

# Magnetic properties of charge-transfer complexes based on TEMPO radicals

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**TEMPO (2,2,6,6-tetramethylpiperidinyloxy) radical 1 and its derivatives 2–5 are found to form charge-transfer complexes with some acceptors such as TCNQF<sub>4</sub> (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) being isolated as solid substances.**

The development of new molecular magnetic materials, especially organomagnetic materials is current interest and a number of compounds carrying stable radicals as the key building blocks have been prepared and their magnetic behaviour has been elucidated in recent years.<sup>1</sup> In the course of our study for the development of new organomagnetic compounds, we have been interested in preparing some donor or acceptor molecules carrying stable radicals, especially TEMPO radicals, and the charge-transfer (CT) complexes derived therefrom to build up and to arrange the spins in the solid state/crystal structures.<sup>2</sup> Here we report 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 which can be isolated as solids.

When TEMPO radical **1** was treated with an equimolar amount of TCNQF<sub>4</sub> in acetonitrile, the resulting deep-blue solid was confirmed by elemental analysis to be the 1 : 1 complex **6**. Moreover, bands corresponding to the TCNQF<sub>4</sub> radical anion, at 856 and 753 nm in acetonitrile were clearly observed in the visible absorption spectrum of **6** and the lower wavenumber of νCN (νCN 2190 cm<sup>-1</sup>) observed in its IR spectrum compared with the neutral acceptor (TCNQF<sub>4</sub>: νCN 2237 cm<sup>-1</sup>) was also consistent with the formation of the CT complex **6** (Table 1).<sup>†</sup> To our knowledge, this is a rare example of a isolated

charge-transfer complex in which a radical acts as a donor (Scheme 1).<sup>3,4,†</sup>

A magnetic susceptibility measurement on **6** was carried out on a polycrystalline sample using a SQUID susceptometer in the temperature range 2–300 K. It was found from the data that while TEMPO **1** itself shows antiferromagnetic interactions with a Weiss constant  $\theta$  of –3.0 K,<sup>5</sup> a drastic decrease of magnetic susceptibility was observed in complex **6** suggesting a strong tendency for singlet formation between the radical centres.<sup>§</sup>

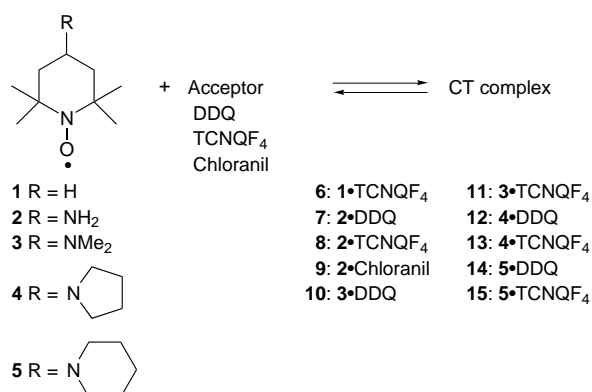
An X-ray analysis of single crystals of **6** grown by recrystallization from acetone gave confirmative structural elucidation of the complex as shown in Fig. 1.<sup>¶</sup> Relatively small bond alternation in each TCNQF<sub>4</sub> molecule of the complex **6** suggests the delocalization of  $\pi$  electrons on the whole molecule upon formation of the radical anion (Fig. 1, upper).<sup>6</sup> It is apparent from Fig. 1 that both donors and acceptors form segregated column structures along the *a*-axis with a zigzag structure in the latter. The following features are also disclosed from the analysis. (i) The nearest O...O distance found is that between donor molecules in the column which amounts to 6.99 Å. (ii) The interplanar stacking distance between TCNQF<sub>4</sub> molecules is ca. 6.99 Å. Partial insertion with some slipping of another TCNQF<sub>4</sub> molecule results in the zigzag column structure. (iii) The nearest distance between oxygen of a donor molecule and a TCNQF<sub>4</sub> molecule is that of O(1)...F(2) of 2.78 Å (Fig. 1, upper), somewhat shorter than the sum of the van der Waals radii of each atom. The magnetic behaviour of the complex would then be interpreted as follows: the charge accepted by the TCNQF<sub>4</sub> species is from TEMPO radicals which leads to the formation of oxoammonium ions, *i.e.* TEMPO is converted into TEMPO<sup>+</sup> resulting a singlet while the loss of the spins of TCNQF<sub>4</sub> radical anions is supposed to be derived from their columnar structure as described above.

Following the results obtained above, we then prepared a series of similar CT complexes derived from 4-amino-TEMPO

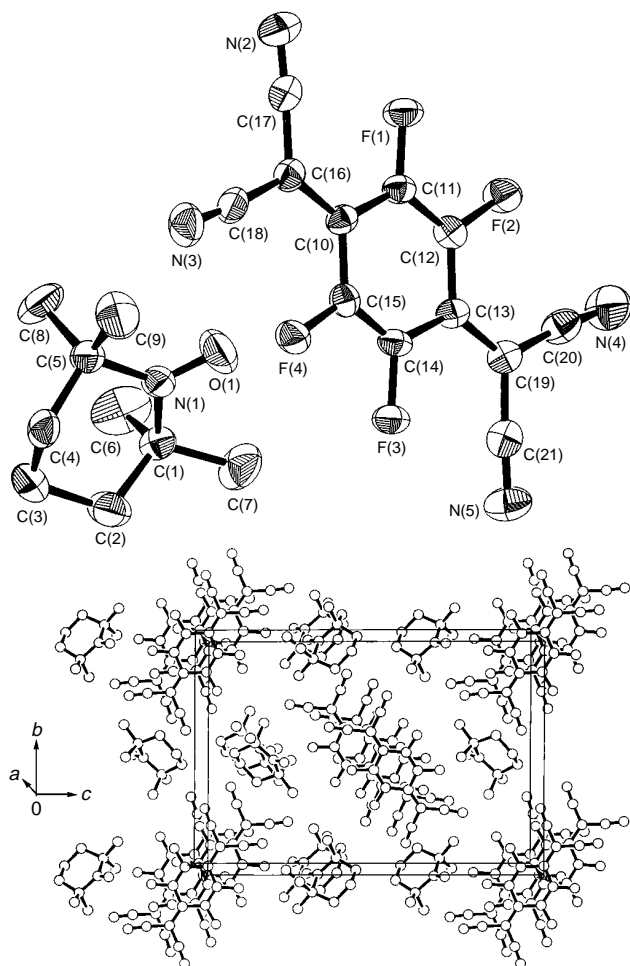
**Table 1** Summary of magnetic data of **1–5** as well as complexes **6–15**

Compound	Magnetic interaction	$\theta^a/K$
<b>1</b>	antiferromagnetic <sup>b</sup>	–3.0 <sup>b</sup>
<b>2</b>	antiferromagnetic	–0.2
<b>3</b>	antiferromagnetic	–7.5 <sup>c</sup>
<b>4</b>	antiferromagnetic	–6.3 <sup>c</sup>
<b>5</b>	ferromagnetic	0.5
<b>6</b>	weak susceptibility	—
<b>7</b>	ferromagnetic	0.1
<b>8</b>	antiferromagnetic	–0.1
<b>9</b>	ferromagnetic	0.1
<b>10</b>	antiferromagnetic	–0.4
<b>11</b>	antiferromagnetic	–1.8
<b>12</b>	antiferromagnetic	–1.1
<b>13</b>	antiferromagnetic	–0.3
<b>14</b>	antiferromagnetic	–6.2 <sup>c</sup>
<b>15</b>	antiferromagnetic	–0.9

<sup>a</sup> Fitting for Curie–Weiss rule. <sup>b</sup> Cf. ref. 5 in text. <sup>c</sup> Short-range order is suggested from the susceptibility data in this case.



**Scheme 1**

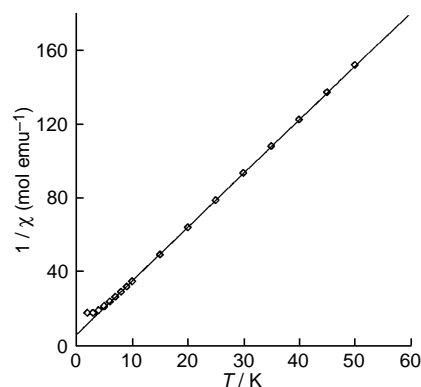


**Fig. 1** Upper: structure of **6**. Lower: crystal structure of **6** viewed almost along the *a* axis. Selected interatomic distances (Å) and angles (°): O(1)–N(1) 1.195(5), N(1)–C(1) 1.526(6), N(1)–C(5) 1.531(6), O(1)–N(1)–C(1) 117.6(5), O(1)–N(1)–C(5) 117.2(5), C(1)–N(1)–C(5) 125.2(5), C(10)–C(11) 1.423(6), C(11)–C(12) 1.350(7), C(12)–C(13) 1.418(7), C(13)–C(14) 1.416(7), C(14)–C(15) 1.340(7), C(10)–C(15) 1.414(7), C(10)–C(16) 1.407(7), C(13)–C(19) 1.398(7).

**2** and its alkylated derivatives **3–5** (Scheme 1) having stronger electron-donating ability than **1**.<sup>4†</sup> The latter radicals (**3–5**) were prepared by the reductive amination of 4-oxo-TEMPO with alkyl amines using sodium cyanoborohydride as a reducing reagent and those radicals **2–5** gave complexes with weaker acceptors than TCNQF<sub>4</sub>, e.g. DDQ or chloranil. As summarized in Table 1, acceptor-dependent antiferromagnetic or ferromagnetic interactions were suggested in each complex on the basis of their Weiss constants, e.g. for the complexes prepared from 4-amino-TEMPO **2**, weak ferromagnetic interactions were suggested in the DDQ complex **7** or chloranil complex **9** ( $\theta = 0.1$  K for both) while antiferromagnetic interactions were suggested in the TCNQF<sub>4</sub> complex ( $\theta = -1.0$  K). Among other complexes prepared from 4-alkylated amino-TEMPO derivatives **3–5**, short-range antiferromagnetic spin order in the very low-temperature region was suggested for the complex **14** as depicted in Fig. 2.

In summary, we have prepared a series of CT complexes **6–15** based on TEMPO radicals having variable and acceptor-dependent magnetic behaviour. The TEMPO–TCNQF<sub>4</sub> complex **6** was structurally elucidated by X-ray analysis to rationalize its low magnetic susceptibility.

Because the CT complexes could be easily prepared from simple nitroxyl radicals and acceptors and because the finding described above may be possibly applied to a variety of hitherto known nitroxyls, it would be expected to enrich sources of novel



**Fig. 2** Temperature dependence of  $1/\chi$  below 50 K for complex **14**. The straight line was drawn to show deviation from Curie–Weiss behaviour in the lower temperature region.

organomagnetic materials and further studies to prepare related complexes and their single crystals are now under way.

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### Footnotes

† In the EPR spectrum of **6**, triplet absorptions due to the nitroxyl radical were observed in acetone solution, suggesting partial dissociation of the complex in the solution.

‡ Independently and almost at the same time, Sugawara and coworkers have prepared and isolated a charge-transfer complex based on *p*-dimethylamino-nitronyl nitroxide and chloranil.

§ The Curie constant *C* for **6** was very low with a value of  $1.57 \times 10^{-3}$  emu K mol<sup>-1</sup>.

¶ *Crystal data* for **6**: C<sub>21</sub>H<sub>18</sub>F<sub>4</sub>N<sub>5</sub>O, *M* = 432.40, monoclinic, space group *P*2<sub>1</sub>/*n* (no. 14), *a* = 6.985(2), *b* = 14.407(4), *c* = 20.427(3) Å,  $\beta$  = 93.70(2)° (*T* = 23.0 °C), *U* = 2051.4(7) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.400 g cm<sup>-3</sup>, *F*(000) = 892.00. 3482 measured reflections, 3188 unique reflections, collected on a Rigaku AFC5R four-circle diffractometer with monochromated Cu-Kα radiation (1.54178 Å). Final conventional *R* factor = 0.059 for 1762 independent reflections with *F*<sub>o</sub> > 3σ(*F*<sub>o</sub>) and 280 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/235.

|| The first oxidation potentials of radicals **1–5** measured by cyclic voltammetry are (*E*/V vs. SCE in acetonitrile, 0.1 mol dm<sup>-3</sup> TBAP as supporting electrolyte, scan rate = 50 mV): **1**, 0.70; **2**, 0.68; **3**, 0.61; **4**, 0.56; **5**, 0.65.

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