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Meridional vs. Facial Coordination Geometries of a Dipodal Ligand Framework Featuring a Secondary Coordination Sphere

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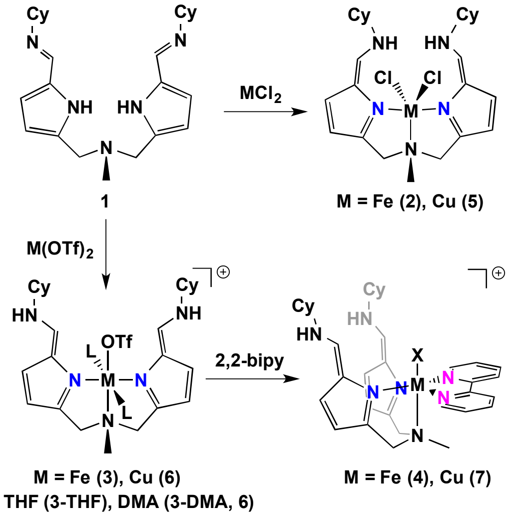
The synthesis of a novel dipodal ligand framework, $H_2[^{Me}N(pi^{Cy})_2]$, is summarized. Upon metalation with MCl_2 salts (M = Fe, Cu), the ligand undergoes a conformational change, resulting in the formation of a trigonal bipyramidal metal center with a pseudoplanar, meridionally-bound ligand framework. This tautomerization positions pendant amines in the metal's secondary coordination sphere. Metalation with $M(OTf)_2$ in coordinating solvent yields octahedral metal complexes, where two solvent molecules bind in the apical positions with one outer sphere counter ion. Reactivity of these complexes, $(^{Me}N(afa^{Cy})_2)M(X)_2$ (X = Cl, OTf), with 2,2'-bypyridine results in ligand reorganization, yielding a facial coordination geometry of the dipodal framework. The described complexes have been characterized by ^1H NMR, EPR, IR, Mössbauer and electronic absorption spectroscopies as well as X-ray crystallography.

Hydrogen bond donating and accepting ligands and redox active amino acids play an important role in reactivity mediated by metalloenzymes.[1] These well-positioned hydrogen bonds or amino acids (e.g. tyrosine, tryptophan, and histidine) ease the electronic burden placed on the metal centre during the activation of small molecules.[1-2] Taking a cue from Nature, we and others have designed ligand scaffolds that feature a secondary coordination sphere capable of tautomerizing to be either hydrogen bond donating or accepting depending on the metal-bound ancillary ligand or desired oxidation state of the metal centre.[3] An additional redox-active ligand may also be incorporated onto the metal centre to facilitate with substrate (i.e. O_2, H_2, N_2) activation while the secondary coordination sphere can stabilize the resulting reactive intermediates. Recently there have been several reports targeting C_3-symmetric ligands on iron centres with additional redox active *o*-phenylene moieties.[4] These complexes were targeted toward understanding multiple proton and electron transfer reactions including water oxidation, hydrogen production and nitrogen fixation.[2] Our studies have focused on iron and copper complexes featuring a dipodal platform with a hydrogen bond donating or accepting secondary coordination sphere and the installation of a redox active moiety, bipyridine (bipy). Herein, we report a structurally diverse family of metal complexes with the dipodal ligand, $H_2[^{Me}N(pi^{Cy})_2]$, demonstrating the flexibility of this framework driven by its interactions with ancillary ligands.

In an effort to synthesize sterically unencumbered dipodal ligand derivatives of the tripodal system recently reported by our group,[3] a platform with a single arm removed was designed based on the pyrrole-derived *N*,*N*-di(pyrrolyl-α-methyl)-*N*-methylamine (H_2dpma) reported previously by Odom and coworkers.[5] Installation of an aldehyde substituent in the 5 position of the pyrrole rings of H_2dmpa was accomplished by a Vilsmeier Haack Formylation.[6] Following workup, addition of an excess of cyclohexylamine in acetonitrile afforded the desired ligand, *N*,*N*-di(5-cyclohexylimmino-pyrrolyl-α-methyl)-*N*-methylamine, $H_2[^{Me}N(pi^{Cy})_2]$ (**1**).

Primarily interested in understanding the affects of the secondary coordination sphere provided by the pendant functional groups of the ligand framework, two pathways were pursued for metalation. The anionic coordination mode of the ligand was found to be undesirable, as attempts to synthesize mononuclear species by the addition of ligand in the presence of a variety of Lewis bases resulted in formation of a dimeric helicate species exclusively.[7] In analogy to the work of Love and co-workers, generation of the azafulvene derivative, $H_2[^{Me}N(afa^{Cy})_2]$, was attempted by addition of $H_2[^{Me}N(pi^{Cy})_2]$ to a THF slurry of $FeCl_2$, resulting in a gradual colour change from tan to orange.[8] Following workup, analysis by ^1H NMR spectroscopy revealed the formation of a new paramagnetic product with 16 resonances ranging from -5.8 to 154.2 ppm and a spectrum which is consistent with C_s symmetry about the metal centre in solution. The electronic absorption spectrum of **2** was relatively featureless, save for a strong band at 333 nm (ε = 63100 $M^{-1}s^{-1}$) assigned to the π-π* of the azafulvene ligand.

Scheme 1. Synthesis of complexes **2-7.**



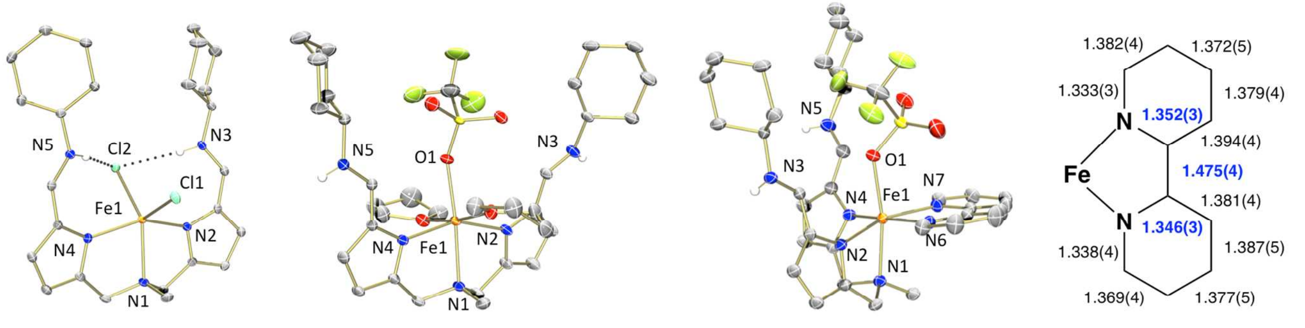
Characterization of the product by X-ray crystallography revealed a five-coordinate iron centre in a distorted trigonal bipyramidal geometry, with the desired di(amino-azafulvene) ligand framework, (^{Me}N(afa^{Cy})$_2$)FeCl$_2$ (**2**) (Fig. 1). The dipodal ligand is coordinated to the metal in an intriguing pseudo-planar fashion. This ligand coordination mode is exemplified by the N2–Fe1–N4 bond angle of 150.60(10)°, which deviates significantly from the N–Fe–N bond angles in the tripodal derivative (~115°). The pendant amines of complex **2** extend outward from the primary coordination sphere of the metal centre, engaging in hydrogen bonding with the coordinated chlorides. Characterization of **2** by Mössbauer spectroscopy reveals a high spin Fe(II) centre with a symmetric ligand field environment (δ = 1.05 mm/s; ΔE_Q = 3.14 mm/s) (Fig 2a),[9] consistent with the measured μ_{eff} of 5.47(4) μB. The measured magnetic moment compares favourably with calculated values for high spin, Fe(II), g=2 ion (μ_{calc}=4.90 μB), and similar species reported by Love and co-workers.[8]

To synthesize a variant of complex **2** with non-coordinating anions, the ligand was added to a THF solution of Fe(OTf)$_2$(MeCN)$_2$. An immediate colour change from tan to yellow was observed. Crystallization of the product via vapour diffusion of diethyl ether into a solution of acetonitrile and THF (1:3) revealed an an octahedral iron species, (^{Me}N(afa^{Cy})$_2$)Fe(OTf)$_2$(THF)$_2$ (**3**) where the ligand framework and one triflate anion occupy the equatorial plane with two THF molecules are coordinated in the axial position (Fig. 1). In contrast to complex **2**, the pendant amines point away from the secondary coordination sphere of the complex, engaging in hydrogen bonding with the outer sphere triflate anion. Similar structural properties were observed when single crystals were grown from a mixture of benzene and dimethylacetamide (DMA) (10:1), where the solvated THF molecules were replaced by DMA (Fig S7, **3-DMA**). The molecular structure of **3-DMA** definitively depicts a distorted octahedral species, but the poor quality of the X-ray data prevents the discussion of any specific metrical parameters.

Characterization of complex **3,** crystallized from a THF/ acetonitrile mixture, by Mössbauer spectroscopy revealed two species. The first is electronically similar to complex **2** (δ = 1.1 mm/s; ΔE_Q = 3 mm/s), suggesting a desolvated structure, and the second resembling an octahedral ligand environment for a high spin Fe(II) species with a nearly identical isomer shift, but dramatically decreased quadrupole splitting (δ = 1.09 mm/s; ΔE_Q = 1.02 mm/s) (Fig 2b). The Mössbauer spectrum of **3-DMA** (δ = 1.14 mm/s; ΔE_Q = 1.49 mm/s) is consistent with the stringent octahedral ligand environment due to the coordination of the DMA solvent compared to the fluxionality of the solvent molecules in complex **3** (Fig. S8)

Attempts to reduce complexes **2** and **3** (or **3-DMA**), resulted in decomposition of the metal species evident by the observance of free ligand in the ^{1}H NMR spectrum. In an effort to elaborate on the electrochemical character of complexes **2** and **3,** and to prevent dimerization upon oxidation, the addition of a redox activity moiety was targeted. An equivalent of 2,2'-bipyridine was added as a solid to a solution of **3** and an immediate color change from yellow to magenta was noted, however, ^{1}H NMR spectroscopy depicted a similar spectrum to that of **3** with free bipyridine. Given the immediate and intense colour change the complex was characterized by X-ray crystallography, which revealed a new, facial coordination geometry of the ligand to the iron centre, resulting in the formation of (^{Me}N(afa^{Cy})$_2$)Fe(bipy)(OTf)$_2$ (**4**) (Fig. 1). Ligand reorganization yields a pseudo-octahedral iron centre, with two azafulvene nitrogens and the nitrogen atoms of the bipyridine forming the equatorial plane; the apical nitrogen of the ligand framework and a triflate occupy the axial positions.

The striking colour change and intensity prompted investigation into the oxidation state of the redox-noninnocent 2,2'-bipyridine ligand in complex **4**. Analysis of the structural data collected at 170 K revealed no bond perturbations that would be consistent with reduction of the bipy ligand. However, the electronic absorption spectrum of **4** has two bands located at 331 nm (ε = 36000 M^{-1}cm^{-1}) and 518 nm (ε = 2300 M^{-1}cm^{-1}) comparing favourably with complexes featuring monoreduced bipyridine ligands (Fig 2b).[10] The solution magnetic moment of 4.11(15) μ_B is consistent with a dynamic electronic state in solution at room temperature, best described as an equilibrium between a neutrally bound bipyridine



[^{Me}N(afa^{Cy})$_2$]FeCl$_2$ (2) [^{Me}N(afa^{Cy})$_2$]Fe(OTf)$_2$(thf)$_2$ (3-THF) [^{Me}N(afa^{Cy})$_2$]Fe(bipy)(OTf)$_2$ (4)

Figure 1. Molecular structures of complexes **2**-**4** shown with 50% probability ellipsoids. Select hydrogen atoms, counter ions and solvent molecules have been removed for clarity. (Right) chart contains structural parameters of bipyridine ligand of complex **4** illustrating bond distances consistent with neutral coordination of the ligand.

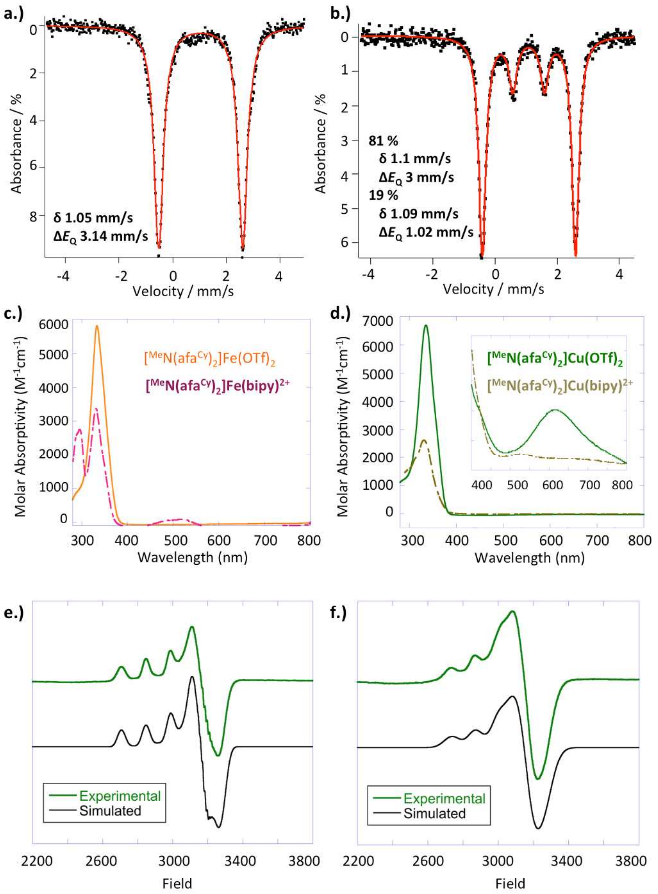


Figure 2. a.) Mössbauer spectrum of **2**. b.) Mössbauer spectrum of **3-THF.** c.) Electronic absorption spectrum of **3** (orange) and **4** (pink) collected in acetonitrile at room temperature. d.) Electronic absorption spectrum of **6** (green) and **7** (brown) collected in acetonitrile at room temperature. Inset shows visible region of spectrum. e.) EPR Spectrum of **6-DMA**. f.) EPR Spectrum of **6**.

ligand and an antiferromagnetically coupled ligand radical. Future investigations will evaluate the solid state, variable temperature magnetic properties of **4** to better develop an understanding of the role of structural reorganization in properties of these complexes. The hypothesis of equilibrium between the Fe^{2+} and Fe^{3+} species has been supported by a complicated Mössbauer spectrum, that depicts the presence of both an Fe(II) high spin species (δ = 0.98 mm/s, ΔE_Q = 2.54 mm/s) and an Fe(III) complex (δ = 0.34 mm/s, ΔE_Q = 0.29 mm/s) (Figure S14).[9]

The cyclic voltammograms for complexes **2**-**4** were recorded in acetonitrile (Fig. S10, **2**; Fig. S11 **3**; Fig. S12, **4**). The spectrum of complex **2** shows a reversible, one electron oxidation to form a stable, trivalent iron species at 0.01 V (vs. $FeCp_2/FeCp_2^+$) (Fig S10), proposed as the oxidation to $[(^{Me}N(afa^{Cy})_2)FeCl_2]^+$. In contrast the triflate derivative shows no reversible processes. The only noticeable electrochemical event for complex **3** occurs in a positive sweep at E = 0.04 V, described as an irreversible oxidation to Fe(III) (Fig S11-S12). However, upon coordination of 2,2'-bipyridine to **3**, the CV becomes more complicated, with reversible, one electron events located at $E_{1/2}$ = -0.16 V and $E_{1/2}$ = 0.55 V, corresponding to the Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV} redox couples, respectively (Fig. S13-S14). The Fe^{II}/Fe^{III} oxidation has been shifted approximately -0.3 V from that of complex **3**, illustrating the effect of the structural rearrangement upon addition of a redox active ligand.

To investigate the electronic properties, the structurally analogous Cu(II) species, were prepared and characterized by EPR spectroscopy. To verify the formation of the analogous compounds, to that of **2-4**, structural parameters for $(^{Me}N(afa^{Cy})_2)CuX_2$ [X = Cl (**5**), OTf (**6**)] and $(^{Me}N(afa^{Cy})_2)Cu(bipy)(OTf)_2$ (**7**) were determined by X-ray crystallography (Figure S9, Table S1). Unlike in the formation of complex **3**, crystallization of complex **6** from a concentrated acetonitrile solution results in the isolation of the trigonal bipyramidal copper, with coordination geoemtries analogous to **2**. Unit cell metrics from a single crystal of **6** grown in the presence of DMA **(6-DMA)** are isomorphous to **3-DMA**.

Complexes **6** and **7** were characterized by electronic absorption spectroscopy (Fig. 2d). Both complexes bear features in the UV region of the spectrum, located at 336 and 331 nm, respectively, assigned to the π-π* transitions of the azafulvene ligand framework.[3] Complex **6** bears a colour-producing band at 616 nm. In contrast to its iron congener, the bipyridine adduct, complex **7**, does not possess any defined transitions in the visible region of the spectrum, indicating neutral coordination of the ligand. This observation is supported by the magnetic moment for complex **7**, 1.79(4) μ_B, which compares favourably to that of **6** (1.78(22) μ_B).

X-band EPR spectra of solutions of **6** and **6-DMA** in MeCN/toluene or DMA/toluene at 120 K were collected to confirm coordination structure of the complexes in solution. As depicted in Figure 2, these complexes exhibit rhombically distorted axial signals, with weak N-superhyperfine coupling observed in **6-DMA**. Parameters from spectral simulations are listed in Table S2 and compare favourable to other copper(II) complexes in both trigonal bipyramidal and octahedral geometries.[4c, 11] The complicated EPR spectrum for **7** is indicative of two unique species in solution, consistent with the decomposition of the bipyridine adduct in strongly coordinating solvents such as DMA.

Conclusions

A family of M(II) complexes (M = Fe, Cu) of the dipodal, azafulvene-amine ligand framework has been synthesized via dative tautomerization of the newly synthesized $H_2[^{Me}N(pi^{Cy})_2]$ ligand. Structural characterization of $(^{Me}N(afa^{Cy})_2)MX_2$ (M = Fe, Cu; X = Cl, OTf) has revealed a trigonal bipyramidal geometry of the metal centre, with a pseudo planar arrangement of the ligand framework. In the case of the triflate species, upon addition of strongly coordinating solvents, the metal centre adopts an octahedral configuration, $(^{Me}N(afa^{Cy})_2)M(OTf)(L)_2(OTf)$ (M = Fe, Cu; L = DMA or THF), where two solvent molecules displace a triflate anion. The structural diversity of the metal species is evident in the Mössbauer spectra in the case of complexes **2-3** and EPR for **6**. Upon addition of an equivalent of 2,2'-bipyridine, the generation of a family of complexes with an additional coordination mode of the ligand has been observed. Future work will probe the complicated electronic structure of $[(^{Me}N(afa^{Cy})_2Fe(bipy)(OTf)](OTf)$ and subsequent reactivity.

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Notes and references

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