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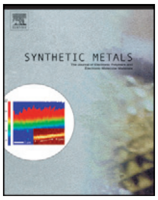

New radical salts based on TEMPO-substituted 2,4,6-triphenylpyridinium and transition metal complexes

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ABSTRACT

Series of radical salts derived from a 2,4,6-triphenylpyridinium (TPP) carrying TEMPO-substituent and transition metal complexes were prepared by the anion exchange of the TPP–TEMPO tetrafluoroborate with [n-Bu$_4$N][Ni(dmit)$_2$], [n-Bu$_4$N]$_2$[Pd(dmit)$_2$], [n-Bu$_4$N]$_2$[Pt(dmit)$_2$], [n-Bu$_4$N][Ni(mnt)$_2$], or [n-Bu$_4$N]$_2$[Ni(mnt)$_2$] to give crystals with different structural features. While weak antiferromagnetic interactions of the Curie–Weiss behavior of $S = 1/2$ spin are predominantly observed in the salts of Pd(dmit)$_2$, Pt(dmit)$_2$ and Ni(mnt)$_2$, the magnetic behavior of 1:1 Ni(dmit)$_2$ salt can be explained by the additional contribution from the spins on Ni(dmit)$_2$ anions ($\chi - \chi_{\text{TEMPO}}$), obeying the 2D Heisenberg model. A couple of the oxidized salts, [TPP][Ni(dmit)$_2$] as well as [TPP]$_2$[Pd(dmit)$_2$], exhibit semi-conducting properties with relatively high room temperature conductivities.

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1. Introduction

Molecular solids with particular functionality are continuously paid much attention by chemists and physicists in the field of materials science [1]. The preparation of new molecular-based spin-bearing systems, among others, has been pursued from the viewpoint of materials/physical organic chemistry to develop novel molecular-based magnetic materials [2]. As regards to molecular-based spin systems, they are roughly classified into two groups; first, organic radical compounds consisting of one component and second, organic charge-transfer (CT) complexes or radical ion salts consisting of two components. The latter group is particularly attractive because a lot of compositional and structural variations are possible and in fact a variety of eminent conductive/magnetic materials with such structural features have been developed, *i.e.*, the first molecular-based ferromagnet [decamethylferrocene][TCNE (tetracyanoethylene)] [3], the first magnetic superconductor [BEDT-TTF (bis-(ethylendithio)tetrathiafulvalene)]$_4$ (H$_2$O) [Fe(C$_2$O$_4$)$_3$](C$_6$H$_5$CN) [4], the first ferromagnetic metal [BEDT-TTF]$_3$ [MnCr(C$_2$O$_4$)$_3$] [5], and many others. Radical salts derived from pyridinium or ammonium ions being composed of respective spin centers of stable radical substituent and counter radical anion are also classified into the latter group. Having relatively strong electrostatic interactions between the components, they are expected to give relatively strong intermolecular magnetic interactions when in suitable positions and conditions. In fact, several examples of this type with intriguing magnetic properties have recently been developed in some pyridinium or ammonium salts with stable radical substituents. Among *N*-alkylaminopyridinium salts with nitronyl nitroxide radical in *p*- or *m*-position [6], a 1:1 salt of *p*-*N*-ethylpyridinium nitronyl nitroxide and Ni(dmit)$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) has been elucidated as an intriguing spin radder system [6c] and three ferromagnets have been discovered from *N*-alkylaminopyridinium salts with an imino nitroxide radical in *p*-position [7]. Several organic/organometallic radical anion salts have been prepared from alkylpyridinium-substituted verdazyl radicals [8], from a trimethylammonium salt with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) [9], or from trialkylanilinium-substituted oxo-verdazyl radicals [10] to show respective semi-conductivities together with interesting magnetic properties.

Concerning the radical salts based on M(dmit)$_2$, extensive studies have so far been performed for the structure/conductivity relationships of the assembled metal complexes (cation)[M(dmit)$_2$]$_2$ (M = Ni, Pd) of a closed-shell cation with M(dmit)$_2$ anion, exhibiting insulating, metallic, or superconducting phases at low temperature under high pressure [11].

In the course of our studies to develop novel spin systems [12], we have been interested in preparing such radical salts that are composed of a cation or an anion carrying a stable radical

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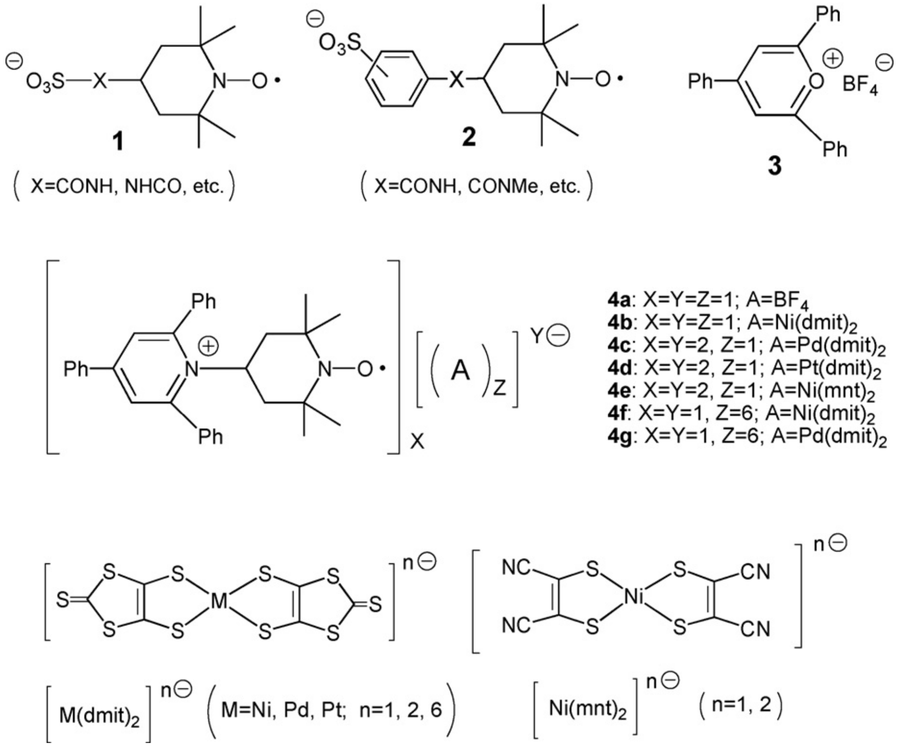


Chart 1.

substituent and appropriate counter anions/cations to develop possible paramagnetic conductors. Hence, series of TEMPO-substituted sulfonates (**1** and **2**) were prepared to form the radical salts with TTF or BEDT-TTF and several materials with semi-conducting properties could be developed among them (Chart 1) [13].

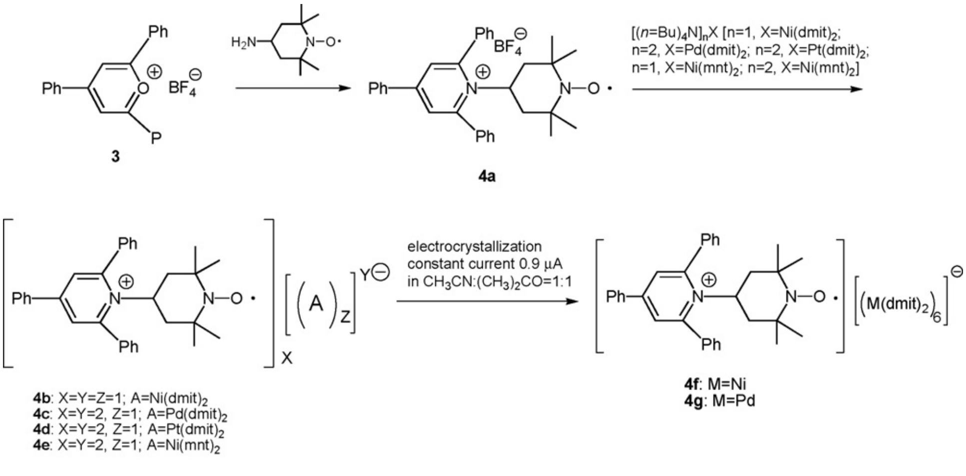
Recently TEMPO substituted 2,4,6-triphenylpyridinium tetrafluoroborate [TPP][BF_4] (**4a**) was found to form radical salts with TCNQ and $TCNQF_4$ through the replacement of BF_4. Different crystal forms were present in each salt, showing apparent differences in their magnetic properties, even though no eminent conductivities could be observed [14]. We then tried to prepare the radical salt derived from the 2,4,6-triphenylpyridinium with a $M(dmit)_2$ anion (M = Ni, Pd, Pt) to obtain salts with better conducing properties and the following will report the details of preparation, structures and magnetic properties of these and related $Ni(mnt)_2$ (mnt = maleonitriledithiolate) salts (**4b**–**4e**) together with the conducting properties of a couple of oxidized salts of $M(dmit)_2$ (**4f**, **4g**) [15].

2. Results and discussion

2.1. Preparation of pyridinium radical salts *4a*–*4h*

As shown in Scheme 1, [TPP][BF_4] **4a** was prepared in 20% yield from the corresponding pyrylium tetrafluoroborate **3** by the nucleophilic insertion of 4-amino-TEMPO in a mixed solution of ethanol and dichloromethane [16].

The metathesis reaction of equimolar amount of [TPP][BF_4] **4a** with [n-Bu_4N][$Ni(dmit)_2$] in an acetone solution produced a dark greenish solid which then was filtered and recrystallized from a mixed solution of acetone and dichloromethane to yield a 1:1



Scheme 1.

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