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Preparation, Crystal and Molecular Structure, and Properties of Tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II). A Structure Containing both Eclipsed and Staggered Ferrocenyl Fragments

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Reaction of copper(II) acetate monohydrate, $Cu(CH_3CO_2)_2\cdot H_2O$, with ferrocenecarboxylic acid gives the antiferromagnetic (μ = 1.20 μ_B/Cu, 293 K) compound tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II). This complex crystallizes from THF as the 1:1 solvate, $Cu_2(O_2C{-}C_5H_4FeC_5H_5)_4(THF)_2\cdot THF$. Crystals belong to the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with a = 9.5837 (15) Å, b = 10.1178 (19) Å, c = 13.6314 (33) Å, α = 92.460 (17)°, β = 91.859 (16)°, γ = 104.946 (14)°, V = 1274.6 (4) Å^3 and Z = 1. Diffraction data were collected on a Syntex P2$_1$ automated four-circle diffractometer and were refined to R_F = 7.7% and R_{wF} = 6.3% for all 2346 independent data. The $Cu_2(O_2C{-}C_5H_4FeC_5H_5)_4(THF)_2$ molecule has a crystallographically imposed inversion center and is based on the classical "dimeric cupric acetate dihydrate" structure. The Cu···Cu distance within the $Cu_2(O_2C{-}R)_4(THF)_2$ core is 2.605 (1) Å, the Cu–O(THF) distance is 2.226 (6) Å, and Cu–O(carboxylate) distances are in the range 1.955 (7)–1.982 (6) Å. The "R" groups in the $Cu_2(O_2C{-}R)_4(THF)_2$ molecule are ferrocenyl groups ($-(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$); two of these have an eclipsed conformation and two have a staggered arrangement. Attempts to oxidize this complex electrochemically are discussed.

Introduction

Transition-metal salts of carboxylic acids, particularly those containing Cu(II), are well documented, and reviews dealing with their preparation and magnetic and spectroscopic properties have been reported.[1-4] Our interest in this area lies in the preparation of new ligand–metal complexes containing polynuclear metal centers that might exhibit unusual effects derived from the interaction of neighboring metal sites.

During the course of our synthetic studies, we attempted to obtain information concerning the nature of the interaction of various bridgehead metals with the π network in ferrocenecarboxylic acid and dithiocarboxylic acid derivatives.[5] However, solubility problems and a lack of correspondence between the copper spectral and ESR features prevented us from accurately assessing the role of the ferrocenyl unit on the electron delocalization in the compounds. We have now been successful in isolating single crystals of the title complex. In this paper we discuss the magnetic, electrochemical, and structural features of tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II).

While this work was in progress, a preliminary report of the dimolybdenum complex of ferrocenecarboxylate, $Mo_2[O_2C{-}C_5H_4FeC_5H_5]_4$ appeared.[6] Analogous complexes with W_2^{4+} and Cr_2^{4+} cores have also been prepared as has the trans pyridine adduct, $Mo_2(O_2C{-}C_5H_4FeC_5H_5)_2(CH_3CO_2)_2\cdot 2C_5H_5N$.[7]

Experimental Section

Tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II). A solution of ferrocenecarboxylic acid (2 g, 8.69 mmol) in 25 mL of THF was mixed with a solution of $Cu(CH_3CO_2)_2\cdot H_2O$ (0.87 g, 4.35 mmol) in 25 mL of THF. A green precipitate formed after 15 min. After the mixture was stirred for an additional 3 h, the microcrystalline precipitate was collected by filtration and washed with three 25-mL portions of THF. After drying at ambient temperature, 2.4 g (88%) of the complex $Cu_2(O_2C{-}C_5H_4FeC_5H_5)_4(THF)_2\cdot THF$ was isolated; mp > 250 °C. IR (KBr): ν_{COOH} 1570 cm^{-1}. UV-VIS: 705 nm (ϵ 250 M^{-1} cm^{-1}), 430 nm (ϵ 860 M^{-1} cm^{-1}), 35 nm (sh). Anal. Calcd for $C_{56}H_{60}O_{11}Cu_2Fe_2$: C, 53.40; H, 4.80; Cu, 10.09. Found: C, 53.60; H, 4.69; Cu, 10.50.

A second product tentatively assigned as the partially substituted complex $Cu_2(O_2C{-}C_5H_4FeC_5H_5)_2(CH_3CO_2)_2(THF)_2$ was isolated from the intensely green filtrate. The purification and characterization of this complex is still under investigation.

Table I. Experimental Data for the X-ray Diffraction Study of $Cu_2(O_2C{-}C_5H_4FeC_5H_5)_4(THF)_2\cdot THF$

(A) Crystallographic Parameters

cryst syst: triclinic	a = 9.5837 (15) Å
space group: $P\bar{1}$ (No. 2)	b = 10.1178 (19) Å
Z = 1	c = 13.6314 (33) Å
formula: $C_{52}H_{52}O_{10}Cu_2Fe_4\cdot(C_4H_8O)$	α = 92.460 (17)°
mol wt = 1259.6	β = 91.859 (16)°
D(calcd) = 1.641 g cm^{-3}	γ = 104.946 (14)°
T = 23 °C (296 K)	V = 1274.6 (4) Å^3

(B) Data Collection

diffraction: Syntex P2$_1$
radiation: Mo K$\bar{\alpha}$ ($\bar{\lambda}$ 0.710730 Å)
monochromator: pyrolytic graphite, equatorial geometry, 2θ(m) = 12.2°; assumed 50% perfect
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan width: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
bkgd measurements: stationary cryst, stationary counter at the extremities of each 2θ scan; each for half of total scan time
std reflcns: 3 approximately orthogonal check reflections were remeasured after each 97 reflections. A significant amount of decay was noted (to 70% of initial intensity) and was corrected for
reflcns collcd: one-half shell (i.e., $+h,\pm k,\pm l$) for 2θ = 4.0°–40.0°; 2370 total reflections were merged to 2356 unique data
abs correction: μ(Mo Kα) = 20.5 cm^{-1}; empirical correction applied

Collection of X-ray Data. Black-green crystals suitable for X-ray analysis were grown by slowly diffusing 1:2 molar solutions of $Cu(CH_3CO_2)_2\cdot H_2O$ and $C_5H_5FeC_5H_4CO_2H$ in a three-chamber apparatus.[8,9]

The crystal selected for the X-ray diffraction study (dimensions 0.27 × 0.20 × 0.13 mm) was sealed into a 0.2-mm-diameter thin-walled glass capillary, which was then set into an aluminum pin (with beeswax) on an eucentric goniometer and mounted on the Syntex P2$_1$ automated four-circle diffractometer at SUNY—Buffalo. All subsequent setup operations (determination of unit cell parameters and the crystal's ori-

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Table II. Atomic Coordinates for $Cu_2(O_2C–C_5H_4FeC_5H_5)_4(THF)_2·THF$

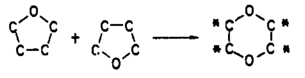
(A) Atoms in Dicopper–Tetrairon Complex[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	*B*, Å²
Cu	0.53825 (12)	0.38628 (10)	−0.01374 (7)	C(27)	0.1291 (15)	0.1659 (11)	0.31871 (73)	
Fe(1)	0.79863 (16)	0.64176 (14)	0.34126 (9)	C(28)	0.2447 (12)	0.2689 (12)	0.28423 (71)	
Fe(2)	0.05776 (15)	0.25715 (13)	0.20347 (9)	C(29)	0.2077 (13)	0.3915 (11)	0.29314 (71)	
O(11′)	0.48440 (67)	0.41174 (64)	−0.15194 (39)	H(1A)	0.4044	0.0340	−0.0618	6.0
O(12)	0.58700 (68)	0.39590 (60)	0.12795 (41)	H(1B)	0.4001	0.1307	−0.1466	6.0
O(21′)	0.73198 (62)	0.50162 (63)	−0.03387 (41)	H(2A)	0.4680	−0.0210	−0.2346	6.0
O(22)	0.33583 (72)	0.30288 (59)	0.01178 (42)	H(2B)	0.5273	−0.0796	−0.1436	6.0
O(1)	0.58060 (76)	0.18815 (56)	−0.06289 (41)	H(3A)	0.6744	0.1174	−0.2562	6.0
C(O1)	0.5708 (10)	0.4940 (11)	0.18086 (63)	H(3B)	0.7382	0.0309	−0.1843	6.0
C(O2)	0.2459 (10)	0.3679 (10)	0.03157 (59)	H(4A)	0.7248	0.2787	−0.1541	6.0
C(1)	0.4598 (11)	0.0875 (10)	−0.10958 (76)	H(4B)	0.7836	0.1906	−0.0809	6.0
C(2)	0.5234 (18)	0.0018 (13)	−0.1744 (10)	H(11)	0.5247	0.6551	0.3496	6.0
C(3)	0.6709 (17)	0.0846 (16)	−0.1918 (11)	H(12)	0.6532	0.6231	0.5089	6.0
C(4)	0.7029 (12)	0.1951 (11)	−0.12170 (86)	H(13)	0.7937	0.4473	0.4753	6.0
C(10)	0.6144 (10)	0.50402 (89)	0.28487 (63)	H(14)	0.7498	0.3706	0.2958	6.0
C(11)	0.5838 (11)	0.5939 (10)	0.35827 (71)	H(15)	0.8475	0.7472	0.1658	6.0
C(12)	0.6567 (13)	0.5766 (12)	0.44744 (69)	H(16)	0.7907	0.9004	0.3001	6.0
C(13)	0.7349 (13)	0.4786 (12)	0.42905 (77)	H(17)	0.3244	0.8653	0.4527	6.0
C(14)	0.7093 (12)	0.43566 (95)	0.32876 (69)	H(18)	1.0698	0.6989	0.4150	6.0
C(15)	0.8872 (14)	0.7586 (13)	0.23140 (79)	H(19)	1.0359	0.6366	0.2325	6.0
C(16)	0.8533 (13)	0.8418 (10)	0.30589 (89)	H(21)	0.1137	0.0852	0.0639	6.0
C(17)	0.9285 (16)	0.8222 (12)	0.38992 (81)	H(22)	−0.1375	0.0295	0.1238	6.0
C(18)	1.0105 (14)	0.7308 (15)	0.36941 (94)	H(23)	−0.2209	0.2432	0.1412	6.0
C(19)	0.9897 (15)	0.6942 (13)	0.2687 (11)	H(24)	−0.0186	0.4404	0.0876	6.0
C(20)	0.1020 (11)	0.29295 (92)	0.06020 (59)	H(25)	0.0220	0.4366	0.3477	6.0
C(21)	0.0576 (13)	0.1489 (10)	0.07519 (69)	H(26)	−0.0676	0.1823	0.3746	6.0
C(22)	−0.0826 (13)	0.1184 (10)	0.10929 (70)	H(27)	0.1254	0.0713	0.3209	6.0
C(23)	−0.1300 (11)	0.2369 (12)	0.11884 (66)	H(28)	0.3318	0.2556	0.2594	6.0
C(24)	−0.0164 (12)	0.3472 (10)	0.08871 (65)	H(29)	0.2652	0.4775	0.2749	6.0
C(25)	0.0721 (15)	0.3689 (12)	0.33327 (76)					
C(26)	0.0221 (12)	0.2271 (13)	0.34869 (67)					

(B) Atoms in the THF Molecule of Solvation[b]

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
O(2)	0.4631 (59)	0.0552 (53)	0.4932 (37)		H(6B)	0.5185	0.1523	0.4228	6.0
C(6)	0.5176 (62)	0.1051 (29)	0.4817 (26)		H(7A)	0.3639	0.0105	0.5950	6.0
C(7)	0.3712 (49)	−0.0170 (81)	0.5283 (26)		H(7B)	0.2784	−0.0658	0.5017	6.0
H(6A)	0.5508	0.1694	0.5356	6.0					

[a] The metal complex is centered about the position ($^1/_2$, $^1/_2$, 0); only atoms in the asymmetric unit are defined. Atoms in the other half of the molecule are related to these by the transformation ($1 - x$, $1 - y$, $-z$). [b] The THF molecule is centered about the position ($^1/_2$, 0, $^1/_2$) and is subject to a 2-fold disorder as shown below. Only the oxygen atom and the two "composite carbon atoms" (with calculated hydrogen atom positions) were included. (An asterisk denotes the site of two unresolved half-carbon atoms, termed a "composite carbon atom".)



entation matrix) and data collection were performed as described previously.[10] Details are presented in Table I. No diffraction symmetry other than the Friedel condition was observed, nor were any systematic absences found. The crystal therefore belongs to the triclinic system, the two possible space groups being the noncentrosymmetric $P1$ (C_1^1; No. 1) or the centrosymmetric $P\bar{1}$ (C_i^1; No. 2); the latter was determined as the correct space group via intensity statistics and the successful solution of the structure in the higher symmetry space group. This space group requires that the sole $Cu_2(O_2C–C_5H_4FeC_5H_5)_4(THF)_2$ molecule in the unit cell lie on an inversion center. It also requires that the THF molecule of solvation be disordered about a crystallographic inversion center.

All data were corrected for Lorentz and polarization factors and for the effects of absorption. Redundant data were averaged [$R(I) = 4.2\%$, $R_w(I) = 4.0\%$], and all corrected data were converted to unscaled $|F_o|$ values; these were placed on an approximately absolute scale by means of a Wilson plot.

It should be noted that a substantial decrease in intensity of the check reflections (to 70% of their initial values) occurred during the course of data collection. This was corrected for by use of a linear decay correction. It probably results from loss of THF by the crystal.

Solution and Refinement of the Crystal Structure. All crystallographic calculations were performed by use of the Syntex XTL system (Data General NOVA 1200 computer with parallel floating-point processor, Diablo disk unit, Versatec electrostatic printer/plotter, and the SUNY—Buffalo modified version of the XTL conversational crystallogrpahic program package).[11] The analytical scattering factors[12a] for neutral Cu, Fe, O, C, and H were corrected for both the real ($\Delta f'$) and the imaginary ($\Delta f''$) components of anomalous dispersion.[12b] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma(|F_o|)^2 + 0.015|F_o|^2)^{-1}$. The structure was solved via a three-dimensional Patterson synthesis, which readily yielded the positions of the copper and iron atoms (and confirmed $P\bar{1}$ as the correct space group). All non-hydrogen atoms (including those belonging to a disordered THF molecule of solvation) were located directly via a series of difference-Fourier syntheses. Hydrogen atoms were not located directly but were input in idealized positions (with $B = 6.0$ Å²) based upon d(C–H) = 0.95 Å[13] and the appropriate trigonal-planar (ferrocene moieties) or tetrahedral (THF) stereochemistry about carbon. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with R_F = 7.7%, R_{wF} = 6.3%, and GOF = 2.34 for all 2346 independent data. (R_F = 6.2% and R_{wF} = 6.2% for those 1965 data with $|F_o| > 3.0\sigma(|F_o|)$.)

A final difference-Fourier synthesis showed no significant features save in the vicinity of the disordered THF molecule; the structure is therefore both correct and complete. Final positional parameters are collected in

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Table III. Interatomic Distances (Å) for $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2 \cdot THF$

(A) Copper–Ligand Distances			
Cu–O(11′)	1.982 (6)	Cu–O(21′)	1.956 (6)
Cu–O(12)	1.965 (6)	Cu–O(22)	1.955 (7)
Cu–O(1)	2.226 (6)	Cu···Cu′	2.605 (1)
(B) Iron–Carbon Distances			
Fe(1)–C(10)	2.050 (10)	Fe(2)–C(20)	2.040 (8)
Fe(1)–C(11)	2.014 (11)	Fe(2)–C(21)	2.023 (10)
Fe(1)–C(12)	2.032 (11)	Fe(2)–C(22)	2.047 (11)
Fe(1)–C(13)	2.056 (11)	Fe(2)–C(23)	2.065 (10)
Fe(1)–C(14)	2.037 (9)	Fe(2)–C(24)	2.042 (10)
Fe(1)–C(15)	2.019 (12)	Fe(2)–C(25)	2.040 (11)
Fe(1)–C(16)	2.038 (10)	Fe(2)–C(26)	2.042 (9)
Fe(1)–C(17)	1.998 (12)	Fe(2)–C(27)	2.041 (11)
Fe(1)–C(18)	2.015 (14)	Fe(2)–C(28)	2.046 (11)
Fe(1)–C(19)	2.067 (15)	Fe(2)–C(29)	2.035 (11)
(C) Carbon–Oxygen Distances			
CO(1)–O(11)	1.274 (12)	CO(2)–O(21)	1.281 (11)
CO(1)–O(12)	1.247 (11)	CO(2)–O(22)	1.241 (12)
(D) $O_2C-C_5H_4$ Distances			
CO(1)–C(1O)	1.457 (12)	CO(2)–C(20)	1.467 (14)
(E) Distances within η^5-C_5H_4 Systems			
C(10)–C(11)	1.411 (13)	C(20)–C(21)	1.435 (13)
C(11)–C(12)	1.422 (14)	C(21)–C(22)	1.399 (17)
C(12)–C(13)	1.407 (17)	C(22)–C(23)	1.390 (16)
C(13)–C(14)	1.411 (14)	C(23)–C(24)	1.429 (15)
C(14)–C(10)	1.410 (14)	C(24)–C(20)	1.440 (15)
(F) Distances within η^5-C_5H_5 Systems			
C(15)–C(16)	1.391 (17)	C(25)–C(26)	1.418 (17)
C(16)–C(17)	1.382 (17)	C(26)–C(27)	1.391 (18)
C(17)–C(18)	1.386 (20)	C(27)–C(28)	1.419 (17)
C(18)–C(19)	1.401 (19)	C(28)–C(29)	1.377 (16)
C(19)–C(15)	1.405 (20)	C(29)–C(25)	1.394 (19)
(G) Distances within the THF Ligand			
O(1)–C(1)	1.439 (12)	C(3)–C(4)	1.404 (19)
C(1)–C(2)	1.464 (18)	C(4)–O(1)	1.430 (13)
C(2)–C(3)	1.478 (24)		

Table II; anisotropic thermal parameters are deposited in Table II-S (supplemental material).

Results and Discussion

Tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II). When 1:2 molar THF solutions of $Cu(CH_3CO_2)_2 \cdot H_2O$ and $C_5H_5FeC_5H_4CO_2H$ were allowed to diffuse, black-green prisms of tetrakis(ferrocenecarboxylato)bis(tetrahydrofuran)dicopper(II), $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2 \cdot THF$, were isolated as the 1:1 solvate in 88% yield. Magnetic and spectroscopic examination gave results consistent with the formation of a bridged dinuclear species. The magnetic moment of 1.20 μ_B/Cu is significantly reduced from the spin-only value of 1.83 μ_B indicative of antiferromagnetic coupling. This type of behavior has been observed for most of the classical $Cu_2(CH_3CO_2)_4(H_2O)_2$ structures and their adducts. A comprehensive study of the magnetic behavior and semiempirical MO calculation is currently being performed, and the results will be forthcoming.

Attempts to oxidize this complex electrochemically in a stepwise fashion were also carried out. Electrochemical studies of $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2 \cdot THF$ were performed in Me_2SO as appreciable solubility (~4 mM) could only be obtained in this solvent system. Cyclic voltammograms taken at 100 mV/s revealed an irreversible reduction at ca. −1.0 V (vs. SCE). This $E_{p,c}$ value most likely corresponds to the Cu(II)/Cu(I) couple. Oxidative scans revealed processes corresponding to $E_{p,a} = +0.20$ and +0.62 V, the latter approaching a reversible wave ($i_c/i_a \simeq 1$).

The process at +0.62 V resembles that of ferrocene and is tentatively ascribed to the ferrocenyl groups. The quasi-reversible oxidative process at ca. +0.20 V shows a corresponding weak reduction wave on return scans at ca. −0.10 V. The origin of this process is not apparent but the actual value (+0.20 V vs. SCE) suggests that chemical oxidation should be feasible. The possibility of isolating mixed-valence oxidation products of the title compound is exciting; further experiments are in progress.

Table IV. Selected Interatomic Angles (deg) for $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2 \cdot THF$

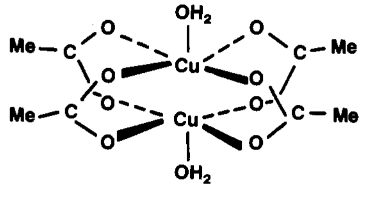
(A) Angles around the Copper Atom			
Cu′···Cu–O(1)	169.6 (2)	O(11′)–Cu–O(12)	169.2 (3)
Cu′···Cu–O(11′)	81.5 (2)	O(11′)–Cu–O(21′)	88.6 (3)
Cu′···Cu–O(12)	87.8 (2)	O(11′)–Cu–O(22)	90.6 (3)
Cu′···Cu–O(21′)	86.4 (2)	O(12)–Cu–O(21′)	89.2 (3)
Cu′···Cu–O(22)	83.1 (2)	O(12)–Cu–O(22)	89.7 (3)
O(1)–Cu–O(11′)	88.7 (2)	O(21′)–Cu–O(22)	169.5 (3)
O(1)–Cu–O(12)	102.1 (2)		
O(1)–Cu–O(21′)	96.7 (2)		
O(1)–Cu–O(22)	93.8 (2)		
(B) Angles within Carboxylate Groups			
O(11)–CO(1)–O(12)	125.2 (9)	O(21)–CO(2)–O(22)	126.0 (8)
O(11)–CO(1)–C(10)	115.5 (8)	O(21)–CO(2)–C(20)	115.0 (8)
O(12)–CO(1)–C(10)	119.3 (8)	O(22)–CO(2)–C(20)	119.0 (8)
Cu–O(12)–CO(1)	119.7 (6)	Cu–O(22)–CO(2)	124.6 (6)
Cu′–O(11)–CO(1)	125.5 (6)	Cu′–O(21)–CO(2)	119.8 (6)
CO(1)–C(10)–C(11)	127.0 (9)	CO(2)–C(20)–C(21)	125.3 (9)
CO(1)–C(10)–C(14)	125.7 (9)	CO(2)–C(20)–C(24)	128.3 (9)
(C) Angles within C_5H_4 and C_5H_5 Systems			
C(14)–C(10)–C(11)	107.0 (8)	C(24)–C(20)–C(21)	106.1 (8)
C(10)–C(11)–C(12)	108.1 (9)	C(20)–C(21)–C(22)	108.1 (9)
C(11)–C(12)–C(13)	108.4 (10)	C(21)–C(22)–C(33)	110.2 (10)
C(12)–C(13)–C(14)	107.0 (10)	C(22)–C(23)–C(24)	107.3 (9)
C(13)–C(14)–C(10)	109.6 (9)	C(23)–C(24)–C(20)	108.3 (9)
C(19)–C(15)–C(16)	109.0 (11)	C(29)–C(25)–C(26)	108.0 (10)
C(15)–C(16)–C(17)	106.5 (11)	C(25)–C(26)–C(27)	107.1 (10)
C(16)–C(17)–C(18)	110.2 (12)	C(26)–C(27)–C(28)	108.3 (10)
C(17)–C(18)–C(19)	107.1 (12)	C(27)–C(28)–C(29)	107.7 (10)
C(18)–C(19)–C(15)	107.0 (12)	C(28)–C(29)–C(20)	108.9 (10)
(D) Selected C–Fe–C Angles[a]			
(E) Angles within the THF Ligand			
Cu–O(1)–C(1)	116.0 (5)	C(1)–C(2)–C(3)	106.0 (12)
Cu–O(1)–C(4)	116.9 (6)	C(2)–C(3)–C(4)	106.9 (13)
C(4)–O(1)–C(1)	107.8 (7)	C(3)–C(4)–O(1)	109.4 (10)
O(1)–C(1)–C(2)	105.4 (9)		

[a] See supplemental material section.

Description of the Molecular Structure. The crystal ideally consists of a 1:1 mixture of $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2$ molecules and THF molecules of solvation. Molecules are separated by normal van der Waals distances; there are no abnormally short intermolecular contacts. Note that the loss of diffracting power by the crystal (vide supra) during the course of the X-ray study *probably* is the result of the loss of some THF of solvation.

The geometry and atomic labeling scheme for the $Cu_2(O_2C-C_5H_4FeC_5H_5)_4(THF)_2$ molecule is illustrated in Figure 1. Interatomic distances are collected in Table III, selected interatomic angles appear in Table IV, and least-squares planes are shown in Table V (supplemental material).

The central portion of the molecule consists of two copper(II) ions mutually linked by four carboxylate groups with each copper atom additionally being coordinated to a THF ligand. As such, this part of the molecule resembles the classical "dimeric cupric acetate dihydrate" structure (I), which was first reported in outline by van Niekerk and Schoening in 1953[14] and has since been



I

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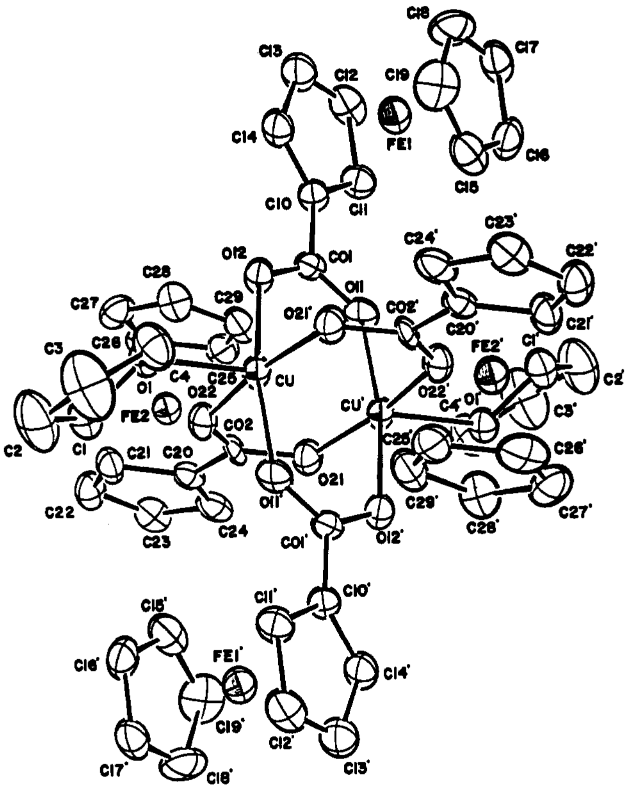

Figure 1. Labeling of atoms in the $Cu_2(O_2C–C_5H_4FeC_5H_5)_4(THF)_2$ molecule (ORTEP-II diagram, 30% probability ellipsoids, all hydrogen atoms omitted).

supplemented by complete X-ray diffraction[15] and neutron diffraction[16] studies; developments in this area have been reviewed.[4,17,18]

The $Cu_2(O_2C–C_5H_4FeC_5H_5)_4(THF)_2$ molecule has a strict, crystallographically imposed, inversion center. Each copper(II) atom is linked to oxygen atoms from four distinct carboxylate groups (Cu–O(11′) = 1.982 (6) Å, Cu–O(12) = 1.965 (6) Å, Cu–O(21′) = 1.956 (6) Å, Cu–O(22) = 1.955 (7) Å) and one THF molecule (Cu–O(1) = 2.226 (6) Å); the Cu···Cu′ distance is 2.605 (1) Å. Each copper(II) atom has a five-coordinate square-pyramidal environment with the copper atom displaced from the basal coordination plane (and toward the apical THF ligand) by 0.182 (1) Å. The Cu′···Cu–O(carboxylate) angles are all acute (Cu′···Cu–O(11′) = 81.5 (2)°, Cu′···Cu–O(12) = 87.8 (2)°, Cu′···Cu–O(21′) = 86.4 (2)° and Cu′···Cu–O(22) = 83.1 (2)°). The angles from the THF ligand to the basal plane range from 88.7 (2) through 102.1 (2)°; this is probably a result of intramolecular crowding involving atom O(1). [Note that the angle Cu′···Cu–O(1) is 169.6 (2)°, rather than having the value of 180° that is expected for a $Cu_2(O_2C–)_4(O–)_2$ core of idealized D_{4h} symmetry.]

The basal coordination plane about Cu (plane A, Table V) makes dihedral angles of 92.83° with the O(11)–CO(1)–O(12) system and 86.07° with the O(21)–CO(2)–O(22) system.

The $O_2C–C_5H_4$ systems are not strictly planar; rather there are torsional angles of 14.39° about the CO(1)–C(10) linkage and 7.73° about the CO(2)C(20) linkage.

The two crystallographically independent ferrocenyl systems have different conformations; that about Fe(1) is eclipsed, while that about Fe(2) is staggered. While the barrier to rotation about the C_5 axis in ferrocene is known to be very small (~0.9 ± 0.3 kcal/mol)[19] and a variety of conformations has been observed,[20] this is perhaps the first example of a structure having unambiguously ordered staggered and eclipsed ferrocenyl fragments.

The dihedral angles between the η^5-C_5H_4 and η^5-C_5H_5 planes are 3.65° for the eclipsed systems about Fe(1) and 3.04° for the staggered systems about Fe(2). Individual Fe–C(η^5-$C_5H_4^-$) distances range from 2.014 (11) through 2.065 (10) Å (average 2.041 Å), whiile Fe–C(η^5-C_5H_5) distances range from 1.998 (12) through 2.067 (15) Å (average 2.034 Å). All other distances and angles in the molecule are normal.

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Registry No. $Cu_2(O_2C–C_5H_4FeC_5H_5)_4(THF)_2·THF$, 97112-53-3; ferrocenecarboxylic acid, 1271-42-7.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters (Table II-S), selected C–Fe–C angles (Table IV-D), and least-squares planes (Table V) (17 pages). Ordering information is given on any current masthead page.

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