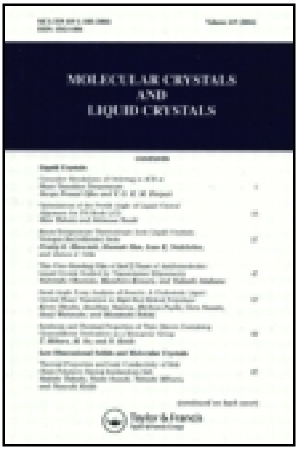

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Novel CT Complexes Derived from 4-Alkylamino-TEMPO and 2,4,6,8-Tetracyanoazulene

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Novel CT Complexes Derived from 4-Alkylamino-TEMPO and 2,4,6,8-Tetracyanoazulene

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Novel CT complexes derived from 4-alkylamino-TEMPO radical and 2,4,6,8-tetracyanoazulene have been prepared. Curie-Weiss behavior has been observed in the magnetic susceptibility of each complex with antiferromagnetic spin-spin interactions in the low temperature region on one hand and rather high conductivity has been found in the electrical conductivity of each complex with semiconducting behavior on the other hand.

Keywords: Nitroxide Radical; TEMPO Radical; Azulene; CT Complex; Magnetic Property; Conductivity

The development of organomagnetic or molecular-based magnetic materials is one of the current interests in materials chemistry. A wide variety of molecular/molecular aggregate spin systems have been developed in recent years in which stable radicals play the crucial roll for the construction of such functional spin systems.[1]

During the course of our studies to develop new organomagnetic materials,[2] we have found recently that some TEMPO radicals (**1**)[3] or verdazyl radicals[4] are able to form CT complexes with appropriate acceptors as $TCNQF_4$ or DDQ. Namely, TEMPO radicals or verdazyl radicals act as donors to form CT complexes and those are isolated as solid substances.

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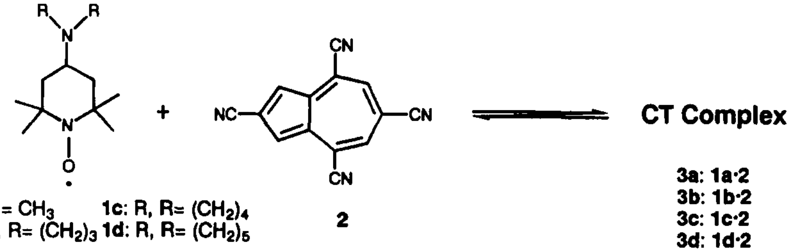
A large number of donor molecules have been prepared until now for organic CT complexes exhibiting carrier transport properties, whereas the number of organic acceptors is still limited being compared to that of organic donors.[5] 2,4,6,8-Tetracyanoazulene (**2**) is a newly developed organic acceptor to be a promising building block for organic metals and thus to join the series of strong acceptors for electrically conductive CT complexes.[6] Actually, relative high conductivities have been found on the novel CT complexes derived from 4-alkylamino-TEMPO radicals and 2,4,6,8-tetracyanoazulene that are rather unusual in such CT complexes based on stable radicals.[7] We report in this communication on the preparation of the CT complexes, their magnetic as well as electrical properties.

The preparation of the CT complexes has been carried out by mixing the acetonitrile solution of equimolecular amounts of 4-alkylamino-TEMPO **1a-1d** with tetracyanoazulene **2** to give black precipitates of the corresponding complexes **3a-3d** (Scheme 1). The donor-to-acceptor ratio was suggested to be 1:2 for the complexes **3a** and **3c**, whereas 1:5 ratio was estimated for **3b** and **3d** by the elemental analysis data.[8]



SCHEME 1

The first oxidation potentials of the radicals **1a-1d** measured by cyclic voltammetry in CH_3CN (*vs.* SCE)[3] fall into 0.56 V – 0.65 V and the first reduction potential of **2** is 0.02 V.[6] The difference ranges from 0.54 to 0.63 V with which the formation of neutral complexes was well anticipated following the criteria proposed by Saito and Ferraris.[9] The formation of neutral complex is also suggested from the above-mentioned stoichiometry of donor-to-acceptor ratio in each complex. However, the decrease of the CN wave numbers from the neutral azulene **2** (2235 cm^{-1}.[6]) has been apparent in each complex showing the stretching frequencies at around 2170–2190 cm^{-1} and the data indicates the existence of partial ionicity in each complex.[10]

Rather complex absorption has been found in their EPR spectra in CH_3CN solution in which the absorption of the radical ion appears to be superimposed with the triplet of the nitroxide radical. Though not so clearly distinguishable as the case of TCNQ/TCNQ$^{\cdot-}$, significant change of the electronic absorption spectra in CH_3CN has been observed in each complex from the neutral azulene, e. g., the longest absorption band in the electronic absorption spectra of each complex in CH_3CN has been appeared at around 1005 nm while that of the original acceptor has been observed at around 912 nm and the data again suggest the radical anion formation of **2** in each complex. Thus, the isolated CT complexes have been satisfactorily characterized by spectroscopic measurements although any attempt to obtain a single crystal for X-ray analysis for further structural information has so far been unsuccessful.

TABLE I Magnetic and electrical properties of CT complex **3**$_a$-**3d**

Compound	*Magnetic interaction*	*C /emu K mol^{-1}*	*θ /K^a*	*σ_{rt}/S cm^{-1b}*	*E_a/eV*
3a	antiferromagnetic	0.30	−0.39	1.40×10^{-2}	0.31
3b	antiferromagnetic	0.19	−0.62	1.93×10^{-4}	0.35
3c	antiferromagnetic	0.31	−0.33	9.38×10^{-4}	0.28
3d	antiferromagnetic	0.23	−0.48	3.95×10^{-5}	0.40

a. Fitting for Curie-Weiss rule.
b. Room temperature conductivity.

The magnetic susceptibility measurements were carried out with the polycrystalline samples by a SQUID susceptometer in the temperature range of 2–300 K and the data are summarized in Table I. It was found from the measurements that the temperature dependence of χT data for the complexes are rather similar showing Curie-Weiss behavior with weak antiferromagnetic spin-spin interactions in the lower temperature region in spite of the difference of their Weiss temperatures. The observed weak and antiferromagnetic spin-spin interactions are considered to be mainly based on the isolated aminoxyl radicals. No significant participation of the spins of the azulenyl radical anion formed by complexation to the spin-spin interactions could be manifested in the complexes. As in the CT complexes derived from 4-alkylamino-TEMPO and other acceptors such as $TCNQF_4$ or DDQ,[3]the slight decrease of their spins from the value of $S=1/2$ was found for **3a** and **3c** being apparent from their Curie constants. On the other hand, relatively large decrease of their spins from the value has been observed in **3b** and **3d** and which suggests the difference of their crystal structures from the former complexes. Although the reason for the relatively large decrease of the spins in the latter complexes is not decisively clear yet, the following possibility might be taken into account; partial singlet formation due to the stronger spin-spin interactions compared with those of the former complexes in the higher temperature region and/or partial decomposition of the spin centers. Thus, the complexes could be assigned into two groups by the magnetic behavior discussed above, although, on the whole, each complex shows weak antiferromagnetic interactions in the lower temperature region. However, further categorizing has been found to be possible through their conducting behavior (*vide infra*).

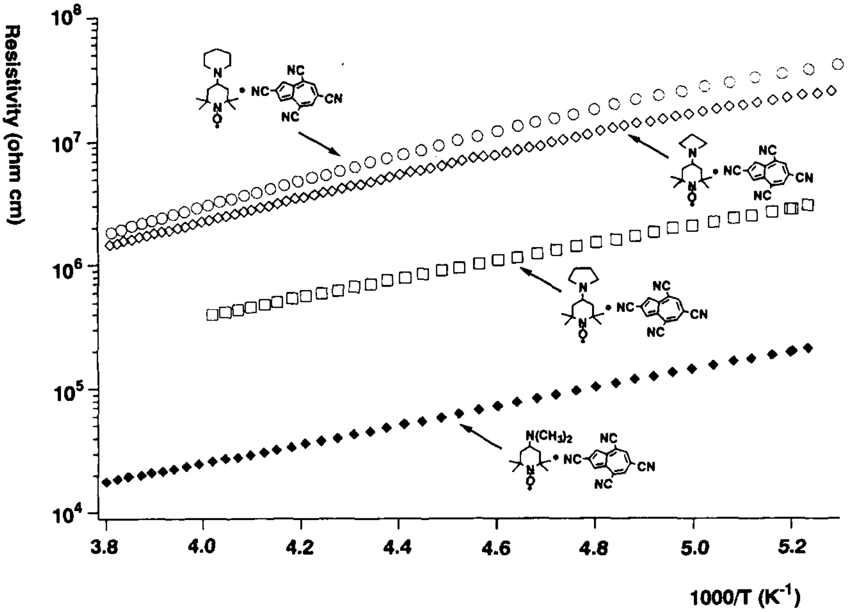


FIGURE 1 Temperature dependence of resistivities of CT complexes

To our surprise, rather high electrical conductivity has been observed in each CT complex at room temperature ranging from 1.40x10^{-2} Scm^{-1} (**3a**) to 3.95x10^{-5} Scm^{-1} (**3d**). The highest room temperature conductivity was found in the CT complex derived from dimethylamino-TEMPO and the lowest one in the CT complex derived from piperidino-TEMPO. The difference indicates the significance of the steric effect for the conducting behaviors in the CT complexes. The conducting behavior shows sharp contrast with each TEMPO derivative itself and other nitroxide based CT complexes showing each conductivity below 10^{-6} Scm^{-1}[3] and the fact indicates the significant participation of azulenyl radical anion for the conductivity in this case. The data of the conducting behavior are comparable to or even 100 times greater for **3a** than that of 2,4-diphenyl-1,3,4-benzotriazolyl/TCNQ complex which have a compressed pellet conductivity of about 10^{-4} Scm^{-1}.[7(e)] The temperature dependence of the resistivity for the four complexes is shown in Fig. 1. Thus, each complex has been found to show simple linear dependence in the resistivity vs. $10^3/T$ plot indicating that they are the semiconductors with activation energy ranging from 0.28 eV (**3c**) to 0.40 eV (**3d**) (Table II). Judging from the magnetic and conducting behaviors described above, the complexes seem to be classified into three groups; high spin concentration with high conductivity (**3a**), low spin concentration with low conductivity (**3b, 3d**), and high spin concentration and intermediate conductivity (**3c**). Such different magnetic/conducting behaviors would be derived from the difference of the packing motives of the TEMPO derivatives and azulene molecules in each complex but the absence of their crystal structure data prevents further discussion and conclusion.

In so far as the complexes **3a** and **3c** are concerned, gradual increase of conductivity and decrease of the activation energy have been observed by the increase of applied pressure for the powder samples in Bridgman anvil (Table II), while an usual pressure dependence has been apparent in the 2,4-diphenyl-1,3,4-benzotriazolyl/TCNQ complex.[7(e)]

TABLE II Pressure dependence of the conductivity of **3a** and **3c**

Compound	*Pressure/GPa*	*Ea/meV*
3a	1.0	107
3a	2.5	94
3c	0.5	144
3c	1.1	130
3c	2.5	123

Further studies including single crystal formation are now in progress.

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8. Also from the elemental analysis data, water molecules are suggested to be incorporated in the complexes **3a** and **3c**; **3a** Found: C, 69.96; H, 4.70; N, 21.22%. Calcd. for $C_{39}H_{31}N_{10}O{\cdot}H_2O$ (D:A=1:2): C, 69.52; H, 4.94; N, 20.79%. **3b**: Found: C, 72.79; H, 2.79; N, 22.44%. Calcd. for $C_{82}H_{47}N_{22}O$ (D:A=1:5): C, 72.82; H, 3.20; N, 22.79%. **3c**: Found: C, 67.60; H, 5.27; N, 18.41%. Calcd. for $C_{41}H_{33}N_{10}O{\cdot}2.5H_2O$ (D:A=1:2): C, 67.75; H, 5.27; N, 19.27%. **3d**: Found: C, 73.14; H, 3.05; N, 22.50%. Calcd. for $C_{84}H_{47}N_{22}O$ (D:A=1:5): C, 73.08; H, 3.43; N, 22.32%.
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10. At first, we expected the existence of the absorption at around 2235 cm^{-1} originated from the neutral azulene molecules in the complexes but, in so far as we examined, no distinct absorption could be observed at the region.