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Magnetic and Electric Properties of a Cation Radical Salt Tris(decacyclene) Bis(hexafluorophosphate), $(Dc)_3(PF_6)_2$

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A cation radical salt between a π-electron donor decacyclene and hexafluorophosphate, $(Dc)_3(PF_6)_2$, was prepared by electrochemical synthesis, and conductivity (90—350 K), electron paramagnetic resonance (4—400 K) and static susceptibility (2—300 K) were measured. The salt was found to be semiconductive with the conductivity of ca. 4×10^{-2} S cm^{-1} at room tempertature and the activation energy of 66±3 meV. The magnetic measurements show that this salt is paramagnetic and spin susceptibility is thermally activated with the activation energy of 17 meV resulting from antiferromagnetic intermolecular interaction, although the dication of electron donor might be expected to have triplet spin multiplicity to stabilize ferromagnetic spin alignment in the ground state. The magnetism of $(Dc)_3(PF_6)_2$ is discussed in terms of charge-transfer interaction among donors.

Since McConnell proposed a model for ferromagnetic (FM) spin alignment in purely organic compounds using ionic charge-transfer (CT) complexes in 1967,[1] some its modifications have been suggested for ionic CT complexes and ion radical salts[2–5] and the model has thoroughly been generalized including organometallic complexes.[6] In these models, it is essential that an ionic CT complex or ion radical salt is consisting of molecules which exhibit high spin multiplicity in the CT excited states and/or in the ground state.[1–6]

For the ion radical salts, virtual disproportionation, where an electron on one molecule which has doubly degenerate orbital (d) occupied by one (d^1) or three (d^3) electrons is transferred to an adjacent molecule with the same electronic configuration, could stabilize FM coupling between the molecules.[2,6] This mechanism may further be extended to the case of a crystal consisting of molecules having higher degeneracy.[6] Similarly, one electron transfer between molecular sites with doubly (or multiply) degenerate orbitals with heterospin configurations (e.g., d^1 and d^2; d^2 and d^3) could result in FM or ferrimagnetic (FIM) coupling.[4,6] In contrast to the situations mentioned above, for the CT complexes, antiferromagnetic (AFM) coupling is predicted for virtual backward CT from a d^1 site to a non-degenerate site (s) with single occupancy (s^1) and also for virtual backward CT from d^3 to s^1,[6] whereas the inverse (forward CT) processes could result in FM coupling.[1–3,6] In other words, whether ion radical salts are in a uni or mixed valence state, they would be more appropriate candidates than ionic CT complexes to realize FM spin alignment, since the FM intermolecular coupling could be stabilized regardless of the direction of CT. Such prescription therefore leads us to study an ion radical salt based on an organic molecule with symmetry higher than C_3. Such a molecule is known to possess degeneracy in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), when it is free.

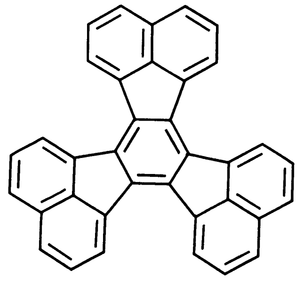

Fig. 1. Molecular structure of decacyclene.

Some aromatic molecules with a three- or six-fold axis of rotation such as decacyclene (diacenaphtho[1,2-*j*:1′,2′-*l*]fluoranthene),[7] 1,3,5-triphenylbenzene,[7,8] hexamethoxytriphenylene,[9] hexachlorobenzene,[10] and hexaazaoctadecahydrocoronene[11] have in fact been shown to have triplet ground state when they were in the dication or dianion state. Therefore, ion radical salts of these aromatic molecules may be a good candidate to establish FM intermolecular coupling in a solid. Cation radical salts of polycyclic aromatic hydrocarbons have been prepared by galvanostatic electrochemical oxidation with an appropriate supporting electrolyte,[12] although some aromatic hydrocarbons such as naphthalene are unstable in atmosphere.[13] We have prepared the cation radical salts of decacyclene (Fig. 1) by the electrochemical oxidation. In this paper, we describe the characterization and investigation of electric and magnetic properties of the cation radical salt with hexafluorophosphate.[14]

Experimental

Decacyclene (Aldrich Chemical Co. Inc.) was recrystallized from a nitrobenzene solution and sublimed twice at 320 °C under 1 Pa. Black single crystals shaped like long needle were prepared by electrochemical oxidation of decacyclene in a dichloromethane solution on a platinum anode under a constant current of 2 μA at 0 °C for 160 hours. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The crystals are stable in a dry atmosphere but mechanically unstable and readily decomposed to yield decacyclene when they are ground in an agate mortar.

A preliminary X-ray diffraction analysis shows that this cation radical salt has 3:2 stoichiometry, i.e., tris(decacyclene) bis(hexafluorophosphate), $(\mathrm{Dc})_3(\mathrm{PF}_6)_2$. The salt crystallizes in the hexagonal system, space group $P6_322$, with the following cell constants: a=27.896(4) Å, c=10.422(1) Å, V=7024(2) Å^3, Z=4, D_x=1.55 Mg m^{-3} and D_{obs}=1.55 Mg m^{-3}.[15] The crystals were elongated along the crystallographic c-axis with dimensions 2—5 mm in length and 0.05—0.1 mm in width.

Direct current electrical conductivity was measured on a single crystal by means of the four probe technique with silver paste (du Pont No. 4929). Electron paramagnetic resonance (EPR) spectra of a single crystal were recorded on a JEOL JES-FE1X spectrometer at 9 GHz with a cylindrical cavity in the TE_{011} mode. Sample temperature was varied and controlled by using an Oxford ESR900 cryostat of continuous flow type and a DTC-2 temperature controller in the range from 4 to 300 K. A JEOL EXDVT-1 temperature controller was also used in the range from 300 to 400 K. The g factor was determined by comparing the resonance position with that of $\mathrm{Li^+TCNQ^-}$ (g=2.0026). The modulation width was always kept much less than one-tenth of the linewidth to prevent line shape from distortion due to overmodulation.

Magnetic susceptibility was measured with a Faraday-type susceptometer over the temperature range from 2 to 300 K on a bundle (1 mg) of the single crystals in a small quartz bucket (ca. 20 mg) at 5 T and on the polycrystalline sample (12 mg) in a quartz bucket (ca. 100 mg) at 3 T. The details of the apparatus were described previously.[16]

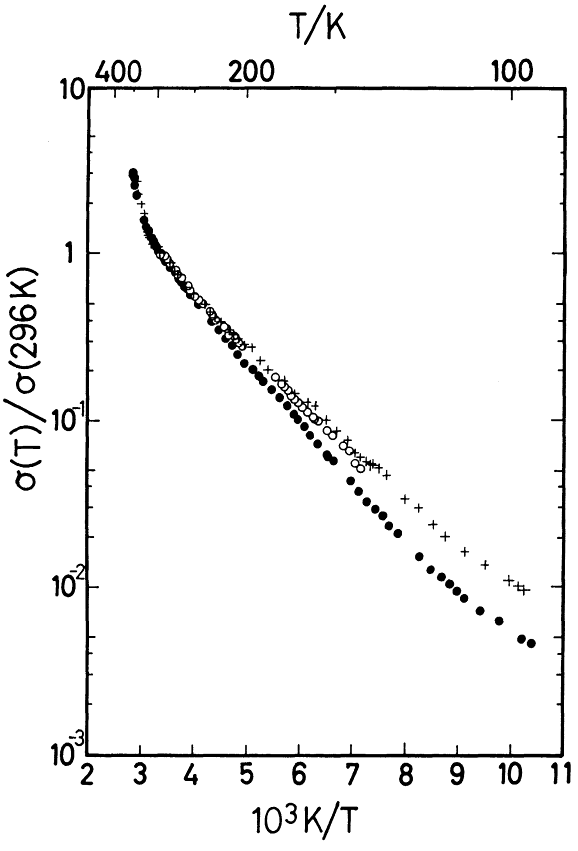

Fig. 2. Temperature dependence of conductivity σ of $(\mathrm{Dc})_3(\mathrm{PF}_6)_2$. The conductivities observed for different crystals are normalized at 296 K and represented by crosses, open and closed circles. The conductivity σ follows $\sigma=\sigma_0\exp(-E_c/kT)$ with $(2—6)\times10^{-2}$ S cm^{-1} at 296 K and the activation energy E_c=66±3 meV.

Results

Semiconductive behavior with the conductivity $(2—6)\times10^{-2}$ S cm^{-1} at 296 K and the activation energy E_c=66±3 meV (1 eV=1.602×10^{-19} J) is observed for $(\mathrm{Dc})_3(\mathrm{PF}_6)_2$ in the range from 90 to 300 K as shown in Fig. 2. Three different crystals gave very similar temperature dependence, although the conductivity values varied from sample to sample in the range indicated, probably due to inaccuracy of sample dimensions used in the conductivity calculation. As the temperature increases from room temperature, the conductivity increases more steeply than that in the low temperature region. This phenomenon was reproducible but no indication for phase transitions in the vicinity of room temperature was observed in the magnetic measurements as described below.

The EPR spectra of the single crystal of $(\mathrm{Dc})_3(\mathrm{PF}_6)_2$ exhibit a Lorentzian shaped line over the whole temperature range between 4 and 403 K examined here as shown in Fig. 3. The g factor is found to be 2.0025(2) and independent of temperature. This indicates that the unpaired electrons in $(\mathrm{Dc})_3(\mathrm{PF}_6)_2$ reside only on the decacyclene molecules. The g factors of aromatic hydrocarbons are given by g=2.00257—$(19\times10^{-5})\lambda$, where λ is the coefficient of the Hückel MO energy level, $\alpha+\lambda\beta$, occupied by an odd electron.[17] We have calculated MO of decacyclene in the Hückel approximation and found that λ=0.4807 for HOMO which are doubly degenerate and occupied by an odd number of electrons when decacyclene is in the monocation radical state. The g factor is then calculated to be 2.00248 with λ=0.4807. This value is in good agreement with the observed value. It is worth noting that the g factor of $\mathrm{PF_5^{-}}$ radical observed under various conditions is known to be 1.9985(6), 2.00174(2), and 2.0039(2).[18]

The EPR absorption intensity is thermally activated except for the low temperature region below about 40 K where the susceptibility follows the Curie law as shown in Fig. 4. Such activation behavior is reminiscent of the moderately conducting ion radical salts.[19]

The peak-to-peak linewidth B_{pp} observed for the decacyclene cation radical salt is sharp, but not very sharp in comparison with that observed for the following cation radical salts of polycyclic aromatic hydrocarbons having metallic conductivity. The line-

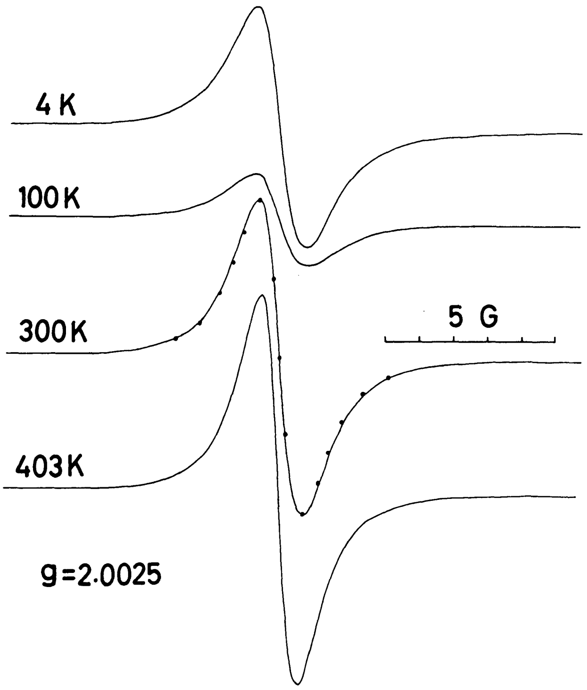

Fig. 3. First derivative curves of EPR spectra of the single crystal of $(Dc)_3(PF_6)_2$ at several temperatures. Closed circles on the 300 K spectrum represent the Lorentzian fit.

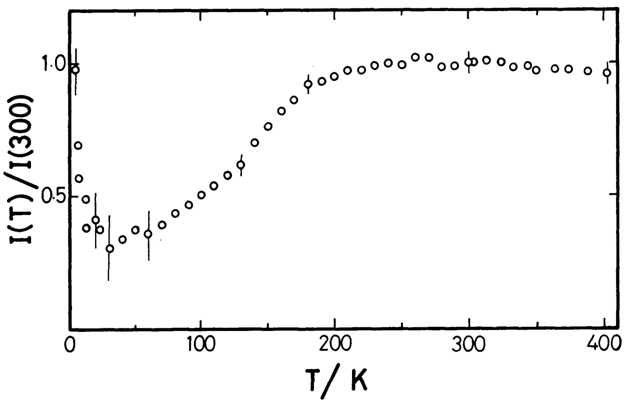

Fig. 4. Temperature dependence of the relative intensity of EPR of $(Dc)_3(PF_6)_2$ normalized at 300 K. Estimated errors are indicated by thin lines. The intensity is thermally activated above 40 K.

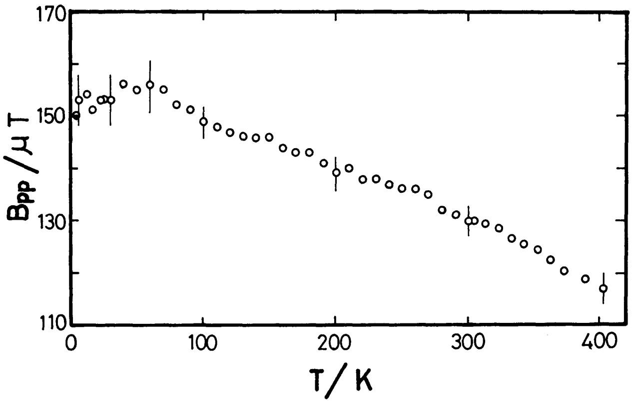

Fig. 5. Temperature dependence of peak-to-peak linewidth of EPR of $(Dc)_3(PF_6)_2$. Estimated errors are indicated by thin lines.

width of $(Dc)_3(PF_6)_2$ varies from 155 μT below 60 K down to 117 μT at 403 K as shown in Fig. 5, while the linewidths of the cation radical salts of other hydrocarbons are reported to be 60—80 μT for $(\text{perylene})_2(XF_6)_{1.1}(CH_2Cl_2)_{0.85}$ (X=As or Sb) at 100—300 K,[20] 1.5 μT for $(\text{fluoranthene})_2PF_6$ at 300 K,[21] and 0.25 μT for $(\text{naphthalene})_2AsF_6$ at 300 K.[22] The linewidth of these salts would be ascribed qualitatively to the motional narrowing effect. The conductivity at room temperature is about 0.04 S cm^{-1} for $(Dc)_3(PF_6)_2$ examined here, 160 S cm^{-1} for $(\text{perylene})_2(XF_6)_{1.1}(CH_2Cl_2)_{0.85}$,[20] 1000 S cm^{-1} for $(\text{fluoranthene})_2PF_6$.[23] Since the motional narrowing becomes effective in highly-conducting solid, the linewidth is expected to decrease in the order of $(Dc)_3(PF_6)_2$, the perylene salt, and the fluoranthene salt, as actually observed. The fact that the linewidth of $(Dc)_3(PF_6)_2$ decreases monotonically upon increasing the temperature also supports the motional narrowing effect because the conductivity increases with the increase of temperature. The linewidth is temperature independent below ca. 60 K. Simultaneously, the Curie contribution becomes dominant in the susceptibility. Therefore, the constant linewidth at low temperatures is ascribed to extrinsic origin such as lattice defects.

The static susceptibility observed for the bundle of the single crystals of $(Dc)_3(PF_6)_2$ exhibits the temperature dependence similar to that of the EPR absorption intensity obtained for the single crystal as shown in Fig. 6. That is, the paramagnetic susceptibility, which is determined by subtracting the diamagnetic contribution $\chi_d=-8.9\times10^{-4}$ emu mol^{-1} (1 emu mol^{-1}=4π cm^3 mol^{-1}) estimated by Pascal's law, is thermally activated except for the low temperature region where the susceptibility follows the Curie law with the Curie constant $C=5.5\times10^{-3}$ emu K mol^{-1} (1 emu K mol^{-1}=4π cm^3 K mol^{-1}) corresponding to 0.7% spins with $S=1/2$.

On the contrary, as shown in Fig. 7, the static susceptibility of the polycrystalline sample is very different from that of the single crystals. Substantial increase in the paramagnetism following the Curie–Weiss law is observed. The Curie constant is $C=0.130$ emu K mol^{-1} (17% spins with $S=1/2$) and the Weiss constant is $\theta=-5$ K. The finite Weiss constant of the polycrystalline sample results from the interaction between the Curie spins of high concentration. Since $(Dc)_3(PF_6)_2$ is mechanically unstable, the polycrystalline sample seems to include greater number of defects than the single crystals. Therefore, the large Curie paramagnetism in the polycrystalline sample is

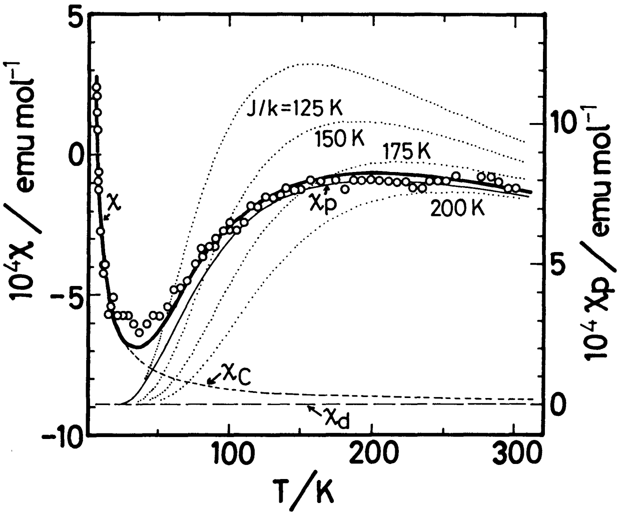

Fig. 6. Temperature dependence of static susceptibility of the bundle of single crystals of $(Dc)_3(PF_6)_2$ is shown by open circles. The diamagnetic (χ_d) and Curie (χ_C) contributions are represented by broken and dashed lines, respectively. The thin line indicates the intrinsic paramagnetic susceptibility (χ_p) calculated by the equation $\chi_p=(C/T)\exp(-E_m/kT)$ with $E_m/k=$ 202 K. The total susceptibility $\chi=\chi_p+\chi_C+\chi_d$ is shown by the thick line. The dotted lines show the theoretical curves calculated in terms of the single-triplet model with $J/k=125$, 150, 175, and 200 K.

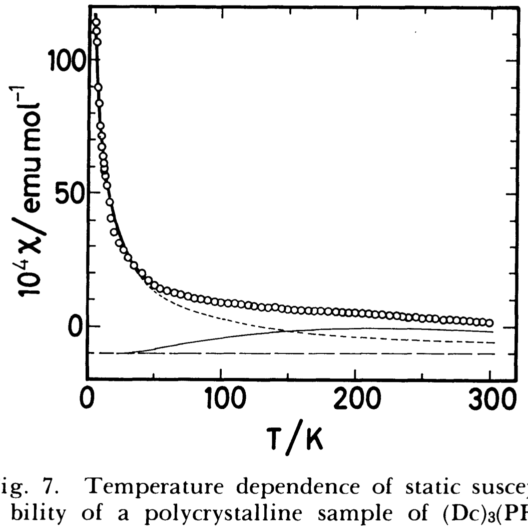

Fig. 7. Temperature dependence of static susceptibility of a polycrystalline sample of $(Dc)_3(PF_6)_2$. The lines represent the same meanings as shown in Fig. 7. It is to be noted that χ_C is about 25 times as large as that of the single crystals, while χ_p and χ_d alter a little.

ascribed to the increase of defects or paramagnetic centers produced by the crystal deterioration. Now it is clear that the Curie contribution observed in the single crystals of $(Dc)_3(PF_6)_2$ is extrinsic in origin and we analyze the paramagnetic susceptibility by subtracting the contribution.

The intrinsic paramagnetic susceptibility χ_p shown by the thin solid line in Fig. 6 is well described by the equation $\chi_p=(C/T)\exp(-E_m/kT)$ with $E_m=17.4$ meV or $E_m/k=202$ K. The diamagnetic (χ_d) and Curie (χ_C) contributions are represented by broken and dashed lines, respectively. The total susceptibility χ calculated by summing χ_p, χ_C, and χ_d is shown by the thick solid line in Fig. 6 and it agrees well, as a matter of course, with the observed susceptibility. The magnetic activation energy E_m obtained is about four times as small as the electric activation energy E_c. Such discrepancy is commonly observed for semiconducting organic ion radical solids and interpreted in terms of on-site Coulomb repulsion between itinerant electrons with AFM coupling.[19] The singlet-triplet model $\chi_p=(4C/T)[3+\exp(2J/kT)]^{-1}$ based on AFM coupling between two doublet sites fails to explain the intrinsic paramagnetism of $(Dc)_3(PF_6)_2$. In this case, the exchange coupling constant J/k should vary from 125 K below 50 K to 200 K above room temperature as shown by dotted lines in Fig. 6. Therefore, the AFM interaction among the spin centers residing on the decacyclene molecules seems to be not restricted within the nearest-neighbor spin centers but extended to second- and third-neighbors.

Discussion

The EPR and static susceptibility investigations demonstrate that $(Dc)_3(PF_6)_2$ is paramagnetic over the whole temperature range between 2 and 400 K. The activation behavior of susceptibility suggests the AFM coupling between unpaired electrons on the decacyclene molecules in spite of its capability to cause FM intermolecular interactions.

The decacyclene molecules seem to be stacked face-to-face taking into account their largely planar molecular structure, although the crystal structure of $(Dc)_3(PF_6)_2$ has not yet been solved. Namely, the decacyclene molecules are expected to form a segregated column structure. The 3:2 stoichiometry of the decacyclene salt with the monovalent anion PF_6^- indicates that two of three decacyclene molecules are formally ionized to monocation radicals and one of them remains neutral. The moderate conductivity observed for the salt supports such a mixed valence state. Therefore, $(Dc)_3(PF_6)_2$ can be regarded as a heterospin system consisting of the d^3 ($Dc^{\dagger}$) and d^4 (Dc) configurations.

The models proposed by McConnell[1] and other authors[2–6] are based on the CT interaction within molecular dyads. Such a molecular dyad approach, however, could not be applicable to $(Dc)_3(PF_6)_2$ in the mixed valence state, because two different pairs of electronic configurations, i.e., d^3d^4 and d^4d^4, must be considered simultaneously. For the semiconducting cation or anion radical salts with 3:2 or 2:3 stoichiometry such as $(TTF)_3(BF_4)_2$,[24] $Cs_2(TCNQ)_3$,[25] and $Rb_2(TCNQ)_3$,[26] where the number of unpaired

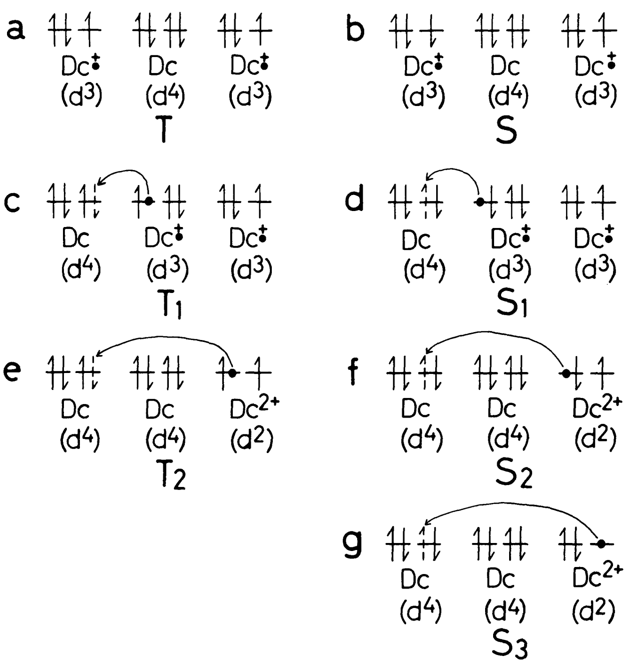

Fig. 8. Ground configurations T and S and excited charge-transfer configurations T_1, T_2, S_1, S_2, and S_3, for an electron transfer among monocation radicals and neutral molecule of decacyclene forming a triad.

electrons per molecule is 2/3 on an average, it is known that molecular triads consisting of the ionized molecules at each terminal and the neutral molecule at the center form an infinite stacking column in the solid. We assume therefore that $(Dc)_3(PF_6)_2$ crystallizes in this type of structure, since it is a semiconductive cation radical salt with 3:2 stoichiometry like $(TTF)_3(BF_4)_2$.

If this is the case, the ground electronic configuration of $(Dc)_3(PF_6)_2$, in the zero-th order approximation, can be described as a heterospin system composed of two d^3 and one d^4 states ($d^3d^4d^3$) as depicted schematically in Fig. 8a for the triplet state (T) and Fig. 8b for the singlet state (S). In terms of this configuration, the interaction is restricted within a triad. However, the discussion on the triad could be generalized to a system of an extended array of triads. Configurations T and S are the no-bond structures and they are nearly degenerate. Strictly speaking, T is slightly more stable than S by the direct exchange interaction represented by the exchange integral. However, such stabilization should be small in the case of intermolecular interaction.

There is a low-lying CT excited configuration ($d^4d^3d^3$ or $d^3d^3d^4$) in each of the triplet (T_1) and singlet (S_1) manifold as shown in Figs. 8c and 8d.[27] These excited configurations T_1 and S_1 admix with the ground configurations, thereby stabilizing T and S, respectively. The magnitude of stabilization is a function of the energy separation (diagonal term) and the magnitudes of the transfer integrals (off-diagonal terms) between the configurations concerned as discussed previously.[28] The diagonal terms in the triplet and singlet manifold would not be very different from each other because the excited configurations consist of two d^3 and one d^4 states as in the ground configurations; only the molecular sites on which the unpaired electrons reside are different. The off-diagonal terms for both manifolds would also not be very different from each other, although numerical calculations of the off-diagonal terms has not been carried out since the crystal structure is not determined yet. Therefore, the ground configurations T and S would be stabilized down to a similar amount by the admixture with the low-lying excited CT configurations T_1 and S_1.

Therefore, we have to consider other excited CT configurations of higher energy. Of these, the configurations T_2, S_2, and S_3 shown in Figs. 8e, 8f, and 8g[29] would contribute considerably to stabilization of the ground configurations T and S. The CT absorption band corresponding to the excitation to the state mainly consisting of S_2 or S_3, as well as that to the state based on S_1, is usually observed in the near-infrared region for most ion radical salts.[30] The diagonal terms for these configurations are, therefore, not too large in spite of on-site Coulomb repulsion on the dication of d^2 configuration. Further, the diagonal term for T_2 must be smaller than that for S_2 and S_3 by the amount of the intramolecular exchange energy. The transfer integral (off-diagonal term) of the salt is expected not to be small, because the transfer integral is known to be large for the cation radical salts of polycyclic hydrocarbons.[31] Therefore, the stabilizations of T and S by admixture of the configurations T_2, S_2, and S_3 are not negligibly small. Since there are two singlet configurations of nearly the same energy, the stabilization of S by admixture of S_2 and S_3 would surpass the stabilization of T, even though the diagonal term for T_2 is more favorable than that for S_2 and S_3. This is a possible reason why $(Dc)_3(PF_6)_2$ does not exhibit FM coupling. There are, of course, many other excited configurations of higher energy and these would also stabilize T and S. However, these would contribute to a similar amount in both manifolds.

Finally, it may be pointed out that there still remain other possibilities of destabilizing ferromagnetically coupled state. For example, there would be Jahn–Teller distortion[32] of a decacyclene molecule removing the orbital degeneracy to increase the diagonal term for the triplet configurations. Although it is known that the dianion of decacyclene has the triplet state as the lowest state in a solution,[7] the electronic structure of its dication is not known. It is therefore of great interest to investigate the molecular and crystal structure of $(Dc)_3(PF_6)_2$ to acquire further insight into the magnetic interaction in this salt.

Conclusion

We have synthesized the cation radical salt between decacyclene and hexafluorophosphate anion with 3:2 stoichiometry. The magnetic and electric properties of the salt were investigated by means of the conductivity, EPR, and static susceptibility measurements. The spin susceptibility of the semiconductive salt is thermally activated with the activation energy of 17 meV, being smaller than that of electrical conduction 66 meV. These results indicate that the unpaired electrons are coupled antiferromagnetically, although the salt apparently meets the requirements of the models for organic ferromagnetism. A possible reason why $(Dc)_3(PF_6)_2$ does not exhibit ferromagnetic intermolecular interaction has been discussed on the basis of the mixed valence state. It is worth noting that magnetic and structural investigations of the salt consisting solely of monovalent decacyclene ions and free from neutral molecules are inevitable to examine the simple and familiar models for ferromagnetic spin alignment based on charge-transfer interaction in organic compounds.

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