Inorg. Chem. **2001,** *40,* 6541−6542

Cu^{II} Coordination Complex Involving TTF-py as Ligand

Fumiyasu Iwahori,† Stéphane Golhen,† Lahcène Ouahab,*,† Roger Carlier,‡ and Jean-Pascal Sutter§

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Institut de Chimie de Rennes, Université de Rennes 1, 35042 Rennes Cedex, France, Laboratoire de Synthèse et Electrosynthèse Organiques, UMR CNRS 6510, Institut de Chimie de Rennes, Université de Rennes 1, 35042 Rennes Cedex, France, and Laboratoire des Sciences Moléculaires, ICMCB, UPR CNRS 9048, 33608 Pessac, France

Received June 12, 2001

Intense investigations are devoted to multifunctional molecular materials both from a fundamental point of view and as active elements in devices. In particular, the synthesis of materials exhibiting synergy between electrical conductivity and magnetic interactions is currently a subject of intensive studies. The goal here is to induce long-range magnetic coupling between localized spins through mobile electrons of the conducting networks (π-electrons).[1−6] The localized spins can be borne by organic radicals[6] targeting all organic materials or by transition metals (d electrons) targeting hybrid organic/inorganic compounds involving the so-called π−d interactions. Many compounds of this kind were obtained and characterized,[1−5] but most of them show a sort of dilemma between the two properties giving rise to the following situations: (i) A superconducting state was stabilized with paramagnetic anions in $(BEDT\text{-}TTF)_4[(H_3O)Fe(C_2O_4)_3]C_6H_5CN$ ($T_c = 8.5$ K)[1a,b] and in $(BETS)_2(FeCl_4)_{0.5}(GaCl_4)_{0.5}$ ($T_c = 4.6$ K)[2] (BETS = bis(ethylenedithio)tetraselenafulvalene). (ii) A metallic state coexists with ferromagnetism in $(BEDT\text{-}TTF)_3[MnCr(C_2O_4)_3]$, the structure of which contains two completely independent metallic and ferromagnetic sublattices.[3] (iii) Magnetic interactions were found in some insulating TTF-derivative salts but not mediated by the conducting electrons.[1d] The achievement of π−d interaction has two important prerequisites, namely, a good conducting organic network and strong interactions between the conducting and the localized-spin systems. To satisfy these conditions, we are investigating materials where the two systems are covalently linked through a conjugated bridge which might enable magnetic exchange interactions between the localized spins and the mobile electrons. Taking advantage of the ability of the pyridine-based organic ligands to coordinate transition metals, we prepared the new Cu^{II} coordination complex formulated as $Cu(hfac)_2(TTF\text{-}py)_2$ (hfac = hexafluoroacetylacetonate; TTF-py = 4-(2-tetrathiafulvalenyl-ethenyl)pyridine). We report here its synthesis, X-ray crystal structure, and electrochemical properties.

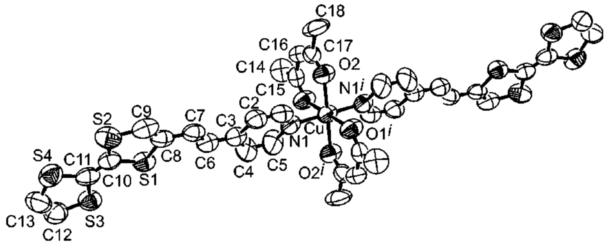

Figure 1. Molecular structure (50% thermal ellipsoids) of *trans*-$Cu(hfac)_2(TTF\text{-}py)_2$. Hydrogen and fluorine atoms are omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Cu(1)−O(1) 2.256(5), Cu(1)−O(2) 2.018(5), Cu(1)−N(1) 2.031(7), S(1)−C(8) 1.756(7), S(1)−C(10) 1.773(8), S(2)−C(9) 1.732(9), S(2)−C(10) 1.754(7), S(3)−C(12) 1.723(9), S(3)−C(11) 1.765(7), S(4)−C(13) 1.724(10), S(4)−C(11) 1.760(8), N(1)−C(1) 1.343(9), N(1)−C(5) 1.351(9), O(2)−C(17) 1.245(8), C(3)−C(6) 1.445(11), C(6)−C(7) 1.319(10), C(7)−C(8) 1.428(10), C(8)−C(9) 1.349(10), C(10)−C(11) 1.317(10), C(12)−C(13) 1.295(13), O(2)−Cu(1)−N(1) 89.9(2), O(2)−Cu(1)−O(1) 88.3(2), N(1)−Cu(1)−O(1) 91.0(2), C(8)−S(1)−C(10) 96.3(3), C(9)−S(2)−C(10) 95.0(4), C(12)−S(3)−C(11) 94.9(4), C(13)−S(4)−C(11) 94.2(4).

TTF-py was synthesized as described in the literature.[7] To a stirred solution of $Cu(hfac)_2{\cdot}H_2O$ (14.1 mg, 0.028 mmol) in boiling *n*-hexane was added TTF-py (19.3 mg, 0.063 mmol) in hot *n*-hexane, and the stirring continued for 10 min. The solution was cooled and kept standing at 4 °C for several days. Microcrystals of *trans*-$Cu(hfac)_2(TTF\text{-}py)_2$ were separated from the mixture. X-ray-quality wine-red single crystals of *trans*-$Cu(hfac)_2(TTF\text{-}py)_2$ were obtained by slow diffusion of *n*-hexane into a dichloromethane solution, and the X-ray structure was solved from data collected at 223 K (Figure 1).[8]

As usually observed for hfac ligand, large thermal coefficients together with residual peaks are found for the fluorine atoms, suggesting high thermal motion and/or positional disorder for these atoms. The crystal structure (Figure 2a) consists of alternate layers of organic (TTF-py) and inorganic $[Cu(hfac)_2]$ parts linked by conjugated bridges. The Cu atom lies on a center of symmetry and adopts a distorted octahedral coordination geometry. It is bonded in the equatorial plane to two bidentate hfac anions through their oxygen atoms with Cu−O bond lengths of 2.018(5) and 2.256(5) Å. The TTF-py ligands occupy the apical positions and are trans to each other; they are bonded to the metal atom through the nitrogen atoms of the pyridyl ring with a Cu−N bond length of 2.031(7) Å. The bond lengths and bond angles of the TTF-py moiety are close to those reported for the noncoordinated neutral unit,[7] indicating that the TTF-py ligand is neutral. Additionally, using the empirical correlation between C=C and

---

* To whom correspondence should be addressed. E-mail: ouahab@univ-rennes1.fr.

† UMR CNRS 6511.

‡ UMR CNRS 6510.

§ UPR CNRS 9048.

(1) (a) Turner, S. S.; Day, P.; Malik, K. M. A.; Hursthouse, M. B.; Teat, S. J.; MacLean, E. J.; Martin, L.; French, S. A. *Inorg. Chem.* **1999**, *38*, 3543. (b) Graham, A. W.; Kurmoo, M.; Day, P. *J. Chem. Soc., Chem. Commun.* **1995**, 2061. (c) Day, P.; Kurmoo, M.; Mallah, T.; Marsden, I. R.; Friend, R. H.; Platt, F. L.; Hayes, W.; Chasseau, D.; Gaultier, J.; Bravic, G.; Ducasse, L. *J. Am. Chem. Soc.* **1992**, *114*, 10722. (d) Turner, S. S.; Le Pevelen, D.; Day, P.; Prout, K. *J. Chem. Soc., Dalton Trans.* **2000**, 2739.

(2) (a) Kobayashi, H.; Kobayashi, A.; Cassoux, P. *Chem. Soc. Rev.* **2000**, *29*, 325. (b) Kobayashi, A.; Udagawa, T.; Tomita, H.; Naito, T.; Kobayashi, H. *Chem. Lett.* **1993**, 2179. (c) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368.

(3) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J. *Nature* **2000**, *408*, 447.

(4) Enoki, T.; Umeyama, T.; Enomoto, M.; Yamaura, J.; Yamaguchi, K.; Miyazaki, A.; Ogura, E.; Kuwatani, Y.; Iyoda, M.; Kikuchi, K. *Synth. Met.* **1999**, *103*, 2275.

(5) Ouahab, L. *Chem. Mater.* **1997**, *9*, 1909.

(6) Sugawara, T. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 257.

(7) Andreu, R.; Malfant, I.; Lacroix, P. G.; Cassoux, P. *Eur. J. Org. Chem.* **2000**, 737.

10.1021/ic015550s CCC: $20.00

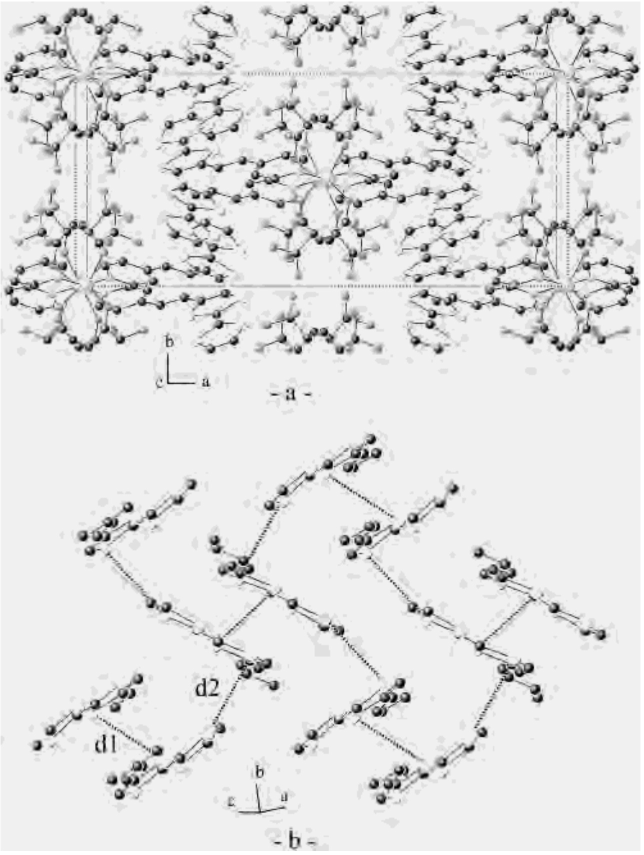

Figure 2. Crystal structure of *trans*-Cu(hfac)$_2$(TTF-py)$_2$: (a) projection in the *ab* plane showing alternate layers of organic and inorganic entities linked by conjugated bridge; (b) structure of the organic part showing shortest S$\cdots$S contacts, d1 = 3.955(4) Å, d2 = 4.057(3) Å.

C−S bond lengths,[9] the calculated charge on the central TTF core is found equal ca. +0.05. In the organic sublattice (Figure 2b) the TTF-py molecules form orthogonal dimers, the shortest S$\cdots$S contact being equal to 3.955(4) Å. This packing is reminiscent of what is usually observed for conducting radical-ion salts containing organic donors and inorganic anions. Therefore, it is favorable for electrical conductivity.

In this complex the two TTF moieties are neutral, and therefore, as expected, an insulating behavior is found from the electrical conductivity measured on a single crystal. The magnetic properties measured on a SQUID magnetometer in the temperature range 5−300 K revealed a paramagnetic behavior corresponding to isolated $S = {}^1/_2$ spins of the Cu^{II} centers.

The complex was investigated by using thin layer cyclic voltammetry (TLCV). Contrary to conventional cyclic voltammetry, in TLCV the number of electrons involved in each oxidation step is directly obtained by integration of the voltammetric peaks and comparison with the standard peak of dichloronaphthoquinone.[10] The TLCV response of the title compound shows two successive reversible oxidation steps at 0.42 and 0.83 V. The integration of the oxidation peaks revealed that each of these peaks is in good agreement with a value of 2 F mol^{-1}, which corresponds to twice the molar value for TTF fragments. This result indicates that two independent TTF-py ligands were simultaneously oxidized in a one-electron process. It is noteworthy that this complex is stable on the oxidation side, thereby allowing further reaction, i.e., partial oxidation of the TTF part without destroying the complex. The oxidation of crystals after several hours of exposure in iodine vapor led to a black powdered compound which is under characterization.

In summary, we synthesized a new transition-metal complex containing organic donors as ligands covalently linked through π-conjugated bridges. The crystal structure and electrochemical properties are appropriate for its potential use as a molecular brick for conducting and magnetic materials. A chemical and/or electrochemical partial oxidation of the complex is under current investigation in our group. This work opens the way for the synthesis and study of analogous coordination complexes using other paramagnetic transition metals and also other functionalized TTF derivatives and might constitute a new approach for π−d interactions in bifunctional conducting and magnetic molecular materials.

Acknowledgment. This work is supported by the Ministère de l'Education Nationale, de la Recherche et de la Technologie (MENRT), CNRS and NEDO. F.I. thanks the MENRT for a postdoctoral grant.

Supporting Information Available: An X-ray crystallographic file in CIF format and a thin layer cyclic voltammogram. This material is available free of charge via the Internet at http://pubs.acs.org.

IC015550S

---

(8) Crystal data for *trans*-Cu(hfac)$_2$(TTF-py)$_2$: $M = 1092.61$, monoclinic, space group $C2/c$ (No.15), $a = 26.7213(12)$ Å, $b = 11.1561(7)$ Å, $c = 15.5802(8)$ Å, $\beta = 107.926(4)°$, $V = 4419.1(4)$ Å^3, $Z = 4$; $D_c = 1.642$ g·cm^{-3}; $T = 223$ K, μ(Mo Kα) = 0.964 mm^{-1}, Nonius KappaCCD; 8770 reflections were collected with 5029 unique and 2264 with $I > 2.0\sigma(I)$ yielding $R = 0.0813$, $R_w = 0.2226$, GOF = 1.032. The structure was solved by direct methods and refined using SHELXS-97 and SHELXL-97 programs, respectively. H atoms were included in the final structure using the appropriate riding model.

(9) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973.

(10) (a) Hubbard, A. T.; Anson, F. C. *Electroanal. Chem.* **1970**, *4*, 129. (b) Carlier, R.; Frère, P.; Sallé, M.; Roncali, J.; Jubaut, M.; Tallec, A.; Gorgues, A. *Adv. Mater.* **1993**, *5*, 445. (c) Frère, P.; Carlier, R.; Boubekeur, K.; Gorgues, A.; Roncali, J.; Tallec, A.; Jubault, M.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2071.