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PREPARATION AND PROPERTIES OF NEW MULTI-SPIN COMPLEXES

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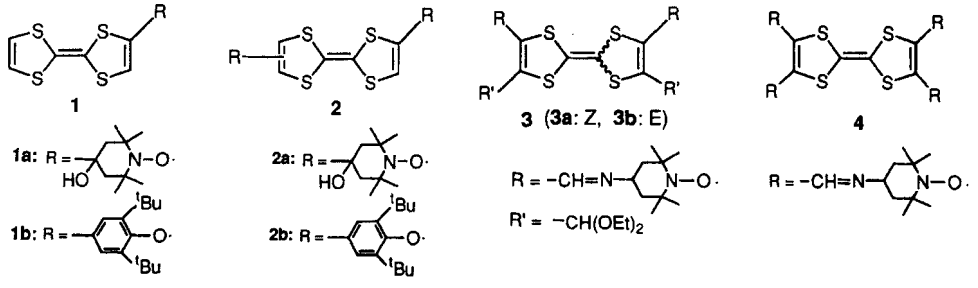
Abstract Two kinds of multi-spin system have been developed; bis- and tetrakis-TEMPO-substituted TTF derivatives have been prepared forming complexes (radical cation salts) with iodine. Several donor-radical-acceptor complexes as multi-spin system with three components (organic ternary alloy) have been prepared.

INTRODUCTION

It is one of current interests to construct new organomagnetic materials through McConnell-Breslow approach and various types of charge-transfer complexes have been developed from the viewpoint to lead important findings including the discovery of new ferromagnetic materials.[1] In the course of our approach for the preparation of new organomagnetic materials, we have been interested in preparing new charge-transfer complexes carring substituents with unpaired electron(s) in either the donor part or the acceptor part or both parts to arrange the spins in column structure.[2]

As the model of such charge-transfer complexes, we have already prepared some TTF derivatives (**1**, **2**) carring substituents with unpaired electron(s) and the charge-transfer complexes derived therefrom, although the desired ferromagnetic properties

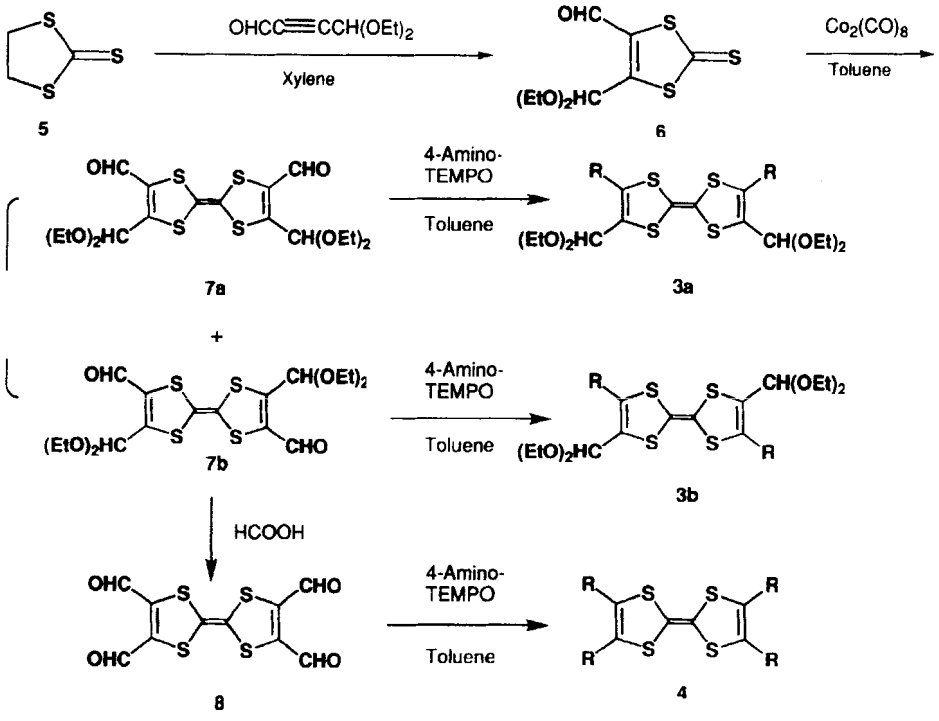


could not be realized yet.[3] As an extension of such approach, we have tried to prepare bis- or tetrakis-TEMPO-substituted TTF derivatives (**3**, **4**) and their charge-transfer complexes to see whether ferro- or ferrimagnetic materials could be realized through the approach.[2] In this paper, we report on the preparative studies and their magnetic properties together with the preliminary results on an alternative approach for the construction of new charge-transfer complexes being constituted of three components, i. e., donor (TTF), radical (4-amino-TEMPO) and acceptor ($TCNQF_4$).

RESULTS AND DISCUSSION

Preparation of Bis- and Tetrakis-TEMPO-substituted TTF Derivatives **3a**, **3b** and **4**

As shown in the following SCHEME, bis- (Z- as well as E-isomers) and tetrakis-TEMPO-substituted TTF derivatives (**3a**, **3b**, **4**) have been prepared through the corresponding formyl drivatives (**7a**, **7b**, **8**), which have been prepared by the coupling reaction of 1,3-dithiole-2-thione derivative **6** following the procedure developed by Gorgues et al.[4] In TABLE 1 cited below are summarized their physical



SCHEME 1

data together with their magnetic data. Although their first oxidation potentials measured by cyclic voltammetry in dichloromethane (V vs. SCE; **3a**: E_1^{ox} = 0.65 V, **3b**: E_1^{ox} = 0.60 V, **3c**: E_1^{ox} = 0.55 V) were found to be relatively higher than that of TTF (E_1^{ox} = 0.49 V), their iodine complexes (**7a**, **7b**, **8**) have been prepared and isolated as black or dark brown solids. In their ESR spectra for the complexes, the values of g-factors as well as coupling constants found were not appreciably changed from the corresponding donor components (**3a**, **3b**, **4**) having g-factors of 2.006-2.007 and couping constants of 15-16 G, respectively.

Magnetic Properties of **3a**, **3b**, **4** and Their Iodine Complexes **7a**, **7b**, **8**

Magnetic susceptibility of **3a**, **3b** and **4** as well as their iodine complexes (**7a**, **7b** and **8**) obtained were measured on their polycrystalline samples by a SQUID susceptometer at temperatures between 2 K and 300 K. The susceptibility data for each compound followed Curie-Weiss curve showing the magnetic behavior with corresponding Weiss constants summarized in TABLE 1.

In FIGURE 1 and in FIGURE 2 are shown the temperature dependence of

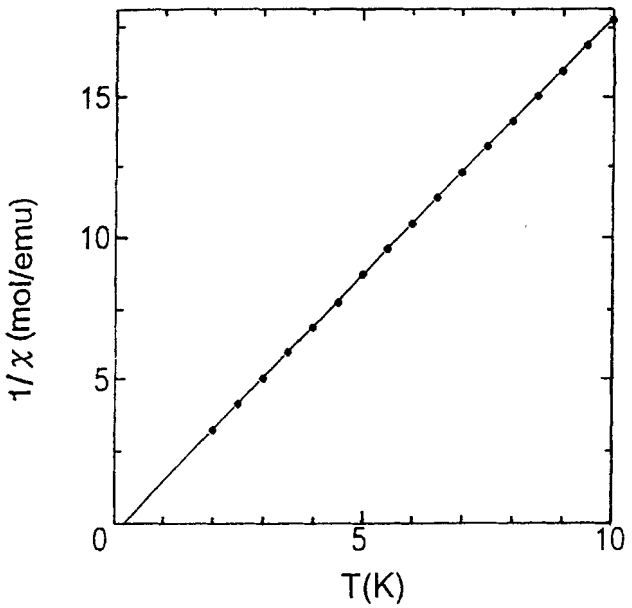


FIGURE 1 Temperature dependence of $1/\chi$ for **3a**.

reciprocals of magnetic susceptibility in the low temperature region for Z-isomer of bis-TEMPO-substituted TTF derivative **3a** and its iodine complex **7a**, respectively. It was found from the data that weak ferromagnetic interactions observed in **3a** turned to weak antiferromagnetic interactions in its iodine complex **7a** with appreciable decrease of magnetic susceptibility in the latter compound compared with **3a** resulting probably

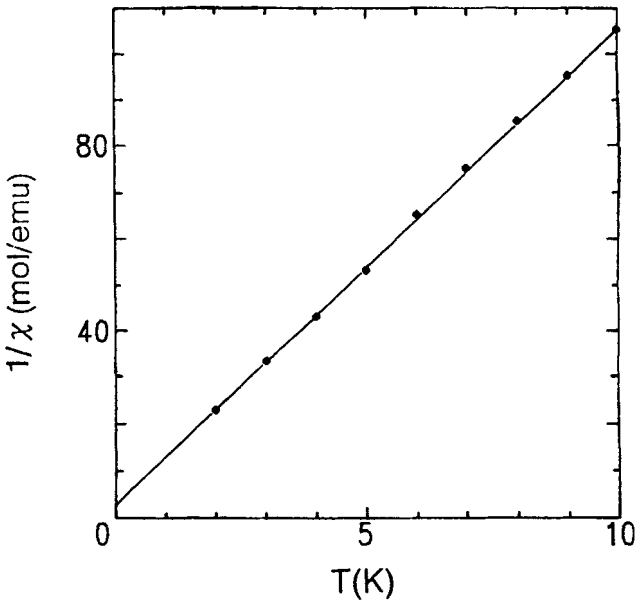


FIGURE 2 Temperature dependence of $1/\chi$ for **7a**.

from the intra- and/or intermolecular singlet formation between unpaired electrons by the complex formation.

Antiferromagnetic behavior with almost the same magnitude of Weiss constant was observed between donor **3a** and its iodine complex **7a** with decrease of magnetic susceptibility in **7a** compared with the donor and the same tendency was observed even

TABLE 1 Summary of physical and magnetic data of **3a**, **3b**, **4** and complexes **7a**, **7b**, **8**

compound	appearence	mp (C°) [a]	magnetic interactions	Weiss constant (K) [b]
3a	orange solid	> ca. 168	ferromagnetic	0.2
3b	orange solid	> ca.160	antiferromagnetic	- 2.3
4	pale red solid	> ca.192	antiferromagnetic	-1.0
7a	black solid	> ca.145	antiferromagnetic	-0.2
7b	black solid	> ca.116	antiferromagnetic	-1.8
8	dark brown solid	> ca.188	antiferromagnetic	-1.0

a) decomposition point. b) Fitting for Curie-Weiss rule.

between tetrakis-substituted derivative **4** and its iodine complex **8** (TABLE 1). In spite of our efforts, so far no single crystals of the complexes for crystallographic studies to clarify their magnetostructural relationships have been available and as far as the complexes examined, it could not be realized to arrange the spins by complex formation in columnar structure and to obtain ferro- or ferrimagnetic materials but serious lost of their spins was observed probably because of singlet formation described above. We then turned our attention to a possibility of the spin alignment by constructing three component system composed of donor, stable radical and acceptor.

Preparation of TTF-4-ATEMPO-TCNQF4 Complexes and Their Properties

According to the recent finding that 4-amino-TEMPO (ATEMPO) radical forms charge-transfer complexes with some acceptors[5] and an earlier study on the growth of mixed crystals of BEDT-TTF-trihalides developed by one of us (H. A.),[6] we extended our study for the preparation of charge-transfer complexes with three component sytem being constituted of TTF, ATEMPO and $TCNQF_4$. Although the results obtained so far are the preliminary one, a variety of complexes were found to be prepared by changing the molecular ratio of each component whose physical data so far obtained are summarized in TABLE 2.

TABLE 2 Summary of physical data of the complexes

complex	composition[a)]	appearence	mp (C°) [b)]
ATEMPO-$TCNQF_4$	1 : 1	green solid	> ca.150
TTF-ATEMPO-$TCNQF_4$	0.3 : 0.7 : 1	dark blue solid	> ca.180
TTF-ATEMPO-$TCNQF_4$ (**9**)	0.5 : 0.5 : 1	dark bluish green solid	> ca.192
TTF-ATEMPO-$TCNQF_4$	0.7 : 0.3 : 1	dark bluish violet solid	> ca.195
TTF-$TCNQF_4$	1 : 1	dark violet solid	> 300

a) theoretical ratio. b) decomposition point.

The magnetic behavior of the complex **9** was found from the temperature dependence of reciprocals of magnetic susceptibility in the low temperature region to follow Curie-Wess law and to have the antiferromagnetic interactions with Weiss

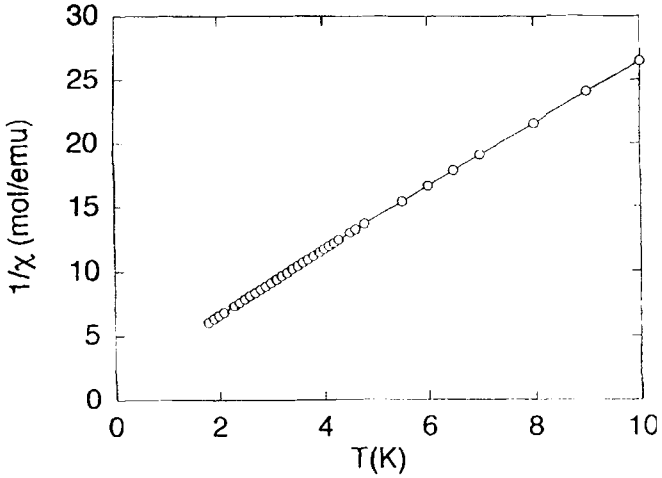


FIGURE 3 Temperature dependence of $1/\chi$ for **9**.

temperature of as large as -0.7 K (FIGURE 3). Although no remarkable interactions have been observed in the complex, it remains still to be investigated in their magneto-constitution relationship because of the interest of such novel three component complexes which are considered as organomagnetic ternary alloys and further studies including their single crystal preparations are now underway.

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