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# Binding of $Cu^I$ and $Cu^{II}$ to the Pendent $O_3$-Face of Iron Arylazo Oximates: Synthesis and Structure of $Cu^IFe^{II}$ and $Cu^{II}Fe^{II}_2$ Families

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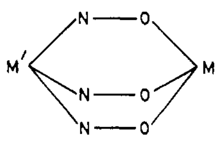
The reaction of the tris(arylazo oximato)iron(II) anion, $Fe(RL)_3^-$ (R = Me, Ph, *p*-$MeC_6H_4$), with $Cu(MeCN)_4^+$ in dichloromethane under air affords the trinuclear complex $Cu^{II}Fe^{II}_2(RL)_6$. In the presence of $PPh_3$ in the reaction mixture, the binuclear complex $Cu^IFe^{II}(RL)_3(PPh_3)$ is isolated. The X-ray structures of $CuFe(MeL)_3(PPh_3)$ and $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$ are reported. In both complexes the $Fe(RL)_3^-$ fragment acts as a facially disposed tridentate oximato-$O_3$ ligand. The $O_3$ face has a natural affinity for the harder copper(II) cation. The stable binding of soft copper(I) becomes possible when a soft coligand like $PPh_3$ is present. The nonbonded Cu···Fe distances are 3.394(1) and 3.483(1) Å in the copper(I) and copper(II) complexes, respectively. The coordination sphere in the former complex is of the unprecedented distorted tetrahedral $CuO_3P$ type. The copper(II) complex is centrosymmetric and the $CuO_6$ coordination sphere is strongly Jahn–Teller elongated along one of the O–Cu–O axes. The N–O lengths corresponding to the elongated Cu–O bonds are shorter. The crystal data for the two complexes are as follows. $CuFe(MeL)_3(PPh_3)$: space group $P\bar{1}$; $a = 9.854(5)$ Å, $b = 12.765(4)$ Å, $c = 17.506(8)$ Å, $\alpha = 94.37(3)°$, $\beta = 103.84(4)°$, $\gamma = 102.47(3)°$; $V = 2068(2)$ Å$^3$; $Z = 2$; $R = 4.46\%$ and $R_w = 5.28\%$. $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$: space group $P2_1/c$; $a = 14.538(7)$ Å, $b = 13.019(8)$ Å, $c = 22.673(11)$ Å, $\beta = 108.89(4)°$; $V = 4060(4)$ Å$^3$; $Z = 2$; $R = 5.85\%$ and $R_w = 6.14\%$. The copper(I) complexes are diamagnetic and display electronic spectra characteristic of the bound $Fe(RL)_3^-$ moiety. In the one-electron paramagnetic copper(II) complexes the $d_{z^2} \rightarrow d_{x^2-y^2}$ ligand field transition is observed near 1200 nm. Parameters for the axially split EPR spectra are $g_\parallel \sim 2.340$, $g_\perp \sim 2.080$, $A_\parallel \sim 110$ G, and $A_\perp \sim 20$ G.

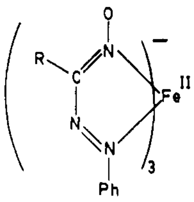
## Introduction

One of the coordination modes of the oxime function is diatomic N,O-bridging between metal atoms.[1–6] The concern of this work is the uncommon $MO_3N_3M'$ motif, **1**, in which the M and M′ polyhedra are held face-to-face by three concurrent bridges. The motif was first authenticated in a mixed-valence iron complex.[7] A few other examples have been reported subsequently,[8–14] in some cases[14] without reference to previous work.[7–11]



—N—O— is oximato bridge

1



$Fe(RL)_3^-$

2

The tris(arylazo oximato)iron(II) anion, $Fe(RL)_3^-$, **2**, is an excellent precursor for assembling **1** (M′ = $Fe^{II}$). Only relatively hard M cations have been used so far.[7–9,13] We have now examined the interaction of $Fe(RL)_3^-$ with an authentic soft cation,[15] copper(I), and the results are reported here. Two families of complexes incorporating motif **1** have been isolated and characterized: binuclear $Cu^IFe^{II}(RL)_3(PPh_3)$ and trinuclear $Cu^{II}Fe^{II}_2(RL)_6$. Structure determination has revealed the presence of the $CuO_3N_3$-Fe motif, the copper coordination spheres being of the types

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**Table I.** Characterization Data

| compounds | $\mu_{eff}$,[a] $\mu_B$ | EPR g(A,G)[c] ∥ | EPR g(A,G)[c] ⊥ | UV–vis–near-IR data[d] $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) |
|---|---|---|---|---|
| $CuFe(MeL)_3(PPh_3)$ | *b* | | | 860[e] (320), 650 (4150), 430 (20 000) |
| $CuFe(PhL)_3(PPh_3)$ | *b* | | | 850[e] (325), 650 (5930), 445 (17 650) |
| $CuFe(p\text{-}MeC_6H_4L)_3(PPh_3)$ | *b* | | | 850[e] (345), 655 (6260), 450 (18 300) |
| $CuFe_2(MeL)_6$ | 2.02 | 2.344 (114) | 2.075 (20) | 1140 (160), 620 (12 540), 415 (45 620) |
| $CuFe_2(PhL)_6$ | 2.20 | 2.345 (110) | 2.078 (23) | 1260 (175), 615 (13 460), 515[e] (17 360), 435 (29 520) |
| $CuFe_2(p\text{-}MeC_6H_4L)_6$ | 2.15 | 2.342 (111) | 2.077 (22) | 1275 (162), 615 (16 210), 520[e] (18 990), 440 (30 780) |

[a] At 296 K. [b] Diamagnetic [c] In 1:1 dichloromethane–toluene frozen glass (77 K). [d] In $CH_2Cl_2$. [e] Shoulder.

$Cu^IO_3P$ and $Cu^{II}O_6$. For stable binding of copper(I) into the motif **1**, the presence of a soft coligand appears to be obligatory.

## Results and Discussion

**Synthetic Studies.** Three $Fe(RL)_3^-$ anions differing in R have been used in the present work: R = Me, Ph, and $p$-$MeC_6H_4$. Under anaerobic conditions the reaction of $Cu(MeCN)_4^+$ with $Fe(RL)_3^-$ fails to afford any tractable solid complex. However, the reaction solution (dichloromethane solvent) is very sensitive—far more than $Cu(MeCN)_4^+$ alone is—to oxygen and the product of the facile oxidation is the trinuclear entity of composition $CuFe_2(RL)_6$ which has been isolated in high yields. It is probable that the oxygen-sensitive species has copper(I) linked to $Fe(RL)_3^-$.

This prompted us to examine the above reaction in the presence of $PPh_3$ which has a high affinity for monovalent copper and might therefore stabilize the oxidation state. The reaction of $Cu(MeCN)_4^+$ with $Fe(RL)_3^-$ indeed proceeded smoothly in dichloromethane solution containing $PPh_3$, affording the complex $CuFe(RL)_3(PPh_3)$ in nearly quantitative yields. The presence of oxygen has no effect on this reaction.

Thus in the redox sense the soft copper(I) ion alone or in MeCN-coordinated form is not suited for stable binding to the oximato oxygen atoms of $Fe(RL)_3^-$ but the harder[15a] copper(II) ion is. Stable coordination of copper(I) becomes achievable once the soft[15a] phosphine coligand is made available.

As a sequel to the above findings, the $CuFe(RL)_3(PPh_3)$ and $CuFe_2(RL)_6$ complexes were successfully synthesized by reacting $Fe(RL)_3^-$ with $Cu(PPh_3)_2NO_3$ and $Cu(ClO_4)_2{\cdot}6H_2O$ respectively. When the complexes are treated with alkali ($OH^-$) in acetone, the copper atom is extruded as hydroxide/oxide and free $Fe(RL)_3^-$ is quantitatively released into the solution. An endless interconversion cycle between $Fe(RL)_3^-$ and its copper complexes can thus be constructed.

**Magnetism and Spectra.** Selected data for the complexes are set out in Table I. The $Fe(RL)_3^-$ moiety is known[16] to be spin-paired ($d^6$, $S = 0$) and consequently the copper(I) and copper(II) complexes are respectively diamagnetic and paramagnetic ($S = {}^1/_2$). Representative examples of the distinctive electronic spectra of the two groups of complexes are displayed in Figure 1. A strong MLCT absorption at ~600 nm often associated with a shoulder at ~900 nm is known[7] to be characteristic of $Fe(RL)_3^-$, and these features are present in the copper(I) complexes.

In the copper(II) complexes the ~600-nm band is present along with a well-defined feature of relatively low intensity (~150 $M^{-1}$ $cm^{-1}$) near 1200 nm. In frozen solution (77 K) $CuFe_2(RL)_6$ gives rise to axially split EPR spectra with $g_\parallel \sim 2.340$, $g_\perp \sim 2.080$, $A_\parallel \sim 110$ G and $A_\perp \sim 20$ G. (Table I). As shown below, the $Cu^{II}O_6$ coordination sphere is indeed strongly elongated along an O–Cu–O axis. The expected ground state is thus $(d_{x^2-y^2})^1$, which is consistent with $g_\parallel \gg g_\perp$. The ~1200-nm optical transition noted above is believed to be largely due to the $d_{z^2} \rightarrow d_{x^2-y^2}$ ligand field excitation.

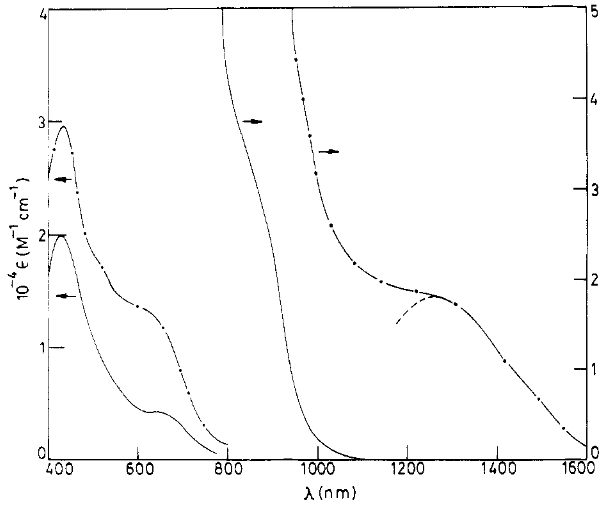

**Figure 1.** Electronic spectra of $CuFe(MeL)_3(PPh_3)$ (—), $CuFe_2(PhL)_6$ (- • -) in dichloromethane solution at 298 K.

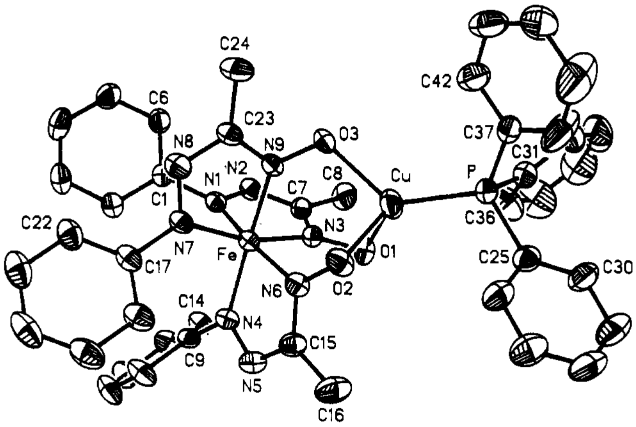

**Figure 2.** ORTEP plot and atom-labeling scheme for $CuFe(MeL)_3(PPh_3)$. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

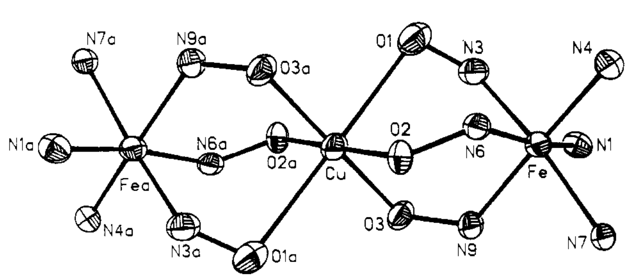

**Figure 3.** View of the coordination spheres of the iron and copper atoms in $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$.

**Structure.** The X-ray structures of $CuFe(MeL)_3(PPh_3)$ and $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$ have been determined. Molecular views are shown in Figures 2–4 and selected bond parameters are listed in Tables II and III. In both complexes $Fe(RL)_3^-$ acts as a facially disposed tridentate $O_3$ ligand and the motif **1** (M = Cu, M′ = Fe) is present. The nonbonded Cu···Fe distances are 3.394(1) and 3.483(1) Å in the $Cu^I$ and $Cu^{II}$ complexes, respectively. The

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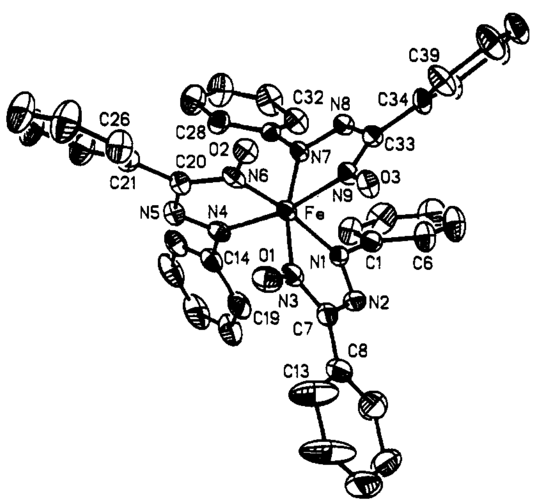

**Figure 4.** ORTEP plot and atom labelling scheme for the $Fe(PhL)_3$ fragment of $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

**Table II.** Selected Bond Lengths (Å) and Angles (deg) for $CuFe(MeL)_3(PPh_3)$

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Cu–P | 2.145(2) | Cu–O(1) | 2.127(3) |
| Cu–O(2) | 2.121(3) | Cu–O(3) | 2.064(3) |
| Fe–N(1) | 1.966(3) | Fe–N(3) | 1.918(3) |
| Fe–N(4) | 1.917(4) | Fe–N(6) | 1.897(4) |
| Fe–N(7) | 1.939(4) | Fe–N(9) | 1.919(3) |
| O(1)–N(3) | 1.293(4) | O(2)–N(6) | 1.300(4) |
| O(3)–N(9) | 1.296(4) | N(1)–N(2) | 1.305(5) |
| N(4)–N(5) | 1.298(5) | N(7)–N(8) | 1.303(5) |
| Bond Angles | | | |
| P–Cu–O(1) | 117.7(1) | P–Cu–O(2) | 120.4(1) |
| O(1)–Cu–O(2) | 91.7(1) | P–Cu–O(3) | 129.1(1) |
| O(1)–Cu–O(3) | 95.1(1) | O(2)–Cu–O(3) | 94.3(1) |
| N(1)–Fe–N(3) | 78.1(1) | N(1)–Fe–N(4) | 99.3(1) |
| N(3)–Fe–N(4) | 96.9(1) | N(1)–Fe–N(6) | 167.3(1) |
| N(3)–Fe–N(6) | 89.5(1) | N(4)–Fe–N(6) | 79.2(2) |
| N(1)–Fe–N(7) | 94.3(1) | N(3)–Fe–N(7) | 164.3(2) |
| N(4)–Fe–N(7) | 97.9(1) | N(6)–Fe–N(7) | 98.3(2) |
| N(1)–Fe–N(9) | 89.6(1) | N(3)–Fe–N(9) | 88.0(2) |
| N(4)–Fe–N(9) | 170.5(2) | N(6)–Fe–N(9) | 92.8(2) |
| N(7)–Fe–N(9) | 78.1(1) | | |

**Table III.** Selected Bond Lengths (Å) and Angles (deg) for $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$

| | | | |
|---|---|---|---|
| Bond Lengths | | | |
| Cu–O(1) | 2.412(7) | Cu–O(2) | 1.973(4) |
| Cu–O(3) | 2.014(6) | Fe–N(1) | 1.962(6) |
| Fe–N(3) | 1.944(7) | Fe–N(4) | 1.941(6) |
| Fe–N(6) | 1.894(7) | Fe–N(7) | 1.957(6) |
| Fe–N(9) | 1.923(6) | O(1)–N(3) | 1.278(11) |
| O(2)–N(6) | 1.325(9) | O(3)–N(9) | 1.325(8) |
| N(1)–N(2) | 1.302(9) | N(4)–N(5) | 1.291(10) |
| N(7)–N(8) | 1.294(9) | | |
| Bond Angles | | | |
| O(1)–Cu–O(2) | 85.9(2) | O(1)–Cu–O(3) | 92.4(2) |
| O(2)–Cu–O(3) | 93.6(2) | O(1)–Cu–O(1A) | 180.0(1) |
| O(1)–Cu–O(2A) | 94.1(2) | O(1)–Cu–O(3A) | 87.6(2) |
| O(2)–Cu–O(3A) | 86.4(2) | N(1)–Fe–N(3) | 78.2(3) |
| N(1)–Fe–N(4) | 102.4(3) | N(3)–Fe–N(4) | 95.9(3) |
| N(1)–Fe–N(6) | 167.1(3) | N(3)–Fe–N(6) | 88.9(3) |
| N(4)–Fe–N(6) | 79.1(3) | N(1)–Fe–N(7) | 92.7(3) |
| N(3)–Fe–N(7) | 166.7(2) | N(4)–Fe–N(7) | 95.5(3) |
| N(6)–Fe–N(7) | 100.0(3) | N(1)–Fe–N(9) | 89.3(3) |
| N(3)–Fe–N(9) | 92.0(3) | N(4)–Fe–N(9) | 167.1(3) |
| N(6)–Fe–N(9) | 90.8(3) | N(7)–Fe–N(9) | 78.2(3) |

corresponding copper coordination spheres are of types $Cu^IO_3P$ and $Cu^{II}O_6$. The three previously reported structural studies[7,8,13] on species of type **1** incorporating $Fe(RL)_3^-$ had the common problem of relatively weakly diffracting crystals. The derived bond parameters were therefore of only moderate accuracy. The present complexes, which do not have this limitation, have afforded more accurate measures of the dimensions of motif **1** engaging $Fe(RL)_3^-$. The $CH_2Cl_2$ of crystallization in the copper(II) complex is disordered.

**a. The $CuO_3P$ Coordination Sphere, $CuFe(MeL)_3(PPh_3)$.** To our knowledge this is the first structural characterization of the $Cu^IO_3P$ coordination sphere. Trigonal β-diketone–phosphine complexes of the type $CuO_2P$ are known.[17] The $CuO_3P$ sphere is tetrahedral but with large angular distortions—the O–Cu–O and P–Cu–O angles lying respectively in the ranges 91–96 and 117–130°. The dimensions of the O–Cu–O angles appear to be controlled more by the geometry of the $Fe(RL)_3^-$ oximato face rather than by any particular requirement of the copper(I) ion.

The Cu–O(2) and Cu–O(3) distances are nearly equal to each other but these are longer than the Cu–O(1) distance, 2.064(3) Å, by ~0.06 Å. The Cu–P length, 2.145(2) Å, is comparable to those in some species incorporating one phosphine per copper(I).[18,19]

**b. The $Cu^{II}O_6$ Center in $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$.** This complex is centrosymmetric with copper(II) lying at a crystallographic inversion center (0, 0, 0). The Fe···Cu···Fe fragment is thus exactly linear. Also there are only three independent Cu–O lengths, and the trans O–Cu–O angles are identically 180°. The cis angles lie in the range 85–95°.

The $CuO_6$ coordination sphere is strongly Jahn–Teller elongated along the O(1)–Cu–O(1A) axis. The Cu–O(1) length, 2.412(7) Å, is ~0.4 Å longer than the other two independent Cu–O lengths, 2.014(6) and 1.973(4) Å. The latter are shorter, as expected (bond contraction due to metal oxidation), than the Cu–O lengths in $CuFe(MeL)_3(PPh_3)$.

Axial elongation similar to that in $CuFe_2(PhL)_6$ has been observed in simpler $CuO_6$ species such as salts of $Cu(H_2O)_6^{2+}$[20] and $Cu(p\text{-}MeC_5H_4NO)_6^{2+}$.[21] For Jahn–Teller-inactive ions the $MO_6$ coordination sphere assembled with $Fe(RL)_3^-$ has near-octahedral geometry as in M = $Fe^{III}$[7] and $Ni^{II}$.[8]

**c. The $Fe(RL)_3^-$ Fragments.** The three arylazo oximate ligands are chelated in the facial manner, Figures 2 and 4. The $FeN_6$ coordination sphere is distorted octahedral. The bite angles of these excellently planar chelate rings are ~78°, and the trans N–Fe–N angles lie in the range 164–171°. The dimensions of the $FeN_6$ spheres in the two complexes do not vary in any marked manner. The average Fe–N(oxime) length is 0.02–0.03 Å shorter than the average Fe–N(azo) length.

The $Fe(RL)_3^-$ chelate is chiral and can occur in Δ and Λ configurations. The centrosymmetry of $CuFe_2(PhL)_6$ implies that within each molecule the $Fe(PhL)_3^-$ units together constitute a racemic Δ–Λ pair. A similar situation occurs in $Fe^{III}Fe^{II}_2(PhL)_6^+$[7] but not in $Ni^{II}Fe^{II}_2(MeL)_6$.[8]

**d. Trends in N–O Length.** In $CuFe_2(PhL)_6$ the N–O lengths are of two types, 1.278(11) and 1.325(9) Å. The shorter length corresponds to the bridge that leads to an elongated Cu–O bond. In the N–O–Cu fragment a weaker Cu–O interaction is logically associated with a stronger N–O bond. The magnitude of the effect on the N–O length is however small—a change of 0.03–0.05 Å only for a ~0.4-Å variation in the Cu–O length.

In $CuFe(MeL)_3(PPh_3)$ there are two Cu–O length types as well, but their difference is only ~0.06 Å. The effect of this on the N–O lengths is unobservably small. Finally, we note that the N–O length in the copper(I) complex (average 1.296(4) Å) is, as expected, shorter than the length corresponding to the

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**Table IV.** Crystallographic Data for $CuFe(MeL)_3(PPh_3)$ and $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$

| | $CuFe(MeL)_3(PPh_3)$ | $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$ |
|---|---|---|
| empirical formula | $C_{42}H_{39}N_9O_3PFeCu$ | $C_{80}H_{64}N_{18}O_6Cl_4Fe_2Cu$ |
| fw | 868.18 | 1690.5 |
| space group | $P\bar{1}$ | $P2_1/c$ |
| $a$, Å | 9.854(5) | 14.538(7) |
| $b$, Å | 12.765(4) | 13.019(8) |
| $c$, Å | 17.506(8) | 22.673(11) |
| $\alpha$, deg | 94.37(3) | |
| $\beta$, deg | 103.84(4) | 108.89(4) |
| $\gamma$, deg | 102.47(3) | |
| $V$, Å$^3$ | 2068(2) | 4060(4) |
| $Z$ | 2 | 2 |
| $T$, °C | 22 | 22 |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.394 | 1.388 |
| $\mu$, cm$^{-1}$ | 9.5 | 8.1 |
| $R$,[a] % | 4.46 | 5.85 |
| $R_w$,[b] % | 5.28 | 6.14 |
| GOF[c] | 1.43 | 0.92 |

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.0005$ for $CuFe(MeL)_3(PPh_3)$ and 0.0001 for $CuFe_2(PhL)_6{\cdot}2CH_2Cl_2$. [c] The goodness of fit is defined as $[w(|F_o|-|F_c|)^2/(n_o - n_v)]^{1/2}$ where $n_o$ and $n_v$ denote the numbers of data and variables, respectively.

nonelongated Cu–O bonds in the copper(II) complex (average 1.325(9) Å).

**Concluding Remarks.** The findings of this work will now be briefly stated. The oximato-$O_3$ face of $Fe(RL)_3^-$ has a natural affinity for relatively hard cations leading to complexes incorporating the uncommon motif **1**. The stable binding of soft copper(I) to $Fe(RL)_3^-$ has been achieved with assistance via coligation of a soft donor ($PPh_3$ in the present case) to copper(I). Complexes of type $CuFe(RL)_3(PPh_3)$ have been isolated and characterized. These constitute unprecedented examples of motif **1** with M = $Cu^I$ and M′ = $Fe^{II}$ and of the distorted tetrahedral $Cu^IO_3P$ coordination sphere.

In the absence of $PPh_3$, solutions containing copper(I) and $Fe(RL)_3^-$ are spontaneously oxidized by oxygen, affording stable complexes of the type $CuFe_2(RL)_6$. In essence, $Fe(RL)_3^-$ assists the oxidation of copper(I) to harder copper(II), which remains bound to $Fe(RL)_3^-$ in a stable manner. In $CuFe_2(RL)_6$, two motifs of type **1** are juxtaposed at the copper(II) center, the $CuO_6$ coordination sphere being strongly Jahn–Teller elongated (by ~0.8 Å in the case of the PhL complex) along one axis. Electronic and EPR spectral features are generally consistent with this.

The X-ray structures of $CuFe(MeL)_3(PPh_3)$ and $CuFe_2(PhL)_6$ have clarified the details of geometry and binding. The latter complex is centrosymmetric and thus the two $Fe(PhL)_3^-$ fragments constitute a Δ–Λ racemic pair. In both complexes the average Fe–N(oxime) length is slightly longer than the average Fe–N(azo) length. A stronger Cu–O interaction is found to lengthen the N–O bond. Using the lessons of the present work we are exploring the binding of other soft cations to $Fe(RL)_3^-$.

**Table V.** Atomic Coordinates (×10$^4$) and Equivalent[a] Isotropic Displacement Coefficients (Å$^2$ × 10$^3$) for $CuFe(MeL)_3(PPh_3)$

| | $x$ | $y$ | $z$ | $U$(eq) |
|---|---|---|---|---|
| Cu | 6777(1) | 10579(1) | 2976(1) | 69(1) |
| Fe | 4458(1) | 8281(1) | 1914(1) | 38(1) |
| P | 8364(1) | 11902(1) | 3739(1) | 59(1) |
| O(1) | 7474(3) | 9202(2) | 2614(2) | 57(1) |
| O(2) | 5174(3) | 9609(2) | 3415(2) | 61(1) |
| O(3) | 5393(3) | 10577(2) | 1885(2) | 57(1) |
| N(1) | 4494(3) | 7943(2) | 806(2) | 40(1) |
| N(2) | 5736(3) | 8249(3) | 646(2) | 45(1) |
| N(3) | 6478(3) | 8720(3) | 1985(2) | 44(1) |
| N(4) | 4463(3) | 6888(3) | 2251(2) | 44(1) |
| N(5) | 4746(4) | 6841(3) | 3009(2) | 53(2) |
| N(6) | 4869(4) | 8640(3) | 3030(2) | 48(1) |
| N(7) | 2396(3) | 8145(3) | 1656(2) | 44(1) |
| N(8) | 1935(4) | 8952(3) | 1367(2) | 53(2) |
| N(9) | 4333(4) | 9723(3) | 1725(2) | 44(1) |
| C(1) | 3329(4) | 7632(3) | 100(2) | 42(2) |
| C(2) | 2219(5) | 6734(3) | 50(3) | 54(2) |
| C(3) | 1088(5) | 6445(4) | −627(3) | 69(2) |
| C(4) | 1062(6) | 7046(5) | −1248(3) | 78(2) |
| C(5) | 2158(6) | 7921(5) | −1195(3) | 72(2) |
| C(6) | 3294(5) | 8224(4) | −527(3) | 57(2) |
| C(7) | 6817(4) | 8651(3) | 1296(3) | 45(2) |
| C(8) | 8319(5) | 9084(4) | 1232(3) | 69(2) |
| C(9) | 4254(4) | 5852(3) | 1795(2) | 43(2) |
| C(10) | 3163(5) | 4988(4) | 1828(3) | 67(2) |
| C(11) | 3013(6) | 4000(4) | 1395(4) | 76(2) |
| C(12) | 3938(6) | 3854(4) | 949(3) | 68(2) |
| C(13) | 5003(6) | 4707(4) | 914(3) | 65(2) |
| C(14) | 5165(5) | 5718(3) | 1334(3) | 54(2) |
| C(15) | 4985(5) | 7817(4) | 3450(3) | 54(2) |
| C(16) | 5431(6) | 7958(5) | 4327(3) | 79(3) |
| C(17) | 1225(5) | 7293(3) | 1717(3) | 50(2) |
| C(18) | 1331(5) | 6863(4) | 2419(3) | 63(2) |
| C(19) | 170(6) | 6079(5) | 2501(4) | 79(3) |
| C(20) | −1037(7) | 5740(5) | 1891(5) | 87(3) |
| C(21) | −1144(6) | 6173(5) | 1191(4) | 85(3) |
| C(22) | −12(5) | 6953(4) | 1105(3) | 66(2) |
| C(23) | 3013(5) | 9822(3) | 1392(3) | 49(2) |
| C(24) | 2697(6) | 10835(4) | 1135(3) | 73(2) |
| C(25) | 8857(5) | 11661(4) | 4765(3) | 60(2) |
| C(26) | 7773(6) | 11116(5) | 5066(3) | 76(3) |
| C(27) | 8050(8) | 10941(5) | 5852(4) | 92(3) |
| C(28) | 9424(9) | 11295(6) | 6330(3) | 95(3) |
| C(29) | 10506(8) | 11798(6) | 6036(4) | 101(3) |
| C(30) | 10233(6) | 11991(5) | 5256(3) | 81(3) |
| C(31) | 10085(6) | 12263(4) | 3505(3) | 71(2) |
| C(32) | 10921(8) | 13303(5) | 3579(3) | 93(3) |
| C(33) | 12257(11) | 13479(8) | 3449(5) | 133(5) |
| C(34) | 12804(9) | 12635(11) | 3242(6) | 143(5) |
| C(35) | 12000(10) | 11623(8) | 3152(5) | 140(5) |
| C(36) | 10627(7) | 11429(5) | 3263(4) | 103(3) |
| C(37) | 7795(5) | 13152(4) | 3790(3) | 71(2) |
| C(38) | 8074(12) | 13844(6) | 4461(5) | 198(6) |
| C(39) | 7556(14) | 14769(8) | 4466(7) | 260(8) |
| C(40) | 6788(10) | 15012(6) | 3777(7) | 149(5) |
| C(41) | 6501(7) | 14345(6) | 3128(5) | 97(3) |
| C(42) | 6986(6) | 13404(5) | 3121(3) | 79(3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

## Experimental Section

**Materials.** Arylazo oximes,[22] $Na[Fe(RL)_3]{\cdot}H_2O$,[16] $[Cu(MeCN)_4]PF_6$,[23] and $Cu(PPh_3)_2NO_3$[24] were prepared by the reported methods. $Cu(ClO_4)_2{\cdot}6H_2O$ was prepared by dissolving cupric hydroxide in 70% aqueous perchloric acid followed by crystallization. For synthetic experiments, the solvents were of analytical grade and were used as obtained.

**Physical Measurements.** UV–vis–near-IR spectra were recorded with a Hitachi 330 spectrophotometer. X-Band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar flask for low-temperature measurements (liquid dinitrogen, 77 K). DPPH ($g$ = 2.0037) was used to calibrate the EPR spectra. Magnetic susceptibilities were measured by using a PAR-155 vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N).

**Preparation of Complexes. (Triphenylphosphine)[tris((phenylazo)benzaldoximato)ferrato(II)]copper(I), $Cu[Fe(PhL)_3](PPh_3)$. a. From $[Cu(MeCN)_4]PF_6$.** To a stirred solution of $[Cu(MeCN)_4]PF_6$ (0.11 g, 0.33 mmol) in dichloromethane (60 mL) were added $PPh_3$ (0.173 g, 0.66 mmol) and then $NaFe(PhL)_3{\cdot}H_2O$ (0.25 g, 0.33 mmol). After 0.5 h the solution was filtered through a medium-porosity frit. The solvent was evaporated to dryness in vacuo. The dark solid obtained was washed with acetonitrile and dried in vacuo over $P_4O_{10}$; yield 0.32 g (94%). Anal. Calcd for $CuFeC_{57}H_{45}N_9O_3P$: C, 64.93; H, 4.27; N, 11.96: Found: C, 64.95; H, 4.19; N, 11.58.

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**Table VI.** Atomic Coordinates (×10$^4$) and Equivalent[a] Isotropic Displacement Coefficients (Å$^2$ × 10$^3$) for $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$

| | *x* | *y* | *z* | *U*(eq) |
|---|---|---|---|---|
| Cu | 0 | 0 | 0 | 45(1) |
| Fe | −1025(1) | −551(1) | 1164(1) | 40(1) |
| O(1) | −522(5) | −1675(5) | 224(3) | 66(3) |
| O(2) | 697(3) | 91(4) | 904(2) | 47(2) |
| O(3) | −1205(4) | 683(4) | 72(2) | 52(2) |
| N(1) | −2426(4) | −824(5) | 906(3) | 44(2) |
| N(2) | −2786(5) | −1372(5) | 403(3) | 58(3) |
| N(3) | −1200(5) | −1456(5) | 451(3) | 51(3) |
| N(4) | −506(5) | −1598(5) | 1794(3) | 45(3) |
| N(5) | 427(5) | −1701(5) | 1992(3) | 48(3) |
| N(6) | 316(5) | −475(5) | 1254(3) | 44(2) |
| N(7) | −1110(4) | 523(5) | 1750(2) | 38(2) |
| N(8) | −1457(4) | 1399(5) | 1507(3) | 41(2) |
| N(9) | −1278(4) | 651(5) | 641(2) | 43(2) |
| C(1) | −3160(6) | −302(6) | 1096(4) | 56(4) |
| C(2) | −3206(7) | −383(8) | 1688(4) | 73(4) |
| C(3) | −3935(9) | 139(12) | 1847(5) | 98(6) |
| C(4) | −4575(9) | 761(11) | 1416(8) | 103(7) |
| C(5) | −4516(9) | 833(10) | 834(7) | 105(6) |
| C(6) | −3805(7) | 329(8) | 671(5) | 78(5) |
| C(7) | −2101(6) | −1770(6) | 169(4) | 53(3) |
| C(8) | −2437(9) | −2475(7) | −368(5) | 76(5) |
| C(9) | −3414(12) | −2783(12) | −538(7) | 141(8) |
| C(10) | −3781(13) | −3478(14) | −1052(11) | 204(11) |
| C(11) | −3160(20) | −3864(13) | −1350(6) | 152(10) |
| C(12) | −2225(17) | −3613(12) | −1164(7) | 140(9) |
| C(13) | −1842(11) | −2940(11) | −660(6) | 116(7) |
| C(14) | −988(6) | −2250(6) | 2120(4) | 56(4) |
| C(15) | −596(7) | −2397(7) | 2759(4) | 65(4) |
| C(16) | −1083(11) | −3029(9) | 3053(6) | 90(6) |
| C(17) | −1911(12) | −3513(11) | 2740(9) | 110(8) |
| C(18) | −2289(8) | −3381(9) | 2103(8) | 108(7) |
| C(19) | −1833(7) | −2745(8) | 1772(5) | 83(5) |
| C(20) | 904(6) | −1084(6) | 1688(3) | 44(3) |
| C(21) | 1959(6) | −1160(7) | 1879(3) | 51(3) |
| C(22) | 2464(8) | −1470(9) | 2492(4) | 74(4) |
| C(23) | 3446(9) | −1559(10) | 2681(5) | 93(5) |
| C(24) | 3975(8) | −1340(12) | 2298(7) | 106(6) |
| C(25) | 3506(8) | −1026(11) | 1691(6) | 99(6) |
| C(26) | 2516(7) | −954(8) | 1485(4) | 69(4) |
| C(27) | −884(5) | 547(6) | 2420(3) | 40(3) |
| C(28) | −2(6) | 180(7) | 2781(3) | 55(3) |
| C(29) | 271(7) | 272(9) | 3440(4) | 82(5) |
| C(30) | −364(9) | 712(10) | 3702(4) | 91(5) |
| C(31) | −1250(8) | 1064(9) | 3341(4) | 81(5) |
| C(32) | −1528(7) | 984(7) | 2693(3) | 60(4) |
| C(33) | −1560(5) | 1476(6) | 879(3) | 42(3) |
| C(34) | −1851(6) | 2485(6) | 591(3) | 47(3) |
| C(35) | −2500(7) | 3062(7) | 797(4) | 58(4) |
| C(36) | −2772(8) | 4068(8) | 569(4) | 73(4) |
| C(37) | −2381(9) | 4454(8) | 136(4) | 82(5) |
| C(38) | −1769(9) | 3921(8) | −74(4) | 83(5) |
| C(39) | −1495(7) | 2918(7) | 138(4) | 67(4) |
| C(40) | 5545(23) | 1768(23) | 3940(17) | 244(20) |
| Cl(1A) | 5033(7) | 1133(9) | 3264(6) | 237(6) |
| Cl(2A) | 4893(9) | 2540(11) | 4182(5) | 251(7) |
| Cl(1B) | 5062(45) | 694(59) | 3991(36) | 270(23) |
| Cl(2B) | 4712(29) | 1219(38) | 4389(22) | 210(15) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

The other two complexes of this type were prepared by similar procedures in similar yields. The analytical data are as follows. Anal. Calcd for $Cu[Fe(MeL)_3](PPh_3)$, $CuFeC_{42}H_{39}N_9O_3P$: C, 58.11; H, 4.50; N, 14.53: Found: C, 57.92; H, 4.54; N, 14.43. Anal. Calcd for $Cu[Fe(p\text{-}MeC_6H_4L)_3](PPh_3)$, $CuFeC_{60}H_{51}N_9O_3P$: C, 65.73; H, 4.66; N, 11.50. Found: C, 65.78; H, 4.73; N, 11.32.

**b. From $Cu(PPh_3)_2NO_3$.** To a methanolic solution (60 mL) of $NaFe(PhL)_3 \cdot H_2O$ (0.5 g, 0.65 mmol) was added, with stirring, a solution of $Cu(PPh_3)_2NO_3$ (0.43 g, 0.66 mmol) in $CH_2Cl_2$ (30 mL). The original green solution immediately turned brown. The mixture was stirred at room temperature for 2 h. A dark solid that deposited was collected by filtration and washed thoroughly with methanol and dried in vacuo over $P_4O_{10}$; yield 0.6 g (88%).

**Bis[tris((phenylazo)benzaldoximato)ferrato(II)]copper(II), $[Cu(Fe(PhL)_3)_2]$. a. From $[Cu(MeCN)_4]PF_6$.** To a solution of $[Cu(MeCN)_4]PF_6$ (0.11 g, 0.33 mmol) in dichloromethane (50 mL) was added $NaFe(PhL)_3 \cdot H_2O$ (0.5 g, 0.65 mmol) in air with stirring which was continued for 0.5 h. The solution was then filtered through a medium-porosity frit. The solvent was evaporated to dryness in vacuo. The dark solid thus obtained was washed with acetonitrile and dried in vacuo over $P_4O_{10}$; yield 0.42 g (85%). Anal. Calcd for $CuFe_2C_{78}H_{60}N_{18}O_6$: C, 61.61; H, 3.95; N, 16.59. Found: C, 61.85; H, 3.90; N, 16.38.

The other two complexes of this family were prepared by similar procedures in similar yields. The analytical data are as follows. Anal. Calcd for $[Cu(Fe(MeL)_3)_2]$, $CuFe_2C_{48}H_{48}N_{18}O_6$: C, 50.21; H, 4.18; N, 21.97. Found: C, 49.92; H, 4.15; N, 21.89. Anal. Calcd for $[Cu(Fe(p\text{-}MeC_6H_4L)_3)_2]$, $CuFe_2C_{84}H_{72}H_{18}O_6$: C, 62.87; H, 4.49; N, 15.72. Found: C, 62.51; H, 4.44; N, 15.86.

**b. From $Cu(ClO_4)_2 \cdot 6H_2O$.** To a solution of $NaFe(PhL)_3 \cdot H_2O$ (0.5 g, 0.65 mmol) in ethanol (50 mL) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.13 g, 0.35 mmol), and the mixture was stirred for 3 h. The dark solid precipitated was collected by filtration, washed thoroughly with ethanol and water, and finally dried in vacuo over $P_4O_{10}$. Yield: 0.36 g (70%).

**X-ray Structure Determination.** Crystals of $CuFe(MeL)_3(PPh_3)$ (0.46 × 0.38 × 0.40 mm$^3$) were grown by slow diffusion of hexane into a dichloromethane solution followed by slow evaporation. A single crystal of $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$ (0.42 × 0.52 × 0.60 mm$^3$) grown by slow diffusion of hexane into a dichloromethane solution was sealed in a capillary containing the mother liquor. In the absence of mother liquor the crystals deteriorated quickly. For both complexes cell parameters were determined by a least-squares fit of 30 machine-centered reflections ($2\theta$, 15–30°). Data were collected by the $\omega$-scan method in the $2\theta$ range 3–52° for $CuFe(MeL)_3(PPh_3)$ and 3–50° for $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$ on a Nicolet R3m/V diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction during 61.95 h ($CuFe(MeL)_3(PPh_3)$) and 64.75 h ($CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$) of exposure to X-rays. Data were corrected for Lorentz–polarization effects. Systematic absences (or the lack thereof) led to the identification of the space group as $P\bar{1}$ for $CuFe(MeL)_3(PPh_3)$ and $P2_1/c$ for $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$. For $CuFe(MeL)_3(PPh_3)$ 8602 reflections were collected, 8088 were unique and 4631 satisfying $I > 3.0\sigma(I)$ were used for structure solution. In the case of $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$ the corresponding numbers are 7721, 7041, and 3054 respectively.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAXII Computer with the programs of SHELXTL-PLUS.[25] The structure of $CuFe(MeL)_3(PPh_3)$ was solved by direct methods and that of $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$ by the heavy atom method. Both the structures were refined by block-matrix least-squares procedures, making all non-hydrogen atoms anisotropic. Hydrogen atoms were included in calculated positions with fixed *U* (=0.08 Å$^2$). The highest difference Fourier peaks were 0.42 and 0.78 e/Å$^3$ for $CuFe(MeL)_3(PPh_3)$ and $CuFe_2(PhL)_6 \cdot 2CH_2Cl_2$ respectively. Significant crystal data are listed in Table IV. Atomic coordinates with isotropic thermal parameters are collected in Tables V and VI.

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**Supplementary Material Available:** Tables SI–SVIII, listing anisotropic thermal parameters, complete bond distances and angles, and hydrogen atom positional parameters (19 pages). Ordering information is given on any current masthead page.

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