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CT complexes based on TEMPO radicals

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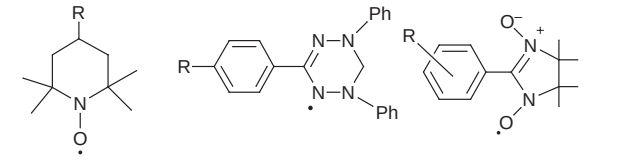
A series of CT (charge-transfer) complexes have been prepared, in which TEMPO (2,2,6,6-tetramethylpiperidinyloxyl) radical **1** and its derivatives (**2** and **6**–**10**) act as donors using $TCNQF_4$ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) or DDQ (2,3-dichloro-5,6-dicyanobenzo-1,4-quinone) as acceptors. A sharp difference was observed in magnetic properties between the charge-transfer complexes derived from the TEMPO radicals **1** or **2** and amino-TEMPO radicals **6**–**10** and the distinct difference observed in the molecular/crystal structures in the complexes is thought to reflect the difference in their magnetic behaviour. The CT complexes from 4-dimethylamino- or 4-azetidino-TEMPO and DDQ formed salt-like complexes of protonated 4-dialkylamino-TEMPO and the substituted benzo-1,4-quinonehydroxylate upon recrystallization from moist acetone.

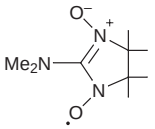
TEMPO radicals are a well-known class of stable radicals mainly used as spin probes for biological studies and a number of derivatives have been prepared for the purpose until now.[1] On the other hand, it is of current interest to develop new molecular-based magnetic materials especially organomagnetic materials and numerous compounds carrying TEMPO radicals as the key building blocks have been prepared and their magnetic behaviour 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 and the CT complexes derived therefrom to build up and to arrange the spins in the solid state/crystal structures[4] and we found recently that some TEMPO radicals (**A**)[5] or verdazyl radicals (**B**)[6]



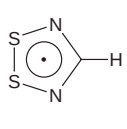
A[4]

B[5]

C[6]



D[7]



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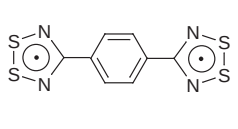
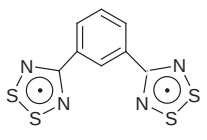
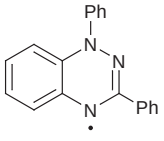


F[10a),b)]



G[10b)]



H[12]

are able to form CT complexes with appropriate acceptors such as $TCNQF_4$ or DDQ, that is to say, TEMPO radicals or verdazyl radicals can act as donors to form CT complexes which can be isolated as solid substances. To our knowledge, these are rare examples in which the radicals act as donors to form CT complexes with appropriate acceptors (*vide infra*). Similar attempts to prepare CT complexes from substituted-phenylnitronyl aminoxyl radicals (**C**) with $TCNQF_4$ or TCNQ in solution gave imine aminoxyl radicals in place of CT complexes[7] although Sugawara *et al.* achieved the formation of the CT complex of dimethylamino nitronyl aminoxyl (**D**) with DDQ by grinding in the solid state.[8]

It was reported as early as 1971 that di-*tert*-butylaminoxyl radical forms CT complexes with various acceptors such as DDQ or TCNE, this being elucidated by electronic spectra as well as EPR measurement in solution, but the complexes have never been isolated nor their solid-state properties reported.[9] Since then, only limited numbers 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. For example, Bryan *et al.* found recently that dithiadiazolyl radical (**E**),[10] its derivatives (**F**,**G**),[11] and their selena-analogues[12] form iodine or bromine complexes when doped with I_2 or Br_2 and some of them show high electrical conductivity at room temperature. Wudl *et al.* prepared the complex of diphenylbenzotriazinyl radical (**H**) with TCNQ (2:5) and observed an anomalous and anisotropic pressure effect on its electric conductivity.[13]

We report in this paper on the results of the preparation and the properties, especially the magnetic properties, of new CT complexes based on TEMPO radicals of type **A** in detail. Furthermore, the facile hydrolysis of the complexes derived from 4-dimethylamino-TEMPO and DDQ as well as 4-azetidino-TEMPO and DDQ to give a salt is also described.[14]

Experimental

Materials

TEMPO radical **1** and its derivatives **2**–**6** as well as 4-oxo-TEMPO are commercially available (Tokyo Kasei Kogyo Co.) and these were used without further purification.

Instrumentation

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 a JASCO Ubest-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 Mn^{2+}/MgO marker as internal standard.

Magnetic measurements

Susceptibility measurements were carried out on a QUANTUM DESIGN MPMS-5 SQUID susceptometer using *ca.* 10 mg for each powdered sample at 0.5–1 T from 4.5 to 300 K and 0.1 T below 4.5 K, respectively. The corrections for the diamagnetic contribution were carried out, using diamagnetic contributions which were corrected from Pascal's constants.

X-Ray structure determination

X-Ray diffraction data were collected on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Ka radiation and a 12 KW rotating anode generator at room temperature. The structures were solved by direct methods and expanded using Fourier techniques. Crystal data are listed in Table 4. 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 and detailed crystallographic data (atomic coordinates, hydrogen atom coordinates, anisotropic displacement parameters, bond lengths and angles) have been deposited with the Cambridge Crystallographic Data Centre.†

Preparation of *N*,*N*-dialkylated-amino-TEMPO derivatives (7–10)

A typical procedure is exemplified for **7** and is as follows. To a stirred mixture of oxo-TEMPO (2.0 g, 12 mmol) and dimethylamine hydrochloride (9.8 g, 120 mmol) in absolute methanol (30 cm^3) was added $NaBH_3CN$ (0.53 g, 8.4 mmol). After being stirred for 5 d at ambient temperature, the reaction mixture was concentrated *in vacuo* and then aqueous potassium hydroxide solution (2 M) was added to neutralize the resulting reaction product. The mixture was extracted with diethyl ether, washed well with water and brine and the organic layer was dried over anhydrous magnesium sulfate. Radical **7** was obtained as orange crystals (1.48 g, 63%) after concentrating the solvent and purified by column chromatography on silica gel. Mp >64 °C (decomp.); EPR (benzene): triplet, $g=2.007$, $a_N=1.55$ mT; *m*/*z* (EI-HRMS) Found: 199.1844. Calcd. for $C_{11}H_{23}ON_2$: 199.1810.

In a similar manner, other derivatives (**8**, **9**, **10**) were prepared.

8: orange crystals mp >79 °C (decomp.); EPR (benzene): triplet, $g=2.007$, $a_N=1.44$ mT; *m*/*z* (EI-HRMS) Found: 211.1776. Calcd. for $C_{12}H_{23}ON_2$: 211.1810.

9: orange crystals mp >54 °C (decomp.); EPR (benzene): triplet, $g=2.007$, $a_N=1.48$ mT; *m*/*z* (EI-HRMS) Found: 225.1938. Calcd. for $C_{13}H_{25}ON_2$: 225.1967.

10: orange crystals mp >70 °C (decomp.); EPR (benzene): triplet, $g=2.007$, $a_N=1.54$ mT; *m*/*z* (EI-HRMS) Found: 239.2086. Calcd. for $C_{14}H_{27}ON_2$: 239.2123.

†CCDC reference number 1145/162. See http://www.rsc.org/suppdata/jm/1999/1747 for crystallographic files in .cif format.

Preparation of charge-transfer complexes (11–25)

A typical procedure is exemplified for **11** and is as follows:

TEMPO (50 mg, 0.32 mmol) was added to an acetonitrile solution (5 cm^3) of $TCNQF_4$ (88 mg, 0.32 mmol) at ambient temperature. The colour of the solution turned immediately to green and the solution was concentrated *in vacuo* carefully to a smaller amount to give dark blue needles. The crystals were filtrated and recrystallized from acetone in a refrigerator and washed several times with diethyl ether to afford **11** as dark blue needles. Mp *ca.* 148 °C (decomp.) [Found: C, 57.71; H, 4.27; N, 16.03. **1**: $TCNQF_4=1:1$ ($C_{21}H_{18}N_5OF_4\cdot 1/4H_2O$) requires: C, 57.73; H, 4.12; N, 16.20%]; ν_{max} (Nujol)/cm^{-1} 2190, 2180 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (2700), 856 (5660).

12: dark blue powder. Mp *ca.* 212 °C (decomp.) [Found: C, 56.76; H, 4.27; N, 15.14. **2**: $TCNQF_4=1:1$ ($C_{21}H_{18}N_5O_2F_4$) requires: C, 56.25; H, 4.05; N, 15.62%]; ν_{max} (Nujol)/cm^{-1} 2200, 2180 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (16 000), 855 (32 800).

13: dark green powder. Mp >146 °C (decomp.) [Found: C, 56.01; H, 4.28; N, 18.38. **6**: $TCNQF_4=1:1$ ($C_{21}H_{19}N_6OF_4$) requires: C, 56.37; H, 4.28; N, 18.79%]; ν_{max} (Nujol)/cm^{-1} 2200 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (11 000), 856 (23 000).

14: dark green powder. Mp >*ca.* 120 °C (decomp.) [Found: C, 49.87; H, 4.98; N, 13.52. **6**: DDQ=1:1 ($C_{17}H_{19}N_4O_3Cl_2$) requires: C, 50.13; H, 4.98; N, 13.96%]; ν_{max} (Nujol)/cm^{-1} 2210 (CN); λ_{max} (CH_3CN)/nm (ε) 457 (3850), 588 (3970).

15: dark green powder. Mp >*ca.* 150 °C (decomp.) [Found: C, 43.37; H, 5.15; N, 6.56. **6**: chloranil=1:1 ($C_{15}H_{19}N_2O_3Cl_4$) requires: C, 43.19; H, 4.59; N, 6.72%]; λ_{max} (CH_3CN)/nm (ε) 421 (870), 428 (1330).

16: dark blue needles. Mp >*ca.* 155 °C (decomp.) [Found: C, 55.26; H, 4.83; N, 16.31. **7**: $TCNQF_4=1:1$ ($C_{23}H_{23}N_6OF_4\cdot 3/2H_2O$) requires: C, 54.97; H, 5.22; N, 16.17%]; ν_{max} (Nujol)/cm^{-1} 2200 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (17 100), 856 (35 900).

17: dark brown powder. Mp >*ca.* 138 °C (decomp.) [Found: C, 53.50; H, 5.42; N, 13.71. **7**: DDQ=1:1 ($C_{19}H_{23}N_4O_3Cl_2$) requires: C, 53.53; H, 5.44; N, 13.14%]; ν_{max} (Nujol)/cm^{-1} 2210 (CN); λ_{max} (CH_3CN)/nm (ε) 457 (2890), 588 (2610).

The complex **17** was dissolved in acetone and recrystallized in a refrigerator at 4 °C to afford new complex **18** as dark brown plates with almost quantitative yield. Mp >132 °C (decomp.) [Found: C, 51.43; H, 6.27; N, 10.60. **7**: A=1:1 ($C_{18}H_{24}N_3O_4Cl_2$) requires: C, 51.80; H, 5.80; N, 10.07%]; ν_{max} (Nujol)/cm^{-1} 3400 br (OH), 2220 (CN); λ_{max} (CH_3CN)/nm (ε) 410 (1480), 585 (490).

19: dark blue needles. Mp >146 °C (decomp.) [Found: C, 57.36; H, 4.89; N, 16.23. **8**: $TCNQF_4=1:1$ ($C_{24}H_{23}N_6OF_4\cdot H_2O$) requires: C, 57.02; H, 4.98; N, 16.63%]; ν_{max} (Nujol)/cm^{-1} 2200, 2180 (CN); λ_{max} (CH_3CN)/nm (ε) 754 (17 400), 851 (37 400).

20: dark brown powder. Mp >*ca.* 180 °C (decomp.); λ_{max} (CH_3CN)/nm (ε) 455 (1860), 585 (1290).

21: dark brown powder. Mp >*ca.* 150 °C (decomp.); ν_{max} (Nujol)/cm^{-1} 3400 br (OH), 2220 (CN); λ_{max} (CH_3CN)/nm (ε) 410 (1480), 585 (490).

22: dark green powder. Mp >145 °C (decomp.) [Found: C, 58.13; H, 4.86; N, 16.15. **9**: $TCNQF_4=1:1$ ($C_{25}H_{25}N_6OF_4\cdot\frac{3}{4}H_2O$) requires: C, 58.30; H, 5.19; N, 16.33%]; ν_{max} (Nujol)/cm^{-1} 2200 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (14 600), 857 (30 700).

23: dark brown powder. Mp >*ca.* 150 °C (decomp.) [Found: C, 55.04; H, 5.70; N, 12.19. **9**: DDQ=1:1 ($C_{21}H_{25}N_4O_3Cl_2\cdot 1/2H_2O$) requires: C, 54.67; H, 5.68; N, 12.15%]; ν_{max} (Nujol)/cm^{-1} 2210 (CN); λ_{max} (CH_3CN)/nm (ε) 456 (2600), 588 (2620).

24: dark green powder. Mp >150 °C (decomp.) [Found: C, 57.64; H, 5.70; N, 15.67. **10**: $TCNQF_4=1:1$

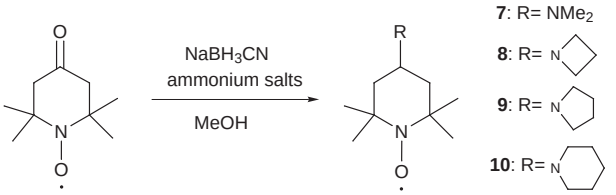
($C_{26}H_{27}N_6OF_4 \cdot \frac{3}{2}H_2O$) requires: C, 57,56; H, 5.57; N, 15.49%]; ν_{max} (Nujol)/cm^{-1} 2200 (CN); λ_{max} (CH_3CN)/nm (ε) 753 (12 700), 852 (23 800).

25: green powder. Mp $>$*ca.* 150 °C (decomp.) [Found: C, 55.58; H, 5.94; N, 11.21. **9**: DDQ = 1 : 1 ($C_{22}H_{27}N_4O_3Cl_2 \cdot \frac{1}{2}H_2O$) requires: C, 55.58; H, 5.94; N, 11.78%]; ν_{max} (Nujol)/cm^{-1} 2210 (CN); λ_{max} (CH_3CN)/nm (ε) 456 (4820), 587 (4810).

Results and discussion

Preparation and electrochemical properties of TEMPO radicals

Although several TEMPO derivatives used in this study are commercially available, we have prepared some alkylamino-TEMPO derivatives expecting enhancement of donor ability. The alkylamino-TEMPO derivatives **7**–**10** were prepared by the reductive amination of 4-oxo-TEMPO with alkyl amines using sodium cyanoborohydride as a reducing reagent (Scheme 1).[15] To estimate their donor ability, we investigated their electrochemical behaviour by cyclic voltammetry. As shown in Table 1, it was observed that 4-amino-TEMPO radicals **6**–**10** show two oxidation potentials (E_1^{ox} and E_2^{ox}) in their redox waves while TEMPO radicals **1**–**5** have only one oxidation potential based on aminoxyl radical in acetonitrile. The donating ability appears to be lowered in **4** and **5** compared to other radicals reflecting the substituent effect of the electron-withdrawing groups (COOH and CN). Each E_1^{ox}- and E_2^{ox}-value of **6**–**10** could be attributed to the oxidation of amino group and aminoxyl radical, respectively and their E_1^{ox}-values are apparently lowered having the lowest value of 0.56 V in **9** among them but, on the contrary, each E_2^{ox}-value is found to be higher compared with those of **1**–**4** and almost equivalent to that of **5**. From the point of view of such redox behaviour



Scheme 1

Table 1 Cyclic voltammetric data for radicals **1**–**10**[a] and acceptors[b]

Radicals	E_1^{ox}	E_2^{ox}	ΔE^c
1 (R = H)	0.70[d]	—	—
2 (R = OH)	0.72[d]	—	—
3 (R = Ome)	0.71[d]	—	—
4 (R = COOH)	0.75[d]	—	—
5 (R = CN)	0.85[d]	—	—
6 (R = NH_2)	0.68[e]	0.87[f]	0.19
7	0.62[e]	0.85[f]	0.23
8	0.64[e]	0.86[f]	0.22
9	0.56[e]	0.85[f]	0.29
10	0.65[e]	0.85[f]	0.20
Acceptors	E_1^{red}	E_2^{red}	ΔE^g
$TCNQF_4$	0.57[d]	0.04[d]	0.53
DDQ[h]	0.47[d]	−0.31[d]	0.78
Chloranil	−0.03[d]	−0.63[d]	0.60

*[a]Oxidation potentials (for radicals) and [b]reduction potentials (for acceptors) (V) *vs.* SCE in CH_3CN with 0.1 M Bu_4NClO_4 at room temp. Scan rate: 50 mV s^{-1}. The standard potential of FcH^+ //FcH is referred to SCE as −0.33 V in CH_3CN; *cf.* G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1988, 56, 461. [c]$\Delta E = E_2^{ox} - E_1^{ox}$ for radicals. [d]Reversible. [e]Irreversible. [f]Quasi-reversible. [g]$\Delta E = E_2^{red} - E_1^{red}$ for acceptors. [h]S. Nakatsuji, N. Akashi, K. Suzuki, T. Enoki and H. Anzai, *J. Chem. Soc., Perkin Trans. 2,* 1996, 2555.

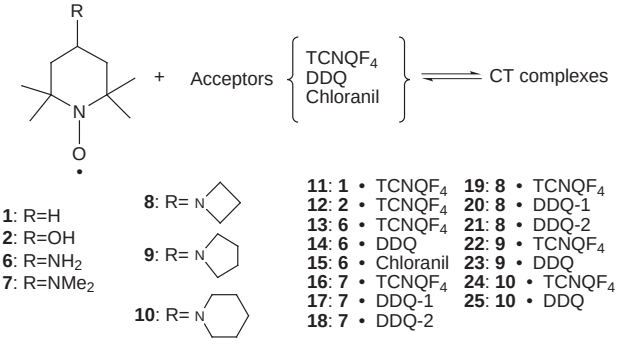
of TEMPO radicals **1**–**10**, it was anticipated that some CT complexes could possibly be formed with appropriate acceptors.

Preparation of CT complexes

When TEMPO radical **1** was reacted with an equimolecular amount of $TCNQF_4$ in acetonitrile, it was observed that the colour of the reaction mixture turned to deep green. The resulting dark blue crystals obtained after working-up the reaction mixture were found to be the CT complex **11** with a radical to acceptor ratio of 1 : 1 being elucidated by elemental analysis. In addition, the bands corresponding to $TCNQF_4$ radical anion, *i.e.*, the bands of 856 and 753 nm in acetonitrile, were clearly observed in the visible absorption spectrum of **11** and the lower shift of ν_{CN} (ν_{CN} = 2190 cm^{-1}) observed in its IR spectrum compared with neutral acceptor ($TCNQF_4$: ν_{CN} = 2237 cm^{-1}) was also consistent with the formation of the CT complex **11**. To our knowledge, this is one of the rare isolated charge-transfer complexes in which a radical works as a donor (Scheme 2).

Following the results described above, we then prepared a series of similar CT complexes derived from other TEMPO derivatives, *i.e.*, 4-hydroxy-4-amino-TEMPO and its alkylated derivatives. Corresponding CT complexes could not be prepared from the 4-carboxy (**4**), 4-cyano (**5**) or even from the 4-methoxy derivative **3** with $TCNQF_4$. The radicals **7**–**10** prepared by the reductive amination of 4-oxo-TEMPO gave complexes with even weaker acceptors than $TCNQF_4$, *i.e.*, DDQ or chloranil. The DDQ complexes were formed by mixing dichloromethane solutions of the TEMPO radicals and DDQ in the usual way (Scheme 2).

We observed in the case of the complexes **17** and **20** that new complexes **18** and **21** were formed upon recrystallization of the complexes from acetone including a trace of water. The structures of the latter complexes are evidenced by the spectroscopic data and the X-ray analysis of **18** as discussed below. No such structural change was observed for the corresponding $TCNQF_4$ complex during similar recrystallization. The electronic absorption spectra of the complexes **17** (λ_{max} 588 and 457 nm in acetonitrile) and **18** (λ_{max} 585 and 410 nm in acetonitrile) showed distinct differences in the longer wavelength region (Fig. 1). Furthermore, different peaks were observed in the negative FAB-MS spectra: while the molecular ion peak of m/z = 227 (DDQ) occurred in the complex **17**, the complex **18** gave a peak at m/z = 217 that fits 2,3-dichloro-5-cyano-6-hydroxybenzo-1,4-quinone. Also a marked difference is observed in the ESR spectra in acetonitrile: **17** exhibits a complicated triplet absorption of the aminoxyl radical (g = 2.007) that is possibly overlapped with the spectra of the DDQ radical anion and/or of the trialkylamino radical cation, whereas the spectrum of **18** shows only the typical triplet of a aminoxyl radical (g = 2.006) and thus excludes further spins. These facts suggest a structural change as formulated in



Scheme 2

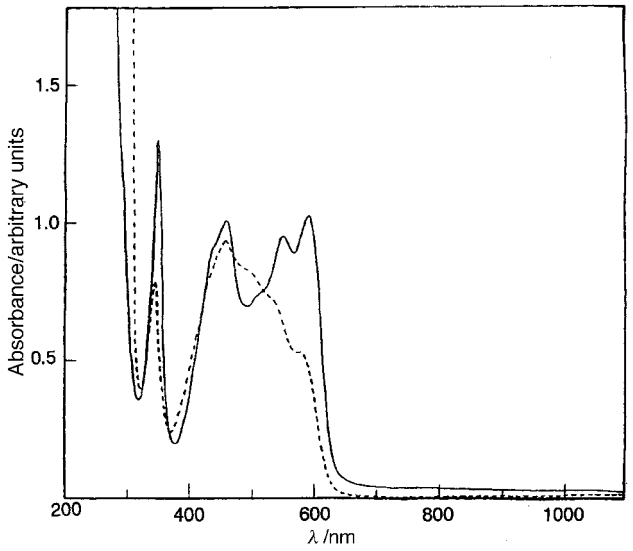


Fig. 1 Absorption spectra of complex **17** (solid line) and **18** (broken line) in CH_3CN.

Scheme 3 and further evidence for that interpretation is provided by X-ray structural analysis of complex **18** (*vide infra*).

Similarly, the 4-azetidino-TEMPO–DDQ complex **20** gave the salt-like complex **21** and similar substitutions of cyano groups by hydroxy groups have been reported in benzamidopyridine–DDQ complexes.[16]

Magnetic properties of radicals as well as complexes

The magnetic susceptibility measurements on the radicals and corresponding CT complexes were carried out on the polycrystalline sample by 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 of −3.0 K (Table 2),[17] a drastic decrease of magnetic susceptibility with a small Curie constant of $C=1.57\times10^{-3}$ emu K mol^{-1} has been observed in the complex **11** being evident from its χ–T data and suggesting a strong tendency to singlet formation between the radical centers. A similar tendency was observed in the complex **12** derived from 4-hydroxy-TEMPO **2**. On the contrary, no such drastic decrease of magnetic susceptibility has been observed for 4-amino- or 4-alkylamino-TEMPO derived complexes **13**–**25** and acceptor-dependent antiferromagnetic or ferromagnetic interactions were suggested in each complex being estimated from their Weiss constants, *e.g.*, for the complexes prepared from 4-amino-TEMPO **6**, weak ferromagnetic interactions were suggested in the DDQ complex **14** or the chloranil complex **15** (each Weiss constant: $\theta=0.1$ K) while the interactions suggested in the $TCNQF_4$ complex **13** were antiferromagnetic ($\theta=-1.0$ K) (*cf.* Fig. 2 and Table 3). Most complexes derived from 4-alkylated amino-TEMPO derivatives **7**–**10** were found to show weak antiferromagnetic interactions with a slight decrease of their spins from the value of $S=\frac{1}{2}$ (*cf.* Table 3) while the short-range antiferromagnetic spin order in the very low temperature region was suggested for the complex **25** derived from **10** being evident from its χ–T data in the low temperature region. Thus, a sharp difference was observed in magnetic behaviour between the complexes **11**, **12** derived from TEMPO **1** or 4-hydroxy-TEMPO **2** and the complexes **13**–**25** from 4-amino-TEMPO **3** or its alkylated derivatives **7**–**10** (Table 3). As regards the comparison of the magnetic behaviour of the DDQ complexes **17**, **20** and the corresponding salt-like complexes **18**, **21**, no distinct difference was observed showing weak antiferromagnetic interactions between the spins in each complex, although the Curie constant of the complex **18** ($C=0.28$ emu K mol^{-1}) is found to be apparently decreased from the original complex **17** with $C=0.35$ emu K mol (*cf.* Fig. 3 and discussion below).

X-Ray crystal structure analysis on the complexes 11, 18, 19

To investigate magneto–structural relationships in the complexes and to clarify the above-mentioned difference, we then tried to study their crystal structures by X-ray analysis. Single crystals were obtained from the complexes **11**, **18** and **19** among the complexes prepared and their crystal data are summarized in Table 4. At first, we discuss the magneto–structural relationship of the complexes **11** and **19** and then we will describe the results of the X-ray analysis of **18**. The

Table 2 Magnetic properties of radicals **1**, **2** and **6**–**10**

Radicals	C/emu K mol^{-1}	Magnetic moment/μB[a]	Weiss-temperature/K	Magnetic interactions
1	—	—	−3.0[b,c]	Antiferromagnetic
2	—	—	−6.4[b,c]	Antiferromagnetic
6	0.34	1.64	−0.2[d]	Antiferromagnetic
7	0.37	1.72	−7.5[c]	Antiferromagnetic
8	0.32	1.61	−4.9[c]	Antiferromagnetic
9	0.32	1.60	−6.3[c]	Antiferromagnetic
10	0.35	1.70	+0.5[d]	Ferromagnetic

*[a]Magnetic moment at 300 K. [b]Ref. 17. [c]Short range ordering is suggested from the susceptibility data in the case. [d]Fitting for Curie–Weiss rule.

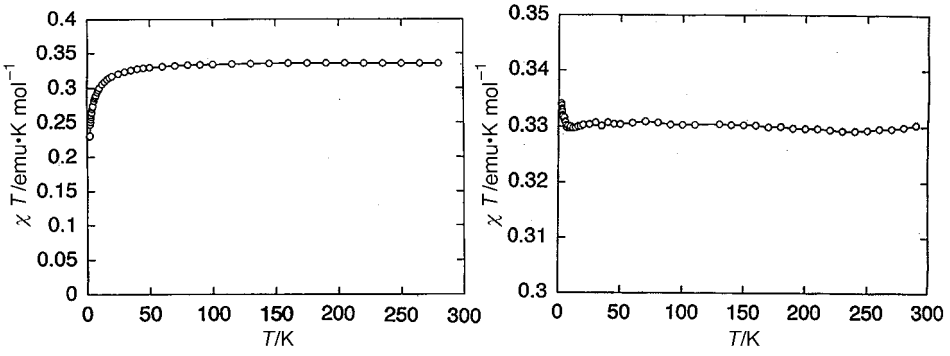


Fig. 2 Temperature dependence of χT for complex **13** (left) and **14** (right).

Table 3 Magnetic properties of CT complexes **11**–**25**

Complex	C/emu K mol^{-1}	Magnetic moment/μB[c]	Weiss-temperature/K	Magnetic interactions
11	0.0016	0.11	−0.1[b]	Antiferromagnetic
12	—	—	—	Diamagnetic
13	0.33	1.64	−1.0[b]	Antiferromagnetic
14	0.33	1.63	+0.1[b]	Ferromagnetic
15	0.35	1.67	+0.1[b]	Ferromagnetic
16	0.34	1.65	−1.8[b]	Antiferromagnetic
17	0.35	1.67	−0.4[b]	Antiferromagnetic
18	0.25	1.42	−1.3[b]	Antiferromagnetic
19	0.34	1.65	−0.3[b]	Antiferromagnetic
20	0.32	1.60	−1.1[b]	Antiferromagnetic
21	0.33	1.63	−1.6[b]	Antiferromagnetic
22	0.27	1.47	−0.3[b]	Antiferromagnetic
23	0.37	1.72	−1.1[b]	Antiferromagnetic
24	0.28	1.50	−0.9[b]	Antiferromagnetic
25	0.34	1.65	−6.2[c]	Antiferromagnetic

*[a]Magnetic moment at 300 K. [b]Fitting for Curie–Weiss rule. [c]Short range ordering is suggested from the susceptibility data in the case.

Table 4 Summary of crystal data for **11**, **18** and **19**

	11	**18**	**19**
Formula	$C_{21}H_{18}N_5OF_4$	$C_{18}H_{23}N_3O_4Cl_2$	$C_{24}H_{23}N_6OF_4$
Formula weight	432.40	416.30	487.48
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	C/c
a/Å	6.985	12.470(4)	20.309(2)
b/Å	14.407(4)	17.279(2)	20.265(3)
c/Å	20.427(3)	9.599(3)	13.452(1)
β/degrees	93.70(2)	101.17(3)	103.987(8)
V/Å^3	2051.4(7)	2029(9)	5372.1(10)
Z	4	4	8
D (calc)/g cm^{-3}	1.400	1.363	1.205
2θ range/degrees	46.2–58.8	55.0	41.6–56.3
No. of reflections measured	3488	5042	4256
No. of reflections used in refinement $F>3\sigma$	1762	2095[a]	2049[a]
No. of parameters refined	280	244	316
R	0.059	0.054	0.098
R_w	0.047	0.077	0.151

*[a]$F>2\sigma$ in this crystal.

X-ray analysis of the single crystal of **11** grown by recrystallization from acetone gave confirmative structural elucidation of the complex as shown in Fig. 4 and 5. Relatively small bond alternation in each $TCNQF_4$ molecule of the complex **11** suggests the delocalization of π-electrons on the whole molecule forming its radical anion (Fig. 4).[18] The shorter N–O bond length (1.20 Å) in the donor molecule of **11** compared with the bond length in ordinary aminoxyl radicals (1.28–1.29 Å)[19] would indicate the formation of an oxoammonium ion from the aminoxyl radical. It is apparent from Fig. 5 that both TEMPO radicals and $TCNQF_4$ radical anions form a column structure 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

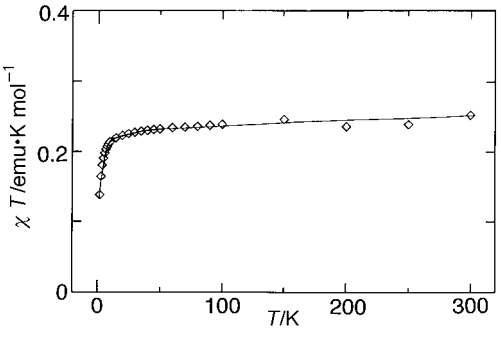


Fig. 3 Temperature dependence of χT for complex **18**.

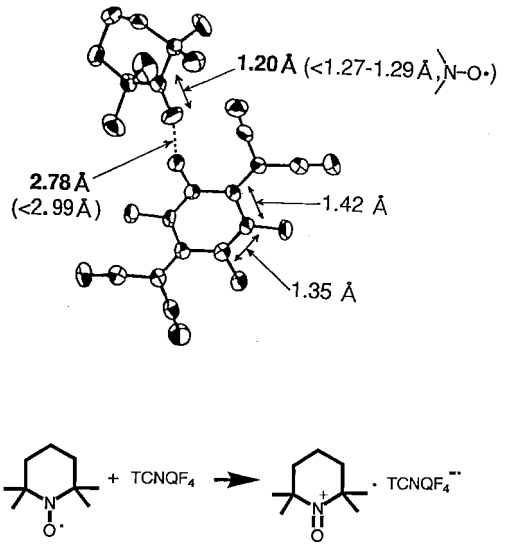


Fig. 4 Molecular structure of complex **11**.

TEMPO radicals in the column which amounts to 6.99 Å. ii) The interplanar stacking distance between $TCNQF_4$ molecules is estimated to be 6.99 Å inserting another $TCNQF_4$ molecule into them with some slipping out to result in a zigzag column structure. iii) The nearest distance between the oxygen of the aminoxyl radical and the $TCNQF_4$ molecule is that of

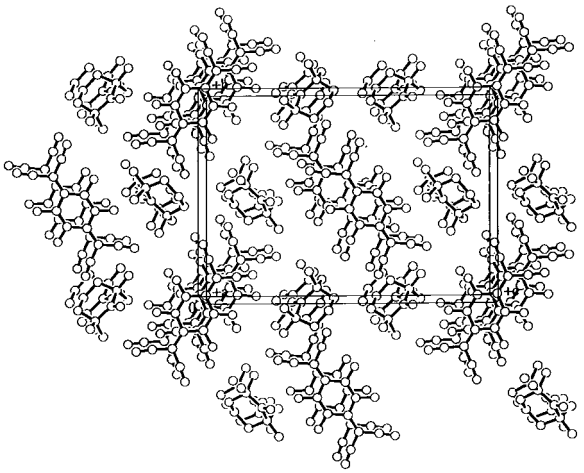


Fig. 5 Crystal structure of **11** viewed almost along the *a* axis.

O(1)–F(2) (Fig. 4) and amounts to 2.78 Å being 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 $TCNQF_4$ species is coming from TEMPO radicals forming oxoammonium ions in the latter, *i.e.*, TEMPO becomes $TEMPO^+$ resulting in a singlet while the loss of the spins of $TCNQF_4$ radical anions is supposed to be derived from their columnar structure as described above.

As shown in Fig. 6 and 7, a distinct difference in the crystal structure of **19** compared with that of **11** was observed. Although the molecular structure of $TCNQF_4$ is similar, *i.e.*, a relatively small bond alternation in each $TCNQF_4$ molecule is estimated to be formed in its radical anion (Fig. 6),[18] the N–O distance (1.29 Å) in the donor molecule in **19** is the ordinary one for an aminoxyl radical indicating that the spins of the radical molecules are not lost and showing a distinct difference from that in **11** described above. The short contact between the nitrogen atom of the amine moiety of the radical **8** and the $TCNQF_4$ molecule suggests that the charge-transfer occurs from the alkylamino group to the acceptor molecule in this case. Also, in contrast to the feature of columnar structure of radical and acceptor observed in complex **11**, a perpendicular and segregated columnar structure is observed in complex

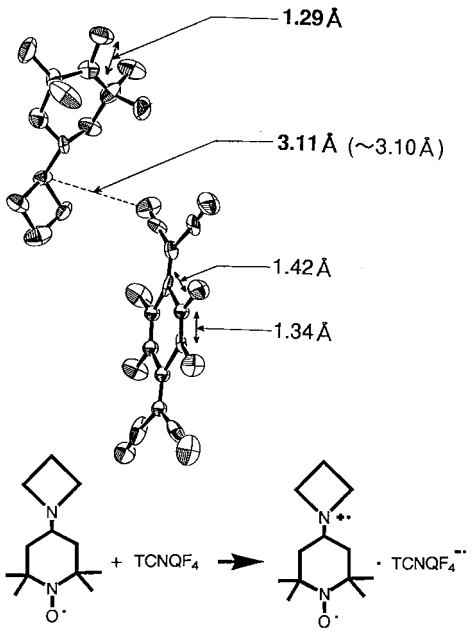


Fig. 6 Molecular structure of complex **19**.

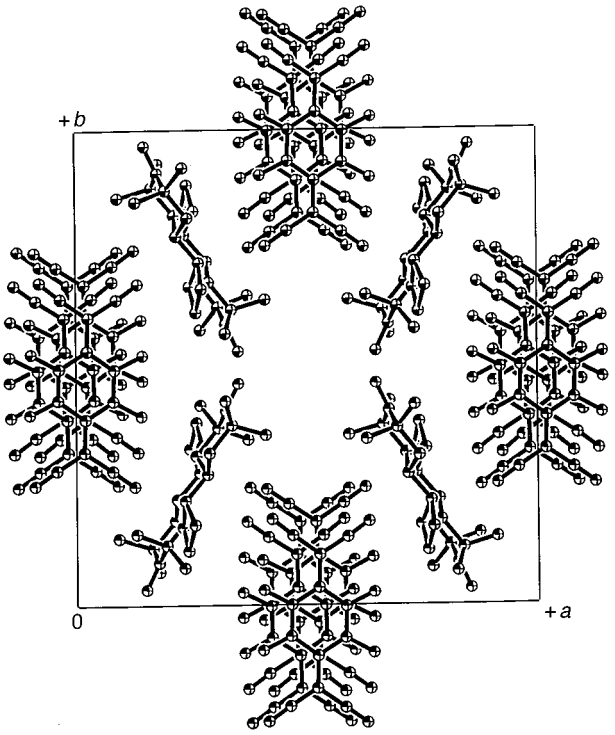


Fig. 7 Crystal structure of **19** viewed along the *c* axis.

19 as shown in Fig. 7 in which each two molecules of $TCNQF_4$ appear to be surrounded by four molecules of radical **8**. The distances between the layers of $TCNQF_4$ molecules stacking along the *c*-axis are 3.2–3.5 Å and the situation is rather similar to the case in complex **11**. Radical molecules, on the other hand, stack along the *a*-axis in a zigzag manner and in a side-by-side, head-to-tail manner along the *c*-axis. It seems to be plausible from such structural features as described above that the spin on the nitrogen atom in the four-membered ring together with the spin on the $TCNQF_4$ anion radical are lost by the singlet formation between them because of the short contact based probably on the fairly strong Coulombic interaction and hence the weak antiferromagnetic interactions observed in **19** would be attributed to the interactions between the spins on TEMPO radicals.

Clearly, the analysis of the complex **18** reveals that one of the cyano groups in the DDQ molecule of the original complex **17** was replaced by hydroxylate (Fig. 8, see also Scheme 3). The C–O bond length (1.25 Å) at that site is found to be shorter than the one that is typical for C–CN. The other C–O bond that is adjacent to the remaining CN group is of almost equal length (1.23 Å), whereas the third is shorter (1.21 Å). Furthermore, similar bond lengths (1.40 and 1.43 Å) of the

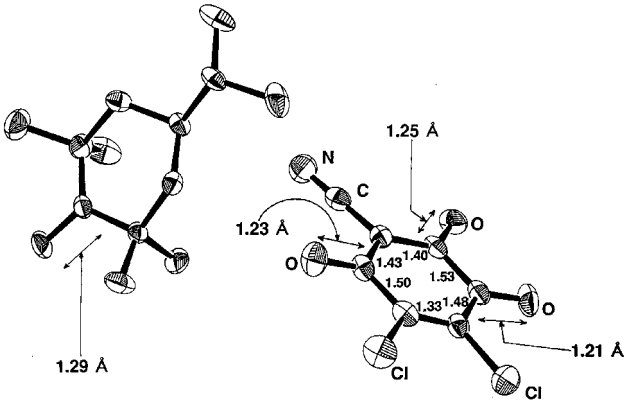
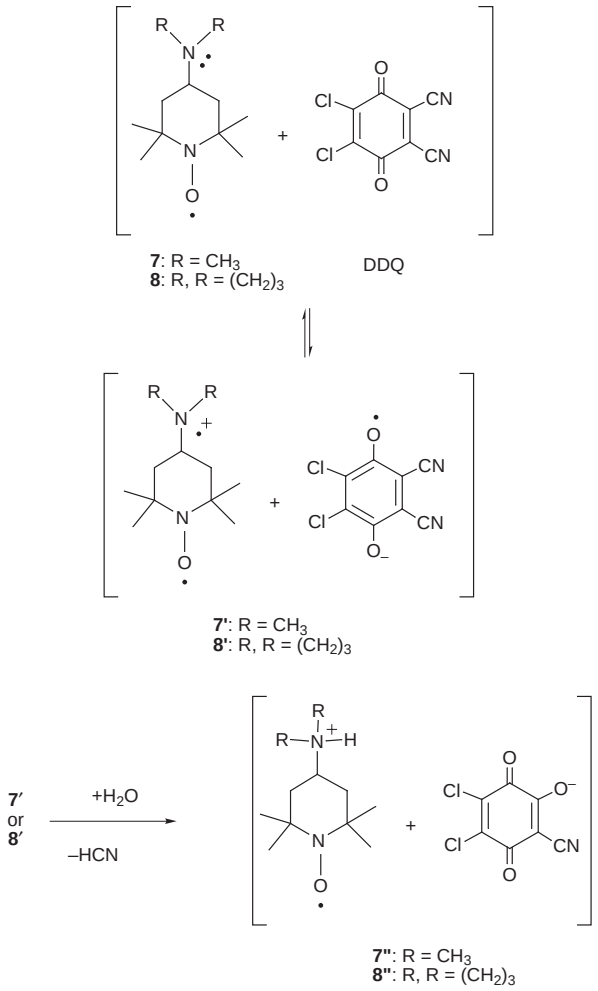


Fig. 8 Molecular structure of complex **18**.



Scheme 3

two C–C bonds in the conjugated enolate moiety indicate the expected delocalization. In the TEMPO part of the complex, the N–O bond length (1.29 Å) of the aminoxyl radical is retained as the normal length. Clearly, no electron is transferred from the aminoxyl radical. Thus, a cyano group of the DDQ moiety in **17** has been substituted by water to form 2,3-dichloro-5-cyano-6-hydroxybenzoquinone and the proton of the latter compound was transferred to the amino-group of the dialkylamino-TEMPO part to form **18**.

As shown in Fig. 9, the crystal packing of the complex exhibits head-to-tail dimer pairs of the enolate that are surrounded by sheets of other radical molecules. Two kinds of short contacts are found between the nitrogen atom of the protonated dimethylamino group in the radical component and the two oxygen atoms attached to C1 and C6 in the enolate (3.18 and 2.76 Å). Another short contact (2.86 Å) is found between the oxygen atom of the aminoxyl group in the radical component and the C1 atom in the enolate component. Thus, a rather markedly different structure of **18** is apparent to the structures in the complexes **11** and **19** which exhibit segregated columnar alignments of both donor and acceptor molecules (*vide supra*). Since the distances between the NO groups of the radicals are not short enough for direct spin–spin interactions (the shortest one is 7.611 Å), only weak antiferromagnetic interactions should be observed in **18**. Although the reason for the relative decrease of the spins compared with other complexes such as **17** is not decisively clear yet, the very hygroscopic nature of the salt seems to account at least in part for the apparent loss of the spins because water and/or solvent molecules tend to be easily incorporated in the salt.

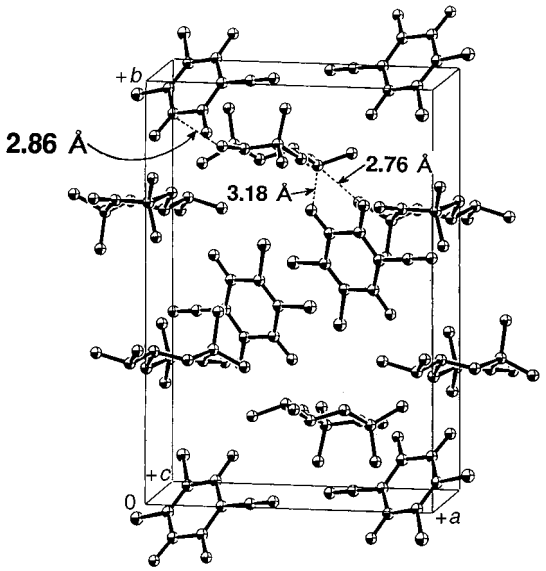


Fig. 9 Crystal structure of **18** viewed almost along the *c* axis.

Conclusion

We have prepared and isolated a series of CT complexes **11**–**25** from TEMPO radicals **1**, **2** and **6**–**10** to exhibit variable and acceptor-dependent magnetic behaviour. The TEMPO–$TCNQF_4$ complex **11** and the 4-azetidino-TEMPO-$TCNQF_4$ **19**, which show sharp differences in their magnetic properties, were structurally elucidated by X-ray analysis to correlate with their magnetic behaviour. As a rare example of a structural change in a CT complex, we observed that the DDQ complexes **17** and **20** afforded new complexes **18** and **21** during recrystallization from acetone, being elucidated by X-ray analysis, and their magnetic behavior was rationally interpreted by the analysis.

Because the CT complexes described in this paper could be easily prepared from simple TEMPO radicals and acceptors and because the method may be applicable to a variety of hitherto known aminoxyls, it would be expected to provide a rich source of novel organomagnetic materials.

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