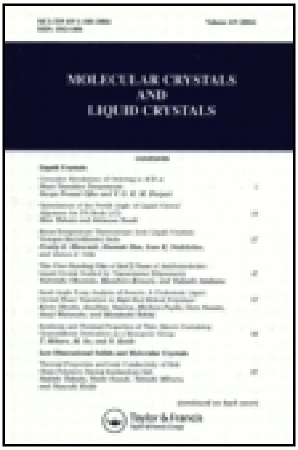

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation and Properties of CT Complexes Derived from 4-Substituted-amino-TEMPO Radicals

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To cite this article: Shin'ichi Nakatsuji, Atsushi Takai, Kazuyoshi Nishikawa, Yukio Morimoto, Noritake Yasuoka & Hiroyuki Anzai (1998): Preparation and Properties of CT Complexes Derived from 4-Substituted-amino-TEMPO Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 229-234

To link to this article: http://dx.doi.org/10.1080/10587259808044280

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 229-234
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Preparation and Properties of CT Complexes Derived from 4-Substituted-amino-TEMPO Radicals

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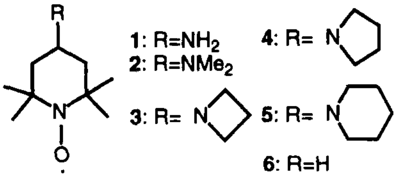
The charge-transfer (CT) complexes of a series of 4-substituted-amino-TEMPO radicals with some acceptors were prepared and their magnetic properties were investigated. The X-ray crystal structural analysis was carried out on the CT complex consisted of 4-azetidyl-TEMPO and TCNQF4; comparison with that of the complex derived from TEMPO and TCNQF4 showed a distinct difference in their molecular/crystal structures, which is considered to reflect the difference in their magnetic properties.

Keywords: TEMPO radicals; CT complexes; magnetic properties; X-ray analysis

INTRODUCTION

TEMPO radicals are a well-known class of stable radicals mainly used as spin probes for biological studies[1]. On the other hand, it is of current interest to develop new molecular-based magnetic materials, especially organomagnetic materials, and numerous compounds carrying TEMPO radicals as the key building blocks have been prepared and their magnetic behavior has been



elucidated in recent years[2]. During the course of our studies to develop new organomagnetic materials, we have been interested in preparing some donor or acceptor molecules carrying stable radicals, especially TEMPO radicals, and the CT complexes derived therefrom to build up and to arrange the spins in the solid state/crystal structures[3]. We have observed during the studies that some TEMPO radicals themselves are able to form CT complexes with appropriate acceptors, that is to say, TEMPO radicals can act as donors to form CT complexes being isolated as solid substances[4]. In this paper, we wish to report on the preparation and the magnetic properties of the CT complexes derived from 4-substituted-amino-TEMPO radicals and on the results of the X-ray analysis of the complex consisted of 4-azetidyl-TEMPO **3** and TCNQF4 in comparison with that of the complex derived from TEMPO **6** and TCNQF4 to show the magneto-structural relationship.

PREPARATION AND ELECTROCHEMICAL BEHAVIOR of 4-SUBSTITUTED-AMINO-TEMPO DERIVATIVES

Although a few TEMPO derivatives used in this study are commercially available, we have prepared some alkylamino-TEMPO derivatives expecting the enhancement of the donor ability. The alkylamino-TEMPO derivatives **2**-**5** were prepared by the reductive amination of 4-oxo-TEMPO with alkyl amines using sodium cyanoborohydride as a reducing reagent[5].

To estimate their donor ability, we investigated their electrochemical behavior by cyclic voltammetry. It was observed as shown in TABLE that 4-

TABLE Cyclic voltammetric data for radicals **1**-**6**[a]

Compound	E_1^{ox}	E_2^{ox}	ΔE^b
1	0.68	0.87	0.19
2	0.62	0.85	0.23
3	0.64	0.86	0.22
4	0.56	0.85	0.29
5	0.65	0.85	0.20
6	0.70	-	-

[a] Oxidation potentials (V) *vs.* SCE in CH_3CN with 0.1 M Bu_4NClO_4 at room temp.

[b] $\Delta E = E_2^{ox} - E_1^{ox}$.

amino-TEMPO radicals **1-5** show two oxidation potentials (E_1^{ox} and E_2^{ox}) in their redox waves while TEMPO radicals **6** has only one oxidation potential based on a nitroxide radical in acetonitrile. Each E_1^{ox}- and E_2^{ox}-value of **1-5** could be attributed to the oxidation of the amino group and the nitroxide radical, respectively, and their E_1^{ox}-values are apparently lowered with the lowest value of 0.56 V in **4** but, on the contrary, each E_2^{ox}-value is found to be higher compared with that of **6**. From the point of view of such redox behavior of TEMPO radicals **1-6**, it was anticipated that some CT complexes could possibly be formed with appropriate acceptors.

PREPARATION AND MAGNETIC PROPERTIES OF CT COMPLEXES

A series of the CT complexes derived from 4-amino-TEMPO **1** or 4-alkylamino-TEMPO derivatives **2-5** or even TEMPO radical **6** were successfully prepared, although DDQ complex of **6** could not be prepared probably because of the poorer donor ability of **6** compared with **1** or **2-5**. Each donor-acceptor ratio of the complexes thus prepared was 1:1 according to elemental analyses and the CT-bands or the bands for their radical anions were clearly observed for each complex in their visible absorption spectra. In their ESR spectra, triplet absorption due to the nitroxy radical was observed in acetone solution, indicating that at least part of the spins remained around the N-O moiety of the donor part.

The magnetic susceptibility measurement on the CT complexes was carried out on the polycrystalline sample by a SQUID susceptometer in the temperature range of 2-300 K. Most CT complexes so far prepared were also found to follow the Curie-Weiss curve showing weak antiferromagnetic interactions. For example, the $TCNQF_4$ complex of **3** was found to follow Curie-Weiss rule and its Weiss-constant was found to be -0.3 K. It was noted that, while TEMPO **6** itself showed antiferromagnetic interactions with a Weiss constant of -3.0 K,[6] drastic decrease of magnetic susceptibility was observed in the $TCNQF_4$ complex suggesting a strong tendency to singlet formation between the radical centers[4]. On the contrary, no such drastic decrease of magnetic susceptibility was observed for 4-amino- or 4-alkylamino-TEMPO derived complexes, and acceptor-dependent antiferromagnetic or ferromagnetic interactions were suggested in each complex which were estimated from their Weiss constants. Thus, sharp difference was observed in the magnetic behavior between the complexes from 4-amino-TEMPO **1** or its alkylated derivatives **2**-**5** and the complex derived from TEMPO **6**.[7]

X-RAY ANALYSIS ON THE COMPLEX CONSISTED OF 3 AND TCNQF$_4$

To investigate the magneto-structural relationship on the complexes and to clarify the above-mentioned difference, we then tried to study of their crystal structures by X-ray analysis. Single crystals were obtained from the complexes **3**-TCNQF$_4$ complex and **6**-TCNQF$_4$ complex[4] among the complexes prepared. The X-ray analysis of the single crystal of **3**-TCNQF$_4$ grown by recrystallization from acetone gave the confirmative structural elucidation of the complex as shown in FIG. 1 and FIG. 2. Relatively small bond alternation in each TCNQF$_4$ molecule of the complex suggests the delocalization of π-electrons on the whole molecule forming its radical anion (FIG. 1, left)[8] and this feature is rather similar with the **6**-TCNQF$_4$

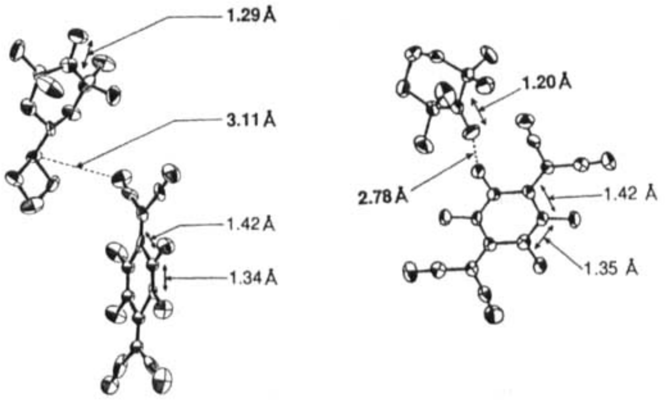


FIGURE 1 Molecular structures of **3**-TCNQF$_4$ (left) and **6**-TCNQF$_4$ (right).

complex (FIG. 1, right). But a distinct difference in the crystal structure of **3**-TCNQF$_4$ compared with that of **6**-TCNQF$_4$ was observed in the point that the N-O distance (1.29 Å) in the donor molecule in **3**-TCNQF$_4$ is the ordinary one for the nitroxide radical (1.28-1.29 Å)[9] indicating the spins of the radical molecules are not lost whereas the shorter N-O bond length (1.20 Å) in the donor molecule in **6**-TCNQF$_4$ compared with the bond length in ordinary nitroxide radicals would indicate the formation of an oxo-ammonium ion from the nitroxide radical. The short contact between the nitrogen atom of the amine moiety of the radical **3** and TCNQF$_4$ molecule suggests that the charge-transfer occurs from the alkylamino group to the acceptor molecule in this case. Also, being different in respect of the columnar structure of the radical and acceptor observed in **6**-TCNQF$_4$, a perpendicular and segregated columnar structure is observed in **3**-TCNQF$_4$ as shown in FIG. 2 in which each two molecules of TCNQF$_4$ are apparently surrounded by four molecules of radical **3**. The distances between the layers of TCNQF$_4$ molecules stacking along the c-axis amounted to 3.2-3.5 Å and the situation is rather

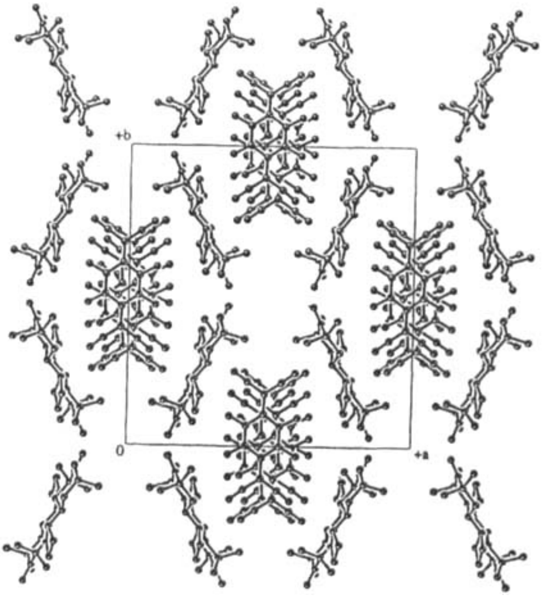


FIGURE 2 Crystal structure of **3**-TCNQF$_4$ viewed along the c-axis.

similar with that in **6**-TCNQF4. Radical molecules, on the other hand, stack along the a-axis in a zig-zag manner and a side-by-side, head-to-tail manner along the c-axis. The nearest O-O distance between the radical molecules amounts to 6.10 Å (-x, y, 1/2-z). From the structural viewpoint mentioned above, antiferromagentic interactions with no appreciable decrease of spins in **3**-TCNQF4 would be attributed mainly to the interactions between the spins on 4-azetidyl-TEMPO radicals while the spins on the TCNQF4 anion radicals would largely be lost by the intermolecular singlet formation which was also found in **6**-TCNQF4 with similar columnar structure for TCNQF4.

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