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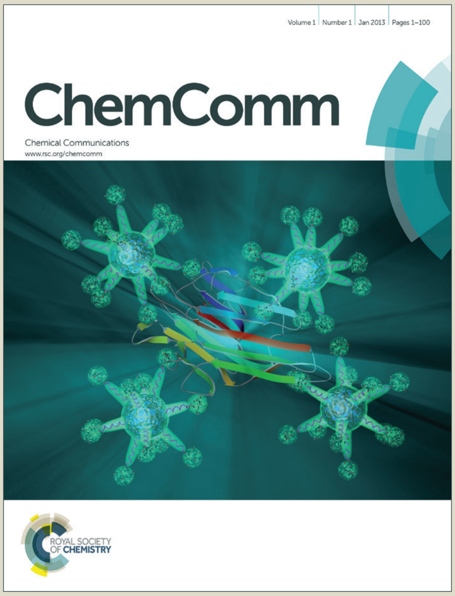

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Redox-induced fluoride ligand dissociation stabilized by intramolecular hydrogen bonding†

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Chemical reduction of a tripodal Cu(II)-F complex containing pendent hydroxyl groups results in the partial dissociation of a F⁻ ligand from Cu. The resulting Cu(I) complex is characterized as containing an outer sphere F⁻ anion 'captured' by hydrogen bonds. The pendent hydroxyl groups were found to be crucial for reductive stability.

Although transition metal fluoride complexes featuring early metals have been well-described in the literature, examples with late metals are considerably rarer.[1] Recent reports have implicated such species as key actors in catalytic fluorination chemistry.[2] Specifically, copper complexes have received considerable interest as cheap, abundant reagents for (catalytic) C-F bond formation[3] and thus, there is a high interest in synthetic strategies that afford Cu-F intermediates.[4] The disparity between the π-donating nature of fluoride and the filled *d*-orbitals of low valent group 11 metals generally leads to highly labile M-F bonds.[5] Despite this, a handful of monomeric copper(I) fluoride complexes have been reported. Prior examples use N-heterocyclic carbenes,[6] bipyridine,[7] and/or phosphines[8] as supporting ligands. Metal fluorides are prolific hydrogen bond (H-bond) acceptors,[9] and in all of the prior reported terminal Cu-F adducts (both Cu^I and Cu^{II}), inter- or intramolecular H-bond interactions with the fluoride ligand accompany metal coordination in the solid state.[10] These interactions are so favorable that even very weak H-bond donors, such as weakly acidic C-H groups participate in non-covalent interactions with the M-F unit.[11] Unfortunately, strategies that incorporate the rational design of these interactions to promote F⁻ binding in close proximity to a metal site (that might support M-F binding) are not well explored.[12]

Recently, we described copper(I/II) chloride complexes supported by *tris*(6-hydroxypyrid-2-ylmethyl)amine (H_3thpa), a tripodal ligand featuring pendent hydroxyl groups capable of engaging in H-bonding interactions with metal bound substrates.[13] By extension, we postulated that an axial fluoride ligand would show enhanced H-bonding interactions when compared to the chloride congener and provide entry into a predictive platform to construct and evaluate M-F interactions. Furthermore, we hypothesized that the highly directed H-bonding interactions provided by H_3thpa would be ideally suited to stabilize reactive, low valent Cu-F units. In this Communication we describe the synthesis of copper fluoride complexes supported by H_3thpa and demonstrate that upon reduction from copper(II) to copper(I), Cu-F bond dissociation occurs to yield a remarkable copper(I) complex with a fluoride anion encapsulated in the secondary coordination sphere *via* H-bonding.

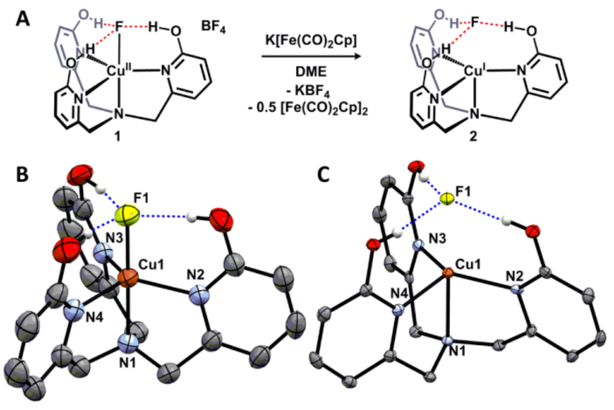

Fig. 1. Synthesis of Cu(I) fluoride adduct **2** (A) and solid state structures of **1** (B; 30% ellipsoids, H atoms not involved in H-bonding and anion removed for clarity) and **2** (C; 50% ellipsoids, H atoms not involved in H-bonding removed for clarity).

We first interrogated H-bonding interactions between H_3thpa and coordinated fluoride by preparing a copper(II) fluoride complex. Treatment of H_3thpa with $Cu(SO_4)•5H_2O$ and $NaBF_4$ in methanol, followed by CsF cleanly provided the copper(II) fluoride complex $CuF(H_3thpa)BF_4$ (**1**) in 77% yield.

The absence of C=O stretches and presence of sharp O-H stretches in the IR spectrum of **1** confirms ligand tautomerization (2-pyridone/2-hydroxypyridine) upon metalation. By using a methodology previously described for copper chloride complexes, the position of the OH stretching frequency can be used to approximate the upper limit of H-bonding strength in **1**.[13,14] As anticipated for the potent H-bond accepting fluoride ligand, each H-bonding interaction in **1** is significantly stronger ($\Delta H^{o}_{H\text{-bond}}$ = -6.0 kcal/mol) than in the corresponding $CuCl(H_3thpa)^+$ complex ($\Delta H^{o}_{H\text{-bond}}$ = -3.8 kcal/mol).[13]

The solution state structure of **1** was interrogated by UV-vis and EPR spectroscopies, both revealing that **1** is trigonal bipyramidal (TBP) in solution.[13] Crystals of **1** were subjected to an X-ray diffraction experiment and the solid state structure is depicted in Fig. 1B.† The TBP coordination geometry in **1** is maintained in the solid state structure. Notably, the F---O separations in **1** (2.578(5), 2.641(5) and 2.668(4) Å) are consistent with intramolecular H-bonding interactions.[15] The Cu-F bond distance in **1** (1.925(2) Å) is elongated in comparison to the 'parent' tpa (tpa = *tris*(2-pyridylmethyl)amine) complex $CuF(tpa)PF_6$ (1.852 Å),[16] and consistent with intramolecular H-bonding interactions serving to remove electron density from the fluoride ligand.

Cyclic voltammetry experiments were conducted in order to ascertain the stability of a putative Cu(I) fluoride supported by H_3thpa. Fig. S3 shows the cyclic voltammogram of **1** in CH_2Cl_2 solution with $[^{n}Bu_4N][PF_6]$ as supporting electrolyte. The reduction of **1** is highly reversible (i_{pa}/i_{pc} = 1.02) and has a peak separation similar to that of ferrocene under identical conditions (Fig. S4). The redox potential of **1** ($E_{1/2}$ = -0.195 V vs. SCE) is cathodic of the corresponding $CuCl(H_3thpa)^+$ complex ($E_{1/2}$ = +0.095 V vs. SCE, Fig. S4), and consistent with the higher electronegativity of the fluoride ligand compared to chloride.

Chemical reduction of **1** with $K[Fe(CO)_2Cp]$ afforded the neutral, copper(I) fluoride adduct **2** (Fig. 1A). Solution (CD_2Cl_2) ^1H NMR spectra of **2** display ligand resonances characteristic of 3-fold symmetry.[17] The OH resonances in **2** appear at 12.90 ppm as a broad singlet ($\nu_{1/2}$ = 26.7 Hz) at 25 °C (Fig. S8). Cooling the sample to -25 °C, the OH signal evolves into a doublet with a coupling constant of 49.5 Hz (Fig. S10). Upon ^{19}F-decoupling at -25 °C, the doublet collapses into a singlet, confirming the observed coupling is due to F (Fig. S11). The magnitude of $^1J_{H\text{-}F}$ (49.5 Hz) is comparable to that observed for the $[F(HF)_3]^-$ anion ($^1J_{H\text{-}F}$ = 41 Hz), which has D_{3h} symmetry.[18] The ^{19}F NMR spectrum of **2** displays a single, broad ($\nu_{1/2}$ = 110 Hz) resonance at -109 ppm (Fig. S9), which is drastically different than previously reported Cu(I)-F complexes (^{19}F NMR signals ranging from -200 to -250 ppm)[6,8] and more closely resembles the ^{19}F chemical shift of hydrated F^- (δ = -119).[19]

The NMR spectroscopic analysis of **2** above alludes to a magnetic environment around fluorine that is weakly (or not) interacting with a copper center. This interaction was clarified by analysis of the solid state structure of **2**, which displays approximate C_{3V} symmetry (Fig. 1C). The separation between Cu and F in the solid state structure is 2.469(2) Å. This value is significantly longer than the sum of the Shannon ionic radii of Cu and F (1.885 Å),[20] suggesting little to no covalent bonding between the two atoms in the solid state structure. The Cu-N1 distance of 2.218(3) Å in **2** is also elongated with respect to **1** (1.995(3) Å), consistent with a decreased Lewis acidic metal center upon reduction. The O---F distances in **2** (2.576(4), 2.581(4) and 2.585(3) Å) are, on average, shorter than those found in **1** (*vide supra*), highlighting the increased electron density on F and stronger H-bonding interactions in **2** with respect to **1**.

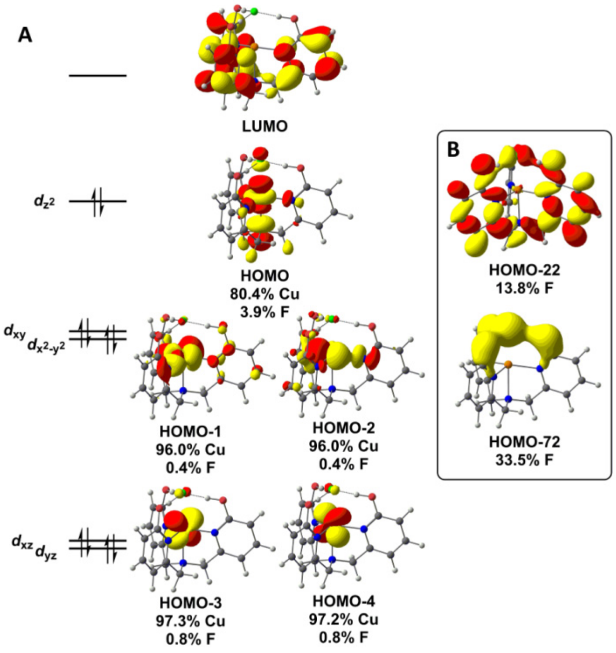

Fig. 2. DFT-calculated qualitative molecular orbital (MO) diagram and orbital compositions of **2** (A; isovalue 0.03) and representative MO's involved in H-bonding with F^- in **2** (B; isovalue 0.03).

To further support the absence of bonding interactions between Cu and F, density functional theory (DFT) calculations of **2** were undertaken.† The B3LYP functional[21] and TZVP basis set[22] were employed and all calculations used an implicit CH_2Cl_2 solvation through a polarizable continuum model.[23] Good agreement between the X-ray structure and calculated structure of **2** was found (Fig. S13 and Table S1). Fig. 2A shows a qualitative molecular orbital diagram of **2**. The highest occupied molecular orbital (HOMO) of **2** primarily arises from the $3d_{z^2}$ orbital on Cu (80.4%) with only a small contribution from the F $2p_z$ orbital (3.9%). The interactions between filled Cu 3*d* (d_{xz}, d_{yz}, d_{xy}, $d_{x^2-y^2}$ and d_{z^2}) orbitals and F 2*p* orbitals all are of anti-bonding character. The lowest unoccupied molecular orbital (LUMO) of **2** primarily consists of π^* orbitals on the pyridine rings of the H_3thpa ligand. Representative molecular orbitals (HOMO-22 and HOMO-72) involved in H-bonding are depicted in Fig. 2B: the σ interactions of F 2p and 2s orbitals (respectively) with the OH groups of H_3thpa. A natural population analysis[24] of **2** found electrostatic charges of +0.54

for Cu and -0.77 for F. The H atoms involved in H-bonding with F were found to have electrostatic charges of +0.523. When the F was removed and natural population analysis was carried out on the cationic fragment Cu(H_3thpa)$^+$, the H atoms were found to have electrostatic charges of +0.470, highlighting the polarization of the H atoms due to H-bonding to F. A natural bond orbital (NBO) analysis[24b] on **2** found no covalent bonding interactions between Cu and F.† Additionally, the donor-acceptor interactions for H-bonding in **2** were found to have a total second order stabilization energy of 65.7 kcal/mol (*ca.* 22 kcal/mol per OH group). A Wiberg bond index[25] between Cu and F was calculated to be 0.12. Taken together, the DFT calculations are consistent with interactions between Cu and F as primarily electrostatic in nature with little covalency between the two atoms.

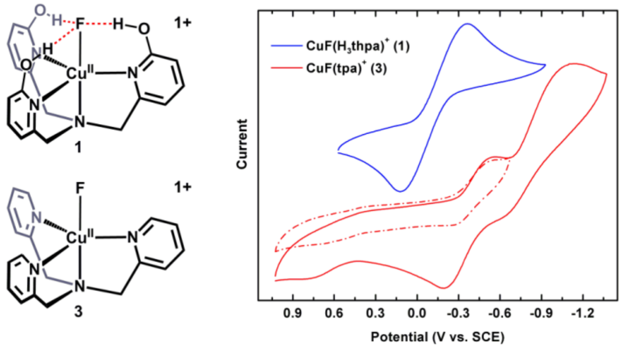

Fig. 3. Comparison of the cyclic voltammograms of **1** and **3** at 100 mV/s scan rate in 0.1 M [^{n}Bu$_4$N][PF$_6$] CH_2Cl_2.

Given the unusual accessibility and stability of both Cu(II) *and* Cu(I) fluoride species, we sought to evaluate the degree to which stability is imparted by the ligand's secondary coordination environment. Unsubstituted tpa was selected as a comparative tripodal ligand that does not contain groups capable of engaging in non-covalent interactions. We prepared Karlin's CuF(tpa)PF_6 (**3**)[16] *via* a modified procedure and examined its reductive electrochemistry. Unlike **1**, the cyclic voltammogram of **3** displays two *irreversible* reductive events (Fig. 3). The first reductive wave centered at *ca.* -0.5 V *vs.* SCE may be due to an irreversible Cu(II/I) redox couple (see dashed inset in Fig. 3) and we propose the second feature centered at *ca.* -1.1 V is due to deposition of Cu^0 on the electrode surface based on the appearance of a stripping wave (ca. -0.2 V) upon reversal of potential during the cyclic voltammetry experiment. This reductive instability of the 'parent' CuF(tpa)$^+$ complex is in stark contrast to **2**, which is reductively stable to -1.5 V *vs* SCE (Fig. S4). Furthermore, attempts to chemically reduce **3** with reductants such as [Co(C_5H_5)$_2$] have led to intractable mixtures containing highly insoluble black material, most consistent with Cu^0. Thus, the presence of the OH groups in **1** serve to greatly enhance the reductive stability of the tripodal copper fluoride complexes and are required for the generation of stable copper(I) fluoride adducts.

In summary, we have shown that the reduction of tripodal Cu(II)-F complexes can be achieved when pendent H-bonding groups are present. Upon reduction, F$^-$ ligand dissociation occurs and the F$^-$ anion is 'captured' by the intramolecular H-bonding network provided by the H_3thpa ligand. DFT calculations confirm that there is little covalency between Cu(I) and F, and that the complex is best described as containing an outer sphere F$^-$ anion. Reactivity studies of **2** are ongoing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed synthetic procedures, EPR and NMR spectra and voltammetry. CCDC 1021516 (**1**) and 1021517 (**2**) contain supplementary crystallographic data. For ESI and crystallographic data in CIF format, see DOI: 10.1039/c000000x/

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