Contents lists available at ScienceDirect

# Physica B



journal homepage: www.elsevier.com/locate/physb

# Syntheses of new TTF-based metal complexes for conducting and magnetic systems: Schiff base-type metal complex with partially oxidized TTF moiety

## H. Nishikawa<sup>\*,1</sup>, H. Oshima, K. Narita, H. Oshio

Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan

#### ARTICLE INFO

Keywords: TTF-based ligand Schiff base Metal complex with TTF Electrical conductivity Magnetic conductor Charge transfer complex

## ABSTRACT

New TTF-based ligands (TTF=tetrathiafulvalene) with Schiff base-type coordination sites have been synthesized: 4,5-bis(4-salicylideneiminophenyl)-4',5'-ethylenedithio-TTF (**1a**), 4,5-bis(4-picolinideneiminophenyl)-4',5'-ethylenedithio-TTF (**1b**), and 4-(2-salicylideneiminoethylthio)-5-methyl-4',5'-ethylenedithio-TTF (Hsae-TTF). X-ray crystallography for **1a** revealed that **1a** has rigid structure around the coordination sites, which prevents it to form metal complexes. On the other hand, Hsae-TTF ligand has flexibility around its coordination sites due to alkyl chain spacer, and gave mononuclear complexes with Ni(II) and Cu(II) ions, [M<sup>II</sup>(saeTTF)<sub>2</sub>] (M<sup>II</sup>=Ni(II) and Cu(II)). The metal ions in [M<sup>II</sup>(saeTTF)<sub>2</sub>] have a square planar coordination structure with two TTF-based ligands, which was sandwiched by two neutral TTF moieties. The Cu(II) complex, [Cu<sup>II</sup>(saeTTF)<sub>2</sub>], yielded charge transfer (CT) complexes with acceptors such as F<sub>4</sub>TCNQ, DDQ, and iodine. CT complexes with F<sub>4</sub>TCNQ and iodine were semiconductive, but that with DDQ was insulator. This is due to the difference of the degree of charge transfer; TTF moiety in F<sub>4</sub>TCNQ salt was partially oxidized but that of DDQ salt was completely oxidized. The radical cation salts of [Cu<sup>II</sup>(saeTTF)<sub>2</sub>] with PF<sub>6</sub> anion was also obtained in 1:1 donor and anion ratio by electrocrystallization. The donor and anion ratio indicates that the oxidation state of TTF moieties in the radical salt, [Cu<sup>II</sup>(saeTTF)<sub>2</sub>]PF<sub>6</sub>, was partial oxidation state.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Multifunctional properties in molecular magnetic conductors, such as paramagnetic superconductor or magnetic field induced superconductivity, have their origin in the interaction between conduction electrons and localized spins [1-7]. In such molecular based materials, organic  $\pi$ -donor molecules usually bear the electrical conduction and inorganic counter anions involving paramagnetic metal ions the magnetism, thus they are generally referred as  $\pi$ -d systems. Interaction between conduction electrons and localized spins in the  $\pi$ -d systems is usually weak, because they are constructed with two component molecules: tetrathiafulvalene (TTF) derivatives and counter anions with paramagnetic metal ions. In order to develop new materials with stronger interaction, a large number of researches for the synthesis of TTF derivatives possessing a direct coordination site to paramagnetic metal ions and their corresponding metal complexes have been conducted [8]. However, the TTF moieties of most of the complexes are in the neutral states, and very few

E-mail address: nishikaw@chem.tsukuba.ac.jp (H. Nishikawa).

examples have completely or partially oxidized TTF moieties. The complexes with oxidized TTF units showed magnetic properties originating from the TTF<sup>+</sup> radical cation, but complete oxidation leads to the low electrical conductivity [9,10]. On the other hand, the Cu(II) complex with the TTF-based ligand having ethenylpyridine as a coordination site reported by Setifi et al. possesses partially oxidized TTF moieties, but the charge on the TTF sites disproportionate to neutral and cation radical, leading to the insulating property [11]. Recently, Ichikawa et al. reported the Cu(I) complex coordinated by partially oxidized pyradine-annulated STF (diselenadithiafulvalene) and relatively high electrical conduction [12]. Thus, it is important for yielding the metal complexes with TTF-based ligands with high electrical conductivity to oxidize the TTF moieties partially.

In order to obtain the TTF-based metal complexes with partial oxidation state, we have prepared several TTF-based ligands involving Schiff base-type coordination sites. Schiff base ligands can coordinate to metal ions by chelate structure, which is expected to stabilize metal complexes upon oxidation through relatively strong coordination bonds. In this context, we prepared new TTF-based ligands with Schiff base coordination site, **1a–b** and Hsae-TTF. While the ligand **1a** and **1b** are derived from bis(4-aminophenyl)-4',5'-ethylenedithio-TTF, therefore they may act as tetradentate ligands, Hsae-TTF possesses one Schiff base coordination site leading to bidentate coordination. In this paper, we



<sup>\*</sup> Corresponding author. Tel./fax: +81 29 8534426.

<sup>&</sup>lt;sup>1</sup> Present address: Department of Chemistry, Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan.

<sup>0921-4526/\$ -</sup> see front matter  $\circledcirc$  2009 Elsevier B.V. All rights reserved. doi:10.1016/j.physb.2009.11.084

will report the syntheses, crystal structure of the Schiff base-type TTF-ligand and their metal complexes. The preparation and physical properties including electrical conductivity of CT complexes and radical salt based on Cu(II) complex with Hsae-TTF ligand are also disclosed.

#### 2. Experimental detail

#### 2.1. Syntheses of TTF-based ligands 1a and 1b

Syntheses of TTF-based ligands **1a** and **1b** were carried out as shown in Scheme 1. 2-Chloro-1,2-bis(4-nitrophenyl)ethanone (**2**) was prepared by the reported procedure [13]. Ethanone **2** was converted to **3** by the reaction with sodium O-isopropyl xanthate in 83% yield, which was treated with  $H_2SO_4$  to give ketone **4** according to the method reported previously [14]. Cross-coupling reaction of ketone **4** and 4,5-ethylenedithio -1,3-dithiole-2-thione using trimethylphosphite in toluene gave TTF derivative **5**. Reduction of **5** with tin dichloride in ethyl acetate provided amino derivative **6** in 52% yield. TTF derivative **6** was reacted with salicylaldehyde and picolinaldehyde to give the corresponding Schiff base-type TTF-ligands **1a** and **1b**, respectively.

#### 2.2. Synthesis of Hsae-TTF and its corresponding metal complexes

Synthesis of Hsae-TTF was performed according to the synthetic route shown in Scheme 2. The cyanoethyl-protected TTF derivative **7** [15] was converted to TTF derivative **8** by deprotection with cesium hydroxide, followed by treatment with BOC-protected 2-bromoethylamine in 70% yield. The BOC-protected TTF **8** was deprotected by trifluoroacetic acid to give aminoethyl-TTF **9** in qualitative yield, which was reacted with salicylaldehyde to give the corresponding Schiff base-type TTF-ligand, Hsae-TTF, in 89% yield.

Metal complex with Hsae-TTF,  $[M^{II}(saeTTF)_2]$   $(M^{2+}=Ni^{2+}, or Cu^{2+})$ , was synthesized by the addition of methanol solution of nickel or copper chloride to dichloromethane solution of Hsae-TTF in the presence of triethylamine.

#### 2.3. X-ray crystallography

Diffraction data were collected at 293 K on a Bruker SMART APEX diffractometer fitted with a CCD type area detector, and a full sphere of data were collected using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$ =0.71073 Å). Total reflections collected were 8111 and 3563 of which independent reflections were 5843 (R(int)=0.1357) and 3217 (R(int)=0.0137) for **1a** and [Ni<sup>II</sup>(saeTTF)<sub>2</sub>],



respectively. The structure was solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELEX 5.1 package (Bruker Analytical X-ray Systems). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those the parent atoms.

Crystal data for **1a**:  $C_{34}H_{24}N_2O_2S_6$ , F. W.=684.91, red plate, triclinic, space group P1,  $\alpha$ =11.846(5), b=12.034(5), c=12.135(5)Å,  $\alpha$ =81.399(5),  $\beta$ =64.420(5),  $\gamma$ =77.270(5)°, V=1519(5)Å<sup>3</sup>, Z=2, R=0.0975, wR=0.1893.

Crystal data for [Ni<sup>II</sup>(saeTTF)<sub>2</sub>]: C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>NiO<sub>2</sub>S<sub>14</sub>, F. W=516.09, orange plate, triclinic, space group PT, *a*=9.731(2), *b*=10.263(2), *c*=11.130(2)Å,  $\alpha$ =109.692(3),  $\beta$ =93.148(3),  $\gamma$ =97.770(2)°, *V*=1031.0(3)Å<sup>3</sup>, *Z*=2, *R*=0.0388, w*R*=0.0996.

#### 2.4. Electrical conductivity and magnetic susceptibility

Temperature dependence of resistivity was measured on compressed pellets for CT complexes of  $[Cu^{II}(saeTTF)_2]$  and on a single crystal for  $[Cu^{II}(saeTTF)_2]PF_6$  by the four probe dc method using gold wire contacted to the samples by carbon paste. Magnetic susceptibility of  $[Cu^{II}(saeTTF)_2]$  was measured for a powder sample in the temperature range of 2–300 K using a superconducting quantum interference device magnetometer

with 10 000 Oe field application. The diamagnetic contribution of  $[Cu^{II}(saeTTF)_2]$  was calculated using Pascal's law.

#### 3. Results and discussions

#### 3.1. Molecular structure of 1a

Fig. 1 shows the molecular structure of 1a. TTF skeleton takes non-planar tub conformation usually seen in the TTF derivatives in neutral states. While the TTF skeleton and salicylideneimino moieties lie in the almost same plane, phenyl groups connecting the Schiff base coordination sites, i.e. salicylideneimino moieties, to the TTF, tilt from the plane made by TTF and salicylidenimino moieties by ca. 50°. In the Schiff base coordination sites, hydrogen bonds exist between phenol group and imino nitrogen. Picolinaldehyde derivative **1b** is expected to have similar molecular structure. We tried to prepare transition metal complexes using **1a** and **1b**, but any metal complexes could not be obtained. This is probably because the TTF-ligands 1a and 1b have rigid conformation around coordination sites, which prevents the proximity of two intramolecular N, O-bidentate chelate sites and complexation to metal ions with these intramolecular coordination sites. Recently, Liu et al. reported Cu(II) and Ni(II) complexes with TTF-based ligands having two Schiff base coordination sites [16]. In this case, Schiff base moieties are placed on the ortho position of phenyl group which



Fig. 1. Molecular structure of 1a: (a) top view and (b) side view.

is annulated to TTF skeleton directly, and the ligand has optimal conformation for complexation.

#### 3.2. Metal complex coordinated by Hsae-TTF

In order to improve the rigid conformation around coordination sites in **1a** and **1b**, we prepared a new Schiff base-type TTF-ligand, Hsae-TTF, which has flexible structure around coordination site due to the connection of Schiff base coordination site to TTF moiety by alkyl chain spacer. Consequently, Ni(II) and Cu(II) complexes were successfully obtained using this ligand.

Molecular and crystal structures of  $[Ni^{II}(saeTTF)_2]$  were shown in Fig. 2. The complex crystallized in space group P1. Central Ni<sup>2+</sup> ion locates on the inversion center, and adopts an N<sub>2</sub>O<sub>2</sub> configuration from Schiff base moieties, which coordinate to the Ni<sup>2+</sup> ion in square planar geometry with *cis* conformation. The square planar Schiff base coordination site was sandwiched by two neutral TTF moieties as shown in Fig. 2b. Fig. 2c shows crystal structure of  $[Ni^{II}(saeTTF)_2]$ , where Ni complexes form onedimensional arrays along *a*-axis. Within the array, sulfur–sulfur contacts shorter than the sum of van der Waals radii (3.70 Å) exist.

The redox potentials of  $[M^{II}(\text{saeTTF})_2]$  ( $M^{2+}=Ni^{2+}$ , or  $Cu^{2+}$ ) were investigated by cyclic voltammetry in  $CH_2Cl_2$ , and two oxidation wave were observed ( $[Ni^{II}(\text{saeTTF})_2]$ :  $E_1=0.44$  V,  $E_2=0.84$  V (vs. SCE);  $[Cu^{II}(\text{saeTTF})_2]$ :  $E_1=0.45$  V,  $E_2=0.83$  V). The redox potentials of the corresponding ligand, Hsae-TTF, are almost similar to those of the metal complexes ( $E_1=0.43$  V,  $E_2=0.85$  V),

suggesting the oxidation of the metal complexes corresponds to that from TTF moieties and the metal complexes retain the redox ability of TTF.

Fig. 3 shows the temperature dependence of magnetic susceptibility of the neutral complex  $[Cu^{II}(saeTTF)_2]$ . The  $\chi_m T$  value at 300 K was  $0.4162 \text{ emu K mol}^{-1}$ . The magnetic susceptibility was well reproduced by Curie–Weiss law as shown by the solid line in Fig. 3. The least-squares fit is found for the Curie constant  $C=0.3434 \text{ emu K mol}^{-1}$ , which is reasonable for the expected value of  $0.375 \text{ emu K mol}^{-1}$  for g=2.0 and S=1/2 system, and Weiss temperature  $\theta = -0.466 \text{ K}$ .

# 3.3. Charge transfer complexes and radical cation salt of [Cu<sup>II</sup>(saeTTF)<sub>2</sub>]

Charge transfer (CT) complexes were prepared by diffusion method of  $CH_2Cl_2$  solution of  $[Cu^{II}(saeTTF)_2]$  and acceptor molecule. We tried five acceptors: 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), 2,3,5,6-tetrafluoro-TCNQ (F<sub>4</sub>TCNQ), chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and iodine. Among them, F<sub>4</sub>TCNQ, DDQ, and iodine provided CT complexes as black powder. Ratios of donor to acceptor of CT complexes were determined by elemental analyses and summarized in Table 1. Temperature dependence of resistivity was shown in Fig. 4. While F<sub>4</sub>TCNQ, and iodine salts were semiconductive, DDQ salt was insulator. Room temperature conductivities and activation energies are summarized in Table 1.



Fig. 2. Molecular structure and crystal structure of  $[Ni^{II}(saeTTF)_2]$ : (a) top view of molecular structure, (b) side view and (c) molecular packing motif showing intermolecular short S...S contacts with dotted line.



**Fig. 3.** Temperature dependence of magnetic susceptibility and  $\chi_m T$  of [Cu<sup>II</sup>(saeTTF)<sub>2</sub>]. The solid line is a fit by Curie–Weiss law.

 Table 1

 Conducting behavior of CT complexes based on [Cu<sup>II</sup>(saeTTF)<sub>2</sub>].

Acceptor	D:A	$\sigma$ (295 K) (S cm <sup>-1</sup> )	<i>E</i> <sub>a</sub> (295–200 K) (eV)
F₄TCNQ	2:3	$\begin{array}{c} 1.1\times 10^{-3} \\ 5.0\times 10^{-8} \\ 5.3\times 10^{-3} \end{array}$	0.14
DDQ	1:4		1.01
I	2:7		0.071



Fig. 4. Temperature dependence of resistivity of CT complexes and  $PF_6$  salt of  $[Cu^{II}(saeTTF)_2]$ .

In order to evaluate the degree of charge transfer of the CT complexes, we measured IR spectra of  $F_4TCNQ$ , and DDQ salts together with neutral  $F_4TCNQ$ , and DDQ molecules and potassium salts of  $F_4TCNQ$  and DDQ, namely the fully ionic accecptors. The electronic states of  $F_4TCNQ$  and DDQ in CT complexes with  $[Cu^{II}(saeTTF)_2]$  were estimated by comparing the CC-streching vibration mode of  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  with those of  $F_4TCNQ^0$  and  $K^+(F_4TCNQ^-)$ , and CN-streching mode of  $[Cu^{II}(saeTTF)_2](DDQ)_4$  with DDQ<sup>0</sup> and  $K^+(DDQ^-)$ , respectively. As a result, the charge on  $F_4TCNQ$  in CT complex was estimated to be -0.5. On the other hand, the valence of DDQ in CT complex

was evaluated to be fully ionic DDQ<sup>-</sup>. Charges on acceptors and stoichiometry of CT complexes, the oxidation states of  $[Cu^{II}(saeTTF)_2]$  in the CT complexes were determined as +0.75 for  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  and +4.0 for  $[Cu^{II}(saeTTF)_2](DDQ)_4$ , respectively, indicating the oxidation states of TTF moieties in the CT complexes were +0.38 for  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  and +2.0 for  $[Cu^{II}(saeTTF)_2](DDQ)_4$ , respectively; the electronic state of TTF moieties in  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  was assigned to the partial oxidation state, but that in  $[Cu^{II}(saeTTF)_2](DDQ)_4$  was to the fully ionic state. The different oxidation states of TTF moieties in  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  and  $[Cu^{II}(saeTTF)_2](DDQ)_4$  leads to the fairly good electrical conductivity for the former salts and insulating behavior for the latter.

We also succeeded in the preparation of a partially oxidized cation radical salt,  $[Cu^{II}(saeTTF)_2]PF_6$  by electrocrystallization with constant current of 0.5  $\mu$ A in THF. Temperature dependence of resistivity of  $[Cu^{II}(saeTTF)_2]PF_6$  is also described in Fig. 4. Although TTF moieties in  $[Cu^{II}(saeTTF)_2]PF_6$  is in the partial oxidation state, the salt exhibited semiconductive behavior with room temperature conductivity of  $6.1 \times 10^{-3} \, \text{S cm}^{-1}$  and activation energy of 67 meV (295–120 K). Preliminary X-ray crystallography for  $[Cu^{II}(saeTTF)_2]PF_6$  indicates that TTF moieties form one-dimensional stacking column with strong dimerization, which may cause the band gap at Fermi level and its semiconductive behavior. The details of crystal structure and electronic structure will be reported elsewhere.

#### 4. Conclusions

New Schiff base-type TTF-ligands (1a, 1b, and Hsae-TTF) and metal complexes using Hsae-TTF ligand have been synthesized towards strong interaction between conduction electrons and magnetic local spins. In contrast to tetradentate ligands 1a and 1b, Hsae-TTF has flexible structure around its coordination site, and gave mononuclear complexes with N<sup>2+</sup> and Cu<sup>2+</sup> ions, [M<sup>II</sup>(saeTTF)<sub>2</sub>]  $(M^{2+}=Ni^{2+} \text{ and } Cu^{2+})$ .  $[Cu^{II}(saeTTF)_2]$  provided CT complexes with F4TCNQ, DDQ, and iodine. Electronic state of TTF moieties in  $[Cu^{II}(saeTTF)_2]_2(F_4TCNQ)_3$  was partial oxidation state, leading to fairly high conducting behavior. On the other hand, TTF moieties in [Cu<sup>II</sup>(saeTTF)<sub>2</sub>](DDQ)<sub>4</sub> was in fully ionic states, which made this complex insulator. Cation radical salt with partially oxidized TTF moiety,  $[Cu^{II}(saeTTF)_2]PF_6$ , was also successfully prepared by electrochemical crystallization method. The conductive behavior of this salt was semiconductor, probably due to the onedimensionality with strong dimerization. Magnetic properties will be reported elsewhere together with the detail of the X-ray crystallographic analysis of this salt.

#### Acknowledgment

This work was supported by Grant-in Aid for Scientific Research on Innovative Areas of Molecular Degree of Freedom (No. 20110007) from the Ministry of Education, Culture, Sports, Science and Technology.

#### References

- P. Day, M. Kurmoo, T. Mallah, I.R. Marsden, R.H. Friend, F.L. Pratt, W. Hayes, D. Chasseau, J. Gaultier, G. Bravic, L. Ducasse, J. Amer. Chem. Soc. 114 (1992) 10722.
- [2] M. Kurmoo, A.W. Graham, P. Day, S.J. Coles, M.B. Hursthouse, J.L. Caulfield, J. Singleton, F.L. Pratt, W. Hayes, L. Ducasse, P. Guionneau, J. Amer. Chem. Soc. 117 (1995) 12209.
- [3] E. Coronado, J.R. Galán-Mascarós, G.J. Gómez-García, V. Laukhin, Nature 408 (2000) 447.

- [4] S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, H. Kobayashi, Nature 410 (2001) 908.
- [5] H. Fujiwara, E. Fujiwara, Y. Nakazawa, B.Z. Narymbetov, K. Kato, H. Kobayashi, A. Kobayshi, M. Tokumoto, P. Cassoux, J. Amer. Chem. Soc. 123 (2001) 306.
- [6] X. Xiao, T. Hayashi, H. Fujiwara, T. Sugimoto, S. Noguchi, Y. Weng, H. Yoshino, K. Murata, H.A. Katori, J. Amer. Chem. Soc. 129 (2007) 12618.
- [7] T. Hayashi, X. Xiao, H. Fujiwara, T. Sugimoto, H. Nakazumi, S. Noguchi, H.A. Katori, Inorg. Chem. 46 (2007) 8478.
- [8] D. Lorcy, N. Bellec, M. Fourmigué, N. Avarvari, Coord. Chem. Rev. 253 (2009) 1398.
- [9] N. Avarvari, M. Fourmigué, Chem. Comm. (2004) 1300.

- [10] S. Liu, C. Ambrus, S. Dolder, A. Neels, S. Decurtins, Inorg. Chem. 45 (2006) 9622.
- [11] F. Setifi, L. Ouahab, S. Golhen, Y. Yoshida, G. Saito, Inorg. Chem. 42 (2003) 1791.
- [12] S. Ichikawa, H. Mori, Inorg. Chem. 48 (2009) 4643.
- [13] M. Fontaine, C. Rivat, C. Hamet, C. Ropartz, C. Caullet, Bull. de la Soc. Chim. de France 5–6 (1975) 1357.
- [14] B.A. Clement, R.L. Soulen, J. Org. Chem. 39 (1974) 97.
- [15] H. Nishikawa, S. Kojima, T. Kodama, I. Ikemoto, S. Suzuki, K. Kikuchi, M. Fujitsuka, H. Luo, Y. Araki, O. Ito, J. Phys. Chem. A 108 (2004) 1881.
- [16] J. Wu, S. Liu, T.D. Keene, A. Neels, V. Mereacre, A.K. Powell, S. Decurtins, Inorg. Chem. 47 (2008) 3452.