Recent progress in the development of organomagnetic materials based on neutral nitroxide radicals and charge transfer complexes derived from nitroxide radicals

Shin′ichi Nakatsuji and Hiroyuki Anzai

Department of Material Science, Faculty of Science, Himeji Institute of Technology, Kanaji 1479-1, Kamigori, Hyogo 678-12, Japan

Nitroxide radicals play a central role in the recent development of organomagnetic materials or molecular-based magnetic materials. This feature article considers the recent progress in the development of molecular-based magnetic materials dealing mainly with nitroxide radical crystals and charge transfer (CT) complexes consisting of nitroxide radicals. We present a view of the progress of this rapidly growing field of materials science over the past few years, showing the results of several research groups (including ours) based on nitroxide radicals in order to introduce the readers to the present situation and to further perspectives to possible degree.

It was in 1856 when W. H. Perkin discovered his famous colourant ‘mauvein’ serendipitously[1] and since then organic compounds have been recognized to be useful for materials besides medicines and perfumes, and have played an important role in industrial and materials chemistry, especially in the field of dyes and pigments. However, it is only in the latter half of this century that in some organic compounds normally having insulating properties electrons have been found to have conducting properties, *i.e.*, several kinds of organic semiconductors, conductors and even superconductors have been discovered and developed.[2] It may be anticipated that much of the progress in modern molecular science is owed to such discovery and development. Compared with the development of organic conducting materials, the more recent development of organomagnetic materials is rather similar to that of organoconducting materials in that unusual properties must be induced in the organic compound; the spin alignment in the organic compound must be arranged with strong interactions between the spins to be parallel. This appears to work against nature because organic compounds normally have a strong tendency to bond together with antiparallel spin alignment.[3] Thus special control of the spin alignment is needed to develop organomagnetic materials, this is the most difficult aspect in this research field. It is therefore not surprising that only a decade or so has passed since high spin molecules with parallel spin alignment within the molecules,[4] and molecular-based organomagnetic materials (decamethylferrocene–TCNE complex **1**),[5] have really come into the world, although the theoretical possibility of molecular-based magnetic materials was predicted as early as 1963[6] and also successively later on.[7] Amazing progress has since followed and an outstanding result was the discovery in 1991 by Kinoshita and coworkers[8] of a bulk ferromagnet consisting of a purely organic compound, *p*-nitrophenyl nitronyl nitroxide radical (β-phase) **2**. The number of organic ferromagnets had grown to almost twenty by the end of 1996; most of them were found in very recent years and large numbers of them are nitroxide radicals, as described below. We show representatives of molecular-based ferromagnets discovered thus far in Fig. 1. It is now much easier than in previous years for preparative organic chemists, such as ourselves, to carry out research projects on organomagnetic materials, because of the possibility of collaborating with physicists or physical chemists who could measure magnetic properties of organic compounds such as magnetic susceptibility, heat capacity and so on. Moreover, it is no longer unusual for organic chemists themselves to measure magnetic susceptibility using a SQUID susceptometer, which was almost inconceivable ten years ago. The rapid progress in this field of science is therefore surely owed to such developments in research circumstances.

Nitroxide radicals (the word ‘nitroxyl’ is also conventionally used for the class of radicals; ‘aminoxyl’ is the recommended term, but we use in this article the conventional word ‘nitroxide’ in order to avoid confusion) are well known, constituting one of the rare classes of radicals capable of being handled under ordinary conditions on the laboratory bench.[9] So far many nitroxide radicals have been prepared and isolated as stable substances; they are usually stabilized either by conjugation with π-electrons of aromatic system(s) or by substitution with bulky substituents. Historically speaking, this class of compounds has been developed and used widely as spin-labelling or spin-trapping reagents for biological studies, to elucidate in particular the structures and functions of cell membranes.[10] The use of TEMPO (2,2,6,6-tetramethylpiperidinyloxy) radicals (which are sometimes referred to as TANOLs) as preparative reagents and above all as mild oxidants has also been recognized in recent years.[11]

Nitroxide radicals have, especially in recent years, been central to the development of molecular-based magnetic materials and among them TEMPO radicals and nitronyl nitroxide (2-substituted 4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide; NN) radicals are the two representative classes of compounds which have been widely used and studied for this purpose (Fig. 2).[12] From the theoretical point of view, it is recognized that the unpaired electrons of nitroxides in the SOMO (singly occupied molecular orbital) energy level are localized mainly on the N—O moiety; they are delocalized between the nitrogen and the oxygen atoms in the TEMPO series, and those in the NN series are evenly distributed between two N—O groups making a node at the α-carbon atom. Without these electronic features the magnetic properties of these radicals would be difficult to understand, and their derivatization could offer a wide variety of magnetic materials with interesting three-dimensional structures and solid-state properties. In this article, we survey the progress and development in this field of materials science from the viewpoint of the preparative organic chemist, with the emphasis on nitroxide radicals aimed at the formation of magnetic materials and, dealing mainly with nitroxide radical crystals and charge transfer (CT) complexes

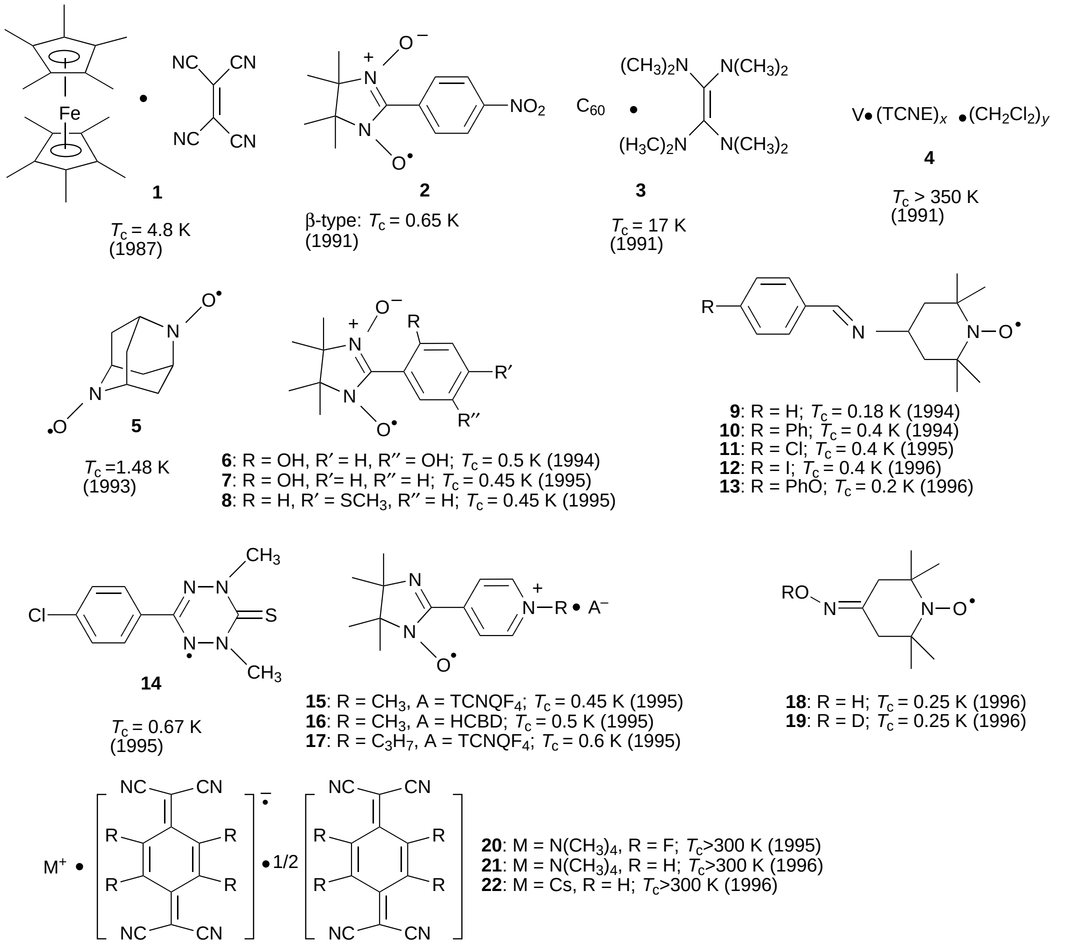
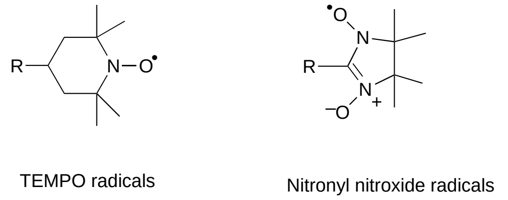


Fig. 1 Various molecular-based ferromagnetic materials reported up to the end of 1996


TEMPO radicals

Nitronyl nitroxide radicals

Fig. 2 TEMPO radicals and nitronyl nitroxide radicals

consisting of nitroxide radicals developed recently. There have been several leading and excellent review articles,[4,13] books[14] and detailed conference proceedings[15] published in recent years, which give comprehensive overviews of magnetic materials in general, including magnetic materials based on macromolecules as well as metal complexes derived from nitroxide radicals, which will not be covered in this article.

Brief survey of the physical concepts for the development of organomagnetic materials

Because rigorous treatment of this topic is available elsewhere,[4–8,12–14,16,17] we survey the physical concepts for the development of organomagnetic materials only briefly here.

It is well known from quantum mechanical consideration that ferromagnetic exchange interactions between spins[18] are expected when, according to Hund's rule, the orbitals in which each spin is occupied are orthogonal, hence to construct the molecular system with spins in orthogonal orbitals is the most useful and simple intramolecular approach to attain ferromagnetic interactions in the system. High spin molecules with carbene or nitrene centres having intrinsic orthogonal orbitals,[19,20] and Rassat's radical with orthogonal spin orbitals, described below,[21,22] have been developed along this line. Besides this, there are two other principal approaches known to couple the spins of radical cations or radical anions in a parallel manner, *i.e.*, to attain ferromagnetic interactions in radicals. Taking the spin polarization effect with induced alternating up and down spins, *i.e.*, α- and β-spins in intra- and/or intermolecular exchange interactions into consideration is one of the leading principles for obtaining ferromagnetic materials with orbital considerations in an intra- or intermolecular fashion. For preparative chemists, the approach to organomagnetic materials controlling the intramolecular spin polarization effect is one of the most attractive routes and the development of new organomagnetic materials including high spin molecules[4] or non-Kekulé hydrocarbon radicals[23] has progressed through topological considerations. Also, the recent success of experimental as well as theoretical verification of the magnetic behaviour of CT complexes consisting of metallocenes and acceptors is based on the intermolecular spin polarization effect which is a through-space modification of the so-called McConnell mechanism I developed by McConnell.[6] A through-space approach also developed by McConnell involving the charge-transfer state of a donor–acceptor pair is known as McConnell mechanism II; this was further modified by Breslow and co-workers in 1980.[7] The basic point of the theoretical consideration is to postulate the triplet ground state of the neutral donor or the acceptor with two degenerate SOMOs, which would result in ferromagnetic spin alignment after charge transfer due to stabilization of the low-lying triplet state, which is derived from the interaction between the two triplet states of before and after the charge transfer; it should be noted that the picture is an oversimplified one.[16] Much experimental effort has been devoted to this approach in recent years, being invoked by the theoretical consideration in connection with the development of CT-type organoconducting materials, and several organoferromagnetic materials have so far been obtained through this approach, although the mechanism of the origin of their magnetism has proved to be neither the one proposed originally[17] nor the definite one. On the other hand, the ferromagnetism of β-PNN **2** was interpreted satisfactorily by the approach, taking the charge transfer from the SOMO to the LUMO, or the doubly occupied NHOMO to the SOMO, into consideration.

It is now generally recognized, from both theoretical consideration and experimental verification, that the route to the preparation of organomagnetic materials with efficient intermolecular ferromagnetic interactions can be summarized as follows: prepare molecules with large intramolecular spin polarization; minimise the intermolecular overlap integrals between the SOMOs of the unpaired electrons of radicals; and then attain large overlap integrals through charge transfer interactions between the SOMO of the unpaired electron of a radical and the vacant or doubly occupied molecular orbital of a neighbouring molecule.

One can see from the brief survey described above that the development of new theoretical considerations invokes the development of new organomagnetic materials, which in turn invokes further progress of theoretical consideration.

Nitroxide radical crystals

Historical survey

In 1972, Veyret *et al.* reported on the magnetic behaviour of several nitroxide radicals,[24] amongst which the ferromagnetic behaviour of TANOL suberate **23** received much attention;[25] TANOL was believed to be the first organoferromagnet for some time. In fact, the substance was not a genuine organic ferromagnet with three-dimensional magnetic order, but was an antiferromagnet with ferromagnetic interactions within two-dimensional sheets having antiparallel spin order between the sheet structures with $T_N = 0.38$ K.[26] Since then, almost twenty years passed before a genuine organic ferromagnet, *i.e.*, the β-phase of *p*-nitrophenyl nitronyl nitroxide (PNN) **2** with $T_c = 0.65$ K, was found in 1991 by Kinoshita and co-workers,[8] although during this period many significant results on organomagnetic materials were achieved, especially in the fields of high spin molecules,[4] coordination complexes on nitroxide radicals[27] and CT complexes derived from metallocenes.[5] It seems that the discovery of the first organic ferromagnet evoked the successive rapid development and discoveries of other organic ferromagnets during the past few years, with almost twenty being known by the end of 1996 (see above), and it is also noteworthy that a large number of them are nitroxide radicals. Also, the number of organic radicals with ferromagnetic interactions, only four at the end of the 1980s, has increased rapidly in the 1990s to over fifty.

Nitroxide radicals developed recently

We discuss here several approaches to obtaining new organomagnetic materials from radical crystals based on nitroxide radicals, after the successful discovery of PNN (Fig. 3 and 4), surveying firstly the results of several research groups and then showing our own results. An elegant example was provided soon after the discovery of PNN in 1993 by Rassat and co-workers, namely 1,3,5,7-tetramethyl-2,6-diazaadamantane-*N*,*N*′-dioxyl **5**.[21] Compound **5** was expected to possess intramolecular ferromagnetic interactions from the orthogonality of the two N—O groups of the biradical,[22] and owing to the favourable three-dimensional network of NO chains for intermolecular ferromagnetic interactions it showed a ferromagnetic transition at 1.48 K, the highest T_c value among the organoferromagnets of radical crystals. Sugawara *et al.* and Veciana and co-workers prepared the phenol derivatives of nitronyl nitroxides **6**[28] and **7**[29] to control the arrangement of spin sources through the phenolic hydrogen bond, and found that they are really ferromagnets, although the mechanisms of the ferromagnetic interactions in **6** and **7** appear to be different. Gatteschi and co-workers succeeded in developing a ferromagnet **8**, which showed evidence of ferromagnetic order with T_c *ca.* 0.2 K.[30] It was found that the donor group SMe played an important role in generating sufficiently strong ferromagnetic interactions even at large distances. The control of the arrangement of spins using Coulombic interactions is another approach; Inoue and Iwamura in compounds **24**[31] and more recently Jackson and co-workers in compounds **25**[32] tried to control the molecular and spin arrangements in these molecules by the interactions with ferromagnetic interactions shown in some of them (**24a**, **25b** and **25c**). Interesting results were found by Inoue and Iwamura; their acetylenic derivatives carrying nitroxide radicals (**26**, **27**) formed different three-dimensional molecular-assembling systems through van der Waals interactions and then different spin arrays in the derivatives, resulting in quite contrasting magnetic behaviour.[33a]

The development of heteroaromatic systems carrying nitroxide radicals is also an attractive way to obtain new organomagnetic materials. Awaga *et al.* developed *p*- and *m*-pyridyl nitronyl nitroxide derivatives (**28**, **29**),[34] which could be further modified chemically by *N*-alkylation[35] or *N*-protonation[36] to afford a group of magnetic materials. 3-Quinolyl nitronyl nitroxide **30** was prepared by Sugano *et al.*[37] and 5-pyrimidinyl derivative **31** and its imino analogue were prepared by Rey and co-workers[38] and each magneto-structural relationship was investigated. Among these, **31** has a unique one-dimentional structural feature with ferromagnetic spin–spin interactions. A triazole nitronyl nitroxide radical **32** was prepared by Kahn and co-workers and was found to show the unique magnetic features of both intermolecular ferromagnetic interactions, assigned to the McConnell mechanism, and weak ferromagnetism with spontaneous magnetization below the critical temperature $T_c = 0.60$ K.[39] Kobayashi and co-workers prepared unique thienothiophene derivatives of nitronyl nitroxide (**33**, **34**) and the corresponding imino nitroxide and observed the differences in their magnetic behaviour due to topological differences by annulation.[40]

Extensive studies were carried out by Nogami and co-workers on 4-arylmethyleneamino-TEMPO derivatives **35** and related radicals; of 165 radicals investigated, 52 radicals were found with ferromagnetic interactions, and 9 radicals with ferromagnetic transitions at very low temperatures were found.[41] They proposed that the spin polarization mechanism through the hydrogen bond of type C—H···O—N, also proposed independently by Veciana and co-workers,[29] is a likely mechanism for the ferromagnetic interactions based on the magneto-structural relationship investigated.[42] The sharp differences in the magnetic behaviour observed between the TEMPO-substituted acrylate **36a** and methacrylate **36b**, and between the TEMPO-substituted acrylamide **36c** and methacrylamide **36d** prepared by Kamachi and co-workers, were rationally interpreted from the differences of the three-dimensional arrangements in the crystals.[43]

Multi-spin systems bearing nitroxide radicals have received attention, especially in connection with high spin molecules. Iwamura and co-workers prepared the triradicals **37** and **38** and investigated their magnetic properties; they found that **38**, which has stronger intramolecular spin interactions than **37**, has a quartet ground state.[44] An interesting approach to the construction of an organic ferrimagnet consisting of purely organic molecules (molecular solid), *i.e.*, monoradical **39** and diradical **40**, was described by Sugawara and co-workers, and a unique spin system was obtained, although ferrimagnetic spin ordering was not achieved.[45]

It is currently of interest to determine whether distorted

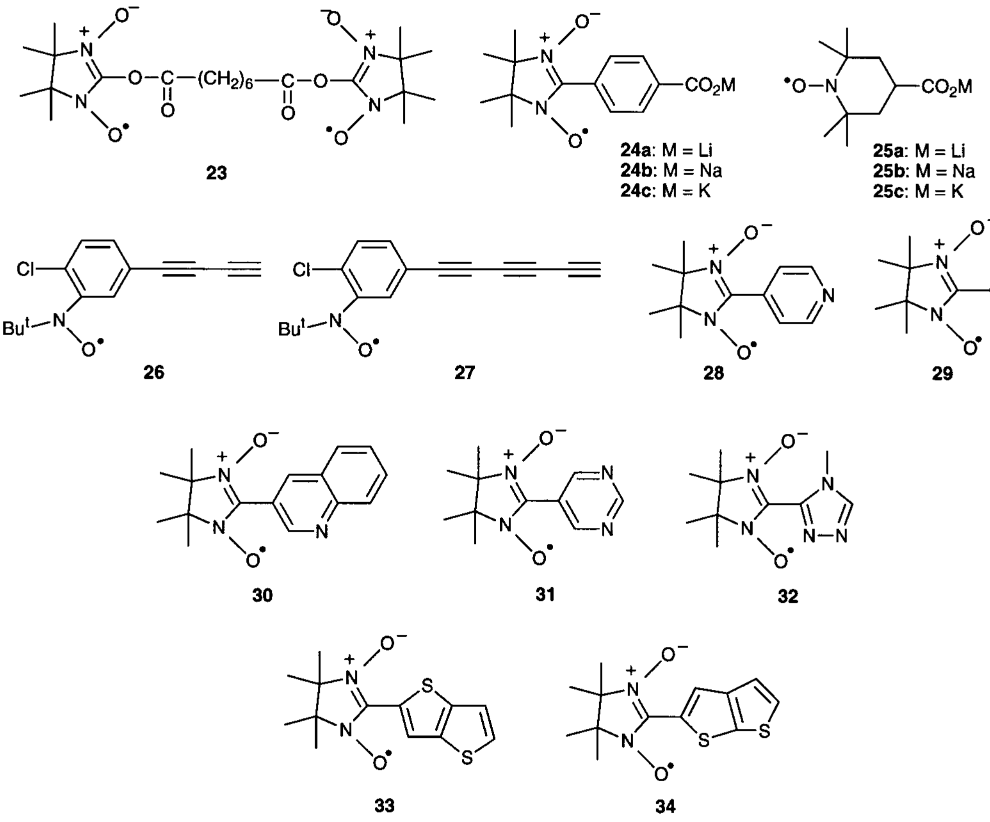


Fig. 3 Various nitroxide radicals developed recently for magnetic materials

molecules between an aromatic system and a radical moiety could possibly violate Hund's rule in non-Kekulé hydrocarbons[46] or the spin polarization effect widely recognized for the design of ferromagnetic materials. Rassat and co-workers[47] and Iwamura and co-workers[48] discovered independently that their bisnitroxide radical isomers **41** and **42** have unexpected ground-state singlets owing to the steric hindrance by bulky substituents.

o-Halophenyl nitronyl nitroxides

We have been interested, from different viewpoints as described above, in investigating the magneto-structural relationship in such molecules as that having a twisted conformation between the π-system and the radical moiety. Our objectives are to eliminate SOMO–SOMO overlap between radical centres, which is considered to be undesirable for ferromagnetic interactions, and also to obtain spin-coupling systems between the radicals constructed by non-bonding interactions; we would like to gain some insights into three-dimensional spin–spin interactions through this approach. We therefore prepared a series of nitronyl nitroxide derivatives of benzene, introducing halogen atoms at the *ortho*-position (Fig. 5) leading to successive distortion between the moieties.[49] As an estimation of the distortion between the phenyl ring and the radical moiety of nitronyl nitroxide in **43**–**46**, we at first calculated the dihedral angles between the plane of the phenyl ring and the five-membered ring of the radicals by MM2 calculations, which gave the result of sequential distortion according to the van der Waals radii of the halogen atoms. It was predicted from the calculated result that the dihedral angle for fluorine derivative **43** was *ca.* 55°. This compound was found from the plot of the reciprocal susceptibility against temperature for the fluorine derivative **43** to follow the Curie–Weiss law between 2 and 300 K, and the Curie and Weiss constants were determined to be 0.375 emu K mol^{-1} and +0.5 K, respectively (Table 1). The positive Weiss constant and the increase of the product χ_pT with decreasing temperature lower than *ca.* 20 K indicated intermolecular ferromagnetic interactions between the spins of radical **43** at low temperature [Fig. 6(*a*)]. The magnetic behaviour of **43** was further investigated by ac susceptibility measurements from 0.04 to 4.2 K to show the phase transition below the Weiss constant at around 0.3 K observed in the temperature dependence data of χ_{ac} [Fig. 6(*b*)] for each applied frequency (20 Hz, 40 Hz, 240 Hz). A distinct peak was detected at T_c revealed by magnetic heat capacity measurements as shown in Fig. 7, and a quasi-one-dimensional magnetic structure was suggested by the measurement, *i.e.*, the ferromagnetic intrachain interactions were considered to be larger than the interchain magnetic interactions with ferromagnetic nature. Thus, ferromagnetic ordering with T_c of around 0.3 K is suggested by the magnetic behaviour of **43**.[50]

Table 1 The Weiss constants (θ)[a] and the degrees of distortion (ψ) of the radicals **43**–**50**

compound	θ/K	$\psi_{calc.}$/degrees[b]	ψ_{found}/degrees[c]
43	0.5	55	48[d]
44	−0.2	66	60[e]
45	−3.3	71	—
46	−3.4	70	—
47	−1.5	—	—
48	−0.9	—	55[e]
49	0.7	—	56,64[e,f]
50	0	—	—

[a]Fitting to the Curie–Weiss rule. The value of the unsubstituted derivative is reported to be θ/K = −1.4; K. Awaga and Y. Maruyama, *J. Chem. Phys.*, 1989, **91**, 2743. [b]Calculated degree of distortion by using MM2 optimized parameters in the CAChe system. [c]Found by X-ray data. [d]Ref. 49. [e]Unpublished results. [f]Two sorts of molecules are found in the crystal, having corresponding values.

In contrast, negative Weiss constants were obtained for radicals **44**, **45** and **46**, indicating that the intermolecular spin–spin interactions are antiferromagnetic in these three radicals; stronger interactions were observed in the latter two (**45** and **46**) than in chlorine derivative **44** (Table 1). It is also

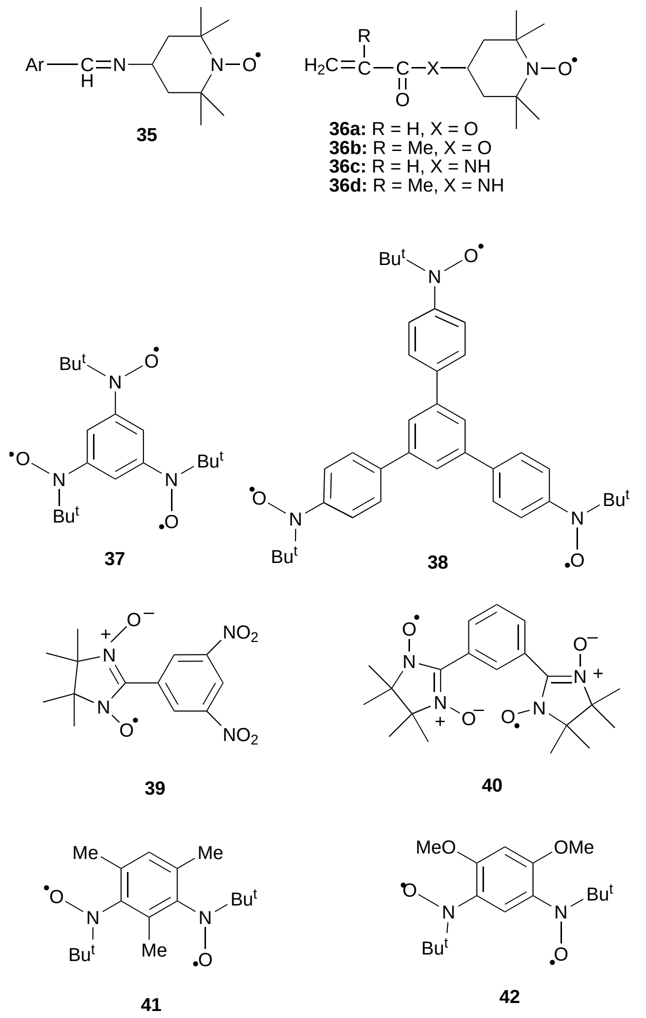


Fig. 4 Various nitroxide radicals developed recently for magnetic materials (continued)

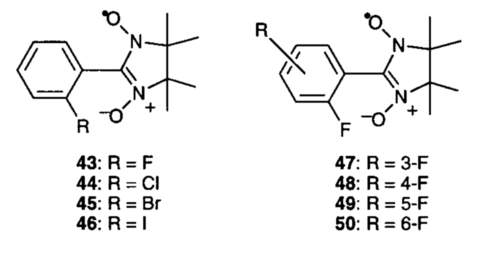


Fig. 5 Nitronyl nitroxide derivatives of benzene with halogen atoms at the *ortho*-position

notable that the Weiss constants for **45** and **46** showed almost the same order of magnitude, possibly reflecting the same order of distortion.

Thus, a sharp difference was observed between the magnetic properties of **43** and the other derivatives and the origin of the difference may be attributable, at least in part, to the degree of their molecular distortion estimated from the van der Waals radii of the halogen atoms and the resulting crystal structural difference in three dimensions. The dihedral angle between the plane of the phenyl ring and the five-membered ring of radical **43** was found to be 48° by X-ray analysis, which is somewhat smaller than the value estimated from MM calculations (Table 1). The following tendency is apparent from the data, *i.e.*, the direct interaction between NO and ON is very small and hence the overlap between SOMOs between the molecules is estimated to be very small, which is relevant to ferromagnetic interactions. Moreover, the interactions between the radicals work through methyl groups or phenyl groups by weak hydrogen bonds of the C—H···O—N type or other non-bonded interactions to build up a three-dimensional network system and then to give an efficient spin polarization effect for the ferromagnetic interactions between the radicals.[29,42] Thus, the ferromagnetic behaviour of fluorine derivative **43** may be interpreted rationally from its crystal structural analysis and it is apparent from the results obtained above that the ferromagnetic behaviour of radical crystals depends subtly upon their molecular/crystal structures as antiferromagnetic, but not ferromagnetic, behaviour was found for radicals **44**, **45** and **46**, which may have more distorted molecular structures than **43** (from recent X-ray analysis results on **44**, the dihedral angle between both planes was found to be 60° as cited in Table 1).

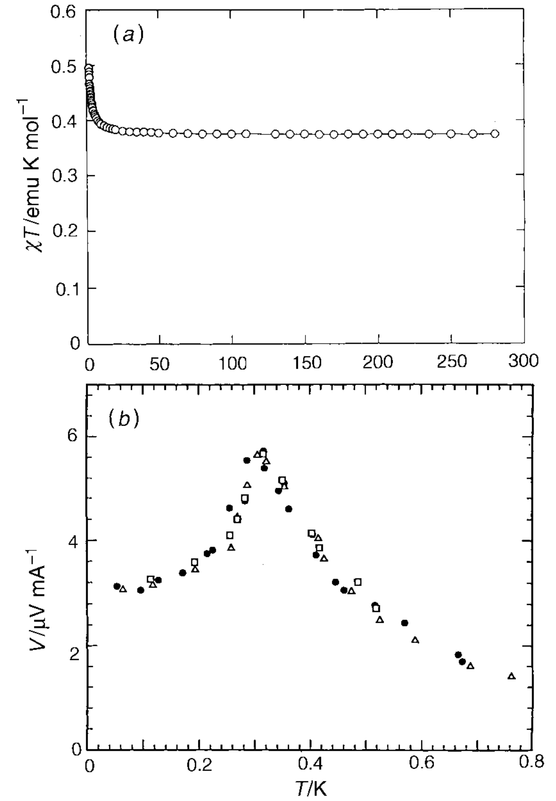


Fig. 6 (*a*) Temperature dependence of χT for **43**. Reproduced by permission from ref. 49. (*b*) Temperature dependence of χ_{ac} for **43**. ●, 40 Hz data; △, 20 Hz data (×2); □, 240 Hz data (×⅙).

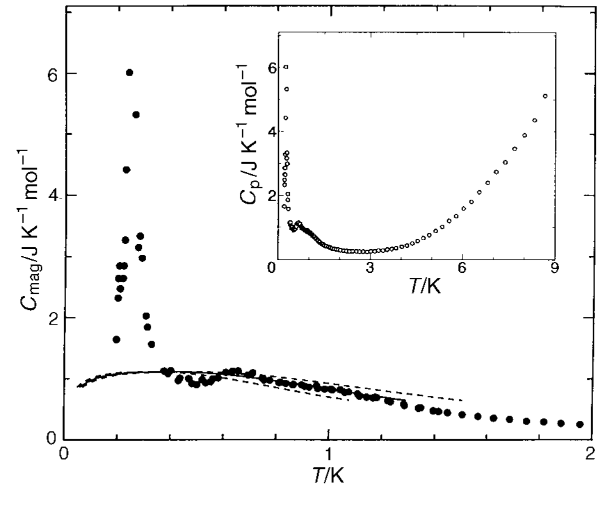


Fig. 7 Temperature dependence of magnetic heat capacity of **43** between 0.2 and 2 K. The solid line represents the theoretical results for the isotropic Heisenberg ferromagnet with $J/k_B = 0.6 \pm 0.1$ K. The data between 0.2 and 9 K are shown in the inset.

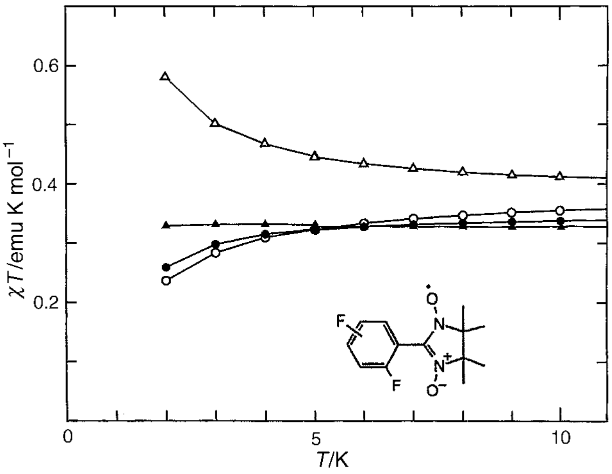


Fig. 8 Temperature dependence of χT for radicals **47**–**50** in the lower temperature region. ○, 2,3-F; ●, 2,4-F; △, 2,5-F; ▲, 2,6-F.

Although no definite conclusion could be drawn from the experimental results obtained in the study, it was recognized that magnetic behaviour of radical crystals depends subtly upon molecular structure and molecular configuration to form three-dimensional crystal structures, and that a moderate degree of distortion could yield ferromagnetic interactions in the system while too much distortion results in the occurrence of antiferromagnetic interactions. Thus, we could find a ferromagnetic system and could identify some interesting features through study, but clarification of the magneto-structural relationship between molecular distortion and magnetism is still required.

In spite of the efforts of the preceding years described above, it is still the Rassat radical which has the highest T_c value known, 1.48 K.[21] Although there is now less optimism about the development of organic radical crystals with very high T_c values, it is important to make steady efforts into the development of new radical crystals systematically, to clarify and to understand the structure–magnetism relationship. A very serious point for development is control of the molecular arrangement in three dimensions, because the magnetic properties of materials depend subtly on the packing mode of molecules. As a typical example, it is known that only the β-phase of the four possible phases (α,β,γ,δ) of PNN crystals is ferromagnetic.[8] In the bis-fluorine-substituted phenyl nitronyl nitroxide derivatives **47**–**50** recently prepared (Fig. 5), such a situation was again found. While antiferromagnetic interactions were observed in 2,3-bis-fluorine-substituted derivative **47** and 2,4-bis-fluorine-substituted derivative **48**, ferromagnetic interactions and paramagnetic interactions were found in 2,5-bis-substituted derivative **49** and 2,6-bis-substituted derivative **50**, respectively (as shown in Fig. 8), reflecting the subtle change of magnetic properties through the change of crystal structures in the regioisomers. It was found from X-ray analysis of **48** and **49** that relatively short NO–ON distances (4.05 Å) in their dimer structures appear to be relevant to the observed antiferromagnetic interactions in **48**, while the ferromagnetic interactions observed in **49** could be rationally understood by a spin polarization effect between the radical centres through fluorine atoms, methyl and phenyl groups in three dimensions.[51]

CT complexes consisting of nitroxide radicals

General aspects

The construction of hitherto unknown organoferromagnetic conductors is undoubtedly one of the aspirations of materials scientists, and efforts to prepare such an interesting material have been carried out by several research groups, including ourselves. The reason for the difficulty in obtaining organomagnetic conductors is based mainly on the difficulty of arranging the spins at both the molecular and the crystal level experimentally, to construct an organoferromagnetic material with conducting electrons, while the theoretical possibility of access to ferromagnetic materials including organoferromagnetic conductors for charge transfer complexes incorporating stable radicals was recently pointed out.[52] As shown in the typical examples in Fig. 9, ferromagnetic behaviour can be observed when the spins of donor molecules carrying radical(s) interact with the spins of radical(s) and the spins of acceptors alternately, stacking ferromagnetically in intramolecular, intermolecular and interchain fashion, *i.e.*, when all the exchange interactions have positive values (upper left). Ferrimagnetic interactions can be observed even if some of the interactions described above are antiferromagnetic, when other ferromagnetic interactions remain, as shown in the upper right of Fig. 9. Even magnetic conductors can be postulated when a segregated column is made to direct the interactions between the spins of conducting electrons of donors and/or acceptors and the localized spins of radicals ferromagnetically (lower part of Fig. 9). A similar situation would be anticipated for CT complexes derived from acceptor molecules carrying radicals and donors. We have therefore been interested in preparing donor and acceptor molecules bearing stable radicals and the CT complexes derived therefrom to build up and arrange the spins in their crystal structures, in which the localized spins could be considered to correlate with conducting electrons. The idea described above was originally based on McConnell's theory to obtain ferromagnetic materials, which was further developed by Breslow as described above.[7] By this approach, several organoferromagnetic materials have so far been realized including decamethylferrocene-TCNE complex **1** ($T_c = 4.8$ K),[5] C_{60}–tetrakis (dimethylamino)ethylene complex **3** (weak ferromagnet, $T_c = 16$ K)[53] and tetramethylammonium-$TCNQF_4 \cdot 1/2TCNQF_4$ complex **20** and related salts reported recently,[54] although there is no clear experimental evidence for their magnetic interactions assigned to the mechanism[16] and actual experimental access to organomagnetic conductors has yet to be achieved, despite the many studies undertaken.

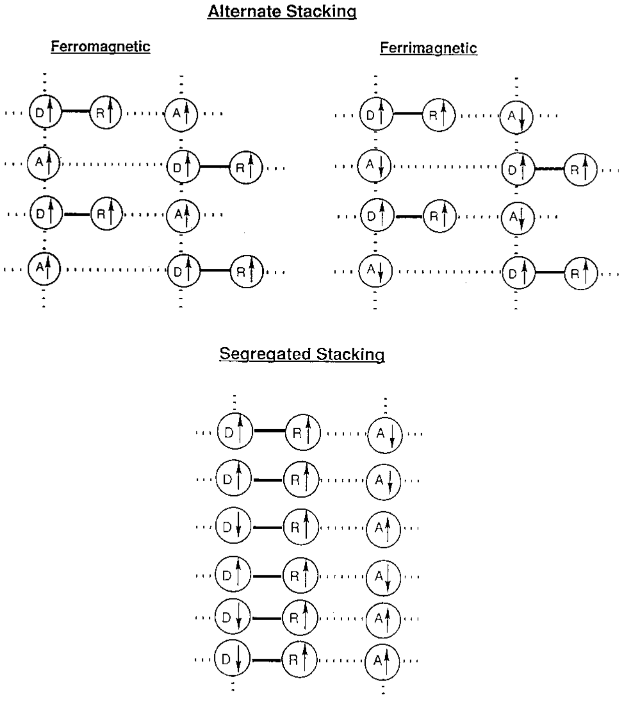


Fig. 9 Possibilities of organoferromagnetic and ferrimagnetic CT complexes as well as organomagnetic metal, where D, A, R denote donor, acceptor and stable radical, respectively

In the next section, we will to survey the experimental efforts and the results obtained so far. The CT complexes with stable radicals developed are classified in the following four categories:

(i) development of charge transfer complexes consisting of donor compounds carrying stable radicals and acceptors;

(ii) development of charge transfer complexes consisting of acceptor compounds carrying stable radicals and donors;

(iii) development of charge transfer complexes consisting of stable radicals and acceptors;

(iv) development of charge transfer complexes consisting of donors, stable radicals and acceptors (organic ternary complexes).

(i) Development of CT complexes consisting of donors carrying nitroxide radicals and acceptors

Several research groups have studied independently and developed their own compounds along the lines of approach (i).[55–60] The prepared and reported compounds are donors carrying nitroxide radicals (**51**–**57**) as depicted in Fig. 10. All of the donors **51**–**57** gave CT complexes with appropriate acceptors showing varying magnetic behaviour which, however have not yet shown the desired ferromagnetism, according to the reported results. Ferrocene derivative **51**[55] and donor molecules **52**–**55**[56] were developed independently in 1991 along the guiding principle described above. Ferrocene derivative **51** formed a CT complex with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), which showed antiferromagnetic coupling between the ferrocenium ion and radical spin at low temperature as evidenced by susceptibility measurements. Donor molecules **52**–**55** were found to form CT complexes with $TCNQF_4$ which, however, showed no remarkable spin–spin interactions between $D^{\cdot +}$ and radical spin at low temperatures. While the EPR spectral data on the radical cations of TTF derivatives **55** and **56**[57] suggested the presence of intramolecular spin–spin exchange between the TTF radical cation and nitroxide radicals in solution, the magnetic behaviour in susceptibility measurements on the CT complexes or radical cation salts of **55** and **56** with $TCNQF_4$ or I_2 indicated that even the short-range spin alignment of radicals could not be achieved in the CT complexes or the radical cation salts, although different magnetic properties in the complexes or in the salts were observed depending on the kind of radical substituents.[58] Significant intramolecular exchange interactions were found for the radical cation salt of cross-conjugated TTF derivative **57** and the radical anion salt derived from benzoquinone derivative **67** (Fig. 11), as estimated from their EPR measurements, in which relatively large antiferromagnetic interactions were found for the former while ferromagnetic interactions were found for the latter.[59] An unusual magnetic property of the DDQ complex of **57** was reported which could not be explained by simple paramagnetism.[60]

Independently, we prepared several TTF derivatives carrying one, two or four radical substituents as shown in Fig. 11. Mono- and bis-hydroxy-TEMPO-substituted TTF derivatives **58**[61] and **59**[62] were prepared through the mono-lithio TTF derivative and bis- or tetrakis-lithio TTF derivative following the steps shown in Scheme 1. In the latter case, no tris- or tetrakis-substituted derivatives could be isolated, probably because of the steric hindrance of the bulky substituent. The redox behaviour of the TTF derivatives **58** and **59** was investigated by cyclic voltammetry in CH_3CN (Table 2) and the first oxidation potentials estimated from the data were found to be comparable with that of TTF, suggesting sufficient donor ability of **58** and **59** to form CT complexes with appropriate acceptors. Moreover, electrons would transfer firstly from the TTF moiety forming TTF radical cations for both **58** and **59** because the first oxidation potential of **1** is apparently lower than that of 4-hydroxy-TEMPO itself. Actually, some CT complexes, *i.e.*, I_3, DDQ and $TCNQF_4$ complexes, can be prepared both from **58** and **59** (radical cation salts in the case of I_3) and their magnetic behaviour was investigated using a SQUID susceptometer. No ferromagnetic, and only weak antiferromagnetic behaviour with a Weiss constant of as large as -1 K for each complex, an apparent decrease of the magnetic susceptibility upon CT complex formation was observed from the susceptibility data, probably resulting from the partial formation of singlets between unpaired electrons although different magnetic behaviour, depending on the acceptor molecules used, was observed at the same time.[63,64]

We next prepared TTF derivatives carrying two or four nitroxide radicals as an extension of the approach described above, to inspect the spin ordering in the complexes derived from them. Bis- (*Z* and *E* isomers) and tetrakis-TEMPO-

Table 2 EPR data[a] and oxidation potentials[b] of the donors **58**, **59**, 4-hydroxy-TEMPO and TTF

compound	*g*-factor	a_N/mT	E_1^{ox}	E_2^{ox}	ΔE^c
58	2.007	1.53	0.44	0.85	0.41
59	2.006	1.53	0.40	0.86	0.40
4-hydroxy-TEMPO	2.006	1.53	0.85	—	—
TTF	—	—	0.49	0.80	0.31

[a]Solvent: benzene. The *g*-factors are estimated from the signals of Mn^{2+}/MgO with $g=1.981$. [b]V *vs.* SCE in CH_3CN with TBAP at room temperature. Scan rate: 50 mV s^{-1}. [c]$\Delta E = E_2^{ox} - E_1^{ox}$.

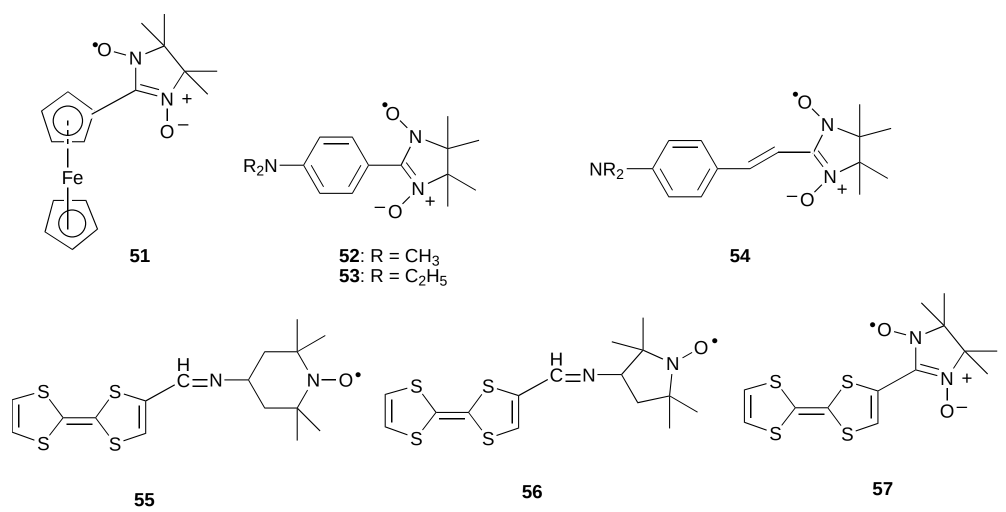


Fig. 10 Donor molecules bearing stable radicals developed recently

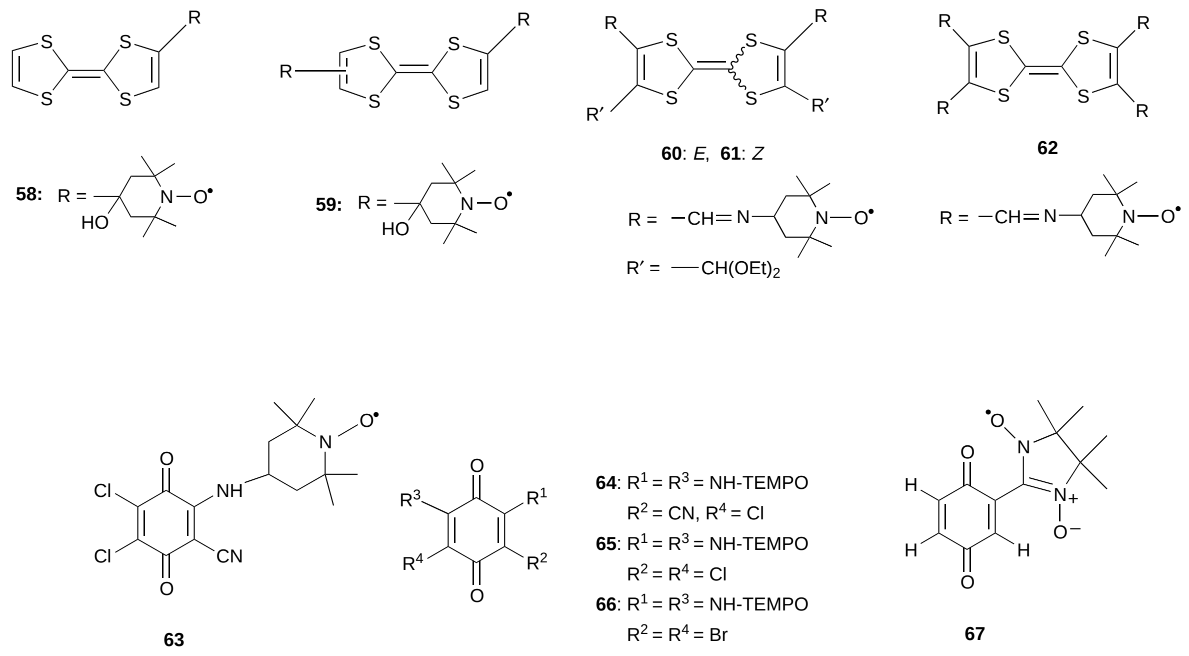
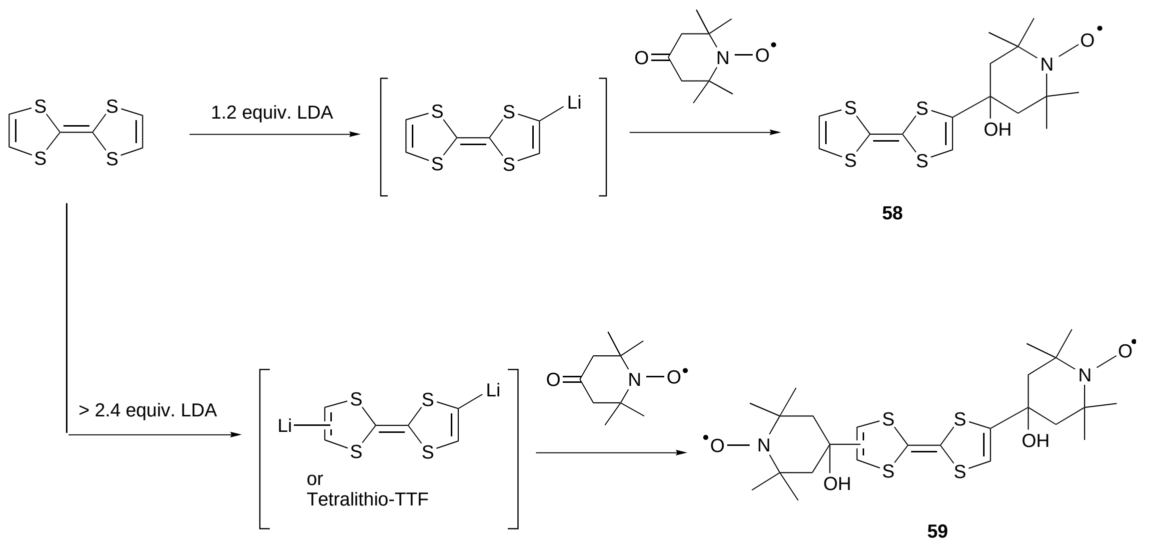


Fig. 11 Donor and acceptor molecules bearing radicals developed recently (continued)



Scheme 1

substituted TTF derivatives **60**, **61** and **62** were prepared *via* the corresponding formyl derivatives, which were prepared by the coupling reaction of the 1,3-dithiole-2-thione derivative following the procedure developed by Gorgues *et al.* (Scheme 2).[65] Although the first oxidation potentials measured by cyclic voltammetry in CH_2Cl_2 (V *vs.* SCE; **60**: $E_1^{ox} = 0.65$ V; **61**: $E_1^{ox} = 0.60$ V; **62**: $E_1^{ox} = 0.55$ V) were found to be higher than that of TTF ($E_1^{ox} = 0.49$ V), their iodine salts could be isolated as black or dark brown solids. The susceptibility data for each compound followed Curie–Weiss curves showing the magnetic behaviour, with corresponding Weiss constants summarized in Table 3. Thus, only weak antiferromagnetic interactions with an appreciable decrease of susceptibility compared with the corresponding donors was again observed for each radical cation salt.[66] For the complexes described above, the spins could not be arranged by complex formation in a columnar structure to obtain ferro- or ferri-magnetic materials, but serious loss of the spins was observed, probably because of singlet formation between unpaired electrons.

Meanwhile, Sugimoto *et al.* succeeded in developing three ferromagnetic CT complexes based on pyridinium-substituted imidazolin-1-oxyl with $TCNQF_4$ or hexacyanobutadiene (HCBD) **15**–**17**, although some spin loss was also observed in their complexes.[67]

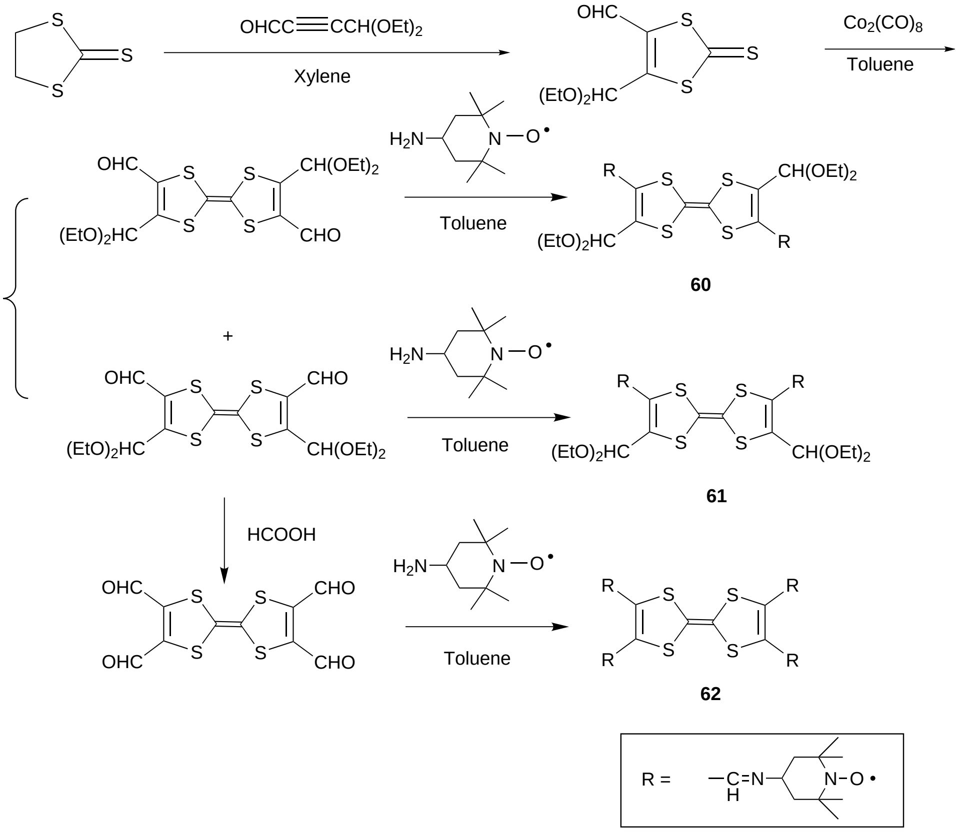
Table 3 Magnetic properties of the radicals **60**–**62** and their iodine complexes

compound	magnetic interactions	Weiss constant/K[a]
60	antiferromagnetic	−2.3
61	ferromagnetic	0.2
62	antiferromagnetic	−1.0
I_2 complex of **60**	antiferromagnetic	−1.8
I_2 complex of **61**	antiferromagnetic	−0.2
I_2 complex of **62**	antiferromagnetic	−1.0

[a] Fitting for Curie–Weiss rule.

(ii) Development of CT complexes consisting of acceptors carrying nitroxide radicals and donors

Alternatively, we intended to prepare acceptor molecules (benzoquinone derivatives) carrying nitroxide radicals, such as



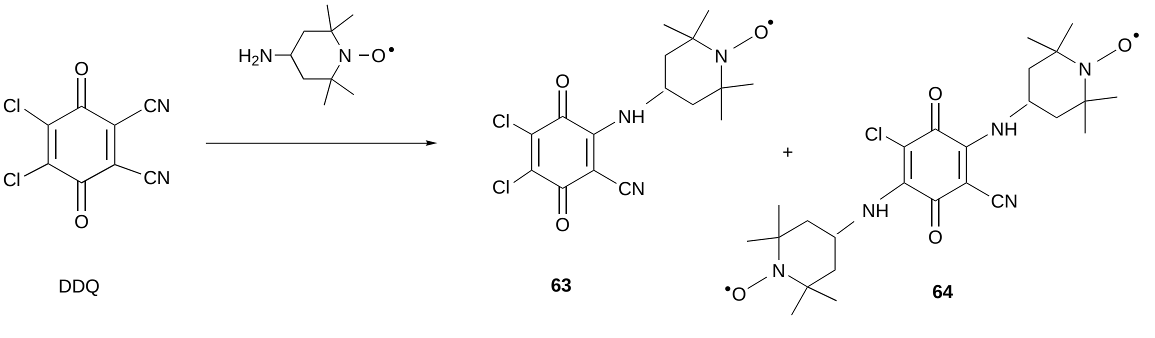
Scheme 2

63–**66** (Fig. 11) to explore approach (ii). The preparation of the TEMPO-substituted benzoquinone derivatives was carried out by using the substitution reaction of 4-amino-TEMPO on acceptor molecules such as DDQ, chloranil and bromanil. Interestingly, when DDQ was used as a substrate, the monosubstituted derivative **63** was the major product, with a small amount of bis-substituted derivative **64** (Scheme 3), whereas bis-substituted derivatives **65** and **66** were obtained as the major products when chloranil and bromanil, respectively, were used as the substrate.[68] It was found from cyclic voltammetry data that the first reduction potentials of the acceptors **63**–**66** were lower than that of DDQ but higher than that of benzoquinone, suggesting that **63**–**66** have intermediate electron-accepting ability (Table 4); the electron-accepting ability of **63** was the highest of these compounds, suggesting it to be the most suitable acceptor for the formation of a CT complex with an appropriate donor molecule. As expected from the redox behaviour, CT complexes were found to be formed between **63** and TTF, and even between **63** and 4-hydroxy-TEMPO-substituted TTF **58**, while there was no evidence for the formation of CT complexes between **64**–**66** and TTF. It was found from the magnetic susceptibility data that the complexes prepared again showed no ferromagnetic, but weak antiferromagnetic, interactions with decrease in magnetic susceptibility compared with **63**, while **63** itself showed antiferromagnetic ordering in one dimension. Thus, as we found through approaches (i) and (ii), no ferromagnetic spin ordering was realized and instead similar tendencies of singlet formation were observed in each case. On the other hand, Sugawara and co-workers observed ferromagnetic interactions in their radical anion salt derived from an acceptor molecule carrying nitronyl

Table 4 Cyclic voltammetric data for the radicals **63–66**[a]

compound	E_1^{red}	E_2^{red}	ΔE^b
benzoquinone	−0.57	−1.27	0.70
DDQ	0.47	−0.31	0.70
63	−0.19	−0.83	0.64
64	−0.34	−0.86	0.52
65	−0.28	−0.87	0.59
66	−0.35	−0.88	0.53

[a]Reduction potentials (V) *vs.* SCE in CH_3CN with 0.1 M TBAP at room temperature. Scan rate: 50 mV s^{-1}. [b]$\Delta E = E_2^{red} - E_1^{red}$.



Scheme 3

nitroxide radical **67**, although the complex was not isolated in the solid state.[59]

(iii) Development of CT complexes consisting of nitroxide radicals and acceptors

In the above-mentioned approach to organomagnetic materials, the groups of stable radicals are covalently bonded to the π-system of the donor or acceptor moiety, while it has been found recently that some CT complexes have been formed between TEMPO radicals and appropriate acceptors, *i.e.*, the TEMPO radical itself could work as a donor forming solid charge transfer complexes [Fig. 12, corresponding to approach (iii)].[69] It was reported as early as 1971 that the di-*tert*-butyl-*N*-oxide radical formed CT complexes with various acceptors, such as DDQ or TCNE, which were elucidated by electronic spectra and EPR measurements in solution but the complexes have never been isolated or their solid-state properties reported.[70] Since then, to our knowledge, there have been no reports on the formation of CT complexes based on nitroxide radical and only a few reports have appeared on the preparation of other types of CT complexes, such as those in which radicals work as donors.[71] We carried out a more extensive study on the CT complexes based on TEMPO radicals. Almost at the same time, Sugawara and co-workers prepared and isolated independently a CT complex based on *p*-dimethylaminonitronyl nitroxide and chloranil.[72]

We prepared a series of CT complexes **75**–**87** from the corresponding TEMPO derivatives **68**–**74** as indicated in Fig. 12. Several TEMPO derivatives (*e.g.*, **68**–**70**) used in the study are now commercially available, but we prepared some alkylamino-TEMPO derivatives expecting the enhancement of the donor ability. The alkylamino-TEMPO derivatives **71**–**74** were prepared by the reductive amination of 4-oxo-TEMPO with alkylamines using sodium cyanoborohydride as a reducing agent (Scheme 4).[73] To estimate their donor ability, their electrochemical behaviour was investigated by cyclic voltammetry. It was observed, as shown in Table 5, that 4-amino- and 4-alkylamino-TEMPO radicals **70**–**74** show two oxidation potentials (E_1^{ox} and E_2^{ox}) in their redox waves while TEMPO radicals **68** and **69** have only one oxidation potential based on nitroxide radical in acetonitrile solution. Each E_1^{ox} and E_2^{ox} value of **70**–**74** could be attributed to the oxidation of the amino group and the nitroxide radical, respectively and their E_1^{ox} values were apparently lowered compared with those of **68** and **69**, with the lowest value of 0.56 V for **73**, while in turn, each E_2^{ox} value was found to be higher than those of **68** and **69**. From the point of view of such redox behaviour of TEMPO radicals **68**–**74**, it was anticipated that some charge transfer complexes could possibly be formed with appropriate acceptors. Actually, when TEMPO radical **68** was reacted with an equimolecular amount of $TCNQF_4$ in acetonitrile, it was observed that the reaction mixture turned deep green. The resulting dark blue crystals obtained after work-up of the reaction mixture was found to be the CT complex **75** 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 at 856 nm and 753 nm, in acetonitrile were clearly observed in the visible absorption spectrum of **75** and the lower shift of ν_{CN} ($\nu_{CN} = 2190\ cm^{-1}$) observed in its IR spectrum compared with that of the neutral acceptor ($TCNQF_4$: $\nu_{CN} = 2237\ cm^{-1}$) was also consistent with the formation of the CT complex. Thus, a CT complex was isolated in which a radical works as a donor. Following the results described above, we then prepared a series of similar CT complexes **76**–**87** derived from the other TEMPO derivatives **69**–**74**. The corresponding CT complexes could not be prepared from 4-methoxy, 4-cyano- or 4-carboxy derivatives. The radicals **71**–**74**, prepared by the reductive amination of 4-oxo-TEMPO, gave complexes with even weaker acceptors than

Table 5 Cyclic voltammetric data for radicals **68**–**74**[a]

compound	E_1^{ox}	E_2^{ox}	ΔE^b
68	0.70	—	—
69	0.72	—	—
70	0.68	0.87	0.19
71	0.62	0.85	0.23
72	0.64	0.86	0.22
73	0.56	0.85	0.29
74	0.65	0.85	0.20

[a] Oxidation potentials (V) *vs.* SCE in CH_3CN with 0.1 M TBAP at room temperature. Scan rate: 50 mV s^{-1}. [b] $\Delta E = E_2^{ox} - E_1^{ox}$.

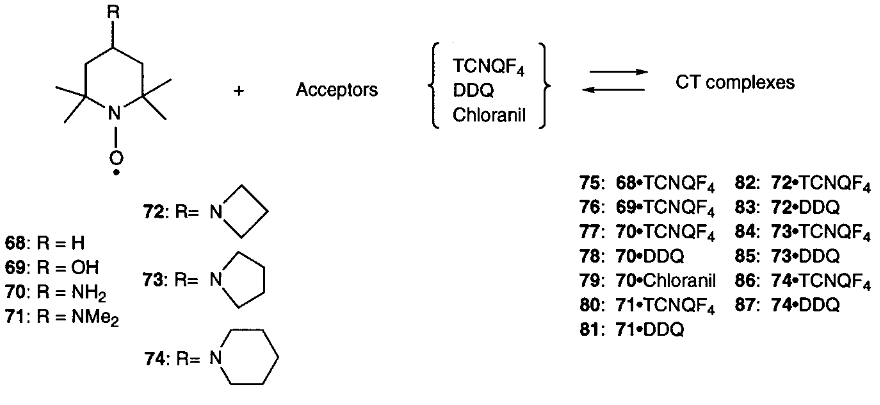
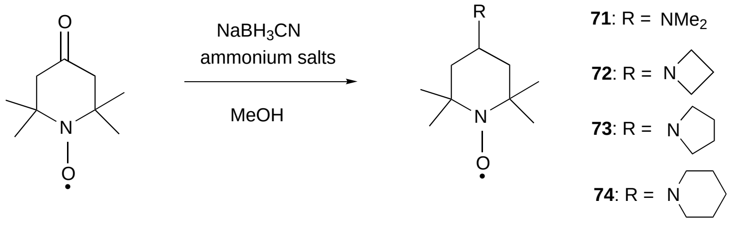


Fig. 12 CT complex formation between TEMPO radicals **68**–**74** and acceptors



Scheme 4

TCNQF$_4$, *i.e.*, DDQ or chloranil. It was found, from the magnetic susceptibility data obtained using a SQUID susceptometer, that while TEMPO **68** itself showed antiferromagnetic interactions with a Weiss constant of -3.0 K (Table 6),[24] a drastic decrease of magnetic susceptibility was observed in complex **75**, suggesting a strong tendency for singlet formation between the radical centres.[74] A similar tendency was observed in complex **76** derived from 4-hydroxy-TEMPO **69**. In contrast, no such drastic decrease of magnetic susceptibility was observed for 4-amino- or 4-alkylamino-TEMPO derived complexes **77**–**87** and acceptor-dependent magnetic interactions were suggested in each complex, which were estimated from their Weiss constants. Interestingly, some complexes were found to show ferromagnetic interactions by SQUID measurements as indicated in Table 6. Although most complexes derived from 4-alkylated amino-TEMPO derivatives showed weak antiferromagnetic interactions; 4-piperidino-TEMPO derivative **74** has ferromagnetic interactions with a Weiss constant of $+0.5$ K and shows weak antiferromagnetic interactions within the complex of TCNQF$_4$ **86** with a Weiss constant of -0.9 K, while short range ordering is observed in DDQ complex **87** with a Weiss constant of -6.2 K (Fig. 13). Thus, a sharp difference was observed in the magnetic behaviour between the complexes **75**, **76** derived from TEMPO **68** or 4-hydroxy-TEMPO **69** and the complexes **77**–**87** from 4-amino-TEMPO **70** or its alkylated derivatives **71**–**74** (Table 6).

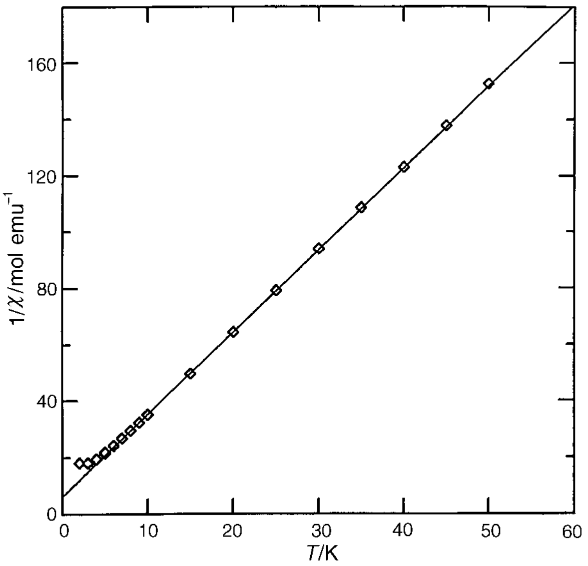


Fig. 13 Temperature dependence of $1/\chi$ below 50 K for complex **87**. Reproduced by permission from ref. 69.

The magneto-structural relationship of the complexes **75** and **82** was investigated by X-ray analysis.[69,75] Relatively small bond alternation in each TCNQF$_4$ molecule in both **75** and **82** suggests the delocalization of π-electrons over the whole molecule, forming its radical anion (Fig. 14, upper and Fig. 15, upper).[54] The shorter N—O bond length (1.20 Å) of the donor molecule in **75** compared with the bond length in ordinary nitroxide radicals (1.28–1.29 Å)[76] indicates the formation of the oxoammonium ion from the nitroxide radical while the bond length of the donor molecule in **82** is 1.29 Å, which is as expected for the nitroxide radical and which indicates that the spins of the radical molecules are not lost in the latter complex. A distinct difference between the crystal structures of **75** and **82** is observed as shown in Fig. 14 (lower) and Fig. 15 (lower). In complex **75**, both TEMPO molecules and TCNQF$_4$ radical anions form columnar structures along the *a*-axis with a zigzag structure in the latter. On the other hand, perpendicularly segregated columnar structures for both donor molecule and radical anion are observed in complex **82**. The following features were also disclosed by the analysis: (i) the shortest NO···ON distance found in both **75** and **82** is that between TEMPO radicals in the column, which amounts to 6.99 Å for **75** and 6.10 Å for **82**; (ii) in both complexes, TCNQF$_4$ molecules stack to form dimer structures with distances of 3.2–3.5 Å, somewhat shorter than the sum of the van der Waals radii (3.54 Å) of the carbon atom, along the *a*-axis in **75** and the *c*-axis in **82**, respectively. That is to say, the stacking mode of TCNQF$_4$ molecules is in this regard rather similar in both complexes; (iii) in complex **75**, the nearest distance between the oxygen of the nitroxide radical and TCNQF$_4$ molecule is that of O(1)···F(2) (Fig. 14, upper) and amounts to 2.78 Å, which is shorter than the sum of the van der Waals radii of each atom. In complex **82**, on the other hand, the shortest contact is that between the nitrogen atom N(2) of the amine moiety of the radical **72** and the nitrogen atoms N(3) or N(4) of the cyano group in the TCNQF$_4$ molecule and amounts to 3.11 Å. The magnetic behaviour of each complex would then be interpreted

Table 6 Summary of physical, spectral and magnetic data of **68–74** and complexes **75–87**

compd.	appearance	mp/°C	D:A[a]	λ_{max} (CH$_3$CN)/nm (ε/dm^3 mol^{-1} cm^{-1})	ν_{max}[b] (Nujol)/cm^{-1}	magnetic interactions	Weiss const./K[c]
68	orange crystals	36–38[d]	—	461 (<10)	—	antiferromagnetic[e]	-3.0[e]
69	orange solid	69–71[d]	—	458 (12)	—	antiferromagnetic[e]	-6.4[e]
70	orange solid	33–35[f]	—	343 (500)	—	antiferromagnetic	-0.2
71	orange crystals	>64[g]	—	460 (100)	—	antiferromagnetic	-7.5[h]
72	red crystals	79	—	450 (<10)	—	antiferromagnetic	-4.9[h]
73	orange crystals	>54[g]	—	458 (<10)	—	antiferromagnetic	-6.3[h]
74	orange crystals	>70[g]	—	451 (20)	—	ferromagnetic	0.5
75	dark blue prisms	148[g]	1:1	856 (5660), 753 (2700)	2190	antiferromagnetic	-0.1
76	blue powder	212[g]	1:1	855 (30200), 753 (16000)	2200	diamagnetic	—
77	dark green powder	>146[g]	1:1	857 (23000), 753 (11000)	2200	antiferromagnetic	-1.0
78	dark green powder	>*ca.* 120[g]	1:1	588 (3970), 457 (3850)	2210	ferromagnetic	0.1
79	dark green powder	>*ca.* 150[g]	1:1	428 (1330), 421 (870)	—	ferromagnetic	0.1
80	dark blue needles	>155[g]	1:1	856 (35900), 753 (17100)	2200	antiferromagnetic	-1.8
81	dark brown powder	>*ca.* 120[g]	1:1	588 (2610), 457 (2890)	2210	antiferromagnetic	-0.4
82	dark blue needles	>140[g]	1:1	851 (37400), 754 (17400)	2200	antiferromagnetic	-0.3
83	dark brown powder	>*ca.* 150[g]	—[i]	585 (500), 460 (1420)	2200	antiferromagnetic	-1.6
84	dark green powder	>145[g]	1:1	857 (30700), 753 (14600)	2200	antiferromagnetic	-0.3
85	dark brown powder	>*ca.* 150[g]	1:1	588 (2620), 456 (2600)	2210	antiferromagnetic	-1.1
86	dark green powder	>150[g]	1:1	852 (23800), 753 (12700)	2200	antiferromagnetic	-0.9
87	green powder	>*ca.* 150[g]	1:1	587 (4810), 456 (4820)	2210	antiferromagnetic	-6.2[h]

[a] Estimated from elemental analysis. [b] Value of ν_{CN}. [c] Fitting for Curie–Weiss rule. [d] Lit.: O. L. Lebedev and S. N. Kazarnovskii, *Zh. Obshch. Khim.*, 1960, **30**, 1631. [e] *Cf.* ref. 24 in text. [f] Lit.: E. G. Rozantsev and Y. V. Kokhanov, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1966, **8**, 1477. [g] Decomposition point. [h] Short range order is suggested from the susceptibility data in this case. [i] Not determined.

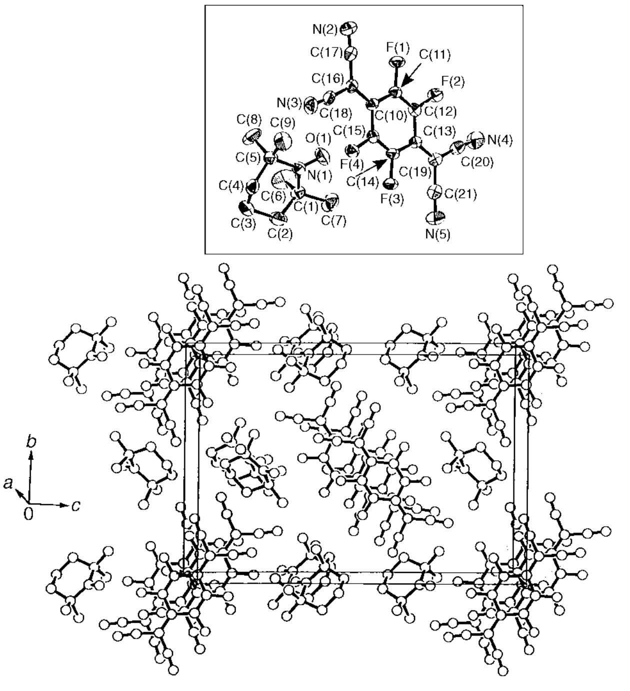


Fig. 14 Upper: molecular structure of complex **75**. Lower: crystal structure of **75** viewed almost along the *a* axis. Reproduced by permission from ref. 69.

as follows: in complex **75**, the charge accepted by the TCNQF$_4$ species comes from TEMPO radicals forming oxoammonium ions in the latter, *i.e.*, TEMPO becomes TEMPO$^+$, while the loss of the spins of TCNQF$_4$ radical anions is supposed to be derived from their columnar structure, resulting in a singlet. In complex **82**, the short contact mentioned above between the nitrogen atom of the amine moiety of radical **72** and the TCNQF$_4$ molecule suggests that the charge transfer occurs from the alkylamino group of the radical to the acceptor molecule in this case and hence antiferromagnetic interactions with no apparent decrease of spins in **82** would be mainly attributed to the interactions between the spins on the TEMPO radicals and the azetidyl radical cations, while the spins on the TCNQF$_4$ radical anions would largely be lost by intermolecular singlet formation. Thus, we prepared and isolated a series of charge transfer complexes **75**–**87** on TEMPO radicals having variable and acceptor-dependent magnetic behaviour. TEMPO–TCNQF$_4$ complex **75** and 4-azetidyl-TEMPO–TCNQF$_4$ complex **82**, showing distinct differences in their magnetic properties, were structurally elucidated by X-ray analysis to correlate with their magnetic behaviour.

Because the charge transfer complexes could be prepared easily from simple TEMPO radicals and acceptors and because the finding described above may be applied to a variety of hitherto known nitroxyls, it would be expected to enrich the source of novel organomagnetic materials.

(iv) Development of CT complexes consisting of donors, nitroxide radicals and acceptors

It was recently found that a series of organic ternary complexes (mixed crystals or alloys) with three-component systems including donor(s), radical(s) and acceptor(s) could be formed by regulating the ratio by stoichiometry.[66,77] As an example, a series of CT complexes derived from TTF, 4-amino-TEMPO (ATEMPO) and TCNQF$_4$ were prepared and their magnetic behaviour was investigated. Although no ferromagnetic behaviour has been found among them yet, as summarized in Table 7, the Weiss temperature (absolute values) was found to decrease along with the decrease of the amount of ATEMPO incorporated into these complexes. Although the study is still a preliminary one and much remains unresolved, we may open a way to obtain a wide variety of ternary CT complexes.

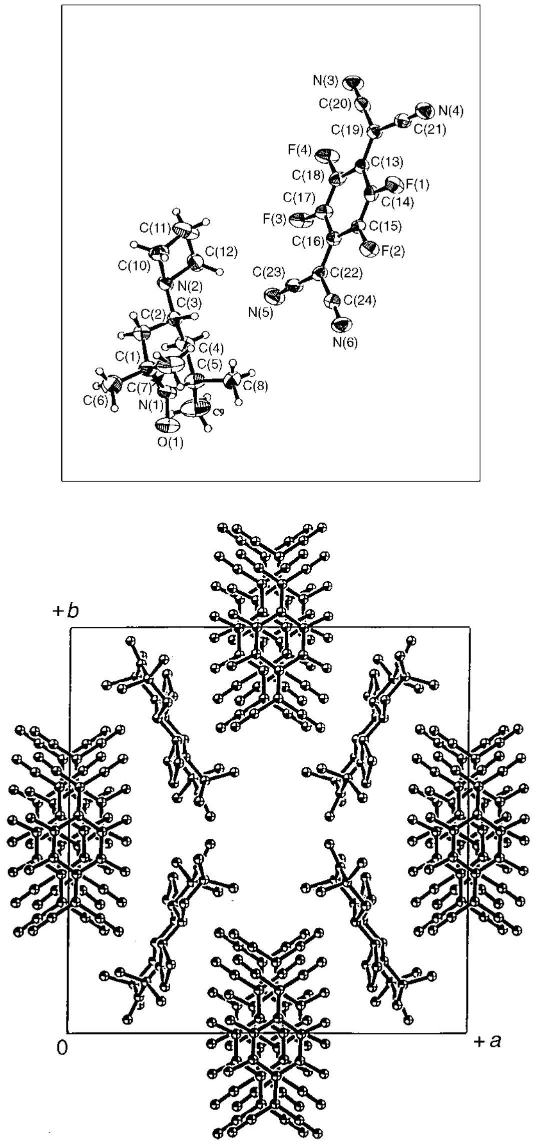


Fig. 15 Upper: molecular structure of complex **82**. Lower: crystal structure of **82** viewed along the *c* axis.

Thus, continuous efforts have been made, and are still being made, to form a step-by-step approach to novel organomagnetic materials such as organomagnetic conductors as shown above, utilizing nitroxide radicals as the key building blocks for magnetic materials.

Summary and future perspectives

We described in this article the recent development of organomagnetic materials based on nitroxide radicals, dealing mainly with nitroxide radical crystals and CT complexes consisting of nitroxide radicals, and introducing different approaches. We have discussed the results of several research groups, as well as our own, in order to give an overview of this rapidly growing field of materials science. We have stressed the remarkable progress made in recent years in the field of nitroxide radical crystals, after the discovery of the first purely organic ferromagnet (β-phase of PNN) in 1991, through various approaches to obtain new organomagnetic materials based on nitroxide radicals. Although the highest T_c known to date among radical crystals and CT complexes consisting of nitroxide radicals is that of the Rassat radical with $T_c = 1.48$ K, much effort has been devoted to the preparation of new

Table 7 Physical and magnetic properties of ternary complexes

compound	composition[a]	appearance	mp[b]/°C	magnetic interactions	Weiss constant/K[c]
ATEMPO–TCNQF$_4$ (**77**)	1:1	green solid	> *ca.* 150	antiferromagnetic	−1.0
TTF–ATEMPO–TCNQF$_4$	0.4:0.6:1	dark blue solid	> *ca.* 180	antiferromagnetic	−0.8
TTF–ATEMPO–TCNQF$_4$	0.5:0.5:1	dark blue–green solid	> *ca.* 192	antiferromagnetic	−0.7
TTF–ATEMPO–TCNQF$_4$	0.8:0.2:1	dark blue–violet solid	> *ca.* 195	antiferromagnetic	−0.6
TTF–TCNQF$_4$	1:1	dark violet solid	> *ca.* 300	paramagnetic	0.0

[a]Estimated by elemental analysis. [b]Decomposition point. [c]Fitting for Curie–Weiss rule.

organomagnetic materials to elucidate the magneto-structural relationship of nitroxide radicals in investigating solid state/crystal (three-dimensional) structures. This should provide feedback for the design and production of more sophisticated or intelligent magnetic materials in the near future. It is therefore still essential that new magnetic materials should be synthesized so that the subtle factors that govern their magnetic properties can be better understood.

We consider that another possible area for future investigation is the development of novel magnetic materials with multi-functionality, *i.e.*, the development of magnetic materials which respond to light, heat, pressure, electricity or other stimulators, which are interesting not only from the viewpoint of basic science but also in technological aspects, to afford examples of molecular devices as thermal or optical switching systems correlated with spins. Actually, interesting examples of spin cross-over systems[78] were proposed and developed in recent years in inorganic compounds[79] and metal complexes[80] having eminent properties, and such systems might be possibly applied to organic compounds as well. Together with the steady efforts on the elucidation of the magneto-structural relationship in magnetic materials, studies in the near future should be focussed along such lines as those described above, and nitroxide radicals must play continuously or even more important roles in the further development of the field.

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