

Preparation and Coordination Complex of the First Imine-Bridged Tetrathiafulvalene–Pyridine Donor Ligand

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Received November 27, 2006

The first imine-bridged pyridyltetrathiafulvalene building block (TTF–CH=N–Py, **1**) has been synthesized via the Schiff base condensation of formyltetrathiafulvalene and 2-aminopyridine. The preparation, X-ray crystal structure, electrochemical and magnetic characterization of a 1:1 copper complex [Cu^{II}(hfac)₂(TTF–CH=N–Py)] (**2**) are reported. The crystal structure reveals that the imine N atom participates in chelation to the paramagnetic center, thus making this ligand an attractive precursor for the assembly of π -d systems.

Charge-transfer (CT) salts based on tetrathiafulvalene (TTF) derivatives have been widely investigated since the discovery of the first organic metal TTF–TCNQ (TCNQ: tetracyanoquinodimethane).^{1,2} One challenge, however, remaining at the forefront of solid-state chemistry is the realization of a dual-property material for which there is interplay between two or more physical properties such as magnetic interactions and electrical conductivity.³ In order to address this challenge, one strategy is to target systems for which d-electron spins are connected to donor π electrons via linkers or bonds.⁴ In this respect, a CT phase transition has been observed in a 2:1 complex of a thiazyl radical and a cobalt dithiolene complex. The close spatial proximity of the thiazyl radical together with the metallic center is responsible for the enhancement of π -d interactions and the observed bistability in this system.⁵

In recent years, we have developed a synthetic strategy to covalently append binding sites onto TTF donors, targeting dual-property electronic and magnetic materials.⁶ In retro-

spect, however, it is clear that although one could introduce d electrons into these systems and exploit the coordination chemistry, for targeting strong π -d interactions, two problems exist: (i) the paramagnetic centers are far from the organic donor radicals and (ii) the compounds have a large degree of conformational flexibility, making it difficult to control their organization in the solid state. In order to address this problem, we have turned our attention to investigate more rigid conjugated linkers. In this respect, we have chosen an imine bridge because it has a N atom that can participate in coordination to a metal ion, bringing the paramagnetic center closer to the organic π system and thus favoring stronger π -d interactions in the solid state.

We report herein the synthesis and characterization of TTF–CH=N–Py (**1**), a new electroactive building block for the assembly of dual-property materials. It contains a TTF unit that can be oxidized, chemically or electrochemically, to provide a source of conducting electrons and a pyridine ligand attached by a conjugated imine bridge, affording a bidentate binding site for the chelation of transition-metal ions carrying a localized spin. The synthesis of this ligand involves the Schiff base condensation of formyltetrathiafulvalene, together with commercially available 2-aminopyridine (Scheme 1). The ¹H NMR spectrum of compound **1** exhibits a resonance at 9.10 ppm for the imine CH proton. The IR absorption band of the imine is clearly visible between 1536 and 1582 cm⁻¹, and a molecular ion peak is observed in the electron impact mass spectrum at *m/z* 309. This methodology opens up the possibility for

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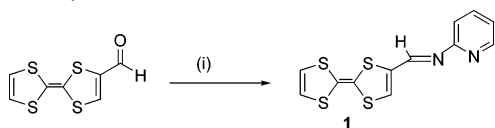
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Scheme 1. Synthetic Route to **1**^a



^a Reagents and conditions: 2-aminopyridine, CH₂Cl₂, 24 h, reflux, 4 Å molecular sieves.

studying the magnetic and electronic interactions of a new family of substituted TTF ligands bearing a diverse range of imine-bridged binding sites and substitution patterns. The reaction of 1 equiv of Cu^{II}(hfac)₂ (hfac = hexafluoroacetylacetonate) with 2 equiv of **1** afforded the 1:1 coordination complex [Cu^{II}(hfac)₂(TTF-CH=N-Py)] (**2**).

Formyltetrathiafulvalene (0.255 g, 1.2 mmol) and 2-aminopyridine (0.110 g, 1.2 mmol) were dissolved in CH₂Cl₂ (50 mL) containing activated 4 Å molecular sieves. After refluxing for 24 h, the solution was filtered over a pad of Celite to afford **1** as a red-purple solid. Yield: 0.280 g, 76%. Mp: 140 °C. ¹H NMR (acetone-*d*₆, 300 MHz): δ 9.10 (s, 1H), 8.46 (d, 1H), 7.87 (t, 1H), 7.34 (s, 1H), 7.30 (m, 2H), 6.68 (s, 2H). ¹³C NMR (acetone-*d*₆, 75 MHz): δ 159.6, 152.9, 148.9, 138.6, 138.4, 133.4, 122.6, 120.8, 119.7, 119.4, 113.2, 107.0. IR (KBr): ν 3022, 1597, 1582, 1555, 1536, 1459, 1430 cm⁻¹. LSIMS: *m/z* 309 (MH⁺, 100%).

Cu(hfac)₂·2H₂O (0.041 g, 0.075 mmol) was added to a solution of **1** (0.046 g, 0.150 mmol) in CH₂Cl₂ (10 mL). The solution was stirred at room temperature for 2 h, after which time pentane (20 mL) was added to precipitate the complex. The solid was washed with pentane (50 mL) and dried to afford **2** as a blue-violet powder. Yield: 0.040 g, 59%. Small black plates suitable for X-ray crystallography were grown via slow evaporation of a pentane–dichloromethane solution. IR (KBr): ν 3070, 1667, 1645, 1590, 1555, 1530, 1495, 1472, 1435 cm⁻¹. FABMS: *m/z* 785 (M⁺, 10%). Anal. Calcd for C₂₂H₁₀N₂O₄S₄CuF₁₂: C, 33.61; H, 1.28; N, 3.56. Found: C, 33.63; H, 1.18; N, 3.52.

Variable-temperature magnetic susceptibility data were collected on a powdered sample of **1** with the use of a Quantum Design SQUID magnetometer in an applied field of 1000 G between 2 and 300 K. Data were corrected for both sample diamagnetism (Pascal's constants) and the sample holder.

Intensity data were collected at 173 K on a Stoe Mark II image-plate diffraction system using Mo Kα graphite-monochromated radiation:⁷ image-plate distance = 100 mm, ω rotation scans = 0–180° at φ = 0° and 0–33° at φ = 90°, step Δω = 1.0°, with an exposure time of 4 min per image, 2θ range = 2.29–59.53°, and *d*_{min}–*d*_{max} = 17.779–0.716 Å. The structure was solved by direct methods using the program *SHELXS-97*.⁸ The refinement and all further calculations were carried out using *SHELXL-97*.⁹ The H atoms were included in calculated positions and treated as riding atoms using *SHELXL* default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on *F*².

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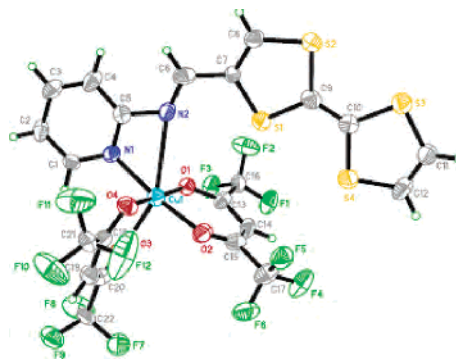


Figure 1. ORTEP¹¹ view of the molecular structure of **2** with the labeling scheme (thermal ellipsoids are plotted at 30% probability).

Table 1. Crystal Data for Complex **2**

empirical formula	C ₂₂ H ₁₀ CuF ₁₂ N ₂ O ₄ S ₄
fw	786.10
<i>T</i> , K	173
λ, Å	0.710 73
space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.0069(5)
<i>b</i> , Å	23.6983(15)
<i>c</i> , Å	10.9874(5)
α, deg	90
β, deg	91.538(15)
γ, deg	90
<i>V</i> , Å ³	2865.0(3)
<i>Z</i>	4
ρ _{calcd} , g cm ⁻³	1.823
μ, mm ⁻¹	1.166
<i>R</i> (<i>F</i> ²)	0.0427
<i>R</i> _w (<i>F</i> ²)	0.0912

The crystallographic data for compound **2** are summarized in Table 1. The X-ray data were collected at 173 K from a single crystal. The molecule crystallizes in the monoclinic space group *P*2₁/*c*. The asymmetric unit contains one molecule of **2**. As is often observed for hfac ligands, one of the CF₃ groups is disordered. The molecular structure of **2** is shown in Figure 1. The crystal structure reveals that the complex is mononuclear with two hfac ligands and one TTF ligand chelated to the metal ion. This is in contrast to previously reported TTF–pyridine complexes, which because of the monodentate nature of their binding sites form 2:1 octahedral complexes with M^{II}(hfac)₂ or M^{II}(acac)₂ salts.¹⁰

The Cu^{II} salt adopts a distorted octahedral geometry. It is bonded in the equatorial plane to three O atoms of two bidentate hfac ligands, O1, O2, and O4, and the N1 atom of the pyridine ring. The imine N2 atom and one hfac O atom (O3) are axial to one another and complete the octahedral coordination geometry. A summary of the bond lengths and angles are given in Table 2.

The axial Cu1–O3 distance of 2.1999(19) Å is slightly longer than the three equatorial Cu–O distances that range from 1.9474(17) to 1.9737(18) Å. The bond angles around the equatorial plane are in the range of 85.31(2)–95.53(8)°.

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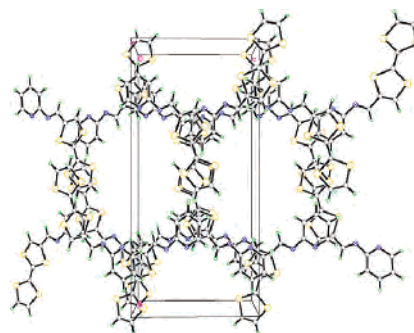
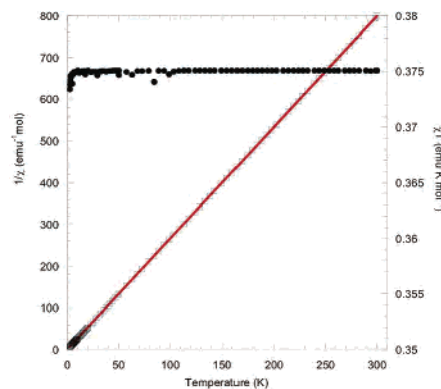
Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complex **2**

Cu1–O1	1.9737(18)	O1–Cu1–O2	91.06(7)
Cu1–O2	1.9474(17)	O1–Cu1–O3	95.72(7)
Cu1–O3	2.1999(19)	O1–Cu1–O4	173.58(7)
Cu1–O4	1.9735(18)	O1–Cu1–N1	95.33(8)
Cu1–N1	1.9938(19)	O1–Cu1–N2	81.68(7)
Cu1–N2	2.690(2)	O2–Cu1–O3	93.36(7)
C9–C10	1.343(3)	O2–Cu1–O4	85.31(7)
C7–C8	1.348(4)	O2–Cu1–N1	167.61(8)
C11–C12	1.322(5)	O2–Cu1–N2	115.38(7)
		O3–Cu1–O4	89.79(7)
		O3–Cu1–N1	96.55(8)
		O3–Cu1–N2	151.12(7)
		O4–Cu1–N1	87.29(8)
		O4–Cu1–N2	95.08(7)
		N1–Cu1–N2	55.43(7)

The imine N atom forms a longer bond to the Cu, where the Cu1–N2 distance is 2.690(2) Å. The Cu1–N1 bond length is consistent with previously reported data for pyridine N–Cu distances.¹⁰ The small 1,3 bite angle of the pyridyl–imine forces the N3–Cu1–O3 bond angle to deviate significantly from linearity by ca. 30°. The central C=C bond length of the TTF core is 1.343(3) Å and is within the range for a neutral donor. The ligand is almost planar, with the largest deviation from planarity being 0.3821 Å for S3. The packing of the neutral donor is unusual in that the TTF donors stack to form a hexagonal arrangement that runs along the *b* axis of the unit cell (Figure 2). The S⋯S distances between TTF ligands in neighboring stacks are 11.007 Å. The cavities formed by this packing arrangement are filled by two Cu(hfac)₂ units. The shortest intermolecular S⋯S distance is 3.810 Å between S3 and S4 atoms of neighboring molecules, which is shorter than the S⋯S distance (3.955 Å) reported previously for the *trans*-Cu(hfac)₂(TTF–Py)₂ coordination complex.^{10a}

The redox properties of ligand **1** and complex **2** were determined by cyclic voltammetry.¹² For both compounds, two reversible single-electron oxidation waves were observed. The E_{ox}^1 and E_{ox}^2 values are 490 and 880 mV for **1** and 530 and 900 mV for **2**. These waves correspond to the formation of the radical cation and dication of TTF, respectively, and are anodically shifted in comparison with the potentials measured for the parent TTF (380 and 770 mV).¹² The electron-withdrawing nature of the pyridine ring via the conjugated bridge makes oxidation of the TTF core more difficult for ligand **1**. Complexation to the Cu^{II} ion enhances the electron-accepting ability of the pyridine ring even further, which, in turn, causes the decrease in the electron density in the TTF core, resulting in larger positive shifts of E_{ox}^1 and E_{ox}^2 when compared to both the uncomplexed ligand and unsubstituted TTF. Similar shifts have been reported for TTF– π -pyridine derivatives complexing Pb^{II} ions.¹³ Figure 3 shows the magnetic behavior of **2** in an applied field of 1000 G in the form of $1/\chi$ vs T (open squares) and χT vs T (closed circles).

The susceptibility of the sample rises monotonically as the temperature decreases following a typical Curie–Weiss behavior, from which the Curie constant C could be determined. The presence one Cu^{II} per molecule is confirmed by a Curie constant of 0.372 emu K mol^{−1} (0.375 is expected for one $S = 1/2$ and $g = 2$) and a very small value for the

**Figure 2.** Packing view of **2** along the *b* axis. Cu(hfac)₂ units are omitted for clarity.**Figure 3.** $1/\chi$ vs T (open squares) with fits to the Curie–Weiss law (red solid line) and χT vs T (closed circles) for compound **2**.

Weiss constant (−0.01 K), as expected for a nearly perfect paramagnetic system with very weak antiferromagnetic interactions between the centers.

The synthesis and characterization of a new imine-bridged TTF–pyridine donor ligand, together with its first coordination complex **2**, have been reported. In this complex, the TTF is neutral and therefore the magnetic properties reveal a paramagnetic behavior corresponding to isolated $S = 1/2$ spins of the Cu^{II} centers. Chemical and electrochemical oxidation of this complex to prepare radical-cation salts is currently under investigation in our group. The rationale of using a conjugated linker that can also participate in chelation to the metal ion constitutes an alternative approach for targeting π –d interactions in dual-property conducting and magnetic molecule based materials.

Acknowledgment. This work was supported by NSERC, CRC (Tier II Chair, M.P.), PREA, Brock University (International Seed Funds), and the MEC (Ramon y Cajal research contract to A.A.).

Supporting Information Available: X-ray crystallographic file in CIF format and magnetization vs field plot for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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