J. Am. Chem. Soc. 1982, 104, 4357-4361

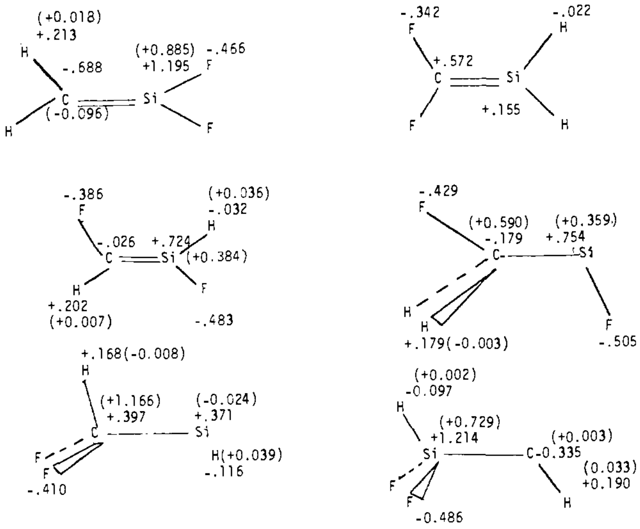

Figure 9. 6-31G*//3-21G charges in difluoro isomers. Numbers in parentheses are the increases in positive charges relative to unsubstituted parents.

stabilize 1,1-dimethyl-1-silaethylene by 9.3 kcal/mol relative to methylethylsilylene. While we have not included the dimethylated species in this work, Hanamura, Nagase, and Morokuma[20] do indeed predict the silaethylene to be rather more stable in this case.

The Mulliken charge densities in the fluoro-substituted species are displayed in Figures 8 and 9. As expected, fluorine substitution increases the positive charge of the attached atom and, through π back-bonding, increases the electron density on the geminal heavy atom. Typically, an increase in positive charge on silicon correlates with a stabilized structure and vice versa.

V. Conclusions

The main conclusions to be drawn from this work are as follows: (a) Fluorine substitution dramatically stabilizes silicon to the degree that normally rather unstable species, such as carbenes, become competitive in stability with their isomers. In the case of silaethyne, a distorted 1-fluoro-1-silaethyne is predicted to be the most stable CSiHF structure. Similarly, $CH_2{=}SiF_2$ is predicted to be much more stable than $CH_2F{-}SiF$. (b) While d orbitals on silicon seem to preferentially stabilize formal triple bonds relative to double bonds and double bonds relative to single bonds, the general effect is quantitative rather than qualitative. Thus, most trends are correctly predicted by the 3-21G basis set. (c) The effects of polarization functions and correlation corrections seem to be approximately additive. While this is certainly not a foolproof approach, it does provide a fast, approximate means for estimating correlation effects.

Acknowledgment. I have benefited from stimulating discussions with Professors K. Krogh-Jespersen, R. D. Koob, and P. Boudjouk. The computer time made available by the North Dakota State University Center is gratefully acknowledged.

Registry No. $H_2C{=}Si$, 65632-07-7; $HC{\equiv}SiH$, 59164-06-6; $C{=}SiH_2$, 74694-33-0; $FHC{=}Si$, 81874-91-1; $HC{\equiv}SiF$, 81874-92-2; $C{=}SiHF$, 81874-93-3; $FC{\equiv}SiH$, 81874-94-4; $LiHC{=}Si$, 81874-95-5; $HC{\equiv}SiLi$, 81874-96-6; $C{=}SiLiH$, 81874-97-7; $LiC{\equiv}SiH$, 81874-98-8; $F_2C{=}Si$, 81874-99-9; $C{=}SiF_2$, 81875-00-5; $FC{\equiv}SiF$, 81875-01-6; $FLiC{=}Si$, 81875-02-7; $LiC{\equiv}SiF$, 81875-03-8; $FC{\equiv}SiLi$, 81875-04-9; $C{=}SiFLi$, 81875-05-0; $H_3CCH{=}Si$, 78442-51-0; $HC{\equiv}SiCH_3$, 81096-75-8; $H_3C{-}C{\equiv}SiH$, 78289-00-6; $C{=}Si(H)CH_3$, 78442-56-5; $H_2C{=}SiH_2$, 51067-84-6; CH_3SiH, 55544-30-4; SiH_3CH, 66605-30-9; $CH_2{=}SiHF$, 81875-06-1; $CH_3{-}SiF$, 81875-07-2; CH_2FSiH, 81875-08-3; $CHF{=}SiH_2$, 81897-63-4; $SIH_3{-}CF$, 81875-09-4; SiH_2FCH, 81875-10-7; $CH_2{=}SiF_2$, 51675-50-4; CH_2FSiF, 81875-11-8; $CHF{=}SiHF$, 81875-12-9; $CHF_2{-}SiH$, 81875-13-0; $CF_2{=}SiH_2$, 51675-51-5; $SiHF_2CH$, 81875-14-1; SiH_2FCF, 81875-15-2; $CH_2{=}Si(H)CH_3$, 38063-40-0; $(CH_3)_2Si$, 6376-86-9; CH_3CH_2SiH, 81875-16-3; $CH_3CH{=}SiH_2$, 76444-54-7.

Cytochrome Oxidase Models. 3. Spin Coupling across Imidazolate Bridges in Binuclear Metalloporphyrin Complexes of Iron and Copper[1]

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Contribution from the Department of Chemistry, William Marsh Rice University, Houston, Texas 77001. *Received July 27, 1981*

Abstract: Four new μ-imidazolato binuclear metalloporphyrin compounds of Fe^{III} and Cu^{II} or Zn^{II} have been synthesized, isolated, and characterized in the solid state as model systems for the active site of cytochrome *c* oxidase. The compounds have been derived from $[Fe^{III}(TPP)X]$ ($X = Cl^-$ or $OSO_2CF_3^-$) and $[M^{II}(imidH)_2DAP]^{2+}$ (M = Zn or Cu) to yield species containing the following μ-imidazolato cationic cores: $[ClFe^{III}(imid)Zn^{II}]^+$ (**1**), $[ClFe^{III}(imid)Cu^{II}]^+$ (**2**), $[(OSO_2CF_3)Fe^{III}(imid)Zn^{II}]^+$ (**3**), and $[(OSO_2CF_3)Fe^{III}(imid)Cu^{II}]^+$ (**4**). Comparative magnetochemical (15–300 K), Mössbauer (100 K), and EPR (10 K) studies of **1** and **2** are consistent with essentially identical electronic environments about Fe^{III} ($S = {}^1/_2$) with $-J_{Fe^{III}-Cu^{II}} \lesssim 15$ cm^{-1} in **2**. Similar comparative studies of **3** and **4** are somewhat complicated by the presence of what appears to be two distinct molecular species of $S = {}^5/_2$ and ${}^1/_2$ coexisting in the same crystalline sample. The magnetic properties and silent EPR behavior of **4** have been rationalized in terms of a ($S = 0, 2$) mixture arising from strong antiferromagnetic coupling between Fe^{III} ($S = {}^1/_2, {}^5/_2$) and Cu^{II} ($S = {}^1/_2$), where $-J_{Fe^{III}-Cu^{II}} \gtrsim 200$ cm^{-1}. The implication of this result to the possible active-site structure of oxidase has been briefly considered.

Cytochrome oxidase is the respiratory enzyme that catalytically reduces 1 mol of dioxygen to 2 mol of water ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) with the concomitant release of energy, which is stored in the ADP–ATP cycle.[3] The enzyme contains four metal centers

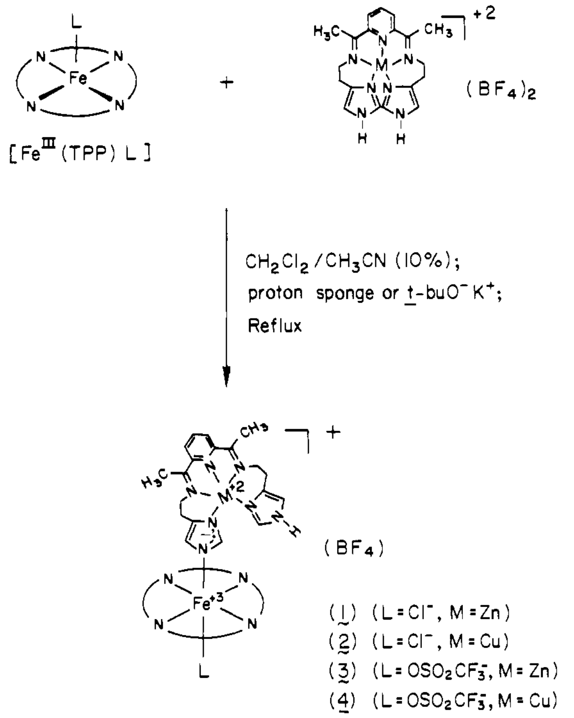

Figure 1. Synthetic scheme for the μ-imidazolato complexes.

(two irons and two coppers) per functioning unit. Furthermore, through various spectroscopic and other studies, it is now know that the enzyme contains one isolated iron heme unit (cytochrome a) that is low spin in both the oxidized and reduced forms and one isolated copper center (Cu$_D$; D for EPR detectable), while at the active or dioxygen binding site there is a high-spin iron heme (cytochrome a_3) and a second copper center (Cu$_U$; U for EPR undetectable).[4] In a full-temperature magnetochemical study,[5] we have shown for the fully oxidized or resting form of the enzyme that the iron center of cyt a_3^{3+} ($S = {}^5/_2$) and Cu$_U^{2+}$ ($S = {}^1/_2$) are strongly coupled antiferromagnetically ($-J \geq 200$ cm^{-1}) to give a resultant $S = 2$ ground state for the binuclear active site. Furthermore, it is now relatively certain, through an ^{15}N-labeled histidine EPR study by Chan et al.,[6] that an endoenous imidazole group axially ligates cyt a_3^{2+} in the fully reduced enzyme. The structure of the presumably ligand-bridged [cyt a_3^{3+}(B)Cu$_U^{2+}$] active site of the resting enzyme[7] and, in particular, the nature of the bridging ligand are still very much in question; however, imidazolato from histidine[5,8] and oxo from dioxygen[1,9,10] or possibly even mercapto[11] have recently emerged as leading candidates. Furthermore, while much of the current literature[9,19-21] has seemingly favored the μ-oxo[cyt a_3^{3+}–O–Cu$_U^{2+}$] possibility for the site structure in the resting enzyme, a recent ^{18}O$_2$ turnover study by Beinert and co-workers[10] has reduced somewhat the appeal of this suggestion.

There seems to be little doubt that single-atom bridges like oxo or mercapto can foster antiferromagnetic exchange interactions approaching or exceeding 200 cm^{-1}; however, in this regard, there is much less certaintly about imidazolate. In fact, past model compound studies by others[12-20] and ourselves[21,22] have suggested that imidazolate and other multiatom heterocyclic bridges are incapable of fostering exchange interactions much greater than ca. 100 cm^{-1}, with most of the values clustered below 30 cm^{-1}.[22] In our continuing efforts to further clarify structural possibilities for the active site of oxidase, we report herein solid-state magnetic and spectroscopic data for the four new μ-imidazolato mixed-metal [LFe^{III}(imid)M^{II}]$^+$ compounds **1–4**, as shown in Figure 1 for M = Zn or Cu and L = Cl$^-$ or OSO$_2$CF$_3^-$ (triflate). While reports of related [Fe^{III}(imid)Cu^{II}]$^{n+}$ oxidase model compounds have appeared in the literature,[17,18] the present work is the first in which such species have been isolated, characterized, and studied as analytically pure solids. The solution-state chemistry of the new μ-imidazolato compounds is complex, involving a binuclear $\rightleftharpoons$ porphyrin + copper fragment type equilibrium, and these results will be reported subsequently.[23]

Experimental Section

Materials and Methods. All compounds were prepared from commercially available reagents, which were used as received. *meso*-Tetraphenylporphine was purchased from Strem Chemicals, Inc.; Cu(BF$_4$)$_2$·6H$_2$O, Zn(BF$_4$)$_2$·6H$_2$O, and anhydrous FeCl$_2$ were from Alfa Products; [1,2-bis(dimethylamino)naphthalene] (Proton Sponge, ps), t-BuO$^-$K$^+$, 2,6-diacetylpyridine (DAP), 2-(2-aminoethyl)pyridine, and silver trifluoromethanesulfonate [Ag(OSO$_2$CF$_3$)] were from Aldrich Chemicals; and histamine, free base, was from Sigma Chemical Co. All solvents were distilled and dried according to literature procedures. Microanalyses were performed by Schwarzkopf Microanalyical Labs. Solid-state infrared spectra were recorded as Nujol mulls on NaCl plates and a Beckman IR-4230 spectrophotometer. Mössbauer spectra were obtained on a previously described spectrometer[25] and computer analyzed by the program of Chrisman and Tumolillo.[26] Temperatures were measured with a copper vs. constantan thermocouple imbedded in the sample. Sodium nitroprusside (SNP) was used as a reference standard for the isomer shift parameter.

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Magnetic susceptibilities of the solids were measured by the Faraday technique on a Cahn Model 6600-1 research magnetic susceptibility system with $Hg[Co(NCS)_4]$ as the calibrant. All measurements were obtained with samples under 1 atm of helium. Corrections for the ligand and anion diamagnetism in all the complexes were made by using the molar susceptibilities calculated from Pascal's constants:[27] $[ClFe(TPP)(imid)Zn](BF_4)\cdot(psH)^+(BF_4)^-$, $\chi_{M,dia} = -690 \times 10^{-6}$ cgsu; $[ClFe(TPP)(imid)Cu](BF_4)\cdot(psH)^+(BF_4)^-$, $\chi_{M,dia} = -685 \times 10^{-6}$ cgsu; $[(OSO_2CF_3)Fe(TPP)(imid)Zn](BF_4)\cdot(psH)^+(BF_4)^-$, $\chi_{M,dia} = -705 \times 10^{-6}$ cgsu; $[(OSO_2CF_3)Fe(TPP)(imid)Cu](BF_4)\cdot(psH)^+(BF_4)^-$, $\chi_{M,dia} = -700 \times 10^{-6}$ cgsu. For the variable-temperature magnetochemical measurements, the cryogenic apparatus consisted of an Air Products Interface Model DMX-19 vacuum shroud, an LT-3-110 B Helitran system, and an APD-TL digital temperature readout monitoring an iron-doped gold vs. chromel thermocouple.

The EPR spectra of the polycrystalline solids were taken at 10 K on a Varian E-line spectrometer. The magnetic field positions were referenced relative to diphenylpicrylhydrazyl (dpph). Analytically pure ammonium sulfate was used as a solid support in the preparation of samples containing ca. 10% of the metal compound.

Syntheses. [Fe(TPP)Cl] was prepared according to the method of Adler et al.[28] $[Fe(TPP)(OSO_2CF_3)]$ was prepared by the metathesis of [Fe(TPP)Cl] with $Ag(OSO_2CF_3)$ by the method of Reed et al.[29] The $[Fe(TPP)(OSO_2CF_3)]$ compound was prepared and recrystallized under an argon atmosphere by using Schlenk techniques to prevent hydrolysis with formation of the μ-oxo dimer, $[Fe(TPP)]_2O$. A mixture of [Fe(TPP)Cl] (0.50 g, 0.710 mmol) and $Ag(OSO_2CF_3)$ (0.18 g, 0.710 mmol) was dissolved in 30 mL of THF and refluxed for 0.5 h, and the solution was then filtered. Heptane (45 mL) was added to the filtrates, and the purple solution was chilled overnight. Crystals were obtained by filtration and recrystallized from hot toluene (40 mL) and heptane (100 mL). The shiny crystals were collected, washed with heptane, and dried in vacuo overnight: μ_{eff} (solid, 298 K) = 5.16 μ_B; IR (Nujol mull) $\nu_{(OSO_2CF_3)^-}$ = 1340 (s), 1240 (s), 1205 (s), 630 (s) cm^{-1}. Anal. Calcd for $FeC_{44}H_{28}N_4O_3SF_3$: C, 66.10; H, 3.45; N, 6.85. Found: C, 65.80; H, 3.69; N, 6.75.

$[M^{II}(imidH)_2DAP](BF_4)_2$, where M = Zn and Cu, was prepared according to the method of Simmons et al.[30]

$[ClFe^{III}(TPP)(imid)M^{II}](BF_4)\cdot(psH)^+(BF_4)^-$ **1** and **2** were prepared by refluxing a 1:1.2 molar ratio of $[Fe^{III}(TPP)L]$ and $[M^{II}(imidH)_2DAP](BF_4)_2$ for ca. 6 h in the presence of 1 mol of Proton Sponge (0.096 g) or t-BuO$^-$K$^+$ (0.05 g) in a dry CH_2Cl_2/CH_3CN (10%) solvent mixture. Removal of the solvent under vacuum resulted in crystalline products, from which excess $[M^{II}(imidH)_2DAP](BF_4)_2$ was removed by washing with water (100 mL). Following a heptane wash, the purple-black solids were dried over P_2O_5 in vacuo at room temperature for 15 h. $[(OSO_2CF_3)Fe^{III}(imid)M^{II}](BF_4)\cdot(psH)^+(BF_4)^-$ **3** and **4** were prepared analogously, by using $[Fe^{III}(TPP)(OSO_2CF_3)]$ and the appropriate $[M^{II}(imidH)_2DAP](BF_4)_2$ complex. Attempted purification by recrystallization invariably resulted in materials with less satisfactory analyses than those obtained before recrysallization attempts. Samples prepared with Proton Sponge (ps) were obtained as $(psH)^+(BF_4)^-$ occludates, while those employing t-BuO$^-$K$^+$ were occludate free. The occludate or occludate-free samples gave essentially identical variable-temperature magnetic and spectroscopic results, although data reported here are for the following $(psH)^+(BF)_4^-$ occludate samples.

Compound 1, $[ClFe^{III}(imid)Zn^{II}]BF_4\cdot(psH)^+(BF_4)^-$. Theory (found): C, 61.38 (61.62); H, 4.62 (4.68); N, 12.08 (12.67); Fe, 3.71 (3.85); Zn, 4.34 (4.96); Cl, 2.35 (2.45).

Compound 2, $[ClFe^{III}(imid)Cu^{II}]BF_4\cdot(psH)^+(BF_4)^-$. Theory (found): C, 61.45 (61.08); H, 4.62 (4.69); N, 12.10 (12.06); Fe, 3.71 (3.61); Cu, 4.22 (3.82); Cl, 2.36 (2.12).

Compound 3, $[(OSO_2CF_3)Fe^{III}(imid)Zn^{II}]BF_4\cdot(psH)^+(BF_4)^-$. Theory (found): C, 57.71 (57.19); H, 4.28 (4.89); N, 11.22 (10.99); Fe, 3.44 (3.40); Zn, 4.03 (4.10).

Compound 4, $[(OSO_2CF_3)Fe^{III}(imid)Cu^{II}]BF_4\cdot(psH)^+(BF_4)^-$. Theory (found): C, 57.78 (57.81); H, 4.29 (5.09); N, 4.29 (4.09); Fe, 3.45 (3.64); Cu, 3.92 (3.85).

Strong absorption bands in the infrared spectrum attributed to occluded $(psH)^+$ are found at ca. 835 and 770 cm^{-1} for all of the compounds, whereas these marker bands are absent in the spectra of t-BuO$^-$K$^+$ samples. In no case were there strong bands at ca. 890 and 870 cm^{-1} that might indicate formation of some μ-oxo porphyrin product.

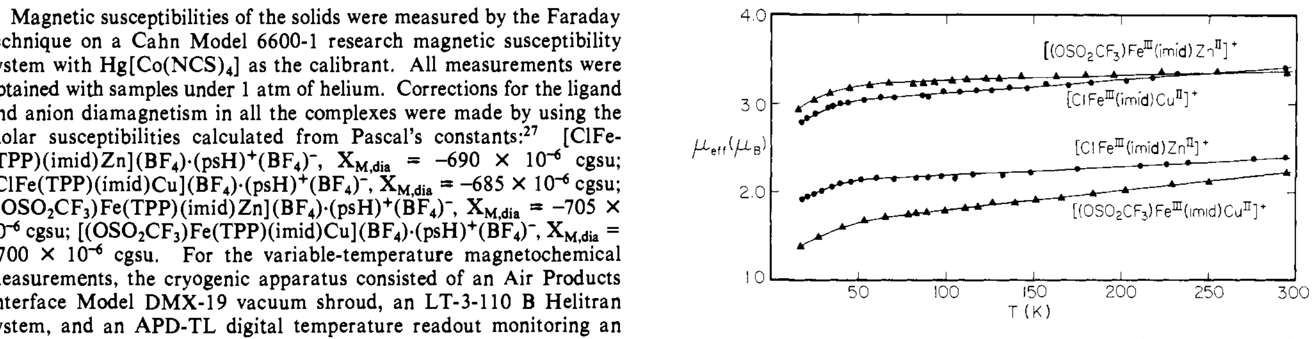

Figure 2. μ_{eff} (μ_B) vs. temperature (15–300 K) data for the μ-imidazolato complexes.

Results and Discussion

As shown in Figure 1, the μ-imidazolato compounds were prepared by the reaction of equimolar amounts of $[Fe^{III}(TPP)L]$ (TPP^{2-} = tetraphenylporphyrinato) and $[M^{II}(imidH)_2DAP]^{2+}$ (M = Zn or Cu)[30,31] in the presence of 1 molar equiv of a base such as [1,2-bis(dimethylamino)naphthalene] (Proton Sponge) or t-BuO$^-$K$^+$. In the presence of a large excess of base and prolonged reaction times, trinuclear or even polynuclear compounds, formulated as $[M^{II}\text{–}Fe^{III}(porphyrin)\text{–}M^{II}]_n$ species, were obtained but not further characterized at this time. No reaction occurred in the absence of base, and the Cu^{II} and Zn^{II} compounds, $[M^{II}(imidH)(py)DAP]^{2+}$ (with one terminal pyridine group replacing an imidazole moiety),[32] also reacted in the presence, but not the absence, of base to form binuclear $[ClFe^{III}(imid)M^{II}]^+$ species analogous to **1** and **2**; furthermore, use of $[Cu^{II}(py)_2DAP]^{2+}$ in the reaction scheme[30,32] produced no binuclear product, in keeping with the absence of a coordinating and bridging imidazolate functional group.

Compounds **1–4** all possess satisfactory elemental analyses consistent with the 1:1 (Fe:M) structural formulations as shown in Figure 1 (see Experimental Section). Unfortunately, the complex equilibrium properties of the systems in solution[23] have, to date, complicated crystal growth attempts for structural verification by X-ray methods; however, the magnetic, spectroscopic, and chemical behavior of **1–4** leave little doubt of their formulation as discrete, mixed-metal μ-imidazolato species in the solid state. In this regard, **2** and **4** represent the first such heteronuclear species of Fe^{III} and Cu^{II} to be prepared and isolated as model compounds for the oxidase active site, although Landrum et al.[20a] have recently reported a μ-imidazolato diporphyrin compound containing Mn^{II} ($S = {}^5/_2$) and Co^{II} ($S = {}^1/_2$) centers as a spin model for the site. In this latter compound, antiferromagnetic coupling was found to be weak (ca. 5 cm^{-1}), which led the authors to argue against imidazolate as a bridging moiety in the enzyme. In this work we present data that serve to temper this conclusion.

Variable-temperature (15–300 K) magnetic susceptibility data for the four μ-imidazolato species are displayed in Figure 2 as plots of μ_{eff} (μ_B) vs. temperature (K). The actual data are listed in the supplemtary material. The curves shown are merely illustrative and not computer-fit to the data. Compound **1** has a room-temperature magnetic moment of 2.67 μ_{eff}^{295K}, a value somewhat high for a simple $S = {}^1/_2$ low-spin ground state of this six-coordinate Fe^{III} porphyrin center having axial Cl^- ligand and a Zn^{II}-metalated imidazolate ligand; however, the gradual decrease in μ_{eff} to ca. 2.15 μ_B at 50 K is in basic agreement with an $S = {}^1/_2$ assignment. Nevertheless, as elaborated upon later, the EPR spectrum of **1** in the polycrstyalline state indicates an electronic

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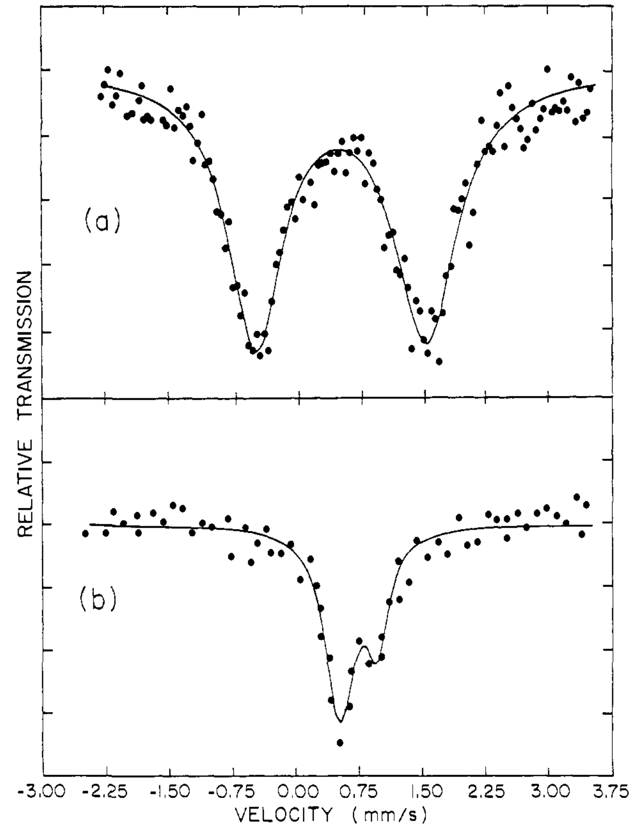

Figure 3. Zero-field Mössbauer spectrum at 100 K of (a) compound **2** and (b) compound **4** relative to sodium nitroprusside.

Table I. EPR Parameters at 10 K for the μ-Imidazolato Complexes in the Polycrystalline State

compd	g factors: Fe	g factors: Cu
1	$g_\perp = 5.67$ $g_\parallel = 1.99; g_{zz} = 2.79$ $g_{yy} = 2.26$ $g_{xx} \simeq 1.71$	
2	$g_\perp = 5.62$ $g_\parallel$ (not fully resolved)	$g_\perp = 2.09$ $g_\parallel = 2.22$
3	$g_\perp = 5.62$ $g_\parallel = 1.99; g_{zz} = 2.72$ $g_{yy} = 2.28$ $g_{xx} = 1.73$	

structure for iron that is not a strict case of a classical $S = {}^1/_2$ system. For compound **2**, in which an $S = {}^1/_2$ Cu^{II} center replaces Zn^{II}, the μ_{eff} vs. temperature curve parallels that found for compound **1** but with the additional paramagnetism expected for an $S = {}^1/_2$ Cu^{II} center having $\mu_{eff} \approx 2.0\ \mu_B$. Thus, comparative full-temperature magnetochemical data for **1** and **2** indicate magnetically isolated $S = {}^1/_2$ centers in **2**, with the bridging imidazolate ligand fostering little ($\lesssim 15$ cm^{-1}), if any, antiferromagnetic coupling between Cu^{II} and Fe^{III}. The zero-field ^{57}Fe Mössbauer spectra of **1** and **2** are also reflective of essentially identical electronic environments about iron, with both compounds exhibiting quadrupole split doublets typical of low-spin Fe^{III} centers having isomer shift and quadrupole splitting parameters that are identical within experimental error: $\delta_{SNP}^{100K} = 0.46$ ($\pm$0.02) mm s^{-1} and $\Delta E_Q^{100K} = 1.94$ ($\pm$0.03) mm s^{-1}. A typical spectrum of **2** is shown in Figure 3a.

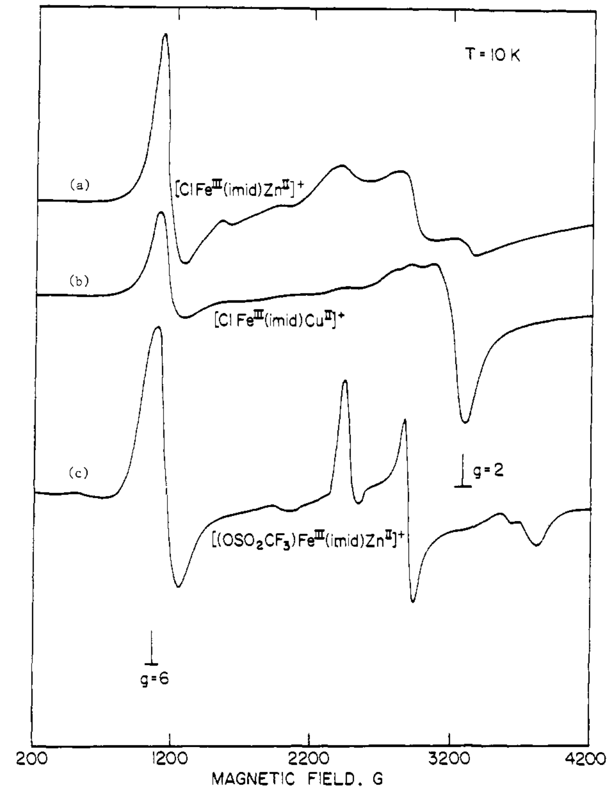

Figure 4. EPR spectrum at 10 K of (a) compound **1**, (b) compound **2**, and (c) compound **3** in the polycrystalline state.

The EPR spectra of **1** and **2** as polycrystalline solids at 10 K are shown in Figure 4, a and b, respectively. EPR parameters for all the EPR-active compounds studied in this work are shown in Table I. In Figure 4a, **1** exhibits a broad, multiple resonance in the $g \approx 2$ region of the spectrum, which is characteristic of low-spin $S = {}^1/_2$ Fe^{III} porphyrin centers. In this same region, compound **2** also displays a similar spectral pattern, but with an additional superimposed component centered around $g = 2$ that can be assigned to Cu^{II}. Furthermore, both compounds also exhibit a $g \approx 6$ resonance that is typical of a rhombically split high-spin $S = {}^5/_2$ state. From relative integration of the $g \approx 2$ and 6 signals, it can be estimated that the $S = {}^1/_2$ state in **1** and **2** is present in approximately 80–90% abundance, although integration of EPR signals from solid samples is not an especially reliable measure of relative paramagnetic concentrations. The $g \approx 6$ signal could arise from some high-spin impurity in **1** and **2**, with the most likely source of such an impurity being the [Fe^{III}(TPP)Cl] precursor. However, the Mössbauer spectra of both **1** and **2** show no indication of any such impurity (in Figure 3a, the $\delta_{SNP}^{100K} = 0.41$ mm s^{-1} singlet for [Fe^{III}(TPP)Cl] should be readily apparent),[33] and, furthermore, the elemental analyses of **1** and **2** are in excellent agreement with their being analytically pure compounds. Of course, a small amount of some $S = {}^5/_2$ impurity could be EPR active and yet escape detection by chemical analyses and Mössbauer spectroscopy, and, if present in only ca. 5%, it would adequately explain the somewhat high value of $\mu_{eff}^{295} = 2.67\ \mu_B$ for **1** as compared to the 2.2–2.4-μ_B range normally found for low-spin Fe^{III}. Since the μ_{eff} vs. temperature plots in Figure 2 are mainly Curie in nature, the observed magnetic behavior is most probably not attributable to a thermally dependent ($S = {}^1/_2$) $\rightleftharpoons$ ($S = {}^5/_2$) spin-equilibrium process unless very small thermodynamic parameters are involved. However, regardless of whether the $g = 6$ signals in question arise from some $S = {}^5/_2$ impurity or from a thermally dependent spin-equilibrium process with small thermodynamic parameters, the basic conclusion of interest here is unchanged: antiferromagnetic exchange through imidazolate in **2** is at best weak and equal to 15 cm^{-1}.

In contrast to the weak exchange interaction found above in **2**, similar magnetic, Mössbauer, and EPR data for **3** and **4** reveal quite a different behavior concerning the ability of imidazolate to foster magnetic coupling between Fe^{III} and Cu^{II}. It is now thought that Fe^{III} in the [Fe^{III}(TPP)(OSO$_2$CF$_3$)] precursor to **3** and **4** exhibits a quantum-mechanical admixture of the $S = {}^3/_2$

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[33] From a spectrum determined in our laboratories.

and $^5/_2$ spin states.[34–41] However, this does not necessarily mean that the μ-imidazolato binuclear species, derived from $[Fe^{III}(TPP)(OSO_2CF_3)]$, would also reflect this unusual electronic structure; and, indeed, the EPR spectrum of **3** discounts the presence of such a spin admixture occurring in **3**, since the spectrum consists of *two* distinct signals at $g = 6, 2$ ($S = {}^5/_2$) and $g = 2$ ($S = {}^1/_2$) rather than a single unique signal expected for some spin admixture of the $S = {}^1/_2$ and $^3/_2$ or $^5/_2$ states. The variable-temperature magnetochemical data for **3** and **4** are shown in Figure 2. The room-temperature moment of **3** is 3.36 $\mu_B{}^{295K}$, which, again, is an unusual value for an Fe^{III} porphyrin compound. Nevertheless, this and the above EPR results can be rationalized by assuming the presence of a simple mixture of two distinct molecular species of $S = {}^5/_2$ and $^1/_2$ coexisting in the same crystalline sample of **3**.[42] Until a crystal structure of **3** is forthcoming, any explanations as to the origin of such a spin mixture would only be speculative at best. It is, however, clear that whatever the explanation, the magnetochemical and EPR results for **3** are reproducible from preparation to preparation. Alternatively, the simultaneous presence of both $g = 6, 2$ and $g = 2$ signals in the EPR spectrum could arise from a thermally dependent $(S = {}^1/_2) \rightleftharpoons (S = {}^5/_2)$ spin equilibrium,[43,44] but, again, the reasonably Curie behavior of the μ_{eff} vs. temperature plots of **3** over a 15–300-K range argue against this possibility. With the assumption that limiting values of μ_{eff} $(S = {}^5/_2) = 5.9$ μ_B and μ_{eff} $(S = {}^1/_2) = 2.3$ μ_B, an ca. 20:80 $(S = {}^5/_2)$: $(S = {}^1/_2)$ mixture would satisfactorily account for the observed full-temperature magnetochemical properties of **3**. Unfortunately, compound **3** failed to yield a resolvable Mössbauer spectrum even at 100 K and long collection times,[45] so additional information about the electronic structure is unavailable from this technique at this time.

The most significant result of this study occurred with compound **4**. As seen in Figure 2, this compound, with its $[Fe^{III}(imid)Cu^{II}]$ core, exhibits a magnetic moment of 2.19 $\mu_B{}^{295K}$ at room temperature, which is a value substantially *depressed* relative to that of compound **3**, where $\mu_{eff} = 3.36$ $\mu_B{}^{295K}$ for a $[Fe^{III}(imid)Zn^{II}]$ core. Furthermore, this magnetochemical pattern is generally maintained over the full 15–300-K temperature range studied, with both compounds nearly Curie in behavior. Probably the most reasonable interpretation of this result (also supported by EPR data) is that a strong antiferromagnetic coupling interaction is mediated by imidazolate between Fe^{III} and Cu^{II} in **4** to generate a fully spin-coupled ground state with $-J_{Fe^{III}-Cu^{II}} \geq 200$ cm^{-1}. The exact nature of this resultant spin-coupled state is open to some interpretation, especially since the electronic structure of Fe^{III} in **3** probably involves a heterogeneous mixture of two spin states, $S = {}^5/_2$ and $^1/_2$, in the same crystalline lattice. However, as for compound **3**, if one assumes an 80:20 $(S = {}^1/_2)$:$(S = {}^5/_2)$ mixture in **4** and strong antiferromagnetic coupling between $S = {}^1/_2$ Cu^{II} and the 80:20 mixture to produce a resulting 80:20 $(S = 0)$:$(S = 2)$ spin-coupled ground state, one calculates a room-temperature magnetic moment of ca. 2.2 μ_B, in excellent agreement with the 2.19 $\mu_B{}^{295K}$ value found experimentally. Furthermore, as to be expected from this analysis in which only even spin states contribute to the ground state, compound **4** should be EPR silent, and, indeed, such is essentially the case.[46] Finally, the zero-field Mössbauer spectrum of this spin-coupled system is shown in Figure 3b, where $\delta_{SNP}{}^{100K} = 0.77$ mm s^{-1} and $\Delta E_Q = 0.36$ mm s^{-1}; it would be instructive to compare this spectrum to that of **3** as further evidence of differing electronic environments for Fe^{III} in these two species, but as mentioned above, compound **3** has as yet failed to yield a resolvable Mössbauer spectrum. Nevertheless, the available magnetic and EPR spectral data for **3** and **4** stand convincingly on their own as indicative of a case in which imidazolate fosters strong antiferromagnetic exchange between Fe^{III} and Cu^{II} in a synthetic metalloporphyrin complex. While the magnitude of this exchange interaction may be as strong $(-J_{Fe^{III}-Cu^{II}} \gtrsim 200$ cm$^{-1})$ as that operating in resting oxidase, this result obviously does not prove the existence of an imidazolate bridge at the active site in the enzyme, especially since compound **2** displays a comparatively weak interaction. Rather, the result serves to rekindle this suggestion as a viable possibility. Continued modeling studies employing the present species and other μ-imidazolato mixed-metal compounds should further elaborate upon this possibility by clarifying what electronic/structural conditions promote magnetic coupling across imidazolate bridges in general.

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Registry No. 1, 82247-38-9; **2**, 82247-37-8; **3**, 82247-40-3; **4**, 82247-39-0; $[Zn^{II}((imid)H)_2DAP](BF_4)_2$, 82135-49-7; $[Cu^{II}((imid)H)_2DAP](BF_4)_2$, 82135-65-7; $Fe^{III}(TPP)Cl$, 16456-81-8; $Fe^{III}(TPP)(OSO_2CF_3)$, 70936-35-5.

Supplementary Material Available: Table listing χ_M (cgsu), μ_{eff} (μ_B), and temperature (K) data for compounds **1**–**4** (5 pages). Ordering information is given on any current masthead page.

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(42) The EPR spectrum of **3** is unusually well-resolved in the $g \approx 2$ region for a magnetically dense polycrystalline sample. Furthermore, the quality of the spectrum in this region is important in this study in that the resolved g factors ($g_{xx} = 2.72$, $g_{yy} = 2.28$, $g_{zz} = 1.73$) closely match those ($g_{xx} = 2.78$, $g_{yy} = 2.26$, $g_{zz} = 1.72$) of the $[Fe^{III}(protoporphyrinato\ IX)(imid)_2]^-$ anion, which also contains axially ligated imidazolate anions, as opposed to those ($g_{xx} = 3.02$, $g_{yy} = 2.24$, $g_{zz} = 1.51$) of the $[Fe^{III}(protoporphyrinato)(imidH)_2]^+$ cation, in which the imidazole groups remain protonated. Peisach, J.; Blumberg, W. E.; Adler, A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 310.

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(45) The signal obtained after 72 h was very broad (hwhh ≈ 1 mm s^{-1}), probably with three or more resolved components. This being the case, it is a considerably different spectrum than that obtained for compound 4 in Figure 4b.

(46) In fact, compound 4 displays very weak signals in both the $g \approx 6$ and $g \approx 2$ regions, but these signals accounted for <0.4% of the Fe^{III} and Cu^{II} present when integrated against signals from solid samples of $[Fe^{III}(TPP)(OSO_2CF_3)]$ and $[Cu^{II}(imidH)_2DAP](BF_4)_2$. Since these signals are so weak, they are best attributed to very small amounts of Fe^{III} and Cu^{II} impurites in the sample and not to the $[Fe^{III}(imid)Cu^{II}]$ core of compound 4. Furthermore, dipolar relaxation broadening, by the so-called Leigh effect (Leigh, J. S., Jr. *J. Chem.* Phys. **1970**, *52*, 2608), is not likely to be responsible for the EPR quietness of 4, since the magnetic susceptibility data are also consistent with strong antiferromagnetic coupling in the compound.