

Molecular Assemblies Containing Unsupported [Fe^{III}–(μ_2 : η^2 -RCO₂)–Cu^{II}] Bridges

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Formate is an inhibitor of cytochrome oxidases and also effects conversion of the bovine heart enzyme from the “fast” to the “slow” cyanide-binding form. The molecular basis of these effects is unknown; one possibility is that formate inserts as a bridge into the binuclear heme a_3 –Cu_B site, impeding the binding of dioxygen or cyanide. Consequently, Fe–Cu–carboxylate interactions are a matter of current interest. We have initiated an examination of such interactions by the synthesis of the first examples of [Fe^{III}–(μ_2 : η^2 -RCO₂)–Cu^{II}] bridges, minimally represented by Fe^{III}–L + Cu^{II}–O₂CR → [Fe^{III}–(RCO₂)–Cu^{II}] + L. A series of Cu(II) precursor complexes and solvate forms have been prepared and their structures determined, including [Cu(Me₅dien)(O₂CH)]⁺ (**3**), [Cu(Me₅dien)(O₂CH)(MeOH)]⁺ (**4**), [Cu(Me₆tren)(O₂CH)]⁺ (**5**), and [Cu(Me₅dien)(OAc)]⁺ (**6**). [**4**](ClO₄) was obtained in monoclinic space group $P2_1/n$ with $a = 8.166(3)$ Å, $b = 15.119(5)$ Å, $c = 15.070(4)$ Å, $\beta = 104.65(2)^\circ$, and $Z = 4$. [**5**](ClO₄)/[**6**](ClO₄) crystallize in orthorhombic space groups $Pnma/Pna2_1$ with $a = 16.788(2)/14.928(5)$ Å, $b = 9.542(1)/9.341(4)$ Å, $c = 12.911(1)/12.554(4)$ Å, and $Z = 4/4$. In all cases, the carboxylate ligand is terminal and is bound in a *syn* orientation. Also prepared for the purpose of structural comparison was [Fe(OEP)(O₂CH)], which occurred in monoclinic space group $P2_1/c$ with $a = 13.342(2)$ Å, $b = 13.621(2)$ Å, $c = 19.333(2)$ Å, $\beta = 106.12(2)^\circ$, and $Z = 4$. The desired bridges were stabilized in the assemblies [(OEP)Fe(O₂CH)Cu(Me₅dien)(OCIO₃)]⁺ (**9**), [(OEP)Fe(OAc)Cu(Me₅dien)]²⁺ (**10**), and {(OEP)Fe[(O₂CH)Cu(Me₆tren)]₂}³⁺ (**11**), which were prepared by the reaction of **3**, **6**, and **5**, respectively, with [Fe(OEP)(OCIO₃)] in acetone or dichloromethane. [**9**](ClO₄)/[**10**](ClO₄)₂·CH₂Cl₂ crystallize in triclinic space group $P\bar{1}$ with $a = 9.016(3)/13.777(3)$ Å, $b = 15.377(5)/13.847(3)$ Å, $c = 19.253(5)/17.608(4)$ Å, $\alpha = 78.12(3)/96.82(3)^\circ$, $\beta = 86.30(4)/108.06(3)^\circ$, $\gamma = 76.23(3)/114.32(3)^\circ$, and $Z = 2/2$. Each assembly contains a [Fe^{III}–(RCO₂)–Cu^{II}] bridge but with the differing orientations *anti-anti* (**9**) and *syn-anti* (**10**, **11**). The compound [**11**](ClO₄)₂(SbF₆) occurs in orthorhombic space group $Pbcn$ with $a = 12.517(6)$ Å, $b = 29.45(1)$ Å, $c = 21.569(8)$ Å, and $Z = 4$. Complex **11** is trinuclear; the Fe(III) site has two axial formate ligands with bond distances indicative of a high-spin configuration. Structural features of **9**–**11** are discussed and are considered in relation to the possible insertion of formate into the binuclear sites of two oxidases whose structures were recently determined. The present results contribute to the series of molecular assemblies with the bridge groups [Fe^{III}–X–Cu^{II}], X = O²⁻, OH⁻, and RCO₂⁻, all with a common high-spin heme, thereby allowing an examination of electronic structure as dependent on the bridging atom or group and bridge structure. (Me₅dien = 1,1,4,7,7-pentamethyldiethylenetriamine; Me₆tren = tris(2-(dimethylamino)ethyl)amine; OEP = octaethylporphyrinate(2-).)

Introduction

Eukaryotic mitochondrial oxidases and many bacterial oxidases form a superfamily of heme–copper respiratory oxidases.¹ These enzymes catalyze the four-electron reduction of dioxygen to water and utilize the free energy of this reaction to produce a transmembrane pH gradient by proton pumping. Among the many common features of members of this family is the presence of an iron–copper (heme a_3 –Cu_B) binuclear site, in which the copper center is ligated by three imidazole groups and the heme is bound to an imidazole distal to copper. This bridged assembly has now been directly confirmed by crystallography for the oxidized cytochrome *c* oxidases of *Paracoccus denitrificans*² and bovine heart.³ Unexpectedly, the metal

centers are rather far apart, 5.2 Å in the bacterial oxidase and 4.5 Å in the bovine oxidase. When evaluated against synthetic compounds with high-spin heme groups and linear Fe^{III}–O–Cu^{II} (3.57 Å,⁴ 3.60 Å⁵) and bent Fe^{III}–(OH)–Cu^{II} (157°, 3.80 Å⁶) bridges, the distances are inconsistent with the presence of oxo or hydroxo bridge atoms. These bridges are known to propagate antiferromagnetic coupling and stabilize the resultant $S = 2$ ground state^{4–6} found for the binuclear site of the oxidized bovine enzyme.⁷ The EXAFS of the cytochrome *aa*₃-type quinol oxidase from *Bacillus subtilis* has been analyzed in terms of a heavy-atom (S/Cl) bridge and an Fe^{III}–Cu separation of 3.70 Å.⁸ A further study of this enzyme by EXAFS and ENDOR spectroscopies has ruled out a linear Fe^{III}–O–Cu^{II} bridge and strongly suggests the existence of a Cu_BN₃O site in which the oxygen ligand has an exchangeable proton.⁹ In the Cu EXAFS, a S/Cl bridge atom was not found in significant

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amount and no strong Cu–Fe scattering was observed. These collective results are consistent with a nonlinear $\text{Fe}^{\text{III}}\text{-(OH)-Cu}^{\text{II}}$ bridge. Possibly the structurally characterized forms of the two oxidases have, as suggested,^{2,3} solvent water molecules interposed in the bridge region, but may be convertible to discrete (hydroxo) bridged forms under other conditions. The separation between the two metal centers would be subject to change by the formation of metal-bridge bonds if the protein structure were sufficiently flexible.

Exogenous ligands such as cyanide, peroxide, CO, NO, and azide have been used as probes of the binuclear site of the oxidases. We note that the range of $\text{Fe}^{\text{III}}\text{-Cu}^{\text{II}}$ separations in synthetic linear and nonlinear $\text{Fe}^{\text{III}}\text{-CN-Cu}^{\text{II}}$ bridges (4.90–5.15 Å),¹⁰ in which Fe(III) is present in a low-spin heme group, falls in the interval of metal separations in the binuclear site of the enzymes. Consequently, cyanide could occupy a bridge position, a matter supported by IR spectroscopic evidence.^{10,11} Such ligands are in general inhibitors, as are formate, fluoride, and others. Formate binding is particularly well documented^{12–18} and exhibits a distinctive property. Bovine heart cytochrome oxidase preparations contain a mixture of “rapid” and “slow” forms of the enzyme,^{14–16,19} so designated on the basis of their relative rates of reaction with cyanide. The rapid \rightarrow slow conversion is accelerated at low pH and is accompanied by a blue shift of the Soret band and development of an EPR spectrum with signals at $g = 12$ and 2.95. Of particular interest is the observation that incubation of the rapid oxidase with formate at alkaline pH produces a form of the enzyme virtually indistinguishable in kinetics and spectroscopic properties from the slow form.^{12–19} The cause of this behavior is unknown but has provoked substantial discussion and speculation. Considerations have ranged from perturbations in protein tertiary structure to specific binding of formate at the binuclear site. No reagent other than formate when added to the rapid enzyme is known to cause simultaneous development of the “ $g' = 12$ ” EPR spectrum and the very slow reaction with cyanide.

Several modes of formate binding to the binuclear site are schematically depicted in Figure 1. In one view,¹³ a ligand at Cu_B is replaced by formate which changes the nature of the

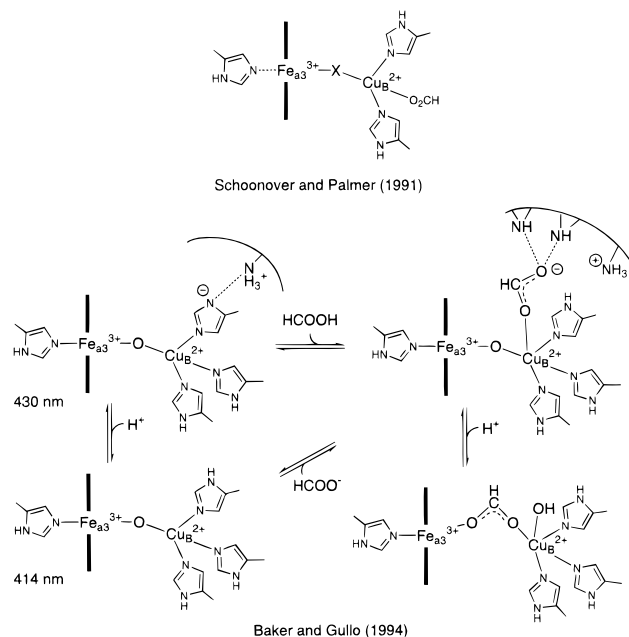


Figure 1. Upper: formate binding as a terminal ligand to Cu_B in the binuclear site of a cytochrome oxidase (adapted from Schoonover and Palmer¹³). Lower: biphasic binding of formate to the binuclear site (adapted from Baker and Gullo¹⁸). Under these proposals, the upper and the $\mu\text{-O}_2\text{CH}$ structures simulate carboxylate-ligated sites in the slow oxidase.

Cu–X bond. This in turn affects the Fe–X bond, which influences the optical spectrum and induces the $g' = 12$ EPR spectrum. Baker and Gullo¹⁸ have provided an explicit structural model for the binding of formate based on a kinetics analysis at pH 8.8. In this scheme, which adopts oxo as the bridging ligand in the resting form, formate interacts in a biphasic manner. It initially binds at the Cu_B site and thereafter in a proton-assisted step is inserted as the bridge between Cu_B and the Fe(III) atom of heme a_3 . In the first proposal, formate simulates the binding of carboxylate as a terminal ligand in the slow enzyme; this ligand would impede the binding of cyanide. Several investigators have suggested that the slow oxidase contains a carboxylate-bridged binuclear site derived from a conserved endogenous residue.^{16,18,20} Exogenous formate would then imitate the role of carboxylate in the slow form.

The foregoing considerations raise significant questions about the properties of the bridge unit $\text{Fe}^{\text{III}}\text{-(}\mu\text{-RCO}_2\text{)-Cu}^{\text{II}}$ which, ideally, is composed of heme iron and copper in a predominantly nitrogen coordination environment. Indeed, no such structurally proven bridge appears to have been prepared. Having synthesized other $\text{Fe}^{\text{III}}\text{-X-Cu}^{\text{II}}$ bridged assemblies containing the inhibitory anions $\text{X} = \text{CN}^-$ ¹⁰ and F^- ,²¹ we turned our attention to the matter of carboxylate-bridged assemblies. We report here the syntheses of three such species, their detailed structures and those of several Cu(II) precursors, and certain reactivity aspects that help define the nature of the bridge unit. Electronic properties will be the subject of a future report.

Experimental Section²²

Preparation of Compounds. Copper(II) and iron(III) porphyrin complexes were prepared in the air using anhydrous commercial solvents. Iron(III)–copper(II) bridged complexes were synthesized

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 (22) Abbreviations: bpy = 2,2'-bipyridyl; dien, diethylenetriamine; Mes-dien, 1,1,4,7,7-pentamethyldiethylenetriamine; Mes₆ten, tris(2-(dimethylamino)ethyl)amine; OEP, octaethylporphyrinate(2-); P = porphyrinate(2-); terpy = 2,2':6',2''-terpyridine; TPP, tetraphenylporphyrinate(2-), TpTP, tetra-*p*-tolylporphyrinate(2-).

under a pure dinitrogen atmosphere using standard glovebox and Schlenk techniques. Solvents were dried according to standard procedures and were degassed as necessary prior to use.

Note! Although we have experienced no instability of the compounds reported here, perchlorate salts are potentially explosive and should be treated accordingly.

(a) Cu(II) Complexes. **[Cu(Me₅dien)Cl](ClO₄).** A solution of 1.16 g (6.72 mmol) of Me₅dien in 10 mL of acetonitrile was added dropwise to a solution of 0.903 g (6.72 mmol) of CuCl₂ in 25 mL of acetonitrile. The dark blue reaction mixture was stirred for 1 h and then treated with 1.39 g (6.72 mmol) of solid AgClO₄. The solution was stirred for 3 h and filtered, and the filtrate was taken to dryness in vacuo. The residue was dissolved in a minimal amount of acetone, the solution was filtered, and several volume equivalents of ether were diffused into the filtrate over 48 h. A dark blue crystalline mass was collected, washed with ether, and dried in vacuo to afford 2.08 g (83%) of pure product. Anal. Calcd for C₉H₂₃Cl₂CuN₃O₄: C, 29.08; H, 6.24; Cl, 19.07; Cu, 17.09; N, 11.30. Found: C, 29.22; H, 6.18; Cl, 19.05; Cu, 17.04; N, 11.25. When this material was recrystallized from acetone/ether for an X-ray structure determination, the product was demonstrated to be [Cu(Me₅dien)Cl(Me₂CO)]ClO₄.

[Cu(Me₅dien)(O₂CH)ClO₄]. A solution of 0.540 g (3.12 mmol) of Me₅dien in 5 mL of methanol was added dropwise to a slurry of 0.703 g (3.12 mmol) of [Cu(OH₂)₄(O₂CH)₂] in 15 mL of methanol. The resulting dark blue solution was stirred for 2 h and treated with 0.382 g (3.12 mmol) of solid NaClO₄, and the mixture was stirred for an additional 4 h. The precipitate was collected, washed with cold methanol and ether, and dried to give the product as 0.640 g (54%) of a blue crystalline solid; ν_{COO} (KBr) 1620 cm⁻¹. Anal. Calcd for C₁₀H₂₄ClCuN₃O₆: C, 31.50; H, 6.34; Cu, 16.66; N, 11.02. Found: C, 31.20; H, 6.54; Cu, 16.39; N, 10.90. When this compound was crystallized from methanol/ether for X-ray diffraction purposes, the product was demonstrated to be [Cu(Me₅dien)(O₂CH)(MeOH)](ClO₄) by a structure determination.

[Cu(Me₆tren)(O₂CH)ClO₄]. A solution of 0.463 g (2.01 mmol) of Me₆tren²³ in 5 mL of methanol was added dropwise to a slurry of 0.453 g (2.01 mmol) of [Cu(OH₂)₄(O₂CH)₂] in 15 mL of methanol. The mixture was stirred for 10 min, and 0.246 g (2.01 mmol) of solid NaClO₄ was added to the light blue solution. The mixture was stirred for 3 h and filtered, and the filtrate was taken to dryness in vacuo. The residue was dissolved in 5 mL of dichloromethane, the solution was filtered, and solvent was removed in vacuo. The residue was dissolved in a minimal amount of acetone, and several volume equivalents of ether were diffused into the solution over 24 h. The solid was collected, washed with ether, and dried in vacuo to give the product as 0.630 g (72%) of light green-blue crystals; ν_{COO} (KBr) 1640 cm⁻¹. Anal. Calcd for C₁₃H₃₁ClCuN₄O₆: C, 35.62; H, 7.13; Cl, 8.09; Cu, 14.49; N, 12.78. Found: C, 35.70; H, 7.10; Cl, 8.15; Cu, 14.55; N, 12.85.

[Cu(Me₅dien)(OAc)](ClO₄). A solution of 0.500 g (1.34 mmol) of [Cu(Me₅dien)Cl](ClO₄) in 15 mL of methanol was treated with 0.110 g (1.34 mmol) of solid NaOAc. The mixture was stirred for 1 h, the solvent was removed in vacuo, and the residue was dissolved in 10 mL of dichloromethane. The solution was filtered, the filtrate was reduced to dryness in vacuo, and the residue was dissolved in a minimal volume of methanol. Diffusion of several volume equivalents of ether into the solution over 3 d resulted in the precipitation of 0.428 g (81%) of product as a blue-purple crystalline solid; ν_{COO} (KBr) 1563 cm⁻¹. Anal. Calcd for C₁₁H₂₆ClCuN₃O₆: C, 33.42; H, 6.63; Cl, 8.97; Cu, 16.07; N, 10.63. Found: C, 33.50; H, 6.51; Cl, 9.00; Cu, 16.05; N, 10.60.

[Cu(Me₅dien)(OAc)(OH₂)](ClO₄). A solution of 1.14 g (5.72 mmol) of [Cu(OAc)₂(OH₂)] in 35 mL of methanol was treated with 0.990 g (5.72 mmol) of Me₅dien. Solid NaClO₄ (0.700 g, 5.72 mmol) was added to the blue solution, which was stirred for 4 h. The solution was taken to dryness in vacuo. The oily residue was dissolved in 15 mL of dichloromethane, the solution was filtered, and the filtrate was reduced to dryness in vacuo. The residue was dissolved in a minimal volume of acetone, the solution was filtered, and several volume equivalents of ether were diffused into the filtrate over 24 h. The solid was collected, washed with ether, and dried to afford 1.81 g (72%) of

product as blue crystals. This compound was identified by an X-ray structure determination.

(b) [Fe(OEP)(O₂CH)]. A solution of 50.0 mg (40 μ mol) of [Fe(OEP)]₂O²⁴ in 10 mL of dichloromethane was shaken vigorously with 2 \times 10 mL portions of 2 M aqueous formic acid. The organic phase was dried (Na₂SO₄), filtered, and taken to dryness in vacuo. The residue was dissolved in a minimal amount of dichloromethane, and the solution was filtered. Several volume equivalents of ether were diffused into the filtrate over 3 d. The solid was collected, washed with ether, and dried in vacuo to give the product as 38.1 mg (72%) of dark blue crystals; ν_{COO} (KBr) 1667 cm⁻¹. Absorption spectrum (CH₂Cl₂): λ_{max} (ϵ_{M}) 367 (sh, 74 700), 394 (92 700), 497 (8210), 530 (7910), 628 (4860) nm. This compound was identified by an X-ray structure determination.

(c) Fe(III)–Cu(II) Bridged Assemblies. **[(OEP)Fe(O₂CH)Cu(Me₅dien)(OCIO₃)](ClO₄).** A solution of 33.1 mg (87 μ mol) of [Cu(Me₅dien)(O₂CH)](ClO₄) in 0.5 mL of acetone was combined with a solution of 59.8 mg (87 μ mol) of [Fe(OEP)(OCIO₃)]²⁵ in 0.5 mL of acetone. The resultant red-brown solution was filtered, and several volume equivalents of ether were diffused into the filtrate over 2 d. A mixture of crystalline products was obtained, including the minor components [Fe(OEP)(O₂CH)], [(OEP)Fe(OH)Cu(Me₅dien)(OCIO₃)](ClO₄) (identified by unit cell parameters⁶), and blue crystals of a copper compound (unidentified). The major product consisted of the desired formate-bridged assembly, which was manually separated from the other components as 44.6 mg (48%) of large red crystals; ν_{COO} (KBr) 1578 cm⁻¹. The compound was identified by an X-ray structure determination.

[(OEP)Fe(OAc)Cu(Me₅dien)](ClO₄). A solid mixture of 50.0 mg (72.5 μ mol) of [Fe(OEP)(OCIO₃)] and 28.8 mg (72.5 μ mol) of [Cu(Me₅dien)(OAc)](ClO₄) was dissolved in 1 mL of dichloromethane, and the solution was filtered. Slow diffusion of ether into the filtrate over 2 d resulted in the precipitation of a mixture of crystalline products. The desired acetate-bridged assembly was manually separated from the other components as red crystals in low yield; ν_{COO} (KBr) 1541 cm⁻¹. The compound was identified by an X-ray structure determination.

{(OEP)Fe[(O₂CH)Cu(Me₆tren)]₂}(ClO₄)₃. A solid mixture of 32.0 mg (73 μ mol) of [Cu(Me₆tren)(O₂CH)](ClO₄) and 50.2 mg (73 μ mol) of [Fe(OEP)(OCIO₃)] was dissolved in 1 mL of acetone, and the solution was filtered. Several volume equivalents of ether were diffused into the filtrate over 2 d, yielding violet crystals of the product as well as green Cu(II) starting material. The crystalline mixture was collected, washed with cold acetone (to remove starting material), and washed with ether. The product was obtained as 36.0 mg (57%) of a violet crystalline solid; ν_{COO} (KBr) 1581 cm⁻¹. Anal. Calcd for C₆₂H₁₀₆Cl₃Cu₂FeN₁₂O₁₆: C, 47.59; H, 6.83; Cl, 6.80; Cu, 8.12; Fe, 3.57; N, 10.74. Found: C, 47.44; H, 6.91; Cl, 6.76; Cu, 8.17; Fe, 3.55; N, 10.66. The compound was further identified by an X-ray structure determination.

The complexes of principal interest in this investigation are designated as follows:

[Cu(Me ₅ dien)Cl] ⁺	1
[Cu(Me ₅ dien)Cl(OCMe ₂) ⁺	2
[Cu(Me ₅ dien)(O ₂ CH)] ⁺	3
[Cu(Me ₅ dien)(O ₂ CH)(MeOH)] ⁺	4
[Cu(Me ₆ tren)(O ₂ CH)] ⁺	5
[Cu(Me ₅ dien)(OAc)] ⁺	6
[Cu(Me ₅ dien)(OAc)(OH ₂)] ⁺	7
[Fe(OEP)(O ₂ CH)]	8
[(OEP)Fe(O ₂ CH)Cu(Me ₅ dien)(OCIO ₃)] ⁺	9
[(OEP)Fe(OAc)Cu(Me ₅ dien)] ²⁺	10
{(OEP)Fe[(O ₂ CH)Cu(Me ₆ tren)] ₂ } ³⁺	11
[(OEP)Fe(OH)Cu(Me ₅ dien)(OCIO ₃)] ⁺	12
[(OEP)FeOCu(Me ₆ tren)] ⁺	13

X-ray Data Collection and Reduction. Structures of the five Cu(II) complexes in Table 1 and the four complexes in Table 2 have been determined. For brevity in this section, all compounds in these tables are referred to by their cation number. Crystals of **2** and **4–11** were

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Table 1. Crystallographic Data^a for [Cu(Me₅dien)Cl(OCMe₂)⁺ (2), [Cu(Me₅dien)(O₂CH)(MeOH)⁺ (4), [Cu(Me₅dien)(OAc)⁺ (6), [Cu(Me₅dien)(OAc)(OH₂)⁺ (7), and [Cu(Me₆tren)(O₂CH)⁺ (5)

	[2](ClO ₄)	[4](ClO ₄)	[6](ClO ₄)	[7](ClO ₄)	[5](ClO ₄)
formula	C ₁₂ H ₂₆ Cl ₂ CuN ₃ O ₅	C ₁₁ H ₂₈ ClCuN ₃ O ₇	C ₁₁ H ₂₆ ClCuN ₃ O ₆	C ₁₁ H ₂₈ ClCuN ₃ O ₇	C ₁₃ H ₃₁ ClCuN ₄ O ₆
fw	429.83	413.38	395.35	413.38	438.43
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>Pnma</i>
Z	4	4	4	4	4
<i>a</i> , Å	7.735(3)	8.166(3)	14.928(5)	14.687(3)	16.788(2)
<i>b</i> , Å	12.564(4)	15.119(5)	9.341(4)	9.285(3)	9.542(1)
<i>c</i> , Å	19.899(7)	15.070(4)	12.554(4)	13.321(4)	12.911(1)
β, deg	96.33(3)	104.65(2)			
<i>V</i> , Å ³	1922(1)	1800(1)	1751(1)	1816.6(9)	2068.1(4)
<i>T</i> , K	223	223	223	223	298
<i>R</i> ^b (<i>R</i> _w ^c), %	5.68 (5.58)	2.93 (3.19)	5.96 (5.23)	6.32 (5.32)	6.74 (7.34)

^a Obtained with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = \{ \sum [w(|F_o|^2 - |F_c|^2)] / \sum [w|F_o|^2] \}^{1/2}$.

Table 2. Crystallographic Data^a for [Fe(OEP)(O₂CH)] (8), [(OEP)Fe(O₂CH)Cu(Me₅dien)(OCIO₃)⁺ (9), [(OEP)Fe(OAc)Cu(Me₅dien)]²⁺ (10), and {(OEP)Fe[(O₂CH)Cu(Me₆tren)]₂}³⁺ (11)

	8	[9](ClO ₄)	[10](ClO ₄) ₂ ·CH ₂ Cl ₂	[11](ClO ₄) ₂ (SbF ₆)
formula	C ₃₇ H ₄₅ FeN ₄ O ₂	C ₄₆ H ₆₈ Cl ₂ CuFeN ₇ O ₁₀	C ₄₈ H ₇₂ Cl ₄ CuFeN ₇ O ₁₀	C ₆₂ H ₁₀₆ Cl ₂ Cu ₂ F ₆ FeN ₁₂ O ₁₂ Sb
fw	633.64	1069.39	1168.31	1701.19
cryst syst	monoclinic	triclinic	triclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1	<i>Pbcn</i>
Z	4	2	2	4
<i>a</i> , Å	13.342(2)	9.016(3)	13.777(3)	12.517(6)
<i>b</i> , Å	13.621(2)	15.377(5)	13.847(3)	29.45(1)
<i>c</i> , Å	19.333(2)	19.253(5)	17.608(4)	21.569(8)
α, deg		78.12(3)	96.82(3)	
β, deg	106.12(2)	86.30(4)	108.06(3)	
γ, deg		76.23(3)	114.32(3)	
<i>V</i> , Å ³	3375.3(8)	2536(1)	2790(1)	7950(6)
<i>T</i> , K	298	223	223	298
<i>R</i> ^b (<i>R</i> _w ^c), %	3.97 (4.08)	4.94 (5.22)	8.92 (<i>R</i> _{w2} ^d = 15.19)	7.17 (7.89)

^a Obtained with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = \{ \sum [w(|F_o|^2 - |F_c|^2)] / \sum [w|F_o|^2] \}^{1/2}$. ^d $R_{w2} = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^2] \}^{1/2}$.

grown by vapor diffusion of ether into saturated solutions in methanol (4, 6), acetone (2, 5, 7, 9, 11), and dichloromethane (8, 10). In the case of 11, a small amount of NaSbF₆ was added to an acetone solution prior to ether diffusion. Single crystals of 2, 4, 6, 7, 9, and 10 were coated with Paratone-N oil, attached to glass fibers, transferred to a Nicolet P3f diffractometer, and cooled in a dinitrogen stream to -50 °C. Crystals of 5, 8, and 11 were coated with epoxy and transferred at room temperature to a Nicolet R3mv (5, 11) or Siemens P4 (8) diffractometer.

Lattice parameters were obtained from least-squares analyses of carefully centered reflections with 15° ≤ 2θ ≤ 30°. Decay corrections were based on measured intensities of one or two reflections monitored periodically throughout the data collections. None of the compounds showed significant decay. The raw intensity data were corrected for scan speed, background, and Lorentz and polarization effects using the program XDISK of the SHELXTL PLUS program package. Empirical absorption corrections based on the observed variations in intensities of the azimuthal (Ψ) scans were applied to the data sets using XEMP. Compounds 2, 4, and 8 crystallize in the monoclinic system with systematic absences unambiguously identifying their space groups. Compounds 5–7 and 11 crystallize in the orthorhombic system. Systematic absences identified the space groups of 5–7 as either *Pnma* or *Pna*2₁. Only the former gave an acceptable solution for 5, while 6 and 7 were consistent with the latter. The space group of 11 was identified by systematic absences. Compounds 9 and 10 crystallize in the triclinic system, with space group *P*1 determined by statistics and successful refinements of the structures.

Structure Solution and Refinement. Structures of 2, 4, 5, and 7–11 were solved by direct methods or from Patterson maps using standard procedures. The structure of 6 could not be solved by either method but was extracted from the phase solution of 5. All structures except that of 10 were refined by full-matrix least-squares and Fourier techniques using SHELXTL-PLUS. Owing to severe disorder problems, the structure of 10 was refined using SHELXTL-93. All non-hydrogen atoms were refined with anisotropic thermal parameters unless

otherwise noted; in some cases disorder prevented anisotropic descriptions of such atoms. Hydrogen atoms were assigned idealized locations with a uniform value of *U*_{iso}.

The asymmetric units of 2, 4, 6, 7, and 9 contain one cation and one anion. In 4, the OH hydrogen atom of the methanol ligand was located in a difference Fourier map; its positional and isotropic thermal parameters were fully refined. The hydrogen atoms of the aquo ligand in 7 were not included in the refinement. The perchlorate ions in 2 and 6 were treated isotropically. Three oxygen atoms of the anion in 6 are disordered over three sites with occupancy factors of 1/3. The anion and cation of 5 are located on a mirror plane. The perchlorate ion is badly disordered, and the oxygen atoms were refined isotropically on six symmetry-equivalent positions. The ethylene and methyl groups of Me₆tren display considerable thermal motion; attempts to refine the structure in a lower-symmetry space group were unsuccessful. The asymmetric unit of 8 consists of one complete molecule, while that of 10 contains one cation, two anions, and one solvate molecule. In the latter, both perchlorate ions display two orientations, each with a site occupancy of 1/2; the oxygen atoms were refined isotropically. The dichloromethane solvate molecule was isotropically refined over two sites with total occupancy constrained to unity and the C–Cl distance fixed at 1.72 Å. In addition, a porphyrin ethyl group is disordered over two positions, each methyl group having a site occupancy of 1/2. In 11, the asymmetric unit contains one-half cation, one-half [SbF₆]⁻, and one disordered perchlorate ion. The iron atom crystallizes on an inversion center, and the antimony atom is located on a 2-fold position. The perchlorate ion is disordered over two positions and was refined isotropically with each position having a site occupancy of 1/2. In the last cycle of refinement of all structures, all parameters shifted by <1% of the esd, and final difference Fourier maps showed no significant electron density. Final agreement factors are contained in Tables 1 and 2.²⁶

(26) See paragraph at the end of this article concerning Supporting Information.

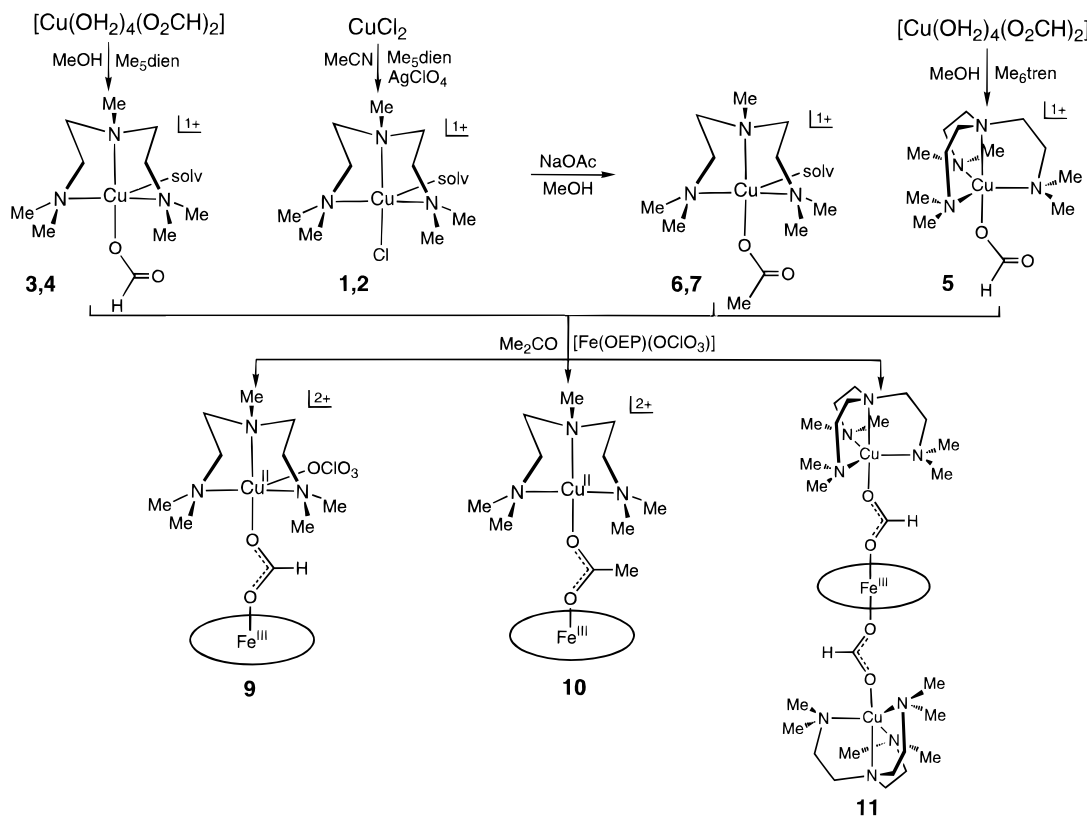
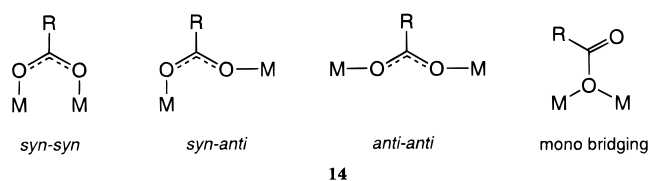


Figure 2. Synthesis of Fe(III)–Cu(II) carboxylate-bridged assemblies **9–11**. Cu(II) precursor complexes **1**, **3**, and **6** are taken to be monosolvated in solution on the basis of the structures of solvate complexes **2**, **4**, and **7**, respectively. The structural formulas are schematic only; **10** and **11** are not depicted in their actual *syn-anti* configurations.

Other Physical Measurements. ^1H NMR spectra were obtained with a Bruker AM-400N spectrometer. FT-IR spectra were recorded with a Nicolet Impact 400D spectrometer.

Results and Discussion

At the outset, we note that carboxylates can act as mono- and bidentate terminal ligands and can assume the four bridging modalities **14**.²⁷ Of the latter, all but the monobridging arrange-



ment have been observed in Cu(II)–formate and –acetate systems. The three triatomic bridges have associated with them particular structural and electronic features. Consequently, matters of particular significance in the context of Fe^{III}–X–Cu^{II} bridged assemblies are (i) means of synthesis, (ii) Cu(II)–carboxylate binding in precursor complexes and any changes associated with forming bridged assemblies, (iii) bridging modality and its conformation in each assembly, and (iv) magnetic properties, particularly magnetic exchange, as modulated by the factors in (iii). The present investigation deals with aspects i–iii.

Bridged Assembly Precursors: Cu(II) Complexes. Because the Cu_B environment in the enzymes was formerly unknown, we have, as in previous work, utilized the ligands Me₅dien and Me₆tren to effect distorted square pyramidal (dSP)

and trigonal bipyramidal Cu(II) coordination units, respectively. Preparations are set out in Figure 2. Complexes **1**, **3**, **5**, and **7** were prepared directly from CuCl₂ (**1**) or a Cu(II) carboxylate. Acetato complex **6** was obtained by chloride substitution of **1**. Solvate species **2** and **4** were formed in crystallization of **1** and **3**, respectively, from the appropriate solvent. All complexes were isolated in good yield as perchlorate salts, which are soluble in acetone. Five of these complexes (**3–7**) contain terminal carboxylate ligands. The structures of **2** and **4–7** have been determined and are provided in Figure 3. Selected interatomic distances and angles are collected in Table 3; parameters describing Cu–N bonding are very similar to those of related Cu(II) complexes^{4,6,10} and require no further discussion.

Five-coordinate complexes **2**, **4**, and **7** exhibit dSP stereochemistry with the acetone (2.418(6) Å), methanol (2.271(3) Å), and water (2.27(1) Å) molecules, respectively, in the axial position, so defined by the indicated, relatively long Cu–O(1) bond distances. Unsolvated complex **6** has a more distant axial ligand, and **5** adopts the expected trigonal bipyramidal structure with formate in an axial position. In the latter, the Cu(II) atom is displaced from the plane N(1,1',3) toward the formate ligand by 0.31 Å; the Cu–O(1) distance of 1.92(1) Å is comparable with the corresponding bond length in [Cu(Me₆tren)(OH)]⁺ (1.875(2) Å).⁴ Carboxylate complexes **4–7** exhibit the constant stereochemical features of η¹-O₂CR coordination and a *syn* orientation of the carboxylate ligand, defined by the position of the Cu and uncoordinated oxygen (O(2)) atoms. In **4** and **7**, hydrogen bonds from the solvate ligand to O(2) stabilize this arrangement. The Cu–O(1) and C(1)–O(1) distances in this set define the ranges 1.911(7)–1.955(2) and 1.19(2)–1.29(1) Å, respectively; asymmetry in C–O distances is observed in all cases but **7**, where possibly the C(1)–O(2) bond is lengthened by hydrogen bonding. In the Me₅dien subset **4**, **6**, **7**, com-

(27) For a more general consideration of the structural aspects of metal–carboxylate interactions, cf.: Carrell, C. J.; Carrell, H. L.; Erlebacher, J.; Glusker, J. P. *J. Am. Chem. Soc.* **1988**, *110*, 8651.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) of Cu(II) Complexes 2, 4–6, and 7

	2	4	5	6	7
Cu–N(1)	2.071(5)	2.045(3)	2.14(1)	2.056(8)	2.060(9)
Cu–N(2)	2.052(5)	2.025(3)	2.00(1)	2.02(1)	2.03(1)
Cu–N(3)	2.061(5)	2.050(3)	2.16(1)	2.042(9)	2.047(9)
Cu–O(1)/Cl ^a	2.247	1.955(2)	1.92(1)	1.911(7)	1.948(8)
Cu–O(3)/N(1')/O(1)	2.418(6)	2.271(3)	2.14(1)		2.27(1)
O(1)–C(1)		1.269(4)	1.19(2)	1.29(1)	1.27(2)
O(2)–C(1)		1.222(5)	1.12(3)	1.21(1)	1.27(2)
N(1)–Cu–O(1)/Cl	93.8(2)	92.4(1)	101.5(3)	93.8(3)	92.5(3)
N(1)–Cu–N(2)	84.8(2)	86.3(1)	84.7(3)	84.9(3)	86.1(4)
N(2)–Cu–N(3)	85.6(2)	86.0(1)	83.7(5)	85.7(3)	86.1(4)
N(3)–Cu–O(1)/Cl	94.3(2)	90.7(1)	84.6(5)	94.9(3)	91.4(3)
O(1)–Cu–O(3)/Cl/N(1')	92.7(1)	92.2(1)	101.5(3)		94.7(4)
N(1)–Cu–O(3)/O(1)/N(1')	105.8(2)	98.0(1)	113.9(5)		102.0(4)
N(2)–Cu–O(3)/O(1)/N(1')	91.5(2)	100.9(1)	100.7(3)		94.4(4)
N(3)–Cu–O(3)/O(1)/N(1')	95.8(2)	102.7(1)	121.6(3)		102.6(4)
N(1)–Cu–N(3)	156.5(2)	158.9(1)	121.6(3)	156.8(4)	154.7(3)
N(2)–Cu–O(1)/Cl	175.7(2)	166.9(1)	168.3(5)	177.9(4)	170.9(4)
Cu–O(1)–C(1)		130.5(2)	133(1)	101.3(7)	127.0(8)
O(1)–C(1)–O(2)		128.3(3)	128(2)	124(1)	125(1)
Cu–O(3)–C(2)	147.1(5) ^b	152.5(2)			

^a Cf. Figure 2 for atom–molecule relationships. ^b Cu–O(1)–C(11).

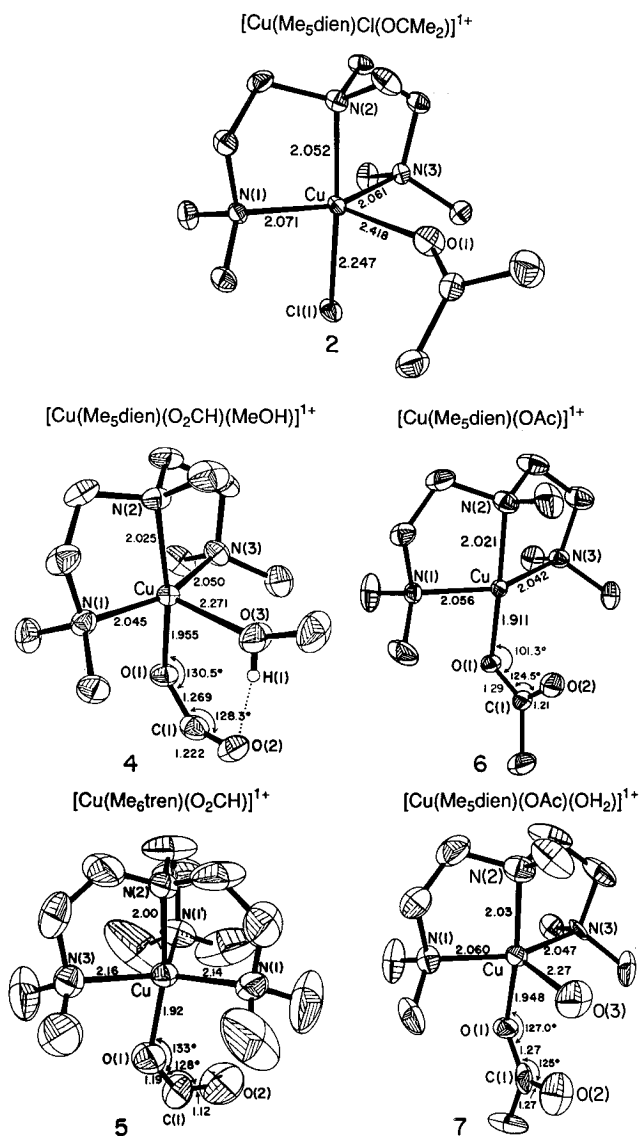


Figure 3. Structures of Cu(II) complexes 2 (30%), 4 (50%), 5 (30%), 6 (30%), and 7 (50%) with the indicated sizes of thermal ellipsoids, the atom-labeling schemes, and selected metric parameters. Note that 5 has imposed mirror symmetry.

plex 6 has (marginally) the shortest Cu–O(1) bond (1.911(7) Å) and by far the smallest Cu–O(1)–C(1) angle (101.3(7)°);

the latter arises from weak binding of the second acetate oxygen atom (Cu–O(2) = 2.50(1) Å). Previously described Cu(II) complexes with one η¹-formate ligand form a small set. Of these, dSP [Cu(terpy)(O₂CH)(OH₂)]⁺,²⁸ with Cu–O_{eq}(formate) = 1.935(3) Å and Cu–O_{ax}(water) = 2.247(3) Å, and dSP [Cu(bpy)₂(O₂CH)]⁺²⁹ are most closely related to 4–7. Complexes 3, 5, and 6 serve as immediate precursors to bridged assemblies.

[Fe(OEP)(O₂CH)]. Compound 8, desired for structural comparison with formate-bridged assemblies, was simply prepared by cleavage of [Fe(OEP)]₂O with formic acid in dichloromethane and was identified by an X-ray structure determination. The structure, shown in Figure 4 with related data in Table 4, closely resembles that of [Fe(TpTP)(OAc)];³⁰ this complex and 8 are additions to a quite small set of [Fe^{III}(P)(O₂CR)] complexes that have been described.³¹ The mean bond length Fe–N = 2.056(1) Å and a displacement of 0.459 Å from the mean plane of the porphyrin toward the axial ligand define 8 as a classic five-coordinate high-spin Fe(III) heme complex.³² In contrast to acetate ligation in [Fe(TpTT)(OAc)], the formate group binds in an *anti* configuration.

Fe^{III}–(RCO₂)–Cu^{II} Bridged Assemblies. Formate-bridged assemblies 9 and 11 and acetate-bridged assembly 10 as perchlorate salts have been prepared by the reactions set out in Figure 2. As in the syntheses of other Fe^{III}–X–Cu^{II} bridged species in this laboratory, having X = F[–],²¹ O^{2–},⁴ OH[–],⁶ and CN[–],¹⁰ condensation of two molecules, one carrying the bridging ligand and the other being coordinatively unsaturated and/or readily substituted, proved effective. In the present case, the latter species is [Fe(OEP)(OCIO₃)], and formate or acetate is introduced as an η¹ ligand in the foregoing Cu(II) complexes. A corresponding set of reactants has been used previously for all bridged assemblies except those containing cyanide, where [Fe(OEP)(CN)L] (L = N-base) was employed as the source of the bridge. In the case of 11, the reaction did not go to completion, as indicated by cocrystallization of starting material.

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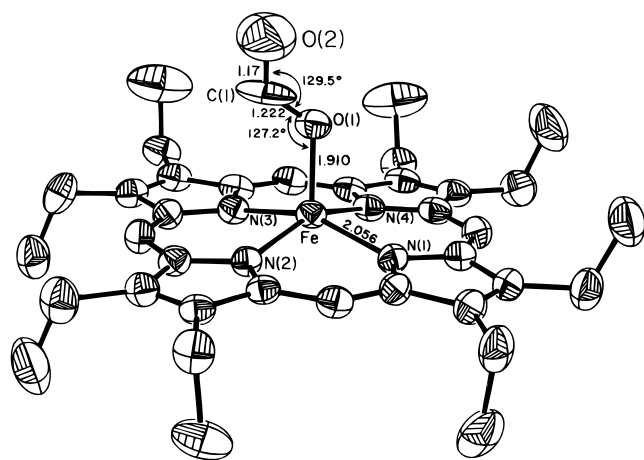
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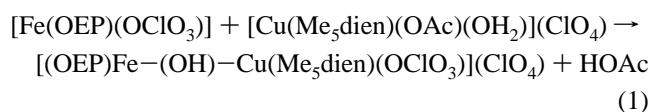
Table 4. Selected Interatomic Distances (Å) and Angles (deg) in Heme Complex **8** and Bridged Assemblies **9** and **10**

	8	9	10
		Bridge	
Fe—O(1)	1.910(4)	1.968(5)	1.961(7)
Cu—O(2)		1.976(6)	1.936(8)
Cu ^{II} —O(1)			2.689
C(1)—O(1)	1.222(9)	1.25(1)	1.28(1)
C(1)—O(2)	1.17(1)	1.227(9)	1.29(1)
Fe—O(1)—C(1)	127.2(4)	131.6(5)	140.6(7)
Cu—O(2)—C(1)		133.7(6)	109.7(7)
O(1)—C(1)—O(2)	129.5(7)	123.1(8)	120(1)
Fe ^{III} —Cu		5.860	4.430
Fe ^{III} —Cl ^d	0.459	0.383	0.407
		Heme	
Fe—N(1)	2.055(4)	2.045(5)	2.024(8)
Fe—N(2)	2.055(4)	2.041(6)	2.042(8)
Fe—N(3)	2.057(4)	2.039(6)	2.045(8)
Fe—N(4)	2.056(4)	2.044(6)	2.050(8)
mean of 4	2.056(1)	2.042(2)	2.04(1)
N _p —Fe—N _p ^b mean	87.7(3)	88.3(2)	88.1(4)
O(1)—Fe—N _p range	99.5(2)—103.7(4)	97.5(2)—102.7(2)	98.3(3)—101.6(3)
		Cu Fragment	
Cu—N(5)		2.038(6)	2.00(1)
Cu—N(6)		2.011(7)	1.98(1)
Cu—N(7)		2.050(6)	2.04(1)
Cu—O(11)		2.282(7)	
N(5)—Cu—N(6)		86.7(3)	85.6(5)
N(6)—Cu—N(7)		86.3(3)	86.7(5)
N(5)—Cu—N(7)		160.0(2)	165.1(4)
O(2)—Cu—N(5)		93.2(3)	95.5(4)
O(2)—Cu—N(6)		168.8(2)	177.8(4)
O(2)—Cu—N(7)		90.0(2)	91.8(4)
O(2)—Cu—O(11)		86.6(2)	
N(5)—Cu—O(11)		100.2(2)	
N(6)—Cu—O(11)		104.4(3)	
N(7)—Cu—O(11)		99.7(2)	
Cu—O(11)—Cl		152.5(5)	

^a Displacement from mean plane of the porphyrin toward Cu. ^b N_p = porphyrin nitrogen atom.

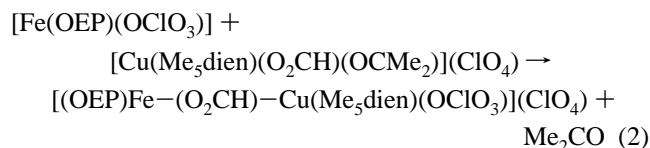
**Figure 4.** Structure of **8** showing 50% probability ellipsoids, the atom-labeling scheme, and selected metric parameters.

Thus, [11](ClO₄)₃ was prepared with a 1:1 reactant ratio inasmuch as product contamination by [5](ClO₄) only worsened upon increasing its amount in the reaction mixture. Preparations of **9** and **10** generated variable amounts of heme complex **8**, an unidentified blue Cu(II) complex, and the recently reported hydroxide-bridged compound [12](ClO₄),⁶ which we have established is formed in high yield in reaction 1 involving the



aquo acetate complex **7**. Presumably, an analogous reaction will occur with a formate complex in the presence of water. We were unable to eliminate completely the formation of [12](ClO₄) even under normally rigorous anhydrous conditions. However, its abundance could be reduced by recrystallizations of the reaction products from dry acetone. Heme **8** presumably formed by ligand substitution with **3**. Far more than casual effort was expended in seeking conditions of synthesis and purification which afforded a single product for each preparation. These endeavors were not successful; consequently, pure samples of [9](ClO₄) (48%) and [10](ClO₄) (13%) were isolated by manual separation from product mixtures in the indicated representative yields.

The structures of complexes **9–11** are presented in Figures 5–7, respectively. Selected interatomic distances and angles are collected in Tables 4 and 5. It is immediately apparent that the desired Fe^{III}—(μ₂-RCO₂)—Cu^{II} bridges have been formed. In all three cases, the stereochemistry and metric features of the Cu^{II}(Me₅dien) or Cu^{II}(Me₆tren) and Fe^{III}(OEP) fragments are not significantly altered upon bridge formation; attention is therefore directed mainly to the bridge units. Reaction 2



describes the formation of **9**. The most important aspect of its structure (Figure 5) is the *anti-anti* bridge configuration, which contributes to the long Fe^{III}—Cu separation of 5.860 Å. Bridge

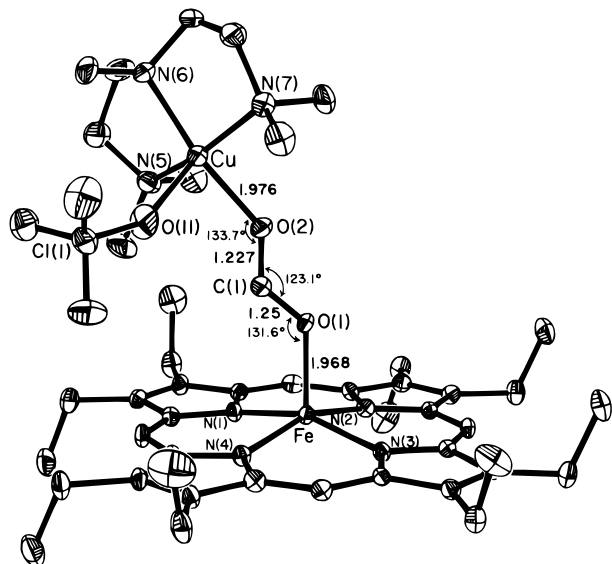


Figure 5. Structure of bridged assembly **9** showing 30% probability ellipsoids, the atom-labeling scheme, and selected bridge metric parameters.

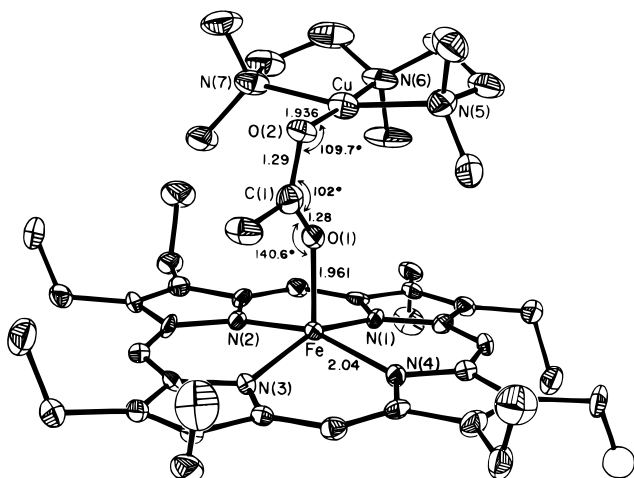


Figure 6. Structure of bridged assembly **10** showing 30% probability ellipsoids, the atom-labeling scheme, and selected bridge metric parameters.

formation requires a switch by formate, which remains equatorial, from the *syn* orientation in reactant **4** to the *anti* configuration in **9**, and the incorporation of perchlorate in an axial position (Cu–O(11) = 2.282(7) Å). As would be expected, the bridge bonds Fe–O(1) and Cu–O(2) are somewhat longer in **9** than in **8** and **4**, respectively, and the associated angles open out by 3–4°. Together with the bridge configuration, these angles dispose the coordination planes N(5,7)O(11) at Cu and N(1–4) at Fe at a dihedral angle of 42.6°. The bridge itself is not planar; its conformation is defined by the dihedral angle FeO(1)C(1)/CuO(2)C(1) = 22.4°. The only other example of an unsupported formate bridge involving metalloporphyrins is found with polymeric [Mn(TPP)(O₂CH)]_n,³³ in which the bridges have the *anti-anti* configuration with angles similar to those of **9**.

The acetate-bridged assembly **10** is produced by reaction 3. In contrast to **9**, the structure of **10** (Figure 6) contains acetate in a *syn-anti* configuration. The Cu fragment, as in **6** and **7**,

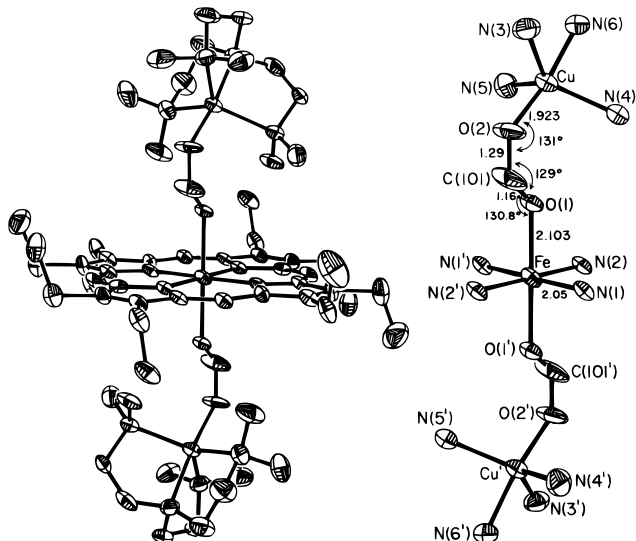
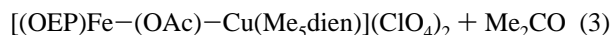
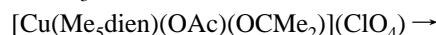
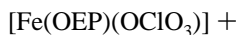


Figure 7. Two views of the structure of bridged assembly **11** showing 30% probability ellipsoids. Left: view of the entire structure. Right: view of the Cu(II) and Fe(III) coordination units including selected bridge metric parameters; primed and unprimed atoms are related by an inversion center.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) in Bridged Assembly **11**

		Bridge	
Cu–O(2)	1.923(9)	Fe–O(1)–C(101)	130.8(9)
Fe–O(1)	2.103(9)	Cu–O(2)–C(101)	131(1)
O(1)–C(101)	1.16(2)	O(1)–C(101)–O(2)	129(2)
O(2)–C(101)	1.29(2)	Fe···Cu	5.422
		Cu Fragment	
Cu–N(3)	2.15(1)	O(2)–Cu–N(3)	86.2(5)
Cu–N(4)	2.16(1)	O(2)–Cu–N(4)	102.7(5)
Cu–N(5)	2.13(1)	O(2)–Cu–N(5)	97.0(5)
Cu–N(6)	2.00(1)	O(2)–Cu–N(6)	170.2(5)
		N(3)–Cu–N(4)	121.4(5)
		N(3)–Cu–N(5)	119.9(5)
		N(4)–Cu–N(5)	116.3(5)
		N(3)–Cu–N(6)	84.7(5)
		N(4)–Cu–N(6)	85.1(5)
		N(5)–Cu–N(6)	84.6(5)
		Heme	
Fe–N(1)	2.04(1)	O(1)–Fe–N(1)	90.8(4)
Fe–N(2)	2.05(1)	O(1)–Fe–N(2)	88.0(4)
		O(1)–Fe–N(2')	92.0(4)
		O(1)–Fe–N(1')	89.2(4)
		N(1)–Fe–N(2)	90.6(4)
		N(2)–Fe–N(1')	89.4(4)

binds acetate in an equatorial *syn* arrangement while the heme acetate is *anti*. Consequently, the Fe···Cu separation of 4.430

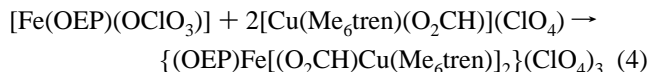


Å is considerably smaller than in **9**. Construction of the bridge requires displacement of the (possible) solvate molecule or the weakly bound O(2) atom at the Cu(II) site and the conversion of acetate to an η^2 ligand, which frees an axial position. The Cu(II) atom is four-coordinate; the nearest perchlorate oxygen atom is 3.67 Å away and has half-site occupancy owing to disorder about the 3-fold axis of the anion. The Cu(II) geometry closely resembles that in polymeric [Cu(dien)(OAc)](ClO₄), which, however, exhibits long axial bridging interactions (2.40,

(33) Turner, P.; Gunter, M. J.; Hambley, T. W.; White, A. H.; Skelton, B. W. *Inorg. Chem.* **1992**, *31*, 2297.

2.65 Å).³⁴ The bridge positions the coordination planes N(5–7) at Cu and N(1–4) at Fe to be nearly parallel (dihedral angle 6.4°). Within the bridge, the Cu–O(1) distance (2.689 Å) appears to convey an extremely weak pseudoaxial interaction. The dihedral angle FeO(1)C(1)/CuO(2)C(1) = 7.1° reveals the bridge conformation to be nearly planar.

When equimolar amounts of **5** and **8** were allowed to react, the trinuclear bridged assembly **11** was formed in reaction 4.



As noted above, contamination by **5**(ClO₄) was lessened when equimolar amounts rather than a 1:2 ratio of reactants were employed. Complex **11** is centrosymmetric with the central heme group bound by two axial formate ligands (Figure 7). In contrast to those in **9**, the bridges in **11** have the *syn-anti* orientation. Thus, **5** was incorporated in the assembly with virtually no change in structure, retaining formate in a *syn* arrangement with a nearly unchanged axial Cu–O(2) bond distance (1.923(9) Å). The axial Fe–O(1) distance has increased by *ca.* 0.13 Å compared to the five-coordinate assemblies **9** and **10**. The mean Fe–N distance of 2.05 Å and the existence of the iron atom in the porphyrin mean plane are consistent with retention of high-spin Fe(III).^{32,35} The longer Fe–O bond and consequent weaker interaction very likely contribute to the marked asymmetry in the formate C–O bond lengths (1.16(2), 1.29(2) Å), the largest observed in **9–11**. The shorter bond is associated with axial ligation to the heme. The Cu(II) and heme fragments are oriented such that the dihedral angle between coordination planes N(3–5) at Cu and N(1,1',2,2') at Fe is 104.3°. With the dihedral angle FeO(1)C(101)/CuO(2)C(101) = 3.1°, the bridge conformation is practically planar. While it is an unexpected reaction product, we note that **11** is preceded by centrosymmetric cyanide-bridged $\{[\text{Cu}(\text{Me}_6\text{tren})]_2\text{Fe}(\text{OEP})(\text{CN})_2\}^{3+}$.^{10b}

Assemblies **9–11** provide the first instances of an *unsupported*²¹ carboxylate bridge between iron and copper, and **9** and **11** exhibit the first structurally proven examples of a heterometal formate bridge of any kind. The two bridge orientations that place the Cu(II) and heme fragments at the largest distances are observed. The *syn-syn* orientation is impossible as a metalloporphyrin bridging modality.

Structure in Solution. A frequently observed NMR feature of five-coordinate [Fe^{III}(OEP)L] complexes is the diastereotopic splitting of the methylene protons into a pair of singlets. The behavior is typified by the L = halide complexes^{36,37} and is also found with bridged assemblies. The following chemical shifts (shift difference) have been observed at ambient temperature: **13**,⁴ 17.4, 20.0 ppm (2.6, Me₂CO); **12**, 33.1, 42.7 ppm (9.6, CD₂Cl₂); **9**, 41.2, 47.4 ppm (6.2, CDCl₃). The downfield progression of shifts stands in the order of decreasing magnetic coupling. Consistent with the proposed origin of splitting is the presence of one methylene signal (48.3 ppm) in the spectrum of centrosymmetric **11** in dichloromethane.

Unlike other bridged assemblies, formate-bridged **9** exhibits fluxional behavior in solution, which can be summarized by the dissociative equilibria (5) and (6). The ¹H NMR spectra of a chloroform solution containing both **9**(ClO₄) and hydroxo-bridged **12**(ClO₄) at 14–56 °C are shown in Figure 8. The

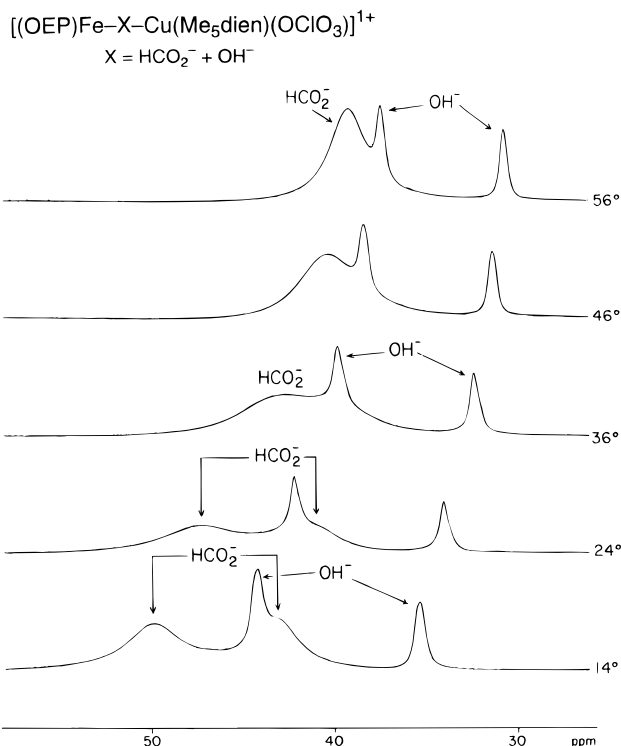
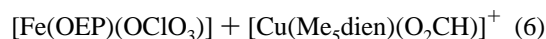
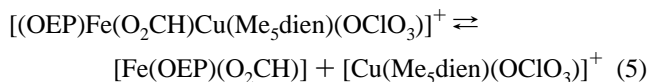


Figure 8. ¹H NMR spectra of OEP CH₂ groups in a mixture of bridged assemblies **9** and **12** in CDCl₃ solution at 14–56 °C. Peak assignments are indicated by the bridging group. At lower temperatures, the diastereotopically split resonances sharpen and shift to lower field.

relatively sharp pair of methylene signals arising from **12** remains well-separated over the temperature range and is a manifestation of a nonfluxional bridged assembly. At 24 °C, **9**



exhibits two broadened methylene signals at 41.2 and 47.4 ppm, very similar to the sharp methylene peaks of **8** (41.1 and 47.0 ppm) in dichloromethane. Thus it is conceivable that the low dielectric chloroform solvent shifts equilibrium 5 to the dissociated region, favoring formation of uncharged **8** over the bridged complex. As the temperature is raised, the methylene signals broaden, coalesce at about 40 °C, and become a broadened singlet at 56 °C and higher temperatures. This averaging of methylene signals at higher temperatures is most likely due to an increased rate of porphyrin inversion processes³⁷ assisted by temporary binding of the dissociated copper complex to the heme fragment, as **8** by itself is not fluxional. Addition of [Cu(Me₅dien)(CF₃SO₃)₂]^{10b} to dichloromethane solutions of **8** simulates ¹H NMR spectra of **9** in dichloromethane, showing a single broadened methylene peak at 45 ppm (midway between methylene peaks of **8**) and providing further evidence for copper-assisted breakage of the formate–Fe bond.

Summary. The following are the principal results and conclusions of this investigation.

1. A series of four- and five-coordinate Cu(II) complexes have been prepared in which formate and acetate are bound in an η^1 *syn* configuration.

2. Molecular assemblies containing carboxylate-bridged heme Fe(III) and Cu(II) can be prepared by the minimal generalized reaction (7), in which carboxylate is introduced in an η^1 Cu-bound form. In the particular systems studied (P =

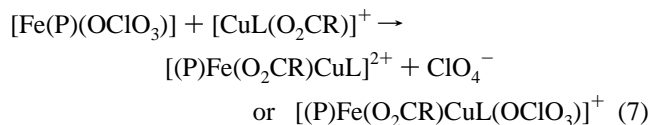
(34) Towle, D. K.; Hoffmann, S. K.; Hatfield, W. E.; Singh, P.; Chaudhuri, P. *Inorg. Chem.* **1988**, *27*, 394.

(35) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 2.

(36) La Mar, G. N. *J. Am. Chem. Soc.* **1973**, *95*, 1662.

(37) Snyder, R. V.; La Mar, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 4419.

OEP, L = Me₅dien, R = H, Me), yields were fair and separation of pure products not inconsequential. Variation of stoichiometry can result in a trinuclear assembly containing two such bridges.



3. The products of reaction 7 contain the first examples of unsupported [Fe^{III}-(μ₂:η²-RCO₂)-Cu^{II}] bridges. These bridges occur with the *anti-anti* (**9**, 22.4°, 5.86 Å) or *syn-anti* (**10**, 7.1°, 4.43 Å) configuration and the indicated FeOC/CuOC dihedral angles and Fe^{III}-Cu separations. The trinuclear assembly also has the *syn-anti* configuration (**11**, 3.1°, 5.42 Å). The high-spin Fe(III) and Cu(II) coordination units are essentially structurally invariant compared to their mononuclear precursors.

4. The insertion of formate between heme a₃ and Cu_B in a *syn-anti* configuration in the binuclear site of cytochrome oxidases (as in the proposal of Figure 1) is dimensionally reasonable, on the basis of the 4.5 and 5.2 Å Fe^{III}-Cu separation in oxidized resting states of the bovine heart³ and bacterial² enzymes, respectively. The *anti-anti* bridge configuration places the two metal centers *ca.* 0.6 Å farther apart than the separation observed in the bacterial oxidase.² These configurations are of course limiting descriptions; the metal-metal distances they induce depend on M-O-C angles.³⁸ Until a larger structural data base is available, these terms remain useful to convey bridge arrangements. The flexibility in distance between the metal centers of native binuclear sites remains to be determined.

Present and past investigations in this laboratory have afforded syntheses and structures of molecular assemblies containing the bridges Fe^{III}-X-Cu^{II} with X = O²⁻,⁴ OH⁻,⁶ and RCO₂⁻, all with a common high-spin heme group. Consequently, this series provides a previously unavailable opportunity to examine ground state electronic structures, including such properties as magnetic exchange and hyperfine coupling, as dependent on the bridging atom or group and bridge structure. Comparison with similar data for oxidases should be useful in interpreting electronic aspects of the latter and assessing structural similarities, at least in the bridge region. A forthcoming report will describe electronic features of the foregoing set of bridged assemblies, a matter of some interest given the possibility that all three bridges may exist under appropriate conditions. We have already noted evidence favorable to a nonlinear Fe^{III}-(OH)-Cu^{II} bridge in a bacterial quinol oxidase.⁹

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Supporting Information Available: For the compounds in Table 1, listings of crystal data and intensity collection parameters, positional and thermal parameters, and interatomic distances and angles (60 pages). Ordering information is given on any current masthead page.

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(38) Note that the bridges in **9** and **11** are both *syn-anti* with comparable Fe-O-C angles (131, 141°) but with Cu-O-C angles that differ by 21° (110, 131°).