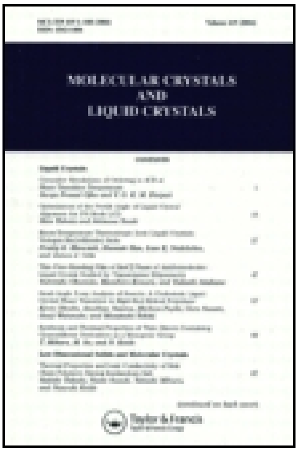

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Preparation and Properties of a Hydroxy-TEMPO-Substituted TTF and ITS CT Complexes

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Preparation and Properties of a Hydroxy-TEMPO-substituted TTF and ITS CT Complexes

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The reaction of lithio derivatives of TTF (tetrathiafulvalene) derived from TTF **1** and LDA in ether solution with 4-oxo-TEMPO (2, 2, 6, 6-tetramethylpiperidine-N-oxy) gave 4-hydroxy-TEMPO-substituted TTF derivative **2**. The magnetic susceptibility and magnetization data on polycrystalline samples of **2** as well as their CT complexes with I_2, DDQ or $TCNQF_4$ revealed only weak intra- or intermolecular antiferromagnetic interactions between unpaired electrons. The decrease of magnetic susceptibility by CT formation together with their solid ESR data showing the decrease of absorption intensity suggested antiparallel spin formation between unpaired electrons in CT complexes.

Keywords: TTF derivative, stable nitroxy radical, magnetic susceptibility, ESR spectra

INTRODUCTION

The search for synthetic organomagnetic materials is of current interest and various types of organic radicals, radical ions as well as polycarbenes (high spin molecules) have been developed from this viewpoint and investigated extensively in recent years.[1] Our approach to construct new organomagnetic materials is directed to build up charge transfer complexes bearing stable radical unit(s) in either the donor part or the acceptor part or both parts and to arrange the unpaired electrons in column structure of the single crystals prepared by a suitable method.[2] As a model of the above mentioned CT complexes bearing stable radical unit(s) in donor part, we were interested in preparing TTF derivatives with stable radical moiety and preserving their donating ability,[3] and hence, we have initiated to prepare TEMPO-substituted TTF derivative(s).

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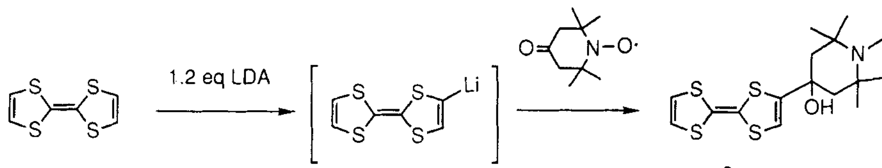
PREPARATION OF 4-HYDROXY-TEMPO-SUBSTITUTED TTF 2 AND ITS CT COMPLEXES

Although Whitesides and Newirth reported that the nitroxy radical (i.e. 2,2,6,6-tetramethylpiperidine-N-oxyl) was destroyed in hexane solution at $-70°C$ when treated with *n*-butyllithium forming several products,[4] we have observed that nitroxy radical was persistent in ether solution with no appreciable destruction of radical moiety when treated with lithium diisopropylamide (LDA). Thus, nitroxy radical substituted TTF derivative was prepared using the reagent and applying 4-oxo-TEMPO as an electrophile. As shown in Scheme 1, when TTF **1** was treated with 1.2 molar amount of LDA in ether at $-78°C$, monolithio-TTF was formed[5] and it gave the mono-4-hydroxy-TEMPO-substituted TTF **2** (yellow crystals, m.p. > ca. 185°C (dec.)) in 33–55% yield after the treatment with 4-oxo-TEMPO.[6,7]



Typical triplet absorptions due to hyperfine splitting with nitrogen-14 atom of nitroxy radicals were observed on their ESR spectra for **2** ($g = 2.007$, $a_N = 15.3$ G in benzene) and no remarkable change was found from 4-hydroxy-TEMPO radical itself ($g = 2.006$, $a_N = 15.3$ G in benzene) suggesting the localized nature of the unpaired electron at the nitroxide group in **2** (Figure 1, left). The redox behavior of **2** was investigated by cyclic voltammetry in CH_2Cl_2 and was found to have oxidation potentials of 0.44 V, 0.85 V vs. SCE suggesting almost comparable electron-donating ability to that of TTF **1** (0.49 V and 0.80 V vs. SCE in CH_2Cl_2) (Figure 2).[8]

As expected from the redox behavior occuring the oxidation first at the TTF moiety on **2**, charge transfer complexes were found to be formed between **2** and some acceptors as I_2, DDQ or $TCNQF_4$ (**3**, **4**, **5**) in benzene or in acetonitrile solution.[9] The absorption maxima in their UV spectra in acetonitrile showing 590 nm ($\varepsilon = 5000$) for **3**, 590 nm ($\varepsilon = 5510$) for **4** and 753 nm ($\varepsilon = 13400$), 857 nn ($\varepsilon = 29500$) for **5** suggested the formation of TTF cation radical for **3** and **4** and $TCNQF_4$ anion radical for **5**, respectively,[9] and the shift to lower frequency of ν_{CN} (2205 cm^{-1} for **4** from 2233 cm^{-1} in neutral DDQ and 2195 cm^{-1} for **5** from 2237 cm^{-1} in neutral $TCNQF_4$) in their IR spectra for **4** and **5** was consistent with the CT complex formation. Triplet absorption with the hyperfine splitting of almost half value ($a_N = 7.6$ G) was observed in I_2 complex in acetone solution (Figure 3, left), indicating the presence of intramolecular spin-spin exchange between TTF cation radical and the nitroxide.[10,11]

More complex splitting patterns were observed for DDQ and $TCNQF_4$ complexes suggesting the presence of intramolecular spin interactions between unpaired electrons in these systems. We have further tried to prepare single crystals of CT complexes of **2** with different acceptors using the electrocrystallization or diffusion method, but every attempt has so far been unsuccessful.

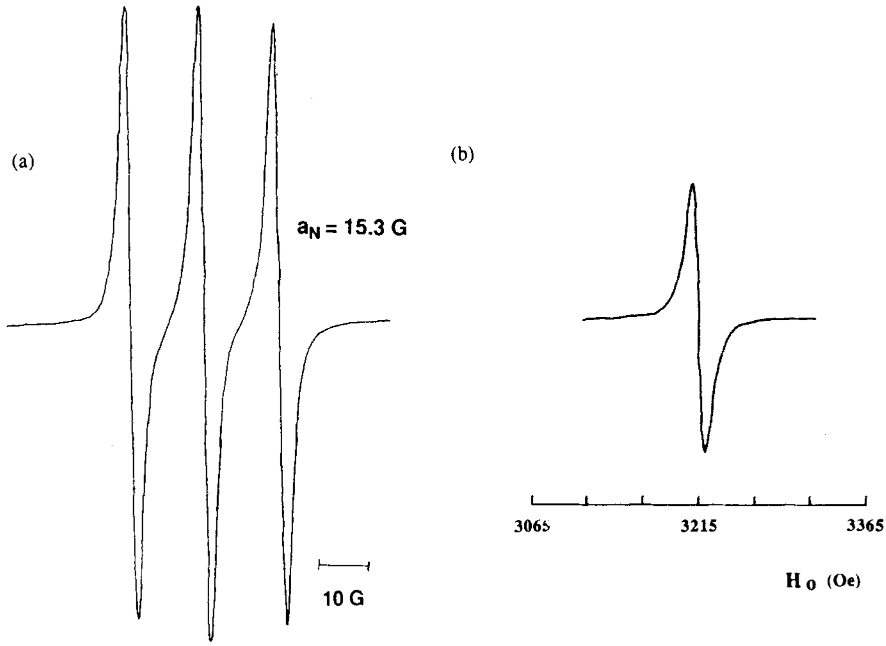


FIGURE 1 ESR spectrum of **2** (a) in benzene (left) and (b) solid state (right) at room temperature.

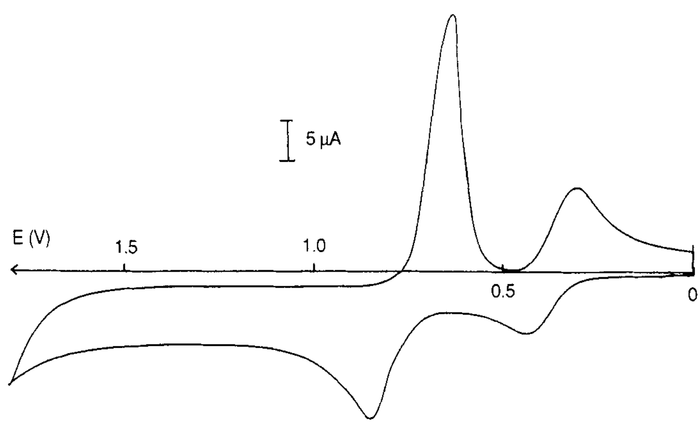


FIGURE 2 Cyclic voltammogram of **2**. V vs. SCE in dichloromethane with 0.1 M $(n\text{-}Bu)_4NClO_4$ at room temperature. Scan rate: 50 mV/s.

MAGNETIC SUSCEPTIBILITY OF 2 AS WELL AS ITS CT COMPLEXES 3, 4, 5

Magnetic susceptibility of **2** as well as its CT complexes **3**, **4**, **5** were measured on their polycrystalline samples by a SQUID susceptometer at temperatures between 2 K and 300 K. As shown in Figure 4, the susceptibility of **2** obeyed Curie's law and the presence of weak antiferromagnetic interaction was suggested from the magnetization curve at

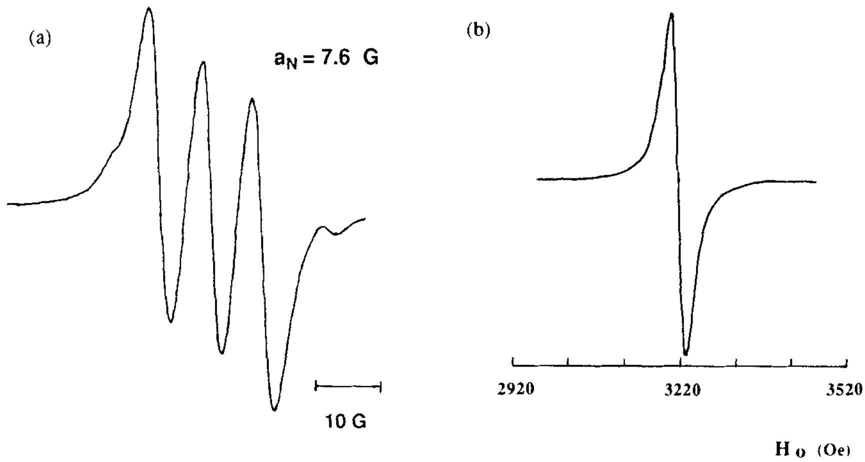


FIGURE 3 ESR spectrum of **3** (a) in acetone (left) and (b) solid state (right) at room temperature.

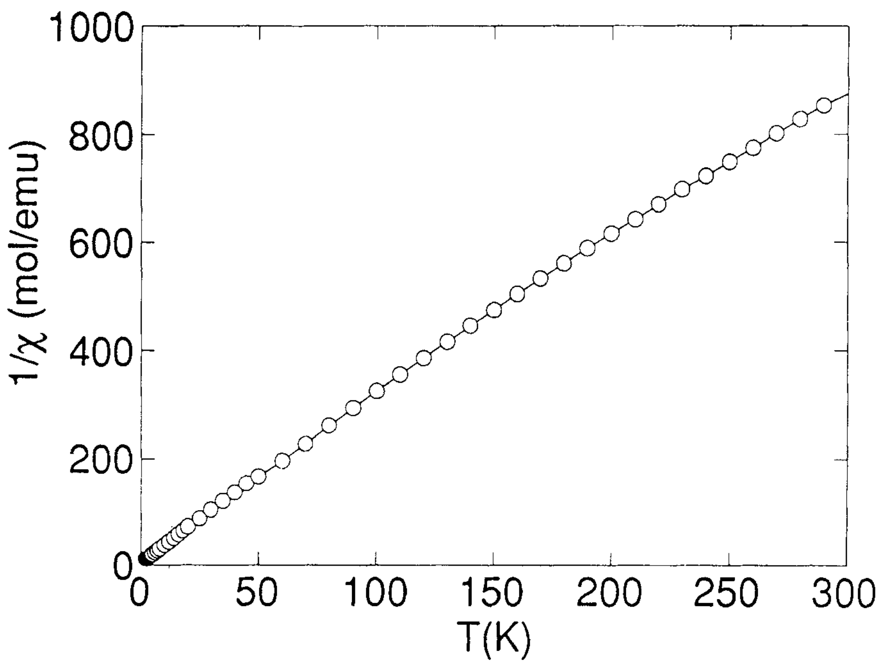


FIGURE 4 Temperature dependence of $1/\chi$ for **2**.

2 K. In Figure 5 are shown the magnetic properties of its CT complexes in low temperature region (2–20 K).

Each Weiss temperature estimated from the Curie-Weiss law was as large as -1 K and the quantity of magnetic moment estimated from the magnetization curve was ca.

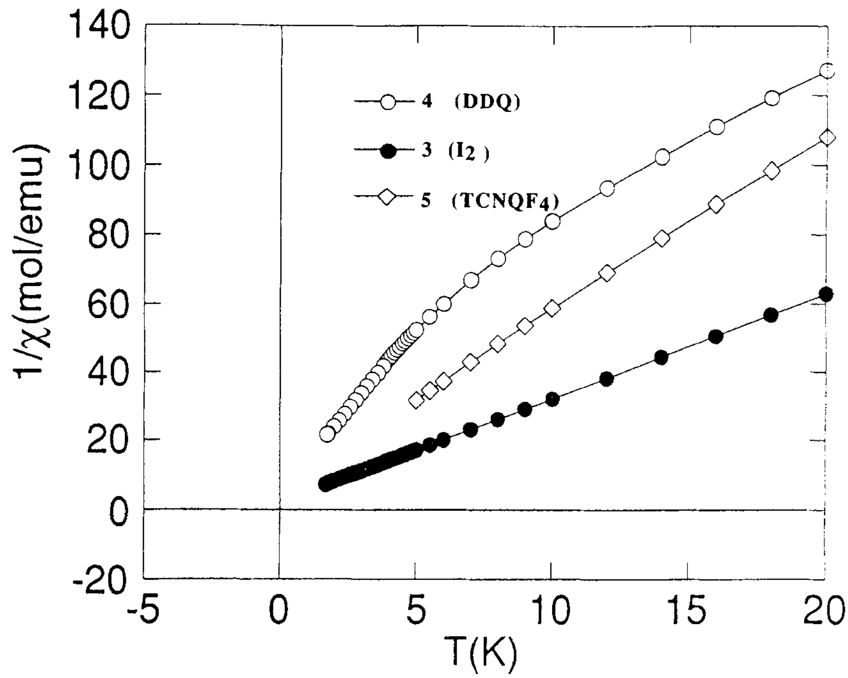


FIGURE 5 Temperature dependence of $1/\chi$ for **3**, **4**, **5** in low temperature region.

$1\,\mu_B$ for I_2 complex, $0.25\,\mu_B$ for DDQ complex and $0.5\,\mu_B$ for $TCNQF_4$ complex,[12] respectively. The small spin numbers found in each complex were beyond our expectation that cation and anion radicals were present in addition to the nitroxyl radicals in CT complexes. We assume that the donor and acceptor molecules are probably dimerized and the cation and anion radicals have disappeared due to the spin singlet formation at ambient temperature. In addition, the small magnetic moments ($< 1\,\mu$B) for the complexes (**3**, **4**, **5**) suggest the intra- and/or intermolecular singlet formation between nitroxyl radicals. Thus, apparent decrease of magnetic susceptibility was observed for each complex (**3**, **4**, **5**) by CT formation resulting probably from the intra- and/or intermolecular singlet formation between unpaired electrons. The significant difference of magnetic behavior depending on anion radicals on their polycrystalline samples prompted us to investigate solid ESR spectral measurement.

SOLID ESR SPECTRA OF 2 AS WELL AS ITS CT COMPLEXES 3, 4, 5

The solid ESR spectral data of the donor **2** and its CT complexes (**3**, **4**, **5**) at ambient temperature are summarized in Table I. Several characteristic features are apparent from the Table, e.g., the broadening tendency of line width in I_2 complex **3**, the smallest g-shift in $TCNQF_4$ complex **5**. Although the exact origin is not clear, the broad line width of **3** is supposed to be due to the spin-orbital interaction between the unpaired

TABLE I

Solid ESR Data of **2** and CT Complexes[a]

	Line Width	g-Factor	Intensity/mg
2	11.7	2.0064	3200
I_2-Complex **3**	26.9	2.0070	1600
DDQ-Complex **4**	14.1	2.0068	1200
$TCNQF_4$-Complex **5**	12.2	2.0050	330

[a] data at 25°C

electron on nitroxyl and I_3 anion and the small g-factor of **5** would be ascribed to the averaging effect of g-factor of nitroxyl radical and anion radical. Thus, an apparent difference for the complexes was observed in their solid ESR data and moreover a noticeable decrease of absorption intensity by CT complex formation was observed for each complex, especially for $TCNQF_4$ complex **5**, suggesting partially antiparallel spin (singlet) formation between unpaired electrons, and which was consistent with the data of susceptibility measurement.

In summary, we have prepared hydroxy-TEMPO-substituted TTF derivative **2** as a stable-radical-substituted organic donor and its I_2, DDQ and $TCNQF_4$ complexes (**3**, **4**, **5**). Only weak antiferromagnetic interactions between unpaired electrons of each complex were observed in the CT complexes and the decrease of their magnetic susceptibility together with the decrease of absorption intensity of their solid ESR by CT complex formation suggested partially antiparallel spin (singlet) formation between unpaired electrons.

Acknowledgement

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6. Found: C, 48.03; H, 5.39; N, 3.82%. Calcd. for $C_{15}H_{20}O_2NS_4$: C, 48.10; H, 5.38; N, 3.74%. EI-MS (m/e): 374 (M^+). IR (Nujol) cm^{-1}: 3450 br.s (OH). ^1H NMR ($CDCl_3$): $\delta = 1.29$ (br.s, 6H, CH_3), 1.34 (br.s, 6H, CH_3), 1.43 (br.s, 4H, CH_2), 6.30 (br.s, 1H, OH), 6.36 (s, 2H, olefinic H), 7.40 (s, 1H, olefinic H). UV (CH_2Cl_2) λ_{max} nm (ε): 310 (12200), 318 (12700), 364 (2100), 450 (310).

7. When > 2.4 molar amount of LDA was used, di- or tetralithio-TTF was formed and small amount of bis (4-hydroxy-TEMPO)- substituted TTF was obtained, and on which we are now trying to study further.
8. Although the first redox couple was reversible, the second one was found to be irreversible. The cyclic voltammogram ascribed to nitroxide group is probably hidden to the second redox region of TTF moiety of 2.
9. I_2 complex **3**: dark violet solid, mp > ca. 115°C (decomp.); DDQ complex **4**: dark brown solid, mp > ca. 225°C (dec.). $TCNQF_4$ complex **5**: dark blue solid, mp > ca. 235°C (dec.). Preliminary elemental analyses indicated that the D:A compositions of I_2 (as I_3 acceptor), DDQ and $TCNQF_4$ complexes are 1:1, 1:1 and 1:1.2, respectively. The UV-VIS-NIR spectra of the solid samples showed broad maxima at ca. 640 nm for **3**, ca. 750 nm for **4**, and ca. 700, 920 nm for **5**.
10. The similar ESR spectral behavior was observed for the recently reported complexes of imino pyrolidine- and piperidine-1-oxyl substituted TTF derivatives (see. ref. 3b), i.e. their hyperfine splitting constants were almost half values of ($a_N = 7.6$ G) of the donors. See also, B. Kirste, A. Kruger and H. Kurreck, *J. Am. Chem. Soc.*, **104**, 3850 (1982).
11. In the ESR measurement of each complex in solution, we have experienced that the initial triplet turned out slowly during the time course to be the triplet of donor itself with $a_N = 15.3$ G, suggesting the slow dissociation of the complexes in solution.
12. We could not rule out some remaining ferromagnetic impurities for the fairly large residual susceptibility of $TCNQF_4$ complex **5** at ambient temperature considering the result of solid ESR, which showed large decrease of intensity in **5**.