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Deconvoluting the Innocent vs. Non-innocent Behavior of *N,N*-diethylphenylazothioformamide Ligands with Copper Sources

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Abstract

Redox-active ligands lead to ambiguity in often clearly defined oxidation states of both the metal centre and the ligand. The arylazothioformamide (ATF) ligand class represents a redox-active ligand with three possible redox states (neutral, singly reduced, and doubly reduced). ATF-metal interactions result in strong colorimetric transitions allowing for the use of ATFs in metal detection and/or separations. While previous reports have discussed dissolution of zerovalent metals, the resulting oxidation states of coordination complexes have proved difficult to interpret through X-ray crystallographic analysis alone. This report describes the X-ray crystallographic analysis combined with computational modelling of the ATF ligand and metal complexes to deconvolute the metal and ligand oxidation state of metal-ATF complexes. Metal(ATF)₂ complexes that originated from zerovalent metals were found to exist as dicationic metal centers containing two singly reduced ATF ligands. When employing Cu(I) salts instead of Cu(0) to generate copper-ATF complexes, the resulting complexes remained Cu(I) and the ATF ligand remained “innocent”, existing in its neutral state. Although the use of CuX (where X = Br or I) or [Cu(NCMe)₄]Y (where Y = BF₄ or PF₆) generated species of the type: [(ATF)Cu(μ-X)]₂ and [Cu(ATF)₂]Y, respectively, the ATF ligand remained in its neutral state for each species type.

Graphical Abstract

Experimental and computational investigation of reactions involving the redox-active arylazothioformamide ligand with multiple Cu(I) sources is described. Cu(I) halides produce dimeric 1:1 coordination species while non-coordinating counter ions (BF₄ and PF₆) gave 2:1 species. Computational comparisons of bond lengths and angles suggest that the Cu remains in the +1 oxidation state.

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Supporting information for this article is given via a link at the end of the document.

Keywords

Copper; Arylazothioformamide; Noncovalent interactions

Introduction

Ligand-metal interactions are central to inorganic, organic, and organometallic reactions. While the valence state of the metal and ligand can be clearly defined for many metal complexes, the discovery and exploration of redox-active ligands in synthesis, results in less clear assignment of the metal-ligand complexes containing redox-active ligands^[1]. Nature is filled with redox-active ligand sites utilizing a variety of metal centers electronically coupled to biochemical systems.^[2] Prediction of the oxidation states of complexes containing redox-active ligands can be challenging.^[3] With advanced capabilities in molecular modelling software connected with X-ray crystallographic analysis, deconvolution of uncertain oxidation states can be undertaken.

Previous work by Bechgaard clearly outlined evidence of redox-active behavior by the ligand N,N-diethylphenylazothioformamide (ATF) **1** with copper (I) tetrakis(acetonitrile) tetrafluoroborate. The resulting copper complex exhibited a Cu(I) center bound through the α -azothiocarbonyl in a 1,3-heterodiene chelate motif with one singly reduced ligand and one neutral ligand, formally $[(\text{Cu}^{\text{I}}(\text{ATF}^{\bullet-})(\text{ATF}))]$ (**2**).^[4] A later report by Krebs and co-workers described the reaction of ATF **1** with the transition metals: Pd, Pt, Ni, and Cu. The resulting metal complexes exhibited four reversible redox events in the electrochemistry, predicting a 2:1 ligand to metal coordination complex.^[5] Krebs and co-workers suggested **2** exists either as $[(\text{Cu}^{\text{I}}(\text{ATF}^{\bullet-})(\text{ATF}))]$ or an antiferromagnetically coupled $[\text{Cu}^{\text{II}}(\text{ATF}^{\bullet-})_2]$ complex.^[6] From crystallographic analysis of the copper complex, the diamagnetic $[(\text{Cu}^{\text{I}}(\text{ATF}^{\bullet-})(\text{ATF}))]$ structure was suggested. Although the former structure should allow for characterization using NMR spectroscopy, the authors noted that ¹H NMR signals were broadened by the presence of some paramagnetic material. Due to the redox behavior of the ATF ligand and the multiple possible valences for both copper and the ATF ligand, the question of the oxidation state remained unsolved. To solve the question of copper and ATF ligand oxidation states, a crystal structure of the ATF ligand itself in addition to computational modelling of the redox states of the ATF ligand are needed. Furthermore, the hetero-1,3-diene chelate motif seen in the azothioformamide functionality of **1** differs from previous studies of noninnocent α -azothiocarbonyls due to the potential for double bond character in the thioamide.^[7]

By achieving a greater understanding of metal-ligand interactions, insight can be provided into the necessary ligand environment to remove metals from consumer products. The removal of metal catalyst residues from consumer care products, such as pharmaceuticals,

polymers, and in electronics applications is a high priority in industrial reactions due to the potential toxicity, lack of therapeutic benefit, side reactions, not to mention the loss of valuable catalyst.^[8] Impurity removal in chemical synthesis, nanomaterial design, and polymers sectors also include concerns of weight, purity, and altered material properties.^[9] Gentle methods for the removal of metal residues that do not harm the consumer product are extremely attractive. A possible solution is the implementation of redox-active ligands. Nielsen, Bechgaard, and Krebs have effectively employed redox-active ATF ligands to remove residual Pd and Cu nanoparticles from conjugated polymers by precipitating the polymer and ligand solution, then separating the insoluble polymer from the soluble ligand-metal complex.^[10]

This report describes the first crystal structure of the ATF ligand, **1**, and its rather “innocent” (non redox-active) behavior with commonly used copper(I) salts specifically copper (I) halides, as well as Cu(I)BF₄ and Cu(I)PF₆. The non-innocent behavior of the coordination complexes was hypothesized and validated through computational analysis. Full characterization and crystal structures for all complexes described within, as well as structural data for the modelled complexes, provide insight into the oxidation states of both the copper center and the ATF ligand. The results strongly support the unique binding of metals with the ATF ligand yet contrast the suggested electronics of Bechgaard/Krebs original Cu(**1**)₂⁰ structure (**2**) (Scheme 1). Subsequently, Bechgaard’s description of the diamagnetic Cu(I)BF₄•(**1**)₂ as monomeric and tetrahedral was re-examined.^[4, 6] The interactions of Cu(I) sources with ligand **1** have implications for further coordination studies and the possibility of being able to recover metals from catalytic reactions.

Results and Discussion

In terms of spectroscopic characterization, one key aspect of **1**•metal coordination is the remarkable color change and rise in extinction coefficient. The dramatic color change upon coordination to a metal center suggests the potential to implement ATF ligands in the quantitative measurement of trace residual metals. Krebs reported an extinction coefficient increase on the order of 10,000 to 20,000 M⁻¹ cm⁻¹ with Cu and Pd, respectively.^[10] Evaluation of **1** with various Cu(I) salts equally gave increased extinction coefficients in both the UV and the visible range (See ESI). This result distinguishes ATF ligands as potential highly sensitive chromophores for trace metal impurities.

Coordination of common synthetic Cu(I) salts with **1** is the result of a larger effort focused on fully exploring the behavior of **1** and related ATF ligands. Cu(I) was chosen as it offered an intriguing difference from the dissolving zero-valent and divalent metal species previously reported by Bechgaard, Krebs and Jensen.^[5] Also, the increased use of Cu(I) in homogeneous and heterogeneous catalysis makes studying ATF coordination with a Cu(I) center and the possibility of stable control of oxidation state warranted.^[11] Further, ATF ligand research provides an improved understanding in multiple areas including redox-active ligand classes, metal centers for synthetic metalloproteins^[2b], and materials development, especially in atom transfer radical polymerization (ATRP) with Cu catalysts.^[12]

For this study, the synthesis of ligand **1** was modified slightly from the one-pot procedure reported by Nielsen and Krebs to ease crystal isolation (See ESI).^[6] The crystalline product was used directly for subsequent coordination with Cu(I). Cyclic voltammetry of ligand **1** produced two reversible redox events with reduction potential peaks at ca. 0.8V and 0.4V vs. the ferrocene/ferrocenium couple (See ESI). Each of the reductions has been modeled to predict the lowest energy conformations prior to coordination to a metal center. Initial explorations successfully replicated the nearly instantaneous reaction of **1** with solid Cu as indicated by a darkening of the solution from transparent orange-red to an intensely light-absorbing, black-blue solution (see ESI). Potential redox induced coordination reactions included attempts with cuprous and cupric halides, followed by spectroscopic evaluation, and crystallization. While darkening of the solution occurred with all cuprous and cupric halides tested (CuCl, CuBr, CuI, [Cu(CH₃CN)₄]BF₄, [Cu(CH₃CN)₄]PF₆, CuCl₂, and CuBr₂), rapid complex formation (in concentrated THF solution) occurred with CuBr, CuI, [Cu(CH₃CN)₄]BF₄, and [Cu(CH₃CN)₄]PF₆ as evidenced by the crystalline material obtained within hours. ¹H NMR spectra for these complexes yielded similar spectra as **1** but with significant downfield shifts in the aryl ortho H's and the methylene H's of the N,N-diethylformamide (See ESI). This trend was seen in all complexes suggesting a change in the electronics around the two coordination sites (N=N, and C=S). Cyclic voltammograms of complexes **3a**, **3b**, **4a**, and **4b** each displayed multiple distinct reduction and oxidation events over a range of -1.4V to 0.4V compared to the ferrocene/ferrocenium couple (See ESI).

Crystal and Computational Modeling of Ligand 1

The molecular structure for ligand **1** is shown in Figure 1. Crystallographic analysis of ligand **1** depicts the thiocarbonyl rotated away from the diazophenyl π system at an angle of 83.5°. This confirmation is intriguing, as a rotation of the thiocarbonyl group into the same plane as the diazophenyl group is required to generate a bidentate ligand. To determine the activation energy for the rotation of the thiocarbonyl group into the plane of the diazophenyl group and the molecular parameters of the singly [1•]¹⁻ and doubly [1••]²⁻ reduced ligands, computational analysis using the B3LYP/6-31G* level of theory was undertaken. To verify the validity of the chosen computational method, five other DFT functionals were used, but B3LYP gave structural parameters that best matched the experimental data. Computational analysis indicated that rotation of the thiocarbonyl group to the plane of the diazophenyl group was 3.4 kcal/mol uphill from ligand **1**. Only a transition state structure (**1***) of the rotated **1** was found, indicating that either the diazophenyl or thiocarbonyl group initially coordinates to the metal center followed by rotation of the remaining group to result in bidentate coordination, when the ligand behaves innocently. Upon examination of the structure of **1***, an increase of the C(1)-N(1) and C(1)-N(2) distance by 0.01 and 0.02 Å, respectively, occurs when compared to **1**.

Reduction of **1** to [1•]¹⁻ results in a lengthening of the N(3)-C(7) bond by almost 0.05 Å. Additionally, the C(7)-S(1) bond and the N(2)-N(1) bond lengths increased suggesting partial double bond character as seen in Table 1 and Figure 2. Addition of a second electron to [1•]¹⁻, generating [1••]²⁻, resulted in a further lengthening of the C(7)-S(1) and N(1)-N(2) bonds by 0.09 and 0.14 Å, respectively, when compared to **1**. Not all bonds lengthened upon

adding electrons to **1**. Addition of one and two electrons to **1** resulted in a contraction of the C(7)-N(2) distance by 0.07 and 0.12 Å, respectively, when compared to **1**. The contraction of the C(7)-N(2) single bond upon the addition of electrons, suggests partial double bond character in $[1^{\bullet}]^{1-}$, and double bond character in $[1^{\bullet\bullet}]^{2-}$. Reduction of **1** decreased the dihedral angle between the thioketone and the diazophenyl group. Electron density distribution maps of **1**, **1***, $[1^{\bullet}]^{1-}$, and $[1^{\bullet\bullet}]^{2-}$ are highlighted in Figure 2. Electron density disperses away from the thiocarbonyl towards the aromatic ring upon reduction.

Crystal and Computational Modeling of $\text{Cu}1_2^0$

Using the computed redox states of **1** and ZnL_n1_{2-n} (where $n = 0, 1$) complexes (see ESI), a comparison of the Bechgaard/Krebs crystalline CuL_2^0 complex was performed. Krebs reported crystals were obtained from the dissolution of copper wire in a concentrated THF solution of **1**.^[5] The report cites that the species recovered was most likely either a Cu^{I} with one singly reduced ligand and one neutral ligand $[\text{Cu}^{\text{I}}(\text{L}^{\bullet-})(\text{L})]$ or an antiferromagnetically coupled $[\text{Cu}^{\text{II}}(\text{L}^{\bullet-})_2]$ complex.^[4] Based on the predicted structures of the ligands in the varied oxidation states our models suggest that the Krebs and Bechgaard complex is most likely the ferromagnetic $[\text{Cu}^{2+}(\text{L}^{\bullet-})_2]$ complex. This species adequately provides an NMR inactive compound (as found) yet provides an adequate neutral species. The reported bond distances and angles exhibit greater similarity to $[1^{\bullet}]^{1-}$ than **1** or $[1^{\bullet\bullet}]^{2-}$, suggesting that the metal center in the $\text{Cu}1_2^0$ complex exists as Cu^{2+} with two singly reduced ligands. With the aid of computational analysis and a crystal structure of the ligand itself, insight into the oxidation states of both ligand and metal center were deduced. This assignment was further verified by the generation of a spin density plot, which showed the majority of the spin density resided on the ligand (see ESI). The other metal center complexes reported previously^[6] were also modelled in similar fashion (Ni, Pd, Pt) and all fit the model of M^{2+} with two singly reduced ligands as suggested by Krebs (see ESI).

Crystal and Computational Modelling of Cu(I) salts

To examine the influence of Cu(I) salts on the ATF oxidation state, **1** was reacted with several Cu(I) species and the resulting products were structurally characterized. For example, when **1** is reacted with one equivalent of Cu(I)Br in THF, a dimeric complex each containing one ATF ligand bridged by the bromide ligand is obtained, as shown in Figure 3. Stabilization of a dimeric bridged Cu(I) halide species has been noted previously; Lobana and coworkers saw similar dimers form with thiosemicarbazones and triphenylphosphine, suggesting that Cu(I) is stable in a tetrahedral geometry containing a bridged halide.^[13] The dimeric, distorted tetrahedral geometry is also structurally similar to the copper A of cytochrome *c* oxidase.^[14] In addition to a bridging bromide, use of CuI instead of CuBr, generated a similar complex with bridging iodides (for crystal structure, see ESI). The bond lengths and angles are provided in table S3 (ESI) in comparison to computational structures. Although dimeric in solid state, the complexes in solution are proposed to exist as monomers with solvent molecules in the coordination sphere. Variable temperature NMR experiments in CDCl_3 and CD_3CN however did not suggest the breakdown of the complex at elevated temperatures of 55°C and 79°C respectively. However, when dissolved in $\text{DMSO}-d_6$ an equilibria of **3a** and a new species with similar aromatic peaks arose and persisted to

101 °C suggesting the presence of another stable coordinative species (See ESI). Computational analysis suggests that dimeric species containing heavier halides were more susceptible to dimer dissociation and solvation.

To determine the oxidation state of the copper center and the ATF ligands of $[(\text{Cu}\cdot\mathbf{1}(\mu\text{-Br}))_2]$ and $[(\text{Cu}\cdot\mathbf{1}(\mu\text{-I}))_2]$ complexes, X-ray crystallographic and computational analysis were undertaken. Both crystallographic and computational analysis suggested that $[(\text{Cu}\cdot\mathbf{1}(\mu\text{-Br}))_2]$ and $[(\text{Cu}\cdot\mathbf{1}(\mu\text{-I}))_2]$ contain neutral ligands with copper in the 1+ oxidation state (See electron density maps and table S2 in ESI).

To examine the influence of non-coordinating anions, reactions of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$, and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ with 0.5–1 equivalents of **1** were undertaken. The addition of ATF to $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ (where X = BF_4 or PF_6) resulted in dark colored solutions that yielded X-ray diffraction quality crystals within hours. NMR spectroscopic analysis of the resulting reaction products resulted in an NMR spectrum similar to the μ -halide complexes yet the crystal structures displayed a 2:1 ligand to metal ratio with either counteranion (BF_4 or PF_6). As seen in Figure 4, the copper center of $\text{Cu}(\text{I})\mathbf{1}_2\cdot\text{PF}_6$ resides in a tetrahedral geometry. As with the μ -halide structures, structural analysis of $\text{Cu}\mathbf{1}_2^{1+}$ shows that both ligands exist in a neutral oxidation state. Bond distances and angles are reported in table S4 (ESI) alongside the Bechgaard/Krebs crystal and computed structure. The ATF ligand in $\text{Cu}(\text{I})\mathbf{1}_2\text{BF}_4/\text{PF}_6$ complexes again compared much more favorably with the neutral ligand in transition state **1*** specifically at the C1-S and N2-N3 bonds. The presence of the counteranion in the outer coordination sphere for both the BF_4 and PF_6 (shown) complexes provided ample indication of the oxidation state for the metal center.

Conclusions

In summary, this report describes the synthesis, characterization and comparative modelling of coordination complexes of ligand **1** with common Cu(I) salts. Single crystal X-ray diffraction combined with a computational study provided insight into the predicted oxidation states of the metal centers and the redox-active ligand for these complexes and previously reported $\text{Cu}\mathbf{1}_2^0$ complexes. Building on previous studies of complexes derived from zero-valent metals, particularly Cu, this report provides important insights into the proposed structure based on the bond distances and angles. Further exploration of the oxidative species present gives potential to separate trace metal impurities, which is significant and applicable in pharmaceuticals and other high value materials. As copper catalysis continues to grow in significance the removal of residual copper species from heterogeneous materials may become more important due to deleterious effects of Cu(I) contamination^[15]. While the Cu(I) species discussed here appear to be stable under standard conditions, further cyclic voltammetry studies are being completed to assess the redox-activity of the Cu (I/II) and ligand system during coordination, complementing the previous work conducted with the tetrafluoroborate complex.

The ability of ligand **1** to complex both zero-valent and cationic transition metals suggests that ATF ligands are attractive ligands for copper catalyzed reactions involving a redox event. Also, a deeper understanding of the electrochemical behavior of these copper-ATF

complexes will provide opportunities for electrochemical refining and stripping of copper from a variety of complex matrices. This information will support further understanding into metal-ligand association and the evaluation of these ligands in separation science.

Experimental Section

Experimental Synthetic procedures

N,N-diethyl phenylazothioformamide (1)—The one-pot procedure reported by Nielsen and Krebs^[5] was modified slightly in the purification to ease the crystal isolation (full experimental is in the ESI). After concentrating the crude product onto silica, a column was run using 9:1 hexane: ethylacetate (EtOAc) yielding 6.03 grams of dense red oil (68%). This oil was subjected to recrystallization using 20:1 heptane: EtOAc. The low melting point of the solid proved a difficult recrystallization therefore once the recrystallization liquor reached room temperature (RT) precipitation of orange crystals was encouraged using a dry ice/acetone bath followed by filtration. The resulting mother liquor, with slow evaporation over time gave large orange crystals of pure product collected in multiple aliquots (5.4g, 61%). ¹H NMR (CDCl₃ δ= 7.26 ppm, 500 MHz) – 7.877–7.899 (m, 2H), 7.495–7.542 (m, 3H), 4.032 (q, 2H, *J* = 2.8 Hz), 3.519 (q, 2H, *J* = 3 Hz), 1.414 (t, 3H, *J* = 2.8 Hz), 1.186 (t, 3H *J* = 2.8 Hz). ¹³C NMR – (CDCl₃ δ–77.00 ppm 125 MHz) – 194.17 (C=S), 151.81, 132.63, 129.25, 123.59, 47.79, 45.09, 13.72, 11.45. FT-IR (cm⁻¹) – 2974, 1515, 1426, 1148, 1085, 791, 685. λ_{max} = 261 nm (CH₃CN). Anal Calcd for C₁₁H₁₅N₃S: C, 59.69; H, 6.83; N, 18.99. Found: C, 59.70; H, 6.83; N, 18.99. m.p. = 56°C.

General Procedure for Crystallization of Copper complexes—Copper salts and **1** were both placed in a clean 4-dram vial. Anhydrous tetrahydrofuran (THF) was added and immediate color change from light orange to dark black as observed. The solution was allowed to slowly evaporate over 2–7 days at RT or at 4°C with repeated decanting for crystal collection.

[(Copper•1(μ-Br))₂ complex (3a)]—4.0 mL of anhydrous THF was added to a vial containing 15.4 mg (0.0696 mol) of **1** and 10.0 mg of Cu(I)Br (0.0696 mol). The solution was heated to 50°C to help promote solvation and then poured into another 4-dram vial and allowed to slowly evaporate over 2 days at room temperature. As crystals formed, the solution was decanted into another vial for further crystallization, collecting a total of 20 mg (78 %) of a dark blue solid. ¹H NMR (CDCl₃ δ –7.26 ppm, 500 MHz) 8.667 (d, 2H *J* = 3.2 Hz); 7.693 (t, 1H *J* = 2.8 Hz); 7.602 (t, 2H *J* = 3.2 Hz); 4.126 (dq, 4H *J* = 2.8 Hz); 1.491 (t, 3H *J* = 2.9 Hz); 1.424 (t, 3H *J* = 2.9 Hz). ¹³C NMR (CDCl₃ δ–77.00 ppm, 125 MHz) 187.88, 150.84, 135.49, 130.02, 127.19, 50.74, 47.84, 14.92, 10.90. FT-IR (cm⁻¹) – 2938, 1663, 1429, 1136, 1045, 1036, 779, 683. λ_{max} = 240 nm (CH₃CN). Anal Calcd for C₂₂H₃₀Br₂Cu₂N₆S₂: C, 36.22; H, 4.15; N, 11.52. Found: C, 38.19; H, 4.33; N, 12.00. m.p. = 160°C.

[(Copper•1(μ-I))₂ complex (3b)]—4.0 mL of anhydrous THF was added to 22 mg (0.099 mmol) of **1** and 18.8 mg (0.099 mmol) of CuI. Dark black crystals were isolated from room temperature evaporation over 3–5 days collecting 40 mg of material (quant.). ¹H NMR

(CDCl₃ δ -7.26 ppm, 500 MHz) 8.740 (d, 2H J = 3.0 Hz), 7.651–7.685 (m, 1H), 7.610–7.571 (m, 2H), 4.177 (dq, 4H J = Hz), 1.482 (t, 3H J = 2.9 Hz), 1.402 (t, 3H J = 2.8 Hz). ¹³C NMR – (CDCl₃ δ -77.00 ppm, 125 MHz) 187.23, 151.34, 134.69, 129.61, 127.03, 50.02, 47.24, 14.89, 11.03. FT-IR (cm⁻¹) – 2932, 1681, 1428, 1135, 1071, 777, 668. Anal Calcd for C₂₂H₃₀I₂Cu₂N₆S₂: C, 32.08; H, 3.67; N, 10.2. Found: C, 32.44; H, 3.70, N, 10.22. m.p. = 178°C.

[Copper•1₂]BF₄ complex (4a)—36 mg (0.162 mmol) of **1** was mixed with 51 mg (0.162 mmol) of [(CH₃CN)₄Cu]BF₄ in 15 mL of THF. After rapid colour change the dark blue solution was quickly decanted into a 20 mL vial to slowly evaporate collecting 10.2 mg of crystals. The remaining solid from the original mixture was washed with hexane, and filtered. The resulting dark blue coloured solid was dissolved in CHCl₃ and separated with 10 mL of deionized H₂O. The aqueous layer was then washed three times with CHCl₃, combined, dried over sodium sulfate and the solvent was slowly evaporated to yield 25.4 mg of dark blue powder (overall 73% yield). ¹H NMR (CDCl₃ δ -7.26 ppm, 500 MHz) 8.054 (m, 2H), 7.618 (tt, 1 H), 7.504 (m, 2H), 4.323 (q, 2H J = 2.8 Hz), 4.133 (q, 2H J = 2.8 Hz), 1.512 (dt, 6H J = 2.8 Hz). ¹³C NMR (CDCl₃ δ -77.00 ppm, 125 MHz) 186.27, 150.65, 136.42, 130.52, 126.42, 51.18, 49.05, 14.98, 10.82. FT-IR (cm⁻¹) – 2977, 1527, 1440, 1136, 1046, 773, 684. Anal Calcd for C₂₂H₃₀BCuF₄N₆S₂: C, 44.56; H, 5.10; N, 14.17. Found: C, 44.67; H, 5.45; N, 13.84. m.p. = 107°C.

[Copper•1₂]PF₆ complex (4b)—350 mg (1.58 mmol) of **1** in 15 mL of THF was added to a suspension of 295 mg (0.79 mmol) of [Cu(CH₃CN)₄]PF₆ in 10 mL of THF. Slow evaporation yielded dark-blue diffracting crystals and dark-blue powder. The powder was washed with hexanes and collected by filtration followed by a deionized H₂O wash and another hexane wash, dried in vacuo yielding overall 507 mg of a dark blue solid (98%). ¹H NMR (CDCl₃ δ -7.26 ppm, 500 MHz) 8.048 (d, 2H J = 3.0 Hz), 7.641 (t, 1H J = 2.9 Hz), 7.500 (t, 2H J = 3.1 Hz), 4.316 (q, 2H J = 2.9 Hz), 4.132 (q, 2H J = 2.9 Hz), 1.518 (dt, 6H J = 2.9, 2.0 Hz). ¹³C NMR (CDCl₃ δ -77.00 ppm, 125 MHz) 186.42, 150.65, 136.34, 130.42, 126.34, 51.03, 48.91, 14.94, 10.77. FT-IR (cm⁻¹) – 2978, 1522, 1419, 1148, 1075, 768, 678. Anal Calcd for C₂₂H₃₀CuF₆N₆PS₂: C 40.58; H, 4.64; N, 12.91. Found: C, 41.39; H, 5.016; N, 12.13. m.p. = 123°C.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Solid-state structure of ATF Ligand **1** with hydrogens omitted for clarity and thermal ellipsoids are displayed at 50% probability.

Figure 2. Reductive pathways and frontier molecular orbitals of **1** (HOMO), rotated transition state **1**^{*} (HOMO), $[1^{\bullet}]^{1-}$ (SOMO), and $[1^{**}]^{2-}$ (HOMO).

Figure 3.
Solid-state structure of **3a** $[(\text{Copper}\cdot\mathbf{1}(\mu\text{-Br}))_2]$ with hydrogens omitted for clarity and thermal ellipsoids displayed at 50% probability.

Figure 4.

Solid-state structure of **4b** [Cu₁₂]PF₆ with hydrogens and the PF₆ counterion omitted for clarity; thermal ellipsoids displayed at 30% probability. The solid-state structure including the PF₆ ion can be found in the ESI.

Scheme 1.

Coordination complexes from mixing ligand **1** with copper sources. Previous studies by Bechgaard and Krebs found structure **2** from $\text{Cu}(0)$ wire while Cu(I) salts generated structures **3** and **4**.

Table 1
Selected Bond Distances and Angles for the Crystal Structure and Computational oxidation states of **1**.

Bond Length	Crystal	Computed	Transition State 1*	Singly Reduced (1 ⁺) ¹⁻	Doubly Reduced (1 ²⁺) ²⁻
N(3)-C(7)	1.322 Å	1.345 Å	1.356 Å	1.396 Å	1.455 Å
C(7)-S(1)	1.662 Å	1.669 Å	1.671 Å	1.720 Å	1.774 Å
C(7)-N(2)	1.440 Å	1.426 Å	1.448 Å	1.357 Å	1.302 Å
N(2)-N(1)	1.244 Å	1.255 Å	1.254 Å	1.329 Å	1.391 Å
Bond Angles					
N(3)-C(7)-S(1)	127.6°	127.8°	125.1°	120.2°	116.1°
S(1)-C(7)-N(2)	117.8°	117.3°	125°	128.1°	130.9°
N(3)-C(7)-N(2)	114.3°	114.6°	109.9°	111.7°	112.9°
Dihedral of SCNN	82.4°	84.14°	0.7°	-4.7°	-3°
Dihedral of PhNN	-9.9°	8.4°	-0.4°	-0.5°	0.3°