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Synthesis and Characterization of 2-Ferrocenyl-4,4,5,5-tetramethyl-2-imidazolin-1-oxyl 3-Oxide and Its CT-Complex with DDQ

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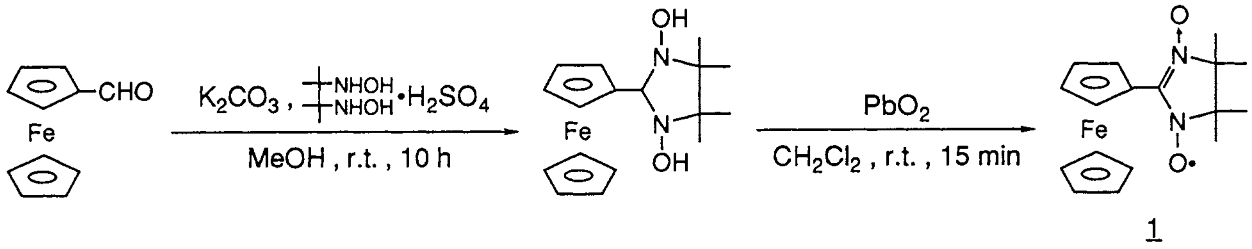
A ferrocene derivative carrying a nitronyl-nitroxide radical was synthesized and its CT salt with DDQ was prepared. There are two S=1/2 spins, ferrocenium ion and nitronyl-nitroxide radical, on the cationic part of the CT-salt. From the temperature dependence of magnetic susceptibility data it is concluded that the interaction between them is antiferromagnetic ($2J \approx -50$ cm^{-1}).

In recent years there has been much interest in the design of molecular ferromagnets, and several approaches have been made.$^{1-4)}$ One of them takes advantage of the charge-transfer (CT) salts, which are composed of S=1/2 donors ($D^{\dot{+}}$) and acceptors ($A^{\dot{-}}$).$^{2-4)}$ When D has a degenerate pair of filled HOMO as in the e_{2g} orbitals of ferrocene, the configurational admixing of a virtual triplet due to D^{2+} should lead to ferromagnetic coupling of the spins on $D^{\dot{+}}$ and $A^{\dot{-}}$.$^{2)}$ Modifying such a scheme, we attempted to construct CT-complexes between a donor (D) carrying a stable radical (R) and an appropriate acceptor (A), as illustrated in Scheme 1. If the spin of R couples with that of $D^{\dot{+}}$ either ferro- or antiferromagnetically, the coupling with $A^{\dot{-}}$ should lead to addition or incomplete cancellation of the total spin, thus showing ferrimagnetic behavior. For the purpose of accomplishing this scheme, 2-ferrocenyl-4,4,5,5-tetramethyl-2-imidazolin-1-oxyl 3-oxide (1) was synthesized, and its CT salt (2) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was prepared. The magnetic behavior of 2 is reported in this article.

Scheme 1.

Radical 1 was synthesized by the modified Ullman's method[5] as shown in Scheme 2. The purification of 1 by column chromatography on silica-gel and recrystallization yielded dark-green needles (mp 150 ℃) which were stable in the air at room temperature. Cyclic voltammetry of 1 showed two reversible waves at 1.07 and 1.41 V vs. Ag/AgI (CH_3CN) corresponding to the oxidation of ferrocene moiety and nitronyl-nitroxide radical, respectively. The former is higher than the oxidation potential of ferrocene (0.88 V) measured under similar conditions, indicating the electron-withdrawing effect of the nitronyl-nitroxide radical. The latter is also higher than those of 2-phenyl- and 2-(1-pyrenyl)- derivatives (1.23 V). Judging from the oxidation potential, the oxidation of 1 into ferrocenium ion is expected to require a fairly strong acceptor.



Scheme 2.

As an acceptor for 1, DDQ was selected, because its reduction potential is located between the two oxidation potentials of 1. Mixing of a solution of 1 in *n*-hexane with that of DDQ in CH_2Cl_2 under an argon atmosphere gave a brown solid (2), which was found by elemental analysis to consist of equimolar 1 and DDQ. All attempts to obtain single crystals have been unsuccessful. Measurement of UV-Vis and ESR spectra of 2 in solution showed that nitronyl-nitroxide radical remained intact without any oxidation and decomposition. A CN-stretching IR absorption was observed at 2216 cm^{-1} in good agreement with that of $K^+DDQ^{\cdot-}$. Consequently it is concluded that 2 is a CT-salt made of the ferrocenium ion of 1 and DDQ anion. DDQ anions are considered to form diamagnetic dimers, $(DDQ)_2^{2-}$, as in other similar cases.[6] On the other hand, there are two S=1/2 spins, ferrocenium ion and nitronyl-nitroxide radical, on the cationic part of 2. ESR spectra and magnetic susceptibility were measured to support the interpretation and clarify their mode of coupling.

ESR spectra of 2 were measured between 4 K and room temperature. The spectrum obtained at 5 K is shown in Fig. 1. A broad signal was observed around 200 mT, and another signal due to a radical around g=2 was very weak. The former was considered to be attributed to a triplet state due to the interaction between ferrocenium ion and nitronyl-nitroxide radical with a g value between g=2 and 4, and the latter to a slightly remaining impurity. The broad signal shifted to higher magnetic field as the temperature was increased.

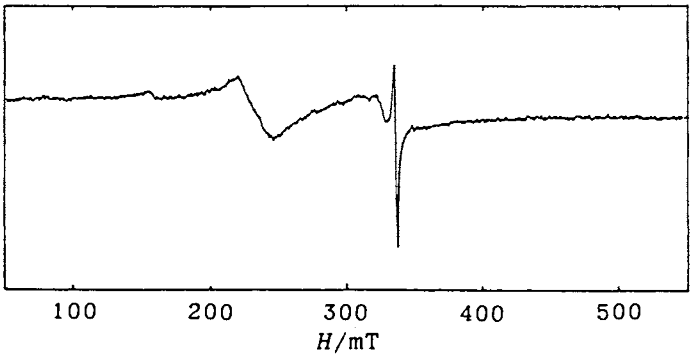


Fig. 1. ESR spectrum of CT salt $\underline{2}$.

The magnetic susceptibility was measured between 2 and 300 K by the Faraday method. The gram susceptibility (χ) and the square of effective magnetic moment (μ_{eff}^2) are shown as a function of temperature in Fig. 2 (a) and (b), respectively. Above 100 K the susceptibility of $\underline{2}$ obeyed a Curie-Weiss law with a Weiss constant of -22 K. Below 100 K the χ vs. T curve gradually deviated from the Curie-Weiss law, and reached a broad maximum at 47 K. After the maximum, the susceptibility fell down as the temperature was decreased toward 10 K, then increased again. The last increase in χ is probably due to independent 1/2 spins of the impurity, which was estimated to be less than 4—5% of the total spins, rather than the ferromagnetic interaction between the cations. The μ_{eff}^2 value at room temperature, $10.2\mu_B^2$, is close to the sum of that of nitronyl-nitroxide ($3.0\mu_B^2$) and ferrocenium ion ($6-7\mu_B^2$).7) μ_{eff}^2 was almost

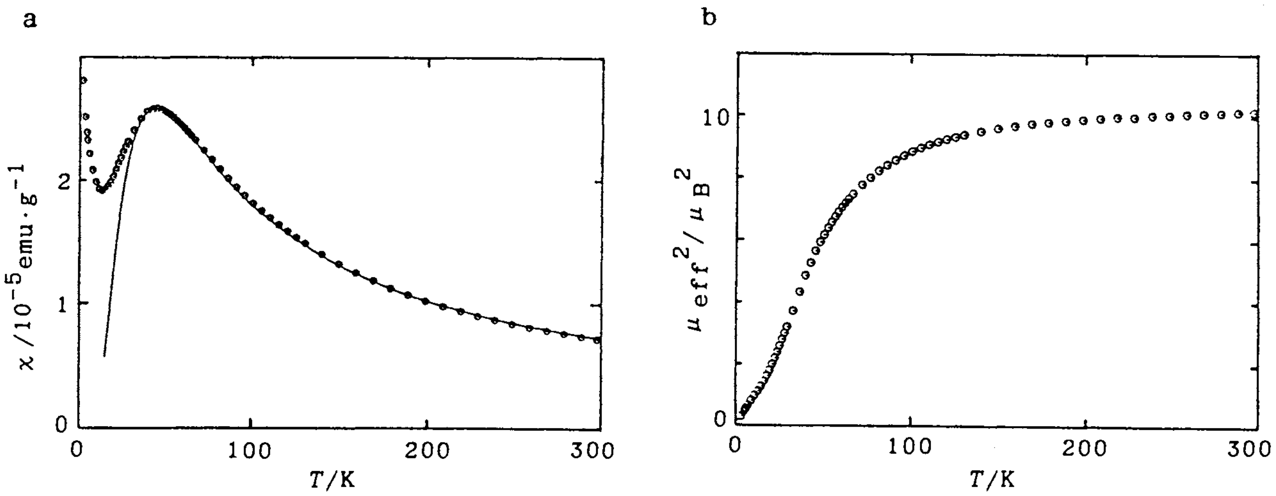


Fig. 2. The temperature dependence of (a) gram susceptibility, χ, and (b) the square of effective magnetic moment, μ_{eff}^2, for $\underline{2}$. The solid curve in (a) represents a calculated one for $2J$=-50 cm^{-1}.

constant as the temperature was lowered from 300 to 150 K, but decreased rapidly below 100 K. This indicates that the interaction between nitronyl-nitroxide radical and ferrocenium ion is antiferromagnetic. On the basis of the ST model,$^{8)}$ the energy gap between the ground singlet and the excited triplet ($=-2J$) is estimated to be about 50 cm^{-1} by fitting the experimental values to theoretical curves as in Fig. 2(a).

In conclusion, ferrocenium ion (D^+) and nitronyl-nitroxide (R) on 2 are not independent but antiferromagnetically coupled. In this case, anions of DDQ (A^-) did not participate in the magnetism of 2 as a result of their dimerization. Studies to find appropriate paramagnetic A^- to realize the model shown in scheme 1 are in progress.

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