

Preparation and Crystal Structure of Dual-Functional Precursor Complex Bis(acetylacetonato)nickel(II) with 4-Pyridyltetrathiafulvalene

Lei Wang,[†] Bin Zhang,[‡] and Jingping Zhang*[†]

Faculty of Chemistry, Northeast Normal University, Changchun 130024, China, and Organic Solid Laboratory, CMS, Institute of Chemistry, Beijing 100080, China

Received January 18, 2006

A tetrathiafulvalene (TTF) derivative 4-pyridyltetrathiafulvalene (Py-TTF) was synthesized. The 1:2 Ni complex **1** of bis(acetylacetonato)nickel(II) coordinated with Py-TTF was prepared. Complex **1** crystallizes in the monoclinic space group $P2_1/c$. Two pyridyl N atoms from two different molecules of Py-TTF are coordinated in the trans configuration to the Ni ion of Ni(acac)₂ to form an octahedral Ni complex, which is a precursor for both conducting and magnetic materials.

Introduction

One of the current challenges in solid-state chemistry is the search for molecule-based materials that are multifunctional.^{1–3} Therefore, great interest is currently devoted to obtain organic/inorganic hybrid materials that combine the electrical conducting properties of the organosulfur donors with the magnetic effects of transition-metal ions.^{3,4} It is deemed that there is a magnetic coupling between the localized spins on d orbitals of the paramagnetic transition-metal ions of the inorganic part through the mobile electrons of the organic conducting networks (π electrons).

Since the first synthesis of tetrathiafulvalene (TTF)⁵ and the discovery of metallic conductivity of an organic charge-transfer complex based on TTF and 7,7,8,8-tetracyanoquino-

dimethane,⁶ in particular the finding of the first organic superconductor,⁷ studies of TTF derivatives and their analogues have received great attention. Various TTF derivatives were designed and synthesized for studies of organic conductors, and even organic superconductors,^{8,9} because TTF derivatives can be converted to the corresponding mono- and dications at easily accessible oxidation potentials.

Our strategy involves the synthesis of TTF derivatives, as shown in Scheme 1, which have metal-ion binding groups directly attached at the periphery without a spacer. Combination with appropriate metal ions would lead to complexes with multiple physical properties, such as electrical conductivity or superconductivity offered by the TTF moiety, coupled with the optical and magnetic properties provided by various transition-metal ions. In this Article, we describe the synthesis and full characterization of 4-pyridyltetrathiafulvalene (Py-TTF), which is the precursor for multifunctional materials. It contains both a TTF unit as a source of conducting electrons upon oxidation and a directly linked pyridine as a ligand to coordinate a transition metal carrying a localized spin, with access for π -d interaction for the expected charge-transfer complex. Then we prepare the new Ni^{II} coordination complex formulated as Ni(acac)₂(Py-TTF)₂

* To whom correspondence should be addressed. E-mail: zhangjp162@nenu.edu.cn.

[†] Northeast Normal University.

[‡] Institute of Chemistry.

- (1) Day, P.; Kurmoo, M.; Mallah, T.; Marsden, I. R.; Friend, R. H.; Pratt, F. L.; Hayes, W.; Chasseau, D.; Gaultier, J.; Bravic, G.; Ducasse, L. *J. Am. Chem. Soc.* **1992**, *114*, 10772.
- (2) Coronado, E.; Favello, L. R.; Galan-Mascaros, J. R.; Rimenez-Saiz, C.; Gomez-Garcia, C. J.; Laukhin, V. N.; Perez-Benitez, A.; Rovira, C.; Veciana, J. *Adv. Mater.* **1997**, *9*, 984.
- (3) Coronado, E.; Galán-Mascarós, J. R.; Gomez-García, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447.
- (4) (a) Iwahori, F.; Golhen, S.; Ouahab, L.; Carlier, R.; Sutter, J.-P. *Inorg. Chem.* **2001**, *40*, 6541. (b) Ouahab, L.; Iwahori, F.; Golhen, S.; Calier, R.; Sutter, J.-P. *Synth. Met.* **2003**, *133–134*, 505. (c) Setiti, F.; Ouahab, L.; Golhen, S.; Yoshida, Y.; Saito, G. *Inorg. Chem.* **2003**, *42*, 1793. (d) Zhang, B.; Wang, Z.; Fujiwara, H.; Kobayashi, H.; Kurmoo, M.; Inoue, K.; Mori, T.; Gao, S.; Zhang, Y.; Zhu, D. *Adv. Mater.* **2005**, *17*, 1988. (e) Massue, J.; Bellec, N.; Chopin, S.; Levillain, E.; Roisnel, T.; Clerac, R.; Lorcy, D. *Inorg. Chem.* **2005**, *44*, 8740.
- (5) Pninzbach, H.; Berger, H.; Lüttringhaus, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 436.

(6) Ferraris, J.; Cowan, D. O.; Walatka, V. J.; Perlstein, H. J. *J. Am. Chem. Soc.* **1973**, *95*, 948.

(7) Andrieux, A.; Duromre, C.; Jérôme, D.; Bechgaard, K. *J. Phys. Lett.* **1979**, *40*, 381.

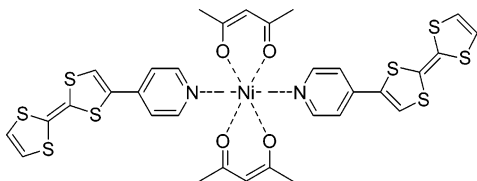
(8) For example, see: Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors (including fullerenes)*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(9) For recent TTF reviews, see: (a) Fabre, J. M. *Chem. Rev.* **2004**, *104*, 5133. (b) Kobayashi, A.; Fujiwara, E.; Kobayashi, H. *Chem. Rev.* **2004**, *104*, 5243.

Scheme 1. Synthesis Route of Py-TTF^a

^a Reagents and conditions: (i) butyllithium, THF, $-78\text{ }^{\circ}\text{C}$; (ii) ClSnBu_3 , $-78\text{ }^{\circ}\text{C}$, then room temperature; (iii) 4-iodopyridine, $\text{Pd}(\text{PPh}_3)_4$, toluene, reflux.

Chart 1



(acac = acetylacetonate) as a precursor for the construction of conducting and magnetic molecular materials.

Experimental Section

Material and Instrumentation. TTF was synthesized according to the previous literature.¹⁰ All other reagents and solvents were bought commercially as analytical reagent grade and used without further purification. ^1H and ^{13}C NMR spectra were recorded on an Inova-500 instrument. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane. Fourier transform infrared (FT-IR) spectra were recorded on a Magna-560 spectrometer in the region of $4000\text{--}400\text{ cm}^{-1}$ as KBr pellets. The mass spectrometry (MS) spectrum of Py-TTF was recorded with a HP GC 6890/MS 5937 spectrometer. The electrochemical properties were measured by an LK98B electrochemistry system. X-ray diffraction data were collected using a Siemens SMART APEX CCD diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Magnetic measurements were performed in the range of $2\text{--}300\text{ K}$ with a Quantum Design MPMS-XL SQUID magnetometer at an applied field of 500 Oe .

Synthesis of Py-TTF. The synthetic route used in making Py-TTF is shown in Scheme 1. After reaction of TTF (2.04 g , 0.01 mol) with butyllithium (6.25 mL , 1.6 M) for half an hour, tributyltin chloride (2.7 mL , 0.01 mol) was added dropwise over 10 min at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred for another 3 h at room temperature. The solvent was evaporated in a vacuum. The mixture was treated by $\text{Pd}(\text{PPh}_3)_4$ (1.0 g) and 4-iodopyridine (2.06 g , 0.01 mol), and the temperature was raised to $130\text{ }^{\circ}\text{C}$ for 1 night. The product was isolated by column chromatography on alumina (activity III) and washed by hot petroleum ether. The products are orange crystals. Yield: 46% . Mp: $216\text{--}218\text{ }^{\circ}\text{C}$. IR spectra (KBr pellet, cm^{-1}): $3430.46(\text{w})$, $3041.04(\text{w})$, $1595.53(\text{w})$, $1451.87(\text{m})$, $733.20(\text{w})$, $402.80(\text{w})$. ^1H NMR (DMSO, δ , ppm): $6.777(\text{s}, 2\text{H})$, $7.424\text{--}7.436(\text{d}, 2\text{H})$, $7.698(\text{s}, 1\text{H})$, $8.582\text{--}8.594(\text{d}, 2\text{H})$. ^{13}C NMR (DMSO, δ , ppm): 105.594 , 109.800 , 113.729 , 120.429 , 120.631 , 120.692 , 122.031 , 132.499 , 138.695 , 150.861 . MS: m/z $281(\text{M}^+)$, 236 , 178 , 146 , 102 , 76 .

Preparation of Complex $\text{Ni}(\text{acac})_2(\text{Py-TTF})_2$. Single crystals of complex $\text{Ni}(\text{acac})_2(\text{Py-TTF})_2$ (**1**, Chart 1) suitable for X-ray diffraction analysis were obtained by slow diffusion. $\text{Ni}(\text{acac})_2$ (20 mg) was dissolved in cyclohexane (10 mL). A methanol solution (20 mL) of Py-TTF (12 mg) was added at room temperature under Ar. The reaction mixture was left to stand undisturbed for 1 week. Small shiny orange crystals were isolated by filtration, washed with

Table 1. Crystal Data and Structure Refinement for Complex 1

empirical formula	$\text{C}_{32}\text{H}_{28}\text{N}_2\text{NiO}_4\text{S}_8$
fw	819.75
T (K)	293(2)
wavelength (\AA)	0.710 73
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a (\AA)	7.3220(5)
b (\AA)	8.5055(5)
c (\AA)	28.6082(18)
α (deg)	90
β (deg)	97.204(1)
γ (deg)	90
V (\AA^3)	1767.58(19)
Z	2
D_c (g cm^{-3})	1.540
abs coeff (mm^{-1})	1.061
$F(000)$	844
cryst size (mm^3)	$0.43 \times 0.34 \times 0.13$
θ range for data collection (deg)	$2.50\text{--}26.07$
limiting indices	$-9 \leq h \leq 8$, $-10 \leq k \leq 10$, $-35 \leq l \leq 24$
reflns collected	9635
indep reflns	3455 [$R(\text{int}) = 0.0581$]
completeness (%) to $\theta = 27.48^\circ$	99.0
abs correction	none
refinement method	full-matrix least squares on F^2
data/restraints/param	3455/0/214
GOF on F^2	1.048
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0442$, $wR2 = 0.1210$
R indices (all data)	$R1 = 0.0519$, $wR2 = 0.1270$
largest diff. peak and hole ($\text{e } \text{\AA}^{-3}$)	0.582 and -0.239

Table 2. Selected Bond Lengths [\AA] and Angles [deg] for Complex 1

Ni1—O2	2.010(2)	Ni1—O1	2.025(2)
Ni1—N1	2.111(2)		
O2A—Ni1—O2	180.0 (1)	O2A—Ni1—O1	87.96(7)
O2—Ni1—O1	92.04(7)	O1A—Ni1—O1	180.00(8)
O2A—Ni1—N1	90.55(8)	O2—Ni1—N1	89.45(8)
O1A—Ni1—N1	89.44(8)	O1—Ni1—N1	90.56(8)
N1—Ni1—N1A	180.0(2)		

^a Symmetry transformations used to generate equivalent atoms: A, $-x$, $-y$, $-z$.

cyclohexane, and air-dried at room temperature. Yield: 22.5 mg (63.9%).

Single-Crystal Structure Determination for Complex $\text{Ni}(\text{acac})_2(\text{Py-TTF})_2$. X-ray diffraction was performed on a CCD area detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.710\text{ 73 } \text{\AA}$) in the range of $2.50 < \theta < 26.07^\circ$. The structure was solved in $P2_1/c$ by direct methods and refined by full-matrix least squares on F^2 using *SHELXTL-97* software. Crystal data for **1** are shown in Tables 1 and 2. CCDC 281109 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre).

Magnetic Measurement of Complex 1. The magnetic susceptibility measurement on complex **1** was obtained on a finely ground polycrystalline sample with the use of a Quantum Design SQUID magnetometer MPMS-XL. The dc measurements were collected from 2.0 to 300 K under 500 Oe . Experimental data were also corrected for the sample holder and for the diamagnetic contribution calculated from Pascal constants.¹¹

(10) Moore, A. J.; Bryce, M. R. *Synthesis* **1997**, 407.

(11) Khan, O. *Molecular Magnetism*; VCH: New York, 1993.

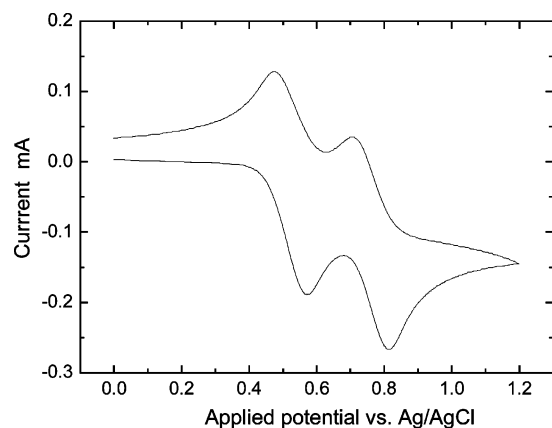


Figure 1. Cyclic voltammetry measurement of Py-TTF.

Results and Discussion

Synthesis of Py-TTF. There are two kinds of available reactions to result in Py-TTF derivatives;^{12,13} we select the use of the organometallic strategy described by Iyoda co-workers¹⁴ because it obtained 4,4',5'-trimethyl-5'-pyridyltetra-thiafulvalene in good yield¹⁵ and recently proved to be successful for a series of heterocyclic aromatic-substituted TTF derivatives.¹⁶ The synthesis of target Py-TTF is shown in Scheme 1 with good yield (46%), which is higher than the reported one.¹⁶

Electrochemical Behavior of Py-TTF. The redox properties of the new molecule were determined by cyclic voltammetry measurements carried out in dimethylformamide at room temperature with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte, Ag/AgCl as the reference electrode, and platinum as working and counter electrodes. The scan speed is 100 mV s⁻¹. The two reversible single-electron oxidation waves were observed (Figure 1). The oxidation half-wave potentials are 474 and 705 mV. They correspond to the TTF fragment (formation of a radical cation and a biradical dication, respectively). Its electrochemical behavior is similar to that of TTF, and it should be a good donor for a molecular conductor.

Structural Data for Complex Ni(acac)₂(Py-TTF)₂. The ORTEP drawing for complex **1** is presented in Figure 2. The Ni atom lies on a center of inversion and adopts a distorted octahedral coordination geometry. It is bonded in the equatorial plane to two bidentate acac anions through their O atoms. The distances between Ni1 and O2 and between Ni1 and O1 are 2.010(2) and 2.025(2) Å, respectively. The Py-TTF ligands occupy the apical positions and are trans to each other; they are bonded to the metal atom through the

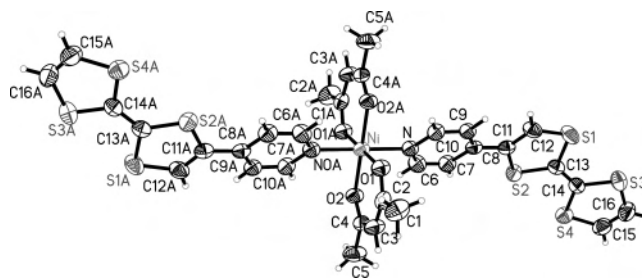


Figure 2. ORTEP drawing of Ni(acac)₂(Py-TTF)₂ at the 50% probability level.

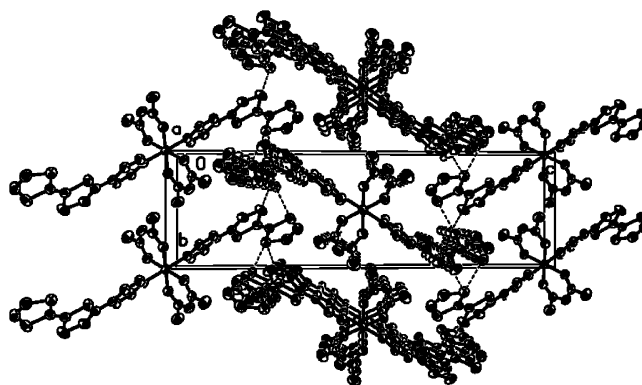


Figure 3. Packing view of complex **1** along the *a* axis.

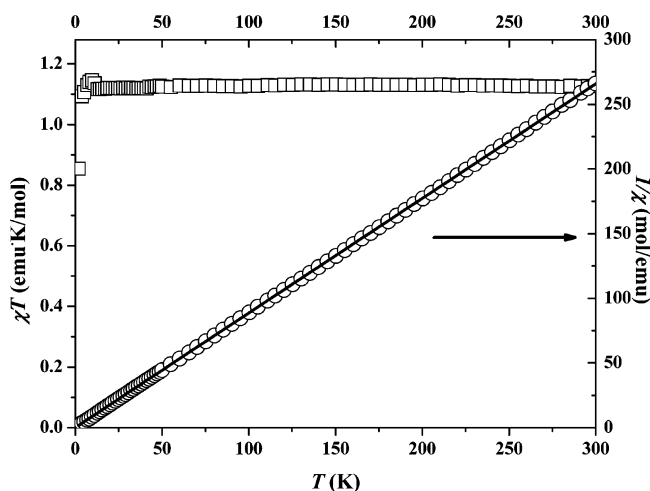


Figure 4. Temperature dependences of χ_{mol} and $\chi_{\text{mol}}T$ for complex **1**. The solid lines represent the best fit of the experimental data to the Curie law.

N atoms of the pyridyl ring with a Ni–N bond length of 2.111(2) Å, and the py planes are perpendicular to the acac planes. The Ni–O and Ni–N bond lengths in this compound are the same as those in Ni(TTFSacac)₂(pyridine)₂.^{4e} In complex **1**, the py planes are perpendicular to the plane of two acac units with a dihedral angle of 89.42(5)°. The torsional angle between the pyridine and the dithio ring is 8.77°. The dihedral angle of TTF and pyridine on a Py-TTF unit is 22.34(9)°, and two Py-TTF units coordinating to Ni are parallel to each other. In one molecule, two TTF units are parallel to each other. The atoms in two acac units and Ni are well coplanar with a deviation of 0.02 Å. Using the empirical correlation between C=C and C–S bond lengths,¹⁷

- (12) (a) Iyoda, M.; Sasaki, S.; Miura, M.; Fukuda, M.; Yamauchi, J. *Tetrahedron Lett.* **1999**, *40*, 2870. (b) Iyoda, M.; Hara, K.; Kuwatani, Y.; Nagase, S. *Org. Lett.* **2000**, *2*, 2217.
 (13) Levi, O. P.; Becker, J. Y.; Ellern, A.; Khodorkovsky, V. *Tetrahedron Lett.* **2001**, *42*, 1571.
 (14) Moore, A. J.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K.; Khodorkovsky, V.; Shapiro, L.; Shames, A. *Eur. J. Org. Chem.* **2001**, 73.
 (15) Bouguessa, S.; Gouasmia, A. K.; Golhen, S.; Ouahab, L.; Fabre, J. M. *Tetrahedron Lett.* **2003**, *44*, 9275.
 (16) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973.

the formal charge on the central TTF core is found to be equal to ca. +0.22 because the C=C and C-S bond lengths of the TTF core are in the average range of neutral donors, so it should be an insulator. Therefore, the Py-TTF ligand can be still be regarded as neutral.

Molecules stack in a face-to-face mode to form a molecular column along the *b* axis; there is no interaction between molecules (see the details in Figure S1 in the Supporting Information). There are intermolecular interactions of 3.557 Å (S3...S1) and 3.413 Å (S3...S4) between columns in the crystal shown in Figure 3.

Magnetic Properties for Complex 1. Figure 4 shows the magnetic behavior of **1** at an applied field of 500 Oe in the form of a $\chi_{\text{mol}}T$ vs *T* plot. The global feature of the $\chi_{\text{mol}}T$ vs *T* curve for **1** is paramagnetic. The $\chi_{\text{mol}}T$ value per Ni^{II} at 300 K is 1.13 emu K mol⁻¹, higher than the spin-only value (1.00 emu K mol⁻¹) expected for a magnetically isolated high-spin Ni^{II} ion with *g* = 2.00. As the sample is cooled from room temperature, the $\chi_{\text{mol}}T$ values are constant in the entire temperature range, decreasing to a value of 0.85 emu K mol⁻¹ at very low temperatures. The 1/ χ_{mol} vs *T* plot is almost linear in the entire temperature range, as shown in Figure 4, and the data can be fitted to the Curie law with *C* = 1.13 cm³ mol⁻¹ K.

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

Concluding Remarks

In this Article, we described the synthesis and full characterization of Py-TTF and its new Ni coordination complex Ni(acac)₂(Py-TTF)₂. Molecules stack in a face-to-face mode along the *b* axis, and there are intermolecular interactions between columns. The magnetic measurement revealed a paramagnetic coupling between the Ni ions. The direct linkage between TTF and pyridine without a spacer between them may facilitate access for π -d interaction between the radical cation of the organic part and the paramagnetic metal ion in the expected charge-transfer complex. Further research on a chemical and/or electrochemical partial oxidation of the complex is under current investigation in our group.

Acknowledgment. Financial support from the NNSFC (Grants 20274006 and 20473095), SRF for ROCS, SEM, and Outstanding Youth Project of Jilin Province is gratefully acknowledged.

Supporting Information Available: Crystallographic information files (CIF) for the crystal structures of Ni(acac)₂(Py-TTF)₂, atomic coordinates and equivalent isotropic displacement parameters, and the packing view along the *b* axis for complex **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC060095R