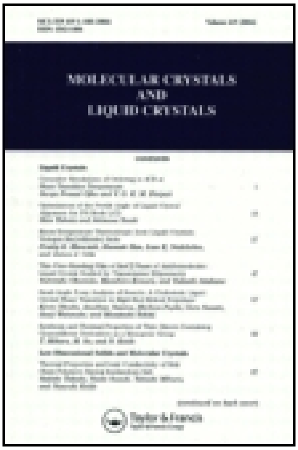

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Shuji Aonuma, Hélène Casellas, Bénédicte Garreau de Bonneval, Christophe Faulmann, Isabelle Malfant, Patrick Cassoux, Yuko Hosokoshi & Katsuya Inoue (2003): STRUCTURE AND PROPERTIES OF M(dmit) 2 SALTS WITH Me 3 N + -TEMPO OR TTF-(HO)TEMPO, Molecular Crystals and Liquid Crystals, 380:1, 263-268

To link to this article: http://dx.doi.org/10.1080/713738697

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 263-268
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1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290101982

STRUCTURE AND PROPERTIES OF M(dmit)$_2$ SALTS WITH Me$_3$N$^+$-TEMPO OR TTF-(HO)TEMPO

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Aiming at obtaining a new magnetic conductor with coupled conducting and magnetic properties, magnetic counter cations based on the TTF donor and the ammonium ion substituted with TEMPO radical are investigated in order to be associated with M(dmit)$_2$ (M = Ni, Pd) molecules.

Keywords: TEMPO; TTF; M(dmit)$_2$; conductivity; magnetism; structure

INTRODUCTION

M(dmit)$_2$ (M = Ni, Pd, etc.) is an acceptor molecule known as a precursor to charge-transfer salts exhibiting metal-like and even superconducting behaviors [1,2]. Co-existence or interplay of conductivity and magnetism is of great interest in the field of molecular material science [3]. In this context, the most spectacular results obtained when using M(dmit)$_2$ are the spin ladder system, (EPYNN)[Ni(dmit)$_2$] [4] and the bulk ferromagnet, [Mn(C$_5$Me$_5$)$_2$][Ni(dmit)$_2$] [5]. Recently, we have developed TEMPO-substituted ammonium ion, Me$_3$N$^+$-TEMPO, as a counter cation in order to introduce magnetic spin into M(dmit)$_2$-based conductor [6].

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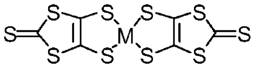
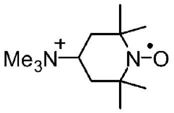
A number of interesting tetrathiafulvalene (TTF) donors bearing nitroxide radicals and their charge-transfer salts have been also reported [7]. Such donor molecules may be profitably associated with the acceptor $M(dmit)_2$ complexes. They are another fascinating candidates for the coupling of conductivity and magnetism. Among these donors, TTF-(HO)TEMPO is readily available and chemically stable.

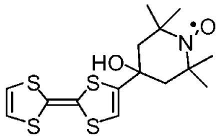
In this paper, we report on some recent results on Me_3N^+-TEMPO radical, electrochemical reinvestigation of TTF-(HO)TEMPO [8], and an attempted association with $[M(dmit)_2]$.



$M(dmit)_2$ (M=Ni, Pd)



Me_3N^+-TEMPO



TTF-(HO)TEMPO

RESULTS AND DISCUSSION

Me_3N^+-TEMPO

We recently reported the preparation, crystal structure, and magnetic properties of $(Me_3N\text{-TEMPO})_x[M(dmit)_2]$ (M = Ni, $x = 2$, 1; M = Pd, $x = 2$). The $(Me_3N\text{-TEMPO})[Ni(dmit)_2]$ salt is a semi-conductor ($E_a = 0.12$ eV with rather high single-crystal conductivity ($4 \times 10^{-3}\,S\,cm^{-1}$ at room temperature) for a mono-valent salt [6]. Magnetic properties of this salt and the further oxidized $(Me_3N\text{-TEMPO})[M(dmit)_2]_x$ (M = Ni, Pd; $x > 2$) salts were obtained for poorly characterized phases. A powder sample which is believed to be the $(Me_3N\text{-TEMPO})[Ni(dmit)_2]_4$ salt (with room-temperature powder conductivity of *ca.* $1 \times 10^{-2}\,S\,cm^{-1}$) shows weak ferromagnetic behavior [9]. $(Me_3N\text{-TEMPO})[Ni(dmit)_2]$ and oxidized $(Me_3N\text{-TEMPO})[Pd(dmit)_2]_2$ show antiferromagnetic behavior.

The Me_3N^+-TEMPO salts with $X = I^-$ and $PF_6{}^-$ show different structure and magnetic properties, i.e., both antiferromagnetic but strongly coupled dimer for $(Me_3N\text{-TEMPO})I$, weakly coupled chain for $(Me_3N\text{-TEMPO})PF_6$ [6]. Thus, solid-state properties of these salts can be controlled by a chemical modification of its counter anion, which can be readily available by metathesis reaction of $(Me_3N\text{-TEMPO})I$ with the potassium or silver salt of the corresponding anion. Following this idea, we have prepared single crystals of salts of tetrahedral anions ($BF_4{}^-$ and $ClO_4{}^-$).

The temperature dependence of the magnetic susceptibility of these salts were well fitted by a Curie-Weiss law with Weiss constants (θ) of -0.7

K for the BF_4^- salt and −0.2 K for the ClO_4^- salt. These values are similar to that obtained for the salt with the octahedral PF_6^- anion ($\theta = -0.2$ K) and much weaker than that in (Me$_3$N-TEMPO)I salt ($\theta = -6.3$ K). (Me$_3$N-TEMPO)ClO$_4$ was found to be isostructural (Figure 1; *Pnma*, $a = 11.170(5)$ Å, $b = 10.650(5)$ Å, $c = 13.264$ (5) Å), and shows similar antiferromagnetic-coupled chain ($2J/k_B = -0.24$ K) as in with (Me$_3$N-TEMPO)PF$_6$ ($a = 11.400(1)$ Å, $b = 10.852(1)$ Å, $c = 13.354$ (2) Å; $2J/k_B = -0.26$ K) [6].

TTF-(HO)TEMPO

A preliminary electrochemical study of TTF-(HO)TEMPO had been previously carried out by cyclic voltammetry in CH_2Cl_2 [8]. Difference between first and second redox potential (ΔE) reported therein is larger compared to that of TTF measured under same condition (Table 1). This suggests that increased Coulombic repulsions in the dicationic state result from substitution with the TEMPO moiety. Moreover, one redox couple was

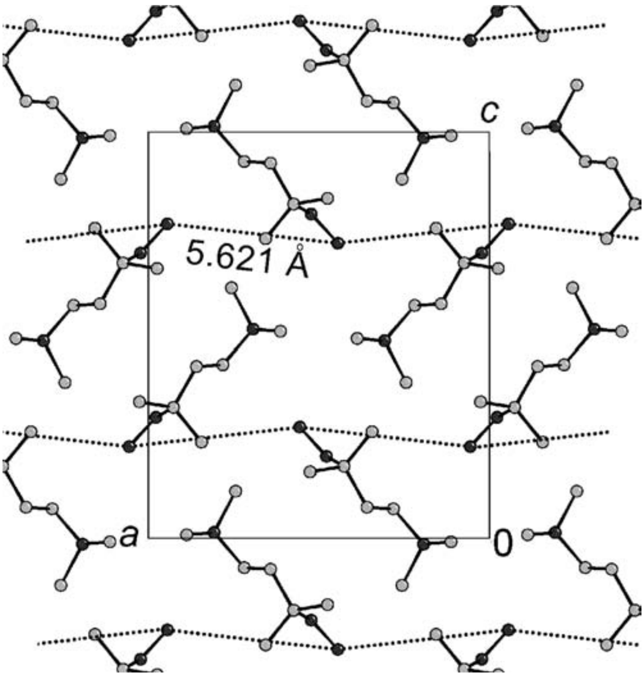


FIGURE 1 Crystal structure of (Me$_3$N-TEMPO)ClO$_4$.

TABLE 1 Redox Potentials (V *vs.* SCE in CH_3CN) for TTF-(HO)TEMPO and Related Compounds

Compound	$E_1^{1/2}$	$E_2^{1/2}$	ΔE $(=E_2-E_1)$	$E_3^{1/2}$
TTF-(HO)TEMPO[a]	0.44	0.85(irrev.)	0.41	
TTF[a]	0.49	0.80	0.31	
TTF-(HO)TEMPO[b]	0.34	0.70	0.36	0.81
TTF[c]	0.38	0.77	0.39	
oxo-TEMPO[b]				0.84
HO-TEMPO[d]				0.85

[a] In CH_2Cl_2, Lit.[8].
[b] This work.
[c] Lit. [10].
[d] Lit. [7].

reported as reversible but the other is irreversible. This prompted us to reinvestigate the redox behavior of the TTF-(HO)TEMPO molecule by cyclic and square-wave voltammetries in CH_3CN (Figure 2). We observed three reversible one-electron waves. By comparison with those observed for TTF [10] and TEMPO derivatives under the similar condition (Table 1), the first and second potentials can be assigned to TTF moiety, and the third one to the TEMPO moiety. The EPR spectra of TTF-(HO)TEMPO in CH_3CN solution shows a triplet ($g = 2.022$, $a_N = 15.7$ G; lit [8]. $a_N = 15.3$ G in benzene). After oxidation by controlled potential electrolysis at 0.5 V *vs.* SCE, another triplet signal with $a_N = 7.7$ G is observed (Figure 3). This a_N value is almost half of that of TTF-(HO)TEMPO, and is indicative of an intramolecular spin-spin exchange between the TTF cation radical and the nitroxide radical [11]. After exhausted electrolysis at 1.0 V *vs.* SCE, this triplet disappears due to further oxidation to the diamagnetic compound TTF^{2+}-(HO)$TEMPO^{+}$.

The $E_1^{1/2} = 0.34$ V *vs.* SCE and $\Delta E = 0.36$ V values for TTF-(HO)TEMPO are very similar to those of TTF under similar conditions. The TEMPO moiety shows higher potential ($E_3^{1/2} = 0.81$ V *vs.* SCE), thus the TTF moiety will be oxidized first. TTF-(HO)TEMPO could be considered as a promising donor for the association with $M(dmit)_2$.

$(TTF\text{-}(HO)TEMPO)_3(BF_4)_2$ was prepared by H_2O_2 oxidation in presence of HBF_4. EPR spectra in CH_3CN solution shows the superposition of two triplets with $a_N = 15$ G and 8 G which indicates TTF-(HO)TEMPO and $TTF^{\bullet+}$-(HO)TEMPO, respectively. Similar feature was also observed in the crystal structure of $(TTF)_3(BF_4)_2$ [12]. Slow diffusion of $(TTF\text{-}(HO)\text{-}TEMPO)_3(BF_4)_2$ and $(n\text{-}Bu_4N)[Ni(dmit)_2]$ solutions, or electrocrystallization using TTF-(HO)TEMPO and $(n\text{-}Bu_4N)[Ni(dmit)_2]$, gave a dark green powder, which shows antiferromagnetic behavior with room-temperature

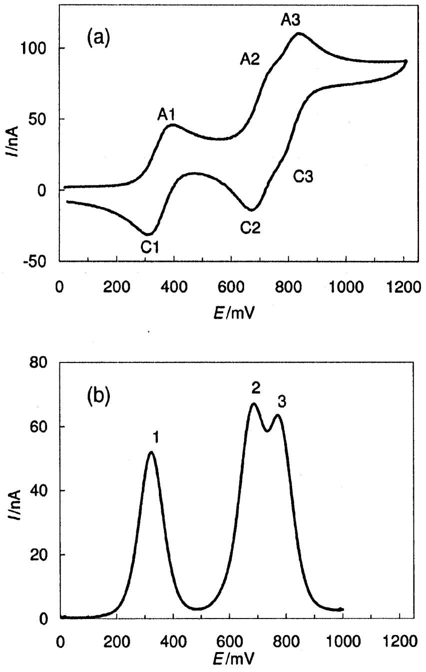


FIGURE 2 (a) Cyclic and (b) square-wave voltammograms of TTF-(HO)TEMPO in CH$_3$CN (0.1 M TBAP, Pt electrodes, scan rate 0.1 Vs^{-1}, V *vs.* SCE).

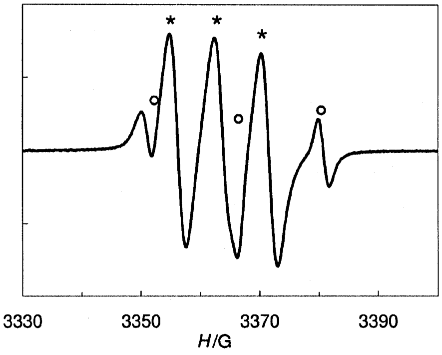


FIGURE 3 The EPR spectra of electrochemically generated TTF$^{\bullet+}$-(HO)TEMPO (shown by ★) in CH$_3$CN at room temperature. The triplet shown by ○ is of TTF-(HO)TEMPO due to incomplete electrolysis.

powder conductivity of $4 \times 10^{-2}\,S\,cm^{-1}$. No well-defined phase has been characterized yet.

CONCLUSION

Associating Me_3N^+-TEMPO with $M(dmit)_2$, affords compounds with interesting structure and properties. However, well-defined phases have not obtained yet for the fractionally oxidized $M(dmit)_2$ salts. Me_3N^+-TEMPO salts with inorganic anions such as BF_4^- and ClO_4^- were also prepared.

The electrochemical property of TTF-(HO)TEMPO was reinvestigated and led to confirm that redox property of this donor is comparable to that of the unsubstituted TTF. Association with $M(dmit)_2$ afforded antiferromgnetic and conducting powder, however failed to afford well-characterised phases.

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