CT Complexes Derived from Verdazyl Radicals

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Several charge-transfer (CT) complexes derived from 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals and TCNQF₄ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-1,4-quinodimethane) or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) were prepared and their magnetic properties were investigated. The X-ray crystal structural analyses on the CT complexes consisted of 3-(4-methoxyphenyl)-, 3-(4-tolyl)- as well as 3-(4-chlorophenyl)-verdazyl radicals and TCNQF₄ were carried out and correlated with their magnetic properties in which large decrease of magnetic susceptibility was observed in each complex.

Introduction

The search of new organomagnetic materials is, together with the search of new organoconducting materials, of growing interest and a lot of neutral stable radicals have been prepared for the purpose in recent years [1]. On the other hand, only the limited members of CT complexes have been reported in which stable radicals act as donor components and they have been prepared mainly for obtaining new organic conductors.

Bryan et al. found recently that dithiadiazolyl radical I and its derivatives 2,3 form iodine or bromine complexes when doped them with I₂ or Br₂ and some of those complexes show high electrical conductivity at room temperature [2]. More recently, Wudl et al. prepared diphenylbenzotriazinyl radical 4-TCNQ (2:5) complex and found its anomalous and anisotropic pressure effect on its electric conductivity [3]. Sugawara et al. reported on the formation of CT complex between dimethylamino nitronyl nitroxide 5 and DDQ by grinding in the solid state which proved to behave paramagnetically by susceptibility measurement [4] (Fig. 1).

We have been interested in preparing such organo compounds that have exotic solid state properties and we found recently that TEMPO and its derivatives 6 also act as donors to form CT complexes with appropriate acceptors showing various and acceptor dependent magnetic properties [5] (Fig. 1).

Verdazyl radicals are also one of the well-known classes of stable radicals having delocalized spin structures of unpaired electrons [6], and we found that several CT complexes could be formed with some acceptors using verdazyl radicals as donors. In this paper, we wish to report in detail on the preparation and the properties, especially magnetic properties, of the CT complexes derived from 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals 7-10 with TCNQF₄ or DDQ and on the results of the X-ray crystal structural analyses of three of the complexes to correlate with their magnetic properties [7].

Results and Discussion

Preparation and properties of verdazyl radicals

A series of 1,5-diphenyl-3-(p-substituted-phenyl)-verdazyl radicals 7-10 were prepared according to the method developed by Kuhn and Trischmann (Scheme 1) [8].

We were initially interested in the electronic effect of p-substituents on formation of the corresponding CT complexes and their magnetic behavior to be regulated by the effect. We then investigated the donating ability of the radicals by
an electrochemical method using cyclic voltammetry, since, to our knowledge, there was no report on the electrochemical behavior of verdazyl radicals and the results obtained are summarized in Table I. It was found from the results that the first oxidation potentials of the verdazyl radicals 7-10 were much lower compared with TEMPO radicals [5] showing their higher donating ability than TEMPO derivatives. The values were, however, not so different within 7-10 suggesting that the donor ability is dominated mainly on the radical moiety. At the same time, gradual increase of the donating ability of the radicals was estimated with increase of the electron-donating ability of substituents. Actually, corresponding CT complexes were found to be formed easily with acceptors as described below.

In their ESR spectra, typical quintet absorptions were observed in each radical with g-factor of 2.004 in benzene solution. The magnetic susceptibility measurement on the radicals was carried out on the polycrystalline sample by a SQUID susceptometer in the temperature range of 2–300 K. It was found from the results that antiferromagnetic interactions were predominant for the

Table I. First oxidation potentials for verdazyl radicals 7-10\(^a,b\) and TEMPO radical\(^a,c\).

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>TEMPO</th>
</tr>
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<tr>
<td>(E_{1}^{\text{ox}})</td>
<td>0.30</td>
<td>0.27</td>
<td>0.28</td>
<td>0.32</td>
<td>0.70</td>
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</table>

\(^a\) Oxidation potentials (V) vs SCE in CH\(_3\)CN with 0.1 M Bu\(_4\)NClO\(_4\) at room temp.; \(^b\) irreversible; \(^c\) reversible.
zyl radicals, and short-range ordering was suggested in 7 [9], 8 and 10 in the very low temperature range [10].

**Preparation and properties of the CT complexes derived from verdazyl radicals**

Considering the results from the electrochemical measurements on the verdazyl radicals, it was well anticipated that some CT complexes would be formed from the radicals with an appropriate acceptors and, actually, several CT complexes (11-15) were found to be formed from 7-10 with TCNQF₄ or DDQ [11] (Scheme 1). They were isolated as relatively stable solids or crystals, and donor/acceptor ratio of the complexes varied from 1:1 for 12, 14, 15 to 1:2 for 11 being estimated from elemental analyses. In 8-TCNQF₄ complex 13 with donor to acceptor ratio of 2:3, solvent molecules (ethyl acetate) were found to be incorporated in the crystal lattice being clarified from X-ray analysis as described below.

In their electronic spectra, typical absorptions ascribed to TCNQF₄ or DDQ radical anion were clearly observed (see Experimental) and the lower frequency-shift of \( v_{CN} \) observed in their IR spectra (\( v_{CN} = 2195-2175 \text{ cm}^{-1} \) in TCNQF₄ complexes and \( v_{CN} = 2237 \text{ cm}^{-1} \) in neutral TCNQF₄; \( v_{CN} = 2205 \text{ cm}^{-1} \) in DDQ complex and \( v_{CN} = 2233 \text{ cm}^{-1} \) in neutral DDQ) together with UV data suggested the occurrence of one-electron transfer from radical to acceptor molecules [12].

As shown in the results from the susceptibility measurements on the CT complexes by using SQUID susceptometer, large decrease of magnetic susceptibility was observed in each complex, irrespective of the type of both donors and acceptors, being apparent from their Curie-constants (normal value for the radical with \( S=+1/2 \) is 0.375) (Table II). The magnitude of decrease was dependent on the kind of complex, but no appreciable regularity was observed in the results indicating no efficient regulation by the substituents could be realized in spite of a-fore-mentioned expectation. Similar large decrease of magnetic susceptibility was also observed in TEMPO-TCNQF₄ and its magnetic behavior was correlated with X-ray analysis data [5]. Weak antiferromagnetic interactions estimated from their values of Weiss constants and compared with original radicals suggest that spin-spin interactions within the complexes are rather weak one (Table II). To clarify the magneto-structure relationship on the class of CT complexes, we then carried out X-ray analyses on three of the complexes (TCNQF₄ complexes of 8, 9 as well as 10) for which single crystals were prepared by recrystallization using appropriate solvents.

**X-ray structure analyses on TCNQF₄ complexes of 8, 9 as well as 10**

The parameters of X-ray structural analyses on TCNQF₄ complexes of 8, 9 as well as 10 (13, 14 and 15) are summarized in Table III. It was found from their X-ray analyses that both 14 and 15 have rather similar molecular/crystal structures among the three complexes elucidated while 13 was somewhat different from them, taking solvent molecules (ethyl acetate) into a crystal lattice. The molecular as well as crystal structure of 14 is shown in Fig. 2 and Fig. 3, respectively. Some features are apparent from the analysis. First, the complex consists of an equimolecular ratio of radical 9 and TCNQF₄ with segregated column structure along c-axis in the crystal. Second, it is estimated from their molecular structures that verdazyl radical 9 is converted into a verdazylum ion by one-electron transfer to TCNQF₄ because both N-N bond length, in the radical moiety (i. e., N5-N6=1.311 Å and N7-N8=1.313 Å) are clearly shortened compared with the normal bond length in the verdazyl radical (1.348–1.353 Å) [13]. Third, the TCNQF₄ molecule is converted into its radical anion owing to the one-electron transfer from the verdazyl radical with relatively small bond alternation in each TCNQF₄ molecule of the complex.
suggesting the delocalization of π-electrons on the whole molecule \[14\] (Scheme 2).

Fourth, it is also apparent from the analysis that TCNQF$_4$ molecules in the complex form a dimer
pair having intra-dimer distances of 3.21–3.23 Å ($r_1$) and inter-dimer distances of 4.78–4.80 Å ($r_2$).
Then, the decrease of magnetic susceptibility in the complexes would largely be due to the singlet

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Table III. Summary of crystal data for 13, 14 and 15.

<table>
<thead>
<tr>
<th></th>
<th>13</th>
<th>14</th>
<th>15</th>
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</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{92}$H$</em>{46}$N$_{20}$O$<em>4$F$</em>{12}$</td>
<td>C$<em>{33}$H$</em>{19}$N$_8$F$_8$</td>
<td>C$<em>{32}$H$</em>{14}$N$_8$F$_4$Cl</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>1603.38</td>
<td>603.56</td>
<td>623.98</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
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<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2$_1$</td>
<td>(#14)</td>
<td>P1 (#1)</td>
</tr>
<tr>
<td><strong>$a$ [Å]</strong></td>
<td>23.303(3)</td>
<td>13.411(1)</td>
<td>7.398(1)</td>
</tr>
<tr>
<td><strong>$b$ [Å]</strong></td>
<td>11.042(6)</td>
<td>14.874(1)</td>
<td>25.170(1)</td>
</tr>
<tr>
<td><strong>$c$ [Å]</strong></td>
<td>19.880(3)</td>
<td>7.403(1)</td>
<td>15.289(1)</td>
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<tr>
<td><strong>$\alpha$ [degrees]</strong></td>
<td>96.021(8)</td>
<td>96.74(1)</td>
<td>90.94(1)</td>
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<tr>
<td><strong>$\beta$ [degrees]</strong></td>
<td>11.042(6)</td>
<td>14.874(1)</td>
<td>25.170(1)</td>
</tr>
<tr>
<td><strong>$\gamma$ [degrees]</strong></td>
<td>23.303(3)</td>
<td>13.411(1)</td>
<td>7.398(1)</td>
</tr>
<tr>
<td><strong>$V$ [Å$^3$]</strong></td>
<td>7673(4)</td>
<td>1430.7(3)</td>
<td>2846.7(6)</td>
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<td><strong>Z</strong></td>
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<td>2</td>
<td>4</td>
</tr>
<tr>
<td><strong>D (calc) [g cm$^{-3}$]</strong></td>
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<td>1.401</td>
<td>1.456</td>
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<td>4647</td>
<td>4748</td>
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<td><strong>No. of reflections used in Refinement F&gt;3σ</strong></td>
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<td>3344</td>
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<tr>
<td><strong>No. of parameters refined</strong></td>
<td>1064</td>
<td>407</td>
<td>406</td>
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<tr>
<td><strong>$R$</strong></td>
<td>0.048</td>
<td>0.044</td>
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<tr>
<td><strong>$R_w$</strong></td>
<td>0.044</td>
<td>0.041</td>
<td>0.055</td>
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</table>
formation between the dimer pairs of TCNQF₄ radical anions although total spin is not completely lost but still slightly remained as suggested from the susceptibility data. Concerning with the composition of the complex, normal stoichiometry is suggested from the X-ray analysis as well as elemental analysis, while the CT complex (salt) derived from a 2,4-diphenylbenzo-1,3,4-triazolyl radical and TCNQ reported by Wudl et al. has an uncommon stoichiometry in which the radical is also converted to the corresponding cation in the complex transferring one electron to one dimer pair of TCNQ molecules [3].

Similar crystal structure to complex 14 was found in complex 15, in which verdazyl radical 10 is turned to verdazylum ion and TCNQF₄ to TCNQF₄ radical anion forming segregated column structure in the crystal and giving dimer pair of TCNQF₄ radical anions along a-axis in TCNQF₄ column (Fig. 4). Again, singlet formation between the dimer pairs should result in the large decrease of magnetic susceptibility in the complex. In the complex 13, on the other hand, the molar ratio of the radical 8, TCNQF₄ and ethyl acetate is found to be 2:3:1 to form the crystal lattice and in which the radicals as well as dimer pairs of TCNQF₄ molecules form a segregated column along the b-axis, but the remaining TCNQF₄ molecules with almost perpendicular molecular orientation to the dimer pairs form a sheet-like structure along the b-axis (Fig. 5). Careful examination of each bond length of both donor and acceptor molecules suggests the formation of verdazylum ion and TCNQF₄ radical anion also in this case. Therefore, the observed large decrease of susceptibility in the complex would be ascribed to the dimer formation within the column to result singlets between them and also the cancellation of their spins within the sheet-like structures of TCNQF₄ radical anions on the whole [15].

Although the molecular ratio of donor to acceptor varies from complex to complex, similar situation as complexes 13 - 15 with dimerizing nature of acceptor molecules within the column would be anticipated in the solid-state structures of other complexes to result predominantly in the singlet formation and then in the large decrease of their magnetic susceptibility.
Electrical conductivity on CT complexes

Because the segregated columnar structures were apparent in three of the TCNQF₄ complexes, relatively high electrical conductivity was expected through the TCNQF₄ columns in the complexes. However, the room temperature conductivity of the complexes investigated was less than the order of 10⁻⁶ S·cm⁻¹ in each case and the applied pressure on the complexes has not improve their conductivity to any appreciable extent.

In summary, we prepared a series of 1,3-5-triphenylverdazyl radicals and corresponding CT complexes derived from the verdazyl radicals and acceptors as TCNQF₄ or DDQ. Although short-range ordering was observed in some of the radicals, large decrease of magnetic susceptibility was predominant in each CT complex prepared irrespective to the ratio of donor to acceptor in the crystal structure and such magnetic behavior in the complexes was structurally correlated with the X-ray analyses data being indicated from three of the complexes. The electrical conductivity of the complexes at room temperature proved to have the values below 10⁻⁶ S·cm⁻¹ in each case with or without applied pressure.
Experimental

General

Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. IR spectra were recorded on a JASCO Report-100 spectrometer. UV-visible spectra were obtained on JASCO Ubist-35 spectrometer. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. ESR spectra were obtained on a JEOL JES-FE3XG spectrometer and each g-value was determined using Mn²⁺/MnO maker as internal standard. Susceptibility measurements were carried out on a QUMTUM DESIGN MPMS-5 SQUID susceptometer using ca. 10 mg for each powdered sample at 0.5 T from 5 K to 300 K and 0.1 T below 5 K, respectively. The corrections for the diamagnetic contribution were carried out, using diamagnetic susceptibilities evaluated by assuming that paramagnetic susceptibilities follow the Curie law at high temperatures. X-ray diffraction data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and a 12KW rotating anode generator at room temperature. The structures were solved by direct methods and expanded using Fourrier techniques. Crystal data are listed in Table III. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Full crystallographic data have been deposited at the Cambridge Crystallographic Centre [16].

Preparation of verdazyl radicals (7 – 10) and their CT complexes (11 – 15)

Verdazyl radicals 7-10 were prepared from corresponding formazan derivatives according to the method of Kuhn and Trischmann [8]. They were characterized by spectroscopic methods and identified by comparing their melting points with literature values.

A typical procedure for the preparation of a CT complex is exemplified for 14 and is as follows; A dichloromethane solution (5 cm³) of verdazyl 9 (10 mg, 0.031 mmol) was added to a dichloromethane solution (15 cm³) of TCNQF₄ (8.4 mg, 0.030 mmol) at ambient temperature. The color of the solution turned immediately to dark greenish blue and after 30 m, diethyl ether was added and the precipitates obtained were filtered to give dark bluish violet crystals (15 mg, 83%). Recrystallized from acetonitrile gave reddish violet plates. M.p. > ca. 154 °C (decomp.). IR (Nujol): ν 2190, 2180sh cm⁻¹ (CN); UV (CH₂Cl₂): λmax (ε) 549 (1.20x10⁵), 753 (1.88x10⁵), 854 (3.68x10⁵) nm.

C₃₃H₁₉N₈F₄ (603.60)
Calcd C 61.06 H 3.17 N 18.97%.
(9: TCNQF₄ = 1:1)
Found C 61.59 H 2.58 N 18.75%.

11: 80% yield. Dark green crystals. M.p. > ca. 155 °C (decomp.). IR (Nujol): ν 2195, 2175sh cm⁻¹ (CN). UV (CH₂Cl₂): λmax (ε) 544 (1.00x10⁵), 753 (1.64x10⁵), 859 (3.38x10⁵) nm.

C₄₄H₁₇N₁₂F₈ (865.74)
Calcd C 61.04 H 1.98 N 19.42%.
(7: TCNQF₄ = 1:2)
Found C 61.08 H 2.14 N 19.82%.

12: 84% yield. Brownish violet crystals. M.p. > ca. 165 °C (decomp.). IR (Nujol): ν 2205 cm⁻¹ (CN); UV (CH₂Cl₂): λmax (ε) 548 (1.70x10⁵) nm.

C₃₈H₂₁N₉O₇Cl₂ (540.40)
Calcd C 62.23 H 3.17 N 15.56%.
(7: DDQ = 1:1)
Found C 62.07 H 3.28 N 15.61%.

13: 76% yield. Reddish violet plates. M.p. > ca. 145 °C (decomp.). IR (Nujol): ν 2195, 2185sh cm⁻¹ (CN). UV (CH₂Cl₂): λmax (ε) 580 (1.03x10⁵), 753 (2.33x10⁵), 857 (4.87x10⁵) nm.

C₇₆H₄₆N₉O₂F₁₂ (1603.47)
Calcd C 61.42 H 2.89 N 17.47%.
(8: TCNQF₄ : CH₂CO₂Et = 2:3:1)
Found C 61.70 H 2.70 N 16.88%.

15: 56% yield. Reddish violet plates. M.p. > ca. 151 °C (decomp.). IR (Nujol): ν 2190, 2175 cm⁻¹ (CN). UV (CH₂Cl₂): λmax (ε) 549 (1.15x10⁵), 753 (1.79x10⁵), 854 (3.76x10⁵) nm.

C₃₂H₁₈N₉F₄Cl (624.01)
Calcd C 61.59 H 2.58 N 17.96%.
(10: TCNQF₄ = 1:1)
Found C 61.05 H 2.24 N 17.50%.

Acknowledgments

We thank to Profs. Kazuo Mukai of Ehime University and Yozo Miura of Osaka City University for their helpful discussions. Financial support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 09640644) is gratefully acknowledged.


[10] The Weiss constants ($\Theta$) and Curie constants ($C$) of the radicals 8–10 were as follows; 8: $\Theta=-29$ K and $C=2.2$ emu·K/mol, 9: $\Theta=-2.8$ K and $C=0.15$ emu·K/mol, 10: $\Theta=-9.9$ K and $C=0.98$ emu·K/mol, respectively.


[15] The early observation described in ref. [7] that there appears to exist two types of TCNQF$_4$ molecules in the crystal of 13, i.e., one with neutral form and another with radical anion form should be corrected as described in the text after careful reexamination of their bond length.

[16] CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB 2 1 EW, UK.