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Unusual Electronic Features and Reactivity of the Dipyridylazaallyl Ligand: Characterizations of $(smif)_2M$ [M = Fe, Co, Co^+, Ni; smif = $\{(2\text{-py})CH\}_2N$] and $[(TMS)_2NFe]_2(smif)_2$

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Nitrogen donor ligands have played a historical and prominent role in coordination chemistry from its beginnings in Werner's time,[1] yet new variants continue to emerge. During the investigation of new chelating ligands, a degradation led to the discovery of an azaallyl ligand, (2-py)CHNCH(2-py) (smif), whose chemical properties are intriguing. A related decomposition of $((2\text{-py})CH_2)_2NH$ led to one previous example, $(smif)_2Zn$.[2] Synthesized from the condensation of 2-pyridylaldehyde and 2-pyridylmethylamine (99%), (smif)H is readily deprotonated by $LiN(TMS)_2$ to afford (smif)Li (73%). Initial synthetic studies and brief insights into the electronic features and reactivity of smif are provided herein.

Treatment of $FeBr_2(THF)_2$, $CoCl_2$, and $NiCl_2(dme)$ in THF with 2 equiv of (smif)Li (generated in situ) afforded $(smif)_2M$ [M = Fe (**1**), 52%; Co (**2**), 87%; Ni (**3**), 67%]. Alternatively, exposure of $Fe[N(SiMe_3)_2]_2THF$[3] with 1 or 2 equiv of (smif)H provided $(smif)FeN(TMS)_2$ (**4**, 74%) or **1** (80%). Solutions of dark-green **1** and deep magenta **2** and **3** were intensely colored and afforded black-purple and gold crystalline solids, respectively, indicative of complementary reflected light. Their structures are roughly D_{2d} according to NMR spectra, which reveal one smif environment, and X-ray crystallography, as the view of **1** in Figure 1 illustrates.

1 is diamagnetic, and its Mössbauer spectrum (Figure 2) is consistent with a covalent, low-spin Fe(II) complex. SQUID data show that **2** exhibits a magnetic moment (μ_{eff}) of 1.7 at 10 K, consistent with an $S = {}^1/_2$ ground state (GS), but μ_{eff} rises to >3.0 at 300 K.[4] Its EPR spectrum at 30 K shows a rhombic signal with Co hyperfine couplings: g [A(Co)] = 2.01 [44 G], 2.135 [66 G] and 2.21 [64 G]. **3** is EPR-silent but manifests a μ_{eff} of 2.8 at 300 K, with only a minor attenuation below 10 K, consistent with an $S = 1$ GS.

The structures of **1**−**3** are reminiscent of axially compressed terpy derivatives.[5] Iron complex **1** displays short aza (N_a) and pyridine (N_{py}) Fe−N distances of 1.9012(14) and 1.9634(12) Å, respectively (Table 1), in a symmetric (i.e., D_{2d}) environment, corroborating its low-spin character. The distortion from idealized O_h coordination is evidenced by the N_{py}−Fe−N_{py} angle of 164.53(11)°. In contrast to **1**, the bis(amide) complex $(dpma)_2Fe$ [dpma = $((2\text{-py})CH_2)_2N$] (**5**) possesses metric parameters consistent with its $S = 2$ (μ_{eff} = 5.0) GS, and its UV−vis spectrum shows no band more intense than 5000 M^{-1} cm^{-1}.

Two independent molecules of **2** exhibit longer average Co−N distances [$d(CoN_a) = 1.93(3)$ Å; $d(CoN_{py}) = 2.08(8)$ Å] and smaller bite angles [e.g., $\angle N_{py}CoN_{py} = 160.9(25)°$], and one smif is slightly canted in the plane perpendicular to the first [$\angle N_aCoN_a' = 176.1(18)°$]. **3** possesses two smif ligands at equivalent long distances [$d(NiN_a) = 2.019(5)$ Å; $d(NiN_{py}) = 2.093(9)$; $\angle N_{py}NiN_{py} = 158.1(4)°$], with a cant similar to that in **2** [$\angle N_aNiN_a' = 176.06(8)°$].

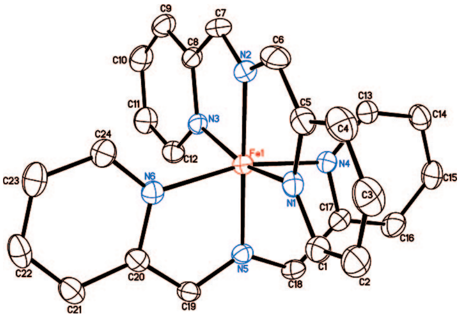

Figure 1. Molecular view of $(smif)_2Fe$ (**1**).

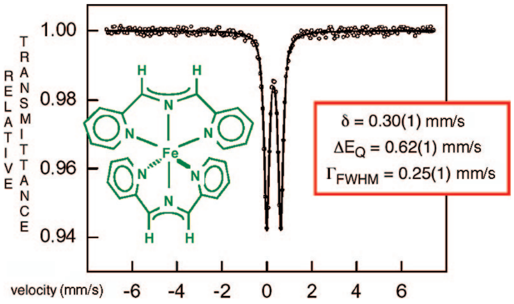

Figure 2. Zero-field Mössbauer spectrum of $(smif)_2Fe$.

A better grasp of the electronic structures, geometries, and optical features of **1**−**3** were obtained from density functional theory (DFT) calculations. Figure 3 shows a simplified orbital diagram, which reveals occupied nonbonding azaallyl carbon-based orbitals that reside *above* the "t_{2g}" set [d_{xy} (b_1); d_{xz}, d_{yz} (e) in D_{2d}]. These orbitals maintain a roughly constant position at about −4.0 eV for **1**−**3** and differentiate smif from related tridentate ligands such as terpy[5,6] by affording high-intensity intraligand (IL) bands. Two large features in the UV−vis spectra of $(smif)_2M$ [**1**, 597 nm (16 000 M^{-1} cm^{-1}), 441 (42 000); **2**, 563 (29 000), 401 (20 000); **3**, 574 (50 000), 399 (18 000)] were assigned as $C^{nb} \rightarrow L\pi^*$ IL bands on the basis of time-dependent DFT (TDDFT) calculations on **1**. Its calculated spectrum, which appeared blue-shifted by ∼0.25 eV, revealed a minor MLCT component in these bands. The TDDFT study permitted a tentative identification of d−d bands at ∼18 000 and 25 000 cm^{-1}. Calculated splittings of the O_h t_{2g} orbitals into $b_1(d_{xy})$ and $e(d_{xz}, d_{yz})$ of D_{2d} and of O_h e_g into $b_2(d_{x^2-y^2})$ and $a_1(d_{z^2})$ of D_{2d} are <1600 cm^{-1}. Consequently, **1** can be estimated (Tanabe−Sugano) to have $\Delta_o \geq 18\,000$ cm^{-1} and $B \approx 470$ cm^{-1}, consistent with the covalency shown in the Mössbauer spectrum.

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Table 1. Structural Parameters for (smif)$_2$M (M = Fe, **1**; Co, **2**; Ni, **3**), [(smif)$_2$Co]OTf (**2+**), (dmpa)$_2$Fe (**5**), and [(TMS)$_2$NFe]$_2$(smif)$_2$ (**4$_2$**)[a]

cmpd	d(MN$_a$)	d(MN$_{py}$)	d(CN$_a$)	∠N$_a$MN$_{py}$	∠N$_a$MN$_{py}$′	∠N$_a$MN$_a$′	∠N$_{py}$MN$_{py}$	∠N$_{py}$MN$_{py}$′
1	1.9012(14)	1.9634(12)	1.333(3)	82.3(2)	97.7(5)	179.11(6)	164.53(11)	91.0(12)
2[b]	1.93(3)	2.08(8)	1.337(7)	80.5(12)	95.1(2)−102.1(2)	177.5(3)	160.9(25)	91.6(18)
2+	1.8768(11)	1.9252(19)	1.331(9)	83.9(2)	96.1(7)	179.05(10)	167.68(9)	90.7(19)
3[b]	2.019(5)	2.093(9)	1.325(4)	79.1(3)	96.6(2)−104.6(2)	176.06(8)	158.1(4)	92.1(16)
5[b]	2.001(13)	2.201(13)	1.418(2)	75.5(4)	99.8(2)−109.5(2)	175.9(16)	150.9(16)	86.90(7)−101.00(7)
4$_2$[c]	1.9432(10)	2.193(3)	1.4345(16)	77.29(13)	102.7(11)	178.53(4)	154.48(4)	

[a] Distances (Å) and angles (deg) are averages unless a range is given. N$_a$ is the aza nitrogen and N$_{py}$ a pyridine nitrogen; primes distinguish different smif ligands. [b] Two molecules in the asymmetric unit. [c] N$_a$′ is (TMS)$_2$N at 1.9538(10) Å.

Figure 3 indicates that smif *may be* redox-active[7−12] in the case of **2**. For **1**, nonbonding, carbon-based azaallyl orbitals are the HOMO and HOMO−1. Ligand-field orbitals drop in energy in going from Fe to Co to Ni, but the additional electron in **2** (vs **1**) may reside in a ligand π^* orbital, rendering **2** formally as Co^{3+}(smif$^{1.5-}$)$_2$. Discrete structural changes are difficult to assess because of delocalization into the py π^* framework. Oxidation of **2** with AgOTf affords magenta [(smif)$_2$Co]OTf (**2+**, 81%), which possesses IL bands at 586 nm (23 000 M^{-1} cm^{-1}) and 383 nm (13 000 M^{-1} cm^{-1}). Symmetric (D_{2d}) structural features of **2+** are consistent with its low-spin d^6 character. In **3**, the d$_{x^2-y^2}$ (b$_2$) and d$_{z^2}$ (a$_1$) orbitals drop below the smif π^* orbitals, and the complex is best described as Ni(II), consistent with its long d(NiN) and EPR silence. The smif-based orbitals stay remarkably consistent for **1**−**3** but may be adjusted in future generations through the appropriate choice of substituents.

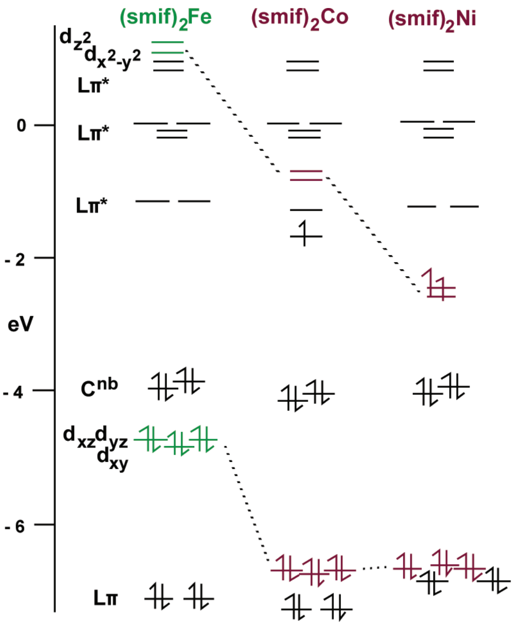

Figure 3. Simplified MO diagrams of **1**−**3**. L stands for smif and C for azaallyl carbon. The dotted lines trace the ligand-field orbitals from Fe to Co to Ni.

The C^{nb} orbitals have ~50% ionic and ~50% covalent character and are "non-innocent" in terms of reactivity. Complex **4** is a dimer in the solid state, as Figure 4 illustrates. In solution, **4** is emerald-green, with IL bands at 633 nm (52 000 M^{-1} cm^{-1}) and 399 nm (37 000 M^{-1} cm^{-1}), but orange crystals reveal its conversion to the amide dimer [(TMS)$_2$NFe]$_2$(smif)$_2$ (**4$_2$**). ^{1}H NMR spectral analysis affords a K_{eq} value of ~4 × 10^{-4} M^{-1} ($\Delta G° \approx 5$ kcal/mol) for the reaction 2 **4** ⇄ **4$_2$**. The dimerization can be construed as either a diradical coupling or a nucleophile/electrophile event, and polar and nonpolar reactivity is anticipated for the smif backbone.

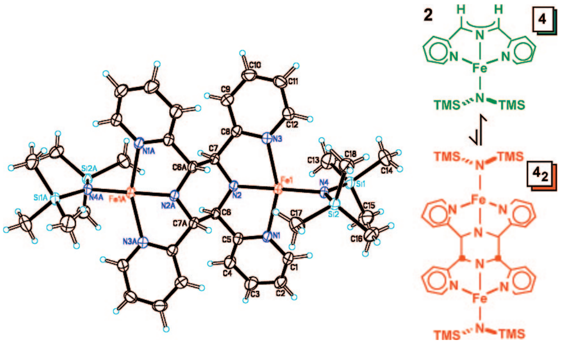

Figure 4. Molecular view of [(TMS)$_2$NFe]$_2$(smif)$_2$ (**4$_2$**), obtained from dimerization of **4**.

The smif ligand provides a rare opportunity to view a *new* homologous series of first-row transition-metal complexes[12] and manifests a unique optical density that may be exploited in various photochemical applications. Physical studies of **1**−**3** and variants as well as (smif)$_2$M (M = V, Cr, Cr$^+$, Mn) are ongoing.

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Supporting Information Available: Experimental details, CIF files, NMR, UV−vis, and EPR spectra, and SQUID data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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