# Fluoride-Bridged Dimers: Binuclear Copper(II) Complexes and Iron(III)–Copper(II) Assemblies

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Preparation of binuclear assemblies containing the $Fe^{III}$–F–$Cu^{II}$ bridge unit gave rise to the problem of distinguishing $[Cu_2(\mu\text{-}OH)_2]^{2+}$ vs $[Cu_2(\mu\text{-}F)_2]^{2+}$ bridges. Reaction of $[Cu(MeCN)_4](PF_6)$ with bnpy$_2$ followed by aerobic oxidation afforded green $[Cu_2F_2(bnpy_2)_2](PF_6)_2$ (**1**), which crystallizes in monoclinic space group $P2_1/c$ with $a$ = 12.337(3) Å, $b$ = 13.065(3) Å, $c$ = 14.916(4) Å, $\beta$ = 113.16(2)°, and $Z$ = 2. Cation $\mathbf{1}^{2+}$ has a parallel-planar dimeric structure in which square pyramidal Cu(II) forms asymmetric axial (2.232(2) Å) and equatorial (1.918(2) Å) bridge bonds. This species has been identified further by elemental analysis and mass spectrometry. These results, together with the structural systematics of the two bridges, indicate that $\mathbf{1}^{2+}$ is the correct formulation of the cation in a previously isolated compound described as $[Cu_2(OH)_2(bnpy_2)_2](PF_6)_2\cdot 2H_2O$. The reaction systems affording $\mathbf{1}^{2+}$ are complex; from them two other dimers have been isolated. $[Cu_2(OMe)_2(bnpy_2)_2](PF_6)_2$ contains a centrosymmetric cation with equatorial Cu–O bridge bonds, following the pattern of hydroxo-bridged species. $[Cu_2(bnOpy)_2](ClO_4)_2$ (**2**) was obtained in space group $P2_1/n$ with $a$ = 10.665(3) Å, $b$ = 9.086(2) Å, $c$ = 21.999(7) Å, $\beta$ = 101.94(2)°, and $Z$ = 2. It contains a centrosymmetric cation with monooxygenated ligands and equatorial Cu–O bridge bonds. Reaction of $Fe(OEP)(OClO_3)$ with **1** in acetone afforded $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(OClO_3)](PF_6)$. The same reaction in acetonitrile gave $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(MeCN)](ClO_4)(PF_6)\cdot MeCN$. Compounds **3**/**4** crystallize in triclinic space group $P\bar{1}$ with $a$ = 12.673(3)/13.96(1) Å, $b$ = 13.832(4)/14.08(2) Å, $c$ = 16.901(5)/18.49(2) Å, $\alpha$ = 93.69(2)°/106.0(1)°, $\beta$ = 105.64(2)°/100.54(8)°, $\gamma$ = 92.91(2)°/111.74(8)°, and $Z$ = 2. These bridged assemblies contain two square pyramidal halves connected by an unsupported asymmetric bridge that approaches linearity (Fe–F–Cu = 171.9(1)° (**3**), 166.2(5)° (**4**)). The Fe–F bond distances (1.865(3) Å (**3**), 1.86(1) Å (**4**)) are only slightly longer than that of Fe(OEP)F (**5**; 1.834(2) Å). Compound **5** was isolated in space group $P2_1/n$ with $a$ = 14.891(4) Å, $b$ = 13.743(3) Å, $c$ = 17.398(5) Å, $\beta$ = 94.24(2)°, and $Z$ = 4. The procedures and results provided here should be of utility in resolving fluoride/hydroxide bridge atom ambiguities in binuclear Cu(II) systems. [bnpy$_2$ = *N*,*N*-bis(2-(2-pyridylethyl))benzylamine, bnOpy$_2$ = *N*-(2-(2-pyridylethyl))-*N*-(2-oxo-2-(2-pyridylethyl))-benzylamine, Me$_6$tren = tris(*N*,*N*-dimethyl-2-aminoethyl)amine, and OEP = octaethylporphyrinate(2–).]

## Introduction

Several metalloproteins have been proven to, or very probably, contain adjacent metal centers connected by a covalent bridge.[2–5] Such constructions may be termed *bridged assemblies*, complexes of two (or more) metal sites spanned by intervening atoms to form an integral unit. Bridged assemblies remain a subject of active study across the breadth of inorganic chemistry, with several standing challenges to their synthesis existent in bioinorganic chemistry alone.[6–8]

As one starting point of description, bridged assemblies can be defined as *symmetric* or *asymmetric*, depending on whether the separate bridged metal environments are identical or different. These terms here refer to the assembly proper, as distinguished from the symmetric/asymmetric bridge descriptors, discussed later, which describe patterns of strong and weak bondings at the bridge. In addition, two limiting bridging motifs can be discerned: *supported*—multiple bridges linking two metal sites, ranging from the simple $M(\mu\text{-}X)_2M$ fragments common in a variety of metal halides to complex polynucleating ligand architectures—and *unsupported*—only a single bridging entity joining separate metal centers. Finally, bridged metal sites that interact electronically may be designated as *intimate*. These terms provide a basis for describing and analyzing synthetic endeavors directed toward biological bridged assemblies, of which the most pertinent here is that of oxidized cytochrome *c* oxidase (CcO).

For CcO, potential bridge entities in various reaction states of the enzyme are now believed to be small atomic or pseudoatomic units: $O^{2-}/OH^-$,[9] $Cl^-$,[4a] $CN^-$,[10] $N_3^-$,[11] present because of either the isolation procedure or the addition of exogenous ligands. Elsewhere, we have reported the synthesis and structure of the first analogue of the bimetallic site of oxidized, as-isolated CcO.[7] This species was formed by the transformation $Cu^{II}\text{–}OH + Fe^{III}\text{–}OClO_3 + B \rightarrow Cu^{II}\text{–}O\text{–}Fe^{III} + BH^+ + ClO_4^-$ and realized as the linear bridged assembly $[(OEP)Fe\text{–}O\text{–}Cu(Me_6tren)]^+$.[12] Terminal cupric hydroxides were unknown at the outset of our study; consequently, we scrutinized the structural and reactivity features reported for species containing the $Cu^{II}{}_2(\mu\text{-}OH)_2$ supported bridge for suitable synthetic precursors. We encountered a potentially useful compound containing curiously asymmetric hydroxo

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(12) Abbreviations: bnpy$_2$ = *N*,*N*-bis(2-(2-pyridylethyl))benzylamine; bnOpy$_2$ = *N*-(2-(2-pyridylethyl))-*N*-(2-oxo-2-(2-pyridylethyl))benzylamine; Me$_6$tren = tris(*N*,*N*-dimethyl-2-aminoethyl)amine; OEP = octaethylporphyrinate(2–).

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bridges which we have reinvestigated. This study, reported here, has led to a reexamination of this compound and produced a set of new observations concerning the function of fluoride in forming supported symmetric and unsupported asymmetric assemblies.

## Experimental Section

**Preparation of Compounds.** All operations were performed under a pure dinitrogen atmosphere unless otherwise indicated. Acetonitrile was distilled from CaH$_2$, degassed, and stored over molecular sieves (4 Å) under dinitrogen before use. Acetone was distilled from B$_2$O$_3$,[13] and methanol, from Mg(OMe)$_2$; both solvents were degassed and stored under dinitrogen. The ligand bnpy$_2$[12,14] was synthesized from 2-vinylpyridine and benzylamine by a procedure analogous to that reported.[15]

**[Cu$_2$F$_2$(bnpy$_2$)$_2$](PF$_6$)$_2$ (1). Method 1.** In 100 mL of methanol, 1.76 g (4.72 mmol) of [Cu(MeCN)$_4$](PF$_6$)[16] and 1.50 g (4.72 mmol) of bnpy$_2$ were combined under anaerobic conditions with stirring for 2 h to give a clear yellow solution. Upon exposure to air, an immediate blue-green color appeared, which deepened as time progressed. After the solution was stirred overnight, a blue supernatant and a crystalline blue product mixed with a light blue powder were obtained. The solid was collected by filtration, washed with ether, and dissolved in the minimum volume of warm acetonitrile. The solution was filtered to remove an insoluble light blue powder. Ether was diffused into the deep blue filtrate, resulting in the formation of a solid, which was collected by filtration and washed with ether to afford 1.2 g (47%) of a blue crystalline product. This method has proven of limited reproducibility. In the majority of attempts, the aforementioned product was not obtained. Instead, exposure to air proceeded to give a blue-green supernatant and a light green powder which, upon crystallization, we have crystallographically characterized as the equatorially bridged Cu(II) dimer [Cu$_2$(OMe)$_2$(bnpy$_2$)$_2$](PF$_6$)$_2$.[17] FD-MS: *m/z* 399 (M$^+$, [Cu(bpny$_2$)F]$^+$ or [Cu(bpny$_2$)F]$_2^{2+}$). Anal. Calcd for C$_{42}$H$_{46}$Cu$_2$F$_{14}$N$_6$P$_2$: C, 46.28; H, 4.26; Cu, 11.66; F, 24.40; N, 7.71; P, 5.68. Found: C, 46.50; H, 4.27; Cu, 11.85; F, 25.67; N, 7.73; P, 5.66. Calcd for C$_{42}$H$_{48}$Cu$_2$F$_{12}$N$_6$O$_2$P$_2$: C, 46.45; H, 4.28; Cu, 11.70; F, 20.99; N, 7.74; P, 5.70 (($\mu$-OH)$_2$-bridged complex).

**Method 2.** In air, a light green suspension of 0.25 g (1.8 mmol) of CuF$_2$·2H$_2$O (Alfa) was stirred in 50 mL of methanol containing 0.58 g (1.8 mmol) of bnpy$_2$ for 36 h. The blue mixture was treated with 0.33 g (1.8 mmol) of KPF$_6$, and the resultant mixture was stirred for 1 h. The blue microcrystalline precipitate was collected by filtration, washed with methanol and ether, and redissolved in 50 mL of boiling dichloromethane. This solution was filtered when hot, and the volume of the dark blue filtrate was reduced in vacuo until blue microcrystals were evident. An excess of ethanol was added and the volume reduction continued until the supernatant was largely colorless. The precipitate was filtered off, washed with ether, and air-dried to afford 0.44 g (44%) of the product as a blue powder. Anal. Found: C, 46.25; H, 4.48; F, 25.89; N, 7.68. This product has crystallographic parameters and an EPR spectrum identical to those of the product from method 1.

**[Cu$_2$(bnOpy$_2$)$_2$](ClO$_4$)$_2$ (2).** Method 1 was followed, but with use of [Cu(MeCN)$_4$](ClO$_4$).[16] The color changed as the reaction progressed, giving a blue-green supernatant and copious quantities of a light green powder, soluble only in very polar aprotic solvents (e.g., DMF or Me$_2$SO) and not further characterized. The mixture was filtered, and the blue-green filtrate was allowed to evaporate over a period of days, ultimately yielding a small quantity of sparingly soluble, small blue-green rectangular crystals imbedded in a sticky blue-green syrup. The crystalline product appears to be a minor component, with the majority of copper removed as the light green solid. The presence of other products is suggested by the sticky residue. This compound was identified by an X-ray structure determination.

**[(OEP)Fe–F–Cu(bnpy$_2$)(OClO$_3$)](PF$_6$) (3).** To an orange-brown solution of 50 mg (0.073 mmol) of Fe(OEP)(OClO$_3$)[12,18] in acetone was added 40 mg (0.037 mmol) of solid **1**. The reaction mixture was stirred for 1 min, yielding a homogeneous black-brown solution. Diffusion of several volume equivalents of ether into the solution over the course of 24–48 h resulted in the crystallization of the product as black blades, which were isolated by decanting the supernatant and washing with ether to give 61 mg (68%). (The yield of this reaction is apparently dependent on the quality of acetone. Wet acetone results in the deposition of a glassy material within the first 12–18 h of ether diffusion. Removal of the mother liquor followed by ether diffusion gives the product in reduced yield.) Atom ratios Fe:Cu:Cl:P = 1:1.0:0.9:0.8 by microprobe analysis; this compound was further identified by an X-ray structure determination.

**[(OEP)Fe–F–Cu(bnpy$_2$)(MeCN)](ClO$_4$)(PF$_6$)·MeCN (4).** An approximately 10 mM solution of Fe(OEP)(OClO$_3$) in acetonitrile was added to 0.5 equiv of solid **1**. A red microcrystalline product immediately precipitated upon mixing. Several volume equivalents of ether were diffused into the black-brown mixture over 24–48 h, yielding dark brown, faceted, blocklike crystals of product, which were isolated by decanting the supernatant and washing with ether. Atom ratios Fe:Cu:Cl:P = 1:1.1:1.1:0.6 by microprobe analysis; the compound was further identified by an X-ray structure determination.

**Fe(OEP)F (5).** In a capped Nalgene bottle under air, 100 mg (0.084 mmol) of [Fe(OEP)]$_2$O[19] was dissolved in 30 mL of dichloromethane and the mixture was vigorously stirred with 20 mL of aqueous 5% HF solution for 1 h. After removal of the acidic aqueous layer by pipet, the organic phase was washed three times with water, separated from the mixture, and dried over Na$_2$SO$_4$ for 1 h. Hexane was added to the deep red solution, and the total solvent volume was reduced in vacuo. After removal of most of the dichloromethane, a black microcrystalline precipitate appeared. This material was collected by filtration and washed with ether to afford 40 mg (39%) of product. A second crop (20 mg) was obtained by addition of hexane to the filtrate, volume reduction, and cooling. Absorption spectrum (CH$_2$Cl$_2$); $\lambda_{max}$, nm ($\epsilon_M$): 352 (48 400), 393 (106 000), 485 (8500), 510 (sh, 7500), 600 (7100). $^1$H NMR (CDCl$_3$): $\delta$ 39.8 (br, 8), 35.8 (br, 8), 5.8 (br, 24), –33.6 (vbr, 4). This compound was further identified by an X-ray structure determination.

**Collection and Reduction of X-ray Data.** Diffraction-quality crystals were obtained by diffusion of ether or *n*-pentane into solutions of the compounds [**1** (acetonitrile/ether) as blue plates,[20] **3** (acetone reaction mixture/ether) as black elongated plates, **4** (acetonitrile reaction mixture/ether) as dark brown faceted blocks, **5** (chloroform/*n*-pentane) as dark brown prisms] or by slow evaporation [**2** (methanol reaction mixture) as green-blue rectangular blocks]. All crystals were mounted as described previously.[21] Diffraction data were collected using graphite-monochromatized Mo K$\alpha$ radiation on a Siemens R3m/v four-circle automated diffractometer equipped with a Siemens LT-2 cryostat operating at 173 K. Following preliminary indexing, refined unit cell parameters were obtained by least-squares fits of machine-centered reflections (**1**, 24 reflections with $25° \leq 2\theta \leq 32°$; **2**, 24 with $20° \leq 2\theta \leq 28°$; **3**, 25 with $25° \leq 2\theta \leq 31°$; **4**, 12 with $13° \leq 2\theta \leq 21°$; **5**, 48 with $20° \leq 2\theta \leq 33°$). Crystals of **4** diffracted poorly, and only a limited data set was obtained. Data were processed and corrected for Lorentz and polarization effects, and peak profiles were fitted (XDISK from the SHELXTL program

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(17) [Cu$_2$(OMe)$_2$(bnpy$_2$)$_2$](PF$_6$)$_2$·2MeCN: $a = 13.817(3)$ Å, $b = 10.276(2)$ Å, $c = 18.348(4)$ Å, monoclinic, $\beta = 91.05(2)°$, $P2_1/n$, $T = 230$ K, $R(R_w) = 6.17\%$ (7.09%). The structure was refined with all atoms anisotropically described; hydrogen atoms were not included in the refinement. Because of the routine nature of the structure, it is not reported in full. The stereochemistry of the cation resembles that in [Cu$_2$(OMe)$_2$L](ClO$_4$)$_2$: Karlin, K. D.; Shi, J.; Hayes, J. C.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chim. Acta* **1984**, *91*, L3. (L = *N,N,N′,N′*-tetrakis-(2-(2-pyridyl)ethyl)propyl-1,3-diamine.)

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(20) Compound **1** has been observed to crystallize from the same system as an acetonitrile solvate, [Cu$_2$F$_2$(bnpy$_2$)$_2$]·MeCN: triclinic, $a = 13.103(3)$ Å, $b = 13.331(4)$ Å, $c = 14.918(4)$ Å, $\alpha = 94.19(2)°$, $\beta = 96.45(2)°$, $\gamma = 112.60(2)°$, $V = 2384(1)$ Å$^3$, $Z = 2$, space group $P\bar{1}$, $T = 243$ K. The solvated crystals tend to be blocklike, in comparison to the flakelike morphology of the solvate-free material. Although we are unsure of the exact conditions necessary to crystallize one morphology versus the other, it appears that bulk recrystallizations yield flakes of the solvate-free material as verified by X-ray powder diffraction. On the other hand, the microscale diffusions used to grow diffraction-quality crystals have been observed on occasion to yield samples with both space groups present. Large, gemlike faceted blocks of the dichloromethane solvate can be obtained by slow cooling of a hot, concentrated dichloromethane solution of **1**. [Cu$_2$F$_2$(bnpy$_2$)$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$: monoclinic, $a = 27.354(9)$ Å, $b = 13.364(5)$ Å, $c = 18.678(6)$ Å, $\beta = 128.86(2)°$, $V = 5317(3)$ Å$^3$, $Z = 4$, space group $C2/c$, $T = 243$ K. These crystals desolvate upon removal from the mother liquor.

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**Table I.** Crystallographic Data[a] for $[Cu_2F_2(bnpy_2)_2](PF_6)_2$ (**1**), $[Cu_2(bnOpy_2)_2](ClO_4)_2$ (**2**), $[(OEP)Fe–F–Cu(bnpy_2)(OClO_3)]PF_6$ (**3**), $[(OEP)Fe–F–Cu(bnpy_2)(MeCN)](ClO_4)(PF_6)\cdot MeCN$ (**4**), and $Fe(OEP)F\cdot CHCl_3$ (**5**)

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| formula | $C_{42}H_{46}Cu_2F_{14}N_6P_2$ | $C_{42}H_{44}Cl_2Cu_2N_6O_{10}$ | $C_{57}H_{67}ClCuF_7FeN_7O_4P$ | $C_{61}H_{73}ClCuF_7FeN_9O_4P$ | $C_{37}H_{45}Cl_3FFeN_4$ |
| fw | 1089.86 | 990.82 | 1232.99 | 1315.09 | 726.97 |
| crystal system | monoclinic | monoclinic | triclinic | triclinic | monoclinic |
| $a$, Å | 12.337(3) | 10.665(3) | 12.673(3) | 13.96(1) | 14.891(4) |
| $b$, Å | 13.065(3) | 9.086(2) | 13.832(4) | 14.08(2) | 13.743(3) |
| $c$, Å | 14.916(4) | 21.999(7) | 16.901(5) | 18.49(2) | 17.398(5) |
| $\alpha$, deg | 90 | 90 | 93.69(2) | 106.0(1) | 90 |
| $\beta$, deg | 113.16(2) | 101.94(2) | 105.64(2) | 100.54(8) | 94.24(2) |
| $\gamma$, deg | 90 | 90 | 92.91(2) | 111.74(8) | 90 |
| $V$, Å$^3$ | 2210(1) | 2086(1) | 2840(1) | 3075(6) | 3551(2) |
| space group | $P2_1/c$ (No. 14) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) |
| $Z$ | 2 | 2 | 2 | 2 | 4 |
| $\rho_{calc}$, g/cm$^3$ | 1.64 | 1.58 | 1.44 | 1.42 | 1.36 |
| $\mu$, mm$^{-1}$ | 1.13 | 1.21 | 0.78 | 0.73 | 0.69 |
| $R^b$ ($R_w{}^c$), % | 3.67 (4.14) | 4.30 (4.60) | 4.84 (4.87) | 7.80 (8.47) | 4.04 (4.63) |

[a] All data collected at $T$ = 173 K with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å) using $\omega$ scans. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum(w|F_o|^2)\}^{1/2}$, with the weighting scheme provided by a three-term Chebyshev polynomial: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr.* **1979**, *A35*, 698.

suite, Siemens XRD Corp., Madison, WI); empirical absorption corrections (XEMP from the SHELXTL package) were applied using azimuthal $\Psi$-scan data. The intensities of three check reflections were monitored every 97 reflections with no significant decay observed for all data collections. Systematic absences uniquely defined the space groups of **1**, **2**, and **5**; simple $E$ statistics suggested the centrosymmetric space group for **3** and **4**. Proper choices of space group were confirmed by successful refinement to convergence. Relevant crystallographic data are listed in Table I.

**Solution and Refinement of Structures.** Atom scattering factors were taken from Cromer and Waber.[22] The initial structural solutions were obtained by direct methods (**1**, **5**) or by interpretation of Patterson maps (**2**–**4**) (XS from the SHELXTL package). Atoms not located from the initial structure solution were found by successive Fourier or difference Fourier maps with intervening cycles of least-squares refinement (CRYSTALS, with graphical interface provided by XP from SHELXTL). All non-hydrogen atoms were treated anisotropically, with the exception of those in **4**, where, owing to limited data, only Fe(1), Cu(1), and F(1) were so treated, with the other non-hydrogen atoms refined isotropically. Blocked-matrix least-squares refinement was employed for **3** due to the number of parameters; full-matrix least-squares refinements were used in all other cases. All hydrogen atoms were located and refined isotropically for **1**. In the final stages of refinement of **2**–**4**, hydrogen atoms were placed at the calculated positions 0.96 Å from, and with isotropic thermal parameters 1.2 times those of, their parent carbon atoms for **2**, **3**, and **5**. Although all hydrogens could be located in the difference map of **5**, only the chloroform hydrogen atom was refined isotropically. Final difference Fourier maps generally showed residual electron density only near the anions ($PF_6^-$, $ClO_4^-$); this, along with their high thermal parameters, suggested some disorder, a common occurrence for these spherical anions. As the bond distances and angles for these anions were adequate and the residual peaks minor, no further treatment was deemed necessary. Final $R$ values are provided in Table I.[23]

**Other Physical Measurements.** Absorption spectra were obtained on a Cary 219 spectrophotometer, EPR spectra on a Bruker ESP 300E spectrometer, and $^1H$ NMR spectra on a Bruker AM500 instrument. Microprobe analyses were performed on crystalline samples by a Cameca MBX electron microprobe using a Tracor Northern TN-1310 wavelength-dispersive spectrometer with a TN-5502 EDS system and a stage automation system. The following standards were used: Fe metal, Cu metal, GaP, sodalite (Cl). We have found metal ratios by microprobe to be generally reliable; analyses for lighter counterion atoms (P, Cl) tend to be less accurate, with sometimes large deviations, particularly for $PF_6^-$. Field desorption (FD) mass spectra were recorded with a JEOL AX-505 spectrometer.

## Results and Discussion

By means of reaction 1, in which X is a suitable leaving group of a porphyrin complex, we sought oxo- or hydroxo-bridged assemblies. Among the Cu(II) hydroxo species considered was

$$(P)Fe^{III}–X + LCu^{II}–OH \rightarrow (P)Fe^{III}–O(H)–Cu^{II}L + X^- \quad (1)$$

the compound formulated as $[Cu_2(OH)_2(bnpy_2)_2](PF_6)_2\cdot 2H_2O$,[14,24] (**1-OH**) which attracted attention because of its markedly asymmetric hydroxo bridges. The centrosymmetric complex cation $[Cu_2(OH)_2(bnpy_2)_2]^{2+}$, which we designate as **[1-OH]**$^{2+}$, is reported to form a parallel-planar dimer structure with Cu–O distances of 1.931(4) and 2.298(3) Å.[24ab,25] This dimer was reported to dissociate to the monomeric form in coordinating solvents.[24a] Employing this complex and exploiting the exceptionally labile axial bond in $Fe(OEP)(OClO_3)$, we have succeeded in isolating bridged Fe/Cu assemblies (vide infra). As will be discussed, unusual features in the structure determinations indicated to us that the bridge in these assemblies was not hydroxide, but actually fluoride. Conceivably, cationic electrophilic $[Fe(OEP)]^+$ could abstract fluoride from the $PF_6^-$ counterion; such behavior has been noted in other Fe(III) porphyrin systems.[26] The Cu(II)-bound hydroxide might then be scavenged by the ensuing, presumably oxophilic, phosphorus species. A simpler alternative would be the presence of bridging fluoride in the Cu(II) starting material. For this reason, we investigated the nature of the Cu(II) dimer in detail.

**Hydroxide or Fluoride Bridges?** The earlier assignment for bridging hydroxide in **[1-OH]**$^{2+}$ was inferred from structural evidence and chemical reactivity arguments concerning dioxygen uptake stoichiometry and the interconversion between this species and a postulated $\mu$-oxo complex, $[Cu_2O(bnpy_2)_2]^{2+}$.[24a] We have not reexamined the reactivity behavior; however, we note that our complex cation $[Cu_2F_2(bnpy_2)_2]^{2+}$ (**1**$^{2+}$) supplies physical characterization data identical with those reported previously. As presented below, the body of evidence points to a fluoride-bridged compound $[Cu_2F_2(bnpy_2)_2](PF_6)_2$ as the proper formulation for compounds **1** and **1-OH**. However, we do not insist that **1-OH** is the only bridged species in previous reaction systems.[14,24a]

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(22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(23) See paragraph at end of paper concerning supplementary material.

(24) (a) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, *23*, 521. (b) Hayes, J. C. Ph.D. Thesis, SUNY—Albany, 1984; University Microfilms International 8503665, 1992. (c) $[Cu_2F_2(bnpy_2)_2](PF_6)_2\cdot 2H_2O$: triclinic, $a$ = 9.452(2) Å, $b$ = 11.419(3) Å, $c$ = 11.573(2) Å, $\alpha$ = 74.81(2)°, $\beta$ = 88.77(2)°, $\gamma$ = 74.12(2)°, $V$ = 1159(1) Å$^3$, $T$ = 293 K.

(25) Karlin, K. D.; Gan, Q.-F.; Farooq, A.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 2549.

(26) (a) Cohen, I. A.; Summerville, D. A.; Su, S. R. *J. Am. Chem. Soc.* **1976**, *98*, 5813. (b) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (c) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325.

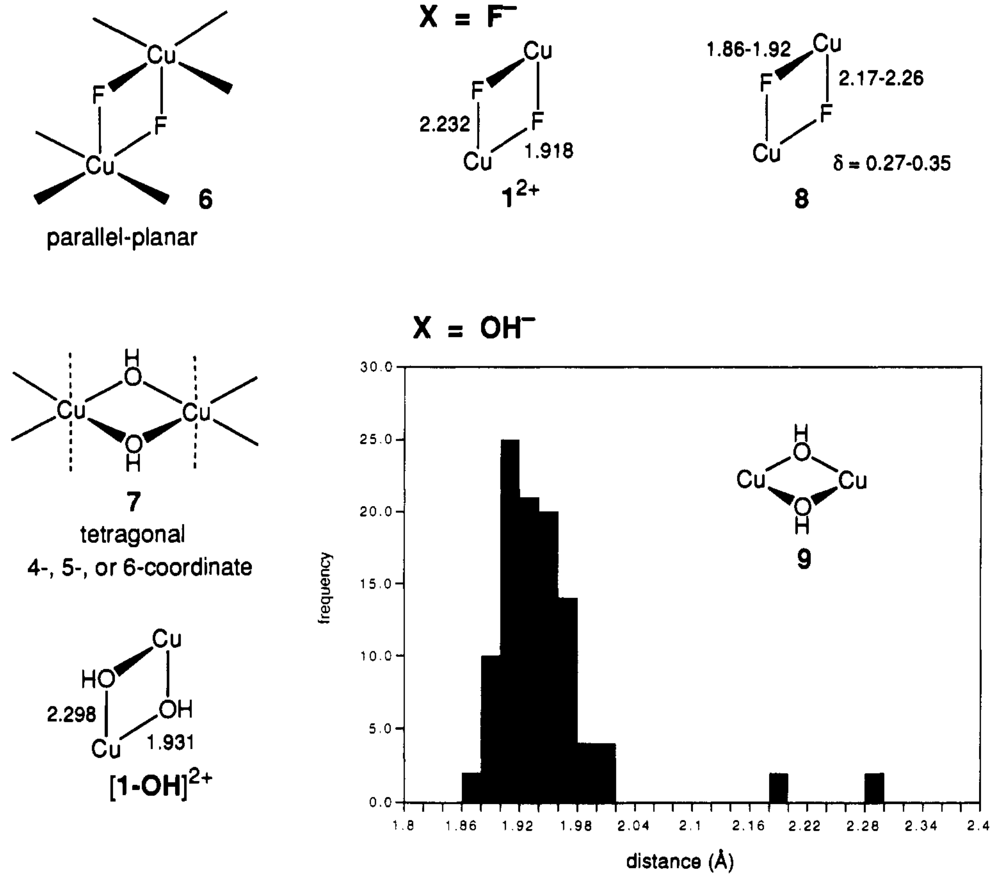

**Figure 1.** Selected structural features of the parallel-planar [Cu$_2$($\mu$-F)$_2$]$^{2+}$ complexes **6** and tetragonal [Cu$_2$($\mu$-OH)$_2$]$^{2+}$ complexes **7** in which the metals may have the indicated coordination numbers. The bridge structures of **1**$^{2+}$ and [**1-OH**]$^{2+}$ are compared, and the ranges of short and long distances in bridge unit **8** (4 examples; two structures of octahedral geometry,[27e,f] with much longer axial contacts, were excluded) and the range of their differences $\delta$ are given. The histogram shows the regime of Cu–O distances in bridge unit **9** (27 examples, from the Cambridge Structural Data Base); the two longer distances are found in [**1-OH**]$^{2+}$ and another dimer described as having asymmetric hydroxo bridges.[25]

**(a) Structural Evidence.** In the discussion that follows, attention is directed to structures **6**-**9** in Figure 1. Highly crystalline **1** can be obtained as diffraction-quality single crystals from a variety of solvents. Slow evaporation of wet methanol solutions gives large crystals having the same cell parameters within experimental tolerance of the previously characterized triclinic structure of **1-OH**.[24] We have determined the structure of compound **1** from a monoclinic crystal obtained by acetonitrile/ether diffusion free of lattice-bound solvent. The structure of **1**$^{2+}$ is provided in Figure 2, and selected bond distances and angles are contained in Table II.

The monoclinic structure of **1**$^{2+}$ is that of a centrosymmetric dimer with the parallel-planar configuration **6** in which the crystallographically unique, square pyramidal Cu(II) center situates the three chelate nitrogen atoms and a bridging fluoride atom in the equatorial plane. As is usual for square pyramidal Cu(II), the coordination sphere is distorted, with axial distances longer than equatorial distances. This is rationalized by the electron configuration ...$\sigma^*(d_{z^2})^2\sigma^*(d_{x^2-y^2})^1$, which leads to the asymmetric bridge with fluoride tightly bound in the equatorial plane (Cu(1)-F(1) = 1.918(2) Å) and weakly so along the axial direction (Cu(1)-F(1′) = 2.232(2) Å). Note that **1** is an example of a *symmetric* dimer with *asymmetric* bridging. The structure of **1**$^{2+}$ is congruous with that reported for [**1-OH**]$^{2+}$ in the triclinic compound; their bridging units are compared in Figure 1. The earlier structure of **1-OH** exhibits a slightly longer distance for the axial bridge bond (2.298(4) Å); this, coupled with some small angular deviations, leads to a longer Cu···Cu separation (3.271 Å) than found in **1** (3.137(1) Å). Given the weak-field nature of axial ligation, distortions attributable to crystal packing influences are not surprising.

To investigate the crystallographic identity of the bridging atom, oxygen was substituted in place of fluorine and subjected to least-squares refinement. The resulting residual at convergence was 0.29% larger with oxygen than with fluorine, and the oxygen thermal ellipsoid was smaller than that of copper. With fluorine in place, the residuals were lower and the bridging atom assumed thermal parameters slightly larger than those of the copper ellipsoid and comparable to those of the nitrogen atoms.[23] The earlier structure of **1-OH**,[24] in which the bridge was refined as oxygen, shows the same trend in temperature factors—equivalent $U_{iso}$ for the bridging oxygen atom (0.022 Å$^2$) was smaller than that for copper (0.036 Å$^2$), which in turn was slightly smaller than that for the nitrogen atoms (0.036, 0.042, 0.042 Å$^2$). In a well-behaved structure, the metal atom should exhibit the lowest extent of motion, with lighter, directly ligated atoms of similar $Z$ displaying similar thermal parameters. These results favor bridging fluorine over oxygen.

Of the seven known structures of complexes containing the [Cu$_2$($\mu$-F)$_2$]$^{2+}$ unit,[27] all but one[27b] manifest the asymmetric axial bridging geometry **8** described above. The only symmetric bridge occurs in a dimer consisting of two planar CuN$_2$F$_2$ units which share equatorial fluoride bridges; the lack of additional ligation presumably dictates the symmetric bridging in this case. In contrast, 27 structures of type **7** complexes containing the [Cu$_2$-

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(27) (a) ten Hoedt, W. M.; Reedijk, J.; Verschoor, G. C. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 400. (b) Velthuizen, W. C.; Haasnoot, J. G.; Kinneging, A. J.; Rietmeijer, F. J.; Reedjik, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1366. (c) Rietmeijer, F. J.; de Graaff, R. A. G.; Reedijk, J. *Inorg. Chem.* **1984**, *23*, 151. (d) van der Voort, E.; van der Sluis, P.; Spek, A. L.; de Boer, J. L. *Acta Crystallogr.* **1987**, *C43*, 887. (e) Oosterling, A.; de Graaff, R. A. G.; Haasnot, J. G.; Keij, F. S.; Reedijk, J.; Pedersen, E. *Inorg. Chim. Acta* **1989**, *163*, 53. (f) Jacobson, R. R.; Tyeklár, Z.; Karlin, K. D.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 2035.

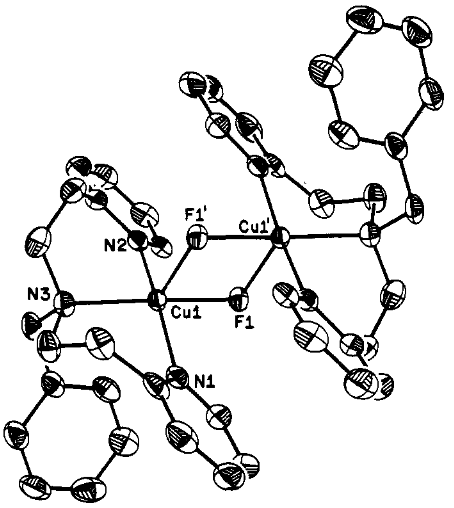

**Figure 2.** Structure of $[Cu_2F_2(bnpy_2)_2]^{2+}$ as its $PF_6^-$ salt showing the labeling scheme for coordination sphere atoms and 50% probability ellipsoids. Primed and unprimed atoms are related by an inversion center.

**Table II.** Selected Interatomic Distances (Å) and Angles (deg) in $[Cu_2F_2(bnpy_2)_2](PF_6)_2$ (**1**)

| | | | |
|---|---|---|---|
| Cu(1)–Cu(1′) | 3.137(1) | Cu(1)–N(1) | 2.020(3) |
| Cu(1)–F(1) | 1.918(2) | Cu(1)–N(2) | 2.014(2) |
| Cu(1)–F(1′) | 2.232(2) | Cu(1)–N(3) | 2.064(2) |

| | | | |
|---|---|---|---|
| Cu(1)–F(1)–Cu(1′) | 97.95(7) | F(1)–Cu(1)–N(2) | 89.18(9) |
| F(1)–Cu(1)–F(1′) | 82.05(7) | F(1)–Cu(1)–N(3) | 174.65(9) |
| F(1′)–Cu(1)–N(1) | 93.60(9) | N(1)–Cu(1)–N(2) | 166.8(1) |
| F(1′)–Cu(1)–N(2) | 98.82(8) | N(1)–Cu(1)–N(3) | 92.5(1) |
| F(1′)–Cu(1)–N(3) | 103.21(9) | N(2)–Cu(1)–N(3) | 89.0(1) |
| F(1)–Cu(1)–N(1) | 88.17(9) | | |

$(\mu\text{-}OH)_2]^{2+}$ unit are known, of which 25 display the planar equatorial bridging geometry **9**. Two axially bridged complexes are the only exceptions, **1-OH** and a second compound that, significantly in the present context, is a $PF_6^-$ salt prepared similarly to **1-OH**.[25] In the set of 25, the bridge units are effectively symmetrical and the Cu–O bond length distribution is relatively narrow[28] compared to that of the bridge in $[\mathbf{1\text{-}OH}]^{2+}$, which is responsible for the datum at 2.29 Å in the histogram in Figure 1. Expanding the sample size, a search of the Cambridge Structural Database[29] reveals 104 examples of the $[Cu_2(\mu\text{-}OH)]^{3+}$ bridge. Of these, only one additional structure has an asymmetric bridge,[30] with all other bridged distances clustering in the 1.9–2.0 Å interval. These statistics reveal a definite stereochemical preference: μ-hydroxide imposes two strong bridge bonds (**7**), whereas fluoride can adopt both strong in-plane and weak axial interactions (**6**). In the present cases, the bnpy₂ ligand itself does not dictate a stereochemical preference. In the square pyramidal dimers $\mathbf{1}^{2+}$ and $[Cu_2(OMe)_2(bnpy_2)_2]^{2+}$,[17,23] the ligand adopts the *mer* and *fac* configurations, respectively.

**(b) Chemical Evidence.** Oxidative reaction 2 (method 1, Experimental Section), on the basis of information available at the start of our studies,[24a] was initially developed for the preparation of the putative hydroxo-bridged dimer. This reaction has proven complex and not entirely reproducible in yielding blue compound **1**. When it succeeds, fluoride is abstracted from $PF_6^-$ by Cu(II), a process with ample precedent.[27] When it fails, other products are indicated by the appearance of greenish solutions and a light green precipitate. Recrystallization of the latter and an X-ray structure determination established one product as $[Cu_2(OMe)_2(bnpy_2)_2](PF_6)_2$,[17] which may form by the reaction of the postulated μ-oxo dimer $[Cu_2O(bnpy_2)_2]^{2+}$ [14] with methanol.

$$2[Cu(bnpy_2)](PF_6) \xrightarrow[MeOH]{O_2} [Cu_2F_2(bnpy_2)_2](PF_6)_2 \quad (2)$$

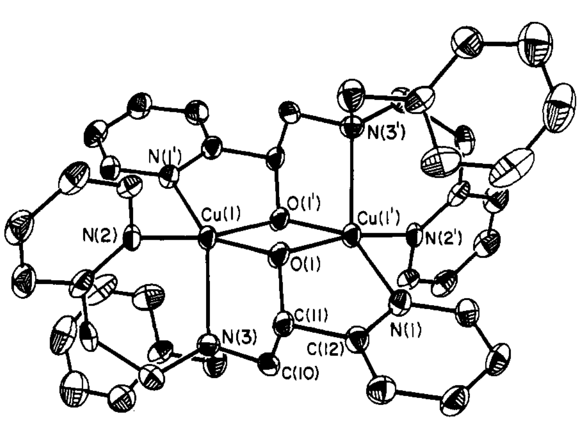

**Figure 3.** Structure of $[Cu_2(bnOpy_2)_2]^{2+}$ as its $ClO_4^-$ salt showing the labeling scheme for coordination sphere atoms and 50% probability ellipsoids. Primed and unprimed atoms are related by an inversion center.

**Table III.** Selected Interatomic Distances (Å) and Angles (deg) in $[Cu_2(bnOpy_2)_2](ClO_4)_2$ (**2**)

| | | | |
|---|---|---|---|
| Cu(1)–Cu(1′) | 3.011(1) | N(3)–C(10) | 1.481(8) |
| Cu(1)–O(1) | 2.028(4) | C(10)–C(11) | 1.515(8) |
| Cu(1)–O(1′) | 1.957(3) | C(11)–C(12) | 1.511(8) |
| Cu(1)–N(1′) | 2.015(4) | C(12)–N(1) | 1.347(7) |
| Cu(1)–N(2) | 2.000(4) | O(1)–C(11) | 1.407(6) |
| Cu(1)–N(3) | 2.265(4) | | |

| | | | |
|---|---|---|---|
| Cu(1)–O(1)–Cu(1′) | 98.1(2) | N(2)–Cu(1)–N(3) | 93.8(2) |
| O(1)–Cu(1)–O(1′) | 81.9(2) | Cu(1)–N(3)–C(10) | 101.3(3) |
| O(1)–Cu(1)–N(1′) | 146.6(2) | C(11)–C(10)–N(3) | 112.8(4) |
| O(1)–Cu(1)–N(2) | 94.5(2) | O(1)–C(11)–C(10) | 112.0(4) |
| O(1)–Cu(1)–N(3) | 83.4(2) | O(1)–C(11)–C(12) | 107.5(4) |
| O(1′)–Cu(1)–N(1′) | 81.8(2) | C(12)–C(11)–C(10) | 108.1(4) |
| O(1′)–Cu(1)–N(2) | 167.3(2) | N(1)–C(12)–C(11) | 112.6(5) |
| O(1′)–Cu(1)–N(3) | 97.9(1) | Cu(1′)–N(1)–C(12) | 111.1(3) |
| N(1′)–Cu(1)–N(2) | 95.0(2) | Cu(1)–O(1)–C(11) | 111.5(3) |
| N(1′)–Cu(1)–N(3) | 127.6(2) | Cu(1′)–O(1)–C(11) | 106.1(3) |

The related reaction, with perchlorate as the counterion, never generated a product analogous to $\mathbf{1}^{2+}$. Instead, complex mixtures were obtained, from which was isolated in low yield the unusual oxygenated compound $[Cu_2(bnOpy_2)_2](ClO_4)_2$ (**2**), identified by an X-ray structure determination. The structure of $\mathbf{2}^{2+}$ is shown in Figure 3, and selected dimensions are compiled in Table III. The configuration is that of a centrosymmetric dimer in which an oxygen atom has been inserted at a methylene carbon atom adjacent to one of the coordinated pyridyl rings; the oxygen atom bridges to another copper atom that is coordinated to the amine nitrogen atom and the other pyridyl group. A symmetric equatorially bridged dimer is formed, with each ligand spanning Cu(1,1′) sites. These sites have distorted square pyramidal stereochemistry with Cu–O bridge bonds (1.957(3), 2.028(4) Å) and Cu–N(1,2) bonds (mean 2.008 Å) in a plane perpendicular to the weak Cu–N(3,3′) axial interactions (2.265(4) Å). Thus, the geometry and metric features of the bridge unit in $\mathbf{2}^{2+}$ are consistent with those of type **7** complexes. Similar ligand oxidation

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(28) Typical structures of complexes containing bridging group **9**: (a) Toofan, M.; Boushehri, A.; Ul-Haque, M. *J. Chem. Soc., Dalton Trans.* **1976**, 217. (b) Chaudhuri, P.; Ventur, D.; Wieghardt, K.; Peters, E.-M.; Peters, K.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 57. (c) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664. (d) The structure in ref 28a is a planar dimer, and those in refs 28b,c are square pyramidal dimers.

(29) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; MacRae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

(30) Gagne, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. D. *Inorg. Chem.* **1979**, *18*, 771. The reported tetranuclear Cu(II) structure possesses several unusual features, including three hydroxide bridges of widely variant Cu–O bond lengths that participate in hydrogen bonding with a "dangling" (unligated) phenolate. We cannot satisfactorily explain the anomalous distances.

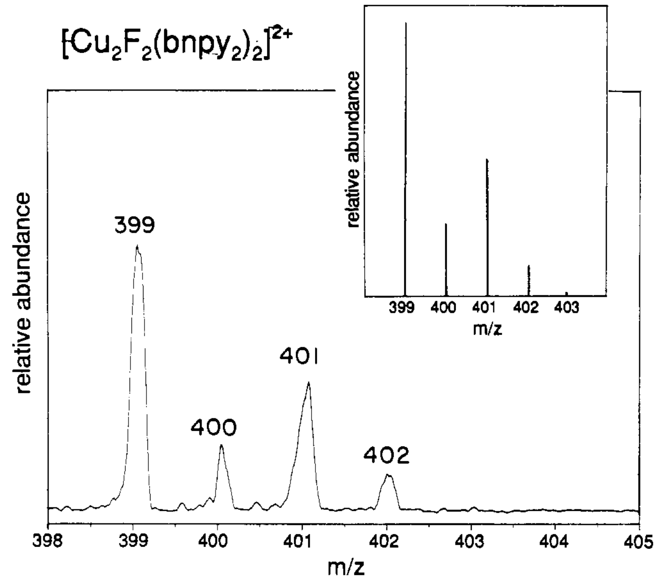

**Figure 4.** Positive-ion FD MS of $[Cu_2F_2(bnpy_2)_2](PF_6)_2$ in the parent-ion region. The inset shows the theoretical isotope pattern for *m/z* = $[CuF(bnpy_2)]^+ = C_{21}H_{23}CuF$.

has been noted in this system, resulting in the formation of benzaldehyde.[14] We note in passing the resemblance of the ligand oxygenation reaction to that catalyzed by the copper enzyme dopamine $\beta$-hydroxylase.[31]

Compound **1** is best prepared by reaction 3 (method 2), from which it has been isolated in 44% yield (unoptimized). Here the metal is initially in the Cu(II) state and metal-bound fluoride is already present. According to elemental analysis, unit cell parameters, and EPR spectra, this material is identical with the product of reaction 2. In addition to providing a reliable synthesis, reaction 3 further supports the fluoride bridge formulation.

$$2CuF_2 \cdot 2H_2O + 2bnpy_2 + 2KPF_6 \xrightarrow{MeOH} [Cu_2F_2(bnpy_2)_2](PF_6)_2 + 2KF + 4H_2O \quad (3)$$

**(c) Physical Evidence.** In addition to crystallographic evidence, other physical data support the presence of fluoride bridges in compound **1**. The positive-ion FD-MS, presented in Figure 4, shows ion flux at *m/z* 399 together with associated isotopomeric signals at higher *m/z* values, corresponding to $[CuF(bnpy_2)]^+$ or $[Cu_2F_2(bnpy_2)_2]^{2+}$. Comparison with the calculated pattern for these species (inset) reveals excellent agreement. No signal was observed at *m/z* 397, the expected dominant position for the corresponding hydroxo species. The *g* values of the X-band EPR spectrum of $\mathbf{1}^{2+}$, set out in Figure 5, match the reported values for **1-OH** in dichloromethane at 77 K,[14] although these are typical for a variety of bridged Cu(II) dimers. This spectrum is essentially identical with that presented for the putative compound $[Cu_2O(bnpy_2)_2](PF_6)_2$,[14,32] whose EPR parameters are closely similar to those of **1-OH**. These results suggest that the actual EPR-active species in these experiments is $\mathbf{1}^{2+}$.

**Bridged Fe–F–Cu Assemblies.** The dissolution of compound **1** in an orange-brown acetone solution of $Fe(OEP)(OClO_3)$ resulted in an immediate color change to black. Diffusion of ether into the solution yielded a black crystalline product, identified as $[(OEP)Fe\text{-}F\text{-}Cu(bnpy_2)(OClO_3)](PF_6)$ (**3**) by an X-ray structural analysis. The same reaction performed in acetonitrile resulted in initial precipitation of red microcrystals and a black supernatant. Introduction of ether by diffusion caused dissolution of the microcrystalline material and deposition of dark brown crystals, structurally identified as $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(MeCN)](ClO_4)(PF_6)\cdot MeCN$ (**4**), on the walls of the container.

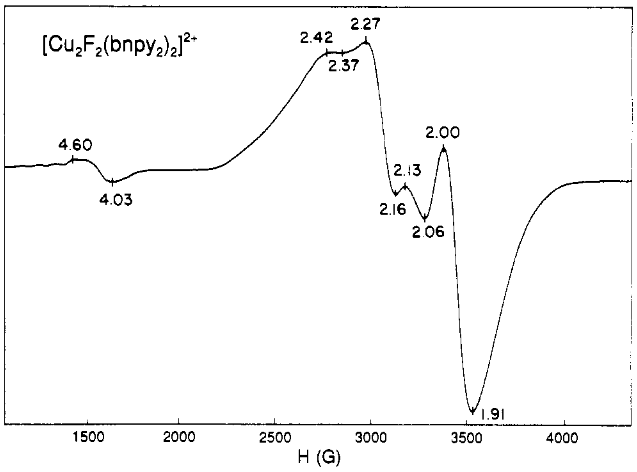

**Figure 5.** X-Band EPR spectrum of an approximately 1 mM solution of $[Cu_2F_2(bnpy_2)_2]^{2+}$ in dichloromethane at 125 K. Apparent *g* values are indicated.

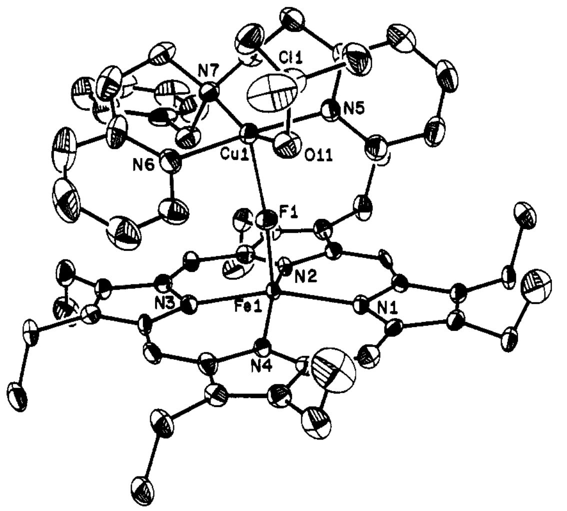

**Figure 6.** Structure of $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(OClO_3)]^+$ as its $PF_6^-$ salt showing the labeling scheme for coordination sphere atoms and 50% probability ellipsoids.

**(a) Structures.** Despite repeated attempts, crystals of **4**, although reasonable in size, diffracted poorly, resulting in relatively imprecise molecular metrics. Parameters about the metal center, however, agree accurately with their equivalents in well-determined **3**, making reliable comparisons possible. The structures of **3** and **4** are presented in Figures 6/7 and 8, respectively; selected metric parameters are contained in Table IV. The two structures are similar, both consisting of separate square pyramidal halves, $[Fe^{III}(OEP)]^+$ and $[Cu(bnpy_2)]^{2+}$, linked by an unsupported fluoride bridge. Displacements of iron atoms from the porphyrin core centroids (0.36 Å (**3**), 0.41 Å (**4**)) and Fe–N bond lengths are typical of high-spin five-coordinate ferric porphyrins,[33] as expected for axial fluoride ligation. The bridges are not linear, the Fe–F–Cu angles being 171.9(1)° in **3** and 166.2° in **4**. The heme structure maps in Figure 9 summarize the OEP structures in the two bridged species and convey the deviations of ligand atoms from the porphyrin mean planes which accompany the five-coordinate $S = {}^5/_2$ state. The Cu(II) coordination sphere resembles that of **1**, except that fluoride is unavailable to take up an equatorial position; instead, the vacant strong-field site is occupied by perchlorate in **3** and acetonitrile

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(31) Stewart, L. C.; Klinman, J. P. *Annu. Rev. Biochem.* **1988**, *57*, 551.

(32) The published spectrum is recorded in the phase opposite to that in Figure 5.

(33) (a) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543. (b) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1.

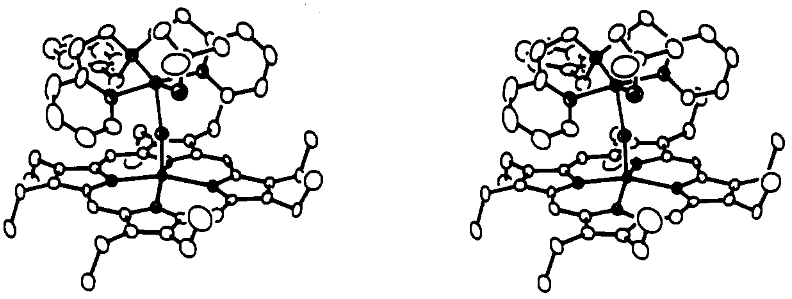

**Figure 7.** Stereoview of the structure in Figure 6.

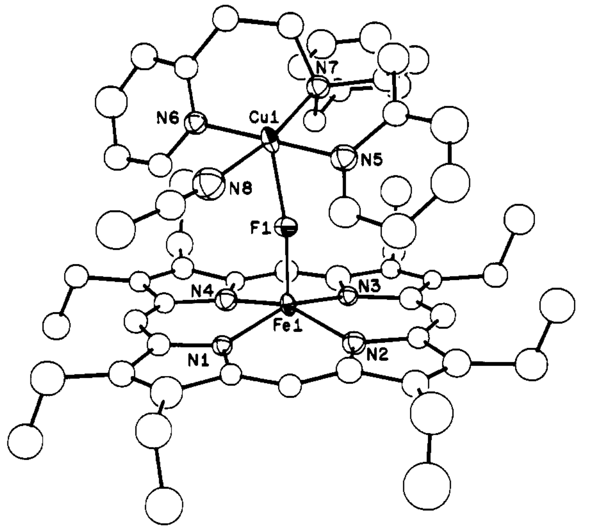

**Figure 8.** Structure of $[(\text{OEP})\text{Fe–F–Cu(bnpy}_2)(\text{MeCN})]^{2+}$ as its acetonitrile monosolvate $\text{ClO}_4^-/\text{PF}_6^-$ salt showing the labeling scheme for coordination sphere atoms and 50% probability ellipsoids. The nitrogen atoms and other atoms represented by open circles were isotropically refined.

in **4**. To our knowledge, strong-field coordination of perchlorate is unprecedented. The Cu–O bond is significantly shorter than those of previously structured $\text{Cu}^{\text{II}}\text{–ClO}_4^-$ complexes, which display a variable and wide range of distances, the shortest at 2.22 Å.[34]

The bridge atom assignment was reached after parallel refinements using oxygen in place of fluorine; for both complexes, residuals were higher and isotropic temperature factors impossibly small (< 0.01 $\text{Å}^2$) for oxygen, thus ruling out a hydroxo bridge. The axial unsupported fluoride bridges in **3** and **4** exhibit the bond asymmetry pattern discerned for **1**. The distances of Cu–F bonds are lengthened, as expected for axial ligation, although shorter than the comparable distance in **1** (2.232(2) Å). The Cu–F distance for **3** (2.101(3) Å) is substantially shorter than that for **4** (2.22(1) Å), an effect possibly reflecting the presence of the weakly donating perchlorate in the equatorial binding site; indeed, the axial Cu–F distance is actually *shorter* in **3** than the equatorial $\text{Cu–OClO}_3$ distance. The copper center in **3** appears to undergo a distortion toward a trigonal bipyramidal geometry relative to **4**; this also supports an electronic basis for the shortened axial distance.

Equatorial bridging does not appear forbidden by any steric/geometric constraint in either assembly; its absence suggests that the Fe(III) affinity for fluoride exceeds the donor capacity necessary for equatorial Cu(II) ligation. The compound Fe(OEP)F (**5**) has been very briefly described,[35] but without physicochemical characterization. For **5**, we report its structure as a chloroform monosolvate in Figure 10; selected metric data are collected in Table V. The UV/visible absorption spectrum of the unsolvated form, presented in Figure 11, and the $^1$H NMR spectrum (Experimental Section) should permit rapid identification of this complex in future work. In support of the structural hypothesis, Fe–F bonds in the bridged assemblies appear to be strong (1.865(3) Å (**3**), 1.86(1) Å (**4**)), with distances comparable to those in **5** (1.834(2) Å) and Fe(TPP)F (1.792(3) Å),[36] the only other five-coordinate $\text{Fe}^{\text{III}}$–porphyrin fluoride of known structure. The potent donor ability of the axial fluoride is demonstrated for **5** by the formation of a hydrogen bond with chloroform.[37] There are 10 other examples of *unsupported* fluoride bridges,[38] but none between heterometals and none involving iron or copper.

**Table IV.** Selected Interatomic Distances (Å) and Angles (deg) for $[(\text{OEP})\text{Fe–F–Cu(bnpy}_2)\text{L}]^{2+}$ (**3**, L = $\text{OClO}_3^-$, Eq = O(11); **4**, L = MeCN, Eq = N(8))[a]

| | 3 | 4 |
|---|---|---|
| Fe(1)–Cu(1) | 3.956(1) | 4.047(3) |
| Fe(1)–F(1) | 1.865(3) | 1.86(1) |
| Fe(1)–N(1) | 2.057(3) | 2.07(1) |
| Fe(1)–N(2) | 2.042(3) | 2.03(1) |
| Fe(1)–N(3) | 2.051(4) | 2.02(1) |
| Fe(1)–N(4) | 2.045(3) | 2.05(1) |
| Fe(1)–$\text{N}_{\text{mean}}$ | 2.049(7) | 2.04(2) |
| Fe(1)···Ct′ | 0.36 | 0.41 |
| Ct′···$\text{N}_{\text{mean}}$ | 2.016 | 2.01 |
| Cu(1)–F(1) | 2.101(3) | 2.22(1) |
| Cu(1)–N(5) | 1.972(4) | 2.01(1) |
| Cu(1)–N(6) | 1.985(4) | 1.99(1) |
| Cu(1)–N(7) | 2.041(4) | 2.08(1) |
| Cu(1)–Eq | 2.139(3) | 2.01(2) |
| Cu(1)–F(1)–Fe(1) | 171.9(1) | 166.2(5) |
| F(1)–Fe(1)–N(1) | 100.3(1) | 100.3(5) |
| F(1)–Fe(1)–N(2) | 102.7(1) | 101.4(5) |
| F(1)–Fe(1)–N(3) | 99.9(1) | 100.4(5) |
| F(1)–Fe(1)–N(4) | 98.5(1) | 100.9(5) |
| N(1)–Fe(1)–N(2) | 88.2(1) | 87.8(5) |
| N(1)–Fe(1)–N(3) | 159.8(1) | 159.4(5) |
| N(1)–Fe(1)–N(4) | 88.2(1) | 88.3(5) |
| N(2)–Fe(1)–N(3) | 87.7(1) | 88.6(6) |
| N(2)–Fe(1)–N(4) | 158.9(1) | 157.7(5) |
| N(3)–Fe(1)–N(4) | 88.5(1) | 87.4(5) |
| F(1)–Cu(1)–N(5) | 89.2(1) | 90.1(5) |
| F(1)–Cu(1)–N(6) | 90.8(1) | 92.6(5) |
| F(1)–Cu(1)–N(7) | 106.5(1) | 97.9(5) |
| Eq–Cu(1)–F(1) | 96.7(1) | 88.7(5) |
| Eq–Cu(1)–N(5) | 84.1(2) | 89.6(6) |
| Eq–Cu(1)–N(6) | 85.7(2) | 85.7(6) |
| Eq–Cu(1)–N(7) | 156.8(1) | 170.8(6) |
| N(5)–Cu(1)–N(6) | 169.7(2) | 174.5(6) |
| N(5)–Cu(1)–N(7) | 96.1(2) | 96.7(6) |
| N(6)–Cu(1)–N(7) | 93.7(2) | 87.6(6) |

[a] Ct′ is the centroid of the 24-atom (C,N) porphyrin core; Eq is the donor atom of the equatorial ligand L on copper.

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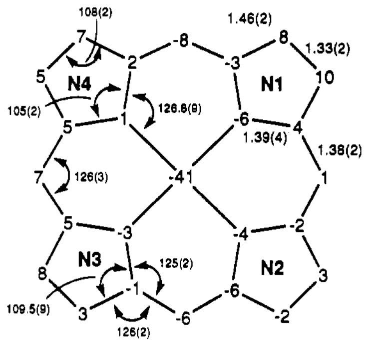
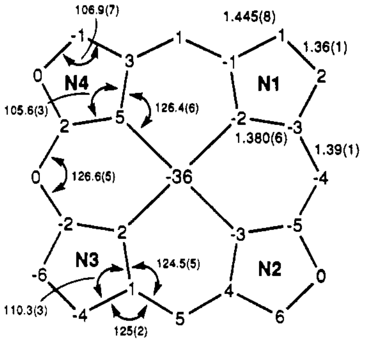


$[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(MeCN)]^{2+}$



$[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(OClO_3)]^+$

**Figure 9.** Heme unit structure maps for $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(MeCN)]^{2+}$ and $[(OEP)Fe\text{–}F\text{–}Cu(bnpy_2)(OClO_3)]^+$ showing selected mean bond angles (deg) and distances (Å) and atom displacements (pm) from the porphyrin mean plane.

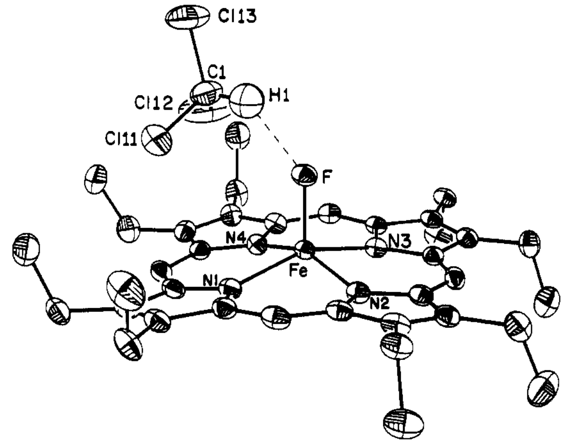


**Figure 10.** Structure of Fe(OEP)F as its chloroform monosolvate showing coordination sphere atom labeling scheme, 50% percent probability ellipsoids, and the $Cl_3C\text{–}H\cdots F$ hydrogen-bonding interaction.

**(b) Syntheses.** With the structural data as a guide, it would appear that the first reaction step in the formation of both compounds is abstraction of fluoride from 1 by electron-deficient $Fe(OEP)(OClO_3)$. The tight Fe–F bond implicates this step, as does the long axial bridge to copper, a structure unlikely to retain integrity in a relatively polar medium. The observation of a microcrystalline precipitate from the reaction system in acetonitrile supports these events; the precipitate is probably Fe(OEP)F inasmuch as neutral Fe(OEP)X species display limited solubility in this solvent. We have observed that ether solubilizes OEP complexes in polar solvents; thus the diffusion of ether serves to maintain the presence of Fe(OEP)F in solution. The formation of the bridged assemblies probably occurs by equilibrium crystallization as the solvent dielectric constant is reduced by the presence of ether.

**Table V.** Selected Interatomic Distances (Å) and Angles (deg) for $Fe(OEP)F\cdot CHCl_3$ (5)[a]

| | | | |
|---|---|---|---|
| Fe(1)–F(1) | 1.834(2) | $Fe(1)\cdots Ct'$ | 0.44 |
| Fe(1)–N(1) | 2.059(2) | $Ct'\cdots N_{mean}$ | 2.016 |
| Fe(1)–N(2) | 2.062(2) | $F(1)\cdots H(1)$ | 2.11(5) |
| Fe(1)–N(3) | 2.060(2) | $F(1)\cdots C(1)$ | 2.878(4) |
| Fe(1)–N(4) | 2.064(2) | C(1)–H(1) | 0.96(5) |
| $Fe(1)\text{–}N_{mean}$ | 2.061(2) | | |
| F(1)–Fe(1)–N(1) | 102.73(9) | N(1)–Fe(1)–N(4) | 87.5(1) |
| F(1)–Fe(1)–N(2) | 99.30(9) | N(2)–Fe(1)–N(3) | 87.7(1) |
| F(1)–Fe(1)–N(3) | 101.23(8) | N(2)–Fe(1)–N(4) | 155.94(9) |
| F(1)–Fe(1)–N(4) | 104.76(9) | N(3)–Fe(1)–N(4) | 87.31(9) |
| N(1)–Fe(1)–N(2) | 87.57(9) | $Fe(1)\text{–}F(1)\cdots H(1)$ | 140(1) |
| N(1)–Fe(1)–N(3) | 156.0(1) | $C(1)\text{–}H(1)\cdots F(1)$ | 136(4) |

[a] Ct′ is the centroid of the 24-atom (C,N) porphyrin core.

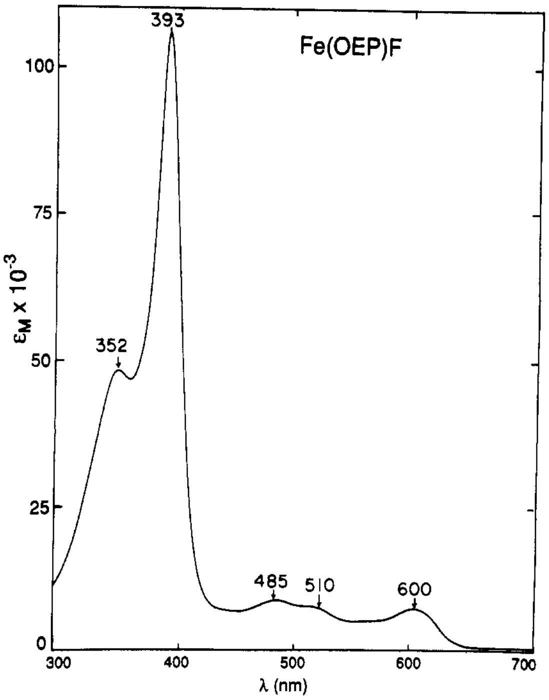


**Figure 11.** Absorption spectrum of Fe(OEP)F in dichloromethane solution. Band maxima are indicated.

## Summary

From these studies, two primary conclusions are emphasized.

(i) Fluorinated counterions of the type $BF_4^-$, $PF_6^-$, and $SbF_6^-$ have long been known to be potentially reactive sources of fluoride ion. In general, simple experimentation would identify the presence of coordinated fluoride with confidence. However, the unfortunate juxtaposition of dioxygen as reactant and $PF_6^-$ as counter-ion in the synthesis of 1 results in ambiguity in the bridge atom identification. The original assignment seemed reasonable when we began our work; only after the refinement of the bridged assemblies, where oxygen clearly did not fit for the bridge, did we realize that something was amiss. Adequately defining the bridging atom required more than casual effort, even with that express purpose in mind; given the difficulty involved in firmly resolving this issue, we recommend the use of a more inert

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counterion (triflate, perchlorate) in studies involving dioxygen or hydroxide. The procedures and results provided here should be of utility to others confronted with the bridging hydroxide/fluoride ambiguity.

(ii) The synthesis and isolation of very weakly bridged assemblies involving a cationic Cu(II) complex and an Fe(III) porphyrin have been accomplished. These results suggest that similar unsupported weak linkages of more direct relevance to CcO, such as bridging $Cl^-$, might also be isolated in crystalline form for study, despite a lack of solution integrity. The observed reactivity with fluoride may also be relevant to the behavior encountered in probing CcO with fluoride ion. Fluoride is observed to disrupt an intimately bridged Fe–Cu form of CcO, by reaction with iron to give fluoroferriheme EPR signals.[39] Our observation of the strong affinity of $[Fe(OEP)]^+$ for fluoride in the presence of Cu(II) is consonant with this behavior. Lastly, the assemblies with X = F represent the case of weak or nil magnetic coupling across roughly linear $Fe^{III}$–X–$Cu^{II}$ bridges, whereas the X = O assembly is the opposite extreme of strong antiferromagnetic coupling.[7] The electronic properties of these and other bridged assemblies will be the subject of future reports.

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**Supplementary Material Available:** For the compounds in Table I and $[Cu_2(OMe)_2(bnpy_2)_2](PF_6)_2$, tables of crystallographic data, atom positional and isotropic thermal parameters, anisotropic thermal parameters bond distances and angles, and calculated hydrogen atom positions and an ORTEP view of $[Cu_2(OMe)_2(bnpy_2)_2]^{2+}$ as its acetonitrile disolvate $PF_6^-$ salt (36 pages). Ordering information is given on any current masthead page.

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