^{-1}$ and $P = [(|F_o|^2 + 2|F_c|^2)/3]$. f, f', and f'' were obtained from the literature.[40] Thermal motions of non-hydrogen atoms were refined anisotropically; H atoms were positioned at calculated distances and refined with a global isotropic thermal factor. The final R factors were R1 = 0.079 and wR2 = 0.196 for $I > 2\sigma(I)$, and the goodness-of-fit was 0.968. A selection of bond lengths and angles is given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cations **A** and **B** of Compound **1** with Their Estimated Standard Deviations in Parentheses

cation **A**		cation **B**	
Cu(1)−O(1)	1.914(6)	Cu(1′)−O(1′)	1.949(6)
Cu(1)−O(3)	1.941(6)	Cu(1′)−O(3′)	1.940(6)
Cu(1)−N(12)	2.003(7)	Cu(1′)−N(12′)	2.008(8)
Cu(1)−N(21)	2.002(7)	Cu(1′)−N(21′)	1.992(8)
Cu(1)−O(14)	2.408(9)	Cu(1′)−O(1M′)	2.174(9)
Cu(2)−O(2)	1.951(6)	Cu(2′)−O(2′)	1.950(7)
Cu(2)−O(4)	1.928(7)	Cu(2′)−O(4′)	1.949(7)
Cu(2)−N(33)	2.016(7)	Cu(2′)−N(33′)	2.000(8)
Cu(2)−N(42)	1.986(7)	Cu(2′)−N(42′)	1.991(8)
Cu(2)−O(2M)	2.219(8)	Cu(2′)−O(2M′)	2.194(8)
O(1)−C(1)	1.252(12)	O(1′)−C(1′)	1.250(11)
O(2)−C(1)	1.271(12)	O(2′)−C(1′)	1.628(11)
O(3)−C(22)	1.231(11)	O(3′)−C(22′)	1.250(11)
O(4)−C(22)	1.262(11)	O(4′)−C(22′)	1.247(11)

cation **A**		cation **B**	
N(12)−Cu(1)−N(21)	80.6(3)	N(12′)−Cu(1′)−N(21′)	80.7(3)
N(12)−Cu(1)−O(3)	92.6(3)	N(12′)−Cu(1′)−O(3′)	93.8(3)
O(1)−Cu(1)−O(3)	94.2(7)	O(1′)−Cu(1′)−O(3′)	87.3(3)
O(1)−Cu(1)−N(21)	92.7(3)	O(1′)−Cu(1′)−N(21′)	96.1(3)
N(12)−Cu(1)−O(14)	84.5(3)	N(12′)−Cu(1′)−O(1M′)	97.2(3)
N(21)−Cu(1)−O(14)	86.5(3)	N(21′)−Cu(1′)−O(1M′)	98.8(3)
N(33)−Cu(2)−N(42)	80.7(3)	N(33′)−Cu(2′)−N(42′)	92.9(3)
N(33)−Cu(2)−O(4)	92.2(3)	N(33′)−Cu(2′)−O(4′)	91.6(3)
O(2)−Cu(2)−O(4)	92.2(3)	O(2′)−Cu(2′)−O(4′)	94.2(3)
N(33)−Cu(2)−O(2M)	101.2(3)	N(33′)−Cu(2′)−O(2M′)	95.7(3)
N(42)−Cu(2)−O(2M)	90.4(3)	N(42′)−Cu(2′)−O(2M′)	93.3(4)
O(1)−C(1)−O(2)	127.0(9)	O(1′)−C(1′)−O(2′)	125.3(9)
O(3)−C(22)−O(4)	126.2(9)	O(3′)−C(22′)−O(4′)	126.7(9)
C(1)−O(1)−Cu(1)	135.0(6)	C(1′)−O(1′)−Cu(1′)	120.1(6)
C(22)−O(3)−Cu(1)	128.8(7)	C(22′)−O(3′)−Cu(1′)	123.8(6)
C(1)−O(2)−Cu(2)	118.8(7)	C(1′)−O(2′)−Cu(2′)	133.6(6)
C(22)−O(4)−Cu(2)	129.8(6)	C(22′)−O(4′)−Cu(2′)	133.6(6)

Results and Discussion

Description of the Structure. The crystal structure of **1** reveals that this compound should be formulated as $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(ClO_4)(CH_3OH)][Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(CH_3OH)_2]\ (ClO_4)_3\cdot CH_3OH$ since it consists of two different doubly bridged dimeric copper(II) cations $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(ClO_4)(CH_3OH)]^+$, **A** (Figure 1), and $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(CH_3OH)_2]^{2+}$, **B** (Figure 2), three ClO_4^- anions, and a methanol crystallization molecule. Both cations contain the [Cu_2{(μ-

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(37) *Gmelins* **1976**, *A3*, 58.

(38) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467.

(39) Sheldrick, G. M. *SHELXL-93: A Computer Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(40) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99, 100, 149.

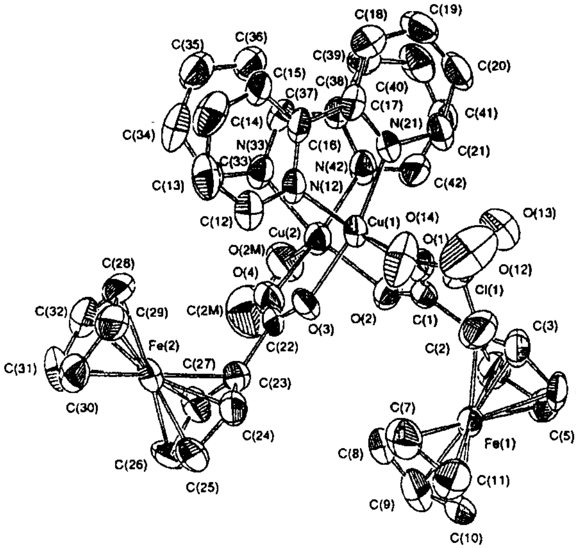

Figure 1. Molecular structure and atom-labeling scheme for $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(ClO_4)(CH_3OH)]^+$, cation **A**.

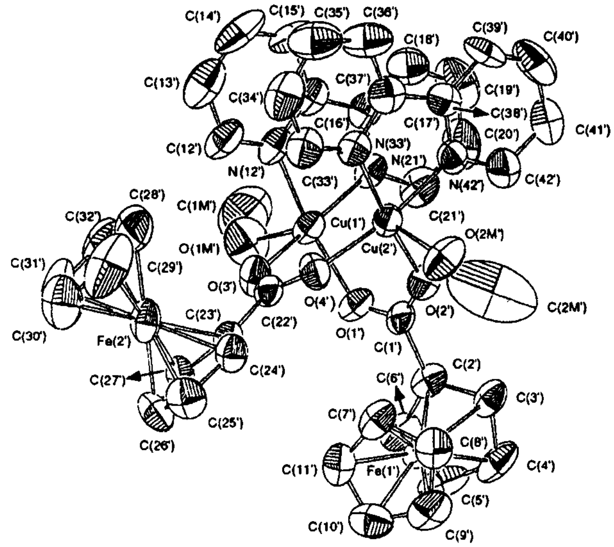

Figure 2. Molecular structure and atom-labeling scheme for $[Cu_2(\mu\text{-}OOCFc)_2(bpy)_2(CH_3OH)_2]^{2+}$, cation **B**.

OOCFc-*O,O′*)}$_2$]$^{2+}$ core where the bridging ligands adopt the syn,syn configuration. The central portions of cations **A** and **B** can be recognized as derived from the $[Cu_2(\mu\text{-}OOCFc)_4(thf)_2]\cdot$thf complex described by Churchill et al.[36] where two contiguous bridging ferrocenecarboxylate groups have been replaced by two chelating bpy ligands. The Cu···Cu intradimer distances are 3.102(5) Å in **A** and 3.061(5) Å in **B**.

The copper atoms have a five-coordinate square-pyramidal environment with a slight trigonal-bipyramidal distortion. The basal plane is defined by two oxygen atoms from two distinct ferrocenecarboxylato groups and two nitrogen atoms from the chelating bpy ligands. The copper atoms are displaced from the basal coordination planes toward the apical position by 0.13 Å for Cu(1) and 0.16 Å for Cu(2) in **A** and by 0.19 Å for Cu(1′) and 0.09 for Cu(2′) in **B**. The apical positions are occupied in cation **A** by one ClO_4^- anion (Cu(1)−O(14) = 2.408(9) Å) and a CH_3OH molecule (Cu(2)−O(2M) = 2.219(8) Å) and in cation **B** by two methanol-solvating molecules (Cu(1′)-O(1M′) = 2.174(9) Å and Cu(2′)-O(2M′) = 2.194(8) Å). In the two cations, the fragments Cu−O−C−O−Cu are nearly planar and their relative orientation is close to the ideal orthogonal, with angles between their mean planes of 95.17 ° in **A** and 91.55 ° in **B**.

The carboxylate groups, with bite angles ranging from 125.3 to 127.0°, are not strictly coplanar with the C_5H_4 rings (angles varying from 7.0 to 1.6° in **A** and from 18.4 to 11.0° in **B**). The average Fe−C_{ring} and C−C_{ring} bond lengths of the ferrocenyl units are similar to those reported in the literature.[41] In each ferrocenyl moiety, the pentagonal rings are planar and nearly parallel (tilt angles 1.5 and 6.0° in cation **A** and 2.0 and 0.1° in **B**) and the twist angles are 21.4° for Fe(1) and 6.0° for Fe(2) in **A** and 10.7° for Fe(1′) and 34.1° for Fe(2′) in **B**. In each cation, the two ferrocenyl fragments are nearly orthogonal. Direct interaction between the Cu and Fe atoms is ruled out since they are more than 5.2 Å apart.

The minimum and maximum distances between main planes of the bpy ligands fall in the ranges 3.14−3.45 Å in **A** and 3.20−3.70 Å in **B**, and their two mean planes form angles of 2.6 and 6.2° in **A** and **B**, respectively. These facts suggest that there is a significant intradimer π-stacking interaction between the bpy ligands. According to the literature, the presence of aromatic N-donor heterocycles in such complexes leads to a syn,syn conformation of the carboxylato bridges[18−25] and, with only one exception where the ligands act as bridges,[18] they show aromatic ring−ring interactions. The conjunction of these two structural factors enhances the formation and the stability of these dinuclear complexes. It is worth noting that intramolecular stacks between such aromatic rings are of great interest since they are present in a number of complexes of biological interest.[42,43]

Magnetic and Electrochemical Studies. Susceptibility measurements for **1** in the 300−4 K temperature range show a room-temperature $\chi_M T$ value of 0.78 cm^3 K mol^{-1} that continuously decreases on cooling to reach a $\chi_M T$ product of 0.005 cm^3 K mol^{-1} at 4 K. This behavior indicates a strong antiferromagnetic superexchange between the two Cu(II) ions inside each dinuclear unit, where no contribution of the ferrocene moiety was observed. To evaluate the coupling constant, the experimental data were fitted using the Bleaney−Bowers[44] expression. As there is no unambiguous way to separate the exchange contributions of each cation, the assumption of similar coupling constants was imposed in the calculations. Minimization of the error function $R = \sum\{[(\chi_M T)_{calc} - (\chi_M T)_{exp}]^2/(\chi_M T)_{exp}{}^2\}$ up to 1.7×10^{-4} leads to an average singlet−triplet gap of −81 cm^{-1} and a mean g_{iso} of 2.16. These values, which agree with those reported for dibridged acetato homologues,[20] are clearly smaller than those obtained for the cage complexes $[Cu_2(\mu\text{-}OOCR)_4L_2]$, which show a more intense coupling (from −280 to −350 cm^{-1}). This fact can be justified by the presence of two additional bridging ligands to transmit the superexchange interactions and a strict square-planar geometry of the Cu(II) ions, which favors the overlap between the magnetic orbitals.

The polycrystalline X-band EPR spectra confirm magnetic data because they show a triplet pattern of axial symmetry ($g_\perp = 2.07$, $g_\| \approx 2.25$, $D = 0.13$ cm^{-1}, and a half-field signal at 1480 G) that vanishes at low temperatures. When the powder is dissolved in acetonitrile, the EPR spectrum of the frozen solution displays the same resonances and behavior, but two new features appear: (a) The 1480 G signal is resolved in seven

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(41) Allen, T. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8*, 146.
(42) Fischer, B. E.; Sigel, H. *J. Am. Chem. Soc.* **1980**, *102*, 2998.
(43) Sigel, H.; Fischer, B. E.; Farkas, E. *Inorg. Chem.* **1983**, *22*, 925.
(44) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

Scheme 1

$$\{[(\mathrm{MeOH})(\mathrm{bpy})\mathrm{Cu}](\mu\text{-}\mathrm{OOCFc})_2[\mathrm{Cu}(\mathrm{bpy})(\mathrm{ClO_4})]\}^+ \ (\mathbf{A}) \rightleftharpoons [\mathrm{Cu}(\mathrm{bpy})(\mathrm{FcCOO})(\mathrm{MeOH})]^+ \ (\mathbf{C}) + [\mathrm{Cu}(\mathrm{bpy})(\mathrm{FcCOO})(\mathrm{ClO_4})] \ (\mathbf{D})$$

$$\{[(\mathrm{MeOH})(\mathrm{bpy})\mathrm{Cu}](\mu\text{-}\mathrm{OOCFc})_2[\mathrm{Cu}(\mathrm{bpy})(\mathrm{MeOH})]\}^{2+} \ (\mathbf{B}) \rightleftharpoons 2\ [\mathrm{Cu}(\mathrm{bpy})(\mathrm{FcCOO})(\mathrm{MeOH})]^+ \ (\mathbf{C})$$

hyperfine lines ($A \approx 75$ G). This fact can be interpreted as the coupling with the two equivalent Cu nuclei ($I = {}^3/_2$) of the cations, confirming that their dinuclear structure is preserved in solution. (b) A new strong signal typical of an isolated Cu(II) ion appears ($g_\perp = 2.07$, $g_\parallel = 2.25$, and four hyperfine coupling lines with $A_\parallel \approx 170$ G), and it does not vanish at 4 K. This finding can be explained by the assumption of equilibrium processes in which the dimeric units dissociate partially into their mononuclear constituents (see Scheme 1). This argument is supported by mass spectrometry analysis of the acetonitrile solution, where two main peaks are detected: one at m/e 995, which corresponds to cation **A** minus MeOH, and a 4 times more intense peak at m/e 448, which can be attributed to the sum of **B** + **C** cations which have also lost their coordinated methanol. The persistence in solution of the perchlorate−copper bond in **A** led us suggest the existence of the neutral species **D** in solution, although it is not detected in the MS experiment probably due to a lack of ionization under those conditions.

The cyclic voltammogram of **1** in the anodic zone displays one signal with a directly associated peak in the reverse scan ($E_{1/2} = 0.18$ V, $\Delta E = 0.10$ V) which is assigned to the envelope of the Fe(II) → Fe(III) redox processes of the coordinated ferrocenecarboxylato groups. When the cyclic voltammogram was recorded in the cathodic area, two irreversible reduction peaks were detected at −1.00 and −1.25 V. This redox behavior differs from that reported by Christou et al.[45] for a related acetato dimer, which exhibits a unique quasi-reversible cathodic process due to the reduction of Cu(II) to Cu(I) at ca. −0.73 V. Due to the complex equilibria detected, we are unable to assign these signals, although they seem to be attributable to the reduction of the coordinated Cu(II) ions of some of the mono- and dinuclear species present in solution. These results suggest that the replacement of the acetato bridges by ferrocenecarboxylato bridges modifies significantly the tendency of the Cu(II) ions to undergo reduction.

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Supporting Information Available: An additional ORTEP diagram of the cores of the two cations of **1** showing the stacking interactions (Figure S1), a plot of the computer fit of $\chi_M T$ vs T (Figure S2), X-band EPR spectra of polycrystalline sample and a frozen solution of **1** (Figure S3), and cyclic voltammograms of an acetonitrile solution of **1** in the anodic zone and in the reduction scan (Figure S4) (5 pages). An X-ray crystallographic file for **1**, in CIF format, is available on the Internet only. Ordering and access information is given on any current masthead page.

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(45) Perlepes, S. P.; Libby, E.; Streib, W. E.; Folting, K.; Christou, G. *Polyhedron* **1992**, *11*, 923.