Inorg. Chem. **1994,** *33,* 4651−4662

Synthesis and Structural Characterization of Unsupported [Fe^{III}−CN−Cu^{II}] Bridges Related to That in Cyanide-Inactivated Cytochrome *c* Oxidase

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Received February 16, 1994®

The syntheses and first crystal structures of molecular examples of the Fe^{III}−CN−Cu^{II} bridge and their heme and Cu(II) precursors and related Cu(II) complexes are reported. The bridged species were sought as analogues to the binuclear site of cyanide-inactivated cytochrome *c* oxidase. Reaction of Cu(II) triflate with tripodal Me_6tren in acetone gave $[Cu(Me_6tren)(OSO_2CF_3)]^+$ (**1**), which was readily converted to $[Cu(Me_6tren)(MeCN)]^{2+}$ (**2**). Compounds [**1**](CF_3SO_3)/[**2**]$(CF_3SO_3)_2$ were found in monoclinic space group $P2_1/c$ with $a = 11.214(4)/11.385(7)$ Å, $b = 13.103(5)/17.069(9)$ Å, $c = 16.251(7)/13.988(6)$ Å, $\beta = 94.16(3)°/90.56(4)°$, and $Z = 4/4$. A similar reaction with tren in acetonitrile produced $[Cu(tren)(MeCN)]^{2+}$. $[Cu(Me_6tren)(OH_2)]^{2+}$ (**4**) with 1 equiv of KCN in methanol formed $[Cu(Me_6tren)(CN)]^+$ (**6**). Compounds [**3**]$(CF_3SO_3)_2$/[**6**](ClO_4) crystallized in trigonal space group $R\bar{3}c$ with $a = 8.038(1)/10.003(3)$ Å, $c = 55.31(2)/32.70(1)$ Å, and $Z = 6/6$. Complexes **1**−**3** and **6** have trigonal bipyramidal (TBP) stereochemistry with unidentate ligands in axial positions. Reaction of **4** in acetonitrile with $^1/_2$ equiv of KCN afforded binuclear $[(Cu(Me_6tren))_2(CN)]^{3+}$ (**5**), which as [**5**]$(ClO_4)_3\cdot 3MeNO_2$ occurred in triclinic space group $P\bar{1}$ with $a = 9.562(2)$ Å, $b = 13.327(3)$ Å, $c = 20.775(6)$ Å, $\alpha = 85.32(2)°$, $\beta = 78.68(2)°$, $\gamma = 70.86(2)°$, and $Z = 2$. The complex contains two TBP halves connected by the disordered linear Cu^{II}−CN−Cu^{II} bridge in axial positions. Copper(II) triflate with Me_5dien in acetone afforded $[Cu(Me_5dien)(OSO_2CF_3)_2]$ (**7**) while reaction of $[Cu(OH_2)_6]^{2+}$ with tridentate Me_5dien in acetonitrile gave $[Cu(Me_5dien)(MeCN)_2]^{2+}$ (**8**). The compounds **7**/[**8**]$(BF_4)_2$ were found in monoclinic space groups $Cc/(P2_1/n)$ with $a = 13.412(8)/8.568(6)$ Å, $b = 10.729(4)/14.800(7)$ Å, $c = 14.876(8)/17.42(1)$ Å, $\beta = 109.11(4)/90.98(6)°$, and $Z = 4/4$. These complexes exhibit distorted tetragonal planar (TP) structures. Complex **7** with 1 equiv of KCN in methanol/acetonitrile formed $[Cu(Me_5dien)(CN)]_n^{n+}$ (**9**), which as [**9**](CF_3SO_3) crystallized in orthorhombic space group *Pnma* with $a = 7.631(2)$ Å, $b = 10.991(2)$ Å, $c = 20.876(4)$ Å, and $Z = 4$. TP **9** is polymerized through cyanide bridges in equatorial positions. $[Fe(OEP)]_2O$ was converted to [Fe(OEP)(CN)L] (L = py (**10**), 1-MeIm (**11**)) by treatment with Me_3SiCN and L in dichloromethane. Compound **11** was found in $P\bar{1}$ with $a = 10.032(4)$ Å, $b = 13.306(5)$ Å, $c = 17.695(7)$ Å, $\alpha = 75.97(3)°$, $\beta = 86.64(3)°$, $\gamma = 73.53(3)°$, and $Z = 2$. Reaction of **10** or **11** with **4** in acetone afforded the bridged assemblies $[L(OEP)Fe{-}CN{-}Cu(Me_6tren)]^{2+}$ (L = py (**13**), 1-MeIm(**14**)), while a similar reaction of **10** and **7** yielded $[(py)(OEP)Fe{-}CN{-}Cu(Me_5dien)(OSO_2CF_3)]^+$ (**15**). The compounds [**13**]$(SbF_6)_2\cdot Me_2CO$/[**15**](CF_3SO_3) crystallize in $P\bar{1}$ with $a = 13.833(3)/11.941(2)$ Å, $b = 16.552(4)/13.576(3)$ Å, $c = 31.532(6)/19.280(5)$ Å, $\alpha = 94.90(2)/84.08(2)°$, $\beta = 94.66(2)/80.38(2)°$, $\gamma = 112.52(2)/70.60(2)°$, and $Z = 4/2$. Both **13** and **15** possess the desired, nearly linear Fe^{III}−CN−Cu^{II} bridge which links a heme to a Cu fragment; their stereochemistries are only slightly altered from those of the precursor complexes. The bridge occupies an axial position in **13** and an equatorial position in **15**. The *doubly* bridged assembly $\{[Cu(Me_6tren)]_2Fe(OEP)(CN)_2]\}^{3+}$ (**16**) was prepared by the reaction of $[Fe(OEP)(OClO_3)]$ with 2 equiv of **6** in acetone. The compound [**16**]$(SbF_6)_3$ occurred in orthorhombic space group *Pbcn* with $a = 13.093(4)$ Å, $b = 28.964(8)$ Å, $c = 21.243(4)$ Å, and $Z = 4$. The bridge unit Cu^{II}−NC−Fe^{III}−CN−Cu^{II} shows small departures from linearity. Metric data of precursor and related complexes are considered and compared with dimensions of bridge units in **13** and **15**, and the structural systematics of the Fe^{III}−CN−Cu^{II} bridge unit are summarized. Cyanide stretching frequencies for terminal and bridged units are collected and compared. For assemblies containing the Fe^{III}−CN−Cu^{II} bridge in the solid and solution phases, $\nu_{CN} = 2174{-}2183$ cm^{-1}, whereas for the enzymes $\nu_{CN} = 2146{-}2151$ cm^{-1}. Possible reasons for the higher frequencies of the synthetic bridges are considered. Both the bridged assemblies and the binuclear center for the cyanide-inhibited enzymes are exchange-coupled to afford an integer spin state, leading to the conclusion that a bridge is formed in the enzymes but may differ in structure from that established in **13** and **15**. (1-MeIm = 1−methylimidazole, Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine, Me_6tren = 2,2′,2″-tris(dimethylaminoethyl)amine, OEP = octaethylporphyrinate(2−), py = pyridine, tren = tris(2-aminoethyl)amine).

Introduction

Eukaryotic cytochrome *c* oxidases[2] (CcO) and prokaryotic cytochrome and quinol oxidases form a giant family of heme−copper enzymes that catalyze the reduction of dioxygen to water, the final step in aerobic metabolism. The four metal centers in CcO have become increasingly well defined as a result of the application of various spectroscopic techniques. These centers and their relative positions in the mitochondrial enzyme are schematically depicted in Figure 1. The Cu_A center has mixed imidazole−sulfur ligation; recent results suggest that it is actually a binuclear Cu(II)/Cu(I) entity.[3] Heme *a* is low-spin with bis(imidazole) axial ligation. These two centers may

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® Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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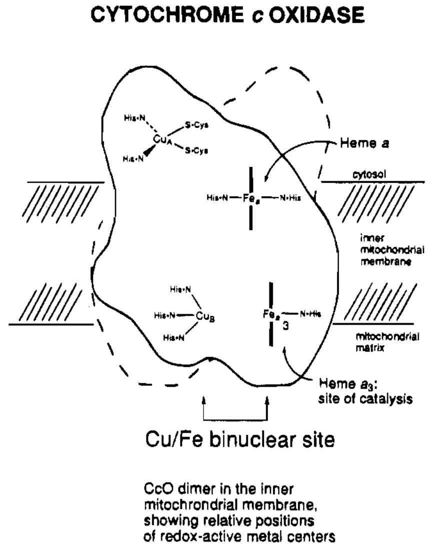

Figure 1. Schematic representation of the relative positions of redox-active metal centers in the mitochondrial CcO dimer (adapted from ref 2c). Note that recent evidence suggests a binuclear Cu_A site.[3]

function in electron transfer to the catalytic size of the enzyme. Here dioxygen is bound and reduced to water by a proximally associated Cu/Fe binuclear reaction center in which the Cu_B site is minimally coordinated by three imidazole groups and the heme a_3 site implicates an axial imidazole ligand distal to Cu_B. In the case of *Rhodobacter sphaeroides* CcO, ligation modes at the heme *a*, heme a_3, and Cu_B sites have been deduced by site-directed mutagenesis.[4] Other than the subset of quinol oxidases which lack Cu_A, the nature of the metal centers appears to be largely conserved over the family.[5-7]

Although all structural and electronic properties of the metal centers in CcO have been derived from spectroscopic analysis of the enzymes themselves, recent results indicate that significant new information can be gained from the synthetic analogue approach. By means of reaction 1 in Figure 2, we have shown that the bridged assembly $[(OEP)Fe-O-Cu(Me_6tren)]^+$ (**12**) containing the linear $Fe^{III}-O-Cu^{II}$ unit can be prepared. Further, antiparallel spin coupling leading to the $S = 2$ ground state of oxidized ("as-isolated") CcO is propagated by the bridging oxo atom.[8] Recently, Nanthakumar *et al.*[9] have prepared a related species with the same bridge unit and ground state. Thus, the oxygen atom is a viable candidate for the as yet unidentified bridge atom in the oxidized enzyme inasmuch as it sustains a prominent electronic property of the binuclear site.

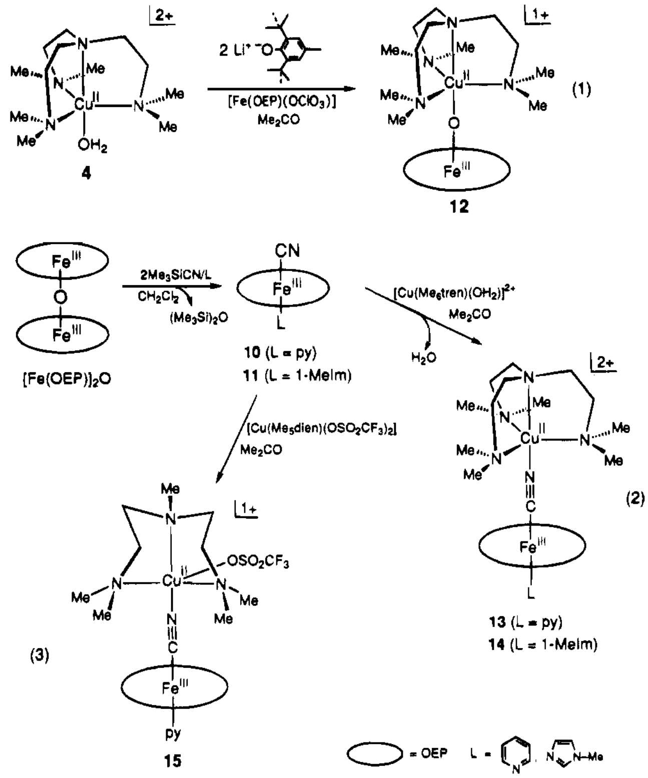

Figure 2. Synthetic routes to Cu(II)−Fe(III) oxo-[8] (**12**) and cyanide-bridged (**13**−**15**) assemblies.

Oxidized and reduced CcO bind a number of exogenous anions,[2] including fluoride, azide, formate, thiocyanate, and cyanide.[10-20] Of these, cyanide is of particular interest and significance. It binds to oxidized and reduced forms of the enzyme and alters all spectroscopic properties (absorption, MCD, resonance Raman, Mössbauer) associated with the binuclear site. When bound to the oxidized enzyme, cyanide causes high-spin heme a_3 to become low-spin and modifies (but does not eliminate) magnetic coupling between Cu(II) and Fe(III) in the binuclear site. Most importantly, cyanide is a potent inhibitor of oxidase activity,[10] and the toxicity of cyanide has been traced to its binding and inhibition of CcO.[21]

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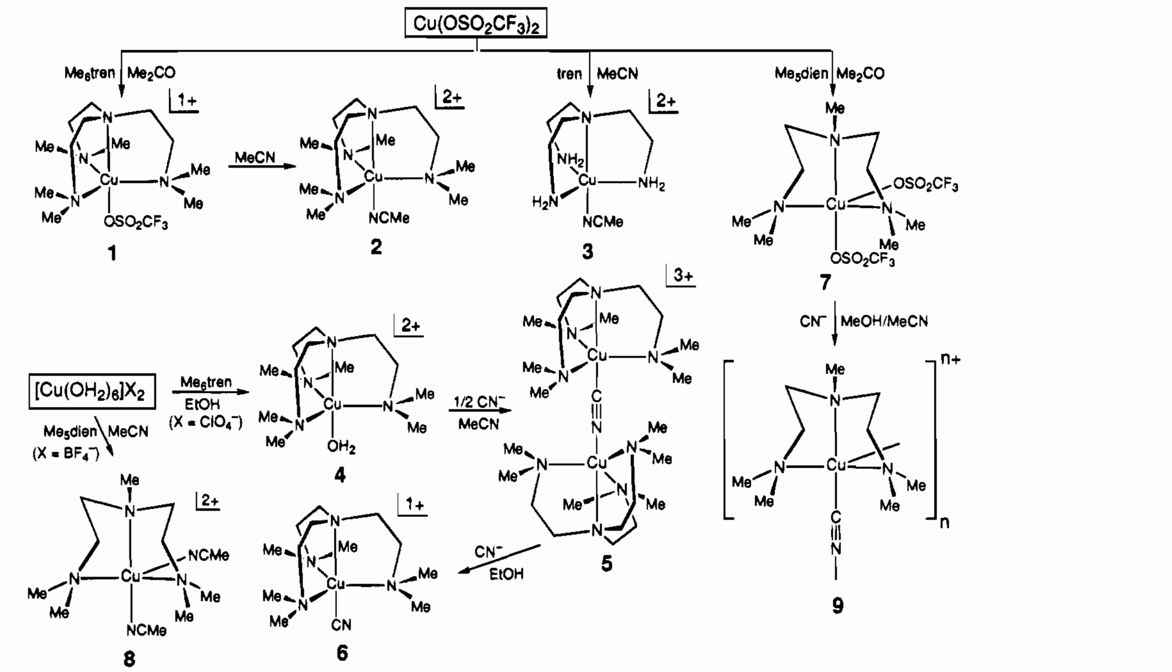

Figure 3. Synthesis of mononuclear Cu(II)–Me_6tren complexes **1**–**3** and **6**, Me_5dien complexes **7**–**9**, and the binuclear cyanide-bridged Me_6tren complex **5**.

There have been numerous proposals that cyanide-bound CcO contains the Fe–CN–Cu bridge unit. While this unit is intuitively acceptable given the ambidentate nature of cyanide,[22,23] its existence in the oxidases is unproven. Recently, using cyanide stretching frequencies as a structural probe, Caughey and co-workers[14] concluded that in oxidized CcO cyanide is coordinated to Cu(II) but is not a bridging ligand, a conclusion that has been contested by Palmer.[20] More recently, the feature at 2151 cm^{-1} has been assigned to the Fe^{III}–CN unit whose nitrogen end is perturbed by hydrogen bonding.[17] Regardless of the merits of these and other arguments concerning the spectroscopic and structural aspects of the cyanide-bound enzyme, it is evident that the existence of one or more structurally proven Fe–CN–Cu molecular species could be of value in assessing the presence or absence of the same bridge in the oxidases. For this reason, we have undertaken a detailed study of this bridge unit, the first structurally proven, heme-based example of which we have recently described;[24] we also note the pioneering work of Gunter, Berry, and Murray,[25] where a similar bridge was apparently prepared although without structural characterization. Here we report the syntheses and solid state structures of heme-based assemblies containing the Fe^{III}–CN–Cu^{II} bridge and of related mononuclear Fe(III) and Cu(II) compounds, and their ν_{CN} values. Future reports will deal with magnetic and other spectroscopic properties and their relationship to corresponding properties of the enzymes.[26]

Experimental Section

Preparation of Compounds.[27] All operations were conducted under a pure dinitrogen atmosphere unless noted otherwise. As appropriate, solvents were degassed and dried by standard methods prior to use.

(a) Iron Complexes. [Fe(OEP)(CN)(py)]. This compound has been reported previously;[28] the following simple alternative procedure results in high yield. To a stirred solution of 500 mg (0.42 mmol) of $[Fe(OEP)]_2O$[29] in 50 mL of pyridine/dichloromethane (1:9 v/v) was added 125 μL (0.94 mmol) of Me_3SiCN. A color change from green-brown to red was evident after 1 h; stirring was continued for 18 h to yield an intensely red solution. The reaction mixture was opened to the air and the solvents were removed by rotary evaporation. The dark microcrystalline residue was dissolved in dichloromethane, the solution was filtered, and *n*-hexane was slowly added to the filtrate, causing some microcrystalline solid to separate. The solution volume was slowly reduced in vacuo, the preferential removal of dichloromethane crystallizing the bulk of the product, which was collected by filtration and washed with *n*-pentane to give 540 mg (92%) of violet microcrystals. Absorption spectrum (acetone): λ_{max} (ϵ_M) 346 (33 900), 406 (103 000), 541 (8100), 553 (sh, 7400) nm.

[Fe(OEP)(CN)(1-MeIm)]. To a rapidly stirred solution of 400 mg (0.334 mmol) of $[Fe(OEP)]_2O$ and 0.50 mL of 1-MeIm in 20 mL of dichloromethane was added 100 μL (0.752 mmol) of Me_3SiCN. The reaction mixture slowly became dark red as it was stirred overnight. All volatiles were removed in vacuo to leave a dark red oily residue, which was treated with 3 mL of dichloromethane. The solution was filtered and several volume equivalents of pentane were diffused into the solution over 48 h. The solid was isolated, washed with several portions of cold ether and with pentane, and dried to give the product as 320 mg (69%) of dark red crystals. Absorption spectrum (acetone): λ_{max} (ϵ_M) 343 (31 000), 409 (123 000), 539 (9300), 579 (sh, 4100) nm. Anal. Calcd for $C_{41}H_{50}N_7Fe{\cdot}CH_2Cl_2$: C, 64.54; H, 6.71; N, 12.54. Found: C, 63.28; H, 6.59; N, 12.85. (These results suggest partial desolvation of the two CH_2Cl_2 solvate molecules identified crystallographically (vide infra).)

(b) Copper Complexes. [Cu(Me_6tren)(OSO_2CF_3)](CF_3SO_3). A solution of 500 mg (2.17 mmol) of Me_6tren[30] was added dropwise to a solution of 785 mg (2.17 mmol) of $Cu(CF_3SO_3)_2$ in 7 mL of acetone. The dark blue solution was stirred overnight 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 afford 1.08 g (84%) of blue crystals. Anal. Calcd for $C_{14}H_{30}CuF_6N_4O_6S_2$: C, 28.40; H, 5.11; Cu, 10.73; N, 9.46. Found: C, 28.27; H, 4.85; Cu, 10.63; N, 9.43.

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(27) Abbreviations of compounds: dien, diethylenetriamine; 1-MeIm, 1-methylimidazole; Me_5dien, 1,1,4,7,7-pentamethyldiethylenetriamine; Me_6tren, 2,2′,2″-tris(dimethylamino)ethyl)amine; OEP, octaethylporphyrinate(2−); py, pyridine; tren, tris(2-aminoethyl)amine; TPP, tetraphenylporphyrinate(2−).

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Table 1. Crystallographic Data[a] for Cu(II)−Me$_6$tren Complexes **1−3**, **5**, and **6**

	[**1**](CF_3SO_3)	[**2**](CF_3SO_3)$_2$	[**3**](CF_3SO_3)$_2$	[**5**](ClO_4)$_3$·3CH_3NO_2	[**6**](ClO_4)
formula	$C_{14}H_{33}CuF_6N_4O_6S_2$	$C_{16}H_{33}CuF_6N_5O_6S_2$	$C_{10}H_{21}CuF_6N_5O_6S_2$	$C_{28}H_{69}Cl_3Cu_2N_{12}O_{18}$	$C_{13}H_{30}ClCuN_5O_4$
fw	595.1	633.1	549.0	1095.4	419.4
cryst syst	monoclinic	monoclinic	trigonal	triclinic	trigonal
space group	$P2_1/c$	$P2_1/c$	$R3c$	$P\bar{1}$	$R3c$
Z	4	4	6	2	6
a, Å	11.214(4)	11.385(7)	8.038(1)	9.562(2)	10.003(3)
b, Å	13.103(5)	17.069(9)		13.327(3)	
c, Å	16.251(7)	13.988(6)	55.308(16)	20.775(6)	32.699(13)
α, deg				85.32(2)	
β, deg	94.16(3)	90.56(4)		78.68(2)	
γ, deg				70.86(2)	
V, Å^3	2381(2)	2718(3)	3095(1)	2451.9(10)	2833(2)
R^b ($R_w{}^c$), %	3.61(3.36)	5.16(5.82)	4.90(5.63)	5.95(6.43)	4.19(4.58)

[a] Obtained with graphite monochromonated Mo Kα (λ = 0.710 73 Å); T = 223 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2/\sum[w|F_o|^2]\}^{1/2}$.

[Cu(Me$_6$tren)(MeCN)](CF_3SO_3)$_2$. [Cu(Me$_6$tren)(OSO_2CF_3)](CF_3SO_3) was dissolved in a minimum volume of acetonitrile, and several volume equivalents to ether were diffused into the solution over 24 h. The solid was collected and washed with ether to give the product in essentially quantitative yield as platelike blue crystals. Anal. Calcd for $C_{16}H_{33}CuF_6N_5O_6S_2$: C, 30.35; H, 5.25; N, 11.06; Cu, 10.03. Found: C, 30.16; H, 5.26; N, 10.95; Cu, 10.27.

[Cu(tren)(MeCN)](CF_3SO_3)$_2$. A solution of 250 mg (0.69 mmol) of tren in 5 mL of acetonitrile was added dropwise to a solution of 101 mg (0.69 mmol) of Cu(CF_3SO_3)$_2$ in 10 mL of acetonitrile. The reaction mixture was stirred for 1 h, and the solvent was removed in vacuo. The dark blue oil was dissolved in the minimum amount of acetonitrile 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 afford the product as 315 mg (83%) of dark blue block-like crystals. Anal. Calcd for $C_{10}H_{21}CuF_6N_5O_6S_2$: Cu, 11.58. Found: Cu, 12.14.

[Cu(Me$_6$tren)(CN)](ClO_4). A mixture of 150 mg (0.294 mmol) of [Cu(Me$_6$tren)(OH_2)](ClO_4)$_2$[8] and 19.2 mg (0.294 mmol) of KCN was treated with 10 mL of methanol. The mixture was stirred overnight and filtered; the filtrate was taken to dryness in vacuo. The residue was dissolved in 2 mL of acetonitrile, the solution was filtered, and ether was diffused into the solution over 48 h. The solid was collected and washed with acetone and with ether; the product was obtained as 98 mg (80%) of dark blue crystals. Anal. Calcd for $C_{13}H_{30}ClCuN_5O_4$: C, 37.23; H, 7.20; N, 16.70; Cu, 15.15. Found: C, 37.16; H, 7.12; N, 16.93; Cu, 15.44.

[(Cu(Me$_6$tren))$_2$(CN)](ClO_4)$_3$. A slurry of 150 mg (0.294 mmol) of [Cu(Me$_6$tren)(OH_2)](ClO_4)$_2$ and 9.6 mg (0.147 mmol) of KCN in 10 mL of acetonitrile was stirred for 12 h. The green solution was filtered and the filtrate taken to dryness in vacuo. The blue-green solid residue was dissolved in the minimum amount of nitromethane and the solution was filtered. Several volume equivalents of ether were diffused into the solution over 24 h. The solid was collected, washed with ether, and dried to afford the product as 106 mg (79%) of blue-green crystals. Anal. Calcd for $C_{25}H_{60}Cl_3Cu_2N_9O_{12}$: C, 32.92; H, 6.63; Cu, 13.93; N, 13.82. Found: C, 32.58; H, 6.85; Cu, 14.04; N, 13.57.

[Cu(Me$_5$dien)(CF_3SO_3)$_2$]. A solution of 0.80 g (4.6 mmol) of Me$_5$dien in 3 mL of acetone was added dropwise to a solution of 1.67 g (4.6 mmol) of Cu(CF_3SO_3)$_2$ in 10 mL of acetone. The mixture was stirred overnight and filtered, and several volume equivalents of ether were diffused into the solution over 24 h. The solid was collected, washed with THF and ether, and dried to afford 2.32 g (94%) of product as large blue crystals. Anal. Calcd for $C_{11}H_{23}CuF_6N_3O_6S_2$: C, 24.70; H, 4.33; Cu, 11.88; N, 7.85. Found: C, 24.91; H, 4.43; Cu, 11.40; N, 7.83.

[Cu(Me$_5$dien)(MeCN)$_2$](BF_4)$_2$. A solution of 0.401 g (2.31 mmol) of Me$_5$dien in 5 mL of acetonitrile was added dropwise to a solution of 0.799 g (2.31 mmol) of Cu(BF_4)$_2$·6H_2O in 30 mL of acetonitrile. The dark blue solution was stirred for 2 h and all volatiles were removed in vacuo. The solid residue was washed with THF and dissolved in 15 mL of acetonitrile, and the solution was filtered. Several volume equivalents of ether were diffused into the filtrate over 48 h, resulting in the formation of a dark blue crystalline mass. This material was collected, washed with THF, and washed with ether to yield 1.07 g (94%) of product as dark blue crystals. Anal. Calcd for $C_{13}H_{29}B_2CuF_8N_5$: C, 31.70; H, 5.93; Cu, 12.90; N, 14.22. Found: C, 31.71; H, 6.25; Cu, 12.60; N, 14.09.

Table 2. Crystallographic Data[a] for Cu(II)−Me$_5$dien Complexes **7−9**

	7	[**8**](BF_4)$_2$	[**9**](CF_3SO_3)
formula	$C_{11}H_{23}CuF_6N_3O_6S_2$	$C_{13}H_{29}B_2CuF_8N_5$	$C_{11}H_{23}CuF_3N_4O_3S_1$
fw	535.0	492.6	411.9
cryst syst	monoclinic	monoclinic	orthorhombic
space group	Cc	$P2_1/n$	$Pnma$
Z	4	4	4
a, Å	13.412(8)	8.568(8)	7.631(2)
b, Å	10.729(4)	14.800(7)	10.991(2)
c, Å	14.876(8)	17.422(11)	20.876(4)
β, deg	109.11(4)	90.98(6)	
V, Å^3	2023(2)	2209(2)	1751.0(5)
R^b ($R_w{}^c$), %	2.49(2.46)	7.62(8.16)	7.71(8.63)

[a] Obtained with graphite monochromated Mo Kα (λ = 0.710 73 Å); T = 223 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$.

[Cu(Me$_5$dien)(CN)]$_n$(CF_3SO_3)$_n$. A mixture of 295 mg (0.55 mmol) of [Cu(Me$_5$dien)(CF_3SO_3)$_2$] and 36 mg (0.55 mmol) of KCN was treated with 15 mL of methanol/acetonitrile (1:1 v/v). The reaction mixture was stirred overnight and filtered; the filtrate was reduced to dryness in vacuo. The solid residue was washed with acetonitrile, acetone, and ether and was dissolved in 2 mL of DMF. The solution was filtered and several volume equivalents of ether were diffused into the filtrate over 48 h. The solid was collected, washed with acetonitrile and ether, and dried in vacuo to afford 127 mg (56%) of product as dark blue crystals. Anal. Calcd for $C_{11}H_{23}CuF_3N_4O_3S$: C, 32.07; H, 5.63; Cu, 15.43; N, 13.60. Found: C, 32.33; H, 5.91; Cu, 15.07; N, 13.72.

(c) **Iron−Copper Bridged Assemblies. [(py)(OEP)Fe−CN−Cu(Me$_6$tren)](ClO_4)$_2$.** Equimolar amounts of [Fe(OEP)(CN)(py)] (100 mg, 0.14 mmol) and [Cu(Me$_6$tren)(OH_2)](ClO_4)$_2$ were dissolved in a minimal volume of acetone (*ca.* 3 mL). Several volume equivalents of ether were diffused into the solution over 48−72 h to afford 145 mg (87%) of violet needles as isolated by removal of the supernatant followed by washing with copious amounts of ether. Absorption spectrum (acetone): λ_{max} (ϵ_m) 348 (27 400), 404 (89 400), 527 (8100), 553 (sh, 6300) nm. An analytical sample was recrystallized from acetone/ether. Anal. Calcd for $C_{54}H_{79}Cl_2CuFeN_{10}O_8$: C, 54.66; H, 6.71; Cl, 5.98; Cu, 5.36; Fe, 4.71; N, 11.80. Found: C, 54.35; H, 6.92; Cl, 6.30; Cu, 5.58; Fe, 4.89; N, 11.25.

[(1-MeIm)(OEP)Fe−CN−Cu(Me$_6$tren)](ClO_4)$_2$. A mixture of 200 mg (0.287 mmol) of [Fe(OEP)(CN)(1-MeIm)] and 146 mg (0.287 mmol) of [Cu(Me$_6$tren)(OH_2)](ClO_4)$_2$ was dissolved in a minimum volume (*ca.* 3 mL) of acetone. The dark violet solution was filtered, and the filtrate was evaporated in vacuo. The residue was dissolved in dichloromethane, the solution was filtered, and the filtrate was evaporated in vacuo. The residue was taken up in a minimum volume of acetone and several volume equivalents of ether were diffused into the solution over 48 h. The solid was collected, washed with THF and ether; the product was obtained as 203 mg (60%) of large needle-like dark violet crystals. Absorption spectrum (acetone): λ_{max} (ϵ_M) 346

Table 3. Crystallographic Data[a] for Heme Complex **11** and Bridged Assemblies **13**, **15**, and **16**

	11·2CH$_2$Cl$_2$	[**13**](SbF$_6$)$_2$·Me$_2$CO	[**15**](CF$_3$SO$_3$)	[**16**](SbF$_6$)$_3$
formula	$C_{43}H_{54}Cl_4FeN_7$	$C_{57}H_{85}CuF_{12}FeN_{10}OSb_2$	$C_{53}H_{72}CuF_6FeN_9O_6S_2$	$C_{62}H_{104}Cu_2F_{18}FeN_{14}Sb_3$
fw	866.6	1517.3	1228.7	1935.8
cryst syst	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbcn*
Z	2	4	2	4
a, Å	10.032(4)	13.833(3)	11.941(2)	13.093(4)
b, Å	13.306(5)	16.552(4)	13.576(3)	28.964(8)
c, Å	17.695(7)	31.532(6)	19.280(5)	21.243(4)
α, deg	75.97(3)	94.90(2)	84.08(2)	
β, deg	86.64(3)	94.66(2)	80.38(2)	
γ, deg	73.53(3)	112.52(2)	70.60(2)	
V, Å^3	2197(2)	6594(3)	2902(1)	8056(4)
R^b ($R_w{}^c$), %	4.32(4.50)	7.63[d]	4.33(4.58)	4.25(4.08)

[a] Obtained with graphite monochromonated Mo Kα (λ = 0.710 73 Å); T = 223 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$. [d] $wR^2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ = 0.1666 (SHELXL-93).

(36 500), 404 (103 000), 526 (8900), 557 (sh, 7000). Anal. Calcd. for $C_{53}H_{80}Cl_2CuFeN_{11}O_8$: C, 53.51; H, 6.78; Cl, 5.96; Cu, 5.34; Fe, 4.69; N, 12.95. Found: C, 53.10; H, 6.75; Cl, 5.85; Cu, 5.15; Fe, 4.64; N, 12.71.

[(Me$_6$tren)Cu−NC−Fe(OEP)−CN−Cu(Me$_6$tren)](ClO$_4$)$_3$. A mixture of 95.6 mg (0.139 mmol) of Fe(OEP)(OClO$_3$)[31] and 116.5 mg (0.278 mmol) of [Cu(Me$_6$tren)(CN)](ClO$_4$) were dissolved in a minimum volume of acetone (*ca.* 2 mL). The dark violet solution was filtered and several equivalents of ether were diffused into the solution over 48 h. The solid was collected, washed with ether, and dried to give 156 mg (73%) of product as large dark violet needle-like crystals. Anal. Calcd for $C_{62}H_{104}Cl_3Cu_2FeN_{14}O_{12}$: C, 48.77; H, 6.84; Cl, 6.97; Cu, 8.32; Fe, 3.66; N, 12.84. Found: C, 48.40; H, 6.83; Cl, 7.11; Cu, 8.38; Fe, 3.62; N, 12.88.

The preceding and several other complexes of primary interest in this work are designated as follows:

[Cu(Me$_6$tren)(OSO$_2$CF$_3$)]$^+$ (**1**)
[Cu(Me$_6$tren)(MeCN)]$^{2+}$ (**2**)
[Cu(tren)(MeCN)]$^{2+}$ (**3**)
[Cu(Me$_6$tren)(OH$_2$)]$^{2+}$ (**4**)
[(Cu(Me$_6$tren))$_2$(CN)]$^{3+}$ (**5**)
[Cu(Me$_6$tren)(CN)]$^+$ (**6**)
[Cu(Me$_5$dien)(OSO$_2$CF$_3$)$_2$] (**7**)
[Cu(Me$_5$dien)(MeCN)$_2$]$^{2+}$ (**8**)
[Cu(Me$_5$dien)(CN)]$_n{}^{n+}$ (**9**)
[Fe(OEP)(CN)(py)] (**10**)
[Fe(OEP)(CN)(1-MeIm)] (**11**)
[(OEP)FeOCu(Me$_6$tren)]$^+$ (**12**)
[(py)(OEP)Fe(CN)Cu(Me$_6$tren)]$^{2+}$ (**13**)
[(1-MeIm)(OEP)Fe(CN)Cu(Me$_6$tren)]$^{2+}$ (**14**)
[(py)(OEP)Fe(CN)Cu(Me$_5$dien)(OSO$_2$CF$_3$)]$^+$ (**15**)
{[Cu(Me$_6$tren)]$_2$Fe(OEP)(CN)$_2$}$^{3+}$ (**16**)

X-ray Data Collection and Reduction. Compounds whose structures were determined are listed in Tables 1−3; in this section, those compounds which are salts are referred to by their cation number. Crystals of **1**−**3**, **5**−**9**, **13**, **15**, and **16** were grown by vapor diffusion of ether into saturated solutions in acetone (**1**, **7**, **13**, **15**, **16**), acetonitrile (**2**, **3**, **6**, **8**), nitromethane (**5**), or DMF (**9**). In the cases of **13** and **16**, small amounts of NaSbF$_6$ were added to the acetone solutions prior to diffusion. Crystals of **11** were obtained by slow diffusion of pentane into a saturated solution in dichloromethane. Single crystals were coated with Paratone-N oil and attached to glass fibers. The crystals were transferred to a Nicolet P3f diffractometer and cooled in a nitrogen stream to −50 °C.

Lattice parameters were obtained from a least-squares analysis of carefully centered reflections with 15° ≤ 2θ ≤ 30°. Decay corrections were based on the measured intensities of two reflections monitored periodically throughout the data collections; none of the compounds showed significant decay. The raw intensity data were converted to structure factor amplitudes and their esd's by correction 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 azimuthal (Ψ) scans were applied to the data sets using the program XEMP. Compounds **1**, **2**, and **8** crystallize in a monoclinic system; systematic absences identified the space groups as $P2_1/c$ (**1**, **2**) and $P2_1/n$ (**8**). Compounds **3** and **6** crystallize in a trigonal system; systematic absences identified the space group as $R3c$ or $R\bar{3}c$. Attempted solution and refinement of both compounds in the two space groups showed that $R3c$ yielded the only acceptable solution. Compounds **5**, **11**, **13**, and **15** crystallize in a triclinic system; space groups were assigned as $P\bar{1}$ by statistics and by successful refinements of the structures. Compound **7** crystallizes in a monoclinic system; systematic absences indicated the space groups Cc or $C2/c$. Of these, only Cc afforded an acceptable solution. Compound **9** was obtained in an orthorhombic system. Systematic absences identified the space group as either *Pnma* or $Pna2_1$; only the former gave an acceptable solution. For compound **16**, systematic absences identified the orthorhombic space group *Pbcn*.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Cu(II)−Me$_6$tren Complexes **1** and **2**

	1	**2**
Cu−N(1)	2.144(3)	2.128(6)
Cu−N(2)	2.146(4)	2.143(7)
Cu−N(3)	2.138(3)	2.156(6)
Cu−N(4)	1.990(3)	2.004(6)
Cu−O(1)/N(5)	1.967(3)	1.965(7)
N(5)−C(51)		1.11(1)
N$_{eq}$−Cu−N$_{eq}$[a]	118.8(1)−120.0(1)	117.6(2)−121.1(2)
N$_{ax}$−Cu−N$_{eq}$[a,b]	86.0(1)−86.9(1)	85.4(2)−85.9(3)
N(1)−Cu−O(1)/N(5)	93.5(1)	94.0(3)
N(2)−Cu−O(1)/N(5)	89.1(1)	94.8(3)
N(3)−Cu−O(1)/N(5)	98.3(1)	93.9(3)
N(4)−Cu−O(1)/N(5)	174.2(1)	179.2(3)
Cu−O(1)−S(1)	148.9(2)	
Cu−N(5)−C(51)		178.9(7)

[a] N$_{eq}$ = N(1−3). [b] N$_{ax}$ = N(4).

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for Cu(II)−Me$_6$tren Complexes **3** and **6**

	3	**6**
Cu−N(2)	2.070(8)	2.184(4)
Cu−N(1)	1.98(1)	2.01(1)
Cu−C(1)		1.96(1)
Cu−N(3)	2.00(2)	
C(3)−N(3)	1.12(3)	
C(1)−N(3)		1.13(1)
N(2)−Cu−N(2′)	119.4(3)	119.0(1)
N(1)−Cu−N(2)	85.5(2)	84.3(1)
N(2)−Cu−C(1)/N(3)	94.5(2)	95.7(1)
N(1)−Cu−C(1)/N(3)	180	180
Cu−C(1)−N(3)		180
Cu−N(3)−C(3)	180	

Structure Solution and Refinement. Structures were solved by direct methods or from Patterson maps using standard procedures. All

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[31] Dolphin, D. H.; Sams, J. R.; Tsin, T. B. *Inorg. Chem.* **1977**, *16*, 711.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for Cu(II)–Me$_5$dien Complexes **7–9**

7		**8**		**9**	
Cu–N(1)	2.052(5)	Cu–N(1)	2.030(9)	Cu–N(1)	2.085(7)
Cu–N(2)	2.041(5)	Cu–N(2)	2.02(1)	Cu–N(2)	2.059(9)
Cu–N(3)	2.027(5)	Cu–N(3)	2.04(1)	Cu–C(1)	1.98(1)
Cu–O(11)	2.036(4)	Cu–N(4)	2.03(1)	Cu–N(3)	2.21(1)
Cu–O(21)	2.212(5)	Cu–N(5)	2.21(1)		
N(1)–Cu–N(2)	85.4(2)	N(1)–Cu–N(2)	86.1(4)	N(1)–Cu–N(2)	85.3(2)
N(2)–Cu–N(3)	86.8(2)	N(2)–Cu–N(3)	87.1(4)		
N(1)–Cu–O(11)	91.7(2)	N(1)–Cu–N(4)	92.6(4)	N(1)–Cu–C(1)	92.5(2)
N(3)–Cu–O(11)	90.6(2)	N(3)–Cu–N(4)	91.1(4)		
O(21)–Cu–N(1)	99.0(2)	N(5)–Cu–N(1)	103.5(4)	N(3)–Cu–N(1)	103.9(2)
O(21)–Cu–N(2)	103.3(2)	N(5)–Cu–N(2)	99.9(4)	N(3)–Cu–N(2)	95.3(4)
O(21)–Cu–N(3)	106.3(2)	N(5)–Cu–N(3)	103.1(4)		
O(21)–Cu–O(11)	89.4(2)	N(5)–Cu–N(4)	87.0(4)	C(1)–Cu–N(3)	93.6(4)
N(1)–Cu–N(3)	154.6(2)	N(1)–Cu–N(3)	153.3(4)	N(1)–Cu–N(1′)	151.3(4)
N(2)–Cu–O(11)	167.3(2)	N(2)–Cu–N(4)	173.0(4)	N(2)–Cu–C(1)	171.1(4)
Cu–O(11)–S(1)	148.2(3)	Cu–N(4)–C(41)	171(1)	Cu–C(1)–N(3)	171.9(9)
Cu–O(21)–S(2)	145.6(3)	Cu–N(5)–C(51)	153(1)	Cu–N(3)–C(1)	172.9(9)

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for Cu^{II}–CN–Cu^{II} Me$_6$tren Bridged Complex **5**[a]

	Bridge		
Cu–C(5)/N(5)[b]	1.951(5)	Cu–C(5)–N(5)	176.4(2)
C(5)–N(5)	1.15(1)		
	Cu Fragment		
Cu–N(1)	2.144(5)	N$_{eq}$–Cu–N$_{eq}$[c]	118.1(2)–120.9(3)
Cu–N(2)	2.162(5)	N$_{ax}$–Cu–N$_{eq}$[d]	85.0(2)–85.5(3)
Cu–N(3)	2.156(7)	N(1)–Cu–C(5)/N(5)	96.8(2)
Cu–N(4)	2.027(5)	N(2)–Cu–C(5)/N(5)	92.8(3)
		N(3)–Cu–C(5)/N(5)	94.5(2)
		N(4)–Cu–C(5)/N(5)	178.0(3)

[a] Two inequivalent cations; data refer to that with the more ordered structure. [b] Atoms C(5) and N(5) were refined as 0.5C + 0.5N. [c] N$_{eq}$ = N(1–3). [d] N$_{ax}$ = N(4).

Table 8. Selected Interatomic Distances (Å) and Angles (deg) for Heme Complex **11**

Fe–N(1)	1.990(5)	N(1)–Fe–N(2)	90.6(2)
Fe–N(2)	1.997(5)	N(2)–Fe–N(3)	89.5(1)
Fe–N(3)	1.986(4)	N(1)–Fe–N(4)	89.6(2)
Fe–N(4)	2.002(5)	N(3)–Fe–N(4)	90.3(2)
Fe–N(5)	2.048(6)	N(1)–Fe–C(1)	90.2(2)
Fe–C(1)	1.927(8)	N(2)–Fe–C(1)	94.1(2)
Fe···Ct[a]	0.006	N(3)–Fe–C(1)	89.0(2)
		N(4)–Fe–C(1)	87.4(2)
		N(1)–Fe–N(5)	90.0(2)
C(1)–N(7)	1.15(1)	N(2)–Fe–N(5)	88.4(2)
Fe–C(1)–N(7)	175.6(5)	N(3)–Fe–N(5)	90.8(2)
C(1)–Fe–N(5)	177.5(2)	N(4)–Fe–N(5)	90.1(2)

[a] Displacement from the 24-atom porphyrin mean plane toward N(5).

structures except that of **13** were refined by full matrix least-squares and Fourier techniques using SHELXTL-PLUS. Owing to the large number of parameters, structure **13** was refined using SHELXL-93. All non-hydrogen atoms were refined with anisotropic thermal parameters unless noted otherwise. Hydrogen atoms were assigned idealized locations and were given a uniform value of B_{iso}.

The asymmetric unit of **1** consists of one cation and one anion, and that of **2** contains one cation and two anions. In **2** three ethylene carbon atoms of the Me$_6$tren ligand are disordered over two positions and were refined with a 0.5 occupancy factor. Complexes **3** and **6** have imposed C_3 axes. The asymmetric unit of **5** consists of crystallographically distinct halves of the cation, three anions, and three nitromethane solvent molecules. The cyanide bridge atoms are disordered across the two inversion centers and were refined with the site occupancy 0.5N + 0.5C. The asymmetric unit of **7** consists of one complete molecule. The asymmetric unit of **8** contains one cation and two anions. In compound **9** the cations are polymerized into infinite chains by cyanide bridges. The cation is situated on a mirror plane. Bridge atoms were refined with both possible orientations; thermal parameters were more consistent, and the structure refined to a lower R value with the carbon atom bound to Cu in an equatorial position. The anion occupies a mirror position and is severely disordered. Attempts to refine the structure in a lower symmetry space group were unsuccessful. Compound **11** crystallized with two dichloromethane solvate molecules. Owing to the limited number of observed data ($F_o^2 > 3\sigma(F_o^2)$), carbon atoms of the imidazole group were isotropically refined. The asymmetric unit of **13** contains two cations, four anions, and two acetone solvate molecules. The asymmetric unit of **15** involves one cation and one anion. The iron atom in **16** crystallizes on an inversion center, and one of the ethyl substituents of the porphyrin was disordered over two positions. The methyl group was refined isotropically with each position having a site occupancy of 0.5. The anions are located on a general and a 2-fold position. Because of the limited number of observed data ($F_o^2 > 3\sigma(F_o^2)$), the carbon atoms of the Me$_6$tren ligand were refined isotropically. Both orientations of the cyanide group were analyzed in the final stages of refinement of bridged assemblies **13**, **15**, and **16**. In each case, the sequence Fe–C–N–Cu was slightly favored over Fe–N–C–Cu. In the last cycle of refinement for all structures, all parameters shifted by <1% of the esd of the parameter, and final difference Fourier maps showed no significant electron density. Selected metric parameters for the 12 structures are contained in Tables 4–10; the structures are depicted in Figures 4–9 and 11.[32]

Other Physical Measurements. All measurements were performed under anaerobic conditions. Absorption spectra were recorded on a Perkin-Elmer Lamba 4C spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker AM-400 spectrometer. FT-IR spectra were measured with a Nicolet IR/42 spectrophotometer.

Results and Discussion

Molecular assemblies **13–15** containing the bridge unit Fe^{III}–CN–Cu^{II} have been prepared by reactions 2 and 3 of Figure 2. Structural analysis of bridges and other features of the assemblies require information concerning (i) the stereochemistry of unbridged Cu(II) and heme fragments and any significant changes upon their incorporation into a bridged assembly and (ii) the interaction of Cu(II) with C- and N-bound cyanide, with nitriles used as simulations of the latter situation, which is unknown in mononuclear Cu(II) chemistry. Inasmuch as the structure at the Cu$_B$ site of the binuclear center in CcO is unestablished, we wished to introduce at least two different stereochemistries in the Cu fragments of the final assemblies. By use of the ligands Me$_6$tren and Me$_5$dien, (distorted) trigonal bipyramidal (TBP) and tetragonal pyramidal (TP) arrangements, respectively, were stabilized with attendant axial (ax) and equatorial (eq) coordination. The ligands chosen also afforded favorable solubility properties of Cu(II) precursor complexes in acetone, where the bridged assemblies are formed.

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(32) See paragraph at the end of this article concerning supplementary material.

Table 9. Selected Interatomic Distances (Å) and Angles (deg) for Fe^{III}−CN−Cu^{II} Bridged Assemblies **13**[a] and **15**

	13a	**13b**	**15**
	Bridge		
Fe−C(1)	1.92(2)	1.88(1)	1.898(5)
C(1)−N_{CN}[b]	1.14(2)	1.15(1)	1.149(7)
Cu−N_{CN}	1.88(1)	1.91(1)	1.949(5)
Fe···Cu	4.94	4.93	4.98
Fe−C(1)−N_{CN}	179(1)	180(1)	177.3(6)
Cu−N_{CN}−C(1)	174(1)	174(1)	170.2(5)
Fe···C_t[c]	0.17	0.15	0.09
	Heme		
Fe−N(1)	2.00(1)	1.984(9)	1.994(4)
Fe−N(2)	2.011(9)	2.00(1)	1.988(5)
Fe−N(3)	1.984(9)	1.98(1)	1.986(4)
Fe−N(4)	2.02(1)	2.00(1)	1.989(5)
mean of 4	2.00(1)	1.99(1)	1.989(3)
Fe−N(5)	2.05(1)	2.057(9)	2.066(4)
N(1)−Fe−N(2)	89.9(4)	89.9(4)	90.4(2)
N(2)−Fe−N(3)	90.3(4)	89.2(4)	89.7(2)
N(3)−Fe−N(4)	89.7(4)	90.5(4)	89.2(2)
N(4)−Fe−N(1)	90.1(4)	90.3(4)	90.7(2)
N_p−Fe−N(5)[d]	91.1(3)	91(1)	91(1)
N_p−Fe−C(1)	89(1)	89(1)	89(2)
C(1)−Fe−N(5)	178.0(5)	178.9(5)	178.1(2)
	Cu Fragment		
Cu−N(6)	2.13(1)	2.14(1)	2.048(4)
Cu−N(7)	2.15(1)	2.14(1)	2.056(4)
Cu−N(8)	2.14(2)	2.14(1)	2.019(4)
Cu−N(9)	1.99(1)	2.01(1)	
Cu−O(11)			2.239(6)
N(6)−Cu−N(9)	86.2(5)	85.7(5)	
N(7)−Cu−N(9)	87.8(6)	86.7(5)	
N(8)−Cu−N(9)	85.3(6)	84.8(5)	
N(6)−Cu−N(7)	118.4(6)	119.8(6)	156.3(2)
N(6)−Cu−N(8)	120.9(6)	118.7(6)	86.4(2)
N(7)−Cu−N(8)	119.5(7)	119.8(6)	86.5(2)
N(6)−Cu−N_{CN}	93.6(5)	92.8(5)	
N(7)−Cu−N_{CN}	94.1(5)	94.1(5)	91.3(2)
N(8)−Cu−C_{CN}	93.1(6)	95.9(5)	92.8(2)
N(6)−Cu−O(11)			98.7(2)
N(7)−Cu−O(11)			104.5(2)
N(8)−Cu−O(11)			96.0(2)
N(9)−Cu−O(11)			91.4(2)
N(9)−Cu−N_{CN}	178.0(6)	178.4(5)	
N(8)−Cu−N_{CN}			172.5(2)

[a] The unit cell contains two crystallographically independent complexes. [b] Nitrogen atom of the cyanide bridge. [c] Displacement from the porphyrin mean plane toward N(5). [d] Mean values, N_p = porphyrin nitrogen atom.

Mononuclear Cu(II) Complexes. Two series of complexes, **1**, **2**, **6** and **7**−**9** derived from Me$_6$tren and Me$_5$dien were prepared by the procedures in Figure 3 to obtain synthetic intermediates and to provide comparative structural data in TBP and TP stereochemistries. The aquo complex **4** is known from previous work.[8] Structures are set out in Figures 4 and 5 and selected metric data are compiled in Tables 4−6. Because of the large amount of structural information presented here and subsequently, some results are expressed as ranges of values rather than as individual values.

(a) Me$_6$tren Complexes. As in all previous complexes of the type $[M(Me_6tren)L]^{2+/1+}$,[8,33] the Me$_6$tren ligand in **1**, **2**, and **6** coordinates in a tripodal tetradentate manner with each ligand arm forming a puckered five-membered ring and ligand L in an axial position. In the resulting TBP stereochemistry, the Cu−N_{ax} distances (1.99−2.01 Å) are always significantly shorter than the Cu−N_{eq} distances (2.13−2.18 Å). Structures are collected in Figure 4; bond distances and angles are summarized in Tables 4 and 5.

Table 10. Selected Interatomic Distances (Å) and Angles (deg) in the Cu^{II}−NC−Fe^{III}−CN−Cu^{II} Bridged Assembly **16**

	Bridge		
Fe−C(1)	1.94(1)	Fe···Cu	4.99
C(1)−N(7)	1.14(2)	Fe−C(1)−N(7)	173(1)
Cu−N(7)	1.94(1)	Cu−N(7)−C(1)	171.8(9)
	Cu Fragment		
Cu−N(3)	2.14(1)	N_{eq}−Cu−N_{eq}[a]	118.4(4)−120.3(4)
Cu−N(4)	2.16(1)	N_{ax}−Cu−N_{eq}[b]	85.2(4)−86.0(4)
Cu−N(5)	2.17(1)	N_{eq}−Cu−N(7)	93.6(4)−95.9(4)
Cu−N(6)	1.99(1)	N(6)−Cu−N(7)	178.8(4)
	Heme		
Fe−N(1)	1.995(8)	N(1)−Fe−N(2)	89.6(3)
Fe−N(2)	1.994(8)	N(2)−Fe−N(1′)	90.4(3)
N_p−Fe−C(1)[c]	88.3(4)−91.7(4)		

[a] N_{eq} = N(3−5). [b] N_{ax} = N(6). [c] N_p, porphyrin N atoms.

The triflate group in **1** is readily displaced by acetonitrile to afford **2**, whose axial ligand is linearly coordinated with a Cu−N(5)−C(51) angle of 178.9(7)° and a Cu−N(5) distance of 1.965(7) Å. The TBP stereochemistry of **3** (Figure 4), which has imposed trigonal symmetry, is precedented in Cu(II)−tren complexes.[34] Comparison with **2** reveals a shorter Cu−N_{eq} distance (2.070(8) Å), presumably arising from the absence of interactions among *N*-methyl groups projecting below the equatorial plane. The bond length to the axial acetonitrile, Cu−N(1) = 1.98(1) Å, is indistinguishable from that in **2**, indicating that the *N*-methyl groups of Me$_6$tren do not sterically influence the Cu−L_{ax} bond distances of linear ligands. Reaction of aquo complex **4** with equimolar cyanide in methanol affords cyanide complex **6**, also with imposed trigonal symmetry. The axial Cu−C(1) distance of 1.96(1) Å is the same as the axial Cu−NCMe bond lengths in **2** and **3**.

(b) Me$_5$dien Complexes. Given the well-documented tendency of Me$_5$dien to stabilize TP geometry or close approaches thereto in complexes of Cu(II),[35] three additional complexes **7**−**9** of this ligand were prepared. Structures are shown in Figure 5, and metric data are compiled in Table 6.

Reaction of Cu(II) triflate with equimolar Me$_5$dien in acetone afforded the bis(triflate) species **7**. Treatment of $[Cu(OH_2)_6](BF_4)_2$ with equimolar Me$_5$dien in acetonitrile gave the bis(acetonitrile) complex **8**.[36] Both complexes have distorted TP stereochemistry, readily recognized by bond angles in the equatorial plane near 90°, displacement of the Cu(II) atom from this plane toward an axial ligand, and elongation of the Cu−ligand bond distance along a pseudotetragonal axis. In the case

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(36) When the perchlorate salt was used as a starting material, a different compound was isolated. Blue $[Cu(Me_5dien)(OH_2)(MeCN)](ClO_4)_2$ has a distorted TP structure with water in the axial and acetonitrile in the equatorial position.

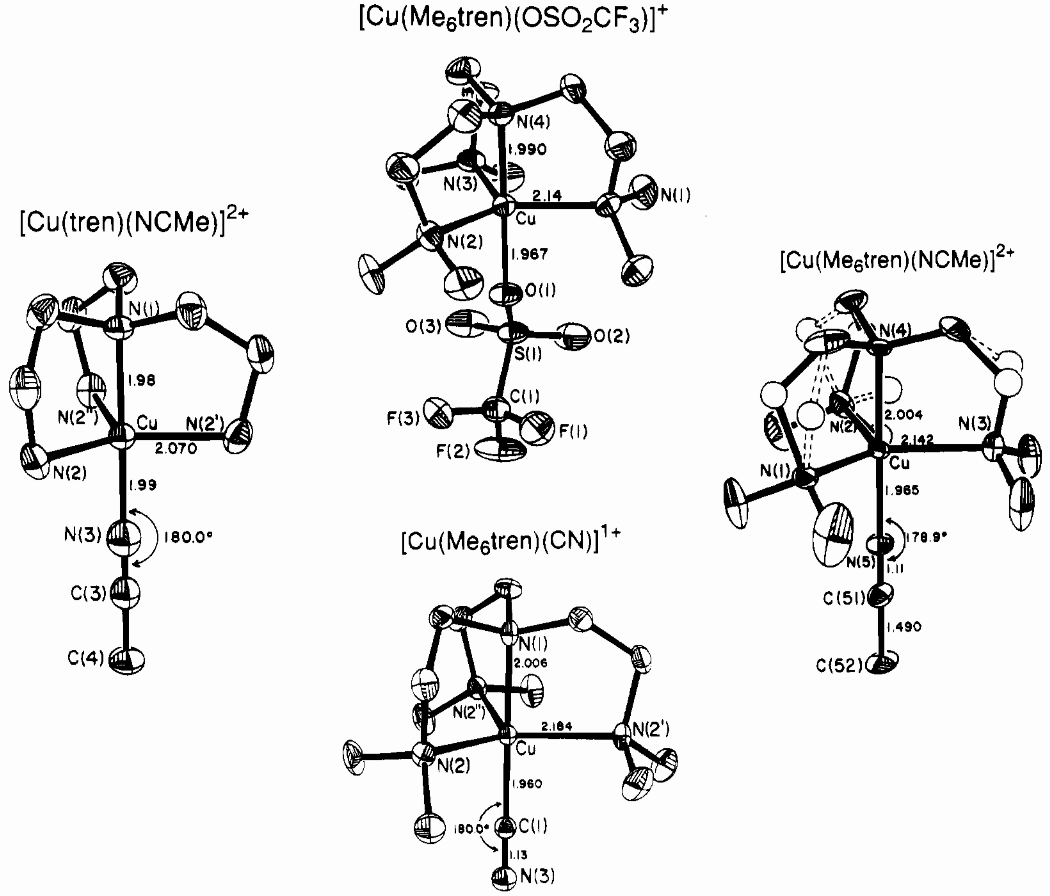

Figure 4. Structures of the trigonal bipyramidal Cu(II)−Me$_6$tren complexes **1**−**3** and **6** showing 50% probability ellipsoids (30% for **2**), atom labeling schemes, and mean equatorial Cu−N bond distance and other metric parameters. Open circles in the structure of **2** represent refined positions of disordered carbon atoms; primed and unprimed atoms are related by a C_3 axis.

of **7**, the equatorial portion is Cu−N(1−3)O(11), with bond distances of 2.027(5)−2.052(5) Å and bond angles of 85.4(2)−91.7(2)°. The axial ligand atom is O(21) bonded at a distance of 2.212(5) Å from the metal. The equatorial portion of **8** is Cu−N(1−4) with bond distances of 2.02(1)−2.04(1) Å and bond angles of 86.1(2)−92.6(2)°. The axial ligand atom N(5) is situated at 2.21 Å from the Cu(II) atom. The equatorial acetonitrile approaches linear coordination (Cu−N(4)−C(41) = 171(1)°) whereas the axial acetonitrile exhibits decidedly nonlinear binding (Cu−N(5)−C(51) = 153(1)°).

Bridged Cu(II) Complexes. Reaction of aquo complex **4** with $^1/_2$ equiv of cyanide in acetonitrile solution (Figure 3) affords the binuclear cyanide complex **5**, whose Cu−CN−Cu bridge structure has been established by an X-ray determination. As shown in Figure 6, the complex when crystallized as a perchlorate salt tris(nitromethane) solvate occurs as a centrosymmetric cation with disordered bridge atoms; metric features are listed in Table 7. The TBP coordination stereochemistry of Me$_6$tren complexes is retained, with an axial cyanide bridge. The Cu−C(5)/N(5) bridge bond length of 1.951(5) Å is indistinguishable from the axial nonbridging distance in **6** and the Cu-NCMe distance in **2**.

Attempts to prepare a monocyano Me$_5$dien complex by reaction of **7** with equimolar KCN in methanol/acetonitrile gave a product **9** with the desired stoichiometry but a polymeric structure (Figure 6). Bond angles and distances (Table 6) are consistent with a distorted TP structure having one cyanide in the equatorial plane (Cu−C(1) = 1.98(1) Å) and the other in an axial position (Cu−N(3) = 2.21(1) Å). Both act as bridging ligands to Cu(II) atoms, resulting in a polymeric crystal structure in which linked units have an imposed mirror plane.

As a class, Cu(II)−cyanide complexes are not entirely common,[23,37] owing to the tendency of Cu(II) to oxidize cyanide to cyanogen. Stable complexes are invariably those containing polydentate aliphatic or aromatic nitrogen ligands,[34b,37−39] a property observed here. Among known mononuclear complexes, TBP $[Cu(tren)(CN)]^+$ [34b] is most closely related to **6**. The Cu^{II}−CN−Cu^{II} bridge has been previously structurally authenticated only in centrosymmetric TBP $[Cu_2([14]\text{-}4,11\text{-}dieneN_4)_2(CN)]^{3+}$, where a linear arrangement obtains and the cyanide bridge occupies an equatorial position (Cu−C/N = 2.125(3) Å).[39b] Magnetic properties indicate its presence in species such as $[Cu_2(tren)_2(CN)]^{3+}$.[39d]

Heme Cyanides. Two monocyano ferriheme complexes have been prepared. Complex **10**, as noted earlier, has been reported[28] and here has been prepared in 92% yield by a more efficient method (Figure 2). Complex **11** was sought because of the closer resemblance of 1-methylimidazole to the coordinated histidine side chain at the iron site of the binuclear center. The structure of **11** is shown in Figure 7; dimensional data are given in Table 8. The detailed stereochemistry resembles that in **10**[28b] and [Fe(TPP)(CN)(py)];[40] the porphyrin ring exhibits S_4 ruffling, but out-of-plane displacements are not as pronounced

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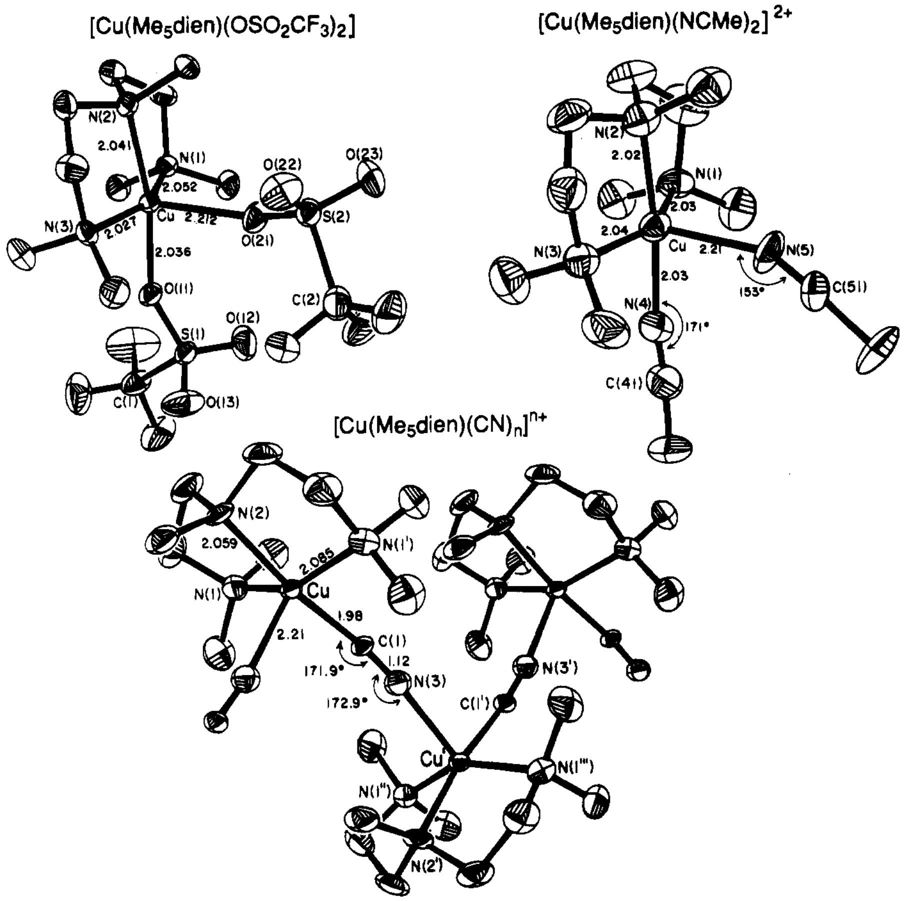
[Cu(Me$_5$dien)(OSO$_2$CF$_3$)$_2$]

[Cu(Me$_5$dien)(NCMe)$_2$]$^{2+}$

[Cu(Me$_5$dien)(CN)$_n$]$^{n+}$

Figure 5. Structures of distorted square-pyramidal Cu(II)–Me$_5$tren complexes **7** and **8** and polymeric cyanide-bridged complex **9**, showing 50% probability ellipsoids, atom labeling schemes, and selected bond distances and angles. Primed and unprimed atoms are related by a mirror plane.

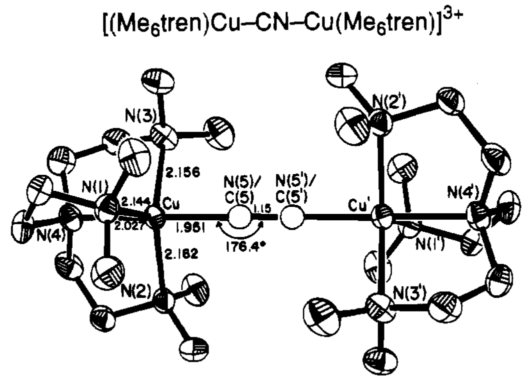
[(Me$_6$tren)Cu–CN–Cu(Me$_6$tren)]$^{3+}$

Figure 6. Structure of one of two crystallographically inequivalent bridged complexes **5** showing 50% probability ellipsoids, the atom labeling scheme, and selected metric parameters. Primed and unprimed atoms are related by an inversion center; open circles are bridge atoms refined as 0.5C + 0.5N. The structure of the other complex is essentially identical to that shown.

as in **10**. The differences in Fe–C and Fe–N$_p$ distances between **10** and **11** are <0.01 Å; the axial Fe–N distance in **10** (2.087(3) Å) is marginally longer than that in **11** (2.048(6) Å). In **10**, the Fe(III) atom is displaced by 0.053 Å from the mean porphyrin plane toward the cyanide carbon atom whereas in **11** the displacement is opposite and very small (0.006 Å) toward the imidazole nitrogen atom. Both **10** and **11** were utilized in the synthesis of cyanide-bridged assemblies.

$\mathrm{Fe^{III}}$–CN–$\mathrm{Cu^{II}}$ Bridged Assemblies. Binuclear singly bridged assemblies **13** and **14** were prepared by reaction 2 and **15**[41] by the analogous reaction 3 of Figure 2. These processes involve displacement of a labile axial ligand (water, triflate) by the nitrogen end of coordinated cyanide in a noncompetitive coordinating solvent (acetone). The compound [**13**](ClO$_4$)$_2$ was isolated in 87% yield as a purple crystalline solid. Metathesis to the [SbF$_6$]$^-$ salt afforded a material more amenable to solution of the crystal structure. We also prepared [**14**](ClO$_4$)$_2$ as a highly crystalline solid, but were unable to determine its structure by X-ray diffraction. The compound was identified by elemental analysis and spectroscopic properties.[26]

Three examples of the $\mathrm{Fe^{III}}$–CN–$\mathrm{Cu^{II}}$ bridge have been crystallographically identified. The asymmetric unit of [**13**](SbF$_6$)$_2$·Me$_2$CO contains two cations per asymmetric unit. Selected metric data for both are provided in Table 9 and the structure of one is depicted in Figure 8, from which the presence of the bridge is immediately apparent. In **13**, the cyanide occupies an axial position in the TBP Cu fragment and the bridge itself is essentially linear, the angles Cu–N–C = 174(1)° departing only slightly from linearity. Comparison of the structure of this assembly with its heme and Cu components as represented by **10**[28b] and **2**/**6**, respectively, reveals only small dimensional changes pursuant to ligand displacement and bridge formation. The bond distances Fe–C, Fe–N$_p$, and C–N are unimportantly different in the assembly compared to the components; in particular, the mean Fe–N$_p$ values of 2.05(1) and 2.057(9) Å demonstrate retention of low-spin Fe(III)[42] in the assembly. Somewhat surprisingly, the bridge Cu–N bond lengths (1.88(1), 1.91(1) Å) are appreciably *shorter* than the best available model axial distances, Cu–CN (**6**), Cu–C/N (**5**), and Cu–NCMe (**2**), which define the narrow interval 1.951(5)–1.965(7) Å. While the effect of negative charge could account for shorter distances when compared to acetonitrile ligation, the situation with C- and N-bound cyanide is unclear.

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[41] The preparation of **15** and other Me$_5$dien assemblies and related complexes will be reported separately.

[42] Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.

These relatively tight Cu−N interactions should result in electron withdrawal from bridging cyanide, an effect that may correlate with the displacement of the Fe atom from the mean porphyrin plane toward the pyridine nitrogen atom by *ca.* 0.15 Å. The porphyrin ring is domed in the same direction, perhaps because packing interactions force the OEP ethyl substituents and their bonded ring carbon atoms to project toward the Cu fragment. This effect would abet the Fe atom displacement. The comparative spectroscopic properties of **13** and **14**[26] insure that both have essentially the same structure.

The structure of assembly **15** is shown in Figure 9; bond distances and angles are summarized is Table 9. With only minor dimensional changes, the Cu fragment has retained the distorted TP stereochemistry of precursor **7**. The long Cu−O(11) bond distance of 2.239(6) Å identifies the axial triflate ligation. The equatorial portion is Cu−N(6−9) with the bridging cyanide in the equatorial plane. The bridge departs somewhat from linearity, mainly because of the angle Cu−N(9)−C(1) = 170.2(5)°, and separates the metal centers by 4.98 Å. The bridge Cu−N(9) bond length of 1.949(5) Å is shorter than the model Cu−NCMe (**8**) and Cu−N/C (**9**) distances of 2.03(1) and 1.99(1) Å, respectively. The Fe(III) atom is displaced by 0.09 Å toward the pyridine nitrogen. The features are akin to those observed in **13** and may have a common origin inasmuch as the porphyrin ring is also domed in the direction of the displacement, but with far less regular deviations from planarity.

Solution Properties. The absorption spectrum of free heme complex **10** and assembly **13** are presented in Figure 10. Consistent with the small structural differences between **10** and its fragment status in **13**, the two chromophores are similar but with some intensity differences. Bridge formation results in a very small shift of the Soret and ultraviolet maxima, and the band shape of the visible features is somewhat altered. The spectrum of **13** is a mildly perturbed version of **10**. The same conclusion follows from the comparison of heme complex **11** and assembly **14**.

Assemblies **13**−**15** exhibit well resolved, isotropically shifted ^{1}H NMR spectra of their heme fragments.[26] A characteristic feature of the Fe(III) complexes $[Fe(OEP)LL']^z$ is the diastereotopic splitting of methylene proton signals when $L \neq L'$.[43] The assemblies manifest this behavior, but with quite different chemical shifts compared to the free hemes, in acetone solution at 298 K: **13**, δ 8.14, 11.57; **14**, δ 6.46, 11.02; **15**, δ 8.35, 11.29. Consequently, we conclude that the bridges remain intact under these conditions. Furthermore, the spectra establish the presence of a single linkage isomer.

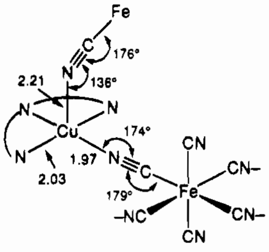
Cu^{II}−NC−Fe^{III}−CN−Cu^{II} Bridged Assembly. The existence of porphyrin complexes of the type $[Fe^{III}(P)(CN)_2]^-$, including structurally authenticated $[Fe(TPP)(CN)_2]^-$,[44] suggested the possibility of a doubly bridged assembly. Reaction 4 afforded such a species, isolated as $[\mathbf{16}](ClO_4)_3$ in 73% yield as dark violet crystals.

$$[Fe(OEP)(OClO_3)] + 2[Cu(Me_6tren)(CN)]^+ \rightarrow \{[Cu(Me_6tren)]_2Fe(OEP)(CN)_2\}^{3+} + ClO_4^- \quad (4)$$

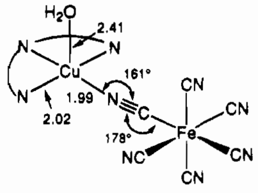
Structural proof of **16** is provided in Figure 11 and dimensional information in Table 10. The complex is centrosymmetric, and the bridge occupies the expected axial position in the Cu fragments and is nonlinear (Fe−C(1)−N(7) = 173(1)°; Cu−N(7)−C(1) = 171.8(9)°). The bridge distance Cu−N(7) = 1.94(1) Å is somewhat shorter than that in **13** and may be influenced by fewer unfavorable interactions between the *N*-methyl groups of the Me$_6$tren ligand and the OEP ethyl groups. Because of the centrosymmetry, adjacent nondisordered groups are directed toward opposite Cu fragments; two symmetry-related ethyl groups are disordered. In acetone solution at 298 K, **16** exhibits a single methylene resonance at δ 9.06 consistent with centrosymmetry.

Synthesis and Structural Precedents. Complexes **13**−**16** are the first structurally authenticated examples of the Fe^{III}−CN−Cu^{II} bridge in discrete assemblies involving a heme component. We are unaware of any previous reactions similar to eqs 2 and 3 (Figure 2), in which an axial cyanide in a metalloporphyrin functions as a ligand to another metal site. However, in the work of Murray and co-workers[25] using a picket-fence heme with four nicotinamido groups positioned above the same face, it appears that this bridge was constructed by displacement of a μ-Cl atom in a binuclear precursor of known structure. Compound identification was inferred from method of synthesis, elemental composition, and magnetic properties; positive structural proof could not be established by X-ray methods because of poor crystal quality.

The Fe$^{III/II}$−CN−Cu^{II} bridge has been structurally demonstrated in compounds obtained from aqueous reaction systems comprised of CuSO$_4$, dien, and ferro- or ferricyanide.[45] The Fe(II) compound $\{[Cu(dien)]_2[Fe(CN)_6]\}\cdot 6H_2O$ is polymerized by such bridges. The fragment **17** of this compound illustrates bridging through nearly linear equatorial and bent axial interactions. Of the six cyano groups, four are involved in bridging interactions. The Fe(III) compound $\{[Cu(dien)]_3[Fe(CN)_6]_2\}\cdot 6H_2O$ contains a cationic polymeric chain $\{[Cu(dien)]_2[Fe(CN)_6]\}^+$, with fragments similar to **17**, and the discrete binuclear anion $\{[Cu(dien)][Fe(CN)_6]\}^-$ (**18**) in which cyanide forms a nonlinear bridge in an equatorial position of the Cu fragment. The indicated equatorial Cu−N bond distances of 1.97(1) and 1.99(1) Å are not significantly different. These values are longer than those of the heme-based assemblies.



17



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From the five molecular Fe^{III}−CN−Cu^{II} bridge structures determined thus far, the following principal features emerge: (i) the apparent range of Cu−N distances is 1.88−1.99 Å; (ii) Fe−CN components are essentially or exactly linear; (iii) bridges occupying TBP axial and TP equatorial positions in Cu fragments approach or achieve linearity, and deviations from nonlinearity are larger in Cu−NC components (minimum Cu−N−C = 161° (**18**)). These features apply also to the Fe(II) compound containing **17**; the bent axial bridge finds a counterpart in the nonlinear axial binding of acetonitrile in TP **8**. These results currently define the structural systematics of the Fe^{III}−CN−Cu^{II} bridge; in the absence of any strong nonbonded interactions across the bridge, we consider the metric features manifested by the heme-based assemblies **13ab**, **15**, and **16** to be intrinsic values.

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[43] The following split methylene resonances are observed in Me$_2$CO solutions at 298 K: **10**, δ 5.79, 6.48; **11**, δ 4.98, 5.12.

[44] Scheidt, W. R.; Haller, K. J.; Hatano, K. *J. Am. Chem. Soc.* **1980**, *102*, 3017.

[45] Morpurgo, G. O.; Mosini, V.; Porta, P.; Dessy, G.; Fares, V. *J. Chem. Soc., Dalton Trans.* **1980**, 1272; **1981**, 111.

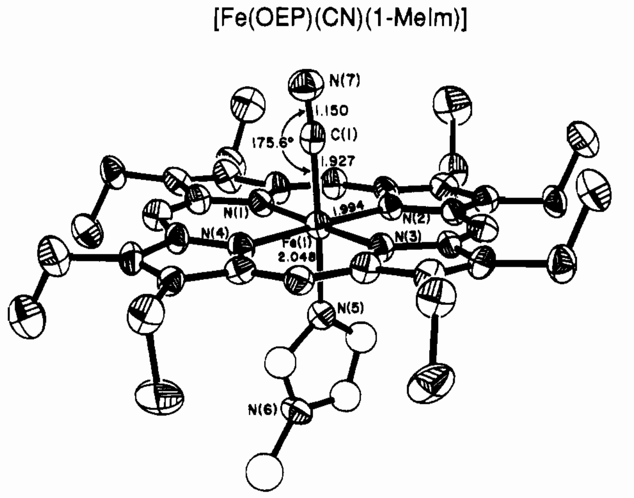

Figure 7. Structure of heme complex **11** showing 50% probability ellipsoids, the atom labeling scheme, and selected metric parameters. Carbon atoms (circles) of the imidazole ligand were refined isotropically.

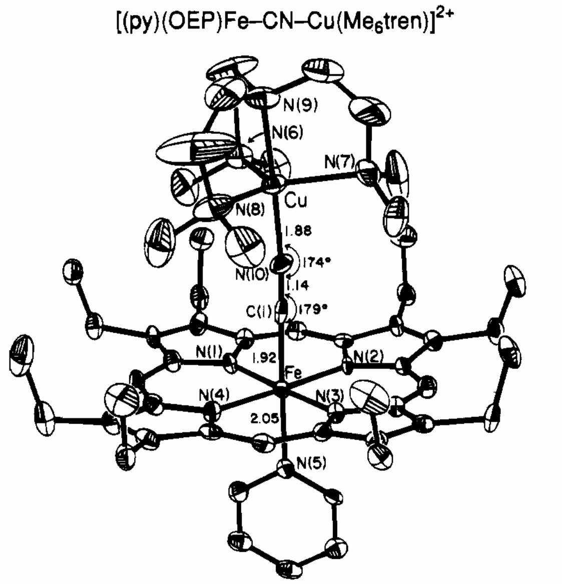

Figure 8. Structure of bridged assembly **13** showing 30% probability ellipsoids, the atom labeling scheme, and selected metric parameters.

Cyanide Stretching Frequencies. In M−CN units where cyanide acts as a σ-donor, electron density is withdrawn from its sp σ^* MO and ν_{CN} is increased relative to that for uncoordinated cyanide. When functioning as a π-acceptor, electron density is added to the empty p π^* MO and ν_{CN} is decreased. In the bridge unit M−CN−M′, where cyanide donates σ electron density to two metals, ν_{CN} is increased further compared to M−CN with M constant. These effects have been amply verified.[22,23,46] Further, recent work with hexacyanometalates has demonstrated the sensitivity of ν_{CN} to (weak) interactions with cations in the crystalline state.[47]

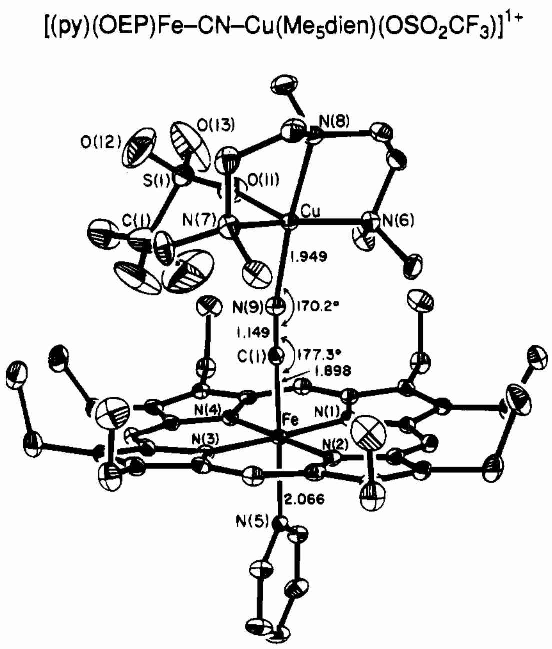

Figure 9. Structure of bridged assembly **15** showing 50% probability ellipsoids, the atom labeling scheme, and selected metric parameters.

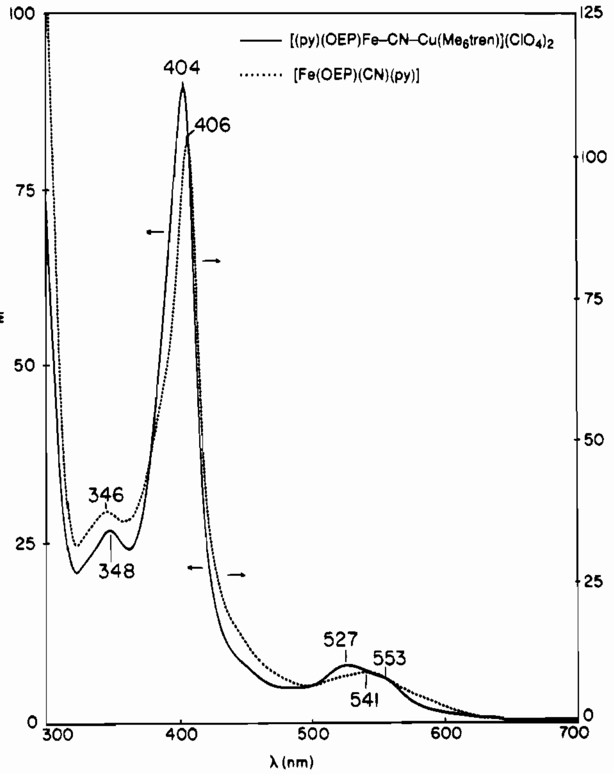

Figure 10. Absorption spectra of heme complex **10** and bridged assembly **13** in acetone solutions. Band maxima are indicated.

Infrared data for five types of metal-cyanide interactions are summarized in Table 11; pertinent results for Cu(II) cyanides from other investigations[39cd,48] are included. Bands are of moderate to weak intensities. All frequencies are higher than that of KCN, indicating that σ-donation dominates. Further, terminal Cu−CN frequencies tend to be lower than Cu−CN−Cu frequencies, but there is some overlap. In the mononuclear complexes, cyanide is tightly bound (Cu−C = 1.94−1.97 Å[38,39bc]). The same is true for bridged species **5** and **9** (Cu−C/N = 1.95 Å (**5**); Cu−C = 1.98 Å (**9**)). The frequencies of these complexes do not overlap. [Cu_2([14]4,11-diene-N_4)$_2$(CN)](ClO_4)$_3$ is the only other structurally proven bridged species and exhibits the lowest ν_{CN} (2130 cm^{-1}). Its previously noted long Cu−C/N distance (2.125(3) Å) indicates relatively weak binding; consequently, the stretching frequency is well below that of species with tighter bridges and invades the terminal Cu^{II}−CN range.

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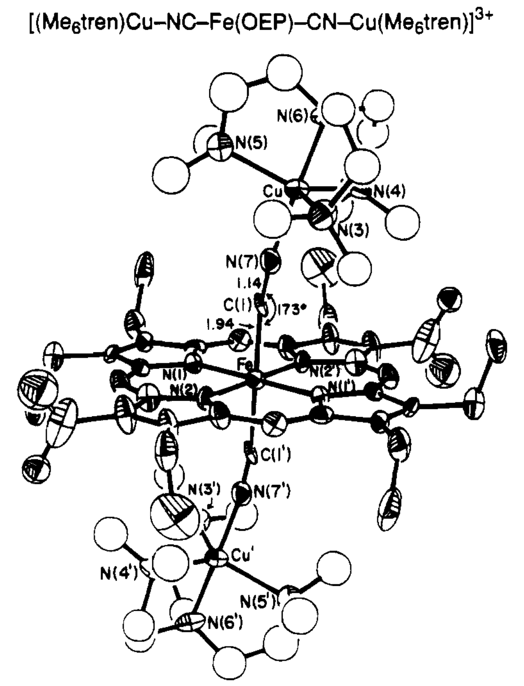

Figure 11. Structure of centrosymmetric doubly bridged assembly **16**, conveying the information in Figure 8. Atoms represented by open circles were described isotropically; two symmetry-related methyl groups are disordered over two positions.

The highest values of ν_{CN} are found for Fe^{III}−CN−Cu^{II} bridges. Excluding the results for doubly-bridged **16**, whose two bands indicate coupled stretches, the values fall into the narrow range 2174−2183 cm^{-1}. They are the same or only slightly different in the solid or solution phase and have no evident dependence on the stereochemistry of the Cu fragment, with the proviso that all bridges are tightly bound (Cu−N = 1.88−1.95 Å). The complex [(py)(OEP)Fe−CN−Cu(Me$_5$dien)-(MeCN)]$^{2+}$ [41] is structurally analogous to **15**. These frequencies are significantly higher than those of oxidized bovine heart CcO, for which there are two independent determinations,[14,18] and of oxidized cytochrome *bo* from *Escherichia coli*[49] (Table 11). The range of enzyme frequencies (2146−2152 cm^{-1}) is just above that for terminal Cu^{II}−CN. In these cases, other spectroscopic evidence suggests the presence of low-spin ferriheme, as in assemblies **13**−**15**.

Interestingly, the low-spin ferriheme−Cu species with the putative Fe^{III}−CN−Cu^{II} bridge described by Murray and coworkers[25] has ν_{CN} = 2150 (solid) and 2143 cm^{-1} (MeOH/CHCl$_3$ solution), in excellent agreement with the enzyme results. The proposed structure of that complex places the bridge nitrogen atom in the axial position of a TP Cu^{II}−N$_4$ unit that is linearly connected to the heme iron atom. Such an arrangement, if not geometrically constrained, would result in a Cu−N bond longer than is the case in **13**−**15**, perhaps in the vicinity of the 2.21 Å axial distance in **8**. This situation would certainly result in a lowering of ν_{CN} relative to the assemblies characterized here. However, any other interaction which increases σ-electron density at the cyanide would have the same consequence. Whatever the exact structural nature of coordinated cyanide in the binuclear center of CcO, its effect of magnetically coupling the Fe and Cu centers to afford an integer electron spin[12,50] is also found in our bridged assemblies.[26] Consequently, it is highly probable that cyanide is a bridge in the enzymatic binuclear center but that, from the IR results, the entire Fe^{III}−CN−Cu^{II} unit including its position in the Cu$_B$ coordination sphere is not structurally congruent with either type of bridged assembly. Current evidence suggests an extent of electronic convergence between the synthetic species and cyanide-treated CcO.[24,26] Future reports will deal with the synthesis and structures of additional bridged assemblies incorporating the Cu^{II}(Me$_5$dien) fragment, and spectroscopic properties of these assemblies and **13**−**15** that bear on the relationship of structurally undefined biological and structurally characterized synthetic bridges.

Table 11. Cyanide Stretching Frequencies[a]

group	compound	ν_{CN}, cm^{-1}
CN$^-$	NaCN	2080
Cu^{II}−CN	[**6**](ClO$_4$)	2136
	MeCN soln	2140
	[Cu(tren)(CN)](BPh$_4$)	2140[b]
	[Cu(phen)$_2$(CN)](NO$_3$)·H$_2$O	2136[c]
Fe^{III}−CN	**10**	2129
	11	2115
	MeCN soln	2120
Cu^{II}−CN−Cu^{II}	[**5**](ClO$_4$)$_3$[d]	2174, 2168
	[**9**]$_n$(CF$_3$SO$_3$)$_n$	2154
	[Cu$_2$([**14**]4,11-diene-N$_4$)$_2$-(CN)](ClO$_4$)$_3$	2130[b]
	[Cu$_2$(tren)$_2$(CN)](PF$_6$)$_3$	2150[e]
	[Cu$_2$(bpy)$_4$(CN)](PF$_6$)$_3$	2140[e]
	[Cu$_2$(phen)$_4$(CN)](PF$_6$)$_3$	2160[e]
Fe^{III}−CN−Cu^{II}	[**13**](ClO$_4$)$_2$	2177
	MeNO$_2$ soln	2179
	MeNO$_2$ (+24 equiv of H$_2$O) soln	2179
	[**14**](ClO$_4$)$_2$	2183
	MeCN soln	2180
	[**15**](CF$_3$SO$_3$)	2181
	[(py)(OEP)Fe−CN−Cu-(Me$_5$dien)(MeCN)](ClO$_4$)$_2$	2174
	ox. CcO (bovine heart)	2151,[f] 2152[g]
	ox. cyt. *bo* (*E. coli*)	2146[h]
Cu^{II}−NC−Fe^{III}−CN−Cu^{II}	[**16**](ClO$_4$)$_3$	2168, 2159

[a] Mulls in Paratone-N oil for compounds prepared in this work. [b] Reference 39c, Nujol mull. [c] Reference 48. [d] Two inequivalent cations. [e] Reference 39d, KBr; X-ray structures have not been determined. [f] Reference 14. [g] Reference 18. [h] Reference 49.

Acknowledgment. This research was supported by NSF Grant CHE 92-08387. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. M.J.S. thanks Professor J. Clardy for a helpful discussion.

Supplementary Material Available: X-ray structural information for the compounds in Tables 1−3, giving tables of crystal and intensity collection data, positional and thermal parameters, interatomic distances and angles (107 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the American Chemical Society; see any current masthead page for ordering information.

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