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# Copper Ion Complexes with Derivatized Chelating Pterin Ligands

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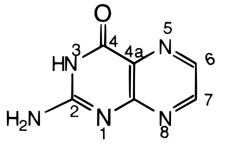
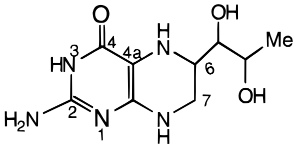
Pterin−copper ion interactions are of interest for possible modeling of enzyme active site chemistry or in coupling reactions of a redox-active metal ion with a redox-active ligand cofactor, Here, we describe the synthesis of derivatized chelating pterins, provided with enhanced organic solubility by introduction of a pivalolyl group at the pterin C2 position and supplied with a good copper ion chelator, through reaction of the 6-(bromomethyl)-pterin with a 2-(2-(methylamino)ethyl)pyridine (to give **L′**) or bis(2-pyrid-2-ylethyl)amine (to give **L**). Copper(I) and copper(II) complexes have been synthesized and characterized. The X-ray structure of [**L′**Cu(Cl)($CH_3CN$)]($PF_6$) (**3**-$PF_6$) is described [space group $P2_1/c$; $a$ = 10.606(3) Å, $b$ = 21.683(3) Å, $c$ = 12.188(3) Å; $\beta$ = 96.67(2)°; $Z$ = 4; $V$ = 2784(1) Å$^3$] and compared with the previously reported structure of [**L**Cu(Cl)]($PF_6$)($NaPF_6$) (**1**-$PF_6$·$NaPF_6$). In **3**-$PF_6$, the Cu(II) is pentacoordinate, including equatorial ligation to the pterin N5 atom, achieving one of the goals of the ligand design. Unlike other pterin−Cu(II) structures, neither **1**-$PF_6$·$NaPF_6$ nor **3**-$PF_6$ binds to the pterin carbonyl oxygen atom (off pterin C4). Other solution spectroscopic data (e.g., IR, UV−vis, EPR) and a magnetic moment of 1.91 $\mu_B$ are provided and are consistent with the solid-state structure observed. Copper(I) complexes [**L**$Cu^I$]($PF_6$) (**5**-$PF_6$) and [**L′**$Cu^I$]($PF_6$)·0.25$CH_2Cl_2$ (**6**-$PF_6$·0.25$CH_2Cl_2$) have been generated and characterized. Observed coordination-induced $^1$H NMR chemical shifts in **6**-$PF_6$·0.25$CH_2Cl_2$) are consistent with binding through the pterin pyrazine N5 donor; a UV−vis feature at 466 nm (sh, $\epsilon$ = 1200) is considered a MLCT transition. A cyclic voltammogram of **6**-$PF_6$·0.25$CH_2Cl_2$ (DMF solvent) reveals a reversible redox process with $E_{1/2}$ = 286 mV ($E_{1/2}$ = 546 mV for ferrocene/ferrocenium; vs Ag/AgCl). [**L′**$Cu^{II}$($CH_3CN$)]($CF_3SO_3$)$_2$ (**4**-($CF_3SO_3$)$_2$) exhibits the identical cyclic voltammogram, indicating common solution structures. The analogue complex [(**MeL**)$Cu^I$($CH_3CN$)]($ClO_4$) (**7**-$ClO_4$) (Me**L** = (2-(2-pyridyl)ethyl)(2-pyridylmethyl)-methylamine) displays a more negative redox potential, $E_{1/2}$ = 24 mV, indicating that the pterin pyrazine ring has an electron-withdrawing effect, which may explain the lack of $O_2$ reactivity of copper(I) complexes of **L** and **L′**.

## Introduction

Pterins (usually C6-substituted) are multinitrogen heterocyclic compounds which serve as cofactors in a variety of enzymes.[1,2] Recent interest in transition metal−pterin coordination chemistry[3−5] has arisen from findings that metal ions are also required constituents and that pterin−metal interactions are observed. With the exception of nitrogenase, all molybdenum enzymes belong to a family known as oxotransferases, which catalyze the transfer of an oxo group to or from a substrate, sharing a commmon component referred to as molybdopterin.[6] Recent protein X-ray structures have authenticated the 1,2-ene dithiolate metal linkage in this cofactor for molybdenum (Mo-co)[6a,7] or tungsten.[8] Tetrahydrobiopterin is also known to be associated with nitric oxide synthases.[9]



pterin



tetrahydrobiopterin

Tetrahydropterin-dependent enzymes, in particular phenylalanine hydroxylase (PAH), also require non-heme iron and dioxygen.[2,10,11] PAH catalyzes the aromatic hydroxylation

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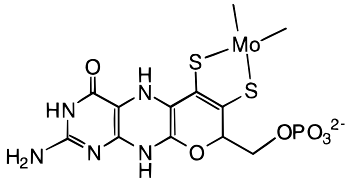

molybdenum cofactor (Mo-co)

reaction forming tyrosine from phenylalanine (Scheme 1). Interests in copper−pterin interactions[4] were spurred in part by the extensive description/characterization of a Cu-dependent phenylalanine hydroxylase from *Chromobacterium violaceum*.[12] These included biochemical and physical studies of the copper(II)-bound form, including direct EPR, electron spin echo,[12c] and EXAFS[12d] spectroscopic studies demonstrating the likelihood of direct Cu(II) binding of the metal through the pterin N5 position. Following arguments made for the mammalian iron enzyme (Scheme 1),[2,10] speculations centered on metal-assisted formation or directed decomposition (and substrate reaction) with an intermediate peroxo- or (hydroperoxo)pterin. However, more recent biochemical reinvestigations have led the same authors to suggest that metal ions might not at all be required for the enzymatic reaction.[13] The role of non-heme iron (and/or possibly copper) ions in this bacterial PAH is still far from clear.[2]

Only limited numbers of studies on synthetic models of potential relevance to the metal site in the pterin-dependent metalloenzymes have been described.[3−5] Our own interests[4d] have not only related to the possible existence of a Cu-PAH but are also directed toward exploring Cu(II)/Cu(I) redox chemistry or $Cu^I/O_2$ reactivity[14] in an environment containing a redox-active cofactor, also capable of proton transfer. Pterins "store" a potential of four electrons/four protons, ranging from the fully reduced tetrahydropterins to the fully oxidized forms.

In our initial study, we synthesized a new kind of pterin-derived ligand (**L**, Chart 1) and its copper complexes.[4d] The ligand was highly soluble in common organic solvents, in contrast to the common behavior of typical pterins. A chelating group was placed in the C6 position to allow for *intra*molecular chemistry of a metal ion and pterin, easing characterization and allowing control of copper ion coordination and redox properties. This positioning was also hoped to generate an interaction of the copper ion with the pterin N5, as has been suggested in the EPR studies of Cu-containing PAH (vide supra). Molecular models indicate the copper ion might also interact with a 4a-OOH or 4a-OH group, if such could be generated. Indeed, the X-ray crystal structure of a Cu(II) complex of **L**, [**L**Cu(Cl)]-($PF_6$)($NaPF_6$) (**1**-$PF_6$·$NaPF_6$) (Chart 2), revealed the pterin moiety is coordinated to the copper ion through the N5 atom.[4d] A copper(I) complex of **L** was synthesized in order to investigate a possible pterin/copper/$O_2$ interaction, but **1**-$PF_6$·$NaPF_6$ was found to be inert toward reaction with dioxygen.[4d]

To obtain a potentially dioxygen-reactive pterin−copper system and to better understand the copper−pterin complex structure, we sought to elaborate the chemistry of the new pterin-derived ligand system. Here, we describe the synthesis and characterization of copper(I) and -(II) complexes of the modified pterin-derived ligand **L′** (Chart 1), including the molecular structure of [**L′**Cu(Cl)($CH_3CN$)]($PF_6$) (**3**-$PF_6$). The rationale for using a bidentate (aminoethyl)pyridine moiety in **L′** at the C6 position was to enhance the potential that an external ligand, e.g., $O_2$, could bind to a resulting coordinately unsaturated copper(I) center. The change in number of potentially coordi-

**Scheme 1**

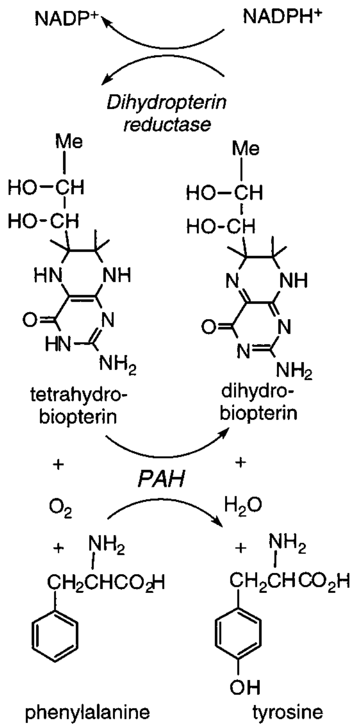

**Chart 1**

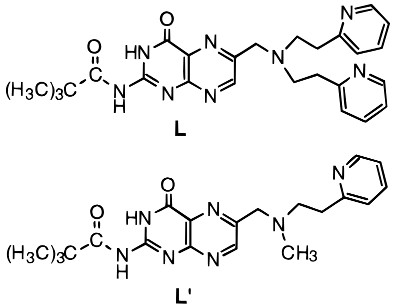

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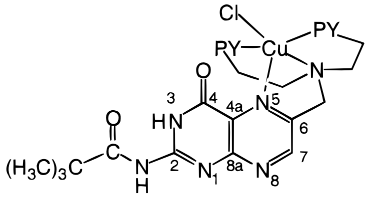
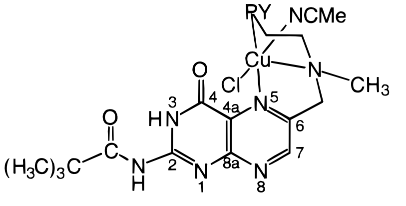
**Chart 2**

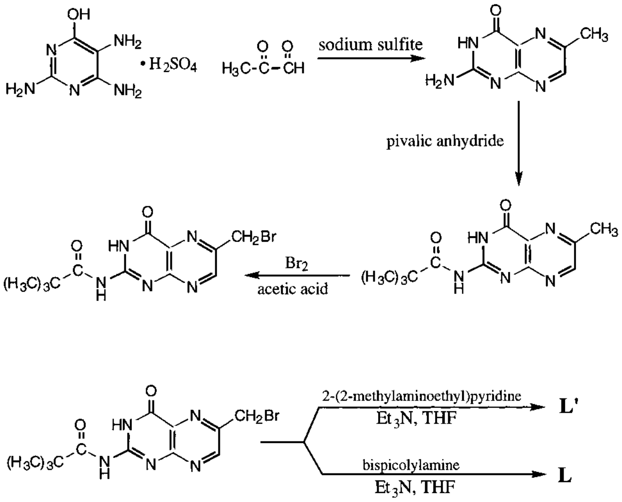


$[\mathbf{L}Cu(Cl)]^+$ (**1**)



$[\mathbf{L'}Cu(Cl)(CH_3CN)]^+$ (**3**)

**Scheme 2**



nating alkylamino or pyridyl donors would also be expected to change the redox properties of the complex relative to the chelate found in **L**.

## Results and Discussion

**Synthesis of Ligands.** Pterin-derived ligands **L** and **L′** were synthesized by the series of organic reactions shown in Scheme 2. The compound 6-methylpterin was prepared according to a literature method,[15] in which 2,5,6-triaminopyrimidin-4(3*H*)-one was reacted with pyruvic aldehyde by an Isay condensation. Pivalic anhydride was used to acylate the 2-amino group of 6-methylpterin;[16] introduction of the *tert*-butyl substituent was carried out in order to increase the solubility of the ligand in organic solvents. The 6-methyl group of the 2-amino-substituted pterin was brominated using bromine in acetic acid, and the chelate groups were then attached.

**Synthesis of Copper(II) Complexes of L and L′.** The copper(II) complexes of **L**, $[\mathbf{L}Cu(Cl)](PF_6)(NaPF_6)$ (**1**-$PF_6$·$NaPF_6$) and $[\mathbf{L}Cu](CF_3SO_3)_2$ (**2**-$(CF_3SO_3)_2$), were synthesized and characterized as described previously,[4d] but the synthetic details are given here (Experimental Section).

The Cu(II) complex $[\mathbf{L'}Cu(Cl)(CH_3CN)](PF_6)$ (**3**-$PF_6$) was synthesized by reacting equivalent amounts of $CuCl_2$·$2H_2O$ and the pterin ligand **L′** in acetonitrile. Excess $NaPF_6$ was added to exchange the $Cl^-$ anion, and then addition of diethyl ether precipitated a green solid, which was purified by recrystallization with acetonitrile/ether. Another Cu(II) complex, $[\mathbf{L'}Cu(CH_3CN)](CF_3SO_3)_2$ (**4**-$(CF_3SO_3)_2$), was prepared by adding 2 equiv of $Cu^{II}(CF_3SO_3)_2$ to an acetonitrile solution of **L′**. Addition of diethyl ether precipitated a green solid, which was purified by recrystallization with acetonitrile/ether. Both compounds were characterized by elemental analysis, conductivity, magnetic moments, and IR and UV−vis spectroscopies.

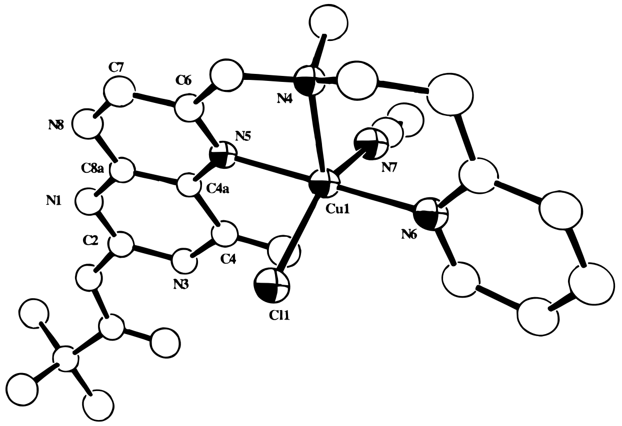


**Figure 1.** ORTEP diagram of $[\mathbf{L'}Cu(Cl)(CH_3CN)](PF_6)$ (**3**-$PF_6$) (20% probability ellipsoids).

**Table 1.** Crystal Data and Details of the Structure Determination for $[\mathbf{L'}Cu(Cl)(CH_3CN)](PF_6)$ (**3**-$PF_6$)

| | |
|---|---|
| formula | $C_{22}H_{28}N_8O_2F_6PClCu$ |
| $T$, K | 296 |
| MW | 681.49 |
| cryst system | monoclinic |
| space group | $P2_1/c$ |
| $a$, Å | 10.606(3) |
| $b$, Å | 21.683(3) |
| $c$, Å | 12.188(3) |
| $\beta$, deg | 96.67(2) |
| $V$, Å$^3$ | 2784(1) |
| $F$(000) | 1392 |
| $Z$ | 4 |
| $\lambda$(Mo Kα), Å | 0.710 69 |
| $D_{calcd}$, g/cm$^3$ | 1.626 |
| abs coeff, cm$^{-1}$ | 10.14 |
| scan type | $\omega-2\theta$ |
| no. of reflns measd | $+h,+k,\pm l$ |
| no. of reflns collcd | 5340 |
| no. of indep reflns | 5054 |
| $R^a$ | 0.045 |
| $R_w{}^b$ | 0.045 |

[a] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**X-ray Structure of $[\mathbf{L'}Cu(Cl)(CH_3CN)](PF_6)$ (3-$PF_6$).** Crystals of $[\mathbf{L'}Cu(Cl)(CH_3CN)](PF_6)$ (**3**-$PF_6$) that were suitable for X-ray structural analysis were obtained by slow diffusion of diethyl ether into a acetonitrile solution of the complex. The molecular structure of (**3**-$PF_6$) is shown as an ORTEP view in Figure 1, with pertinent bond lengths and angles given in Table 2. A summary of crystal parameters and refinement results is given in Table 1.

The structure of the $[(\mathbf{L'})Cu(CH_3CN)(Cl)]^+$ (**3**) cation shows the copper(II) ligated to a nitrogen atom from the pterin ligand (N5), a pyridyl nitrogen (N6), a tertiary amine nitrogen (N4), an acetonitrile nitrogen (N7), and one chloride anion (Cl1). The geometry around a pentacoordinate Cu(II) ion can be analyzed by a method developed by Addison and Reedijk.[17] Here, a

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**Table 2.** Selected Bond Distances (Å) and Angles (deg) for [**L**′Cu(Cl)(CH$_3$CN)](PF$_6$) (**3**-PF$_6$)

| | | | |
|---|---|---|---|
| Intermolecular Distances | | | |
| Cu1−N4 | 2.177(4) | Cu1−N5 | 2.010(4) |
| Cu1−N6 | 1.992(4) | Cu1−Cl | 2.335(2) |
| Cu1−N7 | 2.084 (5) | | |
| Intermolecular Bond Angles | | | |
| N4−Cu1−N6 | 96.7(2) | N6−Cu1−Cl | 90.2(1) |
| N4−Cu1−N7 | 96.6(2) | N7−Cu1−N5 | 94.7(2) |
| N4−Cu1−N5 | 79.8(2) | N7−Cu1−Cl1 | 146.8(1) |
| N4−Cu1−Cl | 116.2(1) | N5−Cu1−Cl1 | 86.7(1) |
| N6−Cu1−N7 | 90.9(2) | Cu1−N7−C21 | 167.5(5) |
| N6−Cu1−N5 | 173.7(2) | | |

structural index parameter, $\tau$, is calculated on the basis of **L**−M−**L**′ basal angles. For a perfect square pyramidal geometry, $\tau$ is equal to zero, while it becomes unity for a perfect trigonal bipyramidal geometry. As applied to compound **3**-PF$_6$, the analysis yields a $\tau$ value of 0.45, indicating that the coordination around the cupric center is intermediate between the two extreme pentacoordinate geometries. As described in terms of being distorted square pyramidal, the equatorial plane consists of the nitrogen atom of pyridine (N6), the N5 atom of pterin, the N7 atom of the acetonitrile, and the chloride anion (Cl1). The axial site is the tertiary amine nitrogen (N4), with a longer Cu−N bond distance (2.177 Å). The copper(II) ion is displaced 0.33 Å out of the basal plane toward N4.

Some other copper−pterin structures have been reported by the Burgmayer, Yamauchi, Karlin, and Nakasuji research groups.[4] With the exception of [**L**Cu(Cl)](PF$_6$)(NaPF$_6$) (**1**-PF$_6$·NaPF$_6$) (Chart 2),[4d] all the pterin−copper complexes display chelation of the metal ions through the carbonyl oxygen atom and a pyrazine nitrogen atom (i.e., N5). However, this O,N5 coordination of the pterin moiety is not observed in [(**L**′)Cu(CH$_3$CN)(Cl)]$^+$ (**3**); instead, there appears to be at best only a weak interaction between the copper ion and the oxygen, with Cu1−O1 = 2.8 Å, outside the sum of their respective covalent radii. The O1,N5 coordination to the Cu ion seen in other compounds results from the deprotonation of N3−H and concomitant formation of a formally anionic oxygen atom of the carbonyl group. The deprotonation of the N3−H hydrogen atom was observed when the complexes were prepared in the presence of base.[4a−c,e,f] The C4−O1 distance of 1.207 Å in **3**-PF$_6$ is shorter than that seen in the anionic pterin−copper complexes having the O,N5-coordination mode (1.226−1.282 Å), consistent with the purely double-bond character of the carbonyl bond and the essentially negligible Cu−O1 interaction. However, lone pair electrons on O1 may point in the direction of the empty axial position of the copper square pyramid with $\angle$C4−O1−Cu1 = 99°.

The copper−N5 distance of 2.010 Å is considerably shorter than that observed in **1**-PF$_6$·NaPF$_6$ (2.328 Å).[4d] This difference is due to the relative orientation of N5 of the pterin plane with respect to the copper plane. In both complexes, the pterin planes are perpendicular to the square plane of copper, but the pterin plane lies within the equatorial plane in [**L**′Cu(Cl)(CH$_3$CN)](PF$_6$) (**3**-PF$_6$) while it occupies an axial position in [**L**Cu(Cl)](PF$_6$)(NaPF$_6$) (**1**-PF$_6$·NaPF$_6$) (Chart 2 and ref 4d). The long axial distance compared to an equatorial bond is typical for a pentacoordinate Cu(II) complex. The axial bonding of the pterin ring in **1**-PF$_6$·NaPF$_6$ may be due to the structural requirements imposed by the more sterically demanding tridentate moiety. For all the other structurally characterized pterin−copper complexes,[4] including **3**-PF$_6$, the pyrazine N5 binds to the copper in an equatorial position and the bond distances are in the range 1.974−2.033 Å, close to the 2.010 Å observed here. The Cu1−Cl1 distance of 2.335(2) Å is comparable with that of [**L**Cu(Cl)](PF$_6$).[4d]

**Other Physical/Spectroscopic Properties of [L′Cu(Cl)(CH$_3$CN)](PF$_6$) (3-PF$_6$).** An IR spectrum of [**L**′Cu(Cl)(CH$_3$CN)](PF$_6$) (**3**-PF$_6$) is similar to that of the free ligand in the spectral region where ligand absorptions are observed. No significant perturbation of the C═O stretching bands occurred in the complexes, further indicating that the pterin ligand is coordinated in its un-deprotonated form. Multiple N−H absorptions observed in the region 3400−3600 cm$^{-1}$ for the copper complexes are due to the presence of different types of N−H bonds in the complexes, N3−H and/or N2−H, indicating that the N3−H bond does not dissociate to give a pterinate anion. Sharp bands of medium intensity located at 1610, 1480, and 1450 cm$^{-1}$ correspond to the C−C, C−N ring vibrations of coordinated pyridne and the pterin moieties.

Electronic absorption spectra of [**L**′Cu(Cl)(CH$_3$CN)](PF$_6$) (**3**-PF$_6$) obtained from CH$_3$CN solution exhibit absorptions with maxima of 717 nm ($\epsilon$ 99) and 1056 nm ($\epsilon$ 71) characteristic of d−d transitions with their typically weak extinction coefficients. Compared with previous data available for pentacoordinate Cu(II) complexes,[18−22] the spectral pattern observed for **3**-PF$_6$ is consistent with a distorted square-based pyramidal structure, suggesting the solid-state structure is maintained in solution. The intense, high-energy band in the ultraviolet region ($\lambda$ = 380 nm, $\epsilon$ = 5450) is associated with the ligand.

An EPR spectrum obtained from a frozen solution of **3**-PF$_6$ in DMF exhibits a typical spectral pattern characteristic of an axial symmetric complex with $g_{\parallel} \sim 2.292 > g_{\perp} \sim 2.057$, and $A_{\parallel} = 155 \times 10^{-4}$ cm$^{-1}$. This result indicates the copper ion is in a $d_{x^2-y^2}$ ground state, in agreement with the solution structure suggested by electronic spectra and the crystal structure. The room-temperature magnetic moment for **3**-PF$_6$ is 1.91 $\mu_B$, which is a typical spin-only value for mononuclear copper(II) complexes. The electrical conductivity of **3**-PF$_6$, measured in acetonitrile, is 150.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, which is characteristic for 1:1 electrolytes[23] and thus consistent with the [**L**′Cu(Cl)(CH$_3$CN)](PF$_6$) formulation. This suggests that the coordinated Cl$^-$ anion is not displaced under the solvent conditions employed.

**Copper(I) Complexes of Ligands L and L′.** A copper(I) complex of ligand **L**, [**L**Cu$^{I}$](PF$_6$) (**5**-PF$_6$), was previously synthesized,[4d] and the synthetic procedure employed is given here (Experimental Section). Reaction of **L**′ with [Cu$^{I}$(CH$_3$CN)$_4$](PF$_6$) in CH$_2$Cl$_2$ under argon, followed by precipitation with ether, gave the dark brown Cu(I) complex [**L**′Cu$^{I}$](PF$_6$)·0.25CH$_2$Cl$_2$ (**6**-PF$_6$·0.25CH$_2$Cl$_2$). The $^1$H NMR spectroscopic resonances of **6**-PF$_6$·0.25CH$_2$Cl$_2$ (CD$_3$CN, room temperature) are sharp and well resolved. The peak positions of protons near the copper binding sites are positively shifted (downfield), especially that of the C7 proton, which suggests that the pterin moiety binds to the Cu(I) ion, probably through the pyrazine ring (N5). **6**-PF$_6$ shows no visible absorption ascribable to d−d transitions, and the absorption observed at 466 nm (sh, $\epsilon$ = 1200) is thus assigned as a copper(I)-to-pterin MLCT transition. This also is consistent with the pterin moiety being coordinated to the copper(I) center, probably through N5.

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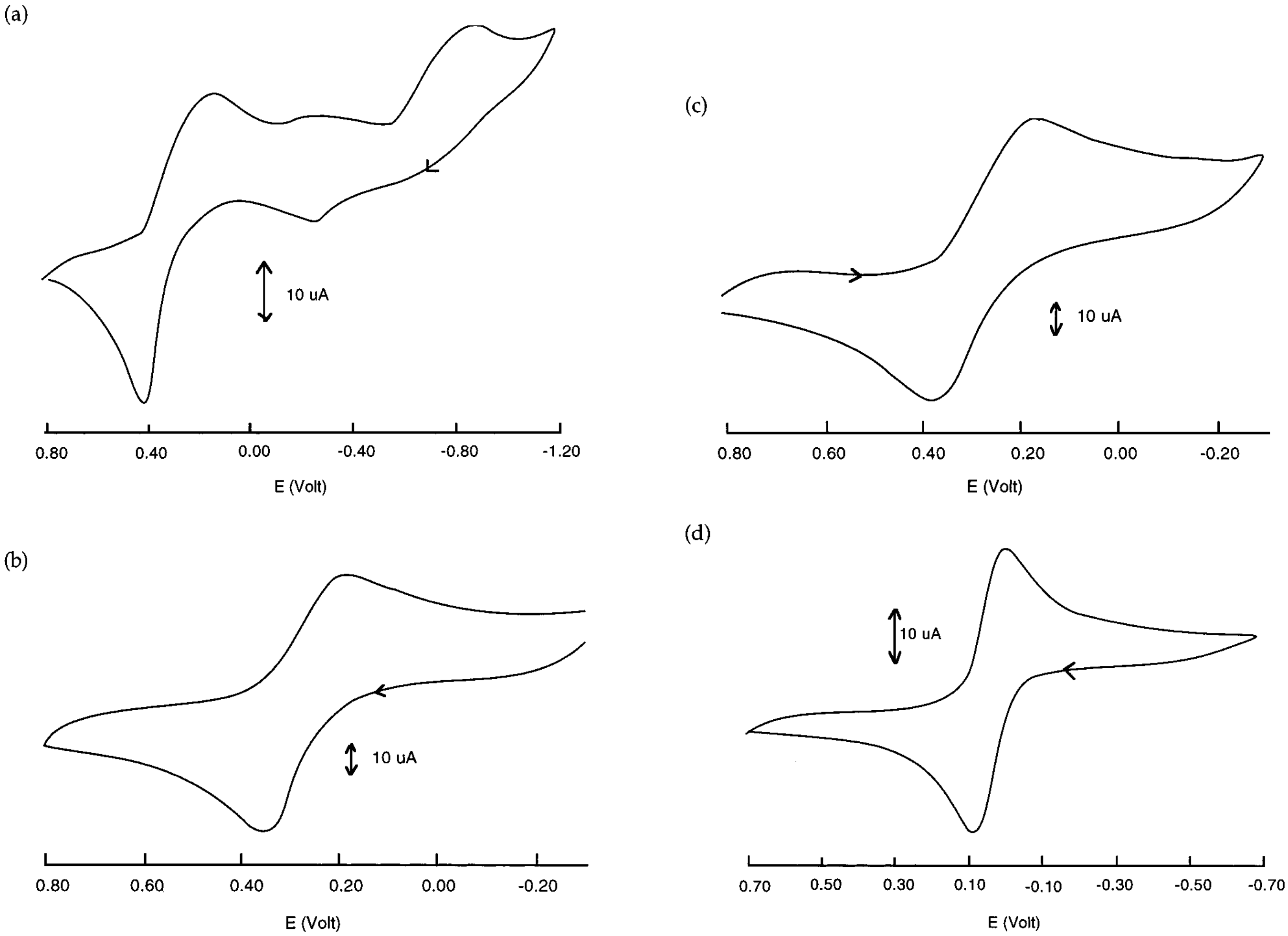
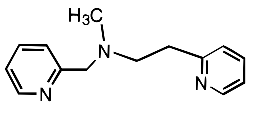


**Figure 2.** Cyclic voltammograms: [**L**′Cu]($PF_6$)•0.25$CH_2Cl_2$ (**6**-$PF_6$•0.25$CH_2Cl_2$); (b) whole range; (c) [**L**′Cu($CH_3CN$)]($CF_3SO_3$)$_2$ (**4**-($CF_3SO_3$)$_2$); (d) [(Me**L**)Cu($CH_3CN$)]($ClO_4$) (**7**-$ClO_4$).

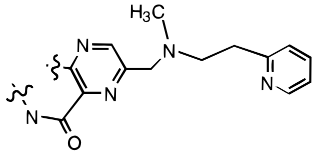
The electrical conductivity of **6**-$PF_6$ measured in acetonitrile is 136.7 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, which is typical for 1:1 electrolytes.[23]

**Electrochemistry.** The electrochemical behavior of [**L**′Cu$^I$]($PF_6$)•0.25$CH_2Cl_2$ (**6**-$PF_6$•0.25$CH_2Cl_2$) and [**L**′Cu$^{II}$($CH_3CN$)]($CF_3SO_3$)$_2$ (**4**-($CF_3SO_3$)$_2$) was measured by cyclic voltammetry (CV) under argon in DMF solution containing 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at a glassy carbon working electrode. Figure 2 depicts a cyclic voltammogram of 1 mM complexes in DMF. A cyclic voltammogram for **6**-$PF_6$•0.25$CH_2Cl_2$ includes a quasi-reversible peak and several other irreversible peaks, in the range −1200 to +800 mV (Figure 2a). The anodic peak at 369 mV (versus Ag/AgCl) and the corresponding cathodic peak at 172 mV are probably associated with a reversible redox process, assumed to be one-electron and metal-based, as revealed by a voltammogram over a limited potential range (Figure 2b). The $E_{1/2}$ value for the quasi-reversible process is 286 mV (with $i_{pa}/i_{pc} = 0.87$ at a scan rate of 100 mV/s. The ferrocene/ferrocenium couple under the same conditions showed $\Delta E_p = 77$ mV and $E_{1/2} = 546$ mV vs Ag/AgCl. The CV of **6**-$PF_6$•0.25$CH_2Cl_2$ exactly matches the CV behavior of [**L**′Cu($CH_3CN$)]($CF_3SO_3$)$_2$ (**4**-($CF_3SO_3$)$_2$) (Figure 2c), suggesting that the two compounds have closely related tetradentate structures in solution, differing from [**L**′Cu(Cl)($CH_3CN$)]($PF_6$) (**3**-$PF_6$) by the additional Cl ligation.

In order to explore the influence of the pterin moiety on the redox properties of the copper complex of the pterin-derived ligand, a coordinatively analogous Cu(I) complex, [(**MeL**)-Cu$^I$($CH_3CN$)]($ClO_4$) (**7**-$ClO_4$), was synthesized (Experimental Section). Here, the pterin moiety is in essence substituted by a pyridine.



**MeL**



**L'**

The $E_{1/2}$ value for [**L**′Cu]($PF_6$)•0.25$CH_2Cl_2$ (**6**-$PF_6$•0.25$CH_2Cl_2$) is considerably more positive than the $E_{1/2} = 24$ mV for Cu(I)/Cu(II) redox processes measured for [(**MeL**)Cu$^I$($CH_3CN$)]($ClO_4$) (**7**-$ClO_4$) (Figure 2d). The higher redox potential for [**L**′Cu]($PF_6$)•0.25$CH_2Cl_2$ (**6**-$PF_6$•0.25$CH_2Cl_2$) may arise from the weak basicity of the heterocyclic complex pterin moiety (p$K_b$ = 11.73)[24] compared to the pyridyl ligand (p$K_b$ = 8.74)[24] in **7**-$ClO_4$. The larger reduction potential value for **6**-$PF_6$•0.25$CH_2Cl_2$ is expected to favor Cu(I) and make the oxidation more difficult. Indeed, it was found **6**-$PF_6$•0.25$CH_2Cl_2$ is very stable to oxidation by dioxygen both as a solid and in solution while [(Me**L**)Cu($CH_3CN$)]($ClO_4$) (**7**-$ClO_4$) rapidly reacts with $O_2$, even at low temperature.[25]

There are also considerable differences in the redox behavior of [**L**′Cu]($PF_6$)•0.25$CH_2Cl_2$ (**6**-$PF_6$•0.25$CH_2Cl_2$) and the analogue Cu(I) complex with **L**, [**L**Cu]($PF_6$) (**5**-$PF_6$). Cyclic

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voltammograms taken in DMF with Ag/AgNO$_3$ as a reference electrode give $E_{1/2} = -253$ mV (vs Ag$^+$/AgNO$_3$) for **6**-PF$_6$·0.25CH$_2$Cl$_2$ and $E_{1/2} = 87$ mV for **5**-PF$_6$. Thus the modification of the ligating group at the C6 position generated a pterin−copper complex with a more negative reduction potential. However, as mentioned above, dioxygen reactivity was still not observed. In order to achieve dioxygen reactivity, further modification of the ligand is required or copper ion complexes of reduced pterins should be examined.

## Summary and Conclusion

A new class of highly soluble pterin-derived ligands and their Cu(I) and Cu(II) complexes have been prepared and characterized. Spectroscopic and structural investigations indicate the pterin ligands interact with the copper ions through N5 of the pterin ring. In contrast to several structurally characterized metal complexes of pterins, these complexes do not exhibit O4−metal binding. The Cu(I) complex [**L′**Cu](PF$_6$)·0.25CH$_2$Cl$_2$ (**6**-PF$_6$·0.25CH$_2$Cl$_2$), displays a relatively positive redox potential and does not react with dioxygen. Coordination by the pterin moiety is seen to shift the redox potential of **6**-PF$_6$·0.25CH$_2$Cl$_2$, when compared to Cu(I) species bound to **MeL**, a tridentate analogue not including a pterin. Further studies will focus on the syntheses and studies of more reactive and possibly biologically relevant transition metal complexes with dihydro- and/or tetrahydropterins.

## Experimental Section

**Materials and Methods.** Reagents and solvents used were of commercially available reagent grade quality unless otherwise stated. Acetonitrile was stirred over CaH$_2$ and then freshly distilled from CaH$_2$ under argon. Anhydrous diethyl ether was distilled from sodium/benzophenone under argon or freshly dried by passing it through a 50 cm long column of activated alumina. All column chromatography procedures for organic compounds were carried out by "flash chromatography" using either silica gel (60−200 mesh) or alumina (80−200 mesh). A 40 × 5 cm column was typically used. Fractions from column chromatography were monitored by using Baker-Flex IB-F (silica or aluminum oxide) TLC plates. Developed plates were analyzed by placing the plate in an iodine chamber or by a UV lamp (366 or 254 nm).

All air-sensitive copper complexes were prepared and handled under an argon atmosphere using standard Schlenk techniques. Solvents and solutions were deoxygenated by either repeated vacuum/purge cycles using argon or bubbling of argon (20−30 min) directly through the solution. Solid samples were stored and transferred, and samples for NMR and IR spectra were prepared in a Vacuum Atmospheres drybox filled with argon.

Elemental analyses were performed by Desert Analytics, Tucson, AZ, and/or National Chemical Consulting Inc., Tenafly, NJ. Electroionization and chemical ionization mass spectra were obtained on a double-focusing vacuum Generator 70-s (VG-70S) gas chromatography/mass spectrometer. Infrared spectra were recorded on neat samples or in Nujol mulls on a Mattson Galaxy 4030 FT-IR spectrometer. $^1$H NMR spectra were obtained in CD$_2$Cl$_2$ or CD$_3$CN or on a Bruker (300 MHz) spectrometer. All spectra were recorded in 5-mm-o.d. NMR tubes. Chemical shifts were reported as $\delta$ values downfield from an internal standard of Me$_4$Si. X-band EPR measurements were taken using a Varian E-4 spectrometer equipped with a liquid-nitrogen Dewer insert. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH; $g = 2.0037$). Frozen DMF solution of copper complexes at ~10$^{-3}$ M in 4-mm-o.d. quartz tubes were studied. Electronic absorption spectra were taken with a Shimadzu UV-160 UV−vis instrument using quartz cuvettes (1 cm). The room-temperature magnetic susceptibility was recorded with a Johnson Mathey magnetometer, which was calibrated by using Hg[Co(SCN)$_4$]. Diamagnetic corrections were calculated from tabulated values of Pascal's constants.[26] Electrical conductivity measurements were carried out in acetonitrile solvent with a Barnstead Model PM-70CB conductivity bridge and a YSI model 3403 conductivity cell.

Cyclic voltammetry was carried out by using a Bioanalytical Systems BAS-100B electrochemistry analyzer connected with an HP-7440A plotter. The cell consisted of a modification of a standard three-chambered design equipped for handling of air-sensitive solutions by utilizing high-vacuum valve (Viton O-ring) seals. A glassy carbon electrode (GCE, BAS MF 2012) was used as the working electrode. Either Ag/AgCl or Ag/AgNO$_3$ was used as a reference electrode. The measurements were performed at room temperature under argon in DMF solvent containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAHP) and 10$^{-3}$−10$^{-4}$ M copper complex. The scan rates of 50−200 mV/s were usually employed, and the ferrocene/ferrocenium (Fe/Fe$^+$) couple was used as calibrant.

**Synthesis of Ligands. 6-Methylpterin.** This compound was synthesized according to a literature preparation.[15]

**2-(*tert*-Butylamido)-6-methylpterin.** This compound was synthesized by a modified procedure of a published method.[16] 6-Methylpterin (10 g, 0.056 mol) was refluxed with stirring in pivalic anhydride (60 mL, 0.30 mol) along with 4-(dimethylamino)pyridine (1 g) as a catalyst for 4−5 h. The mixture was cooled to room temperature, and after addition of 200 mL of ether, it was kept in an ice bath for 2 h. The reaction mixture was filtered, and the solid was washed with ether to give ~10 g of an off-white powder. The crude product was chromatographed on silica gel with CH$_2$Cl$_2$/CH$_3$OH (98:2, $R_f$ 0.5) to give 6 g of a white, pure solid compound (50% yield). $^1$H NMR (DMSO): $\delta$ 1.27 (s, 9H), 2.7 (s, 3 H), 8.75 (s, l H). Mass spectrum (*m/z*): 262 (M + H)$^+$.

**2-(*tert*-Butylamido)-6-(bromomethyl)pterin.** A mixture of 2-(*tert*-butylamido)-6-methylpterin (7.52 g, 29 mmol) and Br$_2$ (5.30 g, 33 mmol) was refluxed in 250 mL of acetic acid with 40 mg of benzoyl peroxide until the color of the reaction mixture turned dark green. The mixture was cooled in an ice bath, and after complete removal of solvent by rotary evaporation, the thick slurry was dissolved in CH$_2$Cl$_2$ (200 mL), and the solution was washed thoroughly with cold water (200 mL). The organic layer was collected, concentrated, and then purified by column chromatography on silica gel with CH$_2$Cl$_2$/methanol (99:l, $R_f$ 0.6) to yield 3.6 g of pure yellow solid (37% yield). $^1$H NMR (CDCl$_3$): $\delta$ 1.3 (9H), 4.7 (s, 2H), 8.9 (s, lH). IR (Nujol, cm$^{-1}$): 1560, 1600, 1680. Mass spectrum (*m/z*): 340 (M).

**L.** To a solution of 2-(*tert*-butylamido)-6-(bromomethyl)pterin (2.30 g, 6.76 mmol) in 150 mL of THF was added bis(pyridylethyl)amine[27,28] (1.53 g, 6.76 mmol). After 0.5 h of stirring at room temperature, triethylamine (0.80 g, 8.00 mmol) was added slowly to the solution. The resulting solution was stirred at room temperature for 4 days, after which it was filtered and the filtrate was rotary-evaporated to give a crude solid, which was chromatographed on silica gel using CH$_2$Cl$_2$/CH$_3$OH (95:5, $R_f$, 0.4). A 1.31 g quantity of pure compound was obtained as a light brown solid (39% yield). $^1$H NMR (CDCl$_3$): $\delta$ 1.34 (s, 9 H), 2.9−3.1 (two triplets, 8 H), 4.05 (s, 2 H), 7.05 (d, 2 H), 7.10 (m, 2 H), 7.55 (m, 2 H), 8.43 (s, 1 H), 8.47 (d, 2 H). Mass spectrum (*m/z*): 487 (M + 1)$^+$.

**L′.** This compound was synthesized in a manner identical to that for **L** by reacting 2-(*tert*-butylamido)-6-(bromomethyl)pterin (2.88 g, 8.47 mmol) and 2-(2-(methylamino)ethyl)pyridine (1.24 g, 9.10 mmol) in 100 mL of THF with triethylamine (1.00 g, 10 mmol). Column chromatography of the crude reaction product on silica gel using CH$_2$Cl$_2$/CH$_3$OH (95:5, $R_f$ 0.5) yielded 1.31 g of pure compound (40% yield). $^1$H NMR (CDCl$_3$): $\delta$ 1.32 (s, 9H), 2.43 (s, 3H), 2.91−3.13 (two triplet, 4H), 4.03 (s, 2H), 7.10−7.73 (m, 3H), 8.52 (d, 1 H), 8.80 (s, 1H). IR (Nujol, cm$^{-1}$): 1570, 1622, 1676, 3400. Mass spectrum (*m/z*): 396 (M + 1)$^+$.

**MeL.** This compound was synthesized according to a literature preparation.[29]

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**Synthesis of the Copper Complexes. [LCu(Cl)]($PF_6$)($NaPF_6$) (1-$PF_6\cdot NaPF_6$).** $CuCl_2\cdot 2H_2O$ (0.175 g, 1.02 mmol) and ligand **L** (0.5 g, 1.02 mmol) were dissolved in 75 mL of $CH_3CN$, and the mixture was allowed to stir for 30 min. To the resulting green solution was slowly added 25 mL of a $CH_3CN$ solution of $NaPF_6$ (0.51 g, 3.06 mmol). After being stirred overnight, the cloudy solution was filtered through a medium-porosity frit. Addition of excess diethyl ether (200 mL) to the clear green filtrate gave a green powder. The resulting solid was recrystallized from $CH_3CN/Et_2O$ to yield 0.63 g (67%) of green crystalline material. X-ray-quality crystals were obtained by dissolving a portion of this powder in a mixture of $CH_3CN/CH_2Cl_2$ (8:2 ratio) and layering with ether at room temperature. Anal. Calcd for $C_{26}H_{29}ClCuF_{12}N_8NaO_2P_2$: C, 34.78; H, 3.23; N, 12.48. Found: C, 34.32; H, 3.57; N, 12.39.

**[LCu]($CF_3SO_3$)$_2$ (2-($CF_3SO_3$)$_2$).** The ligand **L** (0.3 g, 0.61 mmol) and $Cu^{II}(CF_3SO_3)$ (0.223 g, 0.61 mmol) were dissolved in 30 mL of $CH_3CN$, and the mixture was allowed to stir for 30 min, whereupon a green solution developed. Addition of excess diethyl ether (100 mL) gave a dark green oil. The clear liquid was decanted, and the greenish oil was dried under vacuum, dissolved again in 20 mL of $CH_3CN$, and slowly precipitated with diethyl ether. After filtration, the solid was dried to give 0.21 g (40%) of a green powder. Anal. Calcd for $C_{28}H_{30}CuF_6N_8O_8S_2$: C, 39.63, H, 3.4,; N, 13.21. Found: C, 39.41; H, 3.87; N, 12.99.

**[L′Cu(Cl)($CH_3CN$)]($PF_6$) (3-$PF_6$).** **L′** (0.54 g, 1.22 mmol) and $Cu^{II}Cl_2\cdot 2H_2O$ (0.21 g, 1.22 mmol) were mixed in 75 mL of $CH_3CN$ at room temperature, giving a green solution. After 0.5 h of stirring, $NaPF_6$ (0.61 g, 3.66 mmol) in 20 mL of $CH_3CN$ was added. After being stirred overnight, the cloudy solution was filtered through a medium-porosity frit, and addition of 60 mL of $Et_2O$ precipitated a green solid. The solid was recrystallized from $CH_3CN/Et_2O$ and dried under vacuum to yield 0.58 g of a green crystalline compound (70%). Anal. Calcd for $C_{22}H_{28}ClCuF_6N_8O_2P$: C, 38.83; H, 4.15; N, 16.47. Found: C, 39.19; H, 4.10; N, 16.30. UV−vis ($CH_3CN$; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}\,cm^{-1}$)): 380 (5450), 458 (358), 717 (99), 1056 (80). IR (Nujol, $cm^{-1}$): 3580, 3450 (br), 1668, 1610, 1480, 1450, 845 ($PF_6$). Molar conductivity ($CH_3CN$): 150.5 $\Omega^{-1}\,cm^2\,mol^{-1}$. Magnetic moment (solid state, room temperature): $\mu_{eff} = 1.91\ \mu_B$. EPR (DMF, 77 K): $g_{\parallel} = 2.292$, $A_{\parallel} = 155 \times 10^{-4}\ cm^{-1}$, $g_{\perp} = 2.057$.

**[L′Cu($CH_3CN$)]($CF_3SO_3$)$_2$ (4-($CF_3SO_3$)$_2$).** $Cu(CF_3SO_3)_2$ (0.25 g, 0.69 mmol) and **L′** (0.27 g, 0.69 mmol) were dissolved in 30 mL of $CH_3CN$, and the mixture was stirred at room temperature for 1 h. To the green solution was added diethyl ether until the solution became cloudy (ca. 20 mL). The solution was then filtered through a medium-porosity frit, and addition of another 50 mL of diethyl ether gave a green precipitate, which was washed with 50 mL of ether and dried in vacuo to yield 0.33 g (60%) of green powder. Anal. Calcd for $C_{24}H_{28}CuF_6N_8O_8S_2$: C, 36.13; H, 3.54; N, 14.05. Found: C, 36.45; H, 3.77; N, 14.08. UV−vis ($CH_3CN$; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}\,cm^{-1}$)): 365 (6350), 669 (219). IR (Nujol, $cm^{-1}$): 3600, 3400 (br), 1660, 1613, 1564, 1480, 1450, 1244 ($CF_3SO_3$). Solid-state magnetic moment (room temperature): $\mu_{eff} = 1.93\ \mu_B$/Cu. Molar conductivity ($CH_3CN$): 255 $\Omega^{-1}\,cm^2\,mol^{-1}$. EPR (DMF, 77 K): $g_{\parallel} = 2.213$, $A_{\parallel} = 176 \times 10^{-4}\ cm^{-1}$, $g_{\perp} = 2.044$.

**[LCu]($PF_6$) (5-$PF_6$).** **L** (0.43 g, 0.88 mmol) in 20 mL of $CH_2Cl_2$ was added dropwise, with stirring, to solid $[Cu^I(CH_3CN)_4](PF_6)$ (0.32 g, 0.88 mmol) under Ar. The resulting dark brown solution was then allowed to stir for 20 min. Dry diethyl ether (ca. 20 mL) was added to the solution until a slight cloudiness was observed; the solution mixture was then filtered through a medium-porosity frit. An additional portion of diethyl ether (100 mL) was added to completely precipitate the brown solid. The supernate was decanted, and the solid was washed with ether. Drying the brown solid under vacuum yielded 0.27 g (44%). Anal. Calcd for $C_{26}H_{29}CuF_6N_8O_2P$: C, 44.97; H, 4.48; N, 16.09. Found: C, 44.98; H, 4.18; N, 16.14.

**[L′Cu]($PF_6$)·0.25$CH_2Cl_2$ (6-$PF_6$·0.25$CH_2Cl_2$).** **L′** (0.68 g, 1.72 mmol) and $[Cu^I(CH_3CN)_4](PF_6)$ (0.61 g, 1.64 mmol) were placed in a 100-mL Schlenk flask under argon, and 20 mL of oxygen-free $CH_2Cl_2$ was added dropwise with stirring. The resulting dark brown solution was stirred for 20 min, at which time sufficient dry diethyl ether was added to cause a slight cloudiness (ca. 35 mL). The solution was filtered through a medium-porosity frit and the complex precipitated by further addition of ether (90 mL). The supernate was removed and the solid washed with 50 mL additional ether. Drying in vacuo yielded 0.72 g (79% yield) of a dark brown solid. Anal. Calcd for $C_{20}H_{25}CuF_6N_7O_2P\cdot 0.25CH_2Cl_2$: C, 38.86; H, 3.99; N, 15.67. Found: C, 39.21; H, 3.84; N, 15.42. $^1H$ NMR ($CD_3CN$): $\delta$ 1.37 (s, 9H), 2.79 (s, 3H), 2.85−3.02 (m, 4H), 4.01 (s, 2H), 5.25 (s, 0.5 H), 7.31 (m, 2H), 7.81 (m, 1H), 8.90 (m, 2H). UV−vis ($CH_3CN$ (Ar); $\lambda_{max}$, nm ($\epsilon$, $M^{-1}cm^{-1}$)): 324 (9350), 466 (sh, 1200). IR (Nujol, $cm^{-1}$): 3200 (br, NH), 1686, 1618, 1568, 845 ($PF_6$). Molar conductivity ($CH_3CN$): 136.7 $\Omega^{-1}\,cm^2\,mol^{-1}$.

**[(MeL)Cu($CH_3CN$)]($ClO_4$) (7-($ClO_4$)).** The ligand **MeL** (1.30 g, 5.72 mmol), dissolved in 20 mL of $CH_3CN$, was added dropwise to 1.83 g (5.60 mmol) of $[Cu(CH_3CN)_4]ClO_4$ with stirring under argon for 20 min. To the resulting yellow solution was added dried air-free diethyl ether until the solution became slightly cloudy. The solution was then filtered through a medium-porosity frit, the clear solution was layered with more ether (total 200 mL), and the flask was placed in an ice bath. Over a period of 1−2 h, a yellow crystalline material was formed. The supernate was then decanted, and the crystalline material was washed with ether (30 mL) three times. The solid was dried in vacuo to yield 1.90 g (77%) of a bright yellow crystalline powder. Anal. Calcd for $C_{16}H_{20}N_4O_4ClCu$: C, 44.55; H, 4.67; N, 12.99. Found: C, 44.72; H, 4.63; N, 12.51. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.11 (s, 3H, $CH_3CN$), 2.50 (s, 3H), 2.90−3.00 (m, 4H), 3.86 (s, 2H), 7.34 (m, 4H), 7.80 (m, 2H), 8.69 (s, 2H).

**X-ray Crystallography, Crystallization, and Data Collection and Reduction.** X-ray-quality crystals of green, square crystals of [**L′**Cu(Cl)($CH_3CN$)]($PF_6$) (**3**-$PF_6$) were grown by adding diethyl ether over an acetonitrile solution of the copper complex and allowing the solution to stand several days at room temperature. A crystal having approximate dimensions of 0.100 × 0.300 × 0.300 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with a graphite-monochromated Mo X-ray source ($\lambda$(Mo K$\alpha$) = 0.710 69 Å) and a 12-kW rotating-anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $13.49 < 2\theta < 16.40°$, corresponded to a monoclinic cell with dimensions shown in Table 2. All data were collected at 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum $2\theta$ value of 50.0°. Of the 5340 reflections that were collected, 5054 were unique ($R_{int} = 0.076$). The linear absorption coefficient for Mo K$\alpha$ radiation is 10.1 $cm^{-1}$. Azimuthal scans of several reflections indicated no need for an absorption correction. Crystal data, data collection methods, and refinement procedures are provided in Table 1. All ORTEP diagrams were created by using the Johnson programs.

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**Supporting Information Available:** A figure showing the $^1H$ NMR spectra of **L′** in $CDCl_3$ and of **6**-$PF_6\cdot 0.25CH_2Cl_2$ in $CD_3CN$, an ORTEP diagram giving complete atomic labeling for **3**-$PF_6$, and tables listing X-ray experimental details, atomic coordinates, bond lengths, and bond angles for **3**-$PF_6$ (9 pages). Ordering information is given on any current masthead page.

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